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On a simple model of ferroelectricity in liquid crystals

F. Biscarini ^{a,1}, C. Chiccoli ^b, P. Pasini ^b and C. Zannoni ^a

^a *Dipartimento di Chimica Fisica ed Inorganica, Universita', Viale Risorgimento, 4, 40136 Bologna, Italy*

^b *INFN Sez. di Bologna and CNAF, Viale Ercolani, 8, 40138 Bologna, Italy*

A simple model with first and second rank anisotropic interactions that can be viewed as a prototype of bowlic and ferroelectric liquid crystals was studied. This Krieger–James model can have a polar, nematic and isotropic phase. This was investigated by applying two-site cluster theory and Monte Carlo simulations and results are presented for its thermodynamics as well as for its macroscopic polarization as a function of temperature.

1. Introduction

Ferroelectric low molar mass [1] and polymeric liquid crystals [2] have become extremely interesting both for their fundamental properties and for their applicability in fast-switching electro-optic devices [3]. The only liquid crystals that have been prepared and studied to date are, to our knowledge, chiral smectic C phases. However, there are no reasons of principle to exclude other kinds of liquid crystal ferroelectric phases and it is interesting to develop simple molecular models that explore the key ingredients that could give a ferroelectric liquid crystal.

One such model is that first proposed by Krieger and James [4] and later examined also by Lin Lei [5]. We treat a lattice version of the model that consists of a set of particles placed on a simple cubic lattice and interacting with the P_1P_2 pair potential

$$U_{ij} = -\epsilon_{ij} \left[P_2(\cos \beta_{ij}) + \xi P_1(\cos \beta_{ij}) \right], \quad (1)$$

where ϵ_{ij} is a positive constant, ϵ , for nearest-neighbour particles, i and j , β_{ij} is the angle between the axis of these two molecules and P_L is the L th Legendre polynomial. The parameter, ξ , determines the relative importance of the first

rank term with respect to the second one, while its sign determines ferroelectric or antiferroelectric type ordering. Realization of a molecular system with ferroelectric type ordering could be made possible by a combination of steric and dipolar interactions as, for example, in pyramidal systems [6–7].

2. Two-site cluster (TSC) theory

We have employed the classical procedure of Strieb et al. [8] to treat in detail two particles in the field of all the others. The cluster variational parameters have been obtained by direct numerical minimization of the free energy, rather than by solving the system of consistency equations as it is more often done. We have determined the phase transition temperatures for a set of ξ values as well as the first and second rank order parameters, $\langle P_1 \rangle$, $\langle P_2 \rangle$, as a function of temperature. The results are shown below, together with the computer simulation findings.

3. Cluster Monte Carlo (CMC) simulations

Determining transition temperatures and transition behaviour is a challenging exercise in computer simulations [9–11]. Investigating the char-

¹ Present address: Institute of Molecular Biology, University of Oregon, Eugene, OR 97403-1253, USA.

acter of a transition requires a finite size scaling study but even simply obtaining a good estimate of the transition can be rather difficult and complicated by the choice of boundary conditions. The standard method is to use periodic boundary conditions and consists of having exact replicas of the system filling space as needed by the range of the pair interactions. Although vastly superior to, for example, an empty space boundary, using periodic boundary conditions leads to large smearing and broadening of the heat capacity versus temperature peak at a supposed transition. This in turn makes it difficult to obtain a sensible estimate of the transition unless a very high number of particles (typically many thousand) is used [10]. Clearly, such large numbers can be forbidding, even with a simple potential such as that in eq. (1), if the simulation has to be repeated for various values of a physical parameter, here the first to second rank ratio, ξ . Thus we have simulated the P_1P_2 system employing the cluster Monte Carlo method. In this technique, described in detail in ref. [11], periodic boundary conditions are replaced by the weaker condition that the particles outside the sample box have, on the mean, the same observable properties as those inside, rather than being their exact replicas. The desired bulk average of a quantity A is written as an average over the various external configurations, $[W]$, of the average values, $\langle A \rangle_{[W]}$, calculated for a fixed configuration of the ‘world’ outside the sample box. In practice, a finite set M_W of external world configuration samplings is used and one replaces a single Monte Carlo average by an average of Monte Carlo results, each obtained for a fixed environment $[W]$. The external boundary layer orientations are sampled from a distribution

$$P(\cos \beta) = \exp \left[\sum_{L=0}^3 a_L P_L(\cos \beta) \right], \quad (2)$$

where the coefficients a_L are determined from the consistency constraint that the available $\langle P_L \rangle$ can be re-obtained by averaging $P_L(\cos \beta)$ over the distribution in eq. (2) and that the distribution is normalized. In this preliminary study, we have investigated three systems of particles interacting with the P_1P_2 potential of eq. (1), on a simple

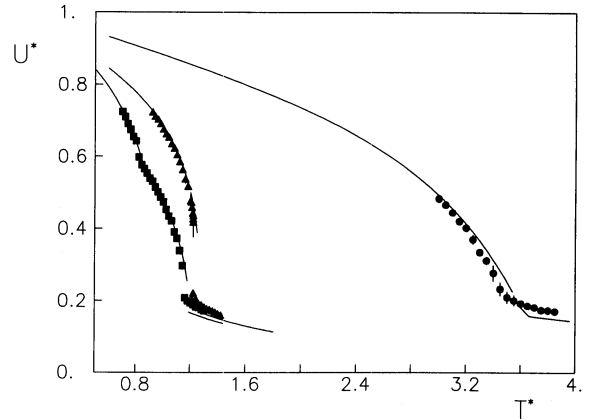


Fig. 1. The reduced energy per particle, U^* , against dimensionless temperature T^* as obtained from $8 \times 8 \times 8$ CMC computer simulations for $\xi = 0.2$ (■), 0.4 (▲), 2.0 (●) compared with the two-site cluster (TSC) results (continuous lines).

cubic lattice with dimensions $8 \times 8 \times 8$ for different values of the parameter ξ , i.e., $\xi = 0.2$, $\xi = 0.4$, $\xi = 2.0$. The simulations have been run in a heating sequence, with the first configuration being completely ordered. In fig. 1, we show the reduced energy, $U^* \equiv U/N\epsilon$, for the three ξ plotted as a function of the dimensionless temperature, $T^* \equiv kT/\epsilon$. We find, by analyzing the temperature derivative of the energy, that when $\xi = 0.2$ the system presents a transition from polar to nematic at $T^* = 0.84 \pm 0.03$ followed by a nematic to isotropic transition at $T^* = 1.16 \pm 0.01$ (see fig. 1). The corresponding TSC results are, respectively, $T^* = 0.8562$ and 1.1727 . When $\xi = 0.4$, we find a sharp, first order, transition from polar to isotropic at $T^* = 1.225 \pm 0.005$ in good accord with the TSC prediction of $T^* = 1.238$. When the first rank contribution is further increased, $\xi = 2.0$, we have again a single transition from polar to isotropic, but now this is a much smoother one, at $T^* = 3.45 \pm 0.02$, while TSC gives $T^* = 3.625$.

Our results are in qualitative agreement with the mean field results in refs. [4,5]. Of course, the TSC results improve on those, as confirmed by the computer simulations.

In fig. 2, we show the temperature dependence of the macroscopic polarization $\langle P_1 \rangle$ for the three values of ξ . This has been calculated from the unit vectors u_i specifying the particle orientation by

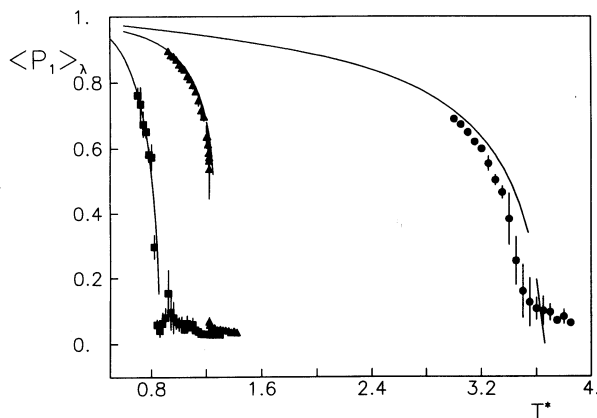


Fig. 2. The first-rank order parameter, $\langle P_1 \rangle$, versus reduced temperature, T^* , obtained from $8 \times 8 \times 8$ CMC for $\xi = 0.2$ (■), 0.4 (▲), 2.0 (●) and TSC theory (continuous lines).

first calculating the director d^J in the J configuration from the eigenvector of the ordering matrix corresponding to the largest eigenvalue, which in turn yields the second rank order parameter $\langle P_2 \rangle_\lambda$ [10,11]. The average over M configurations then gives

$$\langle P_1 \rangle_\lambda = \frac{1}{MN} \sum_J \left| \sum_i^N u_i \cdot d^J \right| \quad (3)$$

We see from fig. 2 that the temperature dependence of the spontaneous polarization is quite different for the three cases studied. At $\xi = 0.2$,

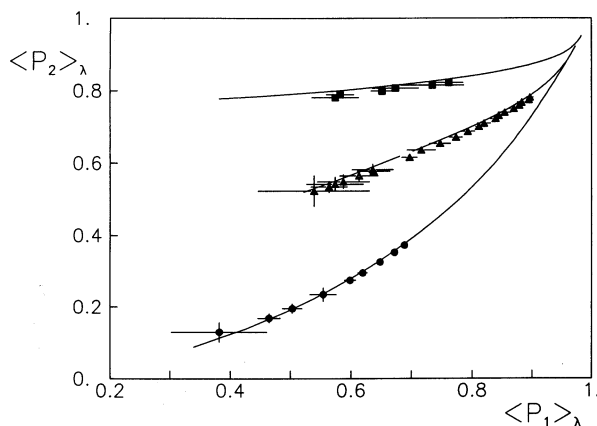


Fig. 3. The second rank order parameter, $\langle P_2 \rangle$, versus the first rank order parameter, $\langle P_1 \rangle$, obtained from $8 \times 8 \times 8$ CMC for $\xi = 0.2$ (■), 0.4 (▲), 2.0 (●) and TSC theory (continuous lines).

$\langle P_1 \rangle$ goes to zero at the first change in slope of U , showing that in the temperature interval between the two transitions the phase is of nematic type. For the other two cases, the polarization only vanishes when going to the isotropic limit. Apart from $\langle P_1 \rangle$ we have determined order parameters up to rank four and these will be reported elsewhere. Here we just show in fig. 3 the second rank versus first rank order parameter together with the TSC prediction. The calculation of both first and second rank order parameter is essential in predicting the molecular contribution to dielectric relaxation in such a phase [12].

4. Conclusions

We have shown that a simple combination of a first rank interaction simulating the head-tail asymmetry and of a second rank interaction is sufficient to obtain a ferroelectric liquid crystal as well as a nematic phase and we have calculated the temperature dependence of the order parameters involved. We believe this simple model [4,5] contains the essential features needed to explain the polar transition and the temperature dependence of the order parameters in its neighbourhood. Moreover, since a liquid crystal can be expected to exist only in a limited temperature range from an orientational phase transition, we think that this model, like the Lebwohl-Lasher model for nematics [10,11], can be taken as a prototype of the behaviour to be expected in real, even though as yet undiscovered uniaxial ferroelectric systems.

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