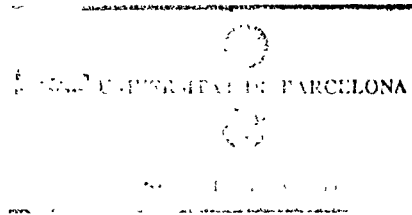


**SIMULACIO MONTE CARLO DE SISTEMES  
AMB ACOBLAMENT DE GRAUS DE LLIBERTAT.**



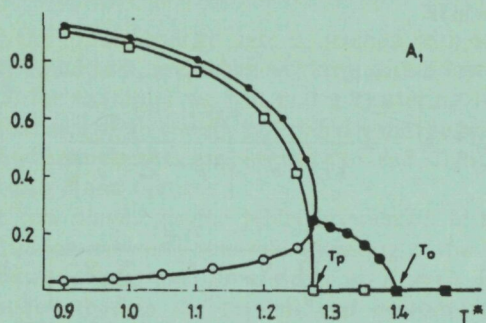


FIG. 5. Evolution of the order parameters vs temperature in the  $A_1$  zone (Fig. 9). The values have been calculated by solving numerically the mean-field equations (15) with  $K_1^* = -0.4$  and  $K_2^* = -1.0$ . ( $\square$ ,  $m_p$ ;  $\bullet$ ,  $m_1^+$ ;  $\circ$ ,  $m_1^-$ .)  $T_p$  and  $T_o$  are the positional and orientational transition temperatures, respectively. This case corresponds to the behavior of a liquid crystal with  $T_p < T_o$ . (The lines are guides to the eye.)

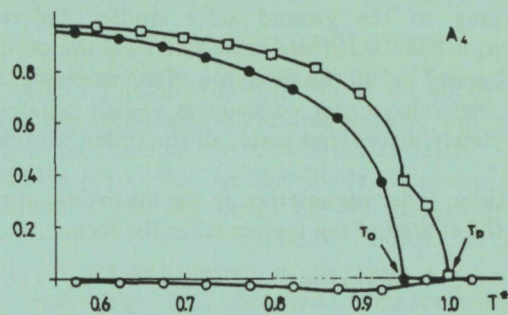


FIG. 8. Evolution of the order parameters vs temperature in the  $A_4$  zone (Fig. 9). The values have been calculated by solving numerically the mean-field equations (15) with  $K_1^* = 0.2$  and  $K_2^* = -0.6$ . ( $\square$ ,  $m_p$ ;  $\bullet$ ,  $m_1^+$ ;  $\circ$ ,  $m_1^-$ .)  $T_p$  and  $T_o$  are the positional and orientational transition temperatures, respectively. (The lines are guides to the eye.)

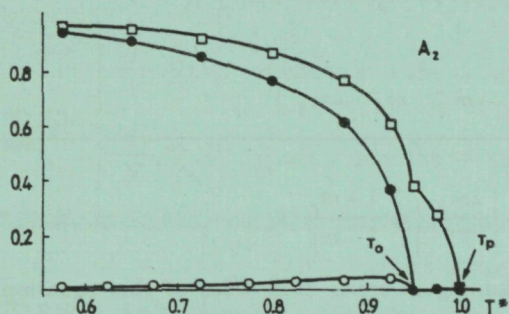


FIG. 6. Evolution of the order parameters vs temperature in the  $A_2$  zone (Fig. 9). The values have been calculated by solving numerically the mean-field equations (15) with  $K_1^* = -0.2$  and  $K_2^* = -0.6$ . ( $\square$ ,  $m_p$ ;  $\bullet$ ,  $m_1^+$ ;  $\circ$ ,  $m_1^-$ .)  $T_p$  and  $T_o$  are the positional and orientational transition temperatures, respectively. This case corresponds to the behavior of a plastic crystal with  $T_p > T_o$ . (The lines are guides to the eye.)

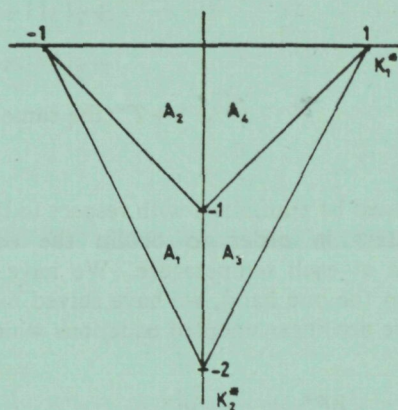


FIG. 9. Detail of the  $T=0$  phase diagram [Fig. 4(a)] showing the regions where the four different mean-field solutions of Figs. 5–8 have been found. All the regions correspond to the same ground state but have different evolutions with rising temperature.

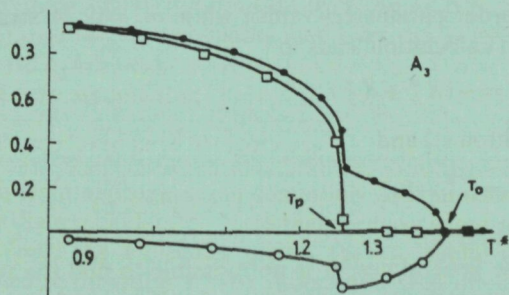


FIG. 7. Evolution of the order parameters vs temperature in the  $A_3$  zone (Fig. 9). The values have been calculated by solving numerically the mean-field equations (15) with  $K_1^* = 0.4$  and  $K_2^* = -1.0$ . ( $\square$ ,  $m_p$ ;  $\bullet$ ,  $m_1^+$ ;  $\circ$ ,  $m_1^-$ .)  $T_p$  and  $T_o$  are the positional and orientational transition temperatures, respectively. (The lines are guides to the eye.)

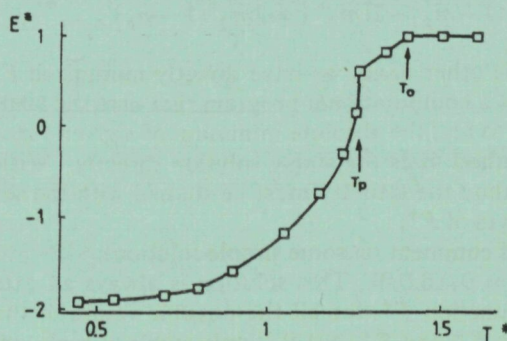


FIG. 10. Plot of the energy  $E^*$  vs temperature  $T^*$  showing the two transitions  $T_p$  and  $T_o$ . The values have been obtained by solving numerically the mean-field equations with  $K_1^* = -0.4$  and  $K_2^* = -1.0$ . (The line is a guide to the eye.)



where each one of the four solutions  $A_1$ ,  $A_2$ ,  $A_3$ , and  $A_4$  is stable. It is worth noting that in the border lines  $A_1$ - $A_2$  and  $A_3$ - $A_4$ ,  $T_p^*$  equals  $T_o^*$ .

In the  $A_1$  region the system behaves as a liquid crystal, while in the  $A_2$  region it behaves as a plastic crystal. In the  $A_3$  and  $A_4$  zones the order parameters show, respectively, the same evolution with temperature as in regions  $A_1$  and  $A_2$ , but with  $m_1^-$  negative.

We note that when one of the two possible modes (orientational or positional) vanishes, the remaining order parameters show a slower decay with increasing temperature. This effect has also been found in general studies of systems with coupled order parameters, using the Landau theory.<sup>3</sup>

Now we will focus our attention on the study of the  $A_1$  region, since it reproduces qualitatively the behavior exhibited by liquid crystals. In Figs. 10 and 11 we have represented, respectively, the energy and the specific heat as a function of the temperature. It is clear that the specific heat shows two singularities associated with both the smectic-nematic and nematic-isotropic phase transitions. Theoretical studies on these transitions<sup>19</sup> and experimental results<sup>20</sup> show that the smectic-nematic transition is continuous and the nematic-isotropic is first order.

Due to the numerical method used to obtain the order parameters as a function of temperature it is difficult to decide if the energy curve presents some discrete jumps or not. Consequently there is a difficulty in knowing the order of the transitions. In our 2D model we have considered molecules with a discrete number of orientations so, *a priori*, it will not exhibit the same transition behavior as real systems. However, it seems clear that the smectic-nematic transition has a continuous character. The order of the nematic-isotropic transition is less evident but also seems to be continuous or at least weakly first order.

Calculating the temperatures  $T_o^*$  and  $T_p^*$  for different values of the parameters  $K_1^*$  and  $K_2^*$  we obtain the phase diagram of the system. In Figs. 12 and 13 some sections of this diagram are plotted. We have also represented the corresponding analytical expressions for the temperatures  $T_o^*$  and  $T_p^*$  previously obtained, with dashed and solid

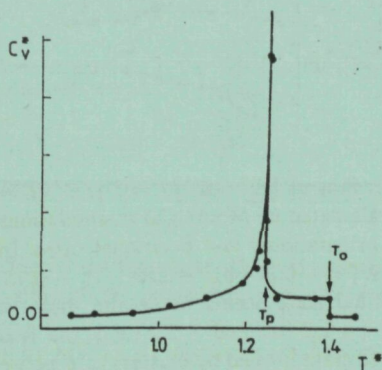


FIG. 11. Numerical derivative of  $E^*$  (Fig. 10), showing the evolution of the specific heat vs temperature in the mean-field approximation.  $T_p^*$  and  $T_o^*$  correspond to the smectic-nematic and nematic-isotropic transition temperatures, respectively. (The line is a guide to the eye, and vertical units are arbitrary.)

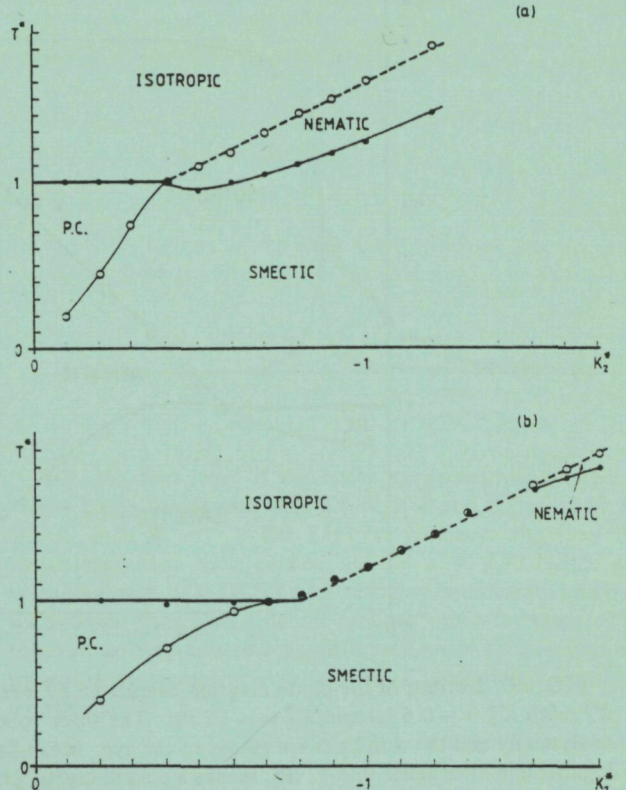


FIG. 12. Sections of the phase diagram calculated by mean-field approximation. The  $T_p^*$  ( $\bullet$ ) and  $T_o^*$  ( $\circ$ ) are plotted for different values of  $K_2^*$  with  $K_1^* = -0.6$  (a) and  $K_1^* = -0.2$  (b). The thick solid and the thick dashed lines are the  $T_p^*$  and  $T_o^*$  calculated analytically and the thin lines are guides to the eye. (PC means a plastic-crystal phase with long-range positional order but not long-range orientational order.)

lines, respectively. As can be seen in the figures there is a good agreement between both numerical and analytical methods. We note that when  $K_2^*$  is very negative the numerical minimization of  $F^*$  is very difficult due to the logarithmic divergence of some terms in  $F^*$ , and the corresponding points in the phase diagrams are obtained with a poor resolution.

#### IV. MONTE CARLO SIMULATION

A numerical simulation of our system is necessary in order to improve the mean-field solution. In most systems Monte Carlo simulation allows us to understand aspects neglected by the mean-field theory. With this idea, we have designed a Monte Carlo simulation program for our model, with the usual method proposed by Metropolis *et al.*<sup>21</sup>

The Monte Carlo simulation of a physical system can be performed using different dynamics. The two principal ones are Glauber dynamics,<sup>22</sup> used when the order parameter is not conserved, and Kawasaki dynamics,<sup>23</sup> which apply to the case of a system with conserved order parameter. The simulation of our system imposes changes keeping the number of molecules  $N_p$  constant, but leaving the number of molecules in a certain orienta-



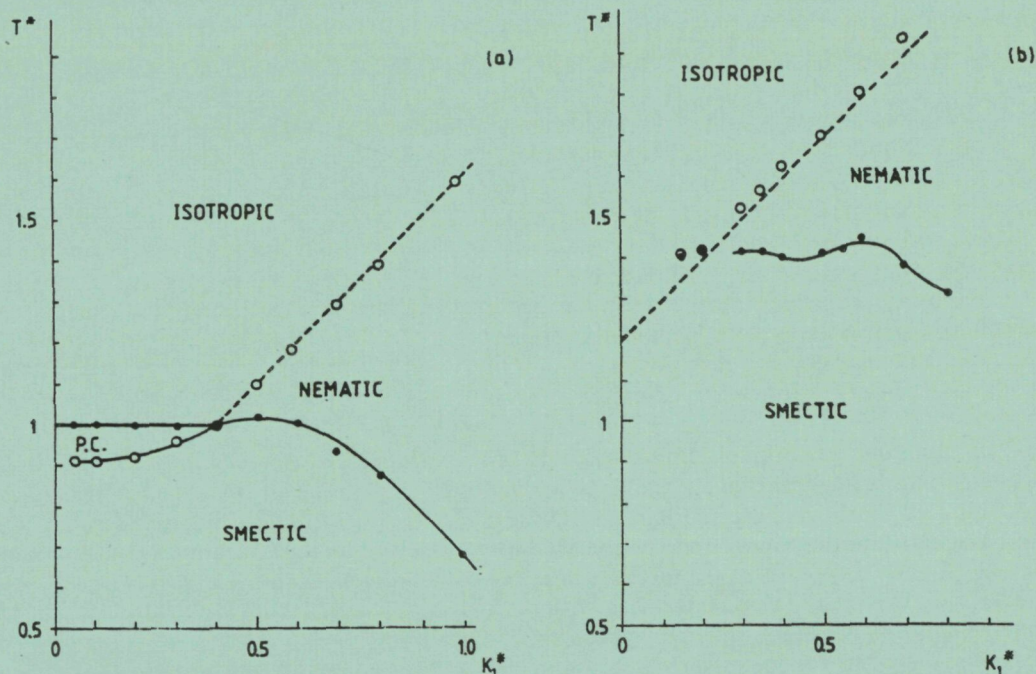


FIG. 13. Sections of the phase diagram calculated by mean-field theory. The  $T_p$  ( $\bullet$ ) and  $T_o$  ( $\circ$ ) are plotted for different values of  $K_1^*$  with  $K_2^* = -0.6$  (a) and  $K_2^* = -1.2$  (b). The thick solid and the thick dashed lines are the  $T_p$  and  $T_o$  temperatures calculated analytically and the thin lines are guides to the eye. Mean-field equations with large values of  $K_2^*$  and  $K_1^*$  are difficult to solve due to logarithmic divergence in  $F^*$ . (PC means a plastic-crystal phase with long-range positional order but not long-range orientational order.)

tion ( $N_\sigma^+, N_\sigma^-$ ) to be variable. This suggests the use of mixing of the two dynamics, exchanging pairs of particles and simply changing their orientation.

Glauber dynamics is faster than Kawasaki dynamics. The use of both simultaneously implies that the mechanism that changes the orientation of the particles is faster than the mechanism that interchanges particles. In fact, this is not a bad hypothesis for our system. We have not studied the relaxation to equilibrium of our system, but of course this would be a very interesting thing to do in order to analyze the competition of both dynamics.

Our simulations have been carried out on lattices with  $30 \times 30$  or  $40 \times 40$  sites with periodic boundary conditions. Usual runs of 3000–5000 Monte Carlo steps (MCS's) (1 MCS = 1 orientational change attempt per site and 1 positional interchange attempt per site) have been performed. The proposed changes are accepted or not by using an exponential transition probability.<sup>24</sup> The calculation of the numerical values of the variables of interest has been done by averaging over 1000 equilibrium configurations and in some cases (order parameters) we have also averaged over six different runs with different random number generator seeds.

In most cases we have performed two kinds of evolutions to equilibrium: first, starting with a complete ordered structure until reaching the equilibrium state at a given temperature, and second, starting with a disordered state. In both cases the final values of the different calcu-

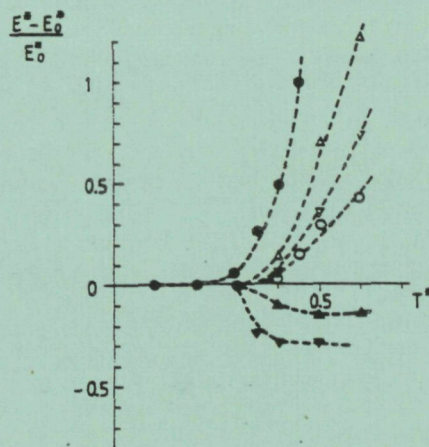


FIG. 14. Plot of  $[E^* - E^*(T=0)]/E^*(T=0)$  at low temperatures calculated by Monte Carlo simulations from an initial state with orientational and positional order [phase A in Fig. 4(c)]. For  $K_1^* = -0.25$  ( $\bullet$ ),  $-0.50$  ( $\Delta$ ),  $-0.75$  ( $\nabla$ ), and  $-1.0$  ( $\circ$ ) the initial state seems to be the most stable, while for greater  $K_1^*$  [ $-1.5$  ( $\blacktriangle$ ) and  $-2.0$  ( $\blacktriangledown$ )], the energy decays to a most ordered state formed by clusters of B phase [Fig. 4(c)]. All the curves are calculated on the line  $K_2^* = K_1^*/\sqrt{2}$ . The A ground-state phase seems to be stable slightly far away from the border line between A and B phases represented in Fig. 4(a). The simulations have been carried out on a  $30 \times 30$  lattice and averaging over 1000 MCS's.



lated quantities agreed quite well.

First of all, we have performed Monte Carlo runs at low temperature in order to obtain the ground state of the system. The structure predicted using Karl's theorem in zone *A* (Fig. 4) has not only been confirmed, but even extended a little into the *B* zone. As discussed in Sec. II, the main reason for this change is certainly the extra energy associated with the boundaries of the clusters in the *B* zone when the particle density is 0.5, as in our case.

In Fig. 14 we have represented  $[E^* - E^*(T^*=0)]/E^*(T^*=0)$  at low  $T^*$  for different values of  $K_1^*$  and with  $K_2^* = K_1^*/\sqrt{2}$ . These values of  $E^*$  have been obtained starting with a configuration corresponding to the theoretical ground state obtained from Karl's theorem, and reaching equilibrium at a given temperature. When  $K_1^* < -1$  the metastable state at very low temperatures decays to a state of lower energy: clusters of the *B* phase are formed. With  $K_1^* > -1$  this effect does not occur since the *A* phase is in the most stable structure. In this particular case ( $K_2^* = K_1^*/\sqrt{2}$ ) the theoretical limit between *A* and *B* phases calculated by using Karl's theorem is reached at  $K_1^* = -0.739$ , but the *A* phase seems to be stable until  $K_1^* = -1.0$ .

In Fig. 15 we show the section of the phase diagram along the line  $K_2^* = K_1^*/\sqrt{2}$  and we compare it with the corresponding phase diagram obtained with the mean-field approximation. The general aspect of both are the same, but the transition temperatures are lower in the Monte Carlo calculations.

This is, in fact, the usual result when comparing

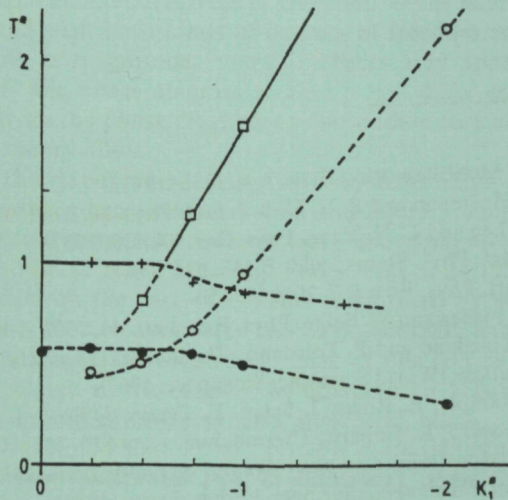


FIG. 15. Section of the phase diagram calculated by Monte Carlo (MC) simulations compared with the mean-field (MF) solution. The section is made over the line  $K_2^* = K_1^*/\sqrt{2}$ . (+,  $T_p$  calculated by MF; □,  $T_o$  calculated by MF; ●,  $T_p$  calculated by MC; and ○,  $T_o$  calculated by MC.) The solid lines are the analytical solutions from Eqs. (15) and the dashed lines are guides to the eye. Both phase diagrams are qualitatively equal; however, MC calculations give lower transition temperatures. The simulations have been carried out on a  $30 \times 30$  lattice and averaging over 1000 MCS's after reaching equilibrium.

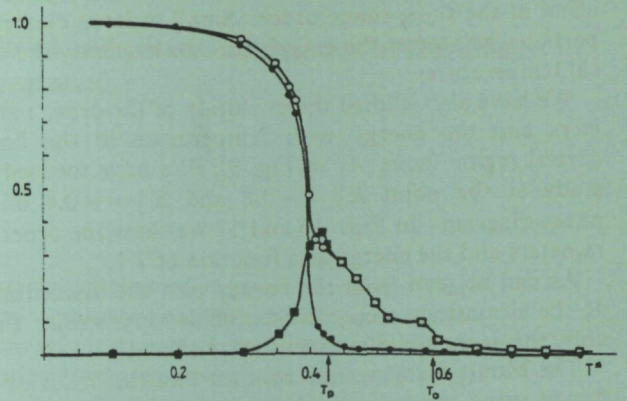


FIG. 16. Evolution of the order parameters calculated by Monte Carlo simulations with  $K_1^* = -0.8$  and  $K_2^* = -0.4$ . (●,  $m_p$ ; ○,  $m_1^+$ ; ■,  $m_1^-$ .) The lines are guides to the eye. The simulations have been carried out on a  $40 \times 40$  lattice and averaging over 1000 MCS's after reaching equilibrium and over six different runs with different random generator seeds. This behavior corresponds to a liquid crystal with  $T_o$  (orientational transition temperature) greater than  $T_p$  (positional transition temperature).

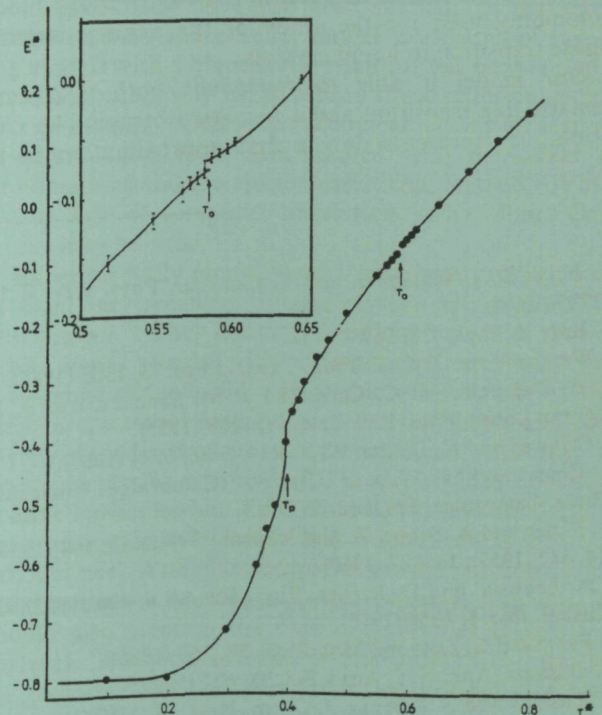


FIG. 17. Evolution of the energy  $E^*$  calculated by Monte Carlo simulations in the same conditions as in Fig. 16. The smectic-nematic transition ( $T_p$ ) and the nematic-isotropic transition ( $T_o$ ) are little masked by the finite-size effects. The inset shows the detail of the orientational transition. (The error bars in the inset show the standard deviation of the values.)



mean-field and exact results, since mean field neglects the effect of the short-range order. Small ordered clusters of particles will lower the energy and consequently the critical temperatures.

We have also studied the evolution of the order parameters and the energy with temperature in the liquid-crystal region (zone  $A_1$  in Fig. 9). We have focused our study at the point  $K_1^* = -0.8$  and  $K_2^* = -0.4$  of the phase diagram. In Figs. 16 and 17 we show the order parameters and the energy as a function of  $T^*$ .

As can be seen from the energy plot the discontinuity at the nematic-isotropic transition is very weak. Probably, this is mainly due to finite-size effects.

The Monte Carlo results confirm that the behavior obtained using the mean-field approximation is correct, at least, at a qualitative level.

## V. SUMMARY

In this work we have studied the phase diagram of a 2D lattice-gas model of rodlike molecules which can exhibit four possible different orientations. In addition to the antiferromagneticlike positional interaction energy between molecules, the Hamiltonian of the system also contains a nonpolar orientational interaction between nearest and next-nearest neighbors. In its dimensionless form, the Hamiltonian depends on two parameters,  $K_1^*$  and  $K_2^*$ , which correspond, respectively, to the ratio between the NN and the NNN orientational interactions and the positional one. The orientational interaction is similar to the one considered in the Maier-Saupe model, commonly used for the study of the nematic-isotropic phase transition in liquid crystals.

Our model is able to reproduce both a smectic-nematic-like transition and a nematic-isotropic-like transition. It represents only a first approximation to the

study of the behavior of real systems. Its relative simplicity, however, allows us to analyze the interdependence of the orientational and the positional components of the interaction determining its influence on the phase diagram of such kinds of systems. The ground state of the model has been investigated on the basis of Karl's theorem. For different values of the two parameters, the system can show a rich variety of structures. We have focused our attention on the region compatible with the expected behavior exhibited in liquid crystals. In this region the Monte Carlo simulation results have confirmed the ground state predicted by Karl's theorem.

We have investigated the properties of the system in this region by mean-field calculation and using the Monte Carlo simulation technique. The mean-field results have been qualitatively confirmed when compared with the Monte Carlo simulations.

The shape of the energy and heat-capacity curves versus temperature, for both the smectic-nematic and nematic-isotropic transitions seems at a qualitative level comparable with those found experimentally in some real systems. Nevertheless, the order of the transitions involved in the model has not been obtained unambiguously. It seems, however, that the smectic-nematic transition has a continuous character, while the nematic-isotropic transition could also present a continuous or at least weakly first-order character.

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# Lattice-gas model of particles with orientational and positional degrees of freedom: Mean-field treatment

We consider a lattice-gas model of particles with internal orientational degrees of freedom. In addition to antiferromagnetic nearest-neighbor (NN) and next-nearest-neighbor (NNN) positional interactions we also consider NN and NNN interactions arising from the internal state of the particles. The system then shows positional and orientational ordering modes with associated phase transitions at  $T_p$  and  $T_o$  temperatures at which long-range positional and orientational ordering are, respectively, lost. We use mean-field techniques to obtain a general approach to the study of these systems. By considering particular forms of the orientational interaction function we study coupling effects between both phase transitions arising from the interplay between orientational and positional degrees of freedom. In mean-field approximation coupling effects appear only for the phase transition taking place at lower temperatures. The strength of the coupling depends on the value of the long-range order parameter that remains finite at that temperature.

## I. INTRODUCTION

The complexity that most of the phase diagrams of real substances exhibit may be attributed to the interplay between the different kinds of internal degrees of freedom of their individual components. A typical example is a binary alloy with one or both kinds of atoms having a magnetic moment.<sup>1</sup> Apart from the configurational interaction leading to the ordering of the two species on the lattice we must consider the magnetic interaction coming from the magnetic degrees of freedom. If the energies associated with both kinds of degrees of freedom are comparable in magnitude, coupling effects may appear and modify the phase diagram so that it can differ considerably from the phase diagram corresponding to a nonmagnetic binary alloy.

In this paper we shall deal with systems exhibiting intermediate phases between solid and liquid phases. Usually their properties emerge from the competition between two or more ordering modes. We shall focus our attention on the case of systems constituted by particles that due to their symmetry can be positionally and orientationally ordered. However, most of our results can be extrapolated to the case of the competition between any two ordering modes (magnetic, structural, etc.).

The ground state of these systems is characterized by a long-range positional and orientational order. By increasing the temperature, the system first loses positional or orientational long-range order, and an intermediate phase between solid and liquid phase is obtained (it can be orientationally ordered only or positionally ordered only). It can usually be classified as a soft condensed matter phase. Finally at higher temperatures the liquid phase with no long-range order is obtained. The comprehension of the main features of these two phase transitions and the intermediate phase is a matter that is closely linked to the problem of coupling between the two

ordering modes, orientational and positional.

Coupling between phase transitions has been extensively studied using different theoretical, computer simulation, and experimental studies. Phenomenological models based on the two-order-parameter Landau theory have been developed.<sup>2</sup> Some microscopical models exhibiting coupling have also been studied. In particular, the two-color Ashkin-Teller model<sup>3</sup> consisting of two Ising models with a biquadratic coupling has been solved in an almost exact way using Monte Carlo renormalization-group theories.<sup>4</sup> Other microscopical models for magnetic binary alloys have been studied using mean-field approximations and the cluster variational method (CVM).<sup>5</sup> In the field of computer simulation, some Monte Carlo works may be cited.<sup>5-7</sup>

Experimentally many systems have been studied, some of them very recently. Liquid crystals are, possibly, the best known.<sup>8</sup> They consist of rodlike molecules that exhibit many phases with orientational and positional long-range order (solid and smectic phases), phases with only orientational long-range order (nematic), and completely disordered phases (isotropic liquid). Another example is plastic crystals<sup>9</sup> (PC's), which also consist of rodlike molecules but differ from liquid crystals (LC's) in that the first ordering mode that reaches zero is the orientational one. At higher temperatures the positional order also vanishes when the isotropic phase is reached. We should also mention the case of molecules adsorbed on surfaces. A typical example is molecules of  $N_2$  adsorbed on graphite<sup>10</sup> which, apart from the possibility of being positionally ordered on the graphite lattice, may be oriented in three different directions.

The main purpose of this work is to introduce a general model for the description of the systems exhibiting coupled phase transitions associated with positional and orientational ordering modes and to solve it using a mean-field approximation in a general case. The lattice-



### III. GROUND STATE

gas model has been extensively used for the study of the solid-liquid phase transition.<sup>11</sup> Our objective is to add orientational degrees of freedom to that model so that it can reproduce intermediate phases. Because of our interest in the study of coupling phenomena we shall eliminate other effects that may distort our model. In particular, we shall avoid dealing with frustration effects that may be important in order to understand the complexity of phase diagrams in real systems.

The paper is organized as follows. First, in Sec. II, we shall introduce the model and discuss its general applicability. In Sec. III we shall comment on some aspects of its ground state. The general solution of the model in the mean-field approximation will be given in Sec. IV. In Sec. V we shall focus our attention on two particular cases (Secs. V A and V B) where the coupling effects can be specifically studied, and finally in Sec. VI we shall summarize the conclusions of the work.

### II. MODEL

Consider a lattice with  $N$  sites ( $I = 1, \dots, N$ ) and let us define in each site two variables:  $s_I$ , which takes values  $\{1, 0\}$  depending on the presence or absence of a particle in site  $I$ ; and  $t_I$ , which takes one of the  $n$  discrete values  $\{1, \dots, i, \dots, n\}$  depending on the orientational state of the particle. In fact,  $t_I$  is only defined when  $s_I = 1$ . We shall write the energy of the system as

$$H = \frac{1}{2}J_1 \sum_{\text{NN}} s_I s_J + \frac{1}{2}J_2 \sum_{\text{NNN}} s_I s_J + \frac{1}{2}K_1 \sum_{\text{NN}} s_I s_J P(t_I, t_J) + \frac{1}{2}K_2 \sum_{\text{NNN}} s_I s_J P(t_I, t_J), \quad (1)$$

where  $J_1, J_2, K_1$ , and  $K_2$  are constants,  $P$  is a symmetric function of the orientations  $t_I$  and  $t_J$  (it will be treated as an  $n \times n$  matrix with  $t_I$  and  $t_J$  taking values between  $1, \dots, n$ ), and  $\sum_{\text{NN}}, \sum_{\text{NNN}}$  are sums over all the nearest-neighbors (NN) and next-nearest-neighbors (NNN) pairs. We shall also assume a conservation law on  $s_I$ ,

$$\sum_I s_I = cN, \quad (2)$$

where  $\sum$  is made over all the lattice sites and  $c$  is the concentration. We shall only consider the case with  $c = 0.5$ .

We exclude the possibility that  $P(t_I, t_J)$  depends on the vector  $r_{IJ}$ , so that we are dealing only with isotropic orientational interactions. It is worth noting that, in this model, the orientational interaction is a slave to the positional one, in the sense that the molecules may only interact orientationally if they are NN or NNN, i.e., they are positionally interacting. This feature makes this model different from the usual models used for the study of coupling between different degrees of freedom where the coupling appears explicitly through a term giving the interaction between the different variables.

Another point worth mentioning is that we have discretized both positions and orientations. This is not always a sufficiently good approximation, but it may be physically justified in many cases and it makes the model suitable for computer simulation.

The system must have a lattice-gas-like ground state, so that we may make the hypothesis that  $J_1$  is positive enough to assure that at  $T \rightarrow 0$  the lattice could be subdivided into two equivalent sublattices (+ and -), one completely full of particles (+) and the other completely empty (-). Here we are also assuming some hypotheses on the symmetry of the lattice so that we shall avoid frustration. In particular, the two-dimensional square lattice, the simple-cubic lattice, and the bcc lattice agree with these hypotheses. This division into two sublattices introduces a positional degeneration  $g_p = 2$ .

In order to characterize the sublattices we define the number of NN  $q_1^{+-}$  and NNN  $q_2^{++}$  between them. For instance, we have  $q_1^{+-} = 4$  and  $q_2^{++} = 4$  for the two-dimensional square lattice and  $q_1^{+-} = 8$  and  $q_2^{++} = 6$  for the bcc lattice. With these assumptions we may write the ground-state energy as

$$H(T=0) = \frac{1}{2}J_2 q_2^{++} cN + \frac{1}{2}K_2 \sum_{\text{NNN}} P(t_I, t_J). \quad (3)$$

Now we suppose that  $K_2 < 0$  and that there is a direction (let us say  $n$ ), so that  $P(n, n)$  has the maximum value of the matrix elements  $P(i, j)$ ,  $i, j = 1, \dots, n$ . Then at the ground state all particles are parallel to each other in the direction  $n$ . We do not exclude the possibility that there are  $k = n-1, \dots, n - (g_o - 1)$  other directions ( $g_o$  is the orientational degeneration), so that  $P(k, k) = P(n, n)$ . In this case the total degeneration of the ground state will be  $g_p g_o$ .

Without losing generality we can also suppose that the matrix  $P$  is normalized so that

$$P(n, n) = 1, \quad (4)$$

$$\sum_{i=1}^n P(n, i) = 0.$$

Should this not be the case, the problem can be solved by defining

$$P'(i, j) = \frac{P(i, j) - \sum_{k=1}^n P(n, k)/n}{P(n, n) - \sum_{k=1}^n P(n, k)/n}$$

and renormalizing  $J_1, J_2, K_1$ , and  $K_2$ .

Cases with a ground state where the molecules are not parallel (for instance, as observed on most of the adsorbed molecules on surfaces<sup>12</sup>) may also be solved with the formalism that we shall develop. However, in this case the order parameters that shall be introduced later should be defined in a different way that is suitable for the considered ground state.

### IV. GENERAL MEAN-FIELD SOLUTION

First, we shall define the occupation numbers of the two different sublattices  $N_i^+$  and  $N_i^-$  ( $i = 1, \dots, n$ ) as the number of particles with orientational state  $i$  in sublattice + and -, respectively. We also define the vector  $\mathbf{N} = (N_1^+, \dots, N_n^+, N_1^-, \dots, N_n^-)$  and the scalars



$N^+ = \sum_i N_i^+$  and  $N^- = \sum_i N_i^-$ . From (2) we have  $N^+ + N^- = cN$ .

Secondly, we shall introduce the order parameters as a function of the occupation numbers. The positional order parameter is defined as

$$m_p = 2(N^+ - N^-)/N,$$

and the orientational order parameters as

$$m_{ok}^\pm = 2(N_n^\pm - N_k^\pm)/N, \quad (5)$$

with  $k = 1, \dots, n-1$

In the ground state the order parameters will take the values  $m_p = 1$ ,  $m_{ok}^+ = 1$ , and  $m_{ok}^- = 0$ . We define the vector

$$\mathbf{m} = (m_{o1}^+, \dots, m_{on-1}^+, m_{o1}^-, \dots, m_{on-1}^-, m_p, c).$$

The relation between the vector  $\mathbf{m}$  and  $N$  is given by the equation

$$\mathbf{m} = [1/(N/2)] \underline{Q} N, \quad (6)$$

where  $\underline{Q}$  is the  $2n \times 2n$  matrix

$$\underline{Q} = \begin{pmatrix} -1 & & & 1 & & & & & 0 \\ & \ddots & & \vdots & & & & & \\ & & -1 & 1 & & & & & \\ & & & & -1 & & & 1 & \\ 0 & & & & & \ddots & & \vdots & \\ & & & & & & -1 & 1 & \\ 1 & \dots & & 1 & -1 & \dots & -1 & & \\ 0.5 & & \dots & \dots & & & & 0.5 & \end{pmatrix}. \quad (7)$$

Inverting relation (6) we obtain

$$N = \frac{1}{2} \underline{Q}^{-1} \mathbf{m}. \quad (8)$$

Assuming the usual mean-field approximations we can write  $H$  as a function of  $N$  as

$$\begin{aligned} NH(N) &= 2J_q N^+ N^- + J_o (N^+ N^+ + N^- N^-) \\ &\quad + 2K_q \sum_k \sum_j P(k, j) N_k^+ N_j^- \\ &\quad + K_o \sum_k \sum_j P(k, j) (N_k^+ N_j^+ + N_k^- N_j^-), \end{aligned} \quad (9)$$

where the differential operators  $\nabla_m$  and  $\nabla_N$  are defined as

$$\begin{aligned} \nabla_m &= (\partial/\partial m_{o1}^+, \dots, \partial/\partial m_{on-1}^+, \partial/\partial m_{o1}^-, \dots, \partial/\partial m_{on-1}^-, \partial/\partial m_p, \partial/\partial c), \\ \nabla_N &= (\partial/\partial N_1^+, \dots, \partial/\partial N_n^+, \partial/\partial N_1^-, \dots, \partial/\partial N_n^-). \end{aligned}$$

In obtaining Eq. (14) we have used the Stirling approximation on (13), the chain rule, and (6) in order to change the  $\nabla_m$  to a  $\nabla_N$  in the second term (that has to be expressed in function of  $\mathbf{m}$ ).

A general solution to Eq. (14) is not easy to find. Nevertheless, we can look for some simple solutions. It is convenient, in order to obtain some analytical results, to make an extra assumption on the interaction  $P(k, j)$ ,

where we have defined

$$\begin{aligned} J_o &= J_2 q_2^{++}, \quad J_q = J_1 q_1^{+-}, \quad K_o = K_2 q_2^{++}, \\ K_q &= K_1 q_1^{+-}. \end{aligned} \quad (10)$$

Now we can calculate the free energy of our system as

$$-\beta F = \ln \left[ \sum_{\mathbf{m}} g(\mathbf{m}) \exp[-\beta H(\mathbf{m})] \right], \quad (11)$$

where  $\sum_{\mathbf{m}}$  is made over all the values of  $\mathbf{m}$  with  $c = 0.5$  and  $g(\mathbf{m})$  is the degeneration of a configuration with order parameter  $\mathbf{m}$  and  $\beta = 1/k_B T$ , where  $k_B$  is the Boltzmann factor and  $T$  is the temperature. If we define the functional  $F(\mathbf{m})$  as

$$-\beta F(\mathbf{m}) = -\beta H(\mathbf{m}) + \ln[g(\mathbf{m})], \quad (12)$$

we can write  $F = F(\mathbf{m}^{\text{eq}})$ , where  $\mathbf{m}^{\text{eq}}$  is the order-parameter vector that minimizes  $F(\mathbf{m})$  keeping  $c = 0.5$ .

We can calculate first  $g'(\mathbf{N})$  as

$$g'(\mathbf{N}) = (g')^+(\mathbf{N})(g')^-(\mathbf{N}),$$

with

$$(g')^\pm(\mathbf{N}) = \frac{(\frac{1}{2}N)!}{N_1^\pm! \dots N_n^\pm! \left[ \frac{1}{2}N - \sum_k N_k^\pm \right]!}. \quad (13)$$

Then, we obtain  $g(\mathbf{m}) = g'(N(\mathbf{m})) = g'(\frac{1}{2}NQ^{-1}\mathbf{m})$ . We can now look for the minimum of  $F(\mathbf{m})$  keeping  $c$  constant. By introducing a Lagrange parameter  $\mu$  and defining a  $2n$ -component vector  $\mu = (0, \dots, 0, \mu)$  we can write concisely the set of  $2n + 1$  equations that determine  $\mathbf{m}^{\text{eq}}$  and  $\mu$  as

$$\beta \underline{Q}^T \nabla_m H(\mathbf{m}) - \beta \underline{Q}^T \mu = \frac{1}{2} N \nabla_N \ln[g'(N(\mathbf{m}))], \quad c = 0.5, \quad (14)$$

$$\sum_k \sum_j P(k, j) N_k^\pm N_j^\pm \approx \left[ \sum_k P(k, n) N_k^\pm \right] \left[ \sum_j P(j, n) N_j^\pm \right], \quad (15)$$

which allows us to write  $H(\mathbf{m})$  as a function of three order parameters only:

$$\begin{aligned} H(\mathbf{m}) &= (J_o + J_q)c^2 + \frac{1}{4}(J_o - J_q)m_p^2 \\ &\quad + \frac{1}{2}K_o(m_o^{+2} + m_o^{-2}) + K_q m_o^+ m_o^-, \end{aligned} \quad (16)$$



where  $m_o^+$  and  $m_o^-$  are linear combinations of the orientational order parameters

$$m_o^\pm = - \sum_{k=1}^{n-1} m_{ok}^\pm P(n, k). \quad (17)$$

This assumption (15) has been extensively discussed<sup>13</sup> and in some cases we are interested in (for instance, in LC's) it has been demonstrated that it is exact in the mean-field approximation. Anyway, numerical solution of Eq. (14) can be obtained without this assumption, and we use it here in order to proceed with an analytical analysis. Let us discuss now the following simple solutions.

(i) Disordered solution: A disordered solution with all the  $N_k^\pm$  equal [or equivalently  $\mathbf{m}=(0, \dots, 0, 0, c=0.5)$ ] is always a solution of Eqs. (14) but is only stable at high enough temperature.

(ii) Solution with only positional order: If we make  $N_k^\pm = N^\pm/n$  for all  $k=1, \dots, n$  [or equivalently  $\mathbf{m}=(0, \dots, 0, m_p, 0.5)$ ] Eqs. (14) reduce to only one equation

$$\exp \left[ \frac{m_p(J_o - J_q)}{2k_B T} \right] = \frac{1 - m_p}{1 + m_p}. \quad (18)$$

This gives a second-order positional phase transition, when the orientational order is not present, at a critical temperature given by

$$k_B T_p(m_{ok}=0) = \frac{1}{4}(J_q - J_o). \quad (19)$$

(iii) Solution with only orientational order: We now look for a solution with  $N_k^+ = N_k^-$  for all  $k=1, \dots, n$  [or equivalently  $\mathbf{m}=(m_{o1}, \dots, m_{on-1}, m_{o1}, \dots, m_{on-1}, m_p=0, 0.5)$ ]. Equations (14) lead to a set of  $n-1$  equations ( $k=1, \dots, n-1$ ),

$$\beta(K_o + K_q)[P(n, n) - P(n, k)] \left[ \sum_{j=1}^{n-1} m_{oj} P(n, j) \right] = \ln \frac{c + \sum_j m_{oj}}{c + \sum_j m_{oj} - m_{ok}}. \quad (20)$$

This set of equations is reduced to the following two:

$$\sum_{k=1}^{n-1} \exp - \frac{x(K_o + K_q)[P(n, n) - P(n, k)]}{k_B T} = (n-1) - \frac{ny}{c+y}, \quad (21)$$

$$\sum_{k=1}^{n-1} P(n, k) \exp - \frac{x(K_o + K_q)[P(n, n) - P(n, k)]}{k_B T} = -P(n, n) - \frac{nx}{c+y},$$

where  $x$  and  $y$  are the following linear combinations of  $m_{ok}$ :

$$x = \sum_{k=1}^{n-1} m_{ok} P(n, k), \quad (22)$$

$$y = \sum_{k=1}^{n-1} m_{ok}.$$

Making  $x \rightarrow 0$  and  $y \rightarrow 0$ , we can obtain the temperature at which the orientational order disappears (supposing that the system is already positionally disordered,  $m_p=0$ ). This temperature is given by

$$k_B T_o(m_p=0) = -c(K_o + K_q)n^{-1} \sum_{k=1}^n P(n, k)^2. \quad (23)$$

In the general case it is difficult to predict the order of the transition, but for a particular  $P(i, j)$  it may be done as we shall see in Sec. V. If the transition is first order,  $T_o$  corresponds to the low-temperature limit of coexistence between the orientationally ordered state and the completely disordered one.

We have found the solutions with one of the two degrees of freedom completely disordered, so we have not found coupling phenomena. In order to do that, the interesting transition temperatures to be found are  $T_o(m_p=0)$  and  $T_p(m_o=0)$  and this will be done in a particular case.

## V. SIMPLE PARTICULAR CASE

### A. Potts-like orientational interaction

In order to obtain analytical solutions for the intermediate transition temperatures and study the coupling phenomena, we shall solve Eqs. (14) choosing a very simple  $P(i, j)$  matrix

$$P(n, k) = -1/(n-1), \quad (24)$$

$$P(n, n) = 1.$$

We suppose that the other terms of the matrix  $P(i, j)$  are defined in such a way that Eq. (15) is exactly verified. It should be pointed out that this definition satisfies the normalization rules (14) defined in Sec. III. Note also that for this case definition (17) may be reduced to

$$m_o^\pm = \left[ \sum_{k=1}^{n-1} m_{ok}^\pm \right] / (n-1). \quad (25)$$

After some algebra, Eqs. (14) reduce to the following equations that determine  $m_p$ ,  $m_o^+$ , and  $m_o^-$ :

$$(K_q - K_o)(m_o^+ - m_o^-) + (J_q - J_o)m_p = k_B T \frac{(1+m_p)[1+m_p+2(n-1)m_o^+]}{(1-m_p)[1-m_p+2(n-1)m_o^-]}, \quad (26a)$$

$$\exp \left[ \frac{n(K_o m_o^\pm + K_q m_o^\mp)}{n-1k_B T} \right] = 1 - \frac{2nm_o^\pm}{1 \pm m_p + 2(n-1)m_o^\pm}. \quad (26b)$$

At  $T=0$  it is easy to prove that the ground-state solution is  $m_p=1$ ,  $m_o^+=1$ , and  $m_o^-=0$ .

We can look for the solutions at  $T > 0$  as before.



(a)  $m_p = 0, m_o^+ = 0, m_o^- = 0$  is always a solution of Eqs. (26) but it may be seen that it is only stable at high enough temperatures. It represents the disordered state with neither positional nor orientational order.

(b)  $m_o^+ = m_o^- = 0, m_p > 0$ . We obtain, as seen before, a second-order phase transition at

$$k_B T_p(m_o = 0) = k_B T_p(0) = \frac{1}{4}(J_q - J_o). \quad (27)$$

(c)  $m_p = 0, m_o^+ = m_o^- = m_o > 0$ . Making  $m_p = 0$  in Eqs. (26), we obtain the transition temperature for this phase

$$k_B T_o(m_p = 0) = k_B T_o(0) = -\frac{1}{2}(n-1)^{-1}(K_o + K_q). \quad (28)$$

We can now study the order of this transition. We have obtained that for  $n=2$  the transition is second order while for  $n > 2$  it becomes first order, as expected from a mean-field theory.

(d)  $m_p > 0, m_o^+ > 0, m_o^- > 0$ . Although the general order-parameter evolution can only be obtained numerically we can find in this case two transition temperatures corresponding to two cases: (i)

$$m_p \rightarrow 0 \text{ with } m_o^+ \rightarrow m_o^*, m_o^- \rightarrow m_o^*.$$

In this case the transition temperature can be expressed in a function of the temperatures found in (27) and (28) as a solution of the following two coupled equations:

$$2T_p(m_o^*) = T_p(0) + \epsilon T_o(0) f(m_o^*) + \{ [T_p(0) - \epsilon T_o(0) f(m_o^*)]^2 + 8T_p(0)\epsilon T_o(0)(n-1)m_o^{*2} \}^{1/2}, \quad (29a)$$

$$\exp[-2nT_o(0)m_o^*/T_p(m_o^*)] = (1 - 2m_o^*) / [1 + 2(n-1)m_o^*], \quad (29b)$$

where

$$\epsilon = (K_o - K_q) / (K_o + K_q),$$

$$f(m_o^*) = 1 + 2(n-2)m_o^* - 2(n-1)m_o^{*2}.$$

$m_o^*$  is the orientational order-parameter value at the transition point  $T_p(m_o^*)$ . Note that if we make  $m_o^* = 0$  we recover the solution (28), and if we take  $m_o^* = \frac{1}{2}$  (this is the maximum value that  $m_o$  can take if  $m_p = 0$ ), we find  $T_p(\frac{1}{2}) = 0$ . It is worth noting again that if the transition is first order this transition temperature corresponds to the low-temperature limit of coexistence of the phase with orientational and positional order and the phase with only orientational order. (ii)  $m_o^+ \rightarrow 0, m_o^- \rightarrow 0, m_p > 0$ . In this case the transition temperature is determined as the solution of

$$2(n-1)k_B T_o(m_p^*) = -K_o + [K_q^2 + (K_o^2 - K_q^2)m_p^{*2}]^{1/2}, \quad (30a)$$

$$\exp[(J_q - J_o)m_p^*/2k_B T_o(m_p^*)] = (1 + m_p^*) / (1 - m_p^*), \quad (30b)$$

and if the transition is first order this temperature corresponds to the low-temperature limit of coexistence be-

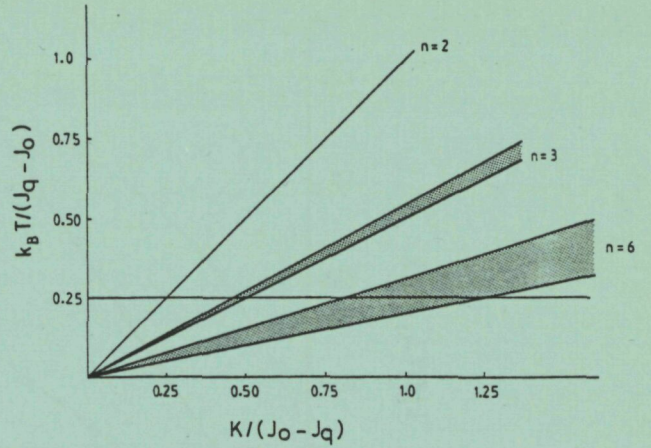


FIG. 1. Phase diagrams for different values on the number  $n$  of particle orientations for the case  $K_q = K_o = K$ . The positional transition is second order and takes place at  $k_B T / (J_q - J_o) = 0.25$  regardless of  $K$  and  $n$ . The orientational transition changes from second order to first order when  $n > 2$ . Shaded areas correspond to metastable coexistence regions in the first-order phase transitions. Transition lines define four regions in the phase space corresponding to the completely disordered phase, the only positionally ordered phase, the only orientationally ordered phase, and the positionally and orientationally ordered phase.

tween a positionally and orientationally ordered phase and an only positionally ordered phase. From Eqs. (29) and (30) one can obtain the transition temperatures as a function of the constants  $(J_o - J_q)$ ,  $(K_o - K_q)$ ,  $(K_o + K_q)$ , and  $n$ . But one can see that this functionality is mainly governed by the value of the order parameter associated with the degree of freedom that remains finite during the transition. ( $m_o^*$  in the case of the positional transition and  $m_p^*$  in the case of the orientational transition). Figures 1 and 2 show the phase diagram calculated from Eqs. (27), (28), (29), and (30) in the cases  $K_q = K_o = K$  and  $K_q = 2K_o = 2K$ , respectively. In the former case ( $K_q = K_o = K$ ) we also show the zone where metastable states are possible during the orientational transition if  $n > 2$ . Comparing both figures, the case  $K_q = K_o$  appears as a special case where there is no coupling effect because the transition lines do not change when crossing. This is due to the fact that the constant  $K_o - K_q$  governs the coupling, as can be clearly seen from Eq. (30a) and via Eq. (29a). When the NN and NN orientational interaction are equal ( $K_o = K_q$ ) the orientational order is not affected by the positional one because the positional transition is associated with a balance between the number of NN and NNN pairs. Another particular case is the case  $J_o = J_q$ . From Eq. (27) one deduces that the positional transition disappears if there is not orientational order, but from Eqs. (29) one can see that  $T_p$  remains finite when  $m_o^*$  is different from zero.

(e) To obtain a complete solution for the order-parameter evolution, solving Eqs. (26) is a very difficult task because of the exponential divergences that make the convergence of the iterative numerical methods very



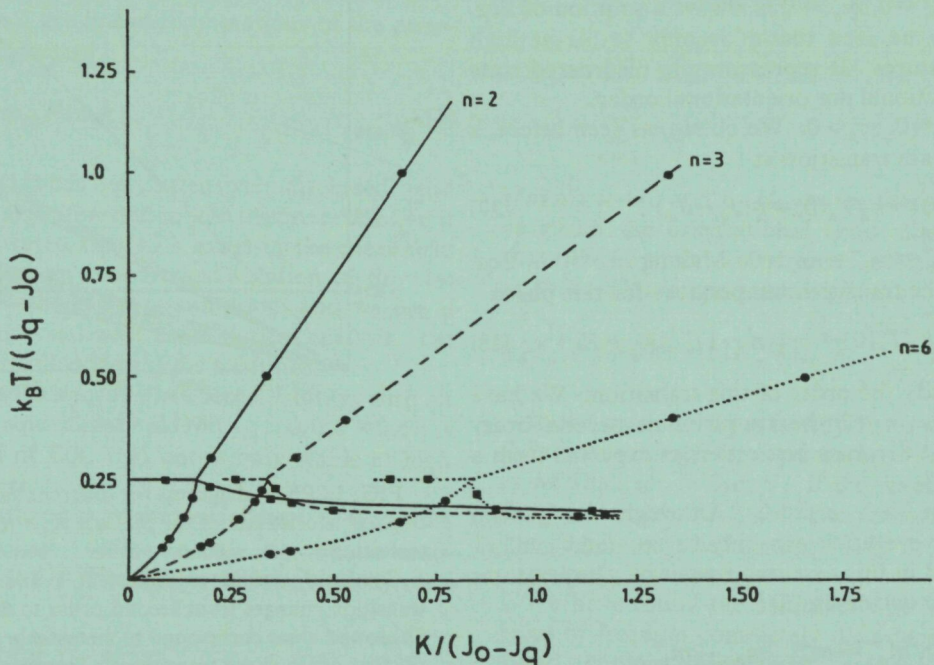


FIG. 2. Phase diagrams for different values of the number  $n$  of particle orientations for the case  $K_q = 2K_o = 2K$ . Dots correspond to the orientational phase transitions while squares correspond to positional phase transitions. Transition lines define four regions in the phase space corresponding to the completely disordered phase, the only positionally ordered phase, the only orientationally ordered phase, the positionally and orientationally ordered phase.

slow. An easier way to proceed is to minimize numerically the effective free energy for this problem. This effective free energy is deduced from (12) noting that symmetry imposes that all the orientational order parameters  $m_{ok}$  be equal. Looking for the deepest minimum one directly obtains the most stable solution, and it is not necessary to calculate the second derivatives in order to

assure the stability of the solutions.

Solutions giving the order parameters as functions of temperature are given in Fig. 3 for a case where  $T_o > T_p$  and in Fig. 4 for a case where  $T_p > T_o$ . Despite the fact that Fig. 3 corresponds to the case  $K_o = K_q$  which does not present coupling effects in the phase diagram (Fig. 1), the order-parameter evolution reflects coupling effects.

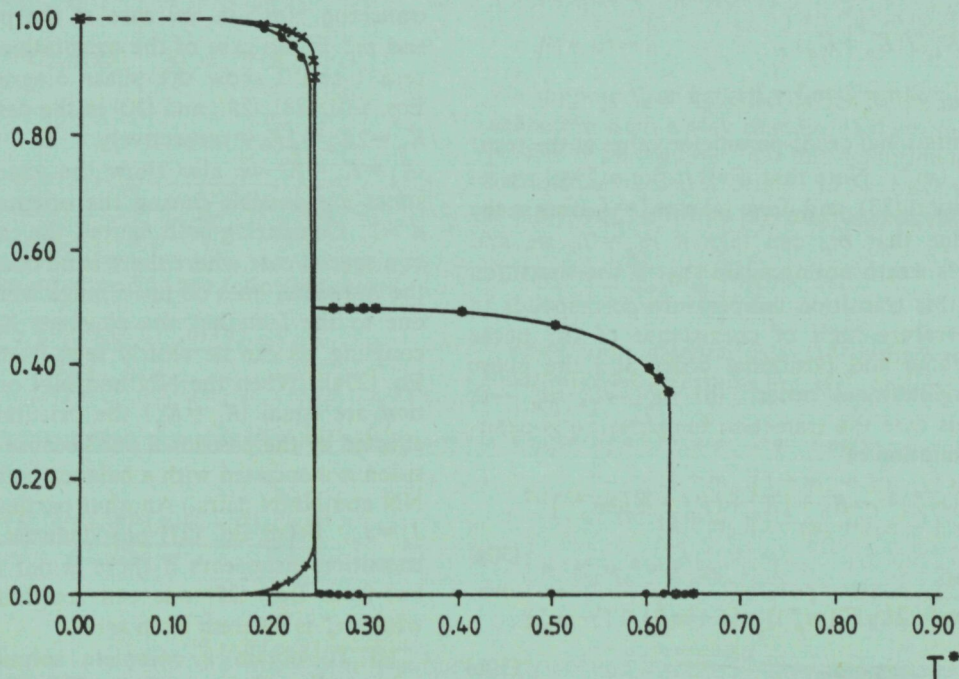


FIG. 3. Order parameters  $m_o^+$  ( $\times$ ),  $m_o^-$  ( $+$ ), and  $m_p$  ( $\bullet$ ) as a function of reduced temperature  $T^* = k_B T / (J_o - J_q)$ , with  $J_q = 1$ ,  $J_o = 0$ ,  $K_o = K_q = -2$ , and  $n = 6$ . The positional transition ( $\bullet$ ) is second order, while the orientational transition is first order. Note that after the positional transition  $m_o^+ = m_o^-$  ( $\star$ ) because the two sublattices  $+$  and  $-$  become equivalent.