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LATTICE SPIN MODELS OF LIQUID CRYSTALS IN AEROGELS

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Abstract Computer simulation results for spin models and liquid crystal ordering in aerogels have been compared in order to assess our understanding of the modeling of these confined systems. The various models adopted so far are compared with experimental results and with simulation data for a new Lebwohl-Lasher type model with sprinkled silica spins and none is found to be completely satisfactory.

INTRODUCTION

The physics of liquid crystals incorporated in a silica porous matrix has recently attracted considerable interest both from the experimental and the theoretical viewpoints [1]. In particular the Isotropic-Nematic transition in these materials has been experimentally characterized, mainly by means of optical, calorimetric and magnetic resonance techniques [1]. Although the macroscopic level interpretation of the observed phenomena is relatively satisfactory, there is a strong need for an adequate microscopic modeling of the system, for instance to clarify the role of the geometry of the solid matrix and of the interactions at the liquid crystal/silica interface. From a theoretical point of view the modeling has been tackled in two ways: *i)* independent pores approximation, where the essential features of the system are assumed to be those of a collection of independent liquid crystal domains with suitable boundary conditions *ii)* description of the aerogel as a fully interconnected system. Lattice spin models of the liquid crystal ordering in aerogels have also been put forward and studied using these two approaches. All the proposed spin models present, in agreement with to the experimental observations, an orientational phase transition characterized by a rounded broader peak in the heat capacity as compared to the bulk, which is shifted to lower temperatures as the silica density increases. However, we shall see that this qualitative similarity turns out to be only apparently satisfactory.

The aim of the present work is to provide a quantitative comparison between experimental data [1], simulation results available in literature [2-6] and predictions of new computer experiments [7]. In particular we shall look at the transition enthalpy and at the shift in the pseudo transition temperature.

THE MODEL SYSTEMS

Lattice spin models have been extensively used to investigate the bulk behavior of liquid crystals [8] and recently they have also been found useful in studying nematics confined in restricted geometries such as, for example, Polymer Dispersed Liquid Crystals [9]. The prototype spin model for nematics, due to Lebwohl and Lasher [8a], is able to reproduce rather well the nematic-isotropic orientational phase transition and its characteristics of weak first order transition, including pretransitional effects. The basic assumption of this and of other spin models is that, as far as orientational properties are concerned, the nematic molecules or, more likely, tightly ordered groups of them [9] could be represented by headless unit vectors ("spins") $\mathbf{s}_i$ which are placed at the lattice points i of a simple cubic lattice. The energy of the system is then defined by the sum of pair interactions between nearest neighbor sites characteristic of the given potential.

The differences between the various models adopted to simulate the ordering of liquid crystals confined in aerogels and described below are obviously due also to the choice of how to model the effect of the silica branches, for instance defining a suitable geometry or adding some form of perturbation to the potential.

Independent Pore Approximation

This approximation is by far the simplest because it considers a single domain of liquid crystal inside a cavity of the aerogel and has also been used within the continuum theory approach [10]. Using Monte Carlo computer simulations we have recently studied such a single domain of nematics [6] considering a droplet carved from a cubic lattice. The effect of the silica twigs has been mimicked in this case by employing various kind of alignment at the droplet surface. Particular attention has been devoted to random boundary conditions, treated as a random field acting only on the particles lying at the surface of the nematic domain [5]. The molecules inside the droplet interact through the pairwise Lebwohl-Lasher (LL) potential and the total energy of the system is then:

$$U = -\sum_{i,j\in\mathcal{S}} \epsilon_{ij}\left[\frac{3}{2}(\mathbf{s}_i\cdot\mathbf{s}_j)^2-\frac{1}{2}\right] - J_B\sum_{i\in\mathcal{S},j\in\mathcal{G}} \epsilon_{ij}\left[\frac{3}{2}(\mathbf{s}_i\cdot\mathbf{s}_j)^2-\frac{1}{2}\right] \qquad (1)$$

where ϵ_{ij} is a positive constant when the spins i and j are nearest neighbors and zero otherwise. $\mathcal{S}$ denotes the liquid crystal domain (here approximately spherical) while $\mathcal{G}$ represents the external environment. This consists of an additional layer of spins which have orientations fixed according to the direction imposed by the chosen boundary conditions B and coupling strength with the spins inside the droplet defined by the parameter J_B.

A variety of surface alignments such as three dimensional random (3DI), tangential (2DI) random, bipolar (BBC), toroidal (TBC) and homeotropic (RBC) alignment has been considered as boundary conditions [6].

We have found that the 3DI boundary conditions cause a dramatic shift in the pseudo-transition temperature. On the other hand, a more ordering surface alignment, such as the BIP and TBC cases works better from this point of view but it does not correctly reproduce the order parameter dependence on temperature [6].

Spin Models with Random Disorder

A first attempt to simulate the behavior of the whole nematic/silica composite material has been made by Maritan and co-workers considering a random field model (RF) acting uniformly on a system of spins [2]. The spins interact through a Lebwohl-Lasher (LL) potential where a second term, describing the random field applied, has been added in the hamiltonian so as to have:

$$U = U_0 + U_1 = -\sum_{<i,j>} \epsilon_{ij}\left[(\mathbf{s}_i\cdot\mathbf{s}_j)^2-\frac{1}{2}\right] - \sum_i(\mathbf{h}_i\cdot\mathbf{s}_j) \qquad (2)$$

where the h_i's are independently chosen quenched fields distributed according to a rotationally invariant probability density. This model has been treated using

Mean Field Theory while the simulation for this case has been performed on a more simplified 3-state Potts model in a random field [2]. However, it should be pointed out that the Potts potential is not a proper model for nematics even in the absence of silica network in the bulk because it only allows for discrete orientations. Thus the results for the confined nematic could be also affected by this further approximation.

In another work, Sluckin *et al.* [5] have simulated a similar system with a weak random field acting on all the particles of a LL system. In both these cases there is no discrimination between molecules close to the silica branches and those fully embedded in a nematic domain.

Yet another model, that we have recently proposed and called the Sprinkled Silica Spin (SSS) model, considers a Lebwohl-Lasher lattice containing a certain concentration of spins with random orientations which are kept frozen during the simulation [7]. These frozen spins represent the silica branches and are randomly dispersed inside the sample. They are assumed to interact with their neighbours as nematic spins with a certain coupling J, here taken as $J = 1$.

The SSS model is somewhat similar to the previous one from a geometrical point of view, but it reduces to the usual LL system when the concentration of the frozen spins goes to zero, correctly reproducing the bulk behavior of a nematic liquid crystals. It should also be noticed that unlike the previous model some of the sites will be occupied by *"silica spins"*, as would be expected in reality.

Model with Interconnected Disorder

A more realistic spin model should attempt to reproduce even more accurately the aerogel including the interconnections between the silica branches, responsible for the disordering effect on the nematic ordering. A first study of this type has been performed by Uzelac *et al.* considering a lattice system with silica branches built up by a Diffusion Limited Aggregation algorithm [3]. Then the simulation of this ID model has been performed on the lattice from which the spins belonging to the silica structure have been removed. Notice that unlike our SSS model [7] the silica twigs simply occupy space without interacting with nematics. Also in this case a major criticism is that a Potts hamiltonian has been employed to simulate the liquid crystal inside the structure.

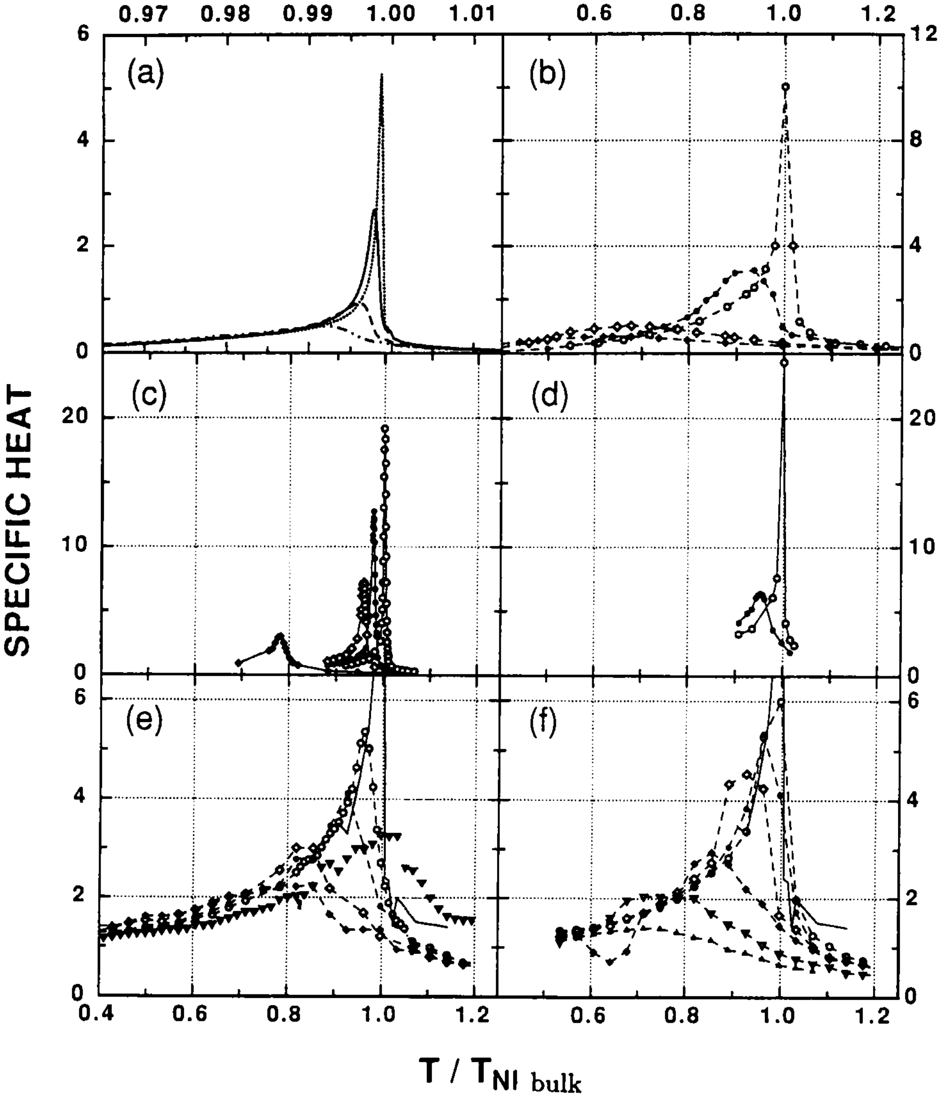

Figure 1. Specific heat vs. the reduced temperature T/T_{NIbulk} as obtained (a) from calorimetry measurements on 8CB in silica aerogel [11] and (b)-(f) from computer simulations of spin models for disordered nematics (see text).

RESULTS

The lattice models briefly described above adopt different kinds of approximations. However, we have already noted that the results of all these models appear to reproduce qualitatively the features observed in real experiments, such as the rounded heat capacity curve with the peak shifted to progressively lower temperatures as the aerogel density increases. This is clearly visible in Figs. 1b-1f, where the heat capacity obtained from the simulations of the different models is reported.

To provide an experimental yardstick, we show in Fig. 1a a plot for the specific heat $C_P(Jg^{-1}K^{-1})$ obtained from measurements on 8CB incorporated in silica aerogels having different densities: $0.08g/cm^3$ (dotted line), $0.17g/cm^3$ (continous line), $0.36g/cm^3$ (dashed line) and $0.60g/cm^3$ (dot-dashed line) with a $T_{NIbulk} = 313.65K$ [11]. We assume for now that this can be compared with the constant volume C_V obtained from theory and simulations; this is reasonable if we recall that there are usually only very small volume changes across a NI transition [12]. In Fig. 1b we plot the C_V^* results from the simulation of a 3-state Potts model on a 14 × 14 × 14 lattice with a strong random field acting on a fraction p of the total spins (from Ref. [2b]). Different values of p have been considered by the authors: $p = 0$ which correspond to the bulk system (empty circles), $p = 0.05$ (full circles), $p = 0.2$ (empty diamonds), $p = 0.3$ (full diamonds). The bulk system shows a transition temperature at $T^*_{NIbulk} = 1.804$. The C_V^* data from the simulation of a 20 × 20 × 20 4-state Potts system where a fraction p of the total spins have been removed to simulate the gel structure, are shown in Fig. 1c (from Ref. [3]). In particular the bulk, $p = 0$ (empty circles), $p = 0.05$ (full circles), $p = 0.1$ (empty diamonds), $p = 0.3$ (full diamonds) are reported. The transition in the bulk occurs in this case at $T^*_{NIbulk} = 1.587$.

The last three plates in Fig. 1 concern systems based on the Lebwhol-Lasher model for nematics which present an orientational phase transition at $T^* = 1.123$. In particular Fig. 1d shows the results, from Ref. [5], of a simulation of a LL model having a weak random field acting on all the spins of a 16 × 16 × 16 lattice (full circles) and for a 30 × 30 × 30 bulk system (open circles).

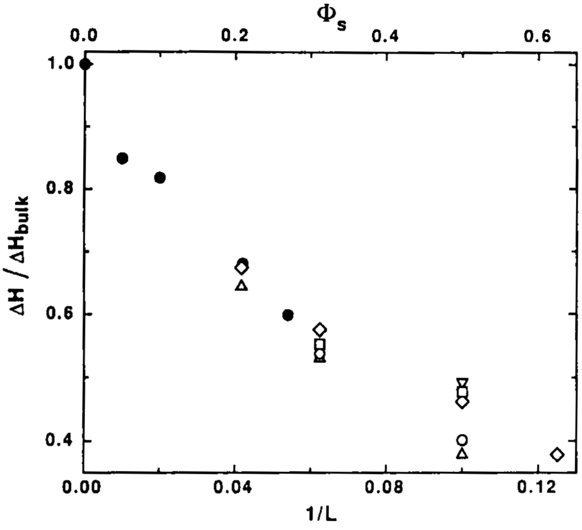

Figure 2. Normalized transition enthalpy $\Delta H/\Delta H_{bulk}$ vs the density of aerogel expressed in silica volume fraction Φ_s (top axis) from experiments (•). The results from the simulations of LL droplets with different boundary conditions, i.e. RBC (△), 2DI (▽), 3DI (◇), BBC (□) and TBC (○), are plotted vs the reciprocal of the droplet size $1/L$ (bottom axis).

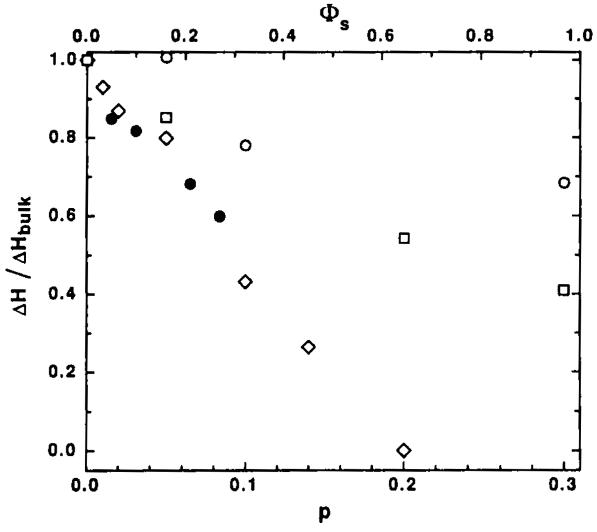

Figure 3. Normalized transition enthalpy $\Delta H/\Delta H_{bulk}$ vs the fraction p of spins that mimic the effect of the silica in the lattice simulations. The data are from the SSS model (◇) [7], the RF model (□) [2b] and the ID model (○) [3]. The experimental results, as in Fig. 2, are also reported.

In Fig. 1e we show the data for the independent pore model, i.e. LL droplets of various sizes with different boundary conditions [6]. The C_V^* results for the bulk (continuous line) are taken from the simulation of a $20 \times 20 \times 20$ system with Periodic Boundary Conditions in order to have the same order of magnitude in the number of spins as for the larger droplet employed and allow for finite size effects. The results are for a 5832 spin droplet with three dimensional random boundary conditions (3DI) (empty circles), a 304 3DI droplet (empty diamonds), a 136 3DI droplet (full diamonds), a 1632 droplet with bipolar boundary conditions (empty triangles).

In Fig. 1f the results for the SSS model, a LL system with a fraction of silica spins (p) having a 3D random orientation frozen during the simulation are shown [7]. The bulk C_V^* behavior is reported in Fig. 1e. The other data are for a $20 \times 20 \times 20$ system with $p = 0.01$ (empty circles), $p = 0.02$ (full circles) $p = 0.05$ (empty diamonds), $p = 0.1$ (full diamonds), $p = 0.14$ (empty triangles) and $p = 0.2$ (full triangles).

As can be seen from Fig 1. even the most drastically simplified model, i.e. independent pores with 3D random boundary conditions, reproduces qualitatively the experimental observations, as we have already mentioned.

In order to obtain a more quantitative comparison between simulations and experiments, we plot in Fig. 2 the normalized transition enthalpy $\Delta H/\Delta H_{bulk}$, obtained by integration of the specific heat curves, as a function of the aerogel density and of the inverse droplet size. Forcing experiment and simulation to have a comparable behavior yields scale factors connecting simulation and experimental lengths. In the case of independent droplets, the dependence of $\Delta H/\Delta H_{bulk}$ on the specific boundary conditions is weak as can be seen from Fig. 2 and we have that one spin represents a cluster of about 10 - 15 molecules.

In Fig. 3 the same analysis is reported as a function of the random field density used in the computer simulations. In the case of random field [2], to obtain agreement between experimental and simulated $\Delta H/\Delta H_{bulk}$ it is necessary to rescale p by a factor of 5. This overestimation of the effect of the disorder in the simulation is probably a consequence both of the fact that each spin represents more than one molecule and of the non connectivity of the disorder that we assume, but could also stem from a more complex alignment effect of the silica twigs on the nematic.

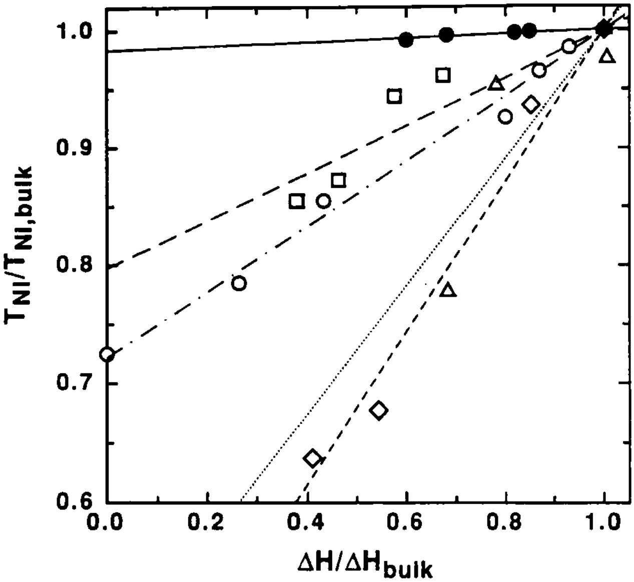

Figure 4. Reduced pseudo - transition temperature $T_{NI}/T_{NI,bulk}$ vs. the normalized transition enthalpy $\Delta H/DeltaH_{bulk}$ as obtained by calorimetric experiments on 8CB in silica aerogels (full circles) and by computer simulation of a $20 \times 20 \times 20$ SSS model (○) [7], LL 3DI droplet (□) [6], a $14 \times 14 \times 14$ 3-state Potts RF model [2b] and a a $20 \times 20 \times 20$ 4-state Potts ID model [3]. The lines represent the best fits of the simulation data.

A more detailed comparison between the experimental and simulated temperature shifts of the pseudo-transitions in the disordered systems with respect to the bulk can be obtained looking at the dependence of the normalized pseudo-transition temperature on the normalized transition enthalpy for the experiment and for the different spin models as shown in Fig. 4. Note that the results plotted in Fig.4 are independent of the scale factors of Figs. 2 and 3 discussed above. As can be seen in Fig.4, all models considered show a dependence of $T/T_{NI,bulk}$ on $\Delta H/\Delta H_{bulk}$ that greatly deviates from the experimental observations. In particular, all the spin models yield pseudo-transition temperature shifts much larger than the ones experimentally observed. One interesting finding shown in Fig.4 is that the nature of the model used to describe the liquid crystal has a great effect on the behavior of the corresponding disordered system: the normalized temperature shifts obtained with two Potts models (diamonds and triangles) are about a factor of two larger that the normalized temperature shifts obtained with the two LL models (circles and squares). Another interesting finding is that, surprisingly, the same kind of quantitative disagreement between experiment and simulation is found in both the LL independent pore model and in the LL random field model. Therefore interconnectivity alone does not account by itself for the described differences. The disagreement may perhaps be a consequence of interface phenomena at the liquid crystal-silica interface that go beyond the random strong coupling so far assumed in the modeling.

ACNOWLEDGMENTS

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REFERENCES

[1] *see for example* Liquid crystals in complex geometries formed by polymer and porous network edited by G.P. Crawford and S. Zumer (Taylor and Francis, London, 1995).

[2] **a)** A. Maritan, M. Cieplak, T. Bellini, J.R. Banavar, Phys. Rev. Lett. 72, 4113 (1994); **b)** A. Maritan, M. Cieplak, J.R. Banavar in Ref. [1].

[3] K. Uzelac, A. Hasmy, R. Jullien, Phys. Rev. Lett. 74, 422 (1995).

[4] Z. Zhang, A. Chakrabarti, preprint, (1995).

[5] D.J. Cleaver, S. Kraly, T.J. Sluckin and M.P. Allen, in Ref. [1].

[6] T. Bellini, C. Chiccoli, P. Pasini, and C. Zannoni, Phys Rev. E. 54, 2647 (1996).

[7] T. Bellini, C. Chiccoli, P. Pasini, and C. Zannoni, (to be published).

[8] **a)**P.A. Lebwohl and G. Lasher, Phys. Rev. A 6, 426 (1972); **b)**U. Fabbri and C. Zannoni, Mol. Phys. 58, 763 (1986); **c)** Z. Zhang, M.J. Zuckermann and O.G. Mouritsen, Phys. Rev. Lett. 69, 1803 (1992).

[9] E. Berggren, C. Chiccoli, P. Pasini, F. Semeria and C. Zannoni, Mol. Cryst. Liq. Cryst. 266, 241 (1995) *and references therein.*

[10] G.S. Iannacchione, G.P. Crawford, S. Zumer, J.W. Doane and D. Finotello, Phys. Rev. Lett. 71, 2595 (1993)

[11] L. Wu, B. Zhou, C.W. Garland, T. Bellini, D.W. Schaefer, Phys. Rev. E 51, 2157 (1995).

[12] P.G. de Gennes, The Physics of Liquid Crystals, (Clarendon, Oxford, 1974).