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Research Paper

A New Classical-Quantum Model for Comparing the Magnetization of Ferromagnetic and Superparamagnetic Nanoparticles During Magnetic Hyperthermia

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ABSTRACT

In the present work, for the first time, a classical-quantum model is established for comparing the magnetization of ferromagnetic/ superparamagnetic nanoparticles under AC magnetic fields (during the magnetic hyperthermia process). For this purpose, the fundamental Brillouin function was used and the physical properties of ferromagnetic and superparamagnetic nanoparticles were separated using this function. In the following, using the presented model, the magnetization of magnetic nanoparticles was compared under AC magnetic field. The results showed that in both classical and quantum states, the magnetization of ferromagnetic nanoparticles under an AC magnetic field was higher than that of superparamagnetic ones. Also, to confirm the correctness of the presented model, the output of the model was adapted to the Curie law in the classical mode and the Curie-Weiss law in the quantum mode. The correspondence between the magnetization obtained from the proposed model and the magnetization obtained from the Weiss molecular field was also confirmed.

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1. Introduction

Magnetic hyperthermia is a process in which magnetic nanoparticles generate heat under alternating magnetic fields [1]. This heat is used to destroy cancer cells [2]. Nowadays, superparamagnetic nanoparticles [3-6] and rarely soft ferromagnetic ones [7-11] are commonly used as heating nuclei in magnetic hyperthermia. The major difference in the diameter of nanoparticles in these two types of materials causes different heating mechanisms to be reported for them.

The issue of whether the magnetization of ferromagnetic or superparamagnetic nanoparticles (under AC magnetic fields) is better has always been investigated experimentally, but it has never been addressed theoretically and within the framework of quantum/classical general rules. This issue is very important because if the parameters affecting these two states of the material are identified by a general rule, the lowest dose of magnetic material with the highest heating rate is obtained in magnetic hyperthermia.

Among the models presented so far for magnetic hyperthermia, the linear response model is the only model that reports the effect of process parameters on the magnetization of magnetic nanoparticles under AC magnetic fields [12]. However, this model is limited to simulating the behavior of superparamagnetic nanoparticles [13] and is not able to analyze the behavior of ferromagnetic nanoparticles. On the other hand, this model and the models derived from this model have always examined the conditions in the classical spectrum but not in the quantum one.

In this research, as a novel work, the linear response model for nanoparticles with soft ferromagnetism is developed in the field and frequency range of magnetic hyperthermia. Also, the range of activities of thermal mechanisms is determined and adapted for physical and experimental studies. Also, by presenting a general relationship for magnetic nanoparticles, their thermal potential is compared and evaluated. On the other hand, by focusing on the study of single domain nanoparticles, the hysteresis loss mechanism is ignored. Moreover, a theoretical law is established for comparing the magnetization of ferromagnetic and superparamagnetic in classical and quantum forms. On the other hands, using the presented model, the magnetization of magnetic nanoparticles under AC magnetic field was compared in classical and quantum states.

2. Calculations-results and discussions

The principle of quantum mechanics is based on the assumption that the energy of a system has discrete values. The magnetic moment (μ_H) in the quantum state is obtained from the following relation (which is equivalent to $\mu\cos\theta$ in the classical form) [14]:

$$\mu_H = gM_J\mu_B \quad (1)$$

where μ_B is the Bohr magneton, g (G-factor) is equal to 2 for net spin moment and 1 for net orbital moment and M_J is the quantum number associated with J [14].

2.1 Development of classical-quantum model

According to the laws of classical physics, the relationship between magnetization and magnetic moment is established using the Brillouin function [14]:

$$M = n\mu\underbrace{\frac{2j+1}{2j}\coth\left(\frac{2j+1}{2j}\right)\lambda-\frac{1}{2j}\coth\left(\frac{\lambda}{2j}\right)}_{B(\lambda)} = n\mu B(\lambda) \quad (2)$$

where $B(\lambda)$ is Brillouin function and *j* is the total angular momentum (the sum of spin and orbital momentum), and λ is calculated from Eq. 3:

$$\lambda = \frac{\mu H}{k_b T} \quad (3)$$

where *H* is the magnetic field, *T* is the temperature and K_b is the Boltzmann constant.

In the quantum form, the magnetization is calculated according to the Brillouin function from Eq. 5:

$$M = n\mu_B Jg\underbrace{(\frac{2j+1}{2j}\coth\left(\frac{2j+1}{2j}\lambda'\right)-\frac{1}{2j}\coth\left(\frac{\lambda'}{2j}\right))}_{B(\lambda')} = n\mu_B JgB(\lambda') \quad (4)$$

where $B(\lambda')$ is the Brillouin function and $\lambda' = Jg\mu_B H / k_b T$.

The Taylor expansion of this function is:

$$B(\lambda') = \frac{j+1}{3j}\lambda' - \frac{\left((j+1)^2+j^2\right)(j+1)}{90j^3}\lambda'^3 + \ldots \quad (5)$$

According to Eq. 2 (Brillouin relation in classical physics), superparamagnetic and ferromagnetic states can be precisely separated based on their physical properties. In the classical form, superparamagnetic materials with a small amount of anisotropy energy will have infinite spin orientation and therefore the total angular momentum will tend to infinity ($j\to\infty$). In other words, in superparamagnetic materials, according to the Brillouin function, the normalized magnetization, *m*, is obtained from Eq. 6:

$$m = \frac{M}{M_s} = \frac{M}{n\mu} = \coth\lambda - \frac{1}{\lambda} = L(\lambda) \quad (6)$$

In this case, the normalized magnetization is equal to the Langevin function, $L(\lambda)$.

In a ferromagnetic state, with the increase in nanoparticle volume and subsequent increase in anisotropy energy, the macrospin will only be able to choose two easy directions for rotation. In other words, *j*=1/2. In this case, according to the Brillouin function (Eq. 2), the normalized magnetization is obtained from Eq. 7:

$$m = \frac{M}{M_s} = \tanh\lambda \tag{7}$$

From **Fig. 1a** and **1b** (In two magnifications), it is clear that the slope of the $tanh\lambda$ graph is greater than that of $L(\lambda)$ one.

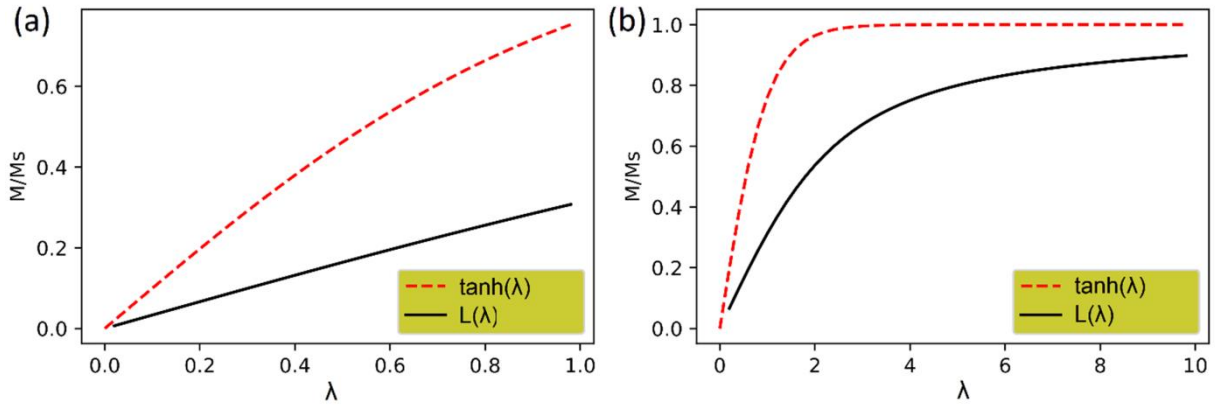

Fig. 1. Comparison between the magnetization of superparamagnetic ($L(\lambda)$) and ferromagnetic ($tanh\lambda$) nanoparticles in two magnifications.

2.2 Correlation of the presented model with magnetic hyperthermia

Applied fields in the magnetic hyperthermia process are approximately in the range of 50 to 400 Oe. If the maximum of these values, i.e. 400 Oe (32kA/m), is considered as a commonly applied field, the value of the λ parameter (λ is dimensionless) will be much less than one:

$$\lambda = \frac{\mu H}{K_b T} = \frac{\mu_0 M_s V H}{K_b T} = \frac{\left(1.2\times10^{-6}\frac{kg.m}{s^2.A^2}\right)\times\left(1.2\times10^{-2}\frac{A}{m}\right)\times\left(4.1\times10^{-24}m^3\right)\times\left(32\times10^{3}A/m\right)}{\left(1.38\times10^{-23}\frac{m^2.kg}{s^2.K}\right)\times\left(300K\right)} << 1 \tag{8}$$

Combining Eq. 6 and Eq. 8, $L(\lambda)$ is convergent to $\frac{\lambda}{3}$ (for small values of λ) and has a linear behavior (**Fig. 1a**). Therefore, it can be concluded (from Eq. 2) that the magnetization always depends on λ and is obtained from $M = n\mu\frac{\lambda}{3}$.

2.3 Adapting the model to classical physics

From section 2-2, it was found that the magnetization of the nanoparticles is obtained from Eq. 9 (under magnetic hyperthermia) as follow:

$$M = 1/3 n\mu\lambda = \frac{M_S \mu H}{3k_b T} \tag{9}$$

According to the definition of susceptibility ($\chi = \frac{M}{H}$) and Eq. 9, one can write:

$$\chi = \frac{M}{H} = \frac{\mu M_S}{3k_b}.\frac{1}{T} = \underset{C}{C/T} \tag{10}$$

which fully obeys Curie's law. Therefore, the presented model is fully compatible with the concepts of classical physics.

2.4 Adapting the model to quantum physics

In the quantum form, according to Eq. 4 (and its Tylor expansion, Eq. 5), and also according to the low amount of λ in magnetic hyperthermia (Eq. 8), the conformity of the model with the Curie's law is quite clear:

$$B(\lambda') = \frac{J+1}{3J}\lambda' = \frac{J+1}{3J}\times\frac{Jg\mu_B H}{k_b T} \rightarrow \chi = \frac{ng^2 J\left(J+1\right)\mu_B^2}{3k_b T} = \frac{C}{T} \tag{11}$$

2.5 Comparing the magnetization of ferromagnetic and superparamagnetic nanoparticles in classical form

As can be seen in **Fig. 1a**, when λ<1 in superparamagnetic nanoparticles, there is a completely linear behavior between magnetization and the applied field (λ is the representative of the applied field). This is while this linear behavior is observed for ferromagnetic nanoparticles at $\lambda < 0.5$ (**Fig. 1a**). If $\lambda = 0.5$ is assumed as the maximum limit of compliance of ferromagnetic (*fm*) and superparamagnetic (*sm*) nanoparticles to the linear behavior, then:

$$\frac{m_{fm}}{m_{sm}} = \frac{\tanh\lambda}{\coth\lambda - \frac{1}{\lambda}} \xrightarrow{\lambda=0.5} \frac{m_{fm}}{m_{sm}} = 2.8 \qquad (12)$$

Combining Eq. 9 and Eq. 12, one can say that the magnetization for ferromagnetic nanoparticles is obtained from Eq. 13:

$$M = 2.8 \times (1/3n\mu\lambda) = 0.93n\mu\lambda \qquad (13)$$

It is clear from Eq. 13 that the magnetization of ferromagnetic materials in the classical form is at least 2.8 times of superparamagnetic materials (under an AC magnetic field during the magnetic hyperthermia process).

2.6 Comparing the magnetization of ferromagnetic and superparamagnetic nanoparticles in quantum form

In the quantum form, the total angular momentum, *j*, consists of discrete values. If it is assumed that there is only pure spin moment without orbital moment, then *j*=1/2. With this assumption, the value of the Brillouin function is in accordance with that presented in Eq. 14 :

$$B(\lambda') = \tanh(\lambda') \qquad (14)$$

λ' in the quantum, form is affected by the applied field ($\lambda' = Jg\mu_B H / k_b T$). This parameter is different in ferromagnetic and superparamagnetic nanoparticles. To explain this matter, we should pay attention to Weiss molecular field ($H_W = \gamma M$, γ is called molecular field constant). For ferromagnetic nanoparticles, the amount of this field is much higher than for superparamagnetic nanoparticles. In other words:

$$H_{W,Ferromagnetic} > H_{W,\mathrm{sup}erparamagnetic} \rightarrow \frac{Jg\mu_B\left(H + H_{W,Ferromagnetic}\right)}{k_b T} > \frac{Jg\mu_B\left(H + H_{W,\mathrm{sup}erparamagnetic}\right)}{k_b T}$$

$$\rightarrow \lambda'_{Ferromagnetic} > \lambda'_{Superparamagnetic}$$

Therefore, the amount of λ' in ferromagnetic nanoparticles will be higher than that of superparamagnetic one, and as a result:

$$\tanh\left(\lambda'\right)_{Ferromagnetic} > \tanh\left(\lambda'\right)_{Superparamagnetic} \qquad (15)$$

These results fully confirm the results of the classical analysis.

2.7 Model compliance with Curie-Weiss law in quantum form

According to the molecular field, γM, the λ' variable is obtained from Eq. 16:

$$\lambda' = \frac{Jg\mu_B\left(H + \gamma M\right)}{k_b T} \rightarrow \frac{M}{M_S} = \left(\frac{k_b T}{Jg\mu_B M_S}\right)\lambda' - \frac{H}{\gamma M_S} \qquad (16)$$

From the combination of Eq. 16 and Eq. 5 and also considering that the applied field in magnetic hyperthermia is small (λ' is very small), then:

$$\chi = \frac{M}{H} = \frac{1}{3k_b}\frac{g\mu_B\left(J+1\right)}{T - \left(g\mu_B\gamma M_S\left(J+1\right)/3k_b\right)} = \frac{C}{T-\theta} \qquad (17)$$

This means that the presented model obeys the Curie-Weiss law.

Fig. 2 shows the comparison between the presented model and the Curie-Weiss law. As can be seen, at the Curie temperature, *T*c, where the spins are completely free, the linearity between the magnetization resulting from the molecular field and the magnetization provided by the presented model is fully established.

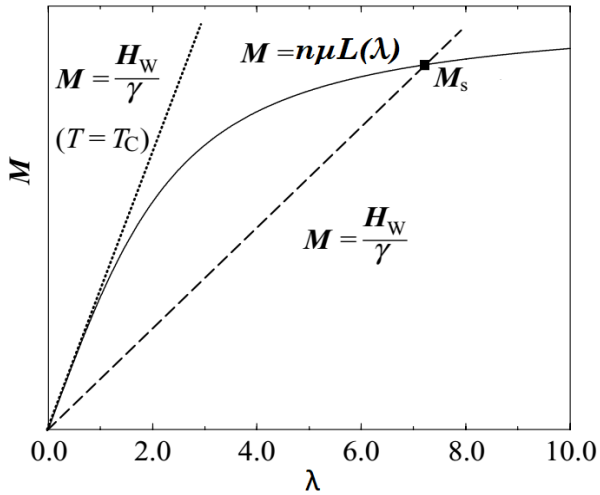

Fig. 2 Matching between the magnetization obtained from the Curie-Weiss molecular field and the magnetization obtained from the model

2.8 Comparison of experimental and model results

Fig. 3 shows the analysis of magnetic hyperthermia or the investigation of heat released by strontium ferrite (superparamagnetic/ferromagnetic) nanoparticles under alternating magnetic fields. As it is clear from this figure, hard ferromagnetic strontium ferrite nanoparticles have the lowest amount of released heat. The reason for this phenomenon can be attributed to two important factors, both of which are caused by the size of nanoparticles. These two factors are:

a- The significant increase in nanoparticle anisotropy (due to the large size of nanoparticles in the hard ferromagnetic state [14]), which makes the macrospin completely resistant to the applied field and without rotation (destruction of the Neel mechanism).

b- Failure of Brown's mechanism due to the enlargement beyond the limit of single-domain nanoparticles so that the applied field is not able to rotate them.

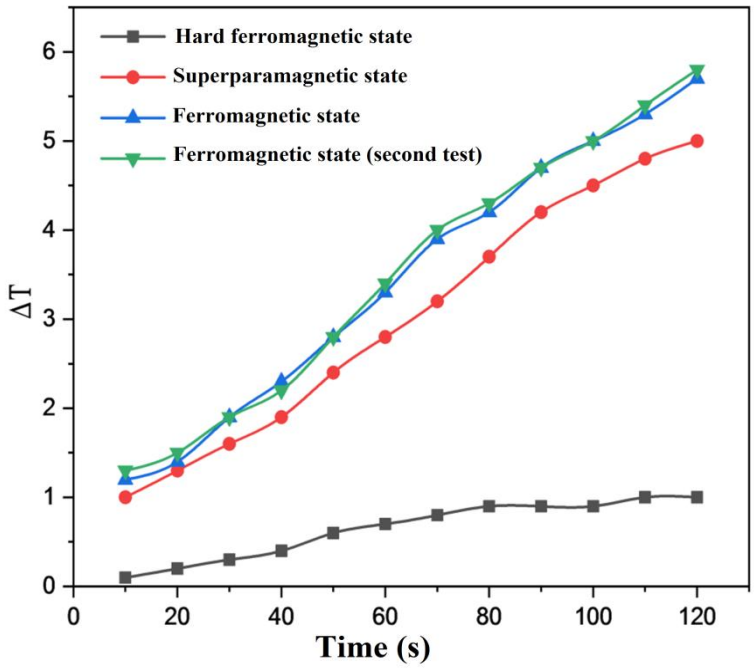

Fig. 3 Magnetic hyperthermia analysis of strontium ferrite nanoparticles at ferromagnetic and superparamagnetic states

In the continuation of the interpretation of the documents related to Fig. 3, superparamagnetic nanoparticles are examined. This category of nanoparticles has the smallest particle size [14] and in this case, the thermal energy caused by atomic vibrations dominates the anisotropy energy. So it can

be said that the macrospin rotate completely freely and the Neel mechanism is fully active in this state. Two important driving forces can be imagined for the Neel mechanism in this state:

a: Heat caused by atomic vibrations that are converted into mechanical energy (macrospin rotation).

b: Applied field with a specific frequency.

It should be noted that when the field is applied to superparamagnetic nanoparticles, due to the free rotation of macrospin and the absence of significant anisotropy, Brown's mechanism cannot be activated.

At the ferromagnetic state, the most released heat is observed (Fig. 3). Here, the increase in the volume of nanoparticles (from the superparamagnetic state to the ferromagnetic one) [14], leads to the occurrence of two events. The first is the reduction of the spin canting process, which leads to the strengthening of the rotation of the spins in the same direction and causes the Neel mechanism to gain more potential. Second, the growth of the size of the macrospin, leads to the production of a larger torque and subsequently more energy during the rotation of the macrospin. This will lead to more heat production.

3. Conclusions

The presented work was written to model the magnetization of ferromagnetic and super-paramagnetic nanoparticles under AC magnetic fields. According to the results obtained, the magnetization of ferromagnetic materials in the classical form is at least 2.8 times of super-paramagnetic ones (under an AC magnetic field during the magnetic hyperthermia process). These results were also confirmed in the quantum state using the Weiss molecular field. According to the proposed model, the magnetization of ferromagnetic and superparamagnetic nanoparticles in the magnetic hyperthermia process is $\xi n\mu\lambda$ and always depends on $\lambda = \mu H / K_b T$. ξ is about 0.98 for ferromagnetic nanoparticles and about 0.33 for superparamagnetic ones.

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