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Harmonics distribution of iron oxide nanoparticles solutions under diamagnetic background

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ABSTRACT

The static and dynamic magnetizations of low concentrated multi-core iron oxide nanoparticles solutions were investigated by a specially developed high-T_c Superconducting Quantum Interference Device (SQUID) magnetometer. The size distribution of iron oxide cores was determined from static magnetization curves concerning different concentrations. The simulated harmonics distribution was compared to the experimental results. Effect of the diamagnetic background from carrier liquid to harmonics distribution was investigated with respect to different intensity and position of peaks in the magnetic moment distribution using a numerical simulation. It was found that the diamagnetic background from carrier liquid of iron oxide nanoparticles affected the harmonics distribution as their concentration decreased and depending on their magnetic moment distribution. The first harmonic component was susceptible to the diamagnetic contribution of carrier liquid when the concentration was lower than 24 μg/ml. The second and third harmonics were affected when the peak position of magnetic moment distribution was smaller than $m = 10^{-19}$ Am^2 and the concentration was 10 ng/ml. A highly sensitive detection up to sub-nanogram of iron oxide nanoparticles in solutions can be achieved by utilizing second and third harmonic components.

1. Introduction

Magnetic nanoparticles (MNPs) have attracted many interests, particularly in bio-medical applications owing to their promising characteristics and detection techniques [1–11]. Detection of MNPs for *in vivo* and *ex-vivo* applications can be performed by utilizing their magnetic properties such as magnetic susceptibility [2–4], relaxation [5–7] and remanence[8,9]. Compared to the latter magnetic properties, magnetic susceptibility is measured in the presence of an excitation magnetic field where the feedthrough generated from the excitation field can reduce the detection sensitivity of MNPs. A cancellation circuit of the excitation magnetic field [12,13] and a band-stop filter [14] can be used to reduce this interference. Furthermore, the nonlinear magnetization characteristic of MNP is commonly utilized in dynamic (AC) magnetization measurements to isolate the frequency component of excitation magnetic fields [15–17]. Since the magnetic response is measured in the presence of excitation magnetic field, this magnetic response contains the induced signal from the environment of MNPs, *i.e.*, diamagnetic carrier liquid [18]. The magnetic response from the diamagnetic carrier liquid such as water can be comparable to the magnetic response of MNPs in the case of high intensity of excitation magnetic field and highly diluted MNP solutions which are used in the most bio-medical applications. Although the magnetization characteristic of the diamagnetic carrier liquid is known to be linear, this diamagnetic background deforms the observed static magnetization curve of MNPs suspended in the diamagnetic carrier liquid. When an AC magnetic field is applied to MNPs, the induced magnetic response reflects the derivatives of the static magnetization curve where it contains harmonic components. Therefore, the effect of the diamagnetic contribution to the induced harmonics must be clarified so that MNPs can be optimized for a highly sensitive detection of MNPs in the suspension of diamagnetic liquid.

In this study, we investigated the magnetization curves and harmonics distribution of commercial multi-core iron oxide nanoparticles in low concentration solutions using our specially developed AC–DC magnetometer. The magnetometer mainly consists of a high-critical-temperature superconducting quantum interference device (high-T_c SQUID) coupled with an optimized flux transformer. We performed reconstructions of magnetization

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curves to analyze the size distribution of iron oxide cores using a non-negative non-regularized inversion method. We compared the measured and simulated harmonics on the basis of particle size distribution. We simulated the ratio of harmonics with respect to different concentrations and magnetic moment distributions to evaluate the effect of the diamagnetic contribution of water as a carrier liquid. The static magnetization curves indicate the deformation due to diamagnetism of water is a function of concentration. The first harmonic component is significantly affected by the diamagnetic background of water and depended on the concentration. Compared to other components, second and third harmonics offer a high signal-to-noise detection of MNPs in low concentration solutions as they are resilient to the diamagnetic background in a wide distribution of magnetic moment and low concentration solutions. Optimization of the magnetic moment of particles will permit a highly sensitive detection on MNPs in the intended applications.

2. Material and measurement system

2.1. Magnetic nanoparticles

We investigated static and dynamic magnetic responses from commercial magnetic nanoparticles: nanomag®-D-spio (Micromod Partikeltechnologie GmbH). These particles are iron oxide multi-core particles where clusters of single-domain iron oxide nanoparticles are coated in dextran. The size of the iron oxide cores and the typical diameter of these multi-core particles are 12 nm and 100 nm, respectively. The composition of iron oxide in these multi-core particles is 35 wt%. These multi-core particles are suspended in water to form a stock solution with a particle concentration of 7.5×10^{12} particles per ml and iron concentration of 2.4 mg/ml. We prepared four sets of low-concentration magnetic fluids by diluting the stock solution in purified water with dilution factors from 25 to 100. The iron concentrations of the diluted solutions were 24 μg/ml, 48 μg/ml, 72 μg/ml, and 96 μg/ml. These solutions were encased in acrylic cases of 20 mm in length, 15 mm in width, and 9 mm in height, which were constructed from 1 mm acrylic plates.

2.2. High-T_c SQUID magnetometer

We have developed a highly sensitive magnetometer utilizing a high-T_c SQUID with a flux transformer for magnetic property evaluation of MNPs in solutions. The developed magnetometer consisted primarily of a high-T_c SQUID with a flux-transformer, a vibrating-sample stage, a computer-controlled electromagnet, and a data acquisition system. The magnetization signal of a sample at room temperature was sensed by a planar differential coil, which was fixed between the poles of the electromagnet. This detection coil was fabricated from 2 elliptical Cu coils with a small compensation coil and was optimized geometrically for detection of static and dynamic magnetizations [12,19]. The magnetization signal was transferred to the high-T_c SQUID via a superconducting flip-chip coil. We measured the static magnetization upon excitation of any given DC magnetic field by modulating the position of the sample along the baseline of the differential coil at a vibration frequency of 2.8 Hz. On the other hand, the dynamic magnetization of a stationary sample upon application of AC and DC magnetic fields was measured by utilizing the gradient characteristic of the differential coil. The DC magnetization output of the developed system was calibrated with a magnetic property measurement system (MPMS3, Quantum Design) by measuring the magnetization of a same paramagnetic MnF_2 sample. The developed system showed a sensitivity of 3×10^{-10} Am^2 at the vibration frequency of 2.8 Hz, which was better in comparison to conventional magnetometers using induction coils and conventional amplifiers. A detailed explanation of the developed system has been reported previously [19,20].

3. Theoretical model

3.1. Static magnetization curve

The magnetization of MNPs can be expressed by the Langevin function for particles with no magnetic interparticle interactions and have isotropic spin governed by thermal fluctuations and the magnetization field [21–24]. For a physical sample, magnetic moments $m = M_sV$ are distributed to some extents due to size distribution. Here, M_s is the intrinsic saturation magnetization and V is the core volume. The magnetization M of MNPs measured at an applied magnetic field $\mu_0 H_j$ can be expressed as

$$M(\mu_0 H_j) = \sum_{i=1}^{N} \rho_i(m) m_i L(m_l \mu_0 H_j / k_B T) \Delta m_i \quad (1)$$

where $\rho_i(m)\Delta m_i = n_i$ represents the number of particles with a magnetic moment between m_i and $m_i + \Delta m_i$, k_B is the Boltzmann constant, T is the absolute temperature, μ_0 is the vacuum permeability, and $L(m_i\mu_0H_j/k_BT) = \mathrm{Coth}(m_i\mu_0H_j/k_BT) - 1/(m_i\mu_0H_j/k_BT)$ is the Langevin function. When the magnetic response of MNPs is measured in a carrier liquid, the magnetization observed by the measurement system can be expressed as

$$M_{observed}(\mu_0 H_j) = \sum_{i=1}^{N} \rho_i(m) m_i L(m_i \mu_0 H_j / k_B T) \Delta m_i - C\mu_0 H_j \quad (2)$$

where C is the diamagnetic parameter of the carrier liquid. The diamagnetic parameter C can be determined by measuring the magnetization curve of the carrier liquid.

3.2. Distribution of magnetic moment

To properly construct the distribution of magnetic moment, a correction to the measured magnetization curves due to the diamagnetic background was performed by subtracting the magnetization curves of the solutions with the water. The distribution of magnetic moment can be constructed by fitting Eq. (1) with the measured data after correction of diamagnetic background. Eq. (1) can be rewritten in a vector form as $\mathbf{M}_{exp} = \mathbf{L}\,\mathbf{w}$ for data measured at J points of the magnetic field. The components of $\mathbf{M}_{exp}$ and $\mathbf{w}$ vectors can be expressed by $M_{exp} \equiv M(\mu_0 H_j)$ $(j = 1,\ldots, J)$ and $w_i \equiv n_i(m) m_i \Delta m_i$ $(i = 1,\ldots, N)$, and $\mathbf{L}$ is a $J \times N$ matrix with the elements of $L_{ji} = L(m_i\mu_0H_j/k_BT)$. Here, w_i represents the magnetic weight of the corresponding magnetic moment m in the distribution. By performing minimization of the mean squares deviation $\xi^2 = \| \mathbf{M}_{exp} - \mathbf{L}\cdot\mathbf{w} \|^2$ between the measured and calculated magnetization values, the distribution of the magnetic weight w_i with respect to m can be determined. We used a non-regularized non-negative inversion method to minimize the deviation in which this method requires no prior information on the shape of the distribution and enforces positive constraints of the solution. The minimization program was coded in Mathematica (Wolfram Research, USA). A detailed explanation of this method can be found in Ref. [24,25].

3.3. Harmonics distribution

To investigate the effect of the diamagnetic background to the harmonics distribution, we consider a low-frequency region where the harmonics are not affected by Neel and Brownian relaxations.