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Mean-field behaviour of the low frequency non-linear dielectric effect in the isotropic phase of nematic and smectic *n*-alkylcyanobiphenyls

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Results are presented of studies on the low frequency ($f = 250$ kHz) non-linear dielectric effect on approaching the nematic and smectic A phases in 4′-cyano-4-*n*-alkylbiphenyls (*n*CB, for $n = 6, 7, 8, 10, 11, 12$). In all cases, the mean-field behaviour was valid up to the clearing temperature. In the case of the isotropic-nematic transition (6CB, 7CB, 8CB), a quantitative agreement with the relation based on the Landau-de Gennes model was also ascertained. The specific feature of the research method applied was that the characteristic time introduced by the measurement field ($T' \approx 1/f$) was always greater than the relaxation time τ, i.e. the condition: $(T'/\tau) > 1$ was satisfied up to T_c.

1. Introduction

The properties of isotropic–liquid crystal phase transitions have been the subject of experimental and theoretical studies over the last several decades [1–9]. The best known experimental fact is the 'critical-like' behaviour of physical properties particularly sensitive to fluctuations in the isotropic phase, on approaching the clearing temperature [1–4 and references therein]. For instance, for the isotropic–nematic (I–N) phase transition, the light scattering (I), the Kerr effect (KE) and the Cotton–Mouton effect (CME) exhibit similar, simple behaviour [1–4]:

$$KE^{-1}, \quad CME^{-1}, \quad I^{-1} \propto (T - T^*)^{\gamma}$$
$$T > T_c, \quad T^* = T_c - \Delta T \qquad (1)$$

where T_c is the clearing (I–N) temperature, T^* denotes the extrapolated temperature of the hypothetical second order phase transition, ΔT is the measure of the discontinuity of the phase transition, and the exponent $\gamma = 1$.

The phenomenological Landau-de Gennes (LdG) model enabled a quantitative description of this mean-field type behaviour [1] to be made. It justified the determination of ΔT in relation (1) and allowed estimation of the amplitude of the susceptibility, molecular anisotropies of electric permittivity, polarizability, magnetic susceptibility and refractive index [1–4, 10–12], and even the position and value of the permanent dipole moment [13, 14]. Based on time resolved Kerr effect studies, the LdG model enabled additionally discussion of the relaxation time changes [11, 15, 16]. However a small deviation from this model in the immediate vicinity of the nematic phase seemed to be a permanent feature of the majority of experimental results [4, 17–20]. This is probably connected with the influence of non-classical fluctuations on approaching the 'critical temperature' T^*, or with the possible vicinity of the tricritical point [4]. These deviations may be responsible for a significant scatter of values of ΔT obtained for the same liquid crystalline material [4, 17–20].

The group of physical magnitudes very sensitive to fluctuations also includes the non-linear dielectric effect (NDE) which describes changes of electric permittivity $\Delta\varepsilon^{E}$ due to the application of a strong, steady electric field $\mathbf{E}$ [21, 22]. Applying the LdG model one can obtain [23]:

$$\frac{\Delta\varepsilon^{E}}{\mathbf{E}^2} + \frac{A_{NDE}}{T - T^*} = \frac{2}{3} a^{-1} \varepsilon_0 \frac{\Delta\varepsilon^{f} \Delta\varepsilon^{o}}{T - T^*} \qquad (2)$$

where: $\Delta\varepsilon^{E}/\mathbf{E}^2$ is the measure of NDE, a is the amplitude of the susceptibility (second rank term in the LdG series), and $\Delta\varepsilon^{o}$, $\Delta\varepsilon^{f}$ are molecular anisotropies of electric permittivity in the zero-frequency limit and for the measurement frequency (radio-range), respectively.

Tests conducted up to now for the isotropic phase of nematogens corroborate the mean-field character of the temperature changes in relations (1, 2), but a significant discrepancy in the value of amplitude A_{NDE} has been found [23–26].

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Markedly more complex behaviour has been observed for smectogens with an isotropic–smectic A ($I-S_A$) phase transition or with a narrow zone of nematic phase separating the smectic from the isotropic liquid. On approaching the clearing point, the reciprocals of the effects mentioned trend up or down from the mean-field linear relation (1) [4, 17–20]. In certain cases near T_c, no changes in value (i.e. 'saturation') have been detected [18, 27]. To the best of our knowledge no theory has yet been reported which would elucidate this variety of behaviours [4].

Comparison of experimental results for NDE [22–26] in the isotropic phase of liquid crystalline materials indicates that deviations from mean-field behaviour (relations (1, 2)) can be associated with the frequency of the weak applied measurement field ($f = 1{\cdot}5$–6 MHz).

We present here the results of studies on the low frequency ($f = 250$ kHz) NDE on approaching the nematic phase and smectic A phase in 4-cyano-4-*n*-alkylbiphenyls (*n*-cyanobiphenyls, *n*CB, for $n = 6$, 7, 8, 10, 11, 12). In all cases, the same mean field pretransitional behaviour up to T_c was observed. For the isotropic–nematic transition quantitative agreement with the LdG model was also ascertained.

2. Experimental

The NDE experiments were conducted using an apparatus constructed based on an idea proposed by Małecki [28], improved and constructed by Górny [29]. It comprises two generators, one a reference generator and the second with the test sample, connected in a differential system. Applying a strong electric field to the sample causes a change in the frequency difference between the generators. In our apparatus this change, which is proportional to the change in permittivity of the liquid tested, was recorded by a 12-bit digitizer (sampling time 10 µs) with a computer system.

A difficult design problem for an apparatus working at low frequency (250 kHz in our case) is to ensure the possibility of using short impulses of the constant field **E** together with sufficient sensitivity of measurement. The first feature could be of particular significance due to the possible influence of electrocaloric and hydrodynamic effects [1, 2]. For the materials tested here, the influence of length of impulse on recorded changes $\Delta\varepsilon$ was observed for impulses of a strong steady electric field **E** of duration greater than 20 ms. Results presented below were obtained using the rectangular impulses of a strong electric field (intensity 2000–7000 V cm^{-1}) lasting for 4–8 ms, repeated every 1–3 s. The intensity of the measurement field of $f = 250$ kHz was 20 V cm^{-1}. Recorded changes in capacitance induced by applying the field **E** had values of 1–5 fF. Typically, accumulations of 10–40 responses to impulses of the strong electric field were used for analyses. For every temperature difference from T_c, the condition $\Delta\varepsilon^E \propto \mathbf{E}^2$ was satisfied with an accuracy better than 2%. The samples were placed in a flat parallel capacitor (radius 10 mm, gap 0·5 mm) made from Invar [30]. The stabilisation of the temperature was better than 0·02 K h^{-1}. The temperature was measured by means of a platinum resistor (A1 class, DIN 43 760) placed in one of the covers of the capacitor and a Keithley 195 A multimeter with a resolution 0·01 K.

Studies have been conducted on 4′-cyano-4-*n*-alkylbiphenyls (*n*-cyanobiphenyls, *n*CB) with an isotropic nematic (I–N) phase transition (6, 7, 8, 11 CB) and an isotropic–smectic A ($I-S_A$) transition (10, 11, 12CB). For the sample of 7CB used, below the nematic phase of temperature width 8 K, a smectic A phase exists. Some authors suggest [18, 19] a narrow zone (0·5 K) of nematic phase between the isotropic and smectic A phases in 11CB. Some materials were purchased from Merck Ltd (UK) (8, 10, 11, 12, CB) and some (6, 7, 8, CB) were synthesised by Professor Dabrowski's group at the Technical Military Academy in Warsaw. All samples tested were degassed immediately prior to measurements. Their conductivity was always less than 3×10^{-11} (Ω^{-1} cm^{-1}). The data were processed using the ORIGIN 3·5 software (Microcal Software Inc.).

3. Results and discussion

Results of NDE measurements on the isotropic phase of the liquid crystalline materials tested are shown in figure 1. On passing from 6CB to 12CB, the pretransitional increment becomes increasingly weak. Remote from T_c, the NDE values for all the materials converge, within the limits of experimental error. Figure 2 shows the reciprocals of the measured pretransitional effects for four of the *n*-cyanobiphenyls on a normalised scale, relative to the amplitude A_{NDE} (table 1) appropriate for each given *n*CB. In all tested materials, NDE^{-1} varies linearly with temperature.

To show more clearly the possible deviations from the mean-field theory, the apparent critical amplitude $NDE\text{x}(T-T^*)$ versus $(T-T^*)$ is plotted on the semi-log scale shown in the inset on figure 2. The constant value of $NDE\text{x}(T-T^*)$, which according to relation (2) determines the amplitude A_{NDE}, shows that the mean-field relation appears to hold over a temperature range of $T - T^* \approx 40°$C, with no 'non-pretransitional' background effect. The quantitative agreement between the pretransitional effects obtained and the relation (2) derived from the Landau-de Gennes model enables a

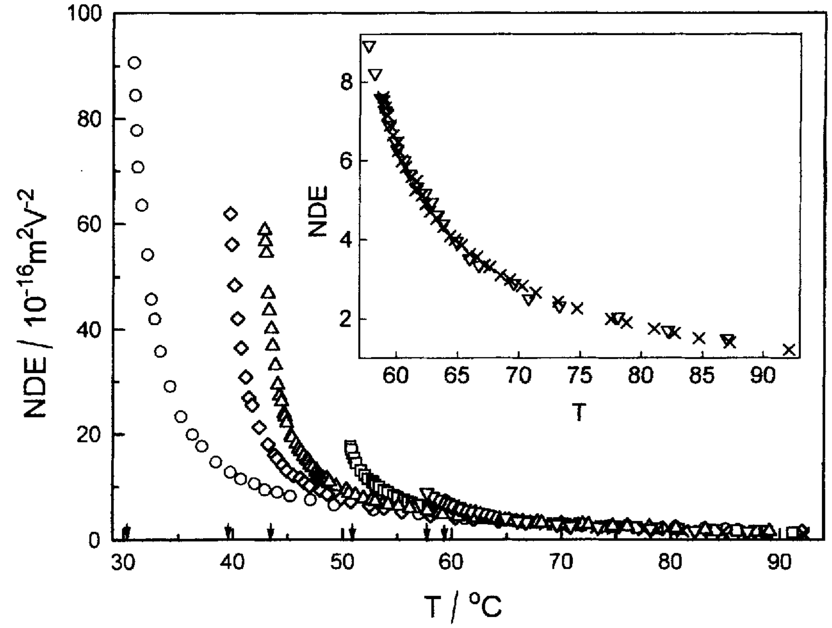

Figure 1. Results of NDE measurements on 6CB (○), 7CB (△), 8CB (◇), 10CB (□), 11CB (▽) and 12CB (X). The arrows show the clearing temperatures, T_c. The inset presents more details of the pretransitional behaviour in 11CB and 12CB.

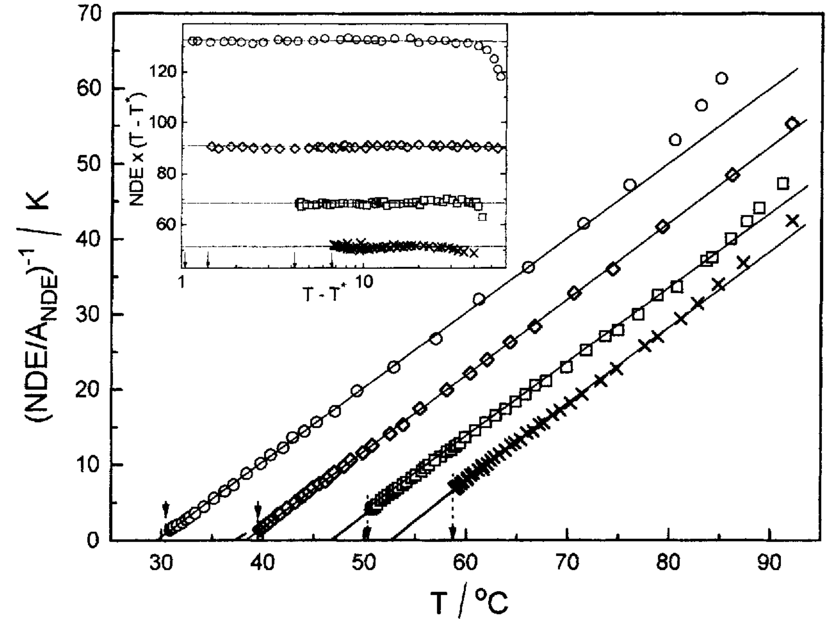

Figure 2. Reciprocals of NDE for 6CB (○), 8CB (◇), 10CB (□) and 12CB (X) on a normalised scale, relative to the amplitude A_{NDE} (table 1). The inset shows the apparent critical amplitude versus the temperature interval from the point of hypothetical continuous transition on a semi-log scale.

Table 1. Values of clearing temperature, discontinuity of the phase transition and pretransitional amplitude in *n*-cyanobiphenyls.

*n*CB	T_c/°C	ΔT/°C	$A_{\mathrm{NDE}}/10^{-16}\ \mathrm{m}^2\ \mathrm{V}^{-2}\ \mathrm{K}$
6CB	30·9	1·1	130 ± 4
7CB	42·7	1·35	87 ± 3
8CB	39·6$_5$	1·65	92 ± 3
10CB	50·7	4·4	69·5 ± 3
11CB	57·5	5·6	51·5 ± 3
12CB	58·9	6·9	52 ± 3

comparison of amplitude ratios. For instance:

$$\left(\frac{A_{\mathrm{NDE}}^{6\mathrm{CB}}}{A_{\mathrm{NDE}}^{8\mathrm{CB}}}\right)_{\mathrm{exp}} \approx 1{\cdot}42 \quad \text{and}$$

$$\left(\frac{A_{\mathrm{NDE}}^{6\mathrm{CB}}}{A_{\mathrm{NDE}}^{8\mathrm{CB}}}\right)_{\mathrm{LdG}} = \frac{((\Delta\varepsilon^{\circ})^2 a^{-1})_{6\mathrm{CB}}}{((\Delta\varepsilon^{\circ})^2 a^{-1})_{8\mathrm{CB}}} \approx 1{\cdot}44 \qquad (3)$$

where $\Delta\varepsilon_0 \approx 10{\cdot}8$ (6CB) and 11·7 (8CB) (measurements for $f = 100\,\mathrm{kHz}$); $a \approx 0{\cdot}053\,\mathrm{J\,cm^{-3}\,K}$ (6CB) and $0{\cdot}09\,\mathrm{J\,cm^{-3}\,K}$ (8CB) [15].

A good agreement between theory and experiment

Table 2. A comparison between the experimental and theoretical (LdG model, relations (2, 3)) ratios of the amplitudes A_{NDE}.

		LdG relation	
n-Cyanobiphenyls	Experiment	Data ref. [15]	Data ref. [11]
$\frac{A_{NDE}^{6CB}}{A_{NDE}^{8CE}}$	$1{\cdot}42 \pm 0{\cdot}08$	1·44	1·59
$\frac{A_{NDE}^{6CB}}{A_{NDE}^{8CE}}$	$0{\cdot}94 \pm 0{\cdot}07$	0·90	0·91
$\frac{A_{NDE}^{6CB}}{A_{NDE}^{8CE}}$	$1{\cdot}49 \pm 0{\cdot}08$	1·31	1·42

can also be found for 6CB/7CB, and 7CB/8CB (table 2). The values of ΔT obtained for these materials (table 1) lie within the limits determined by previous studies using other physical methods mentioned in the introduction [10–19].

The mean-field relation (1) also satisfactorily describes the pretransitional effects for the I–S_A phase transition in 10CB, 11CB and 12CB. This permits the estimation of values of the discontinuity of phase transition, ΔT and also amplitudes, A_{NDE} (figure 2 and table 1). Values of ΔT and A_{NDE} obtained for the *n*CBs tested are collected in table 1 and presented in figure 3.

4. Conclusions

The results presented above show that for the low frequency NDE the simple mean-field description may be valid for approaching both the I–N and I–S_A phase transitions. This conclusion differs from results obtained from previous experiments mentioned in the introduction [1–4, 10–20]. For the I–N transition a very good qualitative agreement with the relation derived from the Landau-de Gennes model has been found. This behaviour is undoubtedly associated with the frequency of the weak measuring field applied ($f = 250\,\text{kHz}$), particularly when taking into account a variety of pretransitional behaviour obtained for higher frequencies (1·5–6 MHz, [21–27]). The reciprocal of the frequency of the applied measurement field (i.e. $T' \approx 1/250\,\text{kHz} = 4\,\mu\text{s}$) may be approximately treated as a characteristic time of measurement. As a natural time scale on approaching the clearing point, the relaxation time (τ) of pre-nematic fluctuations (swarms) [11, 15] may be taken. Comparison of the two indicates that the following relation is valid up to T_c:

$$\frac{T'}{\tau} > 1 \qquad (4)$$

This condition (4) is not valid for methods applying light (KE, CME, I) or for previous NDE studies. Relation (4) could signify that the information obtained may come not from a single, average pre-nematic (pre-smectic) fluctuation, but from a group contained in the region of dimensions $\xi(T'/\tau) > \xi$, where ξ denotes correlation length. This additional averaging could have the effect that only orientational ordering, with a mean-field characteristic, influences the low frequency NDE. A similar influence of the time scale involved in the weak measurement field on the pretransitional behaviour of NDE was recently observed in critical solutions where

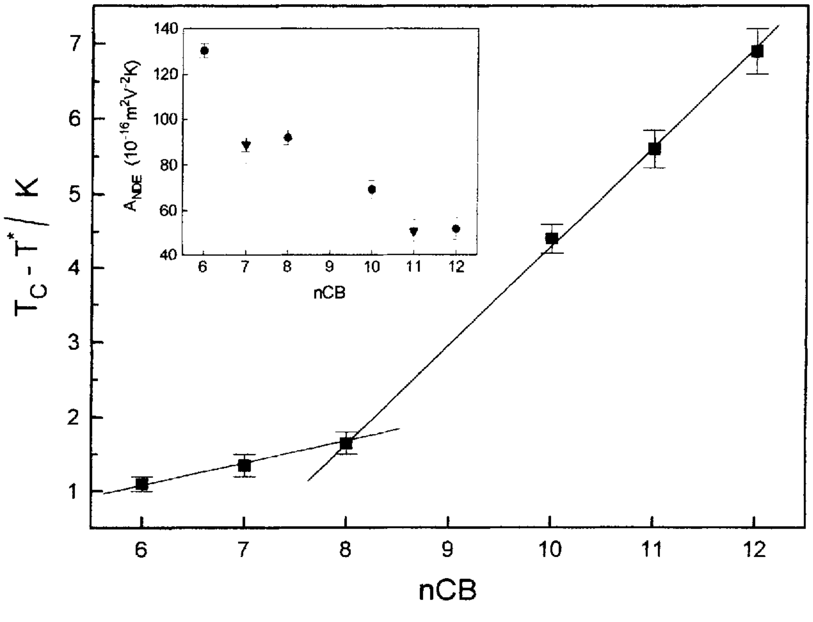

Figure 3. Values of discontinuity of phase transition and amplitude A_{NDE} for the *n*-cynobiphenyls tested.

a strong, steady electric field induces quasi-nematic ordering [29].

Also meriting attention is the systematic change in the value of the temperature discontinuity ΔT obtained in these experiments (figure 3). From this aspect it may be suggested that the *n*-cyanobiphenyls tested here may be divided into two groups (6, 7, 8CB) and (8, 10, 11, 12CB).

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