Dipolar field-induced asymmetric magnetization hysteresis of immobile superparamagnetic nanoclusters

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Abstract

Despite the critical contribution of dipolar interparticle interactions to the hysteretic magnetization curve of superparamagnetic nanoclusters, the quantitative analysis of dipolar field remains a major challenge at room temperature. To investigate such demagnetizing effect due to a close core-to-core distance within a nanocluster, we evaluate the symmetry of ac minor magnetization hysteresis in the presence of static magnetic field. While the nanoclusters are immobilized in a gelatin matrix, we record their dynamic magnetizations for a given 100-kHz sinusoidal magnetic field perpendicular to the static field and further correlate the changes in the coercive fields and remanences with the dipolar field and its demagnetization ratio, respectively. In this work, we also show that the dipolar field-induced shift of the magnetization loop is size-dependent. Under high static bias field, larger core size proportionally enhances the resulting dipolar field. Meanwhile, the cluster size appears to be influential to the dipolar magnetism triggered at low bias field. This study conclusively highlights the distinguishable dynamics between randomly oriented and collaterally aligned magnetic moments.

Keywords: asymmetric hysteresis; dipolar field; dynamic magnetization; magnetic interactions; superparamagnetic nanoclusters.

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1. Introduction

As alternative biomedical agents, magnetic nanoparticles are currently of scientific interest due to their room temperature magnetization dynamics enabling superparamagnetism, dissipative relaxation, or harmonic vibration. [1-3] These excellent properties are beneficial for hyperthermic cancer therapy, imaging, drug delivery/release system, and immunoassay. [4-8] Toward these applications, magnetic nanoparticles are practically involved in polydisperse hydrodynamic forms as they are suspended in a liquid medium. The hydrodynamic polydispersity originated from dipolar interparticle interactions is later critical to alter magnetic response. For instance, large aggregates reduce minor hysteresis in cellular matrixes. [9, 10] Recent works have also reported a concentration-dependent hydrodynamic size and its contribution to the change in hyperthermic efficiency. [11-13] However, the dipolar magnetism is not always identical to a negative contribution. The enhancement of magnetic properties can be expected from chain-like aggregates which improve the uniaxiality of magnetic anisotropy. [14] Thus, a magnetic moment configuration within single hydrodynamic nanostructure is a key factor to decide the magnetizing or demagnetizing effects of dipolar interparticle interactions.

The typical routine to assess how significant the dipolar interaction is by measuring temperature-dependent magnetization under field-cooling and zero-field-cooling (ZFC) protocols. [15-17] The increase of blocking temperature attributed to the maximum ZFC magnetization is an effective indicator to conclude a stronger dipolar magnetism due to the distribution shift of energy barrier. [18] However, it is a challenging issue to quantify dipolar field at room temperature where random fields and torques augmented by thermal energy are influential. In the case of superparamagnetic nanoclusters, for instance, moment dynamics of core particles occur fast due to a small anisotropy energy. The resulting dipolar interparticle interactions are often be qualitatively analyzed from the maximized imaginary part of magnetic susceptibility to address the field-induced cluster rotatability in a liquid medium. [19, 20] For few-nanometer-cores, nevertheless, we confirm that the Brownian relaxation can be insignificant to contribute to the magnetization delay. [21, 22] Therefore, a quantification of finite dipolar field at room-temperature is beneficial for understanding magnetization dynamics of the nanoclusters, further improving their performance in biomedical applications.

The room-temperature magnetopotential energy which principally includes the dipolar interaction, magnetic anisotropy, and Zeeman coupling, can be relatively smaller than thermal energy in the case of superparamagnetic nanoclusters. An increase of Zeeman energy causes the

magnetic moments to align their initial random vectors collaterally in the direction of the external field to minimize the magnetopotential difference. In this condition, magnetic moments let their vectors incoherently relax around the field direction with a small degree of freedom for a large external magnetic field. We utilize this behavior to probe the dipolar field originated from the moment alignment, as well as its demagnetizing effect, by characterizing the dynamic magnetization hysteresis for a given high-frequency sinusoidal magnetic field perpendicular to the static field direction. We hypothesize that the presence of dipolar field components which are parallel to the ac field probe can change the symmetry of the magnetization loops recorded at room temperature. In this study, we later investigate the property of dipolar interparticle magnetism for different superparamagnetic core sizes of maghemite nanoclusters.

2. Materials and Methods

Fig. 1 Frequency-dependent magnetization curves of gelatinized superparamagnetic nanoclusters with various core sizes. The core diameter was evaluated from transmission electron microscopy. The overlap curves between DC magnetization and AC magnetization at 1 kHz in each sample implies the superparamagnetism of the maghemite cores. At 100 kHz, a larger hysteresis area corresponds to the delayed magnetization response. The equilibrium magnetization $\mathbf{M}$ is normalized by each saturated magnetization M_s of the samples; M_s is 0.232, 0.215, and 0.248 emu for the 4-nm, 5-nm, and 7-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters, respectively.

Concerning weak dipolar interparticle interactions in the superparamagnetic nanoclusters, Néel relaxation time τ_N is the key parameter attributed to the temperature-dependent moment dynamics. Despite the conflicting conceptions on whether its effective value increases or decreases for a stronger dipolar interaction, [23, 24] τ_N is unambiguously size-dependent. [25] We thus assess the significance of dipolar interactions in the maghemite nanoclusters (Meito Sangyo Co., Ltd., Kiyosu-shi, Japan) with mean core diameters: 4.59, 5.58, and 6.95 nm. The core particles of those three samples are superparamagnetic according to their static and 1-kHz-

dynamic magnetization responses at room-temperature (**Fig. 1**), showing neither coercivity nor remanence. Meanwhile, in the presence of dipolar interactions, τ_N represents time required to oppositely change the moment vector by overcoming the energy barrier for constant temperature. Instead of slowing down τ_N (e.g., decreasing temperature) to observe such magnetization reversal, we apply a high frequency sinusoidal magnetic field so that the respective observation time can compensate the fast τ_N at room temperature in terms of phase delay. **Figure 1** further shows a larger hysteresis area of magnetization at 100 kHz than that at 1 kHz.

Fig. 2 Change of dynamic magnetization curves of superparamagnetic nanoclusters with core diameter D_c and hydrodynamic diameter D_h , due to the gelation. The larger hysteresis areas observed in the water-based (liquid) samples than those in the gelatinized (solid) samples indicate the contribution of the Brownian relaxation.

Dipolar magnetism generally comprises two interaction ranges: short core-to-core and long cluster-to-cluster. [26, 27] To preserve constant cluster-to-cluster distance, the maghemite nanoclusters coated with dextran-based surfactants were immobilized in a gelatin matrix with the initial concentration of their 0.1-mL colloidal suspensions adjusted to 28 mg-Fe mL⁻¹. From dynamic light scattering, the mean hydrodynamic diameters D_h of each sample prior to the gelation are 38, 56, and 25 nm for the 4-nm, 5-nm, and 7-nm γ -Fe₂O₃ nanoclusters, respectively. From **Fig. 2**, the cluster immobilization leads to a reduction of magnetization due to the absence of Brownian relaxation. Concerning the size dependence, furthermore, we hypothesize that the decreasing hysteresis area for a larger superparamagnetic core diameter D_c should strongly correlate with magnetic interparticle interactions within each hydrodynamic volume. The

quantification of dipolar interactions then starts with identifying the changes in the coercive fields and remanences for a given static bias field perpendicular to the 100-kHz field probe (Fig. 3). The static bias field $\mathbf{H}_{dc}$ is adjustable up to 450 Oe, thus the corresponding equilibrium magnetization $\mathbf{M}/M_S$ may reach 0.404, 0.412, and 0.424 for the immobilized 4-nm, 5-nm and 7-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters, respectively. With a high temporal resolution, we recorded the room-temperature dynamic magnetization of the samples at 100-kHz sinusoidal magnetic field $\mathbf{H}_{ac}$ for various field amplitudes H_0 up to 300 Oe.

Fig. 3 Change in the symmetry of dynamic magnetization for a given sinusoidal magnetic fields $\mathbf{H}_{ac}$ perpendicular to the static bias fields $\mathbf{H}_{dc}$, for the immobilized 4-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters. The negative H_C^- and positive H_C^+ coercive fields are different, as well as for the negative M_R^- and positive M_R^+ remanences, while the field H_0 and magnetization M_0 amplitudes are periodically constant. From the right panel, the values of H_C^- , H_C^+ , M_R^- , and M_R^+ observed under field amplitude $H_0 = 300$ Oe and $\mathbf{H}_{dc} = 450$ Oe are -16.01 Oe, 17.65 Oe, -0.0142 M_S , and 0.0131 M_S , respectively.

In the absence of $\mathbf{H}_{dc}$, we consider that random easy-axis orientations and moment vectors are responsible for the zero-resultant of dipolar fields due to the fast room-temperature moment dynamics. Demonstrated in Fig. 3 for the immobilized 4-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters, applying sufficiently high $\mathbf{H}_{dc}$ should reorient the moment vectors parallel to $\mathbf{H}_{dc}$, thus the resultant of dipolar fields may have a nonzero value with vector parallel to $\mathbf{H}_{dc}$. The coexisting $\mathbf{H}_{ac} \perp \mathbf{H}_{dc}$

is critical to modulate the finite dipolar fields which change the magnetization response. Here, **Fig. 3** also shows the small and asymmetric magnetization hysteresis under $\mathbf{H}_{dc} = 450$ Oe. In this condition, the smaller hysteresis area for the larger $\mathbf{H}_{dc}$ is because of the shorter τ_N attributed to a high energy barrier. Meanwhile, the asymmetric hysteresis caused by the dipolar magnetism can be parametrically decomposed into the negative H_C^- and positive H_C^+ coercive fields, as well as for the negative M_R^- and positive M_R^+ remanences. The dipolar field $\mathbf{H}_d$ and the demagnetization ratio ϕ_N are then defined as

$$\mathbf{H}_d = \frac{H_C^- + H_C^+}{2} \quad (1)$$

$$\phi_N = \frac{M_R^- + M_R^+}{2M_0} \quad (2).$$

Using these terms [**Eqs. (1) and (2)**], we evaluate the magnetization hysteresis of each solid sample both for the increasing H_0 and $\mathbf{H}_{dc}$. Being different from the quasi-static hysteresis analyses (e.g., Henkel or delta- $\mathbf{M}$ plots, and first-order-reversal-curve diagrams), [28, 29] our method highlights the shift of high-frequency minor magnetization loop induced by dipolar field.

3. Results and Discussion

For a uniaxial anisotropic magnetic nanoparticle treated as a single macrospin, the symmetry of its magnetization hysteresis indicates two equivalent easy-axis directions. The stray fields (i.e., dipolar field) of two identical parallel macrospins may magnetize or demagnetize each other, depending on their moment directions. For the same direction, the demagnetizing effect of the stray fields is favorable at close interparticle distance. Therefore, the asymmetric magnetization loop (**Fig. 3**) is an evidence of irreversible magnetization due to the dipolar interaction energy creating a preferred easy magnetization direction. In the framework of magnetic nanoclusters with N number of cores, similarly, the dipolar interaction energy E_d can be expressed as

$$E_d = \frac{1}{4\pi\mu_0} \sum_{i,j=1}^N \left[\frac{\mathbf{m}_i \cdot \mathbf{m}_j - 3(\mathbf{m}_i \cdot \mathbf{r}_{ij})(\mathbf{m}_j \cdot \mathbf{r}_{ij})}{r_{ij}^3} \right] \quad (3),$$

where the neighboring magnetic moments, $\mathbf{m}_i$ and $\mathbf{m}_j$, are distanced by r_{ij} with $\mathbf{r}_{ij}$ unit vector along the direction connecting $\mathbf{m}_i$ to $\mathbf{m}_j$, and μ_0 is magnetic permeability of free space. The effective dipolar field which is typically derived from **Eq. (3)** as $\mathbf{H}_d = dE_d/d\mathbf{m}$ for an effective moment $\mathbf{m}$, may give rise to the irreversible magnetization of the magnetically blocked moments, [30] i.e., a difference in the remanences $\Delta M_R = \phi_N M_0$. In the case of the immobilized 4-nm γ -

158 Fe_2O_3 nanoclusters, for instance, we experimentally evaluate $\mathbf{H}_d$ and ϕ_N from the unidirectional
159 shifts of ac magnetization loops for a given $\mathbf{H}_{ac} \perp \mathbf{H}_{dc}$, shown in Fig. 4.

160
161 **Fig. 4** Changes in the coercive and dipolar fields, as well as the remanences and demagnetization ratio ϕ_N with
162 increasing (a) field amplitude H_0 and (b) static field bias $\mathbf{H}_{dc}$, for the immobilized 4-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters. At
163 constant $\mathbf{H}_{dc} = 450$ Oe (squares), increasing H_0 leads to the higher dipolar field $\mathbf{H}_d$, similarly, the
164 demagnetization ratio ϕ_N has negative value, in comparison to those at zero $\mathbf{H}_{dc}$ (circles). At constant $H_0 = 300$
165 Oe (triangles), increasing $\mathbf{H}_{dc}$ nonlinearly impacts on $\mathbf{H}_d$ and ϕ_N . The fluctuating $\mathbf{H}_d$ and ϕ_N values at
166 $\mathbf{H}_{dc} > 100$ Oe are attributed to the faster moment dynamics (i.e., field-dependent τ_N) increasing error margin.

167 **Figure 4a** shows that increasing H_0 up to 300 Oe results in higher $-H_C^-$ and H_C^+ values. We then
168 numerically fitted these results by exponential functions Eqs. (4) and (5), written as

$$169 \quad H_C^- = - \sum_{i=1}^n a_i [1 - \exp(-b_i H_0)] \quad (4)$$

170 and

$$171 \quad H_C^+ = \sum_{i=1}^n a_i [1 - \exp(-c_i H_0)] \quad (5)$$

172 where a_i , b_i , and c_i are arbitrary constants for i to n integer. The maximum coercive field at
173 frequency f , $H_{C,f} = \sum_{i=1}^n a_i$, is a shared parameter for any $\mathbf{H}_{dc}$. At constant $\mathbf{H}_{dc} = 450$ Oe, the
174 corresponding dipolar fields appear to have a linear trend within H_0 range, while no $\mathbf{H}_d$ is
175 virtually observable in the absence of $\mathbf{H}_{dc}$. Similarly, we confirmed a negative ϕ_N at $\mathbf{H}_{dc} = 450$
176 Oe, whereas ϕ_N equals null at $\mathbf{H}_{dc} = 0$; The negative ϕ_N indicates the demagnetizing effect of
177 the dipolar fields. ϕ_N is obtained by Eq. (2), where M_R^-/M_0 and M_R^+/M_0 can be interpolated by

$$\frac{M_R^-}{M_0} = -u_0 - \sum_{i=1}^n u_i [1 - \exp(-v_i H_0)] \quad (6)$$

and

$$\frac{M_R^+}{M_0} = u_0 + \sum_{i=1}^n u_i [1 - \exp(-w_i H_0)] \quad (7),$$

respectively. In Eqs. (6) and (7), u_0, u_i, v_i and w_i are arbitrary constants, while the maximum remanence at frequency f , $M_{R,f}/M_0 = u_0 + \sum_{i=1}^n u_i$, is set as a global parameter for any $\mathbf{H}_{dc}$. u_0 is a compensating parameter for $M_0 \approx 0$ at extremely low H_0 .

At constant $H_0 = 300$ Oe, Fig. 4b oppositely shows the decreasing both $-H_C^-$ and H_C^+ for the increase of $\mathbf{H}_{dc}$. In this trend, we preferably used polynomial approximants to fit the measured $-H_C^-$ and H_C^+ by Eqs. (8) and (9) as

$$H_C^- = -\frac{a_0 + \sum_{i=1}^n a_i \mathbf{H}_{dc}^i}{1 + \sum_{i=1}^n b_i \mathbf{H}_{dc}^i} \quad (8)$$

and

$$H_C^+ = \frac{a_0 + \sum_{i=1}^n c_i \mathbf{H}_{dc}^i}{1 + \sum_{i=1}^n d_i \mathbf{H}_{dc}^i} \quad (9),$$

respectively with a_i, b_i, c_i , and d_i constants, while a_0 represents the initial coercive field at $\mathbf{H}_{dc} = 0$. Figure 4b further shows that $\mathbf{H}_d$ appears to be maximized in the function of $\mathbf{H}_{dc}$. Meanwhile, concerning the changes in the remanences, M_R^-/M_0 and M_R^+/M_0 are fitted to Eqs. (10) and (11) which are expressed by

$$\frac{M_R^-}{M_0} = -\frac{v_0 + \sum_{i=1}^n v_i \mathbf{H}_{dc}^i}{1 + \sum_{i=1}^n w_i \mathbf{H}_{dc}^i} \quad (10)$$

and

$$\frac{M_R^+}{M_0} = \frac{v_0 + \sum_{i=1}^n x_i \mathbf{H}_{dc}^i}{1 + \sum_{i=1}^n y_i \mathbf{H}_{dc}^i} \quad (11),$$

for the given v_i, w_i, x_i , and y_i constants; v_0 is the initial remanence in the absence of bias field. Shown in Fig. 4b, the resulting ϕ_N implies the nonlinear dependence on $\mathbf{H}_{dc}$ with a minimum value. These extrema will be later correlated with the structural properties of each sample. To investigate the size effect of the dipolar field, as well as the demagnetizing effect, we performed similar dynamic reversal curve analyses (Fig. 4) on the immobilized 5-nm γ -Fe₂O₃ and the 7-nm γ -Fe₂O₃ nanoclusters.

3.1 Size-dependent dipolar field

Fig. 5 Change in the dipolar fields with increasing (a) field amplitude and (b) static bias field, for magnetic nanoclusters with different core sizes. At constant $\mathbf{H}_{dc} = 450$ Oe (squares), $\mathbf{H}_d$ proportionally increases with increasing H_0 , in which the 5-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters (dashed lines) have the largest value due to large D_h . $\mathbf{H}_d$ is insignificant in the absence of $\mathbf{H}_{dc}$ (circles). For single magnetic moment $\mathbf{m}_i$, its rotational dynamics has a small degree of freedom under a large $\mathbf{H}_{dc}$, so that $\mathbf{m}_i$ at $\mathbf{H}_{dc} = 0$ has larger τ_N than $\mathbf{m}_i^*$ denoting $\mathbf{m}_i$ at $\mathbf{H}_{dc} \gg 0$. At constant $H_0 = 300$ Oe (triangles), in contrast, the 7-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters (dash-dotted lines) with the smallest D_h appear to have the largest $\mathbf{H}_d$ for $\mathbf{H}_{dc} > 300$ Oe. The cluster size appears to contribute to the dipolar magnetism at low $\mathbf{H}_{dc}$, indicated by larger $\mathbf{H}_d$ of the 4-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters (solid lines) than that of the 7-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters at $\mathbf{H}_{dc} < 100$ Oe.

Shown in **Fig. 5**, applying $\mathbf{H}_{ac} \perp \mathbf{H}_{dc}$ leads to the observable dipolar fields which are associated with the change in H_C^- and H_C^+ of the asymmetric magnetization hysteresis. To carefully argue the dipolar magnetism in each sample, **Eqs. (4)** and **(5)**, as well as **Eqs. (8)** and **(9)**, are inserted into **Eq. (1)** for H_0 and $\mathbf{H}_{dc}$ dependences of $\mathbf{H}_d$, respectively. In the case of the 5-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters with $D_h = 56$ nm, for instance, **Fig. 5a** shows that they exhibit larger $\mathbf{H}_d$ than 7-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters with smaller D_h , as H_0 increases at constant $\mathbf{H}_{dc} = 450$ Oe. This figure further emphasizes that D_h and D_c should be inseparable factors contributing to the dipolar field. This argument is supported by the fact that the 4-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters have smaller $\mathbf{H}_d$ than the 7-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters despite their larger D_h . Therefore, analyzing the change in $\mathbf{H}_d$ of

each sample for various $\mathbf{H}_{dc}$ at constant H_0 is necessary to address the $\mathbf{H}_{dc}$ -dependent moment alignment.

Regarding Langevin function, the field-induced moment alignment of superparamagnetic nanoparticles principally depends on the magnetic moment and external field strengths, as well as the ambient temperature. [1, 31] While magnetic moment is proportional to the core size, large $\mathbf{H}_{dc}$ improves the collateral alignment of magnetic moments, which is mathematically represented by the ratio equilibrium magnetization over the saturated magnetization, $\mathbf{M}/M_S$. In the case of the aligned moments, the resulting dipolar field will be apparently large. Figure 5b further highlights the nonlinearity of $\mathbf{H}_d(\mathbf{H}_{dc})$ for each sample. In the case of the 7-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters $D_h = 25$ nm, they exhibit small $\mathbf{H}_d$ at low $\mathbf{H}_{dc}$ and large $\mathbf{H}_d$ at high $\mathbf{H}_{dc}$ under constant $H_0 = 300$ Oe; their $\mathbf{H}_d$ is even larger than that of the 5-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters for $\mathbf{H}_{dc} > 300$ Oe. This observation proves the correlation between $\mathbf{H}_d$ and the core size. Referring to Eq. (3), large magnetic moment increases the dipolar interaction energy, thus large core size potentially results in the large dipolar field. However, the moment configuration within each nanocluster should be critical under the low bias field.

Figure 5b implies that $\mathbf{H}_d$ appears to be linearly D_h -dependent at $\mathbf{H}_{dc} < 100$ Oe. As the nanoclusters were immobilized under the same mass concentration, we presumed the intercluster distance should not significantly vary among the samples. Thus, the low bias field-induced $\mathbf{H}_d$ should be associable with the effective number of cores within an immobile nanocluster, in which their moment vectors are still oscillating across their easy-axis directions. The alignment of easy axis significantly enhances the hysteresis properties. [32, 33] For large D_h , nevertheless, the easy-axis configuration of each core, is more sophisticated owing to large number of cores and the anisotropy distribution. Moreover, the evolutionary moment dynamics within nanoclusters from the random orientation to the collateral alignment reveal a unique feature where $\mathbf{H}_d$ is maximized for the increasing $\mathbf{H}_{dc}$, as found in the 4-nm $\gamma\text{-Fe}_2\text{O}_3$ nanoclusters. We consider that this property may be attributed to the competing moment relaxations of cores which should preferably oscillate across the direction of $\mathbf{H}_{dc}$ for large $\mathbf{H}_{dc}$. In this condition, the low moment oscillation decreases the effective $\mathbf{H}_d$. Concerning the anisotropy energy, we expect a higher $\mathbf{H}_{dc}$ maximizing $\mathbf{H}_d$ for larger D_c and D_h of the other samples. Aiming for magnetic hyperthermia or magnetic particle imaging (MPI), therefore, this study suggests a control of the core-to-cluster volume ratio to have positive effect of the dipolar interparticle interactions which is associable with either high hysteresis area and nonlinearity of magnetic response.

3.2 Demagnetizing effect of dipolar field

Fig. 6 (a) Magnetization reversal under sinusoidal magnetic field. The coexisting $H_{ac} \perp H_{dc}$ enables irreversible magnetization indicated by the demagnetization ratio ϕ_N . The changes in ϕ_N with increasing (b) field amplitude and (c) static bias field, for magnetic nanoclusters with different core sizes. At constant $H_{dc} = 450$ Oe (squares), ϕ_N appears to be minimized for the increase of H_0 as apparently seen for the 4-nm γ -Fe₂O₃ nanoclusters (solid lines). No irreversible magnetization observed in the absence of H_{dc} (circles) indicates the symmetric magnetization loops. At constant $H_0 = 300$ Oe (triangles), minimum ϕ_N is also observable for both the 5-nm γ -Fe₂O₃ (dashed lines) and 7-nm γ -Fe₂O₃ (dash-dotted lines) nanoclusters as H_{dc} increases.

The dipolar fields of magnetic moments in a solid dispersion can modify the apparent response of magnetic nanoclusters to the applied field. [34] This phenomenon is effective when the vectors of magnetic moments are collateral. However, most of superparamagnetic nanoclusters consist of magnetic cores with random moment vectors at room temperature so that the magnetizing or demagnetizing effect may not be observable. This situation changes when the nanoclusters are subjected to a strong static bias field or intentionally designed with the strong dipolar interactions of such ferromagnetic cores. [35-37] For the first case, the demagnetization ratio ϕ_N due to dc field-induced moment alignment can be critical to the spatial resolution of MPI as ϕ_N is part of the asymmetric magnetization hysteresis. Illustrated in Fig. 6a,

magnetization reversal under oscillatory magnetic field is typically symmetric in which $-M_R^-$ and M_R^+ remanences are identical. The presence of strong dipolar field may limit the reversal of magnetic moments along their easy axes, thus $-M_R^-$ and M_R^+ vary. **Figure 6b** further shows that ϕ_N has negative values for various H_0 at $\mathbf{H}_{dc} = 450$ Oe, similarly for ϕ_N in the function of $\mathbf{H}_{dc}$ (**Fig. 6c**). This feature represents that contribution of the demagnetizing dipolar fields is not trivial, particularly when the collateral moment alignment is present.

In general, ϕ_N has dependence on both D_h and D_c , similar with $\mathbf{H}_d$. Here, M_R^-/M_0 and M_R^+/M_0 in **Eq. (2)** can be numerically substituted by **Eqs. (6)** and **(7)**, as well as **Eqs. (10)** and **(11)** to fit the field amplitude and static field dependences of ϕ_N , respectively. As shown in **Fig. 6c**, for example, ϕ_N of the 5-nm γ -Fe₂O₃ nanoclusters is the largest one at low $\mathbf{H}_{dc}$. The value changes at high $\mathbf{H}_{dc}$ where the 7-nm γ -Fe₂O₃ nanoclusters with smaller D_h has the largest ϕ_N . Therefore, ϕ_N does not only describe its dependence on the particle size, but it also gives information about the change in the effective moment vector relative to the static bias field. The minimum ϕ_N shown in **Fig. 6c** can be alternatively interpreted as the manifestation of collaterally aligned moment dynamics. Owing to the field-dependent τ_N , [38] the observation time becomes slower relative to the moment dynamics in the presence of bias field. In addition to the smaller hysteresis area, the small fluctuation of moment dynamics results in even smaller ϕ_N . This effect is indeed core size-dependent. From **Fig. 6c**, the minimum ϕ_N are -0.0046, -0.0059, and -0.0071 for the immobilized 4-nm, 5-nm, and 7-nm γ -Fe₂O₃ nanoclusters, respectively. Thus, the evaluation of minimum ϕ_N can be an attribute for how large the effective core size is.

4. Conclusion

We demonstrated the quantification of dipolar interparticle interaction in a superparamagnetic nanoparticle system by analyzing the dynamic magnetization reversal for a given sinusoidal magnetic field perpendicular to the static bias field. The concept is originated from the dipolar field-induced asymmetric magnetization hysteresis which shows a unidirectional shift of the loops. The corresponding changes in both coercive fields and remanences then are attributed to the apparent dipolar field and its demagnetizing effect for three types of superparamagnetic maghemite nanoclusters with different core and cluster sizes. While the dipolar field and demagnetization ratio are zero in the absence of the bias field, they become significant when the bias field increase for an arbitrary field amplitude. In this approach, the collateral alignment of magnetic moments in the static field direction is the key factor signifying the dipolar magnetism. We later confirmed that an increase of core size obviously gives rise to larger dipolar field

observed at high bias field. However, this situation becomes cluster-size-dependent at low bias field, in which large hydrodynamic size may lead to a strong dipolar field. These observations conclusively prove that the dynamic reversal curve analysis of dipolar field-induced asymmetric magnetization hysteresis can be powerful method to quantitatively characterize the dipolar interparticle interactions of magnetic nanoclusters, in the correlation with the core-to-cluster volume ratio.

Acknowledgement

This work was partially supported by JSPS KAKENHI Grant Numbers 15H05764 and 17H03275.

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