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LETTER TO THE EDITOR

Nonlinear dielectric studies in supercooling 4-(2-methylbutyl)-4′-cyanobiphenyl (5*CB)

Aleksandra Drozd-Rzoska†, Sylwester J Rzoska†, Jerzy Zioło† and Krzysztof Czupryński‡

† Institute of Physics, Silesian University, Uniwersytecka 4, 40-007 Katowice, Poland
‡ Military Technical Academy, 01-489 Warsaw, Poland

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Abstract. Results are presented of nonlinear dielectric effect (NDE) in the isotropic phase of 4-(2-methylbutyl)-4′-cyanobiphenyl (5*CB) for three frequencies of a measuring electric field. The critical-like properties of nonlinear changes in dielectric permittivity induced by a strong electric field were found: $\mathcal{E}_{NDE} = A_{NDE}/(T - T^+)^\gamma$ with $A_{NDE} = 135.5 \times 10^{-6}$ (m^2 V^{-2} K^{-1}), $\gamma = 1$ and $T^+ = 12.02\,^\circ$C. The latter may be treated as a temperature of hypothetical continuous phase transition.

The structure of the chiral 4-(2-methylbutyl)-4′-cyanobiphenyl (5*CB) (Gray and McDonnel 1976) molecule is closely related to that of the well known 4-pentyl-4′-cyanobiphenyl (5CB) forming the nematic phase in the range 22–35 °C (Demus *et al* 1998). The presence of the chiral group in the alkyl chain of 5*CB means that the liquid can be easily supercooled, with subsequent possible appearance of the metastable, cholesteric phase and followed by the glassy state (Gray and McDonnel 1976, Massalska-Arodź *et al* 1998, Mayer *et al* 1999, Urban *et al* 1999). The such different phase behaviours of these compounds may be the consequence of the considerable differences in their intermolecular interactions, which may lead to various dynamical properties of molecules in the isotropic phase. It is well known that in the isotropic phase of 5CB on approaching the nematic clearing temperature, strong pretransitional anomalies of the fluctuation-sensitive physical properties appear (Demus *et al* 1988, de Gennes and Prost 1993). The nonlinear dielectric effect (NDE) belongs to this group of magnitudes. It describes changes of dielectric permittivity, for a radio-frequency, induced by an additional strong, steady electric field E. The measure of NDE is the magnitude (Górny *et al* 1996):

$$\mathcal{E}_{NDE} = \frac{\varepsilon^E - \varepsilon}{E^2} \tag{1}$$

where ε^E and ε are the dielectric permittivities under strong and weak electric fields, respectively.

The isotropic phase of nematogens NDE shows a very strong pretransitional effect. The application of the mean-field, Landau–de Gennes (LdG)(de Gennes and Prost 1993) gave (Drozd-Rzoska *et al* 1996, Drozd-Rzoska 1998, 1999):

$$\mathcal{E}_{NDE} = \frac{A_{NDE}}{(T - T^*)^\gamma} = \frac{2}{3a}\varepsilon_0 \frac{\Delta\varepsilon^0 \Delta\varepsilon^f}{T - T^*} \qquad T > T_C,\ T^* = T_C - \Delta T \tag{2}$$

where $\gamma = 1$ is the classical exponent, $\Delta\varepsilon^0$ and $\Delta\varepsilon^f$ represent the molecular anisotropy of dielectric permittivity for the zero-frequency limit and for the measurement frequency f, respectively. The term A_{NDE} is the susceptibility-related amplitude of the second-order term in the LdG expansion. T_C and T^* are the nematic clearing temperature and the temperature of a hypothetical continuous phase transition, respectively. ΔT is the measure of the discontinuity of the isotropic–nematic (I–N) transition.

Relation (2) can also be derived from the relation describing the NDE anomaly in the homogeneous phase of critical, binary mixtures (Rzoska 1993):

$$\mathcal{E}_{NDE} \propto \langle \Delta M^2 \rangle_V \chi \propto (T - T_C^{CCP})^{\psi} = (T - T_C^{CCP})^{2\beta-\gamma} \qquad (3)$$

where T_C^{CCP} denotes the temperature of the critical consolute point (CCP), $\langle \Delta M^2 \rangle_V \propto (T - T^{CCP}C)^{2\beta}$ is the mean square of the order parameter fluctuations, $\beta \approx 0.325$ is the critical exponent of the order parameter, $\chi \propto (T - T_C^{CCP})^{-\gamma}$ is the susceptibility described by the classical critical exponent $\gamma \approx 1$, due to the quasi-nematic structure induced by the strong electric field.

For the non-interacting, prenematic fluctuation relation, equation (3) can be easily reduced to (2) (Drozd-Rzoska 1999). The hypothesis of the fluid-like, critical behaviour, i.e. beyond mean field approximation is strongly supported by the theoretical description recently introduced by Mukherjee *et al* (1998). The model successfully applies an equation of state in which the clearing point lies on a hypothetical co-existence curve (binodal).

Figure 1 shows results of measurements in the isotropic phase of 5*CB and 5CB for several frequencies of the weak measuring field. The experimental set-up is the same as described in details in (Górny *et al* 1996). In 5CB for $f = 70$ kHz the inverse of NDE is a strictly linear function from T_C up to about $T_C + 40$ K and can be well parameterized by means of equation (2), with $\Delta\varepsilon^0 = \Delta\varepsilon^f$. This condition can be applied because the times-scale introduced by the measuring frequency f significantly exceeds the relaxation time (τ) of prenematic (critical) fluctuations: $f^{-1} \gg \tau$ (Drozd-Rzoska *et al* 1996, 1999). Such a relationship is not valid for $f = 2.5$ MHz which leads to a distortion from linearity near T_C. It was shown in (Drozd-Rzoska 1998, Drozd-Rzoska and Rzoska 1998) that it can be described by taking into account the influence of the relaxation of critical fluctuations on the amplitude A_{NDE}.

Figure 1 also shows the reciprocal of measured NDE in 5*CB for several frequencies. By lowering the measurement frequency the linear dependence is extended. It can be written by a critical-like equation:

$$\mathcal{E}_{NDE}^{-1} = A_{NDE}(T - T^+)^{\gamma} \qquad \gamma = 1 \qquad (4)$$

which is the same as for the nematic clearing point.

For the lowest measuring frequency the range of linearity of the inverse of NDE is even greater than that observe in 5CB and other n-cyanobiphenyls (Drozd-Rzoska and Rzoska 1998, Drozd-Rzoska 1999).

Concluding, it has been shown that at least for the lower frequency of the weak measuring field the NDE behaviour in the isotropic phase of 5CB and 5*CB can be portrayed by the same power function with the critical exponent $\gamma = 1$. The amplitude for 5*CB is slightly smaller than that obtained for 5CB and is approximately equal to that obtained for 4-hexyl-4′-cyanobiphenyl (6CB). However, in 5CB a discontinuous transition takes place at T_C, so the low-frequency NDE studies made it possible to obtain a precise estimation of the parameter characterizing the discontinuity, $\Delta T = T_C - T^*$. In 5*CB it is only possible to determine the extrapolated temperature T^+. Nevertheless, there is a striking similarity in the pretransitional behaviour of both compounds despite differences in molecular structure and phase sequence. This points to the existence of pretransitional fluctuations in the tested range of temperatures of 5*CB. It also suggests that $T^+ \approx 12\,^{\circ}$C may be singular temperature of a hypothetical continuous phase transition. However, the following sequence of phases on cooling in 5*CB occurs (Massalska-Arodź *et al* 1998, Mayer *et al* 1999, Urban *et al* 1999): first the isotropic

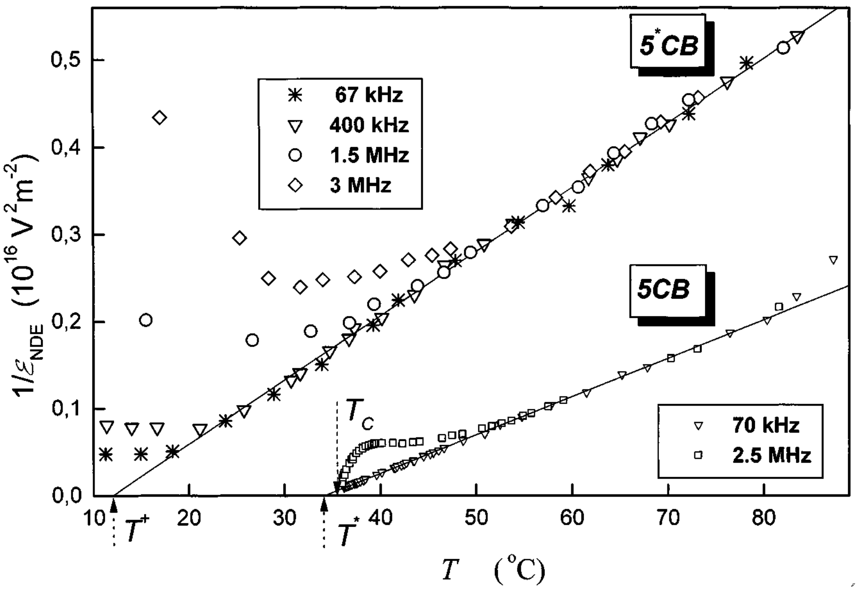

Figure 1. Reciprocals of measured NDE values in the isotropic phase of 5CB and 5*CB. In the case of 5CB a weakly discontinuous phase transition to the nematic phase at CT takes place. Dotted arrows show temperatures T^* and T^+ at which $\varepsilon_{NDE} \to \infty$. Measurements have been conducted for frequencies of the weak measuring field given in the Figure. The strong stead electric was applied in the form of rectangular pulses of duration 1–8 ms (Górny *et al* 1996). The full lines show the linear regression fits.

supercooled liquid with the melting temperature $T_m = 3\,^\circ$C, then at $T_{Ch} = -27\,^\circ$C the metastable cholesteric phase may appear followed by the isotropic glass phase, characterized by the ideal glass temperature $T_0 = -91\,^\circ$C and calorimetric glass temperature $T_g = -63\,^\circ$C. This poses the question of the source of the observed critical-like behaviour. One of the possible explanations is the existence of a hidden nematic phase who formation is not possible due to the damping by the vitrification processes. In the opinion of the authors further studies of the possible relationship between T^+ and the mode-coupling critical temperature (Goetze and Sjoegren 1992) are worth undertaking.

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