Specific loss power in superparamagnetic hyperthermia: nanofluid versus composite

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Abstract. Currently, the magnetic hyperthermia induced by nanoparticles is of great interest in biomedical applications. In the literature, we can find a lot of models for magnetic hyperthermia, but many of them do not give importance to a significant detail, such as the geometry of nanoparticle positions in the system. Usually, a nanofluid is treated by considering random positions of the nanoparticles, geometry that is actually characteristic to the composite nanoparticles. To assess the error which is frequently made, in this paper we propose a comparative analysis between the specific loss power (SLP) in case of a nanofluid and the SLP in case of a composite with magnetic nanoparticles. We are going to use a superparamagnetic hyperthermia model based on the improved model for calculating the Néel relaxation time in a magnetic field oblique to the nanoparticle magnetic anisotropy axes, and on the improved theoretical model LRT (linear response theory) for SLP. To generate the nanoparticle geometry in the system, we are going to apply a Monte Carlo method to a nanofluid, by minimising the interaction potentials in liquid medium and, for a composite environment, a method for generating random positions of the nanoparticles in a given volume.

1. Introduction
The magnetic nanoparticles in suspension in a liquid medium (nanofluid), subjected to a high frequency alternating magnetic field, can generate heat through magnetic losses. This local heat can lead to the destruction of cancer cells. Depending on the increasingly higher nanoparticle diameters, there are, according to the literature, three mechanisms for generating heat by magnetic hyperthermia: susceptibility loss, hysteresis loss and viscous heating (magnetic stirring loss). The specific loss power (SLP) is defined as electromagnetic power lost per magnetic material mass unit and is expressed in watts per kilogram. The mostly used particles in magnetic hyperthermia are the magnetite ones, because of their biocompatibility and low toxicity. The susceptibility loss occurs in superparamagnetic particles. The agglomeration and sedimentation tendency increases considerably with the transition from small nanoparticles to stable single-domain ferromagnetic particles [1], in which case the mechanism of generating hysteresis heat is predominant. Unfortunately, while the particle size is increasing, the agglomeration and sedimentation tendency determines the clogging of blood vessels, situation which is therapeutically unacceptable. The heat generation by magnetic stirring loss occurs when the particles are large enough. Most of these particles are not aligned to the applied field axis, and therefore the particle stirring leads to viscous heating [2]. This stirring can add heat to the system.

These mechanisms for generating heat by magnetic hyperthermia are generally quite complex, because they involve a number of parameters, such as: external magnetic field strength and frequency,
Recent modelling studies have investigated the main mechanisms for generating heat by magnetic hyperthermia, i.e. susceptibilities loss and hysteresis loss, without taking into account the particle positions [3-7].

Other current models take also into account the particle positions, such as the particle concentration. Some of these models are studying the influence of anisotropy axes orientation (with respect to the external magnetic field) on the properties of magnetic hyperthermia, when the particles have random positions in a given volume, as in the case of particles spread in non-magnetic solid matrix [8-10], others take into account the particle organisation (as in liquid matrix), but under the influence of a generic repulsive dimensionless force [11].

In a liquid medium, the particle organisation is clearly different than in a solid medium, and depends on the attractive and repulsive interaction forces exerted on the particle. Some recent papers showed experimentally a tendency to agglomeration, even in the absence of an external magnetic field [12], [13]. This trend, which can determines the clogging of the blood vessels through which the hyperthermia agent is circulating (see [1]), can also increase the influence of magnetic dipolar interactions on the heat generation process. If we apply a nanoparticle positioning like in solid matrix for magnetic hyperthermia therapy, it means to further use an approach beyond reality.

This paper adopts a model for superparamagnetic hyperthermia with spherical nanoparticles. Using this model, we can study how the nanoparticle organisation in non-magnetic liquid or solid matrix influences the SLP. Since the magnetic hyperthermia agent is a nanofluid reaching the affected zone through the bloodstream, it is shown the fact that using in studies a random-type organisation in a given volume, specific to the solid matrix, is not the best choice.

2. Nanoparticle organisation in non-magnetic liquid or solid matrix
In our model, we define a system of $N$ spherical nanoparticles. Each nanoparticle $i$ has a magnetic moment $\mu_i$ and a radius $r_i$. Initially, the orientation of the magnetic moments is random.

In case of solid matrix, the possible positions are: simple-centred cubic lattice, base-centred cubic lattice, and face-centred cubic lattice. Among all the possible positions, the particles have been located in randomly selected suitable locations, according to the ratio between the volumes of the considered nanoparticles and the whole volume of the simulation box. The periodic boundary conditions have been applied on all sides of the simulation box. In Figure 1, we show such arrangement for 500 nanoparticles in a face-centred cubic lattice, where the volume fraction of nanoparticles is 0.05.

![Figure 1. Nanoparticles randomly positioned in a face-centred cubic grid](image)
The nanoparticles dispersed in a carrier fluid form superparamagnetic colloids or nanofluids. The nanofluids are basically classified into two groups: ionic nanofluids and surfactant nanofluids, depending on whether the colloidal stability is provided by electrostatic or steric repulsive interactions, respectively. In the recent years, a new class of ferrofluids, which are ultrastable and often biocompatible, have been developed using a combination of both stabilisation methods [14]. We further describe the positioning in case of liquid matrix. The nanoparticles are coated with a surfactant layer whose thickness is $\delta$, and the number of molecules adsorbed on each nanoparticle surface is $\zeta$. In case of electrosteric stabilisation, the nanoparticle surface charge is $q$. The 3D arrangement of the particles was initially made randomly in grid, and then we fixed the nanoparticle positions in a simple-centred cubic lattice, a body-centred cubic lattice, and a face-centred cubic lattice.

The stability of a magnetic colloidal suspension results from the equilibrium between the attractive and repulsive forces. Theoretically, two types of forces can contribute to the interparticle potential in the system: van der Waals force and electrostatic repulsive force. The Van der Waals forces induce strong short-range isotropic attractions [15-16]. The electrostatic repulsive forces [15], [17-19], can be partially screened by adding salt to the suspension. The steric repulsion forces [20], [21] have to be taken into account for coated nanoparticles. Finally, the magnetic dipolar forces [22] between two particles must be also added in case of magnetic suspensions.

The local magnetic field $\vec{H}_i$ on each nanoparticle results from a vectorial sum of the applied external magnetic field ($\vec{H}_{ext}$) and the internal dipolar magnetic field $\vec{H}_{id}$:

$$\vec{H}_i = \vec{H}_{ext} + \vec{H}_{id}$$

In colloid, the nanoparticles form aggregations leading to an increase in the local concentration of nanoparticles, and so the effect of dipolar magnetic interaction can be significant.

In simulating the positioning of the nanoparticle and the orientation of their magnetic moments, we neglect the internal dynamics of the magnetic moments and consider only their external dynamics caused by the nanoparticle rotation. We considered the initial size of the cubic simulation box (i.e. the size calculated with the algorithm for random 3D layout in grid) in a simple-centred cubic lattice, body-centred cubic lattice, and face-centred cubic lattice.

For positioning and orientation by minimising the potential energy of the system, we are going to use a Monte Carlo method applying the Metropolis Hastings algorithm – the so called “off-lattice” model [23].

The method used in our paper is based on changing the nanoparticle position and orientation of its magnetic moment by minimising the assembly of potentials exercised between the concerned nanoparticle and the other nanoparticles of the colloid. The “assembly of potentials” means: the van der Waals potential, the potential of double layer electrostatic interaction and/or the steric stabilisation potential and magnetostatic potential:

$$V_i = \sum_{j \neq i} V_{vdw,ij} + \sum_{j \neq i} V_{el,DL,ij} + \sum_{j \neq i} V_{steric,ij} + \sum_{j \neq i} V_{d,ij}$$

The dipolar magnetic potential is calculated by direct summation. To equilibrate the system by minimising the potential energy, we use 5000 MCS moves.

In Figure 2, we show the simulation result for 500 spherical magnetite nanoparticles whose volume fraction is 0.08, dispersed in water and positioned in a self-organised system, the intensity of external magnetic field being 15kA/m.
One can easily see a clear tendency of nanoparticles towards self-organisation. The nanoparticles can form chains and other forms of clusters, which can cause a local increase in the nanoparticle volume fraction, influencing therefore the magnetic behaviour of the system.

3. Numerical calculation of the specific loss power
The specific loss power (SLP) is defined as the electromagnetic power lost per nanofluid mass unit, and it is expressed in watt per kilogram. For SLP calculation, within the range of external magnetic field amplitudes suitable for medical applications [16], we can use the linear response theory (LRT) [24]. In this theory, the volumetric power dissipation is expressed as:

$$ P = \pi \mu_0 \chi_0 H_{0,\text{ext}}^2 \nu \frac{2\pi \nu \tau}{1 + (2\pi \nu \tau)^2} $$

(3)

where $\nu$ and $H_{0,\text{ext}}$ are the frequency and magnitude of the applied field, $\mu_0$ is the magnetic permeability of free space, $\chi_0$ is the equilibrium susceptibility and $\tau$ is the magnetic relaxation time. The equation (3), in its original form, applies to nanoparticles monodispersed in sizes, which do not interact magnetically dipolarly, and for which $\chi_0$ is constant [24].

We are going to use a generalised variant of the equation (3) for spherical nanoparticles, polydispersed in sizes, which interact magnetically dipolarly, showing distribution of the magnetic anisotropy constants [24]. Moreover, compared to [25], we will take into account the influence of directions of easy magnetisation axes on the equilibrium susceptibility [26-29]. The power dissipation on nanoparticle is volumetrically calculated, after which we find the average.

For dispersion in solid matrix:

$$ P = \pi \mu_0 H_{0,\text{ext}}^2 \nu \sum_{i=1}^{N} \frac{2\pi \nu \tau_i \chi_0 i}{1 + (2\pi \nu \tau_i \chi_0 i)^2} $$

(4)

where $\tau_i$ stands for “Néel relaxation time”. The Néel relaxation process is the solid state mechanism occurring inside the nanoparticle, which corresponds to the magnetic moment rotation between two equilibrium positions, when considering the nanoparticle as fixed in space.

For dispersion in liquid matrix:
\[
\rho = \pi \mu_0 H_{0,ext}^2 \frac{1}{N} \sum_{i=1}^{N} 2\pi v_i^{eff} \chi_{0i} \left( \frac{1}{1 + (2\pi v_i^{eff})^2} \right) \tag{5}
\]

Using the effective relaxation time for the particle \(i (\tau_i^{eff})\) and the equilibrium susceptibility for the particle \(i (\chi_{0i})\), the effective relaxation time can be described as follows [30]:

\[
\frac{1}{\tau_i^{eff}} = \frac{1}{\tau_i^{N}} + \frac{1}{\tau_i^{B}} \tag{6}
\]

where \(\tau_i^{B}\) is the Brownian relaxation time for the particle \(i\). The Brownian process represents the nanoparticle rotation in the fluid environment. For spherical particles, the Brownian relaxation time is usually described by:

\[
\tau_i^{B} = \frac{3v_i H_0 \eta}{k_B T} \tag{7}
\]

where \(k_B\) is the Boltzmann constant, \(T\) is the temperature, \(v_i\) is the hydrodynamic volume of the particle \(i\), and \(\eta\) is the coefficient of dynamic viscosity.

The relaxation mechanism which dominates the magnetic behaviour of the colloidal suspensions is determined by the nanoparticle properties. This two relaxation processes are treated separately.

For \(\chi_{0i}\), we use the expression [26-29]:

\[
\chi_{0i} = 3\varepsilon_i \chi_L^i 
\]

\[
\varepsilon_i = \left( \frac{\sigma_i}{3.4} \right)^{1.47} \cos^2 \Psi_i + \frac{1}{3}
\]

\[
\Psi_i = \frac{K_{eff,i} V_i}{k_B T} \tag{9}
\]

where \(\sigma_i = \frac{K_{eff,i} V_i}{k_B T}\)

and \(\Psi_i\) is the angle between the easy magnetisation axis and the direction of the applied field (the field direction is the same with the measurement direction). \(K_{eff,i}\) is effective magnetic anisotropy constant of of the \(i\)-th nanoparticle and \(V_i\) is magnetic core volume of the \(i\)-th nanoparticle.

\[
\hat{\chi}_L = \frac{f_m M_s}{H_{0,ext}} \left( \coth\left( \xi_i \right) - \frac{1}{\xi_i} \right) \tag{11}
\]

\[
\xi_i = \frac{H_0 M_s V_i}{k_B T} \tag{12}
\]

and \(f_m\) is magnetic volume fraction of the nanoparticles. \(f_m\) is correlated with volume fraction of nanoparticles by the relation [30]:

\[
\theta = \pi \mu_0 H_{0,ext}^2 \frac{1}{N} \sum_{i=1}^{N} 2\pi v_i^{eff} \chi_{0i} \left( \frac{1}{1 + (2\pi v_i^{eff})^2} \right)
\]

\[
\frac{1}{\tau_i^{eff}} = \frac{1}{\tau_i^{N}} + \frac{1}{\tau_i^{B}}
\]

\[
\tau_i^{B} = \frac{3v_i H_0 \eta}{k_B T}
\]

\[
\chi_{0i} = 3\varepsilon_i \chi_L^i
\]

\[
\varepsilon_i = \left( \frac{\sigma_i}{3.4} \right)^{1.47} \cos^2 \Psi_i + \frac{1}{3}
\]

\[
\Psi_i = \frac{K_{eff,i} V_i}{k_B T}
\]

\[
\hat{\chi}_L = \frac{f_m M_s}{H_{0,ext}} \left( \coth\left( \xi_i \right) - \frac{1}{\xi_i} \right)
\]

\[
\xi_i = \frac{H_0 M_s V_i}{k_B T}
\]
In relation (13) \( d_m \) is the average diameter of the nanoparticles.

Let \( M_s \) be the spontaneous magnetisation, \( k_B \) the Boltzmann constant and \( T \) the temperature. For solid matrix:

\[
SLP = \frac{P}{f_0} = 3\pi\mu_0H_{0,\text{ext}}\mu N \sum_{i} N_{i} \left( \coth(i) - \frac{1}{i} \right) \left( 1 + \frac{2\pi v_\tau N}{f_0} \right) \]

For the nanofluid:

\[
SLP = \frac{P}{f_0} = 3\pi\mu_0H_{0,\text{ext}}\mu N \sum_{i} N_{i} \left( \coth(i) - \frac{1}{i} \right) \left( \frac{2\pi v_\tau N}{f_0} \right) \]

where \( \rho \) is the density of the nanoparticle material.

The numerical calculation of Néel relaxation time is made taking into account the fact that the dipolar magnetic field on the nanoparticle and the external magnetic field create together a resultant magnetic field \( \vec{H}_i \) that does not generally act along the direction of the nanoparticle easy magnetisation axis. If denoting with \( \Psi_i \) the angle between \( \vec{H}_i \) and the easy anisotropy axis of the \( i \)-th nanoparticle, we obtain:

\[
h_i = \frac{\mu_i M_s H_i}{2K_i^{\text{eff}}} \]

where \( K_i^{\text{eff}} \) is the effective magnetic anisotropy constant of the \( i \)-th nanoparticle.

The free diffusion time of magnetisation \( \tau'_{0N} \) for low damping is [31]:

\[
\tau'_{0N} = \frac{v_0 M_s}{2\gamma \alpha k_B T} \]

where \( \alpha \) is the damping constant and \( \gamma \) is the gyromagnetic ratio. For most systems of ferro- and ferrimagnetic nanoparticles, the values of the magnetic damping constant \( \alpha \) are close to the lower limit \( (\alpha \ll 1) \) [32-34].

The nanoparticle relaxation in oblique magnetic fields was studied by Coffey and other colleagues [35]. This calculation shows the relaxation time dependence on the magnetic damping constant \( \alpha \). In these conditions, the relaxation time relationship for an oblique magnetic field is [35]:

\[
\tau'^{i}_{N(\text{oblique \_field})} = \frac{4\pi \tau'_{0N} \left( S_{11}^{-1} + S_{12}^{-1} \right)}{\sqrt{c_{11}^{(1)} c_{12}^{(1)} \cdot e^{-\Delta E_{112}} + c_{11}^{(2)} c_{12}^{(2)} \cdot e^{-\Delta E_{121}}}} \]

where \( \Delta E_{112} \) and \( \Delta E_{121} \) are the normalised energy barriers for magnetic moment re-orientations.

In equation (18):
\[ c_{ii}^{(p)} = 2\sigma_i (\cos 2\theta_p + h_i \cos(\theta_p - \varphi_i)), \quad c_{i2}^{(p)} = 2\sigma_i (\cos^2 \theta_p + h_i \cos(\theta_p - \Psi_i)), \] 
with \( p = 1, 2 \) (19)

where \( \theta_p \) are the solutions of the transcendental equation \( \sin 2\theta_i = 2h_i \sin(\Psi_i - \theta_i) \).

If \( h_i < h_a(\Psi_i) < 1 \):

\[ \cos 2\theta_{i1,2} = \pm \frac{h_i^5}{2} \sin^3 \Psi_i \pm \frac{h_i^4}{16} (3 + 11 \cos 2 \Psi_i) \sin^2 \Psi_i + \frac{h_i^6}{64} (183 + 156 \cos 2 \Psi_i - 19 \cos 4 \Psi_i) \sin^2 \Psi_i + ... \] 

(20)

\[ \Delta E_{i12} = \sigma_i [1 - 2h_i (\sin \Psi_i - \cos \Psi_i)] + \frac{h_i^3}{2} \sin 2\Psi_i (\cos \Psi_i - \sin \Psi_i) + \frac{h_i^4}{2} \sin^2 2\Psi_i + \frac{h_i^5}{32} \sin 2\Psi_i (7 \cos \Psi_i - 3 \cos 3 \Psi_i - 7 \sin \Psi_i - 3 \sin 3 \Psi_i) + \frac{h_i^6}{2} \sin^2 2\Psi_i + ... ] \] 

(21)

\[ \Delta E_{i21} = \sigma_i [1 - 2h_i (\sin \Psi_i + \cos \Psi_i)] + \frac{h_i^3}{2} \sin 2\Psi_i (\cos \Psi_i + \sin \Psi_i) + \frac{h_i^4}{2} \sin^2 2\Psi_i + \frac{h_i^5}{32} \sin 2\Psi_i (7 \cos \Psi_i + 3 \cos 3 \Psi_i + 7 \sin \Psi_i + 3 \sin 3 \Psi_i) + \frac{h_i^6}{2} \sin^2 2\Psi_i + ... ] \] 

(22)

\[ S_{i1,2} = \sigma_i \sqrt{h_i \sin \Psi_i} [16 - \frac{104}{3} h_i \sin \Psi_i + h_i^2 (1 - 21 \cos 2 \Psi_i) + \frac{h_i^4}{2} \sin \Psi_i (45 + 51 \cos 2 \Psi_i) + ... ] \pm \] 

\[ \pm 2\pi \sigma_i h_i^2 \sin 2\Psi_i (4 - 3h_i \sin \Psi_i - 2h_i^2 \sin^2 \Psi_i + ... ) \] 

(23)

In addition to our model presented in [36], we considered the coated nanoparticles, size and uniaxial magnetic anisotropy constants distribution and we incorporates the dependence on the distributions of particle size, anisotropy values, and anisotropy easy axis directions in the equilibrium susceptibility calculs.

4. Results and discussions

We chose a system consisting of 500 spherical magnetite nanoparticles with spontaneous magnetisation \( 4.46 \times 10^5 \) A/m, whose sizes and effective magnetic anisotropy constants had lognormal distribution, were dispersed in water (dynamic viscosity: \( 8.9 \times 10^{-4} \) Pa-s), and the relative electrical permittivity was 78.5.

For this study, we considered the case of a colloid with electrosteric stabilisation. The parameters of the system were: the average diameter of the nanoparticles \( d_m = 10 \) nm and \( d_m' = 15 \) nm with the standard deviation parameter \( 0.25d_m \), the effective magnetic anisotropy constant \( K_{\text{eff}} = 2.5 \times 10^4 \) J/m\(^3\) with the standard deviation parameter \( 0.1K_{\text{eff}} \), the coating thickness of 2 nm, the number of polymer molecules adsorbed on the nanoparticle surface \( \zeta = 10^{-18} \) molecules/m\(^2\), the surface charge \( 1.6 \times 10^{-16} \) C, the concentration of ions in solution \( 10^{26} \) ions/m\(^3\), the Hamaker constant for magnetite in water \( A = 39 \times 10^{-20} \) J and the temperature \( T = 298.15 \) K. We varied the nanoparticle volume fraction from 0.02 to 0.24.

In the first stage, we calculated SLP using the equation (14) for solid matrix and the equation (15) for liquid matrix (Figures 3 and 4).
In the second stage of numerical experiment, we calculated the SLP value using the effective relaxation time, i.e. for the nanofluid, but with random positioning (as in case of solid matrix), and then with the particle positioning like in liquid matrix (Figures 5 and 6).

Figure 3. SLP versus volume fraction of nanoparticles (the average diameter of the nanoparticles 10 nm)

Figure 4. SLP versus volume fraction of nanoparticles (the average diameter of the nanoparticles 15 nm)

Figure 5. SLP versus volume fraction of nanoparticles for a nanofluid (the average diameter of the nanoparticles 10 nm)
Regardless of the average diameter, it can be seen that either in case of solid matrix or liquid matrix stands out a value of the concentration for which SLP is maximal. Similar results with regard to maximum heating at a specific volume fraction were obtained in other studies current experimental [37]. In case of a liquid matrix, the maximum is moving towards higher concentrations of nanoparticles and has higher values than for solid matrix. It can be seen that, at large and very low concentrations, there is no difference between the values of SLP, but the differences are significant at low and medium concentrations. It can be seen that, for nanoparticles with 15 nm average diameter, there is no so much difference between the values of SLP, but the differences are significant, for nanoparticles with 10 nm average diameter, at low and medium concentrations.

5. Conclusions
In this paper, we wanted to point out that, in magnetic hyperthermia modelling, the nanoparticle positioning geometry in a nanofluid, aspect neglected in most models, is especially important for low and medium concentrations of nanoparticles, case used in the therapeutic practice.

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