

A NEW APPROACH FOR CALCULATION OF RELAXATION TIME AND MAGNETIC ANISOTROPY OF FERROFLUIDS CONTAINING SUPERPARAMAGNETIC NANOPARTICLES

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Abstract

In this work, a new approach is described for the calculation of the relaxation time and magnetic anisotropy energy of magnetic nanoparticles. Ferrofluids containing monodispersed magnetite nanoparticles were synthesized via hydrothermal method and then heated using the 10 kA/m external AC magnetic fields in three different frequencies: 10, 50 and 100 kHz. By measuring the temperature variations during the application of the magnetic field, the total magnetic time constant including both Brownian and Neel relaxation times can be calculated. By measuring the magnetic core size and hydrodynamic size of particles, the magnetic anisotropy can be calculated too. Synthesized ferrofluids were characterized via TEM, XRD, VSM and PCS techniques and the results were used for the mentioned calculations.

Keywords: relaxation time; magnetic anisotropy; Ferrofluids; magnetite nanoparticles

1. Introduction

Ferrofluids containing the magnetic nanoparticles have a wide range of biomedical applications such as drug delivery [1], Magnetic Resonance Imaging (MRI) contrast agent [2, 3] and magnetic

hyperthermia [4, 5]. The physical properties of these ferrofluids such as viscosity, particles magnetic anisotropy and heat capacity play an important role in ferrofluid temperature rise used in hyperthermia applications. This temperature rise is mainly due to three types of power loss including

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hysteresis loss, Brownian loss and Neel loss.

In the case of superparamagnetic nanoparticles in which hysteresis loss is zero, power loss can be written as [6]:

$$P = 2\pi^2 \mu_0 \chi_0 H^2 \frac{f^2 \tau}{1 + (2\pi f \tau)^2} \quad \dots(1)$$

Where, μ_0 is the permeability of free space, χ_0 is a magnetic field dependent term, H and f are the amplitude and frequency of the AC field and τ is the total relaxation time:

$$\frac{1}{\tau} = \frac{1}{\tau_N} + \frac{1}{\tau_B} \quad \dots(2)$$

Where, τ_N and τ_B are the Neel and Brownian relaxation times, respectively and can be presented as [7]:

$$\tau_N = \tau_0 \exp\left(\frac{KV_p}{k_B T}\right) \quad \dots(3)$$

$$\tau_B = \frac{3\eta V_h}{k_B T} \quad \dots(4)$$

Where, τ_0 is a time constant approximately equal to 10^{-9} sec, K is the particle magnetic anisotropy, V_p is the particle volume, k_B is the Boltzman constant, T is the absolute temperature, η is the ferrofluid carrier viscosity and V_h is the particle hydrodynamic volume.

Assuming that temperature rise, ΔT , increases linear with power loss, P , the relationship between temperature rise and power loss due to the applied external magnetic field can be written as:

$$P \propto \Delta T \Rightarrow P = C \Delta T \quad \dots(5)$$

Where, C is constant of proportionality. If magnetic field frequency f changes while amounts of other parameters such as physical

properties of ferrofluid, magnetic field strength H and initial ferrofluid temperature T remain constant, the following equations can be written by measurement of ΔT due to frequency variation:

$$\frac{\Delta T_2}{\Delta T_1} = \frac{P_2}{P_1} = a \quad \frac{f_2}{f_1} = b \quad \dots(6)$$

$$a = \frac{P_2}{P_1} = \frac{2\pi^2 \mu_0 \chi_0 H^2 \frac{f_2^2 \tau_2}{1 + (2\pi f_2 \tau_2)^2}}{2\pi^2 \mu_0 \chi_0 H^2 \frac{f_1^2 \tau_1}{1 + (2\pi f_1 \tau_1)^2}} = \frac{b^2 \tau_2}{1 + (2\pi f_2 \tau_2)^2} \Rightarrow \frac{a}{b^2} = \frac{\tau_2 [1 + (2\pi f_1 \tau_1)^2]}{\tau_1 [1 + (2\pi f_2 \tau_2)^2]} \quad \dots(7)$$

$$\Rightarrow \frac{a}{b^2} \tau_1 + \frac{a}{b^2} 4\pi^2 f_2^2 \tau_2^2 \tau_1 = \tau_2 + 4\pi^2 f_1^2 \tau_1^2 \tau_2$$

According to Eqs. 2-4, the total relaxation time, τ , is independent of applied frequency, f , so $\tau_1 = \tau_2$ and Eq. 7 can be simplified as:

$$\frac{a}{b^2} + \frac{a}{b^2} 4\pi^2 f_2^2 \tau^2 = 1 + 4\pi^2 f_1^2 \tau^2$$

$$\Rightarrow \tau = \sqrt{\frac{\frac{a}{b^2} - 1}{4\pi^2 (f_1^2 - \frac{a}{b^2} f_2^2)}} \quad \dots(8)$$

So, the total relaxation time can be calculated via ΔT measurement in two different amounts of frequencies. Equation 8 can be written as:

$$-\ln \left| 4\pi^2 \left(f_1^2 - \frac{a}{b^2} f_2^2 \right) \right| = -\ln \left| \frac{a}{b^2} - 1 \right| + \ln \tau^2 \quad \dots(9)$$

So, in the case of the multi-frequency AC magnetic field, τ is equal to the intercept of the plot $A = -\ln \left| 4\pi^2 \left(f_1^2 - \frac{a}{b^2} f_2^2 \right) \right|$ of versus $B = -\ln \left| \frac{a}{b^2} - 1 \right|$. Obviously, the slope of this plot

should be unity.

According to Eqs. 2-4, τ , is a function of some material properties and environmental conditions and can be written as:

$$\tau = \tau(T, K, V_p, V_h, \eta) \quad \dots(10)$$

So, if the amounts of T , V_p , V_h and τ are known, K can be calculated too. On the other hand, by using this approach in different values of initial ferrofluid temperature, T , amounts of V_p , V_h and η can be calculated too and compared with experimental results.

Among numerous methods of synthesizing magnetic nanoparticles such as co-precipitation [8, 9], sol-gel [10], thermal decomposition [11, 12] and hydrothermal [13-15], thermal methods such as hydrothermal process lead to the formation of monodispersed particles with a narrow size distribution. Since calculation of K via described approach requires a narrow size distribution of particles, magnetite nanoparticles were synthesized via hydrothermal process in this work. Experimental data were used according to the above-mentioned approach and two reasonable amounts of τ and K was calculated for two different ferrofluids. It seems that the described approach can be used in similar cases for the calculation of τ and K for various magnetic nanoparticles.

2. Experimental Procedure

2. 1. Sample preparation

Magnetite nanoparticles were synthesized via hydrothermal process using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as Fe^{2+} source, dimethyl sulfoxide (DMSO) as oxidant to oxidize

Fe^{2+} to Fe^{3+} , tetra methyl ammonium hydroxide (TMAH) as reducing agent and oleic acid as surfactant. All chemical reagents were of analytical grade and used as received without further purification. The detailed hydrothermal process was illustrated elsewhere [13]. Briefly, the relative amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, DMSO, TMAH and oleic acid were magnetically stirred at 140 °C for 60 minutes under argon atmosphere. Then, the black product was washed three times with acetone, magnetically separated and finally dried in oven and used for X-Ray Diffraction (XRD) and Vibration Sample Magnetometer (VSM) characterizations. By changing the system alkalinity, two samples of oleic acid capped nanoparticles were synthesized (samples A1 and A2). The relative molar ratio $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ / DMSO / oleic acid / TMAH was equal to 1/0.08/ 0.008/0.002 and 1/0.08/0.008/0.003 for samples A1 and A2, respectively. 1 mg of samples A1 and A2 were dispersed in 20 ml of hexane and prepared for Transmission Electron Microscopy (TEM) and Photon Correlation Spectroscopy (PCS) characterizations. 50 mg of samples A1 and A2 were dispersed in 10 ml of hexane to prepare ferrofluids with concentration of 5 mg (particle)/ml (ferrofluids F1 and F2, respectively). 0.5 ml of the synthesized ferrofluid was put in a thermal insulation container with minimum heat transfer and AC magnetic field was applied to it. The temperature variation versus time was measured and recorded in a period of 60 seconds (Fig. 1).

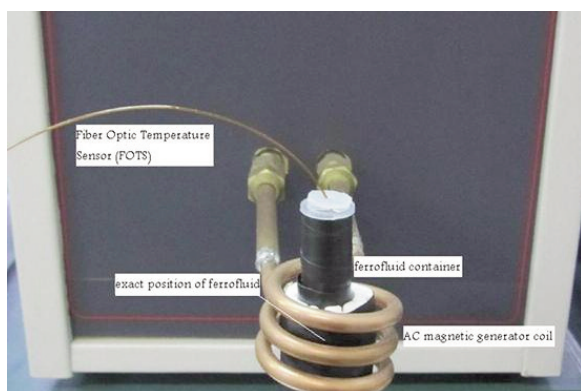


Fig. 1. Used setup for measuring temperature increase due to application of external AC magnetic field.

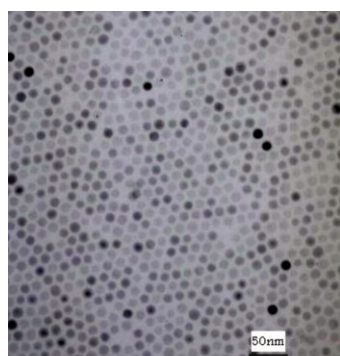
2. Apparatus and characterizations

XRD patterns were taken by a Siemens D5000 X-ray diffractometer using graphite-monochromatized high-intensity $\text{Cu-K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). A JEOL TEM JEM-

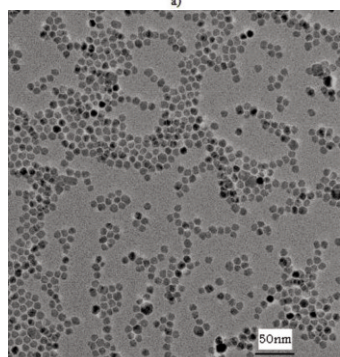
2010F was used to determine the average particle size and morphology of the powders on an accelerating voltage of 200 kV. Beckman particle size analyzer was employed for hydrodynamic diameter measurement via PCS technique. Also, a Lakeshore 7470 VSM was used for magnetic characterization. One AC magnetic field generator was used for heating the synthesized ferrofluid at 10 kA/m and three different amounts of frequency: 10, 50 and 100 kHz. The fiber optic temperature sensor (FOTS) system was employed for exact measurement of temperature variation (Fig. 1).

3. Results and Discussion

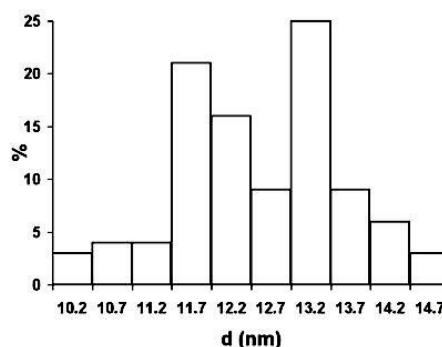
TEM images of samples A1 and A2 are presented in Fig. 2, showing spherical monodispersed particles. So, particle volume can be calculated from, $V_p = \frac{4}{3}\pi r_p^3$ where r_p



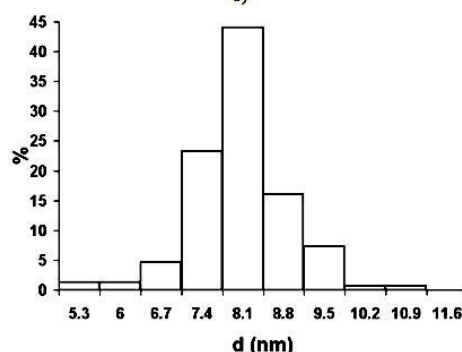
a)



c)



b)



d)

Fig. 2. TEM images and particle size distribution of samples A1 (a, b) and A2 (c, d).

is the particle radius. Measuring 100 particles for each specimen, the mean particle size was calculated as 12.64 and 8.84 nm for the samples A1 and A2, respectively. XRD patterns of samples A1 and A2 are shown in Fig. 3, revealing the inverse spinel structure of these samples, belonging to Fe_3O_4 . The characteristic peaks for these samples ($2\theta = 30.10^\circ, 35.51^\circ, 43.11^\circ, 53.48^\circ, 56.83^\circ$ and 62.77°) are well match with the magnetite characteristic peaks (JCPDS card: 19-0629). VSM diagrams of samples A1 and A2 are shown in Fig. 4, verifying the superparamagnetic behavior of synthesized particles, so hysteresis loss is zero. Saturation magnetizations are equal to 68.1

and 65.4 emu/gr for samples A1 and A2, respectively. Figure 5 shows the size histograms of samples A1 and A2 obtained from PCS measurement. The mean hydrodynamic sizes from these histograms are equal to 52.8 and 43.1 nm for the samples A1 and A2, respectively. The recent measurement was repeated four times for each sample and the mean results were reported as the mean hydrodynamic size.

The amounts of temperature increase (ΔT) after 60 seconds application of the AC magnetic field to 0.5 ml of the ferrofluids A1 and A2 are listed in table 1 and Fig. 6. These amounts are calculated from three

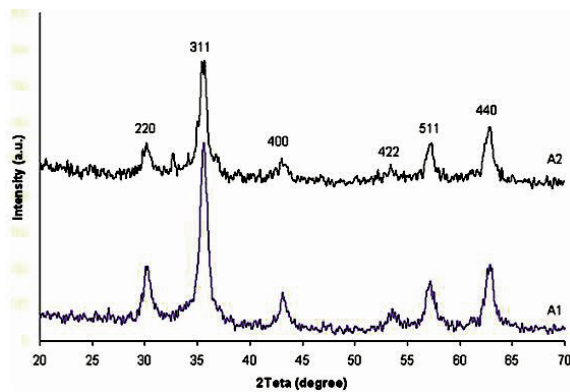


Fig. 3. XRD patterns of samples A1 and A2.

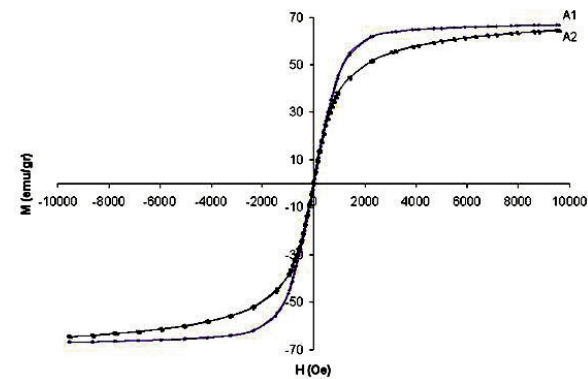


Fig. 4. VSM diagram of samples A1 ($M_s = 68.1$ emu/gr) and A2 ($M_s = 65.4$ emu/gr).

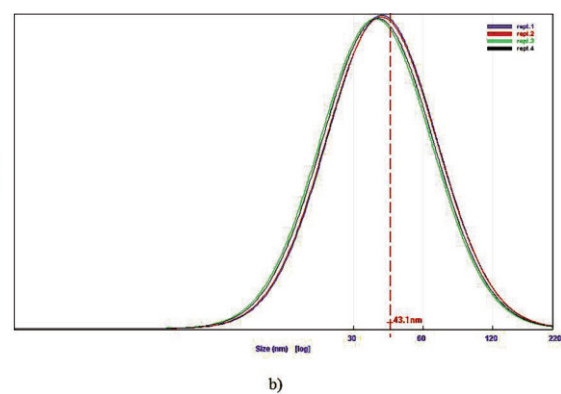
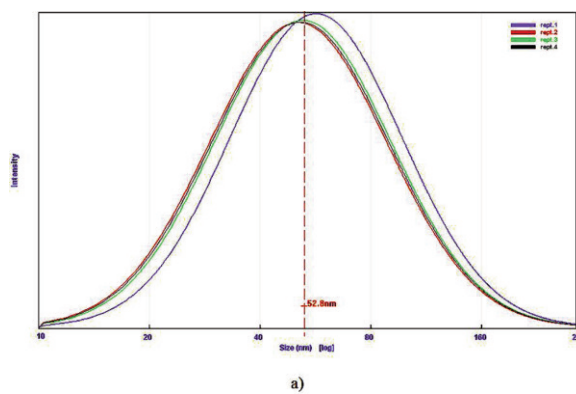


Fig. 5. Mean hydrodynamic size of ferrofluid a) A1 and b) A2. The results were obtained from PCS measurements performed four times for each sample.

measurements at each frequency. According to data listed in table 1, the total magnetic time constant of ferrofluids A1 and A2 can be calculated using Eq. 1. According to the approach described in the introduction section, τ can be calculated by plotting $A = -\ln\left|4\pi^2\left(f_1^2 - \frac{a}{b^2}f_2^2\right)\right|$ versus $B = -\ln\left|\frac{a}{b^2} - 1\right|$ (Fig. 7). As shown in Fig. 7, curve slopes are close to unity so can be calculated from the intercepts, according to Eq. 9. These intercepts are equal to -27.105 and -26.708

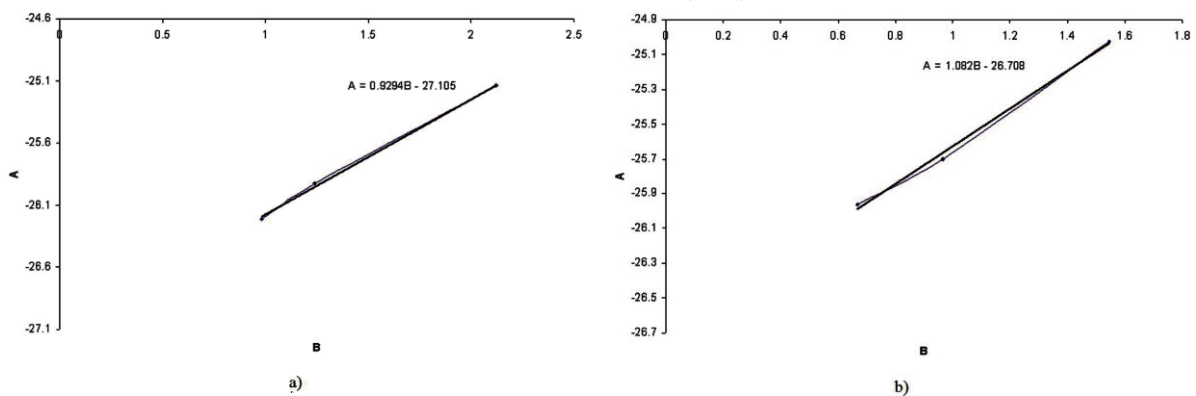


Fig. 7. Diagrams showing $A = -\ln\left|4\pi^2\left(f_1^2 - \frac{a}{b^2}f_2^2\right)\right|$ versus $B = -\ln\left|\frac{a}{b^2} - 1\right|$ for samples a) A1 and b) A2. Intercepts are calculated as -27.105 and -26.708 for samples A1 and A2, respectively.

Table 1. Temperature increase of ferrofluids A1 and A2 at 10 kA/m and various frequencies

Sample	D _{TEM} (nm)	D _{PCS} (nm)	Viscosity ¹ (cP)	$\Delta T_{10\text{kHz}}$ (°C)	$\Delta T_{50\text{kHz}}$ (°C)	$\Delta T_{100\text{kHz}}$ (°C)
A1	12.64	52.8	0.31	0.15	2.95	7.30
A2	8.84	43.1	0.31	0.10	2.20	6.25

¹ viscosity of ferrofluid carrier (hexane) at 20 °C

Table 2. Calculation of $A = -\ln\left|4\pi^2\left(f_1^2 - \frac{a}{b^2}f_2^2\right)\right|$ and $B = -\ln\left|\frac{a}{b^2} - 1\right|$ for samples A1 and A2

sample	f ₁ (kHz)	f ₂ (kHz)	ΔT_1 (°C)	ΔT_2 (°C)	a ¹	b ²	A ³	B ⁴
A1	10	100	0.15	7.30	48.67	10	0.66	-25.96
	50	100	2.95	7.30	2.47	2	0.94	-25.70
	10	50	0.15	2.95	19.67	5	1.54	-25.02
A2	10	100	0.10	6.25	62.5	10	0.98	-26.21
	50	100	2.20	6.25	2.84	2	1.23	-25.92
	10	50	0.10	2.20	22	5	2.12	-25.14

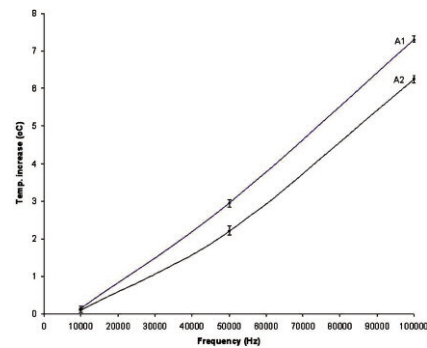


Fig. 6. Temperature increase of ferrofluids A1 and A2 versus AC magnetic field frequency at 10 kA/m ($n=3$).

for samples A1 and A2, respectively. The detailed calculations are listed in table 2 and τ values are determined as 1.58 and 1.06 μsec for ferrofluids A1 and A2, respectively.

Using the data tabulated in table 1, the magnetic anisotropy, K , can be calculated from Eqs. 2-4. Using Eq. 4, values of, $\eta = 0.00031 \text{ Pa}\cdot\text{sec}$, $k_B = 1.38 \times 10^{-23} \frac{J}{K}$, $T = 300 \text{ K}$ and $V_h = \frac{4}{3} \times \pi \times (26.4 \times 10^{-9})^3 = 7.71 \times 10^{-23} \text{ m}^3$, lead to a calculated τ_B of 17.73 μsec for sample A1. So, according Eq. 2 $\tau_N = 1.73 \mu\text{sec}$ and using, $\tau_0 = 10^{-9} \text{ sec}$, $k_B = 1.38 \times 10^{-23} \frac{J}{K}$, $T = 293 \text{ K}$ and $V_p = \frac{4}{3} \times \pi \times (6.32 \times 10^{-9})^3 = 1.06 \times 10^{-24} \text{ m}^3$, is calculated as $28500 \frac{J}{\text{m}^3}$ for A1. Similar approach leads to a calculated value of $81450 \frac{J}{\text{m}^3}$ for A2. These results are reliable according to the literature [16, 17] in which reported K values in the range of 13500 to 100000 $\frac{J}{\text{m}^3}$ for magnetite and according to this fact that K is a size-dependent factor that increases with particle size decrease.

4. Conclusion

In this work, ferrofluids containing monodispersed oleic acid capped magnetite nanoparticles were synthesized via hydrothermal method. By using one calorimetric method, ferrofluids' relaxation time and particles' magnetic anisotropy were calculated. It seems that this approach can employed for similar calculations for various magnetic nanoparticles.

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