Stretched-Exponential Relaxation of Electric Birefringence in Polymer Solutions

Vittorio Degiorgio, Tommaso Bellini, Roberto Piazza, and Francesco Mantegazza
Dipartimento di Elettronica–Sezione di Fisica Applicata, Università di Pavia, 27100 Pavia, Italy

Raymond E. Goldstein
The Research Institutes, The University of Chicago, 5640 Ellis Avenue, Chicago, Illinois 60637
(Received 31 July 1989)

The relaxation of electric birefringence in dilute solutions of a polyelectrolyte is shown to be consistent with a stretched-exponential form, $\exp[-(t/\tau)^{\alpha}]$. The exponent α depends on polymer length L and solvent ionic strength only through the ratio $x \equiv L/L_p$, where L_p is the persistence length, and crosses over from $\alpha \simeq 1$ for stiff chains ($x \simeq 1$) to $\alpha \simeq 0.44 \pm 0.02$ in the self-avoiding-walk regime $x \gg 1$, the latter in accord with a simple scaling theory of polymer statistics and dynamics.

PACS numbers: 78.20.Jq, 36.20.Ey, 61.25.Hq

Scaling arguments[1] suggest that the dynamics of flexible polymers are governed by a single, fundamental relaxation time that varies with the statistical properties of the chains. While confirmation of such scaling concepts has been obtained in recent years, primarily by quasi-elastic-light-scattering experiments,[2] a full description of the time dependence of the chain relaxation is still unavailable. We may remark, however, that studies[3] of transient electric birefringence (TEB) in aqueous solutions of charged polymers have shown that the decay of birefringence after the application of an electric-field pulse is *nonexponential,* and perhaps indicative of a superposition of several exponentially decaying processes. We report here on detailed transient-birefringence experiments whose aim is to test a different interpretation of such experimental data, the motivation for our work coming from two sources; (i) the strong analogy between the statistics of linear, flexible polymers and various features of critical phenomena,[1] and (ii) recent TEB experiments[4] on binary mixtures that have revealed that the relaxation of birefringence near the consolute point is strongly nonexponential, following an asymptotic *stretched-exponential* form of the type

$$R(t) \sim \exp[-(t/\tau)^{\alpha}] \quad (0 \leq \alpha \leq 1), \tag{1}$$

where for binary mixtures α is temperature independent in the critical region, while the effective time constant $\tau(\epsilon)$ exhibits a power-law divergence in the reduced temperature $\epsilon \equiv |T - T_c|/T_c$. These findings are consistent with a simple theory based on static and dynamic scaling laws applicable to critical fluids. The interpretation given to these results is that transient birefringence, unlike more conventional methods such as dynamic light scattering, probes critical fluctuations on all length scales, the resulting broad distribution of relaxation times yielding the new decay form (1).

We have studied five different molecular weights of the linear polyelectrolyte sodium polystyrene sulfonate (NaPSS) in dilute solutions at various ionic strengths I, and have found that in all situations the relaxation of the induced birefringence is very well described by the stretched-exponential form. The apparent value of α is a monotonically decreasing function of the ratio $x \equiv L/L_p$, where L is the extended length of the polymer and L_p is the persistence length. L_p itself, a function of I, has been estimated elsewhere[5] from intrinsic viscosity measurements. The exponent α is found to be close to unity for $x \simeq 1$, and to cross over to $\alpha \simeq 0.44 \pm 0.02$ for $x \gg 1$. We suggest a simple derivation of these observations by noting that birefringence is sensitive to the end-to-end distance of the polymers, and the statistical distribution of this quantity leads to a distribution of relaxation times. That distribution is extremely narrow in the limit of stiff chains ($x \simeq 1$), so the relaxation is a nearly pure exponential, while in the opposite limit ($x \gg 1$) the chains are self-avoiding walks, with a distribution of sizes given by scaling laws related to the universal critical exponents of the polymers. Further, we find that the experimental time constant τ scales as a power of the radius of gyration, as estimated from proposed scaling laws,[6,7] in a way fully consistent with the known dynamic scaling for polymers.

The TEB experiments, described elsewhere,[4] consist of applying a rectangular pulse of electric field to the polymer solution and observing the associated pulse of induced birefringence. The optical path length of the cell is 60 mm, and the electrodes have a separation of 1 mm. All the measurements were performed at room temperature. Voltage pulses with heights of 0.5–5 kV/cm and durations of 20–500 μs were used. The output of the photodetector, which is linearly related to the induced anisotropy of the refractive index of the solution, is sent to a transient digitizer and averager (Data 6000, Data Precision), the decay being sampled over 1000 points, with typically the last 100 points used to evaluate the base line to an accuracy of better than 0.2%. The overall response time of the apparatus is less than 1 μs.

NaPSS presents a large specific Kerr constant because the monomer has a strong optical anisotropy and it is an

electrolyte. It is known, in fact, that the induced polarization can by very large in polyelectrolytes because of the dominant contribution of the counterion atmosphere which surrounds the charged macromolecule.[3,8] Since the conductivity of the sample must be very low in an electric-birefringence experiment, it is possible to study polyelectrolytes only at very low concentrations, below a few millimolar (mM), of both polymer and salt.

Our samples consisted of water solutions of nearly monodisperse ($M_w/M_n \leq 1.1$) NaPSS obtained as molecular-weight standards from Pressure Chemical Co., Pittsburgh, and used without further purification. The five different molecular weights used are $M = 8.8\times10^4$, 2.0×10^5, 3.54×10^5, 6.90×10^5, and 1.06×10^6. The ionic strength of the solvent was varied by the addition of NaCl in the concentration range 0–6 mM. Some measurements have also been performed with no added salt. All solutions were prepared with deionized water and salt of analytical grade. The polyelectrolyte concentration c has been chosen so as to explore only the "dilute" regime, in which the polymer concentration c is smaller than the entanglement concentration[1] c^*, where $c^* = M/N_A R_G^3$, with R_G, the radius of gyration, depending on L, L_p, and the Debye-Hückel screening length.[6] The concentrations used were in the range $(0.25\text{–}10)\times10^{-2}$ mg/cm^3 for the longest polymer, with c progressively increased as M decreased, always satisfying the criterion of $c < c^*$.

All the reported data refer to measurements performed in the Kerr regime, that is, the regime in which the induced birefringence is proportional to the square of the applied field. For the longest polymer, we found (as in a previous study[8]) that the Kerr regime is rather small; e.g., with $c = 0.1$ mg/cm^3 and 1 mM NaCl, saturation effects appear when the applied field exceeds 1.3 kV/cm. We have verified that the shape of the birefringence pulse does not depend on the field strength or the pulse duration in the Kerr regime.

Here we focus on the decay of the birefringence after removal of the applied electric field. With $B(t)$ the observed birefringence at time t after the termination of the applied field, we define a normalized relaxation function $R(t) \equiv B(t)/B(0)$. Figure 1 shows $R(t)$ for three different polymer solutions, plotted as a function of the scaled time $t/\tau(L,I)$, where $\tau(L,I)$ is the fitted relaxation time for each polymer system, varying with both polymer length L and the ionic strength I of the solution. The curve for the shortest polymer is nearly exponential; the other two present strongly nonexponential shapes. We find, however, that all of these curves, and indeed all of the investigated solutions of NaPSS, may be described by the form (1). As for the time constant, the best-fit values of $\alpha(L,I)$ vary with molecular weight and ionic strength. The inset of Fig. 1 shows the same three relaxation functions on a semilog plot as a function of the scaled time $(t/\tau)^\alpha$, using the fitted τ and α for each system; it is seen that they collapse onto a common curve,

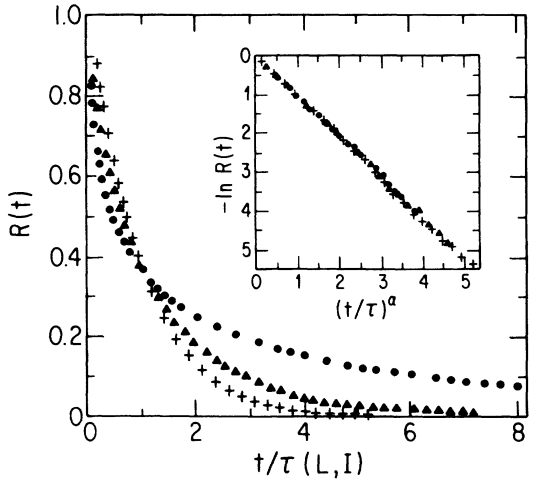

FIG. 1. The normalized electric-birefringence relaxation function plotted vs scaled time, for three polymer solutions. Solution conditions are as follows: +, $M = 8.8\times10^4$, $c = 20$ μg/cm^3, no added salt (residual ionic strength $\simeq 0.05$ mM); ▲, $M = 2.0\times10^5$, $c = 20$ μg/cm^3, 1 mM NaCl; ●, $M = 1.06\times10^6$, $c = 5$ μg/cm^3, 1 mM NaCl. Inset: Semilog plot of $R(t)$ vs $t/\tau(L,I)$, with parameters $\alpha = 1.0$ and $\tau = 6.5$ μs, $\alpha = 0.78$ and $\tau = 13$ μs, and $\alpha = 0.44$ and $\tau = 240$ μs, respectively.

the stretched-exponential form being obeyed essentially over the full range of times accessible experimentally. We find $\alpha \simeq 1$ for the shortest polymer at very low ionic strength, and by increasing the polymer length and (or) the ionic strength decreasing values of α result, with saturation at $\alpha \simeq 0.44 \pm 0.02$ for the longest polymer at ionic strength above 2 mM.

The behavior of the persistence length of polyelectrolytes at very low ionic strength is not clearly understood. We have estimated the persistence length for NaPSS by extrapolating to our conditions the experimental results and numerical studies discussed elsewhere.[5] Significantly, several experiments[5,9] suggest that L_p does not diverge at low I, but rather saturates at a constant value. The empirical formula proposed[5] for L_p reads, in the case of NaPSS, $L_p^{-1} \simeq 0.002 + 0.00258 I^{1/2}$, with L_p in Å and I in mM. The value of L_p we can derive from the relaxation function shown in Fig. 1 (in the absence of added salt), by assuming that the measured decay time is that associated with rotational diffusion of a rigid rod having length L_p, is in fair agreement with the empirical formula. By taking into account both the added salt concentration and the concentration of uncondensed counterions, we arrive at the experimental variation of the exponent α with the ratio L/L_p shown in Fig. 2. Presented this way, we see that the stretch exponent in dilute solutions depends on polymer length, ionic strength, and polymer concentration *only* through the scaled length L/L_p. In addition to the experimentally determined value of τ for each system, we may also define an effective time constant $\bar{\tau}$ directly from the relaxation function as $\bar{\tau} \equiv \int_0^\infty R(t)dt$; for a pure stretched

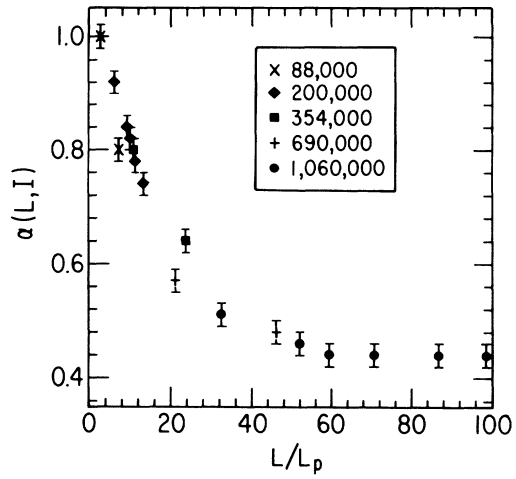

FIG. 2. Experimental stretch exponent α as a function of the ratio of polymer length to persistence length, for varying molecular weights of polymer, as indicated. Concentrations (ionic strengths) in mg/cm^3 (mM) are as follows: ×, 0.05 (0.05), 0.1 (4.0); ◆, 0.02 (0.05), 0.02 (0.4), 0.02 (0.6), 0.02 (1.0), 0.02 (2.0); ■, 0.005 (0.05), 0.05 (2.0); +, 0.005 (0.05), 0.05 (2.0); ●, 0.005 (0.05), 0.01 (0.5), 0.025 (1.0), 0.05 (2.0), 0.1 (4.0), 0.1 (6.0).

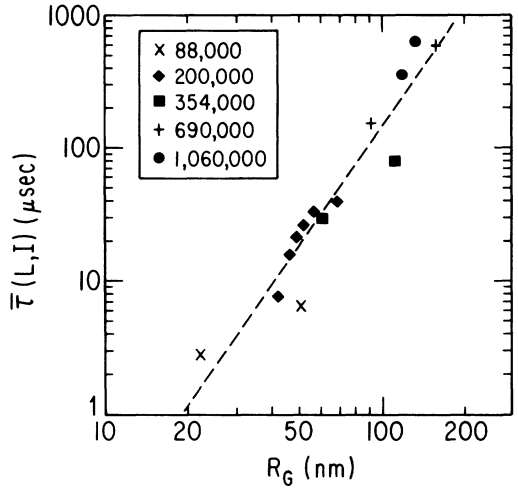

FIG. 3. Relaxation time $\bar{\tau}$ as a function of the estimated radius of gyration of the polyelectrolyte. The dashed line indicates the power-law fit with an exponent of 3.0 ± 0.2.

exponential, $\bar{\tau} = \alpha^{-1}\Gamma(\alpha^{-1})\tau$, Γ being the gamma function, and this relation is confirmed within experimental error. Figure 3 shows the experimental values of $\bar{\tau}$ plotted here as a function of R_G, the latter estimated from the proposed scaling law:[6,7] $R_G \simeq L^{0.6}(L_p/\kappa)^{0.2}$, with κ the inverse screening length. Apart from a slowly varying function (implicitly present in the crossover of α), similar exponents for the variation of both $\bar{\tau}$ and τ with R_G are obtained, namely, $\tau \sim R_G^q$, with $q \simeq 2.9 \pm 0.2$.

The nonexponential dynamics of flexible chains are usually discussed in terms of a discrete set of relaxation modes.[3] Previous work[4] and the analogy between polymer statistics and critical phenomena suggest instead the following interpretation. Following Kuhn,[10] we note that the amplitude of the response of a single chain to an applied electric field is a function of its end-to-end distance R. In considering a dilute solution, we may imagine writing the relaxation of birefringence $B(t)$ as a sum of individual-particle responses, averaged over the probability distribution $P(R)$ of the fluctuating quantity R,

$$B(t) = \int dR\, S(R) P(R) \exp[-t/\tau(R)], \tag{2}$$

where $S(R)$ is some signal function and $\tau(R)$ is the relaxation time appropriate to a chain with end-to-end distance R.

For a non-self-avoiding polymer, $P(R)$ is Gaussian for large R, $P_G \sim \exp[-(R/R_G)^2]$, where R_G scales with polymer length $R_G \sim L^{\nu_G}$, with $\nu_G = \frac{1}{2}$ being the classical value of the critical exponent. For real polymers in good solvents, where excluded-volume constraints swell the chains from their Gaussian size, it has been demonstrated[11] that $P(R)$ also decays as the exponential of a power of R,

$$P(R) \sim f(R) \exp[-(R/R_G)^{\delta}], \tag{3}$$

where now $\delta = 1/(1-\nu)$ is given in terms of the universal exponent $\nu \simeq 0.59$ appropriate to a self-avoiding walk, and the prefactor $f(R)$ varies as some power of R. The dependence of $S(R)$ on R is somewhat complex, although from our data and other studies,[3,7,8] we estimate a power-law dependence of the steady-state anisotropy in the index of refraction; $\Delta n \sim R^s$, with $s \simeq 1$. Finally, the dependence of the relaxation time on the polymer configuration may be obtained by the usual Stokes-Einstein relation for the diffusion constant, $D(R) \sim R^{-1}$, and the diffusive relation $D(R)\tau(R) \sim R^2$, so

$$\tau(R) \sim R^q, \tag{4}$$

with $q \simeq 3$, which may be viewed as the dynamic critical exponent.

With the exponential form for the probability distribution and a power-law variation of the relaxation time, we may determine the long-time behavior of the integrand in (2) by a saddle-point analysis focusing on those two terms, the remaining power-law variations of the prefactors in $S(R)$ and $P(R)$ leading only to slow corrections to the resulting behavior. We obtain a result analogous to that found by Cohen and Grest[12] in their free-volume theory of glassy relaxation, namely, that the stretch exponent α is given by the two exponents δ and q,

$$\alpha = \delta/(\delta+q) = 1/[1+q(1-\nu)]. \tag{5}$$

Thus, in the fully developed self-avoiding limit, *the stretched-exponential form is characterized by a universal value of the stretch exponent α, itself expressed in terms of static (ν) and dynamic (q) critical exponents.*

Moreover, the relaxation time that appears in the stretched-exponential form (1) scales as $\tau \sim R_G^q$. Thus, although the form of relaxation is anomalous, the characteristic time selected by the system is consistent with dynamic scaling. This is analogous to the behavior of critical binary mixtures,[4] namely, anomalous relaxation with a time constant diverging as ξ^z, where ξ is the correlation length associated with composition fluctuations and z is the dynamic critical exponent.

Several previous investigations of polymer dynamics indicate that $q \simeq 3$, and the data presented in Fig. 3 are consistent with such a result. Using the known value $\nu \simeq 0.59$ ($\delta \simeq 2.44$) and $q \simeq 3$, we obtain $\alpha \simeq 0.45$. The measured asymptotic value of the stretch exponent in the limit of a flexible chain ($L/L_p \gg 1$) is seen in Fig. 2 to be in excellent agreement with this prediction. In the opposite extreme, L/L_p of order unity, the macromolecule is a rigid rod, with a very narrow probability distribution, and consequently $R(t)$ is an exponential ($\alpha = 1$). The fact that $R(t)$ appears to be a stretched exponential even at intermediate values of the ratio L/L_p indicates that $P(R)$ presents a rapidly decaying tail which can be described as an exponential of the type $\exp(-AR^p)$, with $p \geq \delta$, although we cannot exclude the possibility that the intermediate values of α reflect slow crossover behavior. In order to derive the precise dependence of α on the scaled variable L/L_p, we would need to know the scaling behavior of $P(R)$ for the case of a semiflexible chain, and this is at present an important open problem.

As a final comment, it should be noted that the stretched-exponential form appears to be a very general law for the relaxation of complex random systems.[13] At variance with most of the previously reported observations of such relaxation, we are here able to suggest a "microscopic" theory of the stretch exponent.[14] In the concentration range where the interparticle interactions are small, and for sufficiently large polymer lengths relative to the persistence length, the observed value of the stretch exponent agrees well with a simple theoretical prediction relating it to critical exponents of polymers.

We thank G. Allegra, D. Bedeaux, B. Duplantier, S. Leibler, and M. Mandel for discussions, and P. G. de Gennes and S. R. Nagel for important comments. This work was supported in part by the Italian Ministero della Pubblica Istruzione (MPI) and by the National Science Foundation, Grant No. CHE-8808378 (R.E.G.).

[1]P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, 1979).

[2]D. W. Schaefer and C. C. Han, in *Dynamic Light Scattering*, edited by R. Pecora (Plenum, New York, 1985), p. 181; P. Wiltzius and D. S. Cannell, Phys. Rev. Lett. **56**, 61 (1986).

[3]S. S. Wijmenga, F. van der Touw, and M. Mandel, Polym. Commun. **26**, 172 (1985).

[4]R. Piazza, T. Bellini, V. Degiorgio, R. E. Goldstein, S. Leibler, and R. Lipowsky, Phys. Rev. B **38**, 7223 (1988); T. Bellini and V. Degiorgio, *ibid.* **39**, 7263 (1989).

[5]M. Tricot, Macromolecules **17**, 1698 (1984).

[6]J. Skolnick and M. Fixman, Macromolecules **10**, 944 (1977).

[7]T. Odijk, Macromolecules **12**, 688 (1979).

[8]M. Tricot and C. Houssier, Macromolecules **15**, 854 (1982); S. S. Wijmenga and M. Mandel, J. Chem. Soc. Faraday Trans. 1 **84**, 2483 (1988).

[9]K. S. Schmitz and J.-W. Yu, Macromolecules **21**, 484 (1988).

[10]See Ref. 1, p. 180; and M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford Univ. Press, Oxford, 1988), p. 122.

[11]M. E. Fisher, J. Chem. Phys. **44**, 616 (1966); D. S. McKenzie and M. A. Moore, J. Phys. A **4**, L82 (1971).

[12]M. H. Cohen and G. S. Grest, Phys. Rev. B **24**, 4091 (1981).

[13]K. L. Ngai, Comments Solid State Phys. **9**, 127 (1979); M. F. Schlesinger, Annu. Rev. Phys. Chem. **39**, 269 (1988); G. D. Patterson and A. Munoz-Rojas, Annu. Rev. Phys. Chem. **38**, 191 (1987).

[14]For proposed relationships between stretched-exponential relaxation and diverging time constants, see, e.g., J. Kakalios, R. A. Street, and W. B. Jackson, Phys. Rev. Lett. **59**, 1037 (1987), and S. R. Nagel and P. K. Dixon, J. Chem. Phys. **90**, 3885 (1989).