Nematics with quenched disorder: violation of self-averaging

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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, 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.

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Liquid crystals confined to quenched disordered media are frequently encountered and 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 at these locations. One consequence of random field disorder on liquid crystal phase transitions 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, 11] 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, 13]. 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, 10, 17] or wipe it out completely [3]. Other known effects include slow dynamics [3, 15, 20], lowering of phase transition temperatures [3, 5], and 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, 24]. 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

$$\epsilon = -J/V \sum_{(i,j)} |\vec{d}_i \cdot \vec{d}_j|^p, \quad J > 0,$$  \hspace{1cm} (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 non-quenched 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 [3].

Most of our analysis is based on the distribution $P_{LT}^{(k)}(\epsilon, s)$, defined as the probability to observe energy density $\epsilon$ 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 ob-
tate \( P_L^{(k)}(\epsilon, s) \). 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 \( M \approx 1000 - 2500 \), based on the convergence of “running averages” of quantities of interest onto plateau values. We also measure correlation functions; the latter are obtained for standard Boltzmann sampling.

For each sample \( k \), we compute the thermally averaged nematic order parameter \( \langle s \rangle \) and measure the fluctuation between samples \( R_s^2 = [\langle s^2 \rangle - \langle s \rangle^2] \), with \([\cdot]\) the disorder average \( [X^m] = (1/M) \sum_{k=1}^{M} X_k^m \). 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 \( G(r) = \langle \hat{d}(0) \cdot \hat{d}(r) \rangle^2 - \frac{1}{2} \) [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 \( k \)-th 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. 11 (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 \( \theta \approx 0.1 \), 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 $\xi$ [23, 24]. The Brout argument [36], which conceives the thermodynamic limit as a large number of independent sub-samples of size $\xi$, thus breaks down. Instead, $\xi$ must be regarded as a random variable. The power law decay of $[G(r)]$ observed by us indicates that $\xi$ 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 $c = V\langle (\epsilon^2) - \langle \epsilon \rangle^2 \rangle$ 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 $c_{\text{max},k}$. Since $\xi$ 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 very large, if not infinite. For $\xi \to \infty$, the Brout argument breaks down in any case [24].

To conclude: the SSS model (with $p = 2$ in Eq. 11 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 non-trivial 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 $T_R$ 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. 11 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 $c_{\text{max},k}$ (b), shifted by their respective averages, and for several $L$. The histograms do not become sharp as $L$ increases.

FIG. 4: Histograms of $(T_\infty - T_{c,k})L^y$ for $p = 10$. The curves for different $L$ collapse, consistent with Eq. (2).
in the presence of random fields is strongly affected by a lack of self-averaging. Certainly for computer simulations, taking a disorder average \[25\] involving many samples is crucial. For a bulk IN transition that is weakly first-order, the violation of self-averaging is so severe, even the correlation length \(\xi\) becomes non-self-averaging \[26, 27\]. 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 \(\xi\) 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.

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\[ q = 0.1, \text{ we show in Fig.}\[1\]b) the variation of \(R_\infty\) 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 \[22\]

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

where \(T_\infty\) is the transition temperature in the thermodynamic limit. This implies that histograms of \((T_\infty - T_{c,k})L^\nu\) become \(L\)-independent, provided correct values of \(T_\infty\) 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, \(T_\infty\) corresponds to an approximate intersection in curves of \(R_\infty\) 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
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