Ordering of dipolar Ising crystals

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We study Ising systems of spins with dipolar interactions. We find a simple approximate relation for the interaction energy between pairs of parallel lattice columns of spins running along the Ising spin direction. This relation provides insight into the relation between lattice geometry and the nature of the ordered state. It can be used to calculate ground state energies. We have also obtained ground state energies and ordering temperatures \( T_0 \) from Monte Carlo simulations. Simple empirical relations, that give \( T_0 \) for simple and body centered tetragonal lattices in terms of lattice parameters are also established. Finally, the nature of the ordered state and \( T_0 \) are determined for Fe\(_8\) clusters, which crystallize on a triclinic lattice.

70.10.Hk, 64.60.Cn

Dipolar interactions can lead to order at low temperature in magnetic \([1]\) as well as in ferroelectric systems \([2,3]\). Interacting dipolar Ising systems (DIS) have recently become the subject of special interest because spin quantum tunneling has been observed in them \([4,5]\). It can take place at temperatures that are well below their ordering temperature \( T_0 \) (see below). The type of order that ensues and \( T_0 \) are not trivially determined owing to the long range nature of dipolar interactions and to their sign changes. Luttinger and Tisza were able to show long ago that the type of ordering depends on the geometry of the lattice \([6]\). The theory was later generalized by Niemeijer and Blötte \([7]\). It enables one to determine, through laborious calculations, the ground state energies and types of
order for simple Bravais lattices with up to two identical magnetic dipoles per unit cell. Ordering temperatures are known from Monte Carlo (MC) simulations for simple cubic lattices [8]. Unfortunately, symmetry forbids the existence of cubic dipolar Ising systems in nature. There are however magnetic systems, such as the so called single-molecule magnets [12] as well as some rare earth sulfides [9], which (1) crystallize in other lattice structures and have sizable single-axis anisotropies, and (2) the organic material around these clusters precludes all magnetic interactions except for the magnetic dipolar one. Consequently, they are expected to behave as DIS, and they indeed seem to do so [9–11]. Magnetic relaxation of some of these single-molecule magnet crystals (Mn$_{12}$ and Fe$_8$) have recently been simulated in connection with spin quantum tunneling experiments [11], but their thermal equilibrium properties have not, as far as we know, been studied.

The aim of this report is twofold. First, we wish to point out that there is a simple approximate relation for the interaction energy between pairs of parallel lattice columns of spins running along the Ising spin direction, and that the nature of the ordered state follows from this relation. Second, we report Monte Carlo results for the ordering temperatures of DIS on cubic lattices, simple and body centered tetragonal lattices (that include Mn$_{12}$ cluster crystals [12]), as well as on the lattice (triclinic) on which Fe$_8$ crystallizes [13].

We treat here systems of spins, on lattices to be specified below, that are restricted to point along the $z$-axis, and interact among themselves only through magnetic dipole interactions. More specifically, let $S_i = \pm S$ be a spin on the $i$-th site of a simple cubic or tetragonal lattice, with Hamiltonian

$$\mathcal{H} = -\frac{v_0}{2} \sum_{ij} V_{ij} s_i s_j, \quad (1)$$

where $s_i = S_i/S$, $V_{ij} = (a_z/r_{ij})^3(1 - 3z_{ij}^2/r_{ij}^2)$, $a_z$ is the nearest neighbor distance along the $z$-axis, $r_{ij}$ is the distance between sites $i$ and $j$,

$$v_0 = \frac{\mu_0}{4\pi}(g\mu_B S)^2/a_z^3, \quad (2)$$

g is the gyromagnetic ratio, $\mu_B$ is the Bohr magneton, and $\mu_0 = 4\pi \times 10^{-7}$ in SI units.
From here on, unless explicitly specified to be in Kelvin, energies and temperatures are given in terms of $v_0$. It may be helpful to keep in mind that, $(\mu_0/4\pi)\mu_B^2/(1\text{Å})^3 \simeq 0.622\text{K}$.

We have used the standard Metropolis algorithm in our Monte Carlo simulations [14]. We have mostly used periodic boundary conditions (PBC). For PBC, a spin at site $i$ is allowed to interact only with spins that lie within a system sized box centered on site $i$. We have also simulated some systems with free boundaries, some shaped like a box, and some bounded by spherical surfaces. With free boundaries, all spins in the system are allowed to interact. The results obtained are in agreement with the expected behavior that follows from Griffith's theorem: that the thermodynamic limit is independent of boundary conditions and of system shape if no external field is applied [13].

We next find the field $B_\lambda$ that an infinitely long column of spins pointing up, as in Fig. 1, produces a distance $a_x$ away from it. First note that, as can be easily checked, $B_\lambda$ would vanish if the moment density were uniformly distributed rather than on a lattice. An exact expression, as an expansion in powers of modified Bessel functions, can be obtained for $B_\lambda$ by writing the magnetic dipole linear density along a column as a Fourier series with period and phase that depend on $a_z$ and $d_z$, respectively (see Fig. 1). The zeroth order term (which corresponds to a constant magnetic dipole density) does not contribute. The leading term is of the form $(a_x/a_z)^{-1/2}\exp(-2\pi a_x/a_z)\cos(2\pi d_z/a_z)$. We have checked numerically that

$$B_\lambda \simeq -\left(\frac{0.1357}{\sqrt{a_x/a_z}}B_0\right)\exp[2\pi(1-a_x/a_z)]\cos(2\pi d_z/a_z),$$

(3)

where

$$B_0 \equiv \frac{\mu_B}{4\pi} \frac{g\mu BS}{a_z^3},$$

(4)

is within 1% of exactness for $a_x/a_z > 0.8$. (Deviations from exactness increase as $a_x/a_z$ decreases, up to 11% for $a_x/a_z = 0.5$.) A $B_\lambda < 0$ value means that a column of spins up produces a field that points down.

On the other hand, the field $B_s$ of an infinite column of spins, all pointing up, at one of its own sites is easily found to be $B_s = 4.808...B_0$. This is much larger than $B_\lambda$ for
any reasonable distance between columns, and gives therefore rise to ferromagnetic order within each column of spins. As shown below, this picture holds for tetragonal lattices for 

\[ \frac{a_x}{a_z} \gtrsim 0.6, \]

but may break down for smaller values of \( \frac{a_x}{a_z} \).

One therefore expects the ordered state on simple cubic and primitive tetragonal lattices, for which \( d_z = 0 \) in Eq. (3), to be a two-dimensional anti-ferromagnetic array of ferromagnetically ordered columns spins as shown in Fig. 1b. On the other hand body-centered cubic and tetragonal lattices, in which \( d_z = a_z/2 \) for nearest neighbor columns, are expected to order ferromagnetically. This is as originally predicted by Luttinger and Tisza [6].

Making use of Eq. (3) and the value of \( B_s \), the ground state energy \( \varepsilon_0 = -(1/2)(g\mu_B S)(B_\lambda + B_s) \) can be easily calculated for a simple cubic or tetragonal lattice. It is,

\[ \varepsilon_0 \simeq -2.404v_0 - 1.8 g\mu_B S B_\lambda. \] (5)

This result is shown in Fig. 2, with data points obtained from Monte Carlo simulations, as a function of the basal plane lattice constant \( a_x \). For ferromagnets the calculation of \( \varepsilon_0 \) is somewhat more involved and is not attempted here. This is because for lines of finite length \( L_z \), equation (3) is applicable only if \( \ln(L_z/a_z) \gg a_x/a_z \). For \( \ln(L_z/a_z) \lesssim a_x/a_z \), \( B_\lambda < 0 \), independently of \( d_z \), which gives rise to magnetic domains in ferromagnets. Equation (3) can be used to obtain the “wall energy” that counterbalances “magnetostatic” energies in domain size and ground state energy calculations [16].

Data points obtained from MC simulations for the ordering temperature of DIS on primitive tetragonal lattices are also shown in Fig. 2a. The equation

\[ T_0 \simeq 2.5 v_0(a_z/a_x)^{1.7} \] (6)

provides the fit shown in Fig. 2a.

For body centered tetragonal lattices, ferromagnetic order ensues, as expected from the fact that \( d_z = a_z/2 \) then. The ground state energy is not simply obtained then, since there are long range contributions. Data points exhibited in Fig. 2b, show that the ordering
temperature follows a slightly different rule from Eq. (3). As shown in the table, the best fit to $T_0$ is then $T_0 \simeq 5.8 v_0(a_z/a_x)^{2.0}$.

Thermal equilibrium results obtained by MC simulations of DIS on simple cubic lattices of (1) up to $16 \times 16 \times 16$ spins with PBC and (2) 2109 and 4169 spins on spherical systems with free boundary conditions are shown in Figs. 3a, 3b, and 3c. These results, together with results (not shown) for smaller systems, as well as for box shaped systems with free boundary conditions of different sizes, lead to ordering temperatures and ground state energies that are, within statistical errors, independent of shape and boundary conditions. Similar results have been obtained for simple and body centered tetragonal lattices, from which the data points for $T_0$ shown in Figs. 2a and 2b, respectively, were obtained.

Triclinic crystals of Fe$_8$ clusters provide an interesting example [13]. Their lattice geometry is exhibited in Fig. 4. Note that lattice sites on columns marked with a diamond, circle, square, etc. are displaced along the $z$-axis a distance $d_z \approx a_z/4$ with respect to sites on columns marked with a circle, square, triangle, etc., respectively. Thus, while all columns on the same row on the right hand side of Fig. 4 interact antiferromagnetically, two columns on adjacent rows do not interact, and two rows on alternate rows (e.g., on rows marked with circles and triangles) interact ferromagnetically. This implies that any given row of columns in Fig. 4 orders antiferromagnetically, but there is near degeneracy (if only nearest nearest neighbor interactions are taken into account) as to how adjacent rows order with respect to each other. How rows order with respect to each other is quite likely determined by longer range interactions, but this question is beyond the scope of this report. To find out how the system actually orders, we turn to MC simulations. The ordered state is depicted in Fig. 4 as follows: ♦, •, ■, ▲, and ▼ stand for columns with spin up, while ◊, ◐, ◆, ◆, and ◆ stand for columns with spins down. This system orders at a temperature given in table I.

It is worth remarking that Eq. (3) is expected to be applicable whether dipoles are point like or extended, or whether they are magnetic or electric, except that the constant $0.1357B_0$ is different in each case. It’s validity only requires that the wave number of the leading fourier component of the dipolar density along the relevant columns be equal to
the smallest reciprocal lattice vector for the columns. Furthermore, Eq. (3) is applicable to other crystal structures, such as hexagonal, not explicitly treated here. It follows, for instance, that DIS, whether magnetic or electric, order antiferromagnetically in a primitive hexagonal structure, but order ferromagnetically in a hexagonal closed packed structure.

In summary, we have shown that Eqs. (3) and (4) provide simple approximate relations for the interaction energy between pairs of parallel lattice columns of spins running along the Ising spin direction, and that the nature of the ordered state follows from this relation. From this simple relation, we have obtained ground state energies. We have also obtained ground state energies and ordering temperatures from Monte Carlo simulations. A simple empirical relation, Eq. (6) gives results for the ordering temperatures of DIS on simple and body centered tetragonal lattices. These results, as well as results for Fe₈ clusters that crystallize on a triclinic lattice, are summarized on table I. (Substituting \( g \approx 2.0 \), \( S = 10 \), and lattice constants (see Fig. 3) of Fe₈ cluster crystals, gives \( T_0 \approx 170 \text{ mK} \). Similarly, \( T_0 \approx 430 \text{ mK} \) is obtained for Mn₁₂ acetate, which crystallizes in a primitive tetragonal lattice with \( a_z = 12.39 \text{Å} \) and \( a_x = 17.32 \text{Å} \).)

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TABLE I. Type of ordered state, ordering temperature $T_0$, and ground state energy $\varepsilon_0$, for dipolar Ising systems on various lattices. All energies and temperatures are given in terms of $v_0$, where $v_0 = (\mu_0/4\pi)(g\mu_B S)^2/a_x^2$, and $(\mu_0/4\pi)\mu_B^2/(1\text{Å})^3 \simeq 0.622\text{K}.$

| LATTICE            | ORDER | $T_0$  | $\varepsilon_0$ | validity         |
|--------------------|-------|--------|-----------------|------------------|
| sc$^{1,2}$         | AF$^3$| 2.50(5)| -2.68(1)        |                  |
| BCC$^1$            | F     | 5.8(2) | -4.0(1)         |                  |
| FCC$^1$            | F     | 11.3(3)| -7.5(1)         |                  |
| Primitive tetragonal | AF$^3$ | $2.5(a_z/a_x)^{1.7}$ | Eqs. (3-5) | $a_x/a_z \gtrsim 0.6$ |
| BC tetragonal$^5$  | F     | $5.8(a_z/a_x)^{2.0}$ | Fig. 2b  | $a_x/a_z \gtrsim 0.6$ |
| Fe$_8$ (triclinic) | AF$^4$| 1.9(1) | -2.73(3)        |                  |

1. Type of order and $\varepsilon_0$ (but not $T_0$) first given in Ref. $^3$.
2. $T_0$, from MC simulations, given in Ref. $^8$.
3. AF order depicted in Fig. 1.
4. AF order depicted in Fig. 4.
5. $T_0$, from MC simulations, given in Ref. $^{17}$ for $a_x/a_z = 0.5$. 


FIG. 1. (a) Parallel lines of spins, showing distances $a_z$, $a_x$, and $d_z$. (b) Antiferromagnetic order in simple cubic lattice.
FIG. 2. (a) Semilog plot of the thermal equilibrium ordering temperature $T_0$ and of the ground state energy $\varepsilon_0$ versus $a_x/a_z$ of the magnetic dipole model on a tetragonal lattice, where $a_x$ and $a_z$ are the nearest neighbor distances along the basal plane and $c$-axis respectively. ○ and • stand for temperature and energy, respectively. The continuous line for energy follows from Eq. (5). The straight line through the temperature data points is a fit; the equation for it is (6). The results for $a_x/a_z = 1.4$ are obtained from columns of $32 \times 32$ spins on the basal plane by 128 spins along the $c$-axis; the result for $a_x/a_y = 1.5$ is from a column of $8 \times 8 \times 512$ spins. All values of $\varepsilon$ and $T$ are given in terms of $v_0$, defined in Eq. (2). (b) Same as in part “a” but for a dipole model on a BC tetragonal lattice. The straight line through the temperature data points is a fit; the equation for it is $5.8(a_z/a_x)^{2.0}$. 
FIG. 3. (a) The thermal equilibrium staggered magnetization $m_s$ versus temperature. ○ and • stand for systems of $8 \times 8 \times 16$ and $16 \times 16 \times 16$ spins, respectively, on a SC lattice with PBC. ◊ and ■ stands for spherically shaped systems of 2109 and 4169 spins, respectively, with free end boundary conditions. (b) Same as in part “a” but for the staggered susceptibility $\chi_s$. (c) Same as in parts “a” and “b”, but for the specific heat.
FIG. 4. Lattice constants of Fe₈ cluster crystals are shown on the left hand side. The lattice parameters are taken from Ref. [13]. On the right hand side, the lattice as seen looking down the \( b \)-axis. Anisotropy constrains all spins to be either up or down along the \( b \)-axis for \( T < 1 \)K in this system. The \( b \)-axis is therefore our \( z \)-axis.