Studies about the attempt frequency influence on the effective relaxation time in a system of nanoparticles for magnetic hyperthermia

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Abstract. This paper presents a series of studies about the modality in which the attempt frequency influences the Néel relaxation time and thus the effective relaxation time, in a spherical-nanoparticle-saturated nanofluid in external magnetic field. The nanoparticles have a random distribution, and their magnetic moments have a magnetic dipole-dipole interaction, along with the distributions of sizes and anisotropy constants. In such a system, the energy of the equilibrium states depends on the total magnetic field experienced by the particle, which includes the magnetic field applied and the dipolar magnetic field produced by the surrounding particles. Because of the high complexity level of the issue, it seems useful to consider the numerical experiments by computational simulation.

1. Introduction

Currently, in nanomagnetism, the study of magnetic nanoparticle systems and especially the iron oxides $\gamma$-Fe$_2$O$_3$ and Fe$_3$O$_4$ occupies a special place because of the biomedical applications, in particular for the nanofluid-based magnetic hyperthermia. In the magnetic hyperthermia with nanofluid, several heating mechanisms are possible, associated with susceptibility loss and hysteresis loss. The susceptibility loss has two associated relaxation processes: the Néel relaxation process and Brownian relaxation process. The Néel relaxation process is the solid state mechanism that takes place inside the nanoparticle, corresponding to the magnetic moment rotation between two equilibrium positions. The nanoparticle is fixed in space, the Brownian relaxation process corresponding to the nanoparticle rotation within the fluid environment. The change in the orientation of the particle causes changes in the orientation of its magnetization. The two processes are treated separately. The Néel relaxation time, $\tau_N$, is usually described for a single barrier, by the Arrhenius law:

$$\tau_N = \frac{1}{f_0} \exp \left( \frac{E_b}{k_BT} \right)$$

(1)

where $k_B$ is the Boltzmann constant, $T$ is the temperature, and $E_b$ is the energy barrier corresponding to the minimum energetic state. The pre-exponential factor $f_0$ is the so-called attempt frequency, which generally depends on the material properties. For spherical particles, the Brownian relaxation time is...
usually described by \( \tau_B = \frac{3V_H \eta}{k_BT} \), where \( V_H \) is the hydrodynamic volume of the particle and \( \eta \) is the coefficient of dynamic viscosity. The relaxation mechanism which dominates the magnetic behaviour of the colloidal suspension is determined by the nanoparticle properties. Hence, the effective relaxation time can be described as

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_N} + \frac{1}{\tau_B}
\]

In many papers, the attempt frequency is considered to be \( f_0 = 10^9 \text{ s}^{-1} \) [1] or to fall within various ranges, such as \((10^{13}-10^9) \text{ s}^{-1} \) [2], and to depend only on the material properties, although, in most cases, the actual system conditions are beyond the single particle model in the absence of the external magnetic field.

2. The Néel-Brown theoretical model for thermal instability of magnetic moments for monodomain nanoparticles with uniaxial anisotropy

The ferromagnetic or ferrimagnetic nanoparticles show an unstable behaviour of their magnetic moments due to thermal agitation. Currently, the thermal fluctuations and relaxation of the magnetic moments of the monodomain nanoparticles play a major role in the biomedical applications. A monodomain nanoparticle is in a state of uniform magnetization for any field applied. The magnetic moment of the monodomain nanoparticle is [3]:

\[
\mu = M_s v \hat{\mu}
\]

where \( M_s \) is the spontaneous magnetization, \( v \) is the particle volume and \( \hat{\mu} \) is the unit vector of the magnetic moments.

The Gilbert equation, for the motion of the magnetization augmented by a random field [4], is:

\[
\dot{\mu}(t) = \mu(t) \left[ r \mu_0 \tilde{H}(t) - \alpha \dot{\mu}(t) + \gamma \tilde{b}(t) \right]
\]

where \( \gamma \) is the gyromagnetic ratio and \( \alpha \) is the dimensionless damping (dissipation) parameter.

Now, let us consider

\[
\tilde{H}(t) = -\frac{1}{\mu_0} \frac{\partial U}{\partial \mu}
\]

as the local magnetic field acting on the nanoparticle, where \( U \) is the Gibbs free energy (characterizing the magnetic anisotropy and Zeeman energy of the nanoparticle).

If the magnetic field is applied along the easy axis, the reduced potential \((U/k_BT)\) is

\[
V(\cos \theta) = -\sigma \cos^2 \theta - \xi \cos \theta = -\sigma \left( \cos^2 \theta + 2 h \cos \theta \right)
\]

where

\[
\xi = \frac{\mu_0 M_s v H}{k_BT}, \quad \sigma = \frac{K}{k_BT}, \quad h = \mu_0 M_s H
\]

In equation (4), \( \tilde{b}(t) \) is a random Gaussian field with white noise properties:

\[
\overline{b_i(t_1)b_j(t_2)} = \delta_{ij} \delta(t_1-t_2)
\]

Here, \( i, j = 1, 2, 3 \) in Kronecker’s delta \( \delta_{ij}, h_i \) are components of \( \tilde{b}(t) \) in the Cartesian coordinate system, \( \delta(t) \) is the Dirac delta function, and overbar means the statistical average over an ensemble of particles which all have the same magnetization at time \( t \). The random field accounts for the thermal fluctuations of magnetization of an individual nanoparticle without which the random orientational motion would not be sustained. Then, Brown deduces from the equation (4) the appropriate Fokker-
Plank equation for the distribution function $W(\theta, \phi, t)$ of the orientation of magnetic moments vector on the surface of unit sphere [5]. In an axially symmetric potential $V$, the complicated Fokker-Planck equation [6], for the distribution function $W(\theta, t)$, is actually a one-space-variable equation:

$$2\tau_{0N} \frac{\partial W}{\partial t} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left[ \sin \theta \left( \frac{\partial W}{\partial \theta} + W \frac{\partial V}{\partial \theta} \right) \right]$$

(9)

$$\tau_{0N} = \frac{\nu M_s (1 + \alpha^2)}{2\gamma c k_b T}$$

(10)

In equation (10) $\tau_{0N}$ denotes the free diffusion time of magnetization (of order $10^{-11} - 10^{-8}$ s) [6].

For low damping ($\alpha << 1$), the precessional motion is the dominant motion. Therefore [6]:

$$\tau_{0N} = \frac{\nu M_s}{2\gamma c k_b T}$$

(11)

For high damping ($\alpha >> 1$) alignment is dominant and [6]:

$$\tau_{0N} = \frac{\nu M_s \alpha}{2\gamma k_b T}$$

(12)

For magnetite nanoparticle with 9 nm diameter, the damping (dissipation) parameter value resulting from experimental measurements is 0.16 [7].

With the potential equation (6), in the high barrier approximation [5] $\sigma (1 - h)^2 >> 1$, and $h < 1$, we obtain:

$$\tau_N = \frac{\tau_{0N} \sqrt{\pi}}{\sigma^{3/2} (1 - h^2)} \left[ (1 + h) e^{-\sigma(1+h)^2} + (1 - h) e^{-\sigma(1-h)^2} \right]^{-1}$$

(13)

For $h = 0$,

$$\tau_N = \frac{\tau_{0N} \sqrt{\pi}}{2\sigma^{3/2}} e^\sigma = \frac{1}{f_0} e^\sigma$$

(14)

where $f_0 = \frac{2\sigma^{3/2}}{\tau_{0N} \sqrt{\pi}}$ is the attempt frequency without magnetic field.

Equation (13) can be written:

$$\frac{1}{\tau_N} = \frac{\sigma^{3/2} (1 - h^2)}{\tau_{0N} \sqrt{\pi}} \left[ (1 + h) e^{-\sigma(1+h)^2} + (1 - h) e^{-\sigma(1-h)^2} \right] = f_{01} e^{-\sigma(1+h)^2} + f_{02} e^{-\sigma(1-h)^2}$$

(15)

where

$$f_{01} = \frac{\sigma^{3/2} (1 - h^2)}{\tau_{0N} \sqrt{\pi}} (1 + h) \text{ and } f_{02} = \frac{\sigma^{3/2} (1 - h^2)}{\tau_{0N} \sqrt{\pi}} (1 - h)$$

(16)

$f_{01}$ and $f_{02}$ are the real attempt frequency factors in the presence of magnetic field.

Usually in the literature [8, 9], the equation (13) is approximated as:

$$\tau'_{N} = \frac{\tau_{0N} \sqrt{\pi}}{\sigma^{3/2}} \left[ e^{-\sigma(1+h)^2} + e^{-\sigma(1-h)^2} \right]^{-1} = \frac{1}{f'_0} \left[ e^{-\sigma(1+h)^2} + e^{-\sigma(1-h)^2} \right]^{-1}$$

(17)

where $f'_0 = \frac{\sigma^{3/2}}{\tau_{0N} \sqrt{\pi}} = f_0 / 2$ is the approximate attempt frequency factor in the presence of magnetic field. This approximation is motivated by the fact that the pre-exponential factors change with the field - in the equation (13) - is much smaller than the change produced in the exponential factor [9].

We intend to verify this statement by numerical simulation, to see if the approximation (17) is valid when working in external magnetic fields typical for applications in hyperthermia (0-14 kA/m), in two
cases: if we do not neglect the internal dipolar field on the particle, and in the real case where the sizes of particles and effective anisotropy constants show a distribution.

In the case of magnetic dipolar interactions among the nanoparticles, if using the Dormann-Bessais-Fiorani approximation [10], only the component on the external magnetic field direction ($\mathbf{H}_{\text{ext}}$) of the dipolar magnetic field ($\mathbf{H}_{\text{dipolar}}$), is taken into account in the above relations $\mathbf{H} = \mathbf{H}_{\text{dipolar}} + \mathbf{H}_{\text{ext}}$.

3. Numerical simulations

Thus, we start from the original Néel-Brown model in an external magnetic field parallel to the aligned easy axes of anisotropy of the spherical nanoparticles. As we showed in the previous paragraph, this model provides a field-dependent expression for the attempt frequency. Then, we generalise the model by introducing, in a stochastic manner, the magnetic dipole–dipole interactions among the nanoparticles. The local magnetic dipolar field produced by the surrounding particles will be calculated using the Dormann-Bessais-Fiorani approximation. We will analyze the Néel relaxation time, simulated by taking into account the customary value for the attempt frequency and the attempt frequency value given by the Néel theory generalized to the local magnetic field. So, we will show how the attempt frequency factors vary depending on the external magnetic field applied.

The simulation was realised for spherical magnetic nanoparticles of uncoated iron oxide, with the saturation magnetization $M_s = 4.46 \times 10^5$ A/m, average diameter $d_m = 10$ nm and uniaxial magnetic anisotropy, and the average value of the effective anisotropy constant $K = 10^4$ J/m$^3$. Either the diameters or the effective anisotropy constants show a lognormal distribution with the parameters $\mu_d = -18.545$ & $\sigma_d = 0.198$ (for diameters), and $\mu_K = 0.198$ & $\sigma_K = 0.0099997$ (for effective anisotropy constants). The external magnetic field applied vary within the range 0 - 14 kA/m, typical values used in magnetic hyperthermia applications.

The analysed systems contain $N=100$ and $N=1000$ nanoparticles, at the temperature $T=298K$ in a base liquid with dynamic viscosity $6 \times 10^{-3}$ Pa·s. The nanoparticles have been located within a base-centred cubic lattice. Among all the possible positions, the particles have been centred 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. The external magnetic field intensity varied in the range (0-14 kA/m), typical values used in magnetic hyperthermia.

4. Results and discussions

This simulation aims to verify the statement made in the literature according to which, the pre-exponential factors modification in the equation (13) with the field is much smaller than the change produced in the exponential factor [9]. For this, because the attempt frequency factors depend also on the volume of nanoparticles, effective anisotropy constants and temperature, we keep unchanged the parameters of the corresponding distributions and the system temperature.

The first study refers to the modality in which the attempt frequency factors vary with the external magnetic field intensity. Thus, we are monitoring the variation of $f_0$, which is the attempt frequency without magnetic field, $f_0'$, which is the approximate attempt frequency factor in the presence of magnetic field, $f_{01}$, and $f_{02}$, which is the exact attempt frequency factor in the presence of magnetic field. The results obtained for a system made of 100 nanoparticles with the volume fraction $f = 0.08$ are presented in Figure 1.

It can be seen that $f_{01}$ shows a peak at about 6500 A/m, and then decreases with increasing external magnetic field. About $f_{02}$, we can say that it decreases with increasing external magnetic field. If we increase the number of nanoparticles in the system, we see that the increase in the nanoparticle number leads to a decrease of the exact attempt frequency values due to the dipolar internal magnetic field variation – Figures 2, 3.
Figure 1. The attempt frequency ($f_0$, $f_0'$ (fop), $f_{01}$ and $f_{02}$) versus the external magnetic field, at the nanoparticle volume fraction $f = 0.08$, for 100 particles in the system.

Figure 2. The exact attempt frequency $f_{01}$ versus the external magnetic field, at the volume fraction $f = 0.1$
Figure 3. The exact attempt frequency $f_{02}$ versus the external magnetic field, at the volume fraction $f = 0.1$.

The second part of the study aims to find how the Néel relaxation time is affected by the attempt frequency variation with the external magnetic field intensity. The results are shown in Figure 4 for a system made of 100 nanoparticles with the volume fraction $f = 0.08$.

Figure 4. Néel relaxation time versus external magnetic field, at the volume fraction of nanoparticles $f = 0.08$, for 100 particles in the system.
It can be seen that, at the small external magnetic fields, there is no significant variation, which means that the constant attempt frequency approximation is valid. But, at more intense fields, there is an almost exponential increase of the relaxation time, calculated using the relation (15), compared with the Néel relaxation time calculated with approximate constant value of the attempt frequency which decreases slightly with increasing external magnetic field intensity.

**Figure 5.** The approximate Néel relaxation time versus the external magnetic field, at the volume fraction $f = 0.1$, for 100 and 1000 nanoparticles.

**Figure 6.** The exact Néel relaxation time versus the external magnetic field, at the volume fraction $f = 0.1$, for 100 and 1000 nanoparticles.
If we vary the number of particles in the system, it is found that, due to the dipolar internal magnetic field variation, the relaxation time increases with increasing number of particles in the system – Figures 5 and 6.

We then simulated the exact Néel relaxation time (calculated using the equation 15) at two different concentrations, \( f = 0.02 \) and \( f = 0.03 \). It was found a slight decrease in the exact Néel relaxation time with increasing concentration – Table 1.

| External magnetic field (A/m) | Exact Néel relaxation time (s) at \( f = 0.02 \) | Exact Néel relaxation time (s) at \( f = 0.03 \) |
|------------------------------|-----------------------------------------------|-----------------------------------------------|
| 0                            | 1.836091589093639e-09                          | 1.83606931144190e-09                          |
| 2000                         | 1.880709887411698e-09                          | 1.877547492722059e-09                          |
| 4000                         | 2.020740803674264e-09                          | 2.013649949075247e-09                          |
| 6000                         | 2.293565438087405e-09                          | 2.280551065183938e-09                          |
| 8000                         | 2.784823253592053e-09                          | 2.761393623573384e-09                          |
| 10000                        | 3.696013390832159e-09                          | 3.651093288259277e-09                          |
| 12000                        | 5.582427455707154e-09                          | 5.482641827927936e-09                          |
| 14000                        | 1.050582994121399e-08                          | 1.020631945091540e-08                          |

This fact was found experimentally in diluted systems. The Mössbauer spectroscopy measurements [10], [11], [12] on weakly interacting \( \gamma \)-Fe\(_2\)O\(_3\) nanoparticles showed a decrease of the relaxation time with increasing interparticle interaction. The publication [12] related about the specific absorption rate (SAR) of a maghemite-based ferrofluid, measured at 315 K, 3 kA/m, and 109 kHz. The magnetic characterization of three different concentrations of this ferrofluid revealed the decrease of the initial susceptibility values and the Néel relaxation times, \( \tau_N \), with increasing concentration.

Given equation (2) and simulation parameters, in the same conditions, no differences between the mean Néel relaxation time and the mean effective relaxation time because Brownian relaxation time is of the order 10\(^{-6}\)s.

5. Conclusions
This paper presents a series of studies regarding the attempt frequency influence on the Néel relaxation time, and thus the effective relaxation time, through their dependence on the external magnetic field and dipolar magnetic field. The studies showed that the statement “the pre-exponential factors change with the field is much smaller than the change produced in the exponential factor”, justifying that the choice of constant exponential prefactors (which depend on the field variation) is truthful only for relatively low external magnetic field intensity. Another obtained result is that the exact relaxation time increases when the number of particles in the system increases, because the particle number in the system leads to the variation of the dipolar internal magnetic field.

It is found also a slight decrease in the exact Néel relaxation time with the concentration increase, in agreement with experimental findings published in the literature. For our simulation parameters, in the same conditions, no differences between the mean Néel relaxation time and the mean effective relaxation time.

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