Optical Extinction Change of Magnetic Nanoparticle Suspension under Pulsed Magnetic Field

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Abstract. We investigated the optical extinction change of γ-Fe₂O₃ magnetic nanoparticle suspension induced by a pulsed magnetic field. The Extinction decrease accompanied by a pulsed magnetic field showed clear relationship with the magnetization of magnetic nanoparticle. However, there observed a different response to the magnetic field between increasing and decreasing of the magnetic field. This indicated that the extinction change followed the time variation of magnetic field with some time constant. The time constant was estimated to be 4.5 μs, but it was different from either of rotational Brownian relaxation (0.23 μs) and Neel relaxation (10 ns) of individual particle. It was thought that the optical density decrease might be attributed to the decrease of Rayleigh scattering cross section by the rotation of the magnetic nanoparticle aggregates.…

1. Introduction
Magnetic nanoparticle (MNP) suspension, which is known as ferrofluid, has attracted wide interest in scientific and engineering fields. The MNP has been used for various purposes, such as a lubricant and seals of rotating shaft [1], a contrast medium of MRI [2], a destroyer of cancer tumors by magnetic hyperthermia [3], a substrate for protein purification [4]. In colloid science, MNP has been utilized as a model magnetic colloidal system, because they have permanent magnetic moment. Attractive or repulsive interaction between MNPs determined the stability and the aggregation [5]. The study of dipolar interactions on the aggregation of MNP will provide a fundamental insight in the behavior of colloidal particles. The aggregation of MNPs under magnetic field has been studied by measuring photo-absorption spectra [6], complex magnetic susceptibility [7], electron microscope [8] and magneto-optical effect [9].

In the present study, we observed the change of optical extinction of MNP suspension accompanied with pulsed magnetic field. The time course of the optical density change was analyzed from the view point of magnetization. The comparison with Langevin function, which describes the magnetization behavior of MNP suspension, suggested that this phenomenon could be attributed to the aggregation of MNPs.

2. Materials and Method
2.1. Ionic maghemite nanoparticle aqueous dispersion
γ-Fe₂O₃ nanoparticle (MNP) was synthesized by the method described by van Ewijk et al.[10]. All regents were used as received without further purification. Two milliliter portion of 25 % NH₃ was
added into 50 mL of 0.04 M FeCl₂ and 0.02 M FeCl₃ aqueous solution, and then, black precipitate was
formed. After the mixture was vigorously agitated, the precipitate was gathered by using a permanent
magnet and the supernatant was removed. Four milliliter of 2 M HNO₃ aqueous solution and 6 mL of
0.35 M Fe(NO₃)₃ was added to the black precipitate and the mixture was boiled for 10 min. During
boiling, the color of the precipitate changed to reddish yellow. After washing several times with 2 M
HNO₃, the precipitate was dispersed in 5 mL of water purified by milli-Q system. MNP dispersion was
diluted to $3.3 \times 10^{-16} - 1.2 \times 10^{-14}$ particles / L before measurement. The concentration of MNP was
estimated from its magnetic susceptibility measured by magnetic balance (MSB-AUTO, Sharewood
Scientific) under the magnetic field of 0.45 T.

Figure 1. The experimental setup for observation of optical density change accompanied with pulsed
magnetic field.

2.2. Photo-extinction measurement under pulsed magnetic field

Figure 1 illustrates the experimental setup to observe the optical transmission change under a pulsed
magnetic field. The pulsed magnetic field was generated by a 2000 µF capacitor bank (MAG-2520L-3A, Toyojiki Co., ltd.) and a 16.4 µH hand made solenoidal coil, whose bore size was 8 mm diameter × 16 mm length. The applied voltage on the capacitor was between 50 V and 500 V. The incident and transmitted lights were guided to a cell in bore of coil and a monochrometer (MD200, Unisoku), respectively, by optical fibers. A cylindrical glass cell, whose optical length was 20 mm, was set in the bore of the coil. The signal from photomultiplier (PM) tube (R2429, Hamamatsu Photonics) was stored on a digital oscilloscope (LT-262, Lecroy) synchronized with a TTL signal from a pulse generator (PG-230, IWATSU) triggered by a signal from a pickup coil. The photo-current signal from the PM was converted to voltage and then the voltage in the absence of magnetic field, $V₀$, was set to be 1.0 V. The oscillogram was transferred to PC and averaged for 10 ~ 50 measurements. The optical
density change, $ΔA$, was obtained from the photo-voltage change, $ΔV$, by using the following equation:

$$ΔA(t) = - \log \left(1 + \frac{ΔV(t)}{V₀}\right)$$ (1)

The temperature of the solenoidal coil was monitored with a thermocouple and, in order to avoid
breaking of the coil, magnetic pulse was controlled not to increase the temperature above 26 °C by a
data acquisition system (NI-compact DAQ, National Instruments) programmed with LabVIEW®
software.
2.3. Magnetic field measurement
Generated magnetic field was evaluated from Faraday effect [11]. Faraday rotation angle of the same glass cell filled by water was measured. Laser light of 640 nm in wavelength after passing a polarizer was irradiated into the cell put in the bore of the coil. Faraday rotation angle was measured from the change of light intensity through an analyzer accompanied with pulsed magnetic field.

3. Results and Discussion
Figure 2 shows the transmission electron microphotograph of the MNP synthesized in the present study. The average diameter was 9.1 ± 3.0 nm. The MNP dispersed in distilled water was very stable without further treatment. Figure 3(A) indicates the optical density decrease at 390 nm accompanied with pulsed magnetic field. The optical density was steeply decreased at the start of applying the field, instantly attained to the constant value, and then gradually increased with the decrease of the magnetic field. The magnetic field was plotted against time in Fig. 3(B). It was found that the time course of the extinction change was different from that of magnetic field. Magnetic field strength increased with the voltage on the condenser bank, while the transmitted light intensity change was not proportional to the magnetic field change.

The wavelength dispersion of the maximum value of optical density change was measured as shown in Fig. 4. The conventional optical extinction spectrum measured with a spectrophotometer indicates the typical Rayleigh scattering pattern, which shows reciprocal dependence on wavelength. The optical density change showed a good correlation with the optical extinction spectrum in the absence of pulsed magnetic field. Therefore, the extinction change induced by magnetic field could be contributed to the variation of the scattering efficiency due to the rotational motion or aggregation of MNP under pulsed magnetic field.

Figure 2. Transmission electron microphotograph of MNPs
Figure 3. Typical time courses of optical density (A) and magnetic field measured from Faraday rotation angle (B): The voltages charged on the condenser bank were 100 V (a), 300 V (b) and 500 V (c). The observed wavelength was 390 nm, each oscillogram was the average of 50 measurements. The concentration of MNP was $1.6 \times 10^{15}$ particles L$^{-3}$.

Figure 4. The spectra of optical extinction under no magnetic field (line) and that of optical density change pulsed magnetic field (filled dots). The voltage on the condenser bank was fixed to 100 V.

For elucidating the observed extinction change, it should be useful to consider the superparamagnetic magnetization behavior of MNP, because that is very sensitive to magnetic field and strongly related to the motion of MNP. In magnetic field, the magnetic moment of MNP, $m_p$, tends to orient along the field direction and the magnetization can be described by Langevin function:

$$\frac{M}{M_\infty} = L(B) = \coth(\beta B) - \frac{1}{\beta B}$$

$$\beta = \frac{m_p}{k_B T}$$

(2)
Figure 5. Optical density change vs. magnetic field: The voltage on the condenser bank was 500 V. The solid curve was fitted by Eq. (4).

where $M_s$ is the saturation magnetization, $m_p$ the magnetic moment of MNP, $T$ the temperature, and $k_B$ the Boltzmann’s constant. The magnetic moment of MNP can be represented as follows:

$$m_p = M_s V$$  \hspace{1cm} (3)

where $M_s$ and $V$ is the spontaneous magnetization and the volume of MNP. The magnetic momentum of examined $\gamma$-Fe$_2$O$_3$ nanoparticle could be estimated to $1.4 \times 10^{-19} \text{ Am}^2$ by substitution of $M_s$ of $3.5 \times 10^5 \text{ Am}^{-1}$ [12] and $V$ of $3.9 \times 10^{-25} \text{ m}^3$ into eq.(3). So as to present clearly the relationship between magnetization and the optical density change, $\Delta A$ was plotted against the magnetic flux density in Fig. 5. The open circles indicate the optical density change in the increasing time region of pulsed magnetic field, and the filled dots show that for the decreasing time region of the magnetic field. A constant sampling frequency of the oscilloscope is responsible for the difference of the number of data between two processes. As shown in Fig. 3(B), the magnetic field quickly increased and comparatively slowly decreased, therefore, the sampling number during increase of magnetic field was smaller than that during decrease. Each plot was fitted by the following equation:

$$\Delta A = \Delta A_S L(B)$$  \hspace{1cm} (4)

where $\Delta A_S$ was the saturated value of $\Delta A$, as indicated by solid lines. The fitted curves seem to be in good agreement with the experimental data. However, it was found that there was a difference between increasing and decreasing time regions. Therefore, the intensity change was attributed to some relaxation behavior that could not follow the pulsed magnetic field.

The relaxation behavior of the MNP magnetization is attributed to two kinds of mechanisms.[5] One is the Brownian relaxation. The magnetic moment of MNP particles suspended in water can orient along the magnetic field accompanied by the rotation of the particle. Therefore, rotational Brownian motion is responsible for the relaxation behavior. The Brownian relaxation time, $\tau_B$, can be written by the following equation:

$$\tau_B = \frac{3\eta V_H}{k_B T}$$  \hspace{1cm} (5)

where $\eta$ is the viscosity of medium and $V_H$ is the hydrodynamic volume of particle. Another one is Néel relaxation. The anisotropic magnetic moment of MNP may also affect its internal orientation.
overcoming the energy barrier constituted by the anisotropy energy. The relaxation time for this process can be expressed as:

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

where $K$ is the anisotropy constant, with $\tau_0$ usually having a value of 1 ns. [13] In the present system, $\tau_0$ and $\tau_N$ were estimated to be 0.23 μs and 10 ns, respectively, by substituting $2.5 \times 10^4$ Jm$^{-3}$ of the anisotropy constant [14]. Since both processes are present simultaneously, an effective relaxation time of magnetization, $\tau_{\text{eff}}$, will be shorter than both relaxation times and can be expressed as:

$$\tau_{\text{eff}} = \frac{\tau_B \tau_N}{\tau_B + \tau_N}$$

Substitution of the values of $\tau_B$ and $\tau_N$ into eq. (7) yields about 10 ns as the value of $\tau_{\text{eff}}$ and therefore it could be said that Néel relaxation controlled the rate of magnetization.

Figure 6 shows the expansion of the time course of the optical density change. In this time region, the magnetic field could be approximated to be proportional to time. We simulated the optical density change, assuming that $\Delta A$ had linear dependence on the magnetization of MNP, that is Langevin function, and that the magnetization could not follow the variation of the pulsed magnetic field. This assumption allowed us to calculate the time course of $\Delta A$ by a convolution integral as represented by following expression:

$$\Delta A(t) = \int_0^t L(\alpha_0) \Delta A_s \exp \left( \frac{t-t_s}{\tau} \right) \frac{dt_s}{\tau}$$

where $\alpha$ was the proportional coefficient of the magnetic field to time. The dashed line in Fig. 6, which indicates the calculated result in the case of $\tau = 10$ ns, did not agree with the experimental results. Therefore, we determined the relaxation constant so as to minimize the squared value of the difference between the experimental results and the calculated results. Thus, the bold line in Fig. 6 and
the value of 4.5 μs were obtained. The calculated results were in good agreement with the experimental results. Therefore, it was suggested that the rate controlling step of the extinction change is not the magnetization step but any other phenomenon after the magnetization should be considered.

One of the most likely explanations for the optical extinction change is that the decrease of the scattering cross section due to the orientation of individual MNP which has anisotropic shape, that is spheroid or ellipsoid. However, from the TEM observation, MNPs were rugged but seem not to be anisotropic shape, and the Brownian relaxation, $\tau_B$, for the present sample was estimated to be much smaller than the observed value from the time course of the extinction change. Furthermore, $\tau_s$ was much smaller than $\tau_B$, because the permanent magnetic moment of MNP could orient within the particle without any rotation of the particle itself. So it is difficult to attribute the extinction change to the orientation of individual MNPs. Finally, the aggregate of MNPs should be considered. MNPs could be spontaneously aggregated by magnetic dipolar-dipolar interaction [5, 8]. In the absence of external magnetic field, MNP aggregates were randomly oriented. Once pulsed magnetic field was exerted, the magnetic moment oriented to the magnetic field by Néel process and then the aggregates rotated to minimize the potential energy. Potential energy should be minimum in the case that the longest axis of aggregate orients along to the magnetic field, and then the scattering cross section decreases.[15] In this case, the relaxation time depends on the rotational Brownian motion and the time constant can be described by eq. (5). The hydrodynamic diameter could be estimated to be 25 nm from the obtained time constant (4.5 μs). This value seems reasonable assuming that the MNPs formed dimmer or trimmer. The other considerable reason is reversible aggregation and dissociation. The magnetic interaction between the MNPs should be changed by the application of magnetic field due to the rotation of magnetic moments. In the case that MNP dimmer aligned perpendicular to magnetic field, the interaction of magnetic moments will be repulsive after Néel relaxation. On the other hand, in the case that the MNPs aligned along the magnetic field, the interaction will be attractive. In the former case, scattering efficiency will become small because that is proportional to the square of volume of particle following Rayleigh scattering mechanism. In the latter case, the MNPs will form chain like structure along the magnetic field, and then the scattering cross section will decrease. In both case, the process needs the translational motion of MNP. However, the extinction change had linear relationship with Langevin function as demonstrated by Fig. 6, and the translational motion attributed to magnetic dipole-dipole moment interaction should be more complicated. Therefore, it is difficult to ascribe the extinction change to the dissociation and aggregation dynamics. As aforementioned discussion, it was suggested that the extinction change could be contributed to the decrease of the scattering cross section by orientation of MNP aggregation. In order to clarify the origin of the extinction change, the dependence of the relaxation time constant on the concentration of MNP, on the ionic strength, on the chemical property of surface, and on the particle size should be investigated.

4. Conclusion

We found the optical extinction change of MNP suspension under pulsed magnetic field. The extinction change had the strong relationship with the magnetization of MNP, because the optical density change could be fitted by Langevin function. However, a hysteresis was observed in the extinction change. The assumption that the optical density change has a linear relationship with Langevin function and it takes $\tau$ to relax the change allowed us to use the convolution integral and simulate the optical density change. The simulation was in good agreement with the experimental result. From this evidence, it was suggested that the aggregate of MNP is ascribed to the extinction change.
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