Simulation Evidence of Critical Behavior of Isotropic-Nematic Phase Transition in a Porous Medium

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We investigate the phase transition from an isotropic to a nematic liquid crystal embedded in a porous network. We model this situation by a simple lattice spin model with a field of finite strength D, but random orientation at a fraction p of randomly selected lattice sites. Monte Carlo simulations show the existence of a nematic phase with *quasi-long-range order* for a large D. The isotropic $\rightarrow$ quasi-long-range nematic transition line has a *tricritical point.* [S0031-9007(98)06536-3]

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Liquid crystalline substances, consisting of anisotropic molecules, in randomly interconnected networks of pores [1], have drawn growing interest recently because of their importance in technological applications and from the fundamental point of view. Such systems raise fundamental issues, such as the effect of finite size and quenched disorder on phase transitions. The simplest liquid crystalline state is the nematic phase where the molecules exhibit only orientational long-range order and no translational long-range order. The isotropic (with neither orientational nor translational long-range order) to nematic (I-N) transition of thermotropic liquid crystals embedded in porous networks has been characterized using various experimental techniques [2,3]. The liquid crystal forming compound 8CB undergoes a weakly first order I-N transition at 313 K in the bulk. A detailed heat capacity study of Wu *et al.* [4] on 8CB in silica aerogel indicates first order I-N coexistence for low aerogel density, but for higher densities the specific-heat peak becomes rounder suggesting no I-N transition at all. On the other hand, 4O.8, another liquid crystalline compound that shows a weakly first order bulk I-N transition, does not exhibit any I-N phase coexistence in silica aerogel even for very low aerogel density [5]. Furthermore, the lowering of the peak position of the specific heat is more pronounced than the 8CB case [4].

Theoretical modeling of such phenomena is difficult. The silica aerogels considered in the experiments of Ref. [4,5] consist of a random network of silica backbones in a multiply connected void space. The effect of such a medium has been described by a random orienting field following the ideas of de Gennes [6]. Maritan *et al.* [7] have carried out mean field analysis of both the discrete three-state Potts model and the Lebwohl-Lasher (LL) model [8], the simplest lattice spin model used to describe the weakly first order bulk I-N transition, where the spins can have arbitrary orientations and interact only with nearest neighbors. In both cases they consider an infinitely strong field oriented randomly on a fraction p of the lattice sites, where p may be interpreted as the fraction of liquid crystalline molecules directly affected by the randomness of the pore geometry [4]. Their analysis [7] predicts a first order I-N transition at a nonzero temperature for all $p \neq 1$, but the transition temperature decreases with increasing p. Maritan *et al.* [7] have also carried out Monte Carlo simulations for the three-state Potts model with random orienting field of infinite strength. They observe in general that the specific-heat peak broadens and decreases in magnitude as p increases, a feature also found in experiment [4]. Their simulations seem to indicate that I-N transition is possible so far as $p \leq 0.5$, which is somewhat below the percolation threshold, p_c. However, we note that the existence of an I-N transition for low p is not clear unless the simulations are carried out systematically for larger system sizes. Moreover, the simulations are carried out for the discrete three-state Potts model with an infinitely strong orienting field. These considerations give an obvious impetus to carry out detailed studies of the continuous orientation LL model for a finite strength random orienting field. In a recent study in this direction, Cleaver *et al.* [9] have carried out a Landau–de Gennes type of mean field analysis, incorporating the effect of a random orienting field, which shows that the I-N transition remains first order for low strength of the random orienting field [10]. They compare their results with their Monte Carlo simulation studies on the LL model with the random orienting field at all lattice sites for different system sizes [9]. Their simulations, however, seem to suggest no I-N transition at a point where their mean field analysis predicts a first order I-N transition. Their results raise important questions. For instance, is the bulk first order transition retained for a low strength of the random field and destroyed beyond a critical strength, thus leading to a nontrivial critical behavior, or is it destroyed for all strength of the random field?

With this backdrop we carry out Monte Carlo simulation studies for the LL model systematically for different p in a finite random orienting field. Our studies differ from other recent simulation studies by Bellini *et al.* [11] where the authors consider the effect of confinement and different anchoring conditions in the LL model. In particular, we analyze the system size dependence of different

thermodynamic quantities at the temperature where the nematic ordering sets in. Our analysis brings out that very low strength of the random orienting field cannot destroy nematic order, resulting in a first order I-N transition for all values of p, including $p = 1$. For large strength, however, the nematic order is replaced by a *quasi-long-range* nematic (QLRN) order. The transition from isotropic to QLRN (I-QLRN) is first order for low p and continuous for large p indicating the presence of a *tricritical point* (TCP) on the transition line.

In our simulations the Hamiltonian is given by $\mathcal{H} = -J\sum_{\langle ij\rangle} P_2(\cos\gamma_{ij}) - D\sum_i' P_2(\vec{n}_i \cdot \vec{s}_i)$. The first term in the Hamiltonian is the usual LL coupling of strength J between the nearest neighbor spins. Here γ_{ij} is the angle between two nearest neighbor spins $\vec{s}_i$ and $\vec{s}_j$ of unit magnitude, and P_2 is the second Legendre polynomial. The second term in the Hamiltonian describes the effect of the local random orienting field: D is the strength of the field, $\vec{n}_i$ is its direction which is a random vector over a unit sphere, and the prime over the second summation indicates that the field is distributed over a randomly selected fraction p of lattice points. We take a simple cubic lattice with periodic boundary conditions in all three directions. The spins are updated by means of standard Metropolis algorithm. For a given D/J and p, we start from a random initial configuration at a high k_BT/J. The final equilibrium configuration is used as the initial configuration for the next lower temperature. Typically 100 000 steps are discarded before any quantity of interest is calculated. The equilibration is monitored by the energy E and nematic scalar order parameter S [defined by the largest eigenvalue of the nematic tensor $Q = \sum_i \frac{1}{2}(3x_\alpha^i x_\beta^i - \delta_{\alpha,\beta})$, where $\{x_\alpha^i\}$ are the spin components at the ith lattice site]. We calculate the equilibrium fluctuation in energy and nematic scalar order parameter which are related to the specific heat $c_V = \frac{1}{N}\langle(E - \langle E\rangle)^2\rangle$ and the order parameter susceptibility $\chi = \frac{1}{N}\langle(S - \langle S\rangle)^2\rangle$, respectively. Here the angular brackets denote the configuration averaging over 10 000 configurations sampled every 10 MC steps during the production runs. We compute c_V and χ for different k_BT/J to locate approximately the peak position of c_V and χ. We repeat the simulation at the approximate peak position for five different realizations of the random orienting field. The two-dimensional histogram of E and S is calculated by averaging over these realizations. Then we apply a histogram reweighting technique [12] to locate the c_V and χ peaks more precisely and to calculate $V_L = 1 - \frac{\langle E^4\rangle}{3\langle E^2\rangle^2}$. To investigate the thermodynamic transition between different possible phases, we check the behavior of the peaks of c_V and χ ($c_V^{\max}$ and $\chi^{\max}$, respectively) with increasing system size, L. In case of true thermodynamic transitions, they should scale with L. V_L shows a minimum, $V_L^{\min}$ at the transition, which has a nice scaling property [13], for $\frac{2}{3} - V_L^{\min}$ scales as L^{-d} for a first order transition, and as $L^{-(d-\alpha/\nu)}$ for a continuous phase transition, where α and ν are critical exponents and d is the dimensionality of the system.

For the bulk case ($D = 0$), c_V and χ show a peak at $k_BT/J = 1.12$, and $c_V^{\max}$ and $\chi^{\max}$ scale as L^3, shown in Fig. 1(a), confirming a first order transition in agreement with previous works [14]. Next we turn on the random orienting field of low field strength ($D/J = 0.1$). The scaling exponents ($= 3$) of $c_V^{\max}$ and $\chi^{\max}$ [Fig. 1(b)] show a first order transition for $p = 1.0$, and for lower p as well. Such is the case for $p = 0.05$ with $D/J = 1.0$ [Fig. 1(c)]. For $p = 1$ at the same D/J, however, c_V (and χ), generated by the histogram reweighting technique, shown in Fig. 2(a), reveals much broader and reduced peaks without any sensible scaling. Nevertheless, V_L shows a clear minimum [Fig. 2(b)] in this case and $\frac{2}{3} - V_L^{\min}$ scales with an exponent (2.9) less than $d = 3$, typical of a continuous transition. The same quantity scales with an exponent $\simeq d = 3$ for the first order cases. Finally, we consider the case of $D/J = 10$. The c_V and χ peaks are featureless here too. But $\frac{2}{3} - V_L^{\min}$ still scales with exponents (ranging from 2.8–2.9) systematically less than $d = 3$, implying continuous transition for p up to 0.2. For $p = 0.25$ we fail to get any sizable S even down to $k_BT/J = 0.5$ [15].

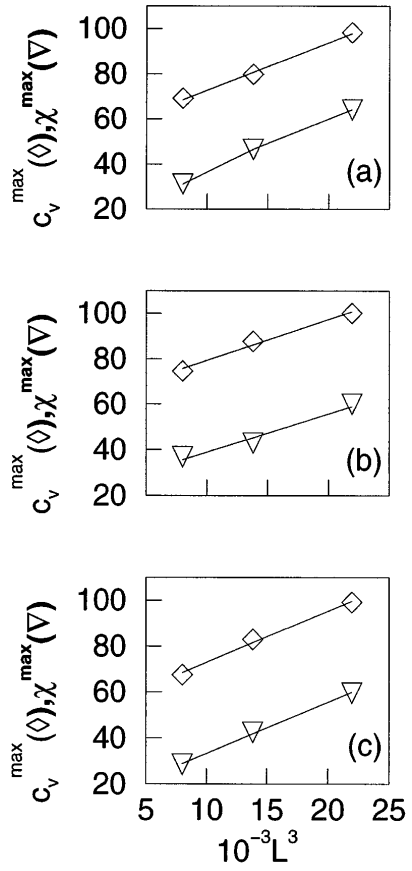

FIG. 1. $c_V^{\max}$ and $\chi^{\max}$, shown by the open diamonds and open triangles, respectively, for (a) bulk case, (b) $p = 1.0$, $D/J = 0.1$, and (c) $p = 0.05$, $D/J = 1.0$ as functions of L^3. The solid lines are the best fitted lines. These cases clearly correspond to first order phase transition.

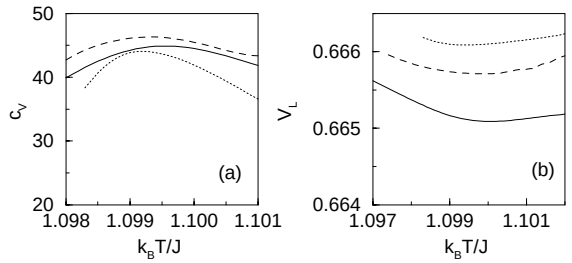

FIG. 2. (a) c_V and (b) V_L as functions of k_BT/J for $p = 1.0$ and $D/J = 1.0$ for different system sizes (solid line for $L = 20$, dashed line for $L = 24$, and dotted line for $L = 28$). The lack of scaling of c_V is evident. χ shows similar behavior. The minimum of V_L is noteworthy, and $V_L^{\min} \to \frac{2}{3}$ with increasing L with a well-defined scaling.

Next we examine the orientational pair correlation function, $g(r)$ [defined by $\langle \sum_{i,j} P_2(\vec{s}_i \cdot \vec{s}_j)\delta(r_{i,j} - r)/\sum_{i,j}\delta(r_{i,j} - r)\rangle$, where $r_{i,j}$ is the minimum image separation of two spins] as a function of r, shown in Fig. 3(a). Clearly $g(r)$ is short ranged for high temperature (isotropic) phases. But the low temperature ($k_BT/J = 1$) phases for $D/J = 0.1$ and $D/J = 1.0$ (with $p = 1.0$ for both cases) show remarkably different behavior. We fit our data with a $g(r) \sim a/r^{1-\eta} + b$ dependence. Note that $b \sim S^2$ for large r in the thermodynamic limit. This makes it worthwhile to check S^2 as a function of L as well. Excluding very short-range contributions to $g(r)$ from the nearest neighbors, we get $\eta \simeq 1$ for $D/J = 0.1$, i.e., a flat $g(r)$ with a finite nonzero b and observe that $S^2 \simeq 0.16$, independent of L, consistent with the finite b. This indicates a true long-range nematic order. For low D/J, the elastic cost of reorientation of randomly oriented nematic domains still wins over the disordering effects to set a true long-range nematic order. In the second case, we obtain $\eta = 0.82$, and S^2 agrees well with a $1/L^{0.18}$ decay as shown in Fig. 3(b), implying

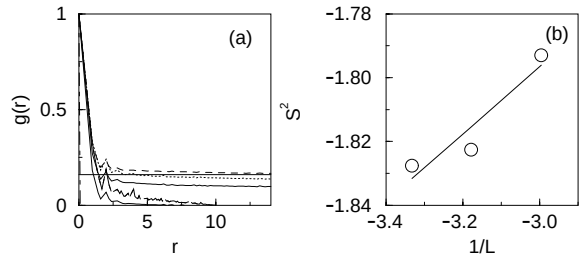

FIG. 3. (a) $g(r)$ vs r plot for different phases: isotropic $k_BT/J = 1.15, p = 1.0, D/J = 1.0$ (solid line), nematic $k_BT/J = 1.0, p = 1.0, D/J = 0.1$ (dashed line), QLRN $k_BT/J = 1.0, p = 1.0, D/J = 1.0$ (dotted line), and $k_BT/J = 0.5, p = 0.25, D/J = 10$ (dot-dashed line). The solid horizontal line corresponds to $b = 0.16$ (obtained from the order parameter estimation in the nematic phase). The steady $g(r)$ for large r in the nematic order and its slow decay in the QLRN order are clear when compared with respect to this line. The correlation length in the isotropic phase exceeds the mean spacing of the random sites. (b) Log-log S^2 vs $1/L$ plot for $D/J = 1.0, p = 1.0$, and $k_BT/J = 1.0$: the circles are the simulated points and the solid line shows a $L^{-0.18}$ dependence.

a slow (algebraic) decay of the nematic order [16], i.e., a QLRN order. For $D/J = 10, p = 0.25$, $g(r)$ is short ranged [Fig. 3(a)] even for a very low temperature ($k_BT/J = 0.5$).

The phase diagram, suggested by our findings on the possible phases and the scaling properties, is illustrated in Fig. 4. We consider the $(k_BT/J, p)$ plane for a given D/J for convenience. For $D/J = 0.1$, there is a first order I-N phase boundary [Fig. 4(a)]. For $D/J = 1.0$, the ordered phase is nematic for very low p but is replaced by QLRN order as p increases. The transition I-QLRN is first order for low p and continuous for large p, implying the existence of a TCP [Fig. 4(b)] on the phase boundary. A possible boundary between nematic and QLRN is shown by dots but has not been numerically tracked down here. For large $D/J = 10$, I-QLRN transition is continuous over $0.05 \le p \le 0.2$. The transition temperature decreases linearly (slope $= -1.6$) with p. We, however, do not rule out the possibility of first order I-N and I-QLRN

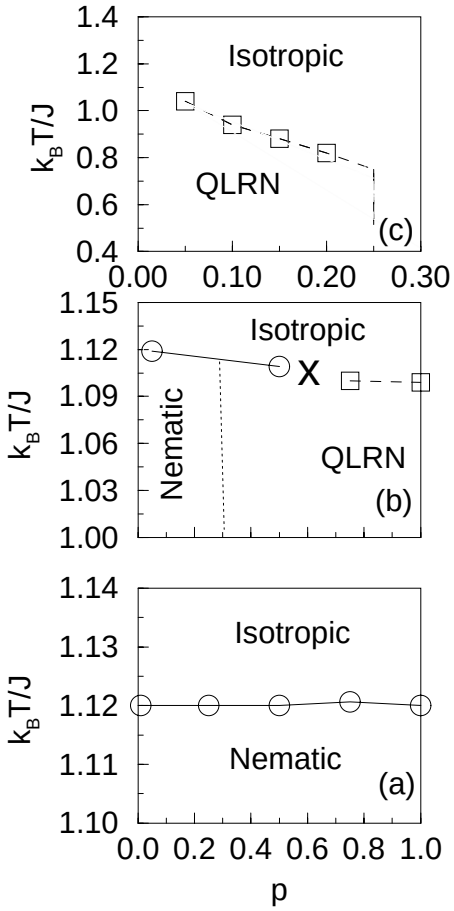

FIG. 4. Phase diagram in $k_BT/J - p$ plane for (a) $D/J = 0.1$, (b) $D/J = 1.0$, and (c) $D/J = 10$. The circles joined by solid line correspond to first order transition and squares joined by dashed line show continuous transition [in (c), however, we show the best fitted line]. The dotted line in (b) is a possible boundary between nematic and QLRN phases. The cross is an approximate location of the TCP. The vertical dot-dashed line in (c) indicates the boundary where the low temperature phases are isotropic. Note the difference in the horizontal scale in (c).

transitions for very low p ($p < 0.05$), not scanned in our work. For $p \geq 0.25$, the long-range order is completely destroyed even at low K_BT/J. The general topology of the phase diagram in $k_BT/J - p - D/J$ space would be as follows. The region in $(k_BT/J, p)$ over which the low temperature nematic phase occurs shrinks with increasing D/J, giving way to low temperature QLRN order. The tricritical line that occurs on the I-QLRN phase boundary would shift to low $(k_BT/J, p)$ with increasing D/J. It could be interesting to compare our phase diagram to the magnetic cases. In spite of the celebrated Imri and Ma argument [17], which says that below four dimensions the ordered state is unstable to an arbitrarily weak random field that couples linearly with order parameter of continuous symmetry, there is mounting evidence of quasi-long-range order in magnetic models, namely, the XY model [18] and the Heisenberg model [19] in random field, presumably due to nonperturbative effects [18] not taken care of in the Imri and Ma argument. Low temperature quasi-long-range order and a TCP on the isotropic $\rightarrow$ quasi-long-range ordered phase transition line, analogous to what we find here, have been reported recently [19] on a discretized version of the Heisenberg model in an infinitely strong random field. However, unlike Ref. [19], our work is a clear evidence of the violation of the Imri and Ma argument, exhibiting quasi-long range, where the full rotational symmetry of the Hamiltonian is retained. We find enhanced stability of the quasi-long-range order compared to Ref. [19]. Especially for large D/J we do not observe any true long-range order for p as low as 0.05. Another interesting difference is that in contrast to Ref. [19], we get first order transition for low p, which is probably due to symmetry difference of the underlying pure models. Finally, a few words are worth regarding a possible mechanism behind QLRN order. We find that the correlation length ξ, defined via $g(r) = e^{-r/\xi}$, in the isotropic phase close to the transition [Fig. 3(a)] exceeds the mean spacing of the random sites. This observation, along with the presence of the quasi-long-range order itself [18,20], would mean that the system is largely vortex-free. Hence, the Kosterlitz-Thouless mechanism which hinges on topological defects seems unlikely. Following the suggestion in Ref. [19], the quasi-long-range order found here could be a manifestation of replica symmetry breaking as in the context of the flux-lattice Hamiltonian in the presence of disorder [20] and the Ising model in a random field [21].

It is worthwhile to discuss the implications of our results to experimental situations. Our results strongly suggest that the experimental phase coexistence observed on 8CB in silica aerogel [4] is essentially the one between isotropic and QLRN phases. The absence of phase coexistence for 4O.8 in silica aerogel [5] is not inconsistent with our strong field results. Although our observations do not rule out the possibility of pure kinetic transition from high temperature isotropic phase to low temperature glassy phase for large $(p, D/J)$, the critical behavior reported here must be interesting to observe in experiments. We hope to report in a future publication on the interesting transition between nematic and QLRN order. Most importantly, our work calls for a thorough theoretical understanding of the phase diagram, more specifically the presence of QLRN order. We believe that similar scaling analysis would be pertinent to other classes of problems related to porous medium, for instance, in the context of nematic to smectic transition and super-fluid transition of helium in silica aerogel.

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