

PHASE DIAGRAM AND ORIENTATIONAL ORDER OF A SYSTEM WITH SECOND AND FOURTH RANK INTERACTIONS

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A simple generalized Lebwohl–Lasher model for liquid crystals, where a fourth rank interaction is added to the usual second rank one, is investigated in detail. We have obtained the phase diagram of the system performing extensive Monte Carlo computer simulations for a range of the fourth to the second rank relative strengths and we compare it with the prediction of Mean Field and Two Site Cluster theories. We show that the addition of a non-negligible fourth rank term significantly changes the temperature dependence of the order parameter. Fourth rank contributions larger than 20% worsen the agreement of the model with the typical temperature behavior of the order in nematics.

1. Introduction

The Lebwohl–Lasher (LL) model has proven to be a simple yet powerful potential for the simulation of the orientational properties of liquid crystals and of the nematic-isotropic (NI) transition.^{1–4} The model potential assumes the molecules to be represented by “spins” \mathbf{u}_i interacting as

$$U_{ij} = -\epsilon_{ij} P_2(\mathbf{u}_i \cdot \mathbf{u}_j), \quad (1)$$

where $\epsilon_{ij} = \epsilon$ for nearest neighbor particles and 0 otherwise and P_2 is a second rank Legendre polynomial. The system has an isotropic and an orientational ordered phase, with the order quantified by the average of the Legendre polynomial $\langle P_2(\cos \beta) \rangle = \langle \frac{3}{2} \cos^2 \beta - \frac{1}{2} \rangle$, where β is the angle between the axis of a molecule and the symmetry axis of the ordered uniaxial phase, the director.

A large number of studies has been performed on this model by groups in the liquid crystals field^{1–4} and, more recently, also by theoretical physicists interested in the phase transitions of RP^N spin models relevant in elementary particle physics.^{5,6} It turns out from these investigations that the system presents the following features:

- (1) an orientational order–disorder (nematic–isotropic) transition at a reduced temperature $T^* = kT/\epsilon = 1.1232$.² The transition is a weak first order one.
- (2) The temperature dependence of the order parameter, $\langle P_2 \rangle(T)$ is similar to the experimental results for nematics. In particular an empirical fitting of $\langle P_2 \rangle$ (Haller law) gives

$$\langle P_2 \rangle = \left(1 - \frac{T}{T_{NI}}\right)^{\beta_2} + \langle P_2 \rangle_{iso}, \quad \text{for } T < T_{NI} \quad (2)$$

with the exponent $\beta_2 \approx 0.22$ similar to that found experimentally, i.e. $\beta_2 = 0.17 - 0.25$, at least for a large series of Schiff bases and cyanobiphenyls.⁷ $\langle P_2 \rangle_{iso}$ is the isotropic value and $\langle P_2 \rangle_{iso} \neq 0$ only for a finite size system, e.g. in computer simulation studies.

- (3) The first two moments $\langle \cos^2 \beta \rangle$, $\langle \cos^4 \beta \rangle$ of the one particle distribution $P(\cos \beta)$ or equivalently the dependence of $\langle P_4 \rangle$ versus $\langle P_2 \rangle$ are compatible with a simple distribution $P(\cos \beta) \propto \exp[aP_2(\cos \beta)]$ as found for real liquid crystals.⁷

The close agreement with experiment is in many ways surprising, especially since non-negligible higher rank contributions are expected for real molecules. Indeed one could think of Eq. (1) as the first term in a more general Legendre polynomial expansion of U_{ij} which should contain higher terms.⁸

The question is then how strictly related are the observed experimental results to the specific second rank nature of the potential? Adding odd rank terms changes the symmetry so it is expected to have important and qualitatively different effects; for instance, we have shown elsewhere that adding a P_1 term can give a ferroelectric phase.⁹ An even rank term might be expected to have less dramatic effects. However, it is interesting to examine the effects of a fourth rank contribution, easily the first neglected term, and indeed some preliminary simulation studies of the mixed P_2P_4 interaction potential have appeared. In Ref. 10 a MC study for $N = 10^3$ particles with a 20% added fourth interaction term (positive and negative) was reported. Another simulation has been performed by Mouritsen and coworkers³ for the case of a 10% P_4 contribution. In Ref. 11 a Mean Field Theory (MFT) of the pure fourth rank model, P_4 , was presented and this was then studied by MC simulations and Two Site Cluster (TSC) theory.¹² However to date no study of the phase diagram in terms of the fourth rank contribution has appeared. This is somewhat surprising also because fourth rank contributions have been often invoked in interpreting experimental results in nematics¹³ and in membrane vesicles.¹⁴

In this work we propose to study systematically the effect of the fourth rank term examining 8 cases with different P_4 contributions and performing a full temperature scan (typically 30 temperatures) for each of them. The simulation results are compared with Mean Field (MF) and Two Site Clusters (TSC) predictions and we comment on the limitations of these methods. We shall also consider how the fourth rank term affects the temperature dependence of the order parameters.

2. The Model and the Simulations

The system studied consists of a number of spins, N , placed at the sites of a cubic lattice. As mentioned above the potential, which is nearest neighbors, is formed by two parts, the usual LL second rank P_2 and the fourth rank contribution P_4 . Thus the Hamiltonian appears as:

$$U_{ij} = -\epsilon_{ij}[P_2(\mathbf{u}_i \cdot \mathbf{u}_j) + C_4 P_4(\mathbf{u}_i \cdot \mathbf{u}_j)]; \quad \text{with } i \neq j, \quad (3)$$

where C_4 designates the relative strength of the interactions. A three dimensional representation of the potential as a function of β_{ij} and C_4 is shown in Fig. 1.

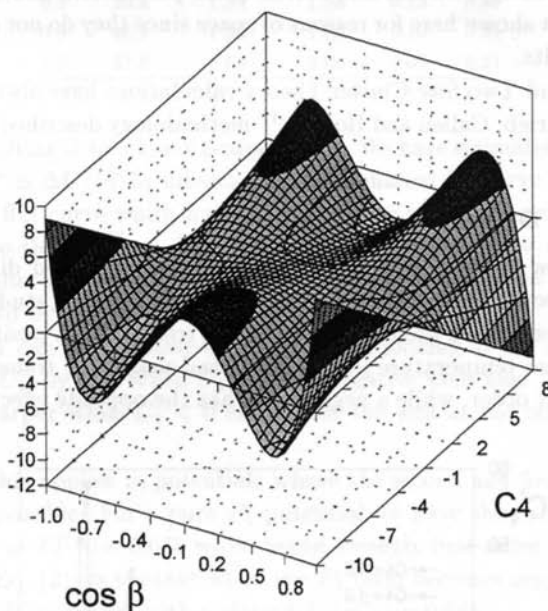


Fig. 1. A plot of the $P_2 P_4$ potential between two spins as a function of their relative orientation $\cos \beta = \mathbf{u}_i \cdot \mathbf{u}_j$ for various fourth rank contributions C_4 .

The simulations have been performed using a spherical sample carved from a cubic lattice so as to minimize the effects due to the surface. This has been made possible by the use of the Cluster Monte Carlo Method (CMC) with a self consistent outside environment described in Ref. 15 instead of employing periodic replicas (PBC). The CMC boundary conditions are obtained considering an additional layer of particles which have, on average, the same ordering as that inside the droplet. The orientations of these *ghost* particles are generated by sampling from a distribution built, using information theory, from a knowledge of the order inside the sample. A detailed description of the procedure is reported in our previous papers.^{9,12,15}

The CMC method, apart from the possibility of using arbitrary sample shapes,¹⁶ has the advantage of allowing a better determination of the phase transition

in comparison with PBC systems of the same size. This is particularly important in cases, like the present one, where the potential depends on an additional parameter whose effect has to be studied and a large number of independent simulations have to be performed to determine a phase diagram.

In the present case we have used the largest droplet contained in a $L \times L \times L$ cubic lattice of edge $L = 16$. Thus our system is constituted by $N = 1472$ spins and we have run simulations at typically 30 different temperatures for each case. Our experience on the simple Lebwohl–Lasher model indicates that CMC simulations of this size can give estimates of T_{N1} to at least 1% of the true value.

We calculate energy, second and fourth order parameters and correlation functions, that are not shown here for reasons of space since they do not add significantly to the other results.

Mean Field and Two Site Cluster Theory calculations have also been performed using the same Strieb, Callen and Horwitz¹⁷ methodology described before in Refs. 9 and 12.

3. Results and Discussion

In Fig. 2 we show the set of curves of specific heat, obtained differentiating the energy with respect to temperature for the various values of C_4 studied. We see that the fourth rank term has a profound effect on the transition. A positive contribution shifts T_{N1}^* at higher temperature (see Table 1) and makes the transition much more pronouncedly first order, while a negative C_4 has the opposite effect, weakening the

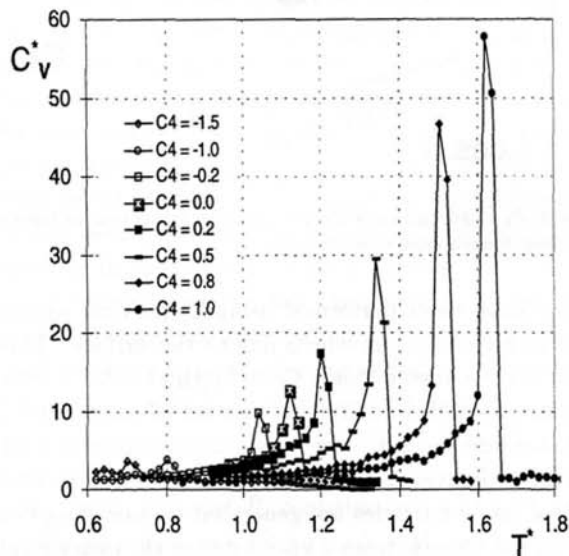


Fig. 2. Heat capacity $C_V^* \equiv C_V/k$ dependence on reduced temperature $T^* \equiv kT/\epsilon$ for various values of C_4 . The lines are a guide for the eye.

Table 1. A summary of the cases investigated. For each value of C_4 we report the values of the maximum of heat capacity from the energy derivative $(C_v^*)_D$, the temperatures at which they occur $(T^*)_D$, and the transition latent heat ΔU^* (see text). The exponent β_2 and β_4 are also reported. Errors are estimated to be $\pm 1\%$.

C_4	$(C_v^*)_D$	$(T^*)_D$	ΔU^*	β_2	β_4
-1.5	3.5	0.70	0.17	0.40	1.10
-1.0	3.8	0.80	0.20	0.36	1.08
-0.2	9.8	1.04	0.61	0.27	0.73
0.0	12.6	1.12	0.95	0.23	0.60
0.2	17.3	1.20	1.35	0.19	0.48
0.5	29.4	1.34	1.58	0.13	0.33
0.8	46.7	1.50	1.81	0.10	0.24
1.0	57.8	1.62	2.06	0.09	0.21

transition and shifting it to a lower temperature. We have estimated the latent heat of transition $\Delta U^* \equiv \Delta U/kT$ by integrating the simulated C_v^* curve and subtracting, as background a flat curve which has the correct low and high temperature values. Notice that while the reported ΔU^* are very useful to compare the effect of C_4 , their absolute value will depend on sample size and that the size dependence will in turn be affected by the character of the transition.

This behavior can be qualitatively understood looking at the changes brought on the potential U_{ij} by C_4 . When $C_4 > 0$ the negative wells near $\beta = 0, \pi$ becomes narrower and sharper while $C_4 < 0$ eliminates the well at the origin in favour of tilted minima.

Notice that this applies to potentials where the second and fourth rank contributions are comparable. For a pure P_4 potential we have shown elsewhere¹² that the transition is at $kT/\epsilon = 0.645$ while being strongly first order. Looking at the $C_4 \gg 1$ limit of Eq. (2) we see that when the P_2 term becomes negligible we reduce to a scaled pure P_4 potential with a slope $kT/(\epsilon C_4) = 0.645$.

In Fig. 3 we see the phase diagram (T_{NI}^*, C_4) obtained from simulations MF and TSC. We notice that MF becomes very seriously incorrect for $C_4 < 0$ where the transition becomes more second order. The overestimation of the transition temperature, typical of MF, goes from $\approx 8\%$ for $C_4 = 0.80$ to $\approx 60\%$ when $C_4 = -1$. TSC is always significantly better than MF. Indeed for $C_4 > 0$ the TSC and MF curves are very similar, even if the agreement is less impressive for $C_4 < 0$. For large positive C_4 , we see that the transition curve becomes indeed a straight line with slope 0.645 as discussed before. We now turn to discussing the order parameters. We see, as already indicated by the specific heat that the transition becomes sharper for $C_4 > 0$ with the order at the transition being much larger. Since $\langle P_2 \rangle$ always starts at very low temperatures ($T \rightarrow 0$) from the same value $\langle P_2 \rangle = 1$ we expect the temperature variation of $\langle P_2 \rangle$ to be different in the various cases. This is indeed the case as we see in Fig. 4 where all the curves are plotted in reduced temperature $T^+ = T^*/T_{NI}^*$. The temperature dependence of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can be

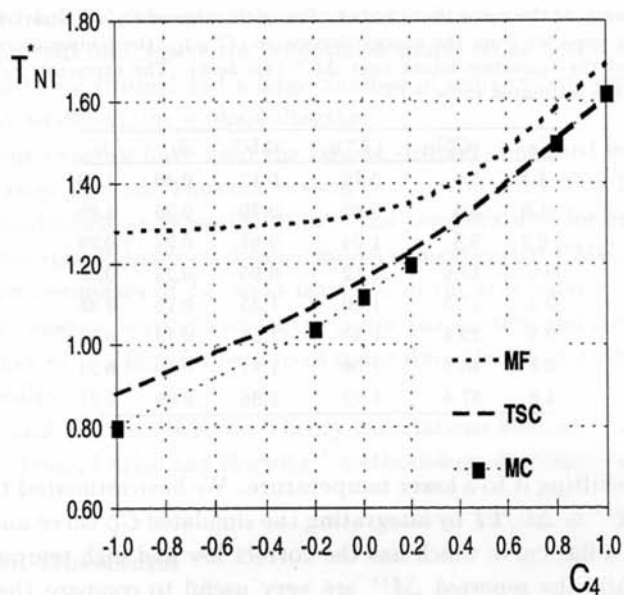


Fig. 3. Phase diagram showing the reduced transition temperature T_{NI}^* versus C_4 as obtained from MC simulation. The Mean Field (MF) and Two Site Cluster (TSC) predictions are also reported.

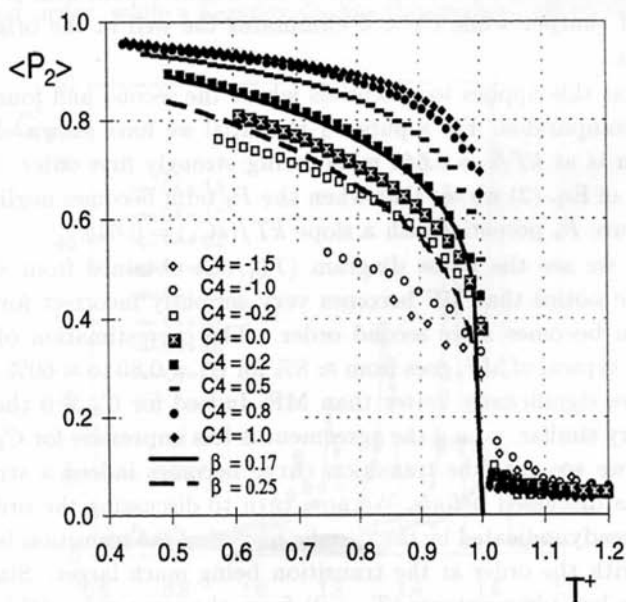


Fig. 4. The second rank order parameter (P_2) dependence on scaled temperature $T^+ \equiv T^*/T_{NI}^*$ for the various cases. The continuous curves denote the region limited by the experimental exponents β in the Haller law as obtained for real liquid crystals.

well-approximated by a formula like equation (2) giving respectively the β_2 and β_4 values reported in Table 1. The type of plot makes the comparison with real experimental data possible and thus we also report as continuous lines the so-called Haller curves for $\beta_2 = 0.17$ and 0.25 , i.e. for the typical range found for a large number of nematic compounds.⁷ It is easy to see that the simple, $C_4 = 0$, LL potential is right in the middle of the region and that while small positive values of C_4 (say $C_4 \leq 0.2$) are still within the experimental higher values or values of the opposite sign would give a temperature dependence of $\langle P_2 \rangle$ in serious disagreement with experiments.

The $\langle P_2 \rangle$, $\langle P_4 \rangle$ order parameters obtained from the simulations are shown in Fig. 5. We notice that, even if both $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can be experimentally obtained on real liquid crystals, measurements of $\langle P_4 \rangle$ are rather scarce and that experimental β_4 are not available at the moment.

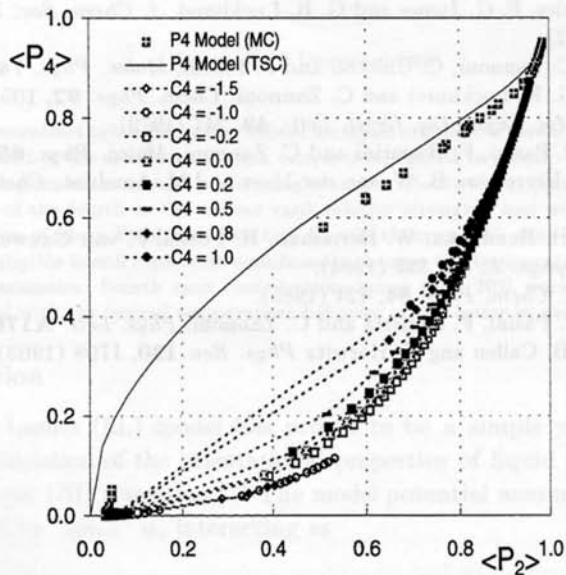


Fig. 5. The fourth rank order parameter $\langle P_4 \rangle$ versus $\langle P_2 \rangle$ for the various cases. The dotted lines are a guide to the eye. The case of a pure P_4 model is also reported (results from Ref. 12).

4. Conclusions

The addition of a fourth rank Legendre polynomial term to the simple LL potential gives significant variations in the absolute value of the order-disorder transition temperature and changes its first order character making it more or less pronounced according to the sign of C_4 . The temperature variation of $\langle P_2 \rangle$ is also changed and the agreement with typical experimental trends⁷ becomes poorer as a significant fourth rank contribution is added.

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