Pretransitional behavior near the isotropic-nematic transition

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8.1. Introduction
Results are presented of the static nonlinear dielectric effect (NDE) and dielectric permittivity measurements in \( n \)-pentylcyanobiphenyl, a rod-like compound with the longitudinal permanent dipole moment. They are compared with the behavior in isotropic MBBA, a compound with the transverse permanent dipole moment. NDE measurement in both compounds showed strong, isomorphic quasi-critical NDE anomalies. For 5CB these measurements were carried out also under hydrostatic pressure. This gave pressure dependencies of the clearing temperature \( T_{IN}(P) \) and the temperature of the hypothetical continuous phase transition \( T^*(P) \) up to \( P = 400\text{MPa} \). The first ever clear extension of \( T_{IN}(P) \) dependence into...
the negative pressure domain with the comprehensive description via the Simon - Glatzel equation is also presented. Results of the application of the distortion-sensitive derivative analysis for the static dielectric permittivity applied for both sides of the I-N transition suggest the pseudospinodal and tricritical nature of the I-N transition.

The isotropic – nematic (I-N) phase transition has been a subject of studies over the last couple of decades [1-72]. The vast majority of experimental results support the simple mean-field description [8, 12-16, 27-32, 38-41, 44-47, 51, 52, 59, 60], strongly advised in basic monographs on the physics of liquid crystals [1-7]. This conclusion was mainly supported by strong pretransitional anomalies of the scattered light \((I_L(T))\) Kerr effect \((KE(T))\) or the Cotton-Mouton effect \((CME(T))\) which are described by the same temperature dependence, namely [1-7, 11-16, 27-30, 32-42, 54, 58, 69]:

\[
I_L, KE, CME \propto \frac{1}{(T - T^*)^\gamma} \tag{8.1}
\]

where \(T > T_{IN} = T^* + \Delta T\), \(T^*\) denotes the virtual, extrapolated, continues phase transition, \(T_{IN}\) is the I-N transition “clearing” temperature and \(T^*\) the hypothetical continuous phase transition, \(\Delta T\) is the measure of the discontinuity of the I-N transition, the exponent \(\gamma = 1\) is related to the singular behavior of susceptibility.

For the broad-band dielectric spectroscopy (BDS) such description agrees with the simple Arrhenius temperature or pressure behavior of relaxation times, its almost Debye distribution and the lack of the pretransitional anomaly of the static dielectric permittivity near the I-N transition [2, 5, 7, 31, 33, 44, 45, 46, 51, 52, 59, 60]. Nevertheless, a reliable reference describing a completely opposite behavior could be noted already in the early eighties [17-22] although it has hardly been cited since then. In 1981 Bradshow and Raynes [17] followed by Thoen and Menu [24] proved the occurrence of a strong pretransitional anomaly for the static dielectric permittivity \(\varepsilon'(T)\). The violation of the Arrhenius dependence was clearly shown by Johari [18, 19], Zeller [20-22] and Benguigi [25] already in the early eighties, although their tests mainly focused on liquid crystalline (LC) mesophases. Starting from the mid nineties these results were clearly confirmed in a set of studies on rod-like isotropic liquid crystals, including \(n\)-cyanobiphenyls [42, 43, 48-50, 54-58, 61-68, 71, 72], regarding both temperature and pressure paths, namely:

\[
\varepsilon' (T) = \varepsilon'^* + a_T^+ (T - T^*) + A_T^+ (T - T^*)^{1-\alpha} \tag{8.2}
\]

\[
\varepsilon' (P) = \varepsilon'^* + a_P (P^* - P) + A_P^* (P^* - P)^{1-\alpha} \tag{8.3}
\]
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where \( f = \text{const.} \) is the measurement frequency (\( 20 \text{Hz} < f < 100 \text{kHz} \), i.e. it is for the weakly ionic and the static regimes). The specific heat anomaly related exponent \( \alpha = 0.5 \). \( T^* \) and \( P^* \) denote temperature and pressure of the virtual, extrapolated “critical” point.

It was shown in refs. [64, 65, 72] that similar description extends also for the evolution of maxima of loss curves peak:

\[
\varepsilon''_p(T) = \varepsilon''_p^* + A_T (T - T^*) + A_T'' (T - T^*)^{1-\alpha}
\]

where \( \varepsilon''_p \) is for \( 20 \text{MHz} < f_{\text{peak}} < 200 \text{MHz} \), \( \varepsilon''_p \) and \( f_{\text{peak}} \) are coordinates of dielectric loss curves.

The validity of the above dependencies was next confirmed by the distortion-sensitive derivative analysis, namely [49, 54, 55, 64, 72]:

\[
\frac{d\varepsilon'}{dT}, \frac{d\varepsilon''}{dT} = \text{const.} + A (T - T^*)^{1-\alpha}
\]

It is noteworthy that the above quasi-critical behavior of dielectric permittivity agrees well with the evidence for the pretransitional anomalies of density \( (\rho(T)) \), and the specific heat \( (c_p(T)) \), namely [5, 6, 9-11, 23, 26]:

\[
c_p(T) \propto (T - T^*)^{-\alpha}
\]

\[
\rho(T) \propto (T - T^*)^{1-\alpha}
\]

The evidence for the pretransitional behavior in the nematic phase is also puzzling. In the early eighties Thoen and Menu [24] gave a clear evidence for the tricritical-like nature of the I-N transition basing on measurements in 8CB, namely they showed that:

\[
\Delta\varepsilon' = \varepsilon'_\parallel - \varepsilon'_\perp = \Delta\varepsilon'^* + (T'^* - T)^\beta
\]

where \( \beta = 0.25 \) is the order parameter related exponent, \( T < T_{\text{IN}} = T'^* - \Delta T'^* \), the temperature \( T'^* \) denotes the extrapolated temperature of the superheated nematic phase and \( \Delta T'^* \) is the related measure of the discontinuity of the N-I transition.

However, in following years most often the simple mean field value of the order parameter \( \beta = 0.5 \) exponent was indicated [1-6 and refs therein]. Instead of relation (8), often the general validity of the empirical relation proposed by Haller was suggested, namely [5, 6, 44]:

\[
\Delta\varepsilon' \propto (T - T_{\text{IN}})^{\beta'}
\]

with the material dependent value of the power exponent \( \beta' \), usually between 0.1 and 0.2. However, it is obvious that the Haller equation can be considered
only as a rough approximation possible to apply far away from the N-I transition where the difference between $T_{IN}$ and $T^*$ is not significant for fitting. Regarding these results noteworthy are the recent state-of-the-art studies in $n$CB, from $n = 5$ to 8, by Marinelli and Mercuri [53] based on photopyroelectric measurements. They obtained a clear $\beta = 0.25$ value for 5CB and a small shift up when moving towards 8CB. The latter fact they associated with the increasing influence of presmectic fluctuations.

This contribution concludes the author’s measurements for the pretransitional behavior near the I-N transition manifested in dielectric measurements, including the fluctuation sensitive nonlinear dielectric effect measurements. It focuses on $n$-pentylcyanobiphenyl (5CB) in isotropic and nematic phase. The hardly explored up to now distortion-sensitive derivative based analysis made it possible to obtain reliable estimations of basic parameters characterizing the I-N transition. The novel experimental evidence for the pressure evolution of $T_{IN}(P)$ and $T^*(P)$ is also given. It includes the first ever evidence for the bulk negative pressure, “stretched liquid”, behavior.

8.2. Experimental

Broad band dielectric spectroscopy (BDS) studies were carried out using the Novocontrol BDS 80 spectrometer with Quattro temperature unit. This enabled measurements with 5 digit resolution and $\pm 0.1 K$ temperature control. Measurements were conducted for the static frequency, $f = 10\, kHz$. Under strong electric dielectric permittivity ceases to be independent from the intensity of the electric field, namely [70]:

$$\varepsilon' (E) = \varepsilon' (E \to 0) + \Delta \varepsilon E^2 + ...$$

(8.10)

The measure of the “nonlinearity” is known as the nonlinear dielectric effect (NDE), ie. $NDE = [\varepsilon(E) - \varepsilon(E \to 0)]/E^2$. In $NDE(T)$ measurements the few millisecond lasting pulse of the strong electric field causes a shift of dielectric permittivity in a given tested liquid, monitored via radio frequency: weak measuring field: in this case the extremely static limit $f_{meas}^{NDE} = 20kHz$ was applied. The NDE was measured using the modulation domain based, single generator and aperiodic HV excitation NDE spectrometer which design is given in ref. [70]. All dielectric measurements were carried out in bulk (the gap of capacitor $d = 0.3 mm$) using temperature and pressure set up described in ref. [64]. Regarding tests in the nematic phase, two identical gold-coated and thermally stabilized capacitors were placed in $B = 1.2 T$ magnetic field. This enabled simultaneous measurements of the parallel ($\varepsilon''_\parallel$) and perpendicular ($\varepsilon''_\perp$) components of dielectric permittivity. Samples of 5CB, synthesized at Military
Technical University (Warsaw) were always carefully degassed immediately prior to measurements.

### 8.3. Results and discussions

Molecular origins of the linear ($\varepsilon$) and the nonlinear ($NDE$) dielectric permittivities in LC compounds are qualitatively different. The linear permittivity is associated with the average ordering of permanent dipole moments [2, 17]. The NDE detects the appearance of heterogeneities which dielectric permittivity is different from the isotropic, fluidlike, surrounding [64, 70]. Hence, in the isotropic phase NDE can register prenematic fluctuation – heterogeneities, similarly to $KE$, $CME$ or $I_L$ measurements mentioned in the introduction. For the simplest static case when the condition $(f^{NDE}_{meas})^{-1} \gg \tau_{fluct}$ (the latter denotes the lifetime of prenematic fluctuations) the following equation is fulfilled [64]:

$$NDE(T) \propto \langle \Delta M^2 \rangle_V \chi^* = \frac{A_{NDE}}{T-T^*} = \frac{2}{3a} \varepsilon_0 \frac{(\Delta \varepsilon^0)^2}{T-T^*}$$

(8.11)

where $\langle \Delta M^2 \rangle_V$ is the mean of the square of the order parameter local fluctuations, the compressibility $\chi^* \sim (T - T^*)^{-\gamma}$, the exponent $\gamma = 1$, $\Delta \varepsilon^0$ denotes the anisotropy of dielectric permittivity of a perfectly ordered sample within the static frequency limit, $a$ is the constant amplitude in the square term in the Landau-de Gennes expansion [3, 48, 64].

Fig. 8.1 shows validity of relation (11) for the isotropic phases of two nematogens: MBBA, with the transverse position of the permanent dipole moment within the molecule, and 5CB with longitudinal dipole moment. For both cases relation (11) is fairly fulfilled. This enables a simple and reliable estimation of $T^*$ and $\Delta T$ from the linear regression of experimental data.

Worth noting is the lack of any distortions in the immediate vicinity of the clearing point, which do not appear also for the I-SmA transition [55,56-58]. This is the unique feature of the static NDE, absent for methods involving light ($KE$, $CME$, $I_L$) [3, 12-16, 27, 38]. Such a difference can be associated with the fact that for methods involving light always in the isotropic phase the condition $(f^{NDE}_{meas})^{-1} \ll \tau_{fluct}$, ie. it is the opposite case to the one applied for the static NDE. Consequently, the NDE studies made the reliable estimation of $T^{N}(n), T^*(P)$ and $\Delta T(P)$ in the homologous series on $n$-cyanobiphenyls possible [56, 70, 72]. NDE studies also enabled estimations of the pressure evolution of these magnitudes [54-58, 64]. Such results for 5CB, based on novel measurements, are shown in Fig. 8.2.
Figure 8.1. Static nonlinear dielectric effect in isotropic 5CB and MBBA: compounds with the longitudinal and the transverse location of the permanent dipole moment within molecule, respectively. The inset shows reciprocals of measured effects from the main plot. Dashed arrows indicate clearing temperatures and solid arrows temperatures of hypothetical continuous phase transitions.

Figure 8.2. Pressure dependence of the clearing temperature (squares) and the temperature of the virtual continuous phase transition (stars). Solid and dashed lines portray the description via the Simon-Glatzel relation, with parameters given in the Figure.

This figure presents the first ever dependence covering a very large range of positive pressures and the extension into the metastable, isotropically stretched liquid, i.e. the negative pressure domain [73]. To the best of the author’s knowledge there is only single experimental result regarding the negative pressure domain in LC compounds. It bases on observations of clearing temperatures of 5CB droplets in the cooling glass sucrose matrix [74]. The value of the negative pressure in ref [74] was estimated from the shift of the clearing temperature, assuming the linear extrapolation of pressure dependence from the positive pressure region. However, it is well known that
such extrapolation hardly or not at all occurs for stretched liquids [73]. Moreover, the clearing temperature is extremely sensitive even to small contaminations [3, 34] which is the inestimable artifact in ref. [74]. Fig. 8.2 presents results of the first ever Berthelot tube [73 and refs therein] based measurements, for which all these parasitic artefacts are absent. It is noteworthy that the negative and the positive pressure data are parameterized by the same Simon-Glatzel (SG) [75-82] function, namely:

\[ T_{IN}(P), T^* (P) = T_{ref} \left(1 + \frac{\Delta P}{\Pi} \right)^{\frac{1}{b}} \]  

(8.12)

where \( \Pi \) is the disposable constant, \( \Delta P = P - P_{ref} \) is the pressure distance from the reference pressure \( P_{ref} \) related to reference temperature \( T_{ref} \). The exponent \( b \) should remain constant in the region of validity of the SG equation.

The SG relation constitutes the basic tool for the parameterizations of pressure dependencies of the melting (i.e. solid - liquid) temperature. In such studies the reference temperature is usually taken as the melting temperature under atmospheric pressure or for some characteristic point in the T-P plane, for instance the triple point [75-82]. It is noteworthy that the SG dependence is the consequence of the Clapeyron-Clausius equation and this underlying physical basis makes its extrapolation beyond the limits of experimental data possible. This is the case of Fig. 8.2 where values of the reference temperature \( T_{ref} \) were taken well below its value under atmospheric pressure what results in the negative pressure value of \( P_{ref} \). Values of optimized fitted parameters are given in Fig. 8.2. It is noteworthy that a liquid can be stretched only down to the cavitation limit where a liquid breaks and the homogeneous nucleation occurs. [73]. This limit is described by the spinodal curve hidden in the negative pressure domain [73]. One may expect that the negative pressure dependence of any physical property should not cross the spinodal curve. In this respect worth noting is the fact that the extrapolation via the SG relation in Fig. 8.2 has a clear asymptote in the negative pressure domain. To the best of the authors knowledge this is the first ever application of the SG relation which includes the negative pressure domain analysis. It is noteworthy that for positive pressures the application of NDE made the precise estimation of the pressure evolution of \( T_{IN}(P), T^*(P) \), and consequently \( \Delta T(P) \) possible. It is visible in Fig. 8.2 that the latter magnitude increases with rising pressure, in agreement with the only available test of such type in MBBA [83]. However, Fig. 8.2 shows that the value of \( \Delta T(P) \) start to increase also when entering the negative pressure domain.

The pretransitional behavior of the static dielectric permittivity \( \varepsilon'(T) \) in the isotropic phase of MBBA and 5CB are qualitatively different as shown in Fig. 8.3. Worth recalling here are NDE results in Fig. 8.1 where the same type of strong the pretransitional anomaly for both compounds occurs.
Figure 8.3. Static dielectric permittivity in isotropic 5CB, MBBA and their solution (concentrations are given in mass fractions). Results are normalized taking coordinates of the hypothetical continuous phase transition as the reference points, respectively for the given system [58].

For 5CB the temperature dependence of $\varepsilon'(T)$ is fairly well portrayed by relation (2) while no such anomaly can be observed for MBBA. The pretransitional anomaly of the static dielectric permittivity is the consequence of the cancellation of permanent dipole moments within prenematic fluctuations, which consequently results in the drop of $\varepsilon'(T)$ on $T \rightarrow T_{IN}$ when the size of prenematic fluctuations strongly increases. However, such cancellation can occur only for components of permanent dipole moment located along the long axis of the rod-like molecule. This factor is absent for MBBA with the transverse location of the permanent dipole moment. It was suggested in refs. [39, 40] that mixtures of rod-like LC compounds with longitudinal and transverse dipole moments can mime a single-component LC with the permanent dipole moment positioned at an arbitrary angle. This is the case of 5CB-MBBA mixture in Fig. 8.3. For this system the amplitude of pretransitional anomaly is much smaller than in MBBA. Moreover the inflection temperature of the temperature dependence of $\varepsilon'(T)$ shifts towards $T^*$ when the mentioned angle increases. It can be even hidden in the nematic phase, below $T_{IN}$.

The evolution of the static dielectric permittivity both in the isotropic and the nematic 5CB is presented in Fig. 8.4. Noteworthy is the fact that the mean dielectric permittivity in the nematic phase exhibits the behavior analogous to the one observed in the isotropic phase, namely:

$$\varepsilon'(T) = \varepsilon'^* + a_T^+ (T - T^*) + A_T^+ (T - T^*)^{1-\alpha}$$ (8.13)
Figure 8.4. Static dielectric permittivity in the isotropic and in the nematic phase of 5CB. The inset shows detailed behavior of dielectric permittivity in the isotropic phase and of the mean permittivity. Solid curves are parameterized by the above relations for $\varepsilon'(T)$ and $\varepsilon'_{\text{mean}}(T)$, respectively.

$$\varepsilon'_{\text{mean}}(T) = \varepsilon^{**} + a^+ (T^{**} - T) + A^+ (T^{**} - T)^{1-\alpha}$$

where $\varepsilon^{**} = 11.19 \pm 0.02$, $a^+ = -0.022 \pm 0.001$, $A^+ = 0.12 \pm 0.01$, $T^* = 309.25 \pm 0.2$, $\alpha = 0.49 \pm 0.02$ for the isotropic phase and $\varepsilon^{**} = 11.28 \pm 0.06$, $a^- = 0.0054 \pm 0.001$, $A^- = 0.11 \pm 0.03$, $T^{**} = 310.9 \pm 0.2$, $\alpha' = 0.51 \pm 0.06$ for the mean permittivity in the nematic phase. The mean permittivity is defined by $\varepsilon'_{\text{mean}} = 2\varepsilon'_{\perp}/3 + \varepsilon'_{\parallel}/3$.

The quasi-critical anomaly of the mean (“diameter”) was firstly found by the authors in 6OCB [62]. Experimental evidence regarding such phenomenon is puzzling. One can find evidence for a clearly linear behavior of the mean as well as for the anomaly of the mean, although without any analysis and even indication for the phenomenon in the text [5, 31, 41, 44, 62]. In the opinion of the authors worth recalling is the case of dielectric permittivity studies for isotropic and nematic 5CB [4] where perfectly no anomaly evidence on both sides of the I-N transition is even presented. This paper shows that a fatal error was probably made in cited in ref. [4] studies. Presented in Fig. 8.5 distortion-sensitive derivative analysis of experimental data from the inset in Fig. 8.4 clearly confirms the presence of the strong anomaly on both sides of the I-N transition in 5CB as well as the discussed via Fig. 8.4 analysis. Particularly it confirms that $\alpha = \alpha'$ and it give the real ration of “critical” amplitudes may be larger that it seems to be from the direct fitting in Fig. 8.5. This may be associated with the distortions on approaching the nematic-solid (N-S) transition, which can be detected due to the application of the derivative analysis. Is this the case of the hypothetical N-S “hidden transition”? In this respect worth mentioning is the fact that the latent heat of the N-S transition is only 10 times larger than the latent heat of the I-N transition [5].
Figure 8.5. The derivative of the mean dielectric permittivity in the nematic phase and of the permittivity in the isotropic phase, based on data from Fig. 8.4. Solid line are portrayed via relations ( ) and ( ) with exponents $\alpha = \alpha'$ and the ration of “critical amplitudes” $A^+/A^- = 1.3$.

Worth recalling is here the fact that the pretransitional anomaly is clearly visible also for the I-SmA transition in 12 CB. The ratio between measures of the discontinuity in 5CB and in 12CB is 8 [56].

On approaching $T_{IN}$ changes of $\Delta \varepsilon' = \varepsilon_{||}' - \varepsilon_{\perp}'$ follows the scalar order parameter evolution. But the discontinuity of the I-N transition matched with the number of adjustable parameters causes that the direct fit via relation (8) does not enable a good estimation of the order parameter exponent $\beta$. Fig. 8.6 shows that this problem can be solved by applying the derivative analysis of experimental data. In such case one may expect the validity of the following relation:

Figure 8.6. The order parameter evolution vs. temperature in the nematic phase of 5CB based on data from Fig. 8.4. The inset shows the derivative analysis of data from the main plot. It enables reliable estimation of the exponent $\beta$ and temperature $T'$. The resulted from the inset power relation parameterizes also the curve in the main plot.
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\[
\frac{d\Delta\varepsilon'}{dT} \propto (T^{**} - T)^{\beta^{-1}}
\]  

(8.15)

This procedure reduces the analysis to the simple linear regression, with one adjustable \((T^{**})\) parameter. Consequently the estimation of the order parameter exponent would be possible even for data located remote from the I-N transition, what is not possible via relation (8). The obtained exponent is definitely beyond the simple mean-field models \((\beta = 1/2)\) and agrees fairly well with the tricritical approximation where \(\beta = 1/4\) [3].

8.3. Conclusions

The results present the comprehensive discussion of static dielectric properties in one of the most classical LC compounds, \(n\)-pentylycyanobiphenyl (5CB). They show that properties of both linear and non-linear dielectric properties are dominated by pretransitional fluctuations regarding the isotropic and the nematic phase. This enormous sensitivity to pretransitional, fluctuation-related, artifacts is supported by the hardly applied up to now distortion – sensitive derivative analysis of experimental data. This made the reliable estimation of basic parameters defining the still puzzling nature of the I-N transition possible. The obtained values of exponents \(\alpha^+ = \alpha^- = 1/2\) and \(\beta = 1/4\) suggest the almost tricritical nature of this transition. Also the experimental ration of “critical” amplitudes \(A^+/A^-\) is reasonably agreement with the value predicted for the specific heat anomaly amplitudes near the tricritical point, what additionally suggest the possible general validity of the mentioned Mistura’s analysis, originally proposed for critical mixtures [49].

Systematic studies of the discontinuity of the isotropic – mesophase transition in \(n\)CB homologous series revealed a systematic increase of the discontinuity of the I-N transition \(\Delta T\) from ca 0.6\(K\) in 4CB to 8\(K\) in 12CB [56, 70]. Another factor which can increase the value of \(\Delta T\) is the hydrostatic pressure. These facts can suggest that the hypothetical decrease of \(\Delta T\) down to zero, i. e. the continuous I-N transition in a rod-like compound, can be eventually also possible in \(n\)CB series for decreasing length of the alkyl chain or for stretching the liquid. It is noteworthy, that for “longer” \(n\)CB with the isotropic - smectic A transition the increase of pressure always induces the I-N transition. Results of this paper cover the range of positive pressures and does not explored up to now the negative pressure domain. It was found the lowering of pressure below \(P = 0\) limit also may cause the increase of the discontinuity of the I-N transition. In the opinion of the authors this may suggest that at least for 5CB minimum value of \(\Delta T(P)\) exists. It may also suggest that for 5CB a smectic phase hidden in the negative pressure region may exist. Precursors of such hypothetical phase can also be responsible for
the distortions of the derivative of the mean dielectric permittivity observed on approaching the nematic - solid transition.

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**Bibliography**


