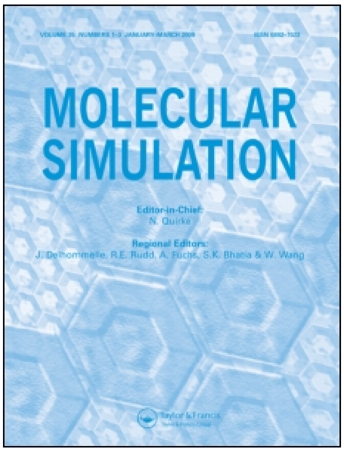

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Jayashree Saha[a]; M. Saha[b]
[a] S. N. Bose National Centre for Basic Sciences, Calcutta, India [b] Department of Physics, University of Calcutta, Calcutta, India

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A LATTICE MODEL MONTE CARLO SIMULATION OF CHOLESTERIC LIQUID CRYSTAL WITH FREELY ROTATING MOLECULES

JAYASHREE SAHA[a] and M. SAHA[b]

[a]*S. N. Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Calcutta 700 091, India;*
[b]*Department of Physics, University of Calcutta, 92, Acharya Prafulla Chandra Road, Calcutta 700 009, India*

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An earlier Monte-Carlo simulation of a cholesteric configuration of molecules is generalised in the present work allowing for full rotational degrees of freedom. The effect of temperature on pitch has been studied and the results are compared with the results obtained from mean field and plane rotator model simulation studies.

Keywords: Chiral molecules; Monte-Carlo; phase transition

INTRODUCTION

There exists a number of computer simulation studies on liquid crystals. One approach considers only anisotropic attractive interactions to be responsible for mesogenic behaviour. A quite different approach follows Onsager's model [1] for excluded volume effect and considers that liquid crystal formation is only due to anisotropic repulsive interaction. Though either kind of interaction is sufficient for the development of the mesophase, in actual liquid crystals both these factors are believed to be important. There exists a third kind of phenomenological approach, closer to real mesogenic systems which considers both the anisotropic short range repulsive and the long range attractive interactions. Modified forms of Lennard-Jones potentials, among which Gay-Berne potential [2] is most realistic, can be used for this type of simulation studies.

Though detailed and extensive studies have been done on other phases of liquid crystals, there exists a very few computer simulation studies for chiral systems. Allen and Masters [3] performed computer simulation of twisted nematic liquid crystals using non-spherical hard particles. Following the third kind of approach mentioned earlier, chiral forms of Gay-Berne potential were used by Memmer *et al.* [4] to generate chiral phases. However, this kind of simulation which involves large computation time is not suitable for performing exact calculation of statistical models because only systems consisting of relatively small number of particles can be studied. Temperature variation of pitch was also not studied. In this respect, lattice model can be used quite efficiently. Furthermore, confinement of molecular centres of mass is necessary for simulating statistical models of liquid crystals (having only orientational ordering) which consider only attractive interactions.

Lattice model version of computer simulation was first done by Lebwhol-Lasher [5] for nematic phase. Recently, we reported the first simulation study of cholesteric phase using lattice model, where molecular rotation was confined in planes [6]. Goosens [7] developed statistical model for cholesteric considering this type of planar structure. But the planar structure prohibited the said model's reduction to the Maier-Saupe model [8] for the nematic phase when chirality was removed. In this paper, we report the results of the computer simulation study for a system of chiral molecules, where the molecular centres of mass were constrained on lattice sites but the molecular symmetry axis had full rotational degrees of freedom.

MODEL

Nematic mesophase of elongated molecules are characterized by the tendency of the long molecular axis to align along a common 'director' represented by a unit vector $\hat{n}$. With reference to right handed Cartesian system with $\hat{n}(0)$ as the Z-axis and the twist axis as the X-axis of the laboratory frame, the vectors $\hat{n}(x,0,0)$ form a helix with pitch $p = 2\pi/q$, where q is the wave number. In most cholesteric liquid crystals pitch is a decreasing function of temperature i.e. $[dp(T)/dT] < 0$.

The anisotropic nematic interaction potential between two neighbouring molecules, as provided by the well known Maier-Saupe theory [8]

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

where J is the coupling constant, $\hat{a}_i$ is the unit vector along the long axis of the ith molecule and $P_2(x)$ is the second order Legendre polymial.

The presence of chiral molecules forms the basis of molecular statistical theory of cholesteric mesophase which was first developed by Goosen's assuming planar structure of the phase. Later, van der Meer *et al.* [10] with the help of a model system showed that cylindrically symmetric molecules can give rise to a cholesteric phase. Their model consists of N identical linear polarizabilities on a twisted cylindrical surface.

From the multipole expansion of electrostatic interaction between two molecules van der Meer *et al.* [10] considered interaction energy between two cylindrically symmetric chiral molecules as

$$V_{ij} = -JP_2(\hat{a}_i\cdot\hat{a}_j) - K(\hat{a}_i\cdot\hat{a}_j)(\hat{a}_i\cdot\hat{a}_j \times \hat{u}_{ij}) \tag{2}$$

where $\hat{u}_{ij}(\equiv \vec{r}_{ij}/|r_{ij}|)$ is a unit vector pointing from the centre of mass of molecule i towards that of j. K is the coupling constant that vanishes for achiral molecules. Though they calculated the expression of J and K from multipole expansion, later they preferred to take them as phenomenological parameters. The first term of equation (2) is the Maier-Saupe induced dipole-dipole interaction and is due to the anisotropy of the molecules giving rise to the nematic phase. The second term which is due to the asymmetry of the molecules, induces a twist in the system and is responsible for giving rise to cholesteric phase.

If the molecules can have θ, ϕ rotations the nematic part of the potential will be

$$(\hat{a}_i\cdot\hat{a}_j) = (\sin\theta_i\cos\phi_i\sin\theta_j\cos\theta_j + \sin\theta_i\sin\phi_i\sin\theta_j\sin\phi_j + \cos\theta_i\cos\theta_j) \tag{3}$$

The box product of the cholesteric part gives

$$(\hat{a}_i \times \hat{a}_j\cdot\hat{u}_{ij}) = \sin\theta_i\sin\phi_i\cos\theta_j - \cos\theta_i\sin\theta_j\sin\phi_j$$

if $\hat{u}_{ij} \parallel X$-axis

$$= \sin\theta_i\cos\phi_i\cos\theta_j - \cos\theta_i\sin\theta_j\cos\phi_j \tag{4}$$

if $\hat{u}_{ij} \parallel Y$-axis

$$= \sin\theta_i\cos\phi_i\sin\theta_j\sin\phi_j - \sin\theta_i\sin\theta_j\sin\phi_i\cos\phi_j$$

if $\hat{u}_{ij} \parallel Z$-axis

The orientation θ_0, ϕ_0 of the director with respect to the laboratory frame was determined in the following way.

If (X', Y', Z') represents the director frame of reference and (X, Y, Z) represents the laboratory frame of reference then

$$\begin{vmatrix} \sin\theta'\cos\phi' \\ \sin\theta'\sin\phi' \\ \cos\theta' \end{vmatrix} = \begin{vmatrix} \sin\theta\cos\phi\cos\phi_0 + \sin\theta\sin\phi\sin\phi_0 \\ -\sin\theta\cos\phi\cos\theta_0\sin\phi_0 + \sin\theta\sin\phi\cos\theta_0\cos\phi_0 + \cos\theta\sin\theta_0 \\ \sin\theta\cos\phi\sin\theta_0\sin\phi_0 - \sin\theta\sin\phi\sin\theta_0\cos\phi_0 + \cos\theta\cos\theta_0 \end{vmatrix} \tag{5}$$

The orientation θ_0, ϕ_0 of the director of each plane with respect to the laboratory frame of reference has been determined in the following way.

Because of ϕ symmetry

$$\overline{\sin\theta\cos\phi}\cos\phi_0 + \overline{\sin\theta\sin\phi}\sin\phi_0 = 0 \tag{6}$$

Therefore,

$$\phi_0 = \tan^{-1}(\overline{\sin\theta\cos\phi}/\overline{\sin\theta\sin\phi}) \tag{7}$$

Maximizing the order parameter $P_2(\cos\theta')$, we get

$$\theta_0 = \tan^{-1}(\overline{\cos\theta}/\overline{-\sin\theta\cos\phi\sin\phi_0 + \sin\theta\sin\phi\cos\phi_0}) \tag{8a}$$

or

$$\theta_0 = \tan^{-1}(\overline{\sin\theta}/\overline{\cos\theta\cos\phi\sin\phi_0 - \cos\theta\sin\phi\cos\phi_0}) \tag{8b}$$

Respective orientational order parameter for each plane is

$$\eta = \langle P_2(\cos\theta')\rangle = \left\langle \frac{3}{2}(\cos\theta\sin\phi\sin\theta_0\sin\phi_0 - \sin\theta\sin\phi\sin\theta_0 + \cos\theta\cos\theta_0)^2 - \frac{1}{2}\right\rangle \tag{9}$$

MONTE-CARLO SIMULATION

For Monte-Carlo simulation the centres of mass of molecules are placed in a $10 \times 10 \times 10$ cubic lattice. To reduce surface effects we used periodic boundary condition after modifying it suitably for this kind of twisted configuration. To ensure that the sites belonging to the uppermost and lowermost plane had an upper and lower neighbour respectively, the lattice was extended by two buffer planes one on the top and another at the bottom of the cubic lattice system. The up-down direction was chosen along the direction of the helix axis. The molecules on upper buffer plane were rotated with respect to the director of the topmost plane which was adjacent to it by an angle equal to an average twist per layer maintaining appropriate sense of twist. Same treatment was applied to the molecules of the lower buffer plane.

The initial configuration chosen is an absolutely ordered phase and for all the molecules the direction θ and ϕ are zero and $\pi/2$ respectively with respect to the laboratory frame. Unlike the planar model [6] in the present work the molecules can have ϕ rotation in addition to the θ orientation with respect to the laboratory frame. For this simulation, we first assigned a random (θ, ϕ) orientation to the molecule belonging to the first lattice site. The value of $\cos\theta$ was uniformly distributed in the range -1 to $+1$. ϕ was uniformly distributed from 0 to π. The value of ϕ was confined between 0 to π instead of 0 to 2π, because the sign of the chiral part of the potential used to change in reflected configurations of the pair of molecules under consideration. In cholesterics the director $\hat{n}$ describes a helix, i.e., the director rotates around an axis. This rotation can be represented by a pseudovector along the helix axis. The dot product of the rotation vector with the unit vector along the helix axis in the direction of observer's moment is equal to $2\pi/p$. The pitch p is inversely proportional to an inner product of an axial vector and a polar vector, hence it is a pseudoscalar. Therefore, pitch changes sign under inversion operation. The chiral coupling constant K takes opposite sign in the range $\pi \leqslant \phi \leqslant 2\pi$. This makes the system a racemic mixture and therefore if full range of ϕ is used we get a nematic phase instead of a cholesteric phase.

Standard Metropolis [11] method was applied for the selection of a new configuration. Treating all the molecules of the system one after another with the same prescription we got a final configuration of the system. Then the orientation of the director (θ_0, ϕ_0) with respect to laboratory frame were calculated for each plane perpendicular to the laboratory X-axis using relations (7), (8a), (8b). We get two values of θ_0 using relations (8a), (8b), which are nearly $\pi/2$ different from each other. Both were used to calculate the order parameter η. The positive value of the order parameter and the corresponding θ_0 was considered as the correct values. Then we calculated the average energy $\langle E \rangle$, the pitch p and the order parameter η of the whole system at a constant temperature. This whole procedure constitutes an iteration. After each iteration the director orientation of the buffer planes were updated accordingly. Iterations were performed till equilibrium was reached.

RESULTS AND DISCUSSION

In this simulation we have chosen $K/J = 2.0$, which is much larger than the actual value. The natural twist found in experiments is always small ($qR \sim 10^{-2}$ to 10^{-3} where R is the length of the molecule). For such a large pitch mean-field theory inferred that $K/J \ll 1$. But, it is impossible to simulate such large pitch value because it means huge enlargement of the system size.

We have calculated the variation of twist angle with plane number of $T_{\text{red}} = 0.2$ (Fig. 1). The variation is more or less linear. The small deviation from strict linearity is due to the small size of the system. The temperature

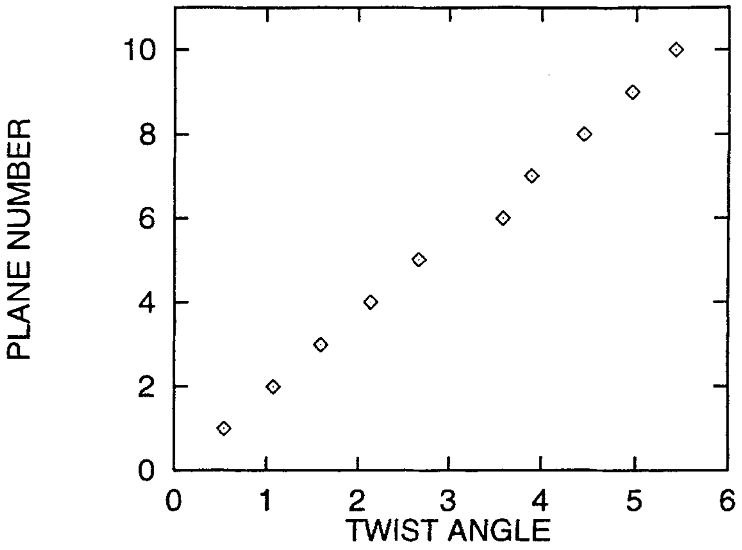

FIGURE 1 Variation of twist angle with plane number at $T_{\text{red}} = 0.2$.

variation of the order parameter η is shown in Figure 2. The plot shows a jump in the value of η between $T_{\text{red}} = 0.45$ and $T_{\text{red}} = 0.5$. This sudden discontinuity in order parameter value indicates phase transition. The temperature vs pitch plot (Fig. 3) shows that the pitch is independent of temperature. This is in accordance with mean field results obtained by van der Meer *et al.* [10]. Luckhurst *et al.* [12] pointed out with simple argument that this kind of potential should give temperature independent pitch in a planar model. The slight temperature dependence observed in our earlier simulation [6] was later found to be due to insufficient number of iterations for proper equilibration. In this simulation study to be sure enough, we have treated the system at a particular temperature with 300000 steps near transition and 150000 steps near transition.

Cholesteric pitch and its temperature sensitivity is the most important point of interest for both theoretical and experimental studies on chiral systems. It was experimentally observed that in most cholesteric liquid crystals pitch is a decreasing function of temperature. van der Meer *et al.* [10] showed that the pair interaction of equation (2) under mean-field approximation gave temperature independent pitch. To decide whether the discrepancy arose due to simplifications made in the construction of the model or due to mean field approximations used in the calculation, we performed Monte-Carlo simulation [6] which provided essentially the exact

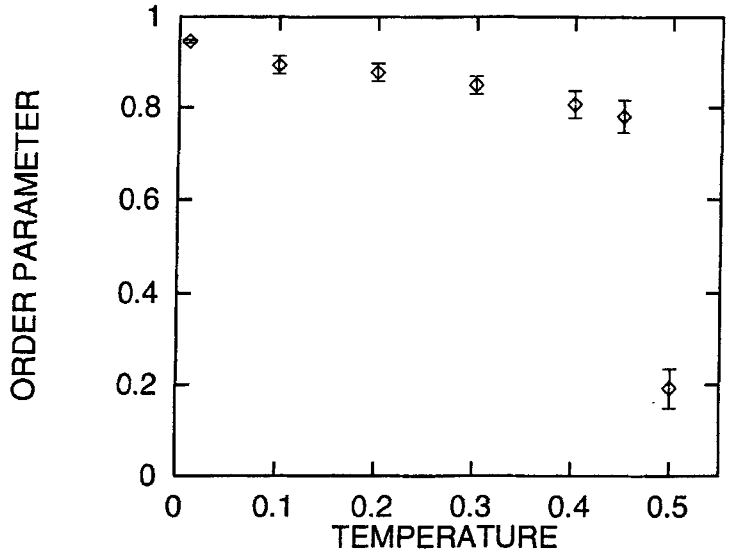

FIGURE 2 Order parameter vs temperature (T_{red}) plot.

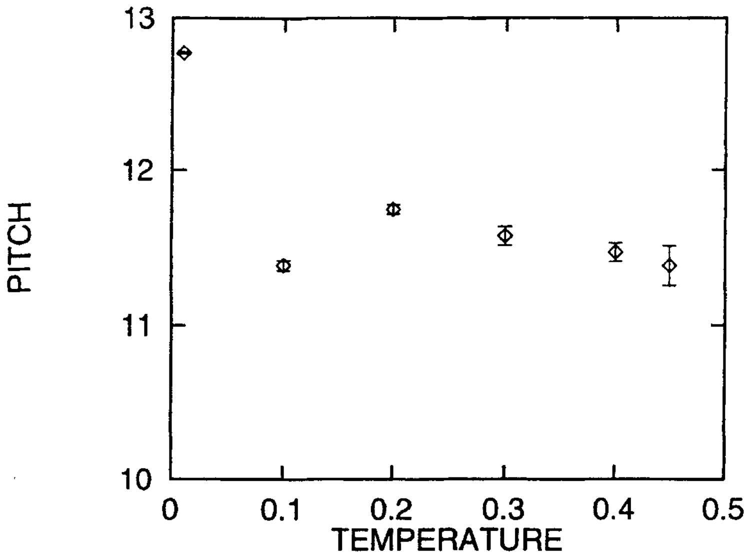

FIGURE 3 Pitch vs temperature (T_{red}) plot.

result of the statistical model. Though that simulation was the first of its kind which investigated temperature sensitivity of the pitch, to simplify it we had assumed that molecules could only rotate in YZ planes. But in the mean field study of van der Meer *et al.* no restriction was imposed on molecular rotation. In the present simulation study we gave full rotational freedom of the molecules. For planar model twisting part of the potential gave non-zero value for two interacting molecules having different x co-ordinates. This term vanishes for interacting molecular pair belonging to same YZ plane. But this is not so in the present case where we removed the restriction on ϕ rotation. This generalization provides proper comparison of simulation with the mean-field results.

Inclusion of higher order terms in this potential might bring out the temperature dependence of the cholesteric pitch as indicated by the mean field theory [10]. Further simulation work is in progress with this kind of potential.

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