LIQUID CRYSTALS, 1988, VOL. 3, NO. 3, 363–368

Can Monte Carlo detect the absence of ordering in a model liquid crystal?

by C. CHICCOLI and P. PASINI
INFN Sez. di Bologna and CNAF, Via Mazzini 2, 40138 Bologna, Italy
and C. ZANNONI
Dipartimento di Chimica Fisica ed Inorganica, Universita', Viale Risorgimento 4, 40136 Bologna, Italy

(*Received 8 September 1987; accepted 9 November 1987*)

We investigate the possibility of inferring the absence of an ordered phase using Monte Carlo simulations. The example we have chosen is that of a one dimensional Lebwohl–Lasher model, where an analytic solution is available. We argue that Monte Carlo can be of help even in this delicate sector notwithstanding the complications created by periodic boundary conditions.

1. Introduction

The Monte Carlo technique is often used to study phase transitions [1, 2]. In particular it has been applied to the investigation of orientational phase transitions in liquid crystal models [3–10]. Here the system goes from a low temperature phase with some sort of orientational order to a high temperature isotropic phase. The analysis has essentially a quantitative character when we already have strong indications that such an order–disorder transformation can take place. Thus, for example, in the three-dimensional Lebwohl–Lasher model [3–8] we expect a low temperature ordered phase. The Monte Carlo simulations aim to locate the transition and to determine the relevant observables together with their temperature variation. The situation is much more delicate for low dimensional systems [9, 10] or in general every time we try to use Monte Carlo computer simulations to infer the existence of an ordered phase. One problem, for example, is linked to the use of periodic boundary conditions and to the ordering that they induce [1, 4, 7]. Another is more intimately connected to the definition of the orientational order parameter as an invariant [4, 11] and to its intrinsically non-negative nature [8, 12]. Thus we may ask first of all if Monte Carlo results are sufficiently accurate to pinpoint the absence of ordering. A somewhat similar kind of check was performed some years ago by Luckhurst and co-workers [13]. They examined a one-dimensional system of particles rotating in a plane (thus a $d = 1, n = 2$ system) and found a small heat capacity anomaly in good agreement with the analytical results of Freasier and Runnels [14]. This was then an important result, bringing confidence into the reliability of the Monte Carlo technique. However, we now face situations where we should decide, based on Monte Carlo evidence, if an ordered system exists or if a phase transition takes place. The observation of a small peak in the heat capacity of a given finite size lattice is certainly not sufficient evidence in itself to prove or disprove the existence of a weak phase transition. One

useful approach, following the introduction of scaling ideas, is that of looking to the size dependence of various observables [1–2, 15–17]. Another fruitful method seems the examination of the pair spatial correlation functions and of their distance dependence. For example, a power law decay of correlation is expected for two-dimensional phases with certain topological order [18] while an exponential decay should occur when no true ordering is present. It seems important, in view of the development of models for the more complex liquid crystal phases, to examine this point in some detail. In this paper we wish to investigate the ability of Monte Carlo simulations to help with this problem. The natural approach will be to look at a simple system were analytical results exist. We shall treat the results as we would do for a simulation on an unknown system and see if the inductions we make are correct.

2. Simulations and results

The system we have chosen belong to the family of Lebwohl–Lasher models and is defined by the hamiltonian

$$U_N = -\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\varepsilon_{ij}P_2(\cos\beta_{ij}), \quad i \neq j. \tag{1}$$

where it is understood that the particles are on a regular one-dimensional lattice of length L with $N = L$ sites, β_{ij} measures the angle between the symmetry axes of the two molecules and ε_{ij} designates the strength of the nearest neighbours attractive interaction.

We have studied three systems of increasing size: $N = 10$, 40, 100 and a few temperatures of a $N = 1000$ particles system. A standard Monte Carlo Metropolis method with periodic, i.e. circular, boundary conditions has been employed to generate equilibrium configurations. The simulation at the lowest temperature studied for each size has been started from a completely aligned system. The simulations at the other temperatures have been run in cascade starting from an equilibrium configuration at the nearest lower temperature. The configuration of the system is given by the set of N orientations $\{\alpha_i, \beta_i\}$ so each particle has two orientational degrees of freedom. A new configuration is generated by randomly choosing a particle amongst those that we have not yet attempted to move during the current lattice sweep with a shuffling algorithm [8]. A new trial orientation of the chosen particle is then generated at random or, in most simulations, using the controlled increment technique of Barker and Watts [19]. No significant difference between the two updating techniques has been found for this model. In any case we have checked that a rejection ratio not too far from 0·5 is achieved. In every simulation a minimum of 10 000 cycles (sets of N attempted moves) has been used for equilibration and thus rejected when calculating averages. Runs were typically between 16 000 and 22 000 production cycles. Any property of interest, A, is evaluated at every cycle. After a number of cycles m_J (typically between 1000 and 2000) an average A^J is calculated. A further grand average is then computed as the weighted average over M such supposedly uncorrelated segments. The attendant weighted standard deviation from the average, σ_A, is also calculated and gives the error estimates. We have calculated for each simulation the energy as well as the second and the fourth rank order parameters. Pair correlation coefficients again of second and fourth rank have been calculated at selected temperatures for the $L = 40$ lattice. The heat capacity of the system has been evaluated by numerical differentiation of the internal energy $\langle U_N \rangle$ resulting from the

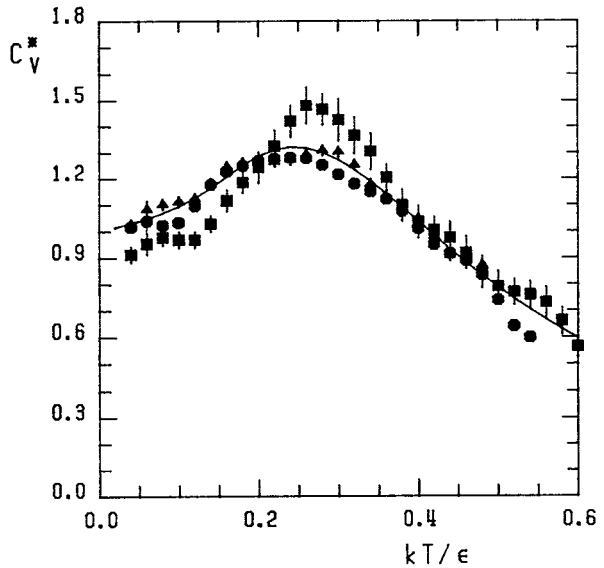

Figure 1. The heat capacity, C_V^*, obtained from differentiation of the energy plotted against the dimensionless temperature, kT/ε, for lattices of length $L = 10$ (squares), 40 (circles), 100 (triangles). The continuous line is the analytic result of Vuillermot and Romerio [20].

simulation. In figure 1 we report the heat capacity C_V^* calculated for the various size lattices as a function of the dimensionless temperature $T^* = kT/\varepsilon$. It is interesting to see that the Monte Carlo results for a linear dimension $L = 10$ differ from those of $L = 40$, but that these are in turn in good agreement with the $L = 100$ size. We have here a first important indication that further increases in size are not going to alter our conclusions. For the linear lattice we know the analytic results of Vuillermot and Romerio [20, 21], i.e.

$$\frac{C_V}{Nk} = \frac{1}{2} - \frac{3}{4T^*}\sqrt{\frac{3}{2T^*}}\left[\frac{T^*}{3} - 1\right] D^{-1}\left(\sqrt{\frac{3}{2T^*}}\right) - \frac{3}{8T^*} D^{-2}\left(\sqrt{\frac{3}{2T^*}}\right), \quad (2)$$

where $D(x)$ is the Dawson function [22] and we also report them here as the continuous line. It is comforting to notice the excellent agreement with the simulation results.

To examine the question of the existence or not of a true ordered phase, we have then computed order parameters. The method we have used is the now-traditional one for periodic boundary conditions simulations [11] based on diagonalization of a suitably defined ordering matrix. Fourth rank order parameters have been computed with the algorithm introduced in [8]. In figure 2 we show our results for this second rank parameter, $\langle P_2 \rangle_\lambda$, at various lattice sizes. $\langle P_4 \rangle_\lambda$ is not given since it presents a qualitatively similar trend, but the results are available from the authors. The order parameter starts from one at $T^* = 0$ and tends to a value $O(L^{-1})$ at high temperatures. The size dependence in the intermediate temperature region is more interesting. We see that the ordering is still significant even in the largest lattice but that it is always smaller than that of its analogues with a smaller number of particles. The decrease with size affects not only the points on the high temperature side of the heat capacity anomaly, but those on the low temperature side as well. This is different from

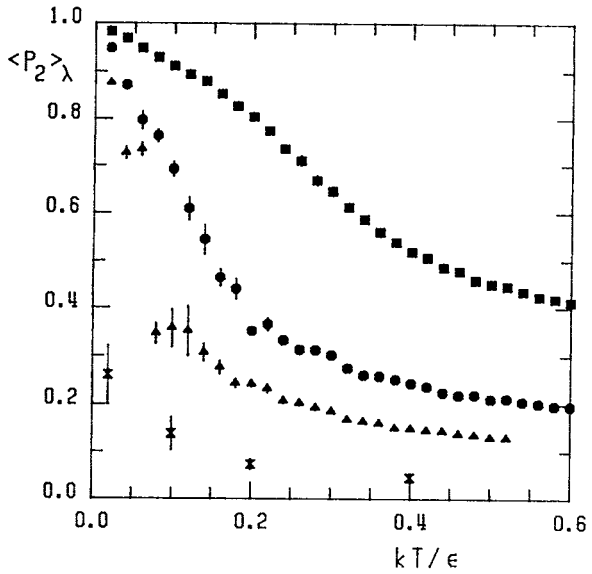

Figure 2. The second rank order parameter $\langle P_2 \rangle_\lambda$ obtained from the largest eigenvalue of the ordering matrix as recalled in the text plotted against the dimensionless temperature, kT/ε. Simulations for systems with $L = 10$ (squares), 40 (circles), 100 (triangles), 1000 (hour glass), are shown with their estimated errors.

the behaviour of three-dimensional and to some extent from that of two-dimensional [10] lattices with the same potential (cf. equation (1)). Thus these observables are not stable against an increase in size, in contrast to what we have seen in the heat capacity. We may have here an indication from our raw experimental observations that there would be no ordering of this kind in an infinite lattice. Interesting indications are offered from the two particle correlation coefficients $G_L(r)$.

The two particle angular correlations coefficients $G_L(r)$ describe a set of expansion coefficients of the rotationally invariant pair correlation function [4, 8, 9]. The calculation is in general time consuming (although not so much in this case) and we have chosen to calculate the first two angular pair correlation coefficients $G_2(r)$ and $G_4(r)$ for about ten temperatures for the $N = 40$ and for a few temperatures for the $N = 1000$ system. We observe a very fast decay above the heat capacity anomaly which becomes somewhat slower as the temperature decreases. In figure 3 we show as an example $G_2(r)$ for two temperatures well below the heat capacity anomaly. We also show the analytic results according to Vuillermot and Romerio [20],

$$G_2(r) = \left[\frac{1}{2}\sqrt{\frac{3T^*}{2}}\, D^{-1}\left(\sqrt{\frac{3}{2T^*}}\right) - \frac{T^*}{2} - \frac{1}{2}\right]^r, \tag{3}$$

as the continuous lines. The agreement between theory and experiment is good for short distances and becomes progressively worse with increasing separations. At low temperatures this may be due to periodic boundary conditions effects leading to spurious increased correlations. However, at high temperatures the simulation data fall below the analytical result, which is harder to explain. We notice that the calculation of the correlation functions is particularly error prone in a one-dimensional lattice. In fact $G_L(r)$ is calculated as a histogram and in a one-dimensional lattice only

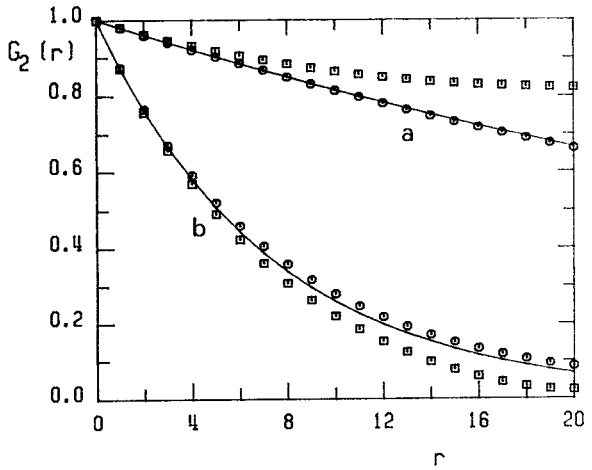

Figure 3. The second rank pair correlation coefficient $G_2(r)$ plotted against the distance r, in lattice units. The results are for the $L = 40$ (squares) and $L = 1000$ (circles) lattices at temperatures (*a*) $T^* = 0{\cdot}02$ and (*b*) $T^* = 0{\cdot}12$. The continuous curves are from Vuillermot and Romerio [20].

buckets at integer distances will be populated. This means that $G_L(r)$ is defined on a smaller number of points than for higher-dimensional lattices. Moreover the statistics on these points will be relatively poor since the coordination number will be just two, independent of the separation. We see, however, that for $N = 1000$ the calculation has improved enough to agree well with the analytic one for this separation range. In any case we shall ignore the analytic results for now, since they would not be available under normal circumstances. We shall then try to obtain some indications by fitting a certain decay law to $G_2(r)$. In practice we perform a non-linear least square fitting of all the second rank correlation coefficients available to either an exponential decay to a plateau

$$G_2(r) = (1 - A_e)\exp(-k_e r) + A_e, \tag{4}$$

or to a power law decay to zero

$$G_2(r) = A_p/r^{k_p}. \tag{5}$$

The non-linear least square fit is performed on raw data up to a certain cut-off length L_f. We have found that the exponential law gives a sensibly better fit at the higher temperatures, but more importantly that the exponential fit is always better even below T_C, so that we have no indication of long short-range order.

3. Discussion and conclusions

For this one-dimensional lattice molecular field theory is completely wrong, since it predicts a first order phase transition at a temperature $T^*_{NI} \approx 0{\cdot}22$ (cf. discussion in [9]). This temperature, which is just the well-known value for the cubic lattice scaled by the reduced number of nearest neighbours is by coincidence similar to the temperature corresponding to the heat capacity anomaly. We have found that studying the size dependence of the results and especially of the order parameters is essential in correctly assessing the lack of existence of a true transition. In this respect we also

find that analysing the pair correlation function decay is particularly helpful in indicating the absence of true ordered phase. We conclude that Monte Carlo simulations indicate correctly the absence of a transition as expected from the analytic results [20, 21].

The simulations were run on a cluster of two DEC VAX 11-780 minicomputers at Dipartimento Fisica—INFN, Bologna, and on a VAX 11-780 at Dipartimento Chimica Fisica. C.Z. thanks C.N.R. and Min. P.I. for grants towards the cost and maintenance of the latter system.

References

[1] BINDER, K., 1979, *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer-Verlag), Chap. 1 and references therein.
[2] MOURITSEN, O. G., 1984, *Computer Studies of Phase Transitions and Critical Phenomena* (Springer-Verlag).
[3] LEBWOHL, P. A., and LASHER, G., 1972, *Phys. Rev.* A, **6**, 426.
[4] ZANNONI, C., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), Chap. 9.
[5] LUCKHURST, G. R., and SIMPSON, P., 1982, *Molec. Phys.*, **47**, 251.
[6] LUCKHURST, G. R., ROMANO, S., and SIMPSON, P., 1982, *Chem. Phys.*, **73**, 337.
[7] ZANNONI, C., 1985, *J. chem. Phys.*, **84**, 424.
[8] FABBRI, U., and ZANNONI, C., 1986, *Molec. Phys.*, **58**, 763.
[9] CHICCOLI, C., PASINI, P., and ZANNONI, C., 1987, *Liq. Crystals*, **2**, 39.
[10] CHICCOLI, C., PASINI, P., and ZANNONI, C., 1987, *Physica* A (in the press).
[11] VIELLARD-BARRON, J., 1974, *Molec. Phys.*, **28**, 809.
[12] EPPENGA, R., and FRENKEL, D., 1984, *Molec. Phys.*, **52**, 1303.
[13] DENHAM, J. Y., HUMPHRIES, R. L., and LUCKHURST, G. R., 1977, *Molec. Crystals liq. Crystals Lett.*, **41**, 67.
[14] FREASIER, B. C., and RUNNELS, L. K., 1973, *J. chem. Phys.*, **58**, 2963.
[15] BINDER, K., 1985, *J. comput. Phys.*, **59**, 1.
[16] TOBOCHNIK, J., and CHESTER, G. V., 1983, *Phys. Rev.* A **27**, 1221.
[17] FRENKEL, D., and EPPENGA, R., 1985, *Phys. Rev.* A, **31**, 1776.
[18] KOSTERLITZ, J. M., and THOULESS, D. J., 1973, *J. Phys.* C, **6**, 1181.
[19] BARKER, J. A., and WATTS, R. O., 1969, *Chem. Phys. Lett.*, **3**, 144.
[20] VUILLERMOT, P. A., and ROMERIO, M. V., 1973, *J. Phys.* C, **6**, 2922.
[21] VUILLERMOT, P. A., and ROMERIO, M. V., 1975, *Commun. math. Phys.*, **41**, 281.
[22] ABRAMOWITZ, M., and SEGUN, I. A., (editors), 1964, *Handbook of Mathematical Functions* (Dover).