Comparative Study of Magnetic Properties of Nanoparticles by High-Frequency Heat Dissipation and Conventional Magnetometry

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Keywords
Nanoparticles, Magnetic hysteresis, Saturation magnetization, Magnetic moments, Magnetometers, Specific absorption rate

Disciplines
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Nanomagnetics

Comparative Study of Magnetic Properties of Nanoparticles by High-Frequency Heat Dissipation and Conventional Magnetometry

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Abstract—The rate of heating of a water-based colloid of uniformly sized 15 nm magnetic nanoparticles by high-amplitude and high-frequency ac magnetic field induced by the resonating LC circuit (nanoTherics Magnetherm) was measured. The results are analyzed in terms of specific energy absorption rate (SAR). Fitting field amplitude and frequency dependences of SAR to the linear response theory, magnetic moment per particles was extracted. The value of magnetic moment was independently evaluated from dc magnetization measurements (Quantum Design MPMS) of a frozen colloid by fitting field-dependent magnetization to Langevin function. The two methods produced similar results, which are compared to the theoretical expectation for this particle size. Additionally, analysis of SAR curves yielded effective relaxation time.

Index Terms—Nanomagnetics, magnetite nanoparticles, specific absorption rate.

I. INTRODUCTION

Magnetic nanoparticles find diverse applications in photonics [Ge 2007], responsive assembly [Malik 2012, He 2012, Malik 2014], drug delivery [Amirfazli 2007], and magnetic hyperthermia cancer treatment [Sonvico 2005, Ortega 2013, Sadhukha 2013], where under an oscillating magnetic field magnetite and maghemite nanoparticles generate heat sufficient to damage or destroy tumor cells [Thiesen 2008, Yang 2012]. Numerous works reported on the particle size [Khandhar 2012, Mehdaoui 2011, Ma 2004, Khandhar 2011], degree of agglomeration [Lima 2013], concentration [Khandhar 2012], magnetic field [Kim 2008], and frequency [Kim 2008] dependent heat generation by magnetic nanoparticles. For example, Persa found that the specific absorption rate (SAR) varies with the applied magnetic field. Recently, Mehdaoui reported that single-domain magnetic nanoparticles are preferred over multidomain nanoparticles for hyperthermia applications [Mehdaoui 2011].

Not surprisingly, there are many fundamental and applied studies of heat-dissipating nanoparticles, and it seems that sufficiently simple linear response theory (LRT) provides an adequate description [Shliomis 1974, Rosensweig 2002, Carrey 2011]. To support the results obtained by LRT, numerical simulations of macroscopic magnetization of nanoparticle assemblies or qualitative observations of magnetic hysteresis were used [Martinez 2013], and Langevin function fitting of the measured magnetization was used to estimate size distribution of magnetic nanoparticles [Khandhar 2012].

AC measurements reported here are conducted at room temperature and only require water for cooling of the coils. Therefore, reliable quantitative correlation between SAR measurements and low-temperature magnetization is important for the analysis of the magnetic properties of nanoparticles derived from relatively simple room-temperature measurements. Here, magnetic moment of magnetic colloidal nanoparticles was calculated independently using the field- and frequency-dependent SAR data. Our results suggest that room-temperature SAR measurements can be used for the magnetic moment determination in colloidal suspension nanoparticles.

II. MATERIALS AND METHODS

A commercial colloidal suspension of magnetite nanoparticles was coated with carboxylic acid (5 mg/mL in water) purchased from Ocean Nanotech Inc. [2014]. The sample was concentrated by repeated centrifugation and redispersion in nanopure water at 10000 rpm to obtain a concentration of 20 mg/mL. A Technai G2 F20 scanning transmission electron microscope was used to image the nanoparticles and to obtain the size of the nanoparticles [inset of Fig. 1(a)]. The average size (15 nm) of the magnetite nanoparticles was determined by statistic average of 200 randomly chosen nanoparticles. This concentrated suspension was used for the magnetic field and temperature-dependent temperature versus time measurements using Magtherm 1.2 (Nanotherics Inc.) [2014]. Magnetic field and temperature-dependent magnetization were performed using the Magnetic Properties Measurement System (MPMS-Quantum Design).

The SAR is defined as [Ma 2004]

\[
SAR = C \frac{dT}{dt} \frac{1}{m_{Fe_3O_4}}
\]

where \( C \) is the heat capacity of the solvent (water in this case), \( \frac{dT}{dt} \) is the initial slope of the time dependent heating curve (temperature versus time, see Fig. 2) and \( m_{Fe_3O_4} \) is the magnetite content per gram of the nanoparticles suspension.
Fig. 1. Experimental magnetization curves: (a) $M(H)$ loop obtained at 260 K. Insets show TEM image of magnetite nanoparticles and their size distribution (the line represents a Gaussian fit). (b) ZFC (dark circles) and FC (open squares) at 500 Oe.

Fig. 2. (a) Heating curves (as a function of time) obtained at different magnetic fields and constant frequency of 173.3 kHz; magnetic field strength corresponding to each curve is shown in the inset of the figure. (b) Heating curves (as a function of time) obtained at different frequencies and constant magnetic field of 82.7 Oe; frequency corresponding to each curve is shown in the inset of the figure.

Fig. 3. (a) SAR obtained at different magnetic field strengths; scattered points, represent the experimental points and lines are the fit obtained using (2); frequency corresponding to each measurement is shown in the legend. (b) SAR obtained at different frequencies; scattered points represent the experimental points and lines are the fit obtained using (2); magnetic field corresponding to each measurement is shown in the legend.

III. RESULTS AND DISCUSSION

The size and morphology of these nanoparticles were also independently analyzed using TEM as described Section II [inset of Fig. 1(a)] [OceanNanotech 2014].

The temperature versus time heating curves at different magnetic fields and a fixed frequency of 173.3 kHz are shown in Fig. 2(a). The frequency-dependent heating curves were obtained at a fixed value of the magnetic field amplitude of 82.7 Oe [see Fig. 2(b)]. As a general trend, we observed temperature increase that saturates approximately after half an hour. The value of saturation temperature depends almost linearly on the strength of the applied magnetic field. The same can be said about increasing frequency. When the field is turned OFF, a decrease of temperature due to dissipation of heat to the environment was detected. The SAR, which indicates the heating efficiency of the nanoparticles suspension, was calculated by using (1). The slope ($\Delta T/\Delta t$) was calculated in the range of 20–100 s of each frequency and magnetic field data point. The calculated SAR values were then plotted as a function magnetic field and frequency, shown in Fig. 2. The experimental data were fitted with the expectation of the LRT [Shliomis 1974, Rosensweig 2002, Carrey 2011].

$$\text{SAR}(H, f) = \frac{\mu_0^2 M_s^2 V H^2 \tau_B (2\pi f)^2}{(3k_B T \rho_{Fe_3O_4})^2 \left(1 + (2\pi T \tau_B f)^2\right)^2} \quad (2)$$
where $\mu_0$ is the permeability of the free space, $M_s$ is the mass magnetization, $V$ is the particle volume, $k_B T$ is the thermal energy, $\tau_s$ is the effective relaxation time, and $\rho_f, \alpha_f$ is the density of magnetite. Magnetic field, $H$, and frequency $f$, are used as independent variables to fit the experimental SAR values to (2). Also, unknown from the first principles relaxation time, $\tau_s$, was used as a fitting parameter. The experimental curves and fitting are shown in Fig. 3(a) (versus field) and Fig. 3(b) (versus frequency). Apparently, the fitting is quite good, especially considering different functional behavior of the SAR($H$) versus SAR($f$) curves, both predicted by (2). In both cases, the only unknown is the value of saturation magnetization, $M_s$. Then, the value of magnetic moment per particle, $\mu = M_s V$, is calculated.

The fitting procedure was performed for each of the measured curves, and therefore, the inferred values must be averaged, both for field- and frequency-dependent SAR data. The calculated average values of magnetic moment per particle using (separately) field and frequency-dependent curves are $3.09 \times 10^{-19}$ J/T. Surprisingly, both field and frequency-dependent SAR curves yield very similar values of magnetic moment per particle. We believe this is due to the highly uniform nature of the studied colloidal suspension.

To validate these results, the magnetic field dependent magnetization curve was obtained at 260 K [see Fig. 1(a)]. The absence of magnetic hysteresis shows that the particles are in superparamagnetic regime at this temperature. The temperature-dependent magnetic properties of these colloids, zero-field cooled (ZFC), and field cooled (FC) data were obtained at 500 Oe [see Fig. 1(b)]. The ZFC and FC curves merge together at 130 K, roughly indicating its blocking temperature. Above the blocking temperature, the $M(H)$ as well as $M(T)$ data can be fitted with the Langevin function

$$M(H, T) = M_s \left[ \coth \frac{\mu H}{k_B T} - \frac{k_B T}{\mu H} \right].$$

Here, $M_s$ is the saturation magnetization. Fig. 4(a) shows $M(H)$ fitting, whereas Fig. 4(b) shows $M(T)$ fitting. The values of the magnetic moment obtained from the fitting are $3.33 \times 10^{-19}$ J/T and $8.44 \times 10^{-19}$ J/T, for $M(H)$ and $M(T)$ curves, respectively. These are of the same order of magnitude as obtained from the SAR curve fitting.

Furthermore, the theoretical value of magnetic moment per magnetite particle is $\mu = N \times (32 \mu_B)$, where $N$ is the number of unit cells present in a single magnetite nanoparticle and $\mu_B$ is the Bohr magneton [Prozorov 2007]. We estimate the theoretical value of magnetic moment per magnetite particle in our study to be $8.88 \times 10^{-19}$ J/T.

Although the value of calculated and experimental magnetic moment lie in the same order of magnitude, the theoretical magnetic moment is higher than the one determined by fitting the experimental data. This discrepancy is due to the fact that the interparticle interaction was not taken into account for the theoretical calculation. Indeed, magnetite nanoparticles in suspension interact with each other. This might lead to the difference in the theoretical and experimental value of magnetic moment. Therefore, this is in a reasonably close agreement with the magnetic moment obtained by fitting the SQUID and Magnetherm data. As a first step toward the development of magnetic characterization techniques, we can reliably use Magnetherm for the determination of the magnetic moment per particle of stable and monodisperse colloids.

**IV. CONCLUSION**

Heating capacity of highly uniform magnetite nanoparticles was studied as a function of magnetic field amplitude and frequency. Magnetic moment per particle was calculated by fitting the frequency- and field-dependent experimental SAR curves. Independently, magnetic field and temperature-dependent magnetization measurements were performed on the same colloid, and the results were fitted to the Langevin function. Overall, the values were found close to each other and close to the theoretical expectation of magnetite nanoparticles of the observed size. This study provides the first direct experimental support for the LRT used for the analysis of heating in the colloidal assemblies of nanoparticles.

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where \( \mu_0 \) is the permeability of the free space, \( M_s \) is the mass magnetization, \( V \) is the particle volume, \( k_B T \) is the thermal energy, \( \tau_e \) is the effective relaxation time, and \( \rho_{Fe} \) is the density of magnetite. Magnetic field, \( H \), and frequency, \( f \), are used as independent variables to fit the experimental SAR values to (2). Also, unknown from the first principles relaxation time, \( \tau_e \), was used as a fitting parameter. The experimental curves and fitting are shown in Fig. 3(a) (versus field) and Fig. 3(b) (versus frequency). Apparently, the fitting is quite good, especially considering different functional behavior of the SAR(\( H \)) versus SAR(\( f \)) curves, both predicted by (2). In both cases, the only unknown is the value of saturation magnetization, \( M_s \). Then, the value of magnetic moment per particle, \( \mu = M_s V \), is calculated.

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