Nematics with Quenched Disorder: How Long Will It Take to Heal?

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Nematics with quenched disorder have been repeatedly predicted to form glass phases. Here we present turbidity experiments and computer simulations aimed at studying glass key features such as dynamics and history dependence in randomly perturbed nematics. Electric field-cooling alignment has been employed to prepare samples in suitably oriented starting states. Remarkable remnant order and slow dynamics are found both by experiment and simulations, indicating that random disorder can, by itself, induce a nematic glass state even without perturber restructuring.

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Quenched disorder, even in minute amounts, is known to produce dramatic transformations in the equilibrium properties of a variety of self-organized systems ranging from superconductors to liquid crystals (LC) [1–7]. In particular, it has recently been shown [6] that nanostructured random silica interfaces destroy the long-range nematic order of the cyanobiphenyl liquid crystals and yield an exponentially decaying local nematic order, with a correlation length depending on the disorder density. Computer simulations of lattice spin models [6] indicate that this result is quite general, as it follows even from a simple representation of the quenched disorder as a random dispersion of a fraction of randomly oriented frozen spins. These results agree with a recent renormalization group analysis of nematics with quenched disorder [8], which predicts, besides the trivial isotropic phase, a second short-ranged ordered phase, which could match the current experimental findings, and a quasi-long-range ordered phase, so far never observed. Theory [8] indicates that both phases should be glassy states. Thus, to fully determine the behavior of nematics in the extended temperature-quenched disorder phase diagram, it is crucial to characterize also their relaxation properties in the presence of random perturbers. In particular, it is of central interest to understand whether the ground state energy landscape has a single or multiple minima and what is the contribution of topology and topological defects to determining the landscape features. It is worth stressing that it is still experimentally not demonstrated that nematics with quenched disorder can be classified as glass states. Dynamic light scattering measurements [9] have revealed the existence of a slow intensity fluctuation of tiny amplitude, indicative of activated processes and possibly nonergodic orientational dynamics. Parallel studies of the electro-optical [10] and magnetic [11] response of nematics confined in the random geometries formed by aggregated silica nanocolloids have showed memory effects which have, however, been interpreted as a consequence of restructuring of the solid network. In such systems, memory effects strongly depend on the LC-surface coupling [12]. Even on the modeling side the connection between random quenched disorder and glassy behavior does not appear to be more obvious. Many contributions have appeared on random anisotropy and random field Heisenberg models. While it is accepted that the former leads to a real (Ising) spin glass phase [13], it is generally believed that the latter does not produce glass states [14]. Much less attention has been devoted to the addition of quenched disorder to the Lebwohl-Lasher (LL) model for nematics [15]. Given the inversion symmetry of the nematic ordering, random anisotropy and random field coupling with disorder cannot be distinguished and analogies between disordered Heisenberg and LL are not easily established.

The presence of memory effects and glassy dynamics even in the absence of network restructuring is the central issue that we wish to address here, both with experiments and simulations. For the latter we have studied the evolution of LL lattices with a random and frozen distribution of disordered sites. Experimentally, we have focused on systems where network rearrangements cannot conceivably occur and on others where the solid network is more fragile. Namely, we have studied three different samples [7], all etherogeneous mixtures of a random structure and a cyanobiphenyl LC. We prepared two "filled nematic" (FN) samples, with 3.5% vol. hydrophilic silica nanoparticles (Degussa A380) in 8CB (sample FN1), and with 9% hydrophobic silica nanoparticles (Degussa R812) in 6CB (FN2). The third sample was made by imbibing a mixed cellulose esters millipore membrane (MM) [16] with 5CB. The membrane has a mean pore size of 3 μm, 17% vol. solid fraction, and a typical thickness of the solid structure of about 0.5 μm. All samples have a thickness of about 20 μm, obtained, in the case of MM-5CB, by microtome slicing. FN and MM-LC are both considered experimental realizations of LC with random quenched disorder [6,17], even though the characteristic length of their disorder is quite different.

We have measured the transmitted intensity of a 5 mm diameter He-Ne laser beam through the samples. Transmitted light has been selected by spatially filtering the beam before and after the sample. Disordered LC samples have very large turbidity τ, a consequence of the local LC birefringence and of the disorder-induced spatial fluctuations of the optical axis [4]. Application of an electric field E has the well known effect of forcing alignment, thus reducing τ [5]. The samples have been prepared by cooling from the isotropic into the nematic phase either while applying a 1 kHz ac field ("field cooling"—FC) or with no field applied ("zero FC"—ZFC). Figure 1 shows the time t dependence of the turbidity τ_{FC} of different FC samples after turning off the field ($t = 0$). In Fig. 1, $\tau_{\mathrm{FC}}(t)$ is normalized to τ_{ZFC} measured at the same temperature T. The relaxations start from low values of τ at $t = 0$, i.e., from a high level of field induced transparency. MM and FN samples show two distinct processes, a faster viscoelastic intrapore relaxation [18] in the ms regime, and a much slower one which saturates, after a few days (or even *weeks*), to a value of τ smaller than the ZFC one. In the MM and in the FN2 samples, where the FC memory is relevant, negligible memory is found if the same field is applied on a ZFC sample, and then removed. Similar FC memory has been found studying nematics incorporated in other, less controlled, random interconnected polymeric structures [19]. To enlighten the dependence of the observations on the structure of the solid fraction, we have performed a few comparative tests with a polymer dispersed LC (PDLC), where the nematic LC E7 (Merck) is confined in droplets of mean radius $r \approx 1.5\ \mu$m. For E up to 10 V/μm, no memory was found in PDLC (see Fig. 1), thus supporting the notion that randomness and interconnectivity are necessary to induce memory in confined nematics.

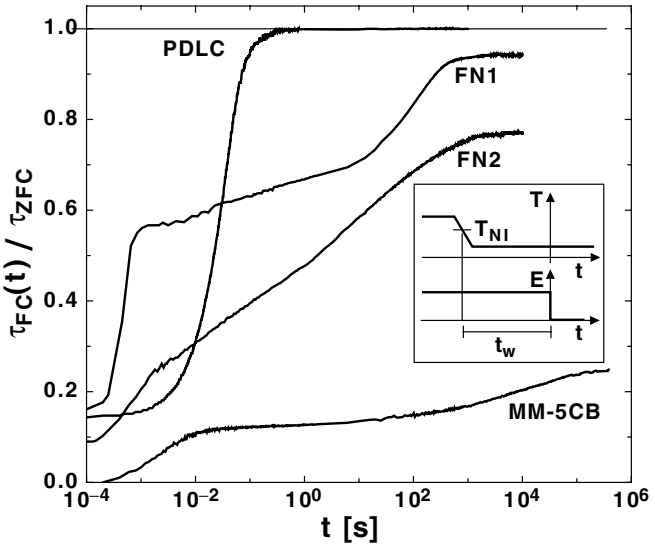

FIG. 1. Time dependence of the turbidity of FC samples after the removal of the field, normalized to τ_{ZFC} at the same T. The waiting time $t_w = 20$ min is the same for every sample. T_{NI} is the isotropic-nematic phase transition T. Parameters: MM-5CB, $T = 25$ °C, $T_{\mathrm{NI}} = 35$ °C, $E = 1.2$ V/μm, $\tau_{\mathrm{ZFC}} = 0.36\ \mu\mathrm{m}^{-1}$; FN1, $T = 32$ °C, $T_{\mathrm{NI}} = 40.5$ °C, $E = 6$ V/μm, $\tau_{\mathrm{ZFC}} = 0.22\ \mu\mathrm{m}^{-1}$; FN2, $T = 22$ °C, $T_{\mathrm{NI}} = 29$ °C, $E = 2.5$ V/μm, $\tau_{\mathrm{ZFC}} = 0.16\ \mu\mathrm{m}^{-1}$; PDLC, $T = 35$ °C, $T_{\mathrm{NI}} = 55$ °C, $E = 2.1$ V/μm, $\tau_{\mathrm{ZFC}} = 0.22\ \mu\mathrm{m}^{-1}$.

Since the scattering efficiency of disordered nematics comes from director distortions, it is clear, at least qualitatively, that memory in Fig. 1 depends on remnant orientational order in the system. We envisage the system as composed of nematic correlated volumes of typical size ζ with molecular order parameter $\langle P_2 \rangle$ and a local director $\mathbf{n}$ making an angle θ_D with the field direction. The correlated volumes are oriented according to a distribution $P(\theta_D)$, in turn corresponding to a certain domain order $\langle P_2 \rangle_D$. To interpret quantitatively the data, we have first extracted ζ from $\tau_{\mathrm{ZFC}}(T)$ by means of the scattering model previously used for analogous investigations [4,6] and obtained $\zeta = 1.1\ \mu$m (MM-5CB), $\zeta = 0.32\ \mu$m (FN1), and $\zeta = 0.18\ \mu$m (FN2). Using an extension of the same model it is also possible to extract $\langle P_2 \rangle_D$ for the FC samples [7]. To do so, we assume that the FC sample is characterized by the same ζ as the ZFC sample, the difference being only in $P(\theta_D)$, uniform in ZFC samples and biased in the field direction in the FC samples. For $E \neq 0$, and in ZFC samples, $P(\theta_D, E)$ can be obtained by balancing electric and elastic torques on each correlated volume [18]. To extract $\langle P_2 \rangle_D$ from τ_{FC}, we additionally assume that the $E = 0$ remnant order is characterized by the same $P(\theta_D, \eta)$, where η plays the role, in this case, of a pseudofield allowing for the degree of nonuniformity of the distribution. Upon exploring various kinds of nematics with quenched disorder at different T, we have found the FC remnant $\langle P_2 \rangle_D$ ranging from 0 to 0.7. In Fig. 2 we show the time dependence of τ_{FC} and $\langle P_2 \rangle_D$ after switching off the field for MM-5CB samples field cooled to different T. Remarkably, the asymptotic value of $\langle P_2 \rangle_D$ appears to be T independent, suggesting that the memory effect crucially depends on phenomena taking place *during* the phase transition. The slow relaxation of $\langle P_2 \rangle_D$ can be well described by a stretched-exponential $\exp[-(t/\tau_s)^{\beta}]$, with the β and τ_s shown in the inset. The increase in τ_s by 2 orders of magnitude by lowering T of 9 °C indicates that the relaxation takes place through activated processes. The strong analogy of the present behavior with the relaxations of FC spin glasses [20] suggests that this slow dynamics should be ascribed to nonlocal "multidomain" motions. We stress that the freeze-out here described takes place at a mesoscopic level, the molecular dynamics being probably unaffected.

Analogous results have been obtained by Monte Carlo (MC) simulations [21]. We explored the effects of initial conditions on the pseudoequilibrium state of a modified LL model, the sprinkled silica spin (SSS) model [6] in which the quenched disorder has been included by freezing a fraction p of randomly chosen spins endowed with random orientations. The SSS Hamiltonian is

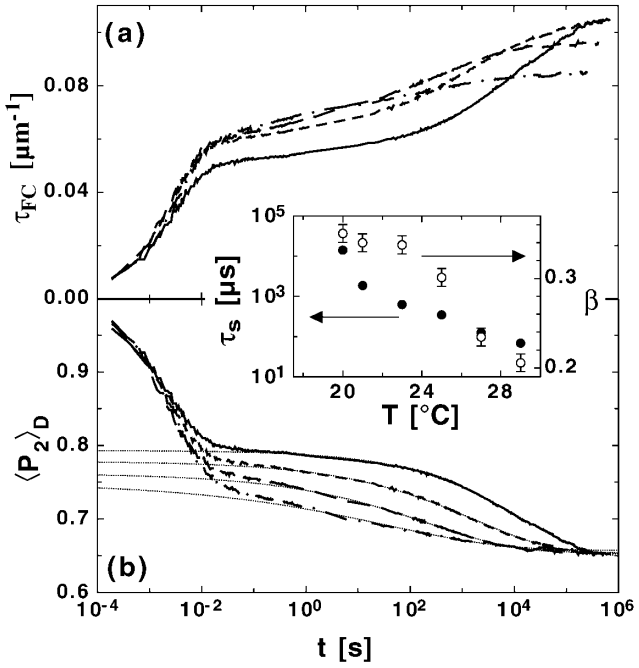

FIG. 2. Time dependence of $\tau_{\rm FC}$ (panel a) and $\langle P_2\rangle_D$ (panel b) of MM 5CB samples field cooled to different temperatures: $T = 29\,^{\circ}$C (dot-dashed line); $T = 25\,^{\circ}$C (long dashed line); $T = 21\,^{\circ}$C (short dashed line); $T = 20\,^{\circ}$C (continuous line). Waiting time $t_w = 20$ min, $E = 1.2$ V/μm, and cooling rate (1 deg/min) are the same for every sample. Thin lines: stretched exponential fit; the fitted parameters β and τ_s vs T are shown in the inset.

$$U = -\epsilon\left[\sum_{i,j\in\mathcal{N}} P_2(\mathbf{s}_i\cdot\mathbf{s}_j) + \sum_{k\in\mathcal{N},l\in S} P_2(\mathbf{s}_k\cdot\mathbf{r}_l)\right], \quad (1)$$

where $\mathcal{N}$ is the set of nematic spins ($\mathbf{s}$) and S is the set of silica spins ($\mathbf{r}$) of concentration $p = \frac{S}{(\mathcal{N}+S)}$. ϵ is a positive coupling constant for nearest neighbor spins and zero otherwise. P_2 is the second Legendre polynomial.

We have explored the disorder densities $p = 0.14, 0.21$ for lattices up to $60\times60\times60$ spins, choosing a low temperature $T^* = k_BT/\epsilon = 0.2$, and letting the systems evolve, from a random initial spin configuration (RIC), to be compared with the ZFC samples, and from a perfectly aligned initial state (AIC), mimicking the FC samples. The simulations have been followed for at least 2×10^5 MC cycles (where a cycle is a set of N attempted moves), or anyway when no evolution was observed for at least 5×10^4 cycles. Figure 3 shows the evolution of $\langle P_2\rangle_\lambda$, calculated from the diagonalization of the ordering matrix [21] for the different p and initial conditions. Systems evolving from an AIC state retain a residual order approached through a very slow stretched-exponential relaxation. Simulations with RIC evolve instead to a much smaller value of $\langle P_2\rangle_\lambda$.

In Fig. 4 we show the asymptotic value of $\langle P_2\rangle_\lambda$ at $T^* = 0.2$ for both AIC (full symbols) and RIC (open symbols) as a function of cube size L for $p = 0.14, 0.21$. The

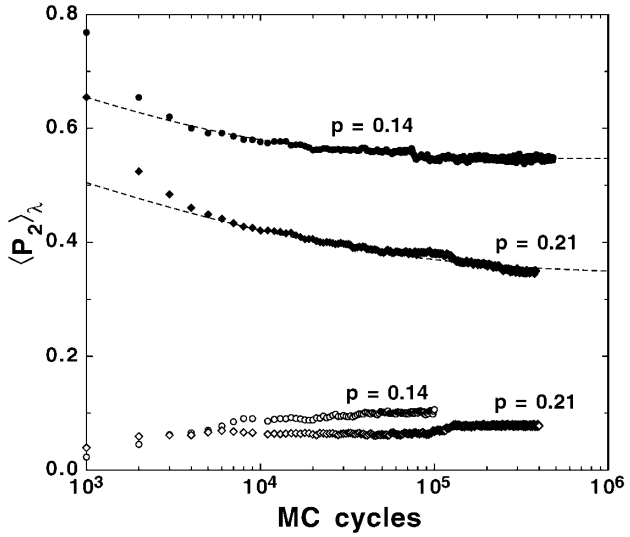

FIG. 3. Dependence of the order parameter $\langle P_2\rangle_\lambda$ on MC cycles from the simulations of a 60^3 SSS system for disorder densities $p = 0.14, 0.21$. The data are obtained by starting from an AIC state (top curves) and from a RIC one (bottom curves). Dashed lines: stretched exponential fits, with $\beta \approx 0.25$; asymptotic values are $\langle P_2\rangle_\lambda = 0.54$ ($p = 0.14$) and $\langle P_2\rangle_\lambda = 0.34$ ($p = 0.21$).

remnant order for AIC appears to reach an asymptotic value as L increases. In the inset of Fig. 4 we show the nematic correlation function $\langle G_2^{NN}(r)\rangle = \langle P_2(\mathbf{s}_i\cdot\mathbf{s}_j)\rangle_r$ [6], calculated from the long time configurations with AIC (curve a) and RIC (curve b). The spatial decay of $\langle G_2^{NN}(r)\rangle$ is well represented by an exponential as shown in the

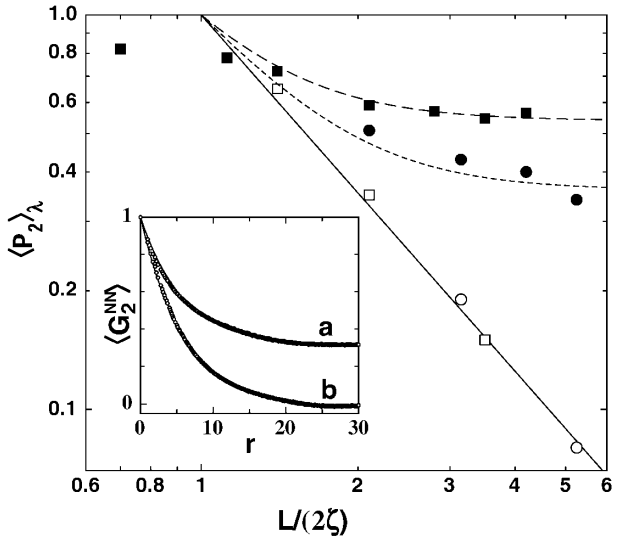

FIG. 4. Dependence of $\langle P_2\rangle_\lambda$ on lattice size from simulations with AIC (full symbols) and RIC (open symbols) states for disorder densities $p = 0.14$ (squares) and $p = 0.21$ (circles). Dashed curves: function f_2 with $\langle P_2\rangle_\infty = 0.52$ (long dashed line) and $\langle P_2\rangle_\infty = 0.39$ (short dashed line). Continuous line: f_1 function. The inset shows the $p = 0.14$ nematic correlation $\langle G_2^{NN}\rangle(r)$ vs lattice units with its exponential fits (buried in the data), for AIC (a) and RIC (b). We obtain $\zeta = 6.6$ (AIC) and $\zeta = 6.5$ (RIC).

inset. The extracted correlation length ζ is basically identical in the two situations, in agreement with the assumption used in interpreting the FC data. Thus, our lattice of size L contains, on average, $N = (L/2\zeta)^3$ correlated domains of "diameter" 2ζ. The fitting lines in Fig. 4 are $f_1 = 1/\sqrt{N}$ (continuous line), describing the L dependence of $\langle P_2\rangle_\lambda$ with RIC [6], and $f_2 = [\langle P_2\rangle_\infty^2 + (1 - \langle P_2\rangle_\infty^2)/N]^{1/2}$ (dashed line). f_2, a generalization of f_1, is the root mean square of the sum of N random numbers having mean value $\langle P_2\rangle_\infty$. $\langle P_2\rangle_\infty$ is determined by fitting the AIC data vs L. The good fit of f_2 to the data, together with the invariance of ζ on the initial conditions, indicates that the simulated system, as the experimental one, can be described as a collection of correlated volumes, whose distribution is biased in the direction of the initial condition.

On the whole, we find a strong analogy between experimental and simulated behavior, both showing remnant order for systems prepared with ordered initial states (FC and AIC), both showing slow relaxation processes. This coherent picture suggests that nematics with dilute but strong quenched disorder have a ground state rich enough to induce permanent history dependent orientational configurations. In particular, the simulations display a significant dependence of the amount of residual order on p, the memory being stronger for more diluted disorder. This suggests that the different memory effects of the various experimental samples should be ascribed to the different effective amount of disorder provided by the solid networks. The hydrophilic FN has, very likely, the best dispersed structure, probably corresponding to a larger disorder density and thus to a smaller remnant order.

Memory effects, slow dynamics and the difference between FC and ZFC response to external fields, are defining properties of glass states [20]. The behavior here described indicates that nematics with quenched disorder correspond in some sense to the glass phase predicted for this class of systems [8]. However, there is a significant difference between well known glass states and the behavior here reported: our data show definite, very slow but measurable, relaxation processes leading to a steady state condition, which, to the best of our determination, displays no sign of decay. In spin glasses, instead, the remnant magnetization is the result of relaxation processes that are too slow to be measured and it appears as a slowly decreasing signal. Inspection of simulation snapshots suggests that the presence of topological defects could be at the origin of this difference. Comparing an AIC and a RIC simulation having identical configuration of the frozen spins, it is apparent that the number and location of disclination defects is different in the two cases. Moreover, analysis of nematics in simpler interconnected porous geometries reveals that disclination lines are generally present and they stretch out through interpore openings [22]. Thus it is reasonable to assume that, when the system is left to evolve from a prepared aligned state, disclination lines form and assign a specific topological connectivity to the system, which relaxes to the lowest energy state compatible with the topological constraints. Switching from a topological setting to a different one costs a much larger amount of energy and thus leads to relaxation of time scales too long to be, even partly, measured. It will be interesting to see if the role of topological defects suggested by our results is of importance also in other condensed matter systems with quenched disorder, thus uncovering a universal feature.

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