Mol. Cryst. and Liq. Cryst., 1999, Vol. 336, pp. 123-131
Reprints available directly from the publisher
Photocopying permitted by license only

Hybridly Aligned Liquid Crystal Films. A Monte Carlo Study of Molecular Organization and Thermodynamics

C. CHICCOLI[a], P. PASINI[a] and C. ZANNONI[b]

[a]*INFN, Sezione di Bologna. Via Irnerio 46, 40126 Bologna. Italy and* [b]*Dip.to di Chimica Fisica ed Inorganica and INSTM, Università, Viale Risorgimento 4, 40136 Bologna, Italy*

A Monte Carlo simulation of a nematic Lebwohl-Lasher hybrid liquid crystal film, confined between two surfaces with antagonistic anchoring alignment, is presented. We have calculated the ordering and the molecular organization inside the film for different lateral sizes. The influence of these boundary conditions on the nematic isotropic phase transition is also investigated.

Keywords: HAND; Phase Transitions; Monte Carlo

INTRODUCTION

We consider a model of an hybrid cell, with random planar anchoring on the bottom surface and homeotropic, surface normal, alignment on the top [1,2]. These conditions have been experimentally realized by Lavrentovich and coworkers placing a suitable liquid crystal, e.g. 4-cyano 4'-n-pentyl biphenyl (5CB) film on the surface of an isotropic liquid substrate such as polyethylenglycol or glycerine and leaving a free air/liquid crystal surface [1]. The interest on these systems is related to one of the most important and telling properties of liquid crystals: the structure of their topological defects [1,2] as well as the possibility of using hybrid boundary conditions in novel types of displays [3].

Here we investigate a Lebwohl-Lasher [4] lattice model of this system where the molecules (or rather small ordered clusters of them) are represented by headless unit vectors (spins), with Monte Carlo simulations. We devote our attention to the changes from the bulk values in the thermodynamics and transition properties and in the microscopic ordering resulting from these conflicting surface boundaries. The molecular organization is in fact inhomogeneous across the sample going from the disordered configuration of the bottom layer to the aligned one of the top layer.

THE MODEL

We deal with a lattice spin model where the particles, assumed to be three dimensional "headless spins" as already mentioned, interact through the second rank Lebwohl - Lasher (LL) potential [4.5]:

$$U_{ij} = -\epsilon_{ij} P_2(\cos \beta_{ij}) \tag{1}$$

where ϵ_{ij} equals $\epsilon > 0$ for nearest neighbors particles i and j and is zero otherwise, P_2 is the second rank Legendre polynomial, β_{ij} is the angle between the axis, $\mathbf{u}_i$, $\mathbf{u}_j$ of the two spins i, j representing a cluster of molecules whose short range order is maintained through the temperature range examined [6]. Clearly the LL potential is only useful as a model for liquid crystals when, like in the present case, nematics and their alignment are treated and in this respect the model reproduces very well the bulk orientational ordering of a nematic and its transition to the isotropic phase [4.5].

We mimic a hybrid aligned nematic (HAN) cell [1] considering the particular type of boundary conditions imposed on the system through layers of spins with suitably fixed orientations. Thus we take the spins of the bottom layer, $z = 0$, to have random fixed orientations in the horizontal (x, y) plane, while those of the top layer, $z = h$, to be fixed along the surface normal (*see Fig. 1*). The anchoring of the liquid crystal to the surface spins is assumed to be of the same functional form and strength as that between the nematic spins, eq. 1. The lateral surfaces surrounding the cell are chosen in two different ways: with open boundary conditions (HEBC), i.e., empty space, or periodic (HPBC) to mimic an infinite cell.

We have seen in [2] that the use of periodic BC might be incompatible when the ground state contains topological defects and in this case it should be better to use HEBC [2]. However, the artificial periodicity causes no fundamental artefacts in the modelling of uniform states and, as we will show here, in the thermodynamic behavior of the nematic film.

Independent simulations for various lattice sizes have been performed here using a standard canonical (constant number of spins N, volume V and temperature $T^* = kT/\epsilon$) Metropolis algorithm to update the lattice, as previously described in detail [2.5]. In particular, in this work, we have investigated films containing S layers in addition to the two, top and bottom, fixed surfaces. The dependence on the system size has been investigated keeping the thickness h fixed and varying the side L, i.e. $L = 10, 20, 30$ of the square film. A wide range of temperatures, about 30, as needed to investigate the thermodynamic behavior has been simulated.

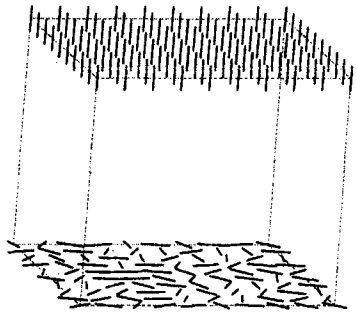

FIGURE 1 The imposed boundary conditions at the horizontal surfaces of the lattice (here a $10 \times 10 \times 10$ system is shown).

RESULTS

We report simulation results for several thermodynamic observables: energy, heat capacity, second rank order parameters. Fourth rank order and spatial - orientational correlation functions [5] have also been calculated but are not presented for conciseness, since they do not modify the picture that emerges for the system.

Heat capacity

We have calculated the heat capacity by differentiating the energy versus the temperature. The results, reported in *Fig. 2* and in *Fig. 3* in dimensionless units, show a depression of the maximum in comparison with the results of a bulk system of a comparable size [5].

Moreover the peaks are shifted at a lower temperature and this clearly indicates that the nematic is relatively destabilized with respect to the isotropic phase because of the disordering effect provoked by the film surfaces, which overcome what might be expected to be the opposite effect of the aligned top layer.

The character of the transition seems also to be changed. We recall that the LL model well reproduces the weak first order characteristic of the phase transition in the bulk. In particular in that case the C_V peak grows and sharpens with sample size. In the present model the transition seems instead to be second order with a specific heat peak that remains, within our computer simulation error, fairly constant if not decreasing as

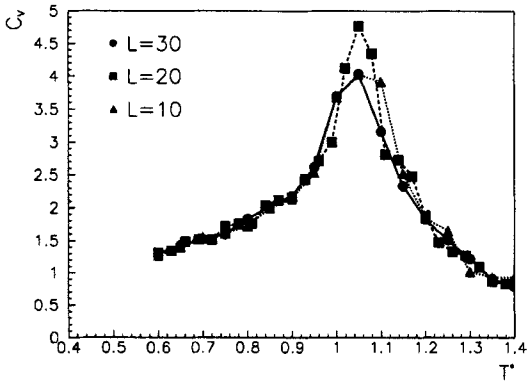

FIGURE 2 The heat capacity as obtained from MC simulations of films of the same thickness ($h = 10$) and with different widths (L).

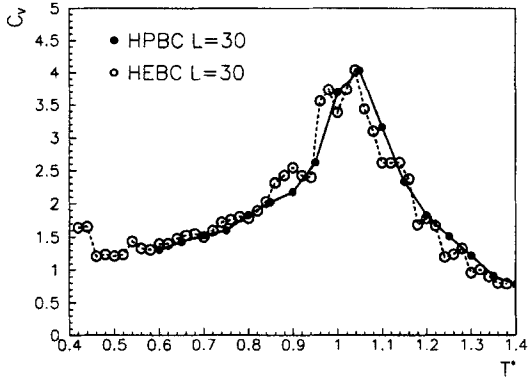

FIGURE 3 The heat capacity as obtained from the simulations of a $30 \times 30 \times 10$ lattice with two different types of boundary conditions at the four vertical surfaces of the film: empty (HEBC) or periodic (HPBC).

the number of particles increases.

The two different type of boundary conditions employed at the four lateral planes do not seem to significantly modify the thermodynamic results, as we see from *Fig. 3*.

The order parameters

We have calculated first the standard nematic second rank order parameter of the whole system with respect to the instantaneous director, $\langle P_2 \rangle_\lambda$ [5].

In *Fig. 4* we report the results for this overall order of the model film with three different lateral sizes with empty boundary conditions and, for the largest size system, a comparison of the results of the film with different boundaries against those of the bulk [5]. We see that $\langle P_2 \rangle_\lambda$, that expresses how the molecular organization deviates from a perfectly aligned configuration [5], has a predictable decrease with temperature and is quite different from the bulk but also that it is not, on the whole, so informative. In particular it cannot, by its very nature, describe orientational the inhomogeneities present in the sample.

On the other hand one of the most important advantages in using microscopic computer simulations to model confined liquid crystals is the possibility of investigating how the boundary conditions influence the molecular organization and the ordering not just on the whole sample but at every point across the nematic cell. Thus we have also calculated the

rotationally invariant second rank order parameter $\langle P_2 \rangle_\lambda^{(L)}$ at each layer.

Considering one layer this local order parameter can be written as:

$$\langle P_2 \rangle_\lambda^{(L)} = \frac{1}{N_L} \sum_{i=1}^{N_L} P_2(\mathbf{u}_i \cdot \mathbf{d}_L). \tag{2}$$

where N_L is the number of spins belonging to the layer L, $\mathbf{u}_i$ is the unit vector defining the orientation of the i-th spin and $\mathbf{d}_L$ is the local layer nematic director, determined as the eigenvector corresponding to the largest eigenvalue of the ordering matrix of the spins of the layer under investigation.

The results, shown for some selected temperatures in *Fig. 5* for open lateral BC, indicate how the influence of the surfaces is modified by the lateral size of the system.

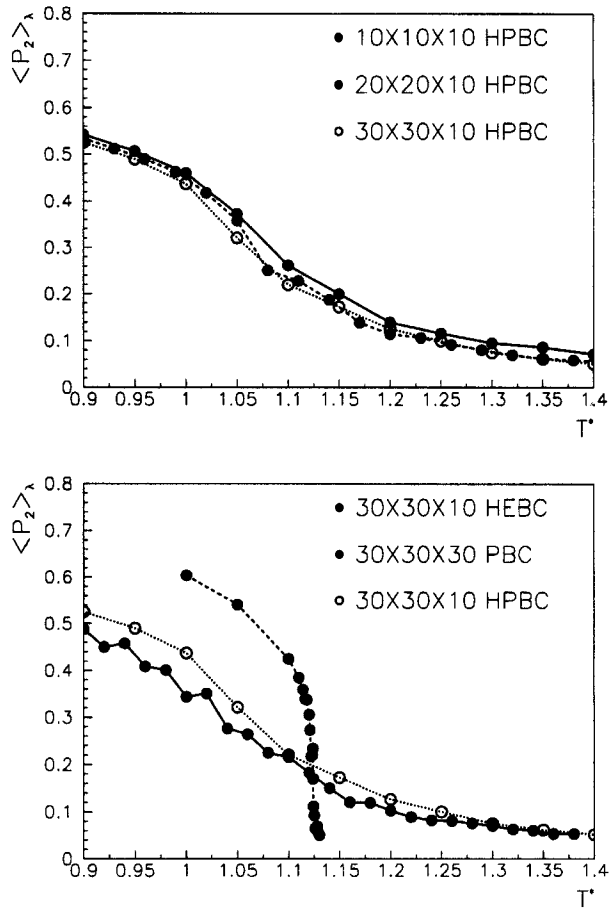

FIGURE 4 The second rank order nematic parameter dependence on reduced temperature as obtained from the MC simulations of a hybrid nematic cell for three different horizontal lengths and empty boundary conditions (top). The comparison among the cases with two different lateral boundary conditions (HEBC and HPBC) and the bulk (PBC) (bottom).

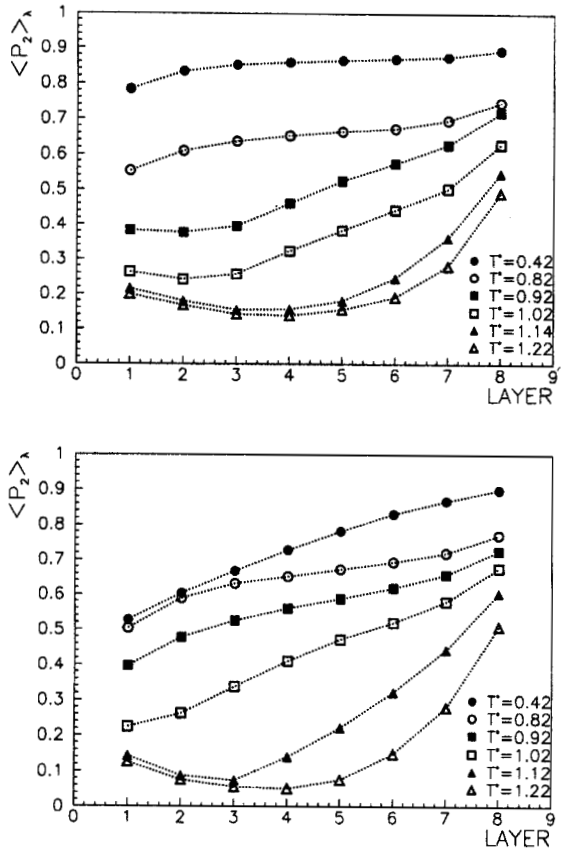

FIGURE 5 The nematic order parameter, $\langle P_2 \rangle_\lambda^L$ plotted against distance , in lattice units, from the bottom to the top of the hybrid cell at some selected temperatures. Results are for a $10 \times 10 \times 10$ (top) and for a $30 \times 30 \times 10$ system (bottom).

We start considering the case of high temperatures (e.g. $T = 1.22, 1.14$) above the order-disorder pseudo-transition. We see that in this case the order is strongly inhomogeneous across the sample and that the main features are the same both for the $10 \times 10 \times 10$ cubic lattice (top plate) and for $30 \times 30 \times 10$ film (bottom plate). Thus the order is enhanced near the top, homeotropic, anchoring surface, as expected, but also near the planar disordered counter surface where the 2D isotropic average of $\langle P_2 \rangle_\lambda = 0.25$ is approached, with respect to the bulk disordered value expected at these temperatures and that the system tries to adopt in the middle of the sample ($\langle P_2 \rangle_\lambda = \mathcal{O}(1/\sqrt{N})$). This combination of effects explains the concave trend of $\langle P_2 \rangle_\lambda$ versus distance at the higher temperatures. As the temperature decreases the cubic sample and the film differ as we can expect, with the $30 \times 30 \times 10$ film being more conditioned by the surfaces, with a strong ordering inhomogeneity even at the lowest temperature, and the cubic sample becoming essentially homogeneous, except at the layer closest to the boundaries. We have seen in Ref. [2] that certain topological defects also become stabilized for a hybrid film where lateral sizes is sufficiently large compared to thickness.

CONCLUSIONS

We have investigated a lattice spin model of a hybrid aligned nematic system. The confinement of the system and the antagonistic boundary conditions at the two cell walls induce a depression in the nematic isotropic phase transition with a change from the first order character of the bulk LL model. The heat capacity peak is lower in comparison to simulation results obtained for bulk systems on similar lattice sizes and the C_V curves appear more broadened. We find that the system goes from an ordered to a disordered phase at a temperature which is approximately 5 to 10% lower than that exhibited by the simulation of the same microscopic model in the bulk. Moreover we find no evident changes in the phase transition behavior by increasing the horizontal dimensions of the cell or by employing Periodic or Empty boundaries at the lateral sides of the system. The second rank order parameter calculated at every layer of the model hybrid cell shows that the system is always strongly inhomogeneous at the higher temperatures, while at low temperature a strong change in ordering across the sample is only observed for large ($30 \times 30 \times 10$) films.

Acknowledgments

We are grateful to University of Bologna, MURST, CNR and INFN (grant I.S. BO12) for support.

References

[1] O.D. Lavrentovich and Yu A. Nastishin, *Europhys. Lett 12*.135 (1990); O.D. Lavrentovich and V.M. Pergamenshchik. *Int. J. Mod. Phys. B 9,* 2839 (1995).
[2] C. Chiccoli, O.D. Lavrentovich, P. Pasini and C. Zannoni, *Phys. Rev. Lett., 79,* 4401 (1997).
[3] R. Barberi, M. Giocondo, J. Li, R. Bartolino, I. Dozov and G. Durand, *Proc. SPIE, 3013,* 229 (1997).
[4] P Lebwohl and G. Lasher, *Phys. Rev. A 6,* 426 (1972).
[5] U. Fabbri and C. Zannoni, *Mol. Phys., 58,* 763 (1986).
[6] E. Berggren, C. Zannoni, C. Chiccoli, P. Pasini and F. Semeria, *Phys. Rev. E 50,* 2929 (1994).