

Stretched-exponential relaxation of birefringence in a critical binary mixture

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Transient electric birefringence in near-critical binary mixtures is found to exhibit stretched-exponential relaxation of the form $\exp[-(t/\tau)^x]$, with x constant and τ diverging as a power law in reduced temperature. A simple scaling theory of this phenomenon is proposed, relating x and the relaxation-time exponent to static and dynamic critical exponents, with values in good agreement with experiment. The results yield information about the distribution of fluctuations in the one-phase region of critical fluids and mixtures.

When the elementary relaxation processes in a system are characterized by a broad distribution of relaxation times, its time evolution following a perturbation may be highly nonexponential. In systems as diverse as amorphous solids, materials with random "traps," polymers, and spin glasses,^{1,2} the time dependence of the relaxation function $R(t)$ of some dynamical variable may take on the so-called stretched-exponential form^{3,4}

$$R(t) \sim \exp[-(t/\tau)^x], \quad (1)$$

where the exponent $x \lesssim 1$, and τ may be interpreted as a mean relaxation time. In contrast, when the distribution of relaxation rates is very narrow, one finds $x = 1$. In understanding the nonexponential relaxation found in a given experiment, it is often postulated⁴ that $R(t)$ may be written as a sum, over the distribution of processes $P(l)$, of the exponential behavior each would have in isolation, characterized by a time constant τ_l ;

$$R(t) \sim \int dl P(l) S(l) \exp(-t/\tau_l), \quad (2)$$

where $S(l)$ is a signal function describing the contribution of each process to the observed signal. The index l may represent, for instance, the heights of barriers hindering rotation of molecules within a host crystal.⁵ The stretched form (1) can be derived from a saddle-point analysis of (2), in the limit of long times, with the exponent x and time constant τ related to the relaxation mechanisms and the form of the distribution. While a description such as (2) is a useful representation of the data, there are few systems in which there exist microscopic theories of both the distribution $P(l)$ and of the relaxation time τ_l so that the origin of the particular exponent x in (1) is not clear.

We report⁶ here experimental studies of the time dependence of electric birefringence⁷ near the consolute point of the binary mixture 2,6-lutidine and water which demonstrate stretched-exponential growth and decay of polarization consistent with Eq. (1), with $x \approx 0.4$ independent of temperature and $\tau \equiv \tau(\epsilon)$ diverging with reduced temperature $\epsilon = |T - T_c|/T_c$ as

$$\tau(\epsilon) \sim \epsilon^{-y}, \quad (3)$$

with $y \approx 1.8$. A simple scaling theory is developed which relates the exponents x and y to static and dynamic critical exponents

$$x \approx \frac{2-\eta}{5-\eta}, \quad y = z\nu, \quad (4)$$

where $\eta \approx 0.04$ describes the decay of correlations at T_c , $z \approx 3$ is the dynamic exponent for a conserved order parameter,⁸ and $\nu \approx 0.63$ is that of correlation length ξ .

The present work was motivated by the discovery of analogous stretched-exponential relaxation in micellar solutions of nonionic surfactants near their lower consolute points.⁹ In order to ascertain whether the anomalous relaxation was a property attributable to the specific microstructure of the systems, with their polydisperse distribution of large micellar aggregates, or, rather, was intrinsic to the critical-point region, we undertook the present experiments on the well-studied lutidine-water solutions.¹⁰ Similar results, particularly with regard to the stretched exponential form of the transients, have been found in the butoxiethanol-plus-water system.¹¹

The experimental methods are essentially unchanged from previous work.⁹ The transient electric birefringence (TEB) experiment consists of applying a rectangular pulse of electric field to the liquid mixture and observing the transient as well as the steady-state induced birefringence. A detailed description of the TEB apparatus can be found in Ref. 10. Here, we simply recall that the setup used in this work includes a quarter-wave plate inserted between the Kerr cell and the analyzer to increase the sensitivity and reduce parasitic effects due to stress birefringence of the cell windows.¹⁰ The cell itself was made from an optical glass cuvette which was selected for its low residual stress birefringence. The optical path-length is 60 mm, and the electrodes have a separation of 2.5 mm. Temperature control within the thermostated cell was maintained to $\pm 0.01^\circ\text{C}$ (reduced temperature to $\pm 3 \times 10^{-5}$). Voltage pulses with heights of 0.3–1 kV and durations of 10–300 μs were used. The samples consisted of high-purity 2,6-lutidine and deionized and filtered water (Germann Instruments Water 1 system). The electrical resistivity of the samples was ca. 200–300 $\text{k}\Omega\text{ cm}$ at 20°C .

The output of the photodetector, which is linearly related to the difference Δn between the index of refraction n_{\parallel} (polarization parallel to the applied electric field) and n_{\perp} (polarization perpendicular to the applied field) is sent to a transient digitizer (Data 6000, Data Precision) which performs the averaging over a prescribed number of runs (typically 50). The duty cycle was extremely low to avoid cumulative heating effects.

The mixture 2,6-lutidine plus water has a lower consolute boundary with a critical point at 33.5°C and 29% by weight of lutidine. By fixing the lutidine concentration at the critical value, we have studied the temperature dependence of the electric birefringence transients in the range 20–33.4°C. In the investigated range of conditions, we have verified that the shape of the birefringence transient does not depend on the applied electric field E , and that the steady-state value Δn_s is proportional to the square of the field. The Kerr constant B , defined as $B = \Delta n_s / \lambda E^2$, with λ the wavelength of probing light, is found to increase from a value of $B \approx 1.3 \times 10^{-13} \text{ mV}^{-2}$ far from T_c to a value of 2.5×10^{-12} at $T_c - T = 0.15^\circ\text{C}$. In the range $2^\circ\text{C} \geq T_c - T \geq 0.15^\circ\text{C}$ ($\epsilon \approx 7 \times 10^{-3}$ to 5×10^{-4}), B is described rather accurately by a power law of the form $B = B_0 t^{-\psi}$, with $B_0 \approx 2 \times 10^{-15} \text{ mV}^{-2}$ and $\psi \approx 0.88 \pm 0.04$. The experimental value for the critical exponent is strikingly different from the value $\psi = \nu(1 - 2\eta) \approx 0.58$ which is the common prediction of both a phenomenological droplet model¹² and a more microscopic theory of the dielectric properties of a polarizable fluid.¹³ We have no explanation for this result.

The birefringence was monitored during the application of a square-wave pulse of the electric field of a duration t_0 which was typically many multiples of the mean relaxation time τ . With $B(t)$ the observed birefringence at time t , we define normalized rise and decay relaxation functions $R_r(t) = [B(\infty) - B(t)] / B(\infty)$ and $R_d(t) = B(t_0 + t) / B(t_0)$. The behavior of these functions is qualitatively like that found in Ref. 10, to which the reader is referred for typical data.

For a relaxation function obeying (1), the exponent x may be determined as the slope of a log-log plot of $-\ln[R(t)]$ vs t , and τ determined from the appropriate intercept. Figure 1 shows data from six of the decay curves spanning the range $1.56 \times 10^{-3} < \epsilon < 1.17 \times 10^{-2}$, plotted as a function of the scaled time $t/\tau(\epsilon)$. In general, we find that linear behavior is obeyed over a larger and larger time range as $\epsilon \rightarrow 0$, with systems closest to the critical point obeying a stretched-exponential decay over almost two decades in the reduced variable t/τ . Mindful of the somewhat limited range of time over which the data collapse, we estimate the slope of the best-fit straight line to the linear portions of the data for $t/\tau \gtrsim 1$ to be $x = 0.39 \pm 0.07$. The power-law divergence of the mean relaxation time $\tau(\epsilon)$ is shown in Fig. 2, and a linear least-squares fit yields $y = 1.80 \pm 0.20$ for the decay curves, where the quoted uncertainty is one standard deviation. Similar exponents appear for the birefringence rise data. An anomalous behavior of the birefringence relaxation in the critical region has also been found in studies of microemulsions.¹⁴

To describe the observed birefringence transients, we

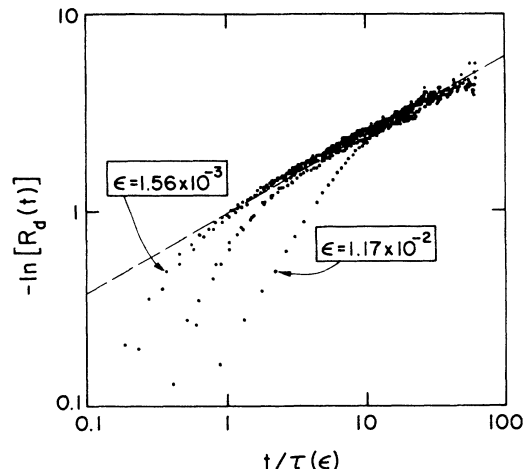


FIG. 1. Normalized decay functions R_d of electric birefringence in lutidine-water mixtures as functions of scaled time, demonstrating stretched-exponential relaxation. Dashed line corresponds to a stretch exponent $x = 0.4$. Maximum and minimum reduced temperatures studied are indicated. Note how the range of reduced temperature over which a stretched-exponential is seen increases as $\epsilon \rightarrow 0$.

draw an analogy with the description of the birefringence behavior of polydisperse fluids along the lines of Eq. (2) and propose that the spectrum of relaxation times in (2) arises from the distribution of sizes of order-parameter fluctuations in a critical fluid. These fluctuations are distorted by the application of an electric field, in much the

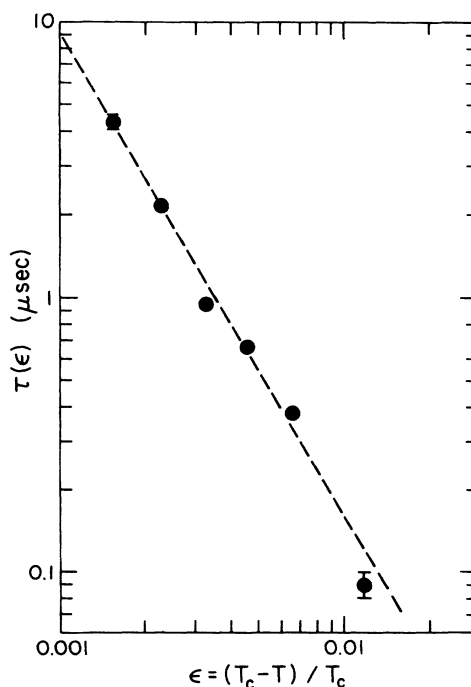


FIG. 2. Power-law divergence of the decay time constants τ_d with reduced temperature ϵ . The slope of the fitted line is $y_d = 1.8 \pm 0.2$.

same way as occurs with aerosol droplets,¹⁵ and will relax back to their equilibrium distribution diffusively. Quite generally, the probability distribution of large-amplitude clusters with characteristic size l has appreciable weight only for $l < \xi$, where ξ is the correlation length. As ξ grows on approach to the critical point, the cluster distribution becomes ever broader, thus producing a correspondingly broader distribution of relaxation times, and stretched-exponential relaxation over a larger and larger time span. That the large-amplitude clusters are important for this experiment can be seen from the analysis of polarized droplets,¹⁵ demonstrating that it is the *contrast* in dielectric constant between the droplet and its surrounding medium which determines its contribution to the optical signal.

We note that the notion that a near-critical fluid may be thought of in terms of a *polydisperse* fluid of fluctuations on broadly-distributed length scales has been used before; it is implicit in the droplet models¹⁶ developed for subcritical temperatures, and has found application in the theory of light scattering and transport properties near critical points.^{17,18}

On the critical isochore, and as reduced temperature $\varepsilon \rightarrow 0$, we write the distribution $P(l)$ as the Boltzmann factor of an excess free energy $F(l)$ for an inhomogeneity of size l , and for $F(l)$ we assume a form

$$F(l) \sim l^d \varepsilon^p l^{-n}. \tag{5}$$

In this form, $F(l)$ satisfies the hyperscaling relation that on length scales of order the correlation length, the free-energy density satisfies

$$f(l) \equiv l^{-d} F(l) \sim \varepsilon^{p+nv} \sim \varepsilon^{2-a} \sim \xi^{-d}, \tag{6}$$

provided that $p = (d - n)v$.

As with the probability distribution, the relaxation function is taken to have a product form

$$\tau_l \sim \varepsilon^q l^r. \tag{7}$$

The requirement of consistency with the dynamic scaling hypothesis, namely that on length scales of order ξ , $\tau_\xi \sim \xi^z$, yields $r - q/v = z$.

In calculating the birefringence signal and, hence, the relaxation function $R(t)$, there will be in the integrand of Eq. (2) additional multiplicative factors which describe the l -dependence of the signal from each of the clusters, but these introduce presumably only logarithmic corrections to the dominant stretched-exponential behavior discussed below, and will be neglected henceforth. Within previous phenomenological studies of critical birefringence,¹² these optical factors were indeed found to be only powers of the size l . With this simplification, we analyze the expression (2) with a saddle-point analysis. The dominant contribution to the integral comes from that length scale $\tilde{l}(t)$ for which the exponential

$$\exp \left[- \left(a \frac{t}{\varepsilon^q l^r} + b \varepsilon^p l^{d-n} \right) \right] \tag{8}$$

is stationary, with a and b representing some constants.

One finds.

$$\tilde{l}(t) \sim \left(\frac{t}{\varepsilon^{p+q}} \right)^{1/(d-n+r)} \tag{9}$$

Substituting (9) back into (8) we obtain relaxation of the form (1) and (3) with

$$x = \frac{1}{1+r\nu/p}, \quad y = \frac{pr}{d-n} - q = z\nu, \tag{10}$$

where in the last relation we have substituted the results from static and dynamic scaling. Note that the value of y is *independent of any model-specific assumptions about the form of the free-energy density $f(l)$* .

The consistency of the result for the exponent of the time constant can also be seen directly from the saddle-point equation. From (10) and the relation $p = (d - n)v$ we find $\tau \sim \varepsilon^{-(r\nu - q)}$ so that the length probed at the characteristic time τ_ξ scales like $\tilde{l}(\tau) \sim \varepsilon^{-\nu}$ and so is proportional to the correlation length. Further, the scale $\tilde{l}(t)$ grows very slowly with time, roughly proportional to $t^{1/5}$ (see below), so even over the duration of the experiments reported here, \tilde{l} varies only by a factor of order unity. Surely at sufficiently long times we expect deviations from the results obtained here, when the length scales probed are much larger than the bulk correlation length.

With four new exponents in Eqs. (5) and (7) and only two scaling relations invoked thus far, the determination of the specific values of the exponents p and r , and, hence, the power x in the stretched exponential, requires more structure to the free-energy density $f(l)$. We propose first that $f(l)$ have a generalized Landau form

$$f(l) \sim \chi^{-1} m(l)^2, \tag{11}$$

where χ is the compressibility, whose inverse measures the distance from the critical point, and $m(l)$ is the magnetization (amplitude of the order parameter fluctuation) on length scales l . If we coarse-grain the system on the length scale l , we find that the mean magnetization in boxes of this size is distributed around $m = 0$ according to some distribution $P(m)$. The width of $P(m)$ has the interpretation of the mean magnetization $m(l)$. From various renormalization-group arguments, from studies of droplet models, and from Monte Carlo simulations, it is known^{19,20} that for l on the order of the correlation length

$$m(l) \sim l^{-\beta/\nu}, \tag{12}$$

β being the usual order-parameter exponent.

With the *ansatz* (12) and with (11) we find $p = \gamma$ and $n = 2\beta/\nu$, consistent with static scaling. Finally, from the dynamic scaling hypothesis extended to the hydrodynamic regime, the relaxation time is expected to behave as $\tau_l \sim \tilde{\eta} l^3 / k_B T$, $\tilde{\eta}$ being the viscosity, which has a weak divergence with a power-law exponent of $x_\eta \approx 0.03$. From the above, we find a stretch exponent $x = (d - 2\beta/\nu) / (d - 2\beta/\nu + 3) = (2 - \eta) / (5 - \eta)$ as in Eq. (4).

Finally, we note that stretched-exponential relaxation with a diverging time constant is also a signature of the

glass transition in certain materials. It has been found that the exponent x is somewhat material-dependent, falling in the range of $\approx 0.5-0.8$, and that τ diverges with the so-called Vogel-Fulcher law $\tau \sim \exp\{A/(T - T_0)\}$, with T_0 somewhat less than the glass transition temperature T_g . The experimental data may also be consistent with a power-law divergence in $T - T_0$.²¹ Whether a scaling theory of these phenomena may be developed along the lines of that which we have presented for binary

mixtures remains an open question, as does a microscopic theory of the phenomena described here.

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