Nematic ordering in a Vycor-like restrictive geometry: A two-dimensional model

Zhengping Zhang and Amitabha Chakrabarti
Department of Physics, Kansas State University, Manhattan, Kansas 66506
(Received 21 April 1995)

We report results from Monte Carlo simulations of the orientational ordering of the two-dimensional Lebwohl-Lasher model for nematic liquid crystals confined inside a model porous medium of Vycor-like tortuous geometry. We find that the magnitude of the order parameter and the susceptibility are strongly suppressed in the presence of the porous medium. The system breaks into many nematic domains with a random distribution of nematic directors. This feature is similar to the "nematic-glass" behavior that is seen in experiments. We find that the relaxation of the order parameter autocorrelation function satisfies an activated dynamical scaling, which is in agreement with recent simulations of random-field models and some recent experiments.

PACS number(s): 64.70.Md, 05.40.+j, 64.60.Cn

I. INTRODUCTION

The usual course of bulk phase separation in binary liquid mixtures [1] and phase transition in liquid crystals [2] is completely altered when these systems are confined in a porous medium of random geometry (such as a Vycor glass or a silica gel). For example, during the phase separation of binary fluid imbedded in Vycor glasses [3,4] the two phases do not separate completely even deep inside the coexistence region; instead, they form many long-lived microdomains, rich in one phase or the other. Two different theoretical interpretations of these phenomena have been introduced. In one interpretation, the metastability and the slow dynamics are explained in terms of the conserved dynamics of a random-field Ising model [5], which is obtained from a coarse-grained description of the phase separation process in the presence of the random convolutions of the pore surface [5]. Criticism has been expressed, however, that such a mapping onto the random-field Ising model is not applicable for low-porosity media such as Vycor glasses [6,7]. The second interpretation is to relate the metastability to the geometric confinement of the binary mixture inside a pore [6]. Such a single-pore model without any randomness has been used as a model system [6–9] to understand various effects observed in experiments of binary liquid mixtures in Vycor glasses [3,4].

The ordering of nematic liquid crystals in a restricted geometry is another rich area of study. Surface effects on the ordering of this system are reasonably well understood for well-characterized confined geometries [10]. Studies have clearly shown the existence of ordered surface layers above the phase transition temperature [11] and a continuous development of nematic ordering [12,13] instead of the weakly first-order nematic-isotropic transition. The complexity of the situation increases considerably when the confining medium has a disordered geometric structure. More recent work [14–19] has been directed to addressing the effect of such randomly constraining media (such as porous glasses like Vycor or silica gels) on both the statics and dynamics of the nematic-isotropic phase transition. In recent experiments the dynamics of the nematic ordering process in various gels has been explored in detail by using quasielastic light scattering measurements [14,18]. The results indicate that the random preferential orientation of the liquid crystals along the pore surface (whose normal changes direction randomly) profoundly influences the dynamics of an isotropic to nematic phase transition in such a system, and fluctuations of the orientational order parameter relax at a much slower rate than in bulk liquid crystals. These experimental findings have stimulated theoretical work [20,21], and a random-field model for nematic liquid crystals has been proposed to qualitatively explain the glasslike behavior seen in experiments. In experimental situations, the surface interaction between the molecules and the porous medium leads to a preferential orientation of the molecules with respect to the random local normal of the porous medium. The random fields in the theoretical model appear then after a coarse-graining of the system on the length scale of the pore size. We should point out that although the random-field term in the Hamiltonian of the nematic liquid crystals looks similar to a random anisotropy term in a magnetic system [22], for the headless symmetry of nematic liquid crystals, this term actually represents the lowest-order random-field term because of its linear coupling to the order parameter [20]. The strength of the random field in the random-field model should directly depend on the anchoring strength of the molecules to the surface of the gel and indirectly on the porosity.

Wu *et al.* [14] have carried out a quasielastic light scattering study of the isotropic-nematic phase transition of 4-(*n*-octyl)-4-cyanobiphenyl (8CB) liquid crystals kept inside sintered silica gels of porosity 30–35 %. They found that the intensity autocorrelation function obeys an activated dynamical scaling as seen in simulations of the random-field Ising model (RFIM) [23]. The experimentally obtained functional form for the scaled autocorrelation function, however, is quite different from that obtained in simulations of the RFIM [23]. This is not surprising since the order parameter of the liquid crystals

has a different symmetry. Bellini, Clark, and Schaefer [18] have carried out a similar study of the 8CB-aerogel system for three different porosities (63%, 79%, and 94% pore volume fraction). However, the slow nematic relaxation observed in this experiment has been fitted to a stretched-exponential form with a temperature dependent exponent. Recent simulations [24] of a microscopic lattice model for nematic liquid crystals in the presence of random fields suggest that the order parameter autocorrelation function obeys a standard dynamical scaling for weak random fields and an activated dynamical scaling for strong random fields. Although these results are consistent with recent experiments, the details of the scaling functions do not agree with results of recent experiments, suggesting that the random-field model for the nematics may not be capable of quantitatively explaining experiment results. It has been argued that this difference arises from important local correlations in the orientation of the liquid crystals along the pore surface [24].

In contrast to the studies carried out with silica gels as the confining media, experimental results of the ordering of nematic liquid crystals in a Vycor glass show that the random-field model is clearly inapplicable [15]. It has been argued that in Vycor glasses and the pore structure minimizes the pore-pore interactions. Hence interactions in a single independent pore plus a suitable distribution of pores to mimic the confining medium should be an appropriate model. Note that this model is quite similar to the single-pore model introduced by Liu *et al.* [6] for binary liquid mixtures confined in Vycor glasses. This single-pore model for the nematic liquid crystals seems to explain the static measurements reasonably well. However, no fluctuation effects have been considered in this Landau–de Gennes type of model [15]. Moreover, the dynamical relaxation process measured in time-resolved optical Kerr effect measurements cannot be explained satisfactorily by such a model [19].

It is quite clear that more theoretical work is necessary at this stage, when experiments alone cannot clarify the physics behind such a complex problem. As we have mentioned before, most of the theoretical interpretation of the slow dynamics seen in experiments has been *qualitatively* explained by the random-field model. However, there is mounting evidence from simulations and experiments that the random-field model is incapable of explaining experimental results *quantitatively*. Computer simulations in a realistic model system will be extremely important for an insight into the ordering problem of nematic liquid crystals kept inside a porous medium. Instead of considering any simplified model (such as the random-field model), simulations should address the ordering of liquid crystals in a model porous medium of interconnected and tortuous structure resembling Vycor glasses or silica gels. Such simulations have already been used for studying phase separation in binary liquid mixtures [25,26] and phase transition in He^3-He^4 mixtures [27]. As a first step in understanding the effects of a porous medium on the ordering of nematic liquid crystals, we have carried out a simulation of a two-dimensional model of nematic liquid crystals kept inside a Vycor-like restrictive geometry. We have studied both the static properties as a function of temperature and the strength of surface interaction and the dynamic relaxation process of the order parameter at low temperatures.

In Sec. II we present the model studied in this paper, which consists of the two-dimensional (2D) Lebwohl-Lasher (LL) model [28] in the presence of a Vycor-like porous medium. We also describe the computational techniques used and the quantities measured in the simulations. The equivalence between the 2D LL model and the 2D XY model is also discussed. The results are presented in Sec. III, and the paper concludes with a discussion in Sec. IV of the results in the context of previous theoretical work and experiments.

II. MODEL AND COMPUTATIONAL METHODS

We study a two-dimensional lattice model for liquid crystals in the presence of a model porous medium in our simulations. The lattice model is a two-dimensional analog of the three-dimensional Lebwohl-Lasher model (LL model) [28], the lattice version of the Maier-Saupe model [29] for liquid crystals. In the model, planar rotors are located at lattice sites and interact via the potential

$$U_{ij} = -\epsilon \cos 2(\phi_i - \phi_j) , \tag{1}$$

where ϵ is a positive coupling constant and $\phi_{i,j}$ are orientational angles of the rotors i and j with respect to an arbitrary fixed axis. The uniaxial property of the rotors is accounted for in the factor of 2 in the form of the potential. Thus the angle ϕ_i varies in a range of $0 \le \phi_i < \pi$. The interaction is restricted to the nearest neighbors. In our simulations, the planar rotors ar positioned on a square lattice with periodic boundary conditions.

The 2D LL model described in Eq. (1) is actually identical to the 2D XY model. It can be easily understood from the potential energy point of view. In the XY model, spins interact with their nearest neighbors via a potential $U_{ij} = -\epsilon \cos(\theta_i - \theta_j)$, where θ_i is a variable in a range of $0 \le \theta_i < 2\pi$, which is the mass as that for $2\phi_i$ in the potential (1). As in the 2D XY model, topological defects called "vortices" are also present in the 2D LL model. However, as we discuss later in this section, there is a difference in the topological defect structure between these two models. Furthermore, there is a uniaxial symmetry in the 2D LL model that is absent in the 2D XY model. A similar difference in symmetry between the 3D LL model and the 3D Heisenberg model results in the very different nature of the phase transitions observed in the two models [2,30,31]. But what would be the consequence of the difference in symmetry in the 2D case? The difference usually affects the way the order parameter is defined. The spontaneous magnetization is normally used as the order parameter for a spin system. The magnetization goes to zero in the thermodynamic limit for the 2D XY model, predicted by the Kosterlitz-Thouless (KT) theory [32], although this quantity can still be used to study the relaxation time by using Monte Carlo simulations [33]. For the 2D LL model, the global order parameter Q was defined [34] to be the maximum of $T^{(j)} = 1/N \sum_i^N \cos 2(\phi_i - \alpha^{(j)})$, where $\alpha^{(j)}$ is the orientation

of the direction that renders $T^{(j)}$ maximum, and the index j refers to the fact that the quantities need to be determined for each configuration j. This order parameter is an analog of that of the 3D LL model [31]. The condition for a maximum, i.e,. $dT^{(j)}/d\alpha^{(j)}=0$, results in $\tan 2\alpha^{(j)}=s/c$, where $c=1/N\sum_i^N \sin 2\phi_i$ and $s=1/N\sum_i^N \cos 2\phi_i$. Thus $Q=c\cos 2\alpha^{(j)}+s\sin 2\alpha^{(j)}=\cos(2\alpha^{(j)})(c^2+s^2)/c$. Since $\cos 2\alpha^{(j)}=c/\sqrt{c^2+s^2}$, one finally has

$$Q=\sqrt{c^2+s^2}\ . \tag{2}$$

The above expression is actually the magnitude of the magnetization per spin for the 2D XY model. Therefore, the uniaxial property of the 2D LL model does not result in any special consequence. That is, there is no phase transition in the thermodynamic sense in the 2D LL model, in contrast to the 3D LL model, which leads to a weak first-order phase transition.

The model porous medium used in our simulations is constructed by using a method suggested by Chakrabarti for modeling a Vycor-like porous medium [25]. Vycor is made commercially by quenching a borosilicate glass into the spinodal reign and then etching out the soft phase with acid so that all the pores are interconnected. Chakrabrati proposed following the same procedure is simulating the quenching process of critical mixtures of two components on a lattice by using a cell-dynamics scheme [35]. An interconnected morphology of the pores can be created by stopping the phase separation process after some reduced time τ_0 and removing one of the two phases. The porosity and the pore radius of the model porous medium can be varied by choosing a different τ_0. There is, however, a limit on the lowest porosity because of the site percolation threshold for the lattice. A similar construction in three dimensions has been made recently [36] by carrying out spinodal decomposition in a long-range Ising model. In our simulations, we started form a 256^2 square lattice consisting of a 50%-50% mixture of two components. We stopped the phase separation at a reduced time of $\tau_0=10^4$ and "etched out" one of the two phases. The porosity, which is defined as the fraction of the vacancies on the lattice, of the model porous medium is about 61%, with an averaged pore radius of about 15 lattice spacings. It should be pointed out that the porosity in our two-dimensional model is much larger than that in real Vycor glass (about 28%). In this respect, the model porous medium more resembles silica gels [18] than it does the Vycor glass used by Iannacchione *et al.* [15].

This kind of model porous medium has originally been created for liquid mixtures [25]. However, for liquid crystals, the direction of the surface anchoring field on the surface of the porous media needs to be determined. To take into account local correlations in the direction, due to the presence of the surface, we propose one possible way to simulate the correlations as follows. The surface of the porous medium is made of the lattice sites of the wall that have at least one nearest-neighbor vacancy. A fictitious rotor system, σ_i, is set on the surface, where σ_i is a unit vector at the site i of the surface and is associated with the direction of the surface field. The rotor system then relaxes at zero temperature through the fictitious interaction that is of the form $-(\hat{\mathbf{r}}_{ij}\cdot\boldsymbol{\sigma}_i)(\hat{\mathbf{r}}_{ij}\cdot\boldsymbol{\sigma}_j)(\boldsymbol{\sigma}_i\cdot\boldsymbol{\sigma}_j)$, where i and j are either the nearest-neighbor sites or the next-nearest-neighbor sites, and $\hat{\mathbf{r}}_{ij}$ is a unit vector pointing from site j to site i. This method of relaxation aligns the fictitious fields σ_i parallel to the local convoluted surface. The direction of the surface anchoring field is given by the final relaxed configuration of σ_i.

We fill up the vacancies of the model porous medium with planar rotors. The Hamiltonian describing our model system is, then, of the form

$$\mathcal{H}=-\frac{\epsilon}{2}\sum_{\langle i,j\rangle}\cos 2(\phi_i-\phi_j)-h^2\sum_{\langle i,s\rangle}\cos^2(\phi_i-\theta_s)\ , \tag{3}$$

where h is the strength of the surface anchoring field, $\langle i,j\rangle$ denote the sites i and j as nearest neighbors, s specifies a site on the surface, and θ_s refers to the orientational angle of σ_s at site s.

Our simulations are performed by using a Monte Carlo procedure, which is based on the traditional Metropolis–Monte Carlo method [37] and modified in order to take advantage of the vectorizing facilities of a Cray 90 computer in the Pittsburgh Supercomputing Center. The vacancies in the model porous medium are grouped into two sublattices, which are the nearest-neighbor sites of each other. The rotors on each sublattice are updated simultaneously. The updatings involve attempts to randomly rotate the direction of the individual rotors in a range from 0 to π.

We calculate the specific heat $c_v(T)$ and the susceptibility $\chi(T)$ by using fluctuations of energy and the order parameter

$$c_v(T)=\frac{1}{Nk_BT^2}(\langle\mathcal{H}^2\rangle-\langle\mathcal{H}\rangle^2)\ , \tag{4}$$

$$\chi(t)=\frac{1}{Nk_BT}(\langle Q^2\rangle-\langle Q\rangle^2)\ , \tag{5}$$

where N is the number of rotors in the system, T is the absolute temperature, k_B is Boltzmann's constant, and the notation $\langle\ \rangle$ indicates thermal equilibrium. We also calculate the order parameter autocorrelation function in equilibrium:

$$c(\tau)=\langle\delta Q(t)\delta Q(t+\tau)\rangle/\langle[\delta Q(t)]^2\rangle\ , \tag{6}$$

where $\delta Q(t)=Q(t)-\langle Q\rangle$.

To find a vortex within any region, one merely travels around a closed loop and calculates the change in direction of the rotors along the path. If there is a single vortex within the loop, then the net change in rotor direction will be π (2π in the XY model) times an integer. The integer is known as the *vorticity* or *vortex strength*. To calculate the change in direction from one rotor to another, one always counts the smaller of the two angles between the two rotors and determines the sign of the change from the anticlockwise or clockwise change in the angle. On a square lattice, the core of a vortex consists of four rotors at the corners of a plaquette. The vorticity is, therefore, almost always unity for a vortex in the plaquette [38]. Furthermore, the vorticity of a single vortex

can be positive or negative. The vorticity within a region is the sum of the vortex strengths of those vortices contained in the region. In the presence of the model porous medium, we follow the same procedure to calculate the vorticity except for the plaquettes near the wall, where at least one corner of the plaquette is occupied by a boundary site. In such a case, we do not consider this plaquette for computing the vorticity. Since the sites on the edge have fewer near neighbors than do the interior sites, effectively this system is open to the outside. A singularity can enter the edge, and so the total vortex change is not conserved in this case. We should mention here that we focus on the thermodynamics of the system in this work although it would be very interesting to study the vortex dynamics in such a system [39].

III. RESULTS

Before we discuss the effects of the model porous medium on various properties of the nematic-liquid-crystal-like molecules, let us first start with a bulk two-dimensional system. The system is initialized with a random orientational configuration and relaxed at a high temperature, $T=1.6$, in units of ϵ. Then the system is cooled down gradually and equilibrated at each intermediate temperature. At each temperature, the system starts with the final configuration of the previous temperatures and equilibrates for 10^4 Monte Carlo steps per rotor (MCS). Next, various quantities are calculated and averaged every 20 MCS for a total of 2×10^5 MCS. Several square lattice systems of up to 200^2 rotors are studied to compute both thermodynamic quantities and topological defects. The number of rotors in the largest system in our simulations is almost the same as that in the model porous medium of 256^2 system with about 61% porosity.

We now summarize results for the bulk system. The temperature dependence of the order parameter, $Q(T)$, shows that the order parameter is small at higher temperatures and tends to be unity at low temperatures. This indicates that at low temperature the range of ordering described by Q is still large in comparison with the system size of 200^2. We find a strong peak in the susceptibility $\chi(T)$ and the KT transition temperature, $T_{XY}\approx0.89$ [38,40–43]. Near the KT transition in a finite system of linear size L, the correlation length $\xi\approx L$, and hence the size dependence of the peak of the susceptibility should be given by $\chi_{\max}\sim L^{2-\eta}$. Our results for η are consistent with previous, more accurate simulations of the 2D XY model [42,43]. In contrast, no obvious size dependence is found for either internal energy or its fluctuations, the specific heat c_v. This is also in agreement with previous simulations of the 2D XY model. There is a peak in the specific heat at temperature around $T=1.05$. The result is consistent with previous simulation results [38,42]. The observation that the peak temperature is far above T_{XY} is certainly not due to finite size effects. It has been explained as follows. According to the KT scenario, the KT transition occurs when a single vortex-antivortex pair unbinds at T_{XY}, whereas the peak in the specific heat is associated with the unbinding of a large number of pairs, which should occur at $T>T_{XY}$ [38,42] since the defects carry most of the energy fluctuations.

We have computed the vortex-pair density v as a function of temperature. The data obtained from systems of sizes 30^2 and 60^2 with periodic boundary conditions do not show any appreciable finite size effects. The numbers of positive and negative vortices are exactly the same at all temperatures and instances, as expected. At low temperatures, according to the KT theory, $v\sim e^{-2\mu/T}$, where 2μ is the energy necessary to crate a vortex pair. This is the so-called dilute gas approximation, where one assumes that vortices are created by thermal fluctuations and that there is no interaction between vortices because the separation between vortex pairs is much larger than that between a vortex-antivortex pair. When we plot the logarithm of vortex-pair density $\ln v$ vs the inverse of temperature T^{-1}, our data do show the above relation in the low-temperature region. A linear behavior suggests that the dilute-gas approximation is valid at low temperatures. However, the energy, as given by the slope of the above semilog plot, is 7.31 ± 0.07, which is inconsistent with the KT prediction of 10.2 [32]. We point out that this result is consistent with more accurate simulations of the 2D XY model [42], where $2\mu\approx7.55$ was found for $T<T_{XY}$. We also observe that the $\ln v$ vs T^{-1} curve levels off near the temperature at which the specific heat is maximum ($T^{-1}\approx0.95$) as it becomes easier to generate more vortices when many vortices are already present to disorder the rotors, as pointed out in previous simulations [38,42].

We now present the results for the two-dimensional liquid crystals confined in the model porous medium. Figure 1 shows the model porous medium used in the simulations. Although this has a Vycor-like structure, the porosity is much higher than commercial Vycor glasses.

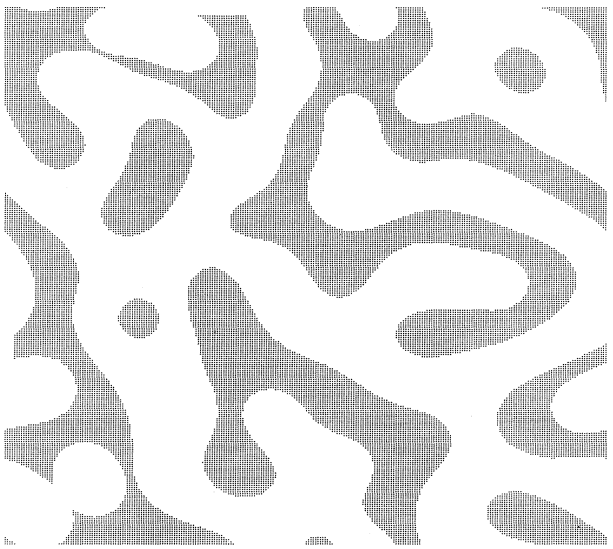

FIG. 1. The model porous medium used in the simulations. The white region corresponds to the "pores" and the black region corresponds to the "glass."

The average pore diameter of this structure is about 30 lattice spacings. Moreover, the ratio of the average pore diameter d to the average pore length l is quite low in comparison with real Vycor glasses. In our model porous medium, $d/l \leq 2$, which is obviously lower than $d/l \geq 4$ in a real Vycor glass used in the experiments [15]. As we have mentioned earlier, the model porous medium resemble silica gels more than it resembles the real Vycor glasses.

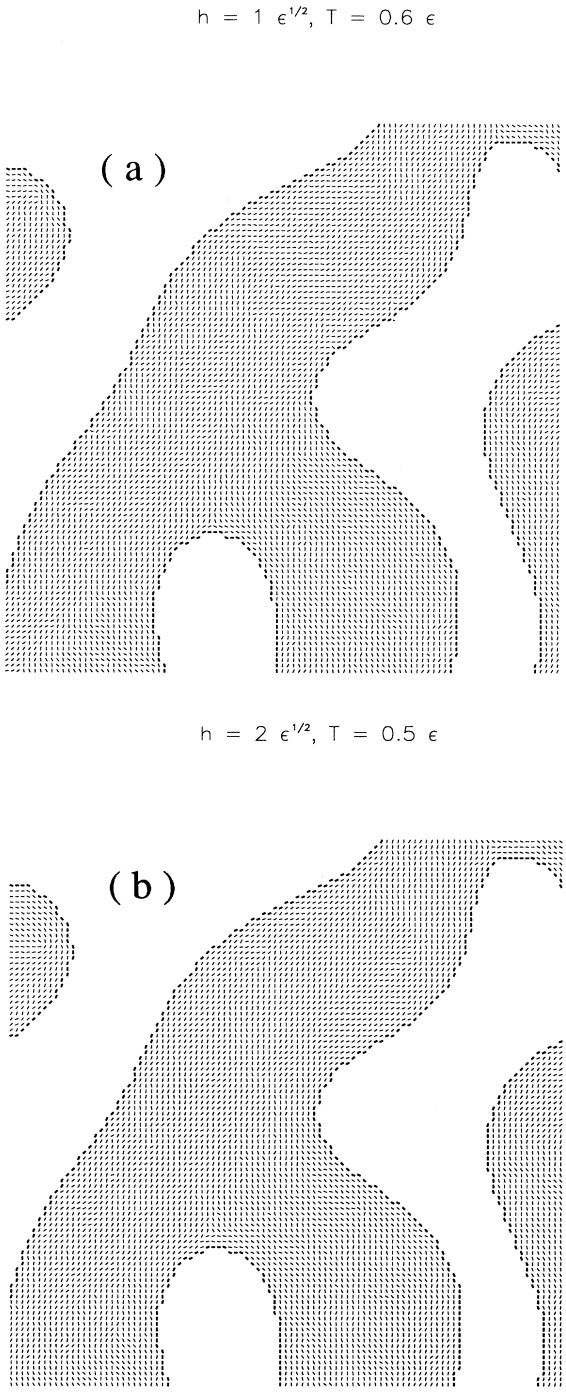

FIG. 2. (a) The snapshot at $T=0.6\epsilon$ for $h^2=1.0\epsilon$; (b) the snapshot at $T=0.5\epsilon$ for $h^2=4.0\epsilon$. The orientations of the rotors and the directions of the surface field are indicated by thin and thick sticks, respectively.

In Figs. 2(a) and 2(b) we show two snapshots at low temperatures for $h^2=1.0\epsilon$ and $h^2=4.0\epsilon$. The snapshots consist of a 100×100 section of the total system. One can observe "domains" with various nematic directions in the system. In the vicinity of the boundary, the directions are determined by the surface field. However, in the middle of the pore, the directions are distributed randomly because of the weak influence of the surface field. As we will discuss shortly, these randomly oriented nematic domains control the statics and the dynamics of the system at low temperatures.

Figure 3(a) shows the temperature dependence of Q for various strengths of surface anchoring fields. The order parameter for a bulk system (of size 200^2, which has approximately the same number of sites as a 256^2 system with 61% porosity) is also shown in the picture for comparison. It can be seen that the order of the system is dramatically suppressed at low temperatures in the presence of the porous medium, which is consistent with experimental results [15] and previous simulations [21]. The suppression is only weakly dependent on the strength of the surface anchoring and is saturated for strong sur-

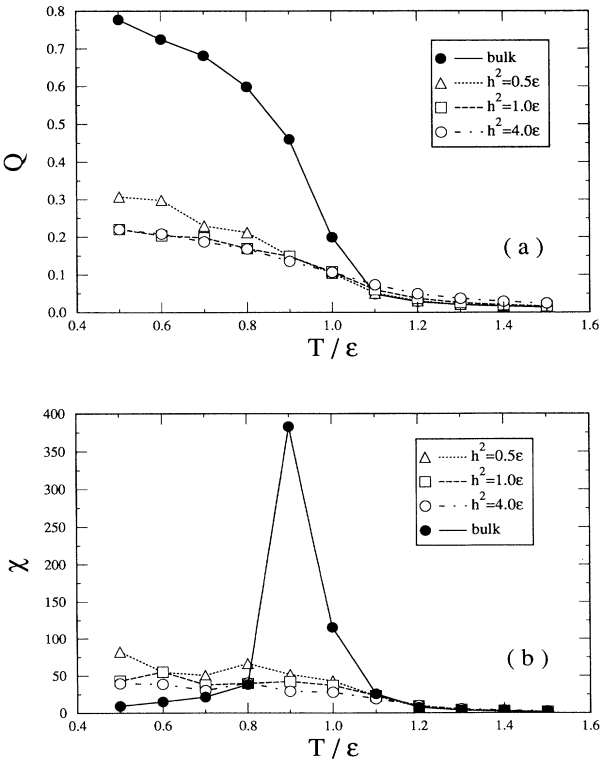

FIG. 3. (a) The order parameter Q as a function of temperature T for various fields; (b) the corresponding susceptibility χ as a function of T.

face anchoring. It indicates that the effects of the pores on the orientational order of the liquid crystals are dominated by the tortuous and confined geometry nature of the model porous medium. Essentially the whose system gets broken into many nematic domains with random nematic directions. A strong anchoring field enables the suppression of the total order parameter to be more efficient at low temperatures. The anchoring field, however, plays an opposite role at high temperatures. It maintains certain local orientational order near the pore surfaces, as indicated by the slight increase of the order parameter at high temperatures in the case of $h^2=4.0\epsilon$.

The susceptibility as a function of T, corresponding to the previous cases mentioned in Fig. 3(a), is shown in Fig. 3(b). In the presence of the porous medium, the strong peak in χ observed at the phase transition temperature in the bulk system disappears and is replaced by very flat (no temperature dependence) curves at low temperatures. The increase in χ at low temperatures in contrast to the bulk case indicates that the fluctuations in the order parameter also increase in the presence of the porous medium at low temperatures. The fluctuations are somewhat smaller though for a stronger anchoring field, as shown in Fig. 3(b).

Because of the large average pore size and the short range of the surface anchoring field in our model porous medium, the energetics of the system is not affected strongly. There surface anchoring field down shifts the internal energy of the system but has little effect on the qualitative features of the temperature dependence of the internal energy. This is seen clearly in Fig. 4 from the temperature dependence of the specific heat $c_v(T)$ in the presence of the porous medium. There is no big change in $c_v(T)$ due to the presence of the porous medium. This is probably because the peak in c_v is not related to a phase transition in the simple model. However the double role that the surface field plays, as already discussed regarding Fig. 3(a), shows up as a slight difference in the specific heat, both above and below the peak temperature, for various strengths of the surface fields. A strong field increases the value of the specific heat above the peak temperature but decreases its value at low temperatures.

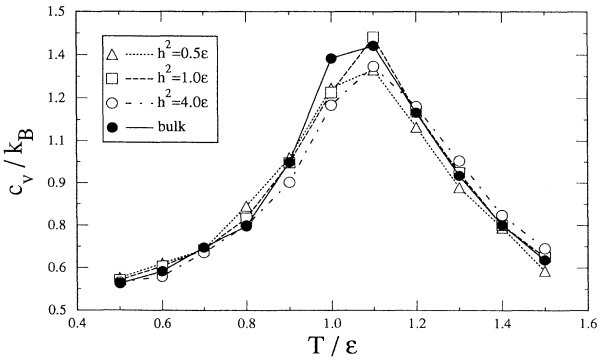

FIG. 4. The specific heat c_v as a function of T in the presence of the porous medium.

The peak in the specific heat is associated with unbinding a large number of vortices. Therefore, the observation we made in Fig. 4 may be connected to the fact that few extra vortices are created in the presence of the porous medium. To check this conjecture, we plot in Fig. 5(a) a comparison of the vortex-pair density v, both above and below the KT transition temperature T_{XY}, in the presence and in the absence of the porous medium. It seems that the density of the vortices is not very sensitive to the presence of the porous medium [44]. However, the qualitative picture concerning the vortices is changed. The number of vortices and antivortices is not always the same anymore, in contrast to a bulk system, because of the presence of the pore boundary. A vortex or an antivortex can easily disappear at the boundary and leave the other one of the pair alone in the pore without any serious consequence, as shown in Fig. 5(b). However, one can observe a small effect of the surface field on the vortex density in Fig. 5(a). The vortex density corresponding to the presence of a surface field is slightly lower than in a bulk system. Also, when we compare our results for $h^2=1$ and $h^2=4$, we find the number of vortices to be smaller for the stronger surface field. It may be related to

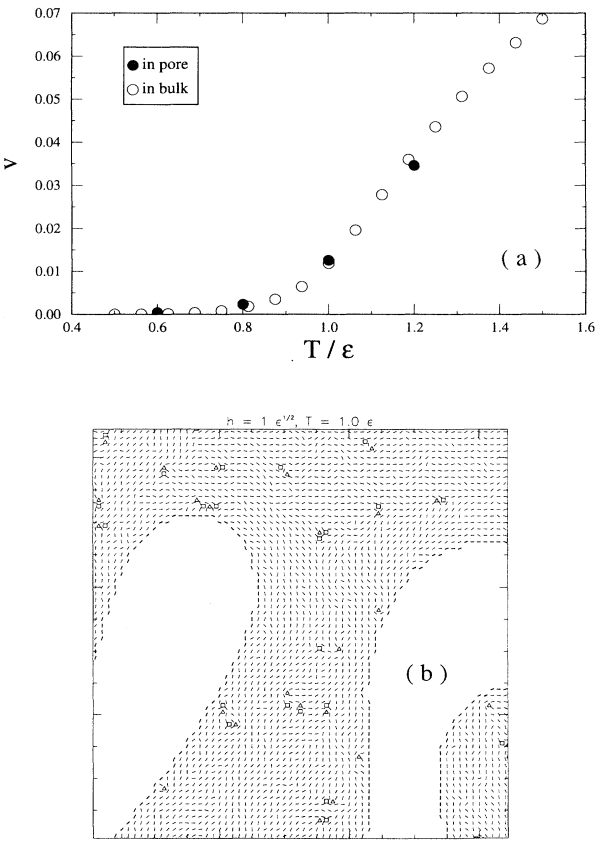

FIG. 5. (a) The comparison of the vortex-pair density v in the presence and the absence of the porous medium; (b) a section of the system at $h^2=1.0\epsilon$ and $T=1.0\epsilon$ in which the vortex and the antivortex are shown by □ and △, respectively.

the fact that the rotors near the surface align smoothly along the surface, under the influence of the anchoring field, so that the possibility of having a vortex (antivortex) near the surface is reduced. To see if the picture is correct, we also calculated the vortex density at the same temperature for $h^2=1\epsilon$ but with a *random orientation* of the new surface fields. In this case, the vortex density is found to be higher than in the previous calculations.

We now present our data for the order parameter relaxation. We compare our results for the order parameter autocorrelation function in the porous medium with two types of relaxation processes. One is known as the *stretched exponential* (SE) [18],

$$c(t)=\exp[-(t/\tau)^{\alpha}] , \quad 0<\alpha\leq 1 , \tag{7}$$

where τ is a relaxation time. The experimental data for many relaxation phenomena in complex random systems seem to obey the SE behavior [16]. The other functional form is suggested by theoretical and simulational studies of model systems in a random field [23,24],

$$c(t)=\exp[-(\ln t/\ln\tau)^{\alpha}] . \tag{8}$$

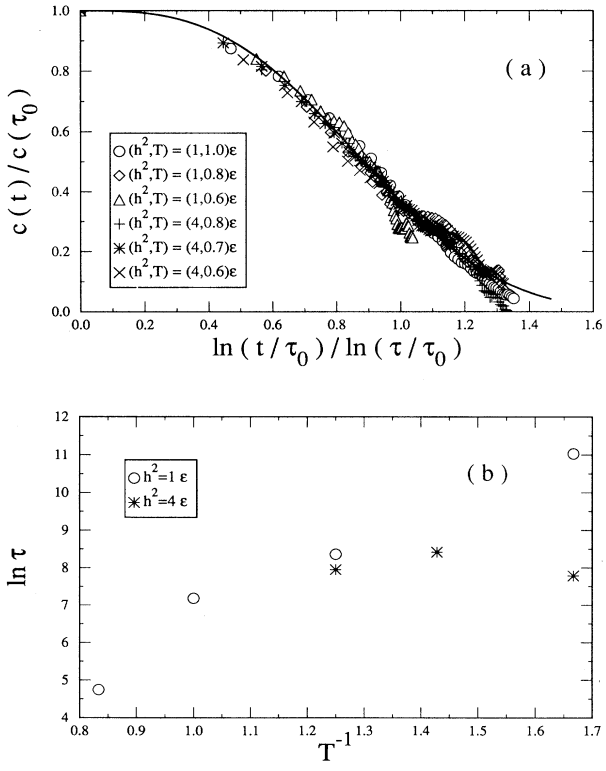

FIG. 6. (a) scaling plot of the order parameter autocorrelation function $c(x)$, demonstrating that the autocorrelation function at different temperatures with surface fields of $h^2=1.0$ and 4.0ϵ satisfies approximately activated dynamical scaling with $x=\ln[t/\tau_0]/\ln[\tau/\tau_0]$, where $\tau_0=20$ MCS. The best fit to the data yields $c(x)\approx\exp(-x^3)$; (b) the corresponding plot of $\ln\tau$ vs $1/T$.

We have computed the autocorrelation function for various T and h. The two types of relaxation functions [Eqs. (7) and (8), respectively] can be fitted to our data almost equally well for each individual T and h with different α and τ. The values of τ obtained by fitting our data to the different forms are always very close. However, the values of α obtained by using the form (7) vary over a range of 0.5–0.8 for different T and h (nonzero field) and do not show universal scaling behavior.

In contrast, the α obtained by using Eq. (8) varies around 3 for all the cases in the range of $\alpha=3\pm0.5$. Therefore, our data seem to scale approximately as $c(t)\sim\exp(-x^3)$, where $x=\ln t/\ln\tau$, as shown in Fig. 6(a) for the case of $h^2=1.0\epsilon$. Since for all temperatures and fields the activated scaling works better, we believe that it is better representation of our data. The corresponding temperature dependence of τ is shown in Fig. 6(b) by plotting $\ln\tau$ vs $1/T$ for $h^2=1.0$ and 4.0. It is clearly shown that τ does not diverge at low temperatures. This strongly indicates that the "glasslike" behavior seen in the simulations does not correspond to a true thermodynamic low-temperature phase.

IV. DISCUSSION

We have carried out a numerical study of a two-dimensional version of the Lebwohl-Lasher model of nematic liquid crystals in the presence of a model porous medium of Vycor-like tortuous geometry. Although it is difficult to relate our results to experimental observations directly, these simulations results are useful for an insight into a complex problem. We find that the magnitude of the order parameter and the susceptibility are strongly suppressed. The system breaks up into many nematic domains with a random distribution of nematic directors. This feature is similar to the "nematic-glass" behavior seen in experiments. We find that the relaxation of the order parameter autocorrelation function satisfies an activated dynamical scaling in agreement with simulations of a random-field model and some recent experiments [4,45]. However, replacement of the model system in terms of a random-field model has its limitations because of the correlations among the surface fields.

Let us now discuss the limitations of our study. We have associated the 2D LL model to the nematic liquid crystals because of the similarity in orientation and uniaxiality between the rotors in the model and the liquid crystal molecules. In contrast to the 3D LL model, the uniaxiality of the rotors in two dimensions does not lead to a first-order phase transition, corresponding to the nematic-isotropic phase transition observed in nematic liquid crystals. The 2D LL model is identical to the 2D XY model in which there is no phase transition in the thermodynamic sense. Instead, there is a Kosterlitz-Thouless type of phase transition. The correlation length of ordering in finite bulk systems, up to 200^2 rotors, is still large enough at low temperatures in comparison with system size to show thermal-phase-transition-like behaviors around T_{XY}. Thus, our results concerning the order parameter and its fluctuations, i.e., the susceptibility, should be valuable for understanding the behavior of

liquid crystals in porous media. However, the specific heat in the model appears at a temperature far above T_{XY}, so it is not associated with the nematiclike ordering. Our results for the specific heat are not very relevant for the liquid crystal systems but may be useful for understanding the behavior of XY-model-like systems, such as superfluids, confined in porous media.

Another limitation of our model, due to the low dimensionality, is the following. Although the model porous medium created in this paper looks like a Vycor glass, the ratio of the average pore diameter d to the average pore length l is quite low in comparison with real Vycor glasses. In our model porous medium, $d/l \leq 2$, which is lower than $d/l \geq 4$ in a real Vycor glass used in the experiments [15]. Thus a detailed comparison with these experiments is not possible in this paper. The order parameter autocorrelation function computed in the simulations shares some common features with recent experiments carried out in silica gels and with simulations of random-field models. However, the combination of the high porosity, the low dimensionality, and the short-range surface anchoring field may lead to the strong deviation of the order parameter autocorrelation function from the experimental results [14] and the previous simulations in three dimensions [24].

ACKNOWLEDGMENTS

We wish to thank Professor D. Finotello, Professor F. Aliev, and Dr. M. Gingras for sharing unpublished results with us. We also thank D. Dimitrov, Professor C. Dasgupta, and Professor G. Wysin for many useful discussions. This work has been supported by a grant from the National Science Foundation (DMR-9312596). The computer calculations were carried out under an NSF grant of computer time from the Pittsburgh Supercomputing Center.

[1] J. D. Gunton, M. San Miguel, and P. S. Sahni, in *Phase Transitions and Critical Phenomena,* edited by C. Domb, and J. L. Lebowitz (Academic, New York, 1983), Vol. 8.
[2] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).
[3] See, for example, W. I. Goldburg, in *Dynamics of Ordering Processes in Condensed Matter,* edited by S. Komura and H. Furukawa (Plenum, New York, 1988).
[4] W. I. Goldburg, F. Aliev, and X. L. Wu, Physica A **213**, 61 (1995), and references therein.
[5] F. Brochard and P. G. de Gennes, J. Phys. (Paris) Lett. **44**, 785 (1983); P. G. de Gennes, J. Phys. Chem. **88**, 6469 (1984); D. Andelman and J. F. Joanny, in *Scaling Phenomena in Disordered Systems,* edited by R. Pynn and A. Skjeltorp (Plenum, New York, 1985).
[6] A. J. Liu, D. J. Durian, E. Herbolzheimer, and S. A. Safran, Phys. Rev. Lett. **65**, 1897 (1990).
[7] A. J. Liu and G. S. Grest, Phys. Rev. A **44**, R7894 (1991); L. Monette, A. J. Liu, and G. S. Grest, *ibid.* **46**, 7664 (1992).
[8] A. Bhattacharya, M. Rao, and A. Chakrabarti, Phys. Rev. E **49**, 524 (1994).
[9] Z. Zhang and A. Chakrabarti, Phys. Rev. E **50**, R4290 (1994).
[10] For a review see, for example, B. Jerome, Rep. Prog. Phys. **54**, 391 (1991).
[11] H. Yokoyama, J. Chem. Soc. Farady Trans. 2 **84**, 1023 (1988); G. P. Crawford, R. Stannarius, and J. W. Doane, Phys. Rev. A **44**, 2558 (1991); G. P. Crawford *et al.*, Phys. Rev. Lett. **66**, 723 (1991); G. P. Crawford *et al.*, *ibid.* **70**, 1838 (1993); S. Kralj, S. Zumer, and D. W. Allender, Phys. Rev. A **43**, 1943 (1991); I. Vilfan, M. Vilfan, and S. Zumer, *ibid.*, **40**, 4724 (1989).
[12] P. Sheng, Phys. Rev. Lett. **37**, 1059 (1976); Phys. Rev. A **26**, 1610 (1982).
[13] A. Golemme *et al.*, Phys. Rev. Lett. **61**, 2937 (1988).
[14] X-l. Wu, W. I. Goldburg, M. X. Liu, and J. Z. Xue, Phys. Rev. Lett. **69**, 470 (1992).
[15] G. S. Iannacchione *et al.*, Phys. Rev. Lett. **71**, 2595 (1993); (unpublished).
[16] T. Bellini *et al.*, Phys. Rev. Lett. **69**, 788 (1992).
[17] S. Tripathi, C. Rosenblatt, and F. M. Aliev, Phys. Rev. Lett. **72**, 2725 (1995).
[18] T. Bellini, N. A. Clark, and D. W. Schaefer, Phys. Rev. Lett. **74**, 2740 (1995).
[19] G. Schwalb and F. W. Deeg, Phys. Rev. Lett. **74**, 1383 (1995).
[20] M. Gingras (unpublished).
[21] A. Maritan, M. Cieplak, T. Bellini, and J. R. Banavar, Phys. Rev. Lett. **72**, 4113 (1993).
[22] Y. Y. Goldschmidt and A. Aharony, Phys. Rev. B **32**, 264 (1985); R. Harris, M. Plischke, and M. J. Zuckermann, Phys. Rev. Lett. **31**, 160 (1973).
[23] A. T. Ogielski and D. A. Huse, Phys. Rev. Lett. **56**, 1298 (1986).
[24] Z. Zhang and A. Chakrabarti (unpublished).
[25] A. Chakrabarti, Phys. Rev. Lett. **69**, 1548 (1992).
[26] D. W. Grunau, T. Lookman, S. Y. Chen, and A. S. Lapedes, Phys. Rev. Lett. **71**, 4198 (1993).
[27] A. Falicov and A. N. Berker, Phys. Rev. Lett. **74**, 426 (1995).
[28] P. A. Lebwohl and G. Lasher, Phys. Rev. A **6**, 426 (1972).
[29] W. Maier and A. Saupe, Z. Naturforsch. Teil A **14**, 882 (1959); **15**, 287 (1960).
[30] Z. Zhang, O. G. Mouritsen, and M. J. Zukermann, Phys. Rev. Lett. **69**, 2803 (1992).
[31] U. Fabbri and C. Zannoni, Mol. Phys. **58**, 763 (1986).
[32] J. M. Kosterlitz and D. J. Thouless, J. Phys. C **6**, 1181 (1973); J. M. Kosterlitz, *ibid.* **7**, 1046 (1974).
[33] J. F. Fernandez, M. F. Ferreira, and J. Stankiewicz, Phys. Rev. B **34**, 292 (1986).
[34] J. Y. Denham, G. R. Luckhurst, C. Zannoni, and J. W. Lewis, Mol. Cryst. Liq. Cryst. **60**, 185 (1980).
[35] Y. Oono and S. Puri, Phys. Rev. Lett. **58**, 863 (1987).
[36] L. Monette, G. S. Grest, and M. P. Anderson, Phys. Rev. E **50**, 3361 (1994).

[37] N. Metropolis *et al.*, J. Chem. Phys. **21**, 1087 (1953).
[38] J. Tobochnik and G. V. Chester, Phys. Rev. B **20**, 3761 (1979).
[39] M. Mondello and N. Goldenfeld, Phys. Rev. A **42**, 5865 (1990); M. Zapotocky, P. M. Goldbart, and N. Goldenfeld, Phys. Rev. E **51**, 1216 (1995).
[40] P. Olsson and P. Minnhagen, Phys. Sci. **43**, 203 (1991).
[41] R. Gupta *et al.*, Phys. Rev. Lett. **61**, 1996 (1988).
[42] R. Gupta and C. F. Bailli, Phys. Rev. B **45**, 2883 (1992).
[43] N. Schultka and E. Manousakis, Phys. Rev. B **49**, 12 071 (1994).
[44] It is interesting to note that a vortex-free pinned phase has been predicted in the random-field XY model. See M. Gingras and D. A. Huse (unpublished).
[45] F. Aliev (private communication).