Semiclassical Dipoles on a Honeycomb Lattice in the Mean Field Approximation

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Abstract

A system of semiclassical dipoles located on a honeycomb lattice is considered within the Mean Field approximation. Energy, entropy, magnetization, susceptibility and specific heat are computed and the phase diagram of the system is constructed. Results are compared with the predictions of the planar classical dipolar model and experimental data on $FeCl_3$ intercalated graphite compounds.

1 Introduction.

The molecules of $FeCl_3$ intercalated into graphite form monomolecular layers sandwiched between graphite layers with the Fe^{3+} ions arranged on a honeycomb lattice. The iron ions are in the spin-$\frac{5}{2}$ state with the dipole moment $\mu = 5.5\mu_B$ and the nearest neighbor distance of $3.5\AA$ [1]-[4]. Since the energy of $0.5K^o$ of the dipolar interaction between two nearest magnetic ions is close to the lowest magnetic phase transition temperature in these compounds ($1.8K^o$) the role of dipole interaction is certainly of crucial importance at low temperatures. There is both experimental and theoretical evidence [1]- [4] that at low temperatures Fe^{3+} dipoles are oriented mostly in a plane parallel to graphite layers. The resulting picture of dipoles confined to rotate in the plane has been adopted by the Planar Dipolar model [4] - [6]. However with temperature increasing the dipoles will tilt out of the plane seeking for the maximum of entropy. To provide this possibility a model with 3-component dipoles is desirable. Moreover, magnetic properties of $FeCl_3$-graphite intercalated compounds in the field pointed along the c-axis have been already measured [7]. To interpret experiments [7] a model of the above-mentioned kind is also necessary. Taking all this into account we will consider a model with magnetic dipoles fixed in the knots of the honeycomb lattice but able to rotate around the knots over the three dimensional space.

As a first step we will apply the Mean Field Approximation (MFA) which is useful only if the long range magnetic order exists. It is well known that neither the ferro- nor the antiferromagnetic Heisenberg model with interactions of the finite range have long range order on 1- or 2-dimensional lattices at any finite temperatures due to the spin waves excitations [8, 9]. In the ferromagnetic classical isotropic planar (XY) model with interactions of the finite range the phase transition occurs at some finite T [10]. However it results [10, 11] from the decoupling of the pairs of the Thoules-Kosterlitz vortices [12] and has nothing to do with the long range magnetic order. The same is true [11, 13] for the antiferromagnetic XY model, which is a close relative of the Planar Dipolar model [4, 5, 6], Thus a question arises whether the Mean Field approximation can give us even a qualitative insight into the system's behavior. Our point of view is that (1) a dipolar system with long-range interaction has long range order at low enough temperatures; and (2) the 3-component dipolar system on a planar lattice with a short range quasi-dipolar interaction (i.e. with the dipole interactions only between nearest neighbors) also has long range magnetic order. The reason for our belief is that the disordered state of a two-dimensional Heisenberg antiferromagnet is very marginal: even a very (if not arbitrarily) small amount of anisotropy or frustration makes the long range order possible [14], even without the long range of the (anisotropic) dipole interaction.

Various antiferromagnetic and dipolar systems had been analyzed within the MFA during last fifty years [15]-[18]. In particular, the Mean Field approximation was applied to the classical antiferromagnetic Heisenberg model and to the dipolar model on bipartite lattices within the Neel approximation of two sublattices [18] as well as to the antiferromagnetic Planar Rotator (XY) model [13] and Planar Dipolar model [4, 5] on the honeycomb lattices assuming different magnetization of each of six sublattices. Nevertheless, without the oversimplifying Neel approximation the behavior of 3-component dipoles on the honeycomb lattice has not been analyzed yet even within the Mean Field Approximation even for the classical dipoles. The possible reason for it is that the ground state of the 3-component dipoles on the honeycomb lattice in nonzero fields (obtained in Section 4 of this paper) has been unknown.

Classical models considered within the MFA do not satisfy the Third Law of Thermodynamics [18]. It means that the MFA treatments [4, 13] of the classical models are not reliable at low temperatures. Since the whole issue of the weak dipole interaction makes sense only at low temperatures, the above mentioned problem is of crucial importance. To clarify the situation we consider the semiclassical dipoles with spin S (the case of $S = 5/2$ of particular interest) and compare their behavior with the classical dipoles.

The outline of this paper is as follows. The problem is described and formulated in Section 2 using the variational Raleigh-Ritz procedure restricted to the Mean Field Approximation. The method of solution including the nearest-neighbor approximation is briefly discussed in Section 3. The ground state of the model in nonzero fields is obtained in Section 4. The paramagnetic and ferromagnetic solutions are given in Section 5 while the dipole configuration in the antiferromagnetic phase is described in Section 6. The thermodynamical properties of the Spin S model are studied (within the MFA) in section 7. Properties of the Spin S, Space Rotator and Planar Rotator models are compared with each other and experiment in Section 8. The most interesting results of this work are summarized in the Conclusion.

2 The Model and the Mean-Field Approximation.

Consider a system of N dipoles on a honeycomb lattice in an external magnetic field $\vec{H}$. We assume the dipoles interact by means of the dipolar interaction

$$U_{ij}^{dip} = J_{ij}^{dip}[\hat{\mu}_i \cdot \hat{\mu}_j - 3(\hat{\mu}_i \cdot \hat{r}_{ij})(\hat{\mu}_j \cdot \hat{r}_{ij})] \tag{1}$$

and write the Hamiltonian as

$$\mathcal{H} = \sum_{<i,j>} U_{ij} - \vec{H} \cdot \sum_i \hat{\mu}_i. \tag{2}$$

Here the summation $\sum_{<i,j>}$ is taken over all pairings of dipoles, a dipole moment at the i^{th} lattice site is $\vec{\mu}_i = g\mu_B\vec{S} = \mu_0\hat{\mu}_i$ (here $\mu_0 = g\mu_B S$, $g = 2$ is the Lande g-factor, $\mu_B = 0.9274\ 10^{-23} J/Tl$ is the Bohr magneton and S is the total moment being equal 5/2 for $FeCl_3$), $\hat{\mu}_i = \vec{\mu}_i/\mu_0$ is a dipole moment of unit magnitude at the i^{th} lattice site, J_{ij}^{dip} is the dipole interaction coupling constant between dipoles $\vec{\mu}_i$ and $\vec{\mu}_j$ ($J_{ij}^{dip} = \mu_{eff}^2/r_{ij}^3, \mu_{eff} =$

$g\mu_B\sqrt{S(S+1)}$), and $\vec{H}$ is an external field multiplied by the magnitude of the magnetic moment μ_0.

The free energy functional $F[\rho]$ of the system is given by the expression

$$F[\rho] = U - TS = Tr\Big[\rho(\sum_{<i,j>} U_{ij} - \vec{H}\cdot\sum_i \hat{\mu}_i + kT\ell n\rho)\Big] \tag{3}$$

where U and S are the energy and entropy functional correspondingly and ρ is the density matrix. In the Mean-Field Approximation we seek to minimize the free energy in the subspace

$$\rho = \prod_{i=1}^{N} \rho_i, \tag{4}$$

where ρ_i is the single particle density matrix normalized to

$$Tr\rho_i = 1. \tag{5}$$

Substitution of (4) into (3) and the use of (1) lead to

$$\begin{aligned} U[\rho] &= \textstyle\sum_{<i,j>} J_{ij}^{dip}\Big[\vec{m}_i\cdot\vec{m}_j - 3(\vec{m}_i\cdot\hat{r}_{ij})(\vec{m}_j\cdot\hat{r}_{ij})\Big] - \vec{H}\cdot\sum_i \vec{m}_i \\ S[\rho] &= -k\textstyle\sum_i Tr(\rho_i\ell n\rho_i) \end{aligned} \tag{6}$$

where

$$\vec{m}_i = Tr(\rho_i\hat{\mu}_i),\ i = 1,2,3,...,N \tag{7}$$

is the average reduced (dimensionless) dipole moment at site i ("magnetization of the dipole $\vec{\mu}_i$").

It is easy to obtain the extremal equation for the functional $F[\rho]$ given by Eq. (6) and subject to the constraint Eq. (5) (see [4]). However analysis of the stability and search for the phase transition points is more difficult. To work around the last problem the direct minimization approach is used in this paper. We choose trial ρ in the form of Eq. (4), where

$$\rho_i = Z_i^{-1} \exp(\frac{\vec{A}_i \cdot \hat{\mu}_i}{kT}) = Z_i^{-1} \exp(\vec{a}_i \cdot \hat{\mu}_i) \tag{8}$$

Here $\vec{a_i} = \vec{A}_i/kT, |\vec{A}_i| < \infty$ and $Z_i = Z_i(a_i)$ does not depend on $\hat{\mu}_i$. The chosen trial function allows us to calculate integrals in Eq. (3) thus reducing the problem to a search for a global minimum of a function instead of a functional. Since ρ of Eq. (8) satisfies the MFA condition Eq. (4) and the MFA extremum equation [4], the resulting a_i will give us the mean field extremals exactly. It will be proven later that the extremum value of the variational parameter $\vec{A}_i$ is the mean field at the i-th site.

For the chosen form of ρ vectors $\vec{m}_i$ and $\vec{a}_i$ are collinear:

$$\vec{m}_i = m(a_i)\hat{e}_i,\ a_i = A_i/kT,\ A_i = |\vec{A}_i|,\ a_i = |\vec{a}_i|,\ \hat{e}_i = \vec{a}_i/a_i\ . \tag{9}$$

There is one-to-one correspondence between $\vec{m}_i$ and $\vec{a}_i$. The direction of vectors $\vec{m}_i$ and $\vec{a}_i$ and the shape of the function $m(a)$ depends on a chosen dipole model. The classical dipoles can be confined to rotate in the lattice plane (the planar dipolar rotator) or to rotate over all space (the space dipolar rotator). The semiclassical dipoles can be allowed to have a finite $2S+1$ number of possible projections onto a given vector $\vec{A}$ (only two in the Ising model, for instance). [1]

In the two-component Planar Rotator model integration over the phase plane leads [4] to

$$\vec{a}_i = (a_{ix}, a_{iy}, 0),\ Z_i = 2\pi I_0(a_i),\ m(a) = I_1(a)/I_0(a), \tag{10}$$

(here $I_n(a) = (\pi)^{-1}\int_0^\pi cos(n\theta)e^{acos\theta}d\theta$ is the modified Bessel function of order n). In the three-component Space Rotator model integration over the space results in the Langevin function:

$$\vec{a}_i = (a_{ix}, a_{iy}, a_{iz}),\ Z_i = 4\pi sinh(a_i)/a_i,\ m(a) = L(a) = coth(a) - 1/a, \tag{11}$$

In the three-component Spin S model we get for $m(a)$ the Brillouin function

$$\vec{a}_i = (a_{ix}, a_{iy}, a_{iz}),\ Z_i = \sum_{m=-S}^{S} e^{ma_i/S} = sinh(\frac{2S+1}{2S}a_i)/sinh(\frac{a_i}{2S}),$$
$$m(a) = B_S(a) = \frac{2S+1}{2S}coth(\frac{2S+1}{2S}a) - \frac{1}{2S}coth(\frac{a}{2S}) \tag{12}$$

In the Ising (spin $S = 1/2$) case the summation over two possible states gives

$$\vec{a}_i = (0, 0, +a_i),\ Z_i = e^{a_i} + e-a_i = 2cosh(a_i),\ m(a) = tanh(a)\ , \tag{13}$$

[1]Besides we can impose restrictions on the direction of the vector $\vec{A}$, for example, assuming a priori that $\vec{A}$ lies along the normal to the lattice plane. Of course in a consistent quantum mechanical picture the projection of the magnetic moment onto some vector $\vec{A}$ is not conserving in the presence of an external magnetic field unless vector $\vec{A}$ is directed along the field.

The classical Langevin function can be obtained from the Brillouin function in a standard way by letting $S \to \infty$ and $\mu_B \to 0$ so that $\lim_{S\to\infty} g\mu_B S = \mu_0 = const.$

The entropy, given in Eq. (6), can now be obtained by combining Eqn. (8) and Eqns. (9)- (13) as

$$S = -k\sum_{i=1}^{N}[a_i m(a_i) - ln(Z_i(a_i))], \tag{14}$$

while the internal energy becomes

$$U = \sum_{i\neq j} J_{ij}^{dip}[\vec{m}_i \cdot \vec{m}_j - 3(\vec{m}_i \cdot \hat{r}_{ij})(\vec{m}_j \cdot \hat{r}_{ij})] - \sum_{i=1}^{N} \vec{H} \cdot \vec{m}_i. \tag{15}$$

It is straightforward to carry out the minimization of the free energy $F = U - TS$ with respect to a_i (or m_i). Using the identity $m_i = \frac{d}{da_i}(lnZ_i)$ we get the equilibrium equation

$$\vec{A}_i - \vec{H} + \sum_j{}' J_{ij}^{dip}[\vec{m}_j - 3\hat{r}_{ij}(\vec{m}_j \cdot \hat{r}_{ij})] = 0 \tag{16}$$

where the prime over the summation sign denotes the restriction of j≠i. As expected, Eqn. (16) coincides with the Euler-Lagrange equation for the free energy functional $F[\rho]$ in the Mean Field Approximation [4], so that $\vec{A}_i$ has meaning of the mean field at site i. The stability properties of the function $F(\vec{m}_i)$ are governed by the Hessian matrix $H = \frac{\partial^2 F}{\partial m_{i\alpha}\partial m_{j\beta}}$, where $\alpha, \beta = x, y, z$. Our goal now is to find $\vec{A}_i$, which minimize the free energy for given $\vec{H}$ and T. Then the per-dipole magnetization is given by

$$\vec{M}(T, \vec{H}) = \frac{1}{N} \sum_{i=1}^{N} \vec{m}_i \tag{17}$$

from which we can directly compute the magnetic susceptibility as

$$\chi^*_{\alpha\beta} = (\frac{\partial \mu_0 M_\alpha}{\partial H_\beta / \mu_0})_T = a^3 \chi_{\alpha\beta}, \tag{18}$$

where

$$\chi_{\alpha\beta} = (\frac{\partial M_\alpha}{\partial h_\beta})_T \tag{19}$$

The specific heat can be obtained either from the internal energy or from the entropy:

$$C = (\frac{\partial U}{\partial T})_H = T(\frac{\partial S}{\partial T})_H. \tag{20}$$

"A word of caution is necessary about calculating the thermodynamic properties of a system under the MFA" [18]. In the MFA the last two expressions for the specific heat are not necessary identical. In the case of the dipole interaction they are different even in zero field (unlike the Heisenberg model), thus providing a useful quantitative measure of the inherent controversy of the MFA.

3 The Method of Solution.

So far we have been careful in the formulation to allow dipolar interactions between *all* pairs. From here on, following [4, 5], we restrict our consideration to nearest-neighbor interactions. A honeycomb lattice of N sites can be decomposed into n=6 equivalent sublattices with $N/6$ sites each, so that spins in the same sublattice do not interact. *A priori*, and guided by our numerical solutions, we expect the magnetization of the six sublattices to be different. Allowing this possibility, enumerating 6 sites of an elementary hexagon as shown in Fig.1 of the work [4] and denoting the number of the nearest neighbors by z($z = 3$ for the honeycomb lattice), we get for the per-site free energy

$$
\begin{aligned}
f &= F/N = u - Ts, \\
u &= \frac{J^{dip}}{2n} \sum_{i=1}^{n} \sum_{j=1'}^{z} [\vec{m}_i \cdot \vec{m}_j - 3(\vec{m}_i \cdot \hat{r}_{ij})(\vec{m}_j \cdot \hat{r}_j)] - \frac{1}{n} \sum_{i=1}^{n} \vec{H} \cdot \vec{m}_i, \\
s &= -\frac{k}{n} \sum_{i=1}^{n} [a_i m(a_i) - ln(Z_i)].
\end{aligned}
\tag{21}
$$

Here u and s are the per-site internal energy and entropy correspondingly. In the nearest neighbor approximation the equilibrium equation (16) reduces to six vector equations as follows:

$$
\begin{aligned}
&\vec{A}_i - \vec{H} + J^{dip} \textstyle\sum_{j'=1'}^{z'} [\vec{m}_{j'} - 3\hat{r}_{ij'}(\vec{m}_{j'} \cdot \hat{r}_{ij'})] = 0, \qquad \text{i = 1, 2, 3} \\
&\vec{A}_{i'} - \vec{H} + J^{dip} \textstyle\sum_{j=1}^{z} [\vec{m}_j - 3\hat{r}_{i'j}(\vec{m}_j \cdot \hat{r}_{i'j})] = 0, \qquad \text{i' = 1', 2', 3'}
\end{aligned}
\tag{22}
$$

where m_j is given by Eqn. (9) , $J^{dip} = \mu^2/a^3$ being the nearest neighbor interaction, and $\hat{r}_{ij'}$ is the unit vector pointing from site i to site j'. The

Hessian becomes the (18*18) matrix with the following elements:

$$\begin{array}{llll}
\frac{\partial^2 f}{\partial m_{i\alpha}{}^2} & = \frac{dA_i}{dm_i} & = kT\ a_i', & i=j, \alpha=\beta, \\
\frac{\partial^2 f}{\partial m_{i\alpha}\partial m_{i\beta}} & & = 0\ , & i=j, \alpha\neq\beta, \\
\frac{\partial^2 f}{\partial m_{i\alpha}\partial m_{j\alpha}} & = A_{ij}^{\alpha} & = J^{dip} - 3J^{dip} r_{ij}^{\alpha} r_{ij}^{\alpha}, & i\neq j, \alpha=\beta, \\
\frac{\partial^2 f}{\partial m_{i\alpha}\partial m_{j\beta}} & = B_{ij}^{\alpha\beta} & = -3J^{dip} r_{ij}^{\alpha} r_{ij}^{\beta}, & i\neq j,\ \alpha\neq\beta,
\end{array} \tag{23}$$

where $i,j = 1,1',2,2',3,3'$ and $\alpha,\beta = x,y,z$, $r_{ij}^{x} = x_{ij}$ and so on. Here

$$(a_i')^{-1} = \begin{cases} 1 - m_i^2 - m_i/a_i, & \text{Planar Rotator model}, \\ -sinh^{-2}(a_i) + a_i^{-2}, & \text{Space Rotator model}, \\ -\left(\frac{2S+1}{2S}\right)^2 sinh^{-2}\left(\frac{2S+1}{2S} a_i\right) + & \\ \frac{1}{4S^2} sinh^{-2}(\frac{a_i}{2S}), & \text{Spin S model}, \\ cosh^{-2}(a_i), & \text{Ising model}, \end{cases} \tag{24}$$

The free energy was minimized numerically. The ground state configuration was used as the initial approximation of the ordered state at low fields and temperatures. The minimum associated with the lowest free energy was identified as the true dipole configuration. The susceptibility and the specific heat were obtained by numeric differentiation with the estimated relative error less than 0.01 and then reevaluated by the Aitken's interpolation formula.

4 The Ground State ($T = 0$).

The ground state is one in which the energy

$$E = \sum_{i=1}^{N} \sum_{j=1'}^{N-1} J_{ij}^{dip} [\hat{\mu}_i \cdot \hat{\mu}_j - 3(\hat{\mu}_i \cdot \hat{r}_{ij})(\hat{\mu}_j \cdot \hat{r}_{ij})] - \sum_{i=1}^{N} \vec{H} \cdot \hat{\mu}_i, \tag{25}$$

has its minimum (in the thermodynamical limit $N \to \infty$). Naturally each of the considered models predicts the same ground state. In spherical coordinates the energy is expressed as follows:

$$E = \sum_{i=1}^{N} \sum_{j=1'}^{N-1} J_{ij}^{dip}[cos(\theta_i)cos(\theta_j) + sin(\theta_i)sin(\theta_j)e_{XY}(\phi_i, \phi_j)]$$
$$-H \sum_{i=1}^{N} cos(\theta_i)cos(\theta_h) - H \sum_{i=1}^{N} sin(\theta_i)cos(\phi_i - \phi_h)sin(\theta_h) \ , \qquad (26)$$

where

$$e_{XY}(\phi_i, \phi_j) = -\frac{3}{2}cos(\phi_i + \phi_j - 2\alpha_{ij}) - \frac{1}{2}cos(\phi_i - \phi_j) \qquad (27)$$

(here $\vec{h} = \vec{H}/J^{dip}$, $\vec{\mu}_i = (1, \theta_i, \phi_i)$ and α_{ij} is the angle that the vector $\vec{r}_{ij}$ makes with the x-axis). The extremum conditions are

$$\frac{\partial E}{\partial \theta_i} = \sum_{j=1}^{N-1} J_{ij}^{dip}[-sin(\theta_i)cos(\theta_j) + cos\theta_i sin\theta_j e_{XY}(\phi_i, \phi_j)]$$
$$+H(sin\theta_i cos\theta_h - cos\theta_i sin\theta_h cos(\phi_i - \phi_h)) = 0, \qquad (28)$$

and

$$\frac{\partial e}{\partial \phi_i} = \sum_{j=1}^{N-1} [sin\theta_i sin\theta_j \frac{\partial e_{XY}(\phi_i, \phi_j)}{\partial \phi_i}] + N sin\theta_i sin\theta_h cos(\phi_i - \phi_h) = 0, \quad (29)$$

A solution of the equilibrium equations (28)- (29) is a minimum if the following stability conditions are satisfied:

$$\frac{\partial^2 e}{\partial x_1 \partial x_1} > 0, det H_{x_i, x_j} > 0, ..., \qquad (30)$$

where H_{x_i,x_j} is the Hessian matrix with respect to the variables $x_i = \theta_i$, θ_j, ϕ_i, ϕ_j.

In the nearest neighbor approximation the energy can be written in the following form:

$$e = \frac{E/J^{dip}}{N} = \frac{1}{n}\sum_{i=1}^{z}\sum_{j=1'}^{z'}[\hat{\mu}_i \cdot \hat{\mu}_j - 3(\hat{\mu}_i \cdot \hat{r}_{ij})(\hat{\mu}_j \cdot \hat{r}_{ij})] - \frac{1}{n}\sum_{i=1}^{n}\vec{h}\cdot\hat{\mu}_i, \quad (31)$$

where for the honeycomb lattice z=3, $z' = 3'$ and $h = H/J^{dip}$. The resulting changes in all other expressions are straightforward.

4.1 $\vec{H} = 0$.

Consider first the ground state for $\vec{H} = 0$. In this case Eqs. (28) have one "planar" solution (1) $\theta_i = \theta_j = \pi/2$, one "parallel" solution (2) $\theta_i = \theta_j = 0$; and "antiparallel" solutions (3) $\theta_i = k_i\pi$ $(k_i = 0, 1)$, which correspond to any other combination of dipoles pointing in any direction along the normal to the plane. The second solution corresponds to a maximum, while the first gives the lowest minimum. Thus, in accordance with the footnote 3 of the work [6], the ground state of the 3-component dipolar system on a honeycomb lattice in zero field coincides with the ground state of the dipolar Planar Rotator model, described in [4, 5, 6]. By symmetry we expect the dipoles to be arranged in a symmetric fashion, namely, the dipoles $\vec{\mu}_1, \vec{\mu}_2, \vec{\mu}_3$, and $\vec{\mu}_{1'}$,$\vec{\mu}_{2'}$, $\vec{\mu}_{3'}$, making 120° with respect to each other, although there can be relative rotations [4]. Clearly, the ground state is continuously degenerate and can be parameterized by one parameter ϕ as follows [6]:

$$\phi_i = (\phi, -\phi - 2\pi/3, \phi - 2\pi/3, -\phi - 4\pi/3, \phi - 4\pi/3, -\phi - 2\pi). \qquad (32)$$

In the nearest neighbor approximation the ground state energy per site equals to $(-3z/4)J^{dip}$ that is $-2.25J^{dip}$ [4] for the hexagonal lattice.

4.2 $\vec{H}$ is collinear to the z-axis.

The normal field is beyond the consideration of the Planar Rotator model. The behavior of the Space Rotator and the Spin S models in the normal field is identical. Eqs. (28) have the stable solution:

$$\begin{array}{ll} cos(\theta_i) = cos(\theta_j) = H/H_z^{cr}, & \text{if } H \leq H_z^{cr}; \\ \theta_i = \theta_j = 0, & \text{if } H \geq H_z^{cr}; \end{array} \qquad (33)$$

where

$$H_z^{cr} = (1 - e_{XY}^0) \sum_{j=1'}^{N-1} J_{ij}^{dip}. \qquad (34)$$

and $e_{XY}^0 = e_{XY}(\phi_i, \phi_j)$ with the angles ϕ_i given for the honeycomb lattice by Eqn. (32). In other words the dipoles tilt out the plane towards the field direction more and more with the increasing field until at $H = H_z^{cr}$ the first order phase transition occurs and all of them become oriented along the normal to the plane. In the nearest neighbor approximation

$$h_z^{cr} = H_z^{cr}/J^{dip} = z(1 - e_{XY}^0). \qquad (35)$$

For the honeycomb lattice $e^0_{XY} = -3/2$ and $h^{cr}_z = 7.5$. It follows that the z-axis susceptibility of the model at $T = 0$ equals $\chi(T = 0) = 1/H^{cr}_z = 2/15 = 0.1(3)$.

4.3 $\vec{H}$ lies in the XY-plane.

The behavior of each of the considered models is the same. Since $cos(\theta_h) = 0$, Eqs. (28) have solution $\theta_i = \theta_j = \pi/2$ with ϕ_i given by Eq. (29). The critical field is the same in each of three considered models ($H_{cr} \approx 2$ for the horizontal $\vec{H}$).

5 The Paramagnetic and Ferromagnetic Phases.

Let us consider the situation when magnetizations of all sublattices are equal and collinear to external field. Using the identity $\sum_{j=1'}^{z}(\vec{m}\hat{r}_{ij})^2 = (z/2)(m_x^2 + m_y^2)$ we get the following expression for the free energy of the para/ferro magnetic phase in the MFA:

$$f = \frac{F/J^{dip}}{N} = \frac{z}{4}(2\vec{m}^2 - 3m_x^2 - 3m_y^2) - \vec{h}\cdot\vec{m} + t[am(a) - \ln Z(a)], \quad (36)$$

where $\vec{h} = \vec{H}/J^{dip}$, $t = kT/J^{dip}$. Let us choose the x axis parallel to $\vec{h}_{XY}$. The equilibrium equations become

$$\frac{\partial f}{\partial m_x} = -\frac{z}{2}m_x - h_x + ta_x = 0, \quad (37)$$

$$\frac{\partial f}{\partial m_z} = zm_z - h_z + ta_z = 0.$$

The equilibrium equation (37) for each (x or z) component is not independent from each other due to Eq. (9). The stability conditions (30) become

$$\frac{\partial^2 f}{\partial m_x^2} > 0 \ , \ detH = \frac{\partial^2 f}{\partial m_x^2}\frac{\partial^2 f}{\partial m_z^2} - \frac{\partial^2 f}{\partial m_x \partial m_z}\frac{\partial^2 f}{\partial m_z \partial m_x} > 0 \ , \qquad (38)$$

where

$$\begin{aligned} \frac{\partial^2 f}{\partial m_x^2} &= -\frac{z}{2} + t[\frac{a}{m} + (a' - \frac{a}{m})(\frac{m_x^2}{m^2})] \\ \frac{\partial^2 f}{\partial m_z{}^2} &= +z + t[\frac{a}{m} + (a' - \frac{a}{m})(\frac{m_z^2}{m^2})] \\ \frac{\partial^2 f}{\partial m_x \partial m_z} = \frac{\partial^2 f}{\partial m_z \partial m_x} &= t[\frac{m_x m_z}{m^2}(a' - \frac{a}{m})] \end{aligned} \qquad (39)$$

and a' is given by Eq. (24)

5.1 Zero temperature ($T = 0$).

The aim of the following calculations is to determine the limiting behavior of the considered models at absolute zero within the MFA, no matter how unphysical it is (due to the fact that the MFA does not have much sense at $T = 0$). Assuming the mean field value A is an analytical function of temperature at $T = 0$, expanding A near $T = 0$ in the powers of the small parameter T: $A = A_0 + A_1 T + O(T^2)$ and using the results of Appendix A one can easily prove that the equilibrium equations Eq. (37) have two solutions at T=0: the ferromagnetic solution ($A \neq 0$)

$$(A + zJ^{dip})cos\theta = H cos(\theta_H), \ (A - \frac{z}{2}J^{dip})sin\theta = H sin(\theta_H), \qquad (40)$$

and the paramagnetic solution ($A = 0$)

$$m_x = -\frac{2}{z}h_x, m_z = \frac{1}{z}h_z, m = \sqrt{4h_x^2 + h_z^2}/z \leq 1. \qquad (41)$$

In zero field the paramagnetic solution is the unstable trivial solution $m = a = 0$, while the ferromagnetic solution becomes either a minimum: $m_z = 1, m_x = 0$, or a maximum $m_z = 0, m_x = 1$. Let us consider two most interesting directions of the external field: $\theta_H = \pi/2$ and $\theta_H = 0$. If $\vec{H}$ lies in the lattice plane ($\theta_H = \pi/2$), then

$$m_z = A_z = 0, A_x = \frac{z}{2}J^{dip} + H, m_x = 1, \qquad (42)$$

or

$$A = -zJ^{dip}, m_x = sin\theta = \frac{-H}{(3/2)zJ^{dip}}, m_z = cos\theta, H \leq \frac{3}{2}zJ^{dip}. \qquad (43)$$

The solution Eq. (43) is unphysical while solution Eq. (42), which becomes the maximum at zero field, does not warrant any discussion. If $\vec{H}$ is normal to the lattice plane ($\theta_H = 0$), then

$$A = \frac{z}{2}J^{dip}, m_x = sin\theta, m_z = cos\theta = \frac{H}{(3/2)zJ^{dip}}, H \leq (3/2)zJ^{dip}. \qquad (44)$$

or

$$A = H - zJ^{dip}, \theta = 0, m_x = 0, m_z = 1, \tag{45}$$

The solution Eq. (44), being a stable minimum, corresponds to unidirectional dipoles tilting out of the lattice plane towards the field direction with the increasing field until all dipoles are oriented along the normal to the plane. The dependence of θ_i is different from one for the ground state. The solution Eq. (45) makes sense only at $H \geq zJ^{dip}$ when the unstable paramagnetic solution reaches the limiting value of $m_x = 1$. The solution Eq. (45) is also unstable untill H reaches the value of $(3/2)zJ^{dip}$ where the solution of Eq. (45) merges with the stable solution of Eq. (44).

5.2 Zero field ($\vec{h} = 0$).

The equilibrium equation (37) for a z-component becomes

$$zm_z + ta_z = zm_z + A_z/J^{dip} = 0 \tag{46}$$

Since m_z and a_z should have the same sign, the only solution is $m_z = a_z = 0$. It follows that in zero field for any considered model

$$m_z = a_z = 0 \ , \ m_x = m(a), -\frac{z}{2}m(a) + ta = 0, \ -\frac{z}{2} + ta' > 0, \tag{47}$$

where $m(a)$, given by Eqs. (9) , is slightly different in shape for different models. The equilibrium equation (47) has a trivial solution $a = 0$ at all temperatures and a nontrivial one at $0 < t < t_{CW}$. The trivial solution approaches $m_x = 0, A = Ta = 0$ at $T \to 0$. For the nontrivial solution $A = (z/2)J^{dip} = const > 0, a = A/T \to \infty, m(a) \to 1, A = (z/2)J^{dip}$. The Z(a), m(a) and s(a) behavior in the limit of the negligibly small and infinitely large a is given in the Appendix A. The most important consequence is that similar to the Planar Rotator model the Space Rotator model does not satisfy the Third Law of Thermodynamics, while the Spin S model does.

At the bifurcation point $(h = 0, t = t_{CW})$ these solutions merge in a degenerate critical point $m_x = 0$. The trivial solution is stable at $t > t_{CW}$, while the nontrivial solution is stable at $0 < t < t_{CW}$. The critical temperature

$$t_{CW} = \frac{z}{2} \lim_{a \to 0} (a')^{-1} = pz/2, \tag{48}$$

where

$$p = \begin{cases} 1/2. & \text{for the Planar Rotator model,} \\ 1/3, & \text{for the Space Rotator model,} \\ (s+1)/(3s), & \text{for the Spin S model,} \\ 1, & \text{for the Ising model,} \\ 7/15. & \text{for S=5/2.} \end{cases} \tag{49}$$

In accordance with the Thom theorem [19] in our case of two control parameters h and t and one behavior (state) parameter a the free energy $f(a)$ in the vicinity of the degenerate critical point is of the cusp catastrophe form.

5.2.1 The high temperature limit ($T \to \infty$).

The behavior of Z(a), m(a) and s(a) in the high temperature limit is described in the Appendix A. In any model

$$m = pa, \text{ as } a \to 0, \tag{50}$$

The equilibrium equation becomes:

$$Tp^{-1}\vec{m} - \vec{H} + \sum_{j=1'}^{z} J_{ij}^{dip}(\vec{m} - 3\hat{r}_{ij}(\vec{m}\hat{r}_{ij})) = 0. \tag{51}$$

Using the identity $\sum_{j=1'}^{z} \hat{r}_{ij}(\vec{m}\hat{r}_{ij})) = (z/6)\vec{m}$ [4], we get the Curie-Weiss law

$$\vec{m} = \frac{\vec{H}}{kT + kT_{CW}} = \frac{\vec{h}}{t + t_{CW}}, \tag{52}$$

As expected in the MFA the Curie-Weiss temperature coincides with the ferromagnetic transition temperature.

6 The Antiferromagnetic Phase: Dipole Configuration.

If field is applied along the plane then the behavior of the dipoles in the Space Rotator or Spin S models differs little from that of the Planar Rotator model [4]. The application of the magnetic field along the plane lifts the infinite degeneracy of the ground state. The configuration with the lowest free energy depends on the direction of the magnetic field. Magnetic fields applied along an axis of lattice symmetry tend to pair up dipole magnetizations with equal magnitudes. This pairing is broken if $\vec{H}$ is not along a direction of symmetry. The flip of the dipoles denotes the occurrence of a phase boundary.

If field is applied along the normal to the plane then the Space Rotator and Spin S models predict a number of new features in the behavior of the system. The dipoles tilt out the plane along the field direction conserving the infinite degeneracy of the ground state and their symmetrical arrangement. At some critical field $h_{cr}(t)$ the projections of the dipoles on the plane become so small that the dipolar interaction could not oppose the tendency of the system to disorder and the phase transition occurs.

7 The Thermodynamical Properties .

To avoid unnecessary discussion of unimportant differences among the three considered models and to make the article shorter we will present in this section the results for the Spin S=5/2 model only. Comparison of the thermodynamic properties of the models will be given in the Section 8.1.

7.1 The magnetization.

The magnetization, normalized to the saturation magnetization M_s, is shown in Fig. 1 as a function of the magnetic field at fixed temperatures, and in

Fig. 2 as a function of temperature at fixed magnetic fields. The figures indicate that for the horizontal fields the magnetization possesses a jump in h when t is less than the critical temperature, t_{cr} and a cusp in t at h less then the critical field h_{cr}. At higher temperatures and fields the discontinuity is replaced by an inflection point. In the fields normal to the lattice plane the magnetization possess cusps in both h and t.

7.2 The susceptibility.

The susceptibility computed from the magnetization using Eq. (18) is shown in Fig. 3 as a function of the applied magnetic field, and in Fig. 4 as a function of the temperature. Figure Fig. 3 shows the existence of the jumps or cusps in the points of the phase transition. The jump in the $\chi(t)$ becomes a gradual maximum at higher in-plane fields.

7.3 The entropy and the specific heat.

The entropy is shown as a function of field and temperature in Figs. 5- 6, while the specific heat computed from the entropy using (15) is shown in Figs. 7- 8. Figures 7- 8 again exhibits sharp jumps in the specific heat at the locations of jumps or cusps in the magnetization and susceptibility.

7.4 The order parameter.

We define an order parameter as follows:

$$\sigma = \frac{1}{2\pi} \sum_{i=1}^{n_{sl}} m_i \delta\theta_i \tag{53}$$

where n_{sl} is a number of sublattices and $\delta\theta_i$ is the smallest angle between dipoles at sites i and $i+1$. In the Neel case of two sublattices the definition gives us the usual antiferromagnetic order parameter $\sigma = m_2 - m_1$. Note that the order parameter equals 1 in the ground state and it equals zero in the disordered phase. A plot of the order parameter σ as a function of temperature and field is shown in Figs. 9-10. It is seen that in nonzero field the order parameter is discontinuous across the boundary between phases while in zero field the dependence $\sigma(t)$ corresponds to the second order phase transition.

7.5 The Phase Diagram.

The energy of the antiferromagentic phase is always lower than the energy of the system of the collinear dipoles whenever the antiferromagentic phase exists. Hence the ferromagnetic phase discussed earlier is metastable and the ferromagnetic phase transition can not be reached in a usual experiment. The only remaining phase transition is one between the paramagnetic and the antiferromagnetic phases. One can now construct a phase diagram in the t-h plane by plotting the locus of the susceptibility or specific heat or order parameter peculiarities between the paramagnetic and the antiferromagnetic phases. This is done in Fig. 11 for the field applied along the horizontal and normal directions. Phase transition curves for fields applied in arbitrary directions along the plane are very similar and do not differ by more than 5%. Fig. 11 shows the existence of two distinct phases I and II. It follows from the behavior of the order parameter (see text above) that phase I is the ordered phase where interactions between the dipoles dominate and there is the sublattice ordering.

The critical temperature in zero field can be obtained analytically for each of the considered dipolar models using the approach of Zimmerman et al. [4]. The result is that

$$kT_N/J^{dip} = \frac{3z}{2}J^{dip}\cdot\lim\frac{m(a)}{a} = \frac{3z}{2}p. \tag{54}$$

substituting z and p from Eq. (49) we get

$$kT_N/J^{dip} = \frac{9}{2}p = \begin{cases} 2.25 & \text{for the Planar Rotator model,} \\ 1.5 & \text{for the Space Rotator model,} \\ 3(s+1)/(2s) & \text{for the Spin S model,} \\ 4.5 & \text{for the Ising model,} \\ 2.1 & \text{for S=5/2.} \end{cases} \tag{55}$$

The critical field at zero temperature is the same for the Space Rotator and Spin S model (and for the Planar Rotator model in the case of fields applied along the plane). For normal direction the critical field is determined only by the energy of the system in zero field having the value of $7.5J^{dip}$. For the horizontal direction the critical field is $2J^{dip}$. At $H = 0$ the phase transition is of the second order. In nonzero fields the system undergoes the first order phase transition.

8 Discussion.

8.1 Comparison of the Spin S, Space Rotator and Plane Rotator dipolar models.

The ground state of the 3-component dipoles on a honeycomb lattice in zero field coincides with the ground state of the Planar Dipolar model. The latter model at nonzero temperatures and nonzero fields directed along the lattice plane was considered within the Mean Field approximation in [4]. The refined phase diagram [4] is represented in Fig. 12. The only substantial difference is that the "high-field" transition curve is not confirmed by our calculations.

The thermodynamic properties of the Space Rotator model are very similar to those of the Spin S model. The major difference is the entropy behavior (see Fig. 13). At $T \to \infty$ the entropy limit ($ln(4\pi) = 2.53$) in the Space Rotator model is substantially greater than that of the Spin S model ($ln(6) = 1.8$) due to extra degrees of freedom. When approaching the absolute zero the entropy of the classical Space Rotator model goes to minus infinity while the entropy of the Spin S model equals zero. However that pathological behavior manifests itself only very close to zero. Hence the first factor plays the key role at all other temperatures and the predicted critical temperature of the Space Rotator model is much smaller ($1.5J^{dip}$) then the critical temperature $2.1J^{dip}$ of the Spin S model.

The entropy of the Planar Rotator model also becomes infinitely negative at absolute zero. But due to the lucky coincidence the entropy contribution into the free energy at infinite temperatures ($ln(2\pi) = 1.8$) is approximately the same as that of the Spin S model. Therefore in the case of the Planar Dipolar model the pathological behavior of the entropy plays the major role in the differences between the models and the critical temperature value of $2.5J^{dip}$ is greater than that of the Spin S model. The resulting phase diagrams for each of the considered models are compared in Fig. 14.

The most important feature of the Space Rotator and Spin S models is their ability to describe the system's behavior in the fields applied along the normal to the lattice plane. Both models predict the existence of two phases and the order-disorder phase transition in the normal field at a value greater than the critical field for directions along the plane. The ratio of the critical fields increases with the temperature going down and reaches approximately 3.75 at $T = 0$ (See Fig. 11).

8.2 Artifacts of the theory.

The considered semiclassical dipolar model is very far from the reality of the $FeCl_3$ graphite intercalated compounds (GIC). In spite of this we believe that the model catches some of the important statistical aspects of the compound behavior. Our belief is confirmed by the comparison of the theoretical predictions with experiment (see next section).

The ordered state of the model in zero fields is continuously degenerate. It means the entropy per spin is infinite so that the system should undergo the zero-th order phase transitions at some critical temperature T_{cr} when changing temperature at zero field, and at zero field when applying it at temperatures below T_{cr}. This behavior is suppressed by thermal and/or dilution and/or field fluctuations reducing the continuous degeneracy to a discrete symmetry [6]. In calculations we have frozen the polar angle of one of the dipoles on one of the sublattices which parameterizes the continuously degenerate ordered state. This primitive way of choosing one of the infinitely degenerate states "by hand" instead of allowing fluctuations to cull it, together with the used MFA, results in a monotonous shape of the critical curve, $T_{cr}(H)$.

It is a well known fact that the MFA predicts wrong critical indices.

The values of the critical field and temperature are also known do differ considerably from the results of more refined approaches. However the predicted differences of critical temperatures for different models should not be substantially affected by this fact.

8.3 Comparison of the theoretical results with experiment.

8.3.1 The phase diagram.

The most important result of our calculations is that the considered model has phase transitions in both normal and in-plane magnetic fields, with the critical field stronger in the normal direction (Fig. 11). Measurements [7] of the in-plane susceptibility in the in-plane and c-axis magnetic fields show that the susceptibility has a peak in both cases (see Fig. 11 of Ref. [7]). Assuming the position of the peak coincides with the critical point (or at least is not far from it), the phase diagram (Fig. 15) can be qualitatively constructed from the data [7]. It is clear from Fig. 15 that the c-axis critical field is several times greater than the in-plane one. The range of experimentally investigated fields and temperatures makes it difficult to estimate the ratio $H^z_{cr}(T = 0)/H^x_{cr}(T = 0)$, but, evidently, theoretical prediction of 3.75 is within the tolerance of the experimental data [2]. Hence the underlying hy-

[2] A rough estimate of the experimental ratio of critical fields, $H^{c-axis}_{cr}(T = 0)/H^{in-plane}_{cr}(T = 0)$, can be obtained from the measured values of H_0, which is close

pothesis of the major role of the dipole interaction in the lowest temperature phase transition in the $FeCl_3$-graphite intercalated compounds is strongly supported by our calculations. The orientational dependence of the experimental phase diagram finds its natural explanation in the two-dimensional nature of the ground state of a dipole system on bipartite plane lattices.

Theoretical (MFA) values of the critical temperature differ substantially from the experimental one. The spin S=5/2 model predicts $T_{cr} = 2.1J^{dip} = 1K^o$, compared with the $T^{cr} = 1.8K^o$ measured for the stage 6 $FeCl_3$ GIC [7].

8.3.2 The in-plane susceptibilty.

Now let us compare theoretical predictions and experimental observations [7] on the susceptibilty in more details.

The interpretation [4] of the maximum of the $\chi(T)$ curves as originated from the critical behavior of the magnetic dipolar subsystem near the orientational order/disorder phase transition is fully supported by our calculations. This is clear from the comparison of Figs. 2-5 of Ref. [7] and Fig. 4 if one takes into account that approximations beyond MFA will smooth out the

to the point where the susceptibility maximum stops shifting towards higher temperatures with the increase of the applied magnetic field. Since the critical field at absolute zero, $H_{cr}(T = 0)$, should grow with the increasing H_0 faster than H_0, the measurements [7] provide us with the lower limit of the ratio of the critical fields: $H_{cr}^{c-axis}(T=0)/H_{cr}^{in-plane}(T=0) \geq H_0^{c-axis}/H_0^{in-plane} = 17/7.5 \approx 2.3$

susceptibilty curve in non-zero fields at the right-hand side of the transition. The shift of the maximum towards high temperatures with the magnetic field increasing is the evident consequence of the critical temperature increase in weak magnetic fields, which is beyond our consideration.

Two distinctive features of the experimental behavior of the in-plane susceptibility versus magnetic field, namely sharp peak at very low fields and decreasing of the susceptibility at higher fields (Figs. 5 and 6 of Ref. [7]) are reproduced by the theory very well (Fig. 3). However, theory also predicts the strong dependence of the peak position of the $\chi(H)$ curves versus the temperature parameter of the curves, which is not observed in the experiments [7]. The theory also fails to explain the origin of the second broad maximum at higher fields (see Fig. 6 of Ref. [7]).

8.3.3 The c-axis susceptibility.

Almost constant value of the c-axis susceptibility and weak anomaly at the critical temperature, observed in the experiments [7], are in an excellent agreement with the theoretical results which predict constant c-axis susceptibility up to the transition point, where the derivative of the susceptibilty changes discontinuously (Fig. 4 (b)).

8.3.4 The high temperature susceptibilty.

The MFA predicts the Curie-Weiss form of the dependence of the susceptibilty upon temperature at high T. The Curie-Weiss law has been observed in the phases 1 and 2 of the $FeCl_3$ GIC [7]. However in phases 3 and 6 the susceptibility behavior is much more complex, indicating the existence of other responses to the applied magnetic field besides the reorientation of magnetic dipoles, interacting by classical magnetic forces.

The MFA also predicts the metastable ferromagnetic phase underneath the antiferromagnetic phase at low enough temperatures. The Curie-Weiss temperature gives the estimate of the critical temperature of the ferromagnetic phase transition.

9 Conclusion.

We have calculated properties of three dipolar models (Planar Rotator, Space Rotator and Spin S=5/2) on a honeycomb lattice using the Raleigh -Ritz minimization approach restricted to the Mean Field Approximation. The behavior of the ground state in nonzero normal fields has been calculated analytically. No profound differences between models have been found except in the very narrow region near absolute zero where the MFA predicts infinite entropy for classical models [18]. The utilized technique allowed us to clarify the phase digram for the Planar Rotator model first calculated in work [4] and to obtain the phase diagram in the wide range of in-plane and normal-plane fields and temperatures taking the quantization of spins into account (in the semi-classical manner of Brillouin). The metastable ferromagnetic phase underneath the antiferromagnetic phase at low enough temperatures has been also predicted.

The results of the calculations of the Spin S=5/2 model have been compared with the experimental data [7] on the $FeCl_3$ graphite intercalated compounds and a surprisingly good agreement has been found. The peculiarities of the measured magnetic properties have been successfully interpreted as the phase transition phenomena; the anisotropy of the magnetic properties has found its natural explanation in the two-dimensional nature of the ground state of a dipole system on bipartite plane lattices. In spite of the fact that the experimentally observed [7] increase of the critical temperature in weak magnetic fields have not been reproduced in the present work, we believe that the considered dipolar model catches the main statistical aspects of the $FeCl_3$ graphite intercalated compounds behavior at temperatures of several degrees above absolute zero.

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APPENDIX

A High and low temperature and field limits for the dipolar models.

For a given dipolar model functions m(a), Z(a) and s(a) depends only on the dimensionless parameter $a = A/T$ which in its turn depends on H and T through $A = A(H,T)$. Let us first find the behaviour of the above mentioned functions in the limits $a \to 0$ and $a \to \infty$.

A.1 The Planar Rotator model.

Using the known expressions [20] for the Bessel functions:

$$I_\nu(a) = (\frac{a}{2})^\nu \sum_{k=0}^{\infty} \frac{(a^2/4)^k}{k!\Gamma(\nu+k+1)}, \text{ at } a \to 0, \nu \neq -1, -1, \ldots \quad (56)$$

$$I_\nu(a) = \frac{e^a}{\sqrt{2\pi a}}(1 - \frac{\mu - 1}{8a} + \frac{(\mu-1)(\mu-9)}{2!(8a)^2} - \ldots), \text{ at } a \to \infty, \mu = 4\nu^2 \quad (57)$$

or

$$I_0(a) = 1 + a^2/4 + \frac{a^2/4}{(2!)^2} + \frac{(a^2/4)^3}{(3!)^2} + \ldots, \text{ at } a \to 0, \quad (58)$$

$$I_1(a) = \frac{a}{2}(1 + \frac{a^2/4}{2!} + \frac{(a^2/4)^2}{(2!)(3!)} + \frac{(a^2/4)^3}{(3!)(4!)} + \ldots), \text{ at } a \to 0, \quad (59)$$

$$I_0(a) = \frac{e^a}{\sqrt{2\pi a}}(1 + \frac{1}{8a} + \frac{3^2}{2!(8a)^2} + \ldots), \text{ at } a \to \infty, \quad (60)$$

$$I_1(a) = \frac{e^a}{\sqrt{2\pi a}}(1 - \frac{3}{8a} - \frac{15}{2!(8a)^2} + \ldots), \text{ at } a \to \infty\ , \quad (61)$$

we get

$$m(a) = \frac{I_1(a)}{I_0(a)} = \frac{a}{2}\frac{1 + a^2/4 + \frac{a^2/4}{(2!)^2} + \frac{(a^2/4)^3}{(3!)^2} + ...}{1 + \frac{a^2/4}{2!} + \frac{(a^2/4)^2}{(2!)(3!)}, + \frac{(a^2/4)^3}{(3!)(4!)} + ...} = \frac{a}{2} - \frac{a^3}{16} + O(a^4), \text{ at } a \to 0, \quad (62)$$

$$m(a) = \frac{I_1(a)}{I_0(a)} = \frac{1 - \frac{3}{8a} - \frac{15}{2!(8a)^2} + ...}{1 + \frac{1}{8a} + \frac{3}{2!(8a)^2} + ...} = 1 - \frac{1}{2a} - \frac{11}{2(8a)^2}, \text{ at } a \to \infty \ , \quad (63)$$

$$Z(a) = 2\pi I_0(a), (64)$$

$$s(a) = \ln Z(a) - am(a) = \ln(2\pi) - a^2/4, \text{ at } a \to 0 \ , \quad (65)$$

$$s(a) = \ln Z(a) - am(a) = \frac{1}{2}(-\ln a + \ln(2\pi) + 1), \text{ at } a \to \infty \ , \quad (66)$$

A.2 The Space Rotator model.

Using known expansions of the hyperbolic functions

$$coth(a) = \frac{1}{a} + \frac{a}{3} - \frac{a^3}{45} + \frac{9a^5}{945} + ... + \frac{2^{2n}}{(2n)!}B_{2n}a^{2n-1}, a^2 < \pi^2, \quad (67)$$

$$coth(a) = 1 + 2(e^{-2a} + e^{-4a} + e^{-6a} + ...), e^{-2a} < 1, \quad (68)$$

$$sinh(a) = a + \frac{a^3}{3!} + \frac{a^5}{5!} + ..., a^2 < \infty, \quad (69)$$

we get

$$m(a) = coth(a) - \frac{1}{a} = \frac{a}{3} - \frac{a^3}{45} + \frac{9a^5}{945} + ... + \frac{2^{2n}}{(2n)!}B_{2n}a^{2n-1}, a^2 < \pi^2, \quad (70)$$

$$m(a) = coth(a) - \frac{1}{a} = 1 - \frac{1}{a} + 2(e^{-2a} + e^{-4a} + e^{-6a} + ...), e^{-2a} < 1, \quad (71)$$

$$Z(a) = 4\pi\frac{sinh(a)}{a} = 4\pi(a + \frac{a^3}{3!} + \frac{a^5}{5!} + ..., a^2 < \infty, \text{ at } a \to 0 \ , \quad (72)$$

$$Z(a) = 2\pi\frac{e^a}{a}(1 - e^{-2a}), \quad (73)$$

$$s(a) = ln(4\pi) - \frac{a^2}{6}, \text{ at } a \to 0 \ , \quad (74)$$

$$s(a) = -ln(a) + ln(2\pi) + 1, \text{ at } a \to \infty \ , \quad (75)$$

A.3 The Spin S model.

Let us denote $\alpha = 2s+1, \beta = 2s$. Expanding coth(x) as before we get the following expressions for the Brillouin function $B_s(a) = \frac{\alpha}{\beta} coth(a\frac{\alpha}{\beta}) - \frac{1}{\beta} coth(a/\beta)$:

$$m(a) = B_s(a) = \frac{\alpha^2 - 1}{s\beta^2} a + \frac{\alpha^4 - 1}{45\beta^4} a^3 + ... + \frac{2^{2n} B_{2n}}{(2n)!} \frac{\alpha^{2n} - 1}{\beta^{2n}} a^{2n-1} + ..., \quad (76)$$

$$a^2 < \pi^2 * \beta^2/\alpha^2,$$

$$m(a) = 1 - \frac{1}{s}(e^{-a/s}(1 - e^{-2a}) + e^{2a/s}(1 - e^{-4a}) + e^{-4a/s}(1 - e^{-6a}) + ...), \quad (77)$$

$$e^{-a/s} < 1, e^{-2a} < 1.$$

Using expansion for sinh(u) (see A.2) we get the expression for the "partition sum" $Z = \frac{sinh(\frac{\alpha}{\beta}a)}{sinh(\frac{a}{\beta})}$ at small arguments:

$$Z(a) = \alpha \frac{1 + \frac{\alpha^2}{\beta^2}\frac{a^3}{3!} + \frac{\alpha^4}{\beta^4}\frac{a^4}{5!} + ... + \frac{\alpha^{2k}}{\beta^{2k}}\frac{a^{2k}}{(2k)!} + ...}{1 + \frac{a^2}{3!} + \frac{a^4}{5!} + ... + \frac{a^{2k}}{(2k)!} + ...} \ , \ a^2 < \infty, \quad (78)$$

The most useful expression for the "partition sum" at large arguments is:

$$Z(a) = e^a(1 - e^{-2\frac{\alpha}{\beta}a})/(1 - e^{-2\frac{a}{\beta}}) \quad (79)$$

Using the well known expansion

$$ln(1 - x) = -(x + \frac{x^2}{2} + \frac{x^3}{3} + ...) \quad (80)$$

we get for the "entropy" $s = lnZ - am$:

$$s = ln(2s+1) - \frac{s+1}{6s}a^2 + ..., a \to 0, \quad (81)$$

$$s = \sum_{n=1}^{\infty}(\frac{e^{-2n\frac{\alpha}{\beta}a}}{n}) + \sum_{n=1}^{\infty}(\frac{e^{-2n\frac{a}{\beta}}}{n}) + \frac{a}{s}\sum_{n=1}^{\infty}\epsilon^{-2^n\frac{a}{s}}(1-\epsilon^{-2na}), a \to \infty \quad (82)$$

A.4 Summary.

The behaviour of the functions m(a), Z(a) and s(a) in the limits of great and small arguments is summarized in the following table.

Table 1. High and low a limits for z, m, s.

Model	lim a	z	m	s/k
Planar rotator	$a \to 0$	2π	$a/2$	$\ln(2\pi) - a^2/4 \to \ln(2\pi) = 1.838$
	$a \to \infty$	$2\pi e^a/(\sqrt{2\pi a})$	$1 - 1/(2a)$	$\frac{1}{2}(-\ln a + \ln(2\pi) + 1) \to -\infty$
Space rotator	$a \to 0$	4π	$a/3$	$\ln(4\pi) - a^2/2 \to \ln(4\pi) = 2.531$
	$a \to \infty$	$2\pi e^a/a$	$1 - 1/a + 2e^{-2a}$	$-\ln a + \ln(2\pi) + 1 \to -\infty$
Spin S	$a \to 0$	$2S + 1$	$\frac{S+1}{3S}a$	$\ln(2S+1) - \frac{S+1}{3S}a^2 \to \ln(2S+1)$
	$a \to \infty$	e^a	$1 - \frac{1}{S}e^{-a/S}$	$(a/S)e^{-a/S} \to 0$
Spin S=5/2	$a \to 0$	6	$(7/15)a$	$\ln 6 - (7/15)a^2 \to \ln 6 = 1.792$
	$a \to 0$	e^a	$1 - (2/5)e^{-2a}$	$(2/5)ae^{-2a} \to 0$
Ising	$a \to 0$	2	a	$\ln 2 - a^2 \to \ln 2 = 0.69315$
	$a \to \infty$	e^a	$1 - 2e^{-2a}$	$2ae^{-2a} \to 0$

Using the obtained asymptotic behaviour of the functions m(a), Z(a) and s(a) and physically evident asymptotic behaviour of the magnetization M as the function of temperature and external field we get the correspondence between limits of a, T and H as represented at Table 2.

Table 2. High and low temperature and field limits for a.

Model	lim T	lim H	lim a
Planar rotator	$T \to \infty$	$H \to 0$	$a \to 0$
	$T \to 0$	$H \to \infty$	$a \to \infty$
Space rotator	$T \to \infty$	$H \to 0$	$a \to 0$
	$T \to 0$	$H \to \infty$	$a \to \infty$
Spin S	$T \to \infty$	$H \to 0$	$a \to 0$
	$T \to 0$	$H \to \infty$	$a \to \infty$
Spin S=5/2	$T \to \infty$	$H \to 0$	$a \to 0$
	$T \to \infty$	$H \to 0$	$a \to \infty$
Ising	$T \to \infty$	$H \to 0$	$a \to 0$
	$T \to 0$	$H \to \infty$	$a \to \infty$

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Figure 1: The magnetization as a function of the magnetic field at fixed temperatures. Fields are applied along the horizontal (a) and normal (b) directions.

Figure 2: The magnetization as a function of the temperature at fixed magnetic fields. Fields are applied along the horizontal (a) and normal (b) directions.

Figure 3: The susceptibility as a function of the magnetic field at fixed temperatures. Fields are applied along the horizontal (a) and normal (b) directions.

Figure 4: The susceptibility as a function of the temperature at fixed magnetic fields. Fields are applied along the horizontal (a) and normal (b) directions.

Figure 5: The entropy as a function of the magnetic field at fixed temperatures. Fields are applied along the horizontal (a) and normal (b) directions.

Figure 6: The entropy as a function of the temperature at fixed magnetic fields. Fields are applied along the horizontal (a) and normal (b) directions.

Figure 7: The specific heat as a function of the magnetic field at fixed temperatures. Fields are applied along the horizontal (a) and normal (b) directions.

Figure 8: The specific heat as a function of the temperature at fixed magnetic fields. Fields are applied along the horizontal (a) and normal (b) directions.

Figure 9: The order parameter as a function of the magnetic field at fixed temperatures. Fields are applied along the horizontal (a) and normal (b) directions.

Figure 10: The order parameter as a function of the temperature at fixed magnetic fields. Fields are applied along the horizontal (a) and normal (b) directions.

Figure 11: The phase diagram of semiclassical dipoles (spin S=5/2) on a honeycomb lattice. Fields are applied along the horizontal and normal directions.

Figure 12: The phase diagram of classical dipoles on a planar honeycomb lattice. Field is applied along the horizontal direction. The "high-field" branch of the critical curve predicted in the work [3] is not confirmed by our calculations.

Figure 13: The entropy of a Planar Rotator, Space Rotator and Spin S=5/2 models as a function of the temperature at zero magnetic field.

Figure 14: The phase diagram of dipole system on a honeycomb lattice for the Planar Rotator, Space Rotator and Spin S=5/2 models. Field is applied in the horizontal direction.

Figure 15: The experimental phase transition curves for the stage 6 of the $FeCl_3$-grpahite intercalated compounds for the lowest temperature phase transition [7]. Field is applied along the c axis (normal direction) or along the plane (in-plane direction). $\mu_{eff} = 5.5\mu_B$, $J^{dip} = 7017\ 10^{-20}$ erg.