

Stretched-exponential relaxation of the nonlinear dielectric effect in a critical binary solution

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An experimental confirmation is given of the existence of a stretched-exponential relaxation of the form $\exp[-(t/\tau)^x]$ with $x \approx 0.39$ in a binary solution with an upper critical point. The nonlinear dielectric effect (NDE) method was used for this experiment. Results obtained are similar to those reported earlier by Piazza *et al.* [J. Opt. Soc. Am. B **3**, 1642 (1986); Phys. Rev. B **38**, 7223 (1988)] based on the Kerr-effect measurements in solutions with a lower critical point. Studies could be carried out in the immediate vicinity of the critical point, because the application of the NDE is not restricted by the appearance of the critical opalescence.

INTRODUCTION

Investigations conducted by Piazza *et al.*^{1,2} on the dynamics of the critical properties of a water–2,6-lutidine solution indicated, on approaching the critical temperature T_c , the existence of a stretched-exponential relaxation² of critical fluctuations of the form $\exp[-(t/\tau)^x]$, with $x \approx 0.4$. This type of relaxation was seen earlier in micellar solutions of nonionic surfactants near their lower consolute points³. The research method used in the quoted papers was the Kerr effect.

In our studies another method was employed, i.e., nonlinear dielectric effect (NDE). This method makes it possible to perform measurements very close to the temperature of phase separation, even in the region of strong critical opalescence, where the Kerr effect cannot be used due to the intensive light scattering (light is here the measuring wave). With the NDE method, radio waves are used, and the turbidity of the medium does not constitute a hindrance. The NDE is defined as the change in electrical susceptibility caused by applying a strong electric field $\Delta\epsilon^E = \epsilon^E - \epsilon^0$, where ϵ^E and ϵ^0 are electric permittivities in a strong and in a weak electric field E , respectively. Because the fact that in practice the electric fields applied have intensities that do not cause deviations from the $\Delta\epsilon \sim E^2$ proportionality, it is generally accepted that the measure of NDE is the magnitude $\Delta\epsilon^E/E^2$.⁴

EXPERIMENT

In our experiment we made use of a modified version of the measurement apparatus proposed by Małecki.⁵ A constant voltage not exceeding 1000 V, of exclusively impulse type, was applied to a flat-parallel capacitor⁶, with a 0.34-mm gap, located in the circuit of the generator working in the range of frequencies of a few MHz. The switch-off impulses had a rectangular form of a time length 3 ms. The slopes of the impulse at the sample's response at the measurement apparatus output had rising (falling) times of about 0.3 ms [Fig. 1(a)]. The impulse repeat time was about 1 s. The application of virtually constant electric field switched impulsively clearly reduced the electric conductance of the solution. We used im-

pulses not longer than 3 ms to avoid distortion due to bandwidth limitation. We hope to solve this problem in the near future.

An analysis was made of the form of the impulse obtained from the cumulation of 50–100 impulses inducing this effect. Measurements were performed for a solution 1-nitropropane–dodecane, with an upper critical point. The critical concentration of the solution was 0.66 mol fraction of 1-nitropropane and the critical temperature was 12.1 °C.⁷ Relaxation times were measured in the temperature interval from 0.25 to 0.005 °C above T_c ; in the scale of reduced temperatures $\epsilon[(T - T_c)/T_c]$ this corresponds to the interval $8 \times 10^{-4} - 1.7 \times 10^{-5}$.

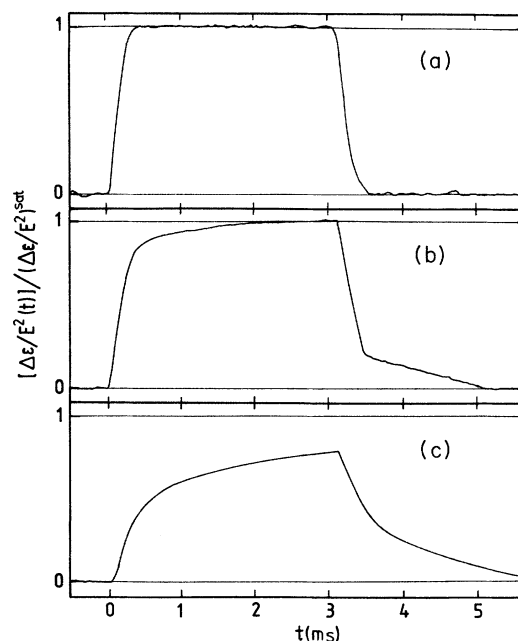


FIG. 1. The shape of the NDE signals observed for (a) $T - T_c = 0.5$ K, (b) $T - T_c = 0.1$ K, and (c) $T - T_c = 0.005$ K.

RESULTS

Figure 1 shows the forms appropriate to the inducing impulses in a critical solution of 1-nitropropane plus dodecane for various temperatures. In Fig. 1(a) is shown the recorded NDE effect at temperature sufficiently high that no influence of relaxation on impulse form is observed. In Fig. 1(b) (temperature $T_c + 0.1^\circ\text{C}$) the influence of relaxation on the form of the impulse is clearly visible. In Fig. 1(c) even more deformation of the impulse may be seen, caused by the very close proximity of T_c (0.005°C above T_c). According to Ref. 2 the form of the NDE impulse ought to be described by the stretched-exponential relaxation function $R(t)$:

$$\begin{aligned} \frac{\Delta\epsilon^E}{E^2}(t) &= \left[\frac{\Delta\epsilon^E}{E^2} \right]^{\text{sat}} \{1 - \exp[-(t/\tau)^x]\} \\ &= \left[\frac{\Delta\epsilon^E}{E^2} \right]^{\text{sat}} R(t) \quad \text{for } \epsilon = \text{const} \end{aligned} \quad (1)$$

where $\Delta\epsilon^E/E^2(t)$ and $(\Delta\epsilon^E/E^2)^{\text{sat}}$ denote values of the NDE for a given time t and for $t \gg \tau$, respectively, τ is the relaxation time, $x \approx (2-\eta)/(5-\eta) \approx 0.39$ is a universal critical exponent of the stretched-exponential relaxation in the critical region, and $\eta \approx 0.04$ is the critical exponent describing the decay of correlation at T_c .⁸

The stretched-exponential relaxation is also observed in noncritical systems, for example, for the liquid-glass transition.⁹ However, in this case the exponent x is material dependent (nonuniversal): $0 < x < 1$. In the recent work of Degiorgio *et al.*¹⁰ on birefringence in polyelectrolyte solutions it has been shown that the value of x may be universal for two cases. The extremely narrow distribution of relaxation times ("stiff chains limit") gave $x \approx 1$. In the opposite case of self-avoiding walks of chains a value of $x \approx 0.44$ was obtained.

Our experimental results confirmed relation (1), which is illustrated by Fig. 2 for an example distance from T_c ($\epsilon = 3.15 \times 10^{-4}$, i.e., $T - T_c = 0.09^\circ\text{C}$). Values of τ (for a given ϵ) and x are determined from the appropriate

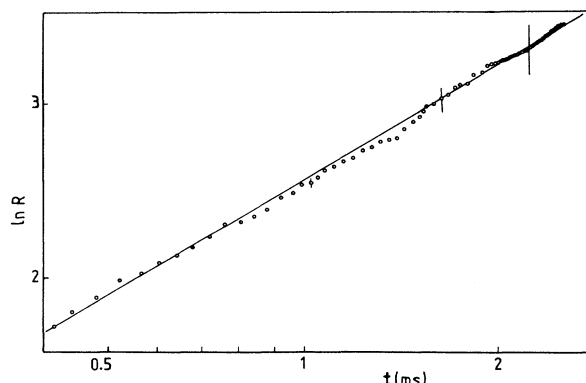


FIG. 2. The log-log plot of the natural logarithm of the relaxation function $R(t)$ as a function of time t .

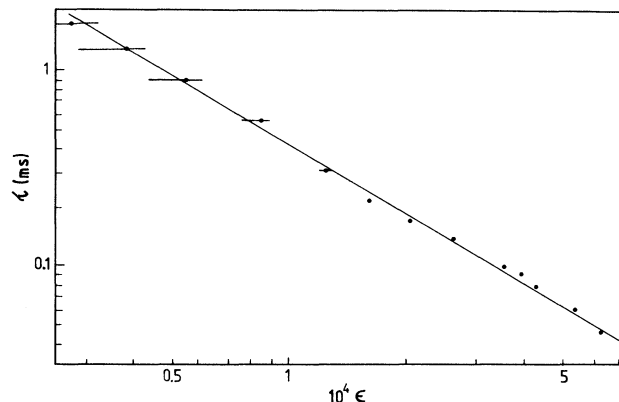


FIG. 3. The log-log plot showing the temperature dependence of the relaxation time τ .

intercept and the slope, respectively. A value of $x = 0.39 \pm 0.01$ has been obtained. All errors in this paper are given as three standard deviations. The numerical analysis was done by means of the least-squares method.¹¹

It is noteworthy that, for all tested temperature distances from the critical point throughout the whole test time interval the experimental points lie, as in Fig. 3, on a straight line. This behavior is in agreement with the results of the Kerr²-effect studies, which were done for $1.56 \times 10^{-3} \leq \epsilon \leq 1.17 \times 10^{-2}$ and where it has been observed that the linear behavior (Fig. 2) is obeyed over an increasing time range as $\epsilon \rightarrow 0$. The temperature character of the relaxation time may be described by the power function (Fig. 3)

$$\tau(\epsilon) \sim \epsilon^{-y}. \quad (2)$$

In Ref. 2 a value of $y = 1.8 \pm 0.6$ is given. The theory² predicts $y \approx zv \approx 1.8$, where $z \approx 3$ is the dynamic critical exponent for a conserved order parameter and $v \approx 0.63$ is the exponent of the correlation length.⁸ The value obtained in our studies of $y = 1.3 \pm 0.3$ differs, for as yet unexplained reasons, from the above values.

Results reported in this paper confirm the existence of the stretched-exponential relaxation in binary solutions, also in the case of a system with an upper critical point. Also important was that this phenomenon was studied in the immediate vicinity of T_c . In exact terms, such measurements by means of the NDE are possible only in this region. This restriction is connected to the dynamics of the measuring apparatus. On the other hand, Kerr-effect measurements are possible only outside this region due to the critical opalescence. Thus the information obtained from both these methods is very complementary.

ACKNOWLEDGMENTS

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- ¹R. Piazza, V. Degiorgio, and T. Bellini, *J. Opt. Soc. Am. B* **3**, 1642 (1986).
- ²R. Piazza, T. Bellini, V. Degiorgio, R. E. Goldstein, S. Leibler, and R. Lipovski, *Phys. Rev. B* **38**, 7223 (1988).
- ³V. Degiorgio and R. Piazza, *Phys. Rev. Lett.* **55**, 288 (1985).
- ⁴A. Chetkowski, *Dielectric Physics* (PWN-Elsevier, Warsaw, 1980).
- ⁵J. Małecki, *J. Chem. Faraday Trans. II* **72**, 104 (1976).
- ⁶S. J. Rzoska, J. Chrapeć, and J. Zioło, *J. Phys. Chem.* **92**, 2064 (1988).
- ⁷J. Zioło, S. J. Rzoska, and J. Chrapeć, *Phase Transitions* **9**, 317 (1987).
- ⁸M. A. Anisimov, *Critical Phenomena in Liquids and Liquid Crystals* (Nauka, Moscow, 1987), in Russian.
- ⁹*Molecular Dynamics and Relaxation Phenomena in Glasses, Lecture Notes in Physics*, edited by T. Dorfmueller and G. Williams (Springer-Verlag, Bielefeld, 1985).
- ¹⁰V. Degiorgio, T. Bellini, F. Mantegazza, and R. E. Goldstein, *Phys. Rev. Lett.* **64**, 1043 (1990).
- ¹¹P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, London, 1969).