ACOUSTIC RELAXATION NEAR THE ISOTROPIC LIQUID-NEMATIC
PHASE TRANSITION IN THE NEMATIC PHASE
IN p-n-OCTYLOXY p’CYANOBI PHENYL

A. DRZYMAŁA, M. CIEŚLAK, H. HERBA and J. MICHALSKI
Chair of Physics, Technical University
(35-959 Rzeszów, ul. W. Pola 2)

The paper presents the results of the completion measurements on p-n-octyloxy
p’cyanobiphenyl [1] of the absorption and the ultrasonic velocity in the smectic-nematic phase
for a frequency range varying from 2.5 MHz to 60 MHz.

In the nematic phase near the isotropic liquid-nematic transition, the contributions to the
quantities αT and α/ν² the critical slowing down of the order parameter, the fluctuations of
the order parameter and the director fluctuations were analyzed. Each ultrasonic absorption
mechanism was characterized by an appropriate relaxation time near the phase transition.

1. Introduction

The classical theories [2, 3] fail to explain ultrasonic absorption in liquid crystals.
The disagreements observed can be explained with the aid of the relaxation theory of
absorption which takes into account both the molecular relaxation and the critical
molecular relaxation associated with present phase transitions. Near the phase transition
temperature, an increase of absorption (decrease of velocity) is observed. However,
during the phase transition the maximum of absorption and minimum (or strong
change) are observed. Now it has generally been agreed that the interaction of
ultrasonic with the order parameter fluctuation [2, 3, 4, 5] is the main mechanism of
absorption in the isotropic liquid crystal.

Near the phase transition in the nematic phase three [3, 4] absorption processes are
present:
1. Coupling of the sound wave and director fluctuations.
2. Coupling of the sound wave and order parameter fluctuations,
3. Coupling of the sound wave and critical slowing down of the order parameter.

The absorption coefficient

\[ \alpha = \alpha_n + \alpha_{\delta_1} + \alpha_2 + \alpha_v \] (1)
is given by components associated with the appropriate absorption mechanism where:
\( \alpha_n \) — described the director fluctuations, \( \alpha_{os} \) — describes the order parameter fluctuations, \( \alpha_s \) — described the slowing down of the order parameter, \( \alpha_v \) — described the absorption which is not related to any relaxation process.

According to the results of Nagai [4], we obtained the following forms for the absorption coefficients referred to the wave length:

\[
\alpha_n \chi(f) = \frac{f}{f_0} \left( 1 - \frac{f}{4\sqrt{2f_0}} \ln \left| \frac{1 + \sqrt{2f_0} + \frac{f}{f_0}}{1 - \sqrt{2f_0} + \frac{f}{f_0}} \right| + 2 \arctg \frac{\sqrt{2f_0}}{f - f_0} \right)
\]

(2)

![Graph showing the contribution of different absorption mechanisms](image_url)

**Fig. 1.** Contribution of different absorption mechanism in \( \alpha/f^2 \) for the mesomorphic nematic phase [5].
\[ \alpha_{o_3} \lambda(f) = E \sqrt{\frac{f}{f_0}} \left( \sqrt{\frac{f_0}{f}} + \sqrt{\frac{(f_0)^2}{f}} + 1 - \sqrt{\frac{2f_0}{f}} \right), \]  

(3)

\[ \alpha_{o} \lambda(f) = F \frac{\frac{f}{f_R}}{1 + \left(\frac{f}{f_R}\right)^2}, \]  

(4)

\[ \alpha_{v} \lambda(f) = Q f, \]  

(5)

where \( f_0, f_0', f_R \) are the relaxation frequencies of the director fluctuation, the order parameter fluctuation and the critical slowing down of the order parameter, respectively. All \( D, E, F \) and \( Q \) are free parameters which require to be adjusted. MANDELSTAMM and LEONTOWICH [6] explained the observed "above Stokes" part of absorption in terms of losses induced by the volume viscosity. It appears during the volume change in space where the substance is condensed. Starting from the theoretical results [5] obtained for the ultrasonic absorption in the nematic liquid crystals phase near the isotropic liquid-nematic transition, we can write [4, 7, 8]:

\[ \alpha \frac{2 \Pi^2}{f^2} \left( \eta_v^{(o)}(f) + \eta_v^{(o_3)}(f) + \eta_v^{(n)}(f) \right) + G \alpha_4, \]  

(6)

where: \( \rho \) – liquid crystal density, \( V \) – ultrasonic velocity, \( \eta_v^{(o)}, \eta_v^{(o_3)}, \eta_v^{(n)} \) denote the contribution of the critical slowing down of the order parameter, the order parameter fluctuating and the director fluctuations in volume viscosity, respectively. \( G \alpha_4 \) denotes the regulator part of the absorption [9]. The components of volume viscosity related to given processes assisting in the critical ultrasonic absorption are given by

\[ \eta_v^{(o)}(f) = \frac{A}{\sqrt{1 + \left(\frac{f}{f_R}\right)^2}}, \]  

(7)

\[ \eta_v^{(o_3)}(f) = \frac{B}{\sqrt{(2\Pi f)^2}} \left[ \sqrt{\sqrt{\frac{2f_0}{f}} + 1 + \frac{2f_0}{f} - \sqrt{\frac{4f_0}{f}}} \right], \]  

(8)

\[ \eta_v^{(n)}(f) = \frac{C}{2\Pi f_0} \left\{ 1 - \frac{1}{2} \sqrt{\frac{f}{2f_0}} \left[ 1 + \frac{1}{2} \ln \left( \frac{f}{f_0} + \sqrt{\frac{2f}{f_0}} + 1 \right) \right] + \right. \]  

\[ \left. + \arctg \left( \sqrt{\frac{2f_0}{f}} + 1 \right) + \arctg \left( \sqrt{\frac{2f_0}{f}} - 1 \right) \right\}. \]  

(9)
Here $A, B, C, G$ are constants which can be calculated from numerical calculations under the experimental results of $\alpha/f^2$. Starting from the measured quantities $\alpha\lambda$ and $\alpha/f^2$, one should determine the concentration of particular mechanisms near the phase transition so as to fit the experimental curves to the theoretical ones given by Eqs. (2)–(6). The dependence of different absorption mechanisms on the quantity $\alpha/f^2$ in the mesomorphic nematic phase is plotted in Fig. 1 [5].

2. Experiment and examined material

The p-n-octyloxy-p'-cyanobiphenyl $C_8H_{17}O$–$<\overline{O}>$–$<\overline{O}>$–CN liquid crystal processes the smectic mesophase and the nematic phase. The temperatures of the phase transitions were determined under the behaviour of the absorption and the velocity during the cooling process (Fig. 2) and the value of enthalpy by the DSC method at the M. Luther University Halle. The obtained results are solid state $\frac{326.35 \text{ K}}{29.3 \text{ KJ/mol}}$ smectic

\[ A \frac{341.45 \text{ K}}{62.5 \text{ J/mol}} \text{ nematic} \frac{348.55 \text{ K}}{754 \text{ J/mol}} \text{ isotropic liquid.} \]

The ultrasonic set US-6 (made at the IFTR in Warsaw) was used for absorption measurements which make possible research of liquid crystals (in the frequency range (9.8–60) MHz [10] or in a modified version in the frequency range: (2.5–7.5) MHz.

3. Experimental results, calculations and discussion

The experimental results of the wave propagation velocity for p-n-octyloxy p'-cyanobiphenyl [1] and calculations of $\alpha\lambda$ for five temperatures near the isotropic liquid-nematic transition (this temperature range contains the mesomorphic nematic phase) and formulas (2)–(4) allow us to find the characteristic relaxation frequencies for appropriate mechanisms for a given frequency range. The description of the main absorption processes near the phase transition formulas (1)–(5) requires the need to fit the set of parameters $f_0, D, f_0', E, f_R, F$ and $Q$ for the appropriate. The $\chi^2$ test was used to estimate the quality of fitting with $\chi^2$ given by

\[ \chi^2 = \sum_f \chi^2(f) = \sum_f \left( \frac{\alpha\lambda_{\exp}(f) - \alpha\lambda_{th}(f)}{\Delta \alpha\lambda(f)} \right)^2, \]
Here $\alpha_\text{exp}^{(0)}$ and $\alpha_\text{th}^{(0)}$ describe the experimental and theoretical values of the absorption coefficient referred to the wavelength respectively. The experimental error to $\alpha_\text{exp}^{(0)}$ described $\Delta[\alpha_\text{exp}^{(0)}]$. The parameters were determined from the minimum condition for $\chi^2$. The values of the absorption components associated with particular mechanisms were calculated with the help of the results presented in [4] and [5] (for a frequency range of the ultrasonic wave from 20 MHz to 60 MHz). The estimated parameters describing the absorption referred to the wave length for particular cases are presented in Table 1. Let $T_{IN}^{*}$ express the temperature for the $N-I$ phase transition which is the minimal temperature for the (metastable) isotropic phase ($T_{IN}^{*} < T_{IN}$) to exist and is very close to $T_{IN}$ the so-called hypothetical second kind phase transition temperature [11, 12]. Next, the behaviour of the relaxation times ($\tau_{\text{rel}} = 1/2.\pi f_{\text{rel}}$) for absorption mechanisms are described by the Fisher function [13]:

$$\tau = A \left( \frac{T_{IN}^{*} - T}{T_{IN}^{*}} \right)^{\lambda}.$$ 

(10)
Here \( \lambda \) is the critical exponent, the amplitude \( A \) is constant and \( T \) is the absolute temperature. The temperature \( T_{IN}^* \) and \( T_{IN} \) satisfy the inequality \( |T_{IN} - T_{IN}^*| \leq 1 \text{ K} \). The critical exponents were determined by least square analysis. The correlation coefficients \( r \) was obtained and was in agreement with the Keller criterion [15] with its limit values \( |r| \) depending on the measurements data number. The obtained values of the relaxation times described by Eq. (10) are presented in Table 2 where \( A_{f0}, \lambda_{f0}, A_{f0}', \lambda_{f0}' \) and \( A_{f}, \lambda_{f} \) denote the amplitudes and critical exponents of the relaxation time for the order parameter fluctuation, the critical slowing down of the order parameter, the correlation coefficient \( r \). The relaxation times of absorption processes for five temperatures are shown in Fig. 3.

We analyzed the variation of \( \alpha \) and \( \nu \) with temperature for the constant value of the ultrasonic incidence frequency (Fig. 3). The results indicate that we are dealing with a

---

### Table 1. Parameters of different absorption mechanisms fitted for ultrasonic frequency wave from 20 MHz to 60 MHz in p-n-octyloxy p'-'cyano biphenyl

<table>
<thead>
<tr>
<th>( T[K] )</th>
<th>( D )</th>
<th>( f_0[MHz] )</th>
<th>( \chi^2 )</th>
<th>( E[s^{-1/2}] )</th>
<th>( f_0[MHz] )</th>
<th>( \chi^2 )</th>
<th>( F )</th>
<th>( f_0[MHz] )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>346.15</td>
<td>0.50</td>
<td>42.5</td>
<td>6.33</td>
<td>153.0</td>
<td>39.77</td>
<td>8.48</td>
<td>1.17</td>
<td>48.77</td>
<td>0.31</td>
</tr>
<tr>
<td>347.15</td>
<td>0.51</td>
<td>42.0</td>
<td>7.21</td>
<td>153.91</td>
<td>38.96</td>
<td>8.78</td>
<td>1.20</td>
<td>45.50</td>
<td>0.56</td>
</tr>
<tr>
<td>348.15</td>
<td>0.48</td>
<td>40.0</td>
<td>10.18</td>
<td>153.17</td>
<td>37.96</td>
<td>9.68</td>
<td>1.22</td>
<td>43.00</td>
<td>0.65</td>
</tr>
<tr>
<td>349.75</td>
<td>1.12</td>
<td>36.8</td>
<td>4.29</td>
<td>130.72</td>
<td>35.97</td>
<td>12.05</td>
<td>1.32</td>
<td>34.40</td>
<td>3.43</td>
</tr>
<tr>
<td>350.35</td>
<td>1.16</td>
<td>34.0</td>
<td>4.63</td>
<td>128.37</td>
<td>34.96</td>
<td>11.84</td>
<td>1.40</td>
<td>27.23</td>
<td>9.36</td>
</tr>
</tbody>
</table>

---

### Table 2. Quantities of p-n-octyloxy p'-'cyano biphenyl describing the relaxation times for different absorption mechanisms

<table>
<thead>
<tr>
<th>( T_{IN}[K] )</th>
<th>( A_{f0} \cdot 10^{-8}[s] )</th>
<th>( \lambda_{f0} )</th>
<th>( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>350.95</td>
<td>0.23</td>
<td>( -0.113 \pm 0.002 )</td>
<td>0.991</td>
</tr>
<tr>
<td>( T_{IN}[K] )</td>
<td>( A_{f0}' \cdot 10^{-8}[s] )</td>
<td>( \lambda_{f0}' )</td>
<td>( r )</td>
</tr>
<tr>
<td>350.95</td>
<td>0.28</td>
<td>( -0.086 \pm 0.003 )</td>
<td>0.994</td>
</tr>
<tr>
<td>( T_{IN}[K] )</td>
<td>( A_{fR} \cdot 10^{-8}[s] )</td>
<td>( \lambda_{fR} )</td>
<td>( r )</td>
</tr>
<tr>
<td>350.95</td>
<td>0.12</td>
<td>( -0.234 \pm 0.004 )</td>
<td>0.995</td>
</tr>
</tbody>
</table>
FIG. 3. Relaxation times of different absorption mechanism for the isotropic liquid-nematic phase transition in p-n-octyloxy p'-cyanobiphenyl.

relaxation process which is conditioned by the character of the phase transition. The calculated characteristic relaxation times for the critical slowing down of the order parameter and the director fluctuation mechanisms are characteristic qualities near the phase transition.

References


Received on August, 10, 1990

Table 1. Quantities of parameters describing the relaxation times of...