

Lattice-gas model of orientable molecules: Application to liquid crystals

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We have analyzed a two-dimensional lattice-gas model of cylindrical molecules which can exhibit four possible orientations. The Hamiltonian of the model contains positional and orientational energy interaction terms. The ground state of the model has been investigated on the basis of Karl's theorem. Monte Carlo simulation results have confirmed the predicted ground state. The model is able to reproduce, with appropriate values of the Hamiltonian parameters, both, a smectic-nematic-like transition and a nematic-isotropic-like transition. We have also analyzed the phase diagram of the system by mean-field techniques and Monte Carlo simulations. Mean-field calculations agree well qualitatively with Monte Carlo results but overestimate transition temperatures.

I. INTRODUCTION

A wide variety of physical systems show properties which may be understood as arising from the interaction of two or more ordering modes. These coupling effects lead to phase diagrams displaying a rich variety of structures. In recent years, many interesting examples have been found in general fields such as magnetism, superconductivity, structural transitions, etc.

Different general studies of systems presenting two ordering modes have been carried out by means of the Landau theory¹⁻³ and have shown that when one of the order parameters vanishes the other one presents some kind of discontinuity. In the case of magnetic alloys microscopic models based on generalized Ising models have been formulated.^{4,5} These models have been solved using different kinds of mean-field approximations and the Monte Carlo simulation technique.

Among the systems that exhibit the above-mentioned behavior, liquid crystals⁶ present a great deal of interest for their multiple applications. These complex systems are basically constituted of rodlike (or disklike) molecules. At low temperatures the system exhibits different crystalline solid phases. In the smectic phase, at higher temperatures, the molecules are oriented parallel to a preferred axis and show some long-range positional order. For example, for the so-called smectic-*A* phase, the center of mass of the molecules sits on planes perpendicular to the preferred axis. These planes can move freely one over the other, and the viscosity is low in the direction of the planes. In the nematic phase, at still higher temperatures, the center of mass of the molecules is placed completely at random, but the system preserves the long-range orientational order. Finally, when not only the positional, but also the orientational order disappears, the isotropic liquid is obtained.

Different microscopic models have been formulated for the study of liquid crystals. On the one hand, the Maier-Saupe model⁷ attempts to describe the nematic-isotropic liquid phase transition. In the original form it has been solved using mean-field approximations. Lebwohl and

Lasher apply first the Monte Carlo simulation technique⁸ to a lattice version of the model. Later, more accurate simulations⁹ have proved that this model contains basically the real orientational interaction between the molecules.

On the other hand, the smectic-nematic phase transition is commonly studied using models of hard cylinders. The original model was formulated by Onsager,¹⁰ and has been simulated numerically by molecular dynamics¹¹ and by the Monte Carlo method.¹²

Some models try to explain simultaneously both the smectic-nematic and the nematic-isotropic transitions. With this idea, the Maier-Saupe model has been reformulated by McMillan,¹³ who introduced a short-range positional interaction in a nonlattice model, which has been solved in the mean-field approximation. Heilmann and Lieb have proposed a lattice model with positional and orientational interactions between the molecules.¹⁴ The model has been studied in two and three dimensions. In the two-dimensional (2D) case the molecules can only be oriented in two perpendicular orientations in the square lattice.

The purpose of this paper is to present a 2D model able to reproduce these two transitions, and analyze their properties. The model is based on a lattice-gas model of cylindrical molecules with orientational degrees of freedom and it represents a first approximation towards the modeling and the complexity displayed by real systems.

The outline of the paper is as follows. In Sec. II we introduce the model mathematically and study its ground state. In Sec. III we present the mean-field solution of the model, and in Sec. IV this solution is compared with the results obtained using the Monte Carlo method. Finally, in Sec. V we summarize the conclusions of the work.

II. MODEL

For simplicity we will restrict ourselves to a two-dimensional square lattice with N_s sites per side and parameter a . The scheme we will reproduce with our model

is presented in Fig. 1. At low temperatures the system exhibits positional and orientational long-range order [Fig. 1(a)]. This phase will represent the smectic phase. At T_p the positional order vanishes and the smectic phase transforms to a nematic one [Fig. 1(b)]. Finally, at a higher temperature, T_o , the orientational order disappears and the isotropic liquid is obtained [Fig. 1(c)]. We will study also the case $T_o < T_p$. This situation would schematically correspond to the case of the so-called plastic crystals.

In each site i of the lattice ($i = 1, \dots, N$; $N = N_s \times N_s$) we define two variables S_i and θ_i . $S_i = +1$ when the i site is occupied by a molecule and $S_i = 0$ otherwise. θ_i (defined only if $S_i = 1$), represents the angular orientation of a molecule. A particular configuration of the lattice will be completely specified when the set of variables $\{S_i, \theta_i\}$ for all the lattice sites is known.

The Hamiltonian of our model is constituted by a positional interaction term plus an orientational interaction term:

$$\mathcal{H} = \mathcal{H}_p + \mathcal{H}_o .$$

On the basis of the lattice-gas model,¹⁵ the positional interaction between molecules is chosen as

$$\mathcal{H}_p = \frac{1}{2} J \sum_{i,j}^{\text{NN}} S_i S_j , \quad (1)$$

where the summation is made over all the different nearest-neighbor (NN) pairs. Taking $J > 0$, the lattice-gas model could be reduced to an Ising model and solved exactly.¹⁶ This model shows a phase transition from an antiferromagnetic positionally ordered state to a disordered state.

We will add now an orientational interaction guided by the Maier-Saupe model.⁷ Originally this is a 3D model with nonpolar NN interactions. The corresponding Hamiltonian reads

$$\mathcal{H}_o = \frac{1}{2} K \sum_{i,j}^{\text{NN}} P_2(\cos\theta_{ij}) , \quad (2)$$

where $P_2(x) = (3x^2 - 1)/2$ and θ_{ij} is the angle between two NN molecules. This model has a transition between an orientationally ordered state and a disordered state (corresponding to the nematic-isotropic transition).

In our case, we will adapt it to two dimensions and we

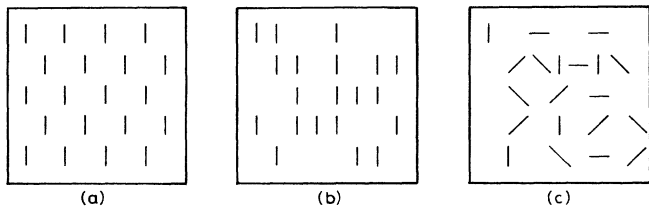


FIG. 1. Schematic picture of the behavior of the presented model that is applicable to liquid crystals. (a) Positional and orientational ordered phase (smectic). (b) Only positional ordered phase (nematic). (c) Completely disordered phase (isotropic).

will assume that only four different orientations are allowed. The rotation symmetry of the continuous angular model is changed by the discrete symmetry of the invariance group of the octagon.

If we take the vertical direction as a reference, θ_i (see Fig. 2) will take values $0, \pi/4, \pi/2, -\pi/4$. Also, θ_{ij} is reduced to $\theta_i - \theta_j$ as a consequence of the change in the dimension of the system. In the original 3D and continuous Maier-Saupe model, the mean value of $P_2(\cos\theta_{ij})$, $\langle P_2(\cos\theta_{ij}) \rangle$, is used as the order parameter. If we want to maintain this, the discretization of the orientations implies changing P_2 by $P(x) = 2x^2 - 1$. With this change $\langle P(x) \rangle$ takes a 0 value in the disordered state and 1 in the completely ordered one.

We will use the following notation:

$$\sigma_i = 3 - \frac{4\theta_i}{\pi} , \quad (3)$$

which will take the values 1, 2, 3, and 4 for the different values of θ_i (see Fig. 3). Now $P(\theta_i - \theta_j)$ will be written as $P(\sigma_i, \sigma_j)$. At this point we are able to propose the complete Hamiltonian for our model as follows:

$$\mathcal{H} = \frac{1}{2} \left[J \sum_{i,j}^{\text{NN}} S_i S_j + K_1 \sum_{i,j}^{\text{NN}} S_i S_j P(\sigma_i, \sigma_j) + K_2 \sum_{i,j}^{\text{NNN}} S_i S_j P(\sigma_i, \sigma_j) \right] . \quad (4)$$

The first term is a lattice-gas positional interaction, the second one is a NN orientational interaction, and the third represents the next-nearest-neighbor (NNN) orientational interactions. The last term has been found to be necessary for stabilizing a ground state with orientational and positional order as we will see in Sec. II A.

We can reduce the number of parameters of the model using the dimensionless quantities

$$\mathcal{H}^* = \frac{\mathcal{H}}{J}, \quad K_1^* = \frac{K_1}{J}, \quad K_2^* = \frac{K_2}{J}, \quad T^* = \frac{k_B T}{J} ,$$

where k_B is the Boltzmann constant. With this notation

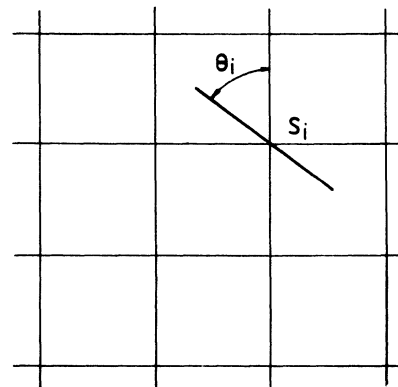


FIG. 2. Variables defined on the two-dimensional square lattice. S_i takes values 1 or 0 if the i site is occupied or not by a molecule. θ_i is the angular orientation of the molecule.

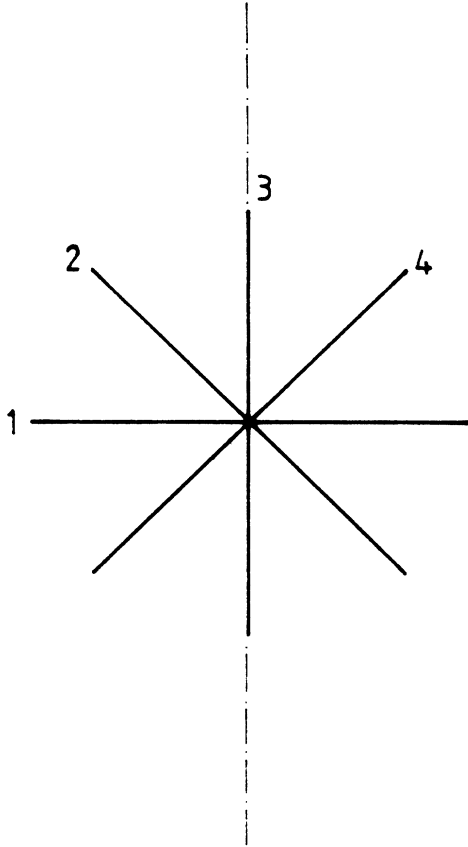


FIG. 3. Discretization of the orientations of the molecules. The number shows the values of σ_i associated with each direction.

the energy depends on only two parameters:

$$\mathcal{H}^* = \frac{1}{2} \left[\sum_{i,j}^{\text{NN}} S_i S_j + K_1^* \sum_{i,j}^{\text{NN}} S_i S_j P(\sigma_i, \sigma_j) + K_2^* \sum_{i,j}^{\text{NNN}} S_i S_j P(\sigma_i, \sigma_j) \right]. \quad (5)$$

Note that this energy may be simply written in the form

$$\mathcal{H}^* = \frac{1}{2} \left[\sum_{i,j}^{\text{NN}} \alpha_{ij}^1 S_i S_j + \sum_{i,j}^{\text{NNN}} \alpha_{ij}^2 S_i S_j \right], \quad (6)$$

with $\alpha_{ij}^1 = 1 + K_1^* P(\sigma_i, \sigma_j)$ and $\alpha_{ij}^2 = K_2^* P(\sigma_i, \sigma_j)$.

A. Ground state

Knowledge of the ground state of the system is necessary if we want, as a first step, to solve the model using the mean-field theory. We are looking for the configuration $\{S_i, \sigma_i\}$ that minimizes the energy given by expression (5). The standard minimization method based on analytical derivation is not impossible but is very complicated. For this reason we have used a different method based on Karl's theorem.¹⁷ Karl proposed that if the interaction between atoms in a lattice system is symmetric and is restricted to NN only, the ground state has a

translational symmetry with parameter $2a$. With NNN interactions (as in our case) the theorem is still true if the interaction is weak enough and probably even if the NNN is of the same order as the NN interaction and has the same sign. When interactions are competing (as in an ANNNI model¹⁸) longer modulated structures could minimize the energy. Using this result and keeping in mind its limitations, we have prepared a computer program for searching the ground state of the system. The program tests the 5^4 possible configurations with $2a$ translational symmetry, and evaluates the corresponding energy. In Fig. 4 we present the phase diagram at $T^* = 0$ obtained for the cases $J^* > 0$ [Fig. 4(a)] and $J^* < 0$ [Fig. 4(b)]. For the present work we will restrict our discussion to the case $J^* > 0$.

Looking at Fig. 4(a) we observe that the zone we are interested in is zone A, since in this zone the particle density is 0.5 and by increasing the temperature it is reasonable that a positional disorder appears. In the B and C

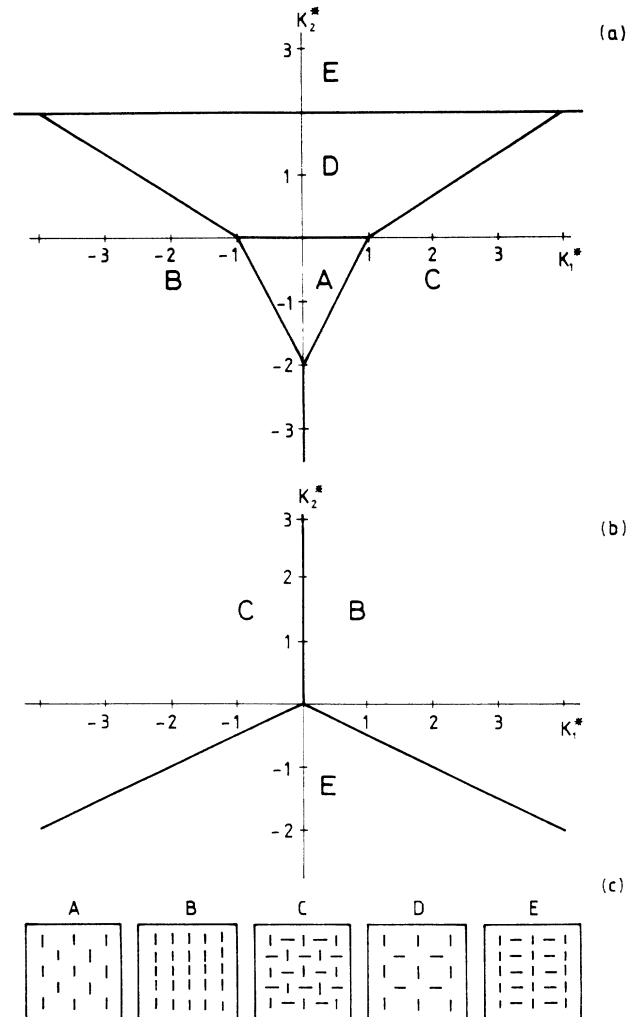


FIG. 4. Phase diagram of the model at $T=0$ calculated by using Karl's theorem. (a) Case $J > 0$. (b) Case $J < 0$. [In case (b) K_1^* and K_2^* are defined as $K_1/|J|$ and $K_2/|J|$.] (c) Structure of the phases in the different regions.

zones, the lowest energy state is reached with a particle density equal to 1, and when working with a lower density (0.5, for example) we will find a clustering tendency. The existence of an energy associated with the boundaries limiting these clusters enables us to extend slightly the A phase into B and C zones.

The role played by the NNN interaction term in the Hamiltonian is clearly seen when looking at the A phase: it stabilizes the orientational order at $T^*=0$. It should be noticed that in the top-left and bottom-right quadrants, Karl's theorem is not applicable; however, the states A , B , and C represented in Fig. 4(a) have been corroborated by means of Monte Carlo simulations as we will discuss in Sec. IV.

Finally, it is worth noting the existence of a high degeneration of the ground state concerning the zone we are dealing with (the A zone). On the one hand, there is a symmetry in exchanging the occupied sublattice with the empty one, and on the other hand, there are four possible orientations, all with the same energy.

$$\sum_{\text{NN}} S_j = \begin{cases} \frac{2q_1}{N} \sum_{\sigma} N_{\sigma}^+ & \text{if site } i \text{ is in the } - \text{ sublattice} \\ \frac{2q_1}{N} \sum_{\sigma} N_{\sigma}^- & \text{if site } i \text{ is in the } + \text{ sublattice,} \end{cases}$$

$$\sum_{\text{NN}} S_j P(\sigma_i, \sigma_j) = \begin{cases} \frac{2q_1}{N} \sum_{\sigma} N_{\sigma}^+ P(\sigma_i, \sigma) & \text{if site } i \text{ is in the } - \text{ sublattice} \\ \frac{2q_1}{N} \sum_{\sigma} N_{\sigma}^- P(\sigma_i, \sigma) & \text{if site } i \text{ is in the } + \text{ sublattice,} \end{cases}$$

$$\sum_{\text{NNN}} S_j P(\sigma_i, \sigma_j) = \begin{cases} \frac{2q_2}{N} \sum_{\sigma} N_{\sigma}^- P(\sigma_i, \sigma) & \text{if } i \text{ is in the } - \text{ sublattice} \\ \frac{2q_2}{N} \sum_{\sigma} N_{\sigma}^+ P(\sigma_i, \sigma) & \text{if } i \text{ is in the } + \text{ sublattice,} \end{cases}$$

where \sum_{NN} represents the sum over the q_1 NN of site i , and \sum_{NNN} the corresponding sum over the q_2 NNN. In our case $q_1 = q_2 = 4$.

We now assume that

$$P(\sigma, \sigma') = P(\sigma, 3)P(3, \sigma'), \quad (8)$$

which is an approximation commonly used in solving the Maier-Saupe model.^{6,13} Note that we have supposed that at $T^*=0$, the molecules are in the $+$ sublattice and oriented in direction 3. We also assume that directions 2 and 4 are completely equivalent since there is no reason for this symmetry to be broken. Under these conditions

$$N_2^+ = N_4^+, \quad N_2^- = N_4^- . \quad (9)$$

With these variables we are able to define the order parameters of our system. It is easy to see that we need five order parameters in order to characterize the phases

III. MEAN-FIELD SOLUTION

In order to obtain the solution of the model, on the basis of the mean-field approximation, we will introduce the notation based on the occupation numbers. Once the ground state is known, we can divide the system into two sublattices which will be called $+$ (occupied) and $-$ (nonoccupied). Then, we define N_{σ}^+ and N_{σ}^- as the number of particles with orientation σ , in the $+$ or $-$ sublattice, respectively. It is clear that these quantities must verify:

$$\sum_{\sigma=1}^4 (N_{\sigma}^+, N_{\sigma}^-) = N_p, \quad (7)$$

where $N_p = cN$ is the number of particles and c is the density. As we are interested in a ground-state-type A , we will take $c=0.5$.

The mean-field approximation is applied by substituting the NN or NNN interaction effects on a molecule in the i site, respectively, by

occurring in the present model. We have chosen them as follows:

$$m_p = \frac{\sum_{\sigma} N_{\sigma}^+ - \sum_{\sigma} N_{\sigma}^-}{N_p},$$

$$m_1^+ = \frac{\sum_{\sigma} N_{\sigma}^+ P(3, \sigma)}{N_p} = (N_3^+ - N_1^+) / N_p,$$

$$m_2^+ = (N_3^+ - N_2^+) / N_p, \quad (10)$$

$$m_1^- = (N_3^- - N_1^-) / N_p,$$

$$m_2^- = (N_3^- - N_2^-) / N_p.$$

The first one, m_p , describes the positional order, and the rest are orientational order parameters. This set of orientational order parameters will be denoted by \mathbf{m}_o , and the complete set of order parameters (m_p, \mathbf{m}_o) by \mathbf{m} .

According to the ground state studied before, at $T^*=0$, $m_p=1$ (or -1 if the sublattice $-$ is the occupied one), $m_1^+=m_2^+=1$ (if the direction of the molecules is 3), and the remaining order parameters vanish, whereas in the completely disordered state, all the order parameters vanish.

With these order parameters, in the mean-field approximation the energy of the system takes the form

$$E^*=(1-m_p^2)+4K_1^*m_1^+m_1^-+2K_2^*(m_1^{+2}+m_1^{-2}). \quad (11)$$

It is worth noting that in the mean-field approximation there is no interaction between the orientational order parameters and the positional one. All coupling effects, will come from the entropy S^* , evaluated as

$$S^*=\ln W, \quad (12)$$

where

$$W(N_\sigma^+, N_\sigma^-)=\frac{N_p!}{\prod_\sigma (N_\sigma^+!) \left[N_p - \sum_\sigma N_\sigma^+ \right]!} \times \frac{N_p!}{\prod_\sigma (N_\sigma^-!) \left[N_p - \sum_\sigma N_\sigma^- \right]!}. \quad (13)$$

S^* can be expressed as a function of the order parameters using (7), (9), and (10). Then the free energy $F^*=E^*-T^*S^*$ is written as

$$\begin{aligned} F^*(m_p, m_1^+, m_2^+, m_1^-, m_2^-) &= (1-m_p^2) + 4k_1^*m_1^+m_1^- + 2K_2^*(m_1^{+2} + m_1^{-2}) \\ &+ T^*\left(\frac{1}{4}\left[\frac{1}{2}(1+m_p) - 3m_1^+ + 2m_2^+\right] \ln\left\{\frac{1}{4}\left[\frac{1}{2}(1+m_p) - 3m_1^+ + 2m_2^+\right]\right\}\right. \\ &\quad \left. + \frac{1}{2}\left[\frac{1}{2}(1+m_p) + m_1^+ + 2m_2^+\right] \ln\left\{\frac{1}{4}\left[\frac{1}{2}(1+m_p) + m_1^+ + 2m_2^+\right]\right\}\right. \\ &\quad \left. + \frac{1}{4}\left[\frac{1}{2}(1+m_p) + m_1^+ + 2m_2^+\right] \ln\left\{\frac{1}{4}\left[\frac{1}{2}(1+m_p) + m_1^+ + 2m_2^+\right]\right\}\right. \\ &\quad \left. + \frac{1}{2}(1-m_p) \ln\left[\frac{1}{2}(1-m_p)\right]\right) \\ &+ T^*(\text{the same but } m_p \rightarrow -m_p, m_1^+ \rightarrow m_1^-, m_2^+ \rightarrow m_2^-). \end{aligned} \quad (14)$$

Now F^* must be minimized with respect to the five order parameters in order to obtain the equilibrium configuration at each temperature. We have used two methods. On the one hand, we have solved numerically the set of five nonlinear coupled equations which are obtained from

$$\begin{aligned} \frac{\partial F^*}{\partial m_p} &= 0, \quad \frac{\partial F^*}{\partial m_1^+} = 0, \quad \frac{\partial F^*}{\partial m_1^-} = 0, \\ \frac{\partial F^*}{\partial m_2^+} &= 0, \quad \frac{\partial F^*}{\partial m_2^-} = 0. \end{aligned} \quad (15)$$

In fact, this set of five equations reduces to three because two of them can be reduced to

$$\begin{aligned} m_1^+(1+m_p) + 2(m_1^+)^2 &= 2m_2^+(1+m_p), \\ m_1^-(1-m_p) + 2(m_1^-)^2 &= 2m_2^-(1-m_p). \end{aligned} \quad (16)$$

On the other hand, we have directly minimized F^* by means of a computational program that uses the SIMPLEX method to find the absolute minimum of a given function. This method finds the stable solution directly. With the first method the stability must be studied with the second derivatives of F^* .

Let us comment on some simple solutions.

(a) $\mathbf{m}=(0,0,0,0,0)$. This solution is always an extreme of the function F^* , for all the possible values of the parameters K_1^* and K_2^* , but it is only stable at high temperatures as we will see later.

(b) $\mathbf{m}=(m_p,0,0,0,0)$. If we restrict ourselves to these kinds of solutions, Eqs. (15) can be easily simplified to the following expression:

$$\exp\left[\frac{2m_p}{T^*}\right] = \frac{1+m_p}{1-m_p}. \quad (17)$$

By expanding in series both sides of this equation, for $m_p \rightarrow 0$, we can find the temperature T_p^* , at which m_p vanishes while $m_o=0$. For all possible values of K_1^* and K_2^* , $T_p^*=1$. This is obviously the mean-field transition temperature of the 2D lattice-gas model with only NN interactions.

(c) $\mathbf{m}=(0, \mathbf{m}_o)$. In this case we can also easily find the variation of the order parameters with temperature. Taking into account Eqs. (16), we need to solve only two equations. If we do not consider degenerated configurations, there are two possible solutions: (1) $m_1^+=m_1^-$ and (2) $m_1^+=-m_1^-$. In this case it is also possible to find the temperature T_o^* at which the orientational order parameters vanish while $m_p=0$. A straightforward calculation leads to

$$T_o^* = -(K_1^* + K_2^*) \quad (18)$$

for solution (1) and

$$T_o^* = K_1^* - K_2^* \quad (19)$$

for solution (2).

In the general case it is not possible to find the transition temperatures analytically. In Figs. 5–8 we have represented the four possible solutions calculated by the method of directly minimizing F^* . In the cases $m_p=0$ and $\mathbf{m}_o=0$, the transition temperatures T_p^* and T_o^* correspond well with those calculated analytically at points (b) and (c). We have only represented m_p , m_1^+ , and m_1^- as a function of temperature. In Fig. 9 we indicate the region

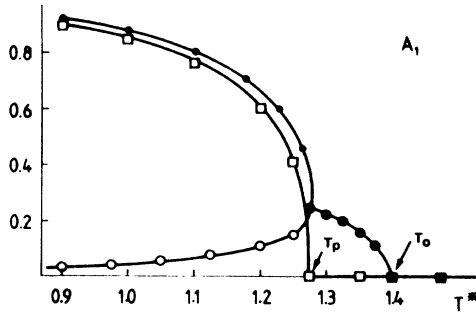


FIG. 5. Evolution of the order parameters vs temperature in the A_1 zone (Fig. 9). The values have been calculated by solving numerically the mean-field equations (15) with $K_1^* = -0.4$ and $K_2^* = -1.0$. (\square , m_p ; \bullet , m_1^+ ; \circ , m_1^- .) T_p and T_o are the positional and orientational 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.)

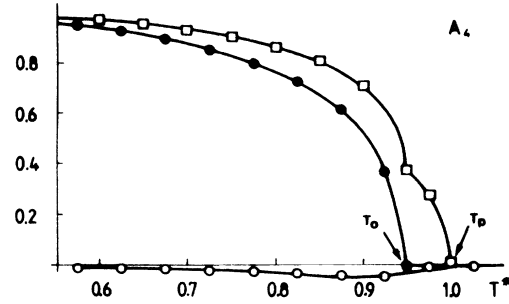


FIG. 8. Evolution of the order parameters vs temperature in the A_4 zone (Fig. 9). The values have been calculated by solving numerically the mean-field equations (15) with $K_1^* = 0.2$ and $K_2^* = -0.6$. (\square , m_p ; \bullet , m_1^+ ; \circ , m_1^- .) T_p and T_o are the positional and orientational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

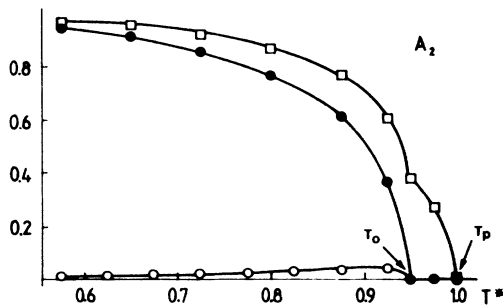


FIG. 6. Evolution of the order parameters vs temperature in the A_2 zone (Fig. 9). The values have been calculated by solving numerically the mean-field equations (15) with $K_1^* = -0.2$ and $K_2^* = -0.6$. (\square , m_p ; \bullet , m_1^+ ; \circ , m_1^- .) T_p and T_o are the positional and orientational 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.)

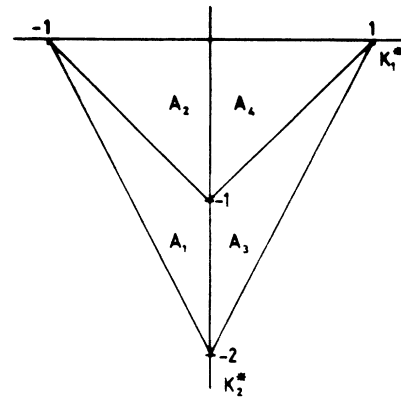


FIG. 9. Detail of the $T=0$ phase diagram [Fig. 4(a)] showing the regions where the four different mean-field solutions of Figs. 5–8 have been found. All the regions correspond to the same ground state but have different evolutions with rising temperature.

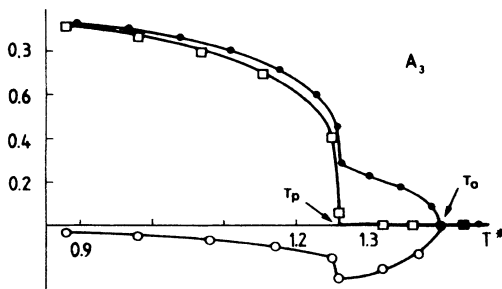


FIG. 7. Evolution of the order parameters vs temperature in the A_3 zone (Fig. 9). The values have been calculated by solving numerically the mean-field equations (15) with $K_1^* = 0.4$ and $K_2^* = -1.0$. (\square , m_p ; \bullet , m_1^+ ; \circ , m_1^- .) T_p and T_o are the positional and orientational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

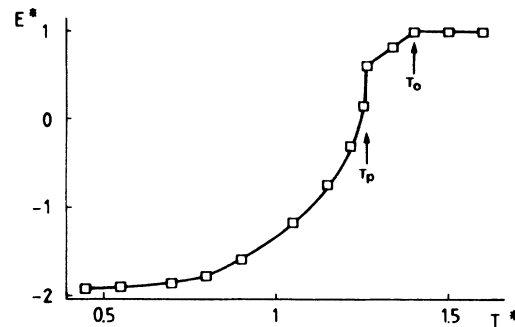


FIG. 10. Plot of the energy E^* vs temperature T^* showing the two transitions T_p and T_o . The values have been obtained by solving numerically the mean-field equations with $K_1^* = -0.4$ and $K_2^* = -0.1$. (The line is a guide to the eye.)

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.³

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 transitions¹⁹ and experimental results²⁰ 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

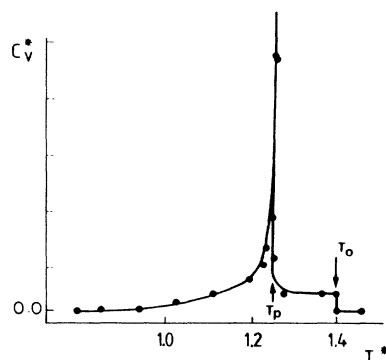


FIG. 11. Numerical derivative of E^* (Fig. 10), showing the evolution of the specific heat vs temperature in the mean-field approximation. T_p and T_o correspond to the smectic-nematic and nematic-isotropic transition temperatures, respectively. (The line is a guide to the eye, and vertical units are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

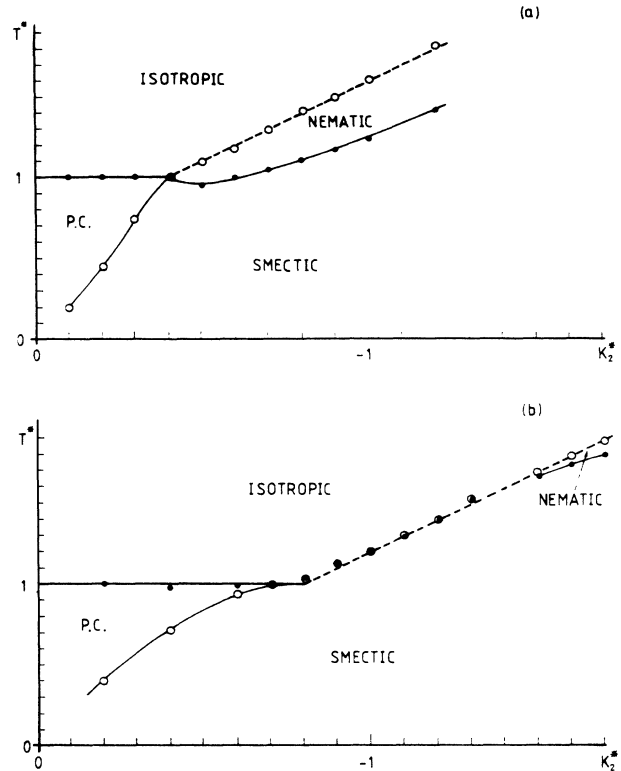


FIG. 12. Sections of the phase diagram calculated by mean-field approximation. The T_p (\bullet) and T_o (\circ) are plotted for different values of K_2^* with $K_1^* = -0.6$ (a) and $K_1^* = -0.2$ (b). The thick solid and the thick dashed lines are the T_p and T_o calculated analytically and the thin 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.*²¹

The Monte Carlo simulation of a physical system can be performed using different dynamics. The two principal ones are Glauber dynamics,²² used when the order parameter is not conserved, and Kawasaki dynamics,²³ 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-

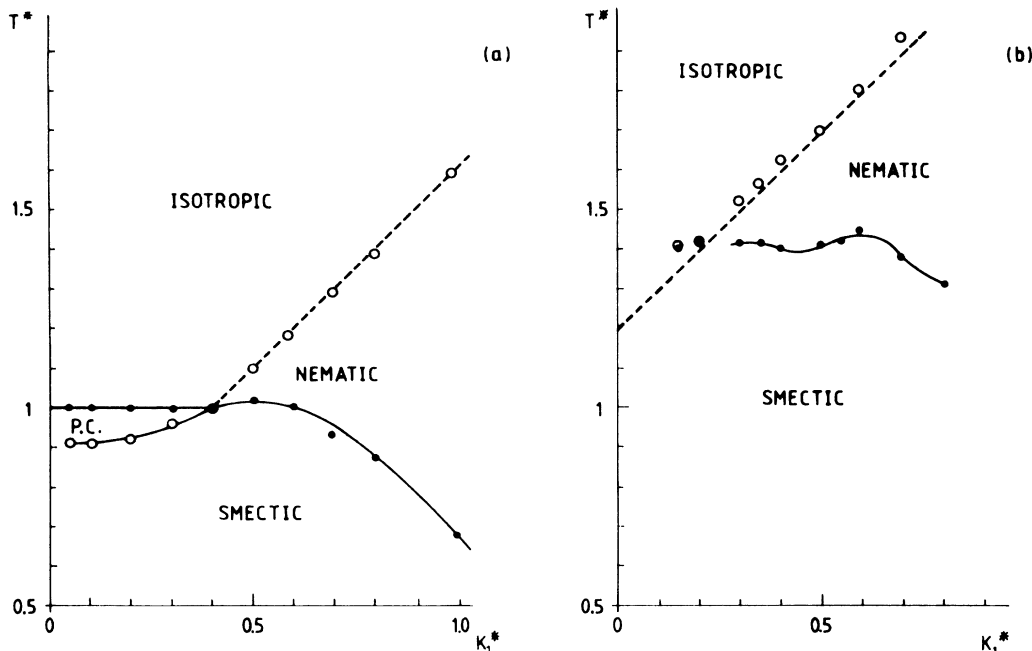


FIG. 13. Sections of the phase diagram calculated by mean-field theory. The T_p (\bullet) and T_o (\circ) are plotted for different values of K_1^* with $K_2^* = -0.6$ (a) and $K_2^* = -1.2$ (b). The thick solid and the thick dashed lines are the T_p and T_o temperatures calculated analytically and the 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_σ^+, N_σ^-) 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 30×30 or 40×40 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.²⁴ 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-

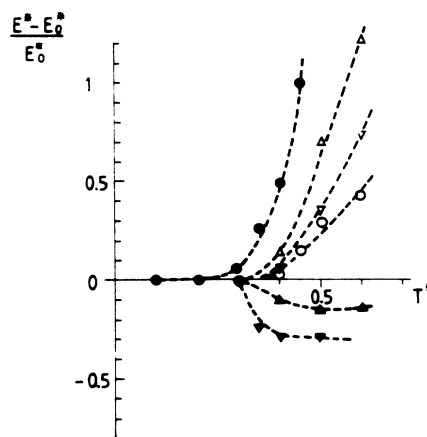


FIG. 14. Plot of $[E^* - E^*(T=0)]/E^*(T=0)$ at low temperatures calculated by Monte Carlo simulations from an initial state with orientational and positional order [phase A in Fig. 4(c)]. For $K_1^* = -0.25$ (\bullet), -0.50 (Δ), -0.75 (∇), and -1.0 (\circ) the initial state seems to be the most stable, 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 30×30 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

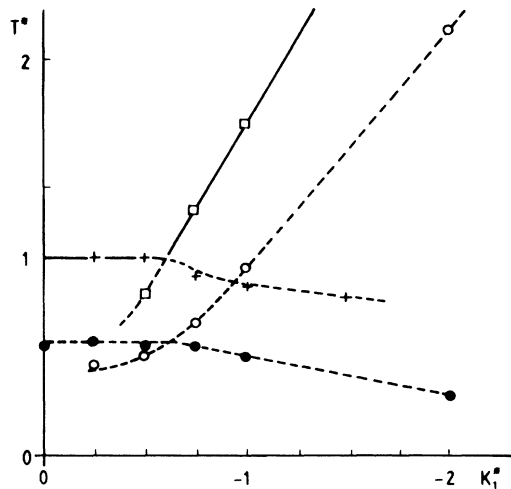


FIG. 15. Section of the phase diagram calculated by Monte Carlo (MC) simulations compared with the mean-field (MF) solution. The section is made over the line $K_2^* = K_1^* / \sqrt{2}$. (+, T_p calculated by MF; □, T_o calculated by MF; ●, T_p calculated by MC; and ○, T_o calculated by MC.) The solid 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 30×30 lattice and averaging over 1000 MCS's after reaching equilibrium.

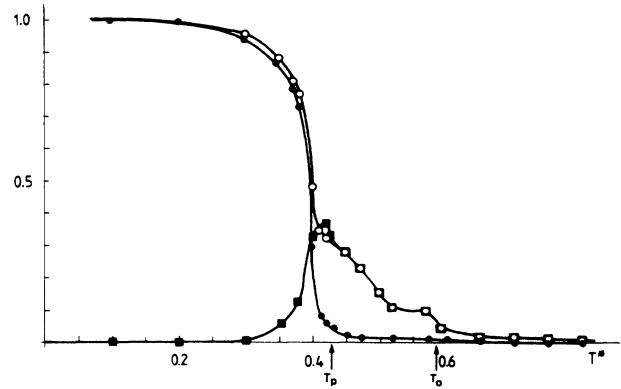


FIG. 16. Evolution of the order parameters calculated by Monte Carlo simulations with $K_1^* = -0.8$ and $K_2^* = -0.4$. (●, m_p ; ○, m_1^+ ; ■, m_1^- .) The lines are guides to the eye. The simulations have been carried out on a 40×40 lattice and averaging over 1000 MCS's after reaching equilibrium 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).

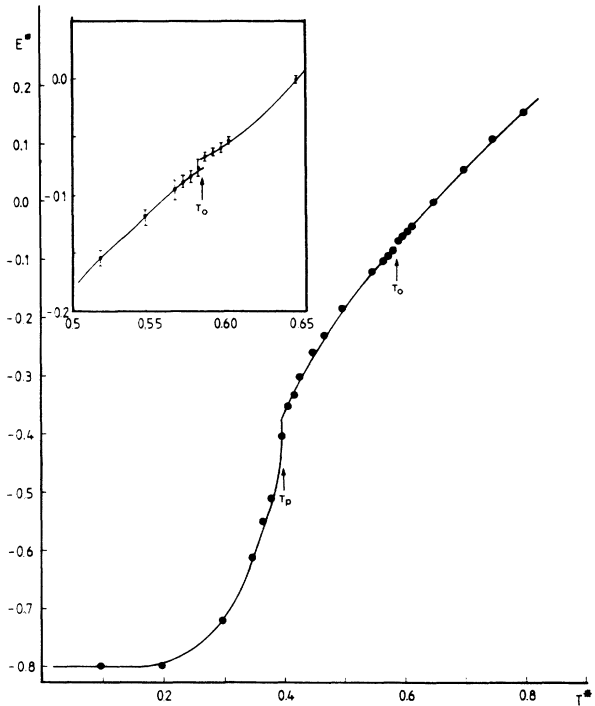


FIG. 17. Evolution of the energy E^* calculated by Monte Carlo simulations in the same conditions as in Fig. 16. The smectic-nematic transition (T_p) and the nematic-isotropic transition (T_o) are little masked by the finite-size effects. The inset shows the detail of the orientational transition. (The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