Classical-nonclassical crossover behavior of critical and noncritical liquid binary solutions in a strong electric field

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A nitrobenzene-dodecane binary mixture has been studied with the use of the nonlinear dielectric effect for one critical and two noncritical concentrations in a series of frequencies (f_m) in a weak measuring electric field. It has been found that for the temperature region where $1/f_m > \tau$ (τ, the lifetime of fluctuations), the critical exponent $\psi = \gamma - 2\beta \approx 0.59$ and consequently exponents γ (susceptibility) and β (order parameter) exhibit nonclassical values. Close to the phase-transition temperature where $1/f_m < \tau$, different patterns appear for critical and noncritical concentrations. For the latter the exponent ψ tends to zero that may point to the classical behavior, with $\gamma \approx 1$ and $\beta \to 0.5$. For the critical concentration $\psi \approx 0.4$, this may be the consequence of the semiclassical behavior with $\gamma \approx 1$ and $\beta \approx 0.325$. [S1063-651X(99)08309-9]

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I. INTRODUCTION

The study of pretransitional effects with the use of nonlinear methods is often employed owing to their high sensitivity to critical fluctuations [1,2]. The nonlinear dielectric effect (NDE), describing changes of dielectric permittivity induced by the application of a strong electric field [3], is used for liquids. It belongs to the same group of research methods as the electro-optic Kerr effect [1,2,4]. Both methods may be treated as a natural tool for studying properties of critical solutions in a strong electric field [2,4–11]. For NDE, on approaching the critical consolute temperature (T_C) [2,9–11]:

$$\mathcal{E}_{\mathrm{NDE}} \propto \langle \Delta M^2 \rangle_v \chi \propto (T - T_C)^{-\psi}, \quad \psi = \gamma - 2\beta \tag{1}$$

where $\mathcal{E}_{\mathrm{NDE}} = \Delta\varepsilon^E/E^2 = (\varepsilon^E - \varepsilon)/E^2$ is the measure of the NDE, and ε and ε^E are dielectric permittivities in a weak, measuring electric field and a strong (E) electric field, respectively. Critical exponents γ and β correspond to the susceptibility (χ) and the order parameter (M).

It can be inferred from Ref. [8] that there are two regions with two different values of the critical exponent ψ, in which Eq. (1) is fulfilled. In the vicinity of T_C, where the time scale introduced by the radio-frequency measuring field $1/f_m < \tau$ (τ is the lifetime of critical fluctuations), the critical exponent $\psi \approx 0.4$, while remote from T_C where $1/f_m > \tau$, the critical exponent $\psi \approx 0.59$. The strong electric field may induce the elongation of critical fluctuations and, consequently, the crossover from the three-dimensional Ising nonclassical behavior to the classical one. Some components of the correlation length $\xi(E \neq 0) = (\xi_\parallel, \xi_\perp, \xi_\perp)$: $\xi_\parallel$ maintains the nonclassical characteristic behavior $\xi_\parallel \propto (T - T_C)^{-\nu} \approx (T - T_C)^{-0.63}$ while other components behave classically $\xi_\perp \propto (T - T_C)^{-0.5}$. Such a property leads to the classical behavior of susceptibility $\chi \propto (T - T_C)^{-1}$ and, consequently, to $\psi \approx 0.4$ after taking into account the corrections-to-scaling terms [2]. The strong electric field interacts with the anisotropic fluctuations in a way similar to that observed in the isotropic phase of liquid-crystalline materials close to the mesomorphic phase [12]. Remote from T_C the time scale associated with f_m causes additional averaging and consequently leads to the change of ψ from about 0.4 to the nonclassical value 0.59. This paper shows the results of NDE studies in a critical solution for a set of frequencies and compares it with the pretransitional effect in noncritical solutions.

II. RESULTS AND DISCUSSION

Description of the experimental setup for performing measurements of NDE as a function of temperature and frequency of the measuring electric fields can be found in [13]. The experiment has been conducted in a nitrobenzene-dodecane (nb-d) solution. Both components were purchased from FLUKA. Dodecane was used as obtained (without further purification) and nitrobenzenze was distilled two times prior to its use. In the presented research, studies have been conducted for wider sets of frequencies than previous [2,5,7,8,12]: 70 kHz, 512 kHz, 2.45 MHz, and 8.6 MHz. It is worth noting that 70 kHz is, up to now, the lowest frequency

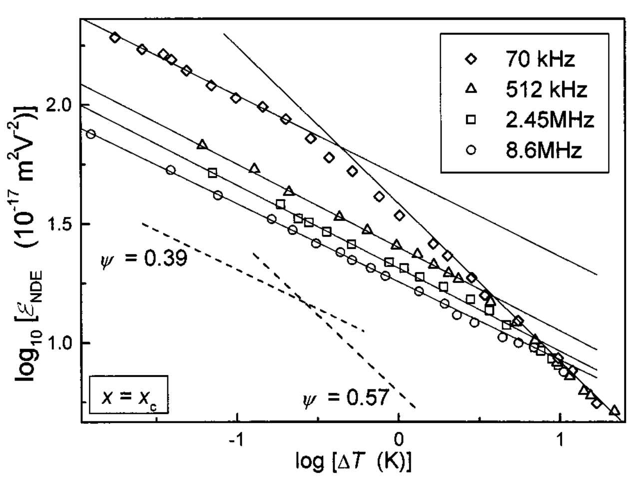

FIG. 1. The critical effect of NDE for a series of tested frequencies in the nitrobenzene-dodecane critical mixture ($\chi = \chi_C = 0.625$ mf of nb). The obtained values of the critical exponent are also shown (the error ± 0.01).

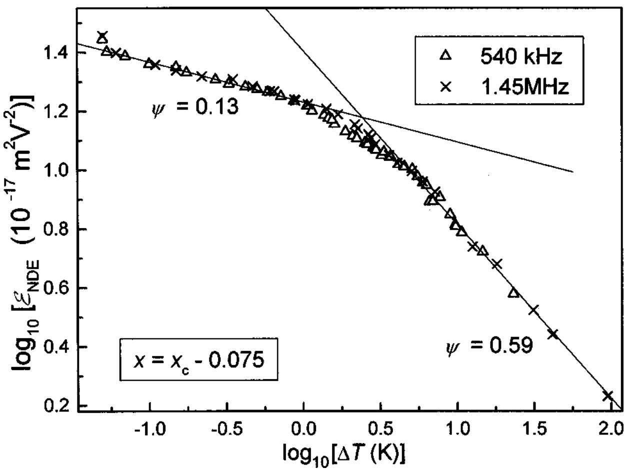

FIG. 2. The pretransitional behavior of NDE in nitrobenzene—dodecane for a noncritical solution. The obtained values of the critical exponent are also shown: the error ± 0.04 near the binodal temperature (T_B) and ± 0.03 remote from T_B.

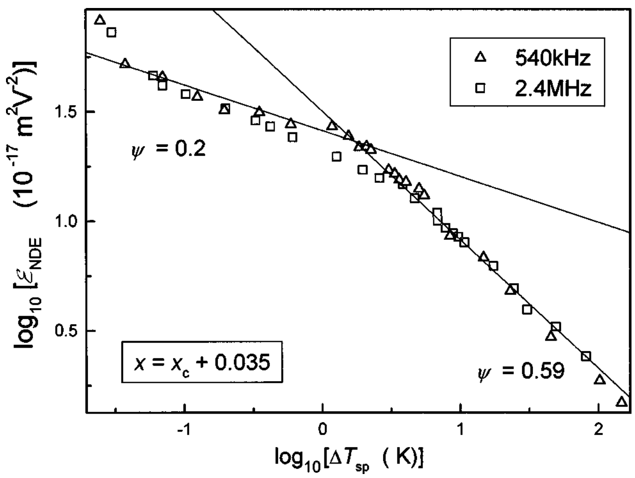

FIG. 3. The pretransitional behavior of NDE in nitrobenzene-dodecane for a noncritical solution. The obtained values of the critical exponent are also shown: the error ± 0.04 near T_B and ± 0.03 remote from T_B.

of measuring electric field applied for NDE measurements in critical solutions. Results of the dependence of $\log(\Delta\varepsilon^E/E^2)$ as a function of $\log(T-T_C)$ for the critical solution are shown in Fig. 1. The experimental pretransitional effects form two regions described by critical exponents $\psi=0.36$–0.38 near T_C and $\psi\approx 0.6$ remote from T_C. By lowering the measurement frequency, the nonclassical region, with $\gamma\approx 1.24$ and consequently $\psi=0.59$, is extended. Simultaneously the mean-field (classical) region with $\gamma\approx 1$ and $\psi\approx 0.39$ is reduced to the temperature range of $T-T_C$ less than 1 K for the measuring frequency 70 kHz. The critical exponent ψ depends on the time scale, since the system needs time to return to equilibrium after having been disturbed by a strong electric field [6,7,12]. It should be noted that NDE is a very sensitive detector of the phase-transition temperature. On crossing T_C, or more generally the separation (binodal) temperature T_B, the NDE apparatus records a very strong change of dielectric permittivity due to the fact that the gap of the measurement capacitor is in the lower phase of the two-phase region.

The results of measurements of NDE for two noncritical solutions with the concentrations $x_C+0.035$ mole fraction (mf) of nb, and $x_C-0.075$ mf of nb are shown in Figs. 2 and 3. One can again notice that in the case of a noncritical mixture the crossover temperature divides the temperature dependence into two regions of NDE described by different exponents. The high-temperature region is described by $\psi\approx 0.6$, whereas close to T_B, the value of the exponent dramatically decreases. The analysis was conducted using the pseudospinodal hypothesis in which the extrapolated temperature $T_{SP}<T_B$ plays the role of the singular temperature in relation (1) [12]. This is due to to the dominance of one kind of fluctuations, which significantly favors deformation by the strong electric field. According to the experimental data [14] and the Landau-Ginzburg theory for $d\geqslant 4$ [15], in the strong fluctuations region the critical exponents $\gamma\approx 1$, $\beta\approx 0.5$, and hence ψ tends to 0. Concluding we can say that

(i) for both critical and noncritical concentrations if $1/f_m>\tau$ is fulfilled then $\gamma\approx 1.23$, $\beta\approx 0.325$, and $\psi=0.59$ (nonclassical case), (ii) for critical concentration if $1/f_m<\tau$ then $\gamma=1.02$ (with the inclusion of logarithmic corrections), $\beta\approx 0.325$, and $\psi\approx 0.39$ (semiclassical case), and (iii) for noncritical concentration if $1/f_m<\tau$ one can observe $\gamma=1.02$, $\beta\to 0.5$, and $\psi\to 0$ (classical case),

The presented results are similar to the ones obtained for binary solutions under shear flow [14] except for those obtained for critical concentration. In our opinion this may be due to the fact that shear flow generates only one kind of fluctuation deformation. In the strong electric field, the deformation of fluctuations with the dielectric permittivity lower or higher than the average permittivity of the solution may be different [16]. For noncritical mixtures one kind of fluctuations dominates and consequently one type of deformation dominates in the external electric field. In this case the situation may be similar for NDE and shear-flow experiments.

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