Stretched relaxation after switching off the strong electric field in a near-critical solution under high pressure

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Experimental investigations of the relaxation of the nonlinear dielectric effect after switching off a strong electric field in a near-critical nitrobenzene-dodecane solution under high pressure are presented. The long-time tail of the decay is described by the stretched exponential function, with the exponent $x = 0.37 \pm 0.04$. The early stages of the decay are portrayed by the power function $R(t) = 1 - 2.29(t/\tau)^{1/3}$, where τ_{OD} denotes the Onuki-Doi relaxation time [Europhys. Lett. **17**, 63 (1992)]. In the immediate vicinity of the critical consolute point a value $\tau_{OD} \approx 0.23$ s was reached. Experimental decays observed at different pressures exhibit a scaling behavior. The pressure evolution of the scaling parameter shows a power behavior with the exponent $y = 1.1 \pm 0.2$. [S1063-651X(97)01109-4]

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INTRODUCTION

Experiments on transient electric birefringence (TEB) [1–4] and the nonlinear dielectric effect (NDE) [5] performed by applying a rectangular pulse of a strong electric field to a near-critical binary solution have shown that the decay after switching off the field is strongly nonexponential and is asymptotically described by the stretched-exponential (SE) function

$$R_{SE}(t) \approx \exp\left[-\left(\frac{t}{\tau_S}\right)^x\right], \tag{1}$$

where $R_{SE}(t)$ is the normalized SE response function [1], t denotes the elapse of time from the moment the electric field is switched off, the time constant τ_S may be interpreted as the measure of the average relaxation time, and the exponent $x \approx 0.39$. The SE response is generally regarded as an important but phenomenological tool to describe the relaxation data in systems as diverse as amorphous solids, complex liquids, polymers, and supercooled glass-forming liquids (see [6–9] and references therein). However, for the TEB and NDE relaxation in critical solutions a unique feature has been proposed: a well-defined relation of the stretch exponent x to universal critical exponents. By applying the dynamic droplet (DD) model, Piazza *et al.* [2] obtained

$$x = \frac{2 - \eta}{5 - \eta} \approx 0.39, \quad \tau_S \propto \xi^{-y} \propto (T - T_C)^{-1.9}, \tag{2}$$

where $\eta = 0.04$ is the exponent for critical correlation function [10], $\xi = \xi_0(T - T_C)^{-v}$ is the correlation length of critical fluctuations, ξ_0 denotes the critical amplitude, the critical exponent $v \approx 0.63$ [10], the exponent $y = zv \approx 1.9$, and $z \approx 3$ is the dynamic exponent for a conserved order parameter. $T > T_C$ and T_C denotes the critical consolute temperature. In 1992 Onuki and Doi [11] applied a less phenomenological theory. They derived a formula that connects the anisotropy of a dielectric tensor in the presence of an external electric field to the anisotropy of the structure factor $S(q)$, induced

by dipole-dipole interactions. From this, they obtained a formula for the normalized response function

$$R_{OD}(t) = \frac{4}{\pi} \int_0^\infty dy\, \frac{y^2}{(1+y^2)^2} \exp[-2K(y)t/\tau_{OD}], \tag{3}$$

where τ_{OD} is the Onuki-Doi relaxation time and

$$K(y) = \tfrac{3}{4}[1 + y^2 + (y^3 - y^{-1})\arctan y] \tag{4}$$

is the Kawasaki function.

In two cases the OD response function is greatly simplified:

$$R_{OD} \approx 1 - 2.29(t/\tau_{OD})^{1/3} \quad \text{for} \quad t/\tau_{OD} \ll 1, \tag{5a}$$

$$R_{OD} \approx 0.199(t/\tau_{OD})^{-3/2} \quad \text{for} \quad t/\tau_{OD} \gg 1. \tag{5b}$$

The OD model relates the time constant τ_{OD} to the average thermal decay rate

$$\tau_{OD} = \frac{6\pi\bar{\eta}\zeta^3}{k_B T} \propto (T - T_C)^{-1.9}, \tag{6}$$

where $\bar{\eta}$ is the shear viscosity and k_B denotes the Boltzmann constant.

Preliminary experiments strongly pointed to the validity of the SE description. TEB studies in near critical mixtures 2,6-lutidine-water [2] and butoxyethanol-water [3] gave $x = 0.39 \pm 0.07$, $y = 1.8 \pm 0.05$, and $x = 0.4 \pm 0.05$, $y = 1.78 \pm 0.05$, respectively. Also noteworthy are earlier studies in a micellar solution $C_{12}Et_6$-H_2O near a critical consolute point where the scaling behavior of experimental decays was found and $y = 1.2 \pm 0.2$ was obtained [1]. NDE studies in 1-nitropropane-dodecane solution gave $x = 0.39 \pm 0.02$ and $y = 1.3 \pm 0.2$ [5]. Recent accurate TEB tests in propylene carbonate- *n*-butylbenzene near-critical mixture gave $x = 0.4 \pm 0.03$ and $y = 1.3 \pm 0.2$ [4]. They also showed that the SE function describes properly the decay for $t/\tau_S > 1$, in agreement with the saddle-point approximation applied in deriving the SE function from the DD model [2]. The numerical evolution of the OD integral (3) showed that it sat-

isfactorily describes experimental data for $0.1 < t/\tau_{OD} < 1$. For $t/\tau_{OD} \rightarrow \infty$ a small, systematic discrepancy was noted [4]. Unfortunately, the appearance of critical opalescence made it impossible to reach the region where the strictly defined power relation (5a) could be tested [4].

Pressure studies of dielectric relaxation processes in liquids exhibiting complex relaxation behavior are, despite its long history (see [9,12–14] and references therein), relatively rare and far from conclusive results [15,16]. To the best of the authors' knowledge, there are no such investigations applying nonlinear dielectric methods. This paper presents results of measurements applying the time-resolved NDE method in a near critical nitrobenzene-dodecane solution. The application of pressure made it possible to test all stages of relaxation, including experimentally untested region just after switching off the strong dielectric field.

EXPERIMENT

The NDE describes changes of dielectric permittivity in liquids induced by an additional, strong steady electric field (E): $\mathcal{E}_{NDE} = (\varepsilon^E - \varepsilon)/E^2$, where ε^E and ε describe dielectric permittivities in strong (E) and weak (measuring) electric fields, respectively. Measurements were performed using an apparatus described in detail in Ref. [17]. The frequency of the weak, measuring field was about 8.9 MHz, with voltage $U = 3$ V. The additional strong, steady electric field was applied in the form of rectangular impulses of duration $\Delta t_D = 1$ ms–1 s ($U = 100$–800 V and repeatability (20–50)Δt_D. Typically 10–50 cumulations of the response signal were registered. The description of the pressure system and the design of the measurement capacitor (a flat parallel, gap 0.3 mm, $C_0 \approx 4.1$ pF) are given in Ref. [18]. At each measurement point the validity of the condition $(\varepsilon^E - \varepsilon) \propto E^2$ was tested. For the time-resolved investigations discussed in this paper the normalized response function is defined as $R(t) = \mathcal{E}_{NDE}(t)/\mathcal{E}_{NDE}^{sat}$, where $\mathcal{E}_{NDE}^{sat} = \mathcal{E}_{NDE}(t=0)$ is the "saturation," stationary, value of the NDE reached if the condition for the application of the strong electric field $\Delta t_D \gg \tau$ is fulfilled. $\mathcal{E}_{NDE}(t)$ describes the decay from this stationary state after switching off a strong electric field.

The temperature of the pressure chamber was stabilized with accuracy 0.02 K/24 h. It was monitored by means of a platinum resistor (A1 class, DIN 40 360) placed in the coat of the chamber and a thermocouple placed inside the chamber using a Keithley 195A multimeter. The pressure was measured by a Nova Swiss tensometric pressure meter with a resolution of ± 0.1 MPa. Studies were conducted in a nitrobenzene-dodecane mixture with $x_C = 0.63$ mole fraction of nitrobenzene, $T_C = 27.1$ °C, and $T_C(P) = 27.1 + 0.07P + 0.000\,09P^2$ [T_C (°C), P (MPa), $P < 200$ MPa] [18,19]. A very small influence of pressure on the critical concentration in this solution was noticed [19]. The relatively large difference of electric permittivity of nitrobenzene and dodecane ($\varepsilon_{nb} \approx 30$ and $\varepsilon_{dod} \approx 2.5$, respectively) guaranteed a large value of NDE critical increase [20]. This feature is of fundamental importance because valves in the pressure chamber introduced parasitic electric capacitances that strongly restricted the sensitivity of the NDE measurement apparatus.

Nitrobenzene (Fluka) was distilled four times, the last time immediately prior to preparing the sample, and dried
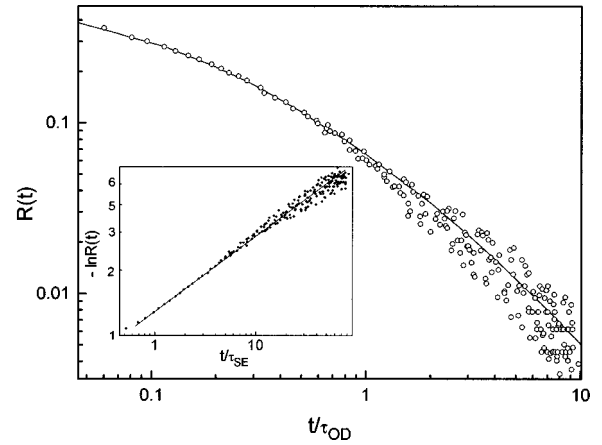

FIG. 1. Comparison between the normalized experimental NDE decay [$(P_c - P) \approx 6$ MPa] and the Onuki-Doi model. The solid line represents the OD response function [relation (3)]. The inset shows the stretched-exponential behavior [relation (1)] for the same experimental data. The slope of the straight line is $x = 0.36 \pm 0.01$.

over molecular sieves. Dodecane (Fluka, HPLC class) was used without further purification. Experimental data were analyzed using ORIGIN 3.5 software (Microcal Inc.). All errors are given as three standard deviations.

RESULTS AND DISCUSSION

The inset in Fig. 1 shows that the experimental response function $R(t)$ follows the stretched exponential pattern over two decades, with a deviation for $t/\tau_S \rightarrow 1$. The average value of the SE exponent obtained from the analysis of over 30 experimental responses, from $P_C - P = 0.5$ to 45 MPa, gave the stretch exponent $x = 0.37 \pm 0.04$, with no systematic deviation from this value at any distance from the critical consolute point. This value is in good agreement with the DD model predictions [2]. The main part of Fig. 1 compares the same data with the OD model [the solid line was plotted from the numerical evaluation of the integral (3)]. The agreement is remarkably good in the tested range $0.1 < t/\tau_{OD} < 10$. The lack of a systematic discrepancy with the OD model for $t/\tau_{OD} > 1$, observed earlier in TEB studies [4], may be the result of a better resolution in TEB experiments. Fits of the decay with the SE relation and OD model yield distinct values of the time constant (τ_S, τ_{OD}). Their ratio is approximately constant for all values of $P_C - P$ distances: $\tau_S : \tau_{OD} = 1:12(\pm 3)$, in agreement with Ref. [4].

In a wide range of reduced pressures $0.5 < P_C - P < 45$ MPa, the shape of the experimental response functions is pressure independent, as shown in the inset in Fig. 2, where different responses are superimposed by simply scaling the time t with the pressure-dependent time constant [for instance, taken in the OD model time scale (τ_{OD}]. Such model-independent scaling behavior was also observed earlier for TEB temperature studies under atmospheric pressure [1,4].

Figure 2 shows also the experimental decay in the immediate vicinity of the critical consolute where a very strong increase of the relaxation time made it possible to test short-time relaxation. Remarkably good agreement with the OD power function [relation (5a)] (solid curve) was found. The
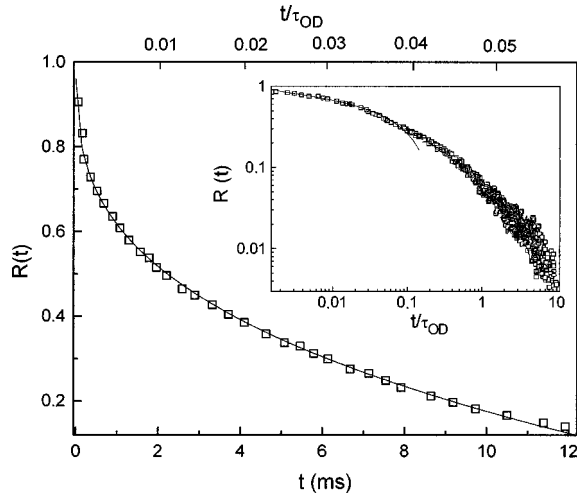
FIG. 2. Experimental NDE decay functions for $P_c - P \approx 0.4$, 6, 15, and 30 MPa. The data are compared with the OD response function for $t/\tau_{OD} \ll 1: R_{OD}(t) = 1 - 2.29(t/\tau_{OD})^{1/3}$ (solid line). The main part of the figure shows details of early stages of the decay for $P_c - P \approx 0.4$ MPa. For these data a value $\tau_{OD} \approx 0.23$ s has been fitted.

validity of the OD model relation for $t/\tau_{OD} \ll 1$ and its range are shown in the inset in Fig. 2 (solid line). Noteworthy is that the value of the time constant in the immediate vicinity of T_C was very high $\tau_{OD} \approx 0.23$ s, whereas for previous temperature studies under atmospheric pressure [1–5] this value did not exceed 10 ms. It seems that such a high value of τ_{OD} is only partially due to the application of pressure. An equally important factor is the shape of the $T_C(P)$ dependence, which consequently allowed us to choose a favorable path of approaching the phase transition point (inset in Fig. 3). The possibility of testing the early stages of the decay was also facilitated by a strong increase of $\mathcal{E}_{NDE}$ from 1.2 $\times 10^{-16}$ m^2 V^{-2} for $P_C - P = 40$ MPa to 28×10^{-16} m^2 V^{-2} for $P_C - P = 0.5$ MPa, which markedly improved the (signal-to-noise) ratio.
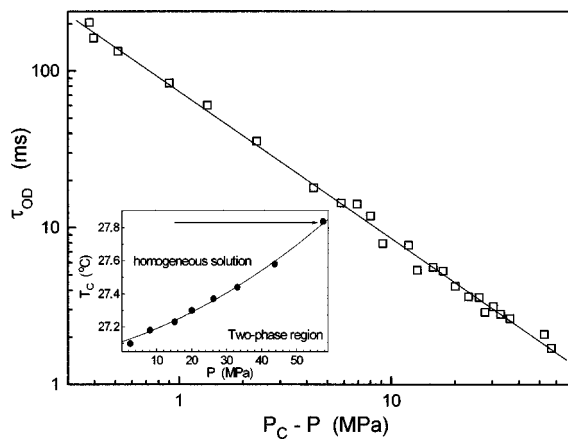

FIG. 3. Logarithmic plot of the dependence of the relaxation time (in the OD model time scale) on the pressure distance from the critical consolute point. The straight line represents a power-law fit with exponent $y = 1.1 \pm 0.2$. The inset shows the pressure dependence of the critical temperature in the tested solution and the path of approaching the critical consolute point applied in these studies (the arrow): $T_c \approx 27.82$ °C (const), $P_c \approx 56.9_5$ MPa.

TABLE I. Experimental values of model-independent scaling factors (time constants) of tested $R(t/\tau)$ experimental decays. The time constants are expressed using the OD model measure of relaxation times.

P (MPa)	τ_{OD} (ms)
4.2	1.4
11.6	2.1
20.6	2.6
24.1	2.8
26.6	3.0
29.2	3.2
30.9	3.6
33.8	3.7
36.9	4.2
39.4	5.3
41.2	5.6
43.6	6
44.9	7.8
47.8	8.1
48.9	11.9
50	14.1
51.1	14.4
52.6	18
54.6	35.7
55.5	60.4
56	84
56.4	133
56.5	162
56.6	227

The main part of Fig. 3 presents the pressure behavior of time constants (scaling factors) obtained by superposing experimental decays on one scaling curve. The data are well described by the power law $\tau_{OD} \propto (P_C - P)^y$, with exponent $y = 1.1 \pm 0.2$. The possible application of τ_S instead of τ_{OD} does not influence the value of the exponent y. It is worth recalling that the temperature studies mentioned in the Introduction [1,4,5] gave values of the exponent y in agreement with the above result. Experimental values of relaxation times are collected in Table I.

CONCLUSION

The results of this paper and that of Ref. [4] point to the fact that at least the main part of the decay, for $t/\tau_{OD} < 1$, is well described by the Onuki-Doi model [relation (3)]. The validity of the OD model seems to cover also the early stages of decay, where the OD response function is reduced to a simple, strictly defined, power function [relation (5a)]. The SE function, with the exponent taken from the DD model, is able to portray the long-time limit decay, for $t/\tau_S > 1$. It is noteworthy that the appearance of two such different types of relaxation was previously observed, e.g., in supercooled, glass-forming liquids where the long-time and short-time regions describe the SE function and von Schweindler power relation [9], respectively. However, there are major differences between critical solutions and glass-forming liquids. For critical solutions the stretch exponent x is a universal,

system-independent magnitude, whereas in supercooled liquids it is a phenomenological, material-dependent parameter [9]. In supercooled liquids the power, critical-like, function is able to describe the evolution of relaxation times only in a limited range of temperatures [9]. The full set of experimental relaxation times in such systems parametrizes the exponential Vogel-Fulcher-Tamman-type equation for both temperature [9] and pressure studies [15,16]. It is noteworthy also that in critical solutions the relaxation processes manifest mainly for ''nonlinear'' dielectric phenomena: the NDE [5] and Kerr effect (KE) [1–4]. For dielectric permittivity (ε) the appearance of dispersion processes is limited to the appearance of the low-frequency Maxwell-Wagner effect in the immediate vicinity of the critical consolute point (see [21] and references therein). For glass-forming liquids the strong influence of relaxation phenomena is clearly visible for both ''linear'' (ε) [9] and ''nonlinear'' (e.g., the KE [22]) dielectric studies. Also worth mentioning is the lack of any evidence of the so-called secondary (β) relaxation [9] in critical solutions [1–5,21].

This paper and Refs. [1,4,5] indicate that the experimental value of the exponent $y = 1.1 – 1.3$ does not agree with the theoretically predicted one $y \approx 1.9$ [2,11]. A possible explanation for this discrepancy may arise from the possible semiclassical, uniaxial character of the correlation length of elongated critical fluctuations in an external field (see [20] and references therein). The fact that $\xi(E) = \xi(\xi_{\parallel}, \xi_{\perp}, \xi_{\perp})$ [20], where the component $\xi_{\parallel}$ holds the nonclassical, critical behavior [$\xi_{\parallel} > \xi(E=0)$ and $\xi(E=0)$, $\xi_{\parallel} \propto (T-T_C)^{-0.63}$, i.e., with $v \approx 0.63$ [10]], and due to its

shortage, the perpendicular component [$\xi_{\perp} < \xi(E=0)$] cross over the Ginzburg [10] criterion becoming classical [$\xi_{\perp} \propto (T-T_C)^{-0.5}$, i.e., $v = 0.5$ [10], together with definitions of the EKE and NDE, enabled us to explain the puzzling behavior of critical exponents describing the temperature behavior of the ''stationary and saturated'' EKE and NDE in critical solutions [20,23,24] and recently also in the isotropic phase of nematogens [25]. In the classical limit the relaxation time ceases to be proportional to the volume of the fluctuation [$\tau \propto \xi^3$ [10], relation (2) and (6)] but follow another pattern [10]: $\tau \propto \xi^2 \propto (T-T_C)^{-1}$, i.e., $y = 2v = 1$. This value seems to be close to the experimental result ($y \approx 1.1$) obtained in this paper.

The results of this paper and Refs. [1–4] suggest also that the temperature and pressure paths of approaching the critical consolute point are equivalent for the stretched-relaxation behavior after switching off a strong electric field. In both cases the behavior of the decay function seems to be described by the same set of universal, system-independent critical exponents. It may be regarded as the consequence of the postulate of isomorphism of critical phenomena [10] applied for dynamic aspects of critical phenomena.

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