Nematics with Quenched Disorder: What Is Left when Long Range Order Is Disrupted?

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It is now generally accepted that even low amounts of quenched disorder disrupt long-range order in anisotropic systems with continuous symmetry. However, very little is known on the key item of the nature of the residual order, if any, and particularly if this has quasi-long-range or truly-short-range character. Here we address this problem both experimentally for the nematic 6CB in dilute aerosils and with computer simulations. We find that the residual order is short ranged and scales with disorder density in agreement with the Imry-Ma argument.

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The effects of quenched random disorder are of fundamental interest for many areas of soft condensed matter [1–4] including superfluids [5], random magnets [6], elastomers [7], and liquid crystals [8,9]. Quenched disorder has also important effects on relaxations, yielding a slow, glass type, dynamics [6,10]. In this Letter, however, we will focus on the far reaching consequences that even minute amounts of a random perturbation have on the extent and nature of order correlations in nematic liquid crystal (LC) systems. The basic reference point to discuss the effect of a random perturbation on ordered phases is still, for its simplicity and generality, the "Imry-Ma argument" which suggests that an arbitrarily low amount of static disorder should suppress long range order (LRO) in a large enough continuous symmetry system in three dimensions [1,6]. While this is to some extent verified experimentally, e.g., in the case of nematics [8,11], very little is known on the nature of the residual order, if any, and in particular if the correlation length ζ for a three-dimensional system has a truly short range, $\exp(-r/\zeta)$, type dependence on distance r or if it is instead quasi-long-range [4,12]. Here we address this problem both experimentally and with computer simulations and we investigate the behavior of a nematic phase distorted by random quenched disorder. This can be achieved in practice for *filled nematics* (FN): nematics where finely dispersed silica at suitably low volume fraction ϕ forms a colloidal gel with at least some nonannealed disorder and with the silica branches creating an aligning effect in random directions [13]. Experiments on FN show that the isotropic-nematic (NI) phase transition is rounded when ϕ is above 0.04 [14]. Parallel investigations on LC incorporated in silica aerogel indicate that the NI coexistence is suppressed when ϕ is above 0.2 [8,11]. While this is certainly sufficient to deduce the loss of LRO, the reciprocal implication is not necessarily true. Therefore the singular calorimetry peak observed at lower ϕ is not conclusive on the loss or permanence of nematic LRO, $\langle P_2 \rangle$ [15] or S [16]. Furthermore, no experiment has, so far, determined the correlation function of the nematics disordered by dispersed silica. On the theoretical side, many different approaches to the problem of the stability of nematic LRO to quenched disorder have also been presented with contrasting conclusions. Maritan *et al.* [2] predicted the existence of a nematic phase at low disorder concentration and temperature from the mean field solution of a random field Lebwohl-Lasher (LL) [15] model. More recently, Radzihovsky and Toner [3], developed an Imry-Ma-like argument which lead to instability of nematic LRO in the presence of arbitrarily weak quenched disorder. They also discussed the possibility for the nematic phase to be replaced by a glassy state characterized by quasi-long-range (QLR) order. A glass phase with QLR order where the correlation length is infinite and the correlation function of the order parameter obeys a power dependence on the distance was also predicted by Feldman [4] using a renormalization group approach.

Computer simulations on various models have also been performed to investigate the behavior of nematics in the presence of disordering fields. In particular, independent pore approximations [17], spin models with random disordering field [2,12,18], and models with interconnected disorder, although for discrete spin orientations [19], have been investigated. Even if all these models reproduce qualitatively the phase transition behavior they have been unable to produce a quantitative account of deviations from bulk behavior and, more seriously, to convincingly determine the existence and nature of residual order. Simulations are also plagued with practical difficulties, like the slowing down and dependence on thermal history induced by quenched disorder which require extremely long runs and the need to explore low disorder concentrations that implies very large sample sizes. Even recent and detailed studies have been performed on relatively small (up to 28^3 spins) systems and with little attention to starting conditions [12].

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In this Letter, we present a body of new results, obtained (i) by measuring the spectral dependence of the total scattering cross section of a FN, and (ii) by performing extensive computer simulations of a modified LL model [15,20].

FN samples were prepared dispersing with a solvent method [14] in the LC 6CB (nematic between 18 and 29 °C) a volume fraction $\phi = 0.015-0.03$ of Degussa Aerosil R812 silica nanoparticles, industrially used as thickeners, and by enclosing the mixture, which is above the gelation threshold [14], in quartz cells of thickness $d = 20$ μm or $d = 50$ μm. The samples, prepared in the isotropic phase and cooled into the nematic phase, were first analyzed by measuring their residual optic anisotropy, i.e., by detecting the depolarized transmitted light when illuminating the samples with a focused He-Ne laser beam as a function of the sample orientation. With this procedure we have repeatedly explored volumes of about 100 μm^3 of FN. Our data indicate that the average birefringence in such volumes is quite small, corresponding to negligible residual nematic order parameter: $\langle P_2 \rangle < 0.02$. The loss of nematic LRO is also, but less directly, confirmed by the quantitative success in interpreting the turbidity data in the same samples [21] since residual LRO would imply smaller optical inhomogeneities and thus smaller scattered intensity.

Given the large turbidity of FN, the structure factor for the orientational fluctuations of the optical axis cannot be simply extracted from the angular dependence of the scattered intensity because multiply scattered photons completely mask the single scattering signal. To explore the local structure factor of FN we propose, as a novel method, to study the total scattered intensity as a function of the light wavelength λ, thus taking advantage of the reliable determination of the transmitted intensity even in highly turbid media. Experiments have been done by illuminating the samples with the expanded and collimated light beam of a UV-VIS lamp with power spectrum $P_0(\lambda)$, and selecting the transmitted power P by coupling the light propagating in the forward direction to a 50 μm optical fiber. $P(\lambda)$, $300 < \lambda < 1100$ nm, is obtained with a spectrum analyzer, finding typical P/P_0 of $10^{-3}-10^{-2}$. From the data we have extracted the turbidity $\tau(\lambda) = -\ln[P(\lambda)/P_0(\lambda)]/d$. We have tested experimental setup and interpretation by studying aqueous colloidal suspensions of polystyrene spheres having radius R of 0.1 and 6 μm (Fig. 1, upper plate). For sufficiently small particles, the Rayleigh-Gans (RG) approximation [22], predicts $\tau \propto \lambda^{-2}$ independently from the particle shape, size, and spacial dependence of the refractive index. This is verified for the data in Fig. 1*B*, as well as for FN with high concentration of silica, and thus short correlation length ζ [21]. A completely different behavior is instead observed, and expected, when the size of the optical fluctuations (R for the spherical particles and ζ in the case of FN) times their amplitude (refractive index mismatch in the case of colloids and LC birefringence Δn in the case of FN) is larger than λ, i.e., when the RG theory cannot be used. In this regime, where the anomalous diffraction (AD) model [22] is instead applicable, $\tau(\lambda)$ strongly depends on amplitude, size, and spacial dependence in the refractive index. The quality of the theoretical predictions in the AD regime is demonstrated by the dashed curve in Fig. 1*A*, obtained with no free parameters. In Fig. 1*D* (continuous curve) we show $\tau(\lambda)$ obtained in a FN whose $\zeta \Delta n > \lambda$, i.e., well outside of the RG regime. We experimentally find, in the case shown in Fig. 1*D* as well as in different FN as reported in the inset of the figure, that $\tau(\lambda)$ is well described by the power law $\tau(\lambda) \propto \lambda^{\alpha}$ with an exponent close to zero, i.e., $\alpha = -0.3 \pm 0.1$, as indicated in the inset. To interpret these results we have extended the AD model previously used to successfully interpret the $\tau(T)$ data in Ref. [21]. This model treats the FN as a collection of independent uniaxial scatterers having uncorrelated optical axes and embedded in an isotropic medium whose refractive index is the mean one of the system. We also suppose that the scatterers have radial symmetry, their birefringence decaying upon moving away from their centers as $\Delta n(r) = \Delta n_B(T) f(r)$, where $\Delta n_B(T)$ is the bulk birefringence of 6CB at the considered temperature and $f(r)$ is a scalar function decaying to zero as the distance r from the scatterer center increases. For each choice of $f(r)$ we then calculate the spatial nematic correlation function $G_2^{NN}(r) = \langle P_2[\mathbf{n}(0) \cdot \mathbf{n}(r)] \rangle$ which, for this model, reduces to $G_2^{NN}(r) \propto \langle \Delta n(0) \Delta n(r) \rangle$, where $\langle\ \rangle$ indicates volume averaging. The result is that $\tau(T)$ is indeed a negative power of λ, the exponent being related to the shape of the correlation function. This is shown in Fig. 2, where we plot the exponent α as a function of k, the parameter controlling the shape of $G_2^{NN}(r)$ for two trial families of stretched exponentials and power laws. We see that the measured α is compatible with a simple exponential decay of $G_2^{NN}(r)$ ($k = 1$), as well as with power law decays having exponent $k = 9 \pm 2$, a value very much larger than the values usually associated with QLR order in condensed phases [16]. Accordingly, our results indicate that the distorted structure of the FN is a true short range nematic order.

Monte Carlo Metropolis simulations have been performed on the sprinkled silica spin (SSS) model proposed in Ref. [20], where molecules (or small clusters of them) are described by units vectors $\mathbf{s}_i$ ("spins") and a fraction p of randomly chosen spins are frozen in randomly chosen orientations $\mathbf{r}_l$ to mimic the disorder induced by the silica gel. The Hamiltonian is

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

where $\mathcal{N}$ is the set of nematic spins and S of silica spins of concentration $p = \frac{S}{(\mathcal{N}+S)}$. ϵ is a positive coupling constant for nearest-neighbor spins and zero otherwise. The model clearly reduces to the LL model for $p \to 0$ and

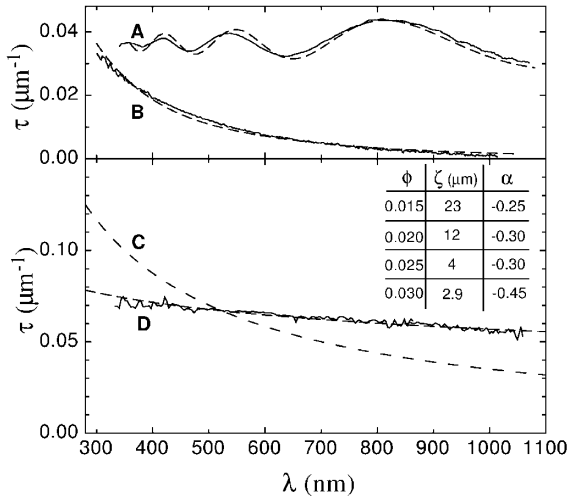

FIG. 1. Experimental (continuous lines) and theoretical (dashed lines) turbidity τ versus wavelength λ. Upper plate: colloidal dispersion of polystyrene spheres of radius $R = 6\ \mu$m (A) and $R = 0.1\ \mu$m (B). Lower plate: FN with $\phi = 0.015$ at $T = 22\,^{\circ}$C (D). Theoretical curves have been obtained from the RG model (B) and from the AD model for spheres (A), for an exponentially decaying G_2^{NN} (D) and, for the sake of comparison, for a power law with $\alpha = -1$ (C). Notice the trend of α towards -0.25 as ζ grows and the system enters the AD regime.

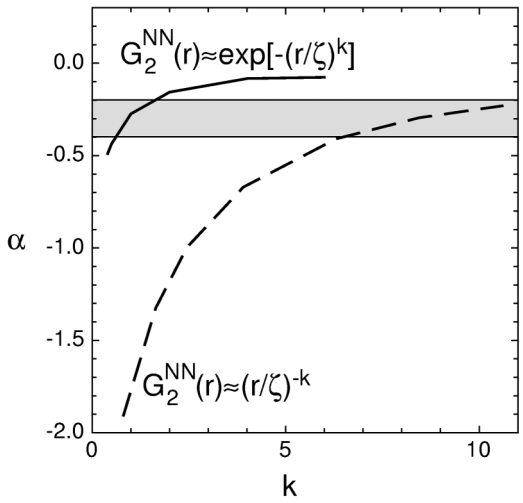

FIG. 2. α vs k parameter predicted by the AD model using a stretched exponential (continuous line) and a power law (dashed line) correlation decay type. The grey area indicates the range of experimental α.

somewhat resembles the uniform random field Hamiltonian employed in [12,18], where the random perturbers are uniformly distributed across the sample. However, the SSS model has some advantage over the uniform random field, since it allows varying the impurity concentration and adds dopant localization so that we can also see how the disorder propagates from the random perturbers and determine if and how this is healed by the nematic. We expect the number of spins of the system to play a crucial role, and here we have investigated the dependence of the simulation results on the lattice size in a series of well-defined cooling runs. In Fig. 3 we show the decay, in lattice units, of the nematic correlation function $G_2^{NN}(r; L)$ calculated in simulation boxes of various linear size L for a system where $p = 0.14$ and at the reduced temperature $T^* = 0.2$. The simulations have been performed starting from isotropic initial configurations. Data analysis reveals the following: (i) the G_2^{NN} are all very well represented by exponential functions decaying to a finite plateau (ii) $\langle P_2\rangle_L$ decreases with the size as $\langle P_2\rangle_L \propto L^{-1.5}$, as better shown in the inset of Fig. 3; (iii) regardless of L, the initial slope of G_2^{NN} is the same. These results coherently support the notion that $G_2^{NN}(r; L \to \infty)$ is an exponential decaying to zero with a decay length ζ extracted from the common initial slope as shown in the figure. Evidence (ii) is thus understood as a decay of $\langle P_2\rangle$ approximately as the inverse square root of the number of correlated ζ^3 subvolumes, while further checks have shown that evidence (iii) holds when $L > \zeta$. Analogous results for the correlation function decay have been obtained for various lattice sizes and $p = 0.05$. Hence simulations, in agreement with experiments, indicate that, at finite values of p the nematic order is short ranged. Systematic extensions to smaller p are increasingly difficult, especially because of the $L > \zeta$ condition, and we have focused on comparing our results with the basic Imry-Ma scaling behavior. The Imry-Ma criterion was based on a magnetic like interaction between the local field **h** and spin **s** in the same lattice position i, i.e., $\mathbf{s}_i \cdot \mathbf{h}_i$ but it is applicable for any local coupling between spin and field which, upon randomly choosing $\mathbf{h}_i$,

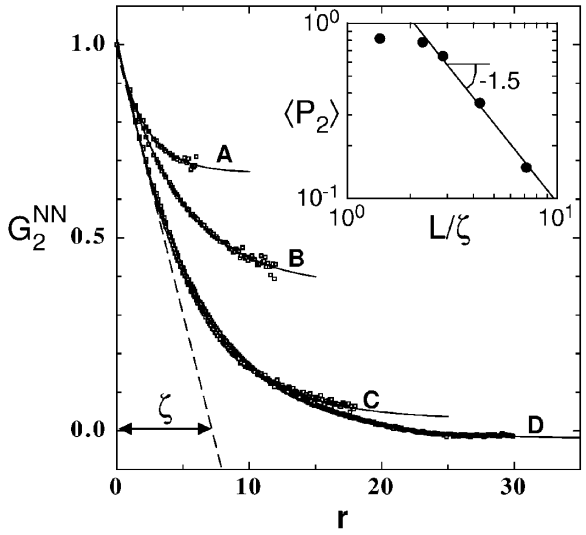

FIG. 3. Orientational correlation $G_2^{NN}(r)$ versus distance r at $T^* = 0.2$ and a density of sprinkled disorder: $p = 0.14$ as obtained from MC simulations of 10^3 (A), 20^3 (B), 30^3(C), and 50^3 (D) lattices. The lines give exponential plus plateau fits to the curves. The correlation ζ is extracted by the common initial slope (straight dashed line). In the inset average nematic order vs scaled L/ζ, including data for $L = 10, 16, 20, 30, 50$.

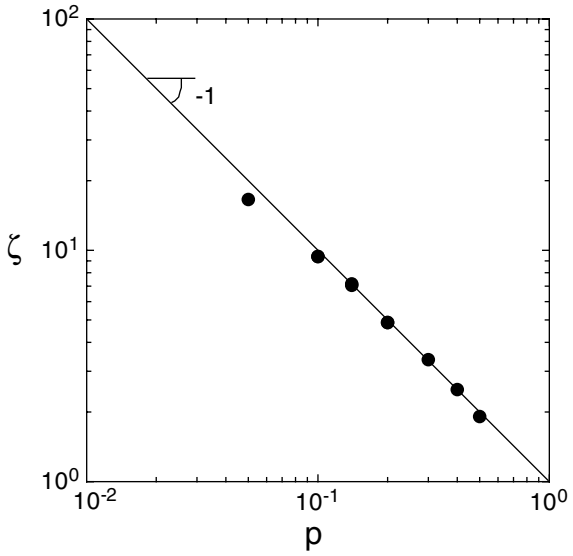

FIG. 4. Correlation length ζ obtained from the simulation at $T^* = 0.2$, plotted as a function of the amount of quenched disorder p. The solid line fits ζ as obtained in the most densely disordered systems.

results in a random variable of zero average, as is the case for $P_2(\mathbf{s}_i \cdot \mathbf{h}_i)$. Consequently, the volume coupling energy E_V of a domain of size L with the random field in the SSS model scales with p and L as $E_V \propto p^{1/2}L^{3/2}$, in turn implying that the typical distortion length scales as $\zeta \propto p^{-1}$ [1]. This prediction can be directly tested by the simulations and, more indirectly, compared with the experiments. In Fig. 4 we show ζ extracted from the initial slope of the simulated $G_2^{NN}(r; L)$ showing that the scaling $\zeta \propto p^{-1}$ is beautifully confirmed. An analogous scaling behavior has been observed in real FN systems, namely $\zeta \propto \phi^{-1.6}$ [21] and $\zeta \propto \phi^{-1.35}$ [23]. The trouble in interpreting this result is the unclear connection between the silica volume fraction and the "disorder density" variable p. Specifically, to compare the experimental results with theory and simulation requires mapping the randomly oriented but spatially structured disorder provided by the silica aggregate in a FN into an "equivalent" spatially and orientationally random disorder. Although only the knowledge of the detailed gel structure would enable a final model, an important clue is provided by the fact that the silica nanoparticles form a fractal structure having fractal dimension $d_f \approx 2.4$ [14]. Fractal gels are generally described as a uniform dispersion of interconnected fractal clusters which, in our case, constitute the "units" providing the disorder. The volume of such clusters grows more than linearly with the number of aggregated particles. Assuming that the aggregation number grows proportionally with ϕ and that p can be identified with the volume filled by the silica structures, we find $p \propto \phi^{3/d_f}$, not far from the experimental findings.

In conclusion, we have shown that experiments and Monte Carlo simulations coherently indicate that, at a given finite amount of disorder, the nematic ordering obtained by cooling into the nematic phase a system prepared in the isotropic phase, is local and short ranged. This proves the short-ranged nature of the nematic ordering at finite disorder concentration and provides a conclusive verification of the basic scaling behavior contained in the Imry-Ma argument, which, in turn, leads to conclude that, even at arbitrarily low density of disorder, the long-ranged nematic order is suppressed.

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