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Numerical micromagnetics of interacting superparamagnetic nanoparticles assembled in clusters with different dimensionalities

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Abstract

We analyze here the equilibrium magnetization state of densely packed interacting superparamagnetic nanoparticles assembled in clusters of various sizes and dimensionalities by comparison with the non-interacting case. We demonstrate that the average magnetization of individual particles is strongly increased in linear chains aligned parallel with the external magnetic field. Two-dimensional (2D) distributions of superparamagnetic nanoparticles present weaker increases of their average magnetization with respect to the non-interacting approximation whereas volume distributions (3D) are almost equivalent with the non-interacting case. A large number of nanoparticles densely packed in 2D superparamagnetic clusters present almost the same magnetic moment as infinite superparamagnetic chains. The effect of mutual interactions on the total magnetic moment of 3D surfaces (spheroids with various aspect ratios) uniformly covered with densely packed monolayers of superparamagnetic nanoparticles is also investigated.

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1. Introduction

Superparamagnetic nanoparticles are of great interest in the area of nano-biotechnology especially in biological applications in which the magnetic nano-carriers can be chemically modified in order to attach with a high degree of specificity to biomolecules. This has opened the way to a large variety of applications using magnetically “tagged” DNA, proteins or cells. One emerging class of applications requiring the use of magnetic nanoparticles and their precise manipulation and positioning is the identification of chemical or biological species in micro total analysis systems (μTAS) [1] or separation devices [2]. The lack of permanent magnetic moment in the absence of the external magnetic field, and the possibility to easily modify the surfaces for specific chemical attachment [3] are crucial properties motivating the use of magnetic nanoparticles in other types of applications such as MRI or NMR imaging

[4]. For both imaging and detection applications, assemblies of several hundreds to several thousands of superparamagnetic particles are needed in order to overcome the inherent difficulty in magnetic manipulation of very small (few nanometer radius) particles [5].

The physical quantity of great importance in magnetic manipulation of clusters formed by assembling of superparamagnetic particles is the total magnetic moment. This parameter needs to be considered in the design of systems used for the capture, manipulation and detection in a microfluidic environment and the effect of the mutual interactions between particles on the total magnetic moment cannot be neglected. Experimental [6] and theoretical [7] studies of assemblies of magnetic nanoparticles have shown a strong influence of the dipolar interactions on their AC susceptibilities. Experimental evaluations of these interactions by the effect induced on the remanence (IRM, DCD) and $\delta-M$ curves [8] or first-order reversal curve (FORC) diagrams [9] revealed their strong influence on the magnetic properties of the agglomerations of superparamagnetic particles. Numerical

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micromagnetic simulations of 2D square arrays of particles with randomly oriented easy axes [10] demonstrated the role played by dipolar interactions in the apparent coercive field and the hysteresis loops of the array. The ability of superparamagnetic particles to self-organize in relatively weak applied magnetic fields was experimentally demonstrated [11–17] and theoretically explained in a dipole–dipole interaction model [11]. The average magnetization of linear chains of superparamagnetic particles in non-uniform magnetic fields has been analytically evaluated [18] using a potential energy approach. More accurate numerical investigations in finite 1D structures of superparamagnetic particles [19,20] revealed the non-uniformity of both mutual interactions and average magnetization along the formed chain especially at its ends.

In this paper, we describe a numerical algorithm for finding the equilibrium magnetization state in assemblies of interacting superparamagnetic nanoparticles and compute the average magnetization of clusters of various sizes (up to thousands of particles) and different dimensionalities (1D, 2D and 3D). The numerical procedure employed here is a generalization of the 1D algorithm proposed by Alward [19], for 2- and 3D distributions of magnetic particles, as described by Yellen [20]. All particles are considered as identical spheres and treated as magnetic dipoles whose moments are proportional to the local magnetic field.

2. Computational method

We consider a collection of n identical superparamagnetic spherical particles located at the points P_i , $i = \overline{1, n}$ in uniform applied magnetic field $\vec{H}_0$. The equilibrium magnetization $\vec{M}_i$ of each particle may be obtained from the equation

$$\vec{M}_i = \chi \cdot (\vec{H}_0 + \vec{H}_i + \vec{h}_i), \quad (1)$$

where χ is the magnetic susceptibility of the particle i , $\vec{H}_i$ is the interaction field i.e. the magnetic field produced by all other particles at the point P_i , and $\vec{h}_i$ is the self-demagnetizing field of the particle i . For spherical and uniformly magnetized particles, the self-demagnetizing field may be expressed as

$$\vec{h}_i = -\frac{1}{3}\vec{M}_i. \quad (2)$$

As for the interaction field $\vec{H}_i$ we have

$$\vec{H}_i = \sum_{j \neq i} \vec{H}_{j \rightarrow i}^{\text{dip}}(\vec{M}_j, \vec{r}_i, \vec{r}_j), \quad (3)$$

where $\vec{H}_{j \rightarrow i}^{\text{dip}}$ is the magnetic field generated by the particle j at the point P_i where the particle i is located. If we consider in a first approximation that this field is mainly due to the dipolar contribution, we can easily express the Cartesian components of $\vec{H}_{j \rightarrow i}^{\text{dip}}$ as linear combinations of the Cartesian components $M_{j,x}$, $M_{j,y}$ and $M_{j,z}$ of the

magnetization, i.e.

$$H_{j \rightarrow i, \alpha}^{\text{dip}}(\vec{M}_j, \vec{r}_i, \vec{r}_j) = \sum_{\beta} A_{\alpha\beta}(\vec{r}_i, \vec{r}_j) M_{j,\beta}, \quad (4)$$

where α and β are one of (x, y, z) and $A(\vec{r}_i, \vec{r}_j)$ a symmetric tensor of second order whose elements are expressed as

$$A_{\alpha\beta}(\vec{r}_i, \vec{r}_j) = \begin{cases} \frac{v}{4\pi} \left[\frac{3\alpha^2}{|\vec{r}_i - \vec{r}_j|^5} - \frac{1}{|\vec{r}_i - \vec{r}_j|^3} \right], & \alpha = \beta, \\ \frac{v}{4\pi} \frac{3\alpha\beta}{|\vec{r}_i - \vec{r}_j|^5}, & \alpha \neq \beta. \end{cases} \quad (5)$$

In the equations above v denotes the particle volume whereas $\vec{r}_i$ and $\vec{r}_j$ are the position vectors for the particles i and j , respectively. The vectorial equation (1) may now be rewritten as a system of three scalar equations:

$$\sum_{k \neq i} A_{xx}(\vec{r}_i, \vec{r}_k) M_{k,x} + \left(-\frac{1}{3} - \frac{1}{\chi} \right) M_{i,x} + \sum_{k \neq i} A_{xy}(\vec{r}_i, \vec{r}_k) M_{k,y} + \sum_{k \neq i} A_{xz}(\vec{r}_i, \vec{r}_k) M_{k,z} = -H_{0x}, \quad (6)$$

$$\sum_{k \neq i} A_{yx}(\vec{r}_i, \vec{r}_k) M_{k,x} + \sum_{k \neq i} A_{yy}(\vec{r}_i, \vec{r}_k) M_{k,y} + \left(-\frac{1}{3} - \frac{1}{\chi} \right) M_{i,y} + \sum_{k \neq i} A_{yz}(\vec{r}_i, \vec{r}_k) M_{k,z} = -H_{0y} \quad (7)$$

and

$$\sum_{k \neq i} A_{zx}(\vec{r}_i, \vec{r}_k) M_{k,x} + \sum_{k \neq i} A_{zy}(\vec{r}_i, \vec{r}_k) M_{k,y} + \sum_{k \neq i} A_{zz}(\vec{r}_i, \vec{r}_k) M_{k,z} + \left(-\frac{1}{3} - \frac{1}{\chi} \right) M_{i,z} = -H_{0z}. \quad (8)$$

We have three scalar equations for each particle so that by taking into account all n particles we obtain a system of $3n$ linear equations with $3n$ scalar components of the magnetization as unknowns. By solving this system we obtain the equilibrium magnetization state of each superparamagnetic particle.

In the next section we find the solutions of such a system for clusters with various dimensionalities and analyze the effect of the interactions on the total magnetic moment of thousands of densely packed superparamagnetic particles assembled in 1D, 2D and 3D structures.

3. Numerical simulations

Firstly we consider a chain of n superparamagnetic particles of radius $R = 5$ nm and susceptibility $\chi = 1$ in a uniform external magnetic field $H_0 = 3000$ A/m. The particles are considered very close to each other so that the distance between the centers of any two neighbor particles is $d = 2R$. For $n = 1$ the system (6)–(8) reduces to three equations with three unknowns—the Cartesian components of the particle magnetization. In this simple situation, the magnetization is always parallel to the

applied field and has the magnitude $M = 2250$ A/m. Because this value could easily be obtained from Eq. (1) by taking $\vec{H}_i = 0$, we will refer to this particular value as the non-interacting (NI) limit. When $n \gg 1$, the mutual interactions will increase the magnetization of particles with respect to the NI value in chains parallel to the applied field (1D $\parallel$), as shown in Fig. 1 for a chain of 50 particles. When the chain is perpendicular to the magnetic field (1D $\perp$), the lateral interactions between particles diminish the local field and the magnetization of particles decreases accordingly (Fig. 1). Both parallel and perpendicular configurations indicate a uniform magnetization for all the particles in the chain except very few of them (3 up to 5) located at the chain ends, where the equilibrium magnetization is less influenced by the mutual magnetic interactions.

As the number of chained particles increases, the topology of the equilibrium magnetization curves remains similar to that shown in Fig. 1 but with an average magnetization asymptotically approaching the analytical limits for infinite chains,

$$M_{1D\parallel}^{\infty} = H_0 \left[\frac{1}{\chi} + \frac{1}{3} - \frac{v\zeta(3)}{\pi d^3} \right]^{-1}, \quad (9)$$

when the applied field $\vec{H}_0$ is parallel to the chain and

$$M_{1D\perp}^{\infty} = H_0 \left[\frac{1}{\chi} + \frac{1}{3} + \frac{v\zeta(3)}{2\pi d^3} \right]^{-1} \quad (10)$$

for the perpendicular case, where we employed the well known notation $\zeta(3)$ for the Riemann Zeta function [21]. As we can see in Fig. 2, these limits are relatively fast reached so that hundreds of chained superparamagnetic particles may already be considered equivalent to infinite chains.

Fig. 1. Magnetization along a chain of 50 densely packed superparamagnetic particles of radius $R = 5$ nm and susceptibility $\chi = 1$ in three situations: NI—non-interacting particles, 1D $\parallel$ —chain parallel to the applied field and 1D $\perp$ —chain perpendicular to the applied field.

Fig. 2. Dependence of the average magnetization on the number of superparamagnetic particles assembled in chains (1D), sheets (2D) and cubes (3D) in uniform applied magnetic field.

We consider now that the particles are located at the nodes of a 2D square lattice of constants $2R$ in both Ox and Oy directions so that the particles form a thin monolayer of superparamagnetic nanoparticles. Two orientation of a uniform applied field $H_0 = 3000$ A/m are again taken into consideration: parallel and perpendicular to the layer. As we may see in Fig. 2, these clusters undergo lower increases of the average magnetization than the superparamagnetic chains, mainly due to the lateral interactions between particles [22]. When compared to the analytical limits corresponding to infinite rectangular arrays

$$M_{2D\parallel}^{\infty} = H_0 \left[\frac{1}{\chi} + \frac{1}{3} - \frac{2.258 \cdot v}{\pi d^3} \right]^{-1} \quad (11)$$

and

$$M_{2D\perp}^{\infty} = H_0 \left[\frac{1}{\chi} + \frac{1}{3} + \frac{2.258 \cdot v}{\pi d^3} \right]^{-1}, \quad (12)$$

the average value of the equilibrium magnetization saturates only for thousands of particles. Moreover, if the effect of interactions is less important in 2D clusters of hundreds of particles, it may become comparable with the 1D case for thousands of particles. It is elementary to find from Eqs. (9) and (11) that the spacing d_1 between particles in infinite 1D chains characterized by the same magnetic moment as for infinite layers of inter-particle spacing d_2 may be expressed as

$$d_1 = d_2 \sqrt[3]{\frac{2\zeta(3)}{2.258}} \approx 1.021 \cdot d_2 \quad (13)$$

so that 1D and 2D configurations of high numbers of particles give almost the same total magnetic moment.

In order to study the influence of mutual interactions on volume distributions of superparamagnetic nanoparticles,

we consider a cubic (3D) lattice of constant $2R$ so that the particles are in contact to each other. A uniform magnetic field $H_0 = 3000$ A/m is applied perpendicular to one of the cube faces and the average magnetization of the cluster is evaluated from the solutions of Eqs. (6)–(8). As expected, volume distributions of superparamagnetic particles are almost equivalent with the NI case even if thousands of particles are assembled in densely packed clusters (Fig. 2). Obviously, this is a consequence of lateral interactions between particles that diminish the local field and so the equilibrium magnetization of the particles.

As the last example, we compute the equilibrium magnetization of clusters obtained by the formation of thousands of uniform and densely packed superparamagnetic particles on the surface of spheroids with various aspect ratios, as shown in Fig. 3(a). As we can see in Fig. 3(b), the influence of mutual interactions is almost negligible for spherical clusters ($\varepsilon = 1$), the relative variation of the total magnetic moment with respect to the NI limit being around 2% only. Prolate (circles) or oblate (triangles) spheroids in magnetic fields applied parallel to their semi-major axis present greater increases of their

magnetic moment with respect to the NI approximation. On the contrary, the magnetic moment is strongly diminished in oblate spheroids when the magnetic field is applied parallel to the semi-minor axis (dashed line). Obviously, the average magnetization of these spheroids has to be limited to the value $M_{1D\parallel}^\infty$ obtained for infinite chains—the optimal configuration for an assembly of superparamagnetic particles. As we can see in Fig. 3(b), the linear dependence of the relative variation of the total magnetic moment on the eccentricity of prolate or oblate spheroids can acceptably be approximated with a simple linear function $\xi(\varepsilon) = k_{1D}(d)(1 - \varepsilon)$. For the particles considered in this study ($R = 5$ nm, $\chi = 1$), which are almost in contact to each other ($d = 2R$), we have $k_{1D} = 17.7\%$.

For the sake of magnetic manipulation of superparamagnetic clusters in microfluidic devices, the total magnetic moment (so the total number of nanoparticles) is of great importance. The mutual magnetic interactions between nanoparticles become also important as they could increase up to 17.7% the total magnetic moment in densely packed chains of nanoparticles. It is obvious from Fig. 2 that the configuration the most suitable in order to maximize the total magnetic moment of superparamagnetic clusters corresponds to NI (spaced) chains of particles almost in contact to each other aligned parallel to the magnetic field. However, in many practical applications related to the trapping of submicronic non-magnetic objects, assemblies of several thousands of superparamagnetic nanoparticles are needed in order to provide the necessary driving force for an efficient capture and manipulation. Consequently, the chaining of such a large amount of particles becomes energetically comparable with the bi-dimensional case (as we can see in Fig. 2, for thousands of particles $M_{1D\parallel}^\infty \approx M_{2D\parallel}^\infty$). The most favorable case of long and NI chains aligned parallel to the magnetic field may be replaced in this case by a densely packed 2D sheet as the inhibiting effect of the lateral interactions on the total magnetic moment would still be minimal for such a large system.

For example, a cylindrical non-magnetic object coated with superparamagnetic nanoparticles and placed in a magnetic field presents the advantage of an important eccentricity (because it will be equivalent to spheroids of small ratios between the semi-minor and the semi-major axis). The influence of the mutual interactions on the total magnetic moment is maximal when the cylinder is coated with NI chains of nanoparticles aligned along the cylinder generators. However, if the cylinder is coated with a densely packed monolayer of nanoparticles, the increasing of the magnetic moment is two-fold: first, the number of particles increases because a densely packed monolayer contains a larger number of nanoparticles than an assembly of NI (spaced) chains and second, the effect of mutual interactions on the magnetic moment increase is still important if the total number of particles is large enough (Fig. 2). Double-, triple- or multi-layered

Fig. 3. (a) Schematic representation of a non-magnetic spheroidal particle uniformly covered with a single layer of densely packed superparamagnetic nanoparticles; (b) relative variation of the magnetic moment with respect to the non-interacting limit for several values of the ratio between the semi-minor and the semi-major axis lengths.

assemblies will have the advantage of a large number of nanoparticles but the influence of mutual interactions on the total magnetic moment will diminish as the distribution approaches the pure 3D case.

4. Conclusions

We have presented a numerical approach to finding the micromagnetic state of assemblies of interacting superparamagnetic particles. We investigated the influence of mutual interactions on the equilibrium magnetization of superparamagnetic monodisperse nanoparticles densely packed in clusters of various sizes and dimensionalities. The most suitable geometry in order to get the maximum magnetic moment from the cluster consists of chained particles along the lines of the applied magnetic field. For a high number of particles, long chains and large sheets of superparamagnetic particles present almost the same magnetic moment. Volume distributions of thousands of superparamagnetic particles are almost equivalent to NI systems so that the mutual interactions in these clusters may be neglected in a first approximation. Future works will deal with generalizations of the numerical algorithm for clusters of polydisperse nanoparticles of various size distributions.

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