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Numerical study of the collective magnetic behavior of nanoparticle assembled films

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Abstract

The magnetic hysteresis and the temperature-dependent magnetization of interacting nanoparticle assemblies are studied by Monte Carlo simulations. By comparison of the simulation results with measurements in Fe/Ag samples grown by low energy cluster beam deposition demonstrate that interparticle exchange interactions dominate over the dipolar interactions and are responsible for the collective magnetic behavior in this system. The simulation of the magnetic properties of quasi-two-dimensional ordered arrays of Co nanoparticles, prepared by self-assembly from a colloidal dispersion, demonstrates that dipolar interactions are responsible for an increase of the blocking temperature relative to the isolated particles. The collective behavior is manifest by oscillations in the magnetization with increasing layer coverage.

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Keywords: Self-assembly; Magnetic nanoparticles; Blocking temperature; Interparticle interactions; Monte Carlo simulation

1. Introduction

Two distinct growth techniques, namely, the low energy cluster beam deposition [1] and the self-assembly [2–4] of nanoparticles prepared in a colloidal dispersion, produce nanostructured films composed of magnetic nanoparticles with an extremely narrow size distribution. However, the nature of the interparticle interactions and the film morphology are different in the two cases. With the former method, random assemblies of nanoparticles are formed and strong interparticle exchange interactions are expected to occur when nanoparticles are in contact. These interactions become the dominant ones at concentrations close to the percolation threshold. In the latter case, nearly planar hexagonal arrays are formed and dipolar interactions dominate. Exchange interactions are suppressed in this case by the presence of a thick surfactant layer.

Recent magnetic measurements in Fe/Ag cluster-assembled films [5] and in self-assembled periodic arrays of Co nanoparticles [2–4] have provided sufficient evidence that these systems are far from the non-interacting (superparamagnetic) limit. In this work, we implement the Monte Carlo simulation method to investigate the magnetic properties of these two categories of nanoparticle assembled systems and verify the importance of different types of interparticle interactions.

2. Model and simulation method

Two different models for the spatial arrangements of the particle assembly are considered. In the first

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model (model I), spherical particles are located randomly with occupation probability P inside a cubic box of edge length LD, where D is the particle diameter. For simplicity, the space inside the box is discretized by a simple cubic (or face centered) lattice with lattice constant equal to the particle diameter. The particles are located only on the nodes of the lattice, thus overlap is avoided. This geometrical model describes the morphology of films formed by co-deposition of preformed particles with non-magnetic atoms [5]. In the second model (model II), the particles form a two-dimensional triangular lattice in the xy-plane with lattice constant $d \geq D$. A film with finite thickness is formed by stacking L_z monolayers of particles in an ABC sequence. The uppermost monolayer is randomly occupied with probability P and the ones below are perfectly periodic. This model describes adequately the morphology of self-assembled ordered arrays of magnetic nanoparticles [3,6].

The magnetic state of the individual nanoparticles is described by the Stoner–Wolfarth model that assumes coherent rotation of the particle's magnetization. An anisotropy axis in a random direction is attributed to each particle. The particles interact via long range dipolar forces and via exchange forces, when they are sufficiently close. The particle assembly is assumed monodisperse in accordance with experimental evidence that both films grown by a cluster beam [5] or by self-assembly on surfaces [3,6] are characterized by extremely low size dispersion. The total energy of the particle assembly:

$$E = g\sum_{i,j}\frac{(\hat{S}_i\cdot\hat{S}_j)-3(\hat{S}_i\cdot\hat{R}_{ij})(\hat{S}_j\cdot\hat{R}_{ij})}{R_{ij}^3} - J\sum_{\langle i,j\rangle}(\hat{S}_i\cdot\hat{S}_j) - k\sum_i(\hat{S}_i\cdot\hat{e}_i)^2 - h\sum_i(\hat{S}_i\cdot\hat{H}) \quad (1)$$

where $\hat{S}_i$ is the magnetic moment direction (spin) of particle i, $\hat{e}_i$ the easy axis direction, R_{ij} the center-to-center distance between particles i and j, measured in units of the particle diameter. The energy parameters entering Eq. (1) are the Zeeman energy $h = \mu H$, where $\mu = M_s V_o$ is the particle magnetic moment, the dipolar energy $g = \mu_0\mu^2/4\pi D^3$, the anisotropy energy $k = K_1 V_o$ and the exchange energy J. The exchange coupling exists only between particles in contact (nearest neighbors). In model I, periodic boundaries in all directions are used, while in model II, mixed periodic boundaries (xy-plane) and open boundaries (z-axis) are used. The spin configuration is obtained by a Metropolis Monte Carlo algorithm [7]. At a given temperature and applied field, the system is allowed to relax towards equilibrium for the first 10^3 Monte Carlo steps per spin and thermal averages are calculated over the subsequent 10^4 steps. The results are averaged over 10–30 samples with different particle locations.

3. Numerical results

3.1. Three-dimensional random assemblies (model I)

We model the magnetic behavior of Fe nanoparticles with diameter $D = 3.0$ nm. The values of the magnetic moment $\mu = 2.44 \times 10^{-20}$ A m^2 and the anisotropy energy density $K = 2.4 \times 10^5$ J m^{-3} have been extracted from magnetic measurements in dilute samples ($P \sim 0.1\%$), where the Fe nanoparticles are to a very good approximation non-interacting. The value of the exchange coupling has been extracted from magnetic measurements in high volume fraction samples [5] and equals $J = 3.11 \times 10^{-20}$ J. Here, we focus in the intermediate concentration regime, that extends up to the percolation threshold, above which the single particle character is lost due to strong coalescence. Simulations are performed on a $L \times L \times L$ box with $L = 10$. In Fig. 1, we show results for the hysteresis behavior at $T = 5$ K. The loop opens and the coercivity (H_c) increases with increasing Fe particle concentration (Fig. 1b). We attribute this

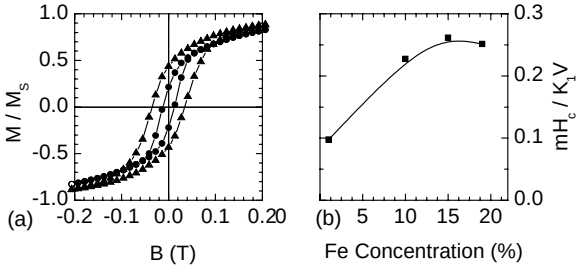

Fig. 1. Low-temperature ($T = 5$ K) hysteresis behavior of Fe cluster-assembled film. (a) Hysteresis loops in the dilute ($P = 1\%$, filled circles) limit and close to percolation ($P = 20\%$, filled triangles). (b) Dependence of coercive field on concentration of Fe nanoparticles (filled squares). The full line serves as a guide to the eye.

behavior to interparticle interactions. Dipolar and exchange interactions *suppress* the coercivity in a random assembly of anisotropic nanoparticles at $T \ll T_b$ [8,9], while dipolar interactions alone can *enhance* the coercivity at $T \sim T_b$ [8,10]. The fraction of blocked particles at $T = 5$ K is estimated from the value of the parameter:

$$b = \left\langle \sum_i \frac{|\hat{S}_i \cdot \hat{e}_i|}{N} \right\rangle_T$$

which is $b = 0.89$ for $P = 1\%$ at $H = 0$ and drops to $b = 0.54$ for $P = 20\%$. The low value of b indicates that in the dense sample a large fraction of the particles are superparamagnetic and consequently, dipolar interactions are responsible for the increase of H_c with concentration at $T = 5$ K.

The evolution of the FC/ZFC magnetization curves with Fe concentration in the temperature range 2–350 K is shown in Fig. 2. For the dilute sample ($P \sim 1\%$), a sharp peak of the ZFC curve occurs at the blocking temperature and a Curie behavior ($M \sim 1/T$) is shown at temperatures well above the blocking ($T \gg T_b$). Finally, a weak variation of T_b with applied field (∼15%) is found, which is in agreement with the analytical model of Dormann et al. [11] that predicts a 10–30% variation of T_b for $H = 100$–500 G. These features indicate that the dilute sample is a non-interacting assembly. The magnetization curves are drastically different in the dense sample (Fig. 2b). The maximum of the ZFC curve is broad indicating a wide distribution of energy barriers in the system. At high temperature ($T \gg T_b$), the dependence is almost linear, deviating seriously from the Curie law. Finally, the position of the ZFC peak is very sensitive to the applied field, as designated by the large upshift (∼50%). These features of the FC/ZFC curves are in good agreement with experimental measurements in Fe cluster-assembled films [5]. The physical picture drawn from these results is that exchange interactions couple individual clusters into (coherent) aggregates giving rise to the increase in T_b and the aggregates interact via dipolar forces that produce the strong field dependence of T_b and the almost linear decay of the magnetization with temperature.

3.2. Quasi-two-dimensional periodic arrays (model II)

We model the magnetic properties of Co nanoparticles arrays formed by self-assembly on a crystal (C, Si) surface. For Co nanoparticles we use the following parameters [12]: diameter $D = 4$ nm, anisotropy density $K_1 = 3.08 \times 10^5$ J m^{-3}, magnetization $M_s = 1.44 \times 10^6$ A m^{-1} and interparticle distance $d = 4.5$ nm. Simulations are performed on a $L \times L \times L_z$ cell with $L = 15d$ and $L_z \leq 4d_z$, where $d_z = d\sqrt{2/3}$ is the inter-layer distance.

In Fig. 3, we show the low-temperature ($T = 2$ K) dependence of the remanence (M_r) and H_c on the layer coverage for an applied field along one of the symmetry axes of the triangular lattice. Results for a strongly dipolar system ($g/k \sim 10$) are also shown to emphasize the fact that the features observed in the Co array (triangles) have their origin in the interparticle dipolar interactions. The Co nanoparticle

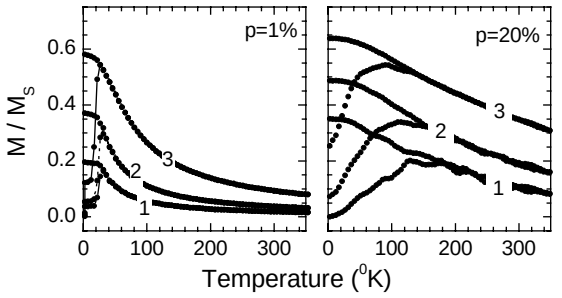

Fig. 2. Zero-field cooled and field-cooled curves of Fe cluster-assembled film in the dilute limit (left panel) and close to percolation (right panel). Labels 1–3 correspond to applied field values of 100, 200 and 500 G, respectively.

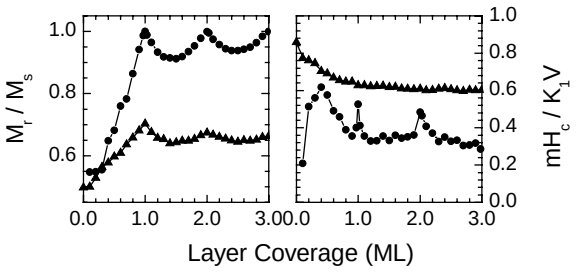

Fig. 3. Low-temperature dependence of remanence (left panel) and coercivity (right panel) on layer coverage for hexagonal arrays {AMIT200}apsusc/of magnetic nanoparticles with ABC stacking sequence. Filled triangles: Co nanoparticles ($g/k = 0.25$); filled circles: soft nanoparticles ($g/k \sim 10$).

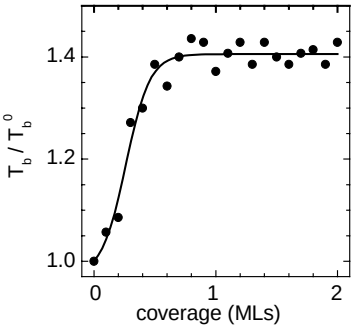

Fig. 4. Increase of blocking temperature (T_b) with layer coverage for hexagonal arrays of Co nanoparticles (filled circles) with ABC stacking sequence. In-plane applied field $H = 100$ Oe. The full line is a guide to the eye.

array shows maxima in the M_r when complete monolayers form ($c = 1$–3 ML), while a incomplete top layer suppresses the magnetic order due to the competing character of the dipolar interactions in a random nanoparticle assembly [8,10]. Peaks in H_c are observed only in the strongly dipolar system at full coverage and they are washed out in the Co array. Given that dipolar interactions in a two-dimensional triangular lattice have an anisotropic ferromagnetic character [13], the peaks observed in M_r and H_c at low T (Fig. 3) indicate that in complete monolayers the ferromagnetically coupled nanoparticles respond collectively to the applied field. The observed decay of H_c with increasing layer thickness, is a result of the transition from a two-dimensional reversal mode ($c = 1$ ML) to a three-dimensional one ($c \gg 1$ ML).

Finally, we calculate the ZFC magnetization curves for different coverage ratios [13] and from those we extract the corresponding blocking temperatures (Fig. 4). An increase of the blocking temperature with layer coverage is seen, that almost reaches saturation as soon as the first complete ML is formed. Below 1 ML coverage, the increase of T_b is due to the anisotropic and ferromagnetic character of dipolar interactions that introduce an additional barrier to the magnetization reversal of the particles. Increased T_b values relative to the dilute samples have been recently measured in self-assembled Co nanoparticle arrays prepared from colloidal dispersions [6,12]. In these experiments it was found that $T_b(1\text{ ML})/T_b^0 \approx 1.3$ [12], which is in good agreement with the results of our simulations and supports the argument that dipolar interactions are the dominant ones in these samples.

4. Conclusions

Different types of interactions at the mesoscopic scale are responsible for the collective magnetic behavior in nanoparticle assembled films. Monte Carlo simulations combined with static magnetic measurements can reveal the nature and the relative strength of the interparticle coupling. In Fe/Ag films grown by cluster deposition strong exchange and weak dipolar interactions are present, while in self-assembled ordered arrays of Co nanoparticles, dipolar interactions can explain the observed collective behavior.

Acknowledgements

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