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Nematic-Liquid-Crystal Order—A Monte Carlo Calculation

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The lattice version of the Maier-Saupe model of a nematic liquid crystal, in which all molecules are restricted to be on a simple-cubic lattice with periodic boundary conditions and to interact only with their nearest neighbors through the interaction energy $E_{ij} = -\epsilon(\frac{3}{2}\cos^2\theta_{ij} - \frac{1}{2})$, is investigated using a Monte Carlo technique. The lattice is found to undergo a first-order phase transition at $\epsilon/kT = 0.890 \pm 0.005$ with a spontaneous order of $\langle P_2(\cos\theta)\rangle = 0.33 \pm 0.04$ at the transition.

INTRODUCTION

For many years, certain liquid crystals have been known to undergo nematic isotropic phase transitions. These substances consist of long molecules which, at the phase transition, are oriented so that their long axes point in some preferred direction; i.e., the quantity

$$M = \langle P_2(\cos\theta)\rangle \tag{1}$$

has a nonzero value.

Maier and Saupe introduced a model of a liquid crystal consisting of rodlike molecules having pairwise interactions that depend only upon the angle between their long axes, θ_{ij},

$$E = -\sum_{ij} J_{ij}\, P_2(\cos\theta_{ij}) . \tag{2}$$

$P_2(x)$ is the second Legendre polynomial; $J_{ij} > 0$ and depend on the distance between the two molecules. Maier and Saupe[1] treated this model in the mean-field approximation and obtained a first-order phase transition.

Because the significance of the results obtained from the mean-field approximation is not clear, we would like to perform a more exact calculation. Before we can accomplish this, however, our system must be defined more precisely. The molecules are restricted to be on a simple-cubic lattice and to interact only with their nearest neighbors; the total energy is

$$E = -\epsilon \sum_{\langle ij\rangle} P_2(\cos\theta_{ij}) , \tag{3}$$

where $\langle i, j\rangle$ indicates nearest neighbors only and ϵ is the maximum interaction energy. Lasher[2] has given a discussion of the motivation for this choice. He has also investigated this model under the restriction that the long axes of the molecules point only along one of 12 directions placed symmetrically over the sphere (i.e., towards the centers of the faces of the inscribed dodecahedron) and has found a first-order phase transition. We have treated this system exactly, allowing the long axes of the molecules to point towards any direction, and have shown that there is a first-order phase transition; the temperature and spontaneous ordering at the transition are significantly different from those found in previous work.

MONTE CARLO CALCULATION

The Monte Carlo calculation was done in the standard manner originated by Metropolis *et al.*[3] We start with a simple-cubic lattice of molecules obeying periodic boundary conditions in some initial state[4] described by the three direction cosines of the long axis of the molecules at each lattice site and calculate the energy of this configuration. The lattice sites are numbered sequentially. A random orientation is chosen for the molecule on the first lattice site, and the energy of the resulting configuration, E_n, is calculated and compared to the energy of the original configuration, E_p. If $E_n < E_p$, the new configuration is retained; if $E_n > E_p$, the new configuration is retained with a probability $P = e^{(E_p - E_n)/kT}$. This same procedure is then applied to each molecule of the lattice in turn. Fosdick[5] has shown that the repetition of this procedure for many passes through the lattice will yield the equilibrium distribution.

We determine the thermodynamic and statistical quantities of interest by averaging over the lattice configurations generated after the system has reached equilibrium. For temperatures far from the transition, only one run, consisting of 2000 different lattice configurations on a $10 \times 10 \times 10$ lattice, was necessary; this run took 5 min on the IBM 360/91 and gave good values for the energy and the order. Runs near the transition required a $20 \times 20 \times 20$ lattice and more than 8000 lattice configurations; these runs took 2 h. The results of these calculations are shown in Fig. 1. All calculations were done using a FORTRAN IV program written expressly for this calculation.

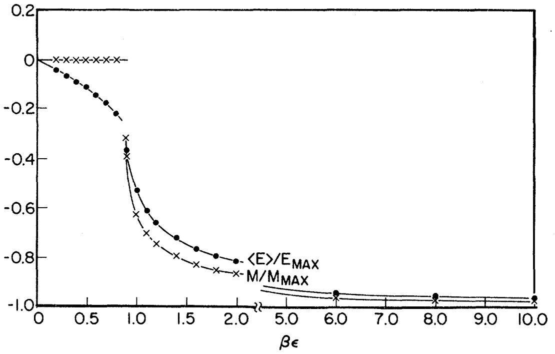

FIG. 1. Plot of the average energy $\langle E\rangle$, normalized to $-1.0 \leq \langle E\rangle \leq 0.0$, and the order M as a function of $\beta\epsilon$. $\beta = 1/kT$, T= temperature, and ϵ is the maximum interaction energy of two molecules. The discontinuity in M and $\langle E\rangle$ indicates a first-order phase transition at approximately $\beta\epsilon \simeq 0.90$.

RESULTS AND DISCUSSION

The apparent discontinuity of the energy $\langle E\rangle$ and order M seen in Fig. 1 suggests that the system has undergone a first-order phase transition; Fig. 2 supports this conclusion. Figure 2 is a histogram of the relative occurrence of all values of the order seen in all the equilibrium configurations of the systems generated at $\epsilon/kT = 0.890$. This histogram shows the bistability of the order, having two peaks at $M = 0.20$ and $M = 0.33$ in which the system spends long periods of time compared to the time spent in transferring from one peak to the other peak. The order of the lattice below the transition is zero. If the identical calculation were done on larger and larger lattices, the histogram would tend to a δ function at $M = 0$ and a δ function at $M = 0.33$. Similar histograms at $\epsilon/kT = 0.885$ and $\epsilon/kT = 0.895$ show single peaks at $M = 0.20$ and $M = 0.37$, respectively; these points, therefore, lie outside the transition region. From the bistability and the other data we conclude that a first-order phase transition occurs at $\epsilon/kT = 0.890 \pm 0.005$ and has a discontinuity in the order of $M = 0.33 \pm 0.04$ and a latent heat of 1.09ϵ.

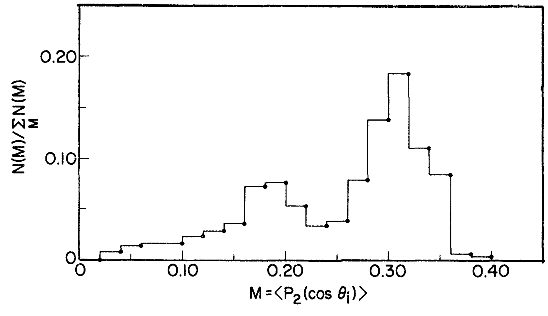

FIG. 2. Histogram of the number of occurrences of a lattice with order M among all equilibrium lattices at $\beta\epsilon = 0.890$. The two peaks indicate that, at this temperature, there are two stable states—one ordered and one disordered—and, therefore, a first-order phase transition occurs near $\beta\epsilon = 0.890$.

A further check on the order of the phase transition is shown in Fig. 3—a plot of the free energy as a function of $\beta\epsilon$. To obtain this plot we evaluate the free energy analytically at very high and very low temperature (see Appendices A and B) and use the formulas[2]

$$\beta f(\beta) = Bf(B) - \int_\beta^B \langle E(x)\rangle\, dx\ , \quad B \gg \beta_{\mathrm{TRANS}} \qquad (4a)$$

$$\beta f(\beta) = bf(b) + \int_b^\beta \langle E(x)\rangle\, dx\ , \quad b \ll \beta_{\mathrm{TRANS}} \qquad (4b)$$

to compute $\beta f(\beta)$ for intermediate values of β. Figure 3 shows the curves integrated from low and high values of β meeting with a discontinuous slope at $\beta\epsilon \simeq 0.890$; this discontinuity is indicative of a first-order phase transition, and its value is the latent heat of ordering.

It is useful to compare our results to the mean-field approximation of Maier and Saupe[1] and the dodecahedral model of Lasher,[2] both of which predict a first-order phase transition. Table I gives the transition temperature, the spontaneous order at the transition temperature, and the latent heat of ordering for all three calculations. It is clear from these figures that, while both models correctly predict the qualitative behavior of the system, neither of them accurately predicts the transition temperature or the spontaneous order.

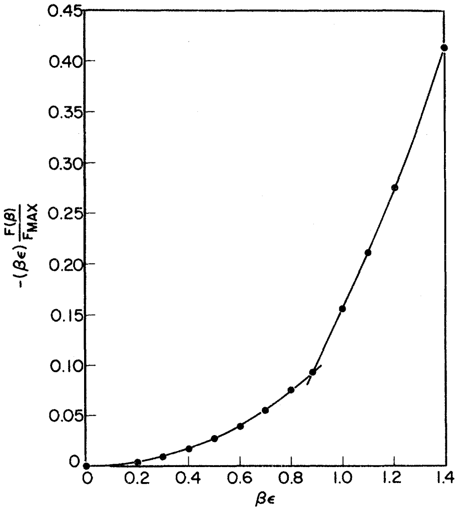

FIG. 3. Plot of the free energy as a function of $\beta\epsilon$. The curves are integrated independently from $\beta\epsilon = 0.20$ and $\beta\epsilon = 20.00$, using (3a) and (3b), and meet with unequal slope at $\beta\epsilon = 0.88$. This discontinuity in the slope is indicative of a first-order phase transition.

TABLE I. Spontaneous ordering at the transition, the transition temperature, and the latent heat of ordering for the mean-field approximation (MFA), the dodecahedral model (DODEC), and the exact calculation (EXACT). The latent heat is given in terms of the energy parameter of Eq. (2), ϵ.

		MFA	DODEC	EXACT
Transition temp	$-\beta\epsilon$	0.77	0.75	0.890
Ordering	ΔM	0.429	0.82	0.33
Latent heat	ΔE	0.522ϵ	1.50ϵ	1.09ϵ

The measured order at the transition of nematic liquid crystals is larger than our result.[6] This disagreement may be explained by the increase in density at the transition, which will increase the intermolecular forces in the ordered phase. A second factor that may contribute to this disagreement is the expectation that the specific choice of lattice will not affect the qualitative behavior of the system, but may affect the precise values of the transition temperature and the spontaneous order.

APPENDIX A: LOW-$\beta\epsilon$ EXPANSION

The N-particle partition function is

$$Z_N=\int\left\{\prod_1^N \frac{d\Omega_i}{4\pi}\right\}\exp\left[\beta\epsilon\sum_{\langle i,j\rangle}P_2(\cos\theta_{ij})\right], \tag{A1}$$

where Ω_i are the angular coordinates of the ith molecule, the energy of (3) is used, and the integration is over the directions of all N molecules. Z_N can be expanded in a power series for $\beta\epsilon$ sufficiently small:

$$Z_N=\int\left\{\prod_1^N \frac{d\Omega_i}{4\pi}\right\}\Big[1+\beta\epsilon\sum_{\langle i,j\rangle}P_2(\cos\theta_{ij})+\tfrac{1}{2}(\beta\epsilon)^2\sum_{\langle i,j\rangle}\sum_{\langle k,l\rangle}P_2(\cos\theta_{ij})P_2(\cos\theta_{kl})+\tfrac{1}{6}(\beta\epsilon)^3$$

$$\times\sum_{\langle i,j\rangle}\sum_{\langle k,l\rangle}\sum_{\langle n,s\rangle}P_2(\cos\theta_{ij})P_2(\cos\theta_{kl})P_2(\cos\theta_{ns})+\cdots\Big], \tag{A2}$$

where each sum runs over all nearest neighbors. The first term of (A2) is 1, since $\int d\Omega_i/4\pi=1$. The second term is zero, since it reduces to a sum of integrals of the form $\int(d\Omega_i/4\pi)P_2(\cos\theta_i)=0$ by judicious choice of coordinate system. The only terms contributing to the third and fourth terms of (A2) are of the form $[P_2(\cos\theta_{ij})]^2$ and $[P_2(\cos\theta_{ij})]^3$, owing to the orthogonality of the $P_n(\cos\theta_{ij})$ and the lack of a closed triangle of bonds on the simple-cubic lattice.

Evaluation of these integrals gives

$$Z_N\simeq 1+\tfrac{3}{10}N(\beta\epsilon)^2+\tfrac{1}{35}N(\beta\epsilon)^3+\ldots\,. \tag{A3}$$

The free energy per particle $(f/3\epsilon)$ and the average energy $\langle E\rangle/3\epsilon$ are

$$\beta\epsilon\frac{f}{3\epsilon}=-\lim_{N\to\infty}\frac{\ln Z_N}{3N}=-\tfrac{1}{10}(\beta\epsilon)^2-\tfrac{1}{105}(\beta\epsilon)^3+\ldots\,, \tag{A4}$$

$$\frac{\langle E\rangle}{3\epsilon}=\frac{\partial[\beta\epsilon(f/3\epsilon)]}{\partial(\beta\epsilon)}=-\tfrac{1}{5}\beta\epsilon-\tfrac{1}{35}(\beta\epsilon)^2+\ldots\,. \tag{A5}$$

Equation (A5) gives a good fit to the computed energies for $\beta\epsilon\leq 0.40$. We used (A4) to start the free-energy calculation described in the text at the low-$(\beta\epsilon)$ end:

$$\beta\epsilon(f/3\epsilon)\big|_{\beta\epsilon=0.20}=-0.00408\,.$$

APPENDIX B: HIGH-$\beta\epsilon$ EXPANSION

We start from the same N-particle partition function (A1). For $\beta\epsilon$ sufficiently large we assume long-range order, i.e., that all molecules point along nearly the same direction. We are thus able to expand the partition function to second order in the variables $\{x_i=\sin\theta_i\cos\psi_i,\ y_i=\sin\theta_i\sin\psi_i\}$, $i=1,2,\ldots,N$, where θ_i is the angle between the ordering direction and the long axis of the ith molecule. If we also take advantage of the invariance of (A1) under simultaneous rotation of all molecules of the lattice through the same angle to orient molecule 1 along the Z axis, we can write the partition function as

$$Z_N=4\pi(2^N)\int_{-\infty}^{\infty}\left\{\prod_{i=1}^N\frac{dx_i\,dy_i}{4\pi}\right\}\delta(x_1)\,\delta(y_1)$$

$$\times\exp\left\{3N\beta\epsilon-\tfrac{3}{2}\beta\epsilon\sum_{\langle i,j\rangle}[(x_i-x_j)^2+(y_i-y_j)^2]\right\}, \tag{B1}$$

where δ is the Dirac δ function and N is the number of molecules in the system. The factor 2^N comes from the degeneracy of the ground state—each molecule can have either $\theta_i=0°$ or $\theta_i=180°$ with respect to the ordering direction of the ground state. We now introduce the running-wave representation

$$x_{\vec{m}}=N^{-1/2}\sum_{\vec{k}}a_k e^{i\vec{k}\cdot\vec{n}}\,,$$

$$y_{\vec{n}}=N^{-1/2}\sum_{\vec{k}}b_k e^{i\vec{k}\cdot\vec{n}}\,, \tag{B2}$$

where n is a triplet of integers locating the lattice site of the molecule. These running waves are analogous to the spin waves of the Heisenberg ferromagnet. Substituting these expressions into (B1) and performing the integrations,

$$Z_N = e^{3N\beta\epsilon}(6\beta\epsilon)^{-N}\,\frac{3\beta\epsilon}{\pi} \times N^{1/2}\Big\{\prod_{k\neq 0}(3-\cos k_x-\cos k_y-\cos k_z)\Big\}\,. \qquad \text{(B3)}$$

In the limit $N\rightarrow\infty$, the free energy, which is the logarithm of the partition function, is

$$\beta f = -3\beta\epsilon + \ln 6\beta\epsilon + \frac{1}{(2\pi)^3} \times \int_{-\pi}^{\pi}\ln(3-\cos k_x-\cos k_y-\cos k_z)\,dk_x\,dk_y\,dk_z\,. \qquad \text{(B4)}$$

The integral in (B4) is the $N\rightarrow\infty$ limit of the sum that is derived from the partition function by taking the logarithm of the product in (B3). Upon evaluating the integral, we can write the free energy per particle as

$$\beta\epsilon\,(f/3\epsilon) = -\beta\epsilon \quad \tfrac{1}{3}\ln\beta\epsilon - 0.924\,. \qquad \text{(B5)}$$

A simple check on this formula is to calculate the energy $\langle E\rangle = [\partial/\partial(\beta\epsilon)]\,\beta\epsilon(f/3\epsilon)$,

$$\langle E\rangle = -1 + 1/3\beta\epsilon\,, \qquad \text{(B6)}$$

and compare it to an independent calculation of the energy. For N molecules with two degress of freedom, the low-temperature excitation spectrum is N independent harmonic oscillators, each having an energy $kT = 1/\beta$. Thus the total energy, including a normalization factor $|E_g| = 3N\epsilon$, is

$$\langle E\rangle = \frac{1}{3N\epsilon}\left(-3N\epsilon + \frac{2N}{2\beta}\right),$$

or

$$\langle E\rangle = -1 + 1/3\beta\epsilon\,. \qquad \text{(B7)}$$

Thus our partition function satisfies this check and (B6) and (B7) both agree with our Monte Carlo results.

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

[2] G. Lasher, Phys. Rev. A 5, 1350 (1972).

[3] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. 21, 1087 (1953).

[4] For all temperatures we could start from a totally disordered state or a fully ordered state and reach the same equilibrium lattice configuration. It was convenient, for reasons of computation speed, to choose a totally disordered initial state for temperatures above the transition or a fully ordered initial state for temperatures below the transition.

[5] L. D. Fosdick, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1963), Vol. 1.

[6] A. Saupe, Angew. Chem. 80, 99 (1968).

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Computer Simulation of Critical Properties and Metastable States in a Finite Square Ising System

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We report some results of a computer simulation of metastable states and critical properties in a finite Ising system consisting of square $n\times n$ lattices with and without periodic boundary conditions.

The description of metastable states on a fundamental level is both an interesting and unsolved problem in statistical mechanics.[1-3] Nature provides many examples of metastable states; they include supercooled vapors and liquids, supersaturated solutions, superheated liquid He^3,[4] ferromagnets in the part of the hysteresis loop where the magnetization and the applied magnetic field are in opposite direction, and diamond. Metastable states can occur in discontinuous phase transitions. Instead of making the appropriate phase transition, however, the system may go over continuously into a one-phase state, called a metastable state, which may have a very long lifetime. The distinguishing feature of a metastable state is that, eventually, either through external disturbances or spontaneous fluctuations which nucleate the missing phase, the system begins an irreversible process which leads to the new stable equilibrium state. The irreversibility of this transition corresponds to a decrease in free energy or an increase in entropy.[3]

In this paper we report some results of a computer simulation of metastable states and critical properties in a finite Ising model consisting of a square $n\times n$ lattice with and without periodic bound-