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Monte Carlo simulations of biaxial structure in thin hybrid nematic film based upon spatially anisotropic pair potential*

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Hybrid nematic films have been studied by Monte Carlo simulations using a lattice spin model, in which the pair potential is spatially anisotropic and dependent on elastic constants of liquid crystals. We confirm in the thin hybrid nematic film the existence of a biaxially nonbent structure and the structure transition from the biaxial to the bent-director structure, which is similar to the result obtained using the Lebwohl–Lasher model. However, the step-like director's profile, characteristic for the biaxial structure, is spatially asymmetric in the film because the pair potential leads to $K_1 \neq K_3$. We estimate the upper cell thickness to be 69 spin layers, in which the biaxial structure can be found.

Keywords: hybrid nematic film, biaxial structure, spatially anisotropic pair potential, Monte Carlo simulation

PACC: 6130, 6470M

1. Introduction

Liquid crystals in restricted geometries are of great interest.[1] In confined nematic liquid crystals with a large surface-to-volume ratio, the aligning effects of the confining surfaces are crucial in determining the equilibrium director configuration.[2,3] A hybrid nematic film consists of a nematic liquid crystal confined by two parallel walls having homeotropic alignment at one wall and homogeneous at the other. Depending on temperature, film thickness, and the anchoring strengths, the hybrid nematic film can be found in one of the three ordered nematic configurations. Deep in the nematic phase, the director distribution is distorted with comparable contributions of splay and bend (hereafter called the bent-director structure). However, if the film is thinner than the critical value $d_{\rm C}$, the director field becomes uniform.[4] The uniform distribution can be homogeneous (when the homogeneous anchoring prevails) or homeotropic (when the homeotropic anchoring dominates). On the other hand, close to the isotropic-nematic phase transition, the nematic wetting layers start to grow at the surfaces, and the third ordered structure has already been predicted within the phenomenological theory.[5−7] It is known that the third configuration has two strata of the film, each with a uniform director orientation dictated by the respective wall, and thus perpendicular to each other, separated by a sharp interface. Chiccoli *et al*[8] has confirmed, by Monte Carlo simulations, the existence of the biaxially ordered structure in highly frustrated hybrid nematic films and reported the observation of the structure transition from the biaxial to the bent-director structure when the temperature of the system is lowered. The simulations performed in their study were based on a Lebwohl–Lasher (L–L) lattice spin model system with interacting pair potential, $U_{ij} = -\varepsilon_{ij} \mathrm{P}_2(\cos\theta_{ij})$ where ε_{ij} is a positive constant for nearest-neighbour spins and zero otherwise, θ_{ij} is the angle between the spins, and P_2 is the second-rank Legendre polynomial. To the best of our knowledge, they are the first to confirm, from the microscopic point of view, the existence of the biaxial state of a hybrid nematic cell and the transition from that state to the usual bent-director structure.

The object of this paper is to study the biaxial structure in highly frustrated hybrid nematic films, based upon spatially anisotropic pair potential depending on the relative position of the particles, which was proposed by Gruhn and Hess.[9] This pair po-

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tential is also built up for lattice spin model system and it approximately reproduces the elastic free energy density, so that the parameters defining the pair potential can be expressed in terms of the elastic constants. Both our study and the investigation presented in Ref.[8] are carried out by means of Monte Carlo simulations, which are effective for simulating such lattice spin models.[10]

2. Theoretical basis

According to the lattice spin model, the single liquid crystal (LC) molecules or clusters of molecules are located at the sites of a simple cubic lattice and are represented by three-component unit vectors $\boldsymbol{u}_i$. From Refs.[9] and [11], the nearest-neighbour pair potential takes the form as follows:

$$\begin{aligned} U_{ik} = \varepsilon\Big\{ & \lambda\left[\mathrm{P}_2(a_i) + \mathrm{P}_2(a_k)\right] \\ & + \mu\left(a_i a_k b_{ik} - \frac{1}{9}\right) + \nu \mathrm{P}_2(b_{ik}) \\ & + \rho\left[\mathrm{P}_2(a_i) + \mathrm{P}_2(a_k)\right]\mathrm{P}_2(b_{ik})\Big\}, \end{aligned} \tag{1}$$

$$\begin{aligned} & \boldsymbol{r} = \boldsymbol{p}_i - \boldsymbol{p}_k, \quad \boldsymbol{s} = \boldsymbol{r}/|\boldsymbol{r}|, \\ & a_i = \boldsymbol{u}_i \cdot \boldsymbol{s}, \quad a_k = \boldsymbol{u}_k \cdot \boldsymbol{s}, \\ & b_{ik} = \boldsymbol{u}_i \cdot \boldsymbol{u}_k. \end{aligned} \tag{2}$$

Here ε denotes a positive quantity setting scaled temperature, i.e. $T^{\mathrm{MC}} = kT/\varepsilon$; $\boldsymbol{p}_i$ and $\boldsymbol{p}_k$ are three-component dimensionless lattice-point coordinates; $\boldsymbol{s}$ is a unit vector pointing from the site i to the site k. And λ, μ, ν and ρ are the potential parameters which can be expressed in terms of the elastic constants:

$$\lambda = \frac{1}{3}\Lambda\left(2K_1 - 3K_2 + K_3\right), \tag{3a}$$

$$\mu = 3\Lambda\left(K_2 - K_1\right), \tag{3b}$$

$$\nu = \frac{1}{3}\Lambda\left(K_1 - 3K_2 - K_3\right), \tag{3c}$$

$$\rho = \frac{1}{3}\Lambda\left(K_1 - K_3\right), \tag{3d}$$

where the factor Λ is defined by setting $\nu = -1$. In the one elastic constant approximation ($K_1 = K_2 = K_3$), the pair potential reduces to that given in the L-L model, i.e. $\lambda = \mu = \rho = 0$. In this paper, the potential parameters are chosen as

$$\lambda = 0.79039, \quad \mu = -1.0611, \quad \nu = -1, \quad \rho = -0.43668.$$

They are taken from the elastic constants of the comparatively simple and extensively studied nematogen 4, 4′- dimethoxyazoxybenzene (para-azoxyanisole, PAA) at 120 °C:

$$\begin{aligned} K_1 &= 7.0 \times 10^{-12} N, \\ K_2 &= 4.3 \times 10^{-12} N, \\ K_3 &= 17.0 \times 10^{-12} N. \end{aligned}$$

The substrate planes are assumed to be normal to the z axis and they remove the homogeneity of the system in the z direction but not in xy plane. There are h nematic LC spin layers parallel to the substrates and two additional layers of fixed spins whose orientation corresponds to the direction induced by the substrates. To mimic a hybrid aligned nematic cell, we let the fixed spins in one additional layer lie along a certain direction in the substrate plane (let it be the x direction) and those in the other layer lie along the plane normal (i.e. the z direction). For simplicity, the LC spin-fixed spin interaction takes the same form as the LC spin-LC spin interaction and the two interactions are of equal strength. In addition, if $\boldsymbol{u}$ is described by the spherical coordinates θ and φ, its three components with respect to axes x, y and z are given by $(\sin\theta\cos\varphi,\ \sin\theta\sin\varphi,\ \cos\theta)$.

3. Monte Carlo simulations

We have performed the simulation on the lattices of $30\times30\times h'$ spins, where $h' = h + 2$ represents h layers of nematic LC spins and two additional layers of fixed spins. The actual thickness of the LC cell is $d = (h-1)l$, where l is the layer distance. At the four lateral faces of the simulation sample, the periodic boundary conditions are employed to mimic the bulk-like conditions. In the course of simulating, simulations at the lowest temperature start from a completely homeotropically aligned configuration and at higher temperatures the starting configuration is the already equilibrated one at a lower temperature. In our procedure, the orientation of a spin is indicated by $\cos\theta_i$ and φ_i ($\cos\theta_i \in [-1,\ 1], \varphi_i \in [0,\ 2\pi]$). Due to the characteristic of an LC molecule (or an LC cluster of molecules), we can take $\cos\theta_i \in [0,\ 1]$. So the initial state with $\cos\theta = 1$ and $\varphi = 0$ is selected. The standard Metropolis[12] procedure 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. In more detail, we choose a random state $(\theta_i,\ \varphi_i)$ for each spin,

and calculate both the random state energy E_n and the last accepted state energy E_p (at the beginning of the simulations, there is only the initial state instead of the last accepted state). If $E_n < E_p$, the random state is accepted. If $E_n \geq E_p$, the random state is accepted according to the probability $p = \mathrm{e}^{-(E_n - E_p)/kT}$. Related studies show that the state of the system will be equilibrated after a number of Monte Carlo cycles (approximately 60,000 MC cycles for thinner cells and up to 80,000 MC cycles for thicker ones).

The tensor order parameter $Q_{\alpha\beta}$, used to describe the state of the system, can be expressed as follows:

$$Q_{\alpha\beta} = \left\langle \frac{3}{2} u_\alpha u_\beta - \frac{1}{2}\delta_\alpha \delta_\beta \right\rangle, \tag{4}$$

where $\langle \ldots \rangle$ represents the ensemble average over each layer and over 30,000 MC cycles after the system has been equilibrated. By diagonalizing the tensor Q, we further obtain director's tilt angles and eigenvalues of the tensor order parameter (Q_1 represents the maximum value, Q_2 represents the minimum one, and Q_3 represents the medium), and the biaxiality ($P = Q_3 - Q_2$) as a function of the reduced temperature in each layer.

4. Numerical results

Taking $h = 10$, a typical plot of director's tilt angle (with respect to the z axis) for each layer as a function of the reduced temperature, resulting from the third component of the eigen-vector corresponding to the scalar order parameter (Q_1), is shown in Fig.1. Director's distribution in the cell under different reduced temperatures is plotted in Fig.2. Eigen-values of the tensor order parameter and biaxiality in the 5-th layer and the director's tilt angles in the 4-th and 5-th layers as functions of the reduced temperature are all depicted in Fig.3

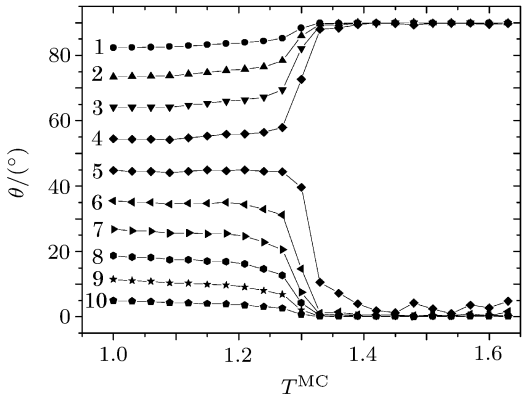


Fig.1. Director's tilt angle in an h=10-layer hybrid cell as a function of MC temperature. Different lines correspond to the tilt angles in distinct layers.

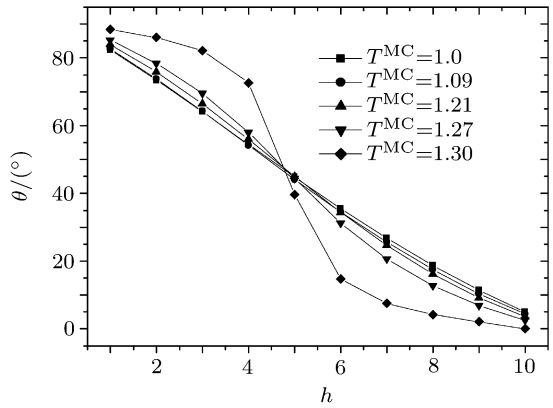


Fig.2. Director's distribution in the cell at different MC temperatures.

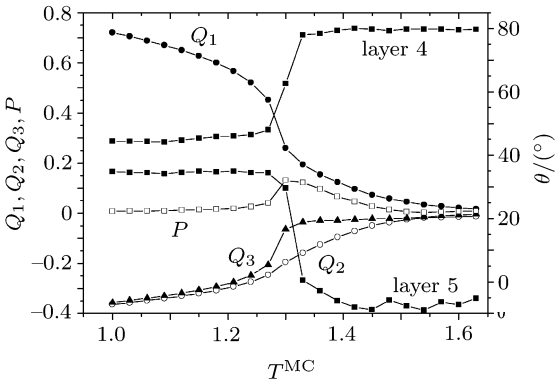


Fig.3. Eigen-values of the tensor order parameter and biaxiality in the 5-th layer; and the director's tilt angles in the 4-th and 5-th layers as functions of MC temperature.

From Fig.1 we can see that at temperatures above a certain temperature $T_{\mathrm{C}}^{\mathrm{MC}}$, the director's tilt angles are close to 90° in the layers 1–4 (instead of in the layers 1–5) and close to 0° in the layers 5–10. This result indicates that in the hybrid nematic film, the bent distortion exhausts more elastic energy than the splay one does, and consequently the separated layers may be no longer the middle ones in the cell. Further, as can be seen in Fig.2, the director's tilt angles as functions of z is nonlinear even at the lowest temperature which is in agreement with the continuum theory. The curves shown in Fig.3 follow the simulation results in the L-L model[8] quite closely, except that the structural transition between bent-director and biaxial structures appears to occur at $T_{\mathrm{C}}^{\mathrm{MC}} \approx 1.29$, higher than that ($T_{\mathrm{C}}^{\mathrm{MC}} \approx 1.10$) given in the L-L model. We note that at the transition, there is a great variation of the order, characterized by a strong decrease of the scalar order parameter and relatively remarkable increase of biaxiality in the 5-th layer. The same can

be observed in other layers, however, less pronounced except in the 4-th layer.

Furthermore, we have performed simulations of hybrid cells by necessity with different numbers of spin layers: h=6, 8, 10, 12, 16, 20, 30. In all of them, the biaxial structure can be found evidently, which is quite different from what has been discussed in the L-L model,[8] where the upper cell thickness is $h_{\max} \approx 17$. Here, we also obtain the temperature of structural transition as a function of the cell thickness, as illustrated in Fig.4, exhibiting the comparison of simulated results for this study with those of the L-L model as well. These results demonstrate that close to the bulk isotropic-nematic phase transition, denoted by $T_{\rm NI}^{\rm MC}$, the bent-director structure changes to the biaxial one and there is $T_{\rm C}^{\rm MC} \leq T_{\rm NI}^{\rm MC}$, where $T_{\rm NI}^{\rm MC} \approx 1.368$, obtained from the specific heat capacity profile in the bulk system.[11] It must be noted that the transition temperature is approximately linearly related to the cell thickness. Allowing of numerical uncertainties and extrapolating the first fit line to the coordinate axis in Fig.4, we will obtain the upper cell thickness, $h_{\max} \approx 69$, much higher than that ($h_{\max} \approx 17$) of the L-L model.

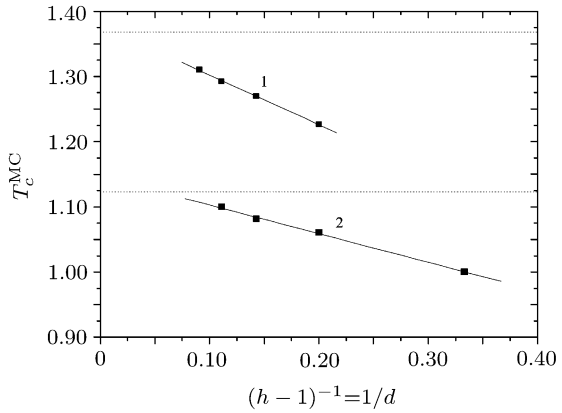


Fig.4. Temperature of the structural transition as a function of the cell thickness. Numbers 1 and 2 denote the linear fits, and the two dotted lines indicate the bulk isotropic-nematic phase transition temperatures for spatially anisotropic pair potential model and for the L-L model.

5. Conclusion and discussion

As an extension of the study conducted in the Refs.[5–8], we have developed the investigation of hybrid nematic films based upon spatially anisotropic pair potential, with valuable insight into the case of $K_1 \neq K_3$. Deep in the nematic phase the director's tilt angle decreases nonuniformly from 90° at the first layer of fixed spins to 0° at the other layer of fixed spins. We confirmed in the thin hybrid nematic film the existence of a biaxially nonbent structure and the structure transition from the biaxial to the bent-director structure. However, the step-like director's profile, characteristic for the biaxial structure, was spatially asymmetric in the cell.

We have estimated the upper cell thickness, in which the biaxial structure can be found, to be $d_{\max} \approx 68l$ or $h_{\max} \approx 69$. In a lattice spin model of liquid crystals, a typical magnitude of the correlation length in the vicinity of the isotropic-nematic phase transition $\xi_{NI} \sim 10\,\text{nm}$ yields approximately 50 molecules per spin. Thus, $d_{\max} \sim 0.7\,\mu$m. In experiments, very thin hybrid nematic films were prepared by depositing 5CB on a nylon coated substrate using isopropanol as a solvent.[13] The nylon surface aligns the 8CB molecules parallel to the surface, on which the molecules tend to align perpendicularly to the free surface. However, even for the smallest thickness ($d = 0.12\,\mu$m), there is no biaxial structure to be found because of too weak anchoring at the free surface. Since the biaxial structure is only realized in hybrid cells with strong and comparable anchoring strengths of the two confining substrates, it is a challenging technology to make a thin hybrid cell within a thickness of half micron.

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