

Molecular Simulation of the Free Surface Order in NLC Samples

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Recently, current vs voltage measurements have revealed a nonstandard behavior of the electric conductivity within some nematic liquid crystals (NLC) samples, and the results have been associated with the local orientational order at the free surfaces of the liquid crystal. We have used Monte Carlo simulation of a liquid crystal in a cell with two free surfaces at the opposite sides to understand how a local director imposed by free surfaces competes with the homeotropic alignment imposed by electrodes of the nematic cell.

I. Introduction

Nematic liquid crystals (NLC) represent thermodynamic phases of a very large class of mainly organic substances. Because of the peculiar forms of their constituent molecules, either strongly elongated or discotic, within a very well-defined temperature interval, the system possesses an orientational order that induces, in turn, anisotropic physical properties. Although these systems are interesting enough from a theoretical point of view, making them worthy to be studied, their industrial applications attracted the attention of hundreds of physicists, chemists, and engineers.

Recently, a nonstandard behavior of electric conductivity within some samples with NLC has been observed, which can be associated with the local orientational order at the free surfaces of the liquid crystal.¹ Current vs voltage measurements have revealed two different conduction zones in a NLC sample. A standard sandwich type sample was filled with K 18 (6 CB) that was aligned (approximately) homeotropically by the two ITO surfaces previously cleaned in orthochromic mixture. On two opposite sides of the cell, the NLC was limited by two Mylar stripes acting as spacers. The other two sides were left open, and the liquid crystal had two free surfaces (limited only by air) in the form of a cylindrical meniscus. The overall conductivity of the cell depended strongly on the length of the free surface. For the same area, samples with a larger free surface experienced a higher overall conductivity. In the absence of an electric field the order in the free zones was planar, the director **n** being normal to the liquid crystal–air interface. For small electric fields, the conduction along the director **n** in the bulk is less than the conduction perpendicular to **n** on the free zone. At higher fields, the Fredericksz transition that operates on the free zones reduces the overall conductivity. This reduced conductivity was practically equal to that obtained when two ITO electrodes were completely immersed in the liquid crystal; that is, the free surfaces do not contribute to the conduction. Considering the measured values, it has been concluded that the order in the free surface zone was planar for a depth of about 50 μm .

The main conclusion depicted from ref 1 was the local orientational order at the free surfaces of the cell plays a certain role on the overall conductivity and the results were explained by the competition between the homeotropic alignment at ITO and free surfaces.

This is why we consider the investigation of the director orientation in the vicinity of the free surfaces to be an important point to clarify. The study can be made by minimization of the free energy described by the continuum model of the liquid crystals,² or by computer simulation, which is a widely used method in the physics of liquid crystals.

II. Molecular Model and Simulation Method

Motivated by the results obtained in ref 1, we have used Monte Carlo simulation as an investigation tool for the molecular order. The simulation model was the well-known Lebwohl–Lasher model,³ which consists of a system of spins **s_i** placed on a cubic lattice, interacting with the attractive energy:

$$U_{ij} = -\epsilon_{ij} P_2(\mathbf{s}_i \cdot \mathbf{s}_j) \quad (1)$$

where ϵ_{ij} is a positive constant (ϵ for nearest neighbors particles and zero otherwise) and P_2 is the second rank Legendre polynomial.

Although the system is very simple, it was widely used to describe the properties of the liquid crystals displays,^{4,5} or nematic structures in various geometries.^{6–8} The main advantage of this simple model is the fact that spins' centers of mass are fixed, saving computer time during the simulation, comparatively with other models considering also translational degrees of freedom. On the other hand, the system is well studied and gives a realistic representation of a nematic, showing a first-order phase transition at a scaled temperature $T_{\text{NI}}^* = (kT_{\text{NI}}/\epsilon) = 1.1232$.⁹

Because we are interested only in the orientational features of the molecules, we used the Lebwohl–Lasher model to simulate the behavior of a liquid crystal cell, Figure 1. The liquid crystal fills a cell of a rectangular shape with electrodes parallel with XOY plane and the free surfaces (menisci) parallel with XOZ ones and we used periodic conditions along the OX

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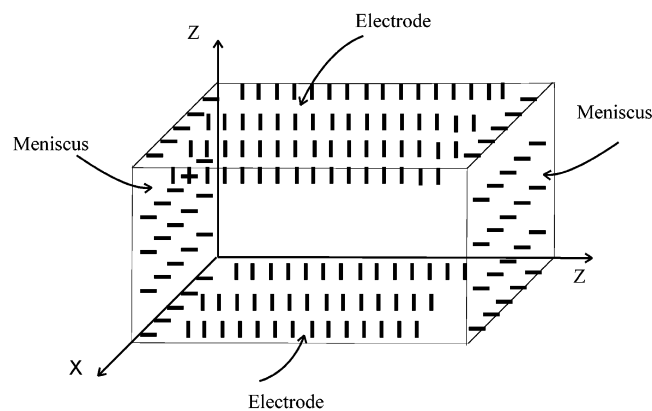


Figure 1. Representation of the simulated cell and orientations of spins in the proximity of the surfaces.

direction to mimic the bulk behavior of a real cell. We denote by N_x , N_y , and N_z the number of cells in each direction.

To impose orientations due to the electrodes and the free surfaces, we considered that spins in layers situated in the first proximity of them are fixed and normally orientated. Interaction of these spins with their first-order neighbor layers may be described by another parameters, ϵ_s in eq 1.

All other spins are free to rotate in their cells. An important aspect is, because the energy of interaction is invariant under a uniform rotation of all spins, the bend, splay, and twist elastic constants are all equal.⁸

An electric field \mathbf{E} parallel with OZ direction is applied between the electrodes. Interaction of this field with spins is described by the potential:^{4,5}

$$U_i = -\epsilon \xi P_2(\mathbf{s}_i \cdot \hat{\mathbf{E}}) \quad (2)$$

where $\xi = (\epsilon_0/3)(\Delta\alpha/\epsilon)\mathbf{E}^2$ is a parameter describing the coupling between spin and the electric field⁵ and $\hat{\mathbf{E}}$ is the direction of the electric field. Here $\Delta\alpha$ is the electrical polarizability anisotropy and its sign and magnitude determines the strength of interaction between spin and field. Note that for $\xi = 0$ we have no external field applied.

The total energy of the system is obtained by combining eqs 1 and 2:

$$U = -\sum_{\substack{i,j=1 \\ i \neq j}}^N \epsilon_{ij} P_2(\mathbf{s}_i \cdot \mathbf{s}_j) - \epsilon \xi \sum_{i=1}^N P_2(\mathbf{s}_i \cdot \hat{\mathbf{E}}) \quad (3)$$

where $N = N_x N_y N_z$ is the total number of spins.

The order of the system is described by the local order tensor:¹⁰

$$Q_{\alpha\beta} = \frac{1}{n} \sum_{k=1}^n \left(\frac{3}{2} \langle s_{k\alpha} s_{k\beta} \rangle - \frac{1}{2} \delta_{\alpha\beta} \right) \quad (4)$$

where $\alpha, \beta = x, y, z$, $\delta_{\alpha\beta}$ is the Kronecker delta, $\langle \dots \rangle$ is the ensemble average and n is the number of spins. If $n = N$, the usual order parameter of the system is obtained from the largest positive eigenvalue of the order tensor $Q_{\alpha\beta}$ and the corresponding eigenvector is the liquid crystal director.¹¹ If we choose $n = 1$, the average is performed on Monte Carlo cycles only and $Q_{\alpha\beta}$ describes the local order.

Because the behavior of the bulk order parameter obtained from the Lebwohl-Lasher model is well understood and because we were interested in local properties of the system, we did not calculate the bulk order parameter to save some

computer time. Instead, we have obtained from the simulations the values of $Q_{\alpha\beta}(y, z)$ in layers parallel with the YOZ plane, averaged on the OX direction.

We also used a field order parameter that describes the order of the system in the direction of the applied field:⁵

$$P_2^E = \frac{1}{n} \sum_{i=1}^n P_2(\mathbf{s}_i \cdot \hat{\mathbf{E}}) \quad (5)$$

where again n is the number of spins. In ref 1, the conductivity of the cell was explained by a mechanism similar to those known in graphite and was linked to the orientations of the molecules under the field applied between electrodes. Because the field order parameter also describes the orientation of the molecules against the direction of the electric field, we used this parameter to qualitatively explain the results from this reference. We have calculated $P_2^E(x, y)$ in a layer parallel with the XOY plane and averaged on the OZ direction. We also defined a total field order parameter $P_2^{E_{\text{tot}}}$, which is the field order parameter averaged on all spins of the cell.

The Monte Carlo procedure was a standard one:^{11,12} we randomly picked a spin and rotated it. We calculated the energies in the old and in the new state and the move was accepted using the Metropolis acceptance criterion.¹¹⁻¹³ The mechanism was repeated for 100 000 Monte Carlo cycles with half of them used for equilibration.

III. Results and Discussions

The system described in the preceding section was used to simulate the behavior of a liquid crystal cell with boundary order imposed by electrodes and by menisci. The number of spins used during the simulation was kept at values $N_x = 10$, $N_y = 32$, and $N_z = 12$, which means we had 3840 spins. Because spins located at electrodes and menisci are fixed and because we have used periodic conditions along the OX direction, the number of free spins is 3000 and a Monte Carlo cycle consisted of 3000 attempted moves.

During the simulations we have used the same value for the coupling interaction between spins, $\epsilon_s = \epsilon$, which means the strength of the coupling is the same between molecules, irrespective of their positions in layers. Experimental results of ref 1 showed that the order imposed by the free surface penetrates the cell to a depth of about 50 μm . This value indicates that the anchoring energy at the meniscus is large and we assumed that it is comparable with the anchoring energy at the electrodes.

First of all, we were interested in investigating the local order in the cell. To do this, we calculated the values of the local order tensor. In the absence of the field, its components in the $y = 15$ layer (middle of the cell) are displayed in Figure 2 as a function of z , at temperature $T^* = 1$, which is in the ordered phase according with ref 9.

The diagonal components of the tensor order defined in eq 6 represent the order with respect to the axes OX, OY, and OZ. The off-diagonal components $Q_{\alpha\beta}$ represent the bending of the director in the plane (α, β) .¹⁴ From Figure 2 we can notice that off-diagonal components of the order tensor are approximately zero. The values of these components indicate that the molecular director does not bend in the corresponding planes. The diagonal components Q_{xx} and Q_{yy} have values close to -0.5 , indicating that the director is normal to the OX and OY axes, observation sustained by larger values of the Q_{zz} component, indicating that the director is parallel with OZ axis.

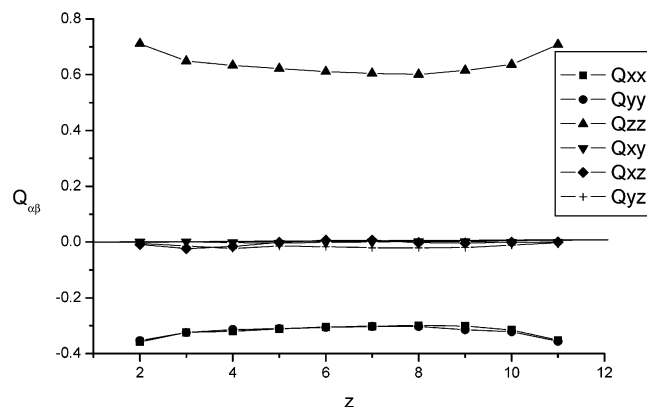


Figure 2. Local order tensor components in the $y = 15$ layer as function of z for the temperature $T^* = 1$ and no electric field. Error bars sizes are of dimension of the symbols and were omitted. Lines are only guide to the eye.

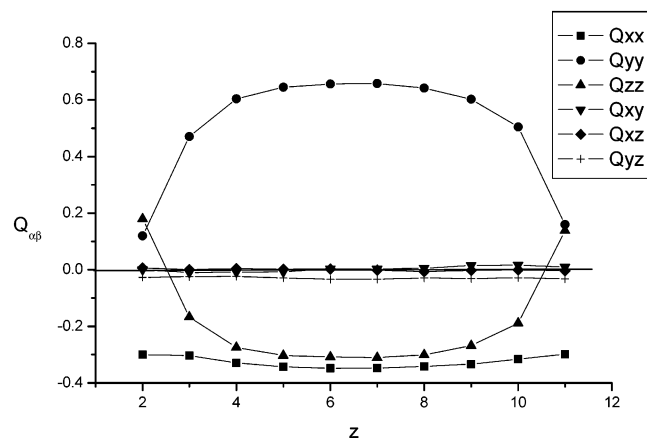


Figure 3. Local order tensor components in the $y = 2$ layer as function of z for the temperature $T^* = 1$ and no electric field. Error bars sizes are of dimension of the symbols and were omitted. Lines are only guide to the eye.

This behavior may be explained by the fact that the order along the OZ axis imposed by the electrodes is propagated inside the cell if the layer is far enough from the menisci. The situation dramatically changes in a layer in the vicinity of one of the meniscus as for $y = 2$, as we can notice from Figure 3.

Values of the off-diagonal tensor components are again zero, Q_{xx} is again close to -0.5 , but Q_{zz} values also approach -0.5 , except the regions near the electrodes. Instead, the values of the Q_{yy} increase from a minimum value near the electrodes toward a maximum at the middle of the cell, indicating that the order along the OY axis imposed by the meniscus is now propagated in the cell.

The main conclusion we can obtain is the molecular director is parallel with the YOZ plane and the order change from director parallel with the OY axis in the vicinity of the menisci to parallel with the OZ axis far away from them. The situation is illustrated in Figure 4 where Q_{zz} is displayed as a function of z for increasing layer number. Near the menisci, Q_{zz} is approximately -0.5 , with the exception of the regions near the electrodes. As the layer number increases, Q_{zz} progressively grows toward a 0.7 value in layers near the center of the cell, indicating that in this region the order is along the OZ axis.

The same simulation was made at the temperature $T^* = 1.5$, above the nematic isotropic transition, and all components of the tensor order parameter were close to zero, indicating the absence of the order.

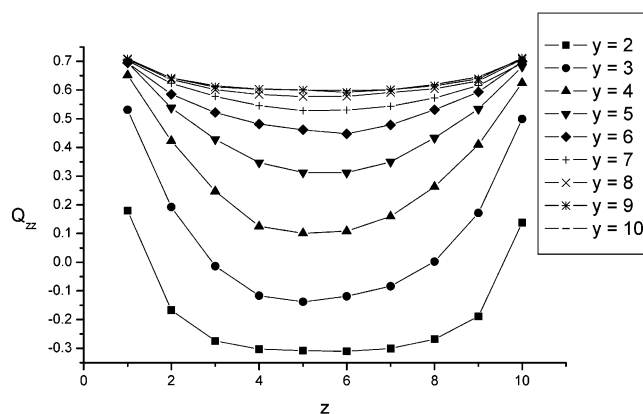


Figure 4. Components Q_{zz} for the local order tensor components as function of z for different layers at no applied field. Parameters are the same as in Figures 3 and 4.

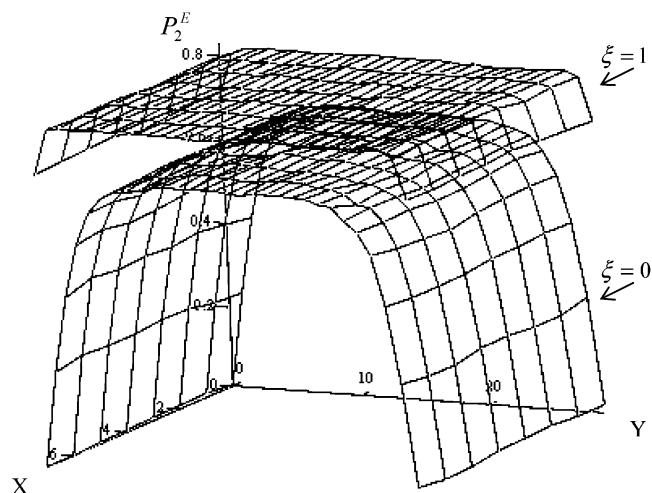


Figure 5. Field order parameter in XOY plane averaged on the OZ direction at temperature $T^* = 1$.

If we impose the presence of an electric field along the OZ axis, the nematic director tends to align the spins along this axis even at temperatures above the nematic isotropic transition temperature and despite the tendencies of the menisci.

A good understanding of the situation may be obtained if we plot the field order parameter P_2^E in the XOY plane, as in Figure 5. If the field is applied along the OZ direction, the shape of the surface changes and its magnitude increases.

As we mentioned above, we believe this parameter is a measure of the conductivity across the liquid crystal cell. We may also assume that all the molecules of the NLC sample contribute to the conductivity in the cell. The applied field is orientated along the OZ axis, and we believe the conductivity above a certain point in the XOY plane is a result of the orientation of all molecules above this point. This is why we have chosen to average the P_2^E parameter along the OZ axis. From Figure 5 we see we have three regions: two marginal regions where P_2^E is small, meaning spins are perpendicular to the OZ axis, and a central region where values of P_2^E are high, meaning spins are parallel with the OZ axis. By applying the electric field, the depth of the marginal zones decreases, indicating that the OZ orientated electric field supplementary tends to orientate molecules perpendicular to the electrodes.

The behavior of the conductivity of the sample was explained in ref 1 by the contribution of the marginal regions to the total cell conductivity. The conductivity of these marginal zones, denoted by σ , has greater values than the conductivity on the

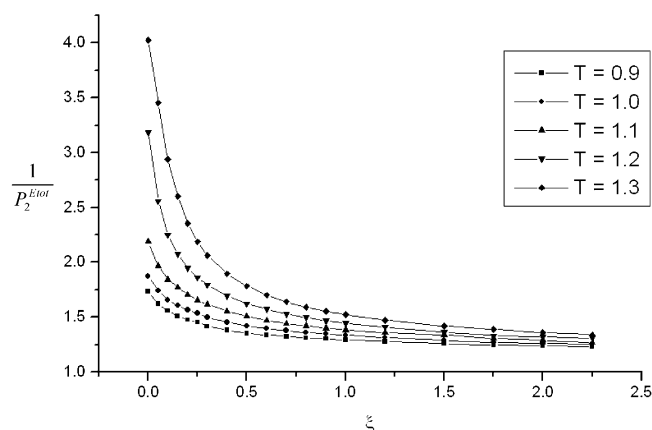


Figure 6. Dependence of $1/P_2^{E_{tot}}$ on field strength for different temperatures.

middle region, $\sigma_{||}$. This is why we believe bulk sample conductivity may be linked with the inverse of the total field order parameter, $1/P_2^{E_{tot}}$.

The dependence of this parameter with field strength at different temperatures is depicted in Figure 6. From this figure we can conclude that the behavior of $1/P_2^{E_{tot}}$ has many similarities with the behavior of the total cell conductivity from ref 1.

First, we should note that $1/P_2^{E_{tot}}$ decreases with field strength, dependence that is similar to the behavior of the conductivity from ref 1.

We can also conclude from Figure 6 that, for temperatures lower than the nematic–isotropic transition temperature, the dependence of the $1/P_2^{E_{tot}}$ on field strength is low, a fact experimentally observed in ref 1.

Depending on values of the field strength, we have two regions where the behavior of $1/P_2^{E_{tot}}$ is different. For small values of the applied field, the quantity decreases very strongly, and for larger values, it remains approximately constant. We believe this behavior is linked to the orientations of spins from layers near menisci, where, when the field increases, we have a Freedericksz transition of spin from these regions.

IV. Conclusions

We have used Monte Carlo simulation to investigate the local order in a liquid crystal cell with competing boundary order due to the electrodes and the free surface. Despite the limitation imposed by relatively small dimensions of the simulated system, the results of our work are in a qualitatively good agreement with those obtained in ref 1.

First, we must point out that the free surfaces of a liquid crystal cell propagate a local order inside the bulk. The director structure in the vicinity of these surfaces depends on the temperature and also on the electric field applied between the electrodes. The shape and dimension of the zone where the direction of \mathbf{n} changes from perpendicular to parallel to the free surface depend on the presence of the applied electric field, as can be seen from Figure 5. Far enough from these air–LC boundaries in the nematic temperature range, the order is imposed by the electrodes, as it is expected.

We have introduced the inverse of the total order field parameter ($1/P_2^{E_{tot}}$) as a measure of total alignment of the molecules in the cell, expected to be proportional with total conductivity of the NLC sample. The results obtained by simulations are in perfect agreement with the experimental facts of ref 1. Perhaps it is worthy to also investigate systems with different dimensions and to see how this parameter depends on the length of the free surface.

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