A Mean Field Theory approach to a Dipole-Quadrupole interaction model

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Abstract

We study a model initially proposed to describe a mixture of \((\text{CO})_{1-x}(\text{N}_2)_x\) adsorbed on exfoliated graphite. The approach used here is that of mean field theory. The Mean Field equations and the Helmholtz Free Energy are found. Phase diagrams are calculated too, and it is possible to find an analytic expression for the second order phase transition line.

1 Introduction

To calculate the fundamental equation of a many particles system, it is necessary first to determinate the allowed energy levels and make the sum of the partition function. Except for a small class of systems, that sum cannot be calculated exactly. One of the solutions for that problem is to look for approximated solutions, in our case we use the so called Mean Field Theory. The importance of this kind of calculation is that it gives us qualitative information about the critical behaviour of the system.

Here we show results for a model of solid mixtures of molecules. We assume that one of the molecules have dipole and quadrupole moments (CO molecules) while the other one has only a quadrupole moment.

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This simple model is in good agreement with experimental results [4]. The interactions between the CO molecules are assumed to be antiferroelectric, but between these and the N$_2$ molecules it is proposed a pseudo dipole-quadrupole coupling. The N$_2$ molecules act like the random fields of the Random Field Ising Model. It is supposed that a crystal of polar molecules diluted with molecules which have quadrupole moments, can have a behaviour qualitatively similar to that predicted in random field models [5].

There are Monte Carlo results for this model [4, 6] which agree very well with experiments. Despite the fact that there are simulations and real experiments for this model, we don’t have analytical results, exact or not, for this model yet. In order to improve our understanding about this kind of system, it is interesting to search for such results. The simplest way to find approximated results is to calculate a Mean Field Approximation for the model, what we do in the next sections. The paper is organized as follows. In section 2 we present the Dipole-Quadrupole model. In section 3 we calculate the mean field approximation using the Bogoliubov Variational Theorem [1] obtaining the mean field equations and the Helmholtz Free Energy of the system. In section 4, we find analytic expressions for the transition lines and these lines are showed for several values of model parameters.

## 2 Dipole-Quadrupole model

This model was proposed to describe a mixture of (CO)$_{1-x}$(N$_2$)$_x$ adsorbed on exfoliated graphite [4]. We associate for each site of the lattice a spin $S_i = -1, 0, 1$. $S_i = \pm 1$ represents the electrical dipole orientations if the site is occupied by a CO molecule and $S_i = 0$ if the site is occupied by a N$_2$ molecule. The interaction between the molecules of CO is antiferromagnetic and the interaction for CO - N$_2$ pairs is described like a pseudo dipole-quadrupole one [4, 6]. The proposed Hamiltonian is

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - J_1 \sum_{\langle ij \rangle} S_i (1 - S_j^2),$$

where $J < 0$ represents the antiferromagnetic coupling, $J_1$ describes the dipole-quadrupole interaction and $S_i = 0, \pm 1$. The symbol $\langle \cdots \rangle$ denotes first neighbors summation. We rewrite the Hamiltonian in
the form

\[ H = -J \sum_{\langle ij \rangle} S_i S_j c_i c_j - J_1 \sum_{\langle ij \rangle} S_i c_i (1 - c_j), \]  

where \( S_i = \pm 1 \) and \( c_i = 1 \) if the site is occupied by a CO molecule and \( c_i = 0 \) otherwise. The probability distribution for the occupation variables is

\[ P(c_i) = p\delta(c_i - 1) + (1 - p)\delta(c_i), \]

with \( 0 \leq p \leq 1 \). The presence of an antiferromagnetic interaction suggests that the system can spontaneously be subdivided into two sub-systems, represented by two sub-lattices (figure 1).

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\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{sublattices.png}
\caption{Sub-lattices A and B in a bidimensional lattice.}
\end{figure}

\section{Mean field calculations}

We propose an unperturbed Hamiltonian \( H_0 \) of the form

\[ H_0 = -(J_1 + \eta_A) \sum_{i \in A} S_i c_i - (J_1 + \eta_B) \sum_{i \in B} S_i c_i, \]  

3
where $\eta_A$ and $\eta_B$ are variational parameters and A and B indicate the inter-penetrating sub-lattices, each one with $N/2$ sites. We choose $H_0$ to be, at the same time, soluble and similar in some manner to the original Hamiltonian.

The Bogoliubov Inequality reads

$$\langle F \rangle \leq \langle F_0 \rangle + \langle (H - H_0)_t \rangle,$$

where $F_0$ is the Helmholtz Free Energy calculated for the unperturbed system and $F$ indicates the complete Helmholtz Free Energy. The symbol $\langle \cdots \rangle$ means a configurational average, while $\langle \cdots \rangle_t$ indicates the thermal average weighted by the factors $\exp (-\beta E_i)$ where $E_i$ is the eigenvalue of energy with indice $i$. The partition function of the soluble Hamiltonian is

$$Z_0 = \text{Tr} \{ e^{-\beta H_0} \} = \prod_{i \in A} \prod_{j \in B} \left[ 2 \cosh \left( \beta c_i (J_1 + \eta_A) \right) \right] \times \left[ 2 \cosh \left( \beta c_j (J_1 + \eta_B) \right) \right],$$

and the mean Free Energy calculated with that partition function becomes

$$\langle F_0 \rangle = -\frac{N}{2\beta} \left[ \langle \ln \left( 2 \cosh \beta c_i (J_1 + \eta_A) \right) \rangle + \langle \ln \left( 2 \cosh \beta c_j (J_1 + \eta_B) \right) \rangle \right],$$

the second part of inequality (5) is written

$$\langle (H - H_0)_t \rangle = \left( \sum_{i \in A} \sum_{j \in B} \langle S_i S_j c_i c_j \rangle_t + \sum_{i \in A} \sum_{j \in B} \langle S_i c_i c_j \rangle_t + \right) \eta_A \sum_{i \in A} \langle S_i c_i \rangle_t + \eta_B \sum_{j \in B} \langle S_j c_j \rangle_t.$$  

If we adjust the variational parameters $\eta_A$ and $\eta_B$ using the stationary condition for the Free Energy and define the magnetizations

$$m_A = \left\langle c_i \tanh \left( c_i \beta (H + \eta_A) \right) \right\rangle,$$
and
\[ m_B = \left\langle c_i \tanh \left[ c_i \beta (H + \eta_B) \right] \right\rangle, \quad (10) \]
it is possible to write the Bogoliubov Inequality like
\[
\langle F \rangle \leq - \frac{N}{2\beta} \left[ \left\langle \ln \left( 2 \cosh \left( \beta c_i (J_1 + \eta_A) \right) \right) \right\rangle + \left\langle \ln \left( 2 \cosh \left( \beta c_i (J_1 + \eta_B) \right) \right) \right\rangle \right] \\
+ J \frac{N z}{2} m_A m_B + J_1 \frac{N z}{4} \left[ \langle c_i \rangle m_A + \langle c_i \rangle m_B \right] + \eta_A \frac{N}{2} m_A + \eta_B \frac{N}{2} m_B. \quad (11)
\]
This expression must be minimized in order to estimate the Free Energy. Differentiating the equation and imposing the stationary condition we find the variational parameters
\[
\eta_A = -J z m_B - J_1 \frac{z}{2} \langle c_i \rangle \quad (12)
\]
and
\[
\eta_B = -J z m_A - J_1 \frac{z}{2} \langle c_i \rangle \quad (13)
\]
then
\[
\langle F \rangle = - \frac{1}{2\beta} \left[ \left\langle \ln \left( 2 \cosh \left( \beta c_i (J_1 - \frac{J_1 z}{2} \langle c_i \rangle - J z m_B) \right) \right) \right\rangle \\
+ \left\langle \ln \left( 2 \cosh \left( \beta c_i (J_1 - \frac{J_1 z}{2} \langle c_i \rangle - J z m_A) \right) \right) \right\rangle \right] - \frac{1}{2} J z m_A m_B. \quad (14)
\]
Again, the antiferromagnetic interaction suggests we should define
\[
M = \frac{m_A + m_B}{2}, \quad (15)
\]
where \( M \) is the total magnetization and
\[
m_s = \frac{m_A - m_B}{2}, \quad (16)
\]
It is also convenient to define
\[
t = \frac{1}{\beta |J| z}, \quad (17)
\]
and

\[ h = \frac{J_1}{|J|z} \left( 1 - \frac{z}{2} \langle c_i \rangle \right), \quad (18) \]

we find

\[ \langle F \rangle = -\frac{1}{2\beta} \left[ \langle \ln \left( 2 \cosh \left( \frac{c_i}{t} (h - M + m_s) \right) \right) \rangle \right] \]

\[ + \langle \ln \left( 2 \cosh \left( \frac{c_i}{t} (h - M - m_s) \right) \right) \rangle \]

\[ - \frac{1}{2\beta t} M^2 + \frac{1}{2\beta t} m_s^2, \quad (19) \]

(23) and (24) define the mean field equations for this model

\[ M = \frac{1}{2} \left[ \langle c_i \tanh \left( \frac{c_i}{t} (h - M + m_s) \right) \rangle + \langle c_i \tanh \left( \frac{c_i}{t} (h - M - m_s) \right) \rangle \right], \quad (20) \]

and

\[ m_s = \frac{1}{2} \left[ \langle c_i \tanh \left( \frac{c_i}{t} (h - M + m_s) \right) \rangle - \langle c_i \tanh \left( \frac{c_i}{t} (h - M - m_s) \right) \rangle \right]. \quad (21) \]

These coupled equations could be solved for \( M \) and \( m_s \) using an iterative scheme.

### 4 Critical lines

The existence of a critical line, critical points and the determination of transition order are made by means of a Landau expansion \([2]\). Then we write the magnetization in the form

\[ M = M_0 + m, \quad (22) \]

where \( M_0 \) is a paramagnetic solution which is a solution of

\[ M_0 = \left\langle c_i \tanh \left( \frac{c_i}{t} (h - M_0) \right) \right\rangle. \quad (23) \]
We define the quantities $m_1 = m - m_s$ and $m_2 = m + m_s$ to expand the right hand side of equation (30) near a paramagnetic solution. Then

$$M = \sum_{n=0}^{\infty} A_n (m_1^n + m_2^n),$$

(24)

eliminating the term corresponding to $n = 0$ we find

$$m = \sum_{n=1}^{\infty} A_n (m_1^n + m_2^n),$$

(25)

it is useful to expand the staggered magnetization too

$$m_s = \sum_{n=1}^{\infty} A_n (m_1^n - m_2^n).$$

(26)

We determine the coefficients $A_n$ in these expressions

$$A_1 = -\frac{1}{t} \left\langle c_i \left(1 - T_2\right) \right\rangle,$$

(27)

$$A_2 = -\frac{1}{2t^2} \left\langle c_i^2 \left(T_1 - T_3\right) \right\rangle,$$

(28)

$$A_3 = \frac{1}{3t^3} \left\langle c_i^3 \left(1 - 4T_2 + 3T_4\right) \right\rangle,$$

(29)

$$A_4 = \frac{1}{3t^4} \left\langle c_i^4 \left(3T_5 - 5T_3 + 2T_1\right) \right\rangle,$$

(30)

$$A_5 = \frac{1}{15t^5} \left\langle c_i^5 \left(15T_6 - 30T_4 + 17T_2 - 2\right) \right\rangle,$$

(31)

where

$$T_k = \tanh^{k} \left[\frac{1}{t}(h - M_0)\right].$$

(32)

It is possible to calculate $m$ in function of $m_s$

$$m = B_1 m_s^2 + B_2 m_s^4 + B_3 m_s^6 + \cdots,$$

(33)
if we substitute this expansion in equation (32) and equal terms of same power in \( m_s \) we find the expressions for the coefficients of expression (40)

\[
B_1 = \frac{A_2}{1 - A_1},
\]

(34)

\[
B_2 = \frac{1}{1 - A_1} \left( \frac{A_2^3}{(1 - A_1)^2} + A_4 + 3 \frac{A_2 A_3}{1 - A_1} \right),
\]

(35)

\[
B_3 = \frac{1}{1 - A_1} \left[ \frac{2A_2^2}{(1 - A_1)^2} \left( \frac{A_2^3}{(1 - A_1)^2} + A_4 + 3 \frac{A_2 A_3}{1 - A_1} \right) + \frac{A_2^3 A_3}{(1 - A_1)^3} + \frac{6A_2^3 A_4}{(1 - A_1)^4} + 5A_2 A_5 \right].
\]

(36)

Here, substituting (41) in (33) we arrive at expression

\[
am_s + bm_s^3 + cm_s^5 + \cdots = 0,
\]

(37)

and finally at the coefficients

\[
a = -(1 + A_1),
\]

(38)

\[
b = - \left( 2 \frac{A_2}{1 - A_1} + A_3 \right),
\]

(39)

\[
c = - \left[ 2 \frac{A_2}{1 - A_1} \left( \frac{A_2^3}{(1 - A_1)^2} + A_4 + 3 \frac{A_2 A_3}{1 - A_1} \right) + 3 \frac{A_2^3 A_3}{(1 - A_1)^2} + 4 \frac{A_2 A_4}{1 - A_1} + A_5 \right].
\]

(40)

A Second order transition is determined by the condition \( a = 0 \) and \( b > 0 \). The existence of a tricritical point will be determined by \( a = b = 0 \) with \( c > 0 \) [3].

With these conditions found, we calculate configurational mean values as indicated for the distribution eq. (10) to find that the critical line condition is equivalent to

\[
1 - \frac{p}{t} \left[ 1 - \tanh \left( \frac{h - M_0}{t} \right)^2 \right] = 0,
\]

(41)
which, together with the configurational mean value of expression (30) give us

\[
\frac{M_0}{p} = [1 - \frac{t}{p}]^{1/2},
\]

(42)

from which we note a limitation on reduced temperature represented by \( t \leq p \). Now the critical line equation is

\[
h = t \tanh^{-1} \left[ 1 - \frac{t}{p} \right]^{1/2} + p \left[ 1 - \frac{t}{p} \right]^{1/2},
\]

(43)

and, finally

\[
\frac{J_1}{J_z} = \frac{1}{(1 - \frac{2p}{z})} \left[ t \tanh^{-1} \left( 1 - \frac{t}{p} \right)^{1/2} + p \left( 1 - \frac{t}{p} \right)^{1/2} \right].
\]

(44)

We should note here that, for a particular lattice of coordination number \( z \), there exist a critical value for the occupation \( p \) where there is a divergence. This point is located at

\[
p_c = \frac{2}{z}.
\]

(45)

The condition \( c > 0 \) for existence of a tricritical point

\[
\frac{2}{3t} \cosh^4 \left( \frac{h - M_0}{t} \right) + \left( \frac{2p}{3t^2} - \frac{p}{2} - \frac{1}{t} \right) \cosh^2 \left( \frac{h - M_0}{t} \right) + \frac{p}{2} - \frac{p}{t^2} > 0.
\]

(46)

Is not satisfied for this model.

In figures (2) and (3) we have two phase diagrams (one for \( p < \frac{2}{z} \) and one for \( p > \frac{2}{z} \)) for the model in the case \( z = 4 \) indicating two possible phases: Antiferromagnetic (AF) and Paramagnetic (P). In figures (4) and (5) we compare the phase diagrams for different values of occupation \( p \).
Figure 2: Second order critical line for $z = 4$ and $p = 0.45$.

Figure 3: Second order critical line for $z = 4$ and $p = 0.75$. 
Figure 4: Comparison for three values of the occupation rate which are less than the critical occupation.

Figure 5: Comparison for three values of the occupation rate which are bigger than the critical occupation.
5 Conclusions

Preliminary mean field results for the model Hamiltonian (2) was presented in this paper. This model describes dipolar systems diluted with quadrupolar molecules. It was possible to determine, using the Bogoliubov Inequality, the mean field equations for the model and the Helmholtz Free Energy. The last one was calculated both, in terms of the magnetizations of the sub-lattices \( m_a \) and \( m_b \) and in terms of total magnetization \( M \) and staggered magnetization \( m_s \). We have also calculated the analytical form for the second order \( \frac{J_z}{|J|} \times t \) critical line.

We found a critical value of occupation probability \( p_c \) in which there is a divergence in expression (44). The critical lines are remarkably different in the regimes of \( p < p_c \) and \( p > p_c \). Another interesting fact is that this model does not have any tricritical or multicritical points, at least in the mean field approximation.

We hope this study is able to stimulate theoretical physicists to search for more theoretical results about this kind of system. It is specially interesting to learn about the possible connections between these and random field models.

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