# Dynamics of critical fluctuations in a binary mixture of limited miscibility under a strong electric field

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Experimental investigations of relaxation after switching off the strong electric field in a nitrobenzene-dodecane mixture are presented. Studies were conducted for mixtures of critical and noncritical concentrations using the time-resolved nonlinear dielectric effect. The decays obtained can be portrayed by means of the stretched exponential function with the value of the exponent in agreement with the dynamic droplet model predictions. It has been shown that experimental decays exhibit a universal scaling behavior. The relaxation time (scaling factor) shows a power behavior with the exponent $y \approx 1.2$ for the critical mixture and $y \to 1$ for the noncritical one. These values are much smaller than theoretically predicted $y = 1.8$–$1.9$. Based on the assumption that a strong electric field induces in the mixture a quasinematic structure with semiclassical critical properties, a quantitative explanation of this difference is proposed.

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## INTRODUCTION

One of the characteristic features of complex liquids is the nonexponential behavior of relaxation times [1–3]. The stretched exponential (SE) function is most often applied to the interval of times ($t$) longer than the relaxation time ($\tau$):

$$R(t) \sim \exp\left[-\left(\frac{t}{\tau}\right)^x\right], \qquad (1)$$

where $0 < x < 1$ is the SE exponent and $t$ is the relaxation decay time. The initial part of the relaxation process can be parametrized by the von Schweidler dependence

$$R(t) = f - h(t/\tau)^b, \quad 0 < b < 1. \qquad (2)$$

Generally, the coefficients in relations (1) and (2) are system dependent [1–3]. To the best of the authors knowledge the only exception is the relaxation in a critical mixture after switching off the strong electric field. This phenomenon was first observed by Degiorgio and Piazza [4] who applied a time-resolved electro-optic Kerr effect (EKE) to micellar solutions of nonionic surfactants near their lower consolute point and next to two other critical binary mixtures [5,6]. They obtained the value of the SE exponent by applying the droplet model (DM) to dynamic phenomena [the dynamic droplet model (DDM)]

$$R(t) = C \int_0^\infty l^{\psi/\nu - 1} \exp\left[\frac{(l/\xi)^2}{k_B T}\right] \exp\left(\frac{t}{Al^3}\right) dl, \qquad (3)$$

where $R(t)$ is the normalized birefringence decay, $C$ denotes the normalizing factor, the index $I$ represents the cluster size, the exponent $\psi \approx 0.59$ describes the temperature evolution of the stationary birefringence, and $\xi \propto (T - T)^{-\nu}$ is the correlation length $\nu \approx 0.63$.

The saddle point approximation simplifies relation (3) tho the SE equation with the exponent [5,6]

$$x = \frac{2 - \eta}{5 - \eta} \approx 0.395, \qquad (4)$$

where $\eta \approx 0.004$ is the correlation-function critical exponent. The DDM also assumes

$$\tau \propto \xi^z \approx (T - T_C)^{-y}, \quad y \approx -1.9, \qquad (5)$$

where $z \approx 3$ is the dynamic exponent. A different approach to the problem was presented by Onuki and Doi [7] who related the anisotropy of the structure factor of a critical solution in a strong electric field to that of the dielectric tensor and obtained

$$R(t) = \frac{4}{\pi} \int_0^\infty dy \frac{y^2}{(1 + y^2)} \exp\left[-2K(y)\frac{t}{\tau_{OD}}\right], \qquad (6)$$

where $K(y)$ is the Kawasaki function and $\tau_{OD}$ is the relaxation time.

It can also be simplified to

$$R(t) \approx 1 - 2.29(t/\tau_{OD})^{1/3} \quad (t \ll \tau_{OD}) \quad \text{and}$$
$$R(t) \approx 0.199(t/\tau_{OD})^{-1.5} \quad (t \gg \tau_{OD}). \qquad (7)$$

The similarity of these equations to the von Schweidler dependence is noteworthy. As for the temperature evolution of the relaxation time

$$\tau_{OD} = \frac{6\pi \eta_s \xi^3}{k_B T} \propto (T - T_C)^{-y}, \quad y \approx -1.85, \qquad (8)$$

where $\eta_s \propto (T - T_C)^{-\phi}$ denotes the shear viscosity with $\phi = 0.032$–$0.041$ [8]. The experiments mentioned above [4–6] and the subsequent tests in propylene carbonate-butylbenzene critical mixture [9] confirmed the validity of the SE description proposed by the DDM model. In Ref. [9] it is shown that the OD formula also portrays the decay well.

In the EKE experiments the strong, steady electric field is applied in the form of rectangular pulses of duration $\Delta t_D$. Such a behavior of a strong electric field also occurs for the

nonlinear dielectric effect (NDE) [10,11] $\mathcal{E}_{NDE}=(\varepsilon^E - \varepsilon)/E^2$, where $\varepsilon^E, \varepsilon$ are dielectric permittivities (for radio frequencies) in a strong and weak electric field, respectively. The first test on time-resolved NDE in 1-nitropropane-dodecane critical mixture was conducted by the authors in 1991 [12]. The next studies were carried out for the isothermal, pressure approaching the critical consolute point in the nitrobenzene-dodecane mixture [13].

This paper shows results of time-resolved NDE studies in nitrobenzene-dodecane under atmospheric pressure for mixtures of critical and noncritical concentration. It is noteworthy that a significant difference between these two cases for the temperature behavior of the stationary NDE has been recently found [14]. Another aim of our investigations was to find further data concerning exponent $y$. The results of only few experiments [5,6] agree with the theoretical predictions mentioned above [relations (5) and (8)] whereas in the majority of investigations [4,9,12,13] a much smaller value of $y=1.1–1.3$ was obtained.

## EXPERIMENT

Measurements were performed using the setup described in Ref. [11]. Tests were conducted for the frequency of the weak measuring filed $f_m=3.5$ MHz, the voltage (peak-peak) of which was 1.5 V. The electric field was applied in the form of dc pulses of duration $\Delta t_D=1$ ms–32 m. The period between pulses was 1–3 s and the voltage 70–1000 V. The capacitor gap was 0.8 mm, $C_0=4.7$ pF. The switching off of the steady electric field induced a shift of capacitance (1–5 fF) which was registered with three-digit resolution. For the results obtained it is important that the strong electric field is switched off in the stationary state for $\Delta t_D \gg \tau$. Temperature was measured by means of a platinum resistor (DIN 43 260) placed in one of the capacitor covers and by a Keithley 195A multimeter. The gradient of temperature across the measurement capacitor, monitored by two thermocouples did not exceed 0.002 K. The data were analyzed using ORIGIN 5.0 software. All errors are given as three standard deviations.

## RESULTS AND DISCUSSION

Figure 1 shows experimental NDE responses for several distances from the critical consolute temperature. The response function was normalized in the following way:

$$R(t)=1-\mathcal{E}_{NDE}(t)/\mathcal{E}_{NDE}^{sat}, \qquad (9)$$

where $\mathcal{E}_{NDE}(t)$ is the value of NDE at time $t$ after switching off the strong electric field and $\mathcal{E}_{NDE}^{sat}$ is the stationary, "saturated" value of NDE for $t \gg \tau$.

The deformation of the NDE responses due to relaxation processes ceases to be visible for $T-T_C > 0.2$ K when the relaxation time is less than 0.02 ms. Then only the saturated value can be measured. This restriction is associated with the internal dynamics of the measuring technique. It is worth noticing the compatibility of time-resolved NDE and EKE methods. For the latter the region in the immediate vicinity of $T_C$ is inaccessible. This is due to loss of transparency caused by critical opalescence. Figure 1 also shows that a simple scaling of the decay-time axis made it possible to
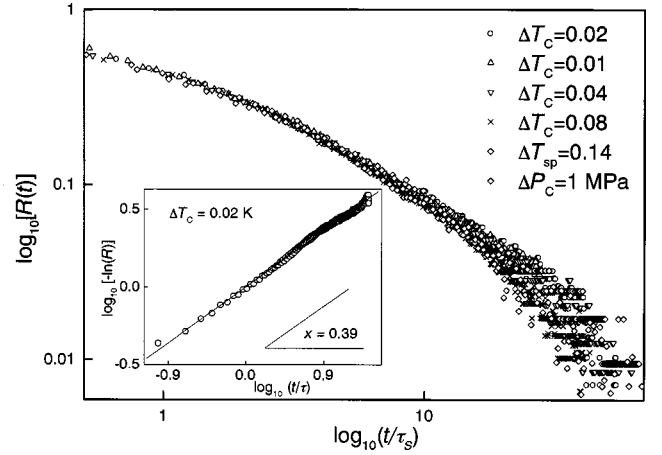


FIG. 1. Normalized relaxation decays in the log-log scale for several distances from the point of the continuous phase transition. $T-T_C$ denotes the distance from the critical consolute point, $T-T_{sp}$ is the distance from the extrapolated point of a hypothetical, continuous pseudospinodal transition for the noncritical concentration ($x=x_C+0.04$ mole fraction of nitrobenzene). $P-P_C$ is the pressure distance from the critical consolute point. Pressure data are taken from Ref. [13]. The inset shows the SE behavior of one of responses.

superpose decays for different distances from $T_C$ into a one scaling curve. The single, scaled decay also contains data for the noncritical mixture and decays obtained from isothermal pressure studies in a critical nitrobenzene-dodecane mixture [13].

The inset clearly shows the validity of the SE description of the decay. The average value for the SE exponent for the critical mixture is $x=0.39\pm0.02$ and for the noncritical one is $x=0.37\pm0.06$. The decay can also be portrayed by means of the DDM integral general response formula (3). However, this is only possible if the exponent $\psi$ is treated as an adjustable parameter but then the results become ambiguous [9]. The OD model [7] decay formula was derived for birefringence for which the wave number $k$ essentially differs from the one in NDE studies. The shape of the OD decay strongly depends on the value of the $k\xi$ factor [16].

It should be noted that the droplet model [15] and the OD model [7] predicted $\psi_{EKE}=\psi_{NDE}=\psi_{theor}\approx0.59$ but experiments (Ref. [17], and references therein) gave $\psi_{EKE} \gtrsim \psi_{theor} > \psi_{NDE}$. The proposal of explaining this discrepancy is given in Refs. [17–19].

Figure 2 shows the critical behavior of the temperature evolution of relaxation times. It should be noted that for the analysis of the noncritical mixture a pseudopinodal hypothesis [20] was used:

$$\tau=\tau_0(T-T_{sp})^{-y} \quad \text{with} \quad T>T_B, \; T_{sp}=T_B-\Delta T \quad (10)$$

where $T_B$ is the binodal temperature, $T_{sp}$ is the pseudospinodal temperature, and $\Delta T$ is a measure of the discontinuity of the transition. For the critical and the noncritical mixture the critical exponent $y$ is much smaller than the value given in relations (5) and (8).

In the opinion of the authors such a behavior may be associated with the quasinematic structure of critical fluctua-
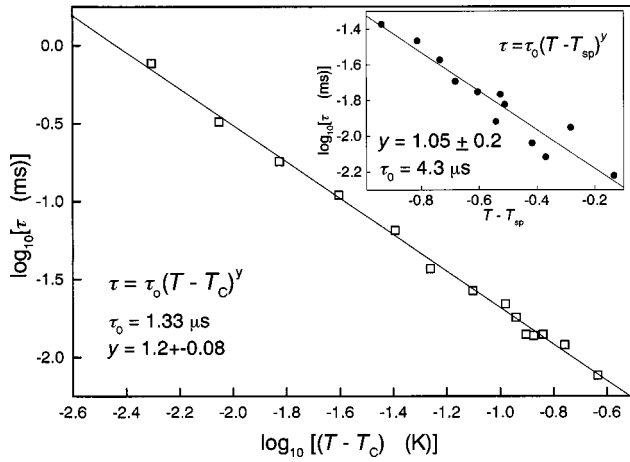
FIG. 2. Logarithmic plot of the temperature dependence of the relaxation time for the critical and the noncritical (the inset) mixture. Parameters of the fit of data (solid lines) are given in the figure.

tions in a strong electric field. This feature strongly influences the critical effects of stationary EKE and NDE [17–19]. For the latter [17]

$$\mathcal{E}_{\text{NDE}}^{\text{sat}} \propto \langle \Delta M^2 \rangle_V \chi \propto (T - T_C)^{-\psi}, \tag{11}$$

where the mean square of the order parameter fluctuations $\langle \Delta M^2 \rangle_V \propto (T - T_C)^\beta$, $\beta$ is the universal critical exponent for the order parameter, and the susceptibility (compressibility) $\chi \propto (T - T_C)^{-\gamma}$. As mentioned above the OD model and the droplet model predict $\psi = \gamma - 2\beta \approx 0.59$ with $\gamma \approx 1.23$ and $\beta \approx 0.325$ (nonclassical values).

However, it has been shown in Ref. [19] that such a value can be only obtained remote from $T_C$, where the condition $f_m^{-1}/\tau > 1$ is fulfilled. Near $T_C$, for $f_m^{-1}/\tau < 1$, the exponent $\gamma \approx 1$ (classical value) and $\beta \approx 0.325$ (nonclassical value) which consequently gave $\psi \approx 0.39$ (semiclassical behavior). Recent studies for a noncritical solution suggest that in this case on approaching the spinodal temperature $\psi \rightarrow 0$ [14]. This may be the consequence of $\beta \approx 0.5$ and $\gamma \approx 1$, i.e., the classical behavior. Such a discrepancy between the NDE behavior in critical and noncritical solutions may be associated with the fact that the strong electric field may act in a different way on fluctuations which have dielectric permittivity larger (e.g., nitrobenzene rich) or smaller (e.g., $n$-alkane rich) than the permittivity of the mixture [21,22]. Due to this difference critical fluctuations under strong electric field may take the form of prolate (rodlike) and oblate (disklike) objects, respectively. However, the oblate deformation was

never found in observations of a liquid droplet immersed in another liquid, for instance an oil droplet in water. Only prolate droplets were observed [23–25]. Such behavior was associated with the nonstability of the oblate forms which unlike the prolate objects are perpendicular to the direction of the strong electric field [26]. However, this factor may not be vital for the relatively small and short lived critical fluctuations. Applying this hypothesis [17] it can be assumed that the correlation length of prolate fluctuations is $\xi = (\xi_{\text{long}}, \xi_{\text{short}}, \xi_{\text{short}})$ and the correlation length of oblate fluctuations is $\xi = (\xi_{\text{short}}, \xi_{\text{long}}, \xi_{\text{long}})$. The component with index ''long'' pertains the nonclassical behavior under field $E$, i.e., the critical exponent $v \approx 0.63$ while the ''short'' components may crossover the Ginzburg criterion and become classical, i.e., $v = 0.5$. For a critical mixture under a strong electric field the number of both types of fluctuations should be equal. Additionally, taking into account the fact that for the nonconserved order parameter the dynamical exponent $z = 2$ [8], one can define the exponent $y$ as an average of contributions from both prolate and oblate components:

$$y = 1/2[z(v_{\text{short}} + z_\eta) + z(v_{\text{long}} + z_\eta)]$$
$$= v_{\text{long}} + v_{\text{short}} + 2z_\eta \approx 1.26, \tag{12}$$

where $z_\eta \approx 0.064$ is the dynamic critical exponent for the critical part of the shear viscosity $\eta_s \propto \xi^{z_\eta}$ and the diffusion coefficient $D \propto \xi^{1 + z_\eta}$ [27].

It should be noted that the value $z = 2$ has been found also for prenematic fluctuations in the isotropic phase of nematogens [28]. In the opinion of authors this coincidence additionally supports the fluidlike, critical hypothesis [29–32] for the isotropic phase of nematogenic liquid crystalline materials.

For noncritical mixtures the domination of one kind of fluctuations may create a structure more similar to the one that observed for the isotropic phase of nematogens and shift $y \rightarrow 1$ (Fig. 3) as well as $\psi \rightarrow 0$ [14].

The hypothesis of the semiclassical, quasinematic characteristics of the critical fluctuations [17–19] was first introduced to remove the long-standing discrepancy between theoretical and experimental behavior of stationary NDE and EKE in critical solutions (Ref. [17], and references therein). Results presented above suggest that this idea can also be applied to explain the experimentally obtained values of exponent $y$.

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