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Model Calculations for Nematic Ordering

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Model Calculations for Nematic Ordering†

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Dimer models with excluded volume interactions and classical anisotropic dispersion interactions are solved exactly in the limit of close packing on the two dimensional square, triangular and honeycomb lattices. These models exhibit nematic phase transitions for the aforementioned three lattices at temperatures of $2.55b/k$, $1.51b/k$ and $3.10b/k$ respectively, where $-b$ is the ground state energy per molecule.

I INTRODUCTION

Early microscopic calculations for nematic liquid crystals fell into two classes, which are (a) calculations on models with short range, anisotropic hard core repulsions[1] and (b) Maier–Saupe mean field type calculations.[1] Mean field calculations have the property of being exact for models with very long range interactions[2] and are therefore reasonable approximations for the long range anisotropic dispersion interactions in liquid crystals. However, estimates indicate that the strength of the anisotropic dispersion interactions are too small by an order of magnitude to account for liquid crystal transition temperatures.[3,4] Thus, the justification of the Maier–Saupe calculations is that they also account for the anisotropic hard core interactions, with reasonable if not complete success.[5] However, since mean

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field theory is best for very long range interactions and poorest for short range excluded volume interactions, it is desirable to treat the hard cores in a better way.

In general for nematic liquid crystals one would like to do calculations for models with (a) short range anisotropic hard cores, (b) long range anisotropic dispersion interactions and (c) long range isotropic dispersion interactions. It is not easy to do accurate statistical mechanical calculations for such ambitious multiterm models. But there is one computational procedure that splits the computational problem into more manageable pieces and whose merits and demerits are known in advance. This procedure has been employed previously for ordinary fluids,[6] magnets[2] and liquid crystals.[7,8] One first chooses a model with a pure hard core interaction (type (a)) and performs the best calculational possible. One then adds the long range interactions (types (b) and (c)) to the free energy in a classical, mean field way and minimizes the new free energy. In additional to the mathematical simplifications the merit of this procedure is that it is exact if the long range interactions (b) and (c) are of sufficiently long range.[2] Compared to real nematics with R^{-6} interactions the effect of this procedure is to suppress pretransition fluctuations, eliminate post-transition effects and to give only classical critical points if the transition is higher order.[7] However, the transition temperatures will be only slightly higher and the order of the transition probably stays the same. Thus, this procedure should be quite useful if one is primarily concerned with the question of the relative strengths of the various interactions (a), (b) and (c) and not with critical properties.

After the decision has been made to split the calculation by using the classical approximation for interactions (b) and (c), further improvement must focus on the hard core calculation. Previous treatments[7,8] for liquid crystals have used approximate mathematical treatments for fairly realistic models. In contrast this paper considers two dimensional short rod lattice models with type (a) and (b) interactions, for which the calculations for the hard core are done exactly. Although these models are obviously not the best for real nematics, they do exhibit nematic ordering and the calculations reveal some trends of interest. Also, we envision these models as the simplest in a sequence of increasingly realistic models, and approximations necessary to treat the more realistic models can be tested on these exactly solvable models in the appropriate limits.

II LATTICE DIMER MODELS

The most realistic models with short range anisotropic excluded volume interactions (type (a)) that can be solved exactly are close packed dimer

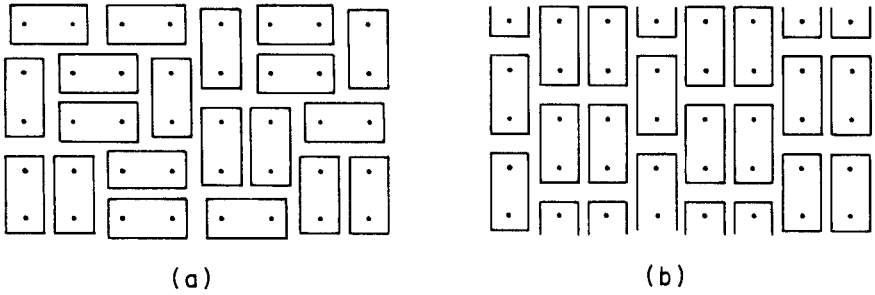

FIGURE 1 (a) Typical isotropic disordered state for dimers on the square lattice. (b) Typical ordered nematic state with order parameter $\Psi = 1$.

models on two dimensional lattices in which each dimer occupies a pair of near neighbor lattice sites and no two dimers occupy the same site and all sites are occupied by a dimer.[2] (See Figure 1.) The obvious objections to these models will be discussed in the next section where the results are interpreted. This section sets forth the procedure for solving these models with both (a) and (b) type interactions.

A Square lattice

The first part of the calculation finds the entropy $S(\rho_v)$ as a function of the density of vertical dimers ρ_v and horizontal dimers $\rho_h = 1 - \rho_v$. (See Figure 1.) This is accomplished through the use of the partition function

$$Z(v, h) = \sum_{n,m} v^n h^m \Omega(n, m) \tag{1}$$

where n is the number of vertical dimers, m is the number of horizontal dimers and $n + m = N$ is the total number of dimers.

$$S = k \ln \Omega(n, m) \tag{2}$$

is obviously the entropy for a state with n horizontal and m vertical dimers. The exact calculations[9] yield

$$(\ln Z)/N = (1/2\pi^2) \iint_0^\pi d\theta d\phi \ln[2(v^2 + h^2 - v^2 \cos\theta - h^2 \cos\phi]$$

$$= \ln h + \sum_{r=0}^{\infty} \pi^{-1}(-1)^r(2r + 1)^{-2}(\tan \pi\rho_v/2)^{2r+1} \tag{3}$$

and

$$\rho_v = (v/N)\partial \ln Z/\partial v = (2/\pi) \tan^{-1}(v/h). \tag{4}$$

By the maximum term principle,

$$\lim_{N\to\infty}(\ln Z)/N = \mathrm{Max}_{n,m}[(\ln \Omega(n, m))/N + \rho_v \ln v + \rho_h \ln h]. \quad (5)$$

From (2-5) one has the entropy per dimer

$$S(\rho_v) = k\left[-(\rho_v/2)\ln(\tan \pi\rho_v/2) + \pi^{-1}\sum_{n=0}^{\infty}(-1)^n(2n+1)^{-2}(\tan \pi\rho_v/2)^{2n+1}\right] \quad (6)$$

which is a function of ρ_v only, because excluded volume models are athermal.

The second part of the calculation expresses the long range interactions $U(\rho_v)$ as a function of ρ_v. For anisotropic dispersion interactions (type (b)) this is done as follows. In the spirit of the classical or mean field approximation the interaction between every pair of vertical dimers is taken to be the same value which we choose to be $-2b/N$, between every pair of horizontal dimers it is taken to be the same $-2b/N$, and between every vertical and horizontal pair it is taken to be $+2b/N$. (The $1/N$ factor ensures thermodynamic stability and justifies the term, weak, very long range interactions.[2]) Thus, the total energy per dimer is

$$\begin{aligned} U(\rho_v) &= [-n(n-1)/2 - m(m-1)/2 + nm](2b/N^2) \\ &= -b(\rho_v - \rho_h)^2 = -b(2\rho_v - 1)^2 \end{aligned} \quad (7)$$

in the limit of large N. In the case of isotropic dispersion interactions (type (c)) one obtains

$$U_{\mathrm{iso}}(\rho) = -c\rho. \quad (8)$$

For the close packed lattice $\rho = \rho_v + \rho_h = 1$ and U_{iso} is just a constant, so type (c) interactions play no role in these models. Future work will allow vacancies (monomer-dimer models) and treat the short range part using series expansions and then type (c) interactions will play a role.

The third part of the calculation treats the combined model with both kinds of interaction by forming the free energy

$$A(T, \rho_v) = U(\rho_v) - TS(\rho_v). \quad (9)$$

This simple addition of the type (b) interactions to the short range free energy, $-TS$, is only possible for classical or mean field type interactions which depend only on a density variable. For a given T the free energy A is then minimized with respect to ρ_v to find the equilibrium state. Consider

$$\partial A/\partial\rho_v = -4b(2\rho_v - 1) + kT\ln(\tan(\pi\rho_v/2)) \quad (10)$$

and

$$\partial^2 A/\partial\rho_v^2 = -8b + \pi kT/(\sin(\pi\rho_v/2)\cos(\pi\rho_v/2)). \quad (11)$$

The first derivative is always 0 at $\rho_v = 1/2$ which is the isotropic state, but the second derivative is negative when $T < T_c = 8b/\pi k$ so the isotropic state is not stable for $T < T_c$. One must also check whether the isotropic state is merely metastable above T_c. If there were metastability for $T > T_c$, then the second derivative would necessarily be negative for some value of ρ_v. However, from (11) the second derivative takes its minimum value at $\rho_v = 1/2$ and is therefore positive for all ρ_v for $T > T_c$. Thus, T_c is a classical second order critical point and the two dimensional nematic order parameter, $\psi = \langle 2\cos^2\theta - 1\rangle = 2\rho_v - 1$ is shown in Figure 2.

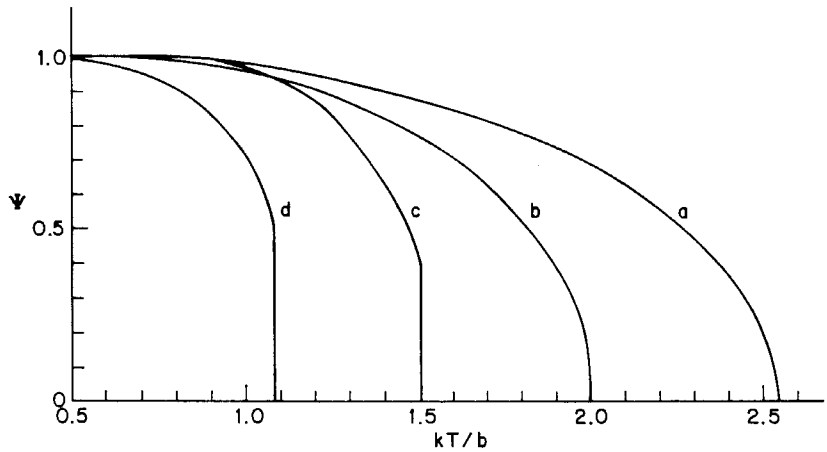

FIGURE 2 The order parameter Ψ versus T for four dimer lattice models. (a) Square lattice with both type (a) and (b) interactions (from Section II). (b) Square lattice with type (b) interactions only. (c) Triangular lattice with both type (a) and (b) interactions (Section II). (d) Triangular lattice with type (b) interaction only.

B Triangular lattice

Dimers on the triangular lattice may have three orientations, 1, 2 and 3, but there are still only two different relative orientations and therefore only two different interaction energies. Thus, the long range anisotropic energy per dimer may be written in the classical or mean field approximation as

$$\begin{aligned} U &= b[-\rho_1^2 - \rho_2^2 - \rho_3^2 + \rho_1\rho_2 + \rho_2\rho_3 + \rho_3\rho_1] \\ &= (-b/2)[(\rho_1 - \rho_2)^2 + (\rho_2 - \rho_3)^2 + (\rho_3 - \rho_1)^2]. \end{aligned} \tag{12}$$

To obtain the entropy one follows the same procedure as for the square lattice

$$Z(x, y, z) = \sum_{n_1, n_2, n_3} x^{n_1} y^{n_2} z^{n_3} \Omega(n_1, n_2, n_3) \tag{13}$$

and the exact calculations give

$$(\ln Z)/N = (2\pi^2)^{-1} \int_0^\pi \int d\theta d\phi \ln 2[x^2 + y^2 + z^2 - y^2 \cos\theta - z^2 \cos\phi + x^2 \cos(\theta + \phi)]. \quad (14)$$

We could not evaluate (14) in as convenient a way as for the square lattice, so we resorted to a series expansion of the logarithm followed by a term by term integration. To facilitate this step we specialized to the case $y = z \neq x$ in the anticipation that the stable state would be at most triply degenerate with at least two densities equal, such as $\rho_2 = \rho_3 \neq \rho_1$. We can not definitely exclude the possibility of six fold degenerate states with no two densities equal, although we consider this to be most unlikely and we did verify that the states with $\rho_2 = \rho_3 \neq \rho_1$ were stable against a variation $\delta\rho_2 = -\delta\rho_3$, $\delta\rho_1 = 0$. With this simplification

$$(\ln Z)/N = (2\pi^2)^{-1} \int_0^\pi \int d\alpha d\beta \ln 4[x^2 + y^2 - x^2 \sin^2\alpha - y^2 \cos\alpha \cos\beta] \quad (15)$$

which is amenable to a term by term integration which was carried far enough to ensure convergence to six figures in the region of interest for $\ln Z$ and also for ρ_1 and ρ_2. Following the procedure for the square lattice the entropy was found from $\ln Z$ and the free energy $A = U - TS$ was calculated as a function of density ρ_1. At high T the isotropic state with $\rho_1 = 1/3 = \rho_2 = \rho_3$ is stable. A first order transition occurs at $kT = 1.5077b$ and ρ_1 jumps to 0.60 (and $\rho_2 = \rho_3$ jump to 0.20). That the transition is first order in classical models with three fold symmetry is expected.[10] Figure 2 shows the order parameter $\psi = \langle 2\cos^2\theta - 1\rangle = (1/2)[3\rho_1 - 1]$.

C Honeycomb lattice

Like the triangular lattice the honeycomb lattice has three dimer orientations and the energy in the mean field approximation is given by Eq. (12). Just as for the triangular lattice we specialize to the case $\rho_1 \neq \rho_2 = \rho_3$. Without loss of generality we may set $z = y$ and $x = 1$ in Eq. (13) and then the exact solution yields

$$\rho_2 = \pi^{-1} \cos^{-1}(1/2y) \quad (16)$$

which may be conveniently integrated to give

$$(\ln Z)/N = \int_0^y (2\rho_2/y')dy' \quad (17)$$

from which $S(\rho_2)$ and $A(\rho_2)$ are calculated. There is a first order transition into a fully ordered nematic state with $\rho_1 = 1$ and $\psi = 1$ at $kT = 3.096b$. The abruptness of the transition and the high transition temperature relative to the triangular and square lattices is related to the fact that, as x, y and z are varied, the purely excluded volume dimer model on the honeycomb lattice has a 3/2 order phase transition[11] at $y = z = 1/2$, $x = 1$, whereas the dimer models on the square and triangular lattices have no such transition.

III DISCUSSION OF RESULTS

The models presented allow one to study the interplay of the effects of the excluded volume and of the anisotropic dispersion interactions in producing the nematic ordering of elongated molecules. However, it is not to be taken literally as a realistic model of a liquid crystal for the following reasons:

1) The models considered so far are only two dimensional. However, it is not certain that two dimensional liquid crystals should not have transitions,[12] unlike xy models with near neighbor interactions, because in liquid crystals one has the infinitely hard excluded volume interactions and long range interactions, either of which can even cause one dimensional system to have transitions.[2,12] Since we are usually dealing with a first order transition and not with critical phenomena, the low dimensionality is not such a severe drawback.

2) Dimers have a length/width ratio R of only 2, compared to an R of about 4 or 5 for nematic liquid crystals. Thus, the hard core in our model is not as effective in producing nematic order as is the hard core in real nematics. In this connection we plan to study longer R-mers with dispersion interactions with the aid of approximations.[14]

3) The model is a lattice model. The centers of the dimers are restricted to the centers of the bonds on a lattice. Loss of continuous translational freedom may tend to make the transition higher order, as for the square lattice, but this is probably not too serious. Much more serious for a nematic transition is the loss of continuous orientational freedom,[15] which raises the transition temperature considerably. This effect is made apparent by doing calculations for models with only type (b) anisotropic long range interactions and no hard core interactions. For such models with p orientations the entropy is simply

$$S = -k \sum_{i=1}^{p} \rho_i \ln \rho_i$$

and the free energy A is minimized as usual. For $p = 2$ there is a second order transition at $kT = 2b$. For $p = 3$ there is a first order transition with a jump in the order parameter to 0.5 (one of the densities jumps to 2/3) at $kT = 1.082b$. For $p = \infty$ the Maier–Saupe result gives a first order transition at $kT = 0.44b$. Once this restricted orientational feature is realized, one compensates for it by comparing to the aforementioned mean field calculations on similarly restricted orientational models as shown in Table I.

TABLE I

$-b$ is the ground state energy per molecule and Ψ is the order parameter.

	$\frac{kT_{\text{transition}}}{b}$	Enhancement factor	Order of transition	$\Delta\Psi$
Square Lattice				
Section II	2.546	1.27	2nd	0
Mean Field Only	2.000		2nd	0
Triangular Lattice				
Section II	1.508	1.39	1st	0.4
Mean Field Only	1.082		1st	0.5
Hexagonal Lattice				
Section II	3.096	2.86	1st	1.0
Mean Field Only	1.082		1st	0.5

The enhancement factor in Table I is the ratio of the transition temperature of the models solved in Section II with both (a) and (b) type interactions to the transition temperature of models with only (b) type interactions mentioned in the preceding paragraph. For the transitions on the square and triangular lattices the anisotropic dispersion interaction is clearly the dominant factor. The hard core does increase the transition temperature significantly, but not enough to reconcile the estimated values of b to the transition temperature of liquid crystals,[4,5] which would require enhancement factors of about 10. The larger enhancement factor for the honeycomb lattice is likely to be anomalous, as discussed in Section II. It would also appear that there may be a trend toward larger enhancement factors with more orientational degrees of freedom. Although it is not possible to predict an enhancement factor for hard cores with continuous orientational freedom from these results, the value of the enhancement factor for the triangular lattice ought to be a reliable lower bound for molecules with length/width ratio $R = 2$.

In conclusion we feel that the general computational method of adding classical Maier–Saupe type interactions, and also isotropic dispersion interactions, to models with anisotropic excluded volume interactions is a fruitful one to use to study ordered phases, such as liquid crystals, which seem to

require more than one interaction. The particular models treated in this paper have the virtue that the excluded volume part is rigorously solvable so these models may provide a testing ground for approximations which can also be applied to more realistic models. One such approximation being planned by the authors is series expansions for monomer–dimer models; this will allow treatment of three dimensional models and the inclusion of a relevant isotropic dispersion interaction.

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