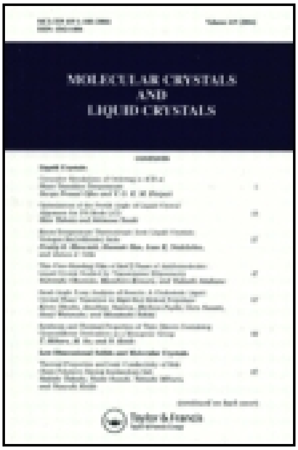

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A PAIRWISE ADDITIVE POTENTIAL FOR THE ELASTIC INTERACTION ENERGY OF A CHIRAL NEMATIC

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We have developed a pairwise additive potential model to describe the macroscopic elastic interactions of a chiral nematic liquid crystal. The potential is obtained from the expression for the elastic free energy density discretized onto a cubic lattice and mapped onto a suitable expansion in scalar invariants. The value of the pair potential is explored by means of a Monte Carlo lattice computer simulation. It allows, in a simple and efficient way, the simulation of liquid crystal devices and samples in confined geometries, taking into account the effect of the temperature of the sample and of the thermal fluctuations in the director distribution, as well as the elastic interactions.

Keywords: chiral nematic; elastic free energy; Monte Carlo lattice simulation

INTRODUCTION

The elastic properties of nematic liquid crystals are of particular interest since they determine the director distribution for a sample in a confined geometry subject to boundary constraints. For example, we can consider

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This work is dedicated to the memory of Prof. Pier Luigi Nordio.
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the nematic phases used in liquid crystals display (LCD) technologies where the sample is contained in thin cells, between parallel plates, and is subject to the orienting effects of the surfaces as well as of an external applied electric field. The transmission of light depends on the director distribution for the nematic inside the cell, which is, in turn, determined by the response of the nematic sample to the orienting forces. Such a response to an external field is, eventually, determined by the elastic constants of the sample, K_1, K_2 and K_3 for the splay, twist and bend deformations, respectively. The equilibrium director distribution for a set of elastic constants and boundary conditions is that which minimises the elastic free energy for the system, obtained by integrating the free energy density given by the Oseen-Zöcher-Frank expression [1]:

$$F = \frac{1}{2}\left(K_1(\nabla \cdot \mathbf{n})^2 + K_2[\mathbf{n} \cdot (\nabla \times \mathbf{n})]^2 + K_3[\mathbf{n} \times (\nabla \times \mathbf{n})]^2\right). \tag{1}$$

It has been shown that the director distribution resulting from a given set of constraints can also be obtained with a Monte Carlo sampling scheme together with an appropriate pair potential which approximately reproduces the elastic free energy of the system [2–5]. This method appears to be convenient when analytical solutions are not available. Moreover, the Monte Carlo simulation approach allows us to include in the description of the system the thermal fluctuations of the director, whereas the solution of Eq. (1) is usually carried out as a simple energy minimisation.

A suitable pair potential for elastic problems was originally proposed by Gruhn and Hess [2] and then parametrised and characterised by Romano [3]. Different parameterisations have also been investigated by Luckhurst and Romano [4]. We have used the pair potential, with the parameterisation given by Romano, to investigate the Fréedericksz transitions of a nematic sample by means of Monte Carlo lattice simulations [5].

The pair potential has been developed for the case of an achiral nematic. However, in applications such as twisted nematic and super twisted nematic displays the samples are normally chiral, produced by doping a nematic with chiral solutes in order to favor the twisting of the director in the cell. It would, therefore, be desirable to extend the derivation of the pair potential to include a chiral term which can then be used to simulate the behaviour of a chiral nematic subject to competing constraints.

The layout of our paper is as follows; in the subsequent section we develop a pair potential with which to represent the elastic energy of a chiral nematic. In the following section we describe simulations based on the elastic pair potential to explore its effectiveness in modelling the unperturbed chiral nematic state. The results of the simulations are also discussed in this section. Our conclusions are given in the final section.

DERIVATION OF THE PAIR POTENTIAL

The derivation of the pair potential elastic energy of the chiral nematic closely follows the steps already used to obtain the pair potential for the achiral case [4]. For the case of a chiral nematic Eq. (1) is modified by an additional contribution to the twist deformation term:

$$F = \frac{1}{2}\left(K_1(\nabla\cdot\mathbf{n})^2 + K_2[\mathbf{n}\cdot(\nabla\times\mathbf{n}) + q_0]^2 + K_3[\mathbf{n}\times(\nabla\times\mathbf{n})]^2\right). \quad (2)$$

where the wavevector, q_0, for the helix is related to the inverse of its pitch, p_0, by the relation [1]

$$p_0 = 2\pi/q_0. \quad (3)$$

For q_0 equal to zero we recover the expression for the elastic free energy density of a non-chiral nematic. In this case it has been shown already that it is possible to obtain the approximate elastic free energy of the system as a sum of pairwise interactions between all neighbouring pairs of directors resulting from the discretization of the sample onto a simple cubic lattice [2–5]. The pair potential, Φ_{jk}, describing the elastic interaction energy between a pair of directors, j and k, each centred in a volume element of dimension Λ^3, is obtained by mapping the expression for the free energy density onto a series expansion in terms of the invariants

$$\begin{aligned} a_j &= \mathbf{n}_j\cdot\mathbf{r}, \\ a_k &= \mathbf{n}_k\cdot\mathbf{r}, \\ b_{jk} &= \mathbf{n}_j\cdot\mathbf{n}_k, \\ c_{jk} &= \mathbf{n}_j\cdot\mathbf{n}_k\times\mathbf{r}. \end{aligned} \quad (4)$$

Here $\mathbf{n}_j$ and $\mathbf{n}_k$ are unit vectors defining the orientation of the neighbouring directors j and k, respectively, while $\mathbf{r}$ is a unit vector defining the orientation of the vector joining the directors at the points j and k. For an achiral nematic the symmetry of the system excludes the last invariant, c_{jk}, from the description of the elastic interaction. It is, however, essential for a description of the elastic behaviour of a chiral nematic phase. The mapping can be done by considering an expansion in powers of the four invariants as shown by Romano [3]

$$\Phi_{jk} = \sum_{lmnp} C_{lmnp} a_j^l a_k^m b_{jk}^n c_{jk}^p, \quad (5)$$

where p is set to zero for the achiral case. Alternatively the invariant S-functions can be used as a basis set for the expansion [4].

As in Ref. [4] we calculate explicitly the free energy for three representative director deformations. We consider, without loss of generality, the director j to be oriented along the laboratory z axis and the director k on a neighbouring lattice site to be slightly displaced with respect to j so that we can write

$$\begin{aligned} \mathbf{n}_j &= (0, 0, 1), \\ \mathbf{n}_k &= (\xi, \eta, \zeta), \end{aligned} \tag{6}$$

where ξ and η are very close to zero, while ζ is close to unity, that is we are in the limit of small displacements as assumed in continuum theory.

We first consider the case where the inter-director vector is oriented along the laboratory x axis. In this case we find that

$$\begin{gathered} \nabla \cdot \mathrm{n} = \xi, \\ \mathbf{n} \cdot (\nabla \times \mathbf{n}) + q_0 = \eta + q_0, \\ \frac{\partial n_z}{\partial x^*} = \zeta - 1, \\ 2F = K_1\xi^2 + K_2\eta^2 + 2K_2q_0\eta + K_2q_0^2. \end{gathered} \tag{7}$$

which are analogous to Eqs. (19)–(22) of Ref. [4]. In these and subsequent expressions the positional coordinates have been scaled with the lattice parameter, Λ. Comparing Eq. (7) with Eq. (22) of Ref. [4] we notice the presence of an additional term in the free energy, which is linear in η (the result for the achiral case can easily be recovered, here and in the following expressions, by setting q_0 to zero). The last term in the expression of the free energy, quadratic in q_0, can be neglected since it is independent of the director orientation.

When the vector linking the two directors is oriented along the laboratory y axis we obtain:

$$\begin{gathered} \nabla \cdot \mathbf{n} = \eta, \\ \mathbf{n} \cdot (\nabla \times \mathbf{n}) + q_0 = -\xi + q_0, \\ \frac{\partial n_z}{\partial y^*} = \zeta - 1, \\ 2F = K_1\eta^2 + K_2\xi^2 - 2K_2q_0\xi + K_2q_0^2. \end{gathered} \tag{8}$$

The result in Eq. (8) has to be compared with the expression in Eq. (26) of Refs. [4,6]. We observe that it differs only by the term linear in ξ. Again the last term, quadratic in q_0, is neglected.

Finally, when the vector linking the two directors is oriented along the laboratory z axis we obtain:

$$\begin{gathered} \nabla \cdot \mathbf{n} = \zeta - 1, \\ \mathbf{n} \cdot (\nabla \times \mathbf{n}) + q_0 = q_0, \\ (\mathbf{n} \times (\nabla \times \mathbf{n}))^2 = \eta^2 + \xi^2, \\ 2F = K_3(\eta^2 + \xi^2), \end{gathered} \tag{9}$$

where this result is obtained after neglecting the constant term $K_2 q_0^2$. To summarize, the presence of the chiral term q_0 in the free energy density in Eq. (2) is responsible for the appearance of a contribution linear in the director displacements η and ξ.

We now consider, for the same three cases, the explicit expressions for the pair potential. As a first approximation we write the expansion as the sum of the achiral contribution plus the lowest order term in the invariant c_{jk}, that is:

$$\Phi_{jk} = \sum_{lmn} C_{lmn0} a_j^l a_k^m b_{jk}^n + C_{0001} c_{jk} = \Phi_{jk}^{ac} + \Phi_{jk}^{c}, \tag{10}$$

where the first term of the right hand side, Φ_{jk}^{nc}, is the achiral expansion of the pair potential already derived in Refs. [3,4] and the second term, Φ_{jk}^{c}, which is simply the invariant c_{jk} times an appropriate coefficient to be determined, is the chiral contribution. Writing explicitly the pair potential for the same three director displacements which we have considered, and equating terms with the same powers in the invariants we finally obtain, after some rearrangement, the expression for the pair potential in terms of the elastic constants, K_1, K_2, and K_3, and the helical wavevector of the chiral nematic, q_0:

$$\begin{aligned}\Phi_{jk} = {} & \lambda\left[P_2(a_j) + P_2(a_k)\right] + \mu\left(a_j a_k b_{jk} - 1/9\right) + \nu P_2\left(b_{jk}\right) \\ & + \rho[P_2(a_j) + P_2(a_k)]P_2(b_{jk}) + \sigma P_1(c_{jk})\mathrm{sgn}(\mathbf{n}_j \cdot \mathbf{n}_k),\end{aligned} \tag{11}$$

where $P_L(\mathrm{x})$ is the Lth order Legendre function and the interaction parameters λ, μ, ν, ρ, σ are defined as [7]:

$$\begin{aligned}\lambda &= \frac{1}{9}\Lambda(2K_1 - 3K_2 + K_3), \\ \mu &= \Lambda(K_2 - K_1), \\ \nu &= \frac{1}{9}\Lambda(K_1 - 3K_2 - K_3), \\ \rho &= \frac{1}{9}\Lambda(K_1 - K_3), \\ \sigma &= -2K_2 q_0 \Lambda^2,\end{aligned} \tag{12}$$

and Λ is the dimension of the unit cell of the cubic lattice. We should note here that the wavevector, q_0, is a pseudo-scalar, that is an inversion operation applied to the system changes q_0 into $-q_0$. It is, therefore, necessary to take into account the sign of the dot product between $\mathbf{n}_j$ and $\mathbf{n}_k$, as shown in Eq. (11). We notice also that the functional form of the chiral contribution is then the simplest, allowed by symmetry considerations, for a chiral interaction. The difference between the chiral term in Eq. (11) and that in the interaction potential between two chiral particles proposed by van der Meer *et al.* [8] is only in the fact that we do not take the dot product between $\mathbf{n}_j$ and $\mathbf{n}_k$, but just its sign. This obtains because the elastic pair potential has been derived in the limit of small director displacements (η and $\xi \sim 0$) where the dot product can be either 1 or -1.

RESULTS AND DISCUSSION

To test the functional form of the elastic pair potential that we have derived, we have simulated the director distribution for a chiral nematic in a partially confined system by means of Monte Carlo simulation. The helical structure of the chiral nematic phase with its spatially varying director orientation precludes the use of standard periodic boundary conditions. This situation occurs because the helical structure of the periodic images will not necessarily be compatible with that in the simulation box. This problem can be solved in a variety of ways as discussed by Luckhurst *et al.* [9]. Here, however, we adopt a different and simpler approach. The helix axis is aligned along the z axis of the simulation box which allows standard periodic boundary conditions to be used in the x and y directions. No periodic images are constructed along the z direction so that the directors at the top (+z) and bottom (−z) of the sample experience a weaker elastic interaction since they only have five and not six nearest neighbours with which to interact. More importantly the chiral interaction, which is in practice confined to directors in neighbouring planes orthogonal to the helix axis, results from just one neighbour for the top and bottom of the sample and not two as for the bulk. The importance of these missing interactions will depend on the size of the system and, as we shall see, it does not appear to be significant for most of the systems we have studied.

The box is rectangular with a dimension of $10 \times 10 \times 100$ along the x, y and z coordinates, respectively. Initially we apply an orienting field along the z axis, taking the sample to have a negative anisotropic susceptibility, so that the preferred orientation of the directors is to lie in the xy plane, perpendicular to the field, thus ensuring that the helix axis is along the z direction. We have equilibrated the sample for 200,000 cycles, then the field was removed and the sample was equilibrated for another 500,000 cycles, at a scaled temperature, T^* ($\equiv k_BT/|\nu|$), of 0.2, for different values of the scaled parameter, $\sigma^*(\equiv -2K_2q_0\Lambda^2/\nu)$. For this series of simulations the elastic constants K_1, K_2 and K_3, were taken to be in the ratio 2:1:3, respectively; these are typical of those for real nematogens.

After equilibrating the sample we have calculated the x and y components of the director as a function of the z coordinate along the box, taking the average over the directors belonging to the xy section at that position along the axis z. The average director orientation for a given xy plane was obtained from the eigenvector associated with the largest eigenvalue of the orientational ordering tensor, **Q**. The sign but not the magnitudes of the components, n_x and n_y, obtained in this way were found to vary in essentially a random manner. To avoid this problem when showing the variation of the director orientation along the helix axis we have used the square of n_x rather than n_x itself. This variation of n_x^2 for the case of σ^* of 0.5625 is shown in Figure 1, as a function of the scaled lattice coordinate z^*, ($\equiv z/\Lambda$). It clearly shows the periodic behaviour expected for a helical structure from which, by performing a non-linear fitting with a squared sinusoidal function, we can obtain the corresponding pitch of the chiral nematic. The best fit is shown in Figure 1 as the solid line.

In Figure 2 we show the section of the box, for the same sample as in Figure 1, at different values of z^*, along the helix axis: the twisting of the director is evident as we move along z. The change in the average director orientation from plane to plane along the helix axis is large in comparison with that for real chiral nematics but this is to be expected for the relatively small system sizes which can be studied in such simulations. The snapshots also show that, because of thermal fluctuations, the directors within a plane are not perfectly aligned. This could be achieved by employing a significantly lower scaled temperature if a comparison with the predictions of continuum theory, which ignores such fluctuations, was required. As expected, we have also found that changing the sign of σ results in a twist

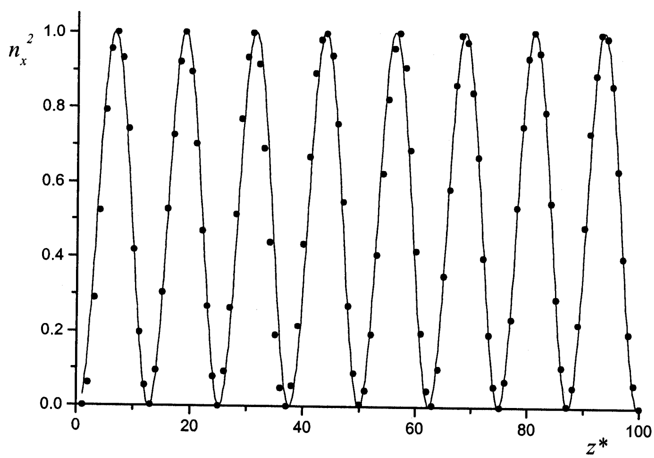

FIGURE 1 The square of the x component of the director n_x^2, as a function of the position $z^*(=z/\Lambda)$ along the z axis for a chiral nematic with σ^* equal to 0.5625 at T* of 0.2. The best fit with a squared sinusoidal function is shown as the solid line.

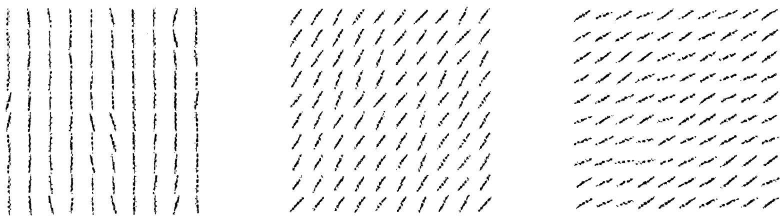

FIGURE 2 From left to right: snapshots of the sample in the *xy* plane for values of z^* of 1, 3 and 5, respectively; σ^* is 0.5625 and T^* is 0.2.

of the director along the helix in the opposite direction, with exactly the same pitch.

In Figure 3 we show the inverse of the scaled pitch p_0^* ($\equiv p_0/\Lambda$) obtained from the simulations for different values of the parameter σ^* used in the potential, as a function of the corresponding scaled helical wavevector q_0^* ($\equiv q_0\Lambda$), given by Eq. (3); the solid line represents the expected pitch given simply by $q_0^*/2\pi$. As we can see, there is almost quantitative agreement with the theoretical prediction. However some minor discrepancies merit a comment: for small values of the helical wavevector, the pitch obtained from the simulation is larger (vide infra) than the value predicted by the theory. This may be due to the effect of the free boundaries at the top and bottom, of the simulation box. As we have seen the

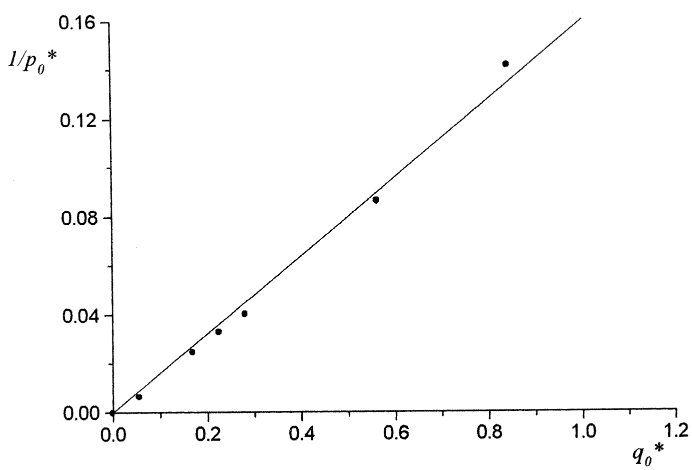

FIGURE 3 The inverse of the simulated pitch, $1/p_0^*$, as a function of the scaled helical wavevector q_0^* used in the simulation; the solid line is the theoretical prediction, $q_0^*/2\pi$.

directors in the first and last xy lattice planes interact with only one set of neighbouring directors, namely the second and second last xy lattice plane, respectively; they do not have any additional interaction with their periodic images. However, the reduced number of chiral interactions to which the directors at the top and bottom of the box are subjected, if it does have effect, would certainly be expected to decrease the total rotation of the director across the sample. We should also note the effect of thermal fluctuations: as we have found when simulating the Fréedericksz transition, [5] a scaled temperature of 0.2, induces relatively large thermal fluctuations in the director distribution, with respect to the distribution predicted by continuum theory. The fluctuations have the effect of weakening the elastic pair interaction and so allow the system to twist less. In fact we have run a simulation at a very low scaled temperature of 0.0001 for the sample with a value for σ^* of 0.1125 and we found that the scaled pitch, p_0^*, changes from a value of 154, obtained at a scaled temperature of 0.2 (see Fig. 3), to a value of 126, where the theoretical pitch is 112. We note that the relatively large disagreement observed at the lower σ^* of 0.1125 between theory and simulation, is related with the fact that the pitch is comparable with the box length and the missing interactions at the top and bottom of the box, which result from the neglect of periodic boundary conditions along the z axis, have an effect. As we see in Figure 3, when the pitch becomes shorter than the box the agreement is almost quantitative. We also observed, for the low temperature case, that the parameter χ^2 for the fitting procedure, not reduced, was of the order of 10^{-6}, while it is of the order of 10^{-3} for a scaled temperature of 0.2.

We also note that, for relatively large values of the helical wavevector a deviation from linearity occurs. This deviation may result from the fact that the potential has been derived in the limit of small director deformations whereas a large helical wavevector combined with a relatively small box dimension means that the director orientation changes significantly between adjacent planes orthogonal to the helix axis.

CONCLUSIONS

We have developed an analytical expression for a pair potential which allows the simulation of the director distribution of a macroscopic sample of a chiral nematic phase characterized by the elastic constants K_1, K_2 and K_3, and helical wavevector, q_0. The pair potential could be employed to simulate the behaviour of chiral nematics in, for example, LCDs by including the additional effect of an orienting field and to investigate the director distribution in confined geometries with the inclusion of thermal fluctuations. Our preliminary Monte Carlo simulations are consistent with the pair potential as a representation of the elastic interactions for a chiral nematic. They also reveal that the removal of periodic boundaries along a direction parallel to the helix axis does not create any anomalies in the behaviour of the system, provided that the pitch of the sample is shorter than the box length.

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