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, which 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.

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 as well as some rare-earth organic compounds,[9] that crystallize in other lattice structures and have sizable single-axis anisotropies, which leads to Ising-like behavior. In addition, magnetic dipolar interactions dominate all others. These systems behave as DIS.[9–11] Magnetic relaxation of some of these single-molecule magnet crystals (such as 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. (Single-molecule magnets, such as Mn_{12} and Fe_8 clusters, relax to equilibrium extremely slowly via quantum tunneling at very low temperatures. Even then, their equilibrium behavior can perhaps be studied experimentally, because the relaxation rate can be controlled by means of an applied transverse field.[12])

The aim of this paper 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 (which include Mn_{12} cluster crystals[13]), as well as on the lattice (triclinic) on which Fe_8 crystallizes.[14]

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 ith site of a simple cubic or tetragonal lattice, with Hamiltonian

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

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,

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

g is the gyromagnetic ratio, μ_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 $(\mu_0/4\pi)\mu_B^2/(1\ \text{Å})^3 \simeq 0.622$ K.

We have used the standard Metropolis algorithm in our Monte Carlo simulations.[15] 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 Griffiths's theorem: that the thermodynamic limit is independent of boundary conditions and of system shape if no external field is applied.[16]

We next find the field B_λ 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 easy checked, B_λ would
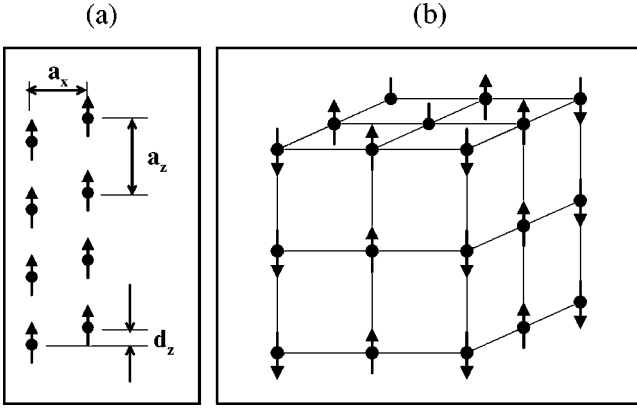
FIG. 1. (a) Parallel lines of spins, showing distances a_z, a_x, and d_z. (b) Antiferromagnetic order in simple cubic lattice.

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_λ 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
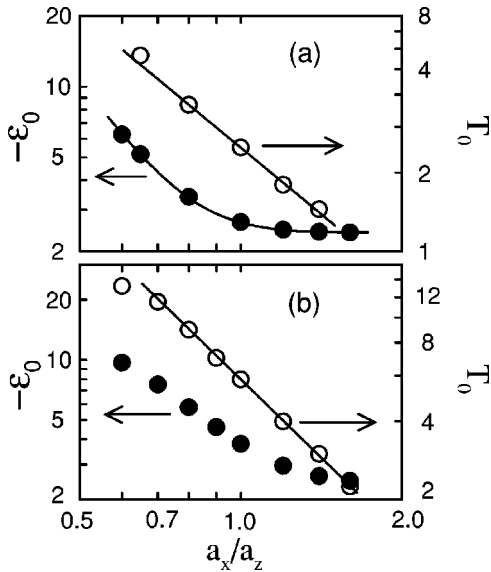

FIG. 2. (a) Semilogarithmic plot of the thermal equilibrium ordering temperature T_0 and of the ground-state energy ε_0 versus a_x/a_z of the magnetic dipole model on a tetragonal lattice, where a_x and a_z are the nearest-neighbor distances along the basal plane and c axis, respectively. ○ and ● stand 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 Eq. (6). The results for $a_x/a_z = 1.4$ are obtained from columns of 32×32 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 ε 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 $5.8(a_z/a_x)^{2.0}$.
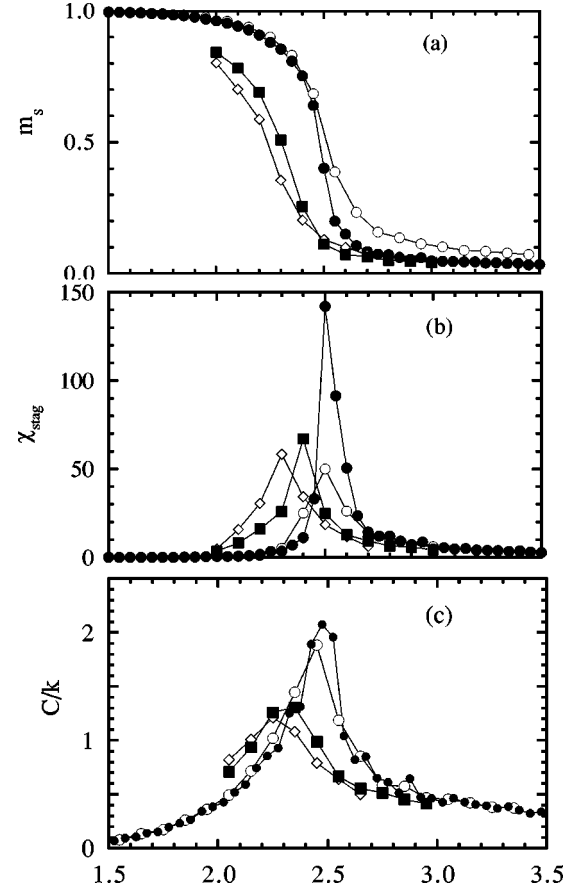

FIG. 3. (a) The thermal equilibrium staggered magnetization m_s versus temperature. ○ and ● stand for systems of $8 \times 8 \times 16$ and $16 \times 16 \times 16$ spins, respectively, on a SC lattice with PBC. ◇ and ■ stand for spherically shaped systems of 2109 and 4169 spins, respectively, with free end boundary conditions. (b) Same as in part (a) but for the staggered susceptibility χ_s. (c) Same as in parts (a) and (b), but for the specific heat.

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

$$(3)$$

where

$$B_0 \equiv \frac{\mu_0}{4\pi}\frac{g\mu_B S}{a_z^3},$$

$$(4)$$

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 $B_s = 4.808 \ldots B_0$. This is much larger than B_λ for any reasonable distance between columns, and, therefore, gives rise to ferromagnetic order within each column of spins. As shown below, this picture holds for tetragonal lattices for $a_x/a_z \gtrsim 0.6$, but may break down for smaller values of 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 *antiferromagnetic* array of ferro-

magnetically ordered column spins as shown in Fig. 1(b). 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

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

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 ε_0 is somewhat more involved and is not attempted here. This is because for lines of *finite* length L_z, Eq. (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.[17]

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

$$T_0 \simeq 2.5 v_0 (a_z/a_x)^{1.7} \qquad (6)$$

provides the fit shown in Fig. 2(a).

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. 2(b), show that the ordering temperature follows a slightly different rule from Eq. (6). 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. 3(a), 3(b), and 3(c). 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. Simi-
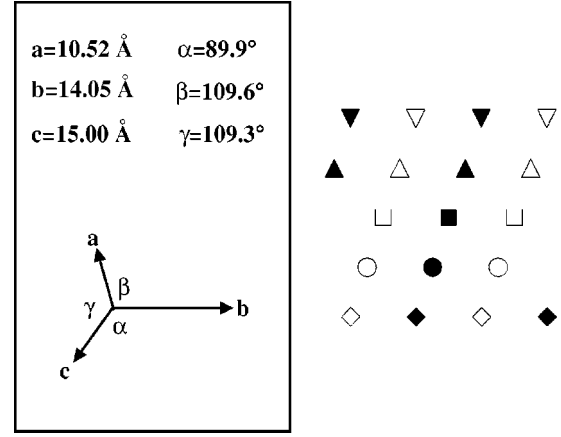

FIG. 4. Lattice constants of Fe_8 cluster crystals are shown on the left-hand side. The lattice parameters are taken from Ref. 14. On the right-hand side, the lattice as seen looking down the b axis. Anisotropy constrains all spins to be either up or down along the b axis for $T < 1$ K in this system. The b axis is therefore our z axis.

lar results have been obtained for simple and body-centered tetragonal lattices, from which the data points for T_0 shown in Figs. 2(a) and 2(b), respectively, were obtained.

Triclinic crystals of Fe_8 clusters provide an interesting example.[14] 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 next-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 paper. 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

TABLE I. Type of ordered state, ordering temperature T_0, and ground-state energy ε_0 for dipolar Ising systems on various lattices. All energies and temperatures are given in terms of v_0, where $v_0 = (\mu_0/4\pi)(g\mu_B S)^2/a_z^3$, and $(\mu_0/4\pi)\mu_B^2/(1\ \text{Å})^3 \simeq 0.622$ K.

Lattice	Order	T_0	ε_0	Validity
sc [a,b]	AF [c]	2.50(5)	-2.68(1)	
bcc [a]	F	5.8(2)	-4.0(1)	
fcc [a]	F	11.3(3)	-7.5(1)	
Primitive tetragonal	AF [c]	$2.5(a_z/a_x)^{1.7}$	Eqs. (3)–(5)	$a_x/a_z \gtrsim 0.6$
BC tetragonal [d]	F	$5.8(a_z/a_x)^{2.0}$	Fig. 2(b)	$a_x/a_z \gtrsim 0.6$
Fe_8 (triclinic)	AF [e]	1.9(1)	-2.73(3)	

[a]Type of order and ε_0 (but not T_0) first given in Ref. 6.
[b]T_0, from MC simulations, given in Ref. 8.
[c]AF order depicted in Fig. 1.
[d]T_0, from MC simulations, given in Ref. 18 for $a_x/a_z = 0.5$.
[e]AF order depicted in Fig. 4.

for columns with spin up, while $\diamond$, $\bigcirc$, $\square$, $\triangle$, 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 pointlike or extended, or whether they are magnetic or electric, except that the constant $0.1357B_0$ is different in each case. Its 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 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 (5) 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 Fe_8 clusters that crystallize on a triclinic lattice, are summarized in Table I. [Substituting $g \simeq 2.0$, $S=10$, and lattice constants (see Fig. 4) of Fe_8 cluster crystals, gives $T_0 \simeq 170$ mK. Similarly, $T_0 \simeq 430$ mK is obtained for Mn_{12} acetate, which crystallizes in a primitive tetragonal lattice with $a_z = 12.39$ Å and $a_x = 17.32$ Å.[13]]

[1] M. Goldman, Phys. Rep., Phys. Lett. **1**, 32 (1971); D. H. Reich, B. Ellman, J. Yang, T. F. Rosenbaum, G. Aeppli, and D. P. Belanger, Phys. Rev. B **42**, 4631 (1990).

[2] W. Luo, S. R. Nagel, T. F. Rosenbaum, and R. Rosensweig, Phys. Rev. Lett. **67**, 2721 (1991).

[3] B. E. Vugmeister and M. D. Glinchuck, Rev. Mod. Phys. **62**, 993 (1990).

[4] For a brief review of spin tunneling through thermally excited states in crystals of Mn_{12} clusters, see, for instance, B. Schwarzschild, Phys. Today **50** (1), 17 (1997).

[5] For reports of tunneling that is independent of temperature in crystals of Fe_8 clusters, see C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gateschi, Phys. Rev. Lett. **78**, 4645 (1997).

[6] J. Luttinger and L. Tisza, Phys. Rev. **72**, 257 (1947).

[7] Th. Niemeijer and H. W. J. Blötte, Physica (Amsterdam) **67**, 125 (1973).

[8] R. Kretschmer and K. Binder, Z. Phys. B **34**, 375 (1979).

[9] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (2000); A. H. Cooke *et al.*, Proc. R. Soc. London, Ser. A **306**, 335 (1968).

[10] G. H. Bellesis, S. Simizu, and S. A. Friedberg, Physica B **165&166**, 221 (1990).

[11] T. Ohm, C. Sangregorio, and C. Paulsen, Eur. Phys. J. B **6**, 195 (1998); A. Cuccoli, A. Rettori, E. Adam, and J. Villain, Eur. Phys. J. B **12**, 39 (1999).

[12] F. Luis (unpublished).

[13] T. Lis, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **36**, 2042 (1980); A. L. Barra, P. Debrunner, D. Getteschi, Ch. E. Schulz, and R. Sessoli, Europhys. Lett. **35**, 133 (1996).

[14] K. Wieghardt, K. Pohl, J. Jibril, and G. Huttner, Angew. Chem. Int. Ed. Engl. **23**, 77 (1984): A. L. Barra, D. Gatteschi, and R. Sessoli, Phys. Rev. B **56**, 8192 (1997); S. Hill, J. A. A. J. Perenboom, N. S. Dalal, T. Hathaway, T. Stalcup, and J. S. Brooks, Phys. Rev. Lett. **80**, 2453 (1998).

[15] See, for instance, N. A. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953); *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer, New York, 1979).

[16] R. B. Griffiths, Phys. Rev. **176**, 655 (1968).

[17] C. Kittel, Rev. Mod. Phys. **21**, 541 (1949).

[18] H. Xu, B. Bergersen, and Z. Rácz, J. Phys.: Condens. Matter **4**, 2035 (1992).