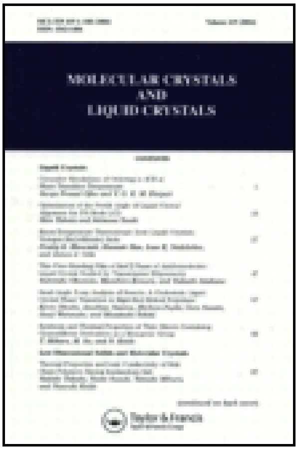

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Monte Carlo Simulations of a Composite Liquid Crystal-Polymer Model System

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Monte Carlo Simulations of a Composite Liquid Crystal-Polymer Model System

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We present a Monte Carlo study of a simple model of a liquid crystal-polymer system under the effect of an external applied field. A lattice spin model, based on the Lebwhol-Lasher Hamiltonian and generalized with suitable boundary conditions, has been employed to investigate the molecular organization and to predict the ordering across a sample cell.

Keywords: computer simulation; confined systems; polycrips; Monte Carlo

INTRODUCTION

Composite materials based on polymers and liquid crystals have recently attracted a lot of attention in view of their possible photonic applications. Some of these composites, consisting of a stack of polymeric sheets alternating with nematic liquid crystal layers, are currently under active study by various experimental groups [1–4] and have attracted a considerable interest both from the basic and the applied research point of view. Here we wish to present a Monte Carlo (MC) simulation [5] study of a single liquid crystal-polymer cell to mimic the main features of the system under the effect of an external applied field. Computer simulations have been successfully used in investigating liquid crystal systems [5,6] since the pioneering work

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of Lebwohl and Lasher (LL) [7] performed on a lattice spin model. This LL model consists of a system of interacting headless vectors ("spins") with three dimensional rotational freedom placed at the sites of a regular lattice. This prototype model is the simplest with the correct symmetry for nematic liquid crystals (in particular the potential is invariant for an head-tail flip of the molecules) and has been the first successful model to simulate the orientational ordering and the nematic-isotropic transition of liquid crystals [7,8]. We have shown that the MC technique is particularly useful in investigating confined systems such as sub-micron droplets with fixed (homeotropic and planar) surface anchoring mimicking polymer dispersed liquid crystals (PDLC), also in the presence of electric fields [9], twisted nematic displays and nematic films with various boundary conditions [5,6,10].

THE SIMULATION MODEL

The model we consider sets out to mimic some of the essential features of a composite system consisting of a very thin film of nematic liquid crystal in contact with a layer of polymer. The polymer surface is porous and soaked by the nematic, while the nematic layer floating above the polymer film can be aligned by a second surface or by a suitably applied external field. We adopt a simple lattice spin model, based on the LL hamiltonian [7], where the spins $\mathbf{u}_i$ represents either the nematic or the polymer molecules. The particles, thus assumed to have uniaxial symmetry, are located at the sites of a $\mathrm{L} \times \mathrm{L} \times (\mathrm{L}+2)$ cubic lattice and interact through a pair potential of the form:

$$U_{ij} = -\varepsilon_{ij} P_2(\mathbf{u}_{ij} \cdot \mathbf{u}_j) \tag{1}$$

where ε_{ij} is a positive constant, ε, for nearest neighbor spins i and j and zero otherwise, P_2 is the second Legendre polynomial. This interaction tends to bring molecules parallel to one another and effectively models whatever underlying intermolecular interaction either attractive or repulsive that does that. The LL model has been studied and generalized, also to non-uniaxial particles [11], by many authors for bulk and confined systems [5,6]. In particular confined systems require several kinds of Boundary Conditions depending on the model to be simulated [10]. Here we assume the potential in Eq. (1) to simulate both nematic and polymer interacting particles but nematic molecules are represented by mobile spins whose orientation is updated during the simulation while polymer chain units are taken as frozen spins. Moreover we simulate the presence of the polymer chains protruding from the bottom of the sample and the consequent decreasing concentration of polymer units moving away from the bottom surface by assuming in the first few bottom layers of the system a decreasing percentage of frozen particles spins.

Monte Carlo simulations are then employed to investigate the creation of structures in the nematic planar layers across the sample with different concentration gradient of frozen oriented particles inside the system. For example, the percentage of frozen (randomly or along Z) oriented particles can change from 50% to 5%, with a 5% variation every 2 layers, going from the bottom to the middle layer of the system. In our system we have chosen the boundary conditions at the top surface with spins all aligned along the Z direction and at the bottom surface aligned along X. At the other four surfaces of the cube we employ periodic boundary conditions. Of particular interest here is the case where an external field is applied to the system and induces an alignment of the molecules along the field direction (the X axis). The application of a uniform electric field, coupled dielectrically to the particles is written as sum of individual terms:

$$U_i = \xi P_2(\mathbf{u}_i \cdot \mathbf{F}_x) \tag{2}$$

The parameter ξ is a dimensionless constant representing the strength of the coupling to the external field $\mathbf{F}_x$. After at least 500 kcycles required to equilibrate the system, where a cycle corresponds to N attempted moves of the N particles, the electric field is applied. The simulation is then continued for at least further 100 kcycles, enough to equilibrate again the system, with the aim to reorient the particles in the X direction. To analyse the influence of the applied field on the duration of the pulse, the procedure of switching OFF is started after different timing of the first field application. The starting configurations of the lattice were chosen to be completely aligned along the Z direction and the evolution of the system was followed according to the classic Metropolis Monte Carlo procedure [12]. We calculate the following thermodynamic observables: the internal energy, which is evaluated directly from the intermolecular potential in Eq. (1) and is an essential part of the Monte Carlo procedure, and the order parameters. The second rank order parameter $\langle \mathrm{P}_2 \rangle$ is calculated from the largest eigenvalue of the ordering matrix [5,8]:

$$\mathrm{Q}_{\alpha\beta} = 1/(2\mathrm{N}) \sum_{i=1,N} (3\ \mathrm{u}_{i,\alpha}\mathrm{u}_{i,\beta} - \delta_{\alpha,\beta}) \tag{3}$$

where $\mathrm{u}_{i,\alpha}$ is the α component (α = x, y, z) of the unit vector along the axis of the particle i and $\delta_{\alpha,\beta}$ is the Kronecker delta. Moreover some more qualitative but informative results, such as the plots of snapshots of the particles and the simulations of polarized microscopy images [13] are obtained off-line. Also these images are analyzed for different field strengths and when these fields are switched ON and OFF, after several cycles of application inside the ON state. Typically the simulation runs are performed on a $N = 40 \times 40 \times 42$ system containing 67200 spins. The simulations were performed on a system of distributed computing tools, called CONDOR [14,15], implemented on the network of the Italian National Institute for Nuclear Physics.

RESULTS

As mentioned above, we have started the simulations from a completely aligned system in the Z direction. In the first 500 kcycles of the simulation (see Figs. 1, 2 red lines) the system is equilibrated, until a stable situation, allowing for a safe computation of physical quantities of interest, such as order parameters and energy is reached. At the end of this equilibration period, an electric field is applied to the system for at least a further 100 kcycles (green lines), sufficient to equilibrate again the system with the resulting overall reorientation of the preferred direction of the molecules along the field direction.

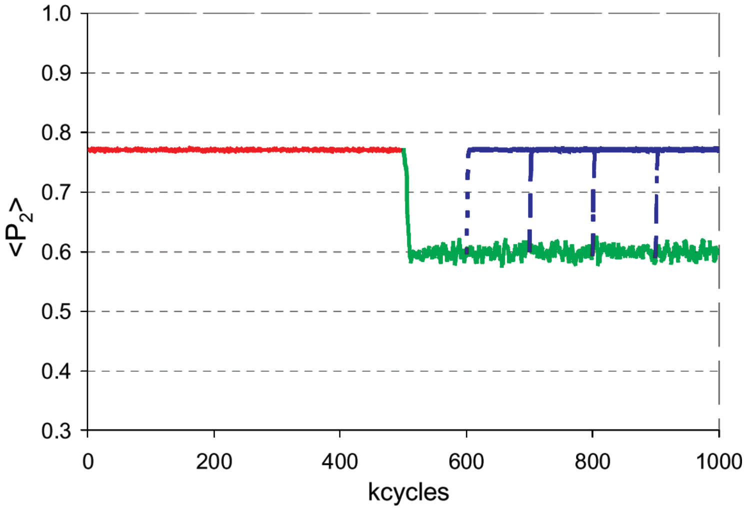


FIGURE 1 Dependence of the nematic order parameter $\langle P_2 \rangle$ on Monte Carlo cycles. The red curve represents the equilibration values of the overall $\langle P_2 \rangle$ when the external field is off, the green curve when the field is turned on and the blue ones when the field is successively again turned off after 100, 200, 300 and 400 kcycles respectively. The field strength is $\xi = 0.03$.

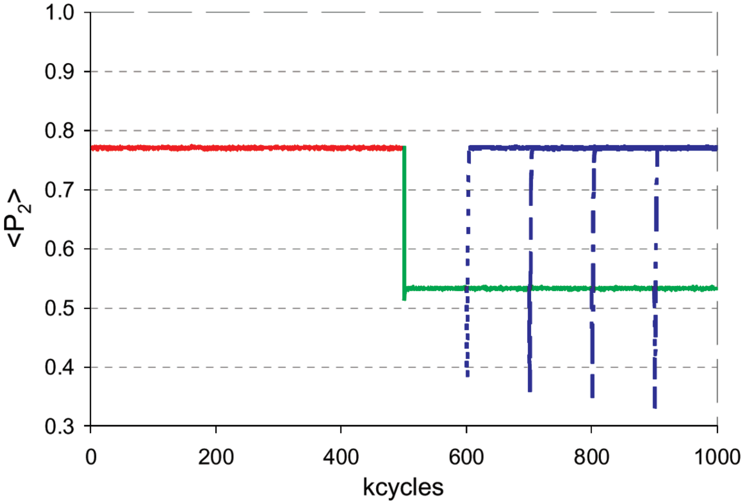
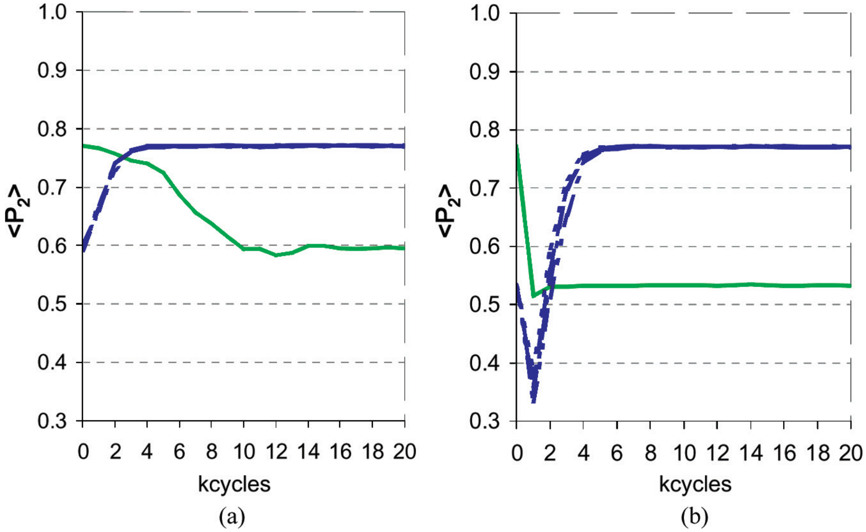


FIGURE 2 As in Figure 1 for an higher value of field strength, i.e. $\xi = 1.0$.

Then to analyze the effect of the duration of the external field pulse we have performed additional simulations, switching OFF the field after different Monte Carlo sequence lengths. In particular we have switched off the field after 100, 200, 300 and 400 kcycles as reported in Figures 1 and 2, respectively for two different field strengths, i.e a very low one, $\xi = 0.03$, and an higher one, $\xi = 1.0$. It is interesting to notice that for the lower field the overall ordering is higher ($\langle P_2 \rangle \approx 0.6$) in comparison with what we have after the application of the higher field ($\langle P_2 \rangle \approx 0.52$) because the alignment of the frozen spins ("the polymer molecules") has still a greater influence in contrasting the field effect. That is also evident by looking at the rapidity of reaching the new ordering when the field is switched on and switched off as reported in Figure 3. For the lower field the alignment along z, induced by the top surface and by the frozen spins, tends to overcome the effect of the external field and then it takes much more MC cycles to reorient the system along the X direction (see Fig. 3a, green line) than to return to the original ordering (Fig. 3a, blue line).

For the higher field intensity the behavior is opposite (see Fig. 3b). It is also interesting to notice that, before recovering the initial ordering, for the higher intensity there is a temporary great decreasing of the overall order as soon as the field is switched off (see Figs. 2 and 3b). This fault in the $\langle P_2 \rangle$ curves is more pronounced as the duration in the field application is longer.



(a)

(b)

FIGURE 3 The curves show the decreasing of the order when the external field is applied along X (green) and the reorientation along Z with the increasing of $\langle P_2 \rangle$ to its initial values (blue) when the field is turned off after different sequences of MC cycles. The results are for two field strengths: $\xi = 0.03$ (plate a) and $\xi = 1.0$ (plate b).

The rapidity of the reorientation of the system when the field is switched off is clearly evident also by looking at the snapshots, reported in Figure 4 for the case $\xi = 1.0$, where a color coding has been employed to better appreciate the changing of orientation of the molecules. The first image (Fig. 4 top left) is taken after 500 kcycles of equilibration without any external field applied. All the molecules of the system tend to be aligned roughly along Z ($\theta = 0°$, red color) as a consequence of the effect induced by the top surface and by the alignment of the frozen spins. The order parameter $\langle P_2 \rangle$ has a value of about 0.78 compatible with the reduced temperature at which the simulation has been performed, i.e. $T^* = 0.8$. We recall that the nematic-isotropic transition temperature for the LL model is $T^* = 1.1232$ [8]. The second snapshot (Fig. 4 bottom left) is taken after 400 kcycles with the external field applied. All the nematic molecules outside the polymer region have changed their orientation and are now directed along X ($\theta = 90°$, yellow color).

The nematic molecules in the liquid crystal-polymer region cannot reorient towards the X direction because the effect of the frozen spins dominates the effect induced by the external field even for the strong

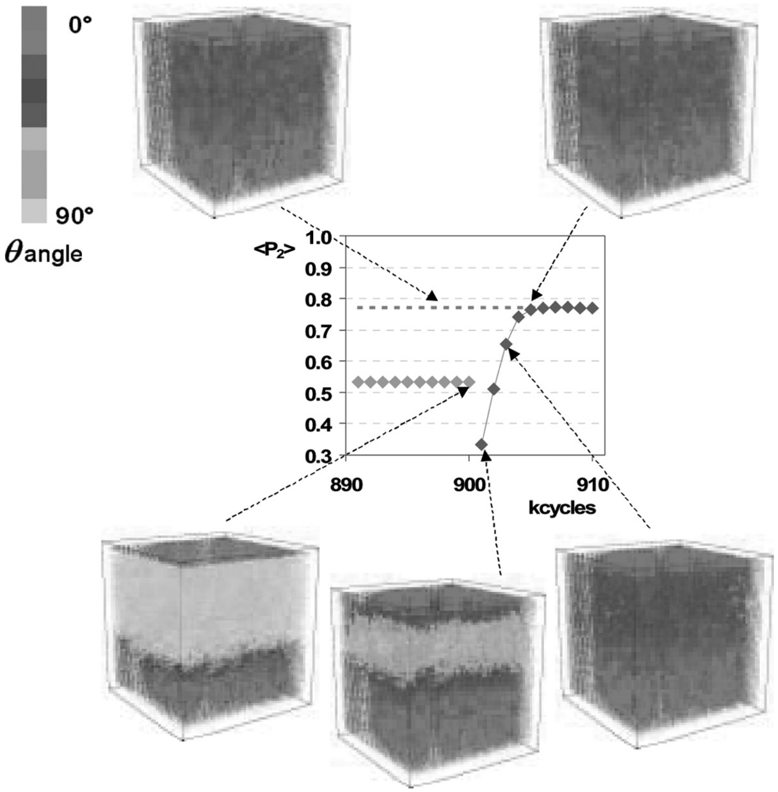


FIGURE 4 Snapshots of the molecular organization as obtained from the Monte Carlo simulations. The different images as indicated in the $\langle P_2 \rangle$ curves. The top left snapshot is taken after the equilibration with the field off and the order parameter $\langle P_2 \rangle$ has the constant value reported with the dashed curve. The bottom left image shows the effect of the application of the field. The other snapshots show the reorientation when the field is turned off reaching a molecular organization similar to the initial one (top right). The results are for field strength $\xi = 1.0$. The color coding shows the deviation from the Z direction ($\theta = 0°$, *see text*).

intensity. The molecules deviate from the Z alignment but cannot reach the X one and accordingly their color code appears almost as blue. Switching off the field, a time lapse of 1000 cycle is sufficient to appreciate the reorientation towards Z, as can be seen from the next image. The decrease in the overall ordering of the system, with respect to the previous configuration, can now be also directly visualized. In a few thousands cycles a configuration similar to the initial one can be reached.

CONCLUSIONS

have presented a Monte Carlo study of a model of a composite liquid crystal polymer system. We have tried to mimic the orientational behavior of a single cell, with suitable boundary conditions, under the effect of an external applied field. We have adopted a simple lattice spin model, based on the Lebwohl-Lasher hamiltonian, which allowed us to calculate the change in the ordering of the system due to the application of the field. The results are in qualitatively agreement with experimental results [4]. However, for a quantitative comparison more detailed simulations (e.g., with larger cells and different cell shapes) will be needed to investigate more completely the molecular organization and the ordering expected across the cell.

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