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Structures and transitions in thin hybrid nematic films: A Monte Carlo study

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We confirm by Monte Carlo simulations of a Lebwohl-Lasher lattice spin model the existence of a biaxially ordered nonbent structure in a liquid-crystalline cell subject to opposing boundary conditions. We report on the observation of the bending transition from the biaxial to the bent-director structure when the temperature of the system is lowered. The structural transition is monitored both by the change of the order parameters and by heat capacity. We discuss the thickness dependence of the transition temperature by means of wetting-induced phenomena and elastic deformations. We propose the correspondence to the phenomenological description, which agrees well without any fitting parameters.

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Liquid crystals confined to various geometries attract a lot of attention both from basic research and from a technological point of view [1]. In the case of the former, one is interested in understanding the combined effect of the confinement, temperature, and anchoring on phase transitions, molecular ordering, and molecular organization inside these systems. For example, if a nematic liquid crystal is subject to competing boundary conditions, its order no longer depends only on the temperature, but it also depends (mainly) on the strength of the interaction of the liquid-crystalline material with the confining substrates (anchoring) and the affinity of the material to elastically deform. In a hybrid nematic film the confining walls tend to align the molecules in different directions, usually, one wall along the direction close to the surface normal while the other substrate forces the molecules to lie in the plane of the wall. In the case of degenerate planar anchoring at one wall, the macroscopic order can either preserve the uniaxial symmetry of the system (yielding negative order parameter at the degenerate planar wall) or the uniaxial symmetry can be broken if the director field changes continuously from one wall to the other. In that case only one of the energetically equivalent directions in the plane is selected at the degenerate planar wall. Due to the broken continuous rotational symmetry, the boundary conditions induce creation of topological defects, which are widely studied [2,3]. Another interesting situation occurs if the degeneracy of planar anchoring is lost and the system exhibits two mutually perpendicular preferred directions. Such hybrid nematic cells are used for studying aligning properties of the confining substrates [4,5] and are the subject of present study.

In the hybrid nematic cell, deep in the nematic phase, the preferred local orientation of molecules either continuously changes from one confinement induced direction to the other (bend and splay deformations of the director field), or the molecules are, on average, oriented along the direction induced by the substrate whose anchoring is much stronger than that of the other. The first case corresponds to strong surface coupling where $d > d_c = |\lambda_1 - \lambda_2|$ (λ is the so-called extrapolation length that measures the affinity of the material to elastically deform with respect to the anchoring strength [6], and d is the thickness of the cell). The latter case occurs for $d < d_c$. Both structures with either bent or uniform director field together with the structural transition between them (the latter is induced by changing the cell thickness) have been observed experimentally and are used to determine anchoring parameters of a given confining substrate in combination with a certain liquid-crystalline material [4,5]. On the other hand, close to the isotropic-nematic phase transition and in the case of high confinement induced frustration, another ordered structure has been predicted within the phenomenological theory of nematic liquid crystals—the biaxial structure with two strata of the film, each with a uniform director orientation dictated by the respective wall and, thus, perpendicular to one another, separated by a sharp interface [7–9]. Up to now there has been no experimental evidence of this structure since its existence is limited to a very narrow temperature interval close to the isotropic-nematic phase transition and since it is only realized in hybrid cells with strong and comparable anchoring strengths of the two confining substrates [9]. The biaxial structure has also not yet been found in numerical experiments within the Monte Carlo simulations, although an attempt has been made in this direction by Cleaver and Teixeira [10] employing the hard Gaussian overlap potential. However, in their study the conditions for the biaxial structure to occur were not fulfilled due to the highly unlike surface potentials they used to mimic homeotropic and planar anchorings. The hybrid conditions in nematics were also studied by means of a density-functional theory [11]. The study revealed the existence of the steplike director's profile characteristic for the biaxial structure [9]; however, the structure was spatially asymmetric because of the interparticle interaction promoting planar alignment.

We have tackled the description of a highly frustrated hybrid nematic cell by performing Monte Carlo (MC) simulations on a Lebwohl-Lasher (LL) lattice spin model system [12–14]. Within this model the spins—single liquid-crystal

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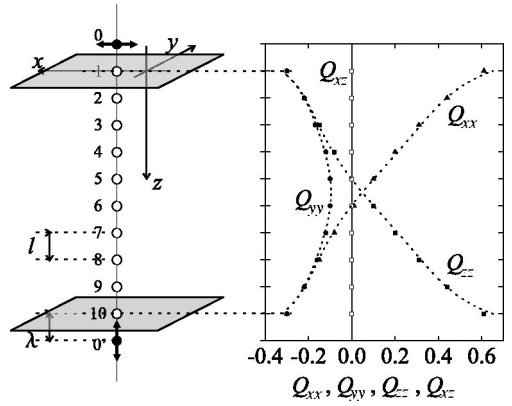

FIG. 1. Left: Sketch of a spin lattice in a $h=10$-layer hybrid cell. Full circles denote fixed layers of spins and arrows denote the orientation of the corresponding easy axis. Right: Typical variation of components of the tensor order parameter above the bending transition ($h=10$, $T^{MC}=1.14$). Symbols correspond to appropriate parameters calculated from the MC simulation and the lines correspond to the results of the phenomenological description for $l=\lambda=0.37\xi_{NI}$.

(LC) molecules or clusters of molecules whose short-range order is maintained in the examined temperature interval—are located at the sites of a cubic lattice and are represented by three-dimensional unit vectors $\hat{u}_i$ corresponding to the director within the cluster. (A typical magnitude of the correlation length in the vicinity of the isotropic-nematic phase transition $\xi_{\mathrm{NI}}\sim 10$ nm yields approximately 50 molecules per spin.) The interaction between the spins is modeled by a second-rank LL potential [12], $U_{ij}=-\epsilon_{ij}P_2(\hat{u}_i\cdot\hat{u}_j)$, where $\epsilon_{ij}=\epsilon>0$ for the nearest-neighbor spins and it is zero otherwise, and P_2 is the second-rank Legendre polynomial. The LL lattice spin model is known to reproduce well the bulk behavior of the nematic liquid crystal [12,15]. In the last decade it has been successfully employed also in the studies of confined nematic systems [3,14]. The confinement is introduced as an additional layer of fixed spins whose orientation corresponds to the direction induced by the walls. In our case the fixed spins in two additional layers lie (i) along a certain direction parallel to the layer (let us say the x direction, in the first layer) and (ii) along the layer normal (let us say the z direction, in the other layer). A sketch of a MC setup is depicted in Fig. 1. In our model, the LC spin-LC spin interaction and the LC spin-fixed spin interaction are of equal strength. In that case, the layer distance can be recognized as the extrapolation length—the length on which the order is extrapolated to the one induced by the confinement—and the actual thickness of the LC cell reads $d=(h-1)l$, where l is the layer distance. With such a choice of interactions one is left with only one variable—the Monte Carlo temperature $T^{MC}=k_BT/\epsilon$, where the bulk isotropic-nematic phase transition occurs at $T_{NI}^{MC}=1.1232\pm 0.0006$ [15].

We have performed our simulation on the lattices of $30\times 30\times h'$ spins, where $h'=h+2$ represents h layers of nematic LC spins and two additional layers of fixed spins. At the four lateral faces of the simulation sample we have employed periodic boundary conditions to mimic the bulklike conditions. The standard Metropolis procedure [16] has been used to update the lattice for a certain number of cycles, where a cycle is a set of $30\times 30\times h$ attempted moves. Simulations at the lowest temperature started from a completely homeotropically aligned configuration. At higher temperatures the starting configuration was the already equilibrated one at a lower temperature. The state of a system was monitored by tensorial nematic order parameter calculated with respect to the fixed frame spanned by the orthonormal triad $(\hat{e}_x,\hat{e}_y,\hat{e}_z)$; $\mathsf{Q}=\langle(3\hat{u}_i\otimes\hat{u}_i-\mathsf{I})/2\rangle$, where $\hat{u}_i$ is a unit vector along the long axis of the ith spin and $\langle\cdots\rangle$ represents the ensemble average over each layer and over 30 000 Monte Carlo cycles after the system has been equilibrated (the equilibration took approximately 60 000 MC cycles for thinner cells and up to 80 000 MC cycles for thicker ones). A typical variation of the tensor order parameter is represented in Fig. 1. The diagonal components of tensor Q represent the degree of order with respect to axes x, y, and z. The off-diagonal components $Q_{\alpha\beta}$ represent the bending of the director field in plane (α,β). In a system with preferred directions $\hat{e}_x$ and $\hat{e}_z$, it can be assumed that the average director does not bend out of the plane of the two preferred directions, i.e., along the y direction. Indeed, parameters Q_{xy} and Q_{yz} were zero within the numerical accuracy and "thermal" fluctuations. On the other hand, the parameter coupling the two preferred directions x and z was used to distinguish between the biaxial and bent-director structure,

$$Q_{xz}=\tfrac{3}{2}\langle \sin 2\beta_i \cos\alpha_i\rangle, \tag{1}$$

where β_i is the azimuthal angle of the ith spin with respect to the layer normal and α_i is the angle between the spin's projection to the layer and the x direction. In the case of a nonzero parameter Q_{xz}, the tensor order parameter was diagonalized. As expected, one of the eigenvectors was fixed along the y direction, whereas the two others (nematic and secondary director) lay in the (x,z) plane.

A typical plot of the director's tilt angle (with respect to the z axis) as a function of temperature is shown in Fig. 2. As an inset, the corresponding bending parameter Q_{xz} is depicted. Deep in the nematic phase the director's tilt angle uniformly decreases from 90° at the first layer of fixed spins (easy axis along $\hat{e}_x$) to 0° at the other layer of fixed spins. The structure corresponds to the continuously changing director field in the bent-director structure. At temperatures above certain temperature $T_C^{MC}\lesssim T_{NI}^{MC}$, the director's tilt profile becomes a steplike function of the position in the cell. In each half of the cell, the director lies along the easy direction of the closest layer of fixed spins, i.e., in the x direction in the first half of the layers and in the z direction in the other half (see the sketch in Fig. 1). The tensor order parameter is diagonal within the frame of the orthonormal triad $(\hat{e}_x,\hat{e}_y,\hat{e}_z)$.

The difference between the director profiles in the two ordered structures is accompanied by the difference between scalar order parameter and biaxiality profiles. Deep in the nematic phase the degree of order along the local director

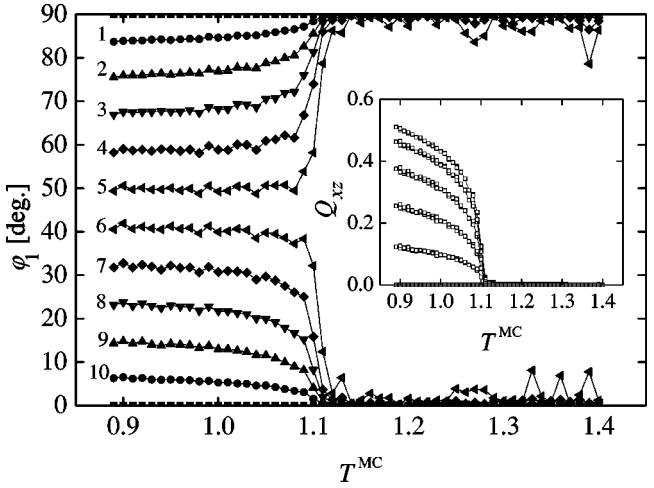

FIG. 2. Director's tilt angle with respect to the z direction in a $h=10$-layer hybrid cell as a function of MC temperature. Different lines correspond to the tilt angle in distinct layers, labels denote position of the layer as denoted in Fig. 1. At high temperatures, the order in the middle of the cell is fairly small, thus, the determination of corresponding tilt angle is delicate. Inset: the bending parameter Q_{xz} in the same cell. The upper the line, the closer is its location to the middle of the cell. Lines are guides to the eye.

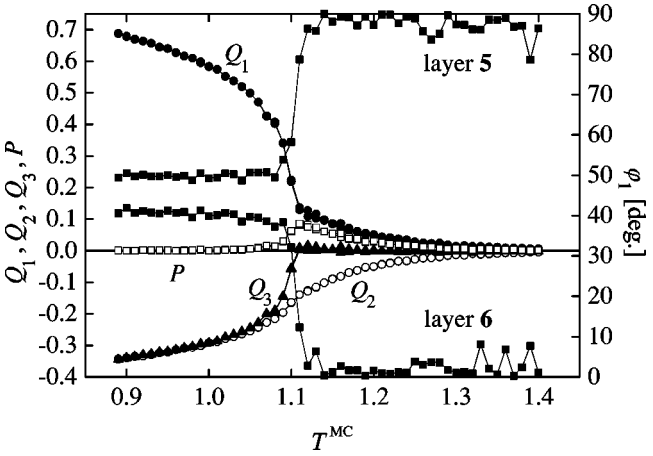

FIG. 3. Eigenvalues of the macroscopic tensor order parameter, biaxiality, and director's tilt angle in the two layers closest to the middle of the $h=10$-layer cell as a function of MC temperature; $Q_1=S$ is the scalar order parameter. Lines are guides to the eye.

only slightly varies through the hybrid cell and the local symmetry around the director is uniaxial. This symmetry is lost in the proximity of the structural transition, however, the biaxiality is fairly small. On the other hand, there is a strong variation of the order in biaxial structure. It is characterized by a strong decrease of the degree of order and relatively strong increase of biaxiality in the middle of the cell, where the two directors (nematic and secondary) exchange. As already discussed within the phenomenological description of the hybrid nematic cell [9], the decrease of order in the middle of the biaxial cell compensates the energy cost of the sharp variation of the director field.

Different properties of both structures can be most easily monitored in the middle of the cell. Eigenvalues of the tensor order parameter and the director's tilt angle in the two layers closest to the middle of the cell are depicted in Fig. 3. At the point where the steplike profile changes to the continuous regime, the slopes of the growth of the scalar order parameters change, indicating that the regions of the two structures are separated by a structural transition. The same can be observed also in other layers, however, less pronounced. Another indication of the structural transition between the two ordered states is given by the inspection of the energy of the system and the corresponding heat capacity. As indicated in Fig. 4(a) the obtained heat capacity profile shows a well-defined peak at temperature of the change of the director's profile. Additionally, a number of weaker peaks can be observed. Due to numerical uncertainties we cannot be sure whether some of them correspond to subsequential ordering transitions in distinct layers.

We have performed simulations of hybrid cells with different number of LC layers—$h=4,6,8,10,14,20$. In all of them, deep in the nematic phase the director field is bent and above the bulk isotropic-nematic transition temperature it is steplike. The temperature of the structural transition depends on the cell thickness: the thicker the cell closer is the transition temperature to the bulk transition temperature. In the two thickest cells the high temperature structures are characterized by two surface ordered layers with mutually perpendicular directors which are not in contact with each other as

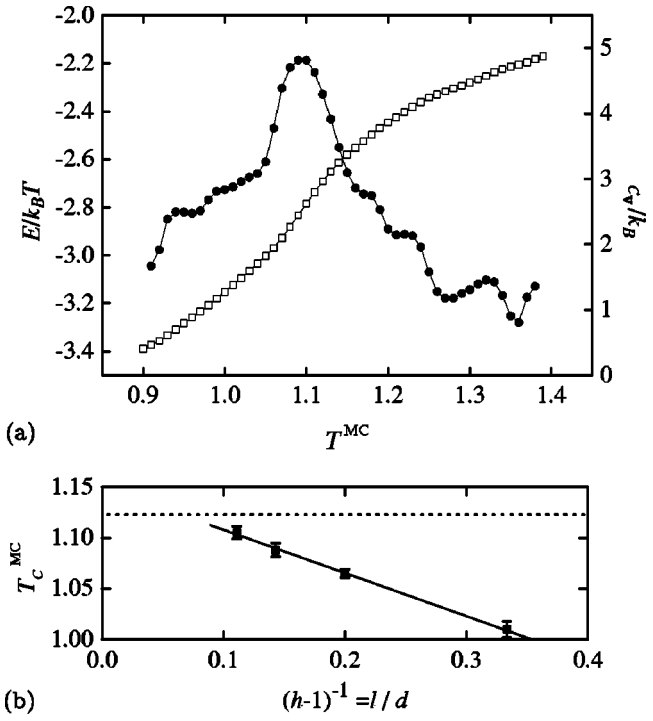

FIG. 4. (a) Energy of the $h=10$-layer hybrid nematic cell (empty squares) and the corresponding heat capacity (full circles). The highest peak located at $T_C^{MC}\approx 1.1$ corresponds to the structural transition between bent-director and biaxial structures. Lines are guides to the eye. (b) The temperature of the structural transition as a function of the cell thickness. The solid line denotes the linear fit and the dotted line indicates the bulk isotropic-nematic phase transition temperature.

is the case in the biaxial structure in thinner cells. On lowering the temperature, the thickness of surface layers grows and once the surface layers meet the transition to the bent-director structure occurs. The width of the biaxial regime and the transition temperature shift are negligible in such a case. In thinner cells there is a finite structural transition temperature shift whose origin is twofold. (i) The wetting properties of substrates which induce high nematic order increase the transition temperature; in the case of nonfrustrating boundary conditions the Clausius-Clapeyron type of equation yields $\Delta T \propto 1/d$ [17]. (ii) The effect of the elastic deformation of the director field causes the negative transition temperature shift; $\Delta T \propto -1/d^2$, for the case of homogeneous degree of order [18,9].

As indicated in Fig. 4(b), in the case of structural transition between the biaxial and bent-director structure the phase shift is negative; however, it exhibits an effective $1/d$ dependence. The negative sign of the temperature shift denotes the promoting effect of elastic deformations. The thickness dependence is different from that characteristic for the elastic deformations, which is a consequence of the nonhomogeneous degree of order. Extrapolating the line in Fig. 4(b), we have estimated the upper cell thickness in which the biaxial structure can be found, $d_{max}=15.6\,l$ or $h_{max}=16.6$. From this we can see that there is no biaxial structure in the thickest cell we have simulated ($h=20$), whereas in the $h=14$ cell the structural transition temperature should be ~ 0.005 below the bulk transition, which we were not able to detect within our resolution.

To relate the results from MC simulations and phenomenological description we have to find a suitable meaning of ''spin.'' Close to the isotropic-nematic phase transition, the comparison of the two corresponding energies associated with a correlated volume of LC molecules, $\epsilon \sim A(T_{NI}-T^*)\mathcal{V}_0$, yields $l=\sqrt[3]{\mathcal{V}_0}\sim 3$ nm$=0.37\,\xi_{NI}$. Here $A(T_{NI}-T^*)$ is a temperature dependent phenomenological coefficient in the Landau free energy associated with order [9,18], and for a typical LC material $A\sim 10^5$ J/m^3, $T_{NI}-T^* \sim 1$ K, $\xi_{NI}\sim 8$ nm, and $\epsilon=k_B T_{NI}/T_{NI}^{MC}\sim 0.024$ eV. By this $\lambda \sim 3$ nm or the strength of the anchoring $G=L/\lambda \sim 0.003$ J/m^2, where L is the elastic constant in the one-elastic-constant approximation. The obtained strength of the surface interaction is experimentally achievable and represents strong anchoring [1,9].

We have used the above values for the description of the same system within the phenomenological theory [9]. As it can be seen from Fig. 1 the proposed relation of the MC simulation to the macroscopic properties yields an excellent agreement between the two descriptions. One should note that there are no free parameters to fit.

In summary, to the best of our knowledge, we are the first to confirm from the microscopic point of view the existence of the biaxial state of the nematic liquid crystal subject to highly frustrating boundary conditions and the transition from that state to the usual bent-director structure. These results were obtained by monitoring the average macroscopic order of the Lebwohl-Lasher lattice spin system, and its energy and heat capacity. The biaxial ordered state and the corresponding transition to the bent-director structure can be found only in cells that are thin enough; we have estimated the upper limit for the ''critical'' cell thickness to be ~ 50 nm which fits well the estimation from the phenomenological description [9]. In addition, we have compared our results to the results obtained within the phenomenological description of a hybrid nematic cell. The excellent agreement between the two models confirms our interpretation of the ''spin'' in the lattice spin model of liquid crystals.

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