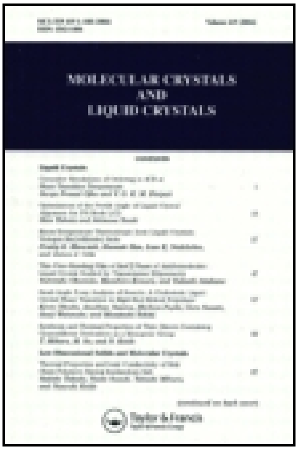

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Quasi-Critical Behaviour of "Linear" and "Nonlinear" Dielectric Permittivity in the Isotropic Phase of Nematogens

Aleksandra Drozd-rzoska [a] & Sylwester J. Rzoska [a]
[a] Institute of Physics, Silesian University, ul. Uniwersytecka 4, 40-007, Katowice, Poland

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Quasi-Critical Behaviour of "Linear" and "Nonlinear" Dielectric Permittivity in the Isotropic Phase of Nematogens

ALEKSANDRA DROZD–RZOSKA and SYLWESTER J. RZOSKA

Institute of Physics, Silesian University, ul. Uniwersytecka 4, 40–007 Katowice, Poland

Results are presented of dielectric permittivity and nonlinear dielectric effect (NDE) studies in the isotropic phase of n-pentylcyanobiphenyl (5CB). Both properties can be described by relations identical to those applied in critical binary solutions. For the isothermal, pressure and isobaric, temperature paths approaching the nematic clearing point pretransitional anomalies of dielectric permittivity and NDE are described by the same relations with critical exponents $\alpha \approx 0.5$ and $\gamma = 1$, respectively This substantiates the postulate of the isomorphism of critical phenomena in the isotropic phase of nematogens. For tested "linear" and "nonlinear" changes of dielectric permittivity the same values of the discontinuity of the isotropic – nematic phase transition was obtained.

Keywords: Pretransitional effect; nematic; nonlinear dielectric effect; dielectric permittivity; critical behaviour

INTRODUCTION

In a strong electric field in liquids dielectric permittivity ceases to be independent of the electric field intensity[1]:

$$\varepsilon^E = \varepsilon + \varepsilon_1 E^2 + 0\left(E^2\right) \qquad (1)$$

where ε^E, ε are dielectric permittivities in a strong (E) and weak, measuring electric field , respectively

The measure of this behaviour, called nonlinear dielectric effect: $NDE = \Delta\varepsilon^E/E^2 = \left(\varepsilon^E - \varepsilon\right)/E^2$, is sensitive to many aspects of molecular properties[1]. In the isotropic phase of nematogens it shows a very strong pretransitional effect, similar to that of the Kerr effect (KE), Cotton-Mouton effect (CME), light scattering (I), relaxation time of prenematic fluctuations (τ) [2]. In case of NDE the application of the Landau - de Gennes model (LdG) gives the following relations [3,4]:

$$\frac{\Delta\varepsilon^{E}}{E^{2}}=\frac{A_{NDE}^{T}}{T-T^{*}}=\frac{2}{3a_{T}}\varepsilon_{0}\frac{\Delta\varepsilon^{0}\Delta\varepsilon^{f}}{(T-T^{*})^{\gamma}},\ T^{*}=T_{C}-\Delta T,\ T>T_{C},\text{(for } P=\text{const)} \tag{2}$$

$$\frac{\Delta\varepsilon^{E}}{E^{2}}=\frac{A_{NDE}^{P}}{P^{*}-P}=\frac{2}{3a_{p}}\varepsilon_{0}\frac{\Delta\varepsilon^{0}\Delta\varepsilon^{f}}{(P^{*}-P)^{\gamma}},P^{*}=P_{C}+\Delta P,\ P<P_{C},\text{(for } T=\text{const)} \tag{3}$$

where the exponent $\gamma=1$, a_T, a_P, are constant amplitudes in the second rank term in the Landau - de Genness (LdG) (isobaric or isothermic) expansion[2]. $\Delta\varepsilon^0$, $\Delta\varepsilon^f$ are molecular anisotropies of dielectric permittivity in the zero-frequency limit and for the measurement frequency. T_C and P_C are coordinates of the isotropic - nematic, *I-N*, transition and T^*, P^* denote coordinates of the extrapolated point of a hypothetical, continuous phase transition.

It is noteworthy that equations (2) and (3) can be also derived beyond the LdG model, basing on the relation describing the critical effect in the homogeneous phase of critical solutions[4]. This indicates that NDE in the isotropic phase of nematogens is sensitive to fluctuations of the order parameter M and pretransitional changes of susceptibility (compressibility) χ[4]: $\Delta\varepsilon^E/E^2\propto\langle|\Delta M|\rangle^2\times\chi$. For the NDE research method the measurement radio-frequency (f) coincide with the time scale introduced by the relaxation time (τ) of pretransitional processes. In the experiment the value of f can be varied what offers possibilities of testing the evolution of relaxation time τ from NDE stationary measurements[5]. Studies carried out in few nematogens with the permanent dipole moment parallel to the long axis of the molecule showed that static dielectric permittivity also reveal a pretransitional effect[4]:

$$\varepsilon = \varepsilon_C + D\left(T - T^*\right)^{1-\alpha} + D_1\left(T - T^*\right) \text{ with } \alpha = 0.5 \pm 0.02 \qquad (4)$$

where ε^* is the extrapolated dielectric permittivity at T^* , D and D_l are amplitudes and α is the critical exponent of the specific heat.

This relation is also analogous to that describing the critical effect in the homogeneous phase of critical solutions[4]. The suggestion of a critical-like behaviour of dielectric permittivity ε in the isotropic phase was first considered in the early eighties by Bradshaw, Raynes[6] and Thoen, Menu[7] but it was hardly explored later[4].

This paper presents studies of the critical-like properties of a „linear" (ε) and „nonlinear" (NDE) dielectric permittivivity in the isotropic phase of a nematogen (n-pentylcyanobiphenyl, 5CB)). In particular, it aims to test the validity of the postulate of isomorphism of a critical phenomena[2] in the isotropic phase. This postulate predicts for a given physical quantity the same forms of relations describing critical effects, with the same values of critical exponents, for isothermal, pressure and isobaric, temperature paths approaching the critical point[2].

EXPERIMENTAL

NDE measurements were conducted using a set - up, described in details in ref. [8]. The parameters of the weak measurement field was f = 70 kHz - 3 MHz and U = 3 V. The strong electric field was applied in the form of a rectangular DC pulses 4 - 16 ms in length, repeatability 3 s and voltage 100 - 700 V. At each measurement point the condition $\Delta\varepsilon^E \propto E^2$ was fulfilled with precision better than 2 %. . The sample was placed in a specially designed flat - parallel capacitor (gap 0.25 mm, $C_0 \approx 7$ pF). The capacitor contained only 0.8 cm^3 of the sample, totally isolated from the pressurized liquid (silicone oil). The pressure was transmitted to the sample via the 50 μm Teflon film. The temperature was measured using a thermocouple placed inside a chamber and a platinum resistor in its jacket. Pressure was measured using a tensometric pressure meter. Temperature and pressure studies were carried out in the same measurement capacitor to minimise a possible systematic error. Dielectric permittivity measurements were conducted by means of SOLARTRON 1260A impedance analyzer, with averaging over 1000 periods. It made it possible to receive the accuracy of five significant digits. The tested material was obtained from Military Technical Academy by the courtesy of Prof. Dąbrowski and Prof. Czupryński. Data were analysed by means of ORIGIN 3.5 software.

RESULTS AND DISCUSSIONS

Figure 1 shows the results of measurements of dielectric permittivity in temperature studies under atmospheric pressure and for isothermal, pressure path approaching the clearing point. In both cases they can be described by similar relations:

$$\varepsilon(T) = 10.774 - 0.0276\times(T - T^*) + 0.125\times(T - T^*)^{0.49}$$

$$\varepsilon(P) = 10.21 - 0.0081\times(P^* - P) + 0.115\times(P^* - P)^{0.52}$$

The error for the exponent $\phi = 1 - \alpha$ is equal to ± 0.03. Figures 2 and 3 present NDE measurement data, in the form which shows the validity of relations (2) and (3). They very well portray the experimental data for the lowest frequency applied (60 kHz): the reciprocal of NDE is a linear function in the ranges from P_C to P_C - 100 MPa and from T_C to T_C + 40 K. In this case the time-scale introduced by the measuring field of $f = 60$ kHz of is equal to 17 μs whereas $\tau(T_C) \approx 0.6$ μs[9]. Hence the condition $f^{-1} >> \tau$ is valid

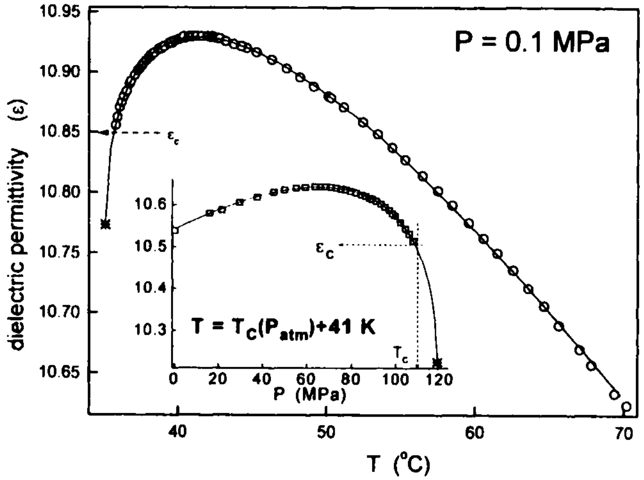

FIGURE 1 Temperature and pressure behaviour of dielectric permittivity in the isotropic phase of 5CB ($f = 10$ kHz).

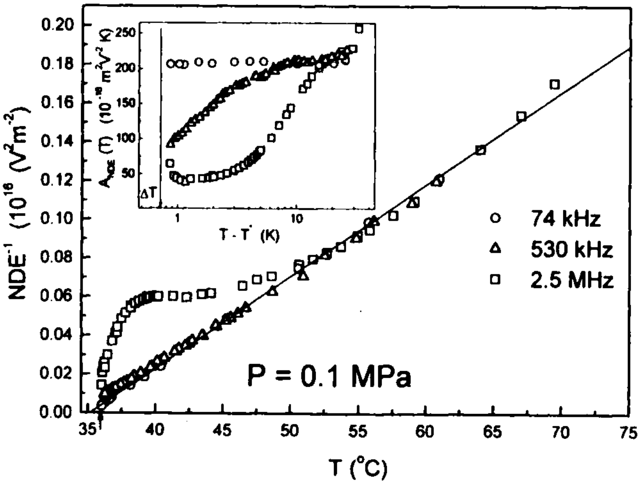

FIGURE 2 Results of NDE temperature measurements in the isotropic phase of 5CB (atmospheric pressure). The inset shows the apparent amplitude analysis.

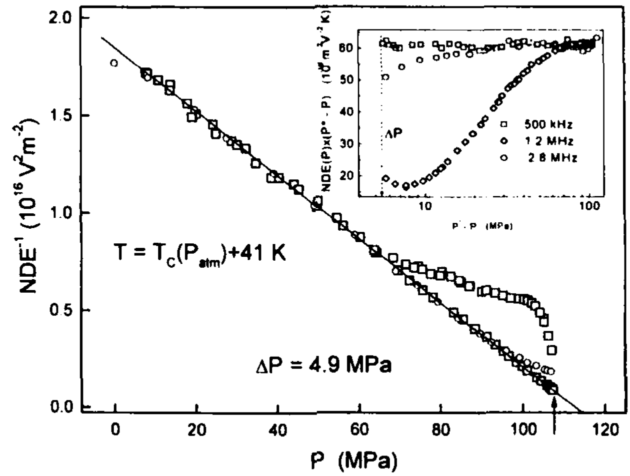

FIGURE 3 Results of isothermic NDE versus pressure measurements in the isotropic phase of 5CB. The inset shows the apparent amplitude analysis.

well above the clearing temperature. The apparent scale analysis presented in the inset shows that discrepancies from relation (2) and (3), for higher frequencies, are caused by the coincidence between the measurement frequency and relaxation time of pretransitional processes. Except for the region of inflexion near the clearing point the apparent amplitude may be portrayed by the relation (solid lines in insets in Figs. 2 and 3):

$$\left.\begin{array}{l} A_{NDE}(T)=NDE(T)\times\left(T-T^{*}\right)\\ \\ A_{NDE}(P)=NDE(P)\times\left(P^{*}-P\right)\end{array}\right| \quad = \quad C_{NDE}^{HF}+\frac{C_{NDE}^{LF}}{1+\omega^{2}\tau^{2}}$$

with $\tau(T)=\tau_{o}^{T}/\left(T-T^{*}\right)^{2\nu}$ and $\tau(P)=\tau_{o}^{P}/\left(P^{*}-P\right)^{2\nu}$, $\nu=0.5$ [2]

The value of the coefficient $\tau_o^T = 0.5 \pm 0.15 \mu s$ obtained by the simultaneous fit of all data given in the inset is in reasonable agreement with the ones found in time-resolved KE studies[9]. For the pressure paths $\tau_o^T \approx 1.6 \mu s$. As was suggested in ref.[5] the inflection near the clearing point may be associated with the influence of yet another factor present in dielectric studies i.e. the intensity of the measuring electric field.

Concluding, the results presented show that pretransitional changes of ε and NDE for the pressure and temperature path of approaching the clearing point are described by isomorphic relations with the same values of critical exponents $\alpha \approx 0.5$, $\gamma = 1$, $\nu = 0.5$. Worthwhile noting that both NDE and ε gave the same values of the discontinuity of the phase transition $\Delta T \approx 0.75$ K and $\Delta P \approx 4.9$ MPa, for the isobaric and isothermal path, respectively. Such behaviour indicates on the validity of the postulate of isomorphism of critical phenomena[2] for the *I-N* transition. This conclusion and the mentioned correlations with the behaviour in critical solutions agrees with idea of a fluidlike, critical behaviour for the *I-N* transition, with clearing temperature lying on a hypothetical coexistence curve, proposed by Mukherjee at al.[10, 11].

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