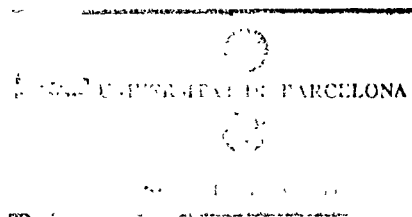


**SIMULACIO MONTE CARLO DE SISTEMES
AMB ACOBLAMENT DE GRAUS DE LLIBERTAT.**



$$H^* = \sum_{i,j}^{n,n} S_i S_j + K_1^* \sum_{i,j}^{n,n} S_i S_j P(R_i, R_j) + K_2^* \sum_{i,j}^{n,n,n} S_i S_j P(R_i, R_j) \quad (5)$$

The phase diagram of this model has been already studied with mean-field techniques¹⁵ and Monte Carlo simulation¹⁶ in previous papers. A detailed study shows that when $-1.0 < K_1^* < 0$ and $-1.0 < K_2^* < 0$ then the ground state of the system is that of Fig. 1b. This ground state is 8 times degenerated because there are 4 possible orientations and 2 possible sublattices to fill. From now on, in a given configuration of the system we will call the + (-) sublattice the one that is more (less) populated.

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

$$m_p = \left(\sum_i^+ S_i - \sum_i^- S_i \right) / N_p \quad (6)$$

$$m_o^+ = \left(\sum_i^+ \delta(R_i - R_{\max}) - \sum_i^+ \delta(R_i - R_{\min}) \right) / N_p \quad (7)$$

$$m_o^- = \left(\sum_i^- \delta(R_i - R_{\max}) - \sum_i^- \delta(R_i - R_{\min}) \right) / N_p \quad (8)$$

where δ is a Kronecker delta function ($\delta(0) = 1$ or 0 otherwise),

Σ^+ (Σ^-) is a summation over the + (-) sublattice, R_{\max} is the preferred direction of the molecules for a given configuration and R_{\min} is the direction perpendicular to R_{\max} . These definitions are used in order to avoid problems associated with the degeneration of the ground state. With these definitions m_p , m_o^+ and m_o^- are always positive.

III MONTE CARLO SIMULATION

Monte Carlo simulations have been performed on a 40×40 lattice with $N_p = 800$ with Periodic Boundary Conditions and using standard Metropolis algorithm^{21,22}. A combination of Glauber dynamics changing the orientations and Kawasaki dynamics exchanging particles and holes has been used. Finite size effects have been corrected using the subblock method²³ which enables to extrapolate the results to the case $L \rightarrow \infty$. Usual runs are carried up to 12000 MC steps per particle. Averages of the quantities of interest like order parameters ($\langle m_p \rangle$, $\langle m_p^2 \rangle$, $\langle m_o \rangle$, $\langle m_o^2 \rangle$), energy ($\langle E \rangle$), etc. are taken over 500 uncorrelated configurations, after discarding the first 10^4 MC steps. The normal correlation time is about 4 MC steps, except near the phase transitions where averages over different evolutions corresponding to different seeds of the random numbers generator have been taken in order to improve the statistics.

Different points of the Phase Diagram have been simulated. Depending on the values of K_1^* and K_2^* one can find two different behaviours (Fig. 2 shows the different sections and points that have been studied and the regions where the two behaviours occur). When K_1^* and K_2^* are sufficiently negative, the positional order disappears at a lower temperature (T_p) than the orientational order (T_o). Between these two temperatures a phase with only long range orientational order (LC phase) is stable. Otherwise, when K_1^* and K_2^* are small, one finds $T_o < T_p$ and a phase with only long range positional order (PC phase) appears.

Figs. 3(a) and 3(b) give the sections of the Phase Diagram

along the dashed lines plotted in Fig.2. The four phases S, LC, PC and L are clearly identified. Changing the value of the orientational constants K_1^* or K_2^* , one can change from a Liquid Crystal behaviour to a Plastic Crystal behaviour.

Figure 4 shows the evolution (extrapolated to $L \rightarrow \infty$) of the positional order parameter in two different cases. Case (a) corresponds to $K_1^* = -0.9$, $K_2^* = -0.9$ and case (b) to $K_1^* = -0.5$, $K_2^* = -0.9$. Performing long enough simulations the results do not depend on the starting configuration any more and a first order transition produces then a broadening due to the existence of long metastable states. For instance in case (b) all data are obtained starting from a disordered state and using several random number generator seeds. The values of the upper branch correspond to runs that have jumped to the high temperature phase while the values of the lower branch correspond to runs that have not jumped. We have suppressed the values corresponding to runs that jump during the average procedure and give spurious values between the two branches. The lines are guides to the eye showing the two envelopes of the obtained results.

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

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

As in the case of the order parameters in case (b) only the envelope of the obtained values is plotted, and the values

corresponding to runs with a jump during the average procedure have been suppressed. The peak of the specific heat has been used in order to have an estimation of the transition temperature T_p with an accuracy of the order of $\Delta T \approx 0.01$.

IV CRITICAL BEHAVIOUR

The orientational transition has previously been identified as a first order phase transition due to the hysteresis shown in the evolution of $\langle m_o \rangle$ and the broad peak in susceptibilities and specific heat. This broadening, due to the hysteresis, appears because the figures are obtained after averaging over different runs with different random number generator seeds. This fact was pointed out by the authors already in the first simulations of this system¹⁶. Here, we will mainly focus our attention on the nature of the positional transition between the S phase and the LC phase.

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

In order to clarify the nature of the positional transition we have used a finite size scaling method proposed recently²⁴. In this method the gaussian character of the energy distribution function is tested using the quantity:

$$V_L = 1 - \frac{\langle E^4 \rangle_L}{3 \langle E^2 \rangle_L^2} \quad (10)$$

In the limit of $L \rightarrow \infty$, V_L should always tend to the value 2/3

except at a first order phase transition where V_L tends to a smaller value related to the latent heat.

Fig. 6 shows the dependence of V_L for the same cases as in figures 4 and 5, for the different subblock sizes ($L = 40, 20, 10, 8, 4$). In both cases one can see the existence of a minimum associated to the positional transition that appears overlapped with another broader well (only partially shown) that corresponds to the first order orientational transition. The position of the peaks of the specific heat curves are always located at the left side of the V_L minima. In case (a) the lack of gaussian character of the energy distribution has practically disappeared at $L=40$, while in case (b) it clearly still remains. This result justifies the continuous nature of the positional phase transition in case (a) and its first order character in case (b), in agreement with the results deduced from the hysteresis considerations.

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

$$m_p = A \left(\frac{T_p - T^*}{T_p} \right)^\beta \quad (11)$$

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

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

This is probably not the best procedure to determine very accurate critical exponents. Methods based on finite size scaling theories²² can produce better estimations, but they are extremely computer time consuming. Since our objective is not to obtain absolute values of the β exponent, but to show possible relative changes, this relatively simple way seems accurate enough.

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

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

The region where the critical behaviour changes is narrower in the case $K_1^* = K_2^*$ than in the case $K_2^* = -0.9$. An explanation to

this behaviour is that, if the orientational interactions at n.n.n. and n.n. are equal, it is reasonable to think that the positional transition (which can be seen as a transition disordering n.n.n pairs to n.n. positions) is less affected. The mean field solution of this model is also in agreement with that explanation¹⁵.

These results can be qualitatively compared with some measurements made with different pure Liquid Crystals or Liquid Crystal mixtures using calorimetric and X-ray scattering techniques^{11,12,17}. Despite the large amount of phases that these systems exhibit we will focus on the so called Smectic-Nematic and Nematic-Isotropic transitions corresponding to the complete vanishing of the long range positional order and the long range orientational order respectively. The temperature separation between these two transitions, or in other words the width of the nematic region, is different in each particular Liquid Crystal and depends mainly on the ratio between the orientational and positional interactions.

Mixing Liquid Crystals with different molecule lengths but similar chemical properties opens the possibility of changing the effective orientational interaction and controlling its value by controlling the composition of the mixtures. This can be compared with the role played by the constants K_1^* and K_2^* in our model. Experiments have been done with mixtures of Alkylbenzoate Liquid Crystals (nCB)¹². The resulting phase diagram can be qualitatively compared to the Liquid Crystal region of the phase diagrams shown in Figs 3(a) and 3(b). The width of the nematic (LC phase) region decreases when the composition of the mixture

is changed. The two transitions, Smectic-Nematic (corresponding to T_p) and Nematic-Isotropic (corresponding to T_o), have been found to overlap at a given composition¹².

In good agreement with our results different authors have reported the existence of a change in the critical behaviour of the smectic-nematic transition and the existence of a tricritical point¹². This agreement is surprising if one notes that in principle a Liquid Crystal is a three-dimensional system, while our model is only two-dimensional. A possible explanation of this fact is that the Smectic phase is basically a layered structure and may behave as if it had a dimensionality less than three.

β effective critical exponents have been measured on different Liquid Crystals and Liquid Crystal mixtures^{11,12,17}. Fig. 8 shows some results of such measurements found in the literature as a function of the Mc Millan parameter M , defined as:

$$M = \frac{T_{\text{Smectic-Nematic}}}{T_{\text{Nematic-Isotropic}}} \quad (12)$$

which measures the relation between the orientational and positional interaction energies, and which can be qualitatively compared to the ratio T_p/T_o . The exponents measured experimentally are scaled by the exponents corresponding to the 3DXY model universality class to which such Liquid Crystals are supposed to belong. The diagram is very similar to those given in Figs 6(a) and 6(b) and shows that when the two transitions are very close, coupling phenomena appear and the behaviour of the positional phase transition changes from second order to first order.

V SUMMARY AND CONCLUSIONS

A model that reproduces some features of pure Liquid Crystals and Liquid Crystal mixtures Phase Diagrams, presented recently^{15,16}, has been studied. The model considers the positional degrees of freedom of the molecules as a lattice gas but introduces an extra variable taking into account the orientational degrees of freedom of the molecules. Two different phase transitions appear, each associated with one of the degrees of freedom. For certain values of the interaction constants we are able to reproduce the Liquid Crystal behaviour, where the transition associated to the positional degrees of freedom (T_p) corresponds to the Smectic-Nematic transition, and the transition associated with the orientational degrees of freedom (T_o) corresponds to the Nematic-Isotropic transition. The model reproduces the fact that the ratio between the positional and orientational interactions controls the width of the Nematic phase.

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

We have also measured the effective β exponent of the positional transition in order to locate the possible tricritical

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

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

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