

HEATING RATE OF COLLOIDAL FERROFLUIDS UNDER ROTATING MAGNETIC FIELD AND SPIN-PHONON COUPLING

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Abstract. *In this work we study the heating process of colloidal ferrofluids (fluid with magnetic nanoparticles embedded in it) by a rotating magnetic field. The heating of the fluid occurs by the magnetic relaxation of the nanoparticles which provide thermal energy for the host liquid in this process. In the limit of small volumes, the relaxation process occurs through the Néel mechanism since the magnetic nanoparticles present superparamagnetic behavior. Within this limit, we have used a microscopic model for spin-phonon coupling in order to model the relaxation mechanism and to obtain an expression for the heating rate of the fluid as a function of the model parameters. Our study allows to determine the appropriated nanoparticles for an optimal heating rate for ferrofluids based on superparamagnetic nanoparticles. Such a study is a relevant contribution in the field of research on fuel droplet combustion with ferrofluids.*

Keywords: *spin-phonon, magnetic nanoparticles, heating rate.*

1. INTRODUCTION

The heating of colloidal ferrofluids is an emerging field due to its potential in technological applications. In fact, one of these applications is the so-called magnetic hyperthermia (MH), where the ferrofluid is used to provide the heating of a system (Ahsen *et al.*, 2010; Cantillon-Murphy *et al.*, 2010). MH can be used in the treatment of cancer, where the magnetic nanoparticles are injected into the tumor tissue. When an external magnetic field is applied, induced magnetization lags the external field which results in heat dissipation at the tissue. As a result, the tumor tissue can be eliminated with fewer collateral effects, in comparison to traditional methods like chemotherapy and radiotherapy (Mornet *et al.*, 2004). Ferrofluids can also be of interest in the construction of combustion chambers, whose projected size increases with the time taken for a complete burn of the fuel droplets. When magnetic nanoparticles are embedded in these fuel droplets, it is possible to accelerate the burn process allowing the construction of more compact chambers (Fachini and Bakuzis, 2010).

Ferrofluids contain magnetic particles whose mobility can be controlled by a magnetic field. Regarding the applications in MH, the interest is the absorption of large amounts of energy when the magnetization of the particles is reversed. Thus, the quantity to be maximized is the heating rate, i.e., the amount of energy absorbed per unit of time. In the process of heating, the reversal of the magnetization can be accomplished by two ways: either the magnetic moment is rotated inside the particle until to be aligned with the field, which is called Néel process, or the particle rotates as a whole, which is called Brownian process (Shliomis, 1974; Shliomis and Morozov, 1994; Rosensweig, 2002). These mechanisms occur with a well defined relaxation time, i.e., the time that the particle takes to revert its magnetization. Besides the magnetization reversal, the heat transfer is different in these two process. In the Brownian process, the heat is transferred directly to the fluid due to the friction generated by the particle rotation in the fluid. In the Néel process, the heat is firstly transferred to the lattice, i.e., to the phonons, and then is delivered to the fluid by heat transfer.

Several research studies have been done in the sense of achieving higher heating rates but considering a regime where both relaxation processes are operating at same time (Rosensweig, 2002; Fachini and Bakuzis, 2010). However, in situations where the size of the particles is very reduced or the particles are immobilized, the Néel mechanism is the only acting in the relaxation process. In fact, as pointed out by Hergt *et al.* (2006), the mobility of the particles trapped in a tumor tissue is not known. In cases like this, it is imperative to study the Néel contribution separately in order to have a deep understanding of the heating process. This case has been addressed in some reports (de Châtel *et al.*, 2009), even though, to our knowledge the connection between the heating rate and the microscopic mechanism of relaxation has not been addressed yet. In this work, the Néel relaxation is considered as being a result of the coupling between the spin of the magnetic nanoparticle with the phonons of its crystalline lattice. To do this a relaxation model of superparamagnetic nanoparticles, considering the spin-phonon interaction, is used (Pfannes *et al.*, 2000). Some results, addressing the importance of the spin-phonon coupling and its relation with external parameters, like the amplitude and frequency of the external magnetic field and the system temperature, are shown.

2. MODEL AND FORMULATION

A ferrofluid composed by immobilized single-domain magnetic nanoparticles under a magnetic field is considered. The application of this field implies in an alignment of the magnetic moment of these nanoparticles, in the same direction of the field, whose net result is a magnetization of the system. A circularly polarized magnetic field is considered, which

is given by:

$$\mathbf{H}(t) = H_0 \cos(\omega t) \hat{\mathbf{x}} + H_0 \sin(\omega t) \hat{\mathbf{y}} \quad (1)$$

with H_0 being the amplitude of the magnetic field and $\omega = 2\pi f$ the angular frequency.

According to Shliomis and Morozov (1994), when the field rotates in the (x, y) -plane, ferrofluid magnetization also rotates in this plane with the same speed as the field but lags behind in phase by a certain angle δ due to the finite relaxation time:

$$\mathbf{M}(t) = M_0 \cos(\omega t - \delta) \hat{\mathbf{x}} + M_0 \sin(\omega t - \delta) \hat{\mathbf{y}}. \quad (2)$$

In order to determine the parameters δ and M , it is used the following expression for the magnetization:

$$\frac{\partial \mathbf{M}(t)}{\partial t} = \frac{1}{\tau} [\mathbf{M}_0(t) - \mathbf{M}(t)] \quad (3)$$

which is the so-called Shliomis relaxation equation, particularized (Shliomis, 1974) for a motionless fluid in a oscillatory field. In Eq. (3), τ is the Néel relaxation time, $\mathbf{M}_0 = \chi_0 \mathbf{H}(t)$ is the equilibrium magnetization and χ_0 is the equilibrium susceptibility. Substitution of Eq. (2) into Eq. (3) leads to:

$$\mathbf{M}(t) = \frac{\chi_0 H_0}{\sqrt{1 + \omega^2 \tau^2}} [\cos(\omega t - \delta) \hat{\mathbf{x}} + \sin(\omega t - \delta) \hat{\mathbf{y}}], \quad (4)$$

where $\tan \delta = \omega \tau$.

Rosensweig (2002) has developed an expression for the energy dissipation per unit volume whose form is given by :

$$E = \mu_0 \int_0^{2\pi/\omega} \mathbf{H} \cdot \frac{\partial \mathbf{M}}{\partial t} dt, \quad (5)$$

where μ_0 is the magnetic permeability of the free space. This function is also called energy density. It is straightforward to obtain an explicit expression for E through substitution of Eqs. (1) and (2) into Eq. (5):

$$E = 2\pi \mu_0 \chi_0 H_0^2 \frac{\omega \tau}{1 + \omega^2 \tau^2}. \quad (6)$$

To describe the heating rate, Rosensweig (2002) has defined the heating rate function, which is given by:

$$\frac{\Delta T}{\Delta t} = \frac{\omega E}{2\pi \rho c} \quad (7)$$

where ΔT is the temperature rise in time step Δt during the heating process. For the ferrofluid, ρ is the density and c the specific heat. In order to investigate the behavior of the heating rate, it is convenient to work with a quantity which does not depend on the parameters ρ and c . Thus, the following heating rate function is defined:

$$H_C = \left(\frac{\rho c}{\mu_0 \chi_0 H_0^2} \right) \frac{\Delta T}{\Delta t} \quad (8)$$

and substituting Eq. (7) and (6) into Eq. (8) leads to:

$$H_C = \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}. \quad (9)$$

The microscopic information regarding the nanoparticles properties are included in the relaxation time, τ . This quantity has been determined by Pfannes *et al.* (2000) where they describe the relaxation process of superparamagnetic nanoparticles under a magnetic field. Within this model, the superparamagnetic particles are considered to present an uniaxial anisotropy whose effect is to produce an energy barrier between two local energy minima. These local energy minima correspond to opposite orientations of the nanoparticle magnetic moment with respect to the easy axis of magnetization. In the presence of the magnetic field, the energy barrier of the nanoparticle will change depending on the orientation of the field, increasing in the sense of the nanoparticle magnetic moment or decreasing in the opposite sense. The coupling of the nanoparticles with a phonon bath introduces a fluctuation in the nanoparticle moment direction with respect to the field and whereby a finite relaxation time. The expression for the relaxation time is given by (Pfannes *et al.*, 2000):

$$\tau^{-1} = \tau_+^{-1} + \tau_-^{-1} \quad (10)$$

with

$$\tau_{\pm} = \frac{S^6 \exp(\alpha_{\pm})}{64C} [\sigma(+h) + \sigma(-h)],$$

and

$$\sigma(\pm h) = \sum_{i=0}^{(S/2)(1\pm h)-1} \frac{\exp\left[-\alpha\left(\frac{2}{S}\right)^2 i^2\right]}{(1+2i)^3[S(1\pm h)-2i][S(1\pm h)-2i-1]} \frac{1 - \exp\left[-\alpha\left(\frac{2}{S}\right)^2 (1+2i)\right]}{[S(1\mp h)+2i+2][S(1\mp h)+2i+1]}.$$

The constants α , h and C are defined by:

$$\alpha_{\pm} = \alpha(1\pm h)^2, \quad \alpha = \frac{KV}{k_B T}, \quad h = \frac{g\mu_B H_0 S}{2KV}, \quad \text{and} \quad C = 4096(KV)^3 \frac{3B^2}{2\pi\hbar^4 \rho a^5}.$$

In Eq. (10), α is the ratio of the anisotropy energy KV to the thermal energy $k_B T$, with K being the anisotropy constant and V the particle volume. In the absence of an external field, KV gives an estimative of the height of the energy barrier between the two energy minima. In the limit of high temperatures ($T \rightarrow \infty$), the energy barrier is too small in comparison to the thermal energy and, as a result, the magnetic moment is randomized, which is known as superparamagnetic limit. Conversely, when the temperature is close to zero, the magnetic moment is fixed, since there is no enough energy to overcome the barrier, and the particle is said blocked. When a magnetic field is applied, it is introduced an asymmetry between the two energy minima which is described by the parameter h , ranging between 0 to 1. It is defined by the ratio of the magnetic energy ($g\mu_B H_0 S$) to the anisotropy energy KV , where g is the well known g-factor and μ_B is the Bohr magneton. The asymmetry between these two minima increases with the applied field until some limit value where one of these minima coincides with the top of the barrier. In this case, the relaxation is quenched and the system becomes saturated. This limit field occurs when $g\mu_B H_0 S = 2KV$, i.e., for $h = 1$. The parameter C contains information about the spin-phonon coupling. In fact, B is a constant describing the intensity of the coupling between the nanoparticle magnetic moment and the phonon bath. It is multiplied by a set of parameters with ρ being the nanoparticle density and a the sound velocity. The substitution of Eq. (9) into Eq. (10) leads to an expression for the heating rate depending on microscopic parameters.

3. RESULTS AND DISCUSSION

In this section, some results obtained from Eqs. (9) and (10) are presented. It is analyzed the behavior of the heating rate (H_R) as function of the field frequency (f) and the spin-phonon coupling (B). In Fig. 1a are shown some curves of H_R vs. f , for different values of the dimensionless field, h . For all the values of h , the heating rate exhibit a general trend, ranging from 0 to the constant value τ^{-1} in the asymptotic limit $f \rightarrow \infty$. This limit can be verified from Eq. (9). The curves in Fig. 1a show that the heating rate first increases with h up to a maximum value for $h \sim 0.80$ and then decreases for $h > 0.80$. In fact, for a frequency $f = 80$ MHz, the heating rate ranges from $\sim 10^8$ for $h = 0.80$ to $\sim 10^6$ for $h = 0.98$, i.e., a reduction of two orders of magnitude. In this range, h is close to unity and, as a result, the relaxation time becomes large enough to produce a significant reduction of the heating rate.

Next, the effect of the spin-phonon coupling on the heating rate is considered. In Fig. 1b, some curves of H_R vs. f for different values of B are shown, in which is observed the same plateau structure as observed in Fig. 1a. By changing the value of B , the plateau also changes going to higher values of the heating rate for larger values of B . This behavior can be understood by considering how the process of heating occurs: the nanoparticle receives energy from the magnetic field which allows its spin to climb to the top of the energy barrier and then go down on the other minimum releasing its energy excess to the phonon bath. Thus, the higher the coupling with the phonons, the faster will be the absorption of heat by the system.

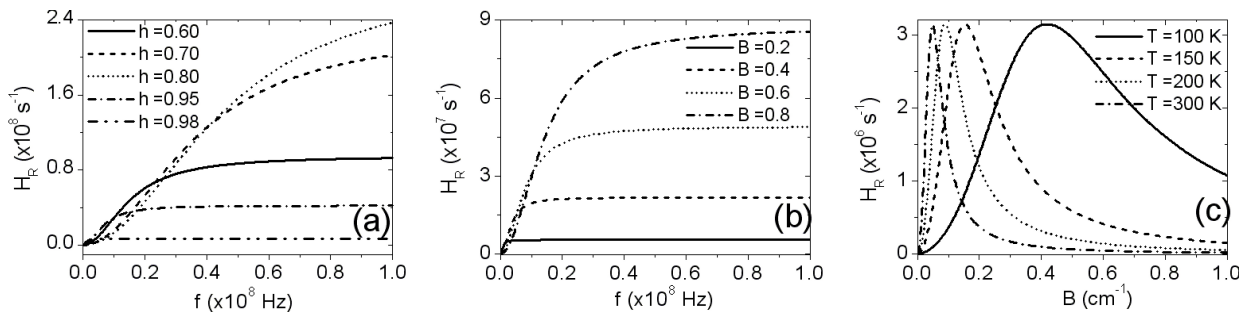


Figure 1. Dimensionless heating rate (H_R) for different values of the model parameters. (a) H_R vs. field frequency (f) for some values of the dimensionless field, h . For these curves, $T = 100$ K and $B = 0.80$. (b) H_R vs. f for some values of spin-phonon coupling (B), with $h = 0.10$ and $T = 300$ K. (c) H_R vs. B for different values of T , $f = 1$ MHz and $h = 0.50$ for all curves. Fixed parameters used in all graphs: $S = 3222$, $K = 7 \times 10^4 \text{ J/m}^3$, $V = 3.82 \times 10^{-25} \text{ m}^3$, $\rho = 5000 \text{ kg/m}^3$, $v = 3000 \text{ m/s}$.

In Fig. 1c, the heating rate as a function of B for different values of the phonon-bath temperature is shown. All curves exhibit the same trend, firstly increasing with B up to some maximum and then decreasing for higher values of B . This behavior stems from the fixed frequency of the magnetic field. In fact, for a given frequency, the corresponding relaxation time (τ_m) for which the heating rate is maximum can be determined from Eq. (9). In all the curves shown in Fig. 1c, the frequency is fixed at 1MHz which leads to $\tau_m = (2\pi f)^{-1} \sim 1.5 \times 10^{-7}$ s. Since $\tau \propto 1/B$, the heating rate increases, when B is reduced from $B = 1.0$, reaching the maximum when B is such that $\tau = \tau_m$. When B is further reduced, the heating rate starts to be reduced being completely suppressed for $B = 0$. When the temperature is increased, the relaxation time decay more rapidly with the spin-phonon coupling. As a result, the value of τ_m is reached at smaller values of B and the heating rate maximum is pushed to smaller values of B for higher values of the temperature. In fact, the maximum ranges from $B \sim 0.41 \text{ cm}^{-1}$ for $T = 100 \text{ K}$ to $B = 0.04 \text{ cm}^{-1}$ when $T = 300 \text{ K}$. This variation shows that it is easier to relaxation process to take place in higher temperatures in such a way that a small coupling with phonons is enough for the system to absorb the energy from the applied field. In the curves shown in Fig. 1, the parameters used were those for Mn-ferrite (MnFe_4) nanoparticles obtained from Pfannes *et al.* (1998). As pointed out by the authors, the value of the spin-phonon coupling, which reproduces the relaxation time observed in experiments, is $B \sim 13 \text{ cm}^{-1}$. Thus, for a fixed frequency of $f = 1\text{MHz}$ the temperature for H_R to be maximum ranges from $T \sim 101.40 \text{ K}$ to $T \sim 19.2 \text{ K}$ as h is changed from $h = 0.20$ to $h = 0.70$.

The results, shown in Fig. 1, allow determining the condition to achieve the maximum heating rate given the spin-phonon coupling. In applications of ferrofluids in combustion, the liquid where the magnetic nanoparticles are dispersed is the fuel to be heated by the magnetic field. Thus, the fuel boiling temperature (T_B) appears as an upper limit for the temperature where the heating rate is a maximum. In fact, for methane (CH_4) with $T_B = 109.15 \text{ K}$, MnFe_4 -nanoparticles may be appropriated since the heating rate is maximum for a temperature range lying below T_B .

4. CONCLUSION

The behavior of the heating rate as a function of spin-phonon coupling and the other parameters of the model has been analyzed. It is clear from the results shown in Fig. 1, that the spin-phonon coupling is a crucial parameter to choose the appropriate material to make the magnetic nanoparticles. In fact, by combining this value along with the field parameters and temperature, it is possible to determine the condition where the heating rate exhibit a maximum value.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

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