

Slow Stress Relaxation in Randomly Disordered Nematic Elastomers and Gels

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Randomly disordered liquid crystalline elastomers align under stress. We study the dynamics of stress relaxation before, during, and after the polydomain-monodomain transition. The results for different materials show a universal logarithmic behavior, especially pronounced in the region of the transition. The data are approximated very well by an equation $\sigma(t) - \sigma_{\text{eq}} \sim 1/(1 + \alpha \ln t)$. We propose a theoretical model based on the cooperative mechanical resistance for the reorientation of each domain, attempting to follow the soft-deformation pathway. [S0031-9007(98)07718-7]

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Liquid crystalline ordering in a confined, randomly quenched geometry has been the subject of considerable research in recent years. Nonaligned polymer-stabilized or dispersed liquid crystals and, in particular, nematics in porous media [1–3] have been studied with an eye on the universal properties of systems with weak random fields. The basic scaling observation, that at long length scales the static random fluctuations dominate over the dynamic thermal fluctuations, has been verified by rigorous theoretical analysis and experimental studies of correlations and susceptibilities in a wide variety of systems [4]. The critical slowing down of all relaxation processes in systems with a random, glasslike order is also a well-established universal phenomenon [5,6], with a characteristic stretched-exponential or power-law behavior as opposed to a normal exponential relaxation of overdamped ordered systems. Accordingly, it has not been surprising to find slow relaxation modes in randomly confined nematic liquid crystals [3,7,8]. However, although the concept of a random orientational effect imposed by the large amount of inner surfaces seems intuitively correct, the direct application of continuum weak random field models to systems with strong local anchoring on length scales equal to or even greater than the correlated domain size may not be fully appropriate.

Nematic elastomers and gels have been a focus of extensive recent research for a number of different, but equally compelling reasons. In these systems the liquid crystal ordering and director are coupled to the mechanical degrees of freedom—stresses and strains of the underlying polymer network. As a result, local elastic torques are unbalanced and the nonsymmetric Cosserat elasticity leads to a number of unique physical effects such as soft elasticity and mechanically driven orientational switching [9]. It has been argued that the network cross-links act as sources of quenched disorder and the nematic gel is analogous to the spin glass with random magnetic anisotropy [10]. One has to make clear the distinction of our system from the structural polymer glass, in spite of our use of similar terminology. The glass transition does exist here, as in most other polymer

systems, but it occurs at a much lower temperature T_g and we deem its effect to be negligible. There are important distinctions from the spin-glass too, in spite of a broad analogy in equilibrium structure and correlations. In nematic networks the order is coupled to the rubber elasticity and is different topologically, making the domain walls into topologically stable disclinations.

The application of external stress to (polydomain) nematic networks disordered on large scales results in a critical transition into the aligned state with an increasing degree of long-range order [10,11], a polydomain-monodomain (P-M) transition, where the director alignment proceeds via the reorientation of correlated regions (“domains”) rather than the growth of the favored ones. Because the polymer chains within each domain are anisotropic, the rotating director causes shape changes, Fig. 1, and thus the materials can accommodate the external deformation without significant stress response. In this Letter we study the dynamics of this transition by increasing the extensional strain ϵ in controlled small steps and monitoring the relaxation of stress $\sigma(t)$.

We find this relaxation to be extremely slow, increasingly so in the vicinity of critical stress for the P-M transition, and following a logarithmic law over several decades of time. Similar logarithmic decays have been observed

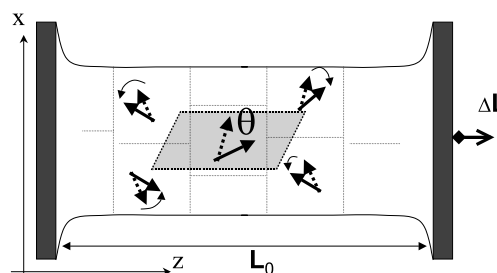


FIG. 1. Schematic illustration of a stretched polydomain elastomer. As each domain rotates its director towards the extension axis, its shape is changing. The shear strain associated with the rotation θ (indicated by shading of a single domain) needs to be compatible with the surrounding elastic medium.

in other systems, apart from glasses, as different as nematics in silica gels [7] and avalanches at the angle of repose [12], and are reminiscent of $1/f$ noise kinetics [13]. However, in contrast to the aging in glasses [14], our results do not visibly depend on the time t_w spent at working temperature. Instead, the main feature we are reporting is the dramatic slowing down during the P-M transition. We propose a model of self-retardation where the rate constant vanishes with an essential singularity due to the cooperative mechanical barriers for each domain's rotation. The resulting kinetic equation, having a form $\dot{\theta} = -m\theta^3 e^{-u/\theta}$, gives a solution which at short times resembles the power law $t^{-1/2}$ and at long times can be approximately interpolated as $1/(1 + 2 \ln t/t^*)$, with the crossover time $t^* = (mu^2)^{-1}$. Both regimes correspond well to the experimental results. We expect this behavior to be universal across the randomly disordered systems where, as in nematic elastomers and gels, the relevant order parameter is coupled to the elastic modes: the mechanical compatibility requires the cooperative nature of elastic barriers.

The materials used in this experiment are three different types of side-chain liquid crystalline polymers: polysiloxanes [15] cross-linked via flexible trifunctional groups, polyacrylates cross-linked by bifunctional chemical groups [16], and by γ radiation [17]. All materials had slightly different cross-linking density, around (5–10)%. The glass transition temperature T_g for polysiloxane is around -5 C (with nematic-isotropic transition $T_{ni} \sim 42$ C), while the polyacrylates become glasses at $T_g \sim 50$ C (with $T_{ni} \sim 110$ C). Hence the experiment was carried at 30 C for polysiloxane elastomer and at around 90 C for both polyacrylates. The results obtained on all materials are very similar and in this Letter we concentrate mostly on the polysiloxane system, which has more dramatic quantitative effects due to the higher chain anisotropy. The experimental approach is straightforward. Strips of polydomain nematic rubber ($\sim 15 \times 5 \times 0.3$ mm) were suspended on a stress gauge and extended in controlled strain fashion in a chamber which was thermostatically controlled. We applied consecutive fixed-step extensions of ~ 0.5 mm every 24 h (thus providing an effective strain rate of $\dot{\epsilon} \sim 3 \times 10^{-7} \text{ s}^{-1}$). The data for variation of response force with time have been collected and then converted to the nominal stress σ (and the extension—to engineering strain $\epsilon = \Delta L/L_0$). The accurate measurement of very small changes in stress over large time intervals demanded the experimental error be brought down to 0.05% in stress and 0.1° in temperature.

The stress-strain dependence of polysiloxane nematic rubber going through the P-M transition is shown in Fig. 2. The sets of data points shown are collected at fixed intervals of 20 s, 100 s, 500 s, and 24 h after the strain increment from the previous-day value. One clearly sees the major trend of the P-M transition, exhibited at all times: When the threshold stress is reached, the correlated nematic domains begin to rotate towards the

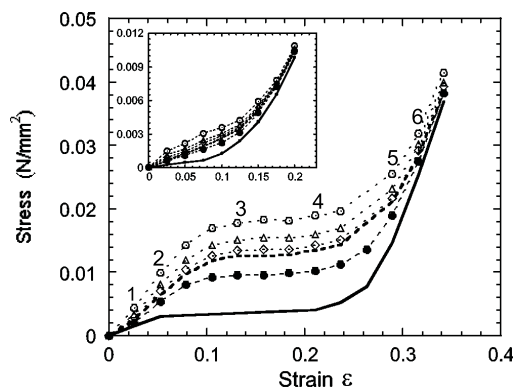


FIG. 2. Experimental values of the nominal stress in polysiloxane nematic rubber, as observed at 20 s (\odot), 100 s (\triangle), 500 s (\diamond), and 24 h (\bullet) after the strain increment. The numbered points correspond to the data sets used in Fig. 3. The thick dashed line is the saturation level of “apparent power law,” Eq. (2); the solid line shows the true equilibrium values $\sigma_{eq}(\epsilon)$ the stress would achieve, if given time for the inverse-logarithmic decay to saturate. The inset shows the same plot for chemically cross-linked polyacrylate.

direction of extension. Because the average polymer backbone is prolate along the local nematic director \mathbf{n} , the aligning of average \mathbf{n} results in the effective lengthening of the whole sample, thus accommodating the imposed strain and creating the stress plateau over a large interval of deformations. The strain at the end of the equilibrium stress plateau is determined by the anisotropy of chain shape $R_{||}/R_{\perp}$ (~ 1.6 in polysiloxanes and 1.06 in polyacrylates). However, the question of what is the equilibrium stress at each value of ϵ requires a detailed analysis of its kinetics. The inset in Fig. 2 shows the analogous plot for a chemically cross-linked polyacrylate, with a much smaller backbone anisotropy and the stress plateau region.

Figure 3 shows the variation of stress with time after the strain increment for several selected points in Fig. 2. One immediately recognizes the fact that the equilibrium stress has not been achieved even after the 24-h interval. Figure 4 gives an example of data analysis. The relaxation of stress at relatively short times accurately follows a power law with a seemingly universal exponent $-\frac{1}{2}$. This variation has been reproduced in all three different materials (studied at different temperatures), for all points on the stress-strain curve of Fig. 2. At longer times a logarithmic decay was evident. Again, this has been a feature for all materials and at all strains; however, the slope of the logarithmic decay was very different, dramatically increasing towards the P-M transition and for the materials with higher chain anisotropy. In fact, the logarithmic decay was hard to detect for the chemically cross-linked polyacrylate, which has very small backbone anisotropy. Also, the samples at large deformations always develop a distinct necking near the rigid clamps. Even at deformations long past the stress plateau and the samples well ordered in the middle, there are still polydomain

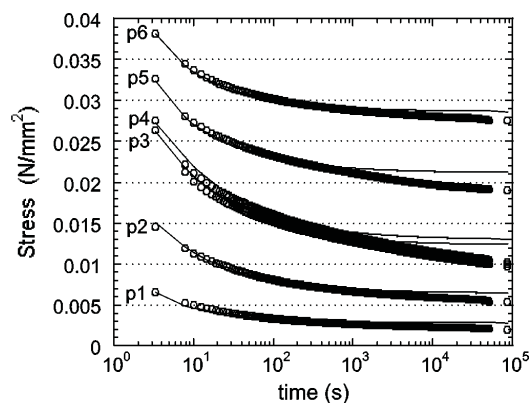


FIG. 3. Six selected relaxation plots $\sigma(t)$ for points, labeled from 1 to 6 in Fig. 2, in polysiloxane sample. Note, that the plots for points $p3$ ($\varepsilon = 0.13$) and $p4$ ($\varepsilon = 0.21$) are hardly distinguishable, even though they are at each end of the stress plateau. The logarithmic relaxation at long times is evident, with the slope significantly increasing as the P-M transition is being approached from both sides. Thin solid lines show the “apparent power-law” model, Eq. (2), which fits only the short-time region of each plot.

regions near the clamps, which are in an incomplete state of alignment (this is clearly seen by the eye and under the microscope). Similarly, before the P-M transition is reached, internal processes associated with domain wall localization [10], may also contribute to slow cooperative relaxation. It is attractive to attribute the residual logarithmic decay away from the P-M transition to such artifacts of nonuniformity and conclude that the main stress relaxation occurs during the P-M transition and is due to the constrained rotation of correlated nematic domains.

To understand the results, one needs to recall the basic concepts of soft elasticity in nematic gels (or any other Cosserat elastic media with an independent Goldstone degree of freedom). Considering a region of lo-

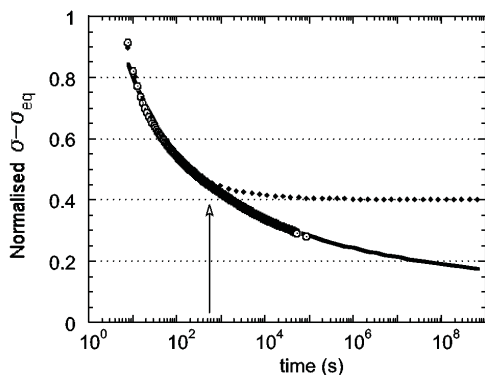


FIG. 4. Analysis of relaxation for the point $p4$ (\odot) where the stress has been normalized for convenience to vary between 1 and 0. The “apparent power-law” model with the exponent $-\frac{1}{2}$ (dots) fits the data well until the crossover time t^* is reached (arrow). A good overall fit of the stress $\sigma(t)$ is given by the inverse-logarithm function $\sigma = \sigma_{eq} + A/(1 + \alpha \ln t)$, the solid line.

cally uniform director (a domain), the rubber-elastic energy can be reduced to zero if the director rotation θ and the Cauchy strain tensor $\underline{\lambda}$ are related by the equation $\underline{\lambda} = \underline{\ell}(\theta)^{1/2}\underline{\ell}(0)^{-1/2}$, where the uniaxially anisotropic polymer step-length matrix is given by $\ell_{ij} = \ell_{\perp}\delta_{ij} + (\ell_{\parallel} - \ell_{\perp})n_in_j$. For a plane stretching and director rotation as in Fig. 1, when the deformation $\varepsilon = \lambda_{zz} - 1$ is applied, the elastic response can be reduced if the director rotates by $\theta \approx \sqrt{2\ell_{\parallel}/(\ell_{\parallel} - \ell_{\perp})} \varepsilon^{1/2}$. To comply with the soft-elasticity pathway, this rotation requires an associated shear $\varepsilon_{zx} \approx \frac{1}{2}(\ell_{\parallel}/\ell_{\perp} - 1) \sin 2\theta$ [9]. Therefore, a given domain subjected to an external extension ε finds itself out of elastic equilibrium, with an effective energy density $\Delta f \approx \frac{1}{2}\mu(\ell_{\parallel}/\ell_{\perp} - 1)^2\theta^4$ at small θ , where $\mu \approx n_x k_B T$ is the rubber modulus. The relaxation of stress then proceeds via the director rotation towards its soft-elasticity equilibrium, $\Delta\sigma(t) \sim \mu(\ell_{\parallel}/\ell_{\perp} - 1)\theta(t)$, while the decay of θ is controlled by the standard model-A equation $\dot{\theta} = -\tilde{m}\theta^3$. Note the cubic force, which is the direct consequence of soft elasticity and leads to the power-law decay $\theta \sim t^{-1/2}$. This power law is indeed observed at early stages of relaxation for all materials and deformations studied.

So far we have discussed the soft response of an individual domain. Surrounded by its neighbors, each of which has its own director and a different set of soft strains, any given domain will face an elastic barrier for its relaxation. In an extreme situation when all neighboring domains are already aligned and cannot find any soft pathway to accommodate the external strain, the shear deformation of the given domain will not be allowed by mechanical compatibility and no relaxation would occur [18]. Therefore, for each individual domain to relax its local stress, one requires a cooperation of its neighbors, providing an opportunity for the required set of strains. We approximate this effect by estimating the effective rate constant \tilde{m} of escape over the average nonsoft barrier. The average of misalignment angles of all different domains $\langle\theta\rangle$ is the measure of nonrelaxed part of the stress. As it decays to zero after each strain increment, fewer domains remain unrotated and the total barrier in the system increases as $\langle\theta_0 - \theta(t)\rangle$ with the initial condition for misalignment θ_0 proportional to the strain step. If we assume that this energy is evenly distributed between all nonrelaxed domains (the number of which is $\propto\langle\theta\rangle$), the effective escape rate becomes $\tilde{m} \sim \exp[-\beta u \frac{\langle\theta_0\rangle - \langle\theta\rangle}{\langle\theta\rangle}]$, leading to the dynamical equation for self-retardation

$$\frac{d}{dt} \langle\theta\rangle = -m e^{-u/\langle\theta\rangle} \langle\theta\rangle^3. \quad (1)$$

We expect the parameter $u \propto \theta_0$ to be proportional to the strain step and also to the overall strain ε , which gives a position on the P-M transition, Fig. 2. Both m and u should be proportional to the chain anisotropy $(\ell_{\parallel}/\ell_{\perp} - 1)$. Equation (1) can be integrated and we plot this solution (Fig. 5) to verify that the essential singularity

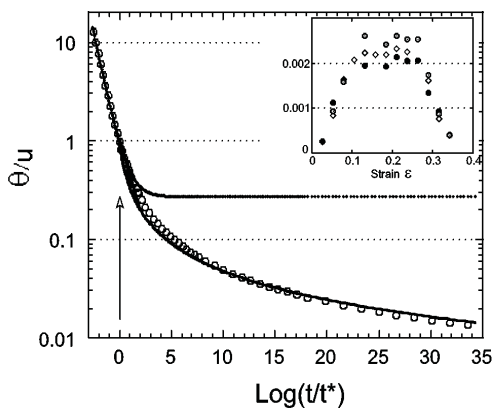


FIG. 5. The log-log plot of scaled solution θ/u against scaled time $t/t^* = mu^2t$, circles. The arrow shows the position of crossover time with two regimes, given by Eqs. (2), shown by dots (apparent power law) and solid line (inverse logarithm). The inset shows the model activation parameter u vs ϵ , determined in three ways described in the text: (i) \diamond , (ii) \circ and (iii) \bullet .

in the rate constant at $\theta \rightarrow 0$, Eq. (1), results in a critical slowing down of the long-time decay. There are several qualitative conclusions to be drawn from Eq. (1). At short times, when θ is not small, the exponential in the decay rate is irrelevant and we recover the power-law behavior. This “apparent power law” becomes invalid at a crossover time $t^* \approx (mu^2)^{-1}$ (when $\theta \sim u$ in the exponent), after which the inverse-logarithm function gives an excellent interpolation:

$$\theta \approx \frac{1}{(2mt)^{1/2}} + 0.27u \quad \text{for } \frac{1}{m\theta_0^2} \ll t \ll t^*, \quad (2)$$

$$\theta \approx \frac{u}{1 + 2 \ln(mu^2t)} \quad \text{for } t \gg t^*.$$

The corresponding stress relaxation behavior, $\sigma(t) = \sigma_{\text{eq}} + \text{const} \cdot \theta(t)$ closely reproduces the data presented in Figs. 3 and 4. The experimental values for crossover time t^* , slope, and saturation level of apparent power law and fit of the long-time logarithmic tail provide a sufficient number of independent measurements for each data set to determine the two model parameters, m and u . The inset of Fig. 5 shows the variation of the parameter u for the polysiloxane sample as a function of position on the stress-strain curve, determined by three different methods: (i) using the difference between σ_{eq} and the apparent power-law saturation being $\approx 0.27u$, (ii) identifying the numerator of the long-time inverse-logarithm fit with u , and (iii) combining the slope of the apparent power law m and the crossover time for each plot, $u = (mt^*)^{-1/2}$. The plateau value $u \approx 0.0023$ (and the corresponding plateau for the parameter $m \approx 700$) strongly depend on the material and temperature, presumably via the chain anisotropy, and are approximately linear functions of the small strain step.

Considering some experimental ambiguities (such as the effect of nonuniform necking) and theoretical simplifica-

tions, we consider the proposed model to provide a good qualitative description of relaxation during the P-M transition. All three materials show the same type of response, with only parameters m and u reflecting the difference. Much remains to be done to build a full understanding of stress relaxation phenomena in nematic elastomers with, it appears, the unavoidable effects of quenched disorder. One needs to study the effect of temperature, in particular, close to the nematic transition point T_{ni} . The detailed role of chain anisotropy R_{\parallel}/R_{\perp} remains to be investigated. Correlating the stress relaxation with equilibrium autocorrelation functions, expected to follow the activated scaling [5] as the spin-glasses and random nematics do, would also be desirable. A refinement of the theoretical model is needed, particularly to address the role of small linear (semisoft) corrections to the cubic force.

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