SIMULACIO MONTE CARLO DE SISTEMES AMB ACOBLAMENT DE GRAUS DE LLIBERTAT.
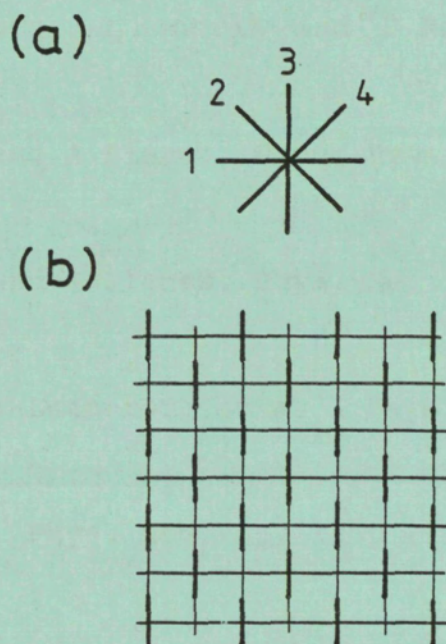
UNIVERSITAT DE BARCELONA
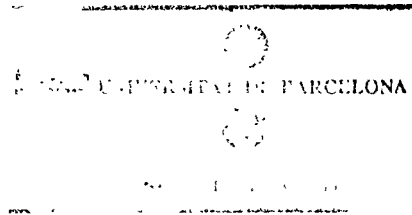
FIG. 1

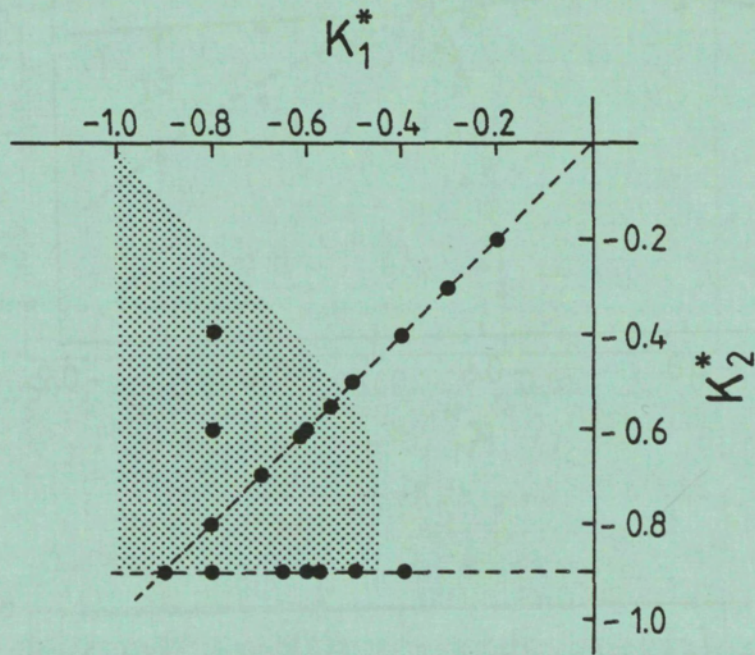a) Four possible directions of the molecules on the surface. b) Ground state configuration.

FIG. 2

Dots represent the different points (K_1^*, K_2^*) that have been
studied by Monte Carlo simulation in the region where the ground
state is that of Fig.1. Discontinuous lines are the sections
along which the phase diagram is represented in Fig. 3. The dot
shadowed area is the region where the Liquid Crystal-like
behaviour has been found and the non shadowed area is the region
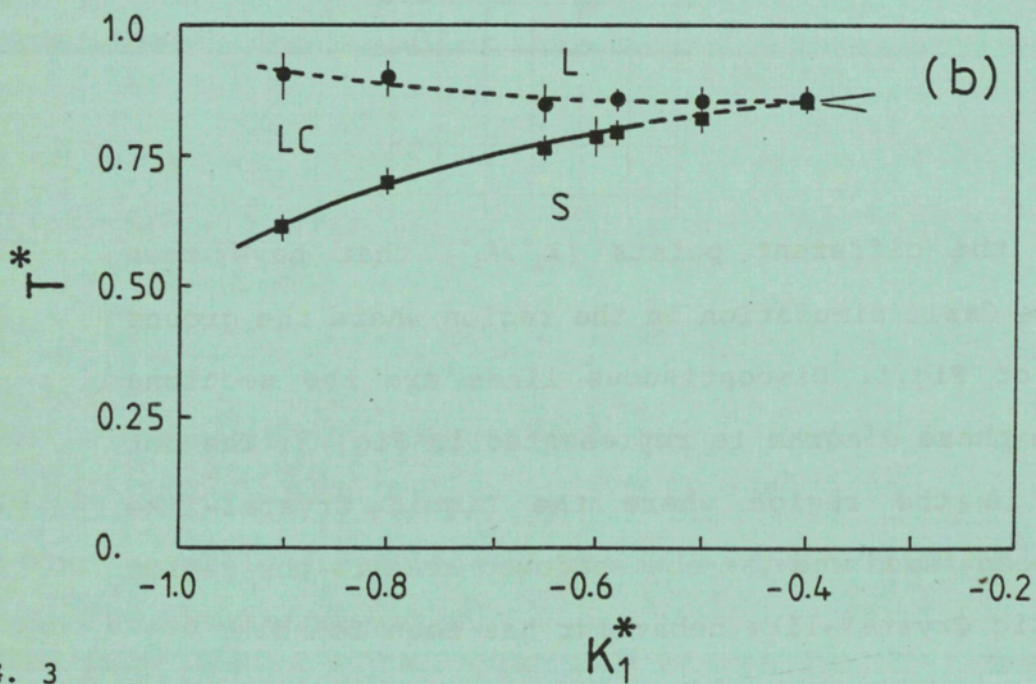where the Plastic Crystal-like behaviour has been found.
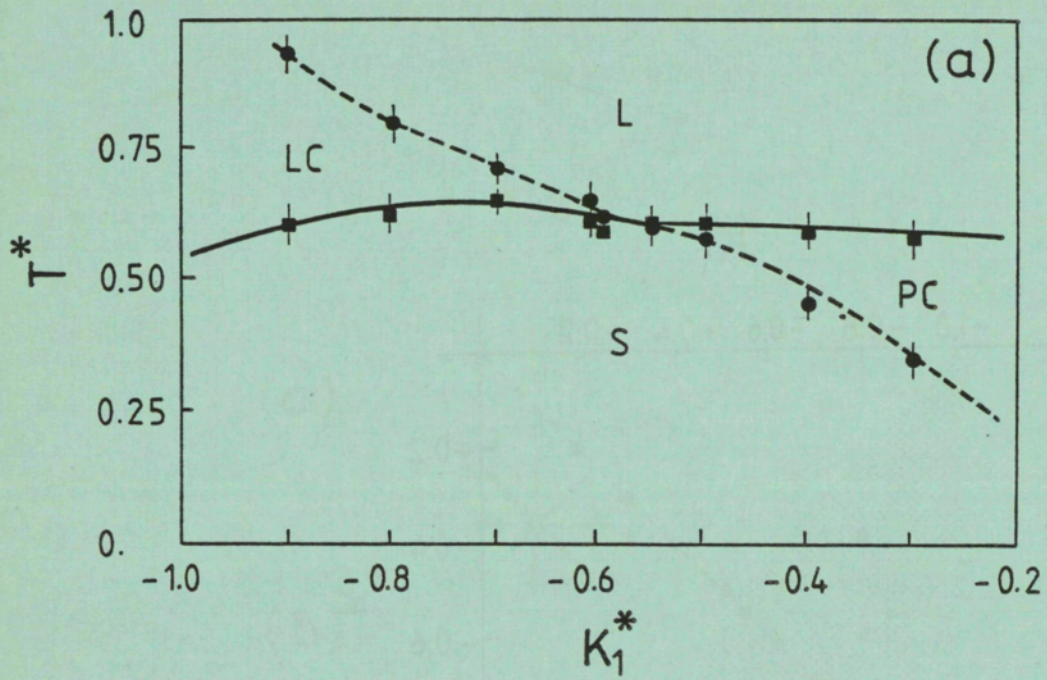
FIG. 3

Sections of the phase diagram along the lines shown in Fig. 2.
a) $K_1^* = K_2^*$ and b) $K_2^* = -0.9$ Lines are guides to the eye.
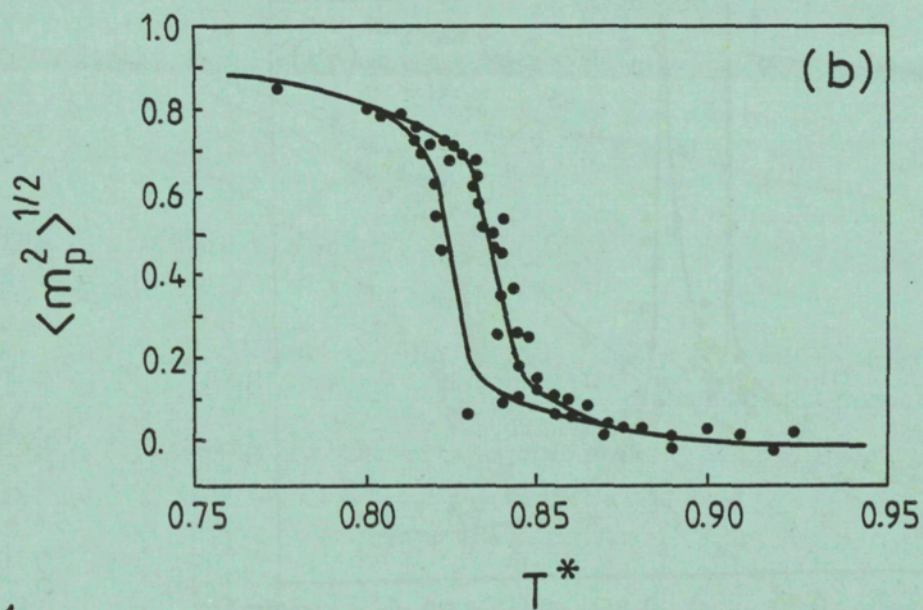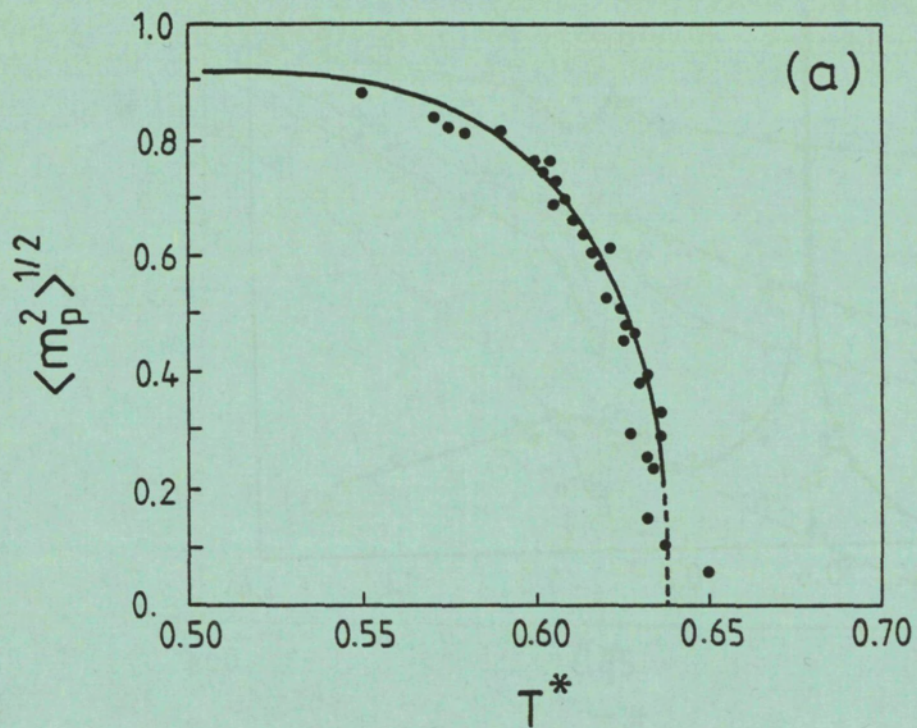
FIG. 4

Detailed order parameter evolution versus temperature. Case a) corresponds to $K_1^* = -0.9$ and $K_2^* = -0.9$, while case b) corresponds with $K_1^* = -0.5$ and $K_2^* = -0.9$. b) exhibits some hystheresis that is not present in a).
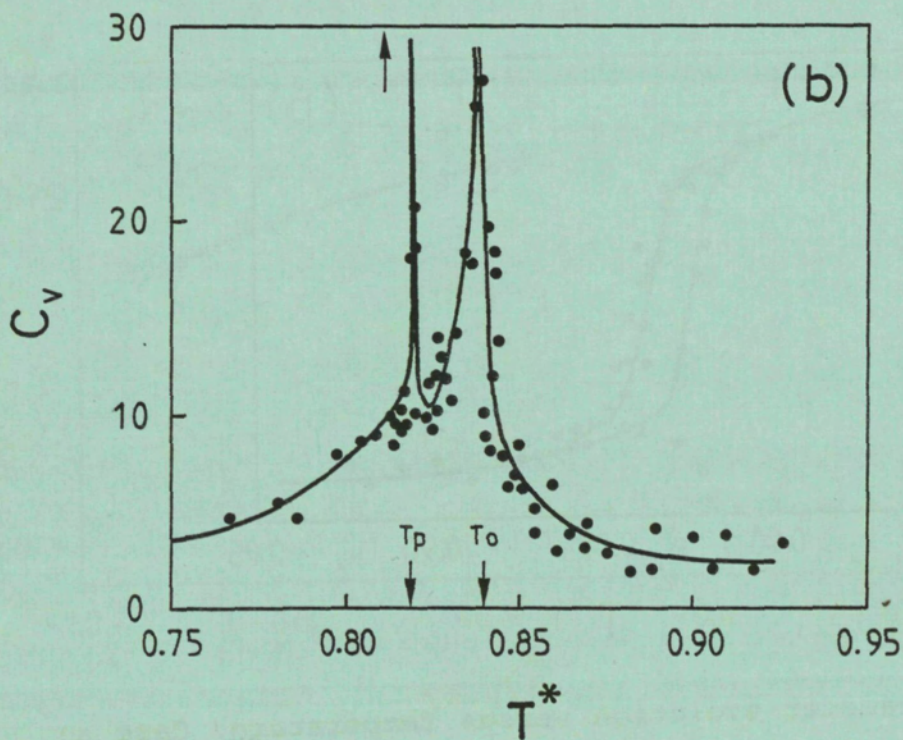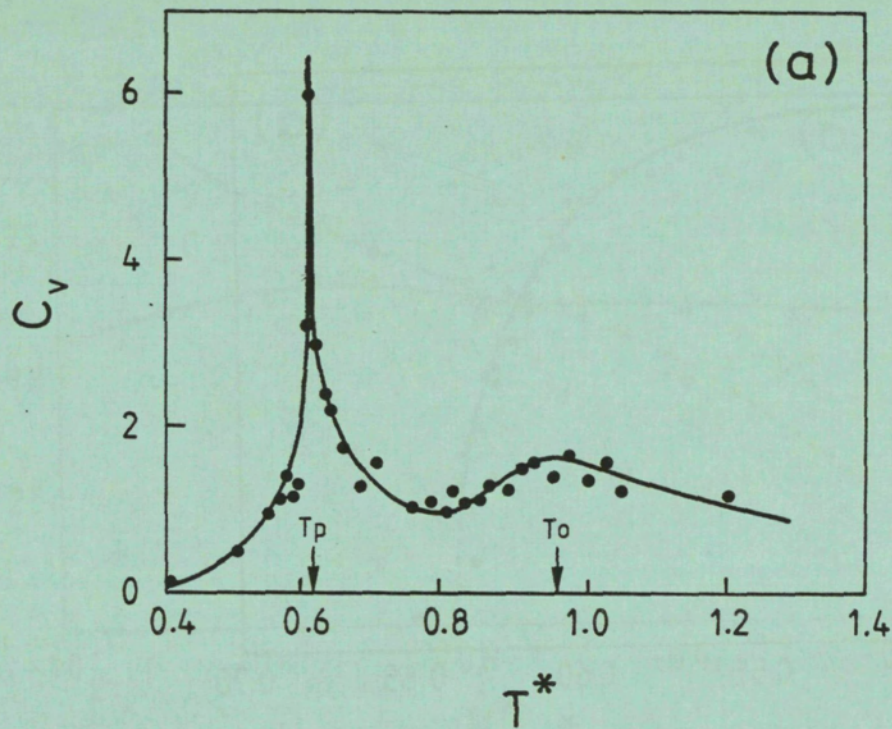
FIG. 5

Specific heat ($<C_v>$) evolution with temperature when (a) $K_1^* = -0.9$, $K_2^* = -0.9$ and (b) $K_1^* = -0.5$, $K_2^* = -0.9$. T_p and T_o indicate the positions of the positional and orientational transition. The line is a guide to the eye.
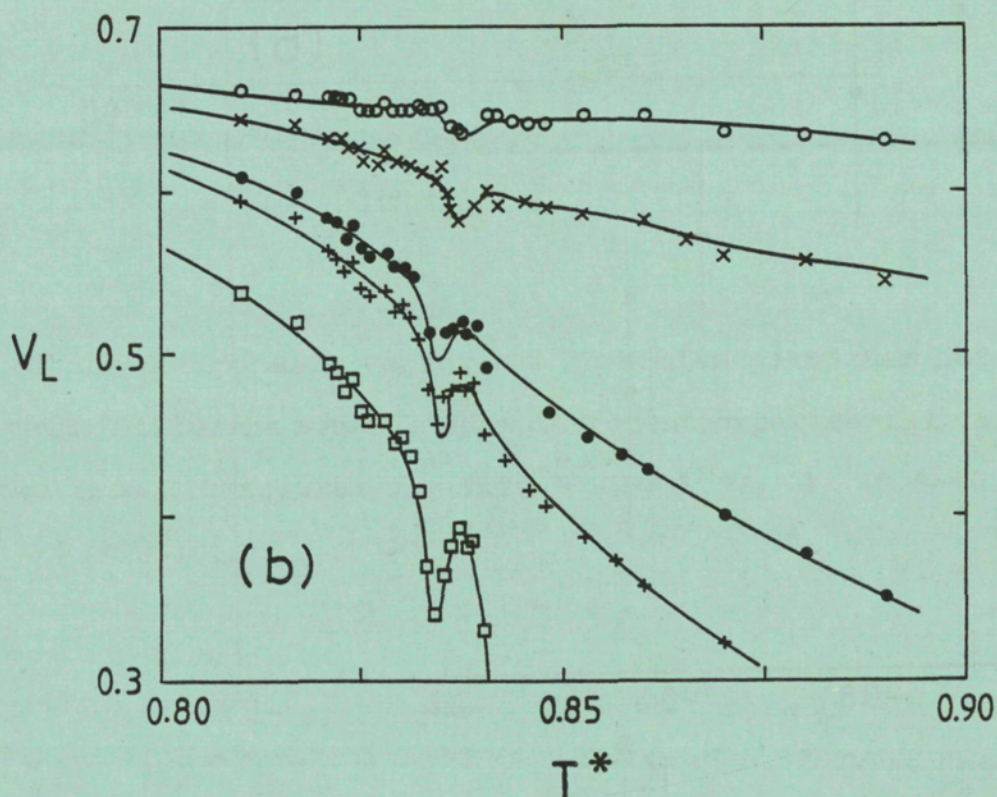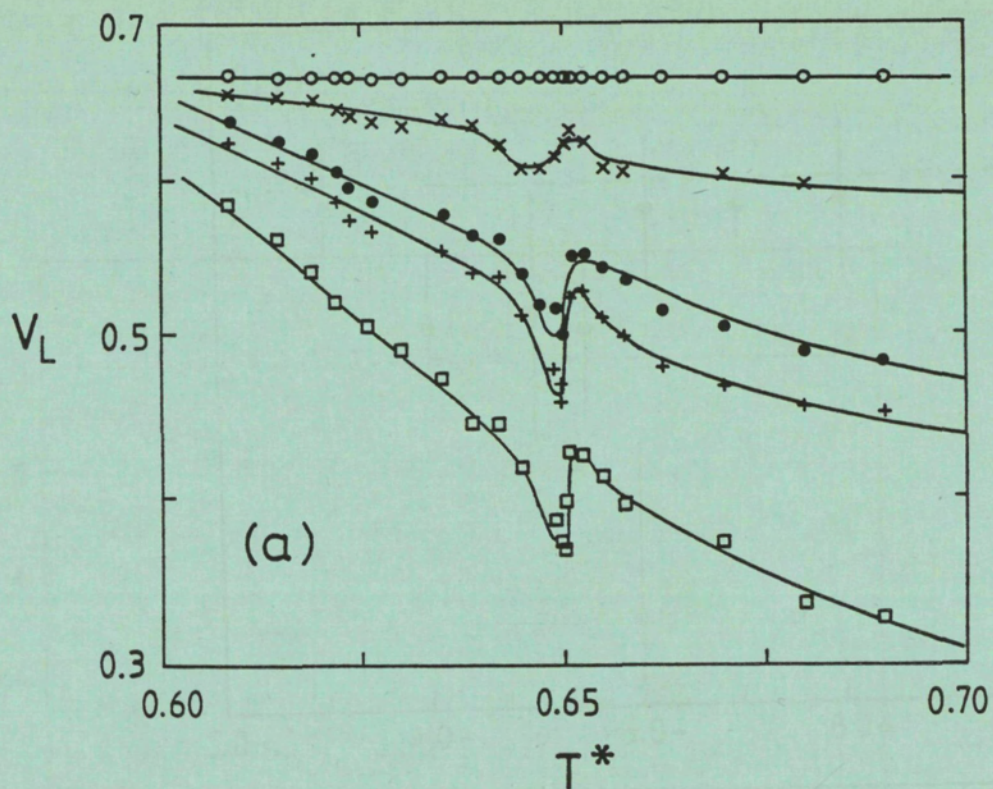
FIG. 6

Dependence of V_L with T^* for the different subblock sizes. (L = O 40, X 20, ● 10, + 8, □ 4). Case (a) corresponds to $K_1^*=-0.9$, $K_2^*=-0.9$ and case (b) to $K_1^*=-0.5$, $K_2^*=-0.9$.
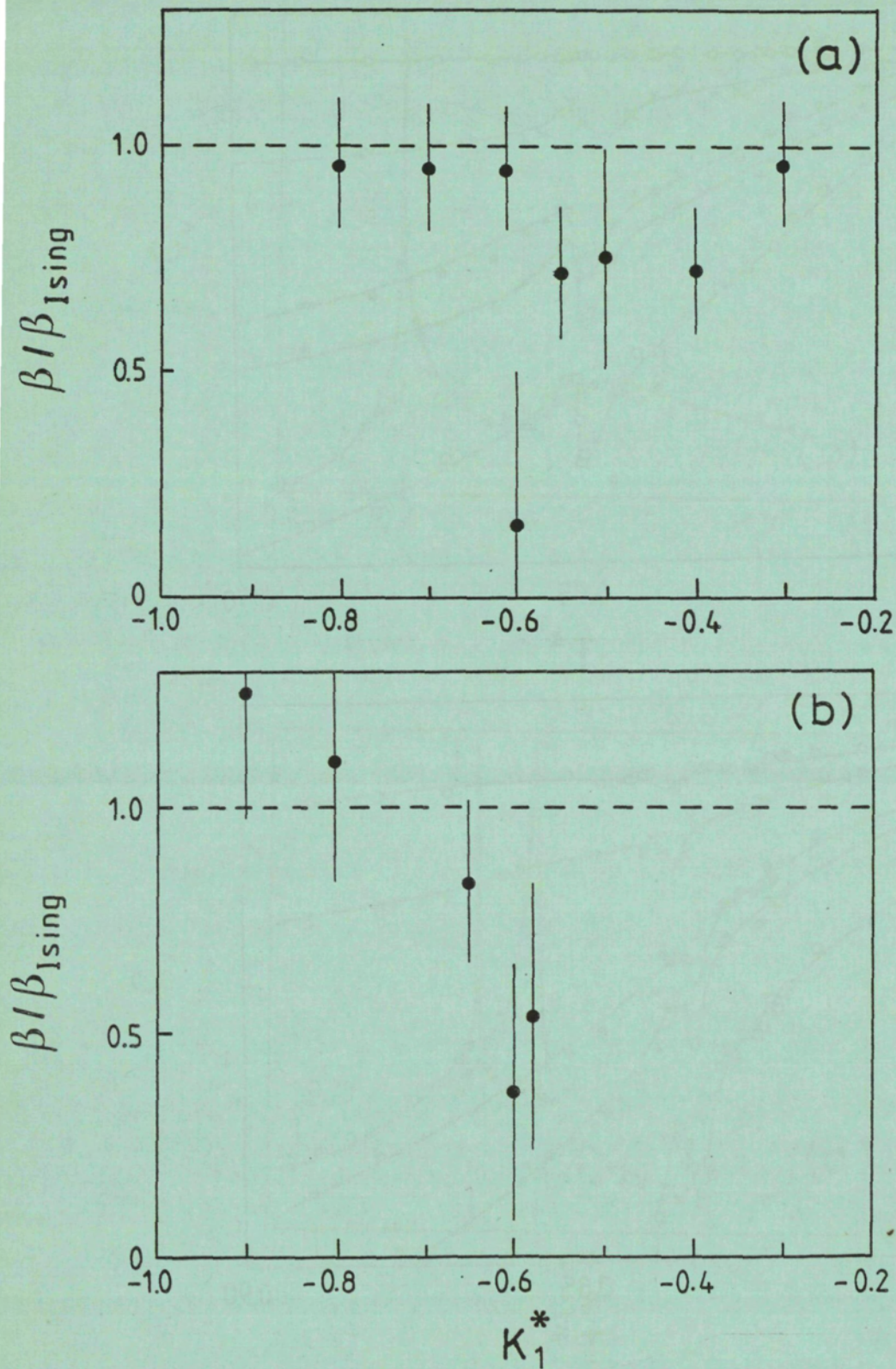
FIG. 7

ß exponents calculated adjusting a power-law to the Monte Carlo data along the lines $K_1^* = K_2^*$ (a) and $K_2^* = -0.9$ (b). Error bars are associated to the deviations on the adjusted exponents due to the indetermination of T_p, as explained in the text.
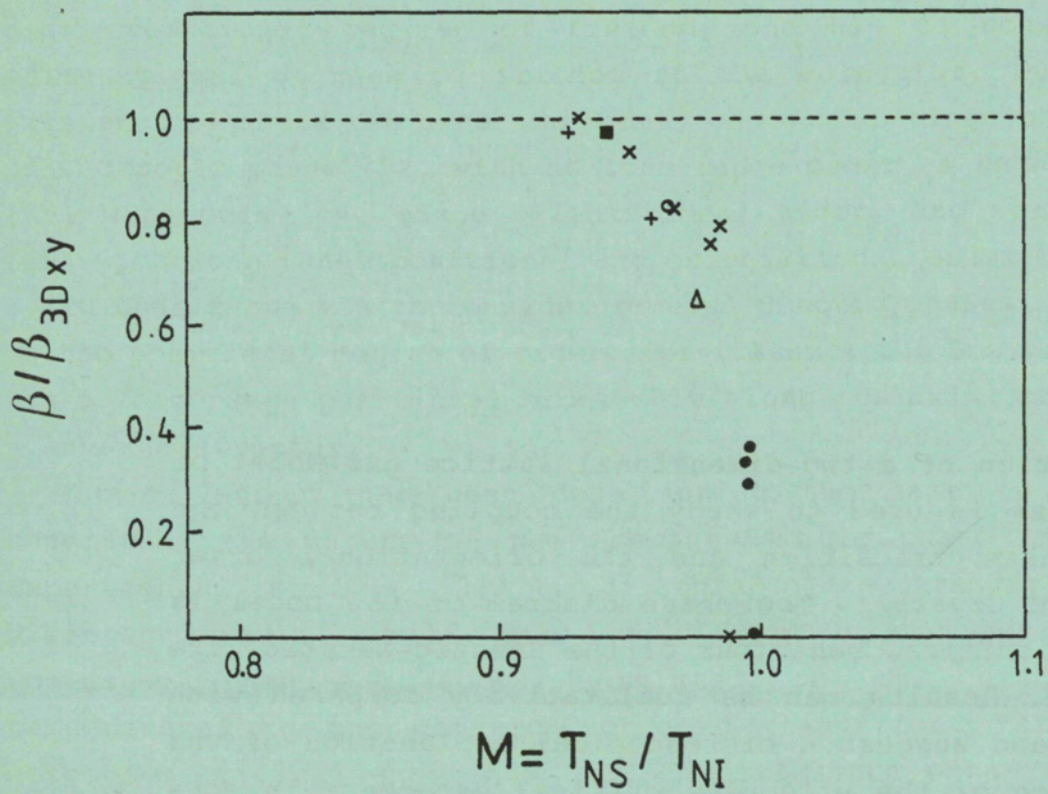
FIG. 8

Values of the ß exponents versus the Mc Millan parameter defined in the text. Different symbols show different experimental values collected from literature: X nS5[12], ■ CBOOA[11,17], + 40.8-40.7[11], Δ 8CB[11], ● 9CB-10CB[12], O 8OCB[11,17].

MONTE CARLO SIMULATION STUDY OF A SMECTIC-NEMATIC-LIKE TRANSITION IN A TWO-DIMENSIONAL LATTICE GAS MODEL OF CYLINDRICAL PARTICLES.

ABSTRACT

Monte Carlo simulation of a two-dimensional lattice gas model of orientable particles is used to study the coupling between the Smectic-Nematic phase transition and the orientational order parameter in Liquid Crystals. The phase diagram of the model is obtained, and the critical behaviour of the Smectic-Nematic-like transition studied. Results can be qualitatively compared with experimental data and suggest a microscopical explanation of the continuous variation of the effective critical exponents in some Liquid Crystal mixtures. The existence of a Tricritical Point is also reproduced. Finally, results are analyzed in terms of a general Landau free energy functional [Anisimov et al. Phys. Rev. **A41**, 6749 (1990)] that suggests that the Tricritical Point is only apparent.

1. Introduction

The main feature of Liquid Crystals [1] that makes them different from other classical many particles systems is that, apart from the usual positional degrees of freedom, one has to consider the orientational degrees of freedom of the molecules. Due to the existence of these two ordering modes, one can distinguish a Liquid or Isotropic phase (LP) with no long range order, a Nematic phase (NP) with only long range orientational order, and solid phases (SP) with long range positional and orientational order. Among the solid phases one has to consider several Smectic phases, depending on the positional degree of order. For instance the Smectic A phase has a long range positional order only along one axis, that favors a layered structure.

A lot of effort has been done during the last 40 years to understand the nature of the Smectic-Nematic phase transition. Experimental studies [2,3,4] of this phase transition using different Liquid Crystals and Liquid Crystals mixtures show that non-usual phenomena appear, related to the distance (in temperature) to the Nematic-Isotropic transition. Variation of effective critical exponents, and the existence of a Tricritical Point (TCP) have been reported by several authors [2,5,6,7].

Figure 1 shows a compilation from the literature of the measurement of critical exponents of the Smectic-Nematic phase transition. α corresponds to the exponents of the specific heat divergence and β to the decay of the order parameter. β results are normalized to the value corresponding to the 3d XY model (the transition under consideration is though to belong to this universality class). The different data correspond to different liquid crystals or different mixtures and they are plotted versus the Mc Millan parameter [8] that measures the ratio between the Smectic-Nematic (T_{NS}) and the Nematic-Isotropic (T_{NI}) temperatures. It can be seen that when the two phase transitions are close one to the other, the measured effective exponents show an important continuous variation. Several authors propose the existence of a TCP near M = 0.994 [5], before the point where the two phase transitions overlap (M=1.0). These

evidences suggest that there is a strong coupling between the orientational and positional order parameters in the system: a small value of the orientational order parameter produces strong effects on the Smectic-Nematic phase transition.

Most progress in the understanding of this problem has been done by means of a Landau theory. The positional order in the Smectic phase can be characterized by the amplitude of the density modulation along the z axis, ψ, while the orientational order is characterized by the fluctuations of a vector (director) that indicates the preferred direction of the molecules δn. When symmetry arguments are used to study, in the Landau frame, the Smectic-Nematic phase transition only even powers of ψ appear in the free energy. An expansion up to ψ^6 allows the transition to be second order or first order and predicts the existence of a tricritical point in the phase diagram of a Liquid Crystal binary mixture at a given composition. This TCP appears when the coefficient of the fourth order term in the free energy expansion (ψ^4) vanishes. This result is in agreement with the early studies of Mc Millan [8].

Nevertheless, Halperin, Lubensky and Ma [9] proposed a free energy expansion in terms of ψ and the orientational fluctuations δn. An effective treatment of the director fluctuations term results in a 3rd order term ψ^3, that suggest that the Smectic-Nematic phase transition is always first order. A very recent paper by Anisimov et al. [10] revises some experimental data and explains the reason why TCP's have been observed experimentally. Only very careful experiments, based on a new dynamical method [11], have been able to show that the Smectic-Nematic transition is always first order. But, there is still a lack of explanation of these phenomena from a more microscopical point of view, starting from a set of variables describing the position of the molecules and performing standard Statistical Mechanics treatment. Such a microscopic model, and its exact solution will be very useful in order to compare Landau expansions predictions with experiments. In this paper we study, by means of Monte Carlo simulation, a simplified microscopic model for the study of the Smectic-Nematic phase transition on the basis of a Lattice-Gas model of molecules with orientational

degrees of freedom presented recently [12]. We study its relation with the results predicted by Halperin, Lubensky and Ma theory [9] and the experimental data. In section 2. we introduce the details of the model. In section 3. we present the main results concerning the phase diagram and the effective critical exponents. Finally in section 4. we discuss our results and conclude.

2. Model

The model is defined on a 2d square lattice with $N = L^2$ sites. On each site we define two variables: S_i taking values 1 or 0 depending on the presence or absence of a molecule in site i, like in a lattice-gas model, and t_i which is a two dimensional unitary vector representing the orientation of a molecule in site i, and that takes values among a discrete set of orientations. The hamiltonian of the system is defined as:

$$H = \sum_{i,j}^{n.n.} S_i S_j + K_1^* \sum_{i,j}^{n.n.} S_i S_j \, P(t_i, t_j) + K_2^* \sum_{i,j}^{n.n.n.} S_i S_j \, P(t_i, t_j)$$

where the first and second summations extend over all the nearest-neighbours (n.n.) pairs, and the third one extends to the next-nearest-neighbours (n.n.n.) pairs. K_1^* and K_2^* are constants and P is a function of the two orientations t_i and t_j.
The first summation is a positional interaction term, and the other two summations are orientational interaction terms to n.n. and n.n.n, governed by the parameters K_1^* and K_2^*
The model has been solved in a very general case using Mean Field techniques [12]. In this work we restrict to the case of having four possible inplane orientations distributed at 0°, 45°, 90° and 135°, and P being the non-polar interaction:

$$P(t_i, t_j) = 2 \cos^2(\theta_{ij}) - 1$$

where θ_{ij} is the angle between the two particles. This interaction has been used several times and is though to describe the main features of liquid crystals orientational interactions.

The density of the system is kept constant and equal to 50% so that:

$$\sum_{i=1}^{N} S_i = \frac{N}{2}$$

Standard Monte Carlo [13] simulations have been performed using a Kawasaki dynamics, exchanging n.n. particles and a Glauber dynamics rotating the molecules. For a large range of values of the hamiltonian parameters, two successive phase transitions have been found. At low temperature an orientationally ordered phase with all molecules parallel and placed in an antiferromagnetic structure (chess-board) is the most stable one. Increasing the temperature the positional antiferromagnetic order is lost and a Nematic phase with the molecules still being parallel but completely placed at random on the lattice appears. Finally at higher temperatures the orientational order also disappears, and a liquid phase is reached. The Solid-Nematic phase transition has been studied measuring the positional order parameter defined as:

$$m = \sum_{i=1}^{N/2 \, +} S_i - \sum_{i=1}^{N/2 \, -} S_i$$

where the + and - sign refer to summations over the two different sublattices of the chess-board structure.

A subblock method proposed by Binder [14], has been used in order to correct the finite-size effects of the Monte Carlo simulation and extrapolate the results to the thermodynamic limit. The evolution of $\langle m \rangle_L$, $\langle |m| \rangle_L$ and $\langle m^2 \rangle_L$ versus the temperature has been studied in a 40x40 system for different subblock sizes (20x20, 10x10, 8x8, 4x4) and for several values of the parameters K_1^* and K_2^*. We have also studied averages of the energy and energy fluctuations values. Monte Carlo runs have been carried up to 12000 Monte Carlo steps per particle and averages over several realizations of the random number sequence have been taken in order to improve statistics.

3. Results

Results concerning the evolution of the Energy, Order parameters and Specific heat have been published recently [15,16].

In this paper we focus on the phase diagram of the model. The main results obtained by our simulations are presented in figure 2. The upper figures show sections of the phase diagrams following different lines in the space of parameters (K_1^*, K_2^*). The different phases SP, NP and LP are clearly identified. Case (a) corresponds to a line with constant $K_2^* = -0.9$ and varying K_1^* between -0.9 and -0.4. Case (b) corresponds to the case $K_1^* = K_2^*$.

The bottom figures (a') and (b') show the corresponding measured values of the effective β exponent normalized to the value corresponding to the 2d Ising model which is a limiting case of our model when there is no orientational interaction. They have been calculated fitting a curve of the form:

$$m = A \cdot (T_0 - T)^\beta$$

T_0 has been fitted according to the maximum of the specific heat curve (calculated from the energy fluctuations), and β using a logarithmic least squares method. No higher order corrections have been included because it is not the aim of this paper to obtain very accurate results of the real critical exponents but to show the existence of an effective variation. Due to the error bars in the determination of T_0, the β values show a variation over a range that is plotted as an error bar.

First of all, we note that our model gives rise to a variation of the effective β critical exponent when the two transitions (positional and orientational) are very close, that is similar to the one showed by experiments (see Fig. 1(b)). This indicates that strong coupling effects with the orientational order are also present in our model. It is also interesting to note that in the case $K_1^* = K_2^*$ the coupling does not appear until the two transitions overlap. A possible explanation to this phenomenon will be presented in the next section. In the case (a) we have indicated a change from second order to first order transition (continuous and

discontinuous lines) in the Smectic-Nematic phase transition. This has been done because long metastable states have been observed in the region where the two transitions are very close in figure (1).

4. Discussion and Conclusions

Our results can be discussed in terms of the Landau expansion proposed by Halperin, Lubensky and Ma [9] and discussed recently by Anisimov et al [10]. We assume that the system can be described by a free energy expansion including the following terms:

$$f(\psi) = \frac{1}{2} A\psi^2 - \frac{1}{3} B\psi^3 + \frac{1}{4} C\psi^4 + \frac{1}{6} D\psi^6$$

The even terms come from the fact that the free energy is invariant under a change in the sign of ψ, and the cubic term is proposed to arise from an effective treatment of the orientational order parameter dependence in a similar way as in [9, 10].
Let us first analyze the case B = 0. A TCP appears as a consequence of the change of sign of C. For C>0 the transition is second order while for C<0 the transition is first order. The TCP is then placed at the point C=0.
The Halperin Lubensky & Ma theory [9] suggests that due to the orientational fluctuations, B is always different from zero, so the transition becomes a fluctuation induced first-order phase transition. Nevertheless, as analyzed by Anisimov et al. [10], the first order character of this phase transition is experimentally quite unaccessible when the orientational fluctuations are very small during the Smectic-Nematic Transition. Only when the Nematic-Isotropic phase transition is close enough, the first order character appears clearly. This justifies the existence of an apparent TCP at a temperature slightly under the true Landau TCP (C=0), which explains the results obtained experimentally [2,5,6,7].
Contrasting such a theory with our results obtained by Monte Carlo simulations, we propose that B depends on $(K_1^*-K_2^*)$ and C on $(1-M)$.

Hence, in the case of $K_1^* \neq K_2^*$ we observe an apparent TCP and when $K_1^* = K_2^*$ we observe a real TCP at the point $M=1$ ($C=0$).

Note that $(K_1^* - K_2^*)$ measures the difference between the orientational interaction at n.n. and n.n.n. It is easy to understand that when the orientational interaction is unsensitive to the change between n.n. and n.n.n, coupling effects between the two order parameters disappear (Remember that such a change is the mechanism of the Smectic-Nematic phase transition in our model). In the general case of a true liquid crystal one can propose that the dependence of the orientational interactions with the distance produces the coupling expressed by the term B of the Landau free energy expansion.

The dependence of C with M comes from the fact that when $K_1^* = K_2^*$ the real TCP seems to be placed just at $M=1$. Then in the case of $K_1^* \neq K_2^*$ the apparent TCP appears slightly before $M=1$. Such a dependence also justifies the experimental fact that the effective critical exponents fall on the same universal curve as seen in Fig. 1. when they are plotted as a function of M. Another dependence with the density (as proposed by Anisimov et al [10]) or the molecular length will not explain such a universal behaviour.

The fact that C depends on M suggest even stronger coupling effects, because not only do the constants A and B depend on the orientational order parameters, but also C seems to depend on the amplitude of the Nematic phase region above the Smectic-Nematic phase transition line.