Relaxation of electric birefringence near a critical consolute point

Sylwester J. Rzoska,* Vittorio Degiorgio, Tommaso Bellini, and Roberto Piazza
Dipartimento di Elettronica, Università di Pavia, 27100 Pavia, Italy
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An experimental investigation of the relaxation of electric birefringence in the critical binary mixture *n*-butylbenzene-propylene carbonate is presented. The decay functions observed at different temperatures in the critical region are clearly nonexponential and show a scaling behavior. The experimental relaxation function is compared with theoretical predictions: the asymptotic decay is a stretched exponential with a stretch exponent 0.40±0.03, in good agreement with the dynamic droplet model, but the earlier stages are very well described also by the Onuki-Doi approach [Europhys. Lett. **17**, 63 (1992)].

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INTRODUCTION

It is known both experimentally [1–3] and theoretically [4–6] that critical fluids become optically anisotropic in the presence of an electric field. Transient electric birefringence (TEB) experiments [7,8], performed by applying a rectangular electric-field pulse to a near-critical binary liquid mixture, have shown that the relaxation of the induced birefringence after switching off the electric field is strongly nonexponential, and is asymptotically well described, in the long-time limit, by a stretched exponential (SE) function:

$$R(t)\approx\exp[-(t/\tau_S)^{\alpha}] \tag{1}$$

where $\alpha\approx 0.4$ and τ_S is a temperature-dependent time constant related to the average lifetime of critical fluctuations. The same behavior was observed for the relaxation of the nonlinear dielectric effect in a critical mixture [9].

In complex systems the time evolution of the response $R(t)$ to an external disturbance is often described by a SE function in a wide time window [10,11]. The stretched exponential character of $R(t)$ can be associated with the existence of a broad distribution of relaxation times. A phenomenological explanation of the observed behavior was given by a dynamic droplet model (DDM) [7] which attributes the origin of the broad distribution of relaxation times to the size polydispersity of critical fluctuations. More recently, Onuki and Doi [6] presented a different approach which relates the anisotropy of the structure factor to that of the dielectric tensor. The Onuki-Doi model (ODM) also predicts a strongly nonexponential decay. The main difference between the two predictions is in the long-time tail which is a power law for the ODM and a stretched exponential for the DDM.

In order to test the models, we have undertaken a set of measurements with an improved apparatus by using an appropriately selected critical binary mixture. In this paper, we present accurate results on the relaxation of the electric birefringence in the binary liquid mixture *n*-butylbenzene and propylene carbonate, and we compare our data with the theoretical models. The experimental results confirm that $R(t)$ is a strongly nonexponential function having a temperature-independent shape in the critical region. The asymptotic decay is a SE function with a stretch exponent coincident with that predicted by the dynamic droplet model. However, the ODM describes very well the decay of $R(t)$ over the range of values $1\geq R(t)\geq 0.1$. We also find that the time constant associated with the relaxation diverges, on approaching the critical temperature, with an exponent 1.3 which is markedly different from the value 1.9 predicted by both models.

THEORETICAL MODELS

The cluster theory proposed in Ref. [7] describes the relaxation of the induced birefringence $\Delta n(t)$, after switching off the applied electric field at $t=0$, by using the superposition integral

$$\Delta n(t)=\int dl P(l)S(l)\exp(-t/\tau_l), \tag{2}$$

where l is the size of the cluster, $P(l)$ its size distribution function, $S(l)$ the signal function, and τ_l the relaxation time associated with a cluster of size l. By using the assumptions $P(l)\approx\exp[-l^2/\xi^2]$, $S(l)\approx l^r$, and $\tau_l\approx l^3$, where ξ is the correlation length of the critical fluctuations, the response $R(t)=\Delta n(t)/\Delta n(0)$ can be written as [7]

$$R(t)=C^{-1}\int dl\,\exp[-l^2/\xi^2]l^r\exp[-(t/\tau_{\mathrm{DM}})(\xi^3/l^3)]\ , \tag{3}$$

where

$$C=\int dl\,\exp[-l^2/\xi^2]l^r\ ,$$

and τ_{DM} is the relaxation time of a cluster of size ξ. It is implicitly assumed that the duration of the electric pulse is sufficiently long to attain the steady-state birefringence Δn_s, that is, $\Delta n(0)=\Delta n_s$, and that the amplitude of E is small enough to confine the experiment to the Kerr regime where $\Delta n_s=\lambda BE^2$, B being the Kerr constant and λ

*Permanent address: Institute of Physics, Silesian University, Universytecka 4, 40-007 Katowice, Poland.

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the wavelength at which the induced birefringence is measured. In the critical region, B diverges according to a power law of the reduced temperature $\epsilon=|T-T_c|/T_c: B\approx\epsilon^{-\psi}$ [1–6]. This implies that the exponent r is given by $(\psi/\nu)-1$, where ν is the critical exponent for ξ.

By applying the saddle-point approximation to the integral of Eq. (3), one obtains, as shown in Ref. [7], a SE function of time with a temperature-independent stretch exponent given by

$$\alpha=\frac{2-\eta}{5-\eta}\cong 0.40\ , \tag{4}$$

where $\eta\cong 0.04$ is the Fisher exponent, and with a time constant τ_S related to $\tau_{\rm DM}$ as follows (DM denotes droplet model):

$$\tau_S=\tau_{\rm DM}\frac{\alpha}{1-\alpha}(1-\alpha)^{1/\alpha}\ . \tag{5}$$

Note that the time constant $\tau_{\rm DM}$ is proportional to ξ^3, and should therefore diverge, on approaching T_c, with an exponent $b=3\nu\cong 1.9$.

Recently, Onuki and Doi [6] applied to electric birefringence and dichroism in critical binary solutions a general theory for the anisotropy of the effective dielectric tensor in the presence of an external field, deriving a formula which connects the anisotropy of the refractive index tensor to the induced anisotropy of the structure factor $S(q)$. Essentially, form birefringence and dichroism are related to the field-induced anisotropy of the scattering cross section, and can be calculated by an appropriate integration over the Fourier components of the field-perturbed $S(q)$. The Onuki-Doi approach is definitely more microscopic and less phenomenological than the DDM. Assuming that the anisotropy of $S(q)$ is due to induced dipole-dipole interactions, and that weak perturbations relax exponentially with a relaxation rate $\Gamma_q=\tau_{\rm OD}K(q\xi)$, where $\tau_{\rm OD}=(6\pi\eta_s\xi^3)/(k_BT)$ is the average thermal decay rate, η_s is the shear viscosity, and

$$K(y)=\tfrac{3}{4}[1+y^2+(y^3-y^{-1})\arctan y\,] \tag{6}$$

is the Kawasaki q dependence of the relaxation rate, the following expression for $R(t)$ is derived:

$$R_{\rm OD}(t)=\frac{4}{\pi}\int_0^\infty dy\frac{y^2}{(1+y^2)^2}\exp[-2K(y)t/\tau_{\rm OD}]\ , \tag{7}$$

which is valid in the limit $k\xi\ll 1$. For $t\ll\tau_{\rm OD}$, $R_{\rm OD}(t)$ decays as $R(t)\approx 1-2.29(t/\tau_{\rm OD})^{1/3}$, and, for $t\gg\tau_{\rm OD}$, $R_{\rm OD}(t)$ decays as a power law: $R(t)\approx 0.199(t/\tau_{\rm OD})^{-1.5}$.

EXPERIMENT

The experiment consists of applying an electric-field rectangular pulse and measuring the time dependence of the birefringence induced into the solution [7,8]. In particular, we focused our attention on the decay of birefringence after the electric field is switched off. If a square pulse of duration t_D is applied at time $t=-t_D$, and if we call $B(t)$ the birefringence observed at time t, we can define the normalized decay function as $R(t)=B(t)/B(0)$. Since t_D has to be at least comparable to the decay time of $R(t)$, the experiment was performed by changing progressively t_D from 50 μs to 8 ms on approaching T_c. Typical applied fields were in the range 1.5–2 kV/cm. All the measurements were performed in the Kerr regime, where the steady-state-induced birefringence is proportional to E^2.

The TEB apparatus was essentially the same as in Refs. [7] and [8]. Some modifications were introduced to ensure the chemical inertness of the Kerr cell to the liquid mixture used. The main body of the cell is made of stainless steel, the remaining parts are made of teflon and glass. The electrodes are platinized, have a length of 6 cm and present a gap of 2.6 mm. The cell is hermetically closed after filling. A temperature stabilization of 0.01 °C over 10 h was obtained by a double-stage water circulation apparatus.

The binary liquid system studied is a mixture of propylene carbonate and n-butylbenzene. As established by the visual method [12], the critical temperature is $T_c=18.9$ °C, and the critical mass fraction of propylene carbonate is $x_c=0.41$. The solution chosen presents some convenient features for the TEB experiment: high electric resistivity, T_c near room temperature, upper critical consolute point, and relatively large precritical effects. These features allow a much better averaging of the TEB response than in the previous experiments [7,8]: typically, the averaging was performed over 1000–2000 pulses.

RESULTS AND DISCUSSION

The observed response $R(t)$ strongly deviates from exponential behavior, consistently with the results of the previous experiments [7,8]. The bilogarithmic plot of $-\ln R(t)$ as a function of t is linear over two decades in time, as shown in Fig. 1. The linearity of the plot is consistent with a stretched exponential behavior [7]. The fit with Eq. (1) gives the time constant τ_S and the stretch ex-

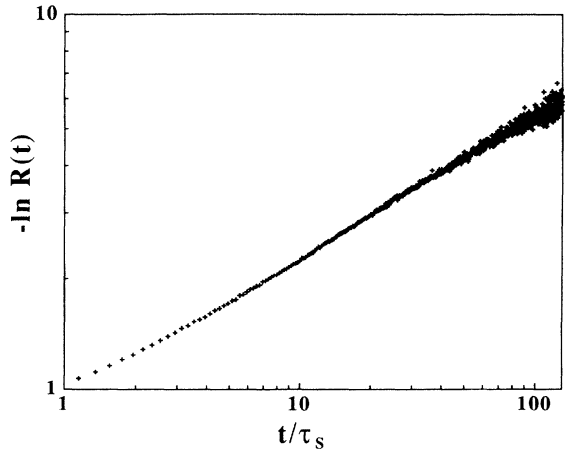

FIG. 1. Logarithmic plot of $-\ln R(t)$ vs t/τ_S for the critical binary mixture n-butylbenzene and propylene carbonate at $T-T_c=0.1$ K. The straight-line behavior indicates a stretched-exponential relaxation.

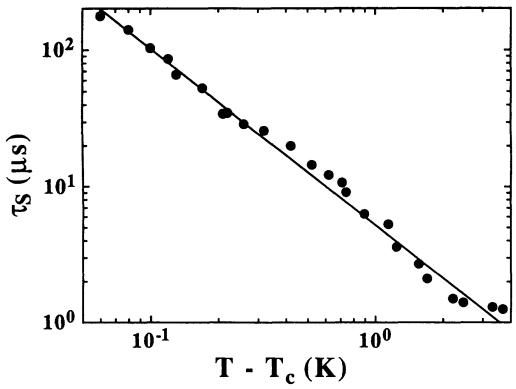

FIG. 2. Logarithmic plot of the dependence of the relaxation time τ_S on the reduced temperature $T-T_c$. The straight line represents a power-law fit with exponent 1.3±0.2.

ponent α. The obtained value of the exponent α is

$$\alpha=0.40\pm0.03 \ . \tag{8}$$

In Fig. 2 we present the behavior of τ_S versus $T-T_c$. The data are well described by a power law $\tau_S \approx (T-T_c)^b$, with exponent $b=1.3\pm0.2$. We recall that the TEB experiments performed with the critical mixtures 2,6-lutidine and water [7], and butoxyethanol and water [8], gave, respectively, $\alpha=0.39\pm0.07$, $b=1.8\pm0.2$, and $\alpha=0.40\pm0.05$, $b=1.78\pm0.05$. The experiment performed on the dynamics of the nonlinear dielectric effect (NDE) with the critical mixture 1-nitropropane and dodecane [9] gave $\alpha=0.39\pm0.02$ and $b=1.3\pm0.2$.

We tried a fit with the full expression predicted by the dynamic droplet model, given in Eq. (2), by using for ψ the measured value 0.83±0.04 [13]. The agreement with the experimental relaxation function, however, is rather poor in the range $t<\tau_{DM}$. We found that the fit becomes

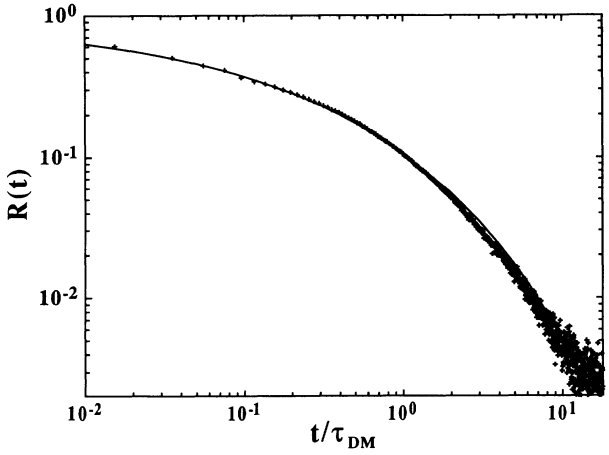

FIG. 3. The comparison between the normalized experimental TEB decay and the dynamic droplet model with the adjustable parameter ψ. The points denote the experimental results, the full curve the DDM prediction.

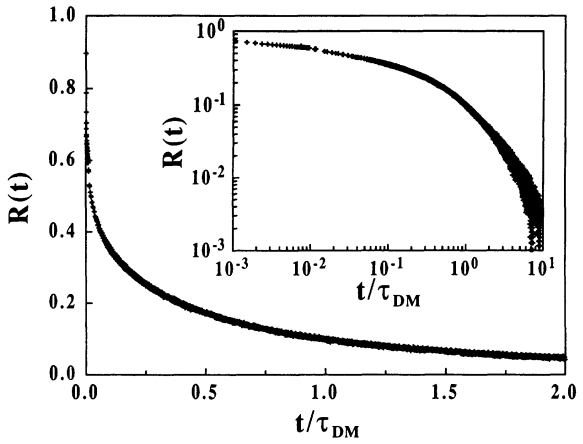

FIG. 4. Four relaxation functions obtained at $T-T_c=0.05$, 0.1, 0.14, and 0.34 K, superposed by appropriately scaling the time.

excellent by leaving ψ as a fit parameter, as shown in Fig. 3. The best-fit value obtained is $\psi=0.52\pm0.03$. In a wide range of reduced temperatures, 0.05 $K<T-T_c<5$ K, the shape of $R(t)$ is temperature independent, as shown by Fig. 4 where different responses are superposed by scaling t with the temperature-dependent time constant τ_{DM}.

The fit with the ODM is shown in Fig. 5. The agreement is remarkably good in the range $0\le t\le\tau_{OD}$, whereas clear deviations are observed for long times (see inset in Fig. 5), as expected from the fact that the ODM predicts asymptotically a power law instead of a stretched exponential. It should be recalled that the ODM formula implies that $\psi=\nu(1-2\eta)$. Therefore, the fit of the short-time behavior of $R(t)$ gives a puzzling result: both the DDM and the ODM describe $R(t)$ well, by using, however, a static exponent ψ which is close to the theoretical prediction, but different from the measured one. It should also be noted that the approximate form for $S(q)$ assumed by Onuki and Doi leads to predic-

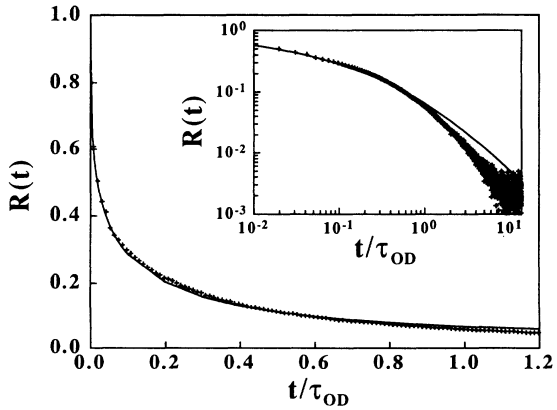

FIG. 5. The comparison between the normalized experimental TEB decay and the Onuki-Doi model. The points denote the experimental results, the full curve the DDM prediction.

tions for the anisotropy of $S(q)$ which seem to be in conflict with recent observations [3]. In any case, even using the form of $S(q)$ proposed in Ref. [3], the asymptotic behavior of $R(t)$ predicted by the Onuki-Doi approach remains a negative power of time.

The fit of $R(t)$ with Eqs. (1), (2), and (4) yields three distinct values for the time constants τ_S, τ_{DM}, and τ_{OD}. We find

$$\tau_S:\tau_{DM}:\tau_{OD}=1:7.5:12.7\ . \tag{9}$$

Since the shape of $R(t)$ does not depend on $T-T_c$, the ratios given in Eq. (8) are temperature independent. Note that the predicted value of the ratio τ_{DM}/τ_S, as calculated from Eq. (5) with $\alpha=0.39$, is 5.6, not too different from the experimental value.

CONCLUSIONS

The shape of the TEB relaxation function $R(t)$ in the critical region of a binary liquid mixture shows a scaling behavior, with the relaxation time scaling as a power law of the reduced temperature. The main part of the decay of $R(t)$ is very well described by the Onuki-Doi model, which is based on a general formula relating the anisotropy in the structure factor to that in the macroscopic dielectric tensor. The long-time decay of $R(t)$ follows a stretched-exponential behavior with a stretch exponent $\alpha=0.4$, in very good agreement with the dynamic droplet model and in disagreement with the ODM, which predicts a power-law decay. However, the complete expression of $R(t)$ obtained from the DDM fits the experimental relaxation function only by taking for the static exponent ψ a value considerably smaller than the measured one. It should be noted that in the case of the comparison with the ODM there is also a discrepancy between the measured ψ and the value of ψ which appears in the model. Both models predict a power-law dependence of the relaxation time on the reduced temperature with an exponent 3ν. The experimental data confirm the power-law behavior, but the measured exponent is smaller.

It has been suggested recently [14] that the discrepancies found with static critical exponents related to the Kerr effect and to the nonlinear dielectric effect in binary mixtures have a common explanation, connected with the possible presence of a crossover between Ising and mean-field behavior. It cannot be excluded that the discrepancies found for the dynamic exponents also have a similar explanation.

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