The effect of dipolar interactions in clusters of magnetic nanocrystals

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Abstract. Monte Carlo simulations are carried out to evaluate the effective magnetic moment \( \mu_{\text{eff}} \) of clusters containing 100 magnetic nanocrystals (MNCs) in a low magnetic field. The true value of the initial magnetic susceptibility, i.e. \( \chi_0 = \frac{\partial M}{\partial H} \) at zero field, can be easily assessed from \( \mu_{\text{eff}} \). Results show that dipolar interactions contribute to reduce the effective magnetic moment. Below a threshold value near the low-field region, clusters of MNCs with smaller diameters possess a larger effective magnetic moment per unit volume compared to clusters with larger MNCs. This is of particular interest for bio-sensing systems relying on the magnetic response of magnetic multi-core nanoparticles in the low-field region.

1. Introduction
In recent years, progress in the synthesis of magnetic nanocrystals (MNCs) with well-controlled dimensions and surface functionalization has opened promising perspectives in biomedical areas such as bio-sensing, targeted drug delivery, magnetic resonance imaging (MRI) and hyperthermia in cancer treatment [1].

More particularly, the possibility to grow many single-domain MNCs into a randomly-packed cluster has led to the development of so-called magnetic multi-core nanoparticles (figure 1) [2-4].

The magnetic response of MNC clusters depends on a subtle interplay between competing energy terms (e.g. magnetic interactions, magnetic anisotropy) and the cluster microstructure. Of particular interest are the inherent magnetic dipole-dipole interactions, owing to their long range, anisotropic and often dominating contributions [5]. To understand the role of dipolar interactions on the magnetic properties of MNC clusters is essential for the proper interpretation of their magnetic response, for instance in bio-sensing systems using multi-core nanoparticles as magnetic markers [6-9].

In this paper, we study the effective magnetic moment of small clusters of MNCs suspended in a liquid using a Monte Carlo method [10]. Our simulations include dipolar interactions between the MNCs within the cluster as well as the Brownian rotation of the entire cluster in the liquid. The results reported here concern the low-field region which is particularly relevant for the bio-sensing systems operating in the mT range [6,7] or below [8,9].

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2. Model
The first step of the simulation is to generate a three-dimensional (3D) cluster of $N$ monodisperse spherical MNCs of diameters $D$ using a procedure reported previously \[10\]. We observe that our method produces clusters that have a realistic microstructure with respect to real systems (figure 1).

![Figure 1](image)

(a) Transmission electron microscopy (TEM) image of a magnetic multi-core nanoparticle FluidMAG-D from Chemicell GmbH. The magnetic multi-core consists of a cluster of several Fe$_3$O$_4$ nanocrystals with a mean diameter of about 12 nm \[11\]. (b) Simulated 3D cluster of $N = 100$ MNCs with diameters $D$ of 12 nm.

Next, the equilibrium magnetization of the MNCs is simulated using a Metropolis algorithm \[10\]. In brief, the magnetic moment of the $i$-th MNC is represented by a single vector $\mu_i$ with a constant magnitude $\mu_i = M_s V$, where $M_s = 350$ kA/m is a typical value of the intrinsic saturation magnetization for small magnetite (Fe$_3$O$_4$) nanocrystals, and $V = (\pi/6)D^3$ is the volume of each MNC. In our model, the total energy for the $i$-th MNC is given by

$$E_{tot}^{(i)} = -\mu_i \cdot B - \frac{\mu_0}{4\pi} \sum_{j \neq i} \left( \frac{3(\mu_i \cdot r_{ij})(\mu_j \cdot r_{ij})}{r_{ij}^3} - \frac{(\mu_i \cdot \mu_j)}{r_{ij}^3} \right).$$

(1)

The first and second terms on the right-hand side of equation (1) represent respectively the coupling energy between $\mu_i$ and the externally applied magnetic field $B$, and the magnetic dipole-dipole interaction energy between $\mu_i$ and the neighboring moment $\mu_j$. The magnetic permeability of vacuum is given by $\mu_0 = 4\pi \times 10^{-7}$ N/A$^2$, and $r_{ij} = r_i - r_j$ is a distance vector joining the two dipoles (with $r_{ij} = ||r_{ij}||$). Owing to the small and finite size of the system, all neighbor pairs are considered in the summation of equation (1). Since the magnetic anisotropy of MNCs with randomly oriented easy axes does not influence the cluster magnetization at low fields \[11\], this contribution is neglected in equation (1). At each iteration step, a new direction of $\mu_i$ is randomly chosen with a uniform distribution in all directions. The move is accepted with probability $p = \min[1, \exp(-\Delta E_{tot}^{(i)}/k_BT)]$, where $k_BT$ is the thermal energy and $\Delta E_{tot}^{(i)}$ is the energy difference between the new and current magnetization orientations calculated from equation (1).

The total magnetic moment of the cluster, $\mu_{tot}$, is calculated as the Euclidian vector norm of the vector sum of the $N$ individual magnetic dipoles $\mu_i$ at the $k$-th iteration step, i.e. $\mu_{tot}^{(k)} = \left| \sum_{i=1}^{N} \mu_i^{(k)} \right|$. We define the effective magnetic moment, $\mu_{eff}$, of the cluster as $\mu_{eff} = \langle \mu_{tot}^2 \rangle_n^{1/2}$. The symbol $\langle \rangle_n$ denotes the average value over $n$ iteration steps after the system has reached thermal equilibrium. The simulation is repeated 64 times at every field with a new cluster created each time.

In addition, we derived an analytical expression of $\mu_{eff}$ in the low-field limit, i.e. $\mu B \ll k_BT$, for an ensemble of $N$ non-interacting MNCs with magnetic moments $\mu$:

$$\mu_{eff} = \sqrt{N\mu^2} \left[ 1 + \frac{(N-1)}{2} \frac{\mu B}{3k_BT} \right]^2.$$

(2)

Equation (2) was obtained under the condition $(N-1)(\mu B/3k_BT)^2 < 1$, which is fulfilled for our simulations with $N = 100$. We note that at zero applied field, equation (2) reduces to $\mu_{eff} = \sqrt{N\mu} = \sqrt{NM_sV}$. 


Calculated initial magnetic susceptibility, $\chi_0$, is often determined from the initial slope of the magnetization curve, i.e. $\chi_0 = \partial M / \partial H|_{H \to 0}$, using a number of calculated magnetization values in the low-field region [12]. Instead, $\chi_0$ can be straightforward derived in a single step from $\mu_{\text{eff}}$ computed at zero applied field:

$$\chi_0 = \mu_0 \frac{\mu_{\text{eff}}^2}{V_{\text{tot}}} \frac{1}{3k_B T}$$

Hence, this is an elegant way to obtain the true value of $\chi_0$ as defined by $\chi_0 = \partial M / \partial H|_{H = 0}$.

Furthermore, this value directly includes the effect of dipolar interactions between the MNCs.

3. Results and discussion

The analytical and simulated values of $\mu_{\text{eff}}$ normalized by the total volume of the cluster, $V_{\text{tot}} = NV$, are illustrated in figure 2 for $D = 8, 10, \text{ and } 12 \text{ nm}$, respectively. The simulation data for clusters of $N$ non-interacting MNCs recover equation (2) for applied fields up to 2 mT.

The simulations also show that dipolar interactions yield a decrease of $\mu_{\text{eff}} / V_{\text{tot}}$ compared to the non-interacting case. Interestingly, whereas the Langevin model, i.e. assuming no interactions, predicts at any applied field a higher magnetic moment per unit volume for larger MNC sizes, our simulations including dipole-dipole interactions reveal the opposite effect for fields up to about 1.8 mT. This effect can be attributed to the significantly stronger dipolar interactions between the 12 nm MNCs compared to the 8 nm MNCs. It should also be noted that $N = 100$ in all the simulations, meaning that $[V_{\text{tot}}]D = 8 \text{ nm} < [V_{\text{tot}}]D = 10 \text{ nm} < [V_{\text{tot}}]D = 12 \text{ nm}$.

From figure 2, one can also evaluate the relative change of $\mu_{\text{eff}}(B) / V_{\text{tot}}$ with respect to $\mu_{\text{eff}}(0) / V_{\text{tot}} = M_s / N^{1/2}$. For a field of 2 mT, $\mu_{\text{eff}}(B) / V_{\text{tot}}$ is nearly 14 percent higher than $\mu_{\text{eff}}(0) / V_{\text{tot}}$ for $D = 12 \text{ nm}$, while the relative increase is about 4 percent for $D = 10 \text{ nm}$ and only 1 percent for $D = 8 \text{ nm}$. Similar results are obtained for the dipolar-interacting MNCs where $\mu_{\text{eff}}(B) / V_{\text{tot}}$ at 2 mT is approximately 1, 4, and 8 percent higher than the zero-field values for $D = 8, 10, \text{ and } 12 \text{ nm}$, respectively. This appears to be of particular interest for applications relying on the low-field response.
of magnetic clusters, such as the bio-sensing systems mentioned above [6-9]. These results suggest indeed that in fields of up to 2 mT the effective magnetic moment of a multi-core particle can be assumed approximately constant when consisting of MNCs with smaller diameters (e.g. 8 nm in our case), whereas a field-dependent value of $\mu_{\text{eff}}$ should preferably be considered in the mT region for larger MNC sizes.

Figure 3 shows the simulated data on a magnified scale around the threshold fields $B_{th} \approx 1.6-1.8$ mT where $\mu_{\text{eff}}(B)/V_{\text{tot}}$ reaches similar values for $D = 8$, 10, and 12 nm when including dipolar interactions. We note that the range of threshold fields is relatively narrow, and with no significant dependence upon $D$, at least for the parameter values of MNCs used here. These results suggest that the effective magnetic moment, i.e. the magnetic response, per unit volume of a cluster with a given number of MNCs can be maximized by synthesizing MNCs with smaller (larger) dimensions depending whether the multi-core particles are intended to be used in the low-field region or not.

4. Conclusion

Monte Carlo simulations were performed to evaluate the influence of dipole-dipole interactions on the effective magnetic moment $\mu_{\text{eff}}$ of clusters of randomly-packed MNCs. Our results show that the value of $\mu_{\text{eff}}$ per unit volume, $\mu_{\text{eff}}/V_{\text{tot}}$, decreases due to the dipolar interactions, and that $\mu_{\text{eff}}$ can be assumed essentially constant in the low-field region (i.e. below 0.5 mT) for the range of MNC sizes considered in this study. Also, we note that for fields above approximately 1.8 mT, clusters of interacting MNCs with larger sizes possess a higher value of $\mu_{\text{eff}}/V_{\text{tot}}$ compared to smaller MNCs, as predicted from the Langevin model. However, for fields below 1.8 mT, the opposite behavior is observed, i.e. $[\mu_{\text{eff}}/V_{\text{tot}}]_{D=8 \, \text{nm}} > [\mu_{\text{eff}}/V_{\text{tot}}]_{D=12 \, \text{nm}}$. These findings are particularly relevant for bio-sensing systems relying on the magnetic response of magnetic multi-core nanoparticles in the low-field region; to account for the influence of the intrinsic dipole-dipole interactions is essential for choosing multi-core particles with appropriate MNC dimensions, and for the proper interpretation of the measurement data.

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