Influence of dipolar interactions on the superparamagnetic relaxation time of $\gamma$-Fe$_2$O$_3$

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Abstract. Influence of dipolar interactions on the Néel superparamagnetic relaxation time, $\tau$, of an assembly of ultrafine ferromagnetic particles ($\gamma$-Fe$_2$O$_3$) with uniaxial anisotropy and of different sizes has been widely studied using Mössbauer technique. These studies, based on different analytical approaches, have shown that $\tau$ decreases with increasing interactions between particles. To interpret these results, we propose a model where interaction effects are considered as being due to a constant and external randomly oriented magnetic field $B(\psi, \phi)$.

The model is based on the resolution of the Fokker-Planck equation (FPE), generalizes previous calculations and gives satisfactory interpretation of the relaxation phenomenon in such systems.

1. Introduction

Due to their interest for technological applications, a great number of both experimental and theoretical studies have been devoted to the study of dynamical properties of nanoparticles [1-28]. Different experimental techniques are used to study superparamagnetic relaxation of fine particles: alternative susceptibility, [3-8], Mössbauer spectroscopy [6, 8, 10, 23], neutrons diffraction [9] and ferromagnetic resonance [11].

In the superparamagnetic domain, the relaxation time of isolated particles is generally expressed by Néel-Brown law [1, 2]:

$$\tau = \tau_0 \exp \left( \frac{\Delta E}{K_BT} \right) \quad (1)$$

where $\tau_0$ is of the order of $10^{10}-10^{13}$ s$^{-1}$, and weakly dependent on temperature, $\Delta E$ is the energy barrier separating two easy magnetization directions, $K_B$ is the Boltzmann constant and $T$ the temperature.

Eq. (1) constitutes a good approximation if $\Delta E \geq 2K_T$. For a particle of uniaxial symmetry, the magnetic anisotropy energy is given by $E(\theta) = -KV\cos^2\theta$, where $K$ is the anisotropy constant, $V$ is the volume of the particle and $\theta$ is the angle between the magnetization vector and the easy magnetization axis; in this case, the energy barrier is equal to $KV$. 
2. Previous results

Magnetic interactions between nearest neighbours nanoparticles have a great influence on the superparamagnetic relaxation phenomenon. The latter has been the subject of numerous experimental and theoretical studies [3-28].

In the presence of a magnetic field, $B$, parallel to the easy magnetization direction, the energy of the particle becomes

$$E = KV\left[\sin^2 \theta - 2h \cos \theta\right]$$  \hspace{1cm} (2)

where $h=\mu B/2KV$. Two situations may be considered depending on the value of $h$. For $h \geq 1$, a stable state exists in which $E$ has a minimum if $\theta=0$ and a maximum if $\theta=\pi$. For $h<1$, $E$ has two minima at $\theta=0$ and at $\pi$, separated by a maximum at $\theta=\arccos(-h)$. The two barriers $\Delta E^\pm=E_0(1\pm h)^2$, corresponding to the crossing from $\theta=0$ to $\pi$, and vice versa, give rise to two relaxation time constants:

$$\left(r_\pm\right)^{-1} = \frac{1}{2\tau_0} \left(1 \pm h\right) \left[1 - h^2\right] \exp\left[-\alpha \left(1 \pm h\right)^2\right]$$  \hspace{1cm} (3)

where $h = \mu B/2KV < 1$ and $\alpha = KV/K_BT > 1$.

The global relaxation time is given by

$$\frac{1}{\tau} = \frac{1}{\tau_+} + \frac{1}{\tau_-}$$  \hspace{1cm} (4)

Shtrikmann and Wohlfarth [12] have considered two cases corresponding to weak and strong couplings, and have represented the action of weak interactions as that of a statistically averaged magnetic field $H_0$, which leads to

$$E_B = KV + H_0M_V\text{th}(H_0M_V/K_B T)$$  \hspace{1cm} (5)

and so gives the Vogel-Fulcher law

$$\tau = \tau_0 \exp\left[\frac{KV}{K_B} \left(\frac{1}{T - T_0}\right)\right]$$  \hspace{1cm} (6)

valid for $T \gg T_0$ with $T_0 = H_0^2M_V^2/VK_B$.

In the case of a strong coupling, they introduced an effective volume with an order temperature

$$V_{\text{eff}} = V_0(V - T/T_0)^{-1}$$  \hspace{1cm} (7)

Chantrell and Wohlfarth [13] have proposed a modified version of the model of Shtrikmann and Wohlfarth [12], and introduced interaction effects; short range interactions and long range ones are represented using an effective volume $VT(T - T_0)^{-1}$, and an effective field $H_0$ respectively. The energy barrier is then given, in the presence of a magnetic field $H$, by

$$E_B = KV\left(\frac{T - T_0}{T - T_0}\right)^{-1}\left(1 \pm h \pm \frac{\mu H}{2KV}\right)^2$$  \hspace{1cm} (8)

where $h=\mu H/2KV$.

Dormann et al. have also proposed a model which predicts that the energy barrier increased with increasing interactions [5]

$$E_B = E_{B_0} + E_{B_{\text{int}}}$$  \hspace{1cm} (9)

and $E_{B_{\text{int}}} \approx n_1M^2\langle b_1 \rangle L\left(M^2\langle b_1 \rangle / K_B T\right)$

where $n_1$ is the number of nearest neighbors and $b=\langle V \rangle/\langle d \rangle$ (regular arrangement).

This model has been successfully applied to interpret magnetic measurements of nanoparticles dispersed in an alumina matrix.

However, Mössbauer measurements on weak interacting Fe$_2$O$_3$ nanoparticles [13-15] revealed a decrease of the relaxation time with increasing interactions between particles.

The increase of the relaxation time with interactions is in accordance with magnetic measurements but disagrees with Mossbauer ones performed on $\gamma$-Fe$_2$O$_3$ nanoparticles. Dormann et al. have explained
this discrepancy as due to the decrease of the damping parameter $\eta_r$ with increasing interactions between particles, appearing in the expression of $\tau_0$ [16-18, 21-25]

$$\tau_0 = \frac{1}{\eta_r} \left[ \frac{m(0)}{E_{J0}} \sqrt{\frac{\pi}{4}} \frac{1}{\alpha} \left( 1 + \frac{1}{\alpha} \right) \right]$$

(10)

Variations of the parameter [18] $\eta_r$ may be a consequence of two contributions. The first one comes from the spin disorder at the surface of the particles which decreases significantly with increasing interactions and then reduces $\eta_r$. The second one is generated by the spatial variation of the dipolar field acting on each particle due to its neighbours.

An other approach has been proposed to interpret Mossbauer experimental observations [15], in which the authors considered that the factor $\tau_0$ as independent of interactions and an effective energy barrier which decreases with increasing interactions.

$$\tau^* \approx \tau_0 \exp \left[ \alpha - \frac{\zeta^2}{3} \left( 1 - \frac{3}{4} \alpha^{-1} \right) \right]$$

(11)

This approach has given results that are in contradiction with experience [23]. Indeed, if the preexponential does not vary, $T_B$ could increase with interactions [14, 22, 23]. However, Mössbauer measurements on weak interacting Fe$_2$O$_3$ nanoparticles [13-15, 22, 23] indicate that relaxation is more fast and $T_B$ more low for interacting particles. Attribution of this systematically observed effect to a decrease of $E_B$ [15] seems to be incorrect. Besides, this model does not take into account of the aleatory character of the field $B_I$.

3. A new approach

We have considered interactions influence on relaxation time, and have developed calculations which give satisfactory interpretation of experimental results.

Consider a monodomain particle of uniaxial symmetry, with magnetic moment $\mu_i$. The other particles of the system act on a particle (i) via a dipolar field $B_I$ at an angle $\psi$ with $e_z$ considered as the easy magnetization axis (Fig.1).

![Figure 1. Dipolar field $B_I$ and magnetic moment in spherical coordinates](image)

The energy anisotropy can be expressed as:

$$E = KV \sin^2 \theta - \tilde{\mu}_i \tilde{B}_I$$

(12)

With the following variables changes, $\beta=1/K_B T$, $\alpha=KV/K_B T$ and $\zeta=\mu_B B_I/K_B T$ this energy may be written in the form:

$$\beta E = \alpha \sin^2 \theta - \zeta \left[ \cos \theta \cos \psi + \sin \theta \cos \phi \sin \psi \cos \varphi - \sin \theta \sin \phi \sin \psi \sin \varphi \right]$$

(13)
Expressing the derivative of Eq. 13 with respect to $\theta$, $(\partial \beta E / \partial \theta) = 0$, gives:

$$\sin \theta \approx h \{ (\sin \psi \cos \phi) / (1 + h \cos \psi) \}$$

where $h = \xi / 2 \alpha$. $h \ll 1$, so $\sin \theta \approx h \sin \psi \cos \phi$, Consequently the minimum value of energy when $\theta$ is close to zero is:

$$\beta E_{\text{min}} = -\alpha \left( h^2 \sin^2 \psi \cos^2 \phi + 2 h \cos \psi \right)$$

When $\theta$ is close to $90^\circ$, a similar approximation to that used above leads to $\cos \theta \approx -h \cos \psi$, and then:

$$\beta E_{\text{max}} = \alpha \left[ 1 + h^2 \sin^2 \psi \cos^2 \phi - 2 h \cos \phi \sin \psi \cos \phi + 2 h \sin \phi \sin \psi \sin \phi \right]$$

The energy barrier, $\Delta E = E_{\text{max}} - E_{\text{min}}$, can be written as:

$$\beta \Delta E = \alpha \left[ 1 + h^2 \sin^2 \psi \cos^2 \phi + 2 h \cos \psi \sin \psi \cos \phi - 2 h \sin \phi \sin \psi \sin \phi \right]$$

The transition probability to overcome the energy barrier is given by

$$f(\psi, \phi) = (2 \pi \tau_0)^{-1} \exp(-\beta \Delta E)$$

Integration of $f(\psi, \phi, \phi)$ with respect to $\phi$ gives:

$$f(\psi, \phi) = \tau_0^{-1} \exp(-\alpha \left[ 1 + h^2 \left( 1 - \sin^2 \psi \sin^2 \phi \right) \right] \times 1 - \xi \cos \psi + \left( \frac{\xi}{2} \right)^2 \left( 1 + \cos^2 \psi \right) \right)$$

And the relaxation time is given by:

$$\tau^{-1} = \frac{\int f(\psi, \phi) \sin \psi \, d\psi \, d\phi}{\int \sin \psi \, d\psi \, d\phi}$$

$$\tau^{-1} = \tau_0^{-1} \frac{2}{4 \pi} \int_0^{2 \pi} \exp(-\alpha \left[ 1 + h^2 \cos^2 \phi \right] \times \left[ 2 + \left( \frac{\xi}{2} \right)^2 \left( \frac{8}{3} - 1 + \frac{2}{3} \alpha h^2 \sin^2 \phi \right) \right] \, d\phi$$

Hence

**Figure 2.** Energy anisotropy $\beta E$ as a function of the parameters $\theta$ and $\phi$:

**a.** $\psi=45^\circ$, $\phi=0$ and $h=0.3$; **b.** $\psi=0$, $\phi=0$ and $h=0$;

$\phi = 0$, $\psi = 45$, $h=0.3$, and $\phi = 0$, $\phi = 35$, $\phi = 75$, $\phi = 90$. 

When $\theta$ is close to zero, $\sin \theta \approx \tan \theta$.
\[ \tau = \frac{\tau_0}{I_0(\frac{ah^2}{2})} \exp \alpha \left[ 1 - \frac{4}{3} \left( h^2 \right) \left( \alpha - \frac{3}{8} \right) \right] \]  

(21)

where \( I_0 \) is the Bessel’s function.

Finally \( \tau \) can be expressed as

\[ \tau = \frac{\tau_0}{1 + \left( \frac{\alpha(h^2)}{4} \right)} \exp \left[ \alpha - \left( \frac{\alpha}{\lambda} \right) \left( 1 - \frac{5}{24} \alpha^{-1} \right) \right] \]  

(22)

Expression (22) may be written as a function of (11).

\[ \tau = \tau' \tau^* \]  

(23)

where

\[ \tau' = \exp \left[ -4\alpha^2 h^2 \left( \frac{2}{3} + \frac{1}{8} \alpha^{-1} \right) - \left( \frac{ah^2}{4} \right)^2 \right] \]  

(24)

We can write with a good approximation

\[ \tau = \frac{\tau_0}{1 + \left( \frac{\alpha h^2}{6} + \frac{8\alpha^2 h^2}{3} + \left( \frac{ah^2}{4} \right)^2 \right) \exp \alpha \left[ 1 - h^2 \left( \frac{4}{3} \alpha - 1 \right) \right]} \]  

(25)

(26)

where \( \alpha \leq 20, \ 0 < h \leq 1 \). In this expression, contributions of the denominator are not negligible.

This relation clearly shows the effect of the relaxation time variation as a consequence of the variation of interactions between particles. \( \tau \) decreases (as a consequence of the increase of the damping factor) with increasing interactions as revealed by Mössbauer experiment and dynamic measurements [23], and hence is in contradiction with the supposition that the parameter \( \tau \) increases as a function of interactions.

The blocking temperature \( T_B \) can be deduced from our approach from equation (21), by writing that the relaxation time value is equal to that of the measuring time, which is given by:

\[ T_B \approx \frac{KV}{C k_B} \left[ 1 - h^2 \left( 4C - \frac{5}{6} \right) \right] \]  

(27)

with \( C = \ln(\tau_m/\tau_0) \), \( \tau_0 = 10^{-10} \text{s} \), \( \tau_m = 10^8 \text{s} \)

For a given value of \( h \), \( T_B \) increases linearly, and is a decreasing function of \( h \) for a fixed value of the parameter KV (Fig. 3).
Figure 3. Blocking temperature, as a function of the average parameter (KV)

4. Conclusion
Superparamagnetic relaxation in the presence of dipolar interactions has been studied. The results are in good agreement with experimental ones, in particular Mössbauer measurements, and show a decrease of the relaxation time with increasing interactions, contrary to previous results indicating an increase of this parameter. The decrease of $\tau$ may be imputed to the decrease of the pre exponential factor.

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