Evaluation of easy-axis dynamics in a magnetic fluid by measurement and analysis of the magnetization curve in an alternating magnetic field

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An understanding of the magnetic relaxation mechanism is critical to the medical application of magnetic nanoparticles. The temporal change in magnetization caused by an applied field can be evaluated by measuring the magnetization curves in the alternating fields. When magnetic nanoparticles are dispersed in a liquid, owing to magnetic torque, the Brownian relaxation influences the magnetization dynamics, in addition to the Néel relaxation. In this study, by evaluating the magnetization curve obtained by subtracting the magnetization curve corresponding to the solid from that of the liquid, the dynamics of the easy axis are observed with respect to the superparamagnetic nanoparticles.

\( \tau_B = \frac{3\eta V_H}{k_B T}, \) (3)

where \( \eta \) is the viscosity and \( V_H \) is the hydrodynamic volume of the MNPs.\textsuperscript{18}

In this study, a water-based \( \gamma \)-Fe\(_2\)O\(_3\) nanoparticle sample, Ferucarbotran, supplied by Meite Sangoy is used. The core diameter of this MNP was determined to be 5 \( \pm \) 1 nm (mean \( \pm \) SD) through transmission electron microscopy. Its mean hydrodynamic diameter and polydispersity index measured by dynamic light scattering were 59 nm and 0.20, respectively. The concentration of this MNP was 28 mg-Fe/mL. To observe the magnetization rotation about the easy axis, measured amounts of samples were fixed with agar to obtain a solid sample and dispersed in water to acquire a liquid sample. It was demonstrated that Ferucarbotran has a multicore structure with effective core diameters of 6.2, 10.7, and 21.6 nm, respectively; the mass fraction of each effective core particle was 0.163, 0.334, and 0.592, respectively.\textsuperscript{16}

Using Eqs. (1) and (2), the calculated Néel relaxation time values of the effective core particles with diameters of 6.2, 10.7, and 21.6 nm were 1.10, 1.60, and 21.2 ns (\( K = 3 \text{ kJ/m}^3 \)), respectively.\textsuperscript{16}

Applying Eq. (3), the Brownian relaxation time of Ferucarbotran was found to be 0.07 ms. The relationship between the relaxation time, \( \tau_B \) and the relaxation peak frequency, \( f_p \), is \( \tau_B = 1/2\pi f_p \). The Néel relaxation time peak frequencies of the effective core particles with diameters of 6.2, 10.7, and 21.6 nm were 145, 100, and 7.50 MHz, respectively. The peak frequency of the Brownian relaxation was 2.3 kHz.

Figure 1 shows the major DC magnetization curves of the solid and liquid Ferucarbotran samples measured by a vibrating sample magnetometer at room temperature. To quantify the magnetization using the value normalized by the saturation magnetization, \( M_s \), expressed in \( M/M_s \), the saturation magnetizations of the measured samples were estimated by fitting the major DC magnetization curve in the solid sample to the magnetization curve calculated by the Langevin function. In the solid sample, the coercivity was marginal, similar to that of the liquid sample, indicating that Ferucarbotran exhibits superparamagnetic behavior.
The AC magnetization curves were measured using a detection circuit composed of pick-up and cancel coils located within an excitation coil at room temperature.\textsuperscript{20) Figures 2(a) and 2(b) show the AC magnetization curves in the solid and liquid Ferucarbotran samples, respectively. For understanding the dynamics of the easy axis experimentally, the AC magnetization curves of the solid sample subtracted from those of the corresponding liquid sample and called as the subtracted curves, were evaluated (Fig. 3). These subtracted curves indicate the differences in the magnetization dynamics, enabling the understanding of the easy-axis dynamics. When the Néel relaxation time is shorter than the Brownian relaxation time, Brownian relaxation occurs in addition to the Néel relaxation. The superimposition of the Brownian relaxation on the Néel relaxation was observed by the numerical simulation of the heat dissipation,\textsuperscript{21) the measurement and calculation of the susceptibility,\textsuperscript{22,23) and the measurement of the AC magnetization curves.\textsuperscript{13,24) However, it is necessary to understand that the rotational degree of the easy axis is not directly depicted by the subtracted curves.

At a frequency of 0.2 kHz, the remanence was marginal [Fig. 3(a)]. This indicates that at zero-field, the magnetizations in the liquid and solid samples had similarly oriented distributions. Therefore, at 0.2 kHz, the easy axis in the liquid sample at zero-field was fully relaxed and randomly oriented, similar to the case of the solid sample, whereas the magnetization in the direction of the applied field remained at zero-field [Fig. 2(b)]. Herein, although the calculated Néel relaxation times are shorter than the Brownian relaxation times, the relaxation of the easy axis was faster than that of...
the magnetization. This is because the Néel and Brownian relaxation times were respectively calculated using the average core and hydrodynamic diameters without considering their distributions. The distribution of the large effective core particles dominantly affects magnetization properties such as the relaxation time.\(^{16,27}\)

However, when the field intensity was increased, the subtracted curves at 0.2 kHz depicted an area that was derived from the difference in the anisotropic energy between the liquid and solid samples. This is similar to the hysteretic phenomenon. The easy axis was oriented along the direction of the applied field, on increasing the field intensity. When the easy axis is uniaxially oriented along the direction of the applied field, the magnetization is bound along the same direction, regardless of the field intensity. This is because, when the magnetization is oriented along the direction of the easy axis, a low anisotropy energy is maintained.

In the general process of hysteresis, when a magnetization curve depicts an counterclockwise loop, the magnetization during the process of increasing the field intensity is lower than that during the process of decreasing the field intensity. However, in Fig. 3(a), the magnetization in the process of increasing the field intensity is higher than that during the process of decreasing the field intensity; this is demonstrated by the magnetization curves, which depict clockwise loops. Thus, when the field intensity increases, the difference between the magnetization in the liquid sample and that in the solid sample is larger than that corresponding to the process of decreasing the field intensity. When a magnetization curve depicts counterclockwise and clockwise loops, positive and negative losses are generated, respectively. At 0.2 kHz, the area of the subtracted curves depicted a negative loss, indicating that the difference between the anisotropy energies in the magnetization and demagnetization processes of the liquid sample was lesser than that of the solid sample. The Stoner–Wohlfarth theory shows that the difference in the magnetization hysteretic process is due to the difference in the anisotropy energy.\(^{25}\) Thus, the subtracted curves show that the orientation of the easy axis temporally changes with the magnetization rotation, i.e., the easy axis is rotated by the magnetic torque. When the easy axis rotates owing to magnetization rotation without phase delay, the anisotropy energy decreases. Consequently, the magnetization can easily relax without being bound by the anisotropy energy. Herein, the magnetization phase delay in the liquid sample was less than that in the solid sample, in the low-frequency region (Fig. 4). For frequency values up to 0.4 kHz, it was observed that the magnetization phase delay with respect to the applied field was less in the liquid sample than in the solid sample. It is indicated that the magnetization phase delay derived from the Néel relaxation decreases with the rotation of the easy axis. Therefore, the rotation of the easy axis without the phase delay that is derived from the Brownian relaxation promotes the magnetization rotation and reduces the magnetization phase delay.

At 1 kHz, the subtracted curve at a maximal field intensity of 8 kA/m depicted both counterclockwise and clockwise loops, whereas the subtracted curves at 2 and 4 kA/m depicted only counterclockwise loops [Fig. 3(b)]. The subtracted curves show coercivities because of the phase delay derived from the rotation and the orientation of the easy axis. At the coercivity of the subtracted curve, the total magnetization in the liquid sample has the same value as that of the solid sample. However, at the coercivity, the oriented distribution of the magnetization in the liquid sample is not necessarily the same as that in the solid sample, even though the total magnetization is the same. At 1 kHz, the easy axis relaxed, on increasing the field intensity from zero-field. On increasing the field intensity further, the easy axis rotated towards the direction of the applied field. However, the field intensity, where the dynamics of the easy axis switches from relaxation to orientation is not specifically determined.

By performing numerical simulation, Yoshida et al. demonstrated that when the Brownian relaxation peak frequency is higher than the frequency of the applied field, the easy axis is rotatable by the magnetic torque owing to magnetization rotation.\(^{26}\) When the Brownian relaxation peak frequency is lower than the frequency of the applied field, the easy axis is oriented along the direction of the applied field and is nearly constant. At frequencies lower than the Brownian relaxation peak frequency, our experimental results, based on the subtracted magnetization curves, agree with the numerical simulation results of Yoshida et al. However, in contrast with the subtracted magnetization that is positive at the maximal field intensity for frequencies up to 10 kHz, the value is negative at 100 kHz [Figs. 3(c) and 3(d)]. Figure 4 also shows that the maximal magnetization in the liquid sample is higher than that in the solid sample, up to 20 kHz. However, the maximal magnetization in the liquid sample is lower than that in the solid sample for frequencies higher than 30 kHz. When the easy axis is uniaxially oriented along the direction of the applied field without rotating, the maximal magnetization increases compared to the magnetization in the randomly oriented easy axis.\(^{27}\) Thus, at 100 kHz, the rotation of the easy axis inhibits magnetization rotation because of the large phase delay with respect to the applied field.

Figure 5 shows the magnetization curves and the corresponding models in terms of the dynamics of the easy axis. When the easy axis rotates towards the direction of the applied field, magnetization rotation is promoted, whereas when the easy axis relaxes, it is inhibited. In addition, when the easy axis is uniaxially oriented towards the direction of the applied field, the magnetization amplitude and phase delay increase, in superparamagnetic nanoparticles.\(^{27,28}\) It is also shown that, with respect to ellipsoidal ferromagnetic nanoparticles, the magnetization amplitude and phase delay increase owing to the orientation of the easy axis along the direction of the applied field.\(^{29}\) The larger phase delay in the
The applied arrows set in a circular pattern show the orientation of the easy axis. The black and white arrows show the rotation processes towards the direction of the applied field and the relaxation with respect to the easy axis, respectively.

In conclusion, the subtracted curves indicate the temporal orientation and relaxation processes of the easy axis with respect to the applied field and magnetization. The difference in magnetization between the solid and liquid samples was significantly less compared to the rotational degree of magnetization. There is a slight rotation and orientation of the easy axis, which affects the magnetization dynamics in a liquid with respect to the phase delay, in particular. For instance, considering the application to MPI, the differences among the magnetization phase delays, dependent on the states and viscosities, can be used as an alternative diagnostic method for detecting the changes in the blood conditions.

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**Fig. 5.** Models with respect to the dynamics of the easy axis and the magnetization curves of the solid and liquid samples at frequencies of (a) 0.2 kHz and (b) 100 kHz at a maximal field intensity of 8 kA/m. The fine arrows set in a circular pattern show the orientation of the easy axis. The black and white arrows show the rotation processes towards the direction of the applied field and the relaxation with respect to the easy axis, respectively.