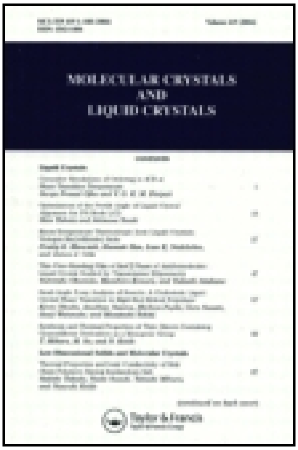

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Monte–Carlo Simulation of the Cholesteric Phase in Liquid Crystals

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Starting from a simple pair interaction potential between chiral molecules, a cholesteric configuration of molecules is generated in a 15 × 15 × 15 system. The effect of temperature on the cholesteric structures is also studied. Unlike the results under the mean field approximation with the same pair potential, the present Monte–Carlo simulation shows a temperature dependence of the pitch.

INTRODUCTION

The cholesteric mesophase is a helically distorted nematic mesophase. In nematic mesophase the long axes of the organic molecules tend to align along a common "director" represented by a unit vector $\hat{n}$. The anisotropic interaction potential between two neighbouring molecules, as provided by the Maier–Saupe theory[1] is

$$V_{ij} = -JP_2(\hat{a}_i \cdot \hat{a}_j) \tag{1}$$

where, J is the coupling constant; $\hat{a}_i$ is a unit vector along the long axis of the ith molecule and $P_2(x)$ is the second order legendre polynomial. The orientational order parameter of the nematic phase

$$\eta = \langle P_2(\cos\theta) \rangle \tag{2}$$

where, θ is the angle between the molecular long axis and the director.

In the cholesteric mesophase the director rotates around an axis normal to $\hat{n}$, so $\hat{n}$ varies as a function of position $\vec{r}$. With reference to a right handed Cartesian coordinate system with $\hat{n}(0)$ as the Z-axis and the twist axis as the X-axis of the laboratory frame, the endpoints of vectors $\hat{n}(x,0,0)$ form a helix with pitch $p = 2\pi/q$, where q is the wave number; $q > 0$ refers to a right handed helix and $q < 0$ to a left handed helix.

The interaction potential between two neighbouring molecules i and j as introduced by Van der Meer *et al.*[2] is

$$V_{ij} = -JP_2(\hat{a}_1 \cdot \hat{a}_j) - K(\hat{a}_1 \cdot \hat{a}_j)(\hat{a}_1 \cdot \hat{a}_j \times \hat{u}_{ij}) \tag{3}$$

where, $\hat{u}_{ij} = \vec{r}_{ij}/r_{ij}$ is the unit vector pointing from the centre of mass of molecule i towards that of j and K is the coupling constant which vanishes if both molecules are achiral. The first term is the Maier–Saupe interaction which gives rise to the nematic phase. The second part of the potential induces a twist into the system resulting in the cholesteric phase.

Van der Meer *et al.* showed that the pair interaction of Equation (3), under mean field approximation, can lead to the stabilization of a cholesteric phase with temperature independent pitch given by

$$p=\frac{2\pi\times 22\,\mathrm{JR}}{21\,\mathrm{K}}$$

where, R is the mean separation of molecules. A slight dependence of R on temperature was ignored. For temperature dependence of the pitch they had to include higher order terms of proper symmetry in the pair interaction. The present Monte–Carlo model shows that the pair interaction considered above without the higher order terms is not only suitable for stabilizing cholesteric phase but also good enough for the temperature dependence of the pitch. The latter aspect, we believe, is due to doing away with the mean field approximation.

In the present work we assumed, for the sake of simplicity, that the molecules are confined to planes parallel to the laboratory YZ plane. Each molecule thus has the freedom to rotate about the X-axis. The simple minded model is similar to the one considered by Lin Liu *et al.*[3] or by W. J. A. Goossens[4] for cholesteric phase and to the work on planar nematic by Denham *et al.*[5] The cholesteric terms of the potential given in Equation (3) vanishes for interacting molecules having the same X co-ordinate, i.e., for molecules belonging to a particular YZ plane. On the other hand this term favours a relatively perpendicular configuration of molecules belonging to neighbouring planes. The first term (the nematic term) however favours parallel arrangement of molecules irrespective of planes. These two opposite tendencies give rise to the cholesteric helix with appropriate pitch which is seen to be temperature dependent. It is to be mentioned that for molecules in a plane the orientation order parameter is to be taken as $\eta=\langle\cos 2\theta\rangle$ where θ is the angle between the molecular long axis and the director in the respective planes. This definition gives the proper normalization of the nematic order parameter in two dimension.

MONTE–CARLO SIMULATION

The centres of mass of molecules are placed in a $15\times 15\times 15$ cubic lattice. As mentioned earlier the long axes of the molecules are confined to parallel planes. The conventional boundary condition of a finite system used to simulate infinite systems is the periodic boundary condition. For the present work we have utilized the helical boundary condition[6] but we had to introduce a modification to make the boundary condition commensurate with the helical structure of the phases. To ensure that the sites on the topmost plane have an upper neighbour and the sites in the lowest plane have a lower neighbour, the lattice is extended by a buffer plane on top of the topmost physical plane and by another buffer plane below the lowest physical plane. The up down direction is chosen along the X-axis, i.e., along the direction of the axis of the helix. The molecules on the buffer planes are made to align along directions commensurate with the helical structure of the physical planes. In other words, the molecules on the upper buffer plane are rotated with respect to the director of the topmost physical plane by an angle equal to the average twist per layer maintaining the appropriate sense of twist. The molecules of the lower buffer plane are made to have similar relation with respect to the lowest physical plane. We have considered the initial configuration to be a highly twisted phase. The particles in a plane make the same angle with the laboratory Z-axis and molecules in adjacent layers are relatively twisted by an angle of 25° which corresponds to the value at ground state, i.e., the minimum of the pair potential. A random orientation θ (uniformly distributed between 0 to π) with respect to the laboratory Z-axis is then assigned to the molecule belonging to the first lattice site. The energy E_R of the resulting configuration is calculated and compared with the previous energy E_P. The condition needed for the acceptance of new configuration is $E_R < E_P$. If $E_R > E_P$ the new configuration is retained with the probability $\exp(E_R - E_P)/T_{\text{red}}$, where T_{red} $(= KT/J)$ is the reduced temperature. Treating all the molecules one after another with the same prescription we get a final configuration of the lattice as a whole. The orientation θ_0 of the director with respect to the laboratory Z-axis is then calculated for molecules of each plane by maximizing respective $\langle \cos 2\theta \rangle$. Maximization procedure leads to the expression

$$\theta_0 = 0.5[\tan^{-1}(\overline{\sin 2\theta}/\overline{\cos 2\theta})].$$

Once this is obtained for each plane, $\eta = \langle \cos 2(\theta - \theta_0) \rangle$ gives the respective orientational order. The whole procedure, i.e., assigning θ from the first lattice point to the last, evaluation of θ_0 and hence η constitutes an iteration. Iterations are performed till equilibrium condition is reached. The criterion for equilibrium was that η's should be stable within 2%. Once equilibrium is reached we have generated 2×10^3 more iteration to get the average value of the orientational order parameter η and θ_0 for each plane. Standard deviation of θ_0 and η are typically ± 0.02 radian ± 0.01 respectively near transition.

The number of iterations needed to reach equilibrium condition in a $15 \times 15 \times 15$ lattice system was 5×10^3 for temperature far away from transition and 9×10^3 near transition.

RESULTS

After some initial trial, we have chosen $K/J = 2.0$. The variation of director orientation from one plane to another has been calculated at various reduced temperatures T_{red}. Figure 1 shows the variation of twist angle with plane number at $T_{\text{red}} = 0.1$. The variation is more or less linear. The deviation of data points from a strict linearity is due the small size of the system and imposition of average twist on the boundary layers in the boundary condition utilized. From such a plot pitch was obtained from the average $\langle \Delta\theta_0 \rangle$, i.e., the change in θ_0 for two adjacent planes. In the cubic lattice considered, the separation between two adjacent planes is one lattice parameter (R) and the pitch $p = (2\pi/\langle \Delta\theta_0 \rangle)R$. The standard deviation in $p \approx \pm 0.3R$. The helical structure starts distorting at about $T_{\text{red}} = 2.0$ (Figure 2). At lower end of temperature the pitch vs. T_{red} curve (Figure 3) approaches a limiting value of 25° twist per plane which is

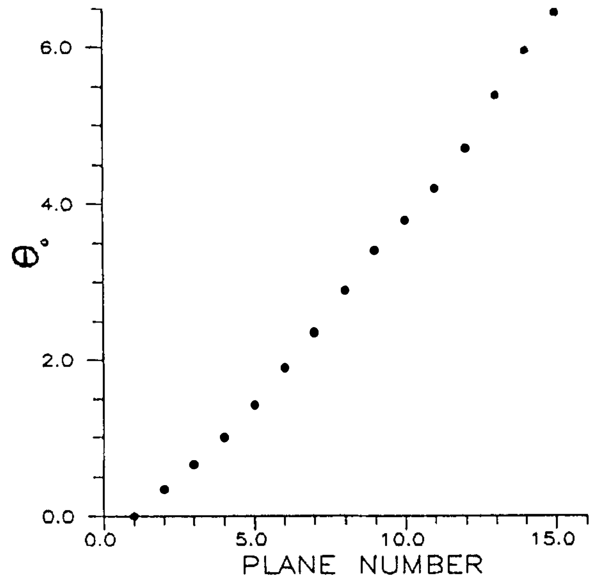

FIGURE 1 θ_0 (in radian) of planes perpendicular to the helix axis at $T_{\text{red}} = 0.1$. Cholesteric phase exists.

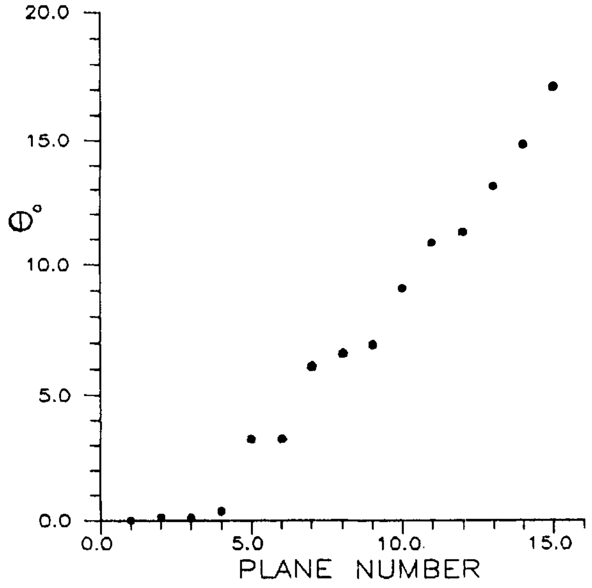

FIGURE 2 θ_0 (in radian) of planes perpendicular to the helix axis at $T_{\text{red}} = 2.0$. The helical structure starts distorting.

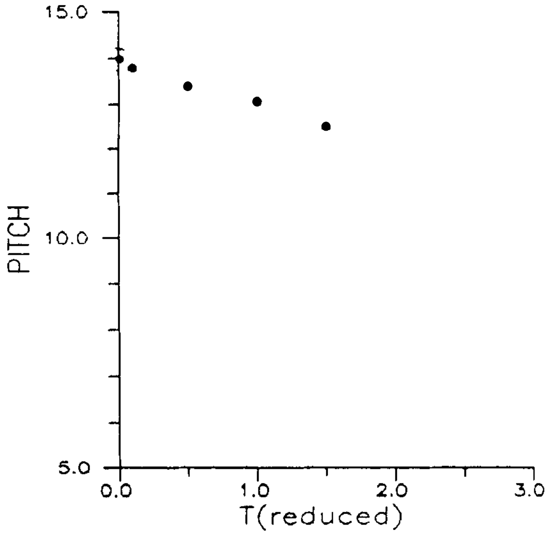

FIGURE 3 Pitch in units of lattice constant vs. reduced temperature.

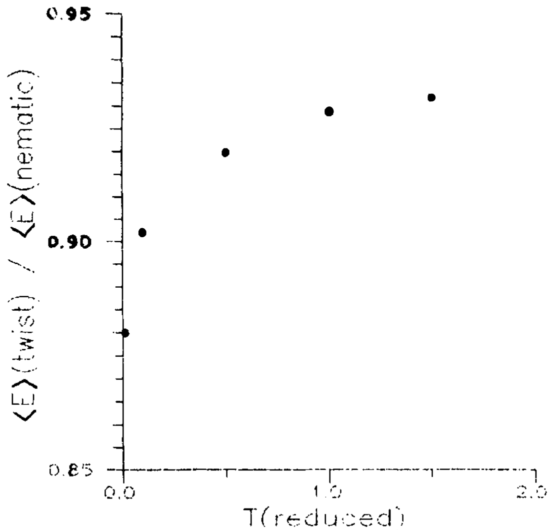

FIGURE 4 Ratio of the average twisting energy and average nematic energy of off planar neighbouring molecules vs. reduced temperature.

consistent with the minimum of pair potential (Equation 3). The decrease in pitch with rising temperature was also looked into. The relative twisting of the two adjacent molecules, belonging to adacent layers, results from the balance between the "nematic" interaction (the first term in Equation 3) and the "twisting" interaction (the second term in Equation 3). The in-plane "nematic" interaction is not relevant to the twist. The

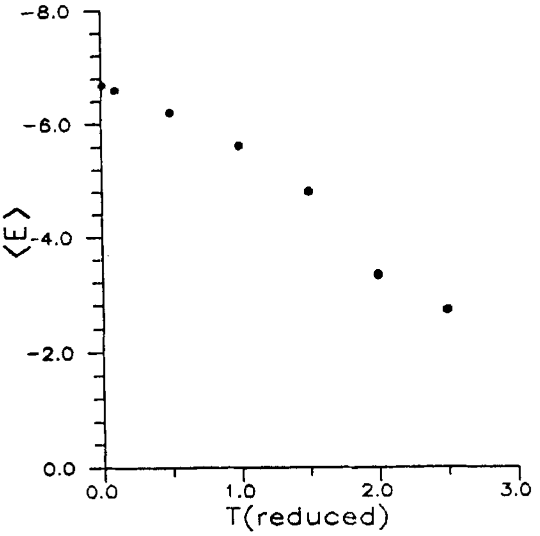

FIGURE 5 Average energy ($\langle V/KT \rangle$) vs. reduced temperature.

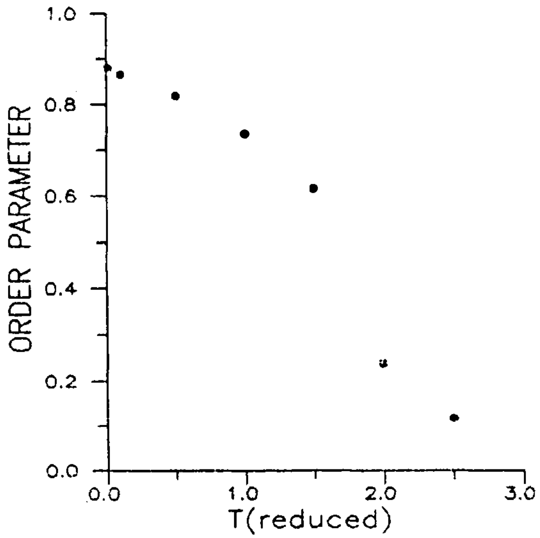

FIGURE 6 Order parameter vs. reduced temperature.

equilibrium average values of the above two parts ("nematic" and "twisting") of interaction energy for pairs of off plane molecules were calculated as a function of temperature. It is seen that the so called "nematic" part decreases faster than the twisting part with rise in temperature (Figure 4). This means that the "twisting" part of the interaction becomes relatively larger (as compared to the nematic part) which in a qualitative sense is equivalent to an increase in K/J ratio, i.e., larger twist par layer and hence smaller pitch.

The temperature variation of $\langle E \rangle$ (Figure 5) and η (Figure 6) are also interesting. A jump in value is obtained in both these plots between $T_{\mathrm{red}} = 1.5$ and $T_{\mathrm{red}} = 2.0$. This is the signature of the nematic isotropic transitions in planes with nematic interaction only. The sudden drop in nematic interaction results into the breaking down of the cholesteric arrangement.

CONCLUSION AND REMARKS

The work presented here reproduces the cholesteric phase for molecules confined in parallel planes. In order to bring down the pitch length so as to be discernable in a $15 \times 15 \times 15$ system we have artificially chosen $|K/J| = 2.0$. As is known from experiment, the cholesteric pitch is of the order of 3000 Å and for such a large pitch, mean field calculation infers that $|K/J| \ll 1.0$. However for us it means an enlargement of the size of the system impossible to be treated in Monte–Carlo simulations because of limitations in computation time. On the other hand the present study though made on a small system reproduces the cholesteric phase and a temperature dependence of the pitch which is qualitatively correct. The latter aspect was not possible in mean field approximation with the same pair interaction.[2] For further comparison with the mean field result, it may be pointed out that the value of the pitch also differs in these two approaches. If one compares with the mean field result mentioned earlier, i.e., $q = (21/22)(K/JR)$ we get a factor of four difference in the value of the pitch at low temperature. When R, the mean separation among molecules are taken as one lattice parameter we get $qR \approx 2$ and $p = 2\pi/\lambda \approx 3R$ with $K/J = 2.0$ in the mean field theory, while our Monte–Carlo result at low temperature shows $p \approx 14R$. These results do differ widely but it is doubtful how far it is meaningful as mean field result was based on assumption $qR \ll 1$ whereas we have here $qR \approx 2$.

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