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Influence of measurement frequency on the pretransitional behaviour of the non-linear dielectric effect in the isotropic phase of liquid crystalline materials

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Results are presented of the non-linear dielectric effect (NDE) as a function of temperature (T) in the isotropic phase on approaching the nematic phase for the liquid crystalline materials 4′-cyano-4-hexylbiphenyl (6CB), 5-heptyl-2-(4′-cyanophenyl)pyrimidine (HCPP) and the smectic A phase of 4′-cyano-4-decylbiphenyl (10CB). For low measurement frequencies (f) the $NDE^{-1}(T)$ exhibits linear behaviour from the clearing temperature (T_C) up to about $T_C + 50$ K. Increase of f causes an increased deviation from this dependence near T_C. The influence of the measurement frequency can be associated with the link between the system time-scale, defined by the relaxation time of pretransitional processes(τ), and the measurement time-scale (f^{-1}). A quantitative agreement with the relation derived from the Landau–de Gennes model—$NDE^{-1}(T)$ analysis—and with the results of time- and frequency-resolved Kerr effect studies is shown. A possible influence of the intensity of the weak measurement field on the pretransitional effect in the immediate vicinity of T_C is discussed. Similarities between pretransitional behaviour in the isotropic phase of the nematogens and in the homogeneous phase of a critical binary solution are considered.

1. Introduction

Studies of the Kerr effect (KE), the Cotton—Mouton effect (CME), light scattering (I) and the non-linear dielectric effect (NDE) make it possible to investigate certain properties of liquid crystalline mesophases still in the isotropic phase. For the isotropic–nematic (I–N) phase transition, application of the Landau–de Gennes (LG) model gives [1–10]:

$$KE^{-1}, CME^{-1}, I^{-1}, NDE^{-1} = C^{-1}(T - T^*)^{\gamma} \qquad (1)$$

with $T > T_C$, $T^* = T_C - \Delta T$ and $\gamma = 1$. Here C is a constant amplitude characteristic for a given measurement method, T_C is the clearing temperature, T^* denotes the extrapolated temperature of the hypothetical continuous phase transition and ΔT is a measure of the discontinuity of the I–N transition.

The validity of the relation (1) leads to the broadly recognized conclusion concerning the mean-field characteristic of the I–N transition [1–4]. In experimental studies, the validity of relation (1) extends typically from T_C to $T_C + (5 \rightarrow 10\,\mathrm{K})$, except for the immediate vicinity of T_C where small, permanent discrepancies appear [4–10]. These are related to the possible vicinity of the tricritical point (TCP) or to the crossover from the mean-field to the critical region [4]. Unfortunately the weakness of these deviations makes their numerical analysis ambiguous [4, 6–10]. The situation for the isotropic–smectic A (I–SmA) phase transition is less clear. Here the linear temperature behaviour predicted by relation (1) is only observed far from the clearing point [4, 6–11]. However, recent theoretical [12–15] and experimental [16] investigations point to yet another possibility leading to this relation, i.e. a classical but simultaneously critical, fluid-like pretransitional behaviour. The I–N phase transition point falls here upon a hypothetical coexistence curve and consequently T^* becomes a pseudo-spinodal temperature [12–15].

Noteworthy is the specific position of the NDE in the group of physical properties mentioned above. In this research method, the frequency of the measuring field f lies in the radio-range. The importance of this feature has been shown by recent low frequency (LF NDE) studies ($f = 250$ kHz) involving the series of n-cyanobiphenyls [17]. They showed a linear dependence of $NDE^{-1}(T)$ in the range from T_C to $T \approx (T_C + 50\,\mathrm{K})$, both for the I–SmA and the I–N phase transitions. This untypical behaviour may be associated with the coincidence between frequency f and the correlation time of pretransitional processes τ, observed previously in the analysis of the critical behaviour in critical solutions [18]. In 1990, Pyżuk [19] pointed out the possible importance of this factor when analysing the NDE for

$f \approx 1{\cdot}5$ MHz for the isotropic phase of 5-heptyl-2-(4′-cyanophenyl)pyrimidine (HCPP, I–N transition). The relation applied by Pyżuk for describing the experimental data can be written in the form:

$$NDE(T) = NDE_{\mathrm{B}} + [NDE_{\mathrm{C}}^{\omega\tau<1} + NDE_{\mathrm{D}}^{\omega\tau>1}], \quad \omega = 2\pi f \tag{2}$$

where subscript B denotes the non-critical background effect and terms in the square bracket are associated with the pretransitional behaviour. $NDE_{\mathrm{C}}^{\omega\tau<1} \propto (T - T^{*})^{-1}$ for $T > T_{\mathrm{C}} = 10$ K and $NDE_{\mathrm{D}}^{\omega\tau>1} \propto (T - T^{*})^{-3\pm0{\cdot}6}$ in the immediate vicinity of T_{C}.

This paper aims to present a preliminary study of the influence of measurement frequency on the pretransitional behaviour in the isotropic phase of some liquid crystalline materials.

2. Experimental

Studies of the non-linear dielectric effect were carried out using the apparatus described in detail in ref. [20]. Measurements involved the application of two electric fields: a weak measurement field of radio frequency (peak–peak voltage $U_{\mathrm{p\text{-}p}} = 1{\cdot}3 \rightarrow 10$ V, $f = 67\,\mathrm{kHz} \rightarrow 9\,\mathrm{MHz}$) and a strong electric field in the form of rectangular pulses of duration $\Delta t = 2 \rightarrow 8$ ms and $V = 200 \rightarrow 1000$ V. For the applied duration of the pulses the condition $\Delta t \gg \tau$ was always fulfilled so that the measured value of the NDE was the stationary one. In such a case: $\varepsilon^{E} = \varepsilon + 3bE^{2} + \ldots$ (where ε, ε^{E} are the dielectric permittivities in a weak and a strong electric field E, respectively) and the experimental value of the NDE is $\Delta\varepsilon^{E}/E^{2} = (\varepsilon^{E} - \varepsilon)/E^{2} = 3b$ [21]. Taking into account this definition, the following relation may be derived from the LG model in the isotropic phase:

$$\frac{\Delta\varepsilon^{E}}{E^{2}} = \frac{C_{\mathrm{NDE}}}{T - T^{*}} = \frac{2}{3} a^{-1} \varepsilon_{0} \times \frac{\Delta\varepsilon^{f} \Delta\varepsilon^{0}}{T - T^{*}},$$

$$T > T_{\mathrm{C}} \quad \text{and } T^{*} = T_{\mathrm{C}} - \Delta T \tag{3}$$

where C_{NDE} is a constant amplitude, $\Delta\varepsilon^{0}$ and $\Delta\varepsilon^{f}$ are the molecular anisotropies of the dielectric permittivity in the zero-frequency limit and for the applied frequency f, respectively. The coefficient a is the constant amplitude in the second rank term in the LG series [1–4]. For the LF NDE mentioned in the introduction, the relation is simplified: $\Delta\varepsilon^{0} \approx \Delta\varepsilon^{f}$ [17].

The samples for test were placed in a flat parallel-capacitor (gap $d = 0{\cdot}2$—1 mm, radius $r = 10$ mm) made of Invar. Changes of capacitance induced by the strong electric field E were of the order $\Delta C^{E} = 1$–5 fF and were registered by a three digit resolution. For every temperature interval from T_{C} the condition $\Delta\varepsilon^{E} \propto E^{2}$ was satisfied with an accuracy of $\pm 2\%$. The temperature stabilization was better than $0{\cdot}02$ K h^{-1}. The temperature was measured by a platinum resistor (DIN 43 760) placed in the cover of the capacitor and a Keithley 195A multimeter. 5-Heptyl-2-(4′-cyanophenyl)pyrimidine (HCPP, $T_{\mathrm{I\text{–}N}} \approx 51{\cdot}9$°C) was prepared by W. Pyżuk from Warsaw University, and 4′-cyano-4-hexylbiphenyl (6CB, $T_{\mathrm{I\text{–}N}} \approx 30{\cdot}8$°C) and 4′-cyano-4-decylbiphenyl (10CB, $T_{\mathrm{I\text{–}SmA}} \approx 50{\cdot}5$°C) in Prof. Dąbrowski's group at the Technical Military Academy, Warsaw, Poland. All these materials have a permanent dipole moment approximately parallel to the long axis of the molecule. The molecular anisotropy of the dielectric permittivity in the zero-frequency limit is about 35 for HCPP [19] and 10·8 for 6CB [22]. All tested samples were degassed immediately prior to each measurement set. The data were analysed by means of ORIGIN 3·5 software.

3. Results and discussion

Figures 1 and 2 show reciprocals of measured values of the NDE in the isotropic phase on approaching the nematic phase for HCPP and 6CB, respectively. Figure 1 also comprises results of the earlier studies by Pyżuk [19] for $f = 1{\cdot}5$ MHz. The pretransitional behaviour for the I–SmA transition is presented in figure 3. In all cases, with increase of f the departure from the linear dependence of $NDE^{-1}(T)$ appears near T_{C}. These discrepancies are much more significant for the I–SmA transition, and this may be due to the more complex nature of pre-smectic fluctuations in comparison with pre-nematic fluctuations. Far from T_{C} all experimental data follow a straight line, up to about $T_{\mathrm{C}} + 50$ K. For lower frequencies the straight line extends to the clearing point, with no distortion near T_{C}. Such a behaviour enables the determination of the amplitude a of the second rank term in the LG expansion. Assuming that $\Delta\varepsilon^{f} = \Delta\varepsilon^{0} \approx 10{\cdot}8$ and taking from figure 2 $C_{\mathrm{NDE}}^{\mathrm{LF}} \approx 13{\cdot}9$, ($10^{-15}\,\mathrm{m^{2}\,V^{-2}}$), relation (3) gives the estimate of $a = 0{\cdot}05 \pm 0{\cdot}002\ \mathrm{J\,cm^{-3}\,K}$. This value is in reasonable agreement with the estimation based on Kerr effect studies [22]: $a \approx 0{\cdot}053\ \mathrm{J\,cm^{-3}\,K}$.

The quantitative agreement with the theoretical predictions of relation (3) and the simple behaviour of $NDE^{-1}(T)$ over a wide temperature range were obtained for the total measured value of the effect, i.e. for $NDE_{\mathrm{B}} \approx 0$ in relation (2). It is noteworthy that the same slope (reciprocal of amplitude C_{NDE} called $C_{\mathrm{NDE}}^{\mathrm{LF}}$ in the sequel) can be determined for low frequencies from T_{C} to ($T_{\mathrm{C}} + 50$ K) and for higher frequencies remote from the clearing point T_{C}.

Recently the existence of pretransitional, slowly relaxing fluctuations has been explicitly shown in transient grating Kerr effect studies of the isotropic phase of liquid crystalline materials [23–25]. It has been found that their existence ceases to influence the behaviour in the isotropic phase when they are reduced to a few molecules

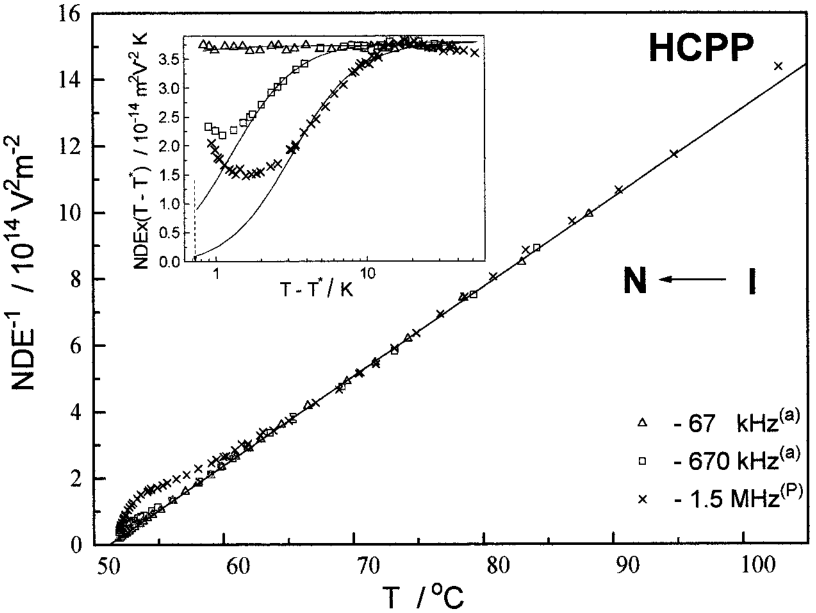

Figure 1. Reciprocals of measured NDE values in the isotropic phase of HCPP for selected measurement frequencies. Data for $f=1{\cdot}5\,\mathrm{MHz}$ are from [19]. Intensity of the measurement field for $f=67\,\mathrm{kHz}$ and $670\,\mathrm{kHz}$ is $E_m \approx 20\,\mathrm{V\,cm^{-1}}$. The value of the pretransitional amplitude (the reciprocal of the slope of the solid line) is equal to $3{\cdot}6\times10^{-4}\,\mathrm{m^2\,V^{-2}}$. The inset shows the apparent amplitude analysis $C_{\mathrm{NDE}}(T)=NDE(T)\times[T-T^*]$. Solid lines represent relation (4). The arrow indicates the clearing point and the value of the discontinuity of the transition.

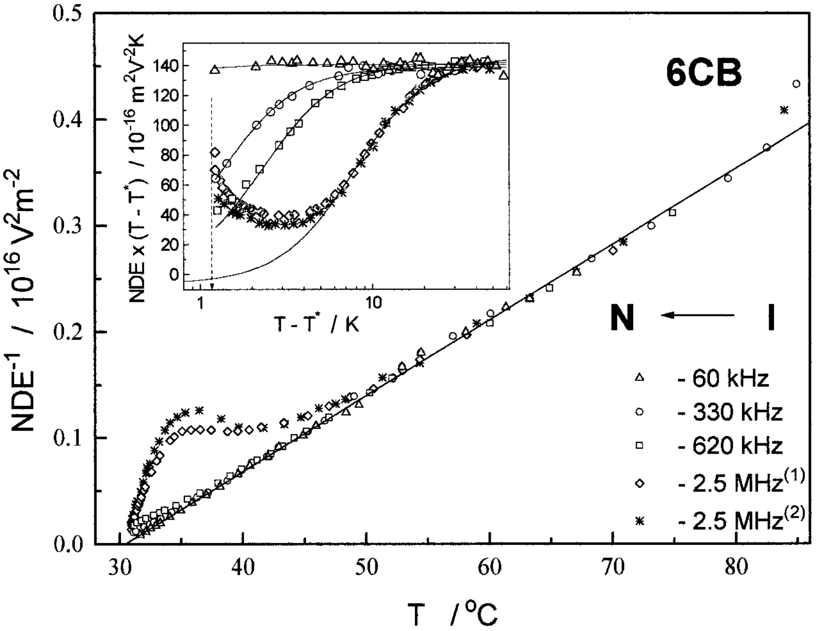

Figure 2. Reciprocals of measured NDE values in the isotropic phase of 6CB for a series of measurement frequencies. For $f=60$, 330 and 620 kHz the studies were carried out at $E_m \approx 20\,\mathrm{V\,cm^{-1}}$. For $f=2{\cdot}5\,\mathrm{MHz}$ index (1) is for $E_m=500\,\mathrm{V\,cm^{-1}}$ and index (2) for $E_m=100\,\mathrm{V\,cm^{-1}}$. The value of the pretransitional amplitude (the reciprocal of the slope of the solid line) is equal to $14\times10^{-15}\,\mathrm{m^2\,V^{-2}}$. The inset shows the apparent amplitude analysis. Solid lines represent relation (4). The arrow indicates the clearing point and the value of ΔT.

for $T > T_C + 50\,\mathrm{K}$, which coincides with the limit of linearity of $NDE^{-1}(T)$.

The insets in figures 1 and 2 represent results of the apparent scale analysis of the experimental data from the main parts. With the exception of the region of inflection near the clearing point, the apparent amplitudes may be portrayed by the relation:

$$C_{\mathrm{NDE}}(T)=NDE(T)\times(T-T^*)=C^{\mathrm{HF}}_{\mathrm{NDE}}+\frac{C^{\mathrm{LF}}_{\mathrm{NDE}}}{1+\omega^2\tau^2} \qquad (4)$$

where $\omega=2\pi f$, and $C^{\mathrm{HF}}_{\mathrm{NDE}}$ and $C^{\mathrm{LF}}_{\mathrm{NDE}}$ are constants. For the relaxation time, the relation $\tau=\tau_0/(T-T^*)^{\gamma}$ with $\gamma=1$ and $\tau_0=const$ has been applied as proposed by the LG model [1–4] and confirmed by experiments [4, 26, 27].

Results of simultaneous fitting for all applied frequencies, presented by the solid lines, are as follows:
$C^{\mathrm{LF}}_{\mathrm{NDE}}=3{\cdot}6\pm0{\cdot}1$, $C^{\mathrm{HF}}_{\mathrm{NDE}}=-0{\cdot}2\pm0{\cdot}1$, $(10^{-14}\,\mathrm{m^2\,V^{-2}\,K})$, and $\tau_0=0{\cdot}32\pm0{\cdot}05\,\mu\mathrm{s}$ for HCPP;
$C^{\mathrm{LF}}_{\mathrm{NDE}}=13{\cdot}9\pm0{\cdot}3$, $C^{\mathrm{HF}}_{\mathrm{NDE}}=-1{\cdot}5\pm0{\cdot}5$, $(10^{-15}\,\mathrm{m^2\,V^{-2}\,K})$, and $\tau_0=0{\cdot}55\pm0{\cdot}08\,\mu\mathrm{s}$ for 6CB.

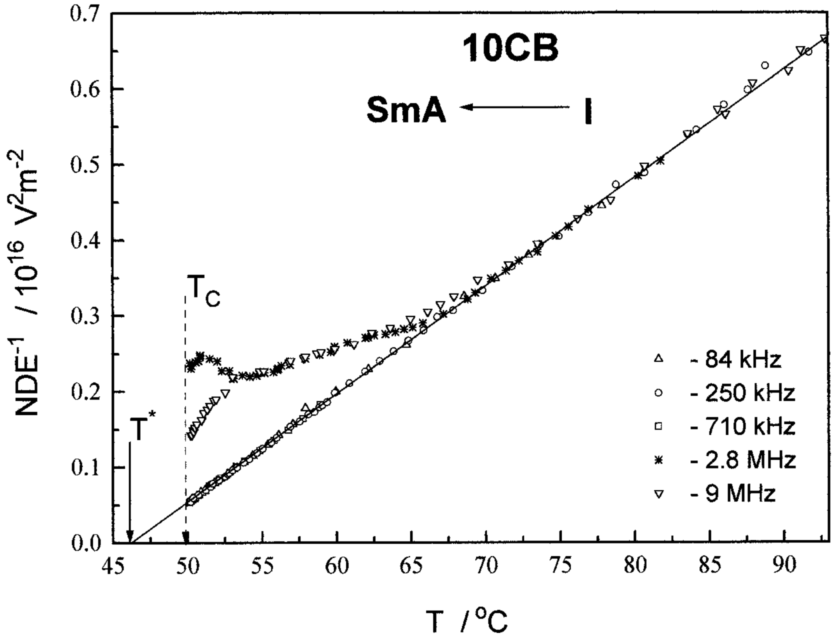

Figure 3. Reciprocals of measured NDE values in the isotropic phase of 10CB for a few of the measurement frequencies. Studies were conducted at $E_m \approx 20\,\mathrm{V\,cm^{-1}}$. The value of the pretransitional amplitude (the reciprocal of the slope of the solid line) is equal to $3 \times 10^{-15}\,\mathrm{m^2\,V^{-2}}$.

The values of τ_0 obtained are in a good agreement with those estimated from time [22, 26, 27] and frequency [28] resolved KE experiments involving the nematogenic n-cyanobiphenyls. These measurements show that the largest value of τ in the isotropic phase of 6CB is about 0·5 µs at $T \approx T_C$. For the lowest tested measurement frequency $f = 60$ kHz, the measurement time-scale may be estimated as $T' = f^{-1} \approx 17$ µs and the condition $T'/\tau > 1$, taking place near T_C, is always fulfilled. For higher frequencies the opposite condition $T'/\tau < 1$ occurs and discrepancies in $NDE^{-1}(T)$ from relation (3) appear on approaching T_C.

The amplitudes C_{NDE}^{LF} and C_{NDE}^{HF} obtained in the apparent scale analysis, relation (4), may be associated with the behaviour for $T'/\tau \gg 1$ and $T'/\tau \ll 1$, respectively. For C_{NDE}^{LF}, a good qualitative agreement with relation (3) exists after the $\Delta\varepsilon^f = \Delta\varepsilon^0$ substitution as was shown above. The small negative value of C_{NDE}^{HF} on approaching T^* may be associated with the anisotropy of the dielectric permittivity ($\Delta\varepsilon^f$) at higher frequencies. Dielectric dispersion studies of similar nematogens in the nematic phase just below T_C have shown that $\Delta\varepsilon^f$ drops to a small negative value in the megahertz region [29] which, according to relations (3) and (5), may lead to a negative sign of the NDE amplitude.

Another feature of the experimental data obtained is the inflection ('bending up') of the apparent amplitude in the immediate vicinity of T_C in figure 2. In the author's opinion the inflection is probably due to the influence of yet another factor which should be taken into account in NDE studies, i.e. the intensity of the weak measurement field (E_m). It is likely that in the immediate vicinity of T_C the E_m is strong enough to infuence the state of the pre-nematic fluctuations. Such a shift of the equilibrium should give an additional positive contribution to NDE. This hypothesis may be supported by two facts shown in the insets in figures 1 and 2. The first is that for the same values of intensity of the measurement field, the inflection near T_C is more pronounced for a molecule with a larger permanent dipole (HCPP) than for 6CB. Secondly, for measurements carried out on 6CB at $f = 2{\cdot}5$ MHz for two different values of E_m, the inflections are different. The values for the apparent amplitude for $E_m = 100\,\mathrm{V\,cm^{-1}}$ equals about $5 \times 10^{-15}\,\mathrm{m^2\,V^{-2}\,K}$ at T_C, whereas for $E_m = 500\,\mathrm{V\,cm^{-1}}$ it equals about $8{\cdot}5 \times 10^{-15}\,\mathrm{m^2\,V^{-2}\,K}$ at T_C. The influence of even weak external disturbances on the state of the system is often observed in complex liquids [30].

In the isotropic phase of nematogens, the temperature behaviour of the NDE and electro-optic Kerr effect (EKE), the fluid-like description can be applied [15, 31]. Taking into account the relation describing the pretransitional behaviour of the NDE in the homogeneous phase of binary solutions with a critical consolute point: $NDE \propto \langle \Delta M^2 \rangle_V \times \chi$, with $\chi = \chi_0 (T - \tilde{T}_C)^{-\gamma}$, denotes the susceptibility ([16] and refs therein) and $\gamma = 1$, i.e. the mean-field value as in relation (3)

$$NDE \propto \langle |\Delta M| \rangle_V^0 \times \langle |\Delta M| \rangle_V^f \times \chi^* \propto \frac{\Delta\varepsilon^0 \Delta\varepsilon^f}{T - T^*} \times \chi_0^* \qquad (5)$$

where $\langle \Delta M^2 \rangle_V$ denotes the mean square of the fluctuation of the order parameter; the amplitude χ^* may be identified with a^{-1} in relation (3).

For $T' \gg \tau$, the characteristic features of a single fluctuation do not influence the NDE value and $\langle \Delta M \rangle_V^f \approx \langle \Delta M \rangle_V^0 \propto \Delta\varepsilon^0$. If the measurement time-scale f^{-1} and the system time-scale $\tau(T)$ are comparable, the symmetry of a single mean fluctuation may influence the NDE pretransitional behaviour and this may induce a departure of $NDE^{-1}(T)$ from linear behaviour near T_C.

When T' and τ approach each other, the NDE pretransitional effect in the isotropic phase is progressively influenced by relaxation processes associated with the diffusion of elongated molecules, which may result in the changing of $\Delta\varepsilon^f$.

It is noteworthy that the dependence for the critical slowing down applied in relation (3) and (5) can also be derived beyond the mean-field model, from the dynamical scaling theory within the hydrodynamic region: $\tau \propto (T - T^*)^{-\nu z}$, with $\nu z = \gamma = 1$, where z is the dynamical scaling exponent and ν is the critical exponent for the correlation length ξ. In the classical approximation $\nu = 0{\cdot}5$ which readily gives $z = 2$, the value characteristic for the non-conserved order parameter and associated with the three-dimensional space $d = 3$ [4, 23]. The same value of z can be obtained for critical solutions in a strong electric field where a 'quasi-nematic' structure of the elongated fluctuation is assumed [16, 31]. Experimental investigations of the NDE relaxation after switching off the strong electric field for such materials showed that the mean relaxation time of the critical fluctuation is governed by the relation: $\tau_S \propto \xi^z \propto (T - T_C)^{-\gamma}$ where $\gamma = \nu z \approx 1{\cdot}3$ ([32] and refs therein) and hence $\nu \approx 0{\cdot}65$, i.e. the value for (3, 1) class universality. According to recent isothermal pressure data $\nu z \cong 1{\cdot}1$ [33]. This value is very close to the observed value in the isotropic phase of nematogens. It is noteworthy here that theories predict that the exponent $\gamma \cong 1{\cdot}9$ and that $z = 3$ is the dynamical exponent of the conserved order parameter [34, 35].

4. Conclusions

The results discussed above suggest that the dynamics of pre-nematic (pre-smectic) fluctuations may significantly influence the pretransitional behaviour of the stationary, non-linear dielectric effect. The behaviour observed is associated with the relation between the system time-scale τ and the measurement time-scale f^{-1}. In the immediate vicinity of T_C the influence of the intensity of the weak measurement field on the pretransitional effect NDE is considered.

It is also noteworthy that the quantitative agreement with theoretical predictions and the simple behaviour of $NDE^{-1}(T)$ over a wide temperature range were obtained for the total measured value of the effect, i.e. $NDE_B \approx 0$ in relation (2) (for $\omega\tau < 1$). The value obtained for the exponent γ also does not exclude the hypothesis of the TCP character of the I–N phase transition mentioned in §1.

Studies carried out in this paper as well as those in [14, 16, 31] point to yet another important problem that still remains open, i.e. the fluid-like, critical behaviour in the isotropic phase of liquid crystalline materials.

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