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Chirality Transfer from Helical Nanostructures to Nematics: A Monte Carlo Study

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We present a simple Monte Carlo study of orientational ordering in a nematic liquid crystal with embedded chiral nanostructures. The nanostructures are shown to impose bulk chiral order in the nematic only for large enough values of the chiral pitch.

Keywords nematics; confinement; chirality; nanostructures; Monte Carlo simulations

Introduction

Over the past two decades, liquid crystals in strongly confined systems, such as nematic droplets, pores, and shells [1,2], have attracted considerable attention both from the theoretical and applicative point of view. A rather intriguing confinement geometry is provided also by engineered submicrometer helical columns capable of inducing chiral nematic order [3]. As such ordering can result in selective reflection of circularly polarized light, this may be particularly appealing for applications, e.g. in photonics [4], and a variety of substrates, such as chiral polymer filaments [5,6] or inorganic twisted structures [3,7–9] designed to template chiral order in a nematic have been and are being continuously proposed. While the idea of using a nematic to transfer chirality from the chiral nanostructure to the medium is clearly appealing, very little is known from the theoretical and simulation point of view on how this chiral transfer effect can be rationalized. For instance, it is not obvious what is the effect of changing the pitch of the chiral structure on the induced order and what is the effect of combining chiral templating agents of opposite handedness.

This paper presents a preliminary attempt to tackle these problems, using a simple Monte Carlo (MC) simulation study of nematic ordering induced by a regular array of straight helical fibers (cylinders). It is focused on identifying the appropriate conditions allowing the cylinder-induced chirality to propagate into the nematic bulk.

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Model and Simulations

To simulate the nematic liquid crystal we use a classical model system proposed by Lebwohl and Lasher (LL) decades ago [10,11] and applied to a variety of confined systems [12,13,14,15]. In the LL model, nematic molecules or rather close-packed molecular clusters are represented by rotors ("spins") arranged into a simple cubic lattice. Denoting the orientation of the ith spin of the LL mesogen by a unit vector $\mathbf{u}_i$ and the interaction strength constant by ϵ_{ij}, the total interaction energy is given by

$$U = -\frac{1}{2}\sum_{i,j\in\mathcal{N}} \epsilon_{ij} P_2(\mathbf{u}_i \cdot \mathbf{u}_j) - J \sum_{k\in\mathcal{N},l\in\mathcal{S}} \epsilon_{kl} P_2(\mathbf{u}_k \cdot \mathbf{s}_l), \tag{1}$$

where $P_2(x) = (3x^2 - 1)/2$ is the second Legendre polynomial, $\mathcal{N}$ is the set of nematic and $\mathcal{S}$ of helical fiber spins. Moreover, ϵ_{ij} is a positive coupling constant, ϵ, for nearest neighbor spins and zero otherwise, and J represents the relative strength of coupling between nematic ($\mathbf{u}_k$) and the fiber spins ($\mathbf{s}_l$), which are kept fixed during the simulation. The confinement agents, i.e. the chiral helical columns, are modeled via straight cylinders of 4 or 6 lattice units diameter, carved from the cubic lattice. Inside the cylinders the rotor orientations are kept fixed and arranged to provide the desired helical boundary conditions (see Fig. 1). For simplicity, the interaction constants ϵ for the nematic-nematic and nematic-cylinder interaction are chosen to be equal ($J = 1$), which implies rather strong surface anchoring.

Two sample types are considered: sample A contains a single chiral cylinder, while sample B contains a pair of cylinders with opposite chirality (Fig. 1). Periodic boundary conditions are applied at the simulation box boundaries, which results in a regular fiber array.

Our MC calculations are performed using the standard Metropolis algorithm, as described in detail in Refs. [11,15], at $k_B T/\epsilon = 1$, which is deep in the orientationally ordered nematic phase, as the bulk LL model has the nematic-isotropic transition at $k_B T/\epsilon = 1.1232$

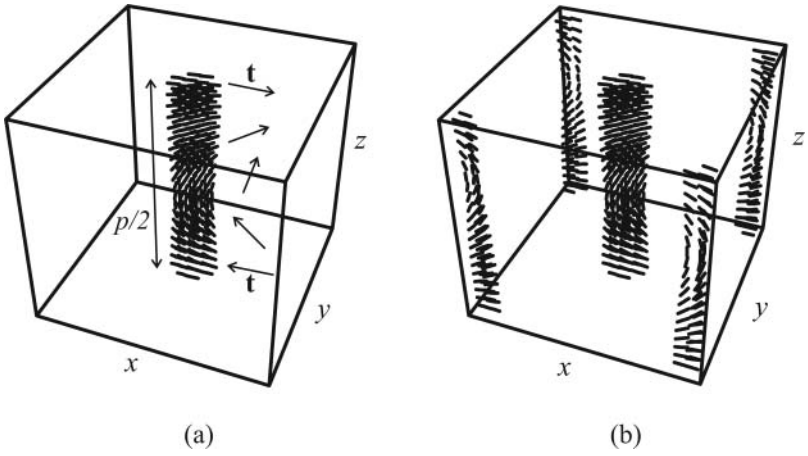

Figure 1. A schematic representation of the simulation box containing chiral cylinder(s): the rods represent the fixed spins imposing the boundary conditions. Above, p denotes the chiral cylinder pitch and **t** is a unit vector along the locally imposed helical easy axis. (a) A single cylinder (sample A), (b) a pair of cylinders with opposite chirality (sample B).

[11]. The simulated system size is $30a \times 30a \times 30a$, where a stands for the lattice spacing, yielding a total of 27000 spins.

To analyze the simulation output, different observables can be calculated. In particular, for a chiral system like ours it is interesting to calculate a local chiral order parameter defined as [14,16]

$$P_2^c = \left\langle \frac{3}{2}(\mathbf{u}_i \cdot \mathbf{t})^2 - \frac{1}{2} \right\rangle \tag{2}$$

for each lattice site i. Here, $\mathbf{t}$ is a unit vector along the easy axis imposed by the chiral cylinder at the corresponding z-layer containing the ith lattice site, and $\langle \cdots \rangle$ denotes an average over MC cycles. P_2^c expresses how well the local structure is twisted and tends to 1 for a perfect helix. It has been used before to quantify how the molecular organization in a pixel of Twisted Nematic display is actually helical in the absence of an external field [14,16]. Here we use it to monitor how chirality is transferred from the helical fiber to the nematic.

As an alternative, one can similarly consider a chiral rotational invariant introduced by Stone [17]

$$S_{221} = -\sqrt{\frac{3}{10}} \left\langle (\mathbf{u}_i \cdot \mathbf{u}_j \times \mathbf{r})(\mathbf{u}_i \cdot \mathbf{u}_j) \right\rangle, \tag{3}$$

where $\mathbf{r}$ is the intermolecular vector connecting the lattice sites i and j. Finally, to visualize the nematic director field, for each lattice site i a MC cycle-averaged nematic ordering matrix

$$\mathsf{Q}_i = \frac{1}{2}(3 \langle \mathbf{u}_i \otimes \mathbf{u}_i \rangle - \mathsf{I}) \tag{4}$$

can be calculated. Then, the local nematic director is obtained by diagonalizing Q_i as the eigenvector corresponding to the largest eigenvalue. (The latter is identified as the standard nematic order parameter [18].)

Results

Let us focus on sample A first. Fig. 2 shows three horizontal director field cross sections for two values of chiral pitch p. It is evident that for large pitch ($p/a = 60$) the director field follows the rotation of the chiral easy axis $\mathbf{t}$ along z; hence, the chiral order of the cylinders is transferred and propagates into the nematic bulk. For the small pitch ($p/a = 30$), on the contrary, the free-energetic cost of a bulk twist deformation is higher; therefore, far enough from the cylinder the nematic remains undeformed. This is also confirmed by Fig. 3 showing the P_2^c order parameter profiles: for $p/a = 60$, P_2^c does not change substantially from layer to layer when moving along the z-axis, while for $p/a = 30$ it does. Similar conclusions can be made also by inspecting the S_{221} profiles shown in Fig. 4. Here nonzero S_{221} values indicate the presence of chiral twist in the system. Indeed, $S_{221} \neq 0$ is observed throughout the sample for large pitch only, while in the small pitch case this is limited to the immediate vicinity of the cylinder.

It is also interesting to explore what happens when the aligning effects of two cylinders with left and right handed chiralities meet in the same simulation box (sample B). We focus on $p/a = 60$, i.e., a large pitch that should facilitate the formation of a bulk chiral phase. However, as it can be deduced from Fig. 5, now there appears to be no net chiral

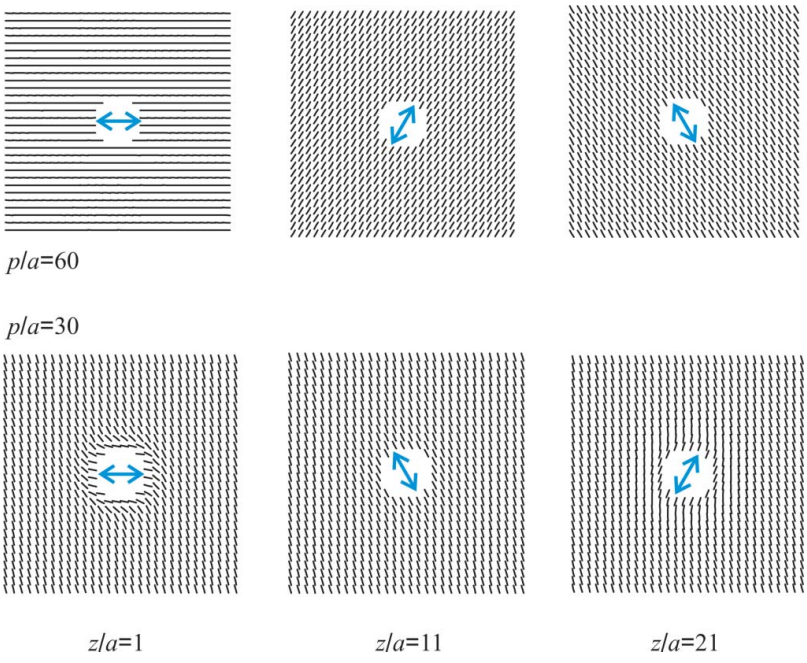

Figure 2. Director fields (xy cross sections) as obtained from MC simulations for sample A. The pictures are for two different pitch lengths: large ($p/a = 60$, *top*), where the nematic follows the twist of the cylinder surface, and small ($p/a = 30$, *bottom*), where this is not the case. Three different horizontal layers at different z/a are shown. The arrows denote the local easy axis **t**.

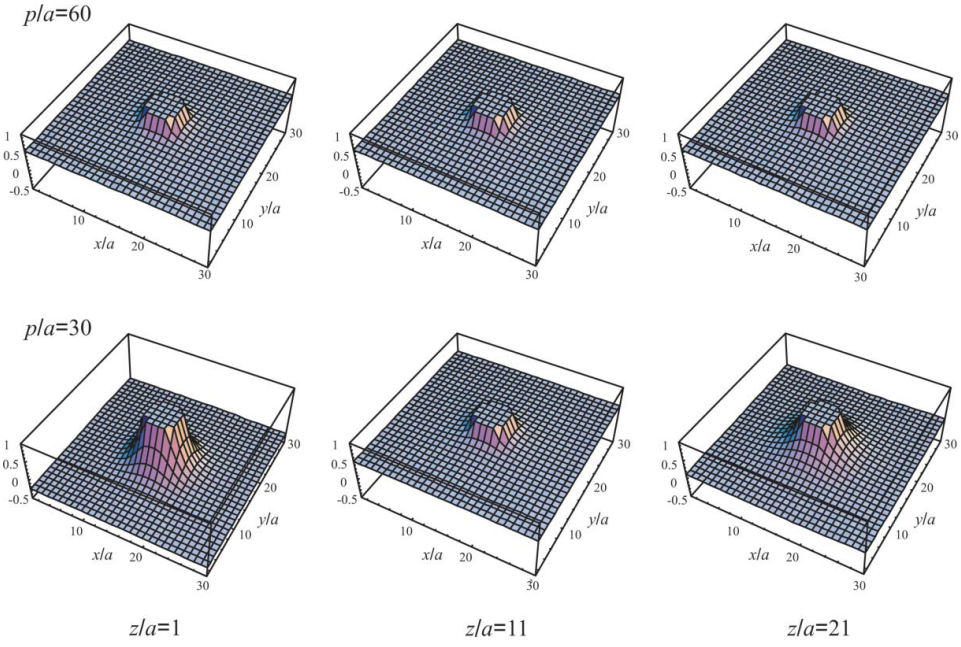

Figure 3. The chiral order parameter P_2^c as obtained for sample A at three different layers. *Top*: large pitch ($p/a = 60$), *bottom*: small pitch ($p/a = 30$).

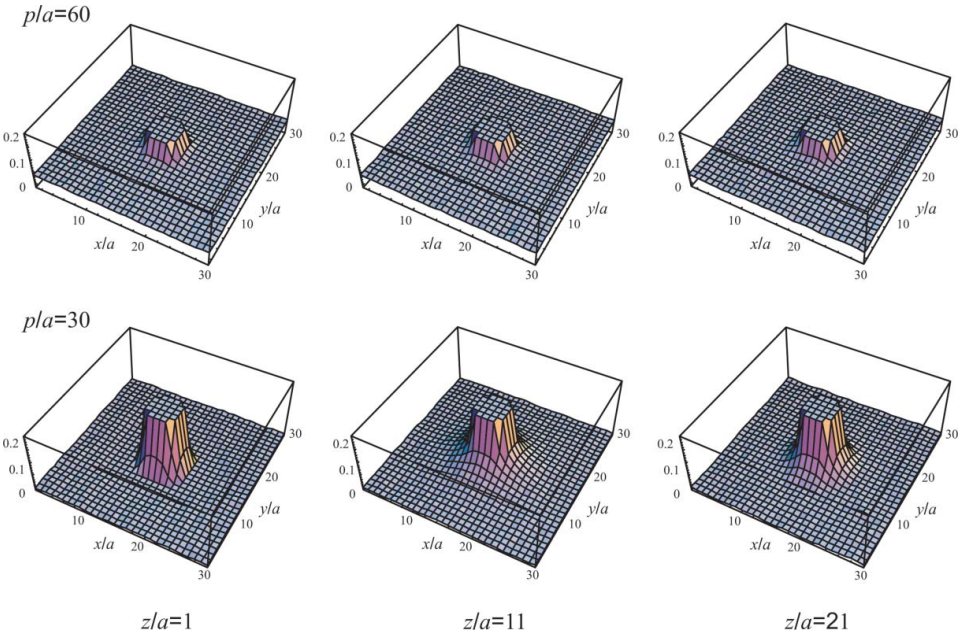

Figure 4. Same as Figure 3, showing the chiral invariant S_{221} instead of P_2^c.

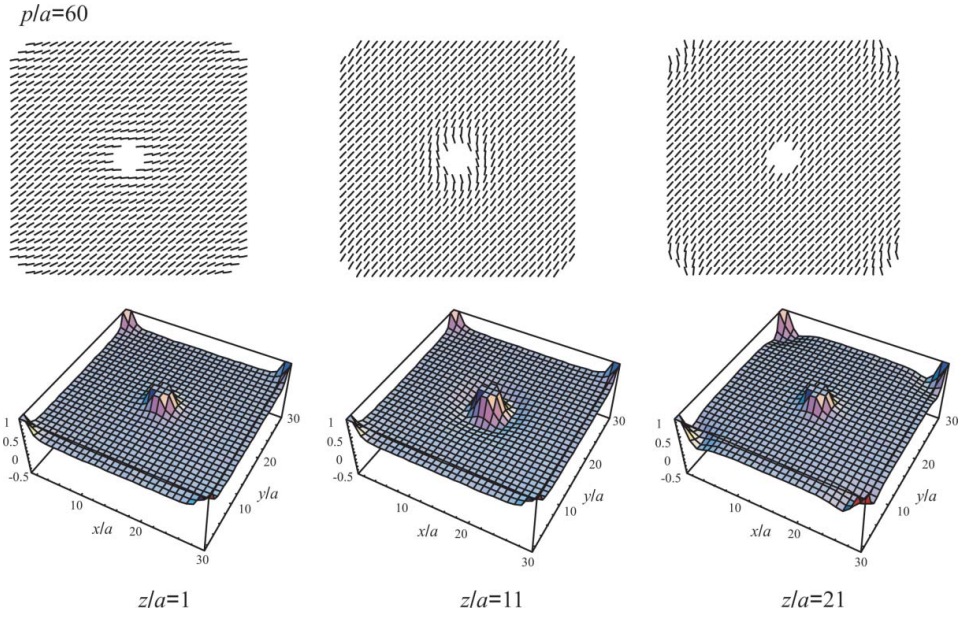

Figure 5. Director fields (xy cross sections, *top*) and the standard nematic order parameter (*bottom*) for sample B and at three different horizontal layers. The results concern the case of large pitch ($p/a = 60$); there is no chiral ordering in the bulk. The residual twist deformation observed close to the cylinders reflects in a slight decrease of the nematic order parameter (*bottom*, $z/a = 11$).

aligning tendency in the system, and even for this value of p/a the chiral ordering does not propagate into the bulk. This in a way is the analogue at mesoscopic level of having a racemic mixture in solution, where chiralities of opposite twist compensate.

Conclusions

We have performed a simple Monte Carlo study based on the Lebwohl-Lasher lattice model to simulate the aligning influence of chiral nanostructures embedded in a nematic liquid crystal. Our results show that significant bulk chiral ordering can be observed only when the chiral pitch is sufficiently long. This is somewhat surprising, since the shorter pitch, i.e. more strongly twisted fiber has a lower chiral templating effect on the nematic it is immersed in. We have also seen that the inclusions with opposite chirality seem to suppress bulk chiral ordering. Although the study is a preliminary one, it shows the potentiality of these mesoscopic level spin lattice simulations in helping to understand chiral nanostructure effects and the conditions required for an effective transfer of chirality from the templating agent to a nematic.

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