SIMULACIO MONTE CARLO DE SISTEMES AMB ACOBLAMENT DE GRAUS DE LLIBERTAT.

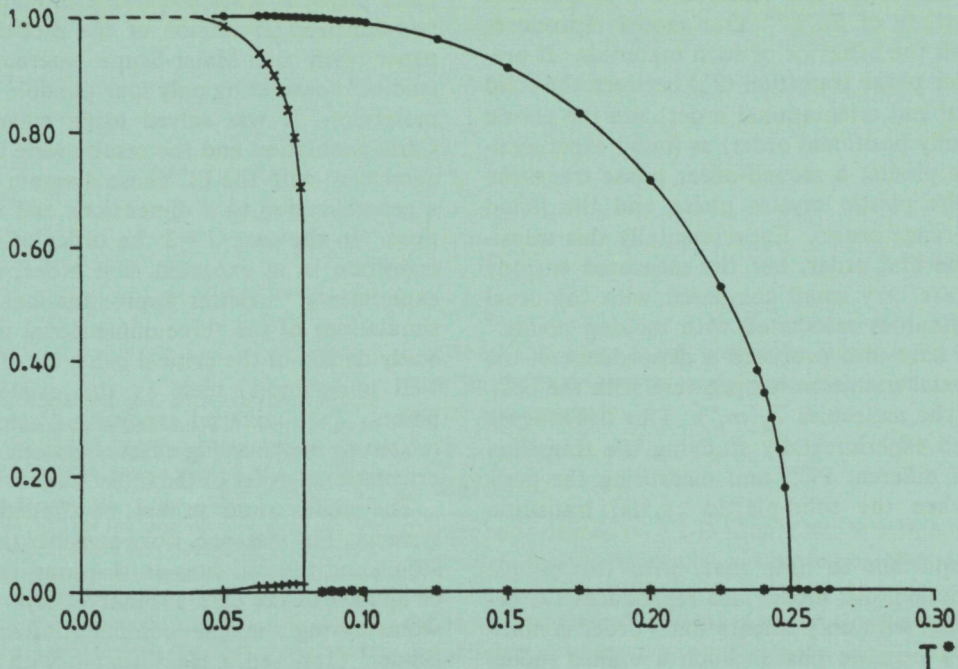UNIVERSITAT DE BARCELONA
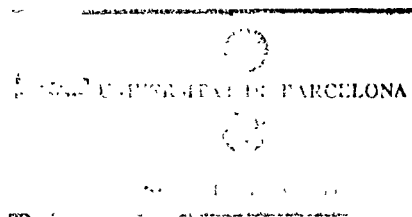
FIG. 4. Order parameters $m_o^+(\times)$, $m_o^-(+)$, and $m_p(\bullet)$ as a function of reduced temperature $T^* = k_B T/(J_o - J_q)$, with $J_q = 4$, $J_o = 0$, $K_o = K_q = -1$, and $n = 6$. The positional transition ($\bullet$) is second order, while the orientational transition is first order.

B. Maier-Saupe interaction

In order to apply our results to the study of the behavior of liquid crystals and plastic crystals, a more realistic interaction should be chosen. The Maier-Saupe interaction was used extensively[14] for this purpose. Originally[15] it was defined as a function of the angle θ_{IJ} between two rodlike molecules of a liquid crystal as follows:

$$P(\theta_{IJ}) = [3\cos^2(\theta_{IJ}) - 1]/2 .$$

In our case we shall define $\{t_I\}$ as a set of unitary vectors giving the discrete orientations that the molecules can have in the space. The Maier-Saupe interaction can then be written in a generalized way as

$$P(t_I, t_J) = a(t_I \cdot t_J)^2 + b , \tag{31}$$

where a and b are constants that can be determined from the normalization conditions (4) and will depend on n and on how the set of directions have been chosen in the space. Note that this interaction is nonpolar so that t_I and $-t_I$ represent the same orientational state.

This interaction has been studied in a previous paper[6] in the particular case of having $n = 4$ in a two-dimensional square lattice. Moreover, these results were compared with a Monte Carlo simulation and it was seen that the liquid-crystal phase diagram was reproduced qualitatively well. With our formalism we can now generalize to a d-dimensional lattice with n discrete orientations. We have studied two cases: (i) $n = d$ orientations along the perpendicular axis (this case includes $d = 2$, $n = 2$ and $d = 3$, $n = 3$); and (ii) $n = d + 2^{d-1}$ orientations along the perpendicular axis and the bisectrices of the quadrants. In both cases, when normalizing P, one finds

$a = d/(d-1)$ and $b = 1/(1-d)$ and $\sum_{k=1}^n P(n, k) = d/(d-1)$. From these results one can study the nematic-isotropic transition T_{N-I} corresponding to $T_o(m_p = 0)$,

$$T_{N-I} = -\tfrac{1}{2}(K_o + K_q)n^{-1}d/(d-1) . \tag{32}$$

Also, in both cases the order of the transition changes from continuous to first order between $d = 2$ and 3. Of course (32) cannot be extrapolated to the case $d = 3$, $n \to \infty$, because that formula has been obtained with constraints between n and d as specified in cases (i) and (ii).

VI. CONCLUSIONS

In this work we have studied the thermodynamics of an antiferromagnetic lattice-gas model of particles with orientational degrees of freedom with density $c = 0.5$. At low temperatures, positional interaction favors an ordered structure of alternating particles an vacancies. The orientational interaction between particles has been introduced as the slave of the positional one, in the sense that the particles only interact orientationally when they are interacting positionally. Physically, this means that the orientational interaction is a perturbation, not necessarily small, of the positional interaction.

The relative simplicity of the model allows the possibility of analyzing the interdependence of the orientational and positional degrees of freedom and its influence on phase diagrams for systems like liquid crystals, plastic crystals, and magnetic binary alloys. The model has been solved using a mean-field treatment for an arbitrary orientational interaction, but we have focused our calculations (analytical and numerical) on two cases of interest for PC and LC.

A Potts-like interaction has been recently proposed as useful for the study of PC's.[16] Our model reproduces qualitatively well the behavior of such materials. It predicts a first-order phase transition (T_o) between the solid phase (positional and orientational order) and the plastic crystal phase (only positional order) as found experimentally.[9] Also we predict a second-order phase transition (T_p) between the plastic crystal phase and the liquid phase (no long-range order). Experimentally this transition seems to be first order, but the measured entropy discontinuities are very small compared with the usual entropy discontinuities associated with melting points.[9] In Eq (30a) we have also proposed a dependence of the solid-plastic crystal transition temperature with the positional order of the molecules $T_o(m_p^*)$. This dependence could be verified experimentally studying the transition temperatures of different PC's and measuring the positional order when the solid-plastic crystal transition occurs.

It is also important to note that, with this simple Potts-like interaction, our model also reproduces LC behavior. The phase with only orientational order is nothing more than a nematic phase. Such a unified model suggests that the differences between PC's and LC's are only due to the different values of the Hamiltonian parameters associated with orientational and positional interaction. In mean-field approximation coupling effects manifest only for the lowest of both T_o and T_p temperatures. The coupling strength depends mainly on the value of the long-range order parameter, which remains finite at the temperature.

Nevertheless, if one wants to study LC's more realistically, it is better to use a Maier-Saupe[15] orientational interaction. This interaction is nearer to the real interaction between LC molecules than the Potts-like interaction considered above, and it is believed that it contains the main physical features of real interaction.[17] In fact, a two-dimensional version of the model proposed in this paper with the Maier-Saupe interaction was recently studied[6] considering only four possible orientations of the molecules. It was solved using mean-field and Monte Carlo simulation and the results were in good qualitative agreement with the LC phase diagram. We propose here a generalization to d dimensions and n possible orientations. In the case $d = 3$ the order of the nematic-liquid transition is, as expected, first order, in agreement with experiments.[18] Better approximations, or Monte Carlo simulations of the three-dimensional model, can help to study details of the critical behavior of LC's that are not well understood, such as the existence of tricritical points,[18] nonuniversal exponents,[19] etc., that are closely related to the coupling effects between the positional and orientational order of the molecules.

The model could, in fact, be applied to other kinds of systems. For instance, if we consider the empty sites as B atoms and the full sites as A atoms, our model can also be applied to the case of binary alloys AB (50%) with A atoms having a magnetic moment. Recently, Düweg and Binder[5] proposed a Hamiltonian with the same kind of slave coupling for the case of a binary alloy A_xB_{1-x} with A atoms having spins $\frac{1}{2}$, with NN magnetic interaction. The solution of our model with an appropriate orientational interaction reproducing the magnetic one, will be a first attempt to extend it to a general case with spin $n/2$ and also with a NNN magnetic interaction.

[1]M. C. Cadeville and J. L. Morán-López, Phys. Rep. 153, 331 (1987).

[2]Y. Imry, J. Phys. C 8, 567 (1975); S. Watanabe and T. Usui, Prog. Theor. Phys. 73, 1305 (1985).

[3]G. S. Grest and M. Widom, Phys. Rev. B 24, 6508 (1981).

[4]J. Chahine, J. R. Drugowich, and N. Caticha, J. Phys. A 22, 1639 (1989).

[5]B. Dünweg and K. Binder, Phys. Rev. B 36, 6935 (1987).

[6]E. Vives and A. Planes, Phys. Rev. A 38, 5391 (1988).

[7]D. B.Carpenter and J. T. Chalker, J. Phys.: Condens. Matter 1, 4907 (1989).

[8]S. Chandrasekhar, Liquid Crystals (Cambridge University Press, Cambridge, England, 1977).

[9]M. Yvinec, Ph.D. thesis, University of Paris, France, 1984; M. Yvinec and R. M. Pick, J. Phys. (Paris) 41, 1045 (1980); R. M. Pick and M. Yvinec, ibid. 41, 1053 (1980); M. Yvinec and R.

M. Pick, ibid. 44, 169 (1983).

[10]M. H. W. Chan, A. D. Migone, K. D. Miner, and Z. R. Li, Phys. Rev. B 30, 2681 (1984).

[11]H. N. V. Temperley, Proc. Phys. Soc. London 74, 183 (1959).

[12]O. G. Mouritsen and J. Berlinsky, Phys. Rev. Lett. 48, 181 (1982).

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

[14]P. A. Lebwohl and G. Lasher, Phys. Rev. A 6, 426 (1972).

[15]W. Maier and A. Saupe, Z. Naturforsch., Teil A 13, 564 (1958).

[16]S. Galam and M. Gabay, Europhys. Lett. 8, 167 (1989).

[17]U. Fabbri and C. Zannoni, Mol. Phys. 58, 763 (1986).

[18]J. Thoen, H. Marynissen, and W. Van Dael, Phys. Rev. Lett. 52, 204 (1984).

[19]K. J. Stine and C. W. Garland, Phys. Rev. A 39, 3148 (1989).

Monte Carlo Study of the Critical Behaviour of a System with Coupled Phase Transitions

Abstract

Using a 2-D lattice gas model of orientable molecules that exhibits two phase transitions, we have performed Monte Carlo simulations in order to study its critical behaviour. One of the phase transitions, associated with positional degrees of freedom, has been found to be second order, while the other, related to orientational degrees of freedom, is first order. Changing the parameters of the hamiltonian we can vary the separation between the two phase transition temperatures. When they are very close to each other the β critical exponent (or at least the effective β critical exponent) of the positional transition varies continuously from the 2-D Ising value to zero when the two transitions overlap. The model is also suitable for qualitatively explaining some experimental results found in Liquid Crystals and other systems showing coupling effects between orientational and positional degrees of freedom.

1. Introduction

Coupling between phase transitions has been widely studied in recent years, experimentally [1, 2], using computer simulation [3] and by means of theoretical approaches [1, 4–6]. The coupling between orientational and positional degrees of freedom is particularly very interesting because it is responsible for the unusual phase diagram features of a great variety of systems. For instance, these phenomena have been observed not only in 3-D systems like Liquid Crystals (L.C.) [7], Plastic Crystals (P.C.) [8], Micellar solutions [9] and microemulsions [10] but also in 2-D systems like adsorbed molecules on crystal surfaces [11]. These coupling effects appear when the system exhibits two phase transitions related to positional and orientational degrees of freedom.

In Liquid Crystals, the smectic-nematic transition is a positional transition that happens when some translational ordering mode of the molecules is lost, while the nematic-isotropic transition is an orientational transition related to the orientational order of the molecule symmetry axes. When these two transitions occur at very close temperatures unusual phenomena can appear. Some authors [2, 12] have reported changes in the critical exponents of the smectic-nematic transition when the nematic-isotropic transition is very close to it, or the existence of tricritical points. These phenomena have also been found in micellar solutions [9] and microemulsions [10].

In this paper we will analyze, using Monte Carlo simulations different coupling phenomena that appear in a 2-D lattice model exhibiting two phase transitions related to positional and orientational degrees of freedom, that can be related to a solid-nematic and a nematic-isotropic phase transition in a liquid crystal film, as shown in a recent paper [3].

The outline of the paper is as follows: in Section 2 we briefly introduce the model, in Section 3 we discuss details of

the Monte Carlo simulation technique, in Section 4 we comment on the main results, and finally in Section 5 we summarize and conclude.

2. Model

The model is defined on a 2-D square lattice with N_s sites per side, where rod-like molecules are placed parallel to the lattice. On each site "i" ($i = 1, \ldots, N$; $N = N_s \times N_s$) we define two variables: S_i that takes values 1 or 0 depending on the presence or absence of a molecule in site "i" and σ_i that represents the angular position of the symmetry axis of the molecule. We allow σ_i to take only 4 different values associated to the 4 directions schematized in Fig. 1.

The interaction energy is:

$$H = J \sum_{nn} S_i S_j + K_1 \sum_{nn} S_i S_j P(\sigma_i, \sigma_j) + K_2 \sum_{nnn} S_i S_j P(\sigma_i, \sigma_j) \tag{1}$$

where J, K_1 and K_2 are constants. Σ_{nn} and Σ_{nnn} are summations over nearest neighbor and next-nearest neighbor pairs and $P(\sigma_i, \sigma_j)$ is the function:

$$P(\sigma_i, \sigma_j) = 2 \cos^2 (\sigma_i - \sigma_j) - 1 \tag{2}$$

Note that with this definition the interaction is non-polar.

The total number of molecules in the system is kept constant:

$$N_p = N/2 \tag{3}$$

In order to reduce the number of parameters we define dimensionless quantities:

$$H^* = H/J, \quad K_1^* = K_1/J, \quad K_2^* = K_2/J, \quad T^* = k_B T/J \tag{4}$$

where k_B is the Boltzmann constant.

When $K_2^* < 0$ and $-1 < K_1^* < 0$ the ground state of the system exhibits long range positional and orientational order as shown in [3] (see. Fig. 2 (A)). When increasing the temperature two phase transitions can occur. A positional phase transition (T_p) when the long range positional order is lost and an orientational phase transition (T_o) when the long range orientational order disappears. In the case $T_o > T_p$ we have a L.C. behaviour (A → B2 → C) while in the case $T_p > T_o$ a P.C. behaviour (A → B1 → C) is obtained.

The ground state structure suggests that we can subdivide the lattice into two sublattices, (+) and (−). The (+) sublattice is the one that is full of particles at the ground state, while the (−) sublattice is the empty one. The structure of the
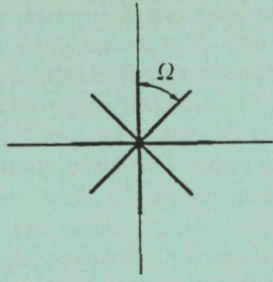
Fig. 1. Schema showing the 4 possible discrete orientations of the molecules with respect to the lattice axis.

system at higher temperatures can be studied by means of the following order parameters [3]:

$$m_p = \left(\sum_+ S_i - \sum_- S_i \right) / N_p \qquad (5)$$

$$m_o^{\pm} = \sum_{\pm} S_i P(\sigma_i, 0) / N_p \qquad (6)$$

where Σ_+ and Σ_- represent sums over all the $(+)$ and $(-)$ sublattice sites respectively.

3. Monte Carlo simulation

Monte Carlo simulations were performed on a 40×40 lattice with 800 particles using the standard Metropolis procedure. We used a Kawasaki dynamic for the interchange of n.n. particles and a Glauber dynamic changing the orientations. In this case, because we are combining two dynamics, the usual definition of the Monte Carlo step must be changed. A Monte Carlo step (MSC) is, in our case, N_p trials of changing orientations and N_p trials of exchanging two particles.

Simulations were carried out on a CRAY-1, an IBM3090 and an IBM9375.

The averages of the magnitudes of interest were taken over 500 non-correlated equilibrium configurations obtained after 9000 MCS in order to be sure the system is in equilibrium.

We also used the subblock finite size scaling method in order to extrapolate the values to the infinite size lattice [13]. This method consists of evaluating the variables (for instance

the order parameters) not only on the whole lattice (40×40) but also on some subblocks (20×20, 10×10, 8×8, 4×4). Plotting the values of the variables in front of $1/L$ (L is the subblock linear size) we can extrapolate these values to the limit $L \to \infty$.

The magnitudes that were measured are:

(i) The energy, calculated as the average of equation (1).

(ii) The specific heat C^*, calculated from the energy fluctuations. In some cases we performed a numerical smoothing before the extrapolation to $L \to \infty$ in order to reduce the noise, and measure in an easier way the position of the phase transition peaks.

(iii) The positional order parameter. Due to the degeneration associated with the $(+)$ and $(-)$ sublattices, m_p must be measured as:

$$m_p = \left\langle \left| \left(\sum_+ S_i - \sum_- S_i \right) / N_p \right| \right\rangle \qquad (7)$$

or as:

$$m_p = \left[\left\langle \left(\sum_+ S_i - \sum_- S_i \right)^2 \right\rangle \right]^{1/2} \qquad (8)$$

(iv) The orientational order parameters. In that case m_o^- and m_o^- are fourfold-degenerated because there are 4 possible equivalent orientations on the lattice (see Fig. 1). We have measured them taking as a reference direction the 4 possible orientations $\simeq = \{0, \pi/4, \pi/2, 3\pi/4\}$ and then taking the averages of the maximum values as:

$$m_o^+ = \langle \max_{\Omega} \{ m_o^+ (\Omega) \} \rangle \qquad (9)$$

$$m_o^- = \langle \max_{\Omega} \{ m_o^- (\Omega) \} \rangle \qquad (10)$$

or as:

$$m_o^+ = [\langle (\max_{\Omega} \{ m_o^+ (\Omega) \})^2 \rangle]^{1/2} \qquad (11)$$

$$m_o^- = [\langle (\max_{\Omega} \{ m_o^- (\Omega) \})^2 \rangle]^{1/2} \qquad (12)$$

4. Results

We studied the behaviour of the positional and orientational order parameters and the specific heat for different values of K_1^* and K_2^* and we have obtained the phase diagram of the model.
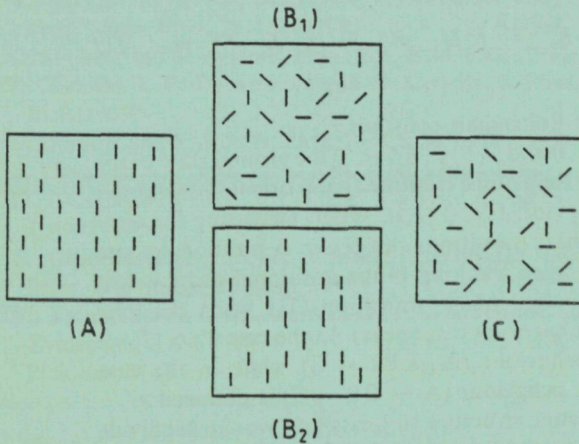

Fig. 2. Structure of the phases exhibited by the model. A is the ground state with orientational and positional order. B1 is a phase with only positional order. B2 is a phase with only orientational order and C is a completely disordered phase.
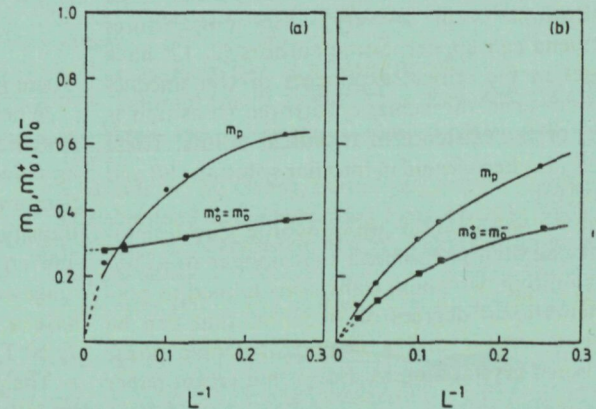

Fig. 3. Order parameters calculated using (7), (9) and (10) vs. the inverse of the subblock size, $1/L$. For $K_1^* = K_2^* = -0.61$ a corresponds to $T^* = 0.625$ (phase with orientational order only) and b corresponds to $T^* = 0.700$ (completely disordered phase).

4.1. Order parameters

In Fig. 3 we represent, as a function of $1/L$, the positional and orientational order parameters at two different temperatures for $K_1^* = 0.61$. Extrapolating their values to $1/L = 0$ we can correct the finite size effects. Fig. 3(a) corresponds to a phase with orientational order but without positional order, while Fig. 3(b) corresponds to a completely disordered phase. Figure 4(a) displays the evolution of the extrapolated order parameters against temperature for the same case as before. Two phase transitions can be distinguished: the positional phase transition T_p corresponding to the m_p decay and the orientational transition T_o, corresponding to the m_o^+ and m_o^- decay. This behaviour may be qualitatively associated to a L.C. behaviour and enables us to identify T_p with the smectic-nematic transition and T_o with the nematic-isotropic one. For some cases (for instance $K_1^* = K_2^* = -0.5$) we found $T_p > T_o$. These cases correspond to a P.C. behaviour.

Note that the orientational order parameter has a hysteresis zone near T_o. This fact indicates that this transition should be first order.

4.2. Specific heat

Figure 4(b) shows the evolution of the specific heat calculated from the energy fluctuations against temperature also for the case $K_1^* = K_2^* = -0.61$. We also extrapolated to $1/L = 0$ after a numerical smoothing. We can clearly distinguish two peaks corresponding to the two phase transitions T_p and T_o.
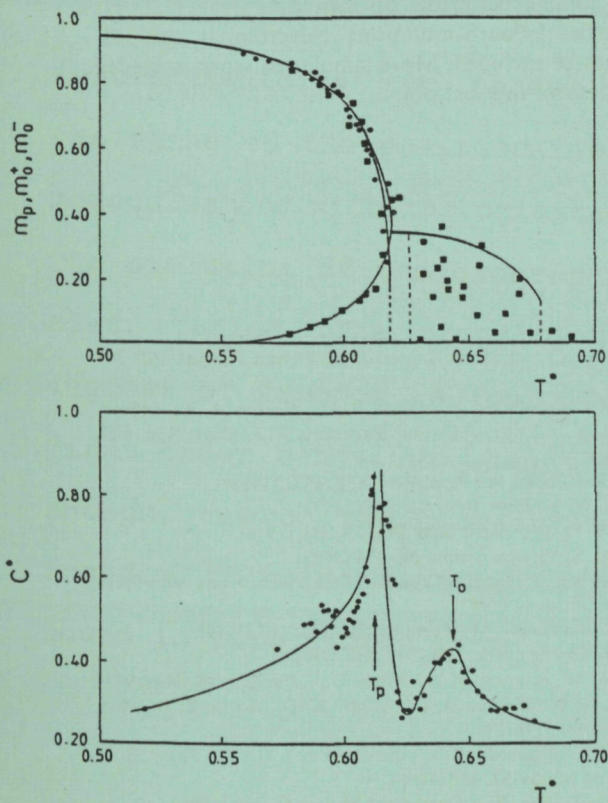

Fig. 4. Order parameter (a) and Specific heat (b) evolution with temperature T^* for the case $K_1^* = K_2^* = -0.61$. In Fig. 4(a), the dots correspond to the positional order parameter calculated using (8), and the squares correspond to the orientational order parameters calculated using (9) and (10). T_p is the positional transition where the positional order parameter vanishes, and T_o is the first-order orientational transition. The noise is due to hysteresis effects.

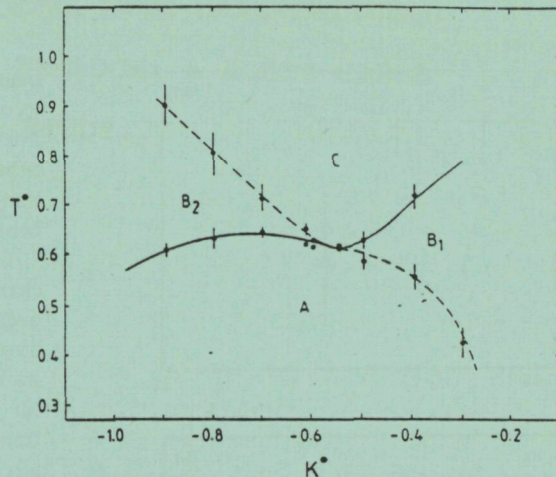Fig. 5. Section of the phase diagram of the model along the line $K_1^* = K_2^*$. A is the phase with long-range positional and orientational order, B_2 is the phase with only orientational order, B_1 is the phase with only positional order and C is the completely disordered phase. The dashed line corresponds to first order phase transitions while the continuous line corresponds to second order phase transitions.

4.3. Phase diagram

We carefully analyzed for 13 different cases with different values of K_1^* and K_2^* the position of the two phase transitions. In Fig. 5 a section of the phase diagram along the line $K_1^* = K_2^*$ is shown. Note that for sufficiently negative values of the constants K_1^* and K_2^* (i.e., higher orientational energies) we have a L.C. behaviour with $T_o > T_p$, while for small values of these constants we have a P.C. behaviour $T_p > T_o$.

All the results are consistent with the hypothesis that the positional transition is second order while the orientational transition is first order, at least in the studied cases. These results are in agreement with other M.C. simulations and a mean field approximate solution of the model [3, 14].

5. Critical behaviour

We analyzed the critical behaviour of the positional transition in the L.C. zone. We focused our attention on the β exponent of the evolution of the positional order parameter near the second order phase transition T_p:

$$m_p \approx A[(T_p - T^*)/T_p]^\beta \quad T^* \to T_p \tag{13}$$

T_p was measured from the position of the specific heat peak extrapolated to $L \to \infty$. Then we have adjusted A and β using a logarithmic fitting to the $m_p(T^*)$ data extrapolated to $L \to \infty$.

Measurements were made for different values of K_1^* and K_2^* on the section of the phase diagram plotted in Fig. 5. For each case we have also measured the distance between the two phase transitions T_p and T_o using the so called McMillan parameter [4] defined as:

$$M = T_p/T_o \tag{14}$$

Figure 6(a) shows the results of the fittings. Note that when the two transitions are separated enough we measure the expected exponent corresponding to the 2-D Ising model, while when the positional transition is closer, the behaviour changes. Our data seem to indicate that the evolution is
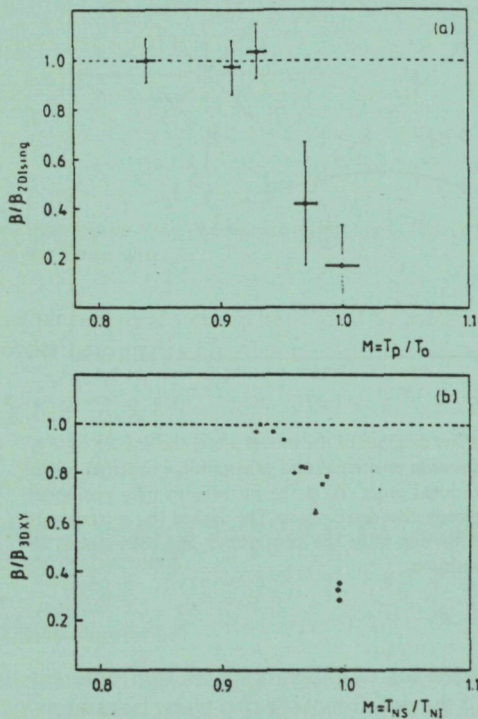
Fig. 6. The effective critical exponent β against the McMillan parameter M. (a) Monte Carlo simulation results using the 2-D model proposed in the text. (b) Experimental values reported by different authors measured using pure Liquid Crystals or mixtures. × nS5 [12]. + 40.8–40.7 [2]. ■ CBOOA [2, 15]. ○ 8OCB [2, 15], △ 8CB [2], ● 9CB–10CB [12].

continuous but we cannot state if a tricritical point before $M = 1$ exists or not.

Figure 6(b) shows a collection of experimental data from different authors [2, 12, 15] of the measured (or calculated from other critical exponents using scaling relations) β exponents for different L.C. mixtures against the distance between the nematic-smectic and the nematic-isotropic transition also measured using the McMillan parameter:

$$M = T_{NS}/T_{NI} \tag{15}$$

Some authors [12] report the existence of a tricritical point before and very near $M = 1$.

Due to the error in the determination of the transition temperatures, this region close to $M = 1$ is difficult to analyze using Monte Carlo simulations.

The two figures 6(a) and 6(b) are not quantitatively comparable because they correspond to different physical systems. Our model is 2-dimensional and the positional transition is associated with an Ising model, while the Nematic–Smectic transition in L.C. is believed to belong to a 3D-XY model universality class. In spite of the difference, we suspect that Fig. 6(a) and 6(b) reflect the same coupling effect between a positional and an orientational phase transition.

6. Summary and conclusions

We have studied a system exhibiting two phase transitions, related to positional (T_p) and orientational (T_o) degrees of freedom. Our results indicate that the positional transition is second order while the orientational transition is first order. The model allows the possibility of studying two different behaviours corresponding to the cases $T_o > T_p$ and $T_p > T_o$ that can be qualitatively compared to a L.C. and a P.C. behaviour.

Changing some parameters of the hamiltonian we can change the distance between the two transitions and also overlap them. In the case of the L.C. behaviour ($T_o > T_p$) we have measured the β exponent of the second order positional transition. We have found that this exponent changes when the transition becomes closer to the orientational first order transition. This behaviour has also been found experimentally in some L.C. mixtures [2, 12].

We suggest two possible explanations of these phenomena. One explanation is that, in fact, the real β exponent does not change, and the exponents measured in our simulations and even experimentally are only effective because the critical region related to the positional transition becomes very narrow when the first order orientational transition is near. A second explanation is that, in fact, the critical exponents change due to the coupling of the two phase transitions. This second explanation has also been proposed in some experimental works [2].

The existence of a tricritical point on the positional transition line before the point where the two transitions overlap, observed in some experiments on Liquid Crystals [12], has not been verified by our simulations. Nevertheless, this possibility cannot be excluded. More simulation work is needed in order to resolve this last point.

References

1. Cadeville. M. C. and Morán-López. J. L.. Physics Reports 153. 331 (1987).
2. Garland. C. W.. Meichle. M.. Ocko. B. M.. Kortan. A. R.. Safinya. C. R.. Yu. L. J.. Lister. J. D. and Birgeneau. R. J.. Phys. Rev. A27. 3234 (1983).
3. Vives. E. and Planes. A.. Phys. Rev. A38. 5391 (1988).
4. McMillan. W. L.. Phys. Rev. A4. 1238 (1971).
5. Imry. Y.. J. Phys. C: Solid State Phys. 8. 567 (1975).
6. Micciancio. S.. Physica Scripta 38. 474 (1988).
7. Chandrasedhar. S.. Liquid Crystals. Cambridge University Press. Cambridge. England (1977).
8. Galam. S. and Gabay. M.. Europhys. Lett. 8. 167 (1989).
9. Fisher. M. E.. Phys. Rev. Lett. 57. 1911 (1986).
10. Bellocq. A. M.. Honorat. P. and Roux. D.. J. Physique 46. 743 (1985).
11. Chan. M. H. W.. Migone. A. D.. Miner. K. D. and Li. Z. R.. Phys. Rev. B30. 2681 (1984).
12. Ocko. B. M.. Birgeneau. R. J. and Litster. J. D.. Z. Phys. B – Condensend Matter 62. 487 (1986).
13. Binder. K.. Z. Phys. B – Condensed Matter 43. 119 (1981).
14. Vives. E. and Planes. A.. Phys. Rev. A ~~submitted~~ 41, 1885 (1990)
15. Evans-Lutterodt. K. W.. Chung. J. W.. Ocko. B. M.. Birgeneau. R. J.. Chiang. C.. Garland. C. W.. Chin. E.. Goodby. J.and Nguyen Huu Tinh.. Phys. Rev. A36. 1387 (1987).

CRITICAL BEHAVIOUR OF A SYSTEM WITH ORIENTATIONAL AND POSITIONAL DEGREES OF FREEDOM: A MONTE CARLO SIMULATION STUDY.

ABSTRACT

The critical behaviour of a system constituted by molecules with a preferred symmetry axis is studied by means of a Monte Carlo simulation of a simplified two-dimensional model. The system exhibits two phase transitions, associated with the vanishing of the positional order of the center of mass of the molecules and with the orientational order of the symmetry axis. The evolution of the order parameters and the specific heat is also studied. The transition associated with the positional degrees of freedom is found to change from a second order to a first order behaviour when the two phase transitions are close enough, due to the coupling with the orientational degrees of freedom. This fact is qualitatively compared with similar results found in pure liquid crystals and liquid crystals mixtures.

I. INTRODUCTION

Systems exhibiting coupling phenomena between different kinds of degrees of freedom have been extensively studied in recent years. Experimentally, it is known that such systems display very rich phase diagrams due to the interplay of the different degrees of freedom. Many models have been developed in order to explain these phase diagrams, and have been solved using mean-field approximations[1] and computer simulations[2].

In this paper, the focus is on systems with coupling between orientational and positional degrees of freedom like Liquid Crystals[3], Plastic Crystals[4] or some molecules adsorbed onto surfaces[5]. These systems are basically constituted by molecules with a preferred symmetry axis. The positional degrees of freedom are associated with the movement of the centre of mass of the molecules in a three-dimensional (or two-dimensional in the case of Adsorbed Molecules) space, while the orientational degrees of freedom are associated with the direction of the symmetry axis.

In principle these degrees of freedom are continuous but, in order to simulate such systems, we will treat them as discontinuous. Discretization of the position of the molecules in the space is usually done by means of the so called Lattice-Gas model[6] which has been extensively used to describe Solid-Liquid and Liquid-Gas phase transitions[7]. This discretization allows the possibility of stabilizing long-range ordered phases in two-dimensional systems[8]. Moreover, the discretization of the orientational degrees of freedom has been used, not only on systems where the symmetry of the interaction potentials clearly

justify it, like some Plastic Crystals[9], but also on Liquid Crystals[10] giving a good agreement with experiments.

One can classify the phases of these systems in four groups. First, Solid phases (S) with long-range orientational and positional order that usually appear at low temperatures. Increasing the temperature, the positional or the orientational long range order may disappear resulting in Liquid Crystalline phases (LC) (no positional long range order) or Plastic Crystalline phases (PC) (no orientational long-range order). At high enough temperatures, all long range order disappears resulting in an isotropic Liquid phase (L). We will call T_p (T_o) the temperature at which all the positional (orientational) long range order vanishes.

In real systems the positional or orientational order usually does not fully disappear at a given temperature. For instance in Liquid Crystals between the fully S phase and the LC phase also called the Nematic phase, there exists other mesophases like Smectic phases with long-range positional order in only one direction of the space forming, for example, layered structures.

Critical behaviour of most of these phase transitions has been individually studied by models taking into account only the relevant degrees of freedom at that temperature (for instance the positional degrees of freedom at T_p) and making some static approximations on the others. The aim of this paper is to study by means of M.C. simulation, and in a very simple case, the whole phase diagram of such systems. The emphasis will be on the coupling phenomena that appear in the critical behaviour of these

systems, and which cannot be understood by a model for an individual phase transition. For instance, some Liquid Crystals exhibit a change in the behaviour of the Smectic-Nematic phase transition (associated with the positional degrees of freedom) from second order, when there is no coupling, to first order when the orientational degrees of freedom begin to play an important role[11,12]. Similar phenomena have been found in micellar solutions[13] and microemulsions[14].

In section II we summarize a 2d model that reproduces the four kinds of phases mentioned above. The phase diagram of this model has been studied previously by the mean-field approximation[15] and qualitatively compared with the Liquid Crystals and Plastic Crystals's phase diagrams. Also some Monte Carlo simulations were performed in order to test the main features of the phase diagram[16]. In section III we present the raw Monte Carlo results. In section IV we focus our attention on the critical behaviour of the positional transition occurring at T_p. Our studies indicate that the behaviour of this phase transition changes from second order to first order due to the coupling with the orientational degrees of freedom. This fact is qualitatively compared with existing experimental data of the critical behaviour of Liquid Crystals found in literature[11,12,17]. Finally, in section V we present the main conclusions of the work.

II. THE MODEL.

The model is defined on a 2d square lattice of $N = L \times L$ sites. On each site i (i = 1,..,N) we define a scalar variable S_i which takes values 1 or 0 depending on the presence or absence of a molecule on site i. The number of molecules in the system is kept constant,

$$N_p = \sum_{i=1}^{N} S_i = N\,c \tag{1}$$

where c = 0.5 is the coverage or density, and the summation extends over all the lattice sites. If $S_i = 1$ we also define another variable R_i that takes values among a set of unitary vectors defining n possible directions in the space. We will restrict to the case of non polar molecules and only n = 4 possible orientations equally distributed on the lattice plane (see Fig.1a).

This restriction of n = 4 is, of course, quite important and is made in order to simplify the M.C. simulation of the model. Nevertheless, a previous Mean Field solution of this model[15] suggest that there are no qualitative changes for n>2. Also, the Monte Carlo simulation of a more restricted but similar model (in 3 dimensions) largely used for the study of the Nematic-Isotropic phase transition[18,19], show that no big differences appear when the number of directions changes from a continuous to a discrete small value. It is also worth noting that as we are interested in the study of the Smectic-Nematic phase transition, that involves a change in the positional order of the molecules, a

simplified treatment of the orientational degrees of freedom does not represent a dramatic approximation.

The Hamiltonian of the system, including only pairwise interactions, is written as:

$$H = J_1 \sum_{i,j}^{n.n} S_i S_j + K_1 \sum_{i,j}^{n.n} S_i S_j \, P(R_i, R_j) + K_2 \sum_{i,j}^{n.n.n.} S_i S_j \, P(R_i, R_j) \qquad (2)$$

where $\sum^{n.n.}$ ($\sum^{n.n.n.}$) is a summation over all nearest-neighbour (next-nearest-neighbour) bonds, and J_1, K_1 and K_2 are constants. P is a scalar function of the directions R_i and R_j defined as:

$$P(R_i, R_j) = 2\left(\cos^2(\theta_{ij}) - 1\right) \qquad (3)$$

where θ_{ij} is the angle between the two directions R_i and R_j. This orientational interaction is the one proposed by Maier and Saupe for the study of the order in Nematic phases[20].

When $J_1 < 0$, the first term of (2) acts as a positional repulsion between nearest-neighbours (n.n). The other two terms, with K_1 and K_2 negative, are orientational interaction terms which favour parallel alignment of the molecules.

In order to simulate this system we will define reduced units as,

$$H^* = \frac{H}{J_1}, \ T^* = \frac{T}{k_B J_1}, \ K_1^* = \frac{K_1}{J_1}, \ K_2^* = \frac{K_2}{J_1} \qquad (4)$$

where T is the thermodynamic temperature of the system and k_B is the Boltzmann constant. With these definitions the Hamiltonian of the system can be written as,