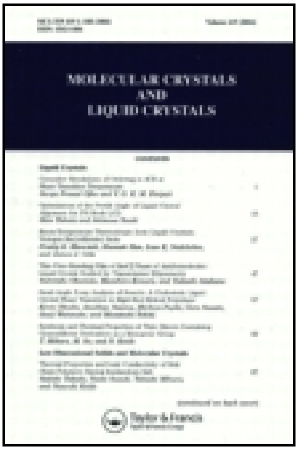

Molecular Crystals and Liquid Crystals

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

Lattice Models of Nematic Liquid Crystals

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Version of record first published: 20 Apr 2011.

To cite this article: S. K. Roy (1986): Lattice Models of Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 133:3-4, 297-311

To link to this article: http://dx.doi.org/10.1080/00268948608080822

Mol. Cryst. Liq. Cryst., 1986, Vol. 133, pp. 297–311
0026-8941/86/1334-0297/$20.00/0

Printed in the United States of America

Lattice Models of Nematic Liquid Crystals

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(*Received July 15, 1985*)

A theory of nematic disorder orginally proposed by Faber[1] has been used to explain some results for the long-range and short-range order parameters in lattice models of nematics, obtained by computer simulation.[5,6] The agreement is good, except for temperatures close to the nematic-isotropic transition.

Keywords: nematic liquid crystals, lattice models

1. INTRODUCTION

Faber[1] has developed a theory of nematic disorder in which the misalignment of the molecules is described in terms of thermally excited modes of distortion in the director field. He has applied the theory[2] to the simple cubic lattic model which is associated with the names of Lasher and Lebwohl[3] and has demonstrated that, except at temperatures close to the nematic-isotropic transition, it provides an accurate description of results generated for the same model by computer simulation.[4]

In the present paper, Faber's theory is applied to four other lattice models for which computer simulations have been performed:

(a) A simple cubic lattice model in which the interaction responsible for aligning the "molecules" is no longer confined to nearest neighbours but has an extended range.

(b) A face-centred cubic lattice model with interaction between nearest neighbours only.

(c) A face-centred cubic lattic model with an interaction of extended range.

(d) A two-dimensional model.

Calculations have been made in each case of both the long-range and the short-range order parameters, at various temperatures and for various specimen sizes. The results are in good agreement with computed values, except close to the nematic-isotropic transition.

2. THEORY

2.1. Simple cubic lattice with extended range interaction

Computer simulations for this model have been performed by Luckhurst, Romano and Simpson.[5] Following these authors, we consider a system of $N(\equiv L^3)$ molecules, confined to a lattice in which the separation between nearest neighbours is a, in a cube of side La with periodic boundary conditions. They interact through an anisotropic potential of the form

$$u_{ij} = -\epsilon(a/r_{ij})^6 P_2(\cos\beta_{ij}), \qquad (1)$$

where ϵ is a positive constant, r_{ij} is the separation between the ith and jth molecules, and β_{ij} is the angle between axes of cylindrical symmetry embedded in each of them. For the 6 nearest neighbours of the ith molecule r_{ij} is of course a; for the 12 in the next coordination shell it is $\sqrt{2}a$; and for the 8 in the third shell it is $\sqrt{3}a$. Beyond that range the interaction is ignored. In what follows we distinguish the coordination shells by a label l which takes three and only three values, these values being the radii of the shells in units of the nearest neighbour separation, i.e. 1, $\sqrt{2}$ and $\sqrt{3}$. The symbol Z_l is used to represent the respective coordination numbers, i.e. 6, 12, or 8.

Following the assumptions and procedures which Faber[2] has fully explained, we first evaluate a quantity $\alpha(l)$, which is defined by the relation

$$\sum_{q\neq 0} \langle(\Delta\psi)_l^2\rangle = \alpha(l) \sum_{q\neq 0} \langle\psi^2\rangle, \qquad (2)$$

where $\langle\psi^2\rangle$ is the mean square angle through which the molecular axes are rotated when a single mode is thermally excited, $\langle(\Delta\psi)_l^2\rangle$ is the mean square value of $(\psi_i - \psi_j)$ for two molecules separated by

$r_{ij} = la$, and the sums are over all possible values (other than zero) for the wave vector $\mathbf{q}$ of the periodic distortion modes of the director field. Once $\alpha(l)$ is known for $l = 1, \sqrt{2}$ and $\sqrt{3}$ we may evaluate, separately for each l, the three roots p', p'' and p''' of equation (14) in paper IV of the series by Faber, and the associated amplitudes Q', Q'' and Q''', and proceed to evaluate the long-range order parameter S_2 as a function of reduced temperature from the equation

$$T^* = (kT/\epsilon) = -\frac{1}{3}\left(\frac{N}{N-1}\right)\ln S_2 \left(\sum_l l^{-6} Z_l (Q'p'S_2^{2p'/3} + Q''p''S_2^{2p''/3} + Q'''p'''S_2^{2p'''/3})_l\right). \quad (3)$$

This long-range order parameter is defined in the usual way as

$$S_2 = \langle P_2(\cos\theta_i)\rangle, \quad (4)$$

where θ_i is the angle between the ith molecular axis and the direction in which it would lie if all the modes other than the $q = 0$ mode could be switched off; the model, like all the models considered in this paper, allows the latter direction to float, because excitation of the $q = 0$ mode costs no energy, but it can be identified in computer simulation work by maximising the right-hand side of (4). The corresponding short-range order parameters for two molecules separated by la, defined as

$$\sigma_2(l) = \langle P_2(\cos\beta_{ij})_l\rangle, \quad (5)$$

are then obtainable from

$$\sigma_2(l) = (Q'S_2^{2p'/3} + Q''S_2^{2p''/3} + Q'''S_2^{2p'''/3})_l \quad (6)$$

and the reduced energy per molecule from

$$u^* = (U/N\epsilon) = \sum_l \frac{1}{2} l^{-6} Z_l \sigma_2(l). \quad (7)$$

To find $\alpha(l)$ we use the following equation, which is a straightforward extension of one of Faber's results:

$$\alpha(l) = 2\left(\sum_{q\neq 0}\left(C_l \Big/ \sum_{l'} (l')^{-6} C_{l'}\right) \Big/ \sum_{q\neq 0}\left(1 \Big/ \sum_{l'} (l')^{-6} C_{l'}\right)\right), \quad (8)$$

where

$$C_l = 1 - (Z_l)^{-1} \sum_j \cos(\mathbf{q} \cdot \mathbf{r}_{ij})_l. \tag{9}$$

The summation on the right-hand side of (9) is over all neighbours of the ith molecule which are separated from it by la. The values of $\mathbf{q}$ permitted by the boundary conditions satisfy

$$q = (2\pi/La)\,(n_1\hat{x} + n_2\hat{y} + n_3\hat{z}) \tag{10}$$

with

$$-L < 2n_1 \leqq L, \qquad -L < 2n_2 \leqq L, \qquad -L < 2n_3 \leqq L. \tag{11}$$

Table I lists computed results for three values of L. The values of S_2 and σ_2 to which they lead are discussed below.

2.2. Face-centred cubic lattice with nearest neighbour interaction

Here again we consider systems which correspond to those of Luckhurst *et al.*[5] They are cubes of side $\sqrt{2}La$, where a is still the separation between nearest neighbours, containing L^3 unit cells of the FCC lattice and $N(\equiv 4L^3)$ molecules. The boundary conditions are again periodic. Equation (1) still describes the interaction but it is truncated after the first coordination cell, for which $Z_l = 12$. Equations (3), (6), (7) and (8) still apply, but the summations over l or l' in (3), (7) and (8) are now to be restricted to one term instead of three. And the permitted values of $\mathbf{q}$ now satisfy

$$\mathbf{q} = (\sqrt{2}\pi/La)(n_1\hat{x} + n_2\hat{y} + n_3\hat{z}) \tag{12}$$

with

$$-\frac{3}{2}L < (n_1 + n_2 - n_3) \leqq \frac{3}{2}L,$$

$$-\frac{3}{2}L < (-n_1 + n_2 + n_3) > \leqq \frac{3}{2}L,$$

$$-\frac{3}{2}L < (n_1 - n_2 + n_3) \leqq \frac{3}{2}L,$$

$$-\frac{3}{2}L < (n_1 + n_2 + n_3) > \leqq \frac{3}{2}L,$$

$$-L < n_1 \leqq L, \qquad -L < n_2 \leqq L, \qquad -L < n_3 \leqq L.$$

TABLE I

L	6	10	20
N	216	1000	8000
$\alpha(1)$	1.5992	1.5085	1.4451
$\alpha(\sqrt{2})$	1.8391	1.7381	1.6659
$\alpha(\sqrt{3})$	1.9246	1.8220	1.7471

Results for $\alpha(1)$ are listed in Table II, and for $\alpha(l)$ with $l > 1$ in Table III; the latter are needed if we wish to compute how the short-range correlations of orientation which make σ_2 exceed S_2^2 decay with distance.

It will be observed that two slightly different values are listed for $\alpha(\sqrt{9})$. This is because the ninth coordination cell in the FCC lattice contains two different types of neighbour, whereas all Z_l neighbours in other shells up to the twelfth are equivalent. The smaller value for $\alpha(\sqrt{9})$ applies for values of $\mathbf{r}_{ij}$ such as

$$(a/\sqrt{2})\ (\hat{x} + \hat{y} + 4\hat{z})$$

and the larger for values of $\mathbf{r}_{ij}$ such as

$$(a/\sqrt{2})\ (3\hat{x} + 3\hat{y}).$$

Corresponding to these different values for $\alpha(\sqrt{9})$ there are slightly different values for $\sigma_2(\sqrt{9})$.

2.3. Face-centred cubic lattice with extended range interaction

This is a straightforward elaboration of the model considered in the previous section, but the interaction, still described by equation (1), is truncated only after the twelfth shell, which means that each molecule interacts with 248 others. There are twelve terms to be included when summing over l' to obtain $\alpha(l)$ from equation (8), or over l to obtain S_2 from equation (3). Results are given in Table IV.

TABLE II

L	5	6	9	10
N	500	864	2916	4000
$\alpha(1)$	1.65190	1.62247	1.57519	1.56601

TABLE III

($L = 6, N = 864$)

l	1	$\sqrt{2}$	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{5}$	$\sqrt{6}$
$\alpha(l)$	1.62247	1.80678	1.86111	1.89922	1.93111	1.94898
	$\sqrt{7}$	$\sqrt{8}$	$\sqrt{9}$	$\sqrt{10}$	$\sqrt{11}$	$\sqrt{12}$
	1.96360	1.97439	1.98363 1.98454	1.99143	2.00008	2.00436

2.4. Two-dimensional triangular lattice

Computer simulations for this model have been reported by Denham, Luckhurst, Zannoni and Lewis.[6] The system is a rectangle of dimensions La and $(\sqrt{3}/2)La$ along the x and y axes respectively. Within this rectangle $N(\equiv L^2)$ molecules are arranged on a triangular lattice of spacing a. The molecular axes are constrained to lie in the xy plane, and they interact via an anisotropic potential

$$u_{ij} = -\epsilon\cos2(\theta_i - \theta_j)$$

which operates between nearest neighbours only. The boundary conditions, as usual, are periodic.

Around each molecule in the lattice neighbouring molecules are coordinated in rings of radius la, where

$$l^2 = l_1^2 + l_2^2 - l_1 l_2 \; (l_{1,2} = 0, 1, 2 \ldots). \qquad (14)$$

In the present calculations attention has been confined to the rings for which l is integral, and in the few cases where these rings are degenerate (in the sense that more than one choice of l_1 and l_2 can be made, e.g. 7 and 0 or 8 and 3, which both correspond to $l = 7$) it has been confined to the six neighbours for which l_2 (say) is zero. These six neighbours, grouped around the central molecule on a regular hexagon, would appear at first sight to be equivalent to one another. The rectangular shape of the system, however, destroys their equivalence, so that on any one of the hexagons $\sigma_2(\mathbf{r}_{ij})$ is liable to

TABLE IV

L	5	9
N	500	2916
$\alpha(1)$	1.7213	1.6556

vary with j. Calculations for the particular case of $l = 1$ have shown that the variations are far too small to be detectable in computer simulation work, so averaged values of $\alpha(l)$ have been computed.

The short-range order parameter for this two-dimensional model needs to be defined by

$$\sigma_2 = \langle \cos 2(\theta_i - \theta_j) \rangle \tag{15}$$

and the long range order parameter by

$$S_2 = \langle \cos 2\theta_i \rangle. \tag{16}$$

It follows that if

$$X = \sum_{q \neq 0} \langle \psi_2^2 \rangle$$

then

$$S_2 = \exp(-2X), \tag{17}$$

and that with $\alpha(l)$ defined as in (2)

$$\sigma_2(l) = S_2^{\alpha(l)}. \tag{18}$$

Equation (18) is approximately true in the three-dimensional case, as Faber[2] has pointed out, but here it applies exactly, which simplifies the calculation of both order parameters. The energy of the system is of course given by

$$U = N\epsilon u^* = -3N\epsilon\sigma_2(1), \tag{19}$$

so the increase of energy when a single mode is switched on is

$$-3N\epsilon\Delta\sigma_2(1) = 6N\epsilon\alpha(1)\sigma_2(1)\Delta X.$$

Equating this to $k_BT/2$ and summing over $(N - 1)$ modes we get

$$12N\epsilon\alpha(1)\sigma_2(1)X = (N - 1)k_BT,$$

or

$$-6(N/(N-1))\sigma_2(1)\ln\sigma_2(1) = k_BT/\epsilon = T^*. \tag{20}$$

Note that $\sigma_2(1)$ is independent of $\alpha(1)$ and hence of L (except in so far as $N/(N - 1)$ varies), which is not the case in three dimensions.

TABLE V

L	12	24	30	60	90
N	144	576	900	3600	8100
$\alpha(1)$	1.23129	1.00002	0.94249	0.79913	0.73369

One may calculate $\sigma_2(1)$ as a function of temperature from (20) and then use (18), given a set of values for $\alpha(l)$, to infer both S_2 and $\sigma_2(l > 1)$. The permitted values of $\mathbf{q}$ satisfy

$$\mathbf{q} = (2\pi/La)\left(n_1\hat{x} + \frac{2}{\sqrt{3}}n_2\hat{y}\right) \tag{21}$$

with

$$-L < 2n_2 \leqq L, \qquad -2L < (3n_1+2n_2) \leqq 2L$$
$$-2L < (3n_1-2n_2) \leqq 2L. \tag{22}$$

The appropriate equation for $\alpha(l)$, averaged as described above, turns out to be

$$\alpha(l) = \frac{2}{3}\left(\left(\sum_{q\neq 0}(B_l/B_1)\right)\bigg/\left(\sum_{q\neq 0}(1/B_1)\right)\right), \tag{23}$$

where

$$B_l = 1 + \frac{1}{3}\left(\cos\left(\frac{2\pi n_1 l}{L}\right) + \cos\left(\frac{\pi(n_1+2n_2)l}{L}\right)\right.$$
$$\left. + \cos\left(\frac{\pi(n_1-2n_2)l}{L}\right)\right). \tag{24}$$

Values of $\alpha(l)$ computed from equation (23) are listed in Tables V and VI.

TABLE VI

(L = 30, N = 900)

l	1	2	3	4	5	6	7	8
$\alpha(l)$	0.9425	1.3017	1.5084	1.6509	1.7576	1.8409	1.9075	1.9613
l	9	10	11	12	13	14	15	16
$\alpha(l)$	2.0049	1.0399	2.0678	2.0894	2.1054	2.1166	2.1235	2.1263

3. RESULTS AND DISCUSSION

Predictions for the three modifications of the Lasher-Lebwohl model which have been discussed in sections 2.1, 2.2 and 2.3 are compared with computer simulation data, taken from reference 5, in Figures 1 to 3. Figure 1 shows the reduced energy per particle, u^*, as a function of reduced temperature T^*. The reduced energy is determined primarily, of course, by the short-range order parameter $\sigma_2(1)$, but where the interaction has an extended range the behaviour of $\sigma_2(l)$ for $l > 1$ is also relevant. This behaviour is shown, for the extended-range FCC model at four different values of T^*, in Figure 2. Figure 3 shows the temperature-dependence of the long-range order parameter, S_2.

Needless to say, the theory is bound to be correct in the limit $T^* \rightarrow 0$, where the magnitude of u^* is determined in a simple fashion by the coordination numbers for the lattice in question and the range of the interaction assumed. One might expect the maximum value of T^* at which an ordered state can be maintained—i.e. the value at

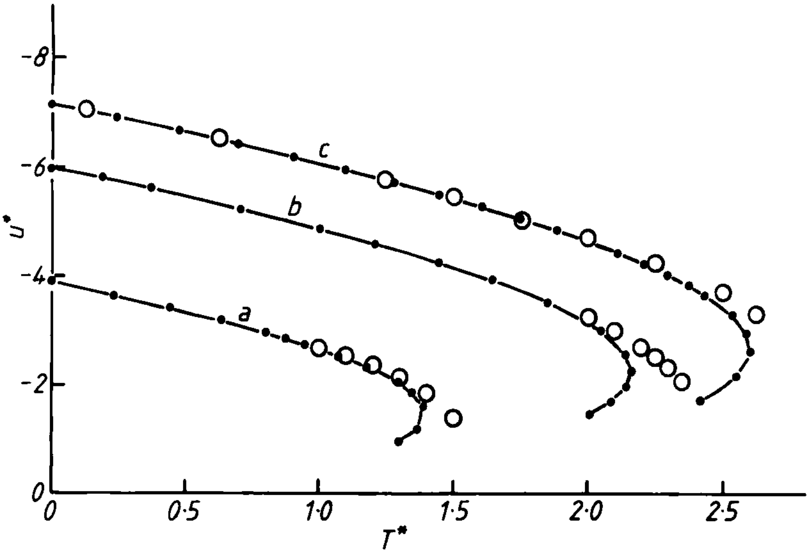

FIGURE 1 Variation of reduced energy per particle with reduced temperature : a, simple cubic lattice with extended-range interaction and N = 1000; b, face-centred cubic lattice with nearest-neighbour interaction and N = 864; c, face-centred lattice with extended-range interaction and N = 500. The filled circles joined by smooth curves are theoretical predictions; the open circles represent data taken from reference (5).

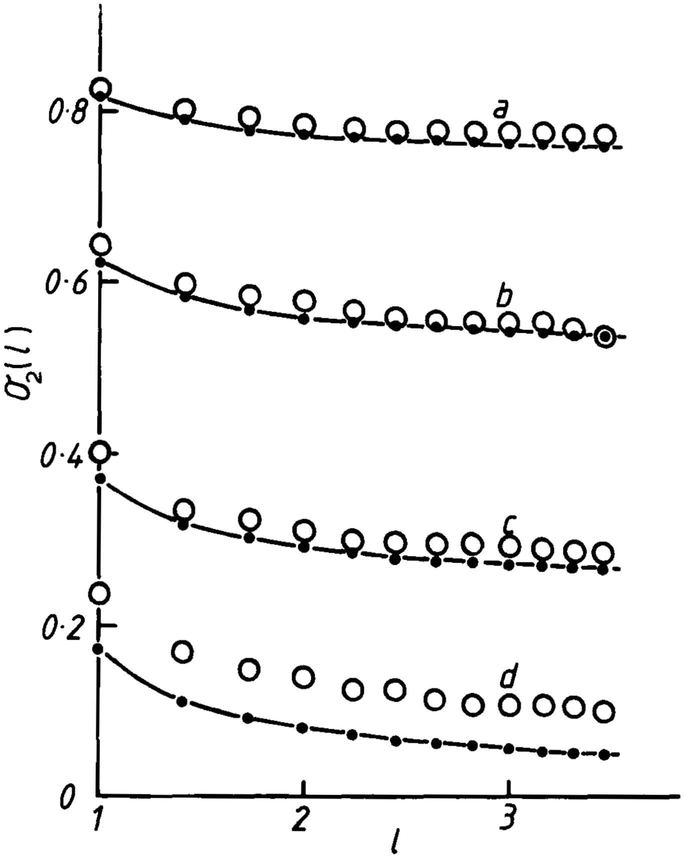

FIGURE 2 Variation of short-range order parameter with l, for the face-centred cubic lattice with extended-range interaction and $N = 500$: a, $T^* = 1.25$; b, $T^* = 1.75$; c, $T^* = 2.25$; d, $T^* = 2.50$. Symbols have the same significance as in Figure 1.

which the curves for u^* and S_2 bend back towards zero—to scale from one model to the next in the same way as $u^*(T^* \rightarrow 0)$, and Figure 1 shows that this expectation is approximately fulfilled. There are some differences of shape between the three curves in this Figure, and similarly the three curves in Figure 3 cannot be brought into exact coincidence by scaling along the temperature axis; the differences are too slight, however, to be of great significance. Thus the agreement that exists between the theoretical curves in Figures 1 to 3 and the computer simulation data, which seems satisfactory except at high temperatures, is not surprising: it mirrors the similar agree-

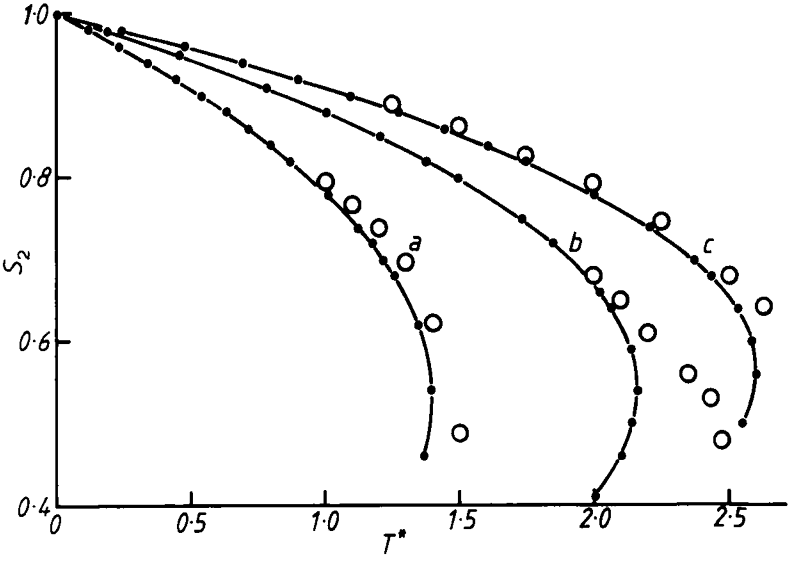

FIGURE 3 Variation of long-range order parameter with reduced temperature : a, simple cubic lattice with extended-range interaction and $N = 1000$; b, face-centred cubic lattice with nearest-neighbour interaction and $N = 864$; c, face-centred lattice with extended-range interaction and $N = 500$. Symbols have the same significance as in Figure 1.

ment which Faber[2] has already demonstrated for the Lasher-Lebwohl model.

The curves presented in Figures 1 to 3 apply for those values of N for which computer simulation data are available. To include curves for other specimen sizes would confuse the Figures, but an indication of the difference which size is liable to make is provided by Figure 4, where the values of T^* at which $S_2 = 0.7$ are plotted against the inverse of $N^{1/3}$. Faber (private communication) has found that straight lines are obtained when his results for the Lasher-Lebwohl model are plotted in this way, and the bottom set of points in Figure 4 derives from his calculations. Evidently, the size-dependence for the three modifications considered in this paper is very similar.

Figures 5 and 6 refer to the two-dimensional model discussed in section 2.4; the computer simulation data with which comparison is made are taken from reference 6. Figure 5 shows that Faber's theory correctly predicts the variation of $\sigma_2(l)$ with l at $T^* = 1.25$, and that it is still reasonably reliable at $T^* = 1.43$; the scatter in the data points in Figure 5 suggest that they are affected by substantial errors of a statistical nature. A similar comparison at $T^* = 1.67$ (not in-

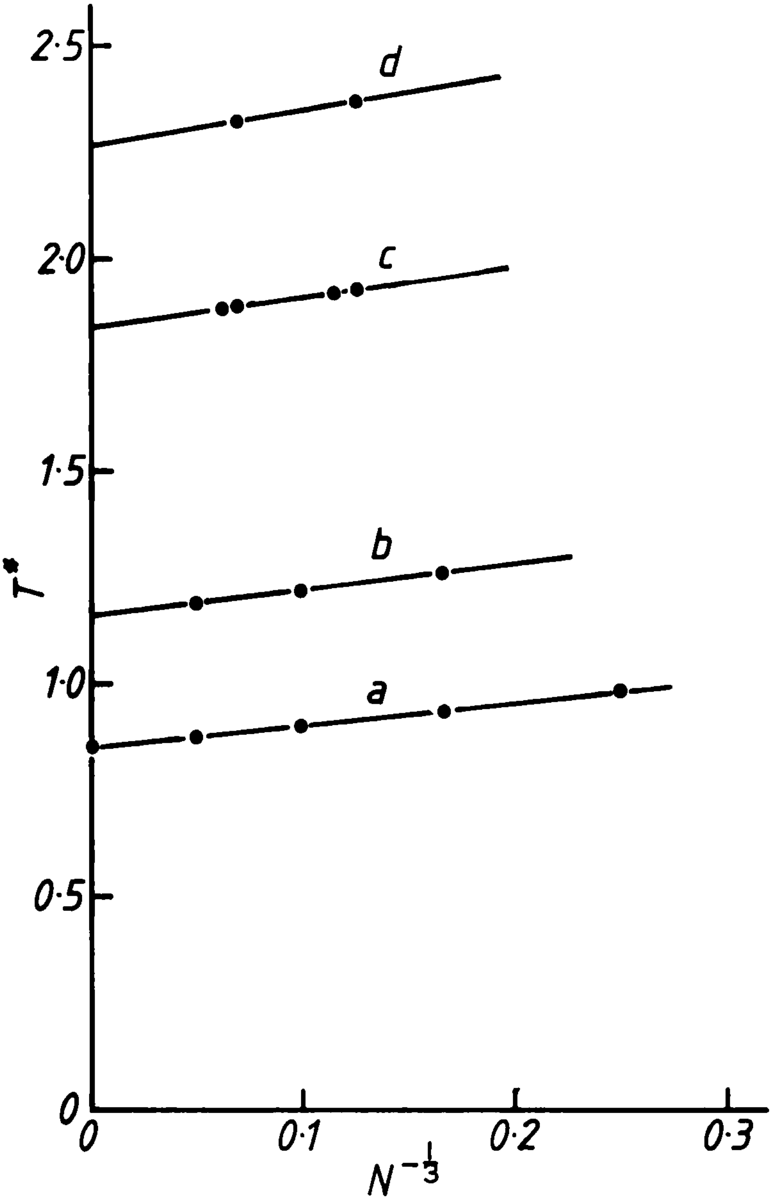

FIGURE 4 Variation with specimen size of the reduced temperature at which S_2 = 0.7 : a, simple cubic lattice with nearest-neighbour interaction, according to Faber; b, simple cubic lattice with extended-range interaction; c, face-centred cubic-lattice with nearest-neighbour interaction; d, face-centred cubic lattice with extended-range interaction.

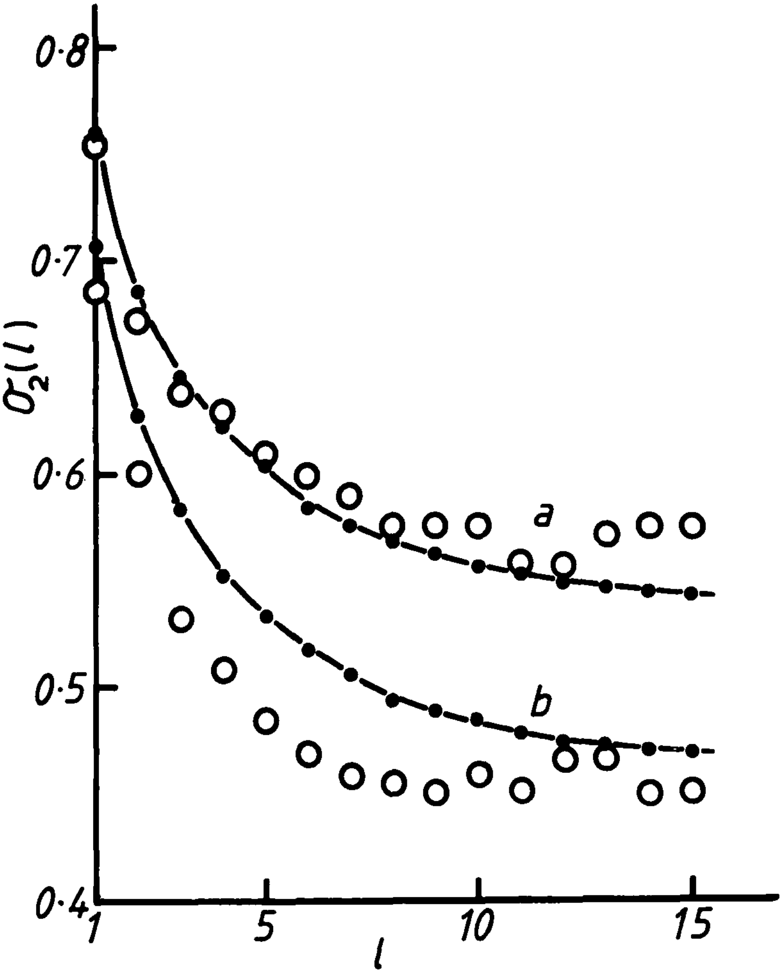

FIGURE 5 Variation of short-range order parameter with l for two-dimensional triangular lattice with $N = 900$: a, $T^* = 1.25$; b, $T^* = 1.43$. The filled circles joined by smooth curves are theoretical predictions; the open circles represent data from reference (6).

cluded in the Figure) shows, however, that at this temperature the theory significantly overestimates σ_2. It is apparent from Figure 6 that at the highest temperatures it also overestimates S_2. The fact that these discrepancies differ in sign from the otherwise similar discrepancies that show up in Figures 1 to 3 may provide some clue as to their origin.

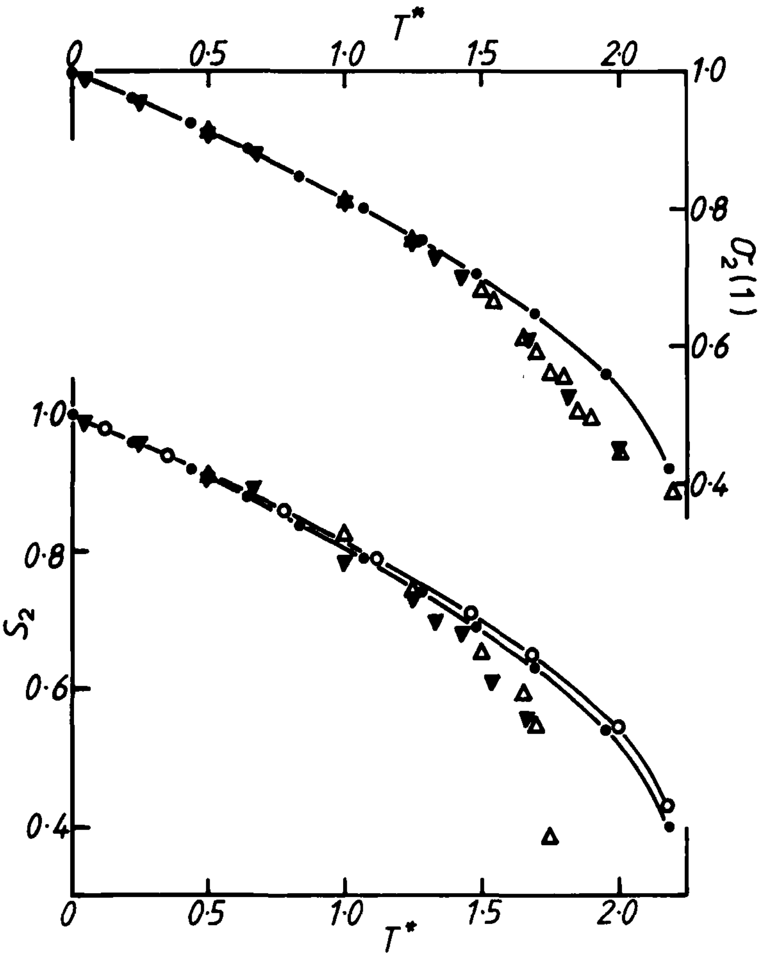

FIGURE 6 Variation of short-range (top half) and long-range (lower half) order parameters with reduced temperature for two dimensional triangular lattice. The filled and open circles joined by smooth curves are theoretical predictions for $N = 900$ and $N = 576$ respectively. The filled and open triangles represent data for the same values of N from reference (6.).

It was pointed out in section 2.4 that $\sigma_2(1)$ should not depend upon N in the two-dimensional case, and indeed no distinction is apparent between the two sets of computer simulation points in the top half of Figure 6, for $N = 576$ and $N = 900$. Both sets converge onto the theoretical curve at low temperatures. The lower half of Figure 6 illustrates the size-dependence that is to be expected for S_2, and this does seem to be apparent, despite some scatter, in the simulated data. As in three dimensions, the effect of decreasing N is to increase the order.

Acknowledgments

The author is indebted to Dr. T. E. Faber for suggesting this work and for help in the preparation of the paper.

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