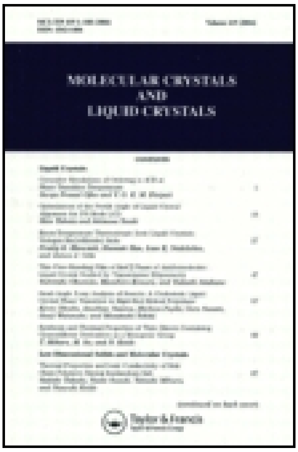

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Induced Nearest-Neighbor Bond Orientational Ordering and Structural Transformation in a Two-Dimensional Liquid Crystal Model

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Induced Nearest-Neighbor Bond Orientational Ordering and Structural Transformation in a Two-Dimensional Liquid Crystal Model

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The intermolecular pair potential responsible for orientational phase transitions in liquid crystal materials are anisotropic and depend on both the orientation of the molecules and on the orientation of the intermolecular vector which connects interacting particles. The induced nearest-neighbor hexatic bond orientational order present in two-dimensional liquid crystalline systems originates from the couplings between the molecular and the intermolecular bond orientation. We show, using an anistropic van der Waals pair potential, that the degree of bond orientational order increases when the strength of these coupling terms is increased. We find that such an increase results in a structural transformation of the nearest-neighbor shell which is similar to the structural phase transitions predicted from zero temperature lattice calculations. Connections are made between the behavior exhibited by the pair potential we study and the behavior of freely-suspended smectic liquid crystal films.

1. INTRODUCTION

A freely-suspended smectic liquid crystal film (FSSLCF) is obtained by spreading a smectic liquid crystal material across a hole in a glass, steel or copper sheet.[1] The lack of substrate in these systems makes them particularly suitable for studying the predictions of defect-mediated two-dimensional ($2D$) melting.[2]

Most of the experimental work on FSSLCFs has, until now, concentrated on the study of the hexatic phase. Bulk hexatic phases of smectic liquid crystals, or hexatic

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liquid crystals, have short-range positional order, as do ordinary fluids, but exhibit long-range order in their intralayer hexagonal nearest-neighbor bond-orientational correlations.[1-3] By varying the number of layers of a FSSLCF in its hexatic phase, one can investigate the three-dimensional to two-dimensional crossover.[4]

In some hexatic liquid crystals, the average orientation of the long molecular axis, $\hat{N}$, is tilted with respect to the normal of the layer. To characterize the local order present within a layer, one introduces two angles, $\phi(\vec{r})$ and $\theta(\vec{r})$. $\phi(\vec{r})$ describes the orientation of the in-plane projection of $\hat{N}$ with respect to a fixed axis, $\hat{x}$, while $\theta(\vec{r})$ characterizes the local orientation of one of the six nearest-neighbor bonds[1,2] with respect to $\hat{x}$.

In tilted hexatics, the anisotropy of the intermolecular pair potential introduces a coupling[5,6] between $\phi(\vec{r})$ and $\theta(\vec{r})$ which can lead to several interesting effects. For example, the presence of a molecular tilt breaks the rotational symmetry within a smectic layer and induces an ordering of the nearest-neighbor bonds.[7,8] Since the molecular anisotropy, or tilt, couples to an applied external field, the phenomenon of induced bond orientational ordering allows one to stabilize single hexatic domains in strong magnetic fields via the tilt-bond coupling,[9] which makes investigations of the multicritical behavior of hexatic liquid crystals possible.[10] Other examples are experiments in which the tilt-bond coupling allows visual observation of nearest-neighbor bond defects[11] and is also responsible for an optical-like locked tilt-bond excitation mode.[12] Furthermore, it has been proposed that the tilt-bond coupling in these systems can drastically modify the behavior of the Fréedericksz transition from that is expected from theories which neglect this coupling.[13,14] Finally, it has recently been shown that the tilt-bond coupling can lead to new types of structural transitions in both thermotropic[12,13,15] and lyotropic[15,16] tilted hexatic liquid crystals.

The structural transitions observed in tilted hexatics[12,16] occur between phases which differ in the average relative orientation of the tilt with respect to the nearest-neighbor bonds or, in other words, by their value of $\langle \phi - \theta \rangle$, where $\langle \quad \rangle$ means that a thermal average is taken. One can distinguish three different cases or phases. The smectic-I and smectic-F have $\langle \phi - \theta \rangle$ equal to 0° and 30° respectively, while $\langle \phi - \theta \rangle$ can take any value between 0° and 30° in the smectic-L phase.

Selinger and Nelson[15] have recently proposed a model which reproduces, within a single theoretical framework, both the first order smectic-I → smectic-F transition observed in thermotropic liquid crystals,[12] and the sequence of second order transitions, smectic-I → smectic-L → smectic-F transitions, observed in lyotropics.[16] Their hypothesis is that the tilt-bond coupling between $\phi(\vec{r})$ and $\theta(\vec{r})$, $V_{T-B}(\phi, \theta)$, which, due to the sixfold symmetry of the nearest-neighbor bond structure, can be written as in the following truncated sixfold periodic Fourier series:

$$V_{T-B}(\phi, \theta) = -h_6 \cos(6\{\phi - \theta\}) - h_{12} \cos(12\{\phi - \theta\}). \qquad (1)$$

with $h_{6n} = 0$ for $n > 2$. A straightforward analysis shows that the value of $\{\phi - \theta\}$ at the minima exhibited by $V_{T-B}(\phi, \theta)$, as well as the order of the transitions between these minima, is determined by the relative sign and magnitude of h_{12}/h_6.

This model, however, does not define the microscopic mechanism which drives the transitions between tilted hexatic phases and one would like to see if similar behavior can be observed in a simple microscopic model. In particular, it raises the first question we ask in this paper, namely: what are the physical mechanisms which determine the $\{\phi - \theta\}$ potential, $V_{T-B}(\phi, \theta)$?

Selinger and Nelson suggest one may employ a lattice model, with an anisotropic pair potential, to extract the h_{6n} coefficients by Fourier transforming the effective $V_{T-B}(\phi, \theta)$. This proposal appears justifiable since both the molecular and nearest-neighbor bond rotational symmetry are broken in tilted hexatic phases and one is interested in transitions between phases which have these two broken symmetries.[17] Hence, one might think that introducing a lattice model where the particles are confined on lattice sites may be a valid starting point for modelling transitions between tilted hexatic phases.

This lattice model approach brings up the second question we ask: does the structural transition exhibited by a lattice model still exist between liquid crystalline phases if translational motion is allowed?

The approach we take to address the above two questions is as follows. Firstly, we introduce in Section II the simple two-dimensional anisotropic van der Waals liquid crystal model which we study in the next sections. Then, in Section III, we use ground state calculations to show that upon variation of a single parameter, γ, the system exhibits a structural phase transition in its solid phase from a distorted triangular lattice to a rectangular lattice. In Section IV we present preliminary results from a Monte Carlo study of the van der Waals system in its two-dimensional nematic liquid crystal phase. These results show that the joint effect of a small anisotropic contribution of the intermolecular pair potential, which is proportional to γ, and of a dense packing of the molecular cores, results in a quasi sixfold periodic $V_{T-B}(\phi - \theta)$ coupling as in Equation 1. By increasing γ, we observe an increase of the induced hexatic ordering. We interpret this behavior as a manifestation of the increase of the strength of the h_{6n} coefficients which enter in the effective $V_{T-B}(\phi - \theta)$ potential. These results provide an explanation for the microscopic origin of the $V_{T-B}(\phi - \theta)$ potential and what controls its strength. However, a further increase in γ leads to a structural transformation from a distorted hexatic phase to a phase with predominant rectangular nearest-neighbor bond structure. This structural transformation is interpreted as a remnant of the structural transition predicted from zero temperature lattice calculations. Finally, we conclude the paper with a discussion.

2. MODEL

We have recently investigated, using Monte Carlo simulations, the thermodynamic behavior of a $2D$ system of particles interacting via an anisotropic van der Waals potential of the form[5,6]:

$$V_{ij}^{VDW}(\vec{r}_{i,j};\, \hat{n}_i, \hat{n}_j) = 4\varepsilon r_{ij}^{-12} - 4\varepsilon r_{ij}^{-6}[\alpha + \beta\{2(\hat{n}_i \cdot \hat{n}_j)^2 - 1\}] - 4\varepsilon\gamma r_{ij}^{-6}(\hat{n}_i \cdot \hat{n}_j - 3\hat{n}_i \cdot \hat{r}_{ij}\hat{r}_{ij} \cdot \hat{n}_j)^2 \quad (2)$$

where we have defined $r_{ij} = |\vec{r}_{ij}|/r_0$. $\vec{r}_{ij}$ is the intermolecular vector which connects particles i and j, and r_0 is an effective molecular diameter. Here $\hat{n}_i = (\cos(\phi_i),$

$\sin(\phi_i))$ is a unit vector in the direction of the molecular anisotropy and $\hat{r}_{ij} = (\cos(\theta_{ij}), \sin(\theta_{ij}))$ is a unit vector in the direction of $\vec{r}_{ij}$. ε is a positive measure of the strength of the interaction and has units of energy.

It is instructive for the purpose of the discussion to expand Equation (2) in terms of its rotational invariants:

$$\begin{aligned} V_{ij}^{VDW} = \frac{4\varepsilon}{r_{ij}^{12}} - \frac{4\alpha + 5\gamma}{r_{ij}^6} - \frac{8\beta + \gamma}{2r_{ij}^6}\cos(2\phi_i - 2\phi_j) \\ - \frac{3\gamma}{r_{ij}^6}[\cos(2\phi_i - 2\theta_{ij}) + \cos(2\phi_j - 2\theta_{ij})] \qquad (3) \\ - \frac{9\gamma}{2r_{ij}^6}[\cos(2\phi_i + 2\phi_j - 4\theta_{ij})]. \end{aligned}$$

We chose the parameters α and β such that

$$\begin{aligned} \alpha &= 1 - \frac{5\gamma}{4} \\ \beta &= J - \frac{\gamma}{8} \qquad (4) \end{aligned}$$

where J and γ are independent and free parameters of the model. With this choice of parameters, we find that integrating V_{ij}^{VDW} over the orientation θ_{ij} of $\hat{r}_{ij}$ reduces it to a suitable potential for the Maier-Saupe model of $2D$ nematic liquid crystals[18,19]:

$$V_{ij}^{MS}(\vec{r}_{i,j}; \hat{n}_i, \hat{n}_j) = 4\varepsilon[r_{ij}^{-12} - r_{ij}^{-6} - J\{2(\hat{n}_i \cdot \hat{n}_j)^2 - 1\}r_{ij}^{-6}]. \qquad (5)$$

The potential V_{ij}^{MS} leads to a nematic fluid phase if J is larger than some critical value. At high temperature, in the isotropic phase, where $\langle e^{2i\theta_{ij}}\rangle \approx \langle e^{4i\theta_{ij}}\rangle \approx 0$ in Equation (3) and $\langle(\hat{n}_i \cdot \hat{n}_j)^2\rangle \approx 1/2$, one recovers an effective Lennard-Jones pair potential from both V_{ij}^{VDW} and V_{ij}^{MS}.

In our previous work[6] we chose the parameter $J = 1/2$ and showed that a system of 400 particles interacting via either V_{ij}^{MS} or V_{ij}^{VDW}, with the particular choice $(\alpha, \beta, \gamma) = (0, 2/5, 4/5)$, leads to an isotropic to nematic phase transition. However, snapshots of particle configurations below the transition showed an important qualitative difference in the positional configurations of the two systems. At the isotropic to nematic transition for potential (2), we observed the build up of considerable nearest-neighbor bond orientational order. In contrast, for potential (5), there was no obvious evidence of such a build up of bond ordering. Calculations of nearest-neighbor bond correlation functions allowed us to interpret these observations as a manifestation of the phenomenon of induced bond orientational ordering[1,7–9] in the system of particles interacting via potential (2).

The terms which couple θ_{ij} with ϕ_i and ϕ_j in Equation (3) are responsible, at the microscopic level, for the induced bond orientational ordering effect observed with potential (2), while the absence of such term in potential (5) means a system of particles interacting via V_{ij}^{MS} exhibits no induced bond orientational order.

In the rest of this paper we study the behavior of the system for $J = 1/2$ and investigate the effects of the $\{\phi - \theta\}$ coupling terms in Equation (3) by varying the parameter γ with α and β still given by Equation (4). As a first step, we present, in the following section, zero temperature (ground state) calculations of the behavior of the system in its solid phase.

3. GROUND STATE CALCULATIONS

In order to determine the lattice structure, we first parameterized the intermolecular vector $\vec{r}_{ij}$ in terms of the basis vectors of the lattice, $\hat{e}_a$ and $\hat{e}_b$. $\hat{e}_b$ makes an angle Θ with respect to $\hat{e}_a$ and the length of the basis vectors along $\hat{e}_b$ and $\hat{e}_b$ are a and b respectively, measured in units of r_o. The total energy per particle, E, is given by

$$E = \frac{1}{2}\sum_j V_{ij}^{VDW} = \frac{1}{2}\sum_{m,n} V_{mn}^{VDW}(\Theta, \Phi_{mn}, \kappa; \gamma, A) \tag{5}$$

where Φ_{mn} is the value of ϕ with respect to $\hat{e}_a$ at lattice site (m, n), and where we have introduced the reduced variable $\kappa = b/a$ with $\kappa \geqslant 1$. A is the area per particle, and is given by $A = ab\sin(\Theta)$. The goal is to minimize E with respect to Θ, Φ_{mn} and κ at fixed value of γ and A.

It is possible to choose a value for J such that the ground state has 'nematic' order[5] with all the molecules pointing in the same direction, $\hat{n}$, and this is the case for $J = 1/2$. Hence, the ground state is a uniform state with Φ_{mn} the same at all lattice sites and equal to Φ. We have calculated E for γ between 0 and 4/5 and A between $0.5r_o^2$ and $1.2r_o^2$ and found, for this range of parameters, all ground states have $\hat{n}$ parallel to $\hat{e}_a$ ($\Phi = 0$). Once the values of Θ and κ which minimize E are found, we calculate the pressure, P, given by $P = -\partial E/\partial A$, and the Gibbs free energy per particle, G, where $G = E + PA$.

These results allow us to construct a zero temperature $\gamma - P$ phase diagram which is shown in Figure 1. We find that for small γ and large P, the system exhibits a slightly distorted triangular (orthorhombic) lattice and, as γ is increased or P decreased, the system undergoes a first order structural transition to a rectangular lattice. The $\{\phi - \theta\}$ couplings in Equation (3) are responsible for the distortion of the lattice which is perfectly triangular for all P at $\gamma = 0$. Because of this distortion, the two lattices have the same symmetry so the transition between the two structures is first order. We found that for γ between 0 and 4/5, the distortion of the lattice away from a perfectly triangular lattice was smaller than 5° at the transition.

The microscopic origin of this transition can be understood by calculating the dependence of V_m on θ_{ij} where V_m is the value of V_{ij}^{VDW} for a separation $r_m(\theta_{ij})$ where V_{ij}^{VDW} is minimum and for $\hat{n}_i \| \hat{n}_j$. V_m has an absolute minimum at $\theta_{ij} = 0$, a local minimum at $\theta_{ij} = 90°$, and an absolute maximum at $\theta_{ij} = \cos^{-1}(\sqrt{3}/3) \approx$

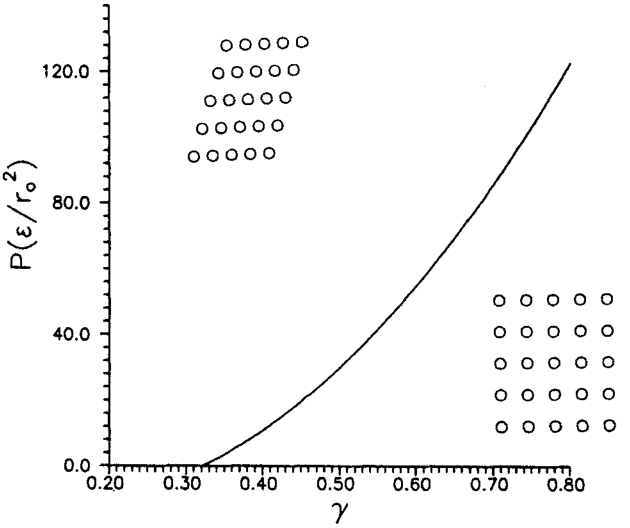

FIGURE 1 $\gamma - P$ phase diagram at $T = 0$. The solid line is a first order phase transition boundary which separates a distorted triangular (orthorhombic) lattice from a rectangular lattice.

55°. The θ_{ij} dependence of r_m and V_m is shown in Figures 2a and 2b for r_m and V_m respectively, for several values of γ. The attractive interactions in Equation (2) favour rectangular packing for all γ, while excluded volume effects favours close packing. If the particles are close packed, the deep minima of the pair potential at $\theta_{ij} = 0$ and 180° ensure that the four equivalent neighbours at, or near 60°, 120°, 240° and 300° must be close to the maxima in the pair potential at 55°, 125°, 235° and 305°. For large γ the close packed configuration becomes unstable and the rectangular configuration becomes the new stable ground state with $\hat{n}\|\hat{e}_a$, and with bonds along $\hat{e}_b$ much weaker than along $\hat{e}_a$.

As explained in the introduction, it is of interest to see if a similar structural transformation occurs when the system is in its liquid crystalline phase. We have investigated this question using a Monte Carlo simulation and present our results in the next section.

4. BEHAVIOR IN THE LIQUID CRYSTAL PHASE—MONTE CARLO RESULTS

In order to observe a structural transformation between two liquid crystalline phases with induced bond orientational ordering, it is necessary to work within a range of parameters such that the system remains in a nematic phase and does not convert either into a solid or isotropic liquid phase as one or several of these parameters are varied.

We performed a simulation at constant area, A, number of particles, N, and temperature, T, and varied γ between 0 and 4/5 and choose[20] $N = 400$, $A = r_o^2$ and $T = 2.7\varepsilon/k_B$. The purpose of this investigation was twofold. Firstly, we wanted to demonstrate that for small but nonzero γ, or $\{\phi - \theta\}$ couplings in Equation (3),

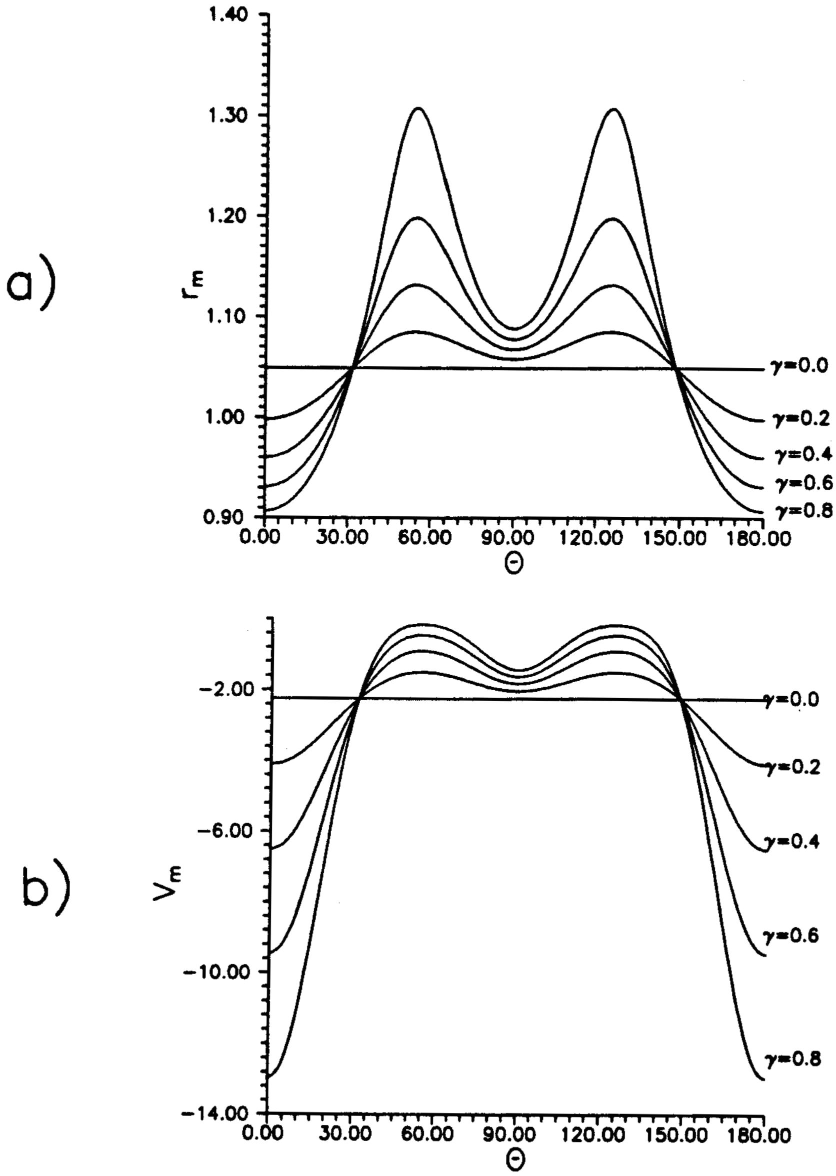

FIGURE 2 (a) θ_{ij} dependence of r_m for potential (2) with $J = 1/2$. (b) θ_{ij} dependence of V_m for potential (2) with $J = 1/2$.

we had induced bond orientational ordering with a liquid crystal phase with predominant sixfold symmetry of the nearest-neighbor bond order. Secondly, we wanted to show that a structural transformation, analogous to the one observed in ground state lattice calculations, could be observed in its liquid crystalline phase.

To measure the degree of induced bond orientational ordering, we introduce a normalized probability distribution function, $\mathcal{P}_1(\theta_1)$. $\mathcal{P}_1(\theta_1)d\theta_1$ measures the probability that the intermolecular vector $\vec{r}_{o1}$, which connected particle o to its first nearest-neighbor, makes an angle $\theta_1 \pm d\theta_1$ with the molecular orientation, $\hat{n}_o$, of particle o. Figure 3 shows $\mathcal{P}_1(\theta_1)$ for various values of γ. We first observe that for $\gamma = 0$, the distribution is uniform between $\theta_1 = 0°$ and $\theta_1 = 360°$, since for $\gamma = 0$, there are no $\{\phi - \theta\}$ couplings. Hence, the system does not exhibit the phenomenon of induced bond orientational ordering and displays only short-range bond orientational order with exponential decay of its nearest-neighbor bond correlation function.[6]

We observed modulation of the distribution function $\mathcal{P}_1(\theta_1)$ for the smallest values of γ studied, indicating that there is a bond orientational field coupled to the molecular orientational field for all finite γ. In the previous section we showed that it is energetically favourable, for finite γ, for a particle to have a configuration of nearest neighbors such that for $\mathcal{P}_1(\theta_1)$ 0°, or 180° (see Figures 2a and 2b). In Figure 3 we see that sharp peaks rapidly develop at these points in the distribution $\mathcal{P}_1(\theta_1)$ as γ increases from zero. As a result, correlations develop between the orientations of the entropically favoured local hexagonal units, and hexagonal bond orientational order develops. This is most easily seen by performing a structure factor calculation of the system. We show in Figure 4 the amplitude squared of the structure factor, $|S(\vec{q})|^2$, as a function of the in-plane components of the momentum transfer, $q_\parallel$ and $q_\perp$. $q_\parallel$ and $q_\perp$ are the components of $\vec{q}$ parallel and perpendicular to the director. The structure factor was calculated from 2000 particle configurations, separated from each other by 5 Monte Carlo steps per particle (2000 Monte Carlo moves). For $\gamma = 0.0$, the structure factor is a ring of uniform intensity, apart from fluctuations due to the finite number of average configurations. For $\gamma = 0.2$, one observes a sixfold modulation of intensity.

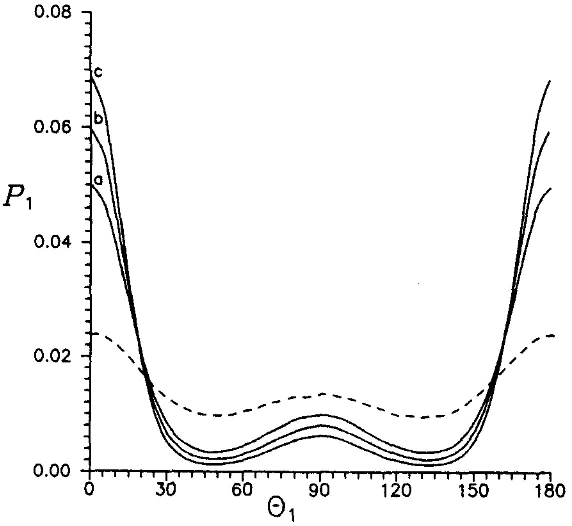

FIGURE 3 θ_1 dependence of probability distribution function $\mathcal{P}_1(\theta_1)$ for several values of γ. The function $\mathcal{P}_1(\theta_1) = \mathcal{P}_1(\theta_1 + \pi)$ and we show the curve only for θ between 0° and 180°. The dashed curve is for $\gamma = 0.2$ and the solid curves are (a) $\gamma = 0.50$, (b) $\gamma = 0.58$, (c) $\gamma = 0.66$.

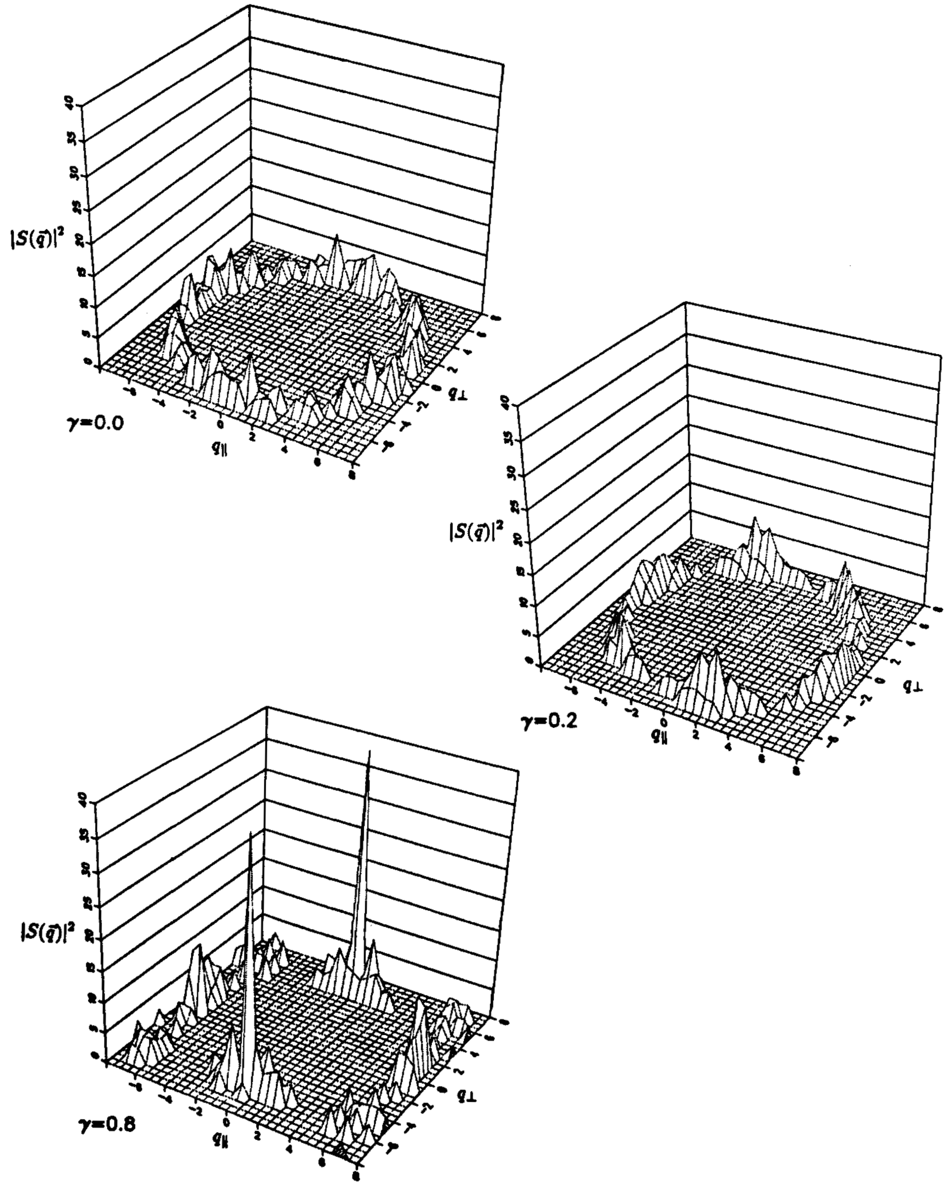

FIGURE 4 Structure factor, $|S(\vec{q})|^2$, for $\gamma = 0.0$, $\gamma = 0.2$ and for $\gamma = 0.8$.

As observed in experiments with smectic-C films, the molecular anisotropy introduces a twofold distortion of the nearest-neighbor bond structure,[9] but which is negligible for sufficiently small γ. These results lead us to speculate that the reason the X-ray diffraction patterns of tilted hexatic[1,9] show an almost perfect sixfold symmetric position of the diffraction is that the effective symmetry breaking couplings, similar to the $\{\phi - \theta\}$ couplings in Equation 3, are small in these systems.

In fact, these couplings may sometimes be so small that they even prevent the observation of induced bond ordering in the smectic-C phase.[21]

As in the ground state calculations, the two body attractive forces favour rectangular order due to the second minimum in the interaction potential for a bond angle of 90° (Figure 2) with respect to the molecular orientation. Hence, for large γ, we expect a change in the bond orientational structure, from hexagonal to rectangular and this is seen in Figure 4c, where $\gamma = 0.8$. In that phase, one can observe long chain-like structures[6] which are remnants of the rectangular solid observed below the melting temperature. In order to examine this structural transformation in more detail we calculated a further normalized probability distribution function, $\mathcal{P}_{13}(\theta_{13})$.

Consider a particle o and its first and third nearest-neighbor. $\mathcal{P}_{13}(\theta_{13})d\theta_{13}$ measures the probability the intermolecular vectors $\vec{r}_{o1}$ and $\vec{r}_{o3}$ make an angle $\theta_{13} \pm d\theta_{13}$ with each other. In an isotropic or hexatic liquid phase, we expect to see the highest peak of $\mathcal{P}_{13}(\theta_{13})$ at 60°. From the ground state calculations, we anticipate finding a $2D$ nematic liquid crystal with considerable rectangular short-range positional structure for sufficiently large γ. In such a state, we expect the highest peak $\mathcal{P}_{13}(\theta_{13})$ to be at 90°. We show, in Figure 5, the function $\mathcal{P}_{13}(\theta_{13})$ for several values of γ between $\gamma = 0$ and $\gamma = 0.7$. The most rapid changes in the distribution occur between $\gamma = 0.5$ and $\gamma = 0.65$ where we observe a rapid development of a peak at θ_{13} at 90° at the expense of the peaks at $\theta_{13} = 60°$ and $\theta_{13} = 120°$.

We interpret this behaviour as a structural transformation from a hexatic phase, with small twofold distortion, to an analogous rectangular bond ordered phase. This behaviour is consistent with the ground state calculations of the previous section, where a first order transition was observed from a triangular to a rectangular lattice structure. However we do not, at present, have sufficiently accurate

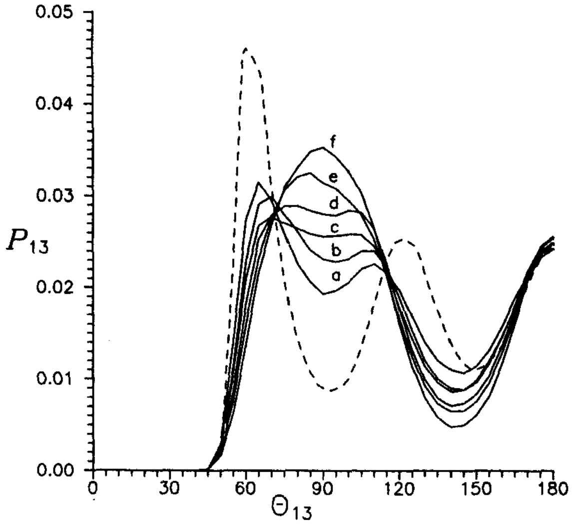

FIGURE 5 θ_{13} dependence of the probability distribution function $\mathcal{P}_{13}(\theta_{13})$ for several values of γ. The function $\mathcal{P}_{13}(\theta_{13}) = \mathcal{P}_{13}(\theta_{13} + \pi)$ and we show the curve only for θ between 0° and 180°. The dashed curve is for $\gamma = 0.2$ and the solid curves are (a) $\gamma = 0.50$, (b) $\gamma = 0.57$, (c) $\gamma = 0.58$, (d) $\gamma = 0.62$, (e) $\gamma = 0.66$, (f) $\gamma = 0.70$.

data to comment on whether the phase transition exists, in the nematic liquid phase or whether it ends at a critical point, due to the presence of orientational and positional fluctuations. This point will be investigated further.

We should emphasize, however, that the bond ordering present in these systems is entirely driven by the nematic ordering via the anisotropy of the intermolecular pair potential, as opposed to the 'true' hexatic phase predicted by the theory of melting of isotropic $2D$ solids.[2,22] The liquid crystalline phases we observe in our simulations are realizations of the anisotropic liquids predicted by the theory of melting of $2D$ anisotropic solids of Ostlund and Halperin.[23] It would be interesting to investigate whether the liquid crystalline phases observed in the present work result from type-II melting of $2D$ anisotropic solids.[23]

We have measured a nematic order parameter,[5,6] Q. Because of their continuous rotational symmetry, $2D$ nematic liquids should exhibit quasi-long-range orientational order and Q should vanish in the thermodynamic limit.[24] However, for a finite system, Q remains a useful indicator of the degree of molecular orientational order. We find that Q increases as γ is increased, which indicates that the structural transformation from the hexatic to the rectangular liquid phase is accompanied by a reduction of the fluctuations in the average molecular orientation.

5. CONCLUSION

Using Monte Carlo simulations, we have studied the behavior of an anisotropic van der Waals nematic liquid crystal as the strength of the components which couple the molecular orientation, $\hat{n}$, with the intermolecular vector orientation, $\hat{r}$, is varied. We have found that an increase of the $\hat{n} - \hat{r}$ coupling results in an increase of the effective field h_6 via the close packing constraint of the molecular cores. As a by-product, an increase of the amount of induced hexatic bond orientational order is also seen.

By increasing the $\hat{n} - \hat{r}$ coupling above some critical value, we observed a structural transformation of the nearest-neighbor bond shell from a slightly distorted hexatic phase to a rectangular analogue of the hexatic phase. This structural transformation was anticipated from zero temperature lattice calculations which predict a first order phase transition from a distorted triangular (orthorhombic) lattice to a rectangular lattice as the strength of the $\hat{n} - \hat{r}$ coupling is increased. These results already give us some confidence that calculations based on lattice model of structural transitions between liquid crystal phases with bond orientational order can provide some insight into the behavior of the system in its liquid phase. However, to increase the confidence in such lattice calculations, it would be interesting to investigate further if a true phase transition occurs in the present anisotropic van der Waals system as γ as varied and the pressure and temperature are held fixed.

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