Critical behavior of a system with orientational and positional degrees of freedom: A Monte Carlo simulation study

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The critical behavior 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 behavior 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-crystal 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 center 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_0) 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 behavior 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 Monte Carlo (MC) 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 behavior 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 behavior 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 Sec. 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 crystal's phase diagrams. Also some Monte Carlo simulations were performed in order to test the main features of the phase dia-

gram.[16] In Sec. III we present the raw Monte Carlo results. In Sec. IV we focus our attention on the critical behavior of the positional transition occurring at T_p. Our studies indicate that the behavior 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 behavior of liquid crystals found in literature.[11,12,17] Finally, in Sec. 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 ($i=1,\ldots,N$) 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:

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

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 nonpolar molecules and only $n=4$ possible orientations equally distributed on the lattice plane [see Fig. 1(a)].

This restriction of $n=4$ is, of course, quite important and is made in order to simplify the MC 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 three 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.

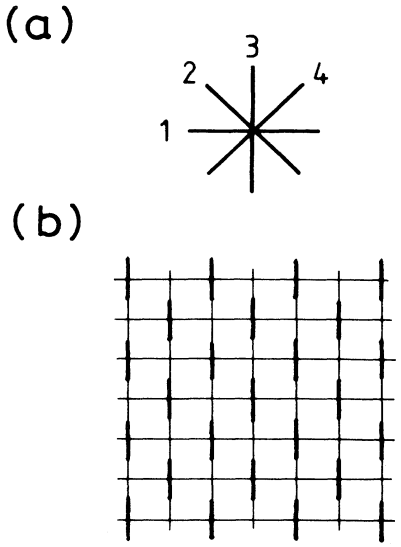

FIG. 1. (a) Four possible directions of the molecules on the surface. (b) Ground-state configuration.

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

$$H=J_1\sum_{i,j}^{\mathrm{NN}} S_iS_j+K_1\sum_{i,j}^{\mathrm{NN}} S_iS_jP(R_i,R_j) +K_2\sum_{i,j}^{\mathrm{NNN}} S_iS_jP(R_i,R_j) \ , \tag{2}$$

where $\sum^{\mathrm{NN}}$ ($\sum^{\mathrm{NNN}}$) is a summation over all nearest-neighbor [next-nearest-neighbor, NNN] 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

$$P(R_i,R_j)=2[\cos^2(\theta_{ij})-1] \ , \tag{3}$$

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 neighbors (NN). The other two terms, with K_1 and K_2 negative, are orientational interaction terms which favor parallel alignment of the molecules.

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

$$H^*=\frac{H}{J_1}, \quad T^*=\frac{T}{k_BJ_1}, \quad K_1^*=\frac{K_1}{J_1}, \quad K_2^*=\frac{K_2}{J_1} \ , \tag{4}$$

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

$$H^*=\sum_{i,j}^{\mathrm{NN}} S_iS_j+K_1^*\sum_{i,j}^{\mathrm{NN}} S_iS_jP(R_i,R_j) +K_2^*\sum_{i,j}^{\mathrm{NNN}} S_iS_jP(R_i,R_j) \ . \tag{5}$$

The phase diagram of this model has been already studied with mean-field techniques[15] and Monte Carlo simulation[16] in previous papers. A detailed study shows that when $-1.0<K_1^*<0$ and $-1.0<K_2^*<0$ then the ground state of the system is that of Fig. 1(b). This ground state is eight times degenerated because there are four possible orientations and two possible sublattices to fill. From now on, in a given configuration of the system we will call the + (−) sublattice the one that is more (less) populated.

As the temperature is increased, this ground state permits the molecules to be positionally and orientationally disordered. In order to study these phenomena, it is useful to define a positional order parameter (m_p) and two orientational order parameters (m_0^+ and m_0^-) associated with the two sublattices + and − as

$$m_p = \left[\sum_i^+ S_i - \sum_i^- S_i \right] / N_p \ , \tag{6}$$

$$m_0^+ = \left[\sum_i^+ \delta(R_i - R_{\max}) - \sum_i^+ \delta(R_i - R_{\min}) \right] / N_p \ , \tag{7}$$

$$m_0^- = \left[\sum_i^- \delta(R_i - R_{\max}) - \sum_i^- \delta(R_i - R_{\min}) \right] / N_p \ , \tag{8}$$

where δ is a Kronecker delta function [$\delta(0)=1$ or 0 otherwise], $\sum^+$ ($\sum^-$) is a summation over the + (−) sublattice, $R_{\max}$ is the preferred direction of the molecules for a given configuration, and $R_{\min}$ is the direction perpendicular to $R_{\max}$. These definitions are used in order to avoid problems associated with the degeneration of the ground state. With these definitions m_p, m_0^+, and m_0^- are always positive.

III. MONTE CARLO SIMULATION

Monte Carlo simulations have been performed on a 40×40 lattice with $N_p=800$ with periodic boundary conditions and using standard Metropolis algorithm.[21,22] A combination of Glauber dynamics changing the orientations and Kawasaki dynamics exchanging particles and holes has been used. Finite-size effects have been corrected using the subblock methd[23] which enables to extrapolate the results to the case $L\to\infty$. Usual runs are carried up to 12 000 MC steps per particle. Averages of the quantities of interest like order parameters ($\langle m_p \rangle$, $\langle m_p^2 \rangle$, $\langle m_0 \rangle$, $\langle m_0^2 \rangle$), energy ($\langle E \rangle$), etc., are taken over 500 uncorrelated configurations, after discarding the first 10^4 MC steps. The normal correlation time is about 4 MC steps, except near the phase transitions where averages over different evolutions corresponding to different seeds of the random numbers generator have been taken in order to improve the statistics.

Different points of the phase diagram have been simulated. Depending on the values of K_1^* and K_2^* one can find two different behaviors (Fig. 2 shows the different

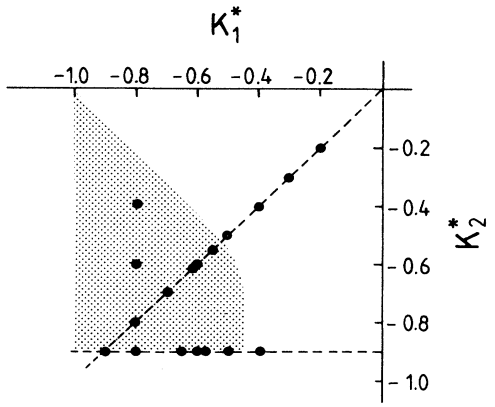

FIG. 2. Dots represent the different points (K_1^*, K_2^*) that have been studied by Monte Carlo simulation in the region where the ground state is that of Fig. 1. Discontinuous lines are the sections along which the phase diagram is represented in Fig. 3. The dot shadowed area is the region where the liquid crystal-like behavior has been found and the nonshadowed area is the region where the plastic crystal-like behavior has been found.

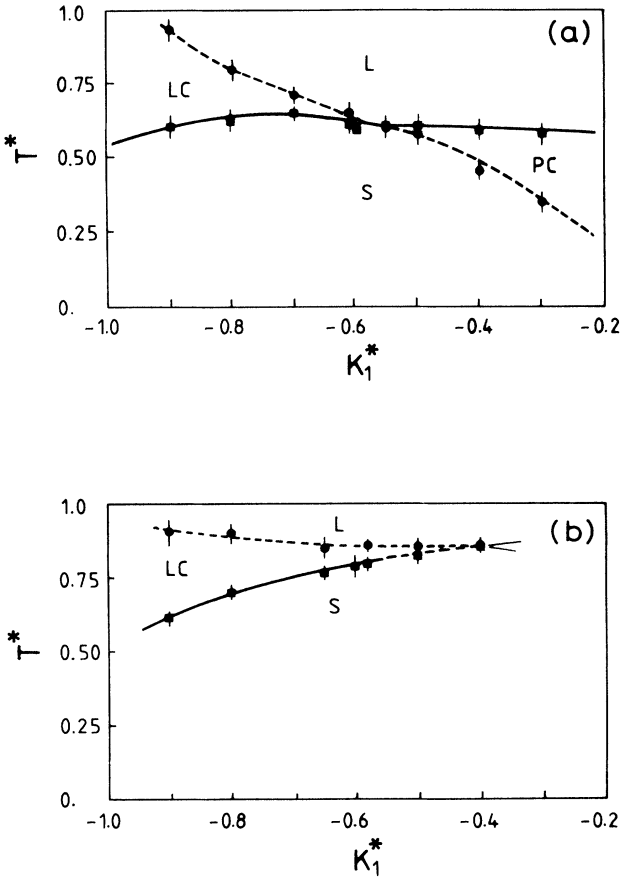

FIG. 3. Sections of the phase diagram along the lines shown in Fig. 2. (a) $K_1^*=K_2^*$ and (b) $K_2^*=-0.9$. Lines are guides to the eye.

sections and points that have been studied and the regions where the two behaviors occur). When K_1^* and K_2^* are sufficiently negative, the positional order disappears at a lower temperature (T_p) than the orientational order (T_0). Between these two temperatures a phase with only long-range orientational order (LC phase) is stable. Otherwise, when K_1^* and K_2^* are small, one finds $T_0<T_p$ and a phase with only long-range positional order (PC phase) appears.

Figures 3(a) and 3(b) give the sections of the phase diagram along the dashed line plotted in Fig. 2. The four phases S, LC, PC, and L are clearly identified. Changing the value of the orientational constants K_1^* or K_2^*, one can change from a liquid crystal behavior to a plastic crystal behavior.

Figure 4 shows the evolution (extrapolated to $L\to\infty$) of the positional order parameter in two different cases. Case (a) corresponds to $K_1^*=-0.9$, $K_2^*=-0.9$ and case (b) to $K_1^*=-0.5$, $K_2^*=-0.9$. Performing long enough simulations the results do not depend on the starting configuration any more and a first-order transition produces then a broadening due to the existence of long metastable states. For instance, in case (b) all data are obtained starting from a disordered state and using several random number generator seeds. The values of

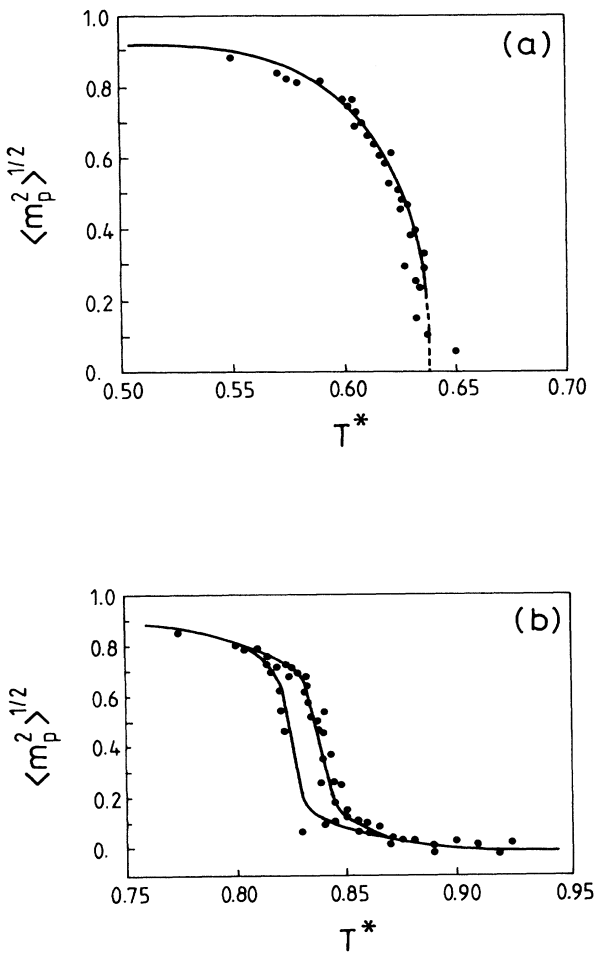

FIG. 4. Detailed order parameter evolution versus temperature. Case (a) corresponds to $K_1^* = -0.9$ and $K_2^* = -0.9$, while case (b) corresponds with $K_1^* = -0.5$ and $K_2^* = -0.9$. (b) Exhibits some hysteresis that is not present in (a).

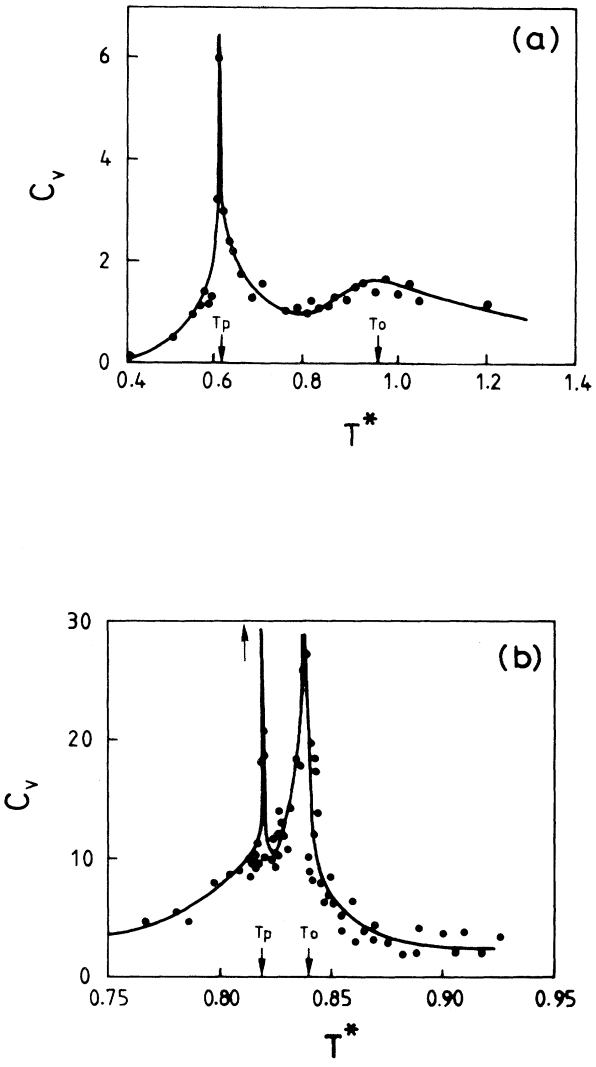

FIG. 5. Specific heat (C_v) evolution with temperature when (a) $K_1^* = -0.9$, $K_2^* = -0.9$ and (b) $K_1^* = -0.5$, $K_2^* = -0.9$. T_p and T_0 indicate the positions of the positional and orientational transition. The line is a guide to the eye.

the upper branch correspond to runs that have jumped to the low-temperature phase while the values of the lower branch correspond to runs that have not jumped. We have suppressed the values corresponding to runs that jump during the average procedure and give spurious values between the two branches. The lines are guides to the eye showing the two envelopes of the obtained results.

In Fig. 5 examples of the variation of the specific heat C_v with T^* are shown for the same two cases (a) and (b) of Fig. 4. It is calculated as the extrapolation to $L \to \infty$ of C_{vL}, calculated as

$$C_{vL} = \frac{N_{pL}}{T^{*2}} (\langle E^2 \rangle_L - \langle E \rangle_L^2) . \tag{9}$$

As in the case of the order parameters in case (b) only the envelope of the obtained values is plotted, and the values corresponding to runs with a jump during the average procedure have been suppressed. The peak of the specific heat has been used in order to have an estimation of the transition temperature T_p with an accuracy of the order of $\Delta T \approx 0.01$.

IV. CRITICAL BEHAVIOR

The orientational transition has previously been identified as a first-order phase transition due to the hysteresis shown in the evolution of $\langle m_0 \rangle$ and the broad peak in susceptibilities and specific heat. This broadening, due to the hysteresis, appears because data are obtained after averaging over different runs with different random number generator seeds. This fact was pointed out by the authors already in the first simulations of this system.[16] Here, we will mainly focus our attention on the nature of the positional transition between the S phase and the LC phase.

As can be seen in the evolution of the positional order parameters (Fig. 4), no hysteresis has been found when the two phase transitions (T_p and T_0) are separated enough (a), while when the LC phase region is narrow hysteresis appears (b). This hysteresis does not produce a broadening of the C_v peak, possibly because it is very weak. These results suggest that there is a change in the character of the positional transition between cases (a) and (b).

In order to clarify the nature of the positional transition we have used a finite-size-scaling method proposed recently.[24] In this method the Gaussian character of the energy distribution function is tested using the quantity

$$V_L = 1 - \frac{\langle E^4 \rangle_L}{3\langle E^2 \rangle_L^2} \ . \tag{10}$$

In the limit of $L \to \infty$, V_L should always tend to the value $\frac{2}{3}$ except at a first-order phase transition where V_L tends to a smaller value related to the latent heat.

Figure 6 shows the dependence of V_L for the same cases as in Figs. 4 and 5, for the different subblock sizes

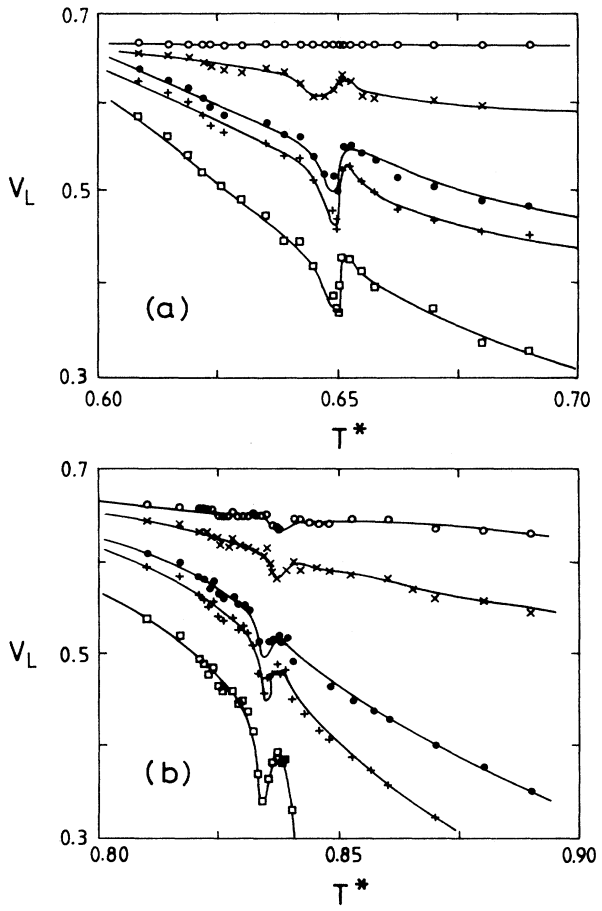

FIG. 6. Dependence of V_L with T^* for the different subblock sizes [$L=40$ (○), 20 (×), 10 ●, 8 (+), 4 (□)]. Case (a) corresponds to $K_1^* = -0.9$, $K_2^* = -0.9$ and case (b) to $K_1^* = -0.5$, $K_2^* = -0.9$.

($L=40$, 20, 10, 8, 4). In both cases one can see the existence of a minimum associated to the positional transition that appears overlapped with another broader well (only partially shown) that corresponds to the first-order orientational transition. The position of the peaks of the specific heat curves are always located at the left side of the V_L minima. In case (a) the lack of Gaussian character of the energy distribution has practically disappeared at $L=40$, while in case (b) it clearly still remains. This result justifies the continuous nature of the positional phase transition in case (a) and its first-order character in case (b), in agreement with the results deduced from the hysteresis considerations.

We have also studied the effective critical exponent β of this positional transition. This exponent is calculated fitting a simple power law,

$$m_p = A \left[\frac{T_p - T^*}{T_p} \right]^{\beta} \tag{11}$$

in a region of temperatures ranging between $0.95T_p$ and T_p. The adjusted effective exponent may differ from the real critical β exponent which is defined by expression (11) in the limit $T \to T_p$. This difference could be quite important if the critical region is very narrow. Nevertheless, this exponent is the one that should be comparable with experiments, due to the finite temperature resolution in most of the experimental systems.

The fit has been done using standard logarithmic least-squares method on the data, corresponding to the evolution of $\langle m_p^2 \rangle$ versus temperature (extrapolated to $L \to \infty$). Two values of β exponents have been adjusted in each case, corresponding to consider a fit with $T_p + \Delta T$ and $T_p - \Delta T$ as transition temperatures.

This is probably not the best procedure to determine very accurate critical exponents. Methods based on finite-size scaling theories[22] can produce better estimations, but they are extremely computer time consuming. Since our objective is not to obtain absolute values of the β exponent, but to show possible relative changes, this relatively simple way seems accurate enough.

Along the two sections indicated in Fig. 2, we have fitted Eq. (11) to the points obtained after extrapolating the Monte Carlo simulation data to $L \to \infty$. Figures 7(a) and 7(b) show the fitted values of the β exponent corresponding to the two sections mentioned before. Error bars arise from the two extreme values of β obtained as indicated before.

The exponent changes from a large value near the two-dimensional Ising-model universality class when the two transitions are separated enough, to a smaller (or vanishing) value when the two transitions are closer. This fact gives further evidence of the change from a second-order transition to a possible first-order transition as indicated on the phase diagram sections [Figs. 3(a) and 3(b)]. We can conjecture, then, the existence of a tricritical point that appears when the two transitions are very close.

The region where the critical behavior changes is narrower in the case $K_1^* = K_2^*$ than in the case $K_2^* = -0.9$. An explanation to this behavior is that, if the orientation-

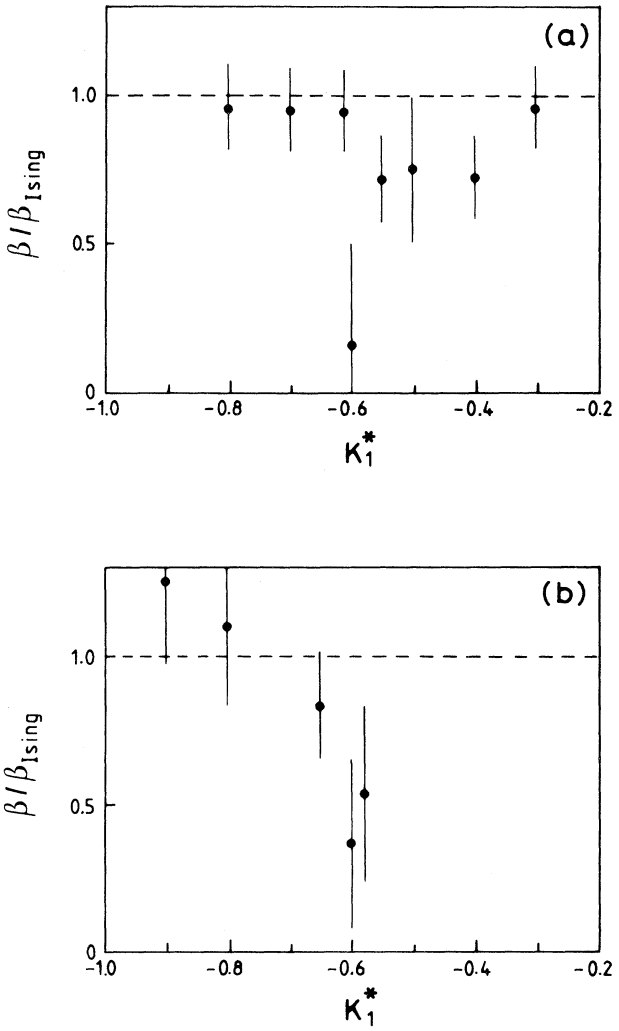

FIG. 7. β exponents calculated adjusting a power-law fit to the Monte Carlo data along the lines $K_1^*=K_2^*$ (a) and $K_2^*=-0.9$ (b). Error bars are associated to the deviations on the adjusted exponents due to the indetermination of T_p, as explained in the text.

al interactions at NNN and NN are equal, it is reasonable to think that the positional transition (which can be seen as a transition disordering NNN pairs to NN positions) is less affected. The mean-field solution of this model is also in agreement with that explanation.[15]

These results can be qualitatively compared with some measurements made with different pure liquid crystals or liquid crystal mixtures using calorimetric and x-ray scattering techniques.[11,12,17] Despite the large amount of phases that these systems exhibit we will focus on the so called smectic-nematic and nematic-isotropic transitions corresponding to the complete vanishing of the long-range positional order and the long-range orientational order, respectively. The temperature separation between these two transitions, or in other words the width of the nematic region, is different in each particular liquid crystal and depends mainly on the ratio between the orientational and positional interactions.

Mixing liquid crystals with different molecule lengths but similar chemical properties opens the possibility of changing the effective orientational interaction and controlling its value by controlling the composition of the mixtures. This can be compared with the role played by the constants K_1^* and K_2^* in our model. Experiments have been done with mixtures of alkylbenzoate liquid crystals (nCB).[12] The resulting phase diagram can be qualitatively compared to the liquid crystal region of the phase diagrams shown in Figs. 3(a) and 3(b). The width of the nematic (LC phase) region decreases when the composition of the mixture is changed. The two transitions, smectic-nematic (corresponding to T_p) and nematic-isotropic (corresponding to T_0), have been found to overlap at a given composition.[12]

In good agreement with our results different authors have reported the existence of a change in the critical behavior of the smectic-nematic transition and the existence of a tricritical point.[12] This agreement is surprising if one notes that in principle a liquid crystal is a three-dimensional system, while our model is only two-dimensional. A possible explanation of this fact is that the smectic phase is basically a layered structure and may behave as if it had a dimensionality less than three.

β effective critical exponents have been measured on different liquid crystals and liquid crystal mixtures.[11,12,17] Figure 8 shows some results of such measurements found in the literature as a function of the McMillan parameter M, defined as

$$M=\frac{T_{SmN}}{T_{NI}} \tag{12}$$

which measures the relation between the orientational and positional interaction energies, and which can be qualitatively compared to the ratio T_p/T_0. The exponents measured experimentally are scaled by the ex-

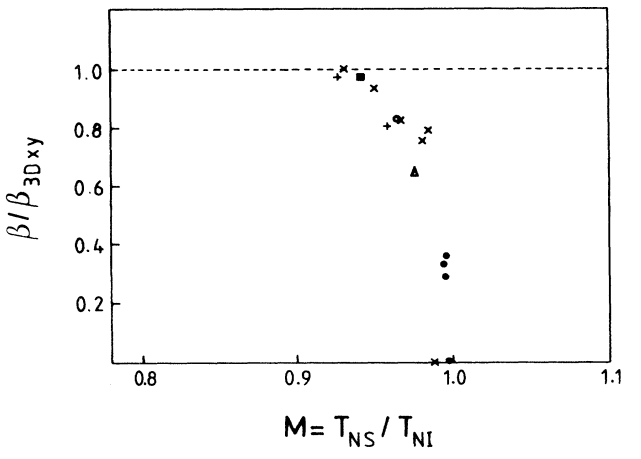

FIG. 8. Values of the β exponents versus the McMillan parameter defined in the text. Different symbols show different experimental values collected from literature: × nS5 (Ref. 12), ■ CBOOA (Refs. 11 and 17), + 40.8-40.7 (Ref. 11), △ 8CB (Ref. 11), ● 9CB-10CB (Ref. 12), ○ 8OCB (Refs. 11 and 17).

ponents corresponding to the 3D XY model universality class to which such liquid crystals are supposed to belong. The diagram is very similar to those given in Figs. 6(a) and 6(b) and shows that when the two transitions are very close, coupling phenomena appear and the behavior of the positional phase transition changes from second order to first order.

V. SUMMARY AND CONCLUSIONS

A model that reproduces some features of pure liquid crystals and liquid crystal mixtures phase diagrams, presented recently,[15,16] has been studied. The model considers the positional degrees of freedom of the molecules as a lattice gas but introduces an extra variable taking into account the orientational degrees of freedom of the molecules. Two different phase transitions appear, each associated with one of the degrees of freedom. For certain values of the interaction constants we are able to reproduce the liquid crystal behavior, where the transition associated to the positional degrees of freedom (T_p) corresponds to the smectic-nematic transition, and the transition associated with the orientational degrees of freedom (T_0) corresponds to the nematic-isotropic transition. The model reproduces the fact that the ratio between the positional and orientational interactions controls the width of the nematic phase.

We have studied by means of Monte Carlo simulations the critical behavior of this model. The orientational transition, as seen in preliminary simulations, is first order, in agreement with the experimental results on the nematic-isotropic transition. The positional transition changes from a second-order behavior to possibly first-order behavior when the nematic region above T_p is narrow enough. This fact has also been reported by experiments on liquid crystal mixtures.

We have also measured the effective β exponent of the positional transition in order to locate the possible tricritical point. We have found that when the two transitions are very close the β exponent decreases indicating a possible change to a first-order phase transition. This fact compares well with experimental data collected from the literature.

Therefore, we can conclude that the coupling phenomena that appear in liquid crystals, like the existence of a tricritical point and its dependence on the nematic phase width, seems to be closely related to the competition between the orientational and positional degrees of freedom, rather than to the detailed microscopic interaction.

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