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Specific Absorption Rate of Fractal-like Aggregates of Magnetic Nanopaticles

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Abstract

A specific absorption rate of fractal-like assemblies of iron oxide nanoparticles in alternating magnetic field has been calculated using stochastic Landau-Lifshitz equation which simultaneously takes into account both the presence of thermal fluctuations of the nanoparticle magnetic moments, and strong magneto-dipole interaction between the nanoparticles of the clusters. No appreciable difference in the magnetic properties of various types of fractal clusters has been revealed. It is also found that the specific absorption rate of dilute assemblies of fractal clusters shows only weak dependence on the number of the nanoparticles within the clusters.

Keywords: Magnetic nanoparticles, Fractal clusters, Magneto- dipole interaction, Low frequency hysteresis loops

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1. Introduction

Magnetic hyperthermia is one of the most promising branches of contemporary cancer treatment technologies [1, 2]. Magnetic nanoparticles have a unique property to generate heat under the influence of alternating magnetic field. However, it has been discovered recently [1-3] that a specific absorption rate (SAR) of an assembly of nanoparticles distributed in liquid is significantly higher then that of the same assembly dispersed in a biological media. One of the reasons of such behavior is the property of magnetic particles to agglomerate [4] and to form fractal-like structures [5] at in-vivo conditions. As a result, SAR of an assembly of magnetic nanoparticles distributed in tissue decreases considerably under the influence of strong magneto-dipole interactions between the nanoparticles of the cluster [4, 6]. It is well known [7] that two different types of fractal clusters can be constructed. In the first process the cluster of the nanoparticles grows by adding isolated nanoparticles moving in a surrounding media. This process of particle-cluster interaction gives fractal clusters of PC type. However, if bigger clusters

grow due to interaction of smaller clusters (cluster – cluster interaction) the clusters of CC type are obtained. The purpose of this paper is to study by means of numerical simulation the influence of the magneto-dipole interaction on SAR of fractal nanoparticle clusters of both PC and CC types.

2. Numerical Simulation

The geometry of fractal clusters of single-domain nanoparticles is characterized [5, 7] by the fractal descriptors D_f and k_f. By definition, the total number of nanoparticles N_p in the fractal cluster is given by the relation $N_p = k_f \left(2R_g/D\right)^{D_f}$, where D_f is the fractal dimension, k_f is the prefactor, D is the nanoparticle diameter, R_g being the radius of cluster gyration. The latter is defined [7] via the mean square of the distances between the particle centers and the geometrical center of mass of the aggregate. In this paper the fractal clusters with various fractal descriptors were created using the well known Filippov's et. al. algorithm [7]. As an example, Fig. 1 shows the geometrical structures of PC and CC types of fractal clusters consisting of N_p = 640 spherical nanoparticles.

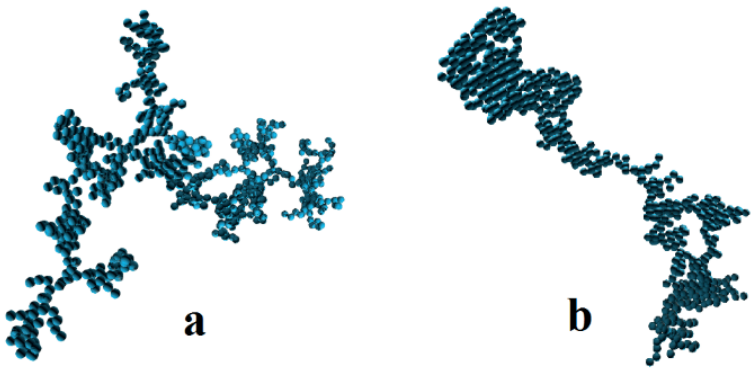

Figure 1: The structures of fractal aggregates of CC (a) and PC (b) types with fractal parameters D_f = 1.8, k_f = 1.3. The number of the nanoparticles in the clusters N_p = 640.

Dynamics of unit magnetization vector $\vec{\alpha}_i$ of i-th single-domain nanoparticle of the cluster is determined by the stochastic Landau- Lifshitz equation

$$\frac{\partial \vec{\alpha}_i}{\partial t} = -\gamma_1 \vec{\alpha}_i \times \left(\vec{H}_{ef,i} + \vec{H}_{th,i}\right) - \kappa\gamma_1 \vec{\alpha}_i \times \left(\vec{\alpha}_i \times \left(\vec{H}_{ef,i} + \vec{H}_{th,i}\right)\right), i = 1, 2, ..N_p, \quad (1)$$

where γ is the gyromagnetic ratio, κ is phenomenological damping parameter, $\gamma_1 = \gamma/(1+\kappa^2)$, $\vec{H}_{ef,i}$ is the effective magnetic field and $\vec{H}_{th,i}$ is the thermal field. The effective magnetic field acting on a separate nanoparticle can be calculated as a derivative of the total cluster energy

$$\vec{H}_{ef,i} = -\frac{\partial W}{VM_s \partial \vec{\alpha}_i}, \quad (2)$$

where V is the nanoparticle volume.

The total magnetic energy of the cluster $W = W_a + W_Z + W_m$ is a sum of the magneto-crystalline anisotropy energy W_a, Zeeman energy W_Z of the particles in applied magnetic field, and the energy of mutual magneto-dipole interaction of the particles W_m.

For nanoparticles with uniaxial type of magnetic anisotropy the magneto-crystalline anisotropy energy is given by

$$W_a = KV\sum_{i=1}^{N_p}\left(1-\left(\vec{\alpha}_i\vec{e}_i\right)^2\right), \tag{3}$$

where $\mathbf{e}_i$ is the unit vector that determines space orientation of the easy anisotropy axis of i-th particle of the cluster. Zeeman energy W_Z of the cluster in applied magnetic field $\vec{H}_0\sin(\omega t)$ is given by

$$W_Z = -M_sV\sum_{i=1}^{N_p}\left(\vec{\alpha}_i\vec{H}_0\sin(\omega t)\right). \tag{4}$$

Next, for spherical uniformly magnetized nanoparticles the magnetostatic energy of the cluster can be represented as the energy of the point interacting dipoles located at the particle centers $\mathbf{r}_i$ within the cluster. Then the magneto-dipole interacting energy is

$$W_m = \frac{M_s^2V^2}{2}\sum_{i\neq j}\frac{\vec{\alpha}_i\vec{\alpha}_j-3\left(\vec{\alpha}_i\vec{n}_{ij}\right)\left(\vec{\alpha}_j\vec{n}_{ij}\right)}{\left|\vec{r}_i-\vec{r}_j\right|^3}, \tag{5}$$

where $\mathbf{n}_{ij}$ is the unit vector along the line connecting the centers of i-th and j-th particles, respectively.

Thus, the effective magnetic field acting on the i-th nanoparticle of the cluster is given by

$$\vec{H}_{ef,i} = H_a\left(\vec{\alpha}_i\vec{e}_i\right)\vec{e}_i + \vec{H}_0\sin(\omega t) - M_sV\sum_{j\neq i}\frac{\vec{\alpha}_j-3\left(\vec{\alpha}_j\vec{n}_{ij}\right)\vec{n}_{ij}}{\left|\vec{r}_i-\vec{r}_j\right|^3}. \tag{6}$$

where $H_a = 2K/M_s$ is the particle anisotropy field.

The thermal fields $\vec{H}_{th,i}$ acting on various nanoparticles of the cluster are statistically independent, with the following statistical properties [8] of their components for every nanoparticle

$$\left\langle H_{th}^{(\alpha)}(t)\right\rangle = 0;\left\langle H_{th}^{(\alpha)}(t)\,H_{th}^{(\beta)}\left(t_1\right)\right\rangle = \frac{2k_BT\kappa}{\gamma M_sV}\delta_{\alpha\beta}\delta\left(t-t_1\right),\alpha,\beta=(x,y,z). \tag{7}$$

Here k_B is the Boltzmann constant, $\delta_{\alpha\beta}$ is the Kroneker symbol, and $\delta(t)$ is the delta function.

The procedure for solving stochastic differential equation (1), (2) and (7) is described in detail in [9-12].

3. Results and Discussion

The low frequency hysteresis loops of fractal clusters of nanoparticles in alternating external magnetic field were calculated using stochastic Landau- Lifshitz equation (1). The clusters of PC and CC types consisting of several hundreds of nanoparticles were created using Filippov's et. al. algorithm [7]. First of all we studied the dependence of the low frequency hysteresis loops of fractal clusters of PC and CC types with fractal dimension D_f = 1.8 and prefactor k_f = 1.3 on the number of the nanoparticles within the cluster. Clusters consist of spherical iron oxide nanoparticles with saturation magnetization Ms = 350 emu/cm^3, effective anisotropy constant K = 10^5 erg/cm^3 and diameter D = 20 nm. The easy anisotropy axes of the nanoparticles are randomly distributed in space. The temperature of the media T = 300 K, the frequency of the alternating magnetic field f = 300 kHz, magnetic field amplitude H_0 = 100 Oe. For every cluster type and fixed number of the nanoparticles within the clusters 10 independent numerical experiments were carried out and their results were averaged. The low frequency hysteresis loops obtained correspond to dilute random assemblies of fractal clusters of magnetic nanoparticles. They are shown in Fig. 2a for PC clusters and in Fig. 2b for CC clusters, respectively.

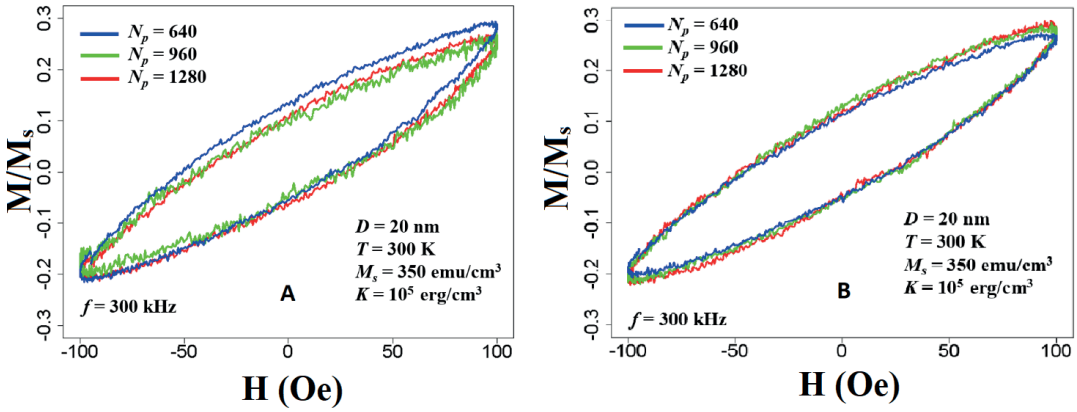

Figure 2: a) Low frequency hysteresis loops of PC type fractal clusters with various numbers of the nanoparticles within the cluster, b) the same as in a), but for fractal clusters of CC type.

As Fig. 2a shows, there is only a weak dependence of the low frequency hysteresis loops on the number of nanoparticles within the PC-type cluster. According to Fig. 2b, it is practically absent for the clusters of CC type. Fig. 3 shows the dependence of SAR on the number of particles within the clusters in the range N_p = 640 - 1280 particles. The SAR of the assemblies was calculated [12] as $SAR = 10^{-7} M_s f A/\rho$ (W/g), where A is the hysteresis loop area in the variables (M/M_s, H) and ρ = 5 g/cm^3 is the density of iron oxide nanoparticles.

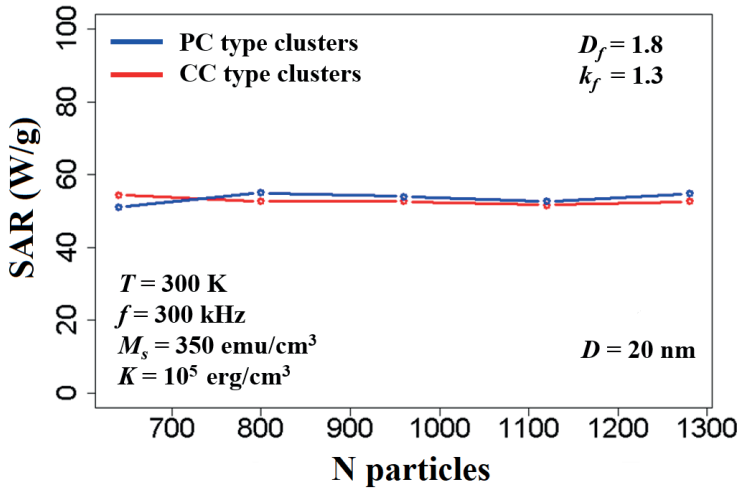

Figure 3: The dependence of SAR on the number of nanoparticles within fractal clusters of PC and CC types.

One can see in Fig. 3 that the SAR of both types of clusters is nearly the same and does not depend in the number of the nanoparticles in the cluster within of the range of N_p investigated.

The calculations in Figs. 2, 3 were carried out assuming that there is no exchange interaction between the closest nanoparticles of the cluster. It is well known that magnetic nanoparticles are usually covered with non magnetic shells to protect them from oxidation. Fig. 4 shows a structure of fractal cluster consisting of magnetic nanoparticles of diameter D having nonmagnetic shells of thickness L_s.

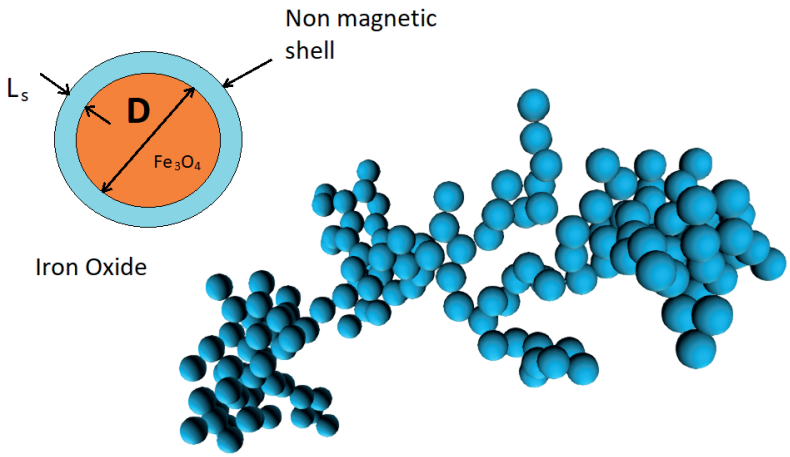

Figure 4: Structure of a CC fractal cluster of spherical magnetic nanoparticles of diameter D, having non magnetic shells of thickness L_s at their surfaces.

From the results obtained by Usov et al. [6], one can expect an increase in SAR with increase of the non magnetic shell thickness at the nanoparticle surfaces for fractal

clusters of both PC and CC types. To check this hypothesis the numerical simulations were carried out with the same magnetic parameters as in Figs. 2, 3, but for fractal clusters of magnetic nanoparticles covered with non magnetic shells with thickness in the range L_s = 1 - 20 nm. Fig. 5 shows the evolution of the hysteresis loop shape depending on the non magnetic shells thickness L_s.

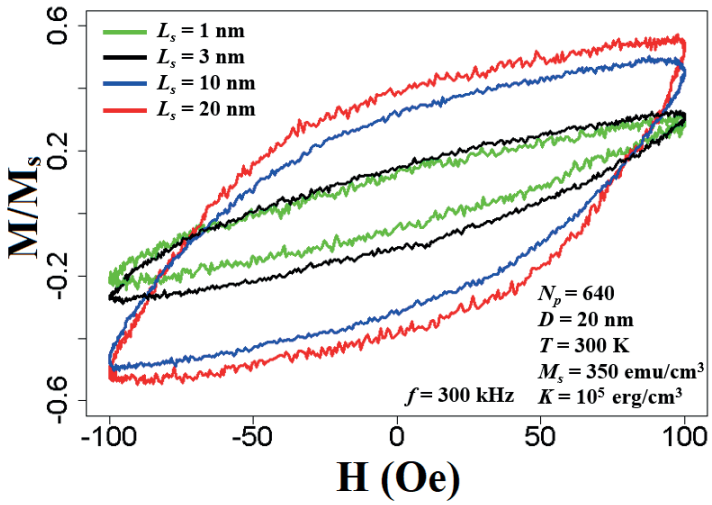

Figure 5: The dependence of the low frequency hysteresis loops of fractal clusters of nanoparticles on the thickness L_s of nonmagnetic shells at the nanoparticle surfaces.

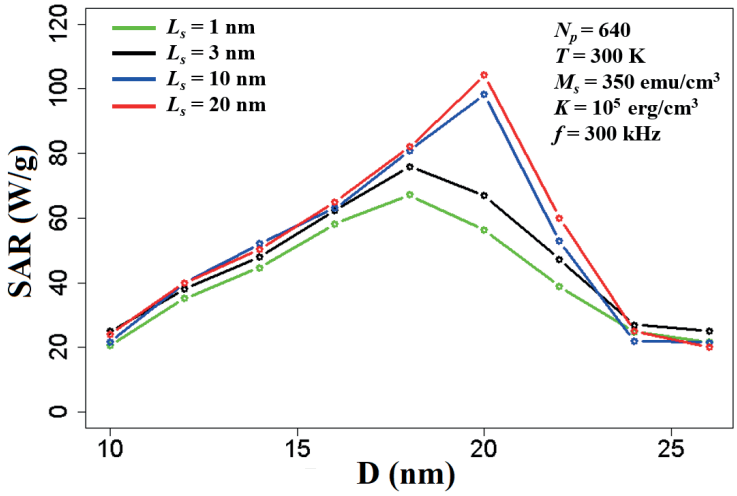

Figure 6: The dependence of the SAR of fractal clusters of nanoparticles on the particle diameter D for various thickness L_s of the non-magnetic shells at the nanoparticle surfaces.

The same calculations were also made for fractal clusters of nanoparticles of different diameters. As Fig. 6 shows, for all cases considered there is an optimal diameter of the nanoparticles corresponding to the maximal SAR value. In addition, in accordance with the results obtained previously [6] for fractal clusters of PC type with relatively

small number of magnetic nanoparticles, N_p = 90, the maximal SAR value increases as a function of the non magnetic shell thickness L_s.

4. Summary

In summary, in this paper it is proved that despite the visual difference in geometrical structures of PC and CC types of fractal clusters shown in Fig. 1, there is no appreciable difference in their magnetic properties in low frequency alternating magnetic field. It is also found that the SAR of dilute assemblies of fractal clusters of nanoparticles shows only weak dependence on the number of the nanoparticles within the cluster. These findings seem to be the consequence of the fact that the fractal clusters of PC and CC types differ mainly in their global structure, at the distances much larger than the average particle diameter. But at large distances the intensity of the magneto-dipole interaction decreases and it has negligible influence on the assembly behaviour.

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