Brownian Relaxation of Interacting Magnetic Nanoparticles in a Colloid Subjected to a Pulsatile Magnetic Field

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We have investigated and modeled the effect of interaction among magnetic particles and the magnitude and duration of external applied magnetic field on Brownian relaxation in a colloidal suspension. In the case of interacting magnetic particles, Brownian relaxation depends on the interparticle dipole–dipole interaction, which slows down the overall Brownian relaxation process of magnetic particles in the colloidal suspension. The individual magnetic particle experiences torque when a pulsatile magnetic field is applied. The torque due to the external field randomizes the particle rotation similar to that of the thermal energy. A faster Brownian relaxation is observed when individual magnetic particles are magnetized for a short duration. Magnetizing the magnetic particle for a longer duration suppresses the rotational motion hence the effect of torque on Brownian relaxation.

Keywords: Magnetic Nanoparticle Colloids, Magnetic Relaxometry, Brownian Relaxation, SQUID.

1. INTRODUCTION

Magnetic particles colloidal suspensions have been proposed for a wide range of biological applications and medical diagnostic1,2 and have been used for years as tracers and contrast agents in medical imaging.3–5 Other applications include magnetic cell separation,6,7 magnetic hyperthermia,8,9 targeted drug delivery,10,11 magnetofection,12 magnetic relaxation immunoassay,13,14 magnetic relaxation imaging,15 remote control,16 and magnetic particle imaging.17 The performances of most of these applications rely on the relaxation mechanism of magnetic particles in the colloidal suspension.

A typical colloidal suspension of magnetic particle contains on the order of 10¹⁴ particles per cm³, which varies with particle size and concentration. After removing the magnetizing field, magnetic particles in a colloidal suspension exhibit two relaxation mechanisms, the Néel relaxation described as the flipping motion of magnetic moment relative to the particle and the Brownian relaxation described as the random rotation of the momentum through the particle’s movement. When the magnetic anisotropy energy is high enough to block the magnetization inside the magnetic particles, then Néel dynamics is much slower than Brownian relaxation and can be ignored. Brownian relaxation of magnetic particles in colloidal suspension depends on the viscosity of the medium, particle’s hydrodynamic volume, which includes coating and surfactant attached to the magnetic cores, and the thermal energy. Since the Brownian relaxation also depends on various other parameters, such as particle core size distribution, dipole–dipole interaction, and other sources of external fluctuations, it is important to clarify these issues prior to applications. Recently Enpuku et al.21 discussed possible models of Brownian relaxation that include particle size distribution and estimated the distribution of magnetic moment, relaxation time, and particle size by comparing experimental results with theoretical predictions. But the effect of interparticle interaction, and magnetic field attributed torque on the Brownian relaxation has not yet been adequately documented.

The interparticle interactions can affect the magnetic relaxation mechanism in several ways. Many phenomena observed in magnetic particle suspensions, such as the viscosity enhancement in a static magnetic field,22 the presence of negative viscosity,23 or the magnetovertical resonance,24 are direct result of the inter-particle interaction. There have been different models proposed25–27 to explain the effect of interaction on dynamic behavior of magnetic particles. For instance, interparticle interactions...
are accounted for by a change of the energy barriers of the isolated particles in some models, whereas the other model includes collective magnetic behavior of the particles. In order to provide a basic understanding, we have investigated the effect of interparticle interaction, magnetizing field, and magnetizing time on the Brownian relaxation of magnetic particle in a colloidal suspension.

2. THEORETICAL MODEL

The Brownian relaxation of monodisperse magnetic particles suspended in a liquid due to random and diffusive motion is exponential. The decay of the remanent field can be phenomenologically described by

\[ B_r(t) = B_0 \exp \left( -\frac{t}{\tau_B} \right) \]  

(1)

Here, \( B_r \) is the remanent fields and \( B_0 \) is the magnetic field produced by the magnetic particles just before relaxation. The exponent \( \beta \) (varies in between 0 and 1) is a measure of the particle size distribution, \( \beta = 1 \) for a sample of mono dispersed particles. The time constant of Brownian relaxation \( \tau_B \) is given by

\[ \tau_B = \frac{3V^*\eta}{k_BT} \]  

(2)

where \( V^* \) is the hydrodynamic volume of the particle, \( \eta \) is the viscosity of the liquid medium, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. Viscosity of water has following temperature dependent expression.

\[ \eta = 2.414 \times 10^{-5} \times 10^{(247.8/(T-140))} \text{ Pa} \cdot \text{s} \]  

(3)

Substituting the value of \( \eta \) in Eq. (2) we have the expression for Brownian relaxation time

\[ \tau_B = \frac{3V^* \times 2.414 \times 10^{-5} \times 10^{(247.8/(T-140))}}{k_BT} \]  

(4)

Equation 2 is valid only for non interacting magnetic particles without considering the effect of other forces such as gravitational, rotational and van der Waals. The interaction among magnetic particles restricts the random diffusive rotation of particles. Applying external magnetic pulse produces torque, which enhances the random walk motions of the magnetic particles in the colloidal suspension. Adding these forms of energy relevant to the diffusive mechanism to the thermal energy \( k_B T \), the new expression for the time constant of Brownian relaxation time is

\[ \tau_B = \frac{3V^*\eta}{(k_BT + E_r - E_{ad})} \]  

(5)

Here \( E_r \) is the average rotational energy and \( E_{ad} \) is the average dipole–dipole interaction energy of magnetic particles in the colloidal suspension.

Assuming the particles are uniformly suspended in the liquid, the average particle–particle separation \( z \) is given by

\[ z = a \left( \frac{4\pi \rho}{3\kappa} \right)^{1/3} \]  

(6)

where \( a \) is the radius and \( \rho \) is the density of particle and \( C \) is the concentration of particles in weight per unit fluid volume. Considering each magnetic particle act as a dipole after the magnetizing field is switched off, the particle–particle magnetic interaction energy \( E_{ad} \) is given by

\[ E_{ad} = \frac{\pi \mu_0 M_r^2 a^3}{(l + 2)^2} \]  

(7)

Here \( M \) is the magnetization per unit volume and \( l = 2z/a \). Substituting the value of \( z \) in Eq. (7), and considering that the average particle–particle separation is much larger than the size of particle, we have \( E_{ad} \) directly proportional to the concentration \( C \)

\[ E_{ad} = \frac{\mu_0 M_r^2 a^3 C}{96\rho} \]  

(9)

The torque \( \tau \) acting on magnetic particles in the colloidal suspension with magnetic moment \( m \) makes an angle \( \theta \) with an applied field \( H_{mag} \) which is given by

\[ \tau = mH_{mag} \sin \theta \]  

(10)

The average rotational energy of the magnetic particles is given by the average integral of torque over angle of individual magnetic particle: \( mH_{mag} \). Because magnetic particle in the colloidal suspension undergoes simple underdamped harmonic motion after applying a magnetizing field, the average rotational energy decays exponentially and can be expressed as

\[ E_r = mH_{mag} e^{-2\tau_{int}} \]  

(11)

Here \( \gamma \) is the damping factor. Substitution of the values of \( E_r \) and \( E_{ad} \) in Eq. (5) leads to a general equation for the Brownian relaxation time

\[ \tau_B = \frac{3V^*\eta}{(k_BT + mH_{mag} e^{-2\tau_{int}} - \frac{\mu_0 M_r^2 a^3 C}{96\rho})} \]  

(12)

Equation (12) quantitatively expresses the effect of interparticle interaction, magnetizing field, and magnetizing time on the overall Brownian relaxation of magnetic particles in a colloidal suspension.

3. EXPERIMENTAL DETAILS

A custom-built single channel Superconducting Quantum Interference Device (SQUID) system was used to measure the decay of magnetic field due to the magnetic relaxation of magnetic particles. The system is equipped
with a low-temperature dc-SQUID coupled to a 12 mm pick-up coil configured as a first-order gradiometer with a baseline of 50 mm and is controlled by dc-SQUID electronics. The total field noise with pick-up coil at 1 kHz is $20\sqrt{T/F}$ dominated by the environmental noise. A Labview®-based interface was used for data acquisition and control of SQUID electronics. In a typical experiment, samples of magnetic particle suspension are exposed to magnetizing fields $H_{\text{mag}}$ from 0.1 to 30 mT and magnetizing time $t_{\text{mag}}$ from 1 to 10 s. After switching off the magnetizing field the SQUID FLL is put into operation with a defined time delay before the remnant magnetization decays is measured. A delay time of 50 ms was chosen. The delay of the recording was to minimize the residual signal due to the exponential decay of magnetizing field when switched off. Averaging of 25 epochs was used for each experiment. To analyze the recorded relaxation curves and to find out best fitting parameters, the curves recorded at different temperature and concentrations were fitted (nonlinear least squares fitting) using Eqs. (1) and (12).

Gamma-ferric oxide ($\gamma$-Fe$_2$O$_3$) magnetic particles were chosen for the experiments. These magnetic particles are spherical in shape and superparamagnetic in nature. The average magnetic core diameter $\sim 40$ nm with $M_s = 1.4 \times 10^9$ A/m. The magnetic particles are coated with Carboxyl to prevent agglomeration. The average hydrodynamic diameter of these magnetic particles was determined to be approximately 1.31 μm. In order to investigate the effects of concentration, the superparamagnetic colloidal suspension was diluted into different volumes of deionized water to obtain the magnetic particle colloid suspensions of various iron concentrations. The magnetic particle suspension was injected into a cylindrical plastic capsule of total volume 290 μL. The concentrations of iron oxide in the capsule varied in between 34 ng to 680 ng per μL to study the effect of inter particle interaction. The capsule was mounted onto a non-magnetic sample holder and the holder was kept inside a water bath for temperature variation experiment. The temperature of the water was maintained and varied from 275 to 321 K (with ±1 K precision) by an external heater. The whole setup was placed on the axis of the magnetization coil and under the SQUID probe.

4. RESULTS AND DISCUSSION

Figure 1 shows the relaxation signal of water-based $\gamma$-Fe$_2$O$_3$ magnetic nanoparticle suspension of highest concentration measured after applying magnetizing pulse ($H_{\text{mag}} = 2$ mT and $t_{\text{mag}} = 1$ s) recorded at different temperature. Solid curves are the corresponding Brownian relaxation fit. The insets show the fit parameters $\tau_B$ and $B_0$ plotted against temperature. The left inset shows the Brownian relaxation time, $\tau_B$ obtained from fitting the relaxation curves at various temperatures. The solid line in the left inset shows the least-mean-square fit to Eq. (4). The parameter $\tau_B$ versus temperature are depicted in the left insert of Figure 1. $\tau_B$ was found to decrease with increasing temperature. The decrease of the Brownian relaxation time is caused directly by increasing temperature and indirectly by the viscosity of water, which tends to fall as temperature increases. The best value of hydrodynamic volume obtained from fitting with Eq. (4) was $3.66 \times 10^{-18}$ m$^3$, which is larger than the expected hydrodynamic volume $V^*$ of magnetic particle used is $1.18 \times 10^{-18}$ m$^3$. We consider the increased hydrodynamic volume as the effective hydrodynamic volume covered by the ordering range of magnetic particles. The increase in hydrodynamic volume is considered to be due to the interaction between magnetic particles. The parameter $B_0$ is nearly independent of temperature and is depicted in the right inset.

In order to examine the correlation between the Brownian relaxation time and particle interaction, we performed concentration variation experiment at five different concentrations. The assumption here is that higher is the concentration stronger is the dipole–dipole interaction as the average particle–particle separation decreases. Figure 2 shows the relaxation signal of magnetic nanoparticle suspension of various concentrations at room temperature (298 K). To analyze the magnetic particle relaxation time versus temperature, the curve was fitted with Eq. (1). The fit parameters are depicted in the insets. At higher concentration, the relaxation process which is because of the random movements of magnetic particles is collective in nature. So the increasing trend of Brownian relaxation time with increasing concentration is due to the interparticle interactions (see the left inset). Considering the uncertainty
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Eq. (12).

in the estimation of the time constant of Brownian relaxation \( \tau_B \), the experimental curve depicted in the left insert of Figure 2 is fitted to Eq. (12). Assuming \( V^* = 1.18 \times 10^{-18} \) m\(^3\), \( \eta = 8.93 \times 10^{-4} \) Pa·s, and \( T = 298 \) K, a good agreement is obtained between experiment and Eq. (12) for \( E_0 \) (for \( H_{\text{mag}} = 2 \) mT and \( t_{\text{mag}} = 1 \) s) = 1.18 \times 10^{-21} \) J. The right insert shows the linear dependence of the parameter \( B_0 \) with increasing concentration.

Figure 3 shows the relaxation signals of magnetic particle suspension measured at \( t_{\text{mag}} = 1 \) s and different magnetizing fields. The data measured at different magnetizing field were fitted with Eq. (1) and the fit parameters are depicted in the insets. The short relaxation time is observed at higher magnetic field. Such behavior is expected because of the increasing rotational motion of magnetic particle with increasing magnetizing field. The individual magnetic particle experiences torque when a pulsatile magnetic field is applied. The torque due to the external field randomizes the particle rotation similar to that of the thermal energy. Initially the magnetization of magnetic particles saturates along the easy axis. The process takes a few ns to ms depending on the magnetizing field and the anisotropy energy constant \( K \) of magnetic particles. Magnetic particle with induced moment \( m \) experiences magnetic torque \( \tau \) and get aligned along the magnetic field direction. The particles become more and more aligned with the field direction which undergoes an under-damped harmonic oscillation. Particles continue to rotate for a while after removal of the magnetizing field depending on the magnetic torque and the viscosity of liquid medium. Angular momentum or rotational motion arises by such a magnetic torque increases with increasing magnetizing field. Larger is the rotational motion faster is the relaxation. Considering the uncertainty in the estimation of the time constant of Brownian relaxation \( \tau_B \), the experimental curve depicted in the left insert of Figure 3 is fitted to Eq. (12). Assuming \( V^* = 1.18 \times 10^{-18} \) m\(^3\), \( \eta = 8.93 \times 10^{-4} \) Pa·s, and \( T = 298 \) K, a good agreement is obtained between experiment and Eq. (12) for \( E_0 \) (at \( C = 0.68 \) µg per µL) = 3.76 \times 10^{-21} \) J.

The parameter \( B_0 \) increases with increasing magnetizing field but begin to saturate at lower field of 20 mT (see right insert). Whereas the values of saturation magnetization \( M_s \) determined from the saturation signal of the static \( M \sim H \) curve specified by the manufacturer is nearly 1.7 T. Similar behavior are also observed by others.\(^{21}\) Enpuku et al. discussed this discrepancy as a result of the aggregation of particles. But we think the discrepancy can be explained better in the context of particle size distribution. Magnetization of magnetic particles saturate at high field, but the initial susceptibility is small when particle size is small; however, the initial susceptibility grows rapidly with increasing particle size. In weak fields most contribution to the magnetization is made by the larger size particles, which are more easily oriented by a magnetic field. But the fine particles require large field to get accumulate saturation of magnetization. Due to this reason most of the magnetic particles which contribute relaxation in the measurement time window (particles of larger diameter) reach to their saturation magnetization at lower field. In the time domain measurement, the fast Néel relaxation (particles of smaller diameter) is seen immediately after the field is switched off. The fast relaxation signal is hidden in the small delay time after switching off the magnetic field and does not contribute for the calculation of parameter \( B_0 \).

The relaxation signal of magnetic particle suspension at \( H_{\text{mag}} = 5 \) mT while varying pulse duration is shown
in Figure 4. The fit parameters are depicted in the insets. The parameter $\tau_2$ increases with increased magnetization time (see the left insert). Such behavior can be explained by the underdamped harmonic oscillatory motion of the magnetic moments along with the magnetic particle. Magnetic moments oscillate along the direction of magnetic field before get aligned to the direction of magnetic field. The oscillation decreases over time due to the drag force in the viscous medium. Angular momentum of a magnetic moments along with the magnetic particle. Magnetic moments oscillate along the direction of magnetic field before get aligned to the direction of magnetic field. The oscillation decreases over time due to the drag force in the viscous medium. Angular momentum of a magnetic particle at a certain point of time is proportional to the amplitude of oscillation. So the angular momentum of magnetic particles decreases over time due to the underdamped oscillation in the viscous medium. Smaller is the angular momentum or the rotational motion less is overall contribution towards the relaxation process. Considering the uncertainty in the estimation of the time constant of Brownian relaxation $\tau_2$, the experimental curve depicted in the left insert of Figure 4 is fitted to Eq. (12). Assuming $V^* = 1.18 \times 10^{-13}$ m$^3$, $\eta = 8.93 \times 10^{-4}$ Pa·s, and $T = 298$ K, a good agreement is obtained between experiment and Eq. (12) for $E_{UA}$ (at $C = 0.68 \, \mu g$ per $\mu L) = 3.63 \times 10^{-1}$ J. The right insert shows the parameter $B_0$ as a function of magnetizing time, which remains nearly independent of magnetizing time. As the magnetization saturates within first few microseconds for a magnetizing pulse of amplitude 5 mT, there is no change observed in varying magnetizing time (100 ms to 10 s).

5. CONCLUSIONS

Magnetic relaxation behavior of magnetic particle suspensions has been investigated by SQUID measurements. The experimental results were quantitatively compared with the theoretical model. Magnetic particle interaction in a colloidal suspension can be correlated to the dipole–dipole interaction. It is found that magnetic particle interaction restricts the overall Brownian relaxation mechanism. Pulsed magnetic field applied to the magnetic particles suspensions enhances the Brownian relaxation process depending on the pulse duration, magnetic moment of individual particle and the viscosity of the medium. Overall, Brownian relaxation time not only depends on the temperature and viscosity of medium and size and size distribution of particles but also depends on the concentration and pulse height and duration of applied magnetic field. This effect needs to be emphasized for various biomedical applications of magnetic particle colloids particularly in the case of magnetic relaxation immunoassay, where magnetic particles bound to biological targets are distinguished from unbound particles because of the different relaxation times.

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References and Notes

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