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MONTE CARLO SIMULATION STUDY FOR A NEGATIVE DIELECTRIC ANISOTROPY NEMATIC LIQUID CRYSTAL PRESENTING A DEFECT NANOPARTICLE UNDER APPLIED ELECTRIC FIELD CONDITIONS

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By using Monte Carlo simulation we study the effect of an electric field on a negative dielectric anisotropy nematic liquid crystal presenting a spherocylindrical shaped particle located inside. We characterize the orientation of the nematic molecules inside the simulation box by means of the scalar and tensorial order parameter, field order parameter and radial order parameter, We also analyze how the system develops a Saturn ring type disclination line having the plane parallel with the direction of the applied electric field.

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1. Introduction

Recently, by using Monte Carlo simulations, we investigated the effect of an electric field on a nematic liquid crystal having immersed inside it a spherocylindrical inclusion [1]. The orientation imposed by the walls of the spherocylinder to the liquid crystal molecules was homeotropic.

In our previous work [1], we have performed a first set of computer simulations in the absence of an electric field. The obtained results were first compared with those of [2], finding that a closed oblate disclination line situated near the diagonal plane of the simulation box was created. The disclination line had a shape of a section of a spherocylinder and corresponded to the Saturn ring line also reported in [3] for the case of a sphere.

It is important to remark that this behaviour was obtained for a strong anchoring regime, the ratio between anchoring energy of a liquid crystal molecule to the walls of the spherocylinder and its interaction energy with a free neighbouring molecule being 1.5.

The simulation was repeated for the same system, this time in the presence of an applied electric field. As expected, sufficiently far away from the spherocylinder, the effect of the electric field acting on the liquid crystals molecules with positive dielectric anisotropy consisted in orientating the molecules parallel with the direction of the electric field. The bulk order parameter value increased from 0.6 to 0.7, whereas in the disclination line, its value dropped to -0.27 and the biaxiality was $\cong 0.25$.

In the case of positive dielectric anisotropy of the nematic molecules, the shape and position of the disclination line were changed [1]. We found that, irrespective of the direction of the electric field with respect to the spherocylinder, the plane of the disclination line became perpendicular to the direction of the field, for field values above a certain threshold [1].

Motivated by these very interesting results, we now present a new set of computer simulations, this time introducing negative dielectric anisotropy nematic liquid crystal molecules.

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2. Molecular Model and Simulation Method

The molecular model of the employed computer simulation was thoroughly discussed in [1], here we only review its main aspects.

We performed Monte Carlo simulations using the Lebwohl-Lasher model of liquid crystals [4]. In this model, the liquid crystal molecules are considered as unit vectors occupying fixed positions in the sites of a cubic lattice and mutually interacting with energy:

$$U_{ij} = -\varepsilon_{ij} P_2\left(\cos\theta_{ij}\right) \tag{1}$$

Here i and j are subscripts of a first order neighbour molecules, with θ_{ij} the angle between their long axis and P_2 the second order Legendre polynomial. Due to its simplicity and versatility, this model was widely used for decades in Monte Carlo simulations of liquid crystals, giving a realistic representation of the order of this class of materials, even in complicated geometries [1,2, 5-13]. The nematic-isotropic reduced transition temperature is $T_{NI}^{*} = \frac{kT_{NI}}{\varepsilon} = 1.1232 \pm 0.0006$ [5-13].

As described in [1], the nematic liquid crystal is placed in a rectangular box with dimensions $\mathrm{N_X} \times \mathrm{N_Y} \times \mathrm{N_Z}$ in lattice spacing. In the middle of the box, a spherocylinder-like particle of length L and diameter D is positioned, as shown in [1].

If we apply an electric field $\vec{E}$ inside the simulation box, the energy of interaction between a certain spin having subscript i with this field is [1,5,10]:

$$U_i = -\xi P_2\left(\hat{e}_i \cdot \hat{E}\right) \tag{2}$$

Here $\xi \sim \Delta\alpha E^2$ is a parameter describing the strength of interaction between the spin and the electric field; $\hat{E}$ is the versor of the electric field [5], and $\hat{e}_i$ is the versor of the spin. $\Delta\alpha$ is the electrical polarizability anisotropy of the liquid crystal molecule. The sign and magnitude of $\Delta\alpha$ determines direction and intensity of interaction between the spin and the applied electric field. For a molecule with positive dielectric anisotropy like in [1] and [5], the electric field tends to align it with the long axis parallel with the field direction, whereas for a molecule with negative dielectric anisotropy, the electric field tends to align it with the long axis perpendicular to the field direction. In this work, as well as in [1], ξ was used as a control parameter for both the strength and direction of interaction between a liquid crystal molecule and the electric field.

The total energy of the system is obtained by summating relation (1) on each pair of molecules and taking the summation of relation (2) for each molecule that interacts with the electric field.

The local order inside the simulation cell was obtained by calculating in each point of the lattice a tensor order parameter [1, 5-13]:

$$\mathrm{Q}_{\alpha\beta} = \frac{3}{2}\left(\langle \mathrm{e}_\alpha \mathrm{e}_\beta \rangle - \frac{1}{2}\delta_{\alpha\beta}\right) \tag{3}$$

whith $\alpha, \beta = x, y, z$ -directions of laboratory coordinate axes, $\delta_{\alpha\beta}$ the Kronecker delta and $\langle \cdots \rangle$ stating the statistical average during the simulation.

The above tensor order parameter is diagonalised and its largest positive eigenvalue is the scalar order parameter, while the corresponding eigenvector is the molecular director [14]. The absolute value of the difference between the remaining two eigenvalues of the order tensor parameter represents the biaxiality of the system [12].

The scalar order parameter obtained by diagonalisation of (3) is used for describing the order inside a liquid crystal [15,16]:

$$S = \langle P_2(\cos\theta) \rangle = \frac{3\langle cos^2\theta - 1 \rangle}{2} \tag{4}$$

3. Results and discussion

The system used in our simulation was identical with the system used in our previous work [1]: the size of the simulation box was $N_X = 64$, $N_Y = 48$, $N_z = 48$ in lattice spacing. The length of the spherocylinder was $L = 32$ and its diameter $D = 16$. The number of spins used in simulation was 141,952 and a Monte Carlo cycle consisted of 141,952 attempted moves. The simulation was performed at the reduced temperature $T^* = 1.0$, corresponding to the room temperature for the 5CB nematic liquid crystal [1,5].

As previously mentioned, we considered a negative anisotropy nematic liquid crystal. In this case, the internal dipole moment of a molecule is oriented along the short axis. As a result, an applied external electric field to our system constrains the nematic molecules to orient with the long axis perpendicular with respect to the field direction.

The coupling between the electric field and the spin for a negative anisotropy media is simulated by considering negative values for ξ.

Figure 1 presents the surface plot for the order parameter, S, in the case of an external applied electric field parallel with the diagonal plane of the simulation box. Here we considered the field intensity as being $\xi = -0.1$.

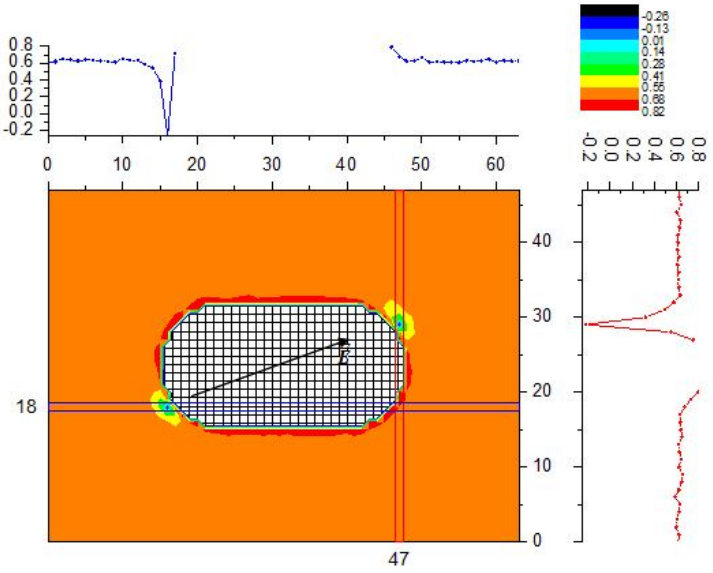

Fig. 1: Surface plot of the scalar order parameter S in the plane z= 24 under applied electric field $\xi = -0.1$ *oriented along a diagonal plane of the simulation box.*

An important remark is the fact that, in this case, the direction of the applied electric field is in the plane of the disclination line, while in the case of a material with positive dielectric anisotropy, this plane is perpendicular to the direction of the electric field. The value for S inside the disclination line is approximately $S \cong -0.27$.and biaxiality is $\cong 0.19$.

By repeating the simulation with the electric field parallel with the other diagonal plane of the system and after considering the order parameter throughout the planes of our simulation box, we conclude that a Saturn ring like disclination line surrounding the spherocylinder, appears with its plane parallel with the electric field

The values for the order parameter in the vicinity of the spherocylinder are quite high, due to the strong superficial anchoring, $S = 0.82$, while in the bulk an average of $S \cong 0.69$ is obtained. For the disclination regions, we report a typical value of $S \cong -0.2$. Figure 2 depicts the projections of the molecular spins in the plane XOY and their surface distribution for the middle section of the simulation box.

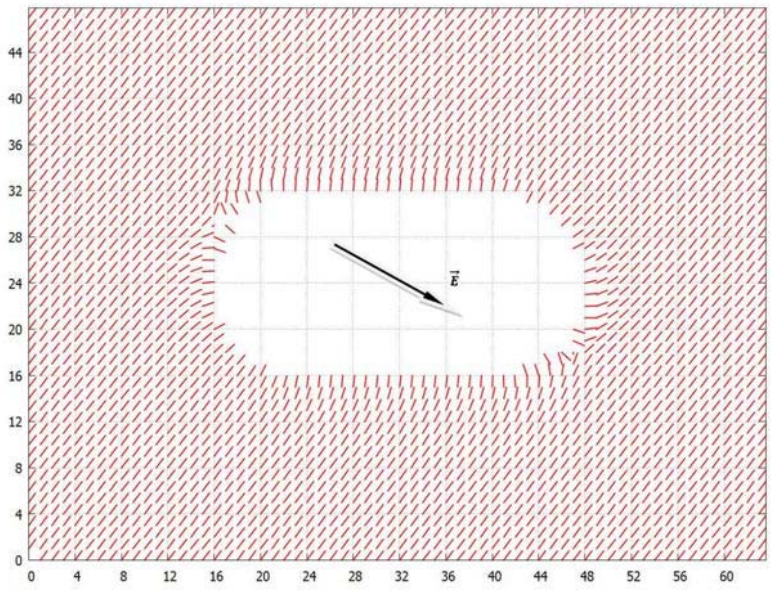

Fig. 2: Projection of the nematic director n (versor components e_x, e_y) in the z=24 plane under applied electric field $\xi = -0.1$ oriented along a diagonal plane of the simulation box.

As expected, the negative anisotropy molecules orient, on average, with the small axis along the applied electric field direction. Nevertheless, in the neighbourhood of the spherocylinder they are homeotropic to its surface, due to the anchoring constraints. The competition between these two types of orientations gives birth to the disclination zones where the symmetry is broken and the molecules re-align themselves, in order to minimize the energy and reach a local equilibrium.

The analysis of the tensorial order parameter, Q, gives us a quantitative description for the local level of order degree. This includes the orientation of the molecules inside the disclination regions, in the bulk and near the surface of the spherocylinder. The results are in good agreement with the description of the system obtained by the molecular director generation, order parameter mappings and other quantities characterizing the simulation. The diagonal components of the tensorial order parameter in the plane $Z = 24$ along the lines $X = 47$ and $Y = 29$ passing through the disclination line are presented in figure 3.

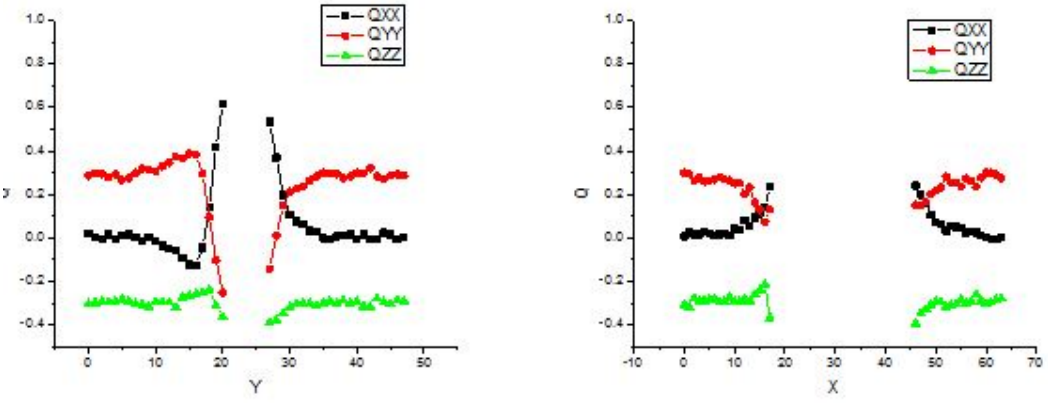

Fig. 3: Qxx, Qyy and Qzz values corresponding to (a) X=47 in the plane Z=24; (b) Y=29 in the plane Z=24.

The biaxiality is zero for all the system, except for the disclination line regions.

A mapping for the median plane of our system presents the field order parameter distribution (figure 4). In the bulk, its value is about -0.31, meaning that the direction of the

molecules is perpendicular on the electric field, as expected. At the same time, in the disclination lines, we estimate positive values between 0.1 and 0.7. In this points, which are very close to the surface of the spherocylinder, the homeotropic anchoring conditions compete with the orientation imposed by the electric field, and because the strong anchoring regime, the molecules become parallel with the field.

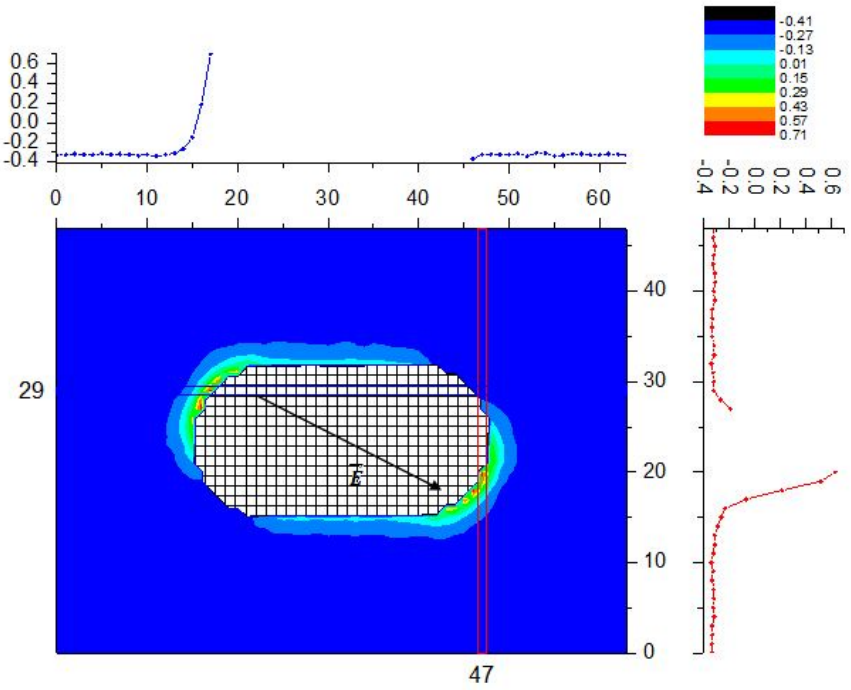

Fig. 4: Field order parameter chart in the z=24 plane, under applied electric field $\xi = -0.1$ *oriented along a diagonal plane of the simulation box.*

The radial order parameter diagram is shown in figure 5. The molecules averagely arrange on the opposite diagonal with respect to the direction of the electric field (here the values are around 0.67). The molecules situated in the proximity of the spherocylinder are radially oriented (the order parameter is around. 0.82), due the strong anchoring regime. A particular situation arises in the defect disclination zones situated near the caps of the spherocylinder, where the molecules are oriented with the long axis parallel to the field direction. In these regions the values of the radial order parameter are positive, whereas along the same direction, but sufficiently far away of the spherocylinder, the radial order parameter decays to -0.3.

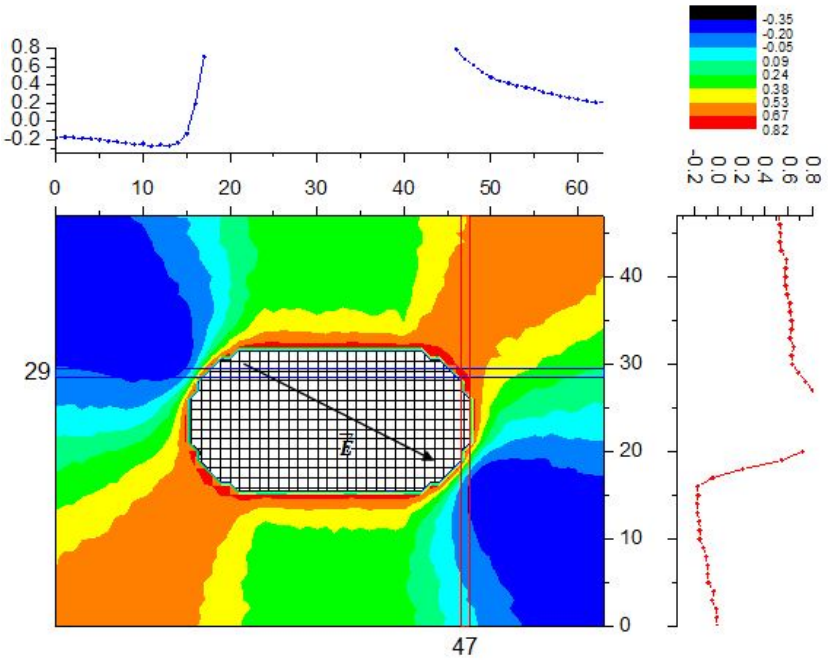

Fig. 5: Radial order parameter plot for the plane z=27, under applied electric field $\xi = -0.1$ *oriented along a diagonal plane of the simulation box*

Monte Carlo simulations were also performed for an electric field applied parallel with the long axis of the spherocylinder, for $\xi = -0.1$. Figure 6 shows the diagram of the scalar order parameter in a longitudinal section plane.

The results show that the plane of the Saturn ring disclination line is again parallel with the direction of the applied electric field.

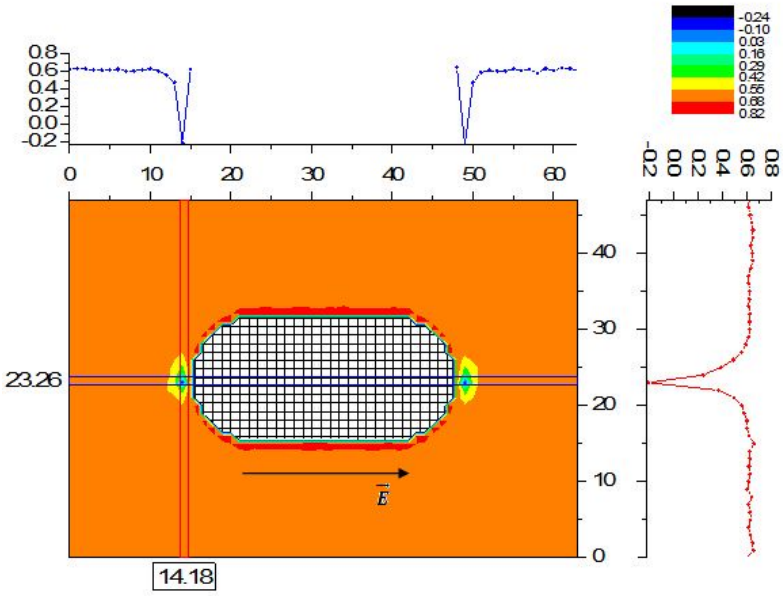

Fig. 6 : Map of the scalar order parameter in the plane Z=24, under electric field $\xi = -0.1.$ *applied along the long axis of the spherocylinder.*

Simulations were also performed for an electric field applied perpendicularly to the long axis of the spherocylinder, but the results are analogous to the ones presented above.

4. Conclusions

Using Monte Carlo simulation, we investigated the effect of the electric field on a nematic liquid crystal with negative dielectric anisotropy having an spherocylindrical nanoparticle inclusion.

We proved that the geometry of the system and the existence of an external perturbation, like an electric field, are very important for the orientation of the nematic liquid crystal, their coupling leading to the formation of defects. Nevertheless, the dielectric properties of the liquid crystal itself play a fundamental role in the orientation of the molecules.

In the presented situation, under the effect of the electric field, the molecules align with the long axis perpendicular on the field direction.

Moreover, the main effect of the electric field on a nematic system with negative dielectric anisotropy is the rotation for the plane of the disclination line until it becomes parallel with the direction of the electric field.

The simulated nematic liquid crystal system and the particular behaviour of the molecular reorientation in the neighbourhood of the spherocylindrical nanoparticle is an interesting example from the soft matter world, as these experiments tackle many issues related to nano sized units and defects, patterned molecular controllers and future nano scale geometries.

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