Critical Point of Magnetic Nanostructures in the Ising Model

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The critical temperature \(T_c\) of magnetic nanostructures is calculated by the variational cumulant expansion in the Ising model. Structures of column, plate and cubic shapes are constructed for the study of shape effects. It is found that \(T_c\) increases with the decreasing surface to volume ratio. The dependence of \(T_c\) on the growth direction is also studied for various cubic lattices.

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I. Introduction

One interesting feature of nanostructures is the bond-length contraction with decreasing size due to the increased surface to volume ratio and charge redistribution [1]. Mössbauer studies of magnetic nanostructures indicate the reduction in the hyperfine magnetic field at the surface [2-4]. Recently, magnetic properties of nanostructures have attracted much attention. In particular, magnetic nano-elements were fabricated to study their domain structure [5-7]. Magnetization of magnetic nano-material was measured [8]. On the other hand, theoretical work on magnetic properties of such a finite system of materials is seldom to be found except for the domain structure [5-7]. The reason is simply that magnetic properties such as the magnetization, critical temperature, and so on, depend strongly on the size of nanostructures, which is not very easy to handle. The critical temperature of magnetic particles is undoubtedly an important property for study, and it is difficult to calculate the magnetization of nano-materials without the knowledge of the critical temperature.

A variational cumulant expansion (VCE) method has been developed [9] for the calculation of the critical point of magnetic films. The theory is in principle capable of dealing with a crystal of any lattice structure and of any geometric shape. We have applied the method [10] to study the critical point \(T_c\) for thin films of cubic lattices with sc, bcc and fcc structures as a function of the number of monolayers \(L\) grown along various directions such as \(<110>, <111>\) and \(<100>\). It is found that \(T_c\) is higher for planes containing more nearest neighbors in the film, provided that the crystal film contains the same number of monolayers but is grown in different directions. Thus, the highest \(T_c\) is found along the \(<100>, <110>\) and \(<111>\) directions in the sc, bcc
fcc structures, respectively. The common feature is that the most populated plane corresponds to the most favorable growth direction and has the highest $T_c$ value. Needless to say, the film tends to a bulk in any case as $L$ approaches infinity.

In this paper, we calculate on the Ising model the critical temperature $T_c$ of nano-particles with cubic lattices. It has been pointed out [6, 7] that magnetic particles smaller than 200 nm remain nearly in a single domain state. Since particles smaller than this size are often made in experiments [2, 3, 8], we consider, for simplicity, only particles with no domain structure. However, the particle should not be too small, because the transition temperature of a finite system smears out, implying that there exists a temperature range $\xi T$, within which the phase transition occurs. $\xi T$ depends on the size of the sample because in this case the correlation length is comparable or exceeds the linear size of the sample. In the case of 3D Ising model, we have $\xi T \approx \frac{1}{0.6 N^{\frac{1}{2}}}$, where $N$ is the number of spins in a nano-particle. If $N$ is too small, $\xi T$ will be so large that the critical point is not well defined. In the present work, we take $250 \cdot N \cdot 2500$, and hence $0.6 \cdot N^{\frac{1}{2}}$. Thus, we can still define $T_c$ as calculated from Eq. (4) below. Furthermore, we assume that the magnetic particle is in the vacuum, neglecting its interaction with the medium.

Consider a spin system with the Hamiltonian

$$H = \frac{1}{s^2} \sum_{i,j} J_{ij} s^z_i s^z_j; \quad (1)$$

where $s^z \cdot s$ and $J_{ij}$ stands for the exchange energy between the spin pair $i$ and $j$. The action $S$ of the system is defined as $S = \sum H = k_B T$, where $k_B$ is the Boltzman constant. The corresponding trial action for the non-interacting system is

$$S_0 = \frac{1}{S} \sum_i \xi_s s^z_i; \quad (2)$$

Here $\xi_s$ are introduced as variation parameters. The $m$th order free energy of the system in VCE is given by:

$$W = W_0 + \frac{1}{n!} H(S; S_0); \quad (3)$$

where $H(S; S_0)$ denotes the cumulant average of the enclosed quantity over the Boltzmann weight $e^{S_0}$. It has been shown [9] that the critical point $T_c$ up to $m$th order is given by

$$k_B T_c^{(m)} = \frac{1}{m!} \frac{\partial m_i}{\partial s^z_i} H^{(m_i)} \frac{\partial}{\partial s^z_i} H^{(m_i)} i_d=0; \quad (4)$$

We assume, for simplicity, the nearest neighbor interaction in a uniform $s = 1=2$ system, namely, $J_{ij} = J$ and $\xi = \xi$ throughout the system. The calculation of $T_c$ is straightforward up to any order by a graphic method outlined in Ref. 10. But it may become tedious in higher orders. Here we do not give long expressions for $T_c$ in each order, but only point out that to each order, all the graphs for topologically equivalent configurations must be summed in order to compute $T_c$. 
Normally, the more neighbors each atom has, the higher $T_c$ will be the nano-particle. A computer code has been developed to handle these graphs.

Apparently, surface atoms have fewer neighbors than interior atoms. Hence larger nano-particles generally possess higher $T_c$. When the particle becomes larger and larger, $T_c$ approaches its bulk value. For ultra-thin films, the critical temperature depends upon the growth direction as is shown in Ref. 11. For nano-particles, at first glance, it seems that $T_c$ is independent of the orientation. Suppose that a nano-particle takes any direction, i.e. it rotates arbitrarily in space. The neighboring configurations remain unchanged. However, as we shall see below, $T_c$ does depend on the growth direction of the particle. In other words, $T_c$ varies when a particle takes planes with different orientations as its own surface. As far as the critical point is concerned, the first order VCE theory yields the same result as that of the mean field (MF) approximation [11]. We therefore calculate up to the second order. Higher order calculation is not expected to change the conclusion qualitatively. Figure 1 shows the first and second order critical temperature $T_c^{(1)}$ and $T_c^{(2)}$ versus the number $N$ of atoms in a nano-particle of sc structure. It is seen that $T_c$ increases with increasing size of the nano-particle. This is because the surface to volume ratio decreases as the nano-particle grows larger. When $N \to \infty$, the critical temperature approaches the corresponding bulk values $k_B T_c^{(1)} = 6$ and $k_B T_c^{(2)} = 5$, respectively.

Nano-particles may be fabricated in shapes other than cubic. For example, they were made in platelet shapes in Ref. 8 with the aspect ratio about 4. To study the shape effect, we also consider the platelet- and column-shaped particles. The aspect ratio of the former is $1 : 4 : 4$, and that of the latter is $1 : 1 : 4$. In either case, the surface to volume ratio is larger than that of a cube for which the ratio is $1 : 1 : 1$. Therefore, one expects lower $T_c$. In any case, it is safe to say that the critical temperature is insensitive to the nano-particle shape. The surface effect diminishes quickly as the nano-particle volume increases. The surface to volume ratio of nano-particles for different shapes is shown in Fig. 2 as a function of the total number of atoms. It is seen that there are still well above 20% surface atoms in a nano-particle consisting of 15000 atoms.
FIG. 2. The surface to volume ratio of atoms (including edges and corners) for the three shapes of sc lattice as a function of $N$.

FIG. 3. The reduced critical temperature of a nano-particle with three different cubic lattices as a function of $N$. Solid line is the first-order result and dashed line is the second-order result.

atoms. But the transition temperature is very close to that of the bulk. It is also noted that for a fixed volume, the ratios of surface areas of four shapes, platelet: column: cube: sphere, are 3.78 : 3.57 : 3.00 : 2.81. Thus, $T_c$ for a cubic particle is quite close to that of a sphere of the same volume.

We have also computed $T_c^{(m)}$ up to the second order as a function of $N$, the total number of atoms in a nano-particle of bcc and fcc lattices. Results are shown in Fig. 3 along with those for a particle of sc lattices. Two different growth directions are considered. The open circles represent $T_c$ of a cubic particle with three faces $<100>$, $<010>$ and $<001>$. The critical temperature $T_c$ of a particle with faces $<110>$, $<110>$ and $<100>$ is given by solid circles. The difference may be called the effect of the growth direction. It comes from different numbers of nearest neighbors in surfaces. On the basis of the previous work on films [12], it is reasonable to expect that the preferable surface plane for nano-particles is such that the particle has the highest $T_c$. 

It should be remarked that when \( N \leq 1 \), the curves in Fig. 3 approach the respective bulk limits as they should. Thus, the limits are \( k_B T_c^{(1)} \) and \( k_B T_c^{(2)} \approx 7 \) or bcc, and for fcc structure they are \( k_B T_c^{(1)} \approx 12 \) and \( k_B T_c^{(2)} \approx 11 \). The limit of sc structure has been mentioned above.

In all the plots, we have limited \( N \) between 250 and 2500 because the theory is basically statistical in nature and does not apply to a small group of atoms. On the other hand, the nanoparticle may have magnetic domains when the total number of atoms is sufficiently large and behaves like the bulk. A rough estimate shows that a magnetic nanoparticle of dimension larger than \( \approx 50 \AA \) will behave like a bulk material as far as the transition temperature is concerned.

In summary, we have calculated the critical temperature of nano-particles with sc, bcc and fcc lattice structures by means of the VCE method. Three different shapes are considered and it is shown that the shape effect is insignificant. Because the surface atoms have fewer neighbors than interior atoms and the proportion of surface atoms in the entire particle decreases as the particle grows, larger nano-particles of the same lattice structure always have higher \( T_c \). It is also found that the orientation of crystal faces in a nano-particle or its direction of growth can affect the critical point significantly.

References

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