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# Computer Simulations and Experimental Dynamical Characterization of a Composite Liquid Crystal-Polymer System

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*We present a Monte Carlo study of a liquid crystal-polymer interface, focusing on a single cell with boundary conditions tailored to mimic the main features of the system and we examine the effect of an external applied field. A simple lattice spin model, based on the Lebwohl-Lasher hamiltonian, has been employed to represent the nematic and the polymer molecules. The orientations of the spins representing the low molar mass nematic molecules are updated during the simulations while the polymer chain units are kept frozen. The model allows us to investigate the molecular organization and the ordering expected across the cell. Moreover the response to the change in external field intensity and duration pulse is also studied.*

**Keywords**   Computer simulation; confined systems; Monte Carlo; polycrips

## Introduction

In the last decades composite materials containing Liquid Crystals (LC) and polymers have attracted the interest of researchers for their potentialities. A number of different technologies based on these composite materials have been proposed for realizing switchable/tunable Bragg diffraction gratings: H-PDLC, POLICRYPS, and POLIPHEM [1–3]. All these structures are produced by curing, under a laser interference pattern, an isotropic photosensitive liquid mixture, containing basically a prepolymeric material, a liquid crystal, and a photoinitiator. In Holographic Polymer Dispersed Liquid Crystals (H-PDLC) the result of the recording process is a grating consisting of a periodic distribution of small LC droplets, embedded in a polymeric matrix: larger droplets and a higher LC concentration are found in correspondence of the dark fringes, whereas smaller LC domains and polymer rich stripes are obtained in correspondence of the bright fringes [1]. An efficient diffraction

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grating is thus obtained due to the mismatch between polymer and LC refractive indices. The grating diffraction efficiency can be switched or tuned by applying an electric field which reorients the LC molecules, thus changing the refractive index modulation sensed by the impinging light. Despite these useful features, the presence of LC droplet in these structures implies problems of scattering loss and high switching fields.

To avoid these problems, POlymer-LIquid CRYstal-Polymer Slices (POLICRYPS) [2] and POlymer LIquid Crystal Polymer Holograms Electrically Manageable (POLIPHEM) [3] are realized with a uniform stripe-like grating morphology, in which the formation of LC droplets is completely avoided through the adoption of particular materials and fabrication processes. Even though POLICRYPS and POLIPHEM are realized according to different patented procedures, they share the same peculiar morphology.

The microscopic structure of POLICRYPS/POLIPHEM (PP) gives them some important features that differentiate their behaviour in comparison to traditional H-PDLCs, such as: i) small light scattering, hence high transparency, because no LC microdroplets are present; ii) the grating pattern is very well defined, thus very high diffraction efficiencies are possible; iii) they need weaker electric fields to be driven; iv) optical response is strongly polarization dependent, as unperturbed LC molecules are aligned parallel to the grating vector. For these peculiar properties, these gratings are very attractive for a number of applications in the field of optical communications [4].

Obviously, optical characterization of PP gratings in different wavelength ranges and a parallel theoretical modelling of their behaviour are mandatory for material optimization in view of real effective applications. Consequently, since few years these composites are under active study by various experimental groups [1–10] and have attracted a considerable interest both from the basic and the applied research point of view.

In particular, the electro-optical characterization of PP gratings has shown a peculiar, and unexpected, dynamical response [7]. The relaxation time (see Fig. 1),
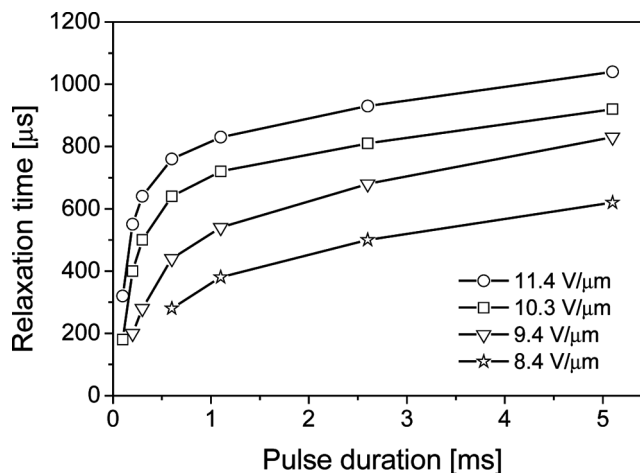


**Figure 1.** Relaxation time dependence on the pulse duration for different pulse amplitudes.

measured after the electric field is switched off, is dependent on the actual field previously applied (amplitude and pulse duration).

The phenomenological conclusion is that some kind of memory of the previously applied electric field remains even when only the elastic restoring torque is effective. The observed behaviour can be explained by assuming a partial anchoring breaking and restoring, for which the role of the LC-polymer interfacial region and its morphology should be fundamental. In fact, due to the fabrication process we cannot assume a 100% completed phase separation: instead a thin interfacial region, of the order of several molecular layers, is likely to exist where the LC and polymer molecules are interdispersed in a complex way. We may assume, on one hand, that it is this interfacial region that ultimately determines the unperturbed LC alignment, and, on the other hand, that the LC mobility in this region is quite different than in the LC bulk (a similar statement can be made also for polymer molecules).

If, for instance, we look at the time behaviour of the diffracted optical signal by a PP grating after removal of the electric field [7], it is evident that the rise of the recorded intensity, shown in Figure 2, cannot be fitted in any case by a single exponential function and requires a two-parameter function for a good fit.

These experimental results, shown in Figures 1 and 2, may suggest that two different phenomena are responsible for LC director reorientation, hence for the time behaviour of the optical response of a PP grating. We can easily indicate that one of them is related to the bulk elastic forces of LC deformation and guess that the second one is related to the interfacial interaction of polymer chains with LC molecules.

Theoretical approaches to understand these phenomena are still very limited [11]. To this aim, we have started Monte Carlo (MC) simulation [12] studies of a model of a composite liquid crystal polymer system to mimic the orientational behavior of a single cell of a PP under the effect of an external applied field. We have adopted a simple lattice spin model, with suitable boundary conditions which allowed us to calculate the change in the ordering of the system due to the application of the field. These simple models provide a very powerful approach to investigate
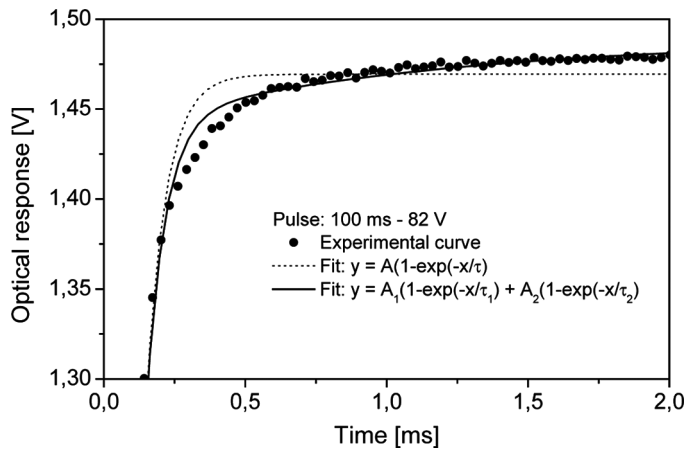


Inside the plot:
Pulse: 100 ms - 82 V
● Experimental curve
····· Fit: y = A(1-exp(-x/τ))
── Fit: y = $A_1$(1-exp(-x/$\tau_1$)) + $A_2$(1-exp(-x/$\tau_2$))

X-axis: Time [ms]
Y-axis: Optical response [V]

**Figure 2.** Time rise of the diffracted-beam optical signal (circles) after removal of the applied field; dashed lines indicates a single exponential fit, while the solid curve a double exponential fit.

both bulk and confined liquid crystal systems [13,14]. Also in this case the results were in qualitatively agreement with experimental results [6].

Here we wish to extend the simulation study modifying the boundary conditions and varying the external field intensity to better analyze the ordering inside a single POLICRYPS cell.

## The Simulation Model

The model studied here consists essentially of a porous polymer surface that is 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. The model is a lattice spin model based on the Lebwhol-Lasher (LL) [15] which consists of a system of interacting three dimensional headless vectors (spins) $\mathbf{u}_i$ located at the sites of a $L \times L \times (L+2)$ cubic lattice. The spins represent either the nematic or the polymer molecules and interact through a pair potential of the form:

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

where $\varepsilon_{ij}$ is a positive constant, $\varepsilon$, for nearest neighbor spins i and j and zero otherwise, $P_2$ is the second Legendre polynomial.

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.

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, we have studied the effect of changing the percentage of frozen (along Z) oriented particles from 50% to 5%, with a 5% variation every 2 layers, going from the bottom to the middle layer of the system. In all cases we assume for simplicity that the polymer unit-mesogen coupling is the same as the mesogen-mesogen one. In addition we have chosen free space boundary conditions at the top and at the bottom surface (layer n. 1), i.e., along the Z direction. 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 so as to induce an alignment of the molecules along the field direction (the X axis). The interaction energy 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 $\xi$ is a dimensionless constant representing the strength of the coupling to the external field $\mathbf{F}_x$.

The simulations were performed at a temperature deep in the nematic phase, i.e., $T^* = kT/\varepsilon = 0.2$, while we recall that the nematic-isotropic transition for the LL

model in the bulk is $T^* = 1.1232$ [16]. The total number of molecules (spins) considered was $N = 40 \times 40 \times 42 = 67200$. The updating of the lattice was performed in accordance with the standard Metropolis procedure [17]. After a certain number of MC equilibration cycles, with a cycle corresponding to N attempted moves, the field is applied to the system for the following 200 kcycles with the aim to reorient the particles in the x direction. To analyse the influence of the switching OFF and ON of the applied field, the procedure of switching OFF-ON-OFF is started after different timing of the first field application.

We calculate the tilt angle $\theta$ of the director with respect to the x-y plane, tilt which is maximum when the director is along z ($\theta = 90°$) and minimum when the director lies on the x-y plane ($\theta = 0°$).

## Results

We have started the simulations from a completely aligned system in the Z direction. In the first 500 kcycles of the simulation (see Fig. 3 red lines) the system is equilibrated, allowing for a reliable computation of physical quantities of interest, such as order parameters and energy. At the end of this equilibration period, a uniform electric field is applied to the system for at least a further 100 kcycles (green lines).
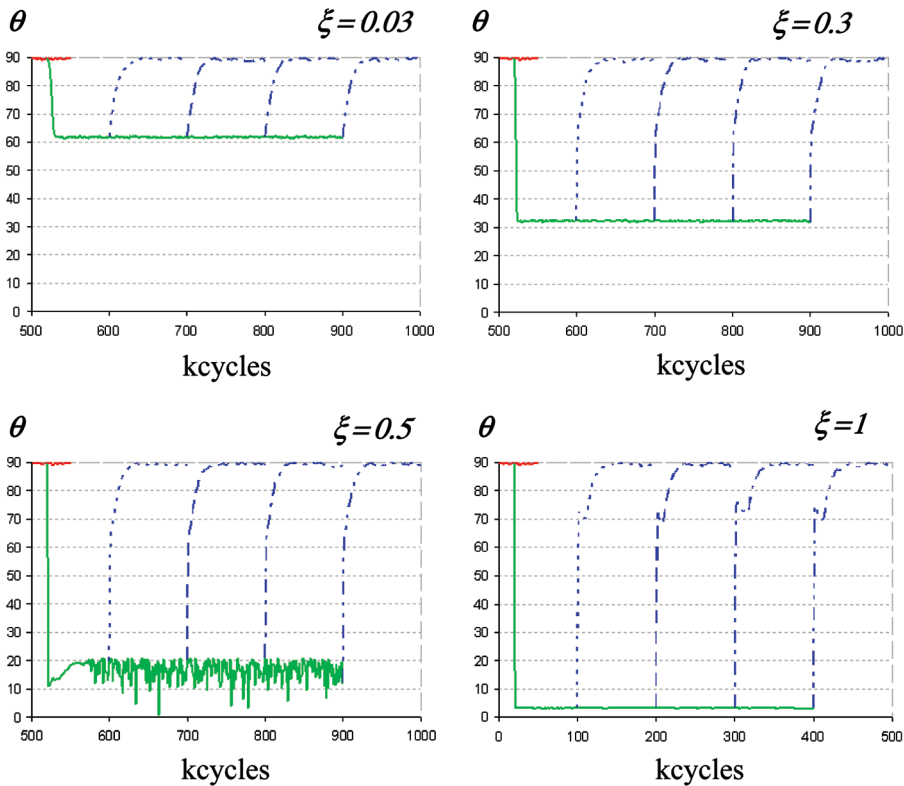


**Figure 3.** Dependence of the director angle $\theta$ with respect to xy plane on Monte Carlo cycles. The curves represent equilibration values of the overall $\theta$ when the external field is off (red–), when the field is turned on (green–) and successively again turned off (blue–) respectively.

sufficient to equilibrate again the system with the resulting overall reorientation of the preferred direction of the molecules along the field direction. 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 Figure 3, for four different field strengths, i.e a very low one, $\xi = 0.03$, two intermediate ones, i.e., $\xi = 0.3$ and $\xi = 0.5$, and a higher one, $\xi = 1.0$. It is interesting to notice that for $\xi = 0.5$ there is a significant fluctuation of the director and only for the higher field the alignment along the field direction is complete. That occurs 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 4.

For the lower field the alignment along z, induced by the frozen spins, tends to overcome the effect of the external field and then it takes more MC cycles to reorient the system along the X direction (see Fig. 4 first plate, green line) than to return to the original ordering (Fig. 4, first plate, blue line).

Increasing the field intensity, the reorientation along the field direction becomes faster (Fig. 4, green lines). When the field is switched off, and the molecules tend to align again along z as influenced by the "polymer" particles, only for the highest
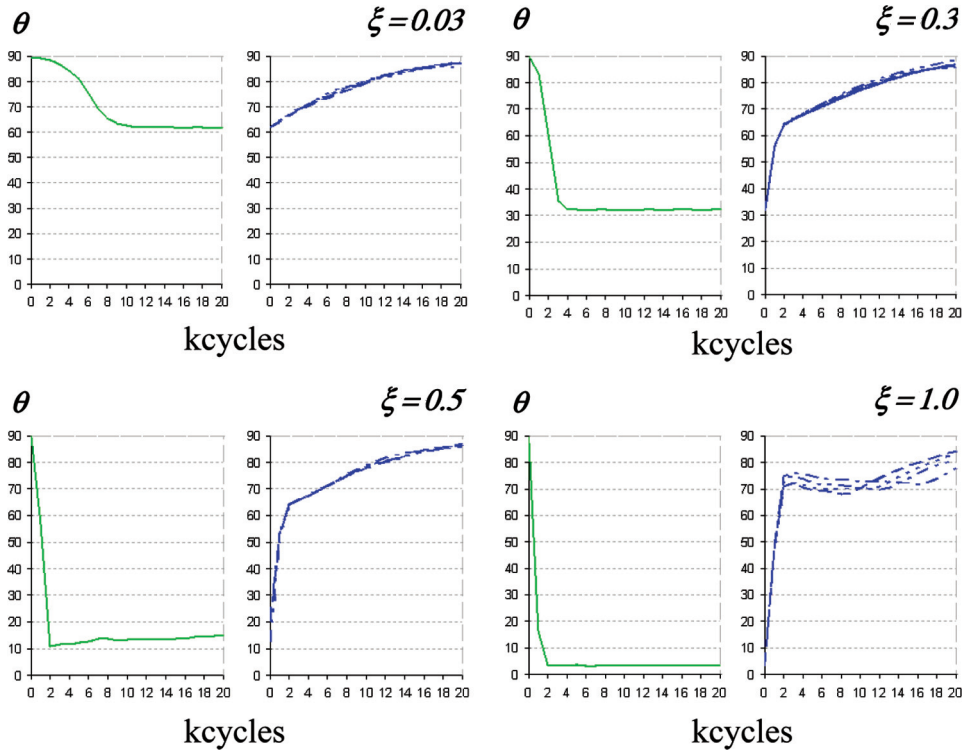


**Figure 4.** Decrease of the $\theta$ angle when the external field is applied along x (green–) and the reorientation along z with $\theta$ increasing to its initial values (blue–) when the field is turned off after different sequences of MC cycles.

field strength there is a rapid realignment. In the other cases it takes about 20 MC kcycles to have a complete realignment. For the case of highest intensity it is important to notice that, apart from the more rapid alignment along the z direction, there is also a memory effect. The alignment along z is not complete and the value of the tilt angle $\theta$, angle which determines the deviation from the xy plane, will not reach the maximum value of 90° (see Fig. 4, last plate).

The alignment of the spins along the field direction and the reorientation towards the Z direction induced by the frozen spins can be appreciated by looking at the snapshots presented in Figure 5 where a colour coding is adopted for the different orientation of the molecules. The nematic molecules in the liquid crystal-polymer region cannot reorient towards the X direction because the influence of the frozen spins dominates over the reorientation effect induced by the external field even for the strong 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 directly visualized as well. In a few thousands cycles a configuration similar to the initial one can be reached.
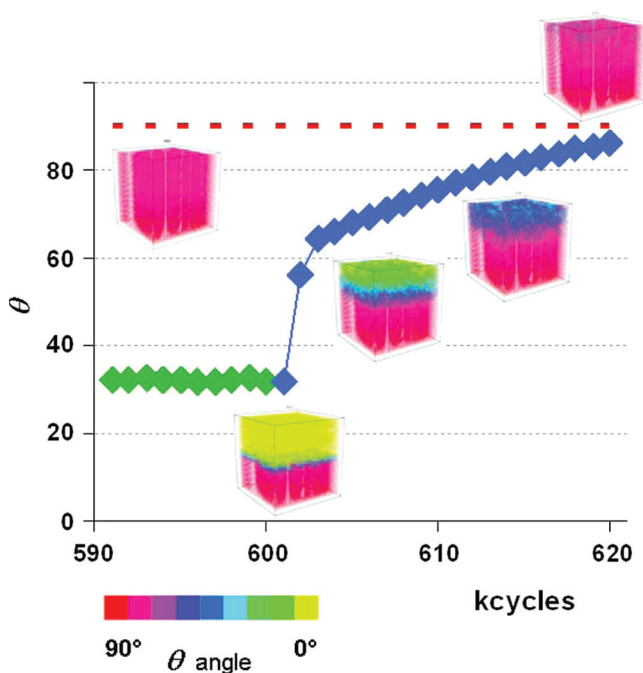


**Figure 5.** Snapshots of the molecular organization as obtained at five different moments of the simulations as indicated in the $\theta$ curves. Starting from top left the snapshots are taken with the field off, i.e., all the particles are aligned along z ($\theta = 90°$) then after the application of the field of strength $\xi = 0.3$. The other snapshots show the reorientation when the field is turned off and a configuration similar to the initial one (top right) is reached. The color coding shows the deviation from the Z direction ($\theta = 90°$, *see text*).

A quantitative evidence of that can be seen by looking at the evolution of the tilt angle $\theta$ across the cell and during the MC cycles in the different cases when the field is off. A complete overview of these results is shown in Figure 6.

Finally, a summary sketch of the simulation results for the director orientation across the cell, as shown in Figure 7, gives a clear view of the behavior of tilt in the different virtual layers of the cell. In fact it is apparent (Fig. 7d) that in the bulk LC region only for the very weak field the nematic director is not completely and rapidly reoriented. On the other hand, in the interfacial region the slow term reorientation is
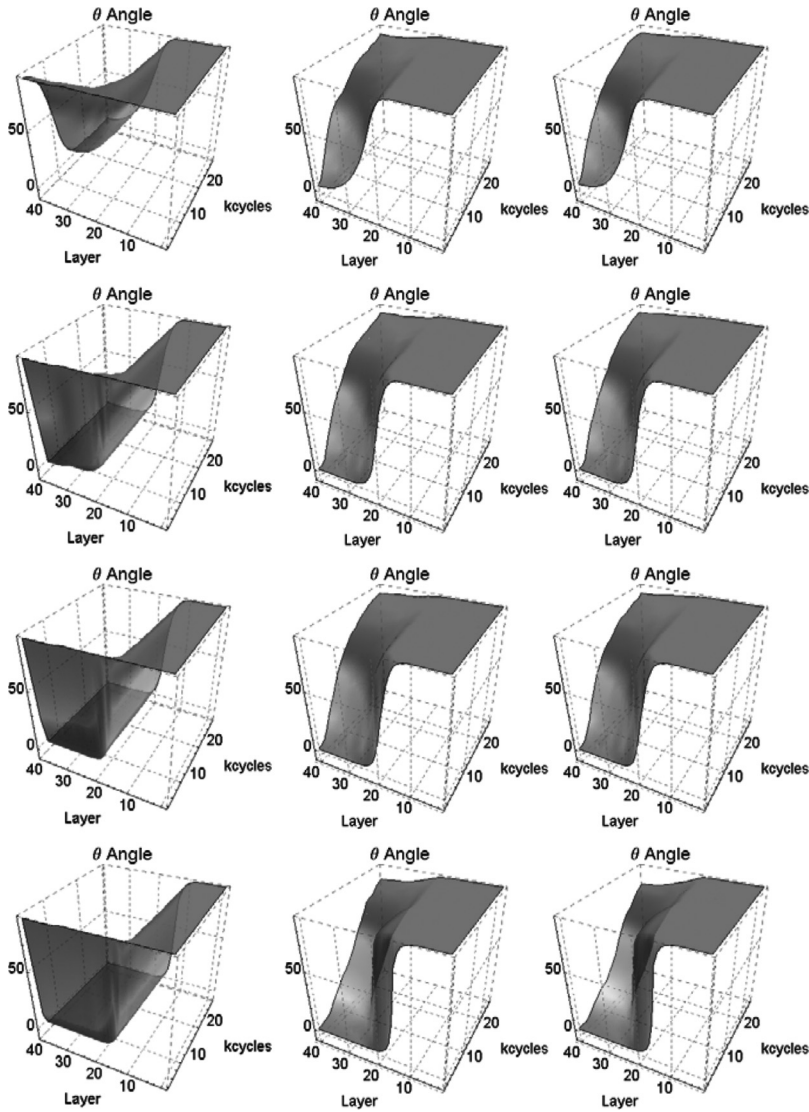


**Figure 6.** MC evolution of the director angle $\theta$ calculated at each layer of the cell when the field is off (1st column) and when the field is applied (2nd and 3rd columns). The calculations are for the field strengths $\xi = 0.03$, $\xi = 0.3$, $\xi = 0.5$, $\xi = 1.0$, from the first to the bottom row, respectively.
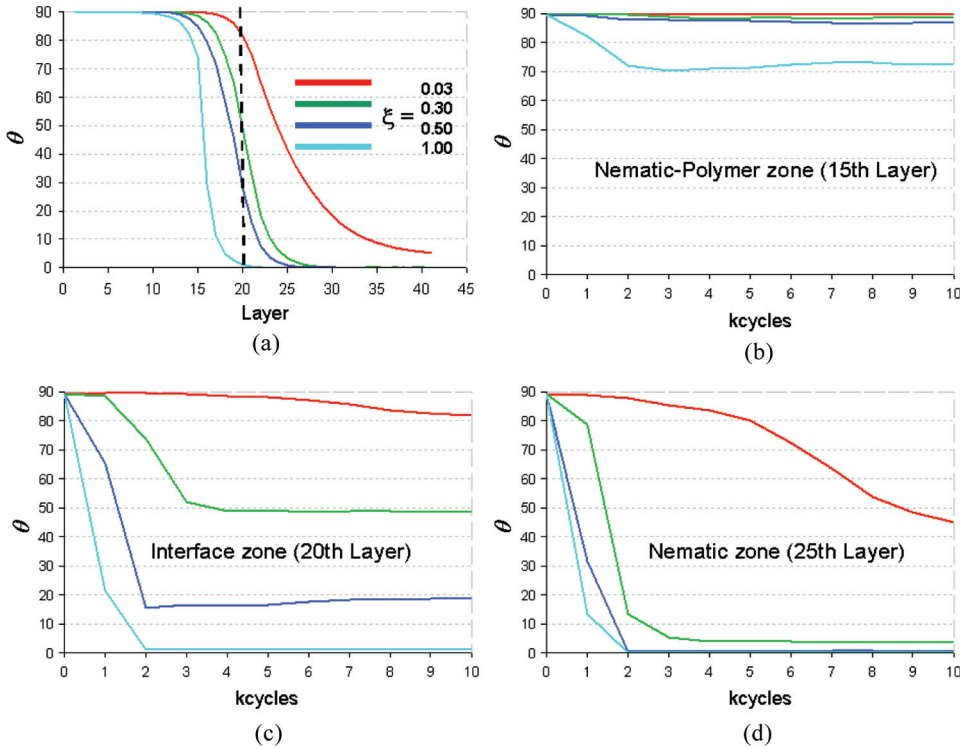
**Figure 7.** (a) The dependence of the $\theta$ angle across the cell, starting from the bottom layer, after 5 kcycles from the application of the fields; (b–d) $\theta$ angle vs. kcycles for the different field strengths in the different regions of the system.

greatly varying with the field strength and, even more important, in the mixed LC-polymer zone, which can be assumed as the region governing the anchoring, only the strongest field is able to reorient the LC director. This fact can be responsible for the memory effect noticed in the fourth plate of Figure 4 where it is shown that the director relaxation after the field removal is not complete up to the initial $\theta = 90°$ but it is lower the longer the pulse applied. A comparison with the experimental findings shown in Figures 1 and 2 is then possible, at least at semi-quantitative level. In fact, considering that the diffracted optical signal is mostly affected by the bulk behaviour we can assume that the optical response upon switching on the field should behave regularly and not depend on the field strength as shown, for instance, in Figure 7d. On the other hand, the optical response during the director relaxation should be dictated by the actual anchoring condition "seen", namely by the behaviour of the interfacial and interdispersed regions. As a consequence, after removal of stronger and longer electric pulses, we observe a fast relaxation but not a complete one. To reach a full relaxation to the unperturbed initial state we should wait for the interfacial and intermixed regions to go back to their initial configuration with a different much slower time constant, thus restoring the unperturbed anchoring conditions.

However, the latter process cannot be well reproduced by our simulations because of our starting assumption that spins representing polymer molecules are kept frozen. We can then state that a comparison of the present study with the

experimental dynamical characterization of PP gratings confirms and renders even stronger the hypothesis of a double process, one occurring in the bulk and the other in the interface region, responsible for the director relaxation. It is also emerging that a quantitative evaluation of the two different time constants ruling the two processes needs a more realistic model for the molecular simulations, in which the rather crude assumption of frozen polymer molecules should be released.

## Conclusions

We have studied a simple anisotropic lattice model for a nematic-polymer inter-disperse interface inducing some homeotropic alignment in the adjacent nematic with the aims of investigating, by means of Monte Carlo simulations, the effect of the application of an external field on the ordering of a composite nematic-polymer system. We have considered a single cell of a prototype POLICRYPS/POLIPHEM system. We have investigated the behaviour of the system under the application of external field pulses of different intensities and duration. The simulation results clearly show a different behaviour in the nematic region, in the nematic-polymer zone and at the interface and that these different behaviour is critically dependent on the field strength. In particular, varying the field strength we find a change in the speed of reorientation along the field direction and, even more importantly, a difference in the final director state reached upon relaxation.

A deep fault in the local ordering, close to the interface region, occurs as the field increases (see Fig. 7a), while no significant difference seems to exist when the external field is applied for longer pulses. These results seem to be in qualitative agreement with experimental observations. The dependence of the relaxation time on the previously applied electric field, a memory effect, possibly connected to the local inhomogeneities introduced the polymers chain segments playing a role similar to that of quenched disorder [18,19] and the possible occurrence of two different physical phenomena at different time scales are confirmed. While these findings highlight a fairly general origin of the sample history effects experimentally observed, it seems clear that a more chemically oriented simulation study at molecular [13] or atomistic [20] resolution, able to mimic in a more realistic way the behaviour of the polymer-LC intermix zone could go further in the detailed understanding of the electro-optical response of PP gratings, thus helping in the design of better performing devices.

## Acknowledgments

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