Nematics with Quenched Disorder: Violation of Self-Averaging

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(Received 17 March 2010; revised manuscript received 2 September 2010; published 28 September 2010)

We consider the isotropic-to-nematic transition in liquid crystals confined to aerogel hosts, and assume that the aerogel acts as a random field. We generally find that self-averaging is violated. For a bulk transition that is weakly first order, the violation of self-averaging is so severe that even the correlation length becomes non-self-averaging: no phase transition remains in this case. For a bulk transition that is more strongly first order, the violation of self-averaging is milder, and a phase transition is observed.

DOI: 10.1103/PhysRevLett.105.147801 PACS numbers: 61.30.Pq, 05.70.Fh, 64.70.mf, 75.10.Hk

Liquid crystals confined to quenched disordered media are frequently encountered and are of practical importance [1]. In certain cases—the prototype example being silica aerogel—the disordered medium induces a quenched random field [2–8]. The random field couples to the liquid crystal at (essentially) arbitrary locations, and imposes a preferred orientation of the nematic director at these locations. One consequence of random-field disorder in liquid crystals is the loss of long-range nematic order in all experimentally relevant dimensions $d \leq 3$ [9–13]. This, however, does not rule out the existence of phase transitions. In contrast, the latter are routinely observed [2,4,8,14] and understanding the influence of random-field disorder on liquid crystal phase transitions is an important topic. One known effect is that random fields can change the order of a transition [3,15]. The bulk isotropic-to-nematic (IN) transition in three dimensions (3D) is usually first order, but random fields can render this transition continuous [2,4,16,17] or wipe it out completely [3]. Other known effects include slow dynamics [5,18–20], lowering of phase transition temperatures [3,5], and the formation of multidomain nematic structures [4,21].

It is also known that systems exposed to random fields generally do not self-average: results obtained for one sample of disorder, even if the sample is large, are not necessarily representative for all disorder samples [22–24]. To what extent lack of self-averaging plays a role at the IN transition is the topic of the present Letter. Our main result is that, for a bulk IN transition in 3D that is weakly first order, i.e., the experimentally most relevant case, the violation of self-averaging in the presence of random fields is so severe, even the correlation length becomes a non-self-averaging quantity [25,26]. The IN transition temperature, as characterized by the temperature of the specific heat maximum, does not become sharp in the thermodynamic limit, but is given by a distribution of finite width. Hence, no sharp phase transition remains.

To illustrate this point, we have simulated the sprinkled silica spin (SSS) model [27]; models such as this are routinely used to describe nematics in disordered media [10,11,27–29]. The SSS model is defined on a 3D periodic $V = L \times L \times L$ lattice. A 3D unit vector $\vec{d}_i$ (spin) is attached to each lattice site i. The energy density is given by

$$\epsilon = -J/V \sum_{\langle i,j \rangle} |\vec{d}_i \cdot \vec{d}_j|^p, \qquad J > 0, \tag{1}$$

with the sum over nearest neighbors (in what follows, the temperature T is expressed in units of J/k_B, with k_B the Boltzmann constant). We set $p = 2$ for now; Eq. (1) then resembles the Lebwohl-Lasher model [30], which undergoes a weak first-order IN transition from a high-T isotropic phase (exponential decay of the nematic correlation function to zero), to a low-T nematic phase with long-range order (exponential decay of the nematic correlation function to a finite positive value). In the SSS model, quenched disorder is introduced by marking a fraction q of randomly selected spins as quenched (we use $q = 0.1$ always). These spins are oriented randomly at the start of the simulation and remain static thereafter, which can be conceived as a random field of infinite strength acting on a fraction of the spins. Even though the random-field strength is infinite, $q = 0.1$ remains in the weak field limit, in the sense that the nonquenched spins still form a percolating network. If q is set above the percolation threshold, any phase transition gets trivially blocked, since then the correlations cannot propagate through the lattice anymore. The SSS model is different from the random-field Ising model because the spins are 3D continuous vectors, as opposed to discrete integers. The SSS model does not support long-range nematic order at any finite temperature [9].

Most of our analysis is based on the distribution $P^{(k)}_{L,T}(\epsilon, s)$, defined as the probability to observe energy density ϵ and nematic order parameter s, at temperature T, system size L, and for some sample of random fields k. We measure the distributions for $L = 7$–15. The nematic order parameter s is defined as the maximum eigenvalue of the 3D orientational tensor. In a perfectly aligned nematic sample $s = 1$, while an isotropic sample yields $s \to 0$ in the thermodynamic limit. We use broad histogram methods, namely, Wang-Landau sampling [31] and successive umbrella sampling [32], to obtain $P^{(k)}_{L,T}(\epsilon, s)$. These

methods ensure that the simulation performs a random walk in phase space. This is crucial because the SSS model is known to exhibit metastable states [20,33], in which standard Monte Carlo simulations (sampling directly from the Boltzmann distribution) may ''get stuck.'' Since we expect self-averaging to be violated, it is crucial that the distributions be measured for $k = 1, \ldots, M$ random-field samples, where M must be large. We use $M \sim 1000$–2500, based on the convergence of ''running averages'' of quantities of interest onto plateau values. We also measure correlation functions; the latter are obtained for $L = 30$ using standard Boltzmann sampling.

For each sample k, we compute the thermally averaged nematic order parameter $\langle s \rangle_k$ and measure the fluctuation between samples $R_s^2 = [\langle s \rangle^2] - [\langle s \rangle]^2$, with $[\cdot]$ the disorder average $[X^n] = (1/M) \sum_{k=1}^{M} X_k^n$. If the system self-averages, $R_s \to 0$ in the thermodynamic limit, in which case a single experiment on a large system will be representative for all samples. In Fig. 1(a), we plot R_s versus T for three system sizes. The striking result is that, at low temperature, R_s does *not* decay to zero with increasing L but remains finite. The onset to the non-self-averaging regime is marked by a maximum in R_s, at temperature $T = T_R$. We thus identify two regimes: a high-T regime ($T > T_R$) where the SSS model self-averages (R_s decreases with L), and a low-T regime ($T < T_R$) where self-averaging is violated (R_s remains finite).

The violation of self-averaging at low T profoundly affects the nematic correlation function $G(r) = \langle \frac{3}{2} (\vec{d}(0) \cdot \vec{d}(r))^2 - \frac{1}{2} \rangle$ [10]. [In this work, $G(r)$ is calculated using all spins, i.e., free and static ones.] Since it holds that $G(L/2) = \langle s \rangle^2$, with L the edge of the simulation box, and since $R_s > 0$, fluctuations in $G(r)$ between disorder samples are automatically implied. We must therefore consider $G_k(r)$, i.e., the nematic correlation function obtained in the kth random-field sample. In the high-T regime, we find that $G_k(r)$ decays exponentially to zero, with negligible fluctuations between samples: the SSS model is isotropic and self-averaging when $T > T_R$. In contrast, in the low-T regime, $G_k(r)$ fluctuates profoundly between disorder samples [Fig. 2(a)]. Note that we concentrate on the tail of $G(r)$ and so the range $r < 5$ is discarded. In some samples, $G_k(r)$ decays very rapidly, while in others the decay is much slower. Clearly, when $T < T_R$ a single measurement of $G_k(r)$ is not representative.

The key point is that, in random-field systems, there exist two correlation functions: the *connected* correlation function $[G(r)]$ (i.e., the nematic correlation function averaged over all samples), and the *disconnected* correlation function $[G(r)^2]$ [34,35]. The solid curve in Fig. 2(a) shows $[G(r)]$: its decay to zero is most consistent with a power law, suggesting quasi-long-range order. This agrees with Ref. [13], but it disagrees with Ref. [10] (where short-ranged exponential decay is observed). Regardless of the precise form of the decay, we confirm that $G_k(r)$ does not self-average. This is shown in Fig. 2(b), where $\kappa \equiv [G(r)^2]/[G(r)]^2$ is plotted. At large r, power law growth $\kappa \propto r^{\theta}$, with $\theta \sim 0.1$, is observed. The disconnected correlations thus decay independently from the connected ones. In contrast, if $G_k(r)$ were self-averaging, the fluctuation $[G(r)^2] - [G(r)]^2$ would be zero at large r: $[G(r)^2]$ and $[G(r)]^2$ then decay with the same exponent. Since the correlation functions do not self-average, it follows that properties extracted from these functions do not self-average either, which includes the correlation length ξ [25,26]. The Brout argument [36], which conceives the thermodynamic limit as a large number of independent

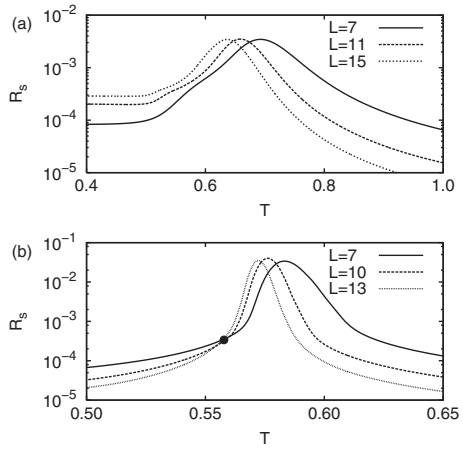

FIG. 1. R_s versus T using $p = 2$ (a) and $p = 10$ (b) for several L. The temperature where R_s is maximal defines T_R. Note that T_R decreases with L. For $p = 2$, there is no self-averaging at low T. In contrast, for $p = 10$, self-averaging is restored at low T, and a sharp phase transition occurs (marked with the dot).

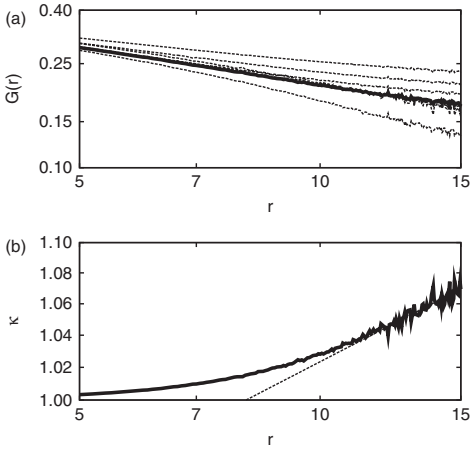

FIG. 2. Correlation functions for $p = 2$, $L = 30$, and $T = 0.5$ (which is well below T_R) on double logarithmic scales; due to periodic boundaries up to $r_{\max} = 15$ can be sampled. (a) $G(r)$ obtained for several samples (dashed curves) together with the disorder-averaged result $[G(r)]$ (solid curve). (b) κ versus r; the dashed line is a power law fit to the large r regime.

subsamples of size ξ, thus breaks down. Instead, ξ must be regarded as a random variable. The power law decay of $[G(r)]$ observed by us indicates that ξ itself is very large, if not infinite. For $\xi \to \infty$, the Brout argument breaks down in any case [24].

How does this affect the IN transition in the SSS model? The usual approach to detect the IN transition is to measure the specific heat $c = V(\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2)$ versus T; at the transition, c reaches a maximum. For each random-field sample k, we measured the temperature $T_{c,k}$ where c was maximal, and the corresponding value $c_{\max,k}$. Since ξ does not self-average, an unusually large fluctuation $[T_c^2] - [T_c]^2$ is expected. This is confirmed in Fig. 3(a), where histograms of $T_{c,k}$ are shown, shifted such that $[T_c]$ is at zero, and for several L. The striking result is that the distributions do not become sharp as L increases. The specific heat itself is also non-self-averaging. This is illustrated in Fig. 3(b), where histograms of $c_{\max,k}$ are shown, shifted by $[c_{\max}]$, and again for several L. We also observed that $[T_c]$ is very close to the temperature T_R where R_s is maximal. A signature of the onset to the low-T regime (where self-averaging is violated) is thus also provided by the specific heat maximum. Both $[T_c]$ and T_R decrease with increasing L: the non-self-averaging regime $T < T_R$ thus gets smaller in larger systems. Unfortunately, finite size scaling with a non-self-averaging correlation length is complicated—a rigorous scaling theory remains elusive—and so it is difficult to estimate T_R in the thermodynamic limit. The decrease of T_R with L, and hence of $[T_c]$, is in any case slow. For instance, if we assume a power law shift $T_R - T_\infty \propto 1/L^y$, $T_\infty \equiv \lim_{L\to\infty} T_R$, a fit to our data yields a maximum value for the exponent $y_{\max} \sim 0.16$; this upper bound is obtained by assuming $T_\infty = 0$.

To conclude, the SSS model (with $p = 2$ in Eq. (1) and quenched spin fraction $q = 0.1$) does not feature a sharp phase transition. For a given sample k of random fields, a well-defined temperature $T_{c,k}$ where the specific heat attains its maximum can be measured, but the fluctuation in $T_{c,k}$ between samples remains finite, even as $L \to \infty$. We attribute this behavior to the existence of a nontrivial *disconnected* correlation function, which implies a non-self-averaging correlation length when $T < T_R \sim [T_c]$. In this regime, the SSS model does not self-average. The temperature T_R decays extremely slowly with system size; whether T_R remains finite in the thermodynamic limit, or whether it decays to zero, cannot be discerned from our data. Since the decay of T_R and $[T_c]$ with L is slow, it is likely that the non-self-averaging regime survives in macroscopic samples (even if $T_\infty = 0$). We expect that by varying T a maximum in the specific heat will be found, but the value of the specific heat at the maximum will vary between samples. There is some experimental evidence for this behavior. The liquid crystal 8CB in bulk undergoes a weak first-order IN transition [2,4], as does Eq. (1) with $p = 2$. Upon insertion in aerogel, the enthalpy obtained in different samples ranges from 3.6–5.23 J/g, which is unusually large [2]. However, since the enthalpy is related to the specific heat, and since the specific heat does not self-average [Fig. 3(b)], a large enthalpy fluctuation between samples would, in fact, not be unexpected.

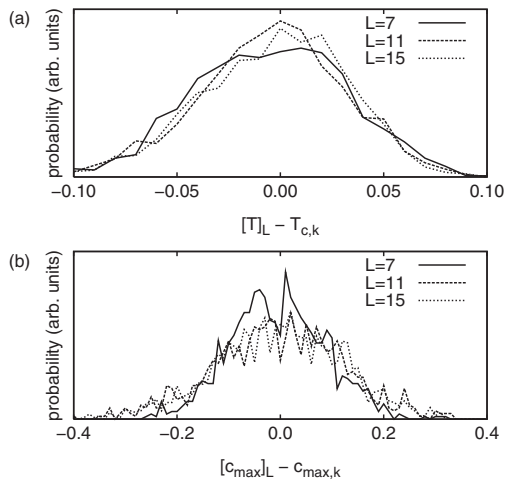

FIG. 3. Histograms of $T_{c,k}$ (a) and $c_{\max,k}$ (b), shifted by their respective averages, and for several L. The histograms do not become sharp as L increases.

Do our results imply the absence of IN transitions, in general, in the presence of random-field disorder? The answer to this question is an unequivocal "no." The phase behavior of liquid crystals is not dictated by any universality class, and by changing details in the particle interaction qualitatively different scenarios may develop [37]. To illustrate this, we reconsider Eq. (1) using $p = 10$; this makes the bulk IN transition more strongly first order [37]. Again using a fraction of quenched spins $q = 0.1$, we show in Fig. 1(b) the variation of R_s with T. The striking difference with $p = 2$ is that self-averaging is restored at low temperatures. There now appears an intermediate regime of temperatures where self-averaging is violated, but this regime becomes smaller as L increases. Hence, in the thermodynamic limit, self-averaging is violated at only one temperature, which then reflects a sharp phase transition, with finite size effects given by [22]

$$\sqrt{[T_c^2] - [T_c]^2} \propto [T_c] - T_\infty \propto 1/L^y, \tag{2}$$

where T_∞ is the transition temperature in the thermodynamic limit. This implies that histograms of $(T_\infty - T_{c,k})L^y$ become L independent, provided correct values of T_∞ and y are used. The scaling is confirmed in Fig. 4, using $T_\infty \approx 0.558$ and $y \approx 0.88$, and the collapse is clearly excellent. Incidentally, T_∞ corresponds to an approximate intersection in curves of R_s versus T for different L [Fig. 1(b)], which offers an alternative route to locate the transition.

In summary, we have shown that the IN transition in the presence of random fields is strongly affected by a lack of self-averaging. Certainly for computer simulations, taking a disorder average $[\cdot]$ involving many samples is crucial.

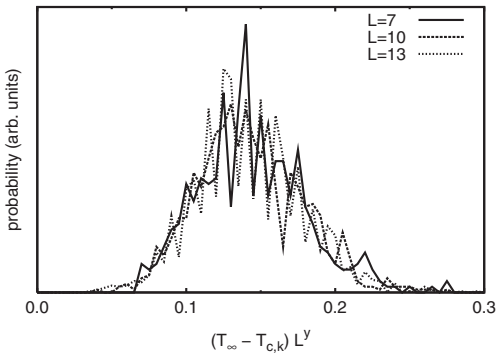

FIG. 4. Histograms of $(T_\infty - T_{c,k})L^y$ for $p = 10$. The curves for different L collapse, consistent with Eq. (2).

For a bulk IN transition that is weakly first order, the violation of self-averaging is so severe, even the correlation length ξ becomes non-self-averaging [25,26]. This manifests itself from the nematic correlation function, which becomes strongly sample dependent. A consequence is that no sharp IN transition remains in this case. For a bulk IN transition that is more strongly first order, the violation of self-averaging is restricted to a single temperature in the thermodynamic limit. In this case, a phase transition does occur, and finite size effects near the transition are well understood [22]. As far as we know, a scaling theory for the case where ξ does not self-average remains elusive. In some sense, the finite size effects observed by us for $p = 2$ resemble those of Eq. (2), but in the limit where $y \to 0$. Perhaps a new scaling theory should be developed keeping this in mind.

This work was supported by the Deutsche Forschungsgemeinschaft, Emmy Noether program: VI 483/1-1.

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