PHYSICAL REVIEW A VOLUME 5, NUMBER 3 MARCH 1972

Monte Carlo Results for a Discrete-Lattice Model of Nematic Ordering

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(Received 29 September 1971)

The lattice version of the Maier-Saupe model for the nematic-liquid-crystal transition consists of an array of unit vectors located at the sites of some regular lattice. The energy of interaction of nearby unit vectors is proportional to $P_2(\cos\theta_{ij}) = \frac{1}{2}(3\cos^2\theta_{ij} - 1)$, where θ_{ij} is the angle between the vectors at sites i and j which represent the directions of the long axes of the molecules of the liquid. A discrete model which we call the dodecahedral model is defined by restricting the vectors to point in the directions of the faces of a regular dodecahedron. Monte Carlo results are obtained for this model, which is among the models discussed by Potts as interesting generalizations of the Ising model. It is also one of the sequence of models solved in the mean-field approximation and two-cluster approximation by Priest. The Monte Carlo results on a $10\times10\times10$ simple-cubic lattice with periodic boundary conditions determine the transition to be of first order. The order at the transition $M = P_2(\cos\theta)$ is found to be 0.82. Attempts to obtain results on the model with vectors pointing in the six directions of the faces of a cube failed because the $10\times10\times10$ lattice was too small in this case to discriminate between a first- and second-order transition.

I. INTRODUCTION

More than ten years ago Maier and Saupe[1] discussed the ordering of nematic liquid crystals in terms of a simple model. In their model the only essential degree of freedom is the direction of the long axes of the molecules of the liquid. Each pair of nearby molecules has an interaction energy proportional to the second Legendre polynomial of the cosine of the angle θ_{ij} between the directions of their long axes:

$$E = -\sum_{i,j} J_{ij}\tfrac{1}{2}(3\cos^2\theta_{ij} - 1) = -\sum_{i,j} J_{ij}P_2(\cos\theta_{ij}), \quad (1)$$

where the sum is over all nearby pairs of molecules i and j. They solved this model in the mean-field approximation, and therefore their solution is independent of the way in which the interaction constants J_{ij} depend on the distance between molecules i and j. Their treatment predicts the average order M as a function of temperature, where

$$M = \langle \tfrac{1}{2}(3\cos^2\theta_i - 1)\rangle = \langle P_2(\cos\theta_i)\rangle \quad (2)$$

and θ_i is the angle between a given molecular axis and the average ordering direction. The angular brackets indicate an average over all the molecules of the liquid. At high temperatures the order M vanishes, at a transition temperature it jumps discontinuously to the value $M_0 = 0.429$, and as the temperature is further reduced it smoothly approaches unity.

In a review article Saupe[2] compared this prediction with the measured order of several nematic materials. They agree to within a few percent. The conclusions to be drawn from the success of this simple model are still a matter of controversy.

We take seriously the fact discussed by Maier and Saupe in the second paper of Ref. 1 that the observed entropy change per molecule across the transition is much smaller than that predicted by their model. They suggest that one should therefore think of each vector of their model as giving the direction of a few neighboring molecules rather than a single one. Another way of saying this is that the model seriously underestimates the short-range order present in the liquid.

In considering more exact treatments of the Maier-Saupe model one first of all must make it more definite. The usual way of doing this is to consider an array of unit vectors arranged on a regular lattice. It is a commonly made observation of lattice models that their qualitative dependence on the type of spatial lattice chosen is slight. This is fortunate since the lattice is completely an artifact in these models, if we take the above suggestion of Maier and Saupe to mean that each vector represents the order in a certain spatial neighborhood. Indeed, one might consider the lattice models to be approximations to some continuum model.[3(a)]

There has been recent discussion on the further questions of whether the mean-field treatment of the lattice models is adequate. The mean-field treatment of a model with the energy (1) is equivalent to the mean-field treatment of the truncated energy,

$$E = -\sum_{i,j} J_{ij}P_2(\cos\theta_i)P_2(\cos\theta_j). \quad (3)$$

This can be demonstrated by taking the spherical-harmonic addition theorem[3(b)] for Eq. (1) and showing that the terms omitted in (3) average to zero. The difference between the energy expressions (1) and (3) depends upon the components of the vectors transverse to the ordering direction. In the mean-field treatment the transverse components of any two vectors are uncorrelated and their contribution to the average energy vanishes. It is particularly significant that the energy expression (1) is invariant under an arbitrary simultaneous rotation of all vectors, but that expression (3) is not.

Raich, Etters, and Flax[4] showed that a cluster approximation which goes beyond mean-field theory gives no transition when applied to a lattice model with the truncated energy (3). Instead of the order M vanishing for some range of temperatures above a transition temperature, the order is finite for all temperatures and merely approaches zero as the temperature approaches infinity.

Schultz[5] found the same result in a quite different treatment of a lattice model with a discrete version of the truncated energy expression (3). In Schultz's model the continuous range for θ_i was replaced by two discrete values with different *a priori* weights. This model was mapped into the Ising model with a certain temperature-dependent magnetic field. Depending upon the J_{ij}, Schultz found that the dependence of the Maier-Saupe model on temperature corresponds to some line in the temperature-field plane of the Ising model. Only if a given lattice site is assumed to interact with more than roughly 70 neighbors does this line intersect the phase-transition line of the Ising model and thus predict a phase transition for the truncated Maier-Saupe model. Although the replacement of the unit vectors by two discrete states is a crude approximation, Schultz's treatment is the only one which treats the correlations between vectors on nearby lattice sites without further approximation.

Apparently the truncation of the rotationally invariant energy (1) to get the expression (3) is not valid if one wishes to go beyond the mean-field approximation. This is the thesis of a letter by Priest[6] in which he argues that an exact treatment of (3) would not give a phase transition. Priest also introduces a series of models that he terms "quantized versions" which represent the unit vectors by various numbers of discrete states. His mean-field and two-cluster approximations of this sequence of models show an increasing value of the order M at the transition as the number of states at a lattice point is increased.

It seems evident to us that the full, rotationally invariant Maier-Saupe model has a phase transition, but certainly rigorous proof of this fact would be desirable. In the Appendix we argue that the order of their model must strictly vanish for the temperature range in which the high-temperature expansion of the partition function converges. At the opposite limit of low temperature the Maier-Saupe model should behave quite like the classical Heisenberg model because the expansion of the energy expression (1) through second order in the angles would be identical in form for both of these models. It would of course follow from the vanishing of the order for a nonzero range of high temperatures and the presence of finite order at low temperatures that the partition function must have a nonanalytic point and that the model must have a phase transition. We therefore believe that a rigorous demonstration could be given that the Maier-Saupe model has a phase transition, although we have not produced such a demonstration.

From our point of view, then, the lattice models with the rotationally invariant energy, Eq. (1), have an ordering phase transition. A principal motivation for the work reported here was to determine whether that phase transition is of first or second order. Briefly stated, our results are that when the spherical array of unit vectors of the Maier-Saupe model is replaced by 12 symmetrically placed directions, the resulting model has a first-order transition. This we take as an indication that the Maier-Saupe model also has a first-order transition.

II. DODECAHEDRAL MODEL AND MONTE CARLO RESULTS

The dodecahedral model is obtained from the Maier-Saupe model by assuming that the unit vectors point only in the directions of the faces of a dodecahedron, as shown in Fig. 1. The rotational symmetry of the collection of unit vectors then survives in the discrete symmetry of the invariance group of the dedocahedron. A similar model is obtained for each of the regular polyhedra. We also did some calculations on the cubic model with its six directions. The 12 faces of the dodecahedron actually give us only six states at each lattice site, because the interaction (1) is the same for oppositely directed vectors.

The six directions indicated in Fig. 1 correspond

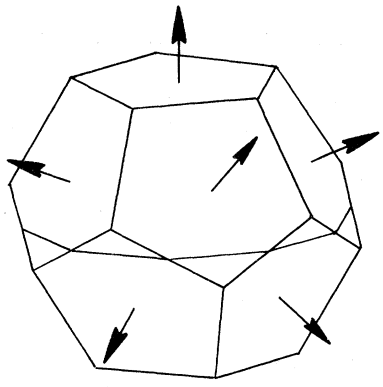

FIG. 1. Dodecahedron with arrows indicating six of the twelve directions from the center of the dodecahedron to the center of the faces. The six directions not shown are oppositely directed to those visible and are therefore equivalent in the dodecahedral model.

to the six allowed states at a single lattice site of the dodecahedral model. Consider the energy assigned by one term of Eq. 1 to some pair of lattice sites. The state at one site can, without loss of generality, be denoted by the arrow in Fig. 1 through the face most nearly facing the reader. The state of the other site of the pair could then be given by the same arrow or one of the five which surround that arrow and which evidently all make the same angle with it. We conclude that in the dodecahedral model there are only two possible values of the energy of a pair of lattice sites. Since it is a trivial change to add or subtract a constant energy to the energy of our model, we can assign zero energy to a pair of lattice sites whose vectors do not point in the same direction. We further simplify by assuming that only vectors at nearest-neighbor lattice sites interact and that their energy is minus one when the vectors are in the same direction. This corresponds to a particular choice for the interaction constants J_{ij} of Eq. (1).

The energy of the dodecahedral model can thus be written as

$$E = - \sum_{(\text{nearest neighbor } i,j)} \delta(\sigma_i, \sigma_j) , \qquad (4)$$

where the σ_i specify the state of the ith lattice site by taking on the values 1, 2, 3 for the cubic model and 1 to 6 for the dodecahedral model. The δ is the Kroneker delta. Models of this type were originally proposed by Potts[7] as interesting generalizations of the Ising model. This model is essentially the same as that of Priest[6] when one takes the parameter r in his equation (6) to be equal to five.

Figure 2 shows the Monte Carlo results for the dodecahedral model. A simple-cubic lattice ten sites on an edge with periodic boundary conditions was used. The discontinuity of the energy and the order at $\beta = (1/T) = 0.75$ (temperature T in energy units) indicates the approximate position of the first-order transition. Calculations of the same size lattice of the cubic model were inconclusive because the fluctuations in the vicinity of the transition were too large to allow us to discriminate between a first- and second-order transition. The weaker the first-order transition the larger the lattice size must be to show that the transition is of first order.

The value of the average order at the transition, $M_0 = 0.82$, is surprisingly large. For the mean-field approximation to the dodecahdral model we find $M_0 = 0.80$, in agreement with a crude extrapolation of the values given by Priest[6] for the mean-field and second-cluster approximations. One might have expected the dodecahedral model to give results closer to the Maier-Saupe model than the cubic model. Apparently this expectation fails because neither of them represent the unit sphere by enough points to be in the region of asymptotic convergence.

The method of the Monte Carlo calculation used here (which is a fairly standard one) obviously could be directly applied to the Maier-Saupe model or to a sequence of discrete models which converge to it. It would be interesting to obtain such results to remove all doubt as to the nature of the transition and to find the order vs temperature.

III. MONTE CARLO CALCULATION

The general form of our calculation is the same as that originated by Metropolis *et al.*[8] for an investigation of a two-dimensional gas of hard disks. Some Monte Carlo calculations have been done on Ising models by Fosdick and others.[9]

The procedure of these calculations is as follows. One starts with some arbitrary state of the lattice, in our case with a 10 × 10 × 10 array of integers with the values 1 to 6. A random process is then applied which changes the state of the lattice in a way that gives detailed balancing for the thermal-equilibrium ensemble at a given temperature. The process must be such that all states of the system can ultimately be reached. It is generated by first considering a small random change of the state of the system and comparing its energy with that of the previous state. If the energy of the new state is lower, then the new state is adopted as a step in the process. If the new state has a higher energy

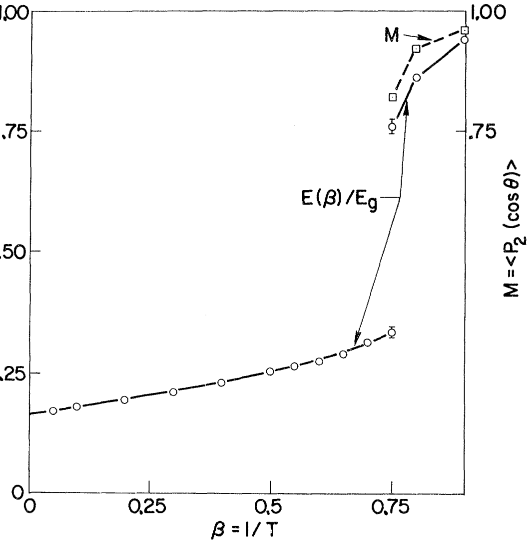

FIG. 2. Monte Carlo results for the dodecahedral model. The normalized energy and the order $M = P_2(\cos\theta)$ are plotted vs $\beta = 1/T$ (T is the temperature in energy units). The discontinuity in these quantities marks the approximate position of the first-order transition. The energy plotted here and in Fig. 3 is normalized by dividing by the ground-state energy which is equal to the negative of three times the number of lattice sites.

it is adopted only with the probability equal to the negative exponential of the change of energy over the temperature in energy units. A little algebra[10] will convince one that this process gives detailed balancing for the thermal-equilibrium ensemble at the given temperature. It also maximizes the probability of adopting the trial state and thus makes the best use of the computer time used in generating the trial state.

In our case we make use of the fact that a simple-cubic lattice separates into two sublattices; the nearest neighbors of each site of one sublattice belong to the other sublattice. For each site of a sublattice a pseudorandom integer from 1 to 6 was chosen as a trial state. The interaction energy of each site with the new trial value was then subtracted from the interaction energy of the previous state of that site. If the new energy was less than the previous energy the new trial value was adopted as the state of the lattice site. If the new energy was greater it was adopted with probability equal to the negative exponential of the change of energy divided by the temperature; otherwise the previous state was maintained. These steps were then repeated for the sites of the other sublattice.

The results shown in Fig. 2 were generated with roughly five h of computation time on an IBM 360/91 with the APL time-sharing system. Points not at the transition point represent averages over sequences of 500 or 100 steps of the method described above. By a step we mean the selection and possible adoption of a new state for each site of *one* sublattice. The points at the transition were determined by 2000 and 4000 steps for the ordered and disordered phases, respectively. The presence of large fluctuations made longer runs necessary at the transition. All of these runs were made only after enough steps had been taken at each new temperature so that any apparent transient had died away.

At $\beta = 1/T = 0.75$ two metastable states were observed. The error bars shown in Fig. 2 are the probable errors derived from the scatter of the results from a few independent runs. No transition between the ordered and disordered states at this temperature was observed during the 6000 total number of steps computed with $\beta = 0.75$. We interpret this behavior to mean that the $10 \times 10 \times 10$ lattice was large enough to make very unlikely any homogeneous fluctuation which could change the phase of the system. On the other hand, this size lattice is presumably too small to contain a transition layer that would allow the two phases to exist in contact and in equilibrium. With a smaller $5 \times 5 \times 5$ lattice transitions were observed between the two phases.

As a further check on our procedure we show that the free energy of the two phases at $\beta = 0.75$ is equal within the accuracy of the calculation. This can be done by numerically integrating certain thermodynamic relations from the high-temperature limit for the disordered phase and from the low-temperature limit for the ordered phase. From the first law of thermodynamics, $dE = TdS$, and the definition of the free energy, $F = E - TS$, where S is the entropy we find for the free energy of the ordered phase, we get

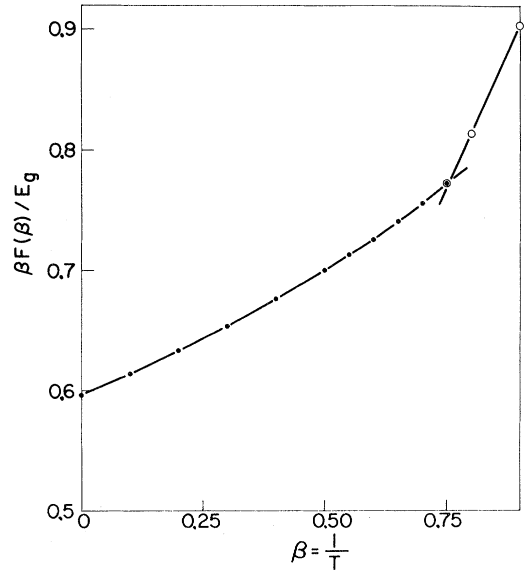

FIG. 3. Free energy of the dodecahedral model vs $\beta = 1/T$. The points were obtained from the results shown in Fig. 2 by numerical integration as indicated in the text. The intersection of the line on the left, which corresponds to the disordered phase, with that on the right, which corresponds to the ordered phase, gives the temperature of the transition. The point of intersection is the result of two independent integrations whose value turned out to be identical to our accuracy.

$$\beta F(\beta) = \beta E_g - \int_\beta^\infty [E(\beta') - E_g]\, d\beta',$$

where E_g is the ground-state energy and is equal to minus three times the number of lattice sites. For the disordered phase

$$\beta F(\beta) = \int_0^\beta E(\beta')\, d\beta' - S_0,$$

where $S_0 = N \ln 6$ is the entropy of the completely disordered phase at $\beta = 0$. Figure 3 shows a plot of these free energies vs β and the consequent determination of the position of the transition point to be $\beta = 0.75$, with an estimated error of 1%.

ACKNOWLEDGMENTS

It is a pleasure to thank M. J. Freiser for many helpful discussions during the course of this work. Thanks are also due to J. P. Straley for pointing out the previous work of Potts, Mittag, and Stephan, and to G. L. Gladstone for a reading of the manuscript. We are indebted to T. D. Schultz for a discussion of his work and for many constructive suggestions for the improvement of the manuscript.

APPENDIX

It is argued here that the convergence of the high-temperature expansion of the classical Heisenberg model or the Maier-Saupe model over a finite region about $\beta = (1/T) = 0$ and zero-field point implies that the order strictly vanishes in the same region. The "proof" is elementary, but seems worth stating explicitly. It depends only on the rotational symmetry of the energy:

$$E(\Omega_i) = -\sum_{i,j} J_{ij} P(\theta_{ij}) - H \sum_{i} P(\theta_i) ,$$

where the Ω_i are the angular coordinates for the unit vector at the ith site, the θ_{ij} are the angles between the unit vectors on the ith and jth lattice sites, and the θ_i are the angles formed by the unit vectors with the direction of the impressed field whose magnitude is H. The J_{ij} are interaction constants which vanish if the distance between the ith and jth sites exceeds some constant. The function $P(\theta)$ is $\cos\theta$ for the calssical Heisenberg model and $P_2(\cos\theta) = \frac{1}{2}(3\cos\theta^2 - 1)$ for the Maier-Saupe model. The partition function for a system with N lattice sites is then given by an integral over the product of N unit spheres,

$$Z_N(\beta, H) = \int \cdots \int \left(\frac{d\Omega_i}{4\Pi}\right)^N e^{-\beta E(\Omega_i)} .$$

The spontaneous moment is given by

$$M(\beta) = \lim_{H\to 0+} \lim_{N\to\infty} \frac{\partial}{\partial H} \frac{1}{\beta N} \ln Z_n(\beta, H) .$$

The next step, which we will not attempt to justify here, is the reversal of the order of taking the limits in the above expression, which is allowed if the power series in H of the logarithm of the partition function of the finite system is well behaved in the thermodynamic limit of $N \to \infty$. From the point of view of those who pursue mathematical rigor in these matters we are merely stating the problem. On the other hand, we believe that most people working with high-temperature series would grant the required properties of this expression. Upon the reversal of the limits, we obtain

$$M(\beta) = \lim_{N\to\infty} \left(\frac{1}{\beta N Z_N(\beta, 0)}\right) \frac{\partial Z_N(\beta, H)}{\partial H}\bigg|_{H=0} ,$$

and the derivative of the partition function is

$$\frac{\partial Z_N}{\partial H}\bigg|_{H=0} = -\beta \sum_{i=1}^{N} \int \cdots \int \left(\frac{d\Omega_i}{4\Pi}\right)^N P(\theta_i)\, e^{-\beta E(\Omega_i)} .$$

This must vanish because one of the N integrations may be done by rotating all N vectors simultaneously. In this integration the θ_{ij} are invariant and the integration of the factor $P(\theta_i)$ gives zero, since both the first and second Legendre polynomials are orthogonal to a constant over the sphere.

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[1] W. Maier and A. Saupe, Z. Naturforsch. 14A, 882 (1959); 15A, 287 (1960).

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[3] (a) In such a model an ensemble would be an integral over a function space whose functions are mappings from three space to the unit sphere. To have convergence, the measure for the integration must neglect the degrees of freedom corresponding to high Fourier components. The lattice models do this in a natural way, but at the cost of removing the invariance to translations appropriate to a liquid. In Ref. 5, T. D. Schultz discusses a different type of continuum model. (b) See, for example, A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton U. P., Princeton, New Jersey, 1957), p. 63.

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[9] Lloyd D. Fosdick, Phys. Rev. 116, 565 (1959); J. R. Ehrman, L. D. Fosdick, and D. C. Handscomb, J. Math. Phys. 1, 547 (1960); Lester Guttman, J. Chem. Phys. 34, 1024 (1961); Chen-Pin Yang, IBM Research Report No. RC564, 1961 (unpublished). This last paper has some interesting discussion of precision and rates of convergence of the Monte Carlo method as applied to lattice models.

[10] A simple procedure is to assume that one has the thermal-equilibrium ensemble, i.e., that the probability of being in the state i with energy E_i is proportional to $e^{-\beta E_i}$. The probability of generating an upward transition by the above procedure to a state j with $E_j > E_i$ is the product of the probability of being in ith state times $e^{-\beta(E_j - E_i)}$, and is therefore proportional to $e^{-\beta E_j}$. The probability of generating the downward transition is just proportional to the probability of being in the jth state or $e^{-\beta E_j}$. Since these are equal we have detailed balancing, and the procedure should generate the thermal-equilibrium ensemble. We have assumed that the i and j states are connected by a single step and that the probability of considering a change to the jth state, given that one is in the ith state, is equal to the probability of considering the opposite transition. It is not necessary that all pairs of states of the lattice be connected by a single transition, but only that they be connected by some sequence of transitions.