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Finite-size versus surface effects in nanoparticles

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Abstract

We study the finite-size and surface effects on the thermal and spatial behaviours of the magnetisation of a small magnetic particle. We consider two systems: (1) A box-shaped particle of simple-cubic structure with either periodic or free boundary conditions. This case is treated analytically using the isotropic model of D-component spin vectors in the limit $D \to \infty$, including the magnetic field. (2) A more realistic particle (γ-Fe_2O_3) of ellipsoidal (or spherical) shape with open boundaries. The magnetic state in this particle is described by the anisotropic classical Dirac–Heisenberg model including exchange and dipolar interactions, and bulk and surface anisotropy. This case is dealt with by the classical Monte Carlo technique.

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1. Introduction

From the physical point of view, nanoparticles exhibit such interesting features as superparamagnetism and exponentially slow relaxation rates at low temperatures due to anisotropy barriers. However, the picture of a single-domain magnetic particle where all spins are pointing into the same direction, leading to coherent relaxation processes, ceases to be valid for very small particles where surface effects become really crucial. For instance, in a particle of radius ~ 4 nm, 50% of atoms lie on the surface. Therefore, it is necessary to understand the effect of free boundaries, first on the static and then on the dynamical properties of nanoparticles. However, one of the difficulties which is inherent to systems of round (spherical or ellipsoidal) geometries, consists in separating surface effects due to symmetry breaking of the crystal field on the boundaries and the unavoidable finite-size effects caused by using systems of finite size. In hypercubic systems, this problem is easily handled by using periodic boundary conditions, but this is not possible in other topologies, and thus surface and finite-size effects are mixed together.

In this article, we discuss surface and finite-size effects on the thermal and spatial behaviours of the intrinsic magnetisation of an isolated small particle. We consider two different systems: (1) A cube of simple-cubic structure with either periodic or free boundary conditions. This system is treated analytically by the isotropic model of D-component

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spin vectors in the limit $D \to \infty$, in magnetic field [1]. (2) The second system, which is more realistic, is the maghemite particle (γ-Fe_2O_3) of ellipsoidal (or spherical) shape with open boundaries. The appropriate model is the anisotropic classical Dirac–Heisenberg model including exchange and dipolar interactions, and taking account of bulk and surface anisotropy. On the contrary, this system can only be dealt with using numerical approaches such as the classical Monte Carlo technique [2]. In the case of a cubic system we obtain the thermal behaviour of local magnetisations at the center of faces, edges and corners. An exact and very useful relation between the intrinsic magnetisation and the magnetisation induced by the magnetic field, valid at all temperatures and fields, was obtained in Ref. [1]. It was shown that the positive contribution of finite-size effects to the magnetisation is lower than the negative one rendered by boundary effects, thus leading to a net decrease of the magnetisation with respect to the bulk. For maghemite, this study has been performed in a very small and constant magnetic field; the surface shell is assumed to be of constant thickness and only the particle size is varied. So, the thermal behaviour of the intrinsic magnetisation is obtained for different particle sizes [2]. This behaviour is compared with that of a cubic maghemite particle with periodic boundary conditions but without anisotropy. In this case the contributions of finite-size and surface effects lead to the same results as for the cube system, but the difference between them is now much larger, due to surface anisotropy. In addition, we show that the magnetisation profile is temperature-dependent.

2. Cubic system: $D \to \infty$ spherical model

We consider an isotropic box-shaped magnetic system of volume $\mathcal{N} = L^3$, with simple-cubic lattice structure, and nearest-neighbour exchange coupling, in a uniform magnetic field. For this we use the Hamiltonian of the isotropic classical D-component vector model [3–5], that is

$$\mathcal{H} = -\boldsymbol{h}\cdot\sum_i \boldsymbol{s}_i - \frac{1}{2}\sum_{i,j}\lambda_{ij}\sum_{\alpha=1}^{D} s_{\alpha i}s_{\alpha j}, \tag{1}$$

where $\boldsymbol{s}_i$ is the normalized D-component vector, $|\boldsymbol{s}_i| = 1$; $\boldsymbol{h} \equiv \mathrm{H}/J_0$ is the magnetic field, and $\lambda_{ij} \equiv J_{ij}/J_0$, the exchange coupling. We also define the reduced temperature $\theta \equiv T/T_c^{\mathrm{MFA}}$, $T_c^{\mathrm{MFA}} = J_0/D$ being the Curie temperature of this model in the mean–field approximation, and J_0 is the zero-momentum Fourier component of J_{ij}. In this model, the magnetisation $\boldsymbol{m}$ is directed along the field $\boldsymbol{h}$, so that $\boldsymbol{h} = h\boldsymbol{e}_z$ and $\boldsymbol{m}_i = m_i\boldsymbol{e}_z$. Using the diagram technique for classical spin systems [3–5] in the limit $D \to \infty$, generalizing it so as to include the magnetic field and adopting a matrix formalism [1], one ends up with a closed system of equations for the average magnetisation component $m_i \equiv \langle s_{zi}\rangle$ and correlation functions $s_{ij} \equiv D\langle s_{\alpha i}s_{\alpha j}\rangle$ with $\alpha \geqslant 2$ [1],

$$\sum_j \mathscr{D}_{ij}m_j = G_i h, \qquad \sum_j \mathscr{D}_{ij}s_{jl} = \theta G_i \delta_{il}, \tag{2}$$

where $\mathscr{D}_{ij} \equiv \delta_{ij} - G_i\lambda_{ij}$ is the Dyson matrix of the problem, and G_i is a local function to be determined from the set of constraint equations on all sites $i = 1, \ldots, \mathcal{N}$ of the lattice

$$s_{ii} + \boldsymbol{m}_i^2 = 1. \tag{3}$$

Now, we define the induced average magnetisation per site by

$$\boldsymbol{m} = \frac{1}{\mathcal{N}}\sum_i \boldsymbol{m}_i, \tag{4}$$

which vanishes for finite-size systems in the absence of magnetic field due to the Golstone mode associated with global rotations of the magnetisation. On the other hand, it is clear that at temperatures $\theta \ll 1$ the spins in the system are aligned with respect to each other and there should exist an *intrinsic* magnetisation. The latter is usually defined for finite–size systems as

$$M = \sqrt{\left\langle\left(\frac{1}{\mathcal{N}}\sum_i \boldsymbol{s}_i\right)^2\right\rangle} = \sqrt{\boldsymbol{m}^2 + \frac{1}{\mathcal{N}^2}\sum_{i,j=1}^{\mathcal{N}} s_{ij}}, \tag{5}$$

where the second equality is valid in the limit $D \to \infty$. Note that $M \geqslant m$ and that M remains non zero for $h = 0$; in this case in the limit $\theta \to 0$, $s_{ij} = 1$ for all i and j, and $M \to 1$. For $\theta \to \infty$ the spins

become uncorrelated and $M \to 1/\sqrt{\mathcal{N}}$. In the limit of $\mathcal{N} \to \infty$, the intrinsic magnetisation M approaches that of the bulk system. In the presence of a magnetic field, the Goldstone mode is suppressed and the magnetisation $\boldsymbol{m}$ of Eq. (4) no longer vanishes, this is why we call it the *supermagnetisation*, in contrast with the intrinsic magnetisation M. If the field is strong the magnitude of the supermagnetisation approaches the intrinsic magnetisation.

An important exact relation was established in Ref. [1] between M and m:

$$m = M\,\frac{2\mathcal{N}Mh/\theta}{1+\sqrt{1+(2\mathcal{N}Mh/\theta)^2}} = MB(\mathcal{N}MH/T), \tag{6}$$

where $B(\xi) = (2\xi/D)/[1+\sqrt{1+(2\xi/D)^2}]$ is the Langevin function for $D \gg 1$. Note that Eq. (6) is usually applied to superparamagnetic systems with the spontaneous bulk magnetisation $m_{\rm b}(T)$ in place of $M(T,H)$. However, unlike $m_b(T)$, the intrinsic magnetisation M of Eq. (5) is a *pertinent* characteristic of a finite magnetic system and depends on both field and temperature.

Solving the above model consists in determining $\boldsymbol{m}_i$ and s_{ij} as functions of G_i from the linear equations (2), and inserting these solutions in the constraint equation (3) in order to obtain G_i. Two types of boundary conditions are considered, free boundary conditions (fbc) and periodic boundary conditions (pbc). In the case of fbc, $\boldsymbol{m}_i$ and G_i are inhomogeneous and s_{ij} nontrivially depends on both indices due to boundary effects. In this case the exact solution is found numerically, though some analytic calculations can be performed at low temperature and field. Whereas in the pbc case the solution becomes homogeneous and the problem greatly simplifies. Although the model with pbc is unphysical, it allows for an analytical treatment and study of finite-size effects separately from boundary effects.

At low temperature, the intrinsic magnetisation in the fbc case, including only the contributions from faces, reads [1]

$$M \cong 1 - \frac{\theta W}{2}\left[1 - \Delta_{\mathcal{N}} + \frac{6}{5}\frac{1}{L}\right], \tag{7}$$

where W is the well–known Watson's integral and

$$\Delta_{\mathcal{N}} = \frac{1}{W}\left(W - \frac{1}{\mathcal{N}}\sum_{\mathbf{q}\neq 0}\frac{1}{1-\lambda_{\mathbf{q}}}\right) > 0 \tag{8}$$

describes the finite–size effects, with $\Delta_{\mathcal{N}} \propto 1/L$, while the last term in Eq. (7) represents the contribution from boundaries. The first term, on the other hand, is the bulk contribution which survives in the limit $L \to \infty$. In contrast with the finite-size effects, boundary effects entail a decrease of the intrinsic magnetisation. The contributions to Eq. (7) from the edges and corners are of order θ/L^2 and θ/L^3, respectively.

Fig. 1 shows the temperature dependence of the intrinsic magnetisation M, Eq. (5), and local magnetisations of the 14^3 cubic system with free and periodic boundary conditions in zero field. For periodic boundary conditions, M exceeds the bulk magnetisation at all temperatures. In particular, at low temperatures this agrees with the positive sign of the finite-size correction to the magnetisation, as in Eq. (7). The magnetisation at the centre of the cube with free boundary conditions is rather close to that for the model with pbc in the whole temperature range and converges with the latter at low temperatures. Local magnetisations at the centre of the faces and edges and those at the corners

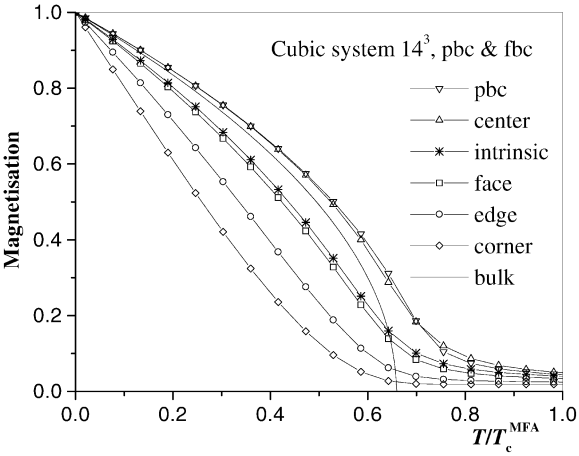

Fig. 1. Temperature dependence of the intrinsic magnetisation M, Eq. (5), and local magnetisations of the 14^3 cubic system with free and periodic boundary conditions in zero field.

decrease with temperature much faster than the magnetisation at the centre. This is also true for the intrinsic magnetisation M which is the average of the local magnetisation M_i over the volume of the system. One can see that, in the temperature range below the bulk critical temperature, M is smaller than the bulk magnetisation. This means that the boundary effects suppressing M are stronger than the finite-size effects which lead to the increase of the latter, and this is in agreement with the low-temperature formula of Eq. (7).

3. Maghemite particles: Monte Carlo simulations

In this section, we consider the more realistic case of (ferrimagnetic) maghemite nanoparticles (γ-Fe_2O_3) of ellipsoidal (or spherical) shape with open boundaries, in a very small and uniform magnetic field. The surface shell is assumed to be of constant thickness ($\sim$0.35 nm) [6], and only the particle size is varied [2].

To deal with spatial magnetisation distributions [7,8] one has to consider exchange, anisotropy and magneto-static energies together. Accordingly, our model for a nanoparticle is the classical Dirac–Heisenberg Hamiltonian including exchange and dipole–dipole interactions, anisotropy, and Zeeman contributions. Denoting (without explicitly writing) the dipole–dipole interaction by $H_{\rm dip}$, our model reads

$$\mathscr{H} = -\sum_{i,\boldsymbol{n}} J_{\alpha\beta} \sum_{\alpha,\beta} \boldsymbol{S}_i^{\alpha} \cdot \boldsymbol{S}_{i+\boldsymbol{n}}^{\beta} - K \sum_{i=1}^{N_t} (\boldsymbol{S}_i \cdot \boldsymbol{e}_i)^2 - (g\mu_B) H \sum_{i=1}^{N_t} \boldsymbol{S}_i + H_{\rm dip},$$

where $J_{\alpha\beta}$ are the exchange couplings between nearest neighbours spanned by the unit vector $\boldsymbol{n}$, $\boldsymbol{S}_i^{\alpha}$ is the (classical) spin vector of the αth atom at site i, H is the uniform field applied to all spins in the particle, $K > 0$ is the anisotropy constant and $\boldsymbol{e}_i$ the single-site anisotropy axis. In both cases of a spherical and ellipsoidal particle, we consider a uniaxial anisotropy in the core along our z reference axis (major axis for the ellipsoid), and single-site anisotropy on the surface, with equal anisotropy constant K_s, and $\boldsymbol{e}_i$ are defined so as to point outward and normal to the surface [9–11].

Our method of simulation proceeds as follows: we start with a regular box of spinel structure, then we cut in a sphere or an ellipsoid that contains the total number N_t of spins of a given particle. We distinguish between spins in the core (of number N_c) from those on the surface (N_s) of the particle according to whether or not their coordination number is equal to that of a system with periodic boundary conditions (pbc). All spins in the core and on the surface are identical but interact via different couplings; exchange interactions between the core and surface spins are taken equal to those inside the core. Our parameters are as follows: the exchange interactions are (in units of K) $J_{AB}/k_B \simeq -28.1$, $J_{BB}/k_B \simeq -8.6$, $J_{AA}/k_B \simeq -21.0$. The bulk and surface anisotropies are $k_c \equiv (K_c/k_B) \simeq 8.13 \times 10^{-3}$, $k_s \equiv (K_s/k_B) \simeq 0.5$, respectively, where k_B is the Boltzmann constant.

In Fig. 2, we plot the thermal variation of the core and surface contributions to the magnetisation (per site) as a function of the reduced temperature $\tau^{\rm core} \equiv T/T_c^{\rm core}$ for $N_t = 909$ and 3766 corresponding to $N_{st} \equiv N_s/N_t = 53\%$ and 41% and diameters of circa 4 and 6 nm, respectively. The core and surface magnetisations are averages over all spins in the core or on the surface, respectively. For both sizes we see that the surface magnetisation $M_{\rm surf}$ decreases more rapidly than the core contribution M_c as the temperature increases, and has a positive curvature while that of M_c is negative.

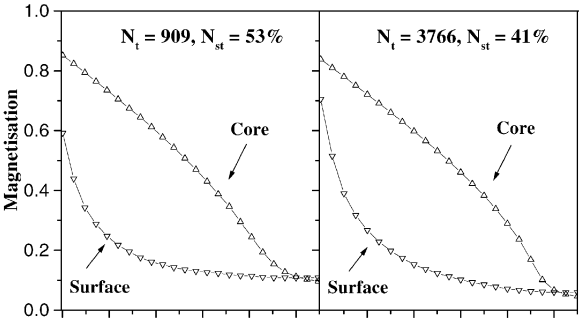

Fig. 2. Temperature dependence of the surface and core magnetisations for $N_t = 909$ and 3766.

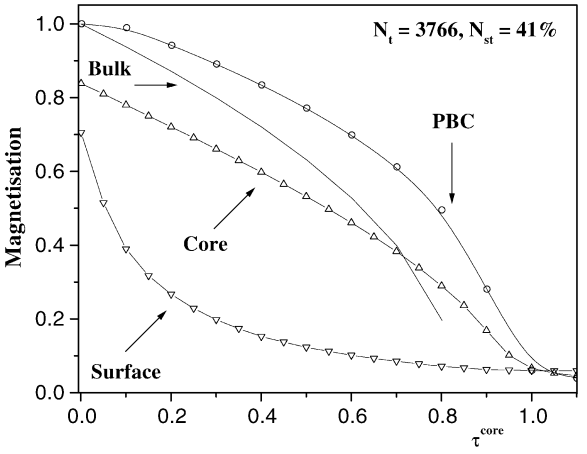

Fig. 3. Temperature dependence of the surface and core magnetisations for $N_t = 3766$, magnetisation of the bulk system ($N_t = \infty$), and the magnetisation of the cube with the spinel structure and periodic boundary conditions (pbc) with $N_t = 40^3$.

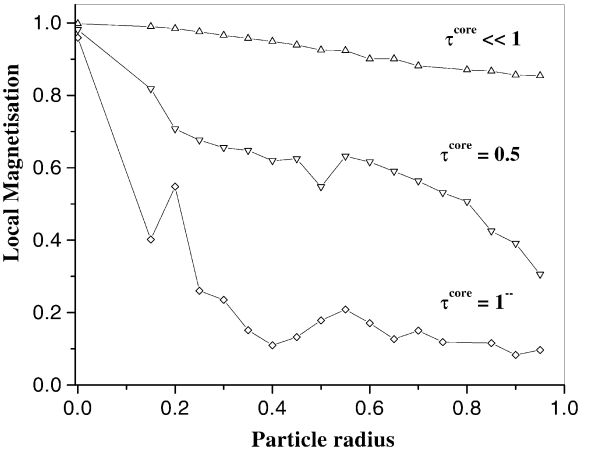

Fig. 4. Spatial variation of the net magnetisation of a spherical nanoparticle of 3140 spins, as a function of the normalised particle radius, for $\tau^{core} \ll 1$, and $\tau^{core} = 0.5$, $\tau^{core} \simeq 1^-$.

Moreover, it is seen that even the (normalised) core magnetisation per site does not reach its saturation value of 1 at very low temperatures, which shows that the magnetic order in the core is disturbed by the surface (see Fig. 4 below). As the size decreases the maximum value of M_{surf} decreases showing that the magnetic disorder is enhanced.

In Fig. 3, we plot the core and surface magnetisations (with $N_t = 3766$, and $N_{st} = 41\%$), the magnetisation of a cube with spinel crystalline structure and pbc, and the bulk magnetisation as functions of the reduced temperature τ^{core}. Apart from the obvious shift to lower temperatures of the critical region due to the finite-size and surface effects, we see that, as was also shown analytically for the cube system, the finite-size effects give a positive contribution to the magnetisation with respect to the bulk, whereas the surface effects yield a negative contribution. Moreover, it is seen that for nanoparticles the contribution from the surface is much larger (in absolute volume) than that coming from finite-size effects. The difference between the two contributions appears to be enhanced by the surface anisotropy in the case of nanoparticles.

In Fig. 4, we plot the spatial evolution of the orientation of the magnetic moment from the centre to the border of the particle, at different temperatures. At all temperatures, the magnetisation decreases with increasing particle radial distance. This obviously suggests that the magnetic disorder starts at the surface and gradually propagates into the core of the particle. At high temperatures, the local magnetisation exhibits a jump of temperature-dependent height, and continues to decrease. This indicates that there is a temperature-dependent radius, smaller than the particle radius, within which the magntisation assumes relatively high values. This result agrees with that of Ref. [12] (for spherical nanoparticles with simple cubic structure) where this radius was called the *magnetic radius*. The local magnetisation also depends on the direction of the radius vector, especially in an ellipsoidal particle.

4. Conclusion

Both in the cube system and the nanoparticle of the maghemite type, surface effects yield a negative contribution to the intrinsic magnetisation, which is larger than the positive contribution of finite-size effects, and this results in a net decrease of the magnetisation with respect to that of the bulk system. In the first case we have been able to separate finite-size effects from surface effects by considering

the same system with periodic and free boundary conditions. On the other hand, the results for a spherical or ellipsoidal nanoparticle with free boundaries have been compared to those of a cube with a spinel structure and periodic-boundary conditions, but without any anisotropy. In this case, it turns out that the contributions from surface and finite-size effects have the same sign as before but the difference between them becomes larger, due to surface anisotropy. These spin models invariably predict that the surface magnetisation (per spin) of systems with free boundaries is smaller than the magnetisation of the bulk system. However, experiments on layered systems, especially of 3d elements, have shown that there is enhancement of the magnetic moment on the surface, which has been attributed to the contribution of orbital moments [13]. It is clear that the models presented here do not account for such effect, but they can be generalised so as to include orbital as well as spin vectors.

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