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Heisenberg model of subdomain fcc clusters: A Monte Carlo study

J. P. Bucher and L. A. Bloomfield
Department of Physics, University of Virginia, Charlottesville, Virginia 22901
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We show that a Heisenberg model of a spin cluster can describe subdomain ferromagnetic particles, from the dynamics of individual spins to the statistical behavior of the total magnetic moment of the cluster. While an analytical solution of the quantum spin problem is given for small clusters, a classical Heisenberg numerical simulation is used to study clusters of up to 561 atoms. We have studied magnetic behavior as a function of particle size, temperature, and magnetic field and find that the magnetization of individual clusters is well described by a Langevin function, in very good agreement with recent experiments on Co clusters in a molecular beam.

It has been observed recently[1] that the behavior of free cobalt clusters containing up to 400 atoms is well described by a picture in which the cluster is considered as a monodomain particle with a giant magnetic moment that fluctuates in direction under thermal agitation.[2] The time-averaged projection of the magnetic moment, measured by the deflection of the cluster beam upon its passage through a gradient magnet, agrees quantitatively with a Langevin function of argument $N\mu H/kT$ where N is the number of atoms in the cluster, μ is the magnetic moment per atom of the monodomain particle, H is the magnetic field, and T the temperature. These observations hint strongly at the superparamagnetic nature[3] of these clusters. The experimental time scale over which the phenomenon of superparamagnetism can be observed is proportional to $\exp(KN/kT)$, where K is the crystal-field anisotropy energy per atom. For particles in a solid-state matrix or in a solution, a wide variety of experimental techniques ranging from Mössbauer spectroscopy to superconducting quantum interference device (SQUID) magnetometry[4,5] can be used to test the mechanism of superparamagnetic relaxation from the ns to the 10 s time scale.

In an attempt to explain early deflection data on Fe clusters,[6] a Monte Carlo Ising model has been proposed recently.[7] The reduction in the measured magnetic moment is attributed to an intraparticle temperature-induced spin disorder. Although the model describes qualitatively part of the experimental data, the high temperatures, necessary to account for the magnitude of the observed magnetic moments are hard to reconcile with real life experimental conditions. In this work, we show that the statistical approach is thoroughly able to explain the experimental results without invoking spin melting. We use a Heisenberg picture in which the spins are located on a fcc lattice because it is conceptually simple, can be solved numerically for reasonably big lattices, and does not possess the artificial monodirectional anisotropy of the Ising model.

The Heisenberg model has contributed in many ways to the understanding of the cooperative effects leading to ferromagnetism and the major consequences of the model have been worked out quite some time ago.[8] Monte Carlo calculations of classical Heisenberg models have also improved our understanding of critical behavior and scaling.[9] While finite systems have been widely used to simulate bulk systems, finite systems have also been studied on their own right. The theory of the Heisenberg superparamagnet is well established.[10] However, since no general analytical solution can be given, numerical techniques have been used to study the impact of the cluster shape on magnetization,[11] as well as the magnetization profiles across the clusters,[12] for simple lattices. Lately, it was shown that sharper transitions are obtained by including magnetic interactions in Monte Carlo simulations of the melting process of ferromagnetic transition metal clusters.[13]

In our analysis, magnetic anisotropies and magnetostatic interactions are neglected. This assumption is justified for a wide range of sizes and temperatures for the ferromagnetic clusters of $3d$ transition metals.[10] We consider the following Hamiltonian:

$$\mathcal{H} = -J\sum_{i>j}\mathbf{S}_i\cdot\mathbf{S}_j - h\sum_i S_i^z . \tag{1}$$

The first summation is over all nearest-neighbor pairs of the cluster while the second summation is over all atoms. The isotropic Heisenberg model considers an effective coupling J between spins which in a molecular-field theory is estimated to be a fraction of the bulk Curie temperature kT_c^{bulk}. The second term is the Zeeman term where S_i^z is the component of spin. Expression (1) is quite general and can be particularized to either the classical (S tending to infinity) or the quantum case. The first step consists in evaluating the partition function: $Z=\mathrm{Tr}e^{-\mathcal{H}/kT}$. Once Z is known, thermodynamic values like the magnetization or specific heat can be calculated by the usual rules of statistical mechanics. In general, the solution of the Hamiltonian for the energy levels must be found numerically. However, since the purpose of this work is to acquire a better insight into the physics of small spin systems, it is quite instructive to start with some basic considerations valid for small systems, in which case the Heisenberg Hamiltonian can be solved analytically for quantum spins.

We can take advantage of the fact that the square of the total spin operator $(S')^2$ of the cluster is given by

$$\left(\sum_i \mathbf{S}_i\right)^2 = \sum_i \mathbf{S}_i^2 + \sum_{i\neq j}\mathbf{S}_i\cdot\mathbf{S}_j = S'(S'+1) . \tag{2}$$

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This provides an easy solution to our Hamiltonian in the case each atom is coupled to every other atom in the cluster. Practically this assumption is only valid for relatively small clusters, smaller than $N=5$ or so. Then, the eigenvalues of $\mathcal{H}$ can be found easily,

$$E(S,S',M')=\tfrac{1}{2}J[NS(S+1)-S'(S'+1)]+hM', \quad (3)$$

where $h=g\mu_B H$, and the z component of the total angular momentum M' has eigenvalues $M'=S',S'-1,\ldots,-(S'-1),-S'$, where $S'=0,1,2,3,\ldots,NS$ for NS integral, and $S'=\frac{1}{2},\frac{3}{2},\frac{5}{2},\ldots,NS$ for NS half-integral. The partition function for the cluster is

$$Z=\sum_{S'}\sum_{M'}\lambda(N,S,S')e^{J\beta S'(S'+1)/2}e^{h\beta M'}, \quad (4)$$

$\beta^{-1}=kT$. We have dropped the terms which depend only on S and are the same for all states since they are of no interest for our problems in magnetism. $\lambda(N,S,S')$ is the number of ways to combine N spin S to obtain a total spin S'. λ can be found in Ref. 8 for any S. Then

$$Z(J,h)=\sum_{S'}\lambda e^{J\beta S'(S'+1)/2}\frac{\sinh[(S'+\frac{1}{2})h\beta]}{\sinh(h\beta/2)}$$
$$=\sum_{S'}P(J,h,S'). \quad (5)$$

By the rules of statistical mechanics, the magnetization is given by $M=\beta^{-1}\partial(\ln Z)/\partial H$; $T=$const. With the use of Eq. (5), the magnetization is found to be

$$M=g\mu_B\frac{\sum_{S'}P(J,h,S')S'B_{S'}(h\beta S')}{\sum_{S'}P(J,h,S')}, \quad (6)$$

where $B_{S'}$ is the Brillouin function.

The quantum-mechanical expression of Eq. (6) is valid for any value of spin S. For bigger clusters, however, individual atoms may no longer be nearest neighbors of each other, Eq. (2) cannot be used anymore, and the geometry of the cluster must be considered explicitly (see the following discussion). However, the general form $M=\sum g(y)f(y)/\sum g(y)$ of Eq. (6) is still conserved.[10] It can be seen that for $S'\to\infty$ (that is, when all orientations of the magnetic moment becomes possible), the phenomenon of superparamagnetism appears as a weighted average of Langevin $L(h\beta S')$ contributions of spin S' with

$$L(x)=\coth x-1/x. \quad (7)$$

An approximation originally used by Heisenberg (quoted by van Vleck[8]), consists of assuming that for big systems (large N), Z has a maximum at some particular value of S' denoted $\tilde{S}$; therefore, it is sufficient to retain only terms through the first order in the Taylor expansion about $\tilde{S}$, and we get $M=g\mu_B\tilde{S}L(h\beta\tilde{S})$.

The results of the quantum treatment for clusters with spin $\frac{1}{2}$ are shown in Fig. 1. The normalized magnetic moment per site, calculated from Eq. (6), is represented as a function of temperature for various sizes N. It is a steeply decreasing function of temperature. One finds that a temperature of 0.02 J (a few K from simple molecular-field considerations) is enough to account for a 50% reduction of the magnetization of a 4-atom cluster.

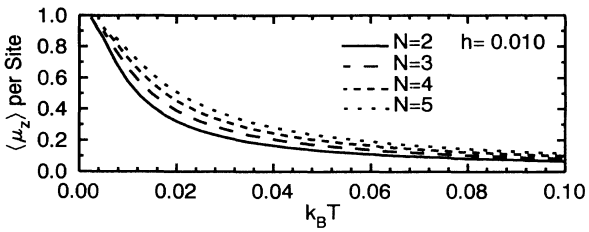

FIG. 1. Magnetic moment per site $\langle\mu_z\rangle$ as a function of temperature, calculated by means of Eq. (6) for small clusters of spin $\frac{1}{2}$. All energies are measured in units of J.

In order to study bigger systems, we use a numerical Monte Carlo technique to solve the classical Heisenberg model. Time averages for the magnitude of the total spin and its projection on the z axis as a function of lattice size, temperature, and applied field are calculated. The exchange interaction in Eq. (1) can be made $J=1$ without losing any generality, since this assignment merely establishes an energy scale. The lattices studied are complete fcc cubo-octahedra having the total numbers of sites $N=13$, 55, 147, 309, and 561 (more information on the geometry can be found in Ref. 14).

Once a random configuration of spin orientation has been generated, the Monte Carlo procedure can be summarized as follows: For a given temperature and a given field, each site is visited in order. A random spin orientation is picked from a 4π solid angle and it is decided whether the state with the old spin orientation of energy E_i will be changed to the state with the new spin orientation of energy E_f. If E_f is lower than E_i, the new state is accepted, otherwise it is accepted conditionally with the probability $e^{-\beta(E_f-E_i)}$. Relevant physical quantities, like the energy E, E^2, and the magnetization are averaged over 5×10^6 MCS (Monte Carlo steps) per site. The technique is well documented (see, for instance, Ref. 15).

Results for the Heisenberg Monte Carlo simulation are presented in Figs. 2–6, along with fits to a very simple theory. In Fig. 2 we see that the individual spins of the 55-site cubo-octahedral cluster are completely aligned at zero temperature, giving a total magnetic moment per site of 1. At higher temperature, the magnitude of the total magnetic moment decreases. The calculations could be fitted to critical parameters from second-order phase transition theory of finite systems: however, since our purpose here is not to study criticality but rather to describe statistical behavior at low temperatures, we find it more con-

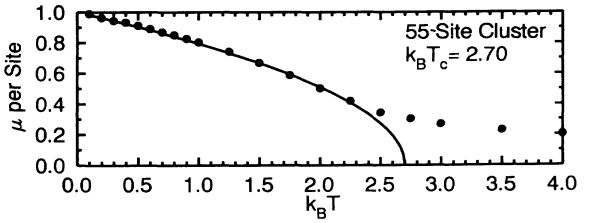

FIG. 2. Magnitude of the total spin per atom as a function of temperature for a 55-site cluster. The curve is the best fit to a power law. Energy in units of J.

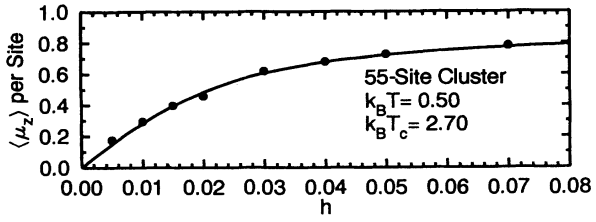

FIG. 3. Time-average projection $\langle \mu_z \rangle$ of the magnetic moment per site on the field axis for 55-site cluster at $T=0.50$ as a function of applied magnetic field. The curve is a parameterless fit by means of a Langevin function.

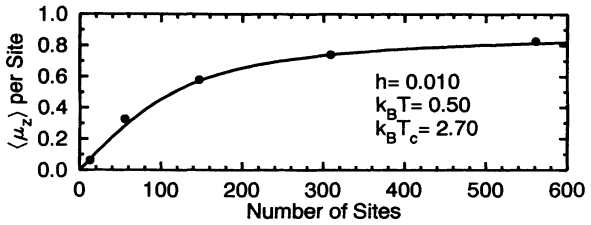

FIG. 5. Time-average projection of the magnetic moment per site on the field axis for particles of various sizes N at $T=0.50$ and $h=0.010$.

venient to fit the calculations to a power law:

$$\mu=(1-T/T_c)^{1/2}, \tag{8}$$

where μ is the average moment per site, and T_c is the critical temperature. The same power-law behavior and T_c are seen for all sized particles. It reflects the temperature-dependent disordering or "melting" of the system when the system goes from an ordered state at low temperature to a disordered state at high temperature. Since the spontaneous symmetry breaking at T_c can occur in the thermodynamic limit only ($N\rightarrow\infty$), the net alignment does not drop to zero at $T=T_c$, as can be seen from Fig. 2. Spin fluctuations lead to some small alignment even at high temperatures. At very low temperature, quantum-mechanical effects come normally into play. However, the standard Bloch $T^{3/2}$ law is only obeyed approximately in clusters and the gap in the spin-wave spectrum is expected to produce a very flat dependence of μ close to zero temperature.

Equation (8) establishes the magnitude of the total magnetic moment but not its orientation. Figure 3 shows the time-averaged projection of spin per site on the field axis for a 55-site cluster at $T=0.50$, as a function of applied magnetic field. The projection increases linearly with field until it saturates at the maximum value given by Eq. (8). Similarly, Fig. 4 shows the spin projection per site for 55-site clusters for a field $h=0.010$, at various temperatures. The projection is maximum at $T=0$ and decreases approximately as $1/T$, reflecting reductions in both the magnitude of the total moment and in the alignment of that total moment with the magnetic field. Figure 4 is the classical analog for $N=55$ of the quantum case ($N=2$–5) of Fig. 1. Finally, Fig. 5 shows the spin projection per site for particles of various sizes N at $T=0.50$ and $h=0.010$. The projection per site increases linearly with particle size before saturating at large sizes.

Despite its simplicity, this model explains quantitatively all the features observed in the cluster beam experiment,[1] namely, the linear variation of the observed magnetic moment as a function of cluster size and field as well as its variation as a function of the inverse of temperature. The overall behavior of the time-averaged projection of the magnetic moment on the field axis $\langle \mu_z \rangle/\mu$ is described accurately by the Langevin function of Eq. (7) with argument $x=\beta N\mu H$, where μ is given by Eq. (8), with $T_c=2.70$. Parameterless fits to the Monte Carlo results, produced with this formula, appear in Figs. 3–5. The fit is extremely good and gives confidence that Eqs. (7) and (8) accurately predict the time averages of the magnetic moment per site and of its projection on the field axis. At the temperatures under consideration here, there is little departure of μ from 1 [Eq. (8)], and the spins within the clusters remain strongly coupled, therefore, each individual cluster has a giant magnetic moment of the order $2N\mu_B$ as obtained from the theoretical ground-state calculations.[16,17] Assuming a magnetic moment μ per atom the same as in the bulk (say $1.7\mu_B$ for Co), a 147-atom cluster at 77 K (liquid-nitrogen temperature) in a typical laboratory field of 0.3 T, would show an observable magnetic moment $\langle \mu_z \rangle=0.212$, in very good agreement with the experiment on Co clusters.[1] Therefore, the cluster beam results do not need to be interpreted in terms of nearly critical high spin temperatures as deduced by Merikoski *et al.*[7] but are a consequence of the fact that clusters exhibit superparamagnetism in the beam. In particular, because of the rapid fluctuation of the total magnetic moment, the model accounts in a natural way for the zero magnetization observed in the absence of a magnetic field.

Due to its continuous spin space symmetry, the Heisenberg model is much more appropriate to describe large

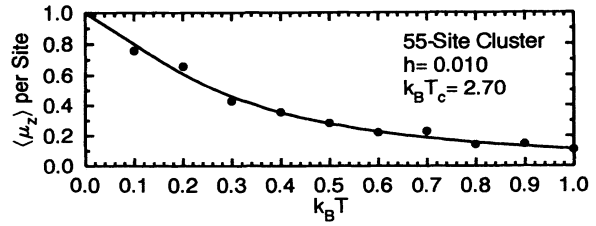

FIG. 4. Time-average projection of the magnetic moment per site on the field axis for a 55-site cluster as a function of temperature in a field of $h=0.010$.

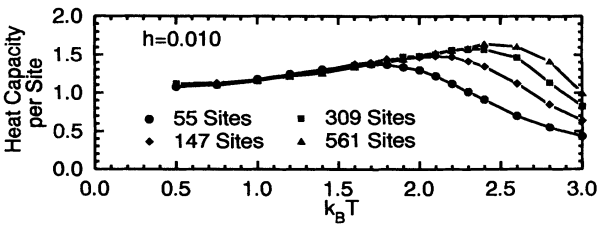

FIG. 6. Specific heat as a function of temperature in a field of $h=0.010$ for various cluster sizes. Energies in units of J.

fluctuations observed in small clusters than is the Ising model. The specific-heat expression $C=(\langle E^2\rangle-\langle E\rangle^2)/kT^2$, obtained from the sampling of E (the energy of the system in the magnetic field), provides a measure of fluctuations, represented by the term inside the parentheses.[15] The calculated specific heat is given in Fig. 6 as a function of temperature for various cluster sizes. The importance of fluctuations is obvious from the nonzero contributions at low and high temperature. Simultaneously, the specific heat shows a rounded peak typical of higher-order phase transitions.

The very good agreement between theory and experiment give strong evidence that the magnetic anisotropy energies are much smaller than the temperatures involved. The fact that in a beam, magnetic moments exchange angular momentum with the particle's lattice through crystal anisotropy coupling does not invalidate the simple picture presented here. At most, it can modify slightly the trajectory in the phase space, away from a purely fluctuating one (a purely coherent trajectory is expected for a strong coupling), but the Boltzman distribution would still be valid to describe the projection of magnetic moments onto the field axis on the time scale of the experiment.

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