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# Time-scale dependence of the critical exponent for the nonlinear dielectric effect in a critical binary solution

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Low frequency [(300 kHz) results for the nonlinear dielectric effect (NDE)] (variation in electric permittivity of liquids induced by a strong, steady electric field) in a critical, binary solution have been obtained. Their comparison with NDE measurements for 9 and 6 MHz indicate that the appearance of a mean-field region near the critical consolute temperature ($T_C$) and the crossover to the nonclassical behavior remote from $T_C$ could be associated not only with the degree of elongation of critical fluctuations but also with the time scale involved. This behavior is possibly due to the correlation between the relaxation time of critical fluctuations and the measurement frequency. The result obtained supplements the analysis given in Phys. Rev. E **48**, 1136 (1993) plus Phys. Rev. E **47**, 1445 (1993) and Phys. Rev. E **50**, 5234 (1994) of the behavior near a critical consolute point of two effects immanently associated with the application of a strong, steady electric field: the electro-optical Kerr effect and nonlinear dielectric effect.

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## I. INTRODUCTION

In the last few years considerable attention has been paid to electric field effects on binary solutions near a critical consolute point [1–9]. The pretransitional behavior of two physical magnitudes immanently associated with the application of a strong, steady electric field—the electro-optic Kerr effect (EKE) and the nonlinear dielectric effect (NDE) [10]—were for a long time a matter of controversy [7].

In critical solutions theoretical models predicted [4,11,12]

$$\frac{\Delta\varepsilon}{E^2},\ \frac{\Delta n}{E^2} \propto (T-T_C)^{-\psi} ,$$

$$\psi=\gamma-2\beta\approx 1.24-2\times 0.325=0.59 , \tag{1}$$

where $\Delta\varepsilon/E^2$ is the measure of NDE, $\Delta\varepsilon=(\varepsilon^E-\varepsilon)$ is the difference between electric permittivity in a strong and a weak steady electric field $E$, $\Delta n/E^2$ is the measure of optical birefringence induced by the steady electric field (EKE), and $T_C$ is the critical consolute temperature ($T>T_C$). Values of critical exponents $\gamma$ (critical susceptibility) and $\beta$ (order parameter) are for the three-dimensional (3D) Ising universality class [13]. However, experiments yielded relations (Ref. [7] and references therein)

$$\psi^{\mathrm{NDE}}(\approx 0.37)<\psi^{\mathrm{theor}}(\approx 0.59)<\psi^{\mathrm{EKE}}(=0.65-0.85) . \tag{2}$$

A proposition for explaining this discrepancy was given in Ref. [7] by assuming that the elongation of the critical fluctuation due to the electric field $E$ can induce a crossover from the "Ising" to the mean-field behavior

$$\xi(E\neq 0)=(\xi_{\parallel},\xi_{\perp},\xi_{\perp}),\quad \xi_{\parallel}>\xi_{\perp} , \tag{3}$$

where the component parallel to the field $E$ maintains the nonclassical characteristic (i.e., $\xi_{\parallel}\propto t^{-\nu}\approx t^{-0.5}$). Then, by taking into account differences in the definitions of EKE and NDE, values $\psi^{\mathrm{NDE}}\approx 0.37$ (or $\psi^{\mathrm{NDE}}\approx 0.4$ if corrections to scaling are taken into account) and $\psi^{\mathrm{EKE}}\approx 0.85$ were obtained. This idea was further developed in Ref. [9], where it was shown that the scatter of $\psi^{\mathrm{EKE}}$ [relation (2)] is associated with the factor related to the degree of elongation of critical fluctuations:

$$e=\frac{(\varepsilon_1-\varepsilon_2)^2}{\varepsilon}E^2 , \tag{4}$$

where $\varepsilon$ and $\varepsilon_1,\varepsilon_2$ are electric permittivities of the solution and its components. In a critical solution with a small mismatch of $\varepsilon_1$ and $\varepsilon_2$ (i.e., small elongation of critical fluctuations), the "Ising" value $\psi^{\mathrm{EKE}}\approx 0.59$ was obtained [9].

However, some unexplained experimental facts still seem to exist for NDE. According to Ref. [7],

$$NDE \propto \langle \Delta M^2\rangle_V \chi \propto t^{2\beta} t^{-\gamma} , \tag{5}$$

where $\langle \Delta M^2\rangle_V$ is the mean (per unit volume) of fluctuation of the order parameter, $\chi$ is the susceptibility, and $t=(T-T_C)/T_C$ is the measure of the dimensionless distance from the critical point. For strongly elongated fluctuations, $\chi$ cross over from the "Ising" to the mean-field behavior and change in value of exponent $\gamma$ from 1.24 to 1.02 (the last value is given with the logarithmic correction [13]) takes place. This is related to the change of $\psi^{\mathrm{NDE}}$ from 0.59 to 0.4. The last value is in agreement with almost all known experimental results.

Recent NDE measurements in a few critical solutions [14] drew attention to the fact that $\psi^{\mathrm{NDE}}$ appears to cross over from $\psi^{\mathrm{NDE}}\approx 0.4$ to $\psi^{\mathrm{NDE}}\approx 0.6$ on moving away from $T_C$. According to the analysis given above, one can suspect that this is associated with the mean-field–nonclassical crossover. For a constant value of an external, anisotropic field (e.g., electric, velocity gra-

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dient), the elongation of critical fluctuations is naturally larger near $T_C$, which can lead to the appearance of mean-field properties in this region. This mechanism was responsible for the classical-nonclassical crossover in light scattering studies in a critical solution under shear flow [15,16] and, to some extent, in the electro-optic Kerr effect studies near the critical consolute point [9]. However, in Ref. [14] we also pointed to the possible relation of this phenomenon to the applied NDE measurement frequency ($f_m = 6$ MHz).

Reported here is an experimental attempt to confirm the existence of this crossover for NDE in critical solutions and to explain its origin. For this purpose results are given of NDE tests in a critical solution implemented by means of two measurement systems especially designed for these studies. The first was for the measurement frequency $f_m = 9$ MHz, with substantially enhanced sensitivity that is of signal importance for the analysis of the critical effect remote from $T_C$. The other was a low frequency apparatus for $f_m = 300$ kHz.

## II. EXPERIMENTAL

The NDE studies were conducted by using an apparatus constructed according to an idea proposed by Malecki [17]. It comprises two generators, a reference generator and one with the tested sample, connected in a differential system. The application of a strong electric field changes the difference of the frequency of generators. This shift, proportional to the change in capacitance $\Delta C$ of the sample, after detection, was recorded by means of a 12 bit digitizer with a computer system.

In earlier reported investigations, the frequency of the measurement generator was 6 MHz and the impulse length of the strong electric field was 1 ms [6,7,14]. The measurement frequency of apparatuses constructed for these tests was 300 kHz and 9 MHz. A difficult design problem for the lower frequency was maintaining suitable sensitivity and at the same time ensuring the possibility of sufficiently short impulses of the strong electric field. Significantly increased sensitivity was possible to achieve for $f_m = 9$ MHz. This feature was in this case of considerable importance in separating the noncritical background effect and the critical effect remote from $T_C$. A description and discussion of this measurement technique are being prepared.

The results presented below were obtained for impulses of duration $\tau_D = 4-8$ ms ($U = 300-1100$ V), repeatability 1–3 s, with 10–40 cumulations. The gap of the flat-parallel measurement capacitor made from Invar was 0.5 mm. The voltage of the measurement field was 2 V. Magnitudes of recorded changes in $\Delta C$ were from 2 to 0.5 fF. At each measurement point the condition $\Delta\varepsilon \propto E^2$ was always satisfied with an accuracy better than 1%. At tested distances from the critical consolute point the condition $\tau_D \gg \tau$ ($\tau$ is the relaxation time of critical fluctuations) was always satisfied.

Temperature of the measurement capacitor was stabilized by means of a water thermostat system with an accuracy better than 0.01 K/h. Temperature was measured by a platinum resistor and multimeter Keithley 195A with a resolution of 0.002°. For testing, a critical nitrobenzene-heptane solution ($x_c = 0.47$ mole fraction of nitrobenzene; $T_C = 19.5\,^\circ$C [13]) was chosen. Nitrobenzene (Merck) was three times distilled, the last time immediately prior to measurements, and dried over molecular sieves. Heptane (POCH, Poland) of "spectral" purity class was used without further purification.

## III. RESULTS AND DISCUSSION

Results of nonlinear dielectric effect measurements in the tested solution are shown in Fig. 1. The marked noncritical background effect ($\mathrm{NDE}_B$) was determined from measurements in a reference (nitrobenzene-carbon tetrachloride) solution of unlimited miscibility [7].

Figures 2 and 3 show the critical effects ($\mathrm{NDE}_C = \mathrm{NDE} - \mathrm{NDE}_B$) for tested frequencies in a log-log scale. For $f_m = 9$ MHz (Fig. 2) the effect is described throughout the greater part of the tested temperature range by means of a power relation with a critical exponent:

$$\psi_{\mathrm{NDE}} = 0.41 \pm 0.01 \ .$$

Remote from $T_C$, the exponent changes its value:

$$\psi_{\mathrm{NDE}} = 0.62 \pm 0.06 \ .$$

For frequency $f_m = 300$ kHz the change in the value of the critical exponent takes place relatively near $T_c$, where critical fluctuations still give the dominating contribution to the total measured nonlinear dielectric effect:

$$\psi_{\mathrm{NDE}} = 0.38 \pm 0.01, \quad \text{for } T - T_C < 1 \text{ K} ,$$

$$\psi_{\mathrm{NDE}} = 0.6 \pm 0.02, \quad \text{for } T - T_C > 1.5 \text{ K} .$$

It is noteworthy to point out a correlation between the reciprocal of the measurement frequency ($T' = 1/f_m$; Figs. 2 and 3) and the value of relaxation time of critical fluctuations for the distance from $T_C$ where the crossover

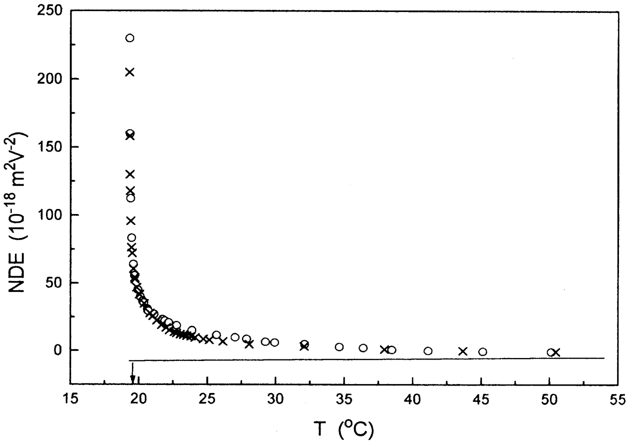

FIG. 1. The nonlinear dielectric effect on approaching the critical consolute temperature in the critical nitrobenzene-heptane solution. Crosses are for the frequency of the weak measurement field $f_m = 300$ kHz, and circles for $f_m = 9$ MHz. The solid line shows the noncritical background effect. The arrow denotes the critical consolute temperature.

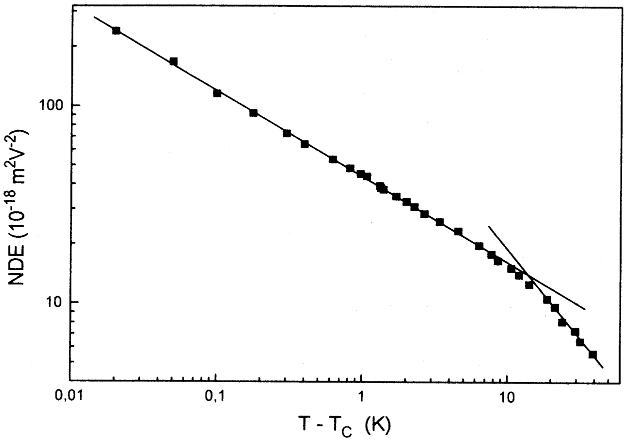

FIG. 2. The critical effect of NDE in the nitrobenzene-heptane solution as a function of the temperature distance from the critical consolute point in a log-log scale for frequency $f_m = 9$ MHz.

in value of the critical exponent takes place:

$$\tau \approx 3.4\ \mu s \text{ at} \Delta T \approx 1 \text{ K}, \quad T'(300 \text{ kHz}) \approx 3.3\ \mu s ,$$

$$\tau \approx 0.18 \mu s \text{ at } \Delta T \approx 9 \text{ K}, T'(6 \text{ MHz}) \approx 0.17\ \mu s ,$$

$$\tau \approx 0.1\ \mu s \text{ at} \Delta T = 12 \text{ K}, T'(9 \text{ MHz}) \approx 12 \text{K} .$$

Relaxation times of critical fluctuations have been estimated on the basis of analysis of the stretched-exponential deformation of the NDE impulse in the vicinity of $T_C$ [5,6,8].

## IV. CONCLUSIONS

Results obtained indicate that in a critical solution under a strong external field (i.e., electric), a crossover from the mean-field behavior near $T_C$ to the totally nonclassical behavior remote from $T_C$ may appear to be due to the time scale involved. Taking $\tau$ as a natural time scale unit in a critical system, we see that the following conditions seem to be fulfilled:

$$\frac{T'}{\tau} < 1 \text{ and } \mathrm{NDE}_C \propto t^{-0.37} \text{ (mean-field region) ,} \tag{6}$$

$$\frac{T'}{\tau} > 1 \text{ and } \mathrm{NDE}_C \propto t^{-0.59} \text{ (nonclassical region) .} \tag{7}$$

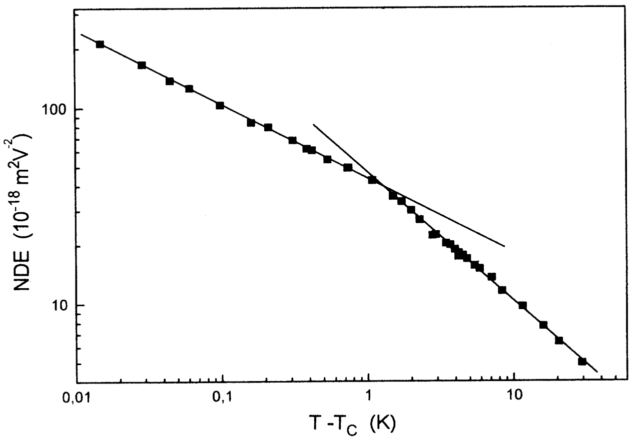

FIG. 3. The critical effect of NDE in the tested solution versus the temperature distance from the critical point in a log-log scale for $f_m = 300$ kHz.

Descriptively it may be said that for $T' < \tau$ (near $T_C$) the measurement field is capable of penetrating regions of dimensions $\xi(T'/\tau) < \xi$. In this case the nonlinear dielectric effect is influenced by the characteristic of a single, mean, critical fluctuation. Its classical-nonclassical anisotropy can be visible [relations (5) and (6)]. For $T' > \tau$ (remote from $T_C$) the measurement process is so slow that the information contained in NDE comes from a group of nonlocalized critical fluctuations within a zone of dimensions $\xi(T'/\tau) > \xi$. This additional averaging means that the specific anisotropy of critical fluctuations is no longer observable. Then NDE has only the nonclassical characteristic [relations (1) and (7)]. For suitably low or high (constant) measurement frequency, in the practically tested experimental range of distances from $T_C$, the critical behavior of NDE may be totally described by a single power relation but with different values of the critical exponent [relation (6) or (7)].

The eventual influence of the degree of elongation of critical fluctuations on the mean-field "Ising" crossover may be estimated from factor $e$ [relation (4)]. Based on results of EKE studies [9], it could be expected that the mean-field behavior would absolutely dominate for $e > 2 \times 10^{12}\ \mathrm{V}^2\,\mathrm{m}^{-2}$. In NDE studies, where for technical reasons the electric fields applied have to be stronger, this factor is virtually always greater than $2 \times 10^{13}\ \mathrm{V}^2\,\mathrm{m}^{-2}$.

Generally, in critical solutions, the nonclassical behavior near the critical point and an eventual crossover to the mean-field behavior on moving away from $T_C$ are expected [13]. This paper and Refs. [7–9] show that the anisotropy induced by a strong, steady electric field can reverse this order. Such an untypical sequence of pretransitional regions was first observed in light scattering studies of a critical solution under shear flow [15,16]. The elongation of critical fluctuations was induced here by the velocity gradient. The results reported above indicate that for the nonlinear dielectric effect, one more factor can be important, i.e., the time scale involved by the measurement frequency.

This paper is complementary to Refs. [7–9] on the analysis of the behavior in critical solutions of two effects associated with the action of a strong electric field: the nonlinear dielectric effect and the eletro-optical Kerr effect.

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