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COMPUTER SIMULATIONS OF CYLINDRICALLY CONFINED NEMATICS

C. CHICCOLI, P. PASINI, F. SEMERIA
INFN Sezione di Bologna, Via Irnerio 46, 40126 Bologna, Italy

E. BERGGREN * AND C. ZANNONI
Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna,
Viale Risorgimento 4, 40136 Bologna, Italy

Abstract A Monte Carlo simulation of a nematic Lebwohl-Lasher liquid crystal confined to a cylindrical pore is presented. We have calculated the ordering and the molecular organisation inside the cavity for cylinders of different size when homeotropic radial boundary conditions and different anchoring strengths are employed. We have not observed escaped radial configurations in the organisations obtained.

INTRODUCTION

Confined nematic systems have attracted and are attracting a great deal of experimental and theoretical attention [1-5]. This interest is, at least in part, due to the need of a better understanding of finite size, confinement, and surface effects in these systems which have found applications in many liquid crystal devices. In the last few years we have started a systematic study of spherical nematic droplets at a microscopic level by means of Monte Carlo computer simulations [4-5] using various boundary conditions, anchoring strenghts, external fields etc.. We have shown that this approach is very useful not only in determining the thermodynamic observables of the system but also the molecular organisation that results from the competition of the above mentioned conditions. Here we have started to

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* present address: European Chemical Bureau Joint Research Centre, TP 280 21020 Ispra (Va), Italy

extend this work to the simulation of nematics confined in cylindrical pores. Even though the model, described in the next section, is very simple, we aim to approach real situations such as, for example, Anopore membranes filled with liquid crystals [1] as it proved possible for spherical PDLC droplets. In the present paper we investigate the effect of planar radial boundary conditions on the thermodynamic observables and on the molecular organisation of a cylindrical nematic sample. Comparison with continuum theory and experimental results, where available, is provided.

THE MODEL

Our model is based on a cylindrical sample carved from a simple cubic lattice where the molecules or more likely short range ordered groups of molecules are represented by three dimensional unit vectors ("spins") and interact through the well known second rank Lebwohl - Lasher pair potential [6]:

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

where β_{ij} is the angle between two spins i and j, P_2 is a second rank Legendre polynomial and ϵ_{ij} is a positive constant for nearest neighbour sites and zero otherwise. This simple potential is a useful model for bulk nematic and reproduces to a good extent the orientational ordering and its temperature dependence, including the nematic - isotropic transition [6]. The cylindrical pores are assumed to be much longer than their diameter and thus periodic boundary conditions, which simulate an infinite vertical dimension, are employed at the top and at the bottom of the sample. Homeotropic radial boundary conditions are instead imposed around the cylinder by adding a surface layer of spins with fixed (in plane) orientations pointing toward the axis of the cavity. In practice the nematic surface interaction is simulated as a pair potential between a liquid crystal molecule i and a molecule j in the polymer matrix as

$$U_{ij} = -\epsilon_{ij} J P_2(\cos \beta_{ij}) \qquad (2).$$

The parameter J gives the relative anchoring strength, i.e. $J < 1$ simulates weak and $J > 1$ strong anchoring at the surface with respect to the standard nematic interactions.

SIMULATIONS AND RESULTS

We have performed a set of independent simulations for some anchoring strengths at various temperatures using different starting conditions. In particular we studied cylinders carved from a cubic lattice of two diameters and different heights: $12 \times 12 \times h$, $22 \times 22 \times h$, with $h = 40, 52, 62, 82$. The first quantity we have considered is the heat capacity C_V which can be obtained during the simulation from the fluctuations of the energy or, as we have done here, to obtain less noisy results, by differentiating the energy against temperature. The results of C_V are shown in Fig. 1 and are in qualitative agreement with the experimental observations of Finotello and co-workers obtained from experiments on Anopore membranes filled with 4-pentyl,4'-cyano-biphenyl (5CB) [7]. The confinement and the planar radial boundary conditions have a rather dramatic effect on the heat capacity. The C_V curve is flattened and the orientational nematic-isotropic phase transition which is weakly first order in the bulk (see Fig. 1) is pratically suppressed. In Fig 1. we consider as " pseudo bulk" a cubic sample with a similar number of particles to that of the cylindrical sample but with periodic boundary conditions in order to limit the unavoidable effects associated to finite size. The bulk nematic order defined by the standard order parameter $< P_2 >_\lambda$ is obtained from the largest eigenvalue of the ordering matrix [8].

The influence of the boundary conditions, with an anchoring parameter $J = 1$, on the nematic order is rather strong and the value of $< P_2 >_\lambda$ in the cylindrical cavity is reduced, for example, to the half of its value for the bulk at the scaled temperature $T^* = kT/\epsilon = 0.6$. This value is reached starting from various initial configurations as shown in Fig. 2 for three different initial conditions. In particular the starting configurations here considered are: *i)* a system with all the spins aligned along the Z axis; *ii)* all the spins perpendicular to Z with in plane orientations pointing towards the axis of the cylinder ("planar radial orientation"); *iii)* spins with three dimensional random orientations. After a certain number of equilibration Monte Carlo cycles (in this case typically 10000) the system reaches an equilibrium state which is determined by the competition of the disordering effect of its finite temperature and of the boundary conditions employed.

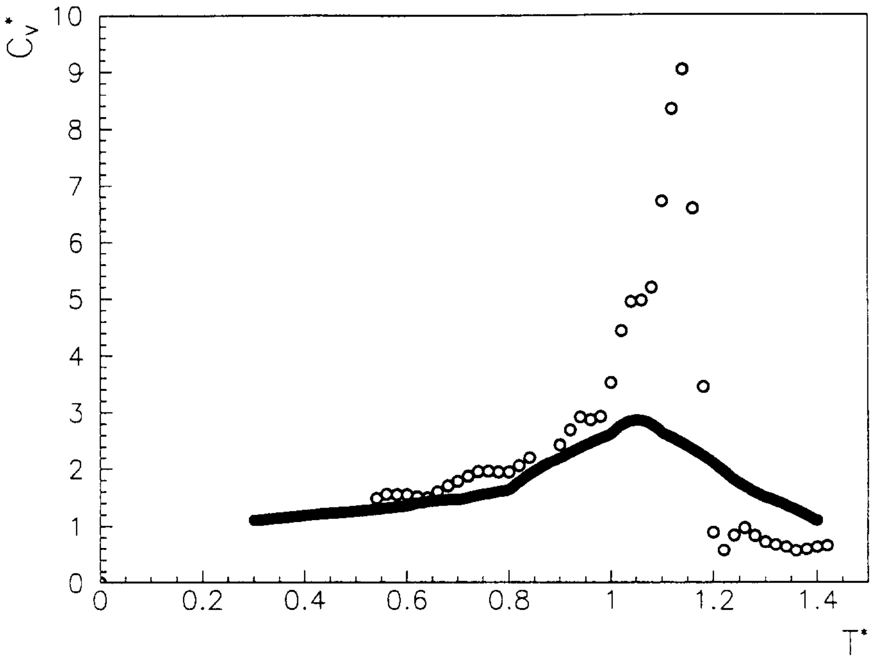

FIGURE 1. The heat capacity as obtained from MC simulation of a pseudo bulk system (empty circles) and of a 12 × 12 × 40 cylindrical system with planar radial boundary conditions (line).

However the standard order parameter $< P_2 >_\lambda$ is quite inappropriate to describe how well the molecular organisation inside the pore is influenced by the homeotropic Boundary Conditions. Thus we have calculated a planar radial order parameter, $< P_2 >_C$ that we have defined as follows:

$$< P_2 >_C = \frac{1}{N} \sum_{i=1}^{N} P_2(\mathbf{u}_i \cdot \mathbf{c}_i), \tag{1}$$

where N is the number of spins in the cavity, $\mathbf{u}_i$ is the orientation vector for the i-th spin and $\mathbf{c}_i$ is the ideal planar radial direction at the point i . This expresses disordering from a perfect planar radial organization, which corresponds to $< P_2 >_C = 1$.

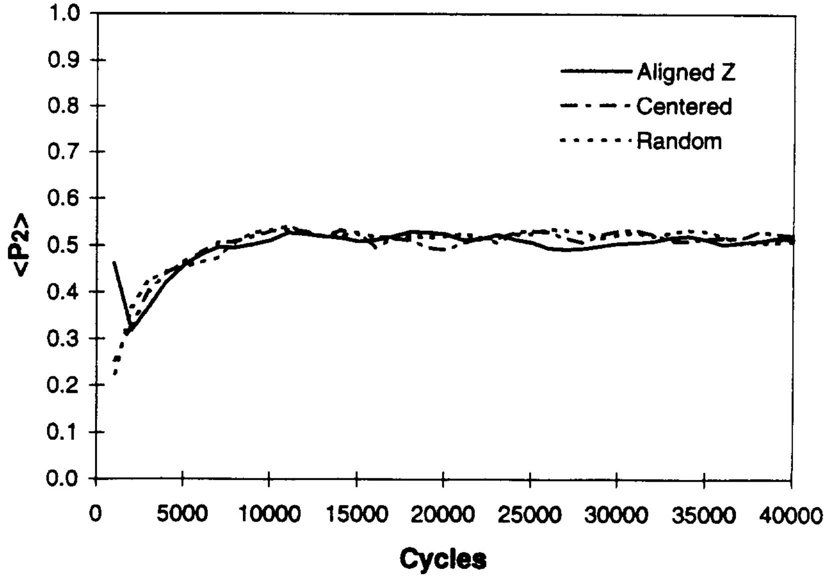

FIGURE 2. The dependence of the standard second rank order parameter $< P_2 >_\lambda$ on the Monte Carlo cycles. Three different starting configurations inside the cylinder are considered at a reduced temperature $T^* = 0.6$.

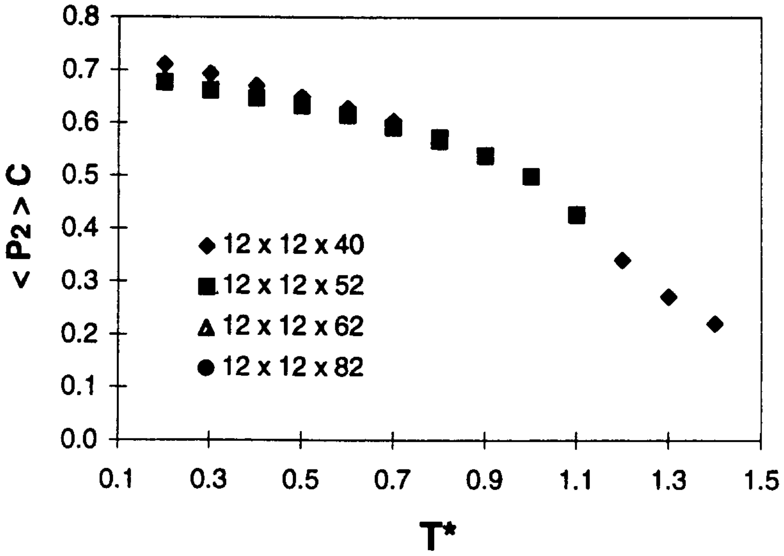

FIGURE 3. The order parameter $< P_2 >_C$ for different cylinder sizes (enclosing lattice sizes: $(12 \times 12 \times 40)$, $(12 \times 12 \times 52)$, $(12 \times 12 \times 62)$ and $(12 \times 12 \times 82)$) at various temperatures.

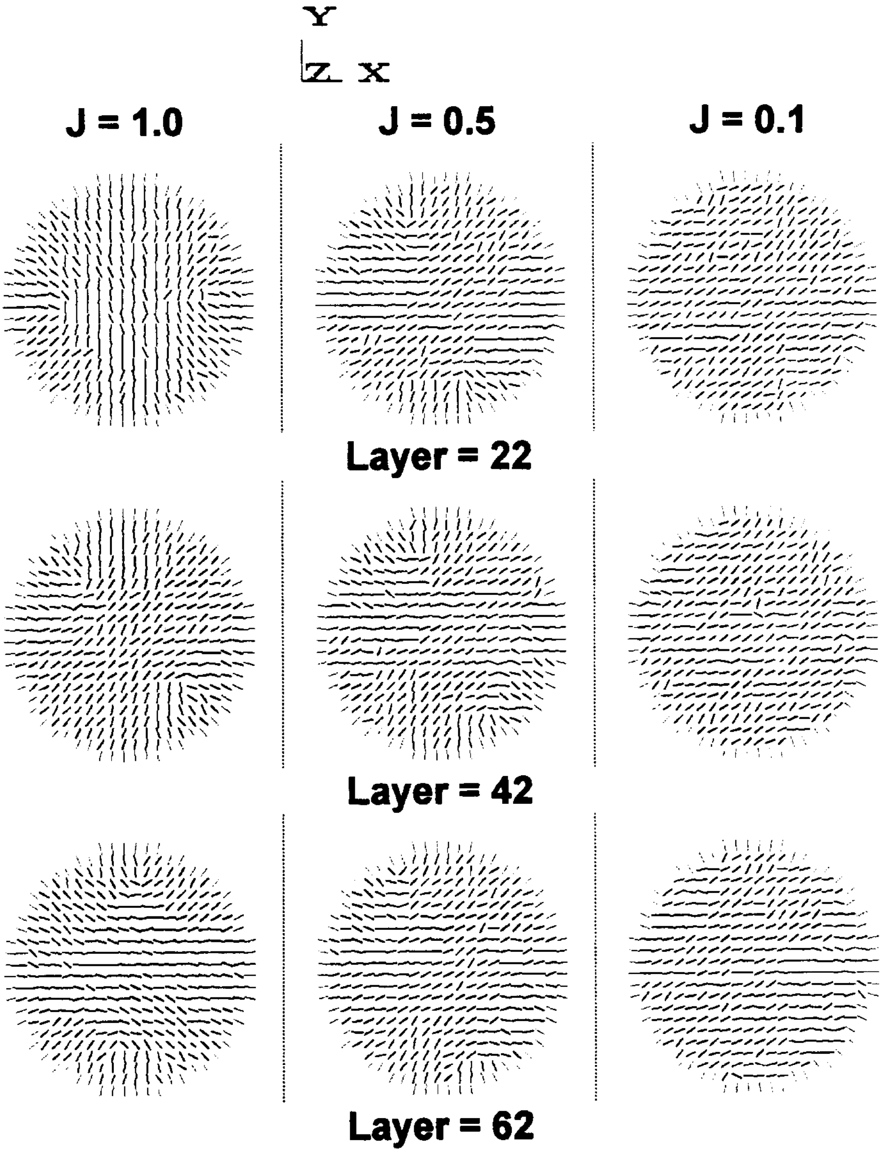

FIGURE 4. Transverse sections of the spins of a simulated configuration viewed along the cylinder z-axis at layer number 22, 42 and 62 for a configuration simulated on a lattice $22 \times 22 \times 82$ at $T^* = 0.6$ for different anchoring strengths, $J = 1.0$ (left), $J = 0.5$ (middle) and $J = 0.1$ (right).

In Fig. 3 we report the temperature dependence of $< P_2 >_C$. We see that a perfect radial ordering, that would imply a single defect line along the axis of the pore is not obtained even at the lowest temperature studied. The dependence on system size has been investigated. The cylindrical order decreases with temperature, as expected, without ever reaching for this system size the real isotropic-like values. This behavior somewhat contrasts with that of similar size spherical samples with radial boundary conditions where an excellent ordering with respect to the boundary field lines was obtained. In that case a small size core defect similar to the expected point defect was easily obtained, while here the situation is less clear cut. It should be said that various types of ordering are to be expected as the diameter of the pore changes as shown by Kraly and Žumer using continuum theory [9]. Here the absolute size of the pores corresponding to our simulation is difficult to estimate even if, according to our previous experience we can expect each spin to correspond to $O(10)$ molecules. We have simulated cylinders with different diameters and also with different lengths to control that the length of the cylinder does not significantly affect the results shown in Fig. 3. According to the estimate just mentioned this range of diameters would correspond to almost $0.1\mu m$. This size seems to be not large enough to obtain the escaped radial configuration but only the planar radial organization. The organization we find is, however, shown in Fig. 4 for different anchoring strengths (decreasing from left to right) and for three different sections. At the strongest anchoring we find a radial ring starting from the surface that is connected to ordered region inside. Reducing J, given that the boundary orientation is the same, is equivalent to a renormalization (and an increase) of the surface temperature. The attendant disordering effect is apparent in the snapshots shown where the defects become, if anything, even less visible.

In conclusion, the molecular organization of liquid crystals inside a pore with radial boundary conditions seems to be more complex than the simple escaped radial and probably varies with pore size as expected from continuum theory. Further computer experiments on a much larger variety of sizes should be performed to see if and under what conditions the escaped radial organisation is obtained.

ACKNOWLEDGMENT

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