A cluster Monte Carlo method for the simulation of anisotropic systems

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A Monte Carlo method for studying anisotropic systems with a new type of boundary conditions is proposed. The missing interactions at the sample box surface are replaced by interactions with ghost molecules. The orientations of these ghost particles are sampled from a "least biased" singlet distribution obtained self-consistently from the order parameter inside the sample. The method is tested on the Lebwohl–Lasher model with 125 and 1000 particles. Results for the transition temperature and order parameters are in good agreement with those obtained from simulation of much larger systems. The method is fairly general and should be applicable in a variety of simulations. Here we show that it can also be used to study director fluctuations in nematogen models.

I. INTRODUCTION

Computer simulations of anisotropic systems[1–16] are complex and especially time consuming. They have been mostly confined to lattice models, where the intermolecular potential is assumed to depend on the orientation of particles whose position is kept fixed.[8] A lot of experience has been accumulated on some of these models and particularly on the Lebwohl–Lasher (LL) model[1] where the pair potential is taken to be

$$U_{ij} = -\epsilon_{ij} P_2(\cos\beta_{ij}), \tag{1}$$

where ϵ_{ij} is a positive constant, ϵ, for nearest-neighbors particles i and j and β_{ij} is the angle between the axis of these two molecules. Study of the LL model has shown that fairly large systems are necessary for an accurate determination of the transition temperature T_{NI}. Monte Carlo calculations with periodic boundary conditions (PBMC) seem to indicate that getting a 1% accuracy on T_{NI} requires at least a $20\times20\times20$ particles system.[1,5,6,8,12,13] A calculation involving a few thousand particles with a single interaction center and short-range couplings can be performed with present computers. However, it rapidly becomes an impracticable task as we increase the number of interaction centers or in general choose a more realistic potential. Thus, for example, a very complex system of *p*, *p'*-pentyl-cyanobiphenyl model molecules has been recently treated[15] but only 64 particles were considered. Facing this computer experimental situation we have, at least for the LL model, a number of approximate theoretical treatments such as a simple molecular field (MF) theory[17] and a few two to four site cluster calculations[18–20] as well as continuum-type theories, etc.[21] For the more complex potentials, e.g., the smectogen ones, only the molecular field treatment is normally available. The MF theory actually works quite well in predicting the temperature dependence of the order parameters vs reduced temperature. On the other hand, MF greatly overestimates the transition temperature, e.g., the MF T_{NI} is at $T^* = kT/\epsilon = 1.321$, while values of 1.119,[5] 1.124,[1] and 1.127[13] have been found from Monte Carlo simulation of the LL model with 8000 particles. The two site cluster treatment gives a better estimate (1.1598) and the four site cluster method gives a value for the transition temperature of 1.142[20] which is 1.5%–2% too high but comparable with what is obtained with the MC method by studying a sample of 1000 particles.[12] However, the order parameter and the change in internal energy at the transition are not so markedly improved so that in this respect things should be improved upon the traditional cluster methods anyway.

The essence of the cluster methods is that of treating exactly interactions within a group of particles, which is in turn embedded in an average field produced by all the neglected particles. It is thus surprising in a way that a MC calculation which treats exactly the interaction between a few hundred molecules should not give even better results for the transition temperature. The answer could lie in the type of boundary conditions employed. We know that in general[22–23] the effect of periodic boundary conditions (PBC) is that of enhancing interparticle correlations and thus that of increasing the transition temperature. On the other extreme, free space boundary conditions underestimate the interaction of our sample with the outside world and generally underestimate the transition temperature. In his pioneering work on spin systems, Binder has used the approximation of an external magnetic field whose strength is adjusted self-consistently.[22] In that approach interactions with the molecules outside the sample box are replaced with interactions with this field. In the next section we wish to propose another type of boundary conditions which seems more general and in particular more easily applicable to the complex situations with multiple order parameters arising in anisotropic systems. The method chooses an environment outside the sample box using self-consistency and information theory[24,25] principles. As we shall see it retains some flavor of the cluster approaches and it seems appropriate calling it cluster Monte Carlo (CMC) method.

II. THE CLUSTER MONTE CARLO (CMC) METHOD

We start by considering a lattice subsystem B of N particles which is part of an asymptotically large system (a "world") W of N_G identical particles. The molecules are defined by their orientational positional state variable X_i and interact through a pairwise potential of a certain effective range. This range defines in turn a natural boundary area

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between the sample of N molecules inside the virtual box B and the world of N_W particles outside. This is schematically represented in two dimensions in Fig. 1 for a square lattice system with nearest-neighbor interactions.

The total potential energy U_G for the global system of $N_G = N + N_W$ particles can be written as

$$U_G = U_B + U_{BW} + U_W, \tag{2}$$

where

$$U_B = \sum_{i=1}^{N} \sum_{j=1}^{N} U_{ij}; \quad \text{with } i<j \tag{3}$$

is the contribution from particles which are all inside the sample box, while

$$U_{BW} = \sum_{i=1}^{N} \sum_{j=N+1}^{N_G} U_{ij} \tag{4}$$

comes from the interaction between molecules inside and outside. Finally U_W is a purely external energy, i.e.,

$$U_W = \sum_{i=N+1}^{N_G} \sum_{j=N+1}^{N_G} U_{ij}; \quad i<j. \tag{5}$$

The global canonical average of a quantity $A = A(\mathbf{X}_1,\mathbf{X}_2,...,\mathbf{X}_N)$ dependent only on the state of the particles in our virtual box is

$$\begin{aligned}\langle A\rangle_G = (1/Z_G)&\int d\mathbf{X}_1\, d\mathbf{X}_2 \cdots d\mathbf{X}_N \\ &\times \exp(-U_B/kT) A(\mathbf{X}_1,\mathbf{X}_2,...,\mathbf{X}_N) \\ &\times \int d\mathbf{X}_{N+1} d\mathbf{X}_{N+2} ... d\mathbf{X}_{N_G} \\ &\times \exp(-U_W/kT)\exp(-U_{BW}/kT),\end{aligned} \tag{6}$$

where k is the Boltzmann constant, T the temperature, and Z_G the global configurational integral,

$$Z_G = \int d\mathbf{X}_1\, d\mathbf{X}_2 \cdots d\mathbf{X}_{N_G} \exp(-U_G/kT). \tag{7}$$

Our aim is to rewrite $\langle A\rangle_G$ in a form amenable to some kind of MC calculation. We notice first that for a certain configuration W of the outside world the average of A is

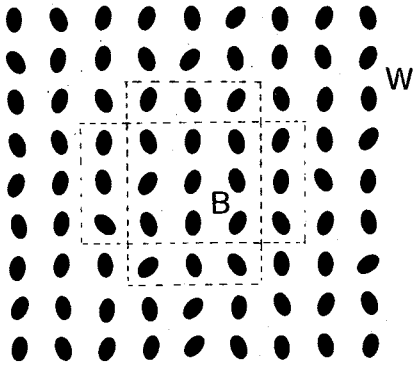

FIG. 1. A schematic representation of a virtual sample box B embedded in a very large system W. The boundary particles of W which directly interact with the internal ones in the case of nearest-neighbor coupling are enclosed by the additional dashed line.

$$\begin{aligned}\langle A\rangle_{[W]} = (1/Z_{B[W]})&\int d\mathbf{X}_1\, d\mathbf{X}_2 \cdots d\mathbf{X}_N \\ &\times \exp[-(U_B + U_{BW})/kT] A(\mathbf{X}_1,...,\mathbf{X}_N),\end{aligned} \tag{8}$$

where we have defined the configuration integral for the box molecules given a certain configuration $[W]$ of the outside world

$$Z_{B[W]} = \int d\mathbf{X}_1\, d\mathbf{X}_2 \cdots d\mathbf{X}_N \exp[-(U_B + U_{BW})/kT]. \tag{9}$$

We can now rewrite $\langle A\rangle_G$ as an average over the outside configurations $\langle\cdots\rangle_W$ of $\langle A\rangle_{[W]}$ since

$$\begin{aligned}\langle A\rangle_G &= (1/Z_G)\int d\mathbf{X}_{N+1} \cdots d\mathbf{X}_{N_G} \\ &\quad \times \exp(-U_W/kT)\langle A\rangle_{[W]} Z_{B[W]} \\ &= \int d\mathbf{X}_{N+1} \cdots d\mathbf{X}_{N_G} P_{\text{out}}(\mathbf{X}_{N+1},...,\mathbf{X}_{N_G})\langle A\rangle_{[W]} \\ &= \langle\langle A\rangle_{[W]}\rangle_W.\end{aligned} \tag{10}$$

Here we have introduced the outside molecules distribution

$$\begin{aligned}P_{\text{out}}(\mathbf{X}_{N+1},...,\mathbf{X}_{N_G}) &= (1/Z_G)\exp(-U_W/kT)\int d\mathbf{X}_1 ... d\mathbf{X}_N \\ &\quad \times \exp[(-U_B + U_{BW})/kT] \\ &= \exp(-U_W/kT) Z_{B[W]}/Z_G\end{aligned} \tag{11}$$

and we have used the fact that $N_W \gg N$. One way of approximating the average over the outside world is through importance sampling, considering a finite number of configurations M_W for the molecules outside the box, i.e.,

$$\langle A\rangle_G \simeq (1/M_W)\sum_{[W]} \langle A\rangle_{[W]}. \tag{12}$$

Notice that each average $\langle A\rangle_{[W]}$ can be calculated with ordinary Monte Carlo when the outside configuration is known. The problem of approximating $\langle A\rangle_G$ based on just an N particles simulation then becomes that of generating suitably sampled outside configurations. To this end we have to discuss the distribution P_{out}. In the idealized simulation over all N_G molecules our N particles MC sample is just a subsystem of a very large one without surface effects. In this case all the m particles distributions inside and outside the virtual box (as well as across the interface) have to be the same:

$$P_{\text{in}}^{(m)}(\mathbf{X}_1,\mathbf{X}_2,...,\mathbf{X}_m) = P_{\text{out}}^{(m)}(\mathbf{X}_1,\mathbf{X}_2,...,\mathbf{X}_m); \quad m \leqslant N. \tag{13}$$

In particular, the distribution needed to average the surface term in Eqs. (9) and (11) would equal the corresponding inside distribution thus giving a self-consistency condition. As a special case this implies that the singlet distribution outside the sample should equal that inside, i.e.,

$$P_{\text{in}}^{(1)}(\mathbf{X}) = P_{\text{out}}^{(1)}(\mathbf{X}). \tag{14}$$

If we expand this singlet distribution inside and outside in the same orthogonal basis set[26] we get at once that the expansion coefficients, i.e., the order parameters inside and

outside should be the same. In the purely orientational case expansion in a Wigner basis gives for a system of rigid particles (see, e.g., Ref. 26)

$$\langle D^L_{mn}\rangle_{\text{in}} = \langle D^L_{mn}\rangle_{\text{out}}. \tag{15}$$

We assume the N-particle sample to be big enough to allow definition of meaningful statistical averages based on just the particles inside, so that, e.g., the left-hand side of Eqs. (13) and (14) can be determined. Thus if we knew at least the singlet distribution inside we could generate all the state variables $\mathbf{X}_i$ necessary to replace the missing interactions by assuming the outside distribution to be a product of singlet ones and sampling from this distribution. This is not trivial since the distribution inside the sample is not known. We shall use Information Theory as an aid in this respect and illustrate this for the simple case where orientations only are relevant. First we assume that there exists a symmetry breaking field direction, say along the Z laboratory axis and that the less symmetric phase is at most uniaxial around this direction. We can then calculate the order parameters with respect to this direction, which for cylindrically symmetric particles are just the Legendre polynomials averages $\langle P_L\rangle$, with L even, i.e., $\langle P_2\rangle$, $\langle P_4\rangle$,... . Armed with these observables we can construct the best information theory[24,25] inference for the molecular distribution outside, i.e.,

$$P(x) = \exp\left\{\sum_L \alpha_L P_L(x)\right\}, \quad x = \cos\beta, \tag{16}$$

where the coefficients α_L are determined from the constraint that the available $\langle P_L\rangle$ can be reobtained by averaging $P_L(x)$ over the distribution in Eq. (16),

$$\langle P_L\rangle = \int_0^1 dx\, P_L(x)P(x) \Big/ \int_0^1 dx\, P(x), \quad \text{with } L \text{ even}. \tag{17}$$

In the present paper we confine ourselves to the simplest approximation in the sequence, i.e., that obtained from a knowledge of just $\langle P_2\rangle_{\text{in}}$. Thus we assume the ghost molecules singlet distribution to be

$$P(x) = (1/Z)\exp[a_2 P_2(x)], \tag{18}$$

with Z a normalization coefficient and a_2 determined from the constraint that $\langle P_2\rangle$ calculated from Eq. (17) satisfies

$$\langle P_2\rangle_{\text{out}} = \langle P_2\rangle_{\text{in}}. \tag{19}$$

Equation (18) represents the least biased inference for the distribution $P(x)$ in terms of its second moment only. In practice ghost molecule orientations are sampled from this distribution thus creating in a self-consistent way a priviledged laboratory direction. In a sense we are simulating interactions with the outside with a inhomogeneously fluctuating surface field whose average strength is proportional to the order parameter inside. The director pinning effect will thus be larger at lower temperatures while it will essentially vanish in the isotropic phase. This is of course different from the case of a true external field which acts on all molecules and whose strength is independent of the ordering inside. In this case a field induced ordering in the isotropic phase is likely to be observed. Notice also that we have a clear pathway for improving upon our approximation. In particular pair distribution sampling can be considered by a straighforward generalization of the present approach. Hence, however, we wish to test the method using the simplest approximation and see how this performs.

III. DETAILS OF THE CALCULATION

We have studied systems of particles interacting with the LL potential Eq. (1) on a simple cubic lattice with dimensions $5\times5\times5$ and $10\times10\times10$. As we have already discussed in the previous section, we consider here a second moment estimate of the singlet distribution for the particles outside the sample box, as in Eq. (18). In practice the calculation is started from a completely aligned system at low temperatures or, where available, from an already equilibrated configuration at a lower temperature. The ordinary Metropolis Monte Carlo procedure is then used to follow the system evolution for a certain number of cycles, i.e., of sets of N attempted moves. Every cycle each particle is selected at random for trial move using a simple random shuffling algorithm.[27] This ensures that each molecule attempts a move every cycle, without the regularity involved in moving the particles sequentially.[28] After a preequilibration period the order parameter $\langle P_2\rangle$ inside the sample is calculated. This identifies the parameter a_2 and thus the distribution in Eq. (18) from which new orientations for the ghost particles outside the box are sampled. We generate the orientations of these external ghosts molecules using a simple rejection technique, as follows. First we extract a uniformly distributed random number x_R, $-1 \leqslant x_R \leqslant 1$ representing a trial orientation, $x_R = \cos\beta$. Then we compare another random number, y, uniform in the range 1 to $P(1)$ with the value of the distribution $P(x_R)$ [cf. Eq. (18)] at that point. The orientation x_R is accepted only if $y \leqslant P(x_R)$. It is then checked that the order parameter outside is the same as that inside to an acceptable threshold (here 0.006) and the generation is repeated if this is not the case. The energy of the system is then recalculated and evolution proceeds as before. Notice that the total energy for the N particles system with N' ghosts is

$$U = -\sum_{i=1}^{N}\sum_{j=N+1}^{N+N'} \epsilon_{ij} P_2(\cos\beta_{ij}); \quad \text{with } i<j. \tag{20}$$

For the simple cubic lattice $N = L^3$, with L the number of particles on each side and $N' = 6L^2$. The total number of interactions in Eq. (20) is $3L^3 + 3L^2$ so that the average energy $U^* = \langle U\rangle/N\epsilon$ per particle is

$$U^* = -(z/2 + 3/L)\sigma_2 \tag{21}$$

in terms of the short-range-order parameter σ_2 while in PBMC we have

$$U^* = -(z/2)\sigma_2. \tag{22}$$

The order parameter with respect to the Z lab direction P_2^J is calculated every cycle J for the molecules inside the box. After a certain number of cycles M an average is calculated for this K trajectory segment

$$\langle P_2\rangle_{\text{in}}^{(K)} = (1/M_K)\sum_J P_2^J, \tag{23}$$

together with the attendant standard deviation σ_K. This order parameter is then compared to the one outside and if the difference between the two is statistically significant to a sat-

isfactory confidence level (here 0.05)[29] a new set of orientations for the ghost molecules is generated using the new order parameter. If the order inside and outside are not significantly different the orientations outside are kept and the next check is made after a longer segment, i.e., $M_{K+1} > M_K$. The number of cycles M_K is instead left unchanged if the order was adjusted. This ensures that on one hand we do not choose an incorrect order parameter outside and leave it unchanged. On the other hand since every change of the outside layer will lower the short-range correlation at the interface this method takes care to do the updating only if really needed and not on every cycle or on the basis of some wild fluctuation.

Equilibration runs of at least 4000 cycles have been discarded before starting production. Production runs were of at least 10 000 cycles and up to 50 000 cycles near the transition for the $5\times5\times5$ system and of 6000 to 30 000 cycles for the $10\times10\times10$ size. Each calculation was divided in runs of 1000 to 2000 cycles. Statistical errors have been estimated as standard deviations from the average over these runs. During the production run various observables have been calculated in addition to the internal energy and second-rank order parameter calculated at every cycle as already described. The results obtained are presented and discussed in the next section.

IV. RESULTS AND DISCUSSION

A. Computer calorimetry

The results of the CMC simulation for the dimensionless energy $U^* = \langle U/N\epsilon \rangle$ at the various reduced temperatures $T^* = kT/\epsilon$ studied are shown in Fig. 2 for the two sample sizes of 125 and 1000 particles. We see clearly that a sharp change of slope occurs for both cases suggesting the onset of a first-order transition. The two curves in Figs. 2(A) and 2(B) have similar shape but the smaller system is, as we might expect, systematically more ordered than the larger one. We notice also that the energy data are somewhat noisier than similar data for PBMC. We think this effect is related to the rather abrupt changes produced in the configurations chain when the outside molecules are updated. This contrasts with the situation in ordinary MC where the various configurations produced by the small changes needed to keep a reasonable acceptance ratio are often too correlated, thus leading to too small and unrealistically low errors when analyzed with a standard statistics which assumes uncorrelated data samples.[30]

The heat capacity of the system C_V^* has been evaluated by differentiating U^* with respect to T^*. This is done by first fitting a smoothing curve to the data points (ICSSCV or ICSMOU from IMSL[31]) then taking the derivative. These results are shown in Fig. 3 for the two systems. They show clearly the peak mimicking the expected divergence both for the $5\times5\times5$ and the $10\times10\times10$ lattice. Notice that even for the small system the peak is sharper than the one obtained for a $10\times10\times10$ system with PBC.[12] We identify the orientational transition temperature with the position of the heat capacity maximum[30] and find the values reported in Table I. The error estimates quoted are obtained from the uncertainty in locating the maximum in C_V^* (cf. Appendix). It is important to notice that the CMC method gives a transition temperature in excellent agreement with that obtained by PBC on larger size systems.[1,12,13] On one hand this is a conforting check of the technique against a very well established one. On the other it indicates that we have not introduced spurious effects with the implementation of the method described in the previous section.

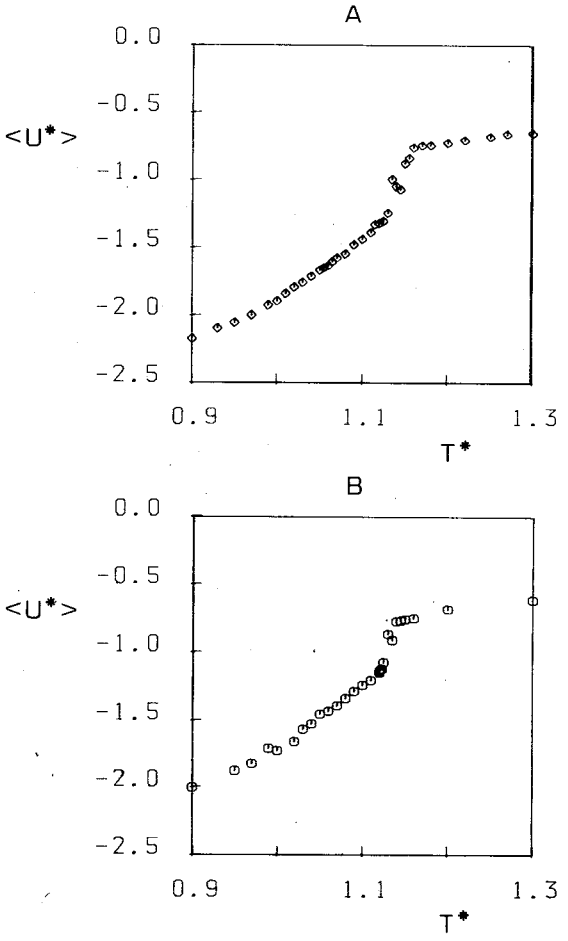

FIG. 2. The average reduced energy $\langle U^* \rangle$ vs temperature T^* obtained from CMC simulation for the $5\times5\times5$ (A) and for the $10\times10\times10$ (B) lattice.

B. Order parameters

One essential part of any simulation of anisotropic systems is the calculation of order parameters. This presents no particular problem in the present method since we have a symmetry breaking direction. We have calculated $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with respect to this direction, finding the results plotted in Figs. 4 and 5. The order parameter calculated for the $10\times10\times10$ system is slightly lower. However, the two curves are very similar and become nearly superimposable if the slight shift in transition temperature is accounted for. Values of the order parameter at the transition were estimated from the values corresponding to the temperature T_{NI}^* previously determined. The values found in this way are again given in Table I. In the transition region the data are rather noisy especially for the smaller system. They also show indications of bistability as expected when solving self-

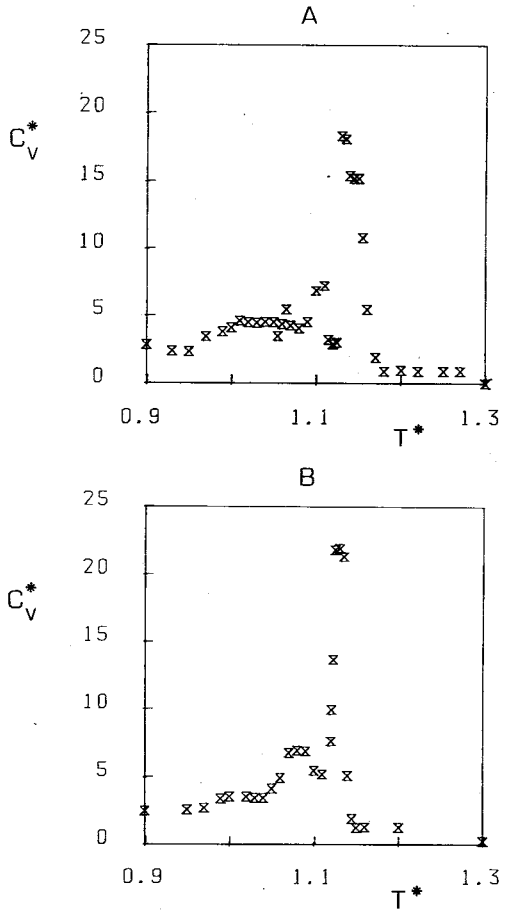

FIG. 3. The heat capacity C_V^* obtained by differentiation of the energy $\langle U^* \rangle$ with respect to T^* for the $5\times5\times5$ (A) and for the $10\times10\times10$ (B) system.

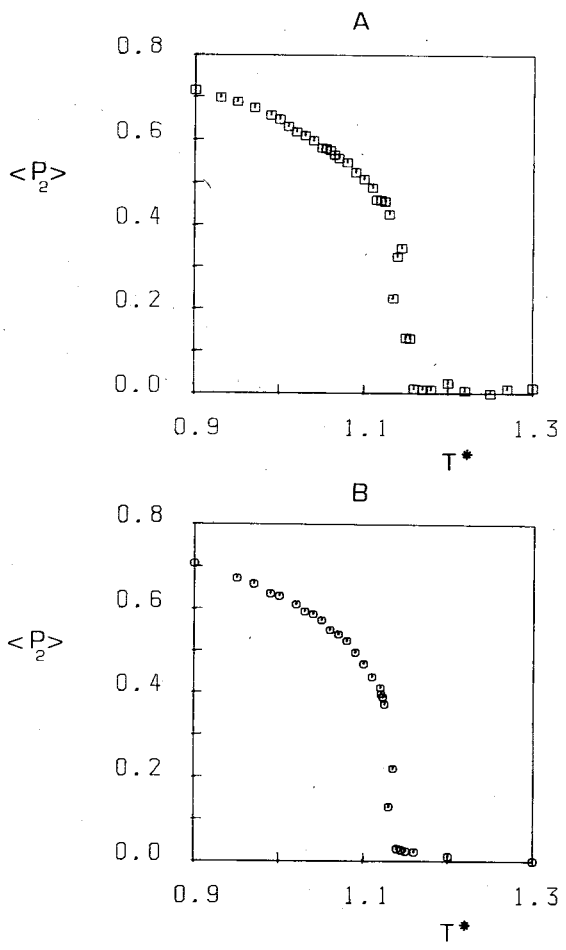

FIG. 4. The second rank order parameter calculated with respect to the laboratory symmetry breaking direction, $\langle P_2 \rangle$, as a function of temperature T^* for lattice size $5\times5\times5$ (A) and $10\times10\times10$ (B).

consistent equations near a first-order transition. However this effect is very close to the error limit of the calculation for these sample sizes and a detailed analysis of the transition region would certainly require further work beyond the scope of the present paper. In the normal PBMC simulations the calculation of order parameters is relatively complicated by the absence of a symmetry breaking direction. Thus an order parameter with respect to the instantaneous director is usually introduced as follows.[2,8] First a suitable ordering matrix is defined as

$$Q_{ab} = \sum_i q_{i,a} q_{i,b} - (1/3)\delta_{a,b}; \quad a,b = x,y,z, \tag{24}$$

where, e.g., $q_{i,x}$ is the x component of the unit vector $\mathbf{q}_i$ specifying the orientation of the ith particle and the sum is extended to all the particles in the system. An order parameter $\langle P_2 \rangle_\lambda$ is then defined in terms of the largest eigenvalue, λ_3, of $\mathbf{Q}$, while the corresponding eigenvector gives the direction of maximum alignment. This order parameter has been calculated in the present work by computing and diagonalizing $\mathbf{Q}$ at every cycle and averaging λ_3,

$$\langle P_2 \rangle_\lambda = (3/2)\langle \lambda_3 \rangle. \tag{25}$$

Notice that $\mathbf{Q}$ is traceless so that $\lambda_3 \geqslant 0$ and $\langle P_2 \rangle_\lambda \geqslant 0$. The order parameter $\langle P_2 \rangle_\lambda$ is plotted in Fig. 6 for the two sys-

TABLE I. A comparison of the orientational transition properties for the Lebwohl–Lasher model obtained in the present work with those of other simulations on the same model using periodic boundary conditions. Here N is the number of particles, T_{NI}^* the estimated transition temperature and $\langle P_2 \rangle$, $\langle P_2 \rangle_\lambda$, and $\langle P_4 \rangle$ are order parameters as described in the text.

N	T_{NI}^*	$\langle P_2 \rangle$	$\langle P_2 \rangle_\lambda$	$\langle P_4 \rangle$	Reference
125	1.133 ± 0.08	0.30 ± 0.05	0.36 ± 0.05	0.070 ± 0.003	this work
1000	1.128 ± 0.003	0.24 ± 0.03	0.27 ± 0.03	0.047 ± 0.002	this work
1000	1.145 ± 0.005	...	...		Ref. 12
8000	1.127 ± 0.003	...	0.27 ± 0.02		Ref. 13
8000	1.119 ± 0.001	...	0.33 ± 0.04		Ref. 5
8000	1.124 ± 0.006	...	0.38 ± 0.04		Ref. 1

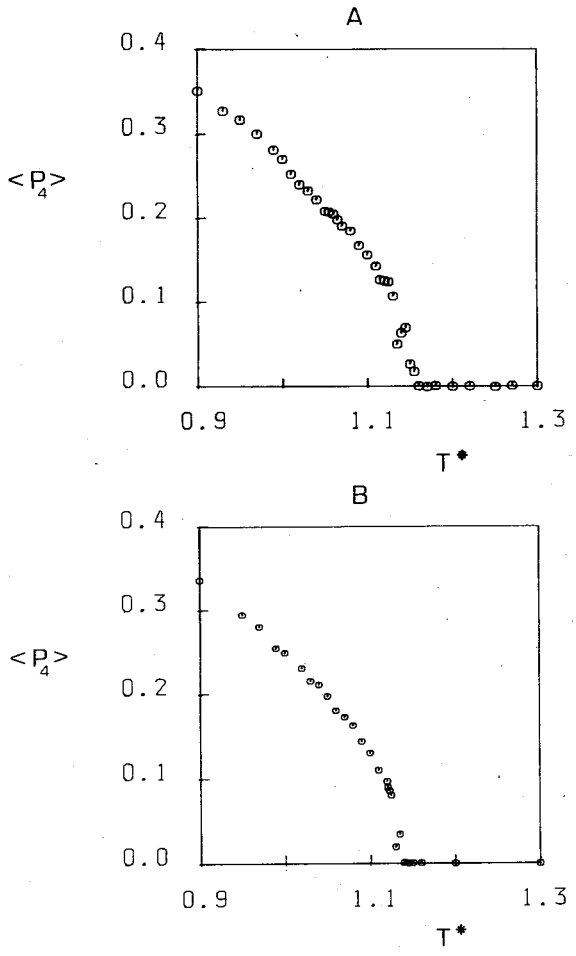

FIG. 5. Same as Fig. 4 but for the fourth rank order parameter $\langle P_4 \rangle$.

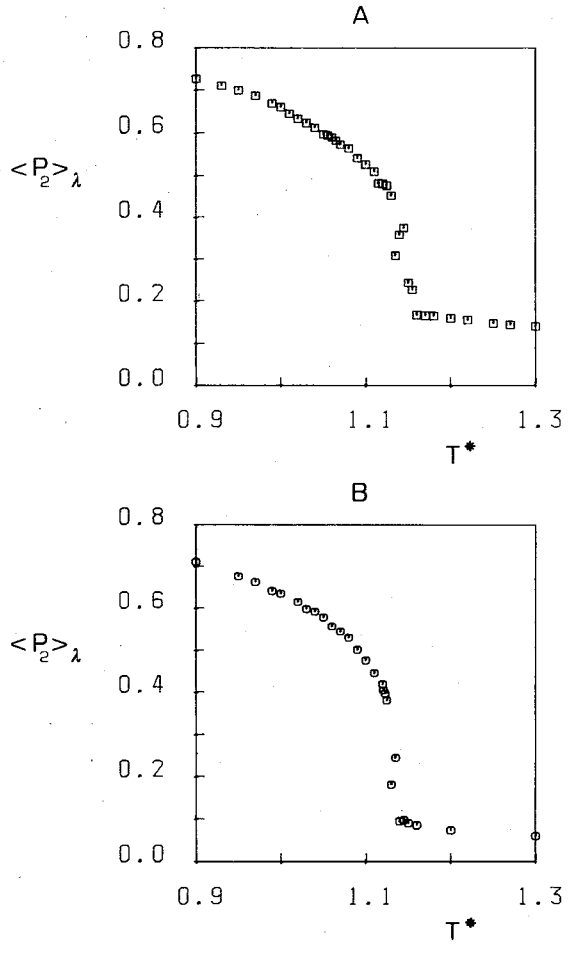

FIG. 6. The second rank order parameter referred to the instantaneous director $\langle P_2 \rangle_\lambda$ for $5\times5\times5$ (A) and $10\times10\times10$ (B) lattices.

tems of different size and we see that it does not go quite to zero above the transition. The same behavior is of course found in PBMC and somewhat contrasts with our expectation of what an order parameter should do above the transition.

The origin of the problem with the diagonalization procedure, here as in PBMC, lies in the fact that it always determines a direction of maximum ordering for every configuration and yields $\langle P_2 \rangle$ with respect to this instantaneous director even in the isotropic phase, where we do not have a bona-fide director. It follows that $\langle P_2 \rangle_\lambda$ being the average of the nonnegative quantity λ_3 is overestimated by the diagonalization algorithm in the isotropic phase. A recent interesting proposal[16] of taking the second, instead than the largest eigenvalue of **Q** to estimate the order parameter in the isotropic phase does not seem to completely solve the problem. On one hand it is clear that the second eigenvalue corresponds to a direction perpendicular to the instantaneous director and that averaging it will give a number approaching zero. It is thus also true that the value obtained in this way for the finite system is a better approximation to the infinite value. On the other hand, the conceptual problem remains since the director does not exist in the disordered phase and cannot be identified with the instantaneous direction of maximum alignment. Indeed the diagonalization procedure would give an order parameter different from zero for any finite isotropic system.

We see from Fig. 7 that the order parameter with respect to the director and that relative to the laboratory are strictly related to one another in the nematic phase. It is interesting to examine the relation between the two[32] even at the cost of

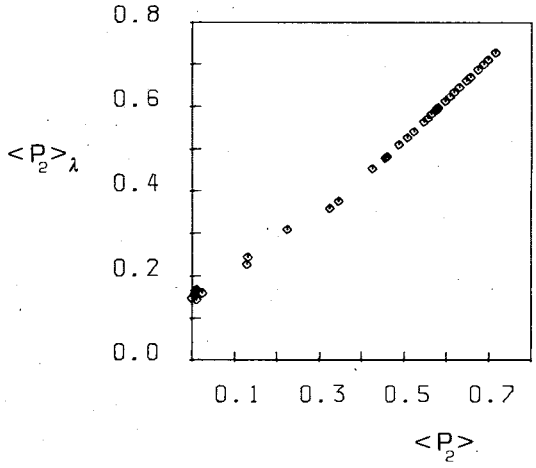

FIG. 7. The relation between the second rank order parameter referred to the average director $\langle P_2 \rangle$ and its counterpart $\langle P_2 \rangle_\lambda$ referred to the fluctuating preferred orientation.

making some simplifying assumptions. Writing the rotation from the laboratory to the molecular frame in two steps gives

$$\langle D^2_{00}(M-L)\rangle_{\rm LAB} = \sum_n \langle D^2_{n0}(D-L)^* D^2_{n0}(M-D)\rangle \tag{26}$$

where we use the notation $D^J_{mn}(B-A)$ for the Wigner rotation matrix connecting frame A to frame B. If we assume that director fluctuations can be decoupled so that they can be averaged separately and if uniaxial symmetry exists, then

$$\langle P_2\rangle = \langle P_2\rangle_{\rm fluc}\langle P_2\rangle_\lambda, \tag{27}$$

where $\langle P_2\rangle_{\rm fluc}$ indicates the dispersion of the director. Notice that we have no *a priori* warranty that performing the decoupling in Eq. (27) is fully justified, even though it is commonly used[32] because of the different time scales of the director and molecular motion. Equation (27) is important in view of a problem recently taken up by Warner.[32] The problem is to assess what part of the laboratory order parameter that is normally measured is to be ascribed to director fluctuations[33] and what part is the bare order parameter referred to the director. One extreme case is that all the disorder is due to reorientational motion, thus with $\langle P_2\rangle_{\rm fluc}\simeq 1$.[34] The other approach is of a continuum type and at its extreme assumes $\langle P_2\rangle_\lambda \simeq 1$ thus considering that disordering is essentially a coherent director fluctuation process.[35] Our results here indicate an intermediate situation with a $\langle P_2\rangle_{\rm fluc}$ corresponding roughly to amplitudes of director fluctuations increasing from about 3 deg at $T^* = 0.90$ to about 30 deg just before the transition. An elastic analysis[32–36] gives

$$\langle P_2\rangle_{\rm fluc} = 1 - \frac{3}{\pi} kT^*/(KL_c), \tag{28}$$

where K is an average elastic constant and L_c a cut off length. Transforming to dimensionless units for the LL model, $K^* = Ka/\epsilon$, $L_c^* = L_c/a$ we find

$$K^* L_c^* = \frac{3}{\pi} T^*/(1 - \langle P_2\rangle_{\rm fluc}). \tag{29}$$

It is well known that elastic constants are expected to vary as the square of the order parameter[37]: $K = K_0\langle P_2\rangle^2$. If this is the case and if we can assume that the cutoff length does not vary with temperature in this range than $K^* L_c^*$ should be linear in $\langle P_2\rangle^2_\lambda$. In Fig. 8 we show that this is the case to a good approximation. We find for the $10\times 10\times 10$ system

$$K^* L_c^* = B\langle P_2\rangle^2_\lambda$$

with $B = 315 \pm 7$ and correlation coefficient $r = 0.943$. An order of magnitude estimate of the quantities involved for a real nematogen (MBBA),[37] i.e., $K_0 \simeq 2\times 10^{-6}$ dyn, $T_{NI} \simeq 320$ K, would give $L_c \simeq 60$ nm. This is an admittedly approximate calculation, but is possibly the first estimate of the cutoff length determining the purely microscopic and fluctuation contributions to the order parameter.[31] The CMC method seems suitable for studying elastic properties of nematogen models even though this should be further investigated.

C. Pair properties

We have calculated the angular pair correlation coefficients $G_L(r)$[6] for rank $L = 2$ and 4. We recall that

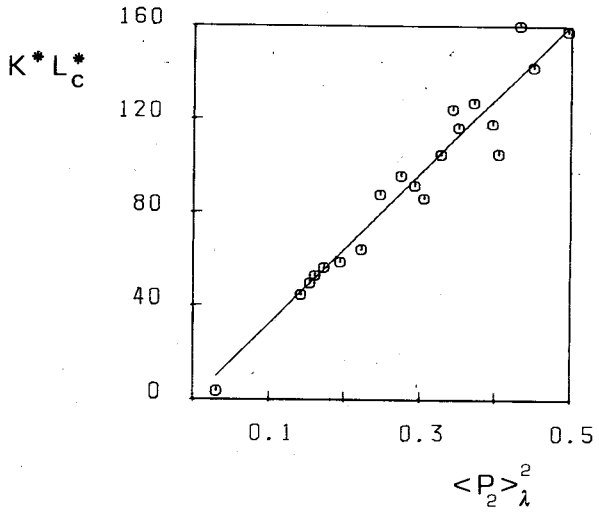

FIG. 8. The product of reduced average elastic constant K^* and cutoff length L_c^*, as obtained from Eqs. (28) and (29), plotted against the order parameter $\langle P_2\rangle_\lambda$ for the $10\times 10\times 10$ lattice. The best linear regression going through the origin is shown as the continuous line.

$$G_L(r) = \langle P_L(\cos\beta_{ij})\rangle_r \tag{30}$$

gives the correlation between the orientation ω_{12} of two particles separated by a distance r. They represent expansion coefficients of the rotationally invariant pair distribution

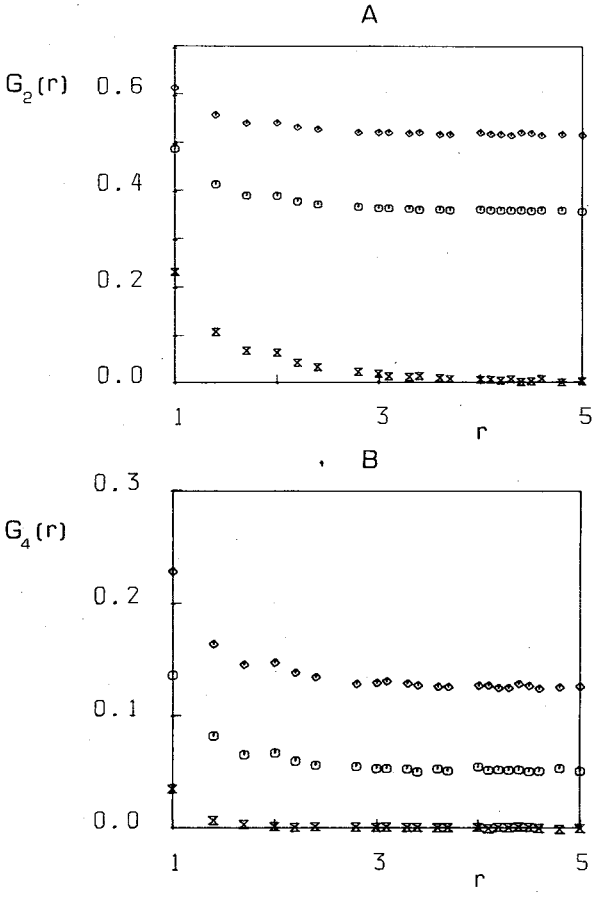

FIG. 9. The angular pair correlation coefficients $G_L(r) = \langle P_2(\cos\beta_{12})\rangle$ with β_{12} relative orientation of two particles at distance r presented for rank $L = 2$ (A) and $L = 4$ (B). Here we show the result for the $5\times 5\times 5$ lattice and for three reduced temperatures: 0.90 (◇), 1.04 (○) and 1.15 (⊠). Dimensionless distances from the nearest neighbor one to the box length are shown.

$G(r_{12},\omega_{12})$,[8,23]

$$G(r_{12},\omega_{12}) = G_0^{00}(r_{12})\sum [(2L+1)/64\pi^4] \times G_L(r_{12})P_L(\cos\beta_{12}), \quad (31)$$

where

$$G_0^{00}(r_{12}) = \int d\omega_1\, d\omega_2 G(r_{12},\omega_{12}). \quad (32)$$

The pair coefficients $G_L(r)$ should start from one and tail off to essentially $\langle P_L\rangle_\lambda^2$.[8] In PBMC, however every distance dependent property is determined modulo the box length. Thus the pair coefficients grow up unphysically for particles whose distance approaches the box length. In the present method this is not the case and the pair correlation has the correct asymptotic behavior. In Figs. 9(A) and 9(B) we show as an example $G_2(r)$ and $G_4(r)$ for these temperatures in the $5\times5\times5$ system and for interparticle separations up to the box length.

V. DISCUSSION AND CONCLUSIONS

In the procedure described we build a ghost environment outside our "small" MC sample that mimicks the true one and its fluctuations by obeying at least approximately Eq. (11). Notice that in an ordinary MC calculation with periodic boundary conditions Eq. (11) is replaced by the much stronger condition that in the various sample replicas the state variables X_i (e.g., orientations) and not just their distribution are the same.

The method proves effective at least for the present system: it gives results on a system of only 125 particles which are comparable to those obtained with much larger samples. Thus quick exploratory studies of small systems could be performed. The procedure allows defining a laboratory frame with the average director identified as the symmetry breaking direction. This allows calculation of order parameters with respect to this external direction, pretty much the same way as it is done in experimental work. Order parameters with respect to the instantaneous director can of course be calculated as usual. A detailed comparison of the two can give information on director fluctuations and thus elastic constants.

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TABLE A1. A summary of the results obtained with the CMC method on a $5\times5\times5$ Lebwohl–Lasher model for energy U^*, heat capacity C_V^* and order parameters $\langle P_2\rangle$, $\langle P_2\rangle_\lambda$, and $\langle P_4\rangle$. Here N_c is the number of production cycles.

T^*	U^*	$\langle P_2\rangle_\lambda$	$\langle P_2\rangle$	$\langle P_4\rangle$	C_V^*	$N_c/10^3$
0.900	−2.173 ± 0.008	0.727 ± 0.0019	0.715 ± 0.0020	0.3701 ± 0.0031	2.8 ± 0.10	27
0.930	−2.095 ± 0.008	0.710 ± 0.0019	0.698 ± 0.0018	0.3465 ± 0.0025	2.4 ± 0.20	31
0.950	−2.054 ± 0.006	0.700 ± 0.0013	0.688 ± 0.0016	0.3352 ± 0.0020	2.3 ± 0.20	36
0.970	−1.999 ± 0.009	0.687 ± 0.0024	0.674 ± 0.0027	0.3184 ± 0.0033	3.4 ± 0.10	25
0.990	−1.925 ± 0.011	0.669 ± 0.0040	0.656 ± 0.0045	0.3001 ± 0.0051	3.8 ± 0.30	24
1.000	−1.895 ± 0.005	0.660 ± 0.0016	0.647 ± 0.0019	0.2901 ± 0.0021	4.1 ± 0.20	32
1.010	−1.842 ± 0.016	0.645 ± 0.0045	0.630 ± 0.0046	0.2746 ± 0.0045	4.6 ± 0.30	24
1.020	−1.794 ± 0.011	0.633 ± 0.0025	0.617 ± 0.0032	0.2614 ± 0.0026	4.5 ± 0.30	31
1.030	−1.759 ± 0.013	0.624 ± 0.0041	0.608 ± 0.0047	0.2528 ± 0.0044	4.4 ± 0.40	24
1.040	−1.714 ± 0.009	0.612 ± 0.0026	0.596 ± 0.0026	0.2436 ± 0.0027	4.5 ± 0.50	36
1.050	−1.669 ± 0.011	0.597 ± 0.0033	0.580 ± 0.0038	0.2299 ± 0.0031	4.5 ± 0.50	54
1.055	−1.650 ± 0.012	0.594 ± 0.0038	0.578 ± 0.0041	0.2271 ± 0.0035	3.5 ± 0.60	29
1.060	−1.636 ± 0.012	0.590 ± 0.0036	0.574 ± 0.0039	0.2243 ± 0.0032	4.3 ± 0.30	44
1.065	−1.606 ± 0.024	0.582 ± 0.0070	0.564 ± 0.0080	0.219 ± 0.0061	5.4 ± 0.40	19
1.070	−1.580 ± 0.017	0.573 ± 0.0055	0.556 ± 0.0058	0.2093 ± 0.0041	4.2 ± 0.30	35
1.080	−1.550 ± 0.018	0.563 ± 0.0057	0.546 ± 0.0062	0.2033 ± 0.0048	4.0 ± 0.40	36
1.090	−1.482 ± 0.013	0.541 ± 0.0047	0.523 ± 0.0048	0.1868 ± 0.0033	4.5 ± 0.50	38
1.100	−1.440 ± 0.013	0.527 ± 0.0045	0.508 ± 0.0046	0.176 ± 0.0033	6.8 ± 1.00	29
1.110	−1.391 ± 0.009	0.510 ± 0.0034	0.488 ± 0.0039	0.1642 ± 0.0023	7.2 ± 1.50	35
1.115	−1.331 ± 0.020	0.482 ± 0.0087	0.460 ± 0.0093	0.1472 ± 0.0045	3.2 ± 1.40	34
1.120	−1.321 ± 0.013	0.481 ± 0.0054	0.459 ± 0.0062	0.1461 ± 0.0032	2.9 ± 1.00	39
1.125	−1.306 ± 0.009	0.477 ± 0.0038	0.456 ± 0.0042	0.1438 ± 0.0026	3.0 ± 1.50	42
1.130	−1.246 ± 0.013	0.452 ± 0.0054	0.425 ± 0.0062	0.1297 ± 0.0031	18.3 ± 2.00	60
1.135	−0.996 ± 0.031	0.308 ± 0.0189	0.224 ± 0.0275	0.0734 ± 0.0070	18.1 ± 2.00	84
1.140	−1.048 ± 0.011	0.358 ± 0.0060	0.325 ± 0.0068	0.0843 ± 0.0025	15.4 ± 1.50	82
1.145	−1.072 ± 0.008	0.375 ± 0.0043	0.346 ± 0.0045	0.0902 ± 0.0021	15.2 ± 1.50	50
1.150	−0.878 ± 0.024	0.244 ± 0.0154	0.132 ± 0.0238	0.0488 ± 0.0054	15.2 ± 1.50	80
1.155	−0.838 ± 0.018	0.227 ± 0.0120	0.129 ± 0.0199	0.0406 ± 0.0036	10.8 ± 0.80	59
1.160	−0.761 ± 0.003	0.168 ± 0.0017	0.011 ± 0.0041	0.0228 ± 0.0005	5.4 ± 0.50	51
1.170	−0.747 ± 0.003	0.166 ± 0.0014	0.009 ± 0.0038	0.0221 ± 0.0005	1.9 ± 0.30	39
1.180	−0.744 ± 0.003	0.165 ± 0.0018	0.009 ± 0.0042	0.0215 ± 0.0008	0.9 ± 0.20	24
1.200	−0.727 ± 0.804	0.160 ± 0.0020	0.024 ± 0.0033	0.0208 ± 0.0004	1.0 ± 0.20	30
1.220	−0.707 ± 0.004	0.156 ± 0.0018	0.006 ± 0.0038	0.0201 ± 0.0005	0.9 ± 0.10	22
1.250	−0.681 ± 0.004	0.147 ± 0.0017	.000 ± 0.0035	0.0181 ± 0.004	0.9 ± 0.10	18
1.270	−0.661 ± 0.007	0.145 ± 0.0026	0.011 ± 0.0047	0.0168 ± 0.0011	0.9 ± 0.10	10
1.300	−0.655 ± 0.006	0.141 ± 0.0021	0.013 ± 0.0029	0.0159 ± 0.0008	.0 ± 0.10	13

TABLE A2. A summary of the results obtained with the CMC method on a $10\times10\times10$ Lebwohl–Lasher model for energy U^*, heat capacity C_V^*, and order parameters $\langle P_2\rangle$, $\langle P_2\rangle_\lambda$, and $\langle P_4\rangle$. Here N_c is the number of production cycles.

T^*	U^*	$\langle P_2\rangle_\lambda$	$\langle P_2\rangle$	$\langle P_4\rangle$	C_V^*	$N_c/10^3$
0.900	-2.005 ± 0.001	0.710 ± 0.001	0.706 ± 0.001	0.3353 ± 0.0014	2.5 ± 0.1	27
0.950	-1.879 ± 0.002	0.677 ± 0.001	0.673 ± 0.001	0.2945 ± 0.0010	2.6 ± 0.3	32
0.970	-1.826 ± 0.002	0.662 ± 0.001	0.658 ± 0.001	0.2793 ± 0.0011	2.7 ± 0.2	24
0.990	-1.768 ± 0.004	0.645 ± 0.001	0.639 ± 0.002	0.2577 ± 0.0019	3.4 ± 0.2	12
1.000	-1.733 ± 0.002	0.635 ± 0.000	0.630 ± 0.001	0.2490 ± 0.0007	3.5 ± 0.1	27
1.020	-1.662 ± 0.003	0.614 ± 0.002	0.609 ± 0.002	0.2293 ± 0.0019	3.5 ± 0.2	25
1.030	-1.627 ± 0.002	0.602 ± 0.001	0.597 ± 0.001	0.2185 ± 0.0012	3.4 ± 0.2	22
1.040	-1.596 ± 0.003	0.592 ± 0.001	0.587 ± 0.001	0.2100 ± 0.0009	3.4 ± 0.2	12
1.050	-1.556 ± 0.004	0.579 ± 0.002	0.574 ± 0.002	0.1999 ± 0.0016	4.1 ± 0.2	19
1.060	-1.512 ± 0.004	0.564 ± 0.002	0.558 ± 0.002	0.1864 ± 0.0018	4.9 ± 0.8	14
1.070	-1.461 ± 0.004	0.545 ± 0.002	0.538 ± 0.002	0.1719 ± 0.0020	6.8 ± 0.8	12
1.080	-1.363 ± 0.019	0.529 ± 0.004	0.523 ± 0.004	0.1620 ± 0.0025	6.9 ± 0.9	26
1.090	-1.315 ± 0.020	0.504 ± 0.004	0.498 ± 0.004	0.1456 ± 0.0025	6.9 ± 0.9	22
1.100	-1.256 ± 0.021	0.477 ± 0.005	0.469 ± 0.005	0.1298 ± 0.0027	5.5 ± 1.0	28
1.110	-1.220 ± 0.010	0.447 ± 0.005	0.439 ± 0.005	0.1109 ± 0.0026	5.2 ± 1.5	33
1.120	-1.154 ± 0.007	0.418 ± 0.003	0.410 ± 0.003	0.0959 ± 0.0014	7.6 ± 1.0	78
1.121	-1.136 ± 0.006	0.403 ± 0.003	0.395 ± 0.003	0.0890 ± 0.0016	9.9 ± 1.0	35
1.123	-1.133 ± 0.006	0.401 ± 0.004	0.393 ± 0.004	0.0877 ± 0.0021	13.7 ± 1.4	32
1.125	-1.086 ± 0.012	0.384 ± 0.007	0.375 ± 0.007	0.0813 ± 0.0028	21.8 ± 1.7	52
1.130	-0.862 ± 0.016	0.170 ± 0.016	0.116 ± 0.021	0.0169 ± 0.0042	21.9 ± 1.8	70
1.135	-0.900 ± 0.016	0.225 ± 0.016	0.194 ± 0.020	0.0299 ± 0.0040	21.3 ± 1.7	62
1.140	-0.779 ± 0.002	0.094 ± 0.002	0.026 ± 0.006	0.0007 ± 0.0004	5.1 ± 1.0	47
1.145	-0.776 ± 0.003	0.097 ± 0.002	0.030 ± 0.006	0.0009 ± 0.0004	1.9 ± 0.5	48
1.150	-0.767 ± 0.002	0.090 ± 0.002	0.020 ± 0.005	0.0004 ± 0.0004	1.2 ± 0.2	55
1.160	-0.757 ± 0.002	0.085 ± 0.003	0.019 ± 0.005	0.0006 ± 0.0004	1.3 ± 0.2	36
1.200	-0.694 ± 0.007	0.073 ± 0.001	0.010 ± 0.003	0.0001 ± 0.0003	1.3 ± 0.2	31
1.300	-0.625 ± 0.002	0.060 ± 0.001	0.000 ± 0.001	-0.0002 ± 0.0002	0.2 ± 0.2	25

system used in this work. I am grateful to Professor G. R. Luckhurst for the interest shown in this work and to NATO for a travel grant.

APPENDIX

Here we give a detailed tabulation of the simulation results for the small $5\times5\times5$ system (see Table A1) and for the $10\times10\times10$ lattice (see Table A2). The average values and the errors quoted have been obtained as follows. Every observable of interest A is calculated with the appropriate algorithm as discussed in Secs. III and IV and is sampled at every cycle. After a certain number of cycles m_J (typically 1000 to 2000) an average A^J is calculated, thus coarse graining the trajectory. A further grand average over M such segments are then calculated as the weighted average

$$\langle A\rangle = (1/N_C)\sum_J^M m_J A^J, \tag{A1}$$

where $N_C = \Sigma_{J=1}^M m_J$ is the total number of production cycles. These averages are reported in Tables A1 and A2. The attendant standard deviation σ_A,

$$\sigma_A = \left\{\sum_{J=1}^M m_J[A^J - \langle A\rangle]^2/[(M-1)N_C]\right\}^{1/2}, \tag{A2}$$

gives the error estimates reported for order parameters and energy in Tables A1 and A2. The heat capacity is obtained as described in Sec. III by smoothing spline fitting the energy, followed by numerical differentiation, so that standard error estimates are more difficult to obtain. The errors quoted here are representative of the spread in the C_V^* values obtained when changing the interpolation and smoothing parameters.

[1]P. A. Lebwohl, and G. Lasher, Phys. Rev. A **6**, 426 (1972).
[2]J. Viellard-Baron, Mol. Phys. **28**, 809 (1974).
[3]H. Meirovitch, Chem. Phys. **21**, 251 (1976).
[4]J. Kushick and B. J. Berne, J. Chem. Phys. **64**, 1362 (1976).
[5]H. J. F. Jansen, G. Vertogen, and J. G. J. Ypma, Mol. Cryst. Liq. Cryst. **38**, 87 (1977).
[6]R. Mountain and Th. W. Ruijgrok, Physica A **89**, 522 (1977).
[7]A. L. Tsykalo and A. D. Bagmet, Mol. Cryst. Liq. Cryst. **46**, 111 (1978).
[8]C. Zannoni, in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, New York, 1979), p. 191.
[9](a) G. R. Luckhurst and S. Romano, Mol. Phys. **40**, 129 (1980); (b) Proc. R. Soc. London Ser. A **373**, 111 (1980).
[10]G. R. Luckhurst, P. Simpson, and C. Zannoni, Chem. Phys. Lett. **78**, 429 (1981).
[11]C. Zannoni and M. Guerra, Mol. Phys. **44**, 849 (1981).
[12]R. L. Humphries and G. R. Luckhurst, Proc. R. Soc. London Ser. A **382**, 307 (1982).
[13]G. R. Luckhurst and P. Simpson, Mol. Phys. **47**, 251 (1982).
[14]G. R. Luckhurst, S. Romano, and P. Simpson, Chem. Phys. **73**, 337 (1982).
[15]H. J. Picken, W. F. van Gusteren, P. Th. van Duynen, and W. H. de Jeu, presented at the 10th Internation Liquid Crystal Conference, York (1984).
[16]R. Eppenga and D. Frenkel, Mol. Phys. **52**, 1303 (1984).
[17]G. R. Luckhurst, in *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic, New York, 1979) p. 85.
[18]P. Sheng and P. J. Wojtowicz, Phys. Rev. A **14**, 1883 (1976).
[19]J. G. Y. Ypma and G. Vertogen, J. Phys. Paris **37**, 557 (1976).
[20]R. Van der Haegen, J. Debruyne, R. Luyckx, and H. N. W. Lekkerkerker, J. Chem. Phys. **73**, 2469 (1980).
[21]T. E. Faber, Proc. R. Soc. London Ser. A **370**, 509 (1980); **396**, 357 (1984).
[22]K. Binder, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, Berlin, 1979), p. 1 and references therein.

[23]O. G. Mouritsen, *Computer Studies of Phase Transitions and Critical Phenomena* (Springer, Berlin, 1984).
[24]*The Maximum Entropy Formalism*, edited by R. D. Levine and M. Tribus (MIT, Cambridge, 1978).
[25]Y. Tikochinsky, N. Z. Tishby, and R. D. Levine, Phys. Rev. Lett. **52**, 1357 (1984).
[26]C. Zannoni, in *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J. W. Emsley (Reidel, Dordrecht, 1985), and Ref. 8, p. 51.
[27](a) *Creative Computing*, edited by D. H. Ahl and G. Burchenal (Creative Computing, Morristown, New Jersey, 1980), Vol. 3, pp. 200–202; (b) D. E. Knuth, *The Art of Computer Programming*, 2nd ed. (Addison–Wesley, Reading, Mass., 1981), Vol. 2.
[28]M. Mezei, J. Comput. Phys. **39**, 128 (1981).
[29]See, e.g., C. Chatfield, *Statistics for Technology*, 3rd ed. (Chapman and Hall, London, 1983).
[30]D. P. Landau, Phys. Rev. A **13**, 2997 (1976); **14**, 255 (1976).
[31]*IMSL Library Reference Manual*, 9th ed. (IMSL, Houston, 1982).
[32]M. Warner, Mol. Phys. **52**, 677 (1984).
[33]P. G. De Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974).
[34]C. Fan and M. J. Stephen, Phys. Rev. Lett. **25**, 500 (1970).
[35]T. E. Faber, Proc. R. Soc. London Ser. A **353**, 247 (1977).
[36]S. A. Brooks, G. R. Luckhurst, and G. F. Pedulli, Chem. Phys. Lett. **11**, 159 (1971).
[37]F. Leenhouts and A. J. Dekker, J. Chem. Phys. **74**, 1956 (1981).