

 Open access • Journal Article • DOI:10.1051/JPHYS:01976003706076900

## Ultrasonic investigation of nematic liquid crystals in the isotropic and nematic phases — [Source link](#)

S. Nagai, P. Martinoty, S. Candau

**Published on:** 01 Jun 1976 - Journal De Physique (Société Française de Physique)

**Topics:** Biaxial nematic, Liquid crystal, Critical exponent and Wavelength

Related papers:

- [The physics of liquid crystals](#)
- [Theory of anomalous ultrasonic absorption and dispersion of nematic liquid crystals just above the clearing point](#)
- [Ultrasonic investigation of the nematic-isotropic phase transition in MBBA](#)
- [Results of Ultrasonic Velocity and Density Investigations of the Nematic Liquid Crystal](#)
- [Acoustic relaxation near the isotropic liquid-nematic phase transition in the nematic phase in p-n-octyloxy p'cyanobiphenyl](#)

Share this paper:    

View more about this paper here: <https://typeset.io/papers/ultrasonic-investigation-of-nematic-liquid-crystals-in-the-4i5ww98k2j>

Classification  
 Physics Abstracts  
 7.130 — 7.240

## ULTRASONIC INVESTIGATION OF NEMATIC LIQUID CRYSTALS IN THE ISOTROPIC AND NEMATIC PHASES

S. NAGAI (\*), P. MARTINOTY and S. CANDAU

Laboratoire d'Acoustique Moléculaire, Université Louis-Pasteur,  
 4, rue Blaise-Pascal, 67070 Strasbourg Cedex, France

(Reçu le 1<sup>er</sup> décembre 1975, révisé le 28 janvier 1976, accepté le 16 février 1976)

**Résumé.** — Nous avons mesuré la variation en fonction de la fréquence de l'atténuation ultrasonore d'un cristal liquide nématique, le *n*-pentyl cyanobiphényle, au voisinage de la transition nématique-isotrope. Les résultats obtenus dans la phase isotrope sont en bon accord avec la théorie récemment proposée par Imura et Okano. En particulier, la fréquence  $\omega_{\max}$  pour laquelle l'absorption par longueur d'onde  $\alpha_\lambda$  est maximum ainsi que la valeur  $(\alpha_\lambda)_{\max}$  de ce maximum divergent à la transition avec des exposants critiques voisins de ceux prévus par la théorie.

Nous avons étendu la théorie d'Imura et Okano à la phase nématique en nous fondant sur l'hypothèse d'un couplage entre la variation thermique produite par l'onde ultrasonore et les constantes de Frank. Ce modèle permet de rendre compte semi-quantitativement des résultats expérimentaux.

Nous avons par ailleurs étudié la variation de l'atténuation ultrasonore basse fréquence en fonction de l'angle entre le directeur et le vecteur d'onde acoustique, pour un cristal liquide nématique (Merck V) présentant une plage étendue de nématicité. Les résultats sont bien décrits par la théorie de Forster *et al.* dans la mesure où les températures sont très inférieures à la température de transition et les fréquences beaucoup plus basses que la fréquence de relaxation intramoléculaire.

**Abstract.** — We report measurements of the frequency dispersion of ultrasonic attenuation for a nematic liquid crystal, the *n*-pentyl cyanobiphenyl in the vicinity of the nematic-isotropic transition. In the isotropic phase, the experimental results are well described by the theory recently proposed by Imura and Okano. The frequency  $\omega_{\max}$  at which the maximum of attenuation per wave length  $\alpha_\lambda$  occurs, as well as the peak value  $(\alpha_\lambda)_{\max}$  diverge at the transition with the critical exponents predicted by the theory.

We have extended the Imura-Okano theory to the nematic phase on the basis of a coupling between sinusoidal temperature variation induced by sound wave and the elastic Frank constants. This model accounts semi-quantitatively for the experimental results.

We have also investigated the dependence of the low frequency attenuation with respect to the angle between the director and the acoustical wave-vector for a nematic liquid crystal (Merck V) which exhibits a broad mesomorphic range. Far below the transition temperature the experimental data are well described by the theory of Forster *et al.*, provided that the frequencies are far below the intramolecular relaxational frequency.

**1. Introduction.** — Many experimental studies [1] have been made on the propagation of longitudinal sound waves in nematic liquid crystals with special emphasis on the region near the nematic-isotropic transition. Strictly speaking the nematic-isotropic transition is of first order but in fact it is nearly of second order. Therefore, several authors [2-6] have observed anomalous behaviour of the longitudinal ultrasonic wave propagation in the nematic-isotropic phase transition region.

A schematic diagram of the frequency and temperature dependence of the attenuation constant  $\alpha/f^2$  ( $\alpha$  attenuation,  $f$  frequency) for a nematic sample which does not exhibit smectic mesophase is shown in figure 1.

In the high frequency range,  $(\alpha/f^2)$  is almost independent of temperature and shows a weak discontinuity at the nematic-isotropic transition temperature. This attenuation, similar to the so-called *classical attenuation* observed in isotropic liquids, can be accounted for by viscous losses. This process has been studied in detail by Bacri [7, 8] who found that the dependence of the attenuation with respect to the

(\*) On leave from National Research Laboratory of Metrology, Itabashi, Tokyo, Japan.

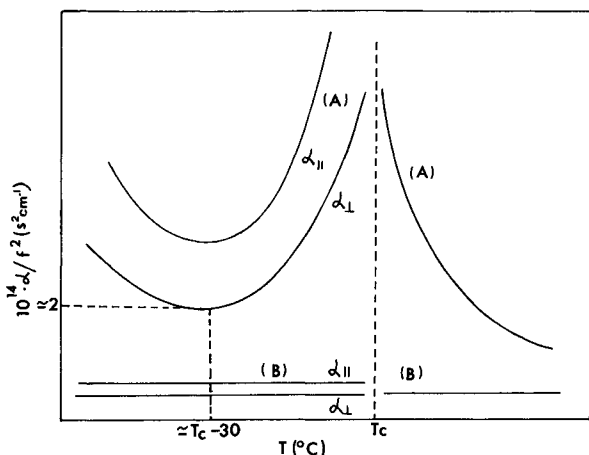


FIG. 1. — Schematic behaviour of the ultrasonic attenuation constant as a function of temperature. Curves (A) and (B) are relative to low frequency ( $\sim 1$  MHz) and high frequency ( $\sim 150$  MHz) ranges, respectively.  $\alpha_{||}$  and  $\alpha_{\perp}$  are the attenuation constants for acoustical wave vectors parallel and perpendicular to the magnetic field.

angle between the director and the acoustical wave vector is well described by the hydrodynamic theory proposed by Forster *et al.* [9].

In addition to this viscous process, a strong relaxational contribution can be observed in the whole temperature range as stressed from the difference shown in figure 1 between the low frequency and high frequency values of  $\alpha/f^2$ . However the behaviour of the relaxational attenuation depends critically on the investigated temperature range.

Far below the transition temperature, the experimental data can be fitted to a single relaxation curve. The amplitude of the dispersion decreases with increasing temperature and at the same time the relaxational frequency increases. This process, which has been investigated by the authors in earlier papers [10, 11], can be assigned to intramolecular trans-gauche isomer transitions occurring in the end chain groups.

Close to the transition temperature, the attenuation increases sharply in both nematic and isotropic regions. In the immediate vicinity of the transition on its nematic side the acoustical properties are characteristic of a multiply relaxing fluid as shown by Eden-Garland-Williamson [4]. The relaxation frequency (or the averaged relaxation frequency for multiple process) diverges at the transition.

This behaviour is typical of a critical process. The nematic-isotropic phase transition, although first order, is nearly of the second and the order parameter relaxes rather slowly. Acoustic waves couple strongly with the fluctuations of the order parameter and this coupling leads to a pretransitional increase of the ultrasonic attenuation.

One can summarize these different contributions to the ultrasonic attenuation by the following equation :

$$\alpha = \alpha_v + \alpha_1 + \alpha_c$$

$\alpha_v$  and  $\alpha_1$  account for viscous and intramolecular losses, respectively, and  $\alpha_c$  is the critical attenuation.

As mentioned before, the behaviour of  $\alpha_v$  and  $\alpha_1$  has been described in detail in earlier papers. In this paper, special attention is given to the critical process.

The anomalous behaviour of the ultrasonic absorption in the critical region has been reported by several authors [2-6].

In a recent work, Eden, Garland and Williamson [4] have studied the nematic and isotropic phases of *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) between 0.3 MHz and 23 MHz. They have observed 1) a sharp increase in the time relaxation  $\tau$  and in the relaxation strength as the phase transition is approached, 2) evidence of a multiple relaxation in the nematic side in the vicinity of the transition, 3) critical exponents for the relaxation time  $\tau$  equal to 0.4 and 1, respectively, in the nematic and isotropic sides. Furthermore, the data are consistent with the earlier high-frequency results of Martinoty and Candau [5] and the two sets of data agree in the region of overlap from 15 to 23 MHz.

At the same time Kawamura *et al.* [2] have also examined MBBA in the frequency range 2-120 MHz. Their results are qualitatively the same as those of Eden *et al.* but there are some discrepancies in the two sets of data. For instance, in the isotropic phase their relaxation frequencies are about twice as low as the values of Eden *et al.* The reason for these discrepancies is not clear but is presumably related to the chemical instability of this compound.

The pretransitional effects observed above the transition temperature were first interpreted theoretically by Hoyer and Nolle [3] in terms of the Frenkel heterophase fluctuations theory. Later Edmonds and Orr [13] applied Fixman's theory of sound attenuation in critical liquid mixtures [14] to explain the anomalies just above the clearing point. More recently, Imura and Okano [15] have proposed a treatment based on the statistical continuum theory of de Gennes [16], including Fixman's results on the anomalous ultrasonic absorption and dispersion in critical liquid mixtures.

Their theory seems to give a satisfactory explanation for the pretransitional effects and is in qualitative agreement with the existing data [2].

In the nematic phase a tentative interpretation has been given by Kawamura *et al.* [2] on the basis of the Landau-Khalatnikov theory.

The present investigation represents a detailed ultrasonic study of the region near the phase transition over a wide frequency range (0.5-120 MHz) on a biphenyl nematic which is more chemically stable than MBBA.

In the first part of this paper, we report measurements of ultrasonic attenuation in the isotropic phase of *p*-*n*-pentyl *p'*-cyanobiphenyl (PCB) and we make a quantitative comparison with Imura and Okano's theory.

In the second part of the paper we propose a semi-quantitative explanation for the anomalous ultrasonic behaviour in the nematic side of the transition, assuming that the order parameter is coupled to the acoustic waves via the elastic constants.

In the third part we discuss the angular dependence of the attenuation constant in a broad nematic temperature range.

**2. Experimental.** — The samples investigated were PCB (*p-n*-pentyl *p'*-cyanobiphenyl) and Merck V (a 2 : 1 molar mixture of *p*-methoxy *p'*-butyl azoxybenzene and *p*-methoxy *p'*-methyl azoxybenzene). These substances were purchased from B.D.H. Chemicals and E. Merck. Co. and used without further purification. They are nematic in a temperature range 22.5 ~ 35 °C and - 5 ~ 75 °C, respectively.

PCB supercools at room temperature, though it is metastable. It was claimed that the transition temperature remains constant even after exposure to the atmosphere for several weeks [17].

The ultrasonic attenuation measurements were carried out in the frequency range 0.5 ~ 115 MHz. The swept acoustical interferometry technique was used at 0.5 ~ 4 MHz with 3 MHz quartz. The description of the measurement cell is given in an earlier paper [11]. In the present study a level measuring set (PSM-5 Wandel and Goltermann) was used to measure the half-width of the resonant curve.

The standard pulse technique was employed for higher frequencies. A 1.285 MHz quartz was driven at 3.9, 6.5, 9.1, 11.7 and 14.2 MHz and a 5 MHz quartz was used at 25, 35, 45, 65, 85 and 115 MHz.

In the pulse technique experiment all measurements were carried out without applied magnetic field. In the swept acoustical interferometry the attenuations  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  relative to the parallel and perpendicular orientations of the acoustical wave vector with respect to a 9 kG magnetic field were measured, as well as the zero-field attenuation  $\bar{\alpha}$ . At several selected temperatures the angular dependence of the attenuation constant with magnetic field was examined. Upon turning on magnetic field, the attenuation constant instantaneously attained the equilibrium value. The temperature of the cells was regulated to better than  $\pm (\frac{1}{15})$  °C. The random error for attenuation measurements was  $\pm 3\%$  with the pulse technique and  $\pm 5\%$  with the swept interferometer technique in the frequency range above 2 MHz. For frequencies lower than 2 MHz, corrections become necessary. These corrections may be achieved by comparison with liquids of known attenuation. Because of the lack of highly attenuating liquids of known attenuation, it is not possible to evaluate the experimental accuracy when  $\alpha/f^2$  exceeds  $10^{-14} \text{ cm}^{-1} \text{ s}^2$ .

**3. Ultrasonic behaviour in the isotropic phase.** —  
2.1 THEORY. — Imura and Okano [15] have explained the anomalous heat capacity and ultrasonic attenua-

tion in the isotropic region within the framework of the phenomenological continuum theory of de Gennes [16]. The basic idea is due to Fixman who calculated the anomalous heat capacity of liquid mixtures in the critical region and explained the anomalous ultrasonic absorption and dispersion. We explain below the principal features of the Imura-Okano-Fixman theory. In section 4 we will apply a similar procedure to explain the anomalous sound attenuation on the nematic side of the transition.

The free energy density  $F$  of the system associated with the fluctuations of the tensorial order parameter  $Q_{\alpha\beta}$  is given by :

$$F - F_0 = \frac{1}{2} A Q_{\alpha\beta} Q_{\alpha\beta} + \frac{1}{2} L \partial_{\alpha} Q_{\beta\gamma} \partial_{\alpha} Q_{\beta\gamma} + \dots \quad (1)$$

The coefficient  $A$  is assumed to have the following temperature ( $T$ ) and pressure ( $P$ ) dependences :

$$A(P, T) = a(P) (T - T_c^*)$$

where the second order transition point  $T_c^*$  is slightly lower than the clearing point  $T_c$ .

The first term of the expansion of the free energy is related to the uniform fluctuations of the local anisotropy and the second term is associated with the spatial variation of  $Q$ .  $L$  is an elastic constant.

The tensor order parameter fluctuations (per unit volume) are described by the correlation function  $G(\mathbf{q})$  given by :

$$G(\mathbf{q}) = \langle | Q_{\alpha\beta} |^2 \rangle = \frac{k_B T}{2(A + Lq^2)} \quad (2)$$

where the brackets stand for an ensemble average and  $k_B$  is the Boltzmann constant. The entropy density associated with the fluctuation is obtained by differentiating eq. (1) with respect to temperature. Thus the average of the entropy change due to the fluctuations is given by :

$$\langle \Delta S(P, T) \rangle = - \frac{1}{2} \sum_{\alpha, \beta} \sum_{\mathbf{q}} \left( \frac{\partial A}{\partial T} \right)_P \langle | Q_{\alpha\beta}(\mathbf{q}) |^2 \rangle$$

with the following substitutions :

$$\sum_{\alpha, \beta} \langle | Q_{\alpha\beta}(\mathbf{q}) |^2 \rangle \rightarrow gG(\mathbf{q})$$

$$\sum_{\mathbf{q}} \rightarrow \frac{V}{2\pi^3} \int_0^{q_{\max}} d\mathbf{q} .$$

The entropy change (per unit volume) can be expressed in terms of the correlation function  $G$

$$\langle \Delta S \rangle = - \frac{g}{16\pi^3} \left( \frac{\partial A}{\partial T} \right)_P \int_0^{q_{\max}} G(\mathbf{q}) d\mathbf{q} \quad (3)$$

where  $g$  is a constant describing the multiplicity of the contribution from the correlation functions to be considered.

Imura and Okano assume that the dominant coupling between sound waves and the orientational correlation function is achieved through the temperature variation of  $A(T)$ . Consequently the local oscillating temperature induces a change in  $A(T)$  and  $G$  as :

$$\begin{aligned} A(T) &\rightarrow A(T) + \left(\frac{\partial A}{\partial T}\right) T_\omega e^{i\omega t} \\ G(q) &\rightarrow G(q) + G_1(q, \omega) e^{i\omega t}. \end{aligned} \quad (4)$$

In the vicinity of  $T_c$  the fluctuation of the order parameter has a strong spatial correlation and the response of  $G(q)$  to local oscillation of temperature induced by sound wave cannot be followed instantaneously. The delay in the response of the system produces the attenuation of sound wave.

The relaxation equation for the correlation function is given by :

$$\zeta \frac{\partial}{\partial t} G(q, t) = - (A + Lq^2) G(q, t) \quad (5)$$

where  $\zeta$  is a kinetic coefficient having the dimension of viscosity. From eq. (4) and (5) we obtain :

$$G_1(q, \omega) = - (A + Lq^2 - i\omega\zeta)^{-1} G(q) \left(\frac{\partial A}{\partial T}\right) T_\omega. \quad (6)$$

The dynamic heat capacity is given by :

$$\Delta c^*(\omega) = T \left\langle \left\langle \frac{\partial}{\partial T} \Delta S_1 \right\rangle \right\rangle$$

where  $\Delta S_1$  is obtained by substituting  $G_1$  in eq. (3) in place of the equilibrium function  $G$ .

Thus the attenuation constant per wave length  $\alpha_\lambda$  is given by :

$$\alpha_\lambda = \pi(\gamma_0 - 1) (C_p^0)^{-1} \text{Im} (\Delta c^*). \quad (7)$$

From eq. (7) the attenuation constant  $\alpha_\lambda$  and the frequency  $\omega_{\max}$  which gives the maximum absorption per wave length  $(\alpha_\lambda)_{\max}$  are expressed as follows (notations of reference [15]) :

$$\begin{aligned} \alpha_\lambda &= \frac{g\pi(\gamma_0 - 1) k_B T^2}{C_p^0} \left(\frac{a}{L}\right)^2 \left(\frac{2L}{\omega\zeta}\right)^{1/2} F_2(x) \\ \omega_{\max} &= 4.2 \omega_0, \quad \omega_0 = A/\zeta \\ (\alpha_\lambda)_{\max} &= \frac{0.3 g\pi(\gamma_0 - 1)}{C_p^0} \times \\ &\quad \times \frac{k_B T^2}{32 \pi} \left(\frac{a}{L}\right)^2 L^{1/2} (T - T_c^*)^{-1/2} \end{aligned} \quad (8)$$

where

$$x = \frac{A(T)}{\zeta\omega} = \frac{\omega_0}{\omega}$$

and

$$F_2(x) = \{ [x + (x^2 + 1)^{1/2}]^{1/2} - (2x) \}^{1/2}$$

where

$$\gamma_0 = \frac{C_p^0}{C_v^0};$$

$C_p^0$  and  $C_v^0$  are, respectively, the heat capacity at constant pressure and at constant volume in the absence of the fluctuations of the nematic order.

From eq. (8) one sees that both  $(\alpha_\lambda)_{\max}$  and  $(1/\zeta\omega_{\max})$  diverge with critical exponents of  $\frac{1}{2}$  and 1, respectively.

The function  $F_2(x)$  has been calculated numerically by Imura and Okano and is given in the original paper [15]. The function  $x^{1/2} F_2(x)$ , which is related to  $\alpha_\lambda$ , is reproduced in figure 2. We have also plotted a standard single relaxation curve according to the equation :

$$\alpha_\lambda = \frac{AV}{2\pi} \frac{\omega}{1 + (\omega/\omega_r)^2} \quad (9)$$

where we have neglected the frequency dispersion of the sound velocity  $V$ .  $A$  is a constant,  $\omega_r$  is the relaxational frequency.

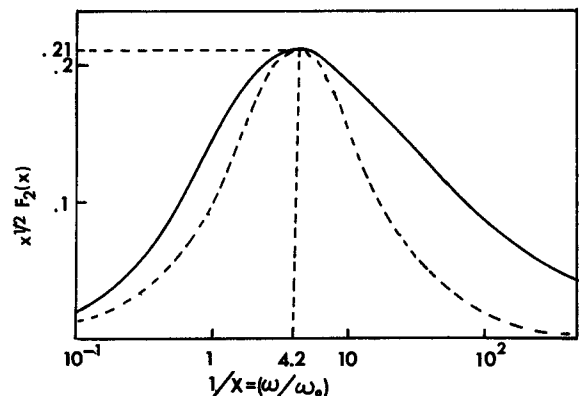


FIG. 2. — The function  $x^{1/2} F_2(x)$  which provides the theoretical frequency dispersion of  $\alpha_\lambda$  in the isotropic phase. The dotted curve represents the frequency dispersion of  $\alpha_\lambda$  for a single relaxation of same peak value assuming  $\omega_r = \omega_{\max}$  as described in the text.

The two curves plotted in figure 2 have been adjusted so that the maxima of  $\alpha_\lambda$  and  $x^{1/2} F_2(x)$  coincide. Both curves are similar in shape, but the single relaxational curve is narrower.

**2.2 EXPERIMENTAL RESULTS.** — Figure 3 represents the ultrasonic attenuation  $(\alpha/f^2)$  of PCB as a function of temperature. At 0.5 MHz the attenuation increases prominently as temperature approaches  $T_c$ . At 115 MHz, the attenuation is almost independent of temperature and does not exhibit any anomalous increase at the transition.

The results of the frequency dispersion of  $(\alpha_\lambda)$  at several selected temperatures are summarized in figure 4. The asymptotic behaviour of  $\alpha_\lambda$  observed in the high frequency range is characteristic of a

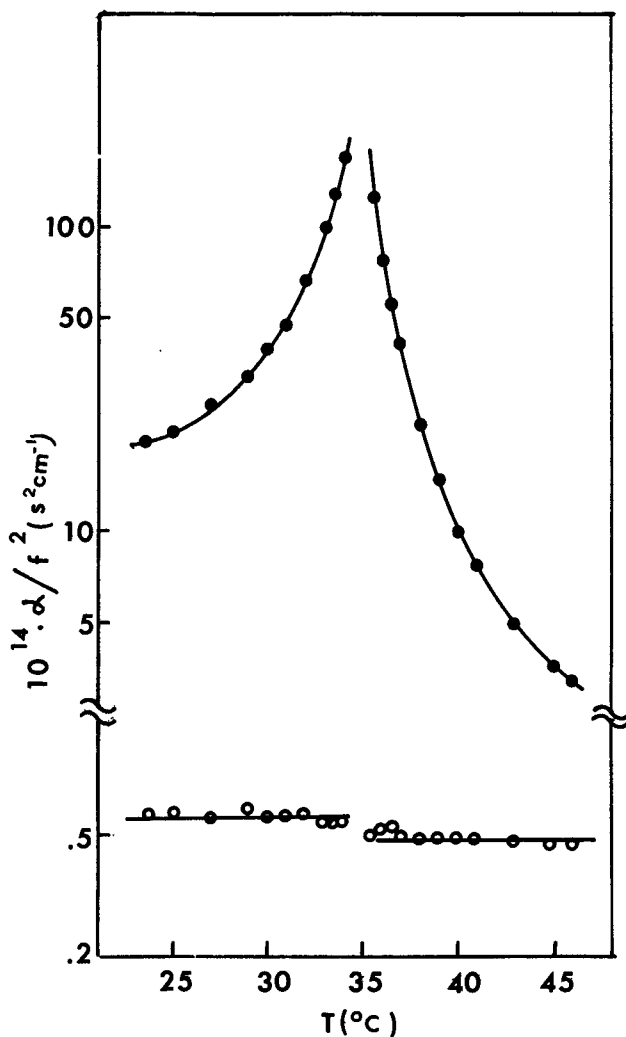


FIG. 3. — Temperature dependence of  $\alpha_\lambda/f^2$  for PCB : ●  $f=0,5$  MHz, ○  $f=115$  MHz,  $T_c = 35$  °C.

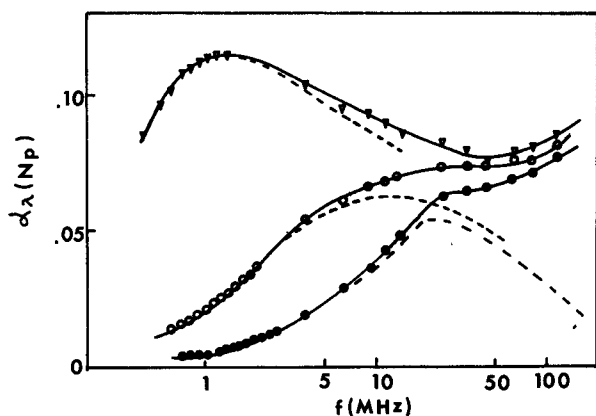


FIG. 4. — Frequency dispersion of  $\alpha_\lambda$  for PCB in the isotropic phase. Individual curves are for various temperatures : ▽ 35.5 °C ○ 39 °C ● 45 °C. The dotted curve has been obtained by subtracting the viscous contribution as described in the text.

residual attenuation arising essentially from viscous losses.

In a first stage, we have compared the experimental

data to the single relaxation curves given by the equation :

$$\alpha_\lambda = \frac{AV}{2\pi} \frac{\omega}{1 + (\omega/\omega_r)^2} + \frac{BV\omega}{2\pi} \quad (10)$$

where the constant  $B$  is an adjustable parameter which accounts for residual attenuation. Figure 5 shows the least square fits to the data by eq. (10). Indeed the frequency dispersion of  $\alpha_\lambda$  deviates appreciably from the single relaxation behaviour, as expected from the theory (Fig. 2).

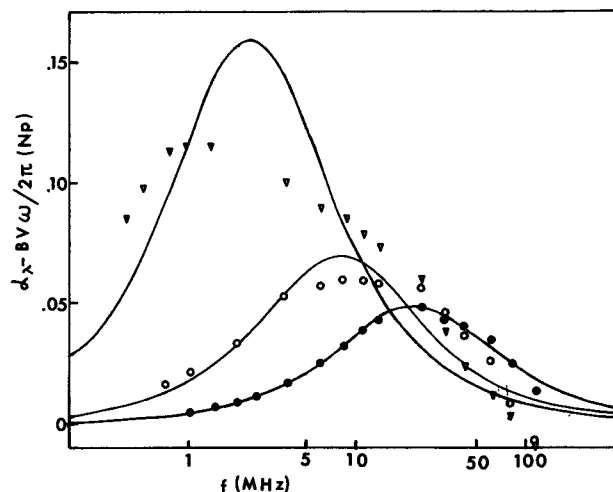


FIG. 5. — Curves least square fitted to the  $\alpha_\lambda$  measurements by a single relaxation curve in the isotropic phase. Symbols identified as in figure 4.

A fitting procedure of the experimental curves to eq. (8) would be meaningless due to the uncertainty in the different parameters involved. However  $(\alpha_\lambda)_{\max}$  and  $\omega_{\max}$  can be directly determined if one knows the  $B$  contribution.

From classical hydrodynamic theory  $B$  is given by :

$$B = \frac{2\pi^2}{\rho V^3} \left| \frac{4}{3} \eta_s + \eta_v \right|$$

For most of liquids,  $(\frac{4}{3}) \eta_s = \eta_v$  in the high frequency range.

Using this assumption, we have calculated the  $B$  contribution and subtracted it from the experimental values of  $\alpha_\lambda$ .

From the resulting dispersion curves shown in figure 4 we have determined both  $\omega_{\max}$  and  $(\alpha_\lambda)_{\max}$ . The temperature dependences of these parameters are reported in figures 6 and 7.

### 2.3 COMPARISON WITH THEORY AND DISCUSSION. —

In order to compare the experimental results of ultrasonic attenuation with eq. (4), one must know  $T_c^*$  and the temperature dependence of  $\zeta$ .  $T_c^*$  has been obtained for PCB from flow birefringence experiments [18] and is given by  $T_c - T_c^* \simeq 0.6$  K.

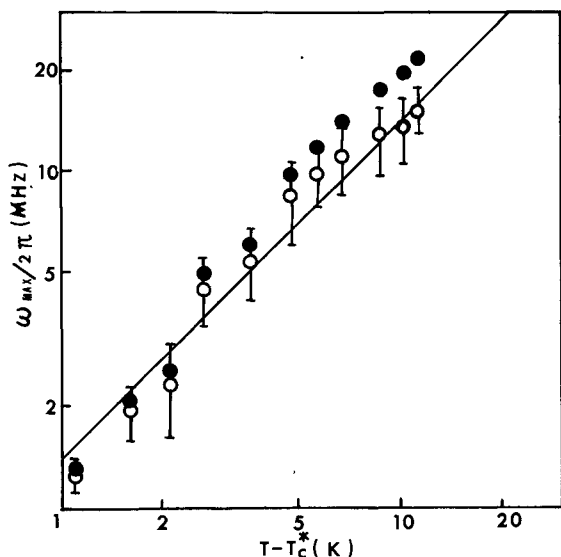


FIG. 6. — Temperature dependence of  $(\omega_{\max}/2\pi)$  for PCB in the isotropic phase. ● Raw data, ○ data corrected for the temperature dependence of the viscosity as described in the text. The solid line is the  $(T - T_c^*)$  power law predicted by the theory.

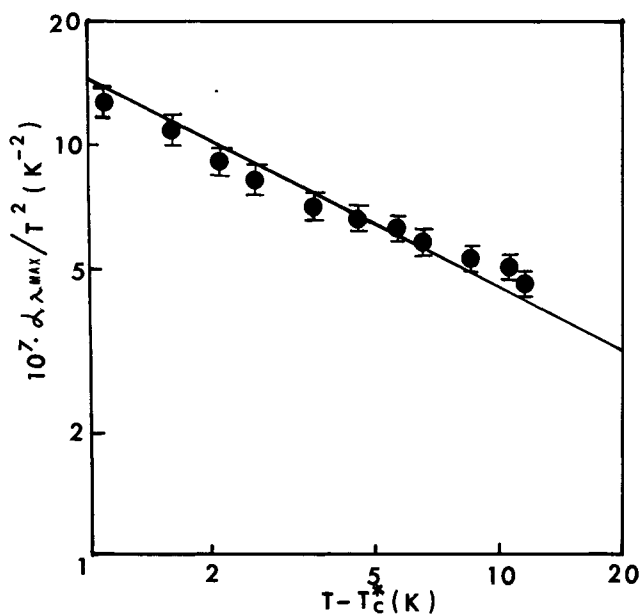


FIG. 7. — Temperature dependence of  $(\alpha_\lambda)_{\max}/T^2$  for PCB in the isotropic phase. The solid line is the  $(T - T_c^*)^{-0.5}$  power law predicted by the theory.

On the other hand, we assume that the temperature dependence of  $\zeta$  is similar to that of low frequency shear viscosity  $\eta_0$ ;  $\eta_0$  has been shown to vary as  $\exp(W/RT)$  with  $W = 8.4$  kcal mole<sup>-1</sup> [18]. The temperature dependence of  $(\omega_{\max}/2\pi)$  has been corrected for the  $\eta_0$  temperature dependence and compared to the  $(T - T_c^*)$  dependence of  $A(T)$  (Fig. 6).

The values of  $(\omega_{\max}/2\pi)_{\text{corr}}$  have been normalized to that  $(\omega_{\max}/2\pi)_{\text{corr}} = (\omega_{\max}/2\pi)$  at  $T = 35$  °C in the isotropic side. The straight line is that predicted by the theory.

The agreement between the theoretical and experimental temperature dependences can be considered as satisfactory due to the uncertainty concerning the activation energy of  $\zeta$  and the experimental errors. We must point out that for MBBA the critical exponent relative to  $\omega_{\max}$  was also close to the theoretical value [2, 4].

Figure 7 shows the temperature dependence of  $(\alpha_\lambda)_{\max}$ . Again, the experimental critical exponent is in good agreement with the theoretical one.

Consequently, an attempt was made to estimate the characteristic constants  $a$  and  $L$  from the acoustical data.

Assuming for the different constants ( $C_p^0$ ,  $\gamma_0$ ) involved in eq. (4) the values relative to PAA (para-azoxyanisole) [19, 20],  $g = 10$  [15] and  $\zeta = \eta_0$ , one obtains at  $\Delta T = 10$  K

$$a = 4.7 \times 10^5 \text{ erg} \times \text{cm}^{-3} \text{ K}^{-1}$$

$$L = 1.3 \times 10^{-7} \text{ dyne.}$$

The values obtained for  $a$  and  $L$  are of the same order of magnitude as that found in MBBA

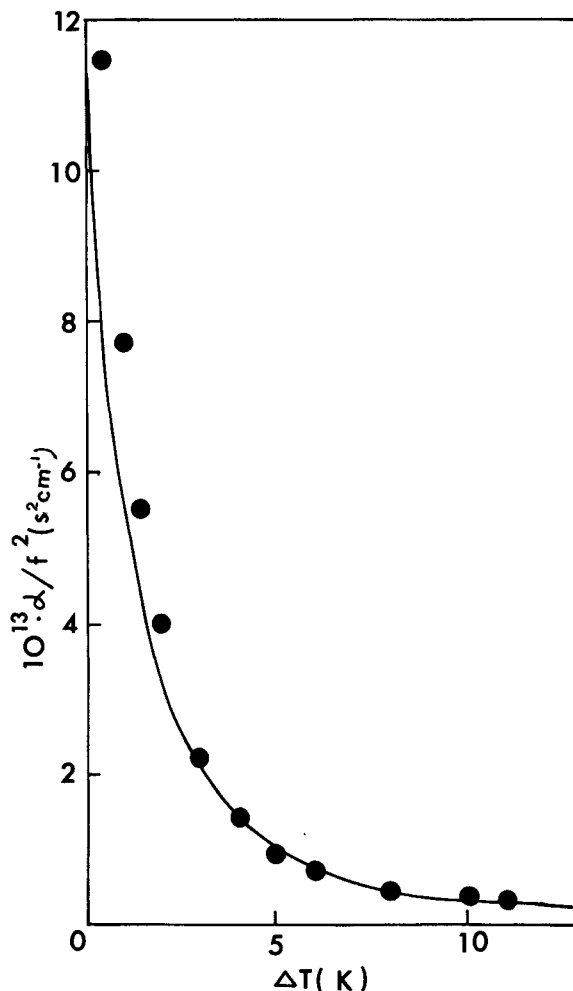


FIG. 8. — Temperature dependence of  $\alpha/f^2$  for PCB at 0.5 MHz in the isotropic phase. The solid line is fitted by eq. (4) to the experimental data as described in the text.

( $a = 6.2 \times 10^5 \text{ erg cm}^{-3} \text{ K}^{-1}$ ,  $L = 9 \times 10^{-7} \text{ dyne}$ ) by Stinson and Litster from magnetic birefringence and light scattering experiments [21].

In figure 8 we have compared the temperature dependence of the experimental values of  $(\alpha/f^2)$  at 0.5 MHz and the curve calculated from eq. (4). Due to the uncertainty in the characteristic parameters, the curves have been normalized at  $\Delta T = 10 \text{ K}$ . For  $T > T_c + 2 \text{ K}$ , the agreement is fairly good. Near  $T_c$  the experimental curve seems to diverge more rapidly than the theoretical one. However this discrepancy is nearly within the experimental accuracy which is fairly poor at low frequency.

#### 4. The critical process in the nematic phase. —

4.1 THEORY — Let us recall first some points concerning the order parameter  $Q_{\alpha\beta}$ . It can be expressed in terms of the director  $n$  and the scalar order parameter  $S$  as :

$$Q_{\alpha\beta} = S(n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta}). \quad (11)$$

The director specifies the direction of the main axis of the tensor  $Q_{\alpha\beta}$  and the magnitude of the tensor is characterized by the order parameter  $S$ . The definition of the order parameter comprises two different aspects of orientational states : in the isotropic phase both the magnitude and the orientation of the order parameter fluctuate widely and we must be concerned with the full order parameter. This is clearly shown in the expression (2), where terms  $A$  and  $L$  both appear. In contrast, in the nematic phase, the fluctuations of  $S$  are weak and the fluctuations of the tensor order parameter are mainly attributed to the fluctuations of the optical axis ( $S$  is fixed).

Coupling between sound waves and fluctuations of the director can be achieved through the temperature variation of Frank's elastic constants. Using this assumption we have attempted to extend the Imura-Okano-Fixman theory to the nematic phase. It is obvious that the coupling mentioned above is not necessarily the only one. Kawamura *et al.* [2] have interpreted the acoustical dispersion of MBBA on the basis of the Landau-Khalatnikov theory as a critical slowing down of the scalar order parameter  $S$ . We shall discuss this point at the end of this section. We have also neglected the intramolecular contribution which leads to an acoustical dispersion in the frequency range investigated.

In order to derive an expression for the anomalous sound attenuation we follow a procedure similar to that of the previous section. In terms of Fourier components for  $n_x$  and  $n_y$ , the distortion free energy is given by [22] :

$$F = \frac{1}{2} \sum_q \sum_{\alpha=1,2} [n_\alpha(q)]^2 [K_{33} q_{//}^2 + K_{\alpha\alpha} q_\perp^2] \quad (12)$$

where we have neglected the magnetic term describing the effects of magnetic field.

With  $\theta$ , the angle between  $z$  axis and the acoustical wave vector, eq. (12) can be written :

$$F = \frac{1}{2} \sum_q \sum_{\alpha=1,2} [n_\alpha(q)]^2 K_\alpha(\theta) q^2 \quad (13)$$

where

$$K_\alpha(\theta) = K_3 \cos^2 \theta + K_\alpha \sin^2 \theta.$$

For a non-oriented sample we assume that eq. (13) is still valid using the average elastic constant

$$K_0 = \frac{1}{3}(K_1 + K_2 + K_3).$$

Hereafter the effective elastic constant  $K$  will represent either  $K(\theta)$  or  $K_0$ .

In the vicinity of the transition, the Frank constants are small and terms of higher order in the Fourier expansion of free energy may become significant. Since the  $q^3$  term is excluded for symmetry considerations, the free energy density can be written as follows :

$$F = \frac{1}{2} \sum_q \sum_{\alpha=1,2} [n_\alpha(q)]^2 [Kq^2 + Qq^4] \quad (14)$$

where the elastic constant  $Q$  is assumed independent of temperature and angle. At this stage we do not make any assumption about the order of magnitude of  $Q$ . Later we will evaluate  $Q$  and verify *a posteriori* that the term  $Qq^4$  is significant only on a molecular length scale.

The equilibrium correlation function  $G(q)$  is derived from eq. (14) using the equi-partition theorem

$$G(q) \approx \langle [n_\alpha(q)]^2 \rangle = \frac{k_B T}{Kq^2 + Qq^4}. \quad (15)$$

We assume now that the dominant coupling of the sound wave and the correlation function is achieved through the temperature variation of the Frank elastic constants.

Consequently the local oscillating temperature produced by the sound wave induces a change in  $K(T)$  and  $G$  as :

$$K \rightarrow K + \frac{\partial K}{\partial T} T_\omega e^{i\omega t}$$

$$G(q) \rightarrow G(q) + G_1(q, \omega) e^{i\omega t}.$$

As with the isotropic phase we assume that the sound attenuation arises from the phase lag in the response of the orientational correlation function to the oscillations of the local temperature.

The relaxation equation for  $G(q)$  is given by :

$$\xi \frac{\partial}{\partial t} G(q, t) = - (Kq^2 + Qq^4) G(q, t) \quad (16)$$

where  $\xi$  is a viscosity coefficient.

This equation has exactly the same form as the relaxation equation of the correlation function derived by Fixman for critical binary mixtures [14]. Thus we may use the results of the Fixman calculation on the



critical sound attenuation. The complex heat capacity is given by :

$$\Delta C^*(\omega) = \frac{gk_B T^2}{4\pi^2} \left(\frac{\partial K}{\partial T}\right)^2 Q^{-2} \left(\frac{Q}{\omega\xi}\right)^{1/4} f(d)$$

$$f(d) = d^{-1/2} \int_0^\infty w^4(w^2 + 1)^{-1} \times$$

$$\times [-id^{-2} + w^2(w^2 + 1)]^{-1} dw$$

$$d = \sqrt{\omega_0/\omega}, \quad \omega_0 = K^2/\xi Q, \quad w = q/\sqrt{K/Q}.$$
(17)

The constant  $g$  describes the multiplicity of the contribution from the correlation functions to be considered.

Then the attenuation constant per wave length is derived from the imaginary part of  $\Delta C^*(\omega)$

$$\alpha_\lambda = \pi(\gamma_0 - 1) C_p^{0-1} \text{Im}(\Delta C^*)$$

$$= \frac{gk_B T^2(\gamma_0 - 1)}{4\pi C_p^0} \left(\frac{\partial K}{\partial T}\right)^2 Q^{-3/2} K^{-1/2} g(d)$$
(18)

$$g(d) = d^{-2} \int_0^\infty w^4(w^2 + 1)^{-1} \times$$

$$\times [d^{-4} + w^4(w^2 + 1)^2]^{-1} dw.$$

Then the frequency dependence of  $\alpha_\lambda$  is provided by the function  $g(d)$ . This function has been numerically calculated and plotted in figure 9;  $\alpha_\lambda$  goes through a maximum for  $\omega = 9.8 \omega_0$ . As in the isotropic phase the peak of attenuation is much broader than in the case of a single relaxation curve.

From eq. (18) and figure 9,  $\omega_{\max}$  and  $(\alpha_\lambda)_{\max}$  in the nematic phase are given by :

$$\omega_{\max} = 9.8 \frac{K^2}{Q\xi}$$
(19)

$$(\alpha_\lambda)_{\max} = 0.13 \frac{(\gamma_0 - 1) gk_B T^2}{4\pi C_p^0} \left(\frac{\partial K}{\partial T}\right)^2 Q^{-3/2} K^{-1/2}.$$

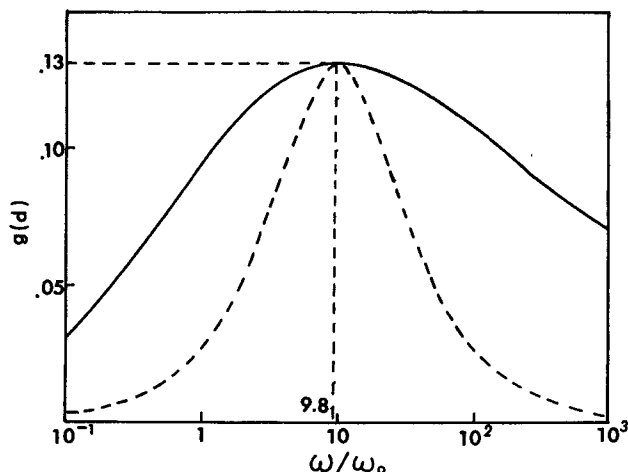


FIG. 9. — The function  $g(d)$  which provides the theoretical frequency dispersion of  $\alpha_\lambda$  in the nematic phase. The dotted curve represents the frequency dispersion of  $\alpha_\lambda$  for a single relaxation of same peak value, assuming  $\omega_r = \omega_{\max}$ .

Eq. (19) predict that both  $(1/\xi\omega_{\max})$  and  $(\alpha_\lambda)_{\max}$  diverge at the transition point as  $K^{-2}$  and  $(\partial K/\partial T)^2 K^{-1/2}$ , respectively. Furthermore, both  $\omega_{\max}$  and  $(\alpha_\lambda)_{\max}$  depend on the angle  $\theta$  between the director and the acoustical wave vector through the  $K(\theta)$  dependence.

4.2 RESULTS AND DISCUSSION. — Our experimental set up did not allow us to measure the attenuation of oriented samples at frequencies higher than 4 MHz. Hence the comparison between the theoretical and experimental behaviours of  $\omega_{\max}$  and  $(\alpha_\lambda)_{\max}$  have been carried out for non-oriented samples, whereas oriented samples were investigated only in the low frequency range.

— *Frequency dispersion of ultrasonic attenuation.* — The frequency dependence of  $\alpha_\lambda$  at different selected temperatures is shown in figure 10. One has mentioned

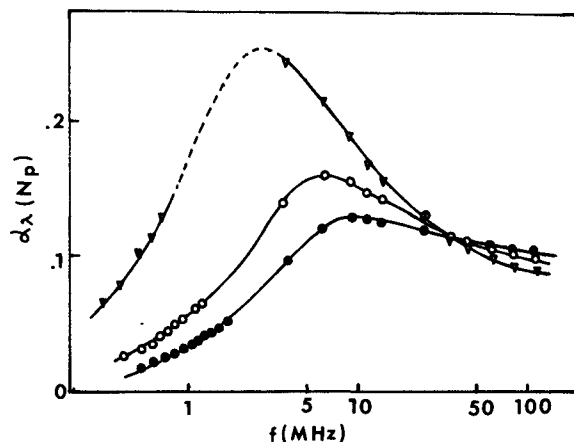


FIG. 10. — The frequency dispersion of  $\alpha_\lambda$  for non-oriented samples of PCB in the nematic phase. Individual curves are for various temperatures :  $\nabla$  33.5 °C,  $\circ$  30 °C,  $\bullet$  25 °C.

above (Fig. 9) that the theoretical frequency dispersion of the ultrasonic attenuation of a nematic phase is characteristic of a multiply relaxing fluid. Indeed, remarkable deviations from the single relaxation behaviour have been found for MBBA by Eden *et al.* [4]. Our experimental results on unoriented samples of PCB also show deviations from the single relaxation curve given by eq. (10), the fits becoming worse as one approaches the transition point.  $(\alpha_\lambda)_{\max}$  and  $\omega_{\max}$  have been determined using the same procedure as in the isotropic phase. Their temperature dependences are plotted in figures 11 and 12.

— *Divergence of  $(1/\omega_{\max})$  and  $(\alpha_\lambda)_{\max}$ .* The theoretical temperature dependences of  $\omega_{\max}$  and  $(\alpha_\lambda)_{\max}$  can be calculated from eq. (19) provided that the temperature dependences of Frank elastic constants and of viscous coefficient  $\xi$  are known.

We have assumed for  $K_i$  the following functions obtained for MBBA [23] :

$$K_1 = 1.5 |\tau|^{0.5} + 2.1 |\tau| + 0.102$$

$$K_3 = 2.43 |\tau|^{0.5} + 0.85 |\tau| + 0.089$$

$$\tau = (T - T_c)/T_c.$$
(20)

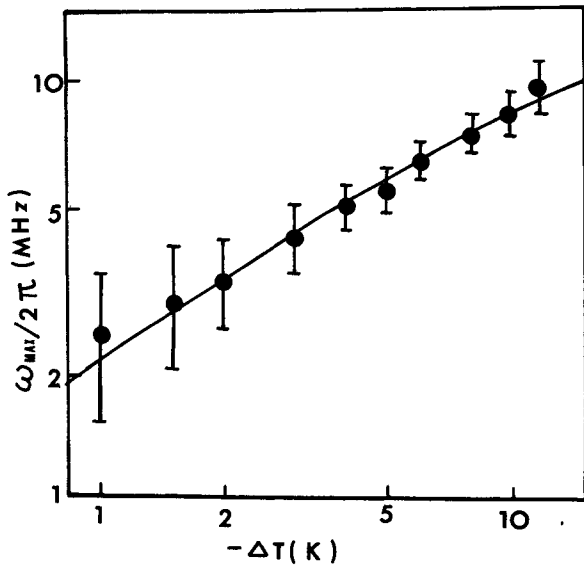


FIG. 11. — Temperature dependence of  $(\omega_{\max}/2\pi)$  for non-oriented samples of PCB in the nematic phase. The solid line is the theoretical one.

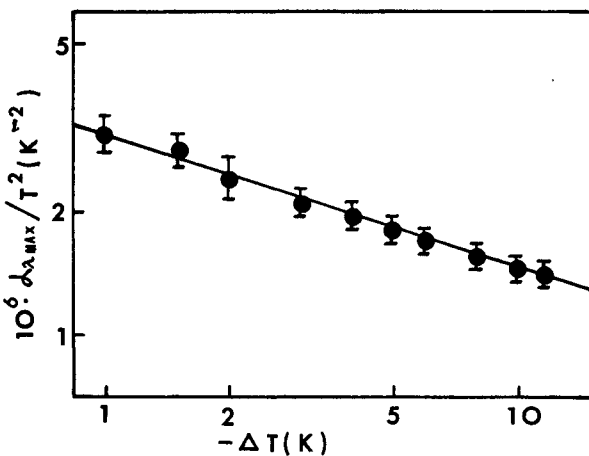


FIG. 12. — Temperature dependence of  $(\alpha_\lambda)_{\max}/T^2$  for non-oriented sample of PCB in the nematic phase. The solid line has been drawn arbitrarily through the points.

As in the isotropic phase the temperature dependence of  $\xi$  was approximated to that of capillary viscosity  $\eta_0$ . The values of  $K_1^2$  and  $K_3^2$  were corrected for the  $\eta_0$  temperature dependence and normalized so that  $K_{\text{corr}}^2 = K^2$  at  $T = 35^\circ\text{C}$ .

Because of the lack of complete data relative to  $K_2$ , the averaged elastic constant  $K_0$  is assumed to be  $\frac{1}{2}(K_1 + K_3)$ . Thus, according to eq. (19) the theoretical temperature dependence of  $\omega_{\max}$  is given by that of  $K_0^2$  corrected for the activation energy of  $\xi$ .

The calculated and experimental temperature dependences of  $\omega_{\max}$  are compared in figure 11; the agreement is fairly good. Let us point out that Eden *et al.* have also found a value (0.4) for the critical exponent of MBBA close to the theoretical value ( $\sim 0.5$ ).

In the same way, we have calculated from eq. (19) the theoretical temperature dependence of  $(\alpha_\lambda)_{\max}$ . According to the calculations  $(\alpha_\lambda)_{\max}$  should diverge

at the transition with a critical exponent approximately equal to 0.9. Experimentally, one finds that  $(\alpha_\lambda)_{\max}$  diverges with an exponent of 0.33 (Fig. 12). We will discuss this point below.

— *Divergence of the low frequency attenuation constant for oriented samples.* — Temperature dependences of the 0.5 MHz values of  $\alpha_{\parallel}/f^2$  and  $\alpha_{\perp}/f^2$  have been calculated from eq. (19) and (20) assuming  $K_\alpha = K_1$ . As shown in figure 13, the experimental attenuation constants diverge more slowly than the theoretical ones, confirming the preceding result concerning the divergence of  $(\alpha_\lambda)_{\max}$  in unoriented samples.

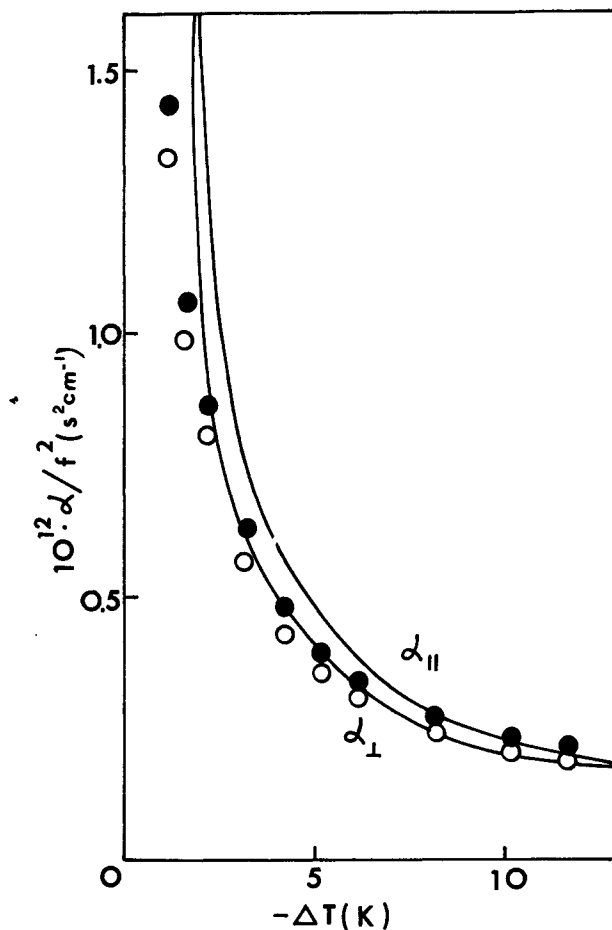


FIG. 13. — Temperature dependence of  $\alpha_{\parallel}/f^2$  and  $\alpha_{\perp}/f^2$  for PCB at 0.5 MHz. The solid lines are fits to the data by eq. (19).

— *Evaluation of Q and  $\xi$ .* — Using the same values of  $\gamma_0$ ,  $Cp_0$  as in the isotropic phase and  $g = 2$ , we have evaluated from the experimental values of  $\omega_{\max}$  and  $\alpha_\lambda$  at  $\Delta T = -1\text{ K}$  the order of magnitude of Q and  $\xi$ :

$$Q \sim 0.6 \times 10^{-20} \text{ dyne cm}^{-2} \quad \xi \sim 4 P.$$

We note that the ratio  $Q/K_0$  is of the order of magnitude of the square of a molecular length

$$Q/K_0 \sim 300 \text{ \AA}^2.$$

On the other hand, the value obtained for  $\xi$  is one order of magnitude higher than the capillary viscosity  $\eta_0$ . Indeed, the macroscopic viscosity may not correspond directly to the microscopic coefficient of friction. Furthermore the evaluation of  $\xi$  and  $Q$  lies on that of the leading factor in eq. (19) which gives  $(\alpha_\lambda)_{\max}$  as a function of  $(Q^{-3/2} K^{-1/2})$ .

In summary, the proposed model can explain at least qualitatively the critical process in the nematic phase. In particular, it accounts for the divergence of  $\omega_{\max}$  at the transition temperature. The major failure of the theory concerns the divergence of  $(\alpha_\lambda)_{\max}$  for non-oriented samples. Three main causes may be at the origin of the observed discrepancy :

— The parameter  $Q$  may decrease with increasing temperature.

— The theoretical temperature dependence of  $(\alpha_\lambda)_{\max}$  is essentially controlled by that of  $(\partial K/\partial T)^2$  which can be seriously in error, whereas  $\omega_{\max}$  diverges as  $K^2$ .

— The intramolecular processes have not been taken into account in the above analysis. One knows from earlier studies that these processes give a contribution to the attenuation in the same range of frequencies. This contribution, unknown for PCB, should be subtracted. In fact, the attenuation constant of PAA which shows no intramolecular relaxation increases more sharply than PCB when approaching the transition in the nematic phase.

At this stage, we compare our experimental results with the model proposed by Kawamura *et al.* [2]. These authors obtained theoretical expressions of  $(\alpha_\lambda)_{\max}$  and  $\omega_{\max}$  in terms of  $(T_1 - T)$ , where  $T_1$  is the *critical point* above which the isotropic phase is the only stable phase [22]. Since  $T_1$  is very close to  $T_c$  ( $T_c - T_1 \simeq 0.1$  K), one may compare directly to their equations the measured variations of  $(\alpha_\lambda)_{\max}$  and  $\omega_{\max}$  versus  $T_c - T$ . Their equations predict that in a narrow temperature range just below  $T_c$ ,  $(\alpha_\lambda)_{\max}$  will be almost constant when  $(T_1 - T)$  is sufficiently small and go to a smaller constant value with increasing  $(T_1 - T)$  via region proportional to  $(T_1 - T)^{-1/2}$ . Indeed our experimental temperature dependence of  $(\alpha_\lambda)_{\max}$  can be approximated to such a behaviour. On the other hand  $\omega_{\max}$  would increase from an almost constant value near  $T_c$  as  $(T_1 - T)$  with increasing  $(T_1 - T)$ . This prediction is not confirmed by our experimental results and those of Eden *et al.* in MBBA since  $\omega_{\max}$  varies approximately as  $(T_c - T)^{0.4}$ .

Therefore from the acoustical data obtained up to now, one cannot conclude in favour of one specific model. Presumably the acoustical attenuation arises from coupling of sound waves with both fluctuations of the director and magnitude of the order parameter. Unfortunately it is not possible at this stage to evaluate the relative orders of magnitude of the contribution provided by the two effects.

**5. Angular dependence of the attenuation constant in the nematic phase.** — 5.1 THEORY. — The hydrodynamic theory of compressible nematic fluids has been examined by Forster *et al.* [9] who derived the following expression for the sound attenuation :

$$\frac{\alpha}{f^2} \frac{\rho V^3}{2 \pi^2} = (2 v_1 + v_2 - v_4 + 2 v_5) + 2(v_4 - v_1 - v_5) \sin^2 \theta - \frac{1}{2}(v_1 + v_2 - 2 v_3) \sin^2 2 \theta \quad (21)$$

where  $v_i$  ( $i = 1 \sim 5$ ) are viscosity coefficients, and  $v_4 - v_2$  and  $v_5$  represent bulk viscosities.

This expression, which does not take explicitly into account the relaxational processes, has been verified experimentally by Bacri [7, 8] in the high frequency range.

On the other hand, in the low frequency range, various groups [24] have shown that the attenuation close to the transition temperature can be fitted to the form

$$\alpha(\theta) = \alpha(0) [1 - \delta \sin^2 \theta] \quad (22)$$

with  $\delta \sim 0.1$ .

The comparison between eq. (22) and (21) indicates that the bulk viscosities ( $v_2 - v_4$ ) and  $v_5$  dominate the attenuation. We have examined whether the proposed model of coupling between sound waves and fluctuations of the director would lead to the observed  $\sin^2 \theta$  dependence.

Since the Frank constants are proportional to the square of the order parameter  $S$  [25], the effective constant  $K(\theta)$  can be written as :

$$K(\theta) = k(\theta) S^2 \quad (23)$$

where  $k(\theta)$  is assumed to be dependent of angle but independent of temperature. Correspondingly, the angular dependence of the attenuation constant is given by :

$$\alpha_\lambda(\theta) \sim \left( \frac{\partial S}{\partial T} \right)^2 S^{-1/2} \times [k_{\parallel} - (k_{\parallel} - k_{\perp}) \sin^2 \theta]^{3/2} g[d(\theta)] \quad (24)$$

The angular dependence of  $g(d)$  is complex. However, in the experimentally investigated range of  $d$  ( $0.5 \sim 1.5$  at 0.5 MHz)  $g(d)$  shows a weak angular dependence and can be approximated as  $b(1 + \delta' \sin^2 \theta)$  ( $b$  and  $\delta'$  vary with temperature).

Thus, neglecting terms of higher order

$$\alpha_\lambda \sim \left( \frac{\partial S}{\partial T} \right)^2 S^{-1/2} b k_{\parallel}^{3/2} \times \left[ 1 - \left( \frac{3}{2} \frac{k_{\parallel} - k_{\perp}}{k_{\parallel}} - \delta' \right) \sin^2 \theta + \dots \right] \quad (25)$$

which reproduces eq. (22).

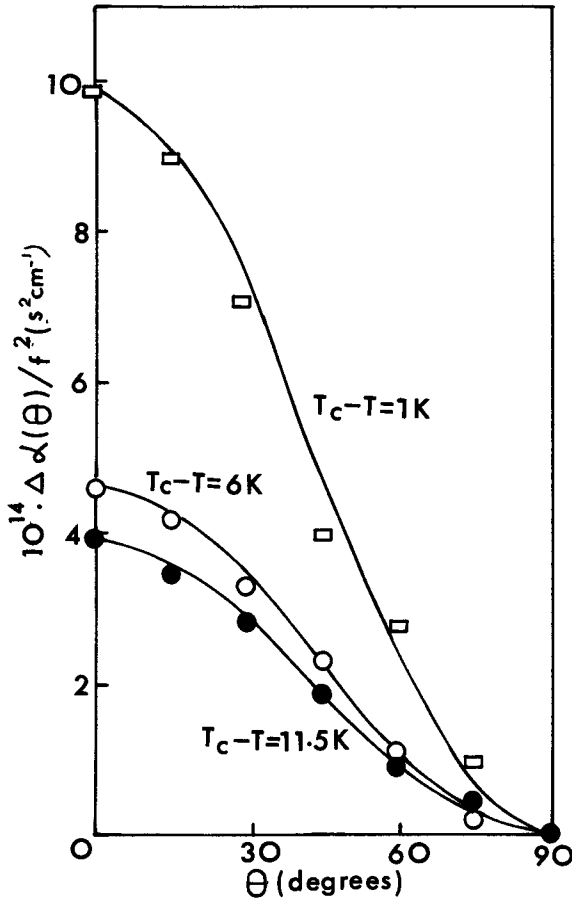


FIG. 14. — Angular dependence of  $\Delta\alpha(\theta)/f^2 = [\alpha(\theta) - \alpha(\pi/2)]/f^2$  for PCB at 1 MHz. The solid lines are fits to the data by eq. (22).

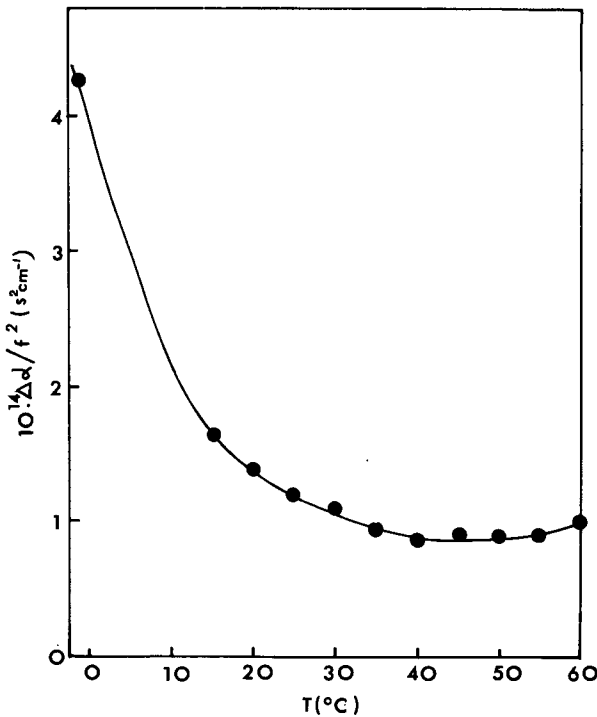


FIG. 15. — Temperature dependence of  $\Delta\alpha/f^2$  for Merck V at 1 MHz.

5.2 EXPERIMENTAL RESULTS AND DISCUSSION. — Figure 14 shows the angular dependence of the low frequency (1 MHz) attenuation constant of PCB for various selected temperatures close to the transition temperature. The experimental results are well described by eq. (22).

We have also examined the angular dependence of the attenuation constant for Merck V, far below the transition, in the temperature range where the intramolecular processes are predominant. In that range, the anisotropy of attenuation  $\Delta\alpha/f^2$  decreases as temperature increases as shown in figure 15. The change of sign of the temperature dependence of  $\Delta\alpha/f^2$  occurs at the same temperature range as the average  $\alpha/f^2$  of an unoriented sample [10].

Unlike the data relative to the critical process, the angular dependence of the attenuation constant is approximated by eq. (21) far below the transition. Eq. (21) can be rewritten as :

$$\Delta\alpha(\theta) = (\alpha_{\parallel} - \alpha_{\perp}) \cos^2 \theta - \alpha_c \sin^2 2\theta \quad (26)$$

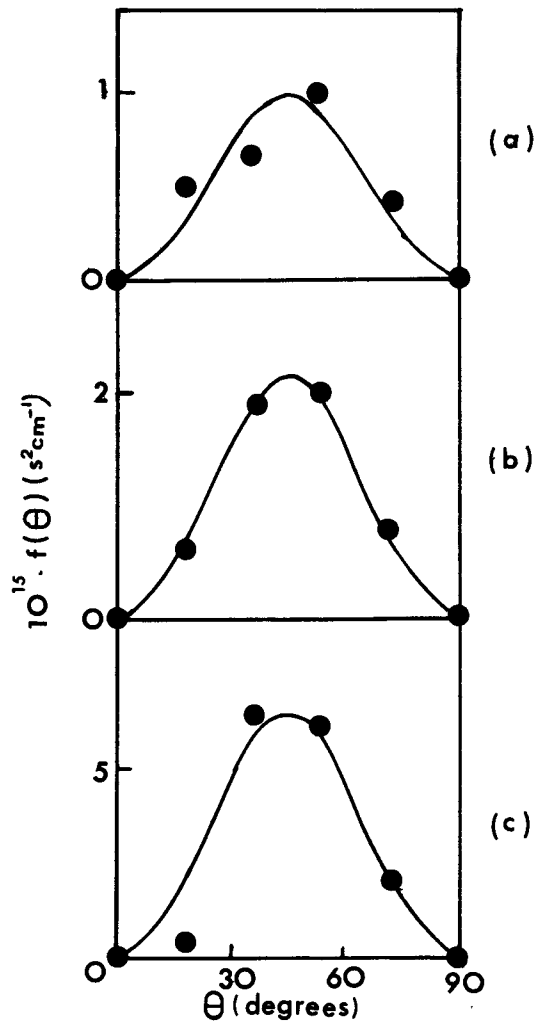


FIG. 16. — The function  $f(\theta)$  for Merck V. The solid lines are least square fits of a  $\sin^2 2\theta$  law. Individual curves are for various temperatures : a) 40 °C, b) 15 °C, c) - 1.5 °C.

with

$$\alpha_c = \frac{2\pi^2 f^2}{\rho V^3} \eta_c, \quad \eta_c = \frac{1}{2}(v_1 + v_2 - 2v_3). \quad (27)$$

One defines a function  $f(\theta)$  :

$$f(\theta) = -\Delta\alpha(\theta) + (\alpha_{//} - \alpha_{\perp}) \cos^2 \theta = \alpha_c \sin^2 2\theta. \quad (28)$$

The results of  $f(\theta)$  relative to Merck V, obtained at a frequency (1 MHz) much lower than the relaxation frequency of the intramolecular process [11] are reported in figure 16 and least square fitted to a  $\sin^2 2\theta$  curve.

The values obtained for  $\alpha_c$  were transformed to  $\eta_c$  according to eq. (27). The values of  $\eta_c$  are given for three temperatures in table I.

In the same table we have reported values of  $\eta_c$  obtained from eq. (27) for PCB in the low temperature range.

For both PCB and Merck V samples,  $\eta_c$  is of the same order of magnitude as that found at high frequency by Bacri for MBBA [7, 8].

TABLE I

$\eta_c$ (Poise)		$\eta_c$ (Poise)	
$T^\circ\text{C}$	Merck V	$T^\circ\text{C}$	PCB
—	—	—	—
— 1.5	1.11	23.5	0.43
15	0.37	29	0.39
40	0.17		

Thus one can conclude that eq. (21) fits the experimental data for frequencies far below the intramolecular relaxational frequency [11]. In the vicinity of the transition temperature, the critical attenuation is so large that the contribution arising from shear viscosities is negligible and the angular dependence of the attenuation fits eq. (22).

**Acknowledgments.** — The authors wish to thank Pr. Cl. Robert and Dr. R. Zana for the generous use of their equipment and Dr. Munch for kindly calculating curves of figure 9.

#### References

- [1] For reviews, see CANDAU, S. and MARTINOTY, P., in the International School of Physics *Enrico Fermi* (1974).
- [2] KAWAMURA, MAEDA, Y., OKANO, K. and IWAYANAGI, S., *Japan. J. Appl. Phys.* **12** (1973) 1510.
- [3] HOYER, W. A. and NOLLE, A. W., *J. Chem. Phys.* **24** (1956) 803.
- [4] EDEN, D., GARLAND, C. W. and WILLIAMSON, R. C., *J. Chem. Phys.* **58** (1973) 1861.
- [5] MARTINOTY, P., Thesis, Strasbourg, France (1972), unpublished.
- MARTINOTY, P., CANDAU, S., *C. R. Hebd. Séan. Acad. Sci., B* **271** (1970) 107.
- [6] CHISTYAKOV, I. G., *Sov. Phys. Usp.* **9** (1967) 551.
- [7] BACRI, J. C., *J. Physique* **35** (1974) 601.
- [8] BACRI, J. C., *J. Physique Lett.* **35** (1974) L-141.
- [9] FORSTER, D., LUBENSKY, T. C., MARTIN, P. C., SWIFT, J. and PERSHAN, P. S., *Phys. Rev. Lett.* **26** (1971) 17.
- [10] CANDAU, S., MARTINOTY, P. and ZANA, R., *J. Physique Lett.* **36** (1975) L-13.
- [11] NAGAI, S., MARTINOTY, P., CANDAU, S. and ZANA, R., *Mol. Cryst. Liq. Cryst.*, to be published.
- [12] LANDAU, L. D. and KHALATONIKOV, E. M., *Collected Papers* of L. D. Landau, Ed. D. Ter Haar (Pergamon Press, New York) 1965, p. 626.
- [13] EDMONDS, P. D. and ORR, D. A., *Mol. Cryst. Liq. Cryst.* **2** (1966) 135.
- [14] FIXMAN, M., *J. Chem. Phys.* **36** (1962) 1961.
- [15] IMURA, F. and OKANO, K., *Chem. Phys. Lett.* **19** (1973) 387.
- [16] DE GENNES, P. G., *Mol. Cryst. Liq. Cryst.* **12** (1971) 193.
- [17] GRAY, G. W., HARRISON, K. J. and NASH, J. A., *Electron. Lett.* **9** (1973) 130.
- [18] Experimental details will be published elsewhere.
- [19] TORGALKOR, A., PORTER, R. S., BARRALL, E. M. and JOHNSON, J. F., *J. Chem. Phys.* **48** (1968) 8897.
- [20] ARNOLD, H., *Z. Phys. Chem.* **226** (1964) 146.
- [21] STINSON, T. W., III and LISTER, J. D., *Phys. Rev. Lett.* **25** (1970) 503. And : The correlation range of fluctuations of short-range order in the isotropic phase of a liquid crystal : preprint.
- [22] DE GENNES, P. G., *Mol. Cryst. Liq. Cryst.* **7** (1969) 325.
- [23] HALLER, I., *J. Chem. Phys.* **57** (1972) 1400.
- [24] DE GENNES, P. G., *The Physics of Liquid Crystals* (Clarendon Press, Oxford) 1974, p. 202.
- [25] LUBENSKY, T. C., *Phys. Rev. A* **2** (1970) 2497.