INFLUENCE OF PARTICLE SIZE DISTRIBUTION ON SPECIFIC LOSS POWER OF MAGNETIC NANOPARTICLE

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ABSTRACT

In this study, the influence of particle size distribution in the range of σ =0-0.4 on the specific loss power (SLP) in magnetic fluids based on nanoparticles (NPs) of 6 materials of FeCo, La₀.₃Sr₀.₇MnO₃, MnFe₂O₄, γ-Fe₂O₃, CoFe₂O₄ and FePt was evaluated using Linear Response Theory (LRT). Results show that while the particle diameters Dcp of maximum SLP remain unchanged, the SLPmax values decrease with increasing size distribution for all the studied materials. The reduction behaviors can be classified into 2 groups, namely group with strong and weak decrease rate for low-anisotropy (FeCo, La₀.₃Sr₀.₇MnO₃, MnFe₂O₄, γ-Fe₂O₃), and high-anisotropy (CoFe₂O₄ and FePt) materials, respectively.

Keywords: specific loss power (SLP); particle size distribution; Néel – Brown; standard deviation.

1. INTRODUCTION

It is now well known that magnetic nanoparticles (MNPs) can absorb energy from an alternating magnetic field (AMF) to create local heating sources, that may be applied in several domains especially in hyperthermia [1,2]. Specific Loss Power (SLP) is commonly used to describe such heating performance of the MNPs [1]. SLP of magnetic fluids depends on many factors including the properties of MNPs suspension such as particle size (D), size distribution (σ), saturation magnetization (Ms), magnetic anisotropy constant (K), viscosity of fluid (η), as well as the amplitude (H₀) and frequency (f) of AMF [1-5]. As an alternative, Intrinsic Loss Power (ILP) is a measure of heating efficiency which normalizes SLP with respect to AMF [6].
According to calculations based on Linear Response Theory (LRT) [1, 3-5], the SLP or ILP against MNPs size has been shown to exhibit a peak-like shape with maximum value, SLP_{max}, appearing at critical particle diameter D_{cp}, which decreases with increasing magnetic anisotropy. To date, the two parameters (SLP_{max}, D_{cp}) have continued to be topic of intensive study. While MNPs were assumed to have the single size in most of theoretical works (standard deviation of particle size distribution, \( \sigma = 0 \)); in reality they are always prepared with some size distribution (\( \sigma > 0 \)) regardless of the synthesis method used [7]. The theoretical calculations for the case of monodisperse ferrofluids found that there had been a vanishing tendency of SLP for small size sides, e.g. for CoFe_{2}O_{4} SLP almost becomes 0 below 9 nm [3]. In contrast, experimental studies reported extremely high SLP values, namely of 400 W/g [4] or 360 W/g [8] for MNPs of 9 nm diameter of this material. This difference between the theoretical and experimental results is supposed to be due to the particle size distribution. So, how do these parameters (SLP_{max}, D_{cp}) of each magnetic fluid change with expanding of the particle size distribution? Rosensweig [1] firstly performed a calculation of the effect for magnetite MNPs in the \( \sigma \) range up to 0.25 and found a reduction of SLP_{max} with \( \sigma \) increasing and noticed an incentive requirement of monodispersity for the heating performance. A few years later, Fortin et. al. [4,5] confirmed the result of Rosensweig when performed a study for the \( \sigma \) range from 0 to 0.4 in the case of \( \gamma \)-Fe_{2}O_{3} and CoFe_{2}O_{4}. The authors remarked on the slower reduction rate observed for the latter material due to its broader SLP versus diameter peak. It is worth to note that in all the reports based on Linear Response Theory (LRT) [1, 3, 4, 5] the peak behavior of SLP vs particle diameter D is resulted from the competition between Néel and Brown relaxation losses. Further investigations of influence of particle polydispersity on the characteristics of SLP vs particle diameter D peak should, therefore, not only shed a light on Neel vs Brown relaxation competition but provide a guide for choosing proper synthesis strategy to minimize the SLP reduction for particular material.

In the present work, the SLP as a function of diameter with various particle size distribution of \( \sigma \) up to 0.4 for a range of six magnetic fluids of FeCo, La_{0.3}Sr_{0.7}MnO_{3}, MnFe_{2}O_{4}, \( \gamma \)-Fe_{2}O_{3}, CoFe_{2}O_{4} and FePt nanoparticles was calculated using LRT. The obtained two parameters SLP_{max}, D_{cp} will be plotted against standard deviation, and discussed in relationship with particle anisotropy.

2. THEORETICAL BACKGROUND AND DATA USED FOR CALCULATION

The calculations were conducted for the field amplitude of \( H_{o} = 6.37 \) kA/m (80 Oe) and the frequency \( f = 236 \) kHz, that the \( H_{o}f \) product is in the region of biological limit (\( H_{o}f < 4.85 \times 10^{8} \) Am^{-1}s^{-1}[9]). Table 1 represents the saturation magnetization, magnetic anisotropy and density of six materials collected from various reports. We used these data for calculation based on Linear Response Theory. We also assumed volume fraction \( \phi = 1 \) mg/ml and surface ligand layer thickness \( \delta = 1 \) nm. Based on LRT, the specific loss power SLP (W/g) was described as [1]:

\[
SLP = \frac{P}{\phi \rho}
\]  

(1)

where \( \phi \) is the volume fraction, \( \rho \) is the mean mass density of the nanoparticles and \( P \) (loss power density) described as [1, 10]:

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\[ P = \pi \mu_0 H_0^2 f \chi \frac{2\pi f \tau}{1 + 2\pi f \tau^2} \]  

(2)

in which \( \mu_0 \) is the permeability of free space; \( H_0 \) and \( f \) are correspondingly the field amplitude and frequency of AMF; \( \chi \) is the equilibrium susceptibility; and \( \tau \) is the effective relaxation time.

The equilibrium susceptibility was presented in details in [1,9,10]. And the effective relaxation time was described as [1,10]:

\[ \frac{1}{\tau_e} = \frac{1}{\tau_N} + \frac{1}{\tau_B} \]  

(3)

where \( \tau_N \) and \( \tau_B \) are the Néel and Brownian relaxation time, respectively.

**Table 1.** The saturation magnetization \( (M_s) \), magnetic anisotropy \( (K) \) and mass density \( (\rho) \) used for calculation.

<table>
<thead>
<tr>
<th>Material</th>
<th>( M_s ) (emu/g)</th>
<th>( K ) (kJ/m(^3))</th>
<th>( \rho ) (kg/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}<em>{0.7}\text{Sr}</em>{0.3}\text{MnO}_3 )</td>
<td>50 [3]</td>
<td>2 [3]</td>
<td>6700 [3]</td>
</tr>
<tr>
<td>( \gamma\text{-Fe}_2\text{O}_3 )</td>
<td>90 [1]</td>
<td>4.6 [1]</td>
<td>4600 [1]</td>
</tr>
</tbody>
</table>

Besides, SLP depends strongly on size, and its distribution [1,4]. Similarly to the previous reports [1,4] we used the log normal particle size distribution \( g(D) \), which was found to fit well to the measured distribution for ferrofluids [12]:

\[ g(D) = \frac{1}{\sqrt{2\pi\sigma D}} \exp \left[ -\frac{\ln(D/D_0)^2}{2\sigma^2} \right] \]  

(4a)

\[ \int_0^\infty g(D)dD = 1 \]  

(4b)

where \( D_0 \) is the mean diameter of particle; \( \sigma \) is standard deviation of the lognormal size distribution. Then, the values of \( P \) (Eq (2)) and relaxation times \( (\tau, \tau_B, \tau_N) \) are the mean \( \overline{\tau}, \overline{\tau_B}, \overline{\tau_N} \) of MNP fluids. The mean loss power density is described as in [1,13]:

\[ \overline{P} = \int_0^\infty \overline{P_g}(D)dD \]  

(5)

Moreover, \( \chi \) is assumed to remain constant with increasing \( H \) in the LRT. The LRT is valid in
the superparamagnetic regime where $H_0 < \frac{k_B T}{\mu_s M_s V}$ and when the magnetization of MNPs is linearly proportional to the AFM amplitude. Thus, we calculated the ratio $\frac{k_B T}{\mu_s H_0 M_s V}$ for the MNPs with $D = 50$ nm, which gave $0.26; 0.05; 0.1; 0.07; 0.07$ and $0.2$ for FeCo, La$_{0.3}$Sr$_{0.7}$MnO$_3$, MnFe$_2$O$_4$, $\gamma$-Fe$_2$O$_3$, CoFe$_2$O$_4$ and FePt, respectively. These values showed that the LRT is valid for the six magnetic fluids with $D \leq 50$ nm. In other words, the Néel relaxation and the Brown relaxation processes mainly contribute to the heating power.

3. RESULTS AND DISCUSSION

We calculated $SLP$ for the six ferrofluid materials in pure water (viscosity of 0.89 mPas) by using their bulk magnetic anisotropies given in Table 1 and for the standard deviation in the range from 0 to 0.4. Figure 1 depicts the plots of the specific loss power versus particle diameter with various standard deviation (representatively for $\sigma = 0; 0.15; 0.25$ and 0.4) for FeCo, La$_{0.3}$Sr$_{0.7}$MnO$_3$, MnFe$_2$O$_4$ and $\gamma$-Fe$_2$O$_3$ nanoparticle fluids. The $SLP$ versus $D$ with various $\sigma$ obtained for CoFe$_2$O$_4$ and FePt magnetic fluids are represented in Figure 2.

![Figure 1](image1.png)

**Figure 1.** Dependence of $SLP$ on particle diameter with various $\sigma$ for:
(a) FeCo, (b) LSMO, (c) MnFe$_2$O$_4$ and (d) $\gamma$-Fe$_2$O$_3$.

As can be seen in Fig. 1 and Fig. 2, with changing $\sigma$ the $SLP$ remains maximized at the same critical diameters ($D_{cp}$) which were obtained for the monodisperse case ($\sigma = 0$) of particular substance as reported in [3]. On the other side, the $SLP_{\text{max}}$ is observed to decrease with increasing deviation parameter in all the studied materials. In order to discuss this observation in more details, we made the graphs of relative $[SLP_{\text{max}}(\sigma)/SLP_{\text{max}}(0)]$ loss power against the standard deviation, as plotted in Fig. 3. As easily noted from this figure, the curves of $SLP_{\text{max}}$ decrease with $\sigma$ can be clearly classified into two groups, namely the group (i) contains FeCo, La$_{0.3}$Sr$_{0.7}$MnO$_3$, MnFe$_2$O$_4$, $\gamma$-Fe$_2$O$_3$, and group (ii) includes CoFe$_2$O$_4$ and FePt. The behaviour of two groups are very strongly distinguished in the $\sigma$ range from 0 to 0.15; namely the mean rates of $SLP$ decrease over 10 % $\sigma$ increase are of about 50 % and 3 % for the (i) and (ii) group, respectively. In the high standard deviation region, the decrease rate of $SLP$ is almost similar for both the groups, i.e. of about $–(7 – 8 \%)$ of $SLP_{\text{max}}$ over +10 % $\sigma$. As indicated by Cabuil in [7] and Fortin et al. in [4], the popularly used synthesis method of coprecipitation can produce
MNPs with $\sigma = 0.3 - 0.4$, while the more sophisticated method as size-sorted technique could enhance dispersity to $\sigma$ around 0.15. Our results, therefore, suggest that the so far used methods for MNPs fabrication result in loosing heating performance of not less than 50 % and 7 % for the (i) and (ii) material group, respectively.

It is now worth to refer to the physical origin of the behavior in the two MNPs groups. Fortin et al. [4] related such a behavior with the difference of peak widths of the SLP vs D curve. We, however, suppose that the more originating reason should be the impact of magnetic anisotropy, $K$. As concluded in several previous works [1, 3-5] the peak behavior of SLP vs D is a result of competition between the Neel and Brown dissipations. With increasing parameter $K$ the critical diameter $D_{cp}$ decreases as because the Brown relaxation becomes dominating. In other words, the Neel relaxation dominates in the “soft” or low $K$ ($< 5$ kJ/m$^3$) nanoparticles of FeCo, $\text{La}_{0.3}\text{Sr}_{0.7}\text{MnO}_3$, $\text{MnFe}_2\text{O}_4$ and $\gamma\text{-Fe}_2\text{O}_3$ while Brown relaxation does in the “hard” or high $K$ ($> 50$ kJ/m$^3$) nanoparticles of CoFe$_2$O$_4$ and FePt magnetic nanoparticles [3]. The dissipation in low $K$ MNPs is characteristic by sharp peak with particle diameter, whereas that of high $K$ MNPs are much more broader [1, 3, 4]. We would also like to remark that different response of low $K$ and high $K$ MNPs was also observed against another ferrofluid parameter, i.e. viscosity, where the high $K$ group is much more impacted than the low $K$ one [4, 14].

Figure 2. Dependence of SLP on particle diameter with various $\sigma$ for: (a) CoFe$_2$O$_4$ and (b) FePt.

Figure 3. Relative specific loss power versus standard deviation parameter obtained for FeCo, $\text{La}_{0.3}\text{Sr}_{0.7}\text{MnO}_3$, $\text{MnFe}_2\text{O}_4$, $\gamma\text{-Fe}_2\text{O}_3$, CoFe$_2$O$_4$, FePt MNPs. Data gained in Ref [4] are shown for comparison.
A question naturally arises, what behavior could be expected for the case of MNPs with magnetic anisotropy in the middle range, i.e. 5 – 50 kJ/m³ such as of Fe₃O₄ [1,9,10]. This subject is a topic of our further study, whose results will be published elsewhere.

4. CONCLUSION

In summary, the research results showed that the dissipation versus particle size remains of peak shape of unchanged critical diameter but the \( SLP_{\text{max}} \) decreases when the standard deviation of the particle size distribution increases. The decrease of \( SLP_{\text{max}} \) in MNPs with anisotropy below 5 kJ/m³ is so strong that a deviation with standard deviation of 0.15 could reduce the optimal heating performance by more than 50%. The impact is much less incentive for the high K MNPs (K > 50 kJ/m³), so that the decrease is less than 30% for the polydisperse NPs even with \( \sigma \) up to 0.4. Systematic study with such enough number of materials has again confirmed different impact of ferrofluid parameters such as viscosity and/or polydispersity on the magnetic heating performance in soft and hard MNPs.

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