

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

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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.¹ 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.² Some microscopical models exhibiting coupling have also been studied. In particular, the two-color Ashkin-Teller model³ consisting of two Ising models with a biquadratic coupling has been solved in an almost exact way using Monte Carlo renormalization-group theories.⁴ Other microscopical models for magnetic binary alloys have been studied using mean-field approximations and the cluster variational method (CVM).⁵ In the field of computer simulation, some Monte Carlo works may be cited.⁵⁻⁷

Experimentally many systems have been studied, some of them very recently. Liquid crystals are, possibly, the best known.⁸ 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 crystals⁹ (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 graphite¹⁰ 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-

gas model has been extensively used for the study of the solid-liquid phase transition.¹¹ 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 \mathbf{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.

III. GROUND STATE

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 \underline{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 surfaces¹²) 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

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 discussed¹³ 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)

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

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-

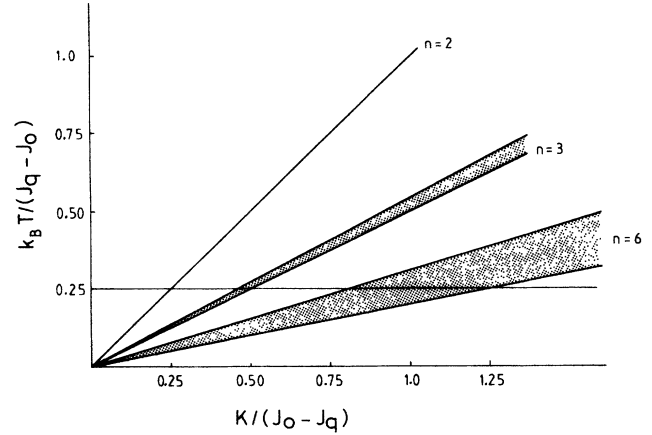


FIG. 1. Phase diagrams for different values on the number n of particle orientations for the case $K_q = K_o = K$. The positional transition is second order and takes place at $k_B T / (J_q - J_o) = 0.25$ regardless of K and n . The orientational transition changes from second order to first order when $n > 2$. 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

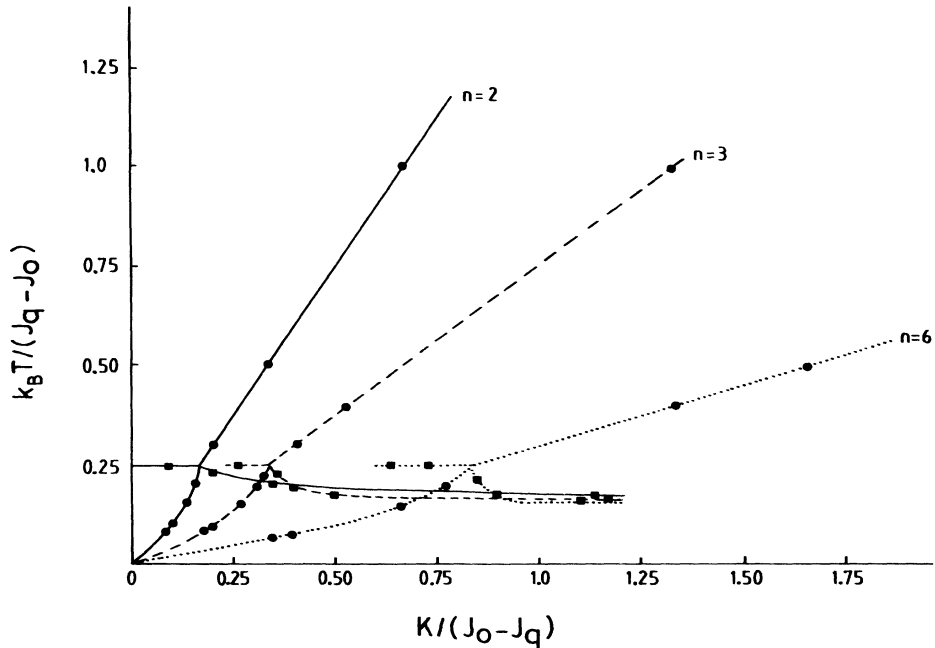


FIG. 2. Phase diagrams for different values of the number n of particle orientations for the case $K_q = 2K_o = 2K$. Dots correspond to the orientational phase transitions while squares correspond to positional phase transitions. Transition lines define four regions in the phase space corresponding to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

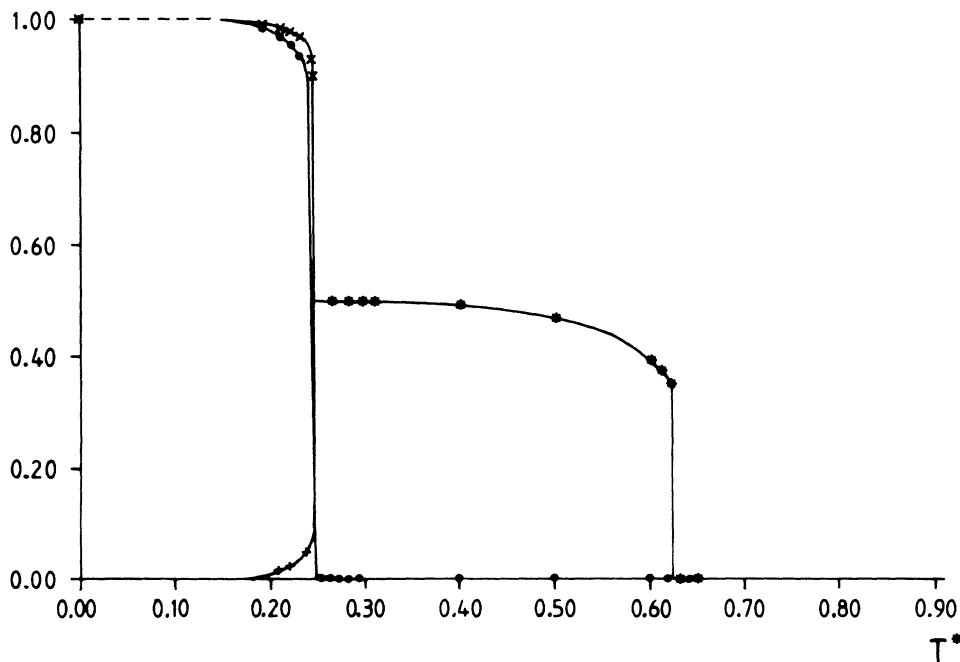


FIG. 3. Order parameters m_o^+ (x), m_o^- (+), and m_p (●) as a function of reduced temperature $T^* = k_B T / (J_O - J_Q)$, with $J_q = 1$, $J_o = 0$, $K_o = K_q = -2$, and $n = 6$. The positional transition (●) is second order, while the orientational transition is first order. Note that after the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

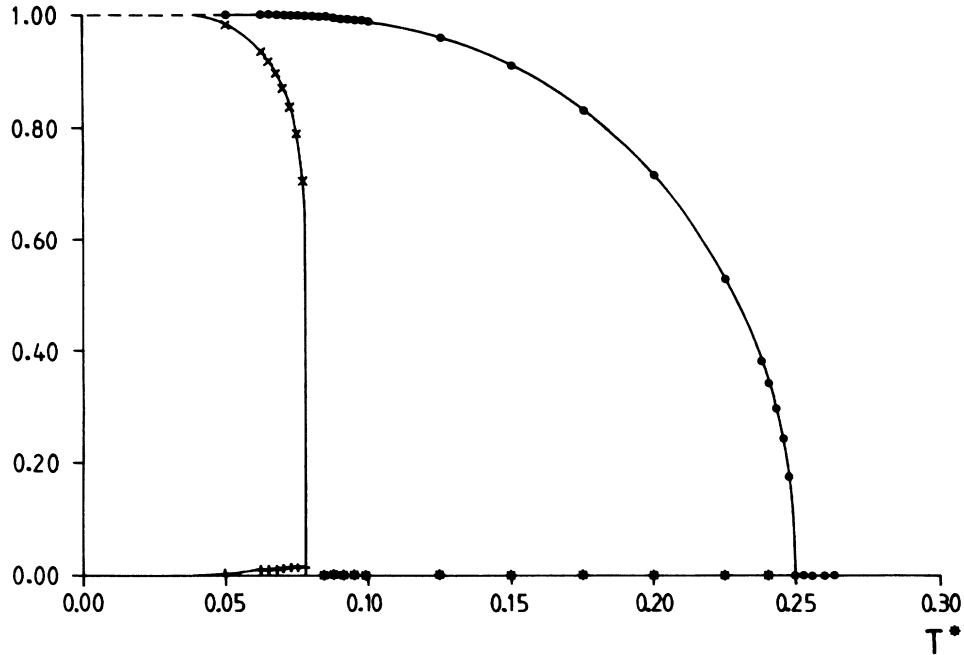


FIG. 4. Order parameters m_o^+ (\times), m_o^- ($+$), and m_p (\bullet) as a function of reduced temperature $T^* = k_B T / (J_o - J_q)$, with $J_q = 4$, $J_o = 0$, $K_o = K_q = -1$, and $n = 6$. The positional transition (\bullet) is second order, while the orientational transition is first order.

B. Maier-Saupe interaction

In order to apply our results to the study of the behavior of liquid crystals and plastic crystals, a more realistic interaction should be chosen. The Maier-Saupe interaction was used extensively¹⁴ for this purpose. Originally¹⁵ it was defined as a function of the angle θ_{IJ} between two rodlike molecules of a liquid crystal as follows:

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

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

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

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

This interaction has been studied in a previous paper⁶ in the particular case of having $n = 4$ in a two-dimensional square lattice. Moreover, these results were compared with a Monte Carlo simulation and it was seen that the liquid-crystal phase diagram was reproduced qualitatively well. With our formalism we can now generalize to a d -dimensional lattice with n discrete orientations. We have studied two cases: (i) $n = d$ orientations along the perpendicular axis (this case includes $d = 2$, $n = 2$ and $d = 3$, $n = 3$); and (ii) $n = d + 2^{d-1}$ orientations along the perpendicular axis and the bisectrices of the quadrants. In both cases, when normalizing P , one finds

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

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

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

VI. CONCLUSIONS

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

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

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

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

Nevertheless, if one wants to study LC's more realistically, it is better to use a Maier-Saupe¹⁵ orientational interaction. This interaction is nearer to the real interaction between LC molecules than the Potts-like interaction considered above, and it is believed that it contains the

main physical features of real interaction.¹⁷ In fact, a two-dimensional version of the model proposed in this paper with the Maier-Saupe interaction was recently studied⁶ considering only four possible orientations of the molecules. It was solved using mean-field and Monte Carlo simulation and the results were in good qualitative agreement with the LC phase diagram. We propose here a generalization to d dimensions and n possible orientations. In the case $d=3$ the order of the nematic-liquid transition is, as expected, first order, in agreement with experiments.¹⁸ Better approximations, or Monte Carlo simulations of the three-dimensional model, can help to study details of the critical behavior of LC's that are not well understood, such as the existence of tricritical points,¹⁸ nonuniversal exponents,¹⁹ etc., that are closely related to the coupling effects between the positional and orientational order of the molecules.

The model could, in fact, be applied to other kinds of systems. For instance, if we consider the empty sites as B atoms and the full sites as A atoms, our model can also be applied to the case of binary alloys AB (50%) with A atoms having a magnetic moment. Recently, Düweg and Binder⁵ proposed a Hamiltonian with the same kind of slave coupling for the case of a binary alloy A_xB_{1-x} with A atoms having spins $\frac{1}{2}$, with NN magnetic interaction. The solution of our model with an appropriate orientational interaction reproducing the magnetic one, will be a first attempt to extend it to a general case with spin $n/2$ and also with a NNN magnetic interaction.

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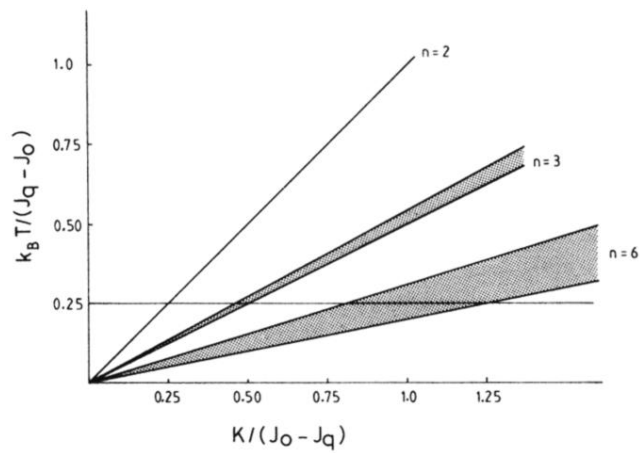


FIG. 1. Phase diagrams for different values on the number n of particle orientations for the case $K_q = K_o = K$. The positional transition is second order and takes place at $k_B T / (J_q - J_o) = 0.25$ regardless of K and n . The orientational transition changes from second order to first order when $n > 2$. 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.