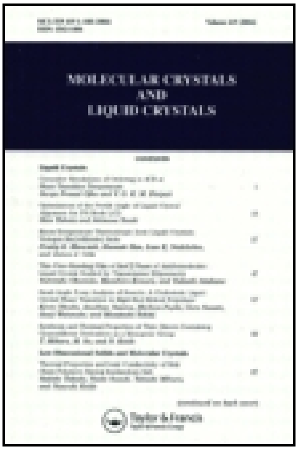


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Computer Simulation Studies of Anisotropic Systems, III. Two-Dimensional Nematic Liquid Crystals

J. Y. Denham [a], G. R. Luckhurst [a], C. Zannoni [a] & J. W. Lewis [b]

[a] Department of Chemistry, The University, Southampton, S09 5NH, U.K.

[b] Science Research Council, Rutherford, Laboratory, Chilton, Didcot, Oxfordshire, OX11 00Y, U.K.

Version of record first published: 20 Apr 2011.

To cite this article: J. Y. Denham, G. R. Luckhurst, C. Zannoni & J. W. Lewis (1980): Computer Simulation Studies of Anisotropic Systems, III. Two-Dimensional Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 60:3, 185-205

To link to this article: http://dx.doi.org/10.1080/00268948008072399

Mol. Cryst. Liq. Cryst., 1980, Vol. 60, pp. 185–207
0026-8941/80/6003-0185$04.50/0

Computer Simulation Studies of Anisotropic Systems, III.

Two-Dimensional Nematic Liquid Crystals

J. Y. DENHAM, G. R. LUCKHURST and C. ZANNONI†
Department of Chemistry, The University, Southampton, S09 5NH, U.K.

and

J. W. LEWIS
Science Research Council, Rutherford, Laboratory,
Chilton, Didcot, Oxfordshire, OX11 0OY, U.K.

(*Received November 26, 1979*)

We have studied a two-dimensional ensemble of cylindrically symmetric particles interacting *via* a weak anisotropic potential using the Monte Carlo technique of computer simulation. The calculation is simplified by confining the particles to the sites of a triangular lattice. The internal energy, specific heat, second rank orientational order parameter and second rank orientational pair correlation function were calculated at various temperatures. The variation of the order parameter and pair correlation function shows that the system exhibits a transition from an orientationally disordered to a partially ordered phase. The temperature dependence of the specific heat suggests that the transition is second order or higher.

The possibility of the existence of order-disorder transitions in two dimensions is discussed. The results of the simulation are then compared with the predictions of a molecular field theory of orientational phase transitions. As expected the theory is found to be in poor agreement with the calculations.

1 INTRODUCTION

A two-dimensional nematic liquid crystal may be visualized as an orientationally ordered system of elongated particles lying on a plane.[1–5] The very possibility that such a phase exists is, however, a matter of some debate.[4–6]

---

† Present and permanent address: Istituto di Chimica Organica, Universita, Viale Risorgimento 4, 40136 Bologna, Italy.

The origin of the problem stems from the fact that an isotropic to nematic transition requires the breaking of the symmetry of the continuous group of rotations. As is well known,[7] there are reasons to believe that true phase transitions, involving the breaking of a continuous symmetry, cannot take place in two dimensions. Thus, for a lattice spin system, we can have a phase transition for the Ising model, where the spins can point in only one of two directions. In contrast, there should not be a true phase transition in the two-dimensional Heisenberg model where the spins can adopt all orientations.

The same is true for crystalline order in two dimensions, in the sense that we should not be able to obtain two-dimensional crystalline ordering. The classical argument for excluding such two-dimensional ordering transitions follows from the elastic behaviour of the system.[8] The relevant mean-square fluctuation of the long-range order is found to diverge logarithmically with the sample size or, equivalently, with the square root of the logarithm of the number of particles. The absence of an aligned phase would depend therefore on the inability of a two-dimensional system to support fluctuations, with the attendant destruction of long-range ordering. This "folk theorem," as it has been called by Fisher[7] was put in a rigorous form by Mermin and Wagner.[9] Their method consists, essentially, of finding an upper bound for the long-range order parameter by using the Bogoliubov inequality.[7] They then show that the bound goes to zero as the size of the system goes to infinity. In two dimensions the divergence is logarithmic, as predicted by the simple, elastic type analysis. The proof was first put forward for spin systems and crystals. Since then Straley[4] has tried to generalize the rigorous proof to the case of two-dimensional orientational ordering, which was not considered explicitly by Mermin and Wagner in their original treatment.[9] Straley was concerned with pair potentials of the kind

$$U_{ij} = u(|\mathbf{r}_i - \mathbf{r}_j|)\cos 2(\theta_i - \theta_j), \tag{1}$$

where $(\mathbf{r}_i, \theta_i)$ and $(\mathbf{r}_j, \theta_j)$ are the positions and orientations of particles i and j with respect to some laboratory coordinate system. This potential is certainly not the most general that could be devised. However, it does include, for example, the two-dimensional analogue of the much-studied Maier–Saupe model[10] that we are going to treat in this paper. In fact we shall consider a two-dimensional lattice where the particles, located at the lattice sites, interact with the potential

$$U_{ij} = -\varepsilon_{ij}\cos 2(\theta_i - \theta_j), \tag{2}$$

where ε_{ij} is a positive constant, ε say, when i and j are nearest neighbours, and zero otherwise. Such a system has also been studied by Vuillermot and

Romerio.[6] They used a generalized version of the Bogoliubov inequality to rule out the existence of long-range ordering in a class of one- and two-dimensional lattice models which seems to include that with molecular interactions given by Eq. (2).

There would, therefore, seem to be little hope of finding a real system exhibiting not only crystalline but also nematic order in two dimensions. It should be noticed, however, that even though this might be the case for an infinite system, the same conclusion does not need to hold for a large but finite sample. This possibility was pointed out by Barker and Henderson[8] with reference to two-dimensional crystals. To understand the reason behind what might seem to be a rather paradoxical statement, let us consider, for example, the expression for the root-mean-square angular fluctuation $\sigma(\mathbf{r}_{ij})$,

$$\sigma(\mathbf{r}_{ij}) = \{\overline{|\theta(\mathbf{r}_i) - \theta(\mathbf{r}_j)|^2}\}^{1/2}. \tag{3}$$

From the classical argument based on the elastic properties,[4,5] it can be shown that, assuming only one elastic constant K,

$$\sigma(r_{ij}) = \left\{\left(\frac{kT}{\pi K}\right)\ln\left(\frac{r_{ij}}{a}\right)\right\}^{1/2}, \tag{4}$$

where a is a molecular length.[5] Orientational correlation is lost therefore when the interparticle separation r_{ij} becomes larger than a certain coherence length $\zeta(T)$, where

$$\zeta(T) \approx a \exp(\pi K/kT). \tag{5}$$

In particular, there is no true long-range order in the infinite separation limit. However, the divergence in σ is only logarithmic. Thus, the relative increase in σ over a thousand molecular lengths is calculated from Eq. (4) to be only a factor of $\sqrt{3 \ln 10}$. It is difficult to be quantitative in our case, but it may be worth quoting a result of Hoover *et al.*[11] They find that a finite two-dimensional crystal of radius 10^{10} light years would have a root-mean-square displacement of only 10 Å. Without going to this extreme, it seems that the problem of the existence of ordering in a finite system, even a relatively large one, is not solved completely by the theorems derived for infinite systems. This in turn does mean that it might still be of interest to study such finite systems, especially as some practical realization of two-dimensional liquid crystals has been proposed.[5] Indeed some experimental observations on nearly two-dimensional systems have already been performed.[12]

In this paper we use Monte Carlo simulations to study finite two-dimensional nematics or pseudo-nematics. We shall use various sample sizes, from 576 up to, in a few cases 3600, particles. These sizes are sensibly larger than that of 170 particles used by Vieillard–Baron[3] in another study of two-dimensional nematics. The system itself was also rather different since he used hard ellipses[3] instead of the soft potential in Eq. (2), and so comparison with our results is not possible.

One of the objectives of our simulation is to test the performance of molecular field theory in a particularly unfavourable situation. Indeed as the molecular field theory tends to overestimate the extent of ordering, this should be particularly bad in a system where we are not supposed to have any long-range order at all.

The plan of the paper is as follows. First we shall introduce the molecular field treatment applied to a system of particles interacting with a very general pair potential. The results will be specialized to the simplest case, equivalent to the potential in Eq. (2) and it will be shown that a second order phase transition is predicted. This result has been obtained by other authors,[13] but we feel that our approach is sufficiently different and more general to warrant some partial duplication. The Monte Carlo results will then be presented and the order parameter and correlation function discussed.

2 THE MOLECULAR FIELD THEORY

The primary objective of a molecular field approach is to determine the potential energy of a single particle resulting from its interaction with all other particles in the system.[10, 14, 15] Armed with this potential or pseudopotential we can then obtain the single particle partition function and hence all the orientational thermodynamic properties and order parameters. Our starting point is a general expression for the intermolecular potential between two cylindrically symmetric molecules lying on a plane. For a translationally invariant system, this potential is a function of the intermolecular separation vector $\mathbf{r}_{ij}$ joining, say, the centres of mass of the two particles, as well as the angles θ_i, θ_j made by the molecular symmetry axes with the intermolecular vector; these coordinates are shown in Figure 1. In general the potential $U(\mathbf{r}_{ij}; \theta_i, \theta_j)$ is a complicated, and unknown, function. However, we shall take advantage of the fact that it can be expanded as a sum of products of angle-dependent terms with distance-dependent coefficients as in the Pople expansion for three-dimensional systems.[16] This is simply an expansion of the pair potential in a suitable product basis set of functions spanning the angular space. The set of functions $\{\exp(ip\theta)\}$ with integer p constitutes a complete set of orthogonal functions in the plane.

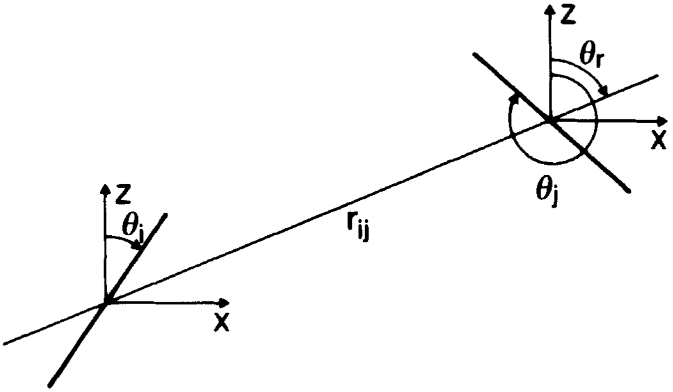


FIGURE 1 The variables defining the orientations θ_i, θ_j and the separation r_{ij} of a pair of linear molecules in two dimensions.

We can therefore write the pair potential as

$$U_{ij}(\mathbf{r}_{ij};\,\theta_i,\theta_j) = \sum_{p,q}{}' u_{pq}(\mathbf{r}_{ij}) \exp(ip\theta_i)\exp(iq\theta_j)\exp\{-i(p+q)\theta_r\}, \qquad (6)$$

where θ_i, θ_j, θ_r are the orientations of particles i, j and of the interparticle vector, respectively in a laboratory fixed frame. The prime indicates that the summation is restricted to even p and q, because we assume that the two ends of the particles are indistinguishable. This expansion is the two-dimensional analogue of that introduced by Blum and Torruella for the pair distribution function.[17]

To obtain the pseudo-potential for particle i starting from Eq. (6) we average over the orientations of the interparticle vector θ_r, the separation r_{ij} between particles and the orientations of particle j. If we assume the intermolecular vector to be isotropically distributed the first average gives

$$\overline{\exp\{-i(p+q)\theta_r\}} = \delta_{p,-q}, \qquad (7)$$

where the upper bar indicates an ensemble average. We now take the average over θ_j with a singlet distribution $f(\theta_j)$ satisfying the symmetry of the hypothetical two-dimensional nematic phase:

$$\begin{aligned} f(\theta) &= f(-\theta),\\ &= f(\theta+\pi). \end{aligned} \qquad (8)$$

We take the director of this phase to be along the laboratory axis from which the angles θ are measured, as in Figure 1. These symmetries yield

$$\overline{\exp(ip\theta_j)} = \overline{T}_p, \qquad (9)$$

where we have defined

$$T_p(\theta) \equiv \cos p\theta. \tag{10}$$

Finally, we average over all intermolecular separations and obtain the pseudo-potential as

$$U(\theta) = \sum_p{}' \bar{u}_p \bar{T}_p T_p(\theta), \tag{11}$$

where the label for a particular molecule has now been omitted. The expansion coefficients $\bar{u}_p$ are defined by

$$\bar{u}_p = \rho \int u_p(r) g(r) \mathrm{d}r \tag{12}$$

in terms of the two-dimensional radial distribution $g(r)$ and ρ, the number of particles per unit area.

The orientational contribution to the molar internal energy, is obtained from the pesudo-potential as

$$U_m = \left(\frac{N_A}{2}\right) \sum_p{}' \bar{u}_p \bar{T}_p^2, \tag{13}$$

where N_A is the Avogadro constant. Within the molecular field approximation the molar orientational entropy is

$$S_m = \left(\frac{N_\mathrm{A}}{T}\right) \sum_p{}' \bar{u}_p \bar{T}_p^2 + R \ln Z, \tag{14}$$

where Z is the single particle orientational partition function

$$Z = \int_0^{2\pi} \exp\left\{-\frac{U(\theta)}{kT}\right\} \mathrm{d}\theta. \tag{15}$$

The molar orientational Helmholtz function is then

$$A_m = -\left(\frac{N_\mathrm{A}}{2}\right) \sum_p{}' \bar{u}_p \bar{T}_p^2 - RT \ln Z. \tag{16}$$

The condition that the Helmholtz free energy should be a minimum with respect to the long-range order parameters $\bar{T}_p$ gives the so-called consistency condition

$$\bar{T}_p = \left(\frac{1}{Z}\right) \int_0^{2\pi} T_p(\theta) \exp\left\{-\frac{U(\theta)}{kT}\right\} \mathrm{d}\theta, \tag{17}$$

Within the molecular field theory these expressions for the order parameters and the thermodynamic functions are exact. However to obtain numerical values for the various properties of the system, it is convenient to approximate the intermolecular potential by truncating the series expansion in Eq. (11). By restricting the series to the term with $p = 2$, we are able to evaluate the order parameter $\overline{T}_2$ and the orientational partition function in terms of modified Bessel functions;[18] thus

$$Z = 2\pi I_0\left(-\frac{\bar{u}_2\overline{T}_2}{kT}\right) \tag{18}$$

and

$$\overline{T}_2 = \frac{I_1(-\bar{u}_2\overline{T}_2/kT)}{I_0(-\bar{u}_2\overline{T}_2/kT)}, \tag{19}$$

where

$$I_n(a) = \int_0^\pi \cos n\theta \exp(a\cos\theta)\mathrm{d}\theta/\pi. \tag{20}$$

These equations are the two-dimensional analogues of those obtained by Maier and Saupe for a three-dimensional system.[10]

The order parameter has been evaluated from Eq. (19) as a function of the reduced temperature $kT/\bar{u}_2$ and found to decrease continuously to zero; this temperature dependence is shown in Figure 2. The orientational Helmholtz free energy was also found to pass continuously to zero and then to vanish when

$$\frac{kT_{\mathrm{NI}}}{\bar{u}_2} = -\frac{1}{2}, \tag{21}$$

where T_{NI} denotes the transition temperature. We are assuming, of course, that the transition occurs at constant volume as in our computer experiments.

The continuous behaviour of the order parameter suggests that the transition from the isotropic phase to the liquid crystal phase is second order. Since $\overline{T}_2$ is small near the transition, we may confirm the second order character of the transition and its exact position by expanding the Helmholtz free energy in powers of $\overline{T}_2$. For small $\overline{T}_2$ we find

$$\frac{A_m}{RT} = \left(\frac{1}{2} - \frac{\bar{u}_2}{4kT}\right)\frac{\bar{u}_2}{kT}\overline{T}_2^2 + \frac{1}{64}\left(\frac{\bar{u}_2}{kT}\right)^4\overline{T}_2^4 + 0(\overline{T}_2^6). \tag{22}$$

The coefficient of the term quadratic in $\overline{T}_2$ vanishes therefore when

$$T = \frac{-\bar{u}_2}{2k} \tag{23}$$

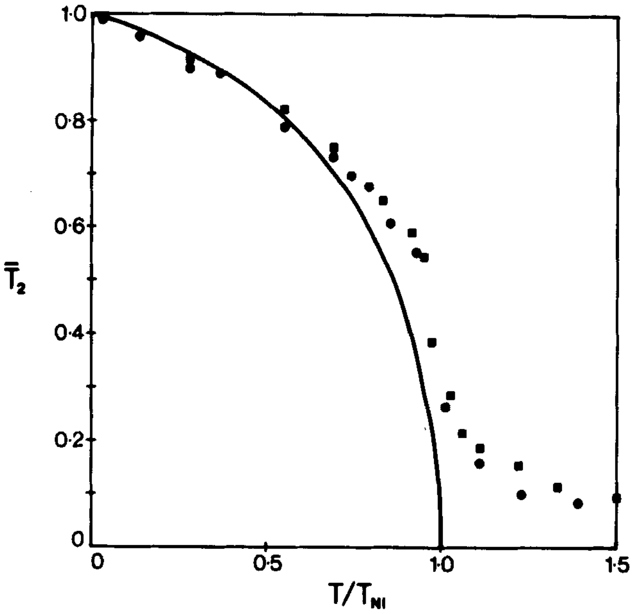


FIGURE 2 The dependence of the orientational order parameter $\overline{T}_2$ on reduced temperature T/T_{NI}; the curve is the molecular field prediction and the points are obtained from the Monte Carlo simulation with ensembles of 24 × 24 (■) and 30 × 30 (●) particles.

and the transition does indeed occur at the temperature found by evaluating the Helmholtz free energy numerically. In addition the coefficient of the cubic term in $\overline{T}_2$ is identically zero while the quartic term is positive as required for a second-order phase transition.[19]

3 THE MONTE CARLO SIMULATION

A system which is the two-dimensional analogue of that proposed by Lebwohl and Lasher[20] in their pioneering study of three-dimensional nematics using the Monte Carlo technique has been chosen for our computer simulation. It consists of a set of N particles at the sites of a certain two-dimensional lattice which interact *via* the pair potential given in Eq. (2). When the properties of such a system are evaluated with the molecular field approximation we find the results shown in Eqs. (11)–(17) with the summation restricted to terms with $p = 2$. The averaged interaction coefficient $\bar{u}_2$ reduces to

$$\bar{u}_2 = -z\varepsilon, \tag{24}$$

for the lattice model where z is the number of nearest neighbours. Thus the molecular field theory predicts, for a triangular lattice ($z = 6$), a reduced transition temperature kT_{NI}/ε of 3.

We have examined the model by Monte Carlo simulation using the standard Metropolis *et al.*, procedure in the canonical ensemble.[21] Periodic boundary conditions have been used, with triangular lattices of various sizes from 24 × 24 up to 60 × 60. The starting configuration was chosen either with all the particles having the same orientation (aligned configuration) or with randomly chosen orientations (random configuration). Up to 10^6 moves in the Monte Carlo stochastic chain were discarded to allow equilibration of the system. For this system it was found possible to reach essentially the same state starting from either a random or an aligned initial configuration. This provided a rather convincing test that equilibration was indeed achieved. After equilibration, a production run of typically 10^6 moves was employed to calculate thermodynamic averages of the relevant observables, i.e., internal energy, specific heat and order parameter $\overline{T}_2$. The orientational internal energy was calculated over M configurations from

$$U = \frac{1}{M}\sum_{j=1}^{M} U^{(j)}, \tag{25}$$

where the energy of the jth configuration $U^{(j)}$ is given by

$$U^{(j)} = -\left(\frac{\varepsilon}{2}\right)\sum_{i,k} \cos 2\theta_{ik}; \tag{26}$$

this last sum is extended to nearest neighbours only. The results for various sample sizes are shown in Table I.

The configurational specific heat may be calculated from fluctuations in the internal energy[21] as

$$\frac{C_V}{k} = \frac{\overline{U^2} - (\overline{U})^2}{k^2T^2}. \tag{27}$$

The results of our calculation for C_V were subject to large uncertainties, as expected for a fluctuation quantity. We therefore fitted the temperature dependence of the internal energy with a cubic spline and evaluated the specific heat from this. The results of the calculation are shown in Figure 3 for two lattice sizes ($N = 900$ and 3600), and the two sets of results are in reasonably good agreement. The specific heat exhibits a maximum at kT/ε of about 1.8 although this does not necessarily indicate a phase transition.[22] However there is a small but discernable jump in C_V at this temperature which is consistent with a second order phase transition.

TABLE I

Orientational internal energy of a two-dimensional triangular lattice for various sample sizes

kT/ε	(24 × 24)	(30 × 30)	(60 × 60)	(30 × 120)
0.05		−2.974		
0.25		−2.873		
0.5	−2.738	−2.738		
0.66667		−2.649		
1.0	−2.440	−2.436		
1.25	−2.260	−2.252	−2.253	
1.33333		−2.187	−2.186	
1.42857		−2.103	−2.096	
1.5	−2.040			
1.53846		−1.984	−1.959	−1.977
1.65	−1.826			
1.66667		−1.834	−1.794	−1.799
1.7	−1.765			
1.75	−1.672			
1.8	−1.650			
1.81818		−1.574	−1.592	−1.602
1.85	−1.516			
1.9	−1.479			
1.90476			−1.445	
2.0	−1.338	−1.351	−1.344	
2.2	−1.154			
2.22222		−1.138	−1.142	
2.4	−1.012			
2.5		−0.949	−0.946	
2.7	−0.840			
3.0	−0.719			
3.33333		−0.631		
4.0		−0.497		
5.0		−0.341		
8.0	−0.213			
12.0	−0.133			
20.0		−0.08		

To investigate the nature of this transition we have computed two quantities related to the extent of orientational ordering in the system. The first is the long-range orientational order parameter $\overline{T}_2$. This quantity is difficult to evaluate because the director orientation α in the arbitrary laboratory frame used in the calculation is unknown and, in addition, can fluctuate from one configuration to the other.[21] Thus $\alpha^{(j)}$ is determined for every configuration j used in the averaging process as the direction which renders the quantity

$$\overline{T}_2^{(j)} = \left(\frac{1}{N}\right) \sum_{i=1}^{N} \cos 2(\theta_i - \alpha^{(j)}) \tag{28}$$

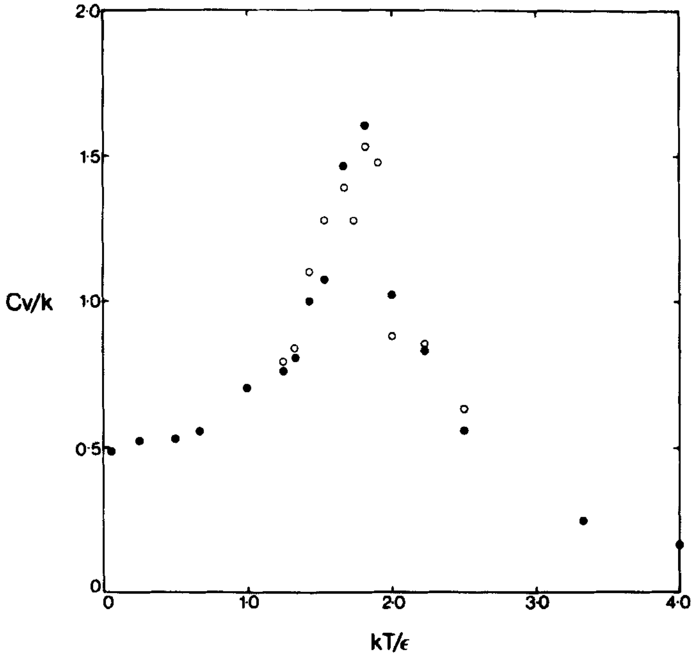


FIGURE 3 The dependence of the specific heat at constant volume C_V/k on temperature, obtained with ensembles of 24 × 24 (○) and 30 × 30 (●) particles.

a maximum. This condition requires that

$$\tan 2\alpha^{(j)} = \frac{\sum_{i=1}^{N} \sin 2\theta_i}{\sum_{i=1}^{N} \cos 2\theta_i} \tag{29}$$

and so the average of sin 2θ and cos 2θ was evaluated for each configuration; given $\alpha^{(j)}$ it is then possible to obtain the order parameter $\overline{T}_2^{(j)}$ for the jth configuration. The order parameter $\overline{T}_2$ is then obtained as an average over M configurations of the value $\overline{T}_2^{(j)}$ determined in this way:

$$\overline{T}_2 = \left(\frac{1}{M}\right) \sum_{j=1}^{M} \overline{T}_2^{(j)}. \tag{30}$$

The temperature dependence of $\overline{T}_2$ obtained for the 24 × 24 triangular lattice is plotted in Figure 4. It can be seen that a pronounced decrease of this long-range order parameter occurs at the apparent transition temperature of kT/ε of 1.8 ± 0.1 in good agreement with that determined from the specific heat. The order parameter seems to decrease smoothly to zero in accord with a second order behaviour. This is sufficient for our present

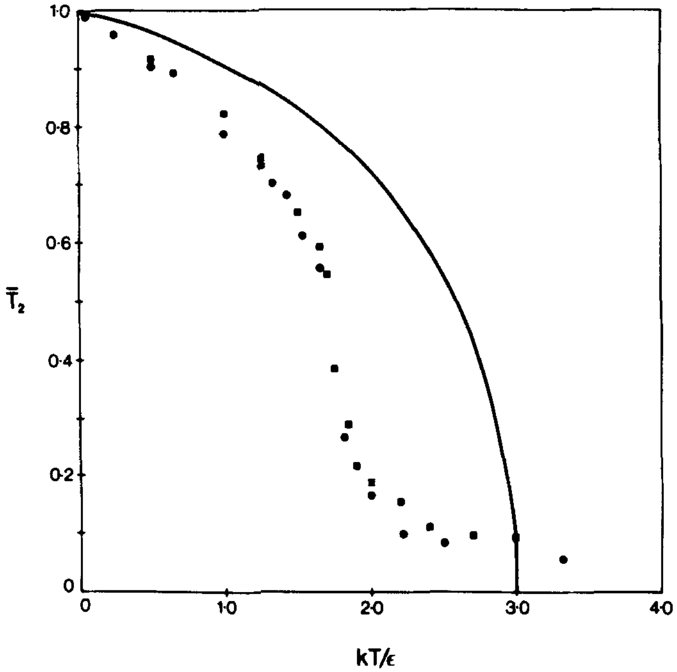


FIGURE 4 The temperature dependence of the order parameter $\overline{T}_2$ for ensembles of 24 × 24 (■) and 30 × 30 (●) particles. The smooth curve is predicted by the molecular field theory.

purposes. However, it should be noted that convergence for $\overline{T}_2$ is rather poor near the transition. Consequently if there is a specific interest in the detailed behaviour near the transition, a separate study with much larger samples and longer runs should be performed.

From the specific heat and order parameter results we can make a comparison with the predictions of the molecular field theory. First we observe that the molecular field theory grossly overestimates the transition temperature. For the triangular lattice the molecular field theory predicts $kT_{NI}/\varepsilon = 3$ while from the computer simulation we find $kT_{NI}/\varepsilon = 1.8 \pm 0.2$. The molecular field theory prediction of the transition temperature would appear, therefore, to be in error by almost 50%, whereas in three dimensions an analogous theory overestimates kT_{NI}/ε by only 16%.[10,21] The more dramatic failure of the molecular field approximation in two dimensions is in complete accord with our previous discussion. Secondly, we can compare the predicted temperature dependence of the order parameter with that obtained from the simulation experiment. The line in Figure 4 shows the prediction of the molecular field theory and this is clearly in poor agreement with the results of the simulation. However much of the disagreement stems from the failure of the theory to predict the transition temperature correctly. We can avoid this difficulty by using a reduced temperature scale (T/T_{NI}) as in the comparison of real experiments with theory. Such a comparison is shown in Figure 2 using $T_{NI} = 1.8\bar{u}_2/k$, and the agreement of the molecular field theory with experiment is much improved.

It is of interest to consider the change in the order parameter $\overline{T}_2$ as the sample size increases. A set of results for the 30 × 30, 60 × 60, 30 × 120 as well as 24 × 24 lattice is listed in Table II. We notice that the tendency is for the order parameter to decrease as the number of particles increases. A similar comparison for the internal energy reveals that this property is a much more insensitive function of the number of particles. Similar results

TABLE II

The temperature dependence of the orientational order parameter $\overline{T}_2$ for systems of various sizes

kT/ε	(24 × 24)	(30 × 30)	(60 × 60)	(30 × 120)
0.05		0.991		
0.25		0.958		
0.5	0.912	0.907		
0.66667		0.894		
1.0	0.824	0.787		
1.25	0.743	0.736	0.649	
1.33333		0.700	0.557	
1.42857		0.681	0.577	
1.5	0.650			
1.53846		0.611	0.303	0.356
1.65	0.593			
1.66667		0.555	0.323	0.164
1.7	0.545			
1.75	0.384			
1.81818		0.266	0.097	0.099
1.85	0.287			
1.9	0.216			
1.90476			0.056	
2.0	0.187	0.166	0.041	
2.2	0.154			
2.22222		0.100	0.053	
2.4	0.115			
2.5		0.084		
2.7	0.098			
3.0	0.094		0.038	
3.33333		0.056		
4.0		0.053		
5.0		0.027		
8.0	0.047			
12.0	0.042			
20.0		0.032		

have been reported[23] for a very similar problem to ours, namely a system consisting of a layer of three-dimensional vectors interacting with a simple $P_2(\cos \beta_{ij})$ pair potential. The difference from the system treated here is, in particular, that in our case the particles are only able to reorient on the plane. Thus the angular volume element is different and, for example, molecular field theory predicts a first order phase transition for the layer system rather than the second order transition found for the plane. Even so it is expected that much of the basic physics is the same for both systems.[7]

To understand the difference in behaviour of energy and order parameter it is helpful to introduce another measure of orientational ordering in the system. We introduce therefore, as in three dimensions,[21,24] a second rank angular pair correlation function

$$G_2(r_{ij}) = \overline{\cos 2\theta_{ij}(r_{ij})}. \tag{31}$$

This gives a measure of the orientational correlation between two particles at a separation r_{ij}. It is a rotationally invariant quantity which is expected to decay to zero fairly quickly in an isotropic system. In contrast it should decay to a limiting value equal to $\overline{T}_2^2$ in an ordered phase. We show in Figure 5 some typical correlation functions obtained for single configurations for a sample of 900 particles and their behaviour is in accord with our expectations. Thus at the highest reduced temperature ($kT/\varepsilon = 3.33$) there is essentially no orientational correlation except for particles which are nearest neighbours. As the temperature is lowered so the magnitude and range of the angular correlation function increase. Near the transition at kT/ε of 1.82, $G_2(r_{ij})$ is appreciable for neighbouring particles but still decays to zero for large separations; this is in only qualitative agreement with the value for $\overline{T}_2^2$ of 0.07. However the agreement improves as the temperature is lowered into the nematic phase. For example, at kT/ε of 1.66 the large separation limit for $G_2(r_{ij})$ is 0.23 which compares well with the value for $\overline{T}_2^2$ of 0.25. Similar agreement is found at still lower temperatures where the angular correlation function is found to decay much more rapidly with intermolecular separation.

The angular correlation function $G_2(r_{ij})$ can be used to calculate the orientational internal energy. In fact

$$\begin{aligned} U &= -\left(\tfrac{1}{2}\right)\sum_{i,j} \varepsilon_{ij} \overline{\cos 2\theta_{ij}}, \\ &= -\frac{zN\varepsilon\sigma_2}{2}, \end{aligned} \tag{32}$$

where

$$\sigma_2 = G_2(a) \tag{33}$$

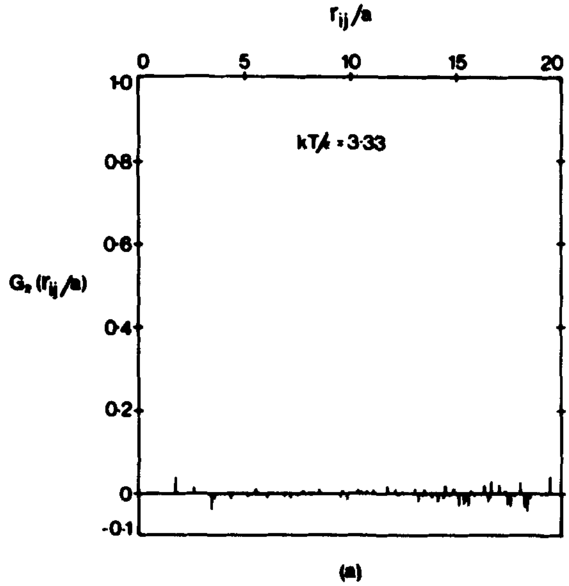
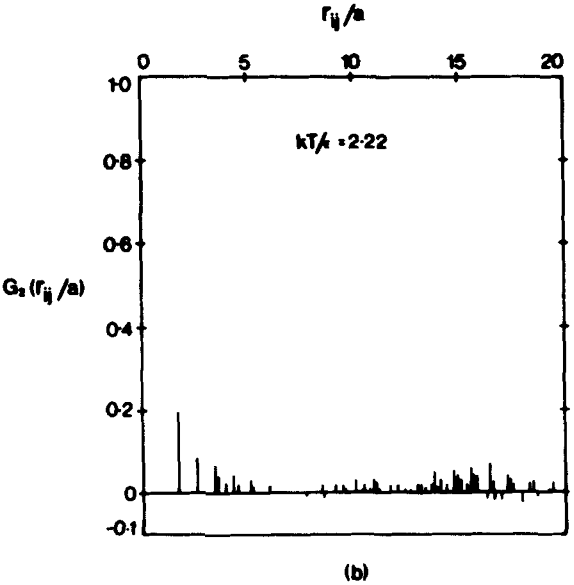
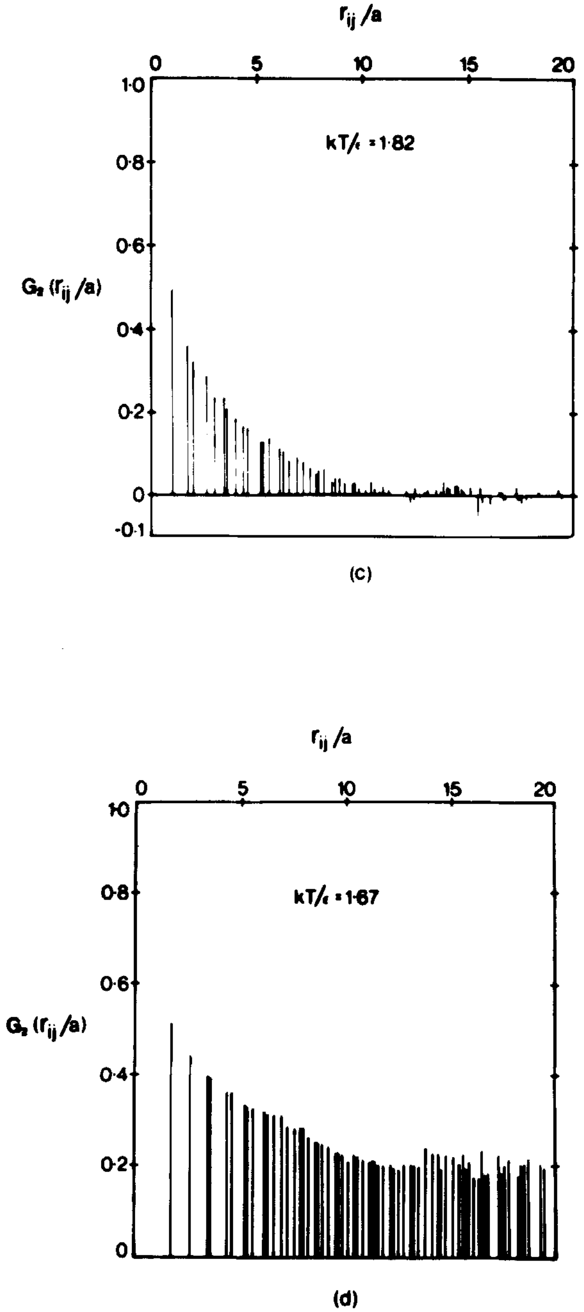


FIGURE 5 The angular correlation function $G_2(r_{ij}/a)$ calculated for an ensemble of 30 × 30 particles at temperatures above and below the order-disorder transition.



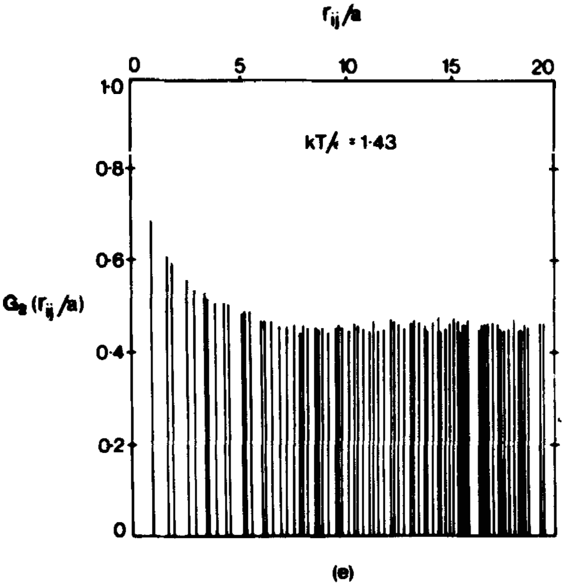
(FIGURE 5 *continued overleaf*)

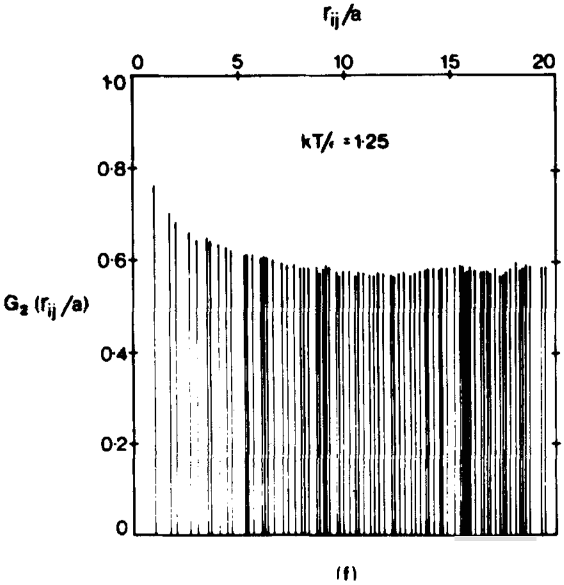


(c)

(d)

FIGURES 5c and d





FIGURES 5e and f

is the value of the angular pair correlation function at the nearest-neighbour separation. The parameter σ_2 represents a measure of the orientational correlation between nearest neighbours; it can, therefore, be called a short-range order parameter. Equation (32) demonstrates that in the present model and indeed in any model based on nearest-neighbour interactions the internal energy is determined entirely by the short-range order parameter.[24] This, incidentally, allows an internal check on the calculation by comparing the short-range order parameter obtained from the pair correlation Eq. (33) and that determined from the internal energy *via* Eq. (32). Such a comparison is effected for lattices of various sizes in Table III. The agreement can be considered to be good, especially if we recall that because of limited computer time, the pair correlation was not averaged over all the particles in the sample, but was computed using just a single particle as origin.

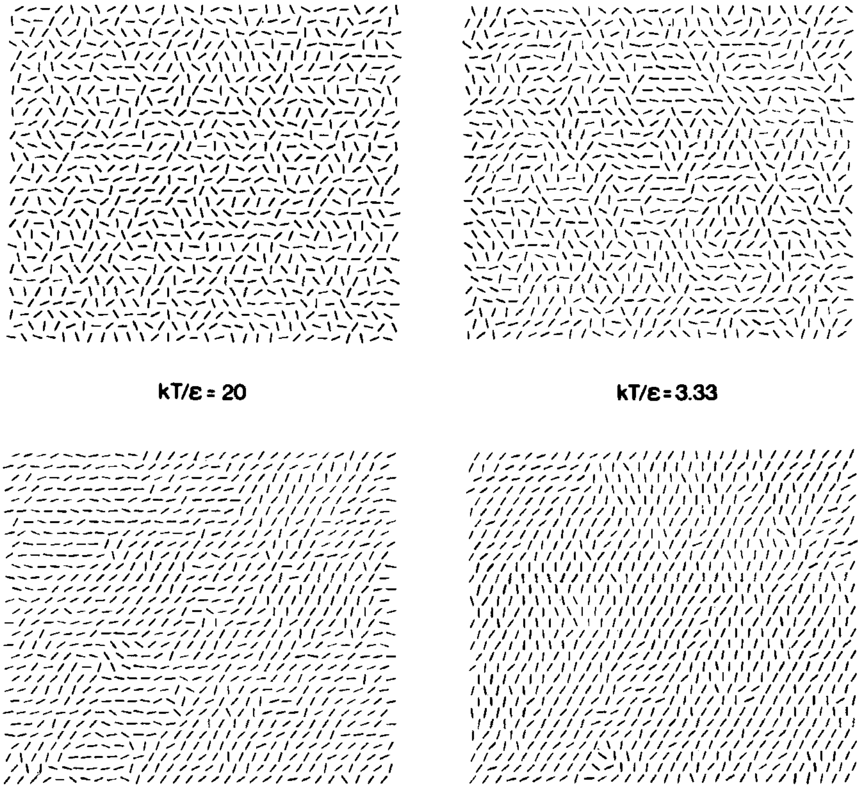
As we have seen, the internal energy is much less influenced than the long-range order parameter $\overline{T}_2$ by the sample size and so the short-range order must also be less sensitive to the size of the system. The picture emerging is, as for similar Monte Carlo calculations on the Heisenberg model,[25,26] not in contrast with the rigorous theorems forbidding the existence of a true transition. For a finite, even if rather large system (a few thousand particles), short-range order develops as the temperature is lowered. This short-range order can actually be fairly long-ranged as we have seen from the tail of the angular pair correlation function. For such finite systems there is an apparent transition, where the long-short range order, as it has been called[7,26] disappears. This transition is continuous and so higher than first order.

We conclude with a cautionary comment. During the course of our computer simulation study we drew certain of the equilibrium configurations for the 30 × 30 ensemble and a representative collection of these is shown in Figure 6. At temperatures well above the order-disorder transition ($kT/\varepsilon = 20$), the system is completely devoid of any angular correlation. As the temperature is lowered, short-range angular correlation begins to develop and this is clearly discernible in the configuration at kT/ε of 3.33. At low temperatures ($kT/\varepsilon = 1.25$), when the orientational order is high the angular correlation extends throughout the sample and is long range. However we notice that for systems with intermediate order ($kT/\varepsilon = 1.54$), the single configuration contains what appear to be quite highly ordered domains. This structure is not in accord with the uniform arrangement anticipated by the molecular field theory. Of course this approximation is known to underestimate the extent of short-range order and so the existence of domains is not really unexpected. Indeed their observation confirms the view that the two dimensional system does not possess true long-range

TABLE III

Comparison of the short-range order parameter (σ_2) obtained from the internal energy (first two columns) and from the angular pair correlation function at the nearest neighbour separation (last four columns). The size of the systems studied were a (30 × 30), b (24 × 24), c (30 × 30), d (24 × 24), e (60 × 60), f (30 × 120)

	From energy		From pair correlation			
kT/ε	a	b	c	d	e	f
0.05	0.991		0.99			
0.25	0.958					
0.5	0.913	0.913				
0.6667	0.883					
1.0	0.812	0.813 0.814				
1.25	0.751	0.753	0.76		0.75	
1.3333	0.729		0.70			
1.42857	0.701		0.68		0.70	
1.5		0.612 0.678 0.682		0.68		
1.53846	0.661		0.67		0.65	0.65
1.65		0.594 0.623				
1.6667	0.611		0.61		0.59	0.61
1.7		0.588				
1.75		0.557				
1.8		0.558 0.545		0.58		
1.81818	0.525		0.49		0.51	0.53
1.85		0.505				
1.9		0.493				
1.90476					0.49	
2.0	0.450	0.446	0.44	0.43		
2.2		0.385				
2.22222	0.379		0.36			
2.4		0.337 0.338				
2.5	0.316		0.26			
2.7		0.279 0.280				
3.0		0.240				
3.3333	0.210		0.20			
4.0	0.166					
5.0	0.114					
8.0		0.071				
12.0		0.044				
30.0	0.026		0.025			



kT/ε = 20

kT/ε = 3.33

kT/ε = 1.54

kT/ε = 1.25

FIGURE 6 Typical equilibrium configurations above and below the order-disorder transition.

order, but rather short-range order with a correlation length which increases as the temperature is lowered.

Acknowledgements

We are grateful to the Science Research Council for the award of a Studentship to Mr. J. Y. Denham, as well as to the University of Southampton, and to C. N. R., Ozzano Emilia (Italy) for partial support of Dr. C. Zannoni.

References

1. K. Lakatos, *J. Chem. Phys.*, **50**, 3822 (1969).
2. K. Timling, *Philips Res. Rept.*, **25**, 223 (1970).
3. J. Vieillard-Baron, *J. Chem. Phys.*, **56**, 4729 (1972).
4. J. P. Straley, *Phys. Rev.*, **A4**, 675 (1971).

5. P. G. de Gennes, *Symp. Faraday Soc.*, **5**, 16 (1971).
6. P. A. Vuillermot and M. V. Romerio, *Commun. Math. Phys.*, **41**, 281 (1975); M. V. Romerio and P. A. Vuillermot, *J. Phys.*, **C7**, 1033 (1974).
7. M. E. Fisher, *Essays in Physics* (G. K. T. Conn and G. N. Fowler, Eds.), Academic Press, 1972.
8. J. A. Barker and D. Henderson, *Rev. Mod. Phys.*, **48**, 587 (1976).
9. N. D. Mermin and H. Wagner, *Phys. Rev. Lett.*, **17**, 1133 (1966).
10. G. R. Luckhurst, *Molecular field theories of nematics*, Chapter 4 in *The Molecular Physics of Liquid Crystals* (G. R. Luckhurst and G. W. Gray, Eds.), Academic Press, 1979, and references therein.
11. W. G. Hoover, W. T. Ashurst, and R. J. Olness, *J. Chem. Phys.*, **60**, 4043 (1974).
12. M. Kleman and G. Ryschenkow, *J. Chem. Phys.*, **64**, 413 (1976).
13. S. Chakravarty and C. W. Woo, *Phys. Rev.*, **A11**, 713 (1975).
14. W. Maier and A. Saupe, *Z. Naturforsch*, **13a**, 564 (1958); **14a**, 882 (1960); **15a**, 287 (1960).
15. R. L. Humphries, P. G. James, and G. R. Luckhurst, *Trans. Farad. Soc.*, **68**, 1031 (1972).
16. J. A. Pople, *Proc. Roy. Soc.* (*London*), **A221**, 498 (1954).
17. L. Blum and A. J. Torruella, *J. Chem. Phys.*, **56**, 303 (1972).
18. A. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, Dover, 1970.
19. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon, 1959.
20. P. A. Lebwohl and G. Lasher, *Phys. Rev.*, **A6**, 426 (1972).
21. C. Zannoni, *Computer simulations*, Chapter 9 in *The Molecular Physics of Liquid Crystals* (G. R. Luckhurst and G. W. Gray, Eds.), Academic Press, 1979, and references therein.
22. J. Y. Denham, R. L. Humphries, and G. R. Luckhurst, *Mol. Cryst. Liq. Cryst. Lett.*, **41**, 67 (1977).
23. R. D. Mountain and Th. W. Rujgrok, *Physica*, **89A**, 522 (1977).
24. C. Zannoni, *Distribution functions and order parameters*, Chapter 3, in *The Molecular Physics of Liquid Crystals* (G. R. Luckhurst and G. W. Gray, Eds.), Academic Press, 1979.
25. R. E. Watson, M. Blume, and G. H. Vineyard, *Phys. Rev.*, **B2**, 684 (1970).
26. H. Betsuyaku, *Solid State Commun.*, **25**, 185 (1978).