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

# A Monte Carlo Calculation of the Nematic-Isotropic Phase Transition

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To cite this article: H. J. F. Jansen , G. Vertogen & J. G. J. Ypma (1977): A Monte Carlo Calculation of the Nematic-Isotropic Phase Transition, Molecular Crystals and Liquid Crystals, 38:1, 87-95

To link to this article: http://dx.doi.org/10.1080/15421407708084377

*Mol. Cryst. Liq. Cryst.*, 1977, Vol. 38, pp. 87–95
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Printed in Holland

# A Monte Carlo Calculation of the Nematic–Isotropic Phase Transition

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(*Received October 18, 1976*)

The behaviour of a lattice version of the Maier–Saupe model near the clearing point is investigated using a biased Monte Carlo technique. The lattice version consists of an array of unit vectors, which are located at the sites of a $n \times n \times n$ ($n = 14, 16, 18, 20$) simple-cubic lattice with periodic boundary conditions and interact by way of a nearest neighbour coupling. The system undergoes a first order phase transition with a spontaneous order $S = 0.333 \pm 0.009$ at the clearing temperature $T_c$ given by $\beta_c \varepsilon = 0.894 \pm 0.001$, where $\varepsilon$ denotes the maximum interaction energy between two nearest neighbours. The pretransitional light scattering in the isotropic phase can be reasonably well described by $[T - T_c^*]^{-1}$, with $(T_c - T_c^*)/T_c = 0.009 \pm 0.007$ for $n = 14$ and $(T_c - T_c^*)/T_c = 0.007 \pm 0.004$ for $n = 16$. This type of divergence is in agreement with experiment.

## 1 INTRODUCTION

The nematic-isotropic phase transition in liquid crystals can be described by a quite simple model proposed by Maier and Saupe.[1] This model was solved in the mean field approximation and the predicted order compared reasonably well with the measured order of several nematics.[2] Doubts have been raised, however, concerning the validity of the mean field results. Notably it has been questioned whether the Maier–Saupe model has a first order phase transition in an exact treatment.[3] In order to answer that question Lasher[4] investigated in first instance a discrete-lattice version of the model by means of a Monte Carlo technique. The lattice version consisted of an array of unit vectors located at the sites of a 10 × 10 × 10 simple-cubic lattice, while the discreteness was obtained by restricting the vectors to point in the directions of the faces of a regular dodecahedron. Further, periodic boundary conditions were imposed and only nearest neighbour interactions were taken into account. A first order phase transition was found. The order at the transition point appeared to be $S = 0.82$. Next, Lebwohl and Lasher[5] improved this lattice model considerably by removing the discreteness, i.e. instead of 12 directions they took all possible orientations into account but they still kept the molecules situated on lattice sites. In order to obtain good results they had to enlarge the 10 × 10 × 10 lattice to a 20 × 20 × 20 lattice. The system appeared to undergo a first order phase transition, which is shown quite clearly by the histogram of the relative occurrences of all values of the order seen in all equilibrium configurations generated at the transition point. Two peaks appear, one at $S_{\text{iso}} = 0.20$, the order in the isotropic phase, and the other at $S_{\text{nem}} = 0.33$, the order in the nematic phase. The fact that spontaneous order exists in the isotropic phase, is due to the finiteness of the lattice. Then they argue without any numerical evidence that $S_{\text{iso}}$ will tend to zero with increasing lattice size, which is not surprising at all, but that $S_{\text{nem}}$ will stay fixed with increasing lattice size. From this and their results at different temperatures Lebwohl and Lasher conclude that the order at the transition point is given by $S = 0.33 \pm 0.04$. It should be remarked here that, although the Monte Carlo calculations do not prove rigorously the existence of a first order phase transition in the Maier–Saupe model, they give very strong indications for the existence of such a phase transition. In our opinion it seems to be possible now to prove rigorously the existence of a phase transition in the Maier–Saupe model by extending the method of Fröhlich, Simon and Spencer,[6] who recently gave a rigorous proof of the existence of a phase transition in the classical isotropic Heisenberg model.

Our motivation to study the lattice version of the Maier–Saupe model by means of the Monte Carlo technique was twofold. First we wanted to improve the accuracy of the calculations of Lebwohl and Lasher in order to get a better insight into the usefulness of approximate solutions, e.g. the mean field approximation, the Bethe approximation[7,8] and cluster variation methods.[9] Notably we wanted to reduce the error in the spontaneous order at the transition point to a few percent. Secondly we wanted to calculate the magnetically induced birefringence and the scattering of light by orientational fluctuations in the isotropic phase. As found experimentally by Stinson and Litster[10] both pretransitional phenomena diverge like $[T - T_c^*]^{-1}$ near the transition point, where $T_c^*$ is slightly less than $T_c : (T_c - T_c^*)/T_c \sim 2 \times 10^{-3}$. It has been suggested on the basis of mean field results,[11] which give a value $(T_c - T_c^*)/T_c = 9 \times 10^{-2}$ in the case of the magnetically induced birefringence, that the Maier–Saupe model or in fact any model with a single coupling constant cannot produce such a small number. Recently, however, it has been shown[8,9] that considerably improved results are obtained for the magnetically induced birefringence by incorporating beforehand a small amount of short range correlation into the calculation. In order to settle the question definitely we decided to try to simulate these pretransitional phenomena on a computer by means of the biased Monte Carlo technique.

## 2 MONTE CARLO CALCULATION OF THE MAIER–SAUPE MODEL

The lattice version of the Maier–Saupe model is described by the following hamiltonian

$$H = -\tfrac{1}{2}\varepsilon \sum_{\mathbf{i},\mathbf{a}} P_2(\cos\theta(\mathbf{i}, \mathbf{i}+\mathbf{a})), \tag{2.1}$$

where $\mathbf{i}$ runs over all lattice sites of a simple-cubic lattice and $\mathbf{a}$ over all nearest neighbours; $\theta(\mathbf{i}, \mathbf{i}+\mathbf{a})$ denotes the angle between the directions of the long axes of the molecules situated at $\mathbf{i}$ and $\mathbf{i}+\mathbf{a}$; $\varepsilon$ is the maximum interaction between two nearest neighbours; $P_2(x)$ is the second Legendre polynomial. In order to determine the thermodynamic and statistical quantities of interest we use the Monte Carlo technique as developed by Metropolis *et al.*[12] Basically it boils down to the following procedure. Calculate the energy of any given configuration of the lattice. Choose a molecule at random and give it a random orientation. Calculate the energy of the new configuration, $E_n$, and compare it with the energy of the preceding configuration, $E_p$. If $E_n < E_p$, the new configuration is accepted; if $E_n > E_p$, the new configuration is accepted with a probability given by the Boltzmann factor $\exp[\beta(E_p - E_n)]$ with $\beta = 1/kT$. Repeating this procedure a sufficient number of times will yield essential equilibrium distributions as shown by Fosdick.[13]

The thermodynamic and statistical quantities are determined by averaging over the lattice configurations generated after the system has reached equilibrium. Note that a crucial step in the calculations is to decide when equilibrium has been reached. We have calculated the following quantities: the order parameter, the internal energy, the specific heat, the latent heat and the scattering of light by orientational fluctuations in order to determine $T_c^*$. It appeared impossible to calculate the magnetically induced birefringence because the order induced by the magnetic field is too small compared with the standard deviation of the order induced by the finiteness of the lattice. All calculations were done on a CDC CYBER 7416 using a program written in PASCAL.[14] First we simulated the one-dimensional Maier–Saupe model, which can also be solved exactly by calculating its partition function.[8] Secondly we compared the results of the low- and high-temperature expansion with the corresponding Monte Carlo results for the present model. Excellent agreement was obtained in both cases. In all our calculations we started, both in the ordered and disordered phase, with the groundstate or a totally disordered configuration. The relevant quantities were obtained by averaging over roughly $10^6$ up to $10^7$ different accepted lattice configurations.

The order of a given lattice configuration is determined by maximizing

$$S = \frac{1}{N} \sum_{\mathbf{i}} P_2(\cos \theta(\mathbf{i}, \mathbf{n})) \tag{2.2}$$

with respect to the unit vector $\mathbf{n}$; the index $\mathbf{i}$ runs over all lattice sites, $N$ is the total number of lattice sites, and $\theta(\mathbf{i}, \mathbf{n})$ denotes the angle between the long axis of a molecule situated at site $\mathbf{i}$ and the vector $\mathbf{n}$, which is the director or the preferred direction of the nematic. This definition of the order parameter is also used by Vieillard–Baron.[14] We cannot use definition (2.2) with fixed $\mathbf{n}$ because the preferred direction changes during the Monte Carlo process. The internal energy $U$ of a given lattice configuration is given by (2.1). For convenience, however, we do not calculate $U$ but

$$E = -\frac{U}{3N\varepsilon}. \tag{2.3}$$

Averaging of $S$ and $E$ over all accepted lattice configurations yields the spontaneous order $S$ and a measure $\langle E \rangle$ for the internal energy of the system. The specific heat $C_v$ is derived from the fluctuations $\Delta U$ in the internal energy. It is well known that

$$(\Delta U)^2 = kT^2 C_v \tag{2.4}$$

or with the aid of (2.2)

$$\frac{C_v}{Nk} = (\beta\varepsilon\Delta E)^2 9N. \tag{2.5}$$

It is clear that this quantity can only be determined at the end of a run after $\langle E \rangle$ and $\Delta E$ have been calculated. A second possibility for calculating $C_v$ is to fit $\langle E \rangle$ to a spline function and to differentiate the resulting function with respect to temperature. Both results for $C_v$ agree well. The latent heat $\Delta U$ is determined by

$$\Delta U = U_{\text{iso}} - U_{\text{nem}}. \tag{2.6}$$

As for the pretransitional effects, we already mentioned that the magnetically induced birefringence cannot be calculated by means of the Monte Carlo method because the long range order, which is induced by the applied magnetic field is much smaller than the standard deviation of the order induced by the finiteness of the lattice with periodic boundary conditions. In order to observe the magnetic field effects we have to use unrealistically high magnetic fields resulting in the behaviour of a free gas interacting with a magnetic field $H$ along the $z$-axis, by way of a hamiltonian

$$W = -\tfrac{1}{3}\Delta\chi H^2 \sum_{\mathbf{i}} P_2(a_z^{\mathbf{i}}) \tag{2.7}$$

where $\mathbf{a}^{\mathbf{i}}$ denotes the direction of the long molecular axis and $\Delta\chi$ is the anisotropy of the diamagnetic susceptibility. A description of the scattering of light has been given by Lubensky.[16] It appears that the intensity $I$ of the scattered light is given by

$$I = \frac{(\Delta\alpha)^2}{\lambda^4} \sum_{i,j} e^{i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)} \langle [(\mathbf{e}^F \cdot Q^i \cdot \mathbf{e}^I) - \langle \mathbf{e}^F \cdot Q^i \cdot \mathbf{e}^I \rangle] \times [(\mathbf{e}^I \cdot Q^j \cdot \mathbf{e}^F) - \langle \mathbf{e}^I \cdot Q^j \cdot \mathbf{e}^F \rangle] \rangle, \tag{2.8}$$

where $\lambda$ is the wavelength of the incident light, $\mathbf{q}$ is the scattering vector and $\mathbf{e}^I$ and $\mathbf{e}^F$ are the polarization vectors of the incident and the outgoing beam. The quantity $\Delta\alpha$ is the difference between the molecular polarizabilities, which are parallel and transverse to the electric field, while

$$Q^i_{\alpha\,\beta} = a^i_\alpha a^i_\beta - \tfrac{1}{3}\delta_{\alpha\beta} \qquad \alpha, \beta = x, y, z. \tag{2.9}$$

Experimentally, two intensities have been measured with polarizations $\mathbf{e}^F$ parallel and perpendicular to the polarization $\mathbf{e}^I$ of the incident light. In order to compare with the experiment we have to calculate for each accepted lattice configuration the following quantities

$$I_{\parallel} = \left(\sum_i Q^i_{zz}\right)^2 - \sum_i (Q^i_{zz})^2 \tag{2.10a}$$

$$I_{\perp} = \left(\sum_i Q^i_{xz}\right)^2 - \sum_i (Q^i_{xz})^2 \tag{2.10b}$$

where we have assumed that $\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j) \ll 1$ which implies that the exponential will be equal to unity. It should be noted here that $\langle \mathbf{e}^F \cdot Q^i \cdot \mathbf{e}^F \rangle = 0$, even in our system with finite long range order in the isotropic phase, because the preferred direction changes more than sufficiently during the simulation. Averaging $I_{\parallel}$ and $I_{\perp}$ over all accepted lattice configurations gives the required quantities.

## 3 RESULTS

Our calculations clearly indicate that the model undergoes a first order phase transition at a clearing temperature $T_c$ given by

$$\beta_c \varepsilon = 0.894 \pm 0.001.$$

In Table I we give the values of $S_{\text{iso}}$, the order in the isotropic phase, and $S_{\text{nem}}$, the order in the nematic phase, at the transition temperature $T_c$ for lattices of different size. Both quantities tend to decrease with increasing lattice size. However, the difference

$$\Delta S = S_{\text{nem}} - S_{\text{iso}}$$

is constant within reasonable limits. It seems, therefore, correct to conclude that the order parameter $S$ of the infinite lattice will tend to $\Delta S$ at the transition temperature. Taking the average of $\Delta S$ yields us the following value of the order parameter at $T_c$

$$S_c = 0.333 \pm 0.009.$$

It should be remarked here that the transition temperature $T_c$ is already independent of the lattice size.

TABLE I

The values of $S_{\text{iso}}$, the order in the isotropic phase, and $S_{\text{nem}}$, the order in the nematic phase, and $\Delta S = S_{\text{nem}} - S_{\text{iso}}$, at the transition temperature $T_c$ for $n \times n \times n$ simple-cubic lattices with $n = 14, 16, 18, 20$ and the results of Lebwohl and Lasher [LL].

| $n$ | $S_{\text{iso}}$ | $S_{\text{nem}}$ | $\Delta S$ |
|---|---|---|---|
| 14 | $0.068 \pm 0.006$ | $0.395 \pm 0.035$ | $0.327 \pm 0.041$ |
| 16 | $0.080 \pm 0.010$ | $0.416 \pm 0.015$ | $0.336 \pm 0.025$ |
| 18 | $0.057 \pm 0.005$ | $0.394 \pm 0.007$ | $0.337 \pm 0.012$ |
| 20 | $0.058 \pm 0.005$ | $0.385 \pm 0.010$ | $0.327 \pm 0.015$ |
| 20[LL] | 0.20 | $0.33 \pm 0.04$ | $0.13 \pm 0.04$ |

The values of $C_v$ near the transition temperature $T_c$ are presented in Table II. They have been obtained by fitting $\langle E \rangle$ to a spline function and then differentiating the resulting function with respect to temperature. A second possibility for the calculation of $C_v$ is to use relation (2.5). Both results for $C_v$ appear to agree well, i.e. the technique used is reliable. The latent heat $\Delta U$ can be easily calculated from the jump in $\langle E \rangle$ at the transition temperature. It follows from our calculations that

$$\Delta \langle E \rangle = 0.10 \pm 0.02.$$

As for the light scattering in the isotropic phase it appeared possible to calculate the quantities $I_{\parallel}$ and $I_{\perp}$ for $n \times n \times n$ lattices with $n = 14, 16,$

TABLE II

The values of $C_v$ near the transition temperature $\beta_c \varepsilon = 0.894$.

| $\beta\varepsilon$ | $C_v/Nk$ |
|---|---|
| 0.80 | 1.40 |
| 0.81 | 1.44 |
| 0.82 | 1.47 |
| 0.83 | 1.51 |
| 0.84 | 1.55 |
| 0.85 | 1.58 |
| 0.86 | 1.62 |
| 0.87 | 1.66 |
| 0.88 | 1.70 |
| 0.89 | 1.73 |
| 0.90 | 4.9 |
| 0.91 | 4.7 |
| 0.92 | 4.4 |
| 0.93 | 4.2 |
| 0.94 | 4.0 |
| 0.95 | 3.7 |
| 0.96 | 3.5 |
| 0.97 | 3.3 |
| 0.98 | 3.0 |
| 0.99 | 2.8 |

although the data show considerable standard deviations. For the cases $n = 18, 20$ the calculations failed because the standard deviation in the scattering intensity was too large due to the fact that the number of configurations involved in the averaging procedure, was too small for lattices of this size. Using the standard deviations in the calculated scattering data as weight factors it appeared possible to fit the inverse scattering data to a straight line. In Table III we present our results for $\beta_c^* \varepsilon$ as determined from the data of $I_{\parallel}$ and $I_{\perp}$. The results for $(T_c - T_c^*)/T_c$ are given in Table IV. They are obtained by averaging the values for $I_{\parallel}$ and $I_{\perp}$. From our calculations it follows that the ratio between $I_{\parallel}$ and $I_{\perp}$, which is experimentally

TABLE III

$\beta_c^* \varepsilon$ as determined from the intensities $I_{\parallel}$ and $I_{\perp}$ of scattered light with polarizations parallel and perpendicular respectively to the polarization of the incident light for lattices with $n = 14, 16$.

| $n$ | $I_{\parallel}$ | $I_{\perp}$ |
|---|---|---|
| 14 | 0.896 | 0.907 |
| 16 | 0.897 | 0.903 |

TABLE IV

The values of $(T_c - T_c^*)/T_c$ for lattices with $n = 14, 16$.

| $n$ | $(T_c - T_c^*)/T_c$ |
|---|---|
| 14 | $0.009 \pm 0.007$ |
| 16 | $0.007 \pm 0.004$ |

found to be close to 4/3, is given by

$$\frac{I_{\parallel}}{I_{\perp}} = 0.83.$$

The disagreement is due to the small size of the lattice, i.e. the existence of long range order in the isotropic phase, which suppresses $I_{\parallel}$ (see e.g., Ref. 11, p. 102).

## 4 CONCLUSION

1) The model undergoes a first order phase transition as clearly shown by the behaviour of $\langle E \rangle$ and $C_v$. The transition temperature can be well determined, is already insensitive to the size of the lattice, and agrees with the value found by Lebwohl and Lasher.

2) The jump in the long range order parameter at the transition temperature can be determined quite well by taking the difference between the order in the nematic phase and the finite order in the isotropic phase. This difference is insensitive to the lattice size, whereas Lebwohl and Lasher assume the nematic order to be independent of the lattice size. It appears that, during a simulation, the histogram of the order parameter versus the accepted lattice configurations displays several order peaks at the phase transition. Only two of them, corresponding with the isotropic and nematic phase, are found to be reproducible.

3) The magnetically induced birefringence in the isotropic phase cannot be determined by Monte Carlo calculations, because the induced order is far too small compared to the standard deviation of the order in the isotropic phase.

4) In spite of the large standard deviations of the intensities of scattered light it appears to be quite well possible, using the standard deviations as weight factors, to fit the inverse intensity as a function of temperature to a straight line. The result indicates that, in contrast to a remark of de Gennes,[11] a one-parameter model is able to produce a value of $(T_c - T_c^*)/T_c$, which is in good agreement with experiment. The ratio $I_{\parallel}/I_{\perp}$ strongly differs from the

experimental value, because we still have long range order in the isotropic phase and consequently $I_{\parallel}$ is reduced.

5) From our experience it appears that the 16 × 16 × 16 lattice was the best candidate for performing the calculations. Good statistics, except for the pretransitional phenomena, were obtained in a reasonable time and we were able to go through the transition at $T_c$, i.e. going from a disordered to an ordered state and vice versa. This is due to the fact that the peaks in the internal energy versus accepted lattice configurations histogram, corresponding with the nematic and isotropic phase, are not totally separated but still contain some overlap. As for the biased Monte Carlo technique itself we should like to remark that this technique readily indicates the existence of a phase transition and yields a good estimate of the transition temperature. A large number of data, however, are needed to get meaningful results for other properties like the long range order and pretransitional behaviour. One might question, therefore, whether this technique is the most suited method for investigating this type of systems; it is definitely the most expensive one.

## Acknowledgements

The authors wish to thank Professor A. J. Dekker and B. W. van der Meer for many interesting and stimulating discussions. This work was performed as part of the research program of the "Stichting voor Fundamenteel Onderzoek der Materie" (F.O.M.) with financial support from the "Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek" (Z.W.O.).

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