Physics Letters A 161 (1992) 369–372
North-Holland

PHYSICS LETTERS A

A Monte Carlo study of smectic–nematic–isotropic phase transitions

B. Nandi, A. Bandyopadhyay, T.R. Bose, J. Saha and M. Saha
Department of Physics, University of Calcutta, 92 A P.C Road, Calcutta 700009, India

Received 29 August 1991; revised manuscript received 16 October 1991; accepted for publication 8 November 1991
Communicated by J. Flouquet

A smectic–nematic–isotropic phase transition sequence is reproduced in a $10\times10\times10$ system. The pair interaction assumed is purely anisotropic and attractive Temperature variations of order parameters show qualitatively the same features as those in the McMillan model.

1. Introduction

There have been quite a few computer simulation studies on nematic–isotropic phase transitions of liquid crystalline systems. The pioneering works of Lasher [1] and Lebwohl and Lasher [2] employed for the first time a computer simulation method to reproduce a nematic to isotropic phase transition in a three-dimensional system. Based on a phenomenological attractive and anisotropic pair interaction, similar to that contained in Maier and Saupe's [3] work, they obtained a first order nematic to isotropic phase transition. Their results are qualitatively in good agreement with the mean field results obtained by Maier and Saupe [3]. Later works of Jansen and Vertogen [4] and Luckhurst et al. [5–7] brought out further facets of simulation studies of a nematic system. In contrast, an extension of the Lebwohl–Lasher method to the smectic ordering was not done for quite some time. The only study we know of is that of Reynolds et al. [8] which could successfully generate smectic ordering utilizing a McMillan [9] type pair interaction. Their results however show a few shortcomings. In their model the smectic ordering is temperature insensitive and is too low (0.03) when the excluded volume is taken as zero. The results improve considerably if one takes the excluded volume into consideration. Even then, the smectic ordering reaches a maximum value of 0.1 at a temperature low enough to generate a long range orientational order of the order of 1. In the present paper we report a study where these inadequacies are successfully removed and the results agree strikingly well with the results of the McMillan model [9].

2. The model

In a smectic-A phase, besides the orientational order, there is translational periodicity in only one direction (director of the orientation field) and the centres of mass of the molecules in the plane perpendicular to the director are randomly placed. We have therefore chosen a pair interaction with this asymmetry. Lee, Tan and Woo [10] proposed such a potential phenomenologically and reproduced excellent phase diagrams showing a crystal–smectic-A–nematic–isotropic phase sequence. Neglecting the purely translational part of their pair interaction, we have taken the interaction energy between two neighbouring molecules as

$$E_{ij} = -\epsilon \exp\{-[(x_j-x_i)^2/a]-[(y_j-y_i)^2/a] - [(z_j-z_i)^2/b]\}P_2(\cos\theta_{ij}) , \quad (1)$$

where θ_{ij} is the angle between the axes of the molecule i and molecule j, P_2 is the second Legendre polynomial and (x, y, z) indicate the position coor-

dinates of the centre of mass of a molecule. In the above expression the z direction has been singled out by introducing the parameter b different from a.

For obtaining the equilibrium angular and spatial distributions of the molecules at a given temperature, the following procedure based on the method of Metropolis et al. [11] is used in the following manner. Initially the molecules are placed in a $10\times10\times10$ cubic lattice with all the molecules pointing along the z axis and the centres of mass at the lattice points. The usual periodic boundary condition is employed by extending the lattice, i.e. by introducing two buffer layers [12]. Starting from a particular spin in the lattice we assign (θ, ϕ) and $(\Delta x, \Delta y, \Delta z)$ from the lattice points by generating five random numbers with appropriate densities. In order to have all directions equally probable, ϕ was uniformly distributed from 0 to 2π and the θ distribution (from 0 to π) had a density $\frac{1}{2}\sin\theta$. The latter distribution corresponds to θ values given by $\cos\theta = 1-2\gamma$, where γ is a random variable distributed uniformly from 0 to 1. Further, the spatial variables were all distributed uniformly from -1 to 1. The total interaction energy of the molecule with the six nearest neighbours is evaluated twice, once with the existing coordinates (E_o) and then with the newly assigned coordinates (E_n). Depending on the values of E_o and E_n, the coordinates of the molecule are kept at the old values or changed to the new values, i.e. a move is accepted. If $E_n < E_o$ the move is accepted and if $E_n > E_o$ the move is accepted with a probability $\exp[-(E_n-E_o)/T]$ by generating one further random number. T in the expression is in fact the parameter k_BT/ϵ, the reduced temperature. This procedure is followed sequentially for each molecule in the lattice. Going over the 10^3 molecules once constitutes a "pass". After each pass the orientational order parameter and the three translational order parameters are evaluated in accordance with the following expressions,

$$\eta = \langle P_2(\cos\theta)\rangle\,, \quad \tau_x = \langle\cos(2\pi x/d)\rangle\,,$$

$$\tau_y = \langle\cos(2\pi y/d)\rangle\,, \quad \tau_z = \langle\cos(2\pi z/d)\rangle\,,$$

where $\langle\ \rangle$ indicates an average over all the 10^3 molecules. The τ_i, as in McMillan's study [9], are the translational order parameters in the three directions. d is the lattice spacing taken as the unit of length. Usually for the first 10^3 passes, the order parameters change and gradually the system equilibrates. To check the equilibrium condition, average order parameters over 10^2 passes were considered and the equilibrium was assumed to be achieved if the average order parameters did not vary by more than 0.001 in a successive hundred passes. For low temperatures, equilibrium could be achieved after usually 1.5×10^3 passes. However for temperatures close to the transition temperatures, 4×10^3 passes were required. For minimizing computation time the final configuration of a low temperature run was taken as an input for the next higher temperature run.

3. Results

The parameters b and a were chosen after some preliminary trial and error to be $b=1.0$ and $a=10.0$. The parameter b is understandably smaller than a as we would like to have a stronger layering interaction along the z direction than in the perpendicular directions. A smaller value of a parameter like a or b means a shorter range of interaction, i.e. neighbouring molecules tend to form layers leaving aside the farther ones which in their turn would form other layers with their respective neighbouring molecules. Fig. 1 shows the variation of order parameters with

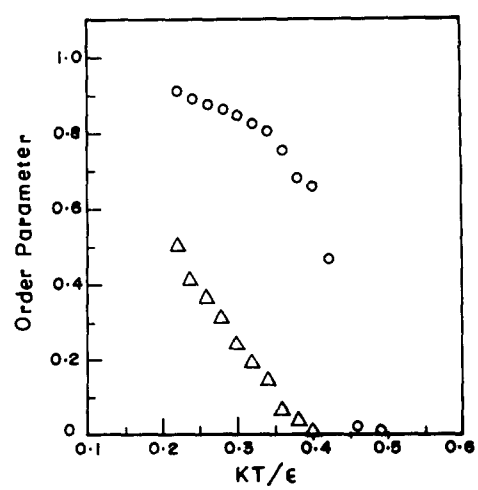

Fig. 1. Order parameters versus reduced temperature (k_BT/ϵ) curve. Circles indicate the orientational order parameter η Triangles indicate the translational order parameter τ_z.

reduced temperature. It is to be noted that in the temperature range plotted, the τ_x and τ_y are very close to zero and have not been shown. It is also interesting to note that τ_- continuously goes to zero near T_{AN}. The nematic order persists for a while and there is a sharp drop at T_{NI}. Because of large fluctuations in the result very near T_{NI}, we have not shown any point there. Figs. 2 and 3 show the distribution of the molecular centres of mass and orientation at a few chosen temperatures. The low temperature figures show clear layering in the X–Z plane and lack of any layering in the X–Y plane. As the temperature is gradually increased layering breaks down and a nematic phase exists. The figures also indicate a gradual low-

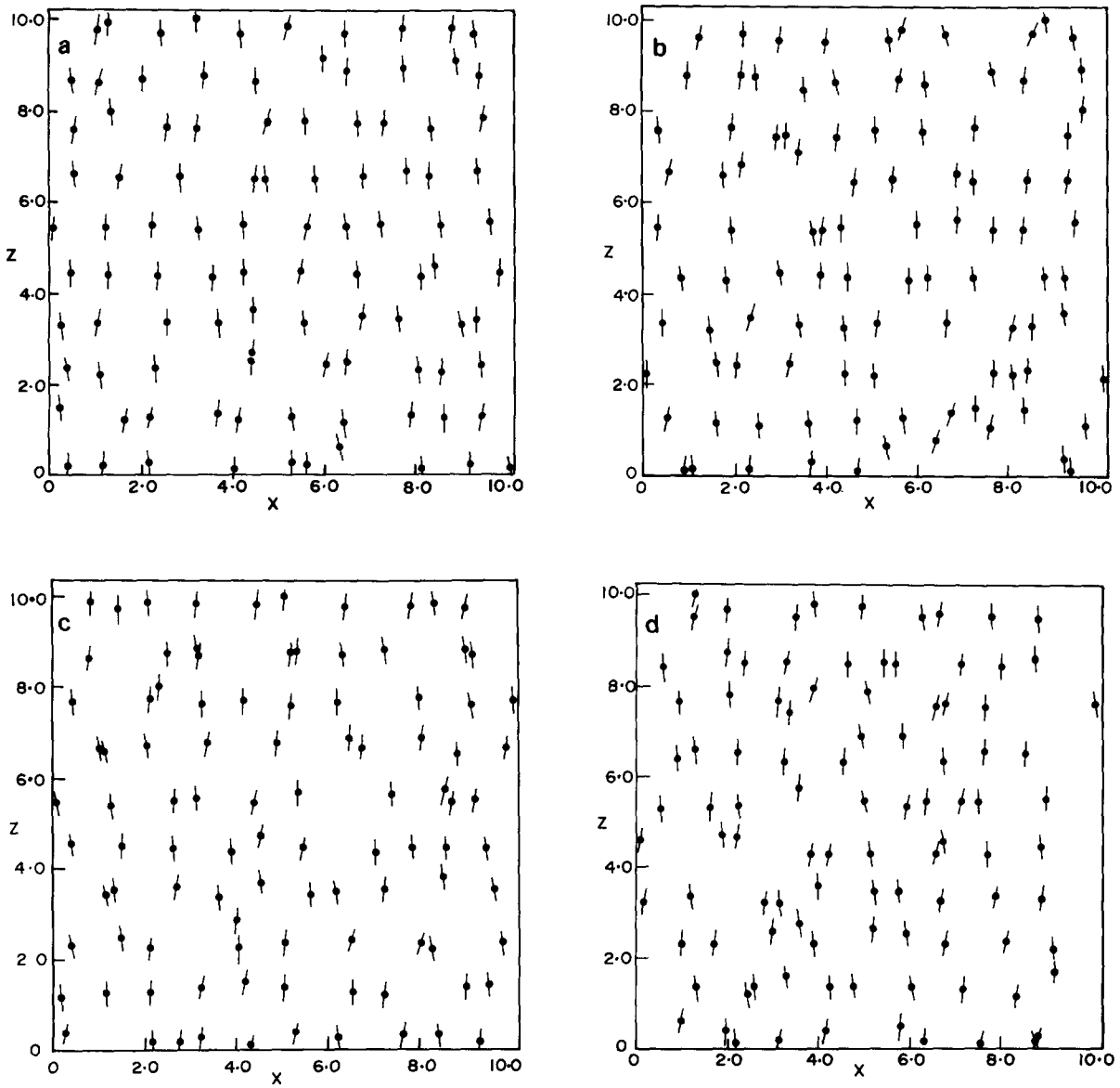

Fig. 2. Spatial and orientational distribution of molecules on the X–Z plane at the reduced temperatures $k_BT/\epsilon=0.22$ (a), 0.24 (b), 0.26 (c), 0.28 (d).

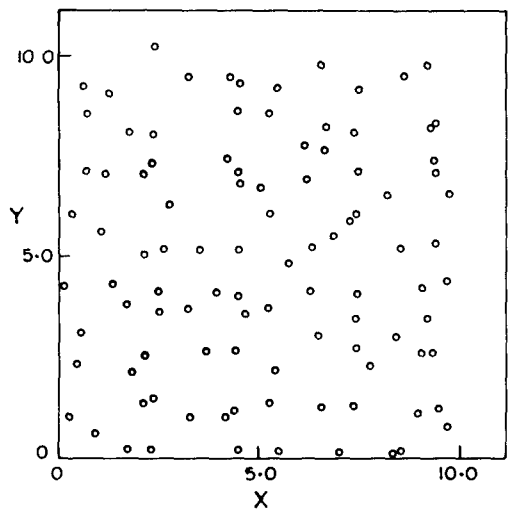

Fig. 3 Distribution of molecular centres of mass on the X–Y plane at the reduced temperature $k_B T/\epsilon = 0.22$

ering of nematic order with rising temperature.

4. Conclusion

The present study successfully reproduces a smectic–nematic–isotropic phase sequence utilizing a Monte Carlo method. The results are definitely superior to those of the earlier study by Reynolds et al. [8]. It is interesting to note that a proper choice of the pair interaction can be fruitful in reproducing phase diagrams of a liquid crystalline system without introducing an excluded volume. Moreover, the values of the order parameters and their temperature variations are in good qualitative agreement with experimental results and also the results obtained in mean field models.

References

[1] G. Lasher, Phys. Rev A 5 (1972) 1350
[2] P A Lebwohl and G Lasher, Phys. Rev A 6 (1972) 429.
[3] W. Maier and A. Saupe, Z. Naturforsch. 14a (1959) 882; 15a (1960) 287
[4] H J F. Jansen and G Vertogen, Mol. Cryst. Liq Cryst 38 (1977) 87.
[5] G R. Luckhurst and S. Romano, Mol. Phys 40 (1980) 129.
[6] G R. Luckhurst, S Romano and P Simpson, Chem. Phys 73 (1982) 337
[7] R. Hashim, G.R Luckhurst and S. Romano, Liq Cryst 1 (1986) 133
[8] D.J Reynolds, A. Hoare and M.C. Holmes, Mol. Cryst Liq Cryst. 152 (1987) 113
[9] W.L. McMillan, Phys Rev A 4 (1971) 1238, 6 (1972) 936
[10] F T Lee, H T Tan and C W. Woo, Phys Lett A 48 (1974) 68
[11] N Metropolis, A W Rosenbluth, M N. Rosenbluth, A.H Teller and E. Teller, J. Chem. Phys 21 (1953) 1087
[12] D Stauffer, F.W Hehl, W. Winkelmann and J.G Zabolitzky, Computer simulation and computer algebra (Springer, Berlin, 1988)