Two-step relaxation process of colloidal magnetic nanoclusters under pulsed fields

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We empirically uncovered a two-step process of a temporal magnetization response under a pulsed field, which was observed by delaying the particle kinetics in a viscous medium. The Brownian alignment of the magnetization easy-axis appeared to occur separately after the rotated moments reached equilibrium, instead of randomly mixed relaxation behavior. The effective cluster moment and anisotropic magnetopotential difference are two key factors for determining each contribution to the steady-state magnetization. This finding adds new insight to the understanding of colloidal magnetic nanoclusters as a semi-rigid dipole system, which has potential applications in biomedical platforms.

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Recent nanotechnological challenges in the biomedical field have revealed the importance of magnetic nanoparticles as a prospective candidate for therapeutic agents.1) Owing to their remarkable room-temperature magnetism, magnetic nanoparticles exclusively contribute to the development of a cellular imaging and heating apparatus for integrated medical service.2,3) Moreover, ranging from material selection to bio-functionalization, there are numerous reports on the fabrication of magnetic nanoparticles for biomedical applications. One of the representative structures is the magnetic nanocluster, which is a three-dimensional (3D) hydrodynamic aggregate of small core particles.4,5) As minimum clinical prerequisites, magnetic nanoclusters should be biocompatible, chemically stable but biodegradable, and well dispersed in ionic cellular matrices. More importantly, they should exhibit excellent magnetic properties in biological environments. Therefore, magnetic characterization has become the first crucial step in assessing whether such nanostructures are feasible for the designed in vivo applications.

The magnetization properties of magnetic nanoclusters strongly correlate with their dissipative relaxation behaviors. The theory on the dynamics of a single magnetic nanoparticle dispersed in a liquid medium, in general, involves two fundamental mechanisms regarding the alignment of the magnetization vector with the direction of minimum magnetopotential energy: Néel and Brownian relaxations.6,7) To address both the moment and particle rotations, the effective relaxation time constant \( \tau = (\tau_N + \tau_B) \) of a linear (Debye) relaxation response is often employed.8) However, such a statistical approach accounting for the fastest mechanism appears implausible, particularly for colloidal magnetic nanoclusters. The dipolar interparticle interactions within a single nanocluster may result in an effective moment to physically rotate the nanocluster with an applied magnetic field.9) Although the Néel time constant \( \tau_N \) of the cores must be shorter than the Brownian time constant \( \tau_B \) of the respective nanocluster, it is hypothesized that the low-frequency regime dominantly belongs to Brownian dynamics.10) The spectral responses of complex magnetization are further evidence with the imaginary parts maximized at \( (2\pi \nu \tau_B) \).11) Instead of \( \tau \approx \tau_B \), \( \tau = (\tau_N + \tau_B) \) mathematically implies that \( \tau \approx \tau_N < \tau_B \), which appears to be practically inconsistent unless the Néel dynamics are completely blocked.

It is critical that the coupled Néel and Brownian dynamics for the polydispersed magnetic nanoparticles are distinguished, while the reduced magnetization of the immobilized nanoparticles demonstrates their coexistence.12) A recent computational study on demagnetizing nanoclusters confirmed a rapid initial decay followed by a long period of relaxation, indicating distinctive Néel and Brownian dynamics.13) Other numerical studies on the ideal monodispersed particle system emphasize no such behavior.14,15) We thus focus on experimentally examining the temporal magnetization response of magnetic nanoclusters dispersed in a viscous medium under a pulsed magnetic field, to provide the first empirical evidence of the two-step relaxation scenario.

As a preliminary analysis, we assessed the water-based suspension of sodium-α-olefin-sulfonate-coated Fe₃O₄ nanoparticles (Sigma Hi-Chemical) with a glycerin-adjusted viscosity to slow the Brownian particle motions. The initial particle concentration was diluted to 35 mg·Fe mL⁻¹. From Fig. 1, a spectral shift of the complex magnetic susceptibility can be confirmed, with the glycerin (volume) ratio varying among 25 (31.8), 50 (56.9), 75 (73.4), and 98 (81.6) vol %, where the numbers in the brackets indicate empirical approximate values based on the ratio of \( \tau_B \) measured at 7.1 Oe rms without a direct-current bias field. The peak intensities of the imaginary parts \( \chi' \) and low-frequency real parts \( \chi'' \) appear to be identical for all samples, indicating a trivial change in the hydrodynamic size distribution. The average distributive primary and secondary particle diameters were approximately 13 and 42 nm, respectively. For such delayed Brownian dynamics on the viscous media (Fig. 1), we expect to observe the moment rotations and easy-axis alignments with a distinguishable timescale. We later exposed the ferrofluid samples to 100-Oe-pulsed fields and recorded the resulting magnetization; the pulse period, width, and time constant were 10, 10⁻¹, and 1.5 x 10⁻⁶ s, respectively.

In the presence of random fields \( \mathbf{\xi} \) and torques \( \mathbf{\Gamma} \) associated with thermal fluctuation, the field-induced magnetization dynamics of a uniaxial anisotropic nanoparticle is as follows:16,17)
Due to the torque balance, we obtain

\[ \frac{de}{dt} = \omega \times e - \frac{\gamma}{1 + \alpha^2} \left[ e \times (H + H_a + \xi - \frac{\omega}{\gamma}) \right] + \alpha e \times \left[ e \times (H + H_a + \xi - \frac{\omega}{\gamma}) \right]. \] (1)

By involving its easy-axis alignment in a viscous medium due to the torque balance, we obtain

\[ I \frac{d\omega}{dt} + \omega = \frac{1}{\xi} \left[ \mu_S \frac{de}{dt} + \mu_S e \times (H + \xi) + \Gamma \right]. \] (2)

Equations (1) and (2) consider that the magnetic moment \( \mu \) (of such a rotatable rigid body) with a constant magnitude \( \mu_S \) and a unit vector \( e = \mu/\mu_S \) performs both internal (Néel) and external (Brownian) relaxation processes with an angular velocity \( \omega \). For the first process, it is not a rare case to omit the precessional effect, depending on the Gilbert damping constant \( \alpha \) and gyromagnetic ratio \( \gamma \). In the rigid-dipole model, for instance, the Néel relaxation is blocked in the liquid because of a large anisotropy energy; thus, only the first right-hand term of Eq. (1) is significant. Similarly, it should be trivial to consider the inertial effect \( I/\xi \) for the small nanoparticle mass and the low frequency regime of the Brownian relaxation;\(^{15}\) \( I \) is the moment of inertia, while \( \xi = 6\eta V_b \) is the friction coefficient depending on the medium viscosity \( \eta \) and hydrodynamic particle volume \( V_b \). For small values of \( I/\xi \) and \( \mu_S/\xi \), the differential terms of Eq. (2) are often eliminated.

The anisotropy field \( H_a = (2k_1/V_m/\mu_S) e \cdot n \) arising from a different vector of the easy axis \( n \) relative to \( e \) is an important factor in determining the equilibrium magnetization of a magnetic nanoparticle with the anisotropy constant \( k_1 \) and primary volume \( V_m \). Under an external pulsed field \( H(t) = H_0[1 - \exp(-t/\tau_p)] \) with the respective magnitude \( H_0 \) and time constant \( \tau_p \), the moment dynamics instantaneously change \( e \cdot n \) in the case of \( \tau_p \leq \tau_p \ll \tau_p \). The resulting anisotropic magnetopotential difference governs Brownian easy-axis alignment \( d\mathbf{n}/dt = \omega \times \mathbf{n} \), while \( \mathbf{e} \) remains in its steady state. Figure 2 presents such two-step relaxation dynamics of the FeO nanoparticles polydispersed in a highly viscous medium.

To support our experimental finding, we computationally simulated 13,824 single-core particles (with primary and secondary diameters of \( D_S = 10 \) and \( D_b = 40 \) nm, respectively) to solve Eqs. (1) and (2). \( I/\xi \) and \( \mu_S/\xi \) were omitted to simplify the rigid-dipole approximation, while \( \xi \) and \( \Gamma \) are Gaussian-distributed with a zero mean\(^{18,19}\). By setting \( k_1 = 10 \) kJ m\(^{-3} \), \( \eta = 0.89 \) cP, \( \alpha = 0.1 \), \( \gamma \) corresponding to the characteristic \( \tau_N \), and the saturated magnetization \( M_S = 52.1 \) emu g\(^{-1} \), the room-temperature magnetization \( M(t) \) and the easy-axis angle \( \psi(t) \) relative to the field direction were calculated as average responses to a pulsed field, similar to the experimental conditions. The mean value of the absolute \( \cos \psi(t) \) settles at 0.514, which is associated with the randomly generated 3D-easy-axis components of the simulated particles. In Fig. 3, the increasing \( M(t) \) at \( 10^{-8} \leq t \leq 10^{-5} \) s indicates the moment rotation, while the easy-axis appears to rotate in the opposite direction to balance the magnetic torque. At \( t > 10^{-5} \) s, the \( M(t) \) of the liquid sample shows an increment from that of the solid sample. The increasing \( \cos \psi(t) \) further suggests that the delayed Brownian rotation is responsible for such a magnitude difference.

Consistent with the experimental and computational results (Figs. 2 and 3), the physical relaxation of a magnetic nanocluster contributes to larger equilibrium magnetization under the external field. One of the determinants is supposed to be the effective cluster moment, which can be defined as \( \mu_S N \sum_{i=1}^{N} \mathbf{e}_i \) for \( N \) core particles within a single hydrodynamic volume, by including the dynamics of each moment vector \( \mathbf{e}_i \). This case considers the dipolar interparticle interactions that limit the moment dynamics relative to the cluster rotation,\(^{13}\) thus governing

\[ \frac{d\mathbf{e}_i}{dt} = -\frac{\gamma}{1 + \alpha^2} \left[ \mathbf{e}_i \times \mathbf{H}_{i,j} + \alpha \mathbf{e}_i \times (\mathbf{e}_i \times \mathbf{H}_{i,j}) \right]. \] (3)
where \( \mathbf{H}_{\text{eff}} = \mathbf{H} + \mathbf{H}_{\text{dip}} + \mathbf{H}_{\text{D}} + \mathbf{H}_{\text{N}} \) is the effective field upon each moment, including the dipolar field \( \mathbf{H}_{\text{dip}} \) from the interaction energy; and \( \omega_{\text{i}}/\gamma \) is zero for the case of immobile cores. While Eq. (3) represents a stochastic Landau–Lifshitz–Gilbert equation for a single core, the cluster may rotate with a constant angular velocity \( \omega_c \) [assuming \( \ell_0 D_{\text{vis}} (\ell^2 \text{d})^{-1} \approx 0 \):]

\[
\omega_c = \frac{M_S}{\xi} \left[ \frac{1}{N} \sum_{i=1}^{N} \frac{\partial \mathbf{e}_i}{\partial t} + \sum_{i=1}^{N} \mathbf{e}_i \times (\mathbf{H} + \mathbf{z} + \frac{\Gamma}{M_S}) \right].
\] (4)

where \( M_S = \mu_0 N \) is the saturated magnetization of the cluster. Therefore, we further investigated the (core–to-cluster) size effect in the field-induced Brownian easy-axis alignment. We used 2.8-mg-Fe maghemite nanoparticles with carboxymethyl-diethy laminoethanol-dextran and carboxy dextran coatings (Meito Sangyo) which were suspended in a 0.1-mL glycerin–water mixture. The average (core, cluster) diameters prior to the viscosity adjustment were (4, 38) and (6, 59) nm, respectively.

Concerning Eqs. (3) and (4), Fig. 4 proves that a large \( M_S \sum_{i=1}^{N} \mathbf{e}_i \) corresponds to a significant contribution to the Brownian relaxation. We presumed that \( \mu_0 \) is proportional to \( D_{\text{vis}} \) whereas \( D_{\text{vis}} \) is associated with \( N \). Thus, compared with the 13-nm \( \gamma \)-Fe_{2}O_{3} sample for the same \( D_{\text{vis}} \), the 4-nm \( \gamma \)-Fe_{2}O_{3} sample has larger steady-state moment dynamics of 0.990\( M_{\text{eff}} \), where \( M_{\text{eff}} \) is the equilibrium magnetization under a static field. Moreover, the value is higher than that of the 6-nm \( \gamma \)-Fe_{2}O_{3} sample, which has a larger \( D_{\text{vis}} \). To discuss this result, we consider that the magnetic nanocluster should sustain its internal relaxation, instead of behaving as a rigid-dipole system; thus, the corresponding magnetization response can be expressed as

\[
\frac{\mathbf{M}(t)}{M_S} = \int_0^t \left( \frac{1}{N} \sum_{i=1}^{N} \frac{\partial \mathbf{e}_i}{\partial t} + \omega_c \times \sum_{i=1}^{N} \mathbf{e}_i \right) \, dt.
\] (5)

Equation (5) indicates that \( \sum_{i=1}^{N} \mathbf{e}_i = 0 \) results in no Brownian cluster rotation; rather, it results in Néel relaxation. We alternatively generalize Eq. (5) into \( \mathbf{M}(t) = \mathbf{M}_N(t) + \mathbf{M}_B(t) \), where \( \mathbf{M}_N(t) \) and \( \mathbf{M}_B(t) \) represent the time-varying magnetization responses, which are attributed to the Néel moment dynamics \( (\partial \mathbf{e}/\partial t) \) and Brownian easy-axis alignment \( (\omega_c \times \sum \mathbf{e}_i) \), respectively.

Figures 2–4 indicate that under the pulsed fields, the resulting magnetization is described by the function \( \mathbf{M}(t) = M_{\text{N0}}[1 - \exp(-t/\tau_{\text{N}})] + M_{\text{B0}}[1 - \exp(-t/\tau_{\text{B}})] \). The equilibrium magnetization \( \mathbf{M}(t) \approx 2\pi \) is then defined as the sum of \( M_{\text{N0}} \) and \( M_{\text{B0}} \) associated with the steady-state moment dynamics and easy-axis alignment, respectively.\(^{20,21}\)

In Fig. 2, the \( M_0 \) of the Fe_{3}O_{4} samples appears to be constant for various viscosities. To obtain \( M_{\text{N0}} \) for each liquid sample, the transient \( \mathbf{M}(t) \) of the gelatin-solidified sample is fitted to the first step of the relaxation responses. Originally, it is possible to fit them all with the same \( M_{\text{N0}} = 0.224 \). However, for low-viscous media (e.g., water and 31.8 vol % glycerin), the Brownian time constant is relatively short (as shown later) to marginally superimpose the particle rotation on the moment rotation at a timescale of approximately \( 10^{-6} \) s, leading to a slightly larger estimate of \( M_{\text{N0}} = 0.229 \). Therefore, specifically for validating the Brownian relaxation, the \( \tau_{\text{B}} \) attributed to the time necessary for reaching \( M_{\text{B0}}(1 - e^{-t}) \) can be extracted and compared with that representing the frequency of the maximum \( \gamma' \). As a result, Fig. 5 confirms that both the spectral and temporal analyses of \( \tau_{\text{B}} \) at the steady-state field of 100 Oe are consistent. In the case of low-medium viscosities, \( \tau_{\text{B}} \) is approximately on the order of \( 10^{-8} \) s. Considering the field-dependent Brownian relaxation [Fig. 5(a)],\(^{8,15,22}\) we further question the minimum field magnitude activating the easy-axis alignment.

The Néel and Brownian dynamics in magnetic nanoclusters are temporally distinguishable from the \( \tau_{\text{N}} \) and \( \tau_{\text{B}} \) values; however, the two-step relaxation behavior is hardly observable at a large \( M_{\text{N0}}/M_0 \) (Fig. 4). In addition to the effective cluster moment, the second reason for the different \( M_{\text{N0}}/M_0 \) lies in the effective anisotropic magnetopotential \( E_{\text{aa}} \). Experiencing the pulsed field, the core particles rapidly change the relative direction of their moments to minimize \( E_{\text{aa}} = -\mu_0 N \sum_{i=1}^{N} \mathbf{e}_i \cdot \mathbf{H} \), which is attributed to the Zeeman energy. Consequently, \( E_{\text{aa}} \) increases to \(-k_{\text{B}} \sum_{i=1}^{N} (\mathbf{e}_i \cdot \mathbf{n})^2 V_{\text{vis}} \), where a Stoner–Wohlfarth core particle with a uniaxial anisotropy defines \(-\mathbf{e}_i \cdot \mathbf{n}^2 = \sin^2 \theta_i, \) with \( \theta_i \) as the angle between \( \mathbf{e}_i \) and \( \mathbf{n}. \)\(^{23,24}\) Without neglecting the dipolar interactions, the field-induced \( \Delta E_{\text{aa}} \) is the origin of the cluster rotation at a
pulsed field of $dH/dt \approx 0$. For the immobile cores [i.e., rigid cluster; $\omega_c/\gamma \approx 0$ with a moment precession $(\alpha \ll 1)$], the respective $\omega_c$ can be obtained by inserting Eq. (3) into Eq. (4):

$$\omega_c = \frac{M_s}{\gamma} \sum_{i=1}^{N} e_i \times (H_{d,i} - H_{a,i}) + \frac{\Gamma}{M_s}.$$

Equation (6) indicates that random cluster motions due to thermal agitation and dipolar interactions readily exist at $H_0 = 0$. After the total magnetopotential of a single magnetic nanocluster is simplified to $E_c \approx E_{d,c} + E_{a,c}$, $M_0(H_0)$ thermodynamically represents $dE_d/dt \approx 0$. To consider $dE_{a,c}/dt \approx -dE_{d,c}/dt$ of the steady state, $|H_{a,i}|$ should increase with $H_0$. Therefore, a sufficiently large $H_0$ allows $H_{a,i}$ to overcome $H_{d,i}$ and $\Gamma/M_s$, enabling easy-axis alignment at $t > 2\pi\tau_n$. Figure 6 confirms that $H_0 > 20$ Oe leads to a clear two-step process of relaxation dynamics in the Fe$_3$O$_4$ sample. For an ideal rigid-dipole model (i.e., $\sum_{i=1}^{N} e_i \times 0 = 0$),\(^\dagger\) in contrast, either the moment or easy-axes should rotate simultaneously with an effective time constant as the field is pulsed with any $H_0$, resulting in a typical exponential response of the magnetization.

In conclusion, we report the first empirical evidence of a two-step relaxation phenomenon in colloidal magnetic nanoclusters under a pulsed field, in which the fast moment dynamics of the cores are followed by Brownian cluster rotation at a delayed timescale. This finding suggests that magnetic nanoclusters are not sufficiently compatible as a rigid-dipole system; instead, it is important to include the Néel relaxation process in each core. Our experimental review further summarizes two key entities for determining the contribution of the easy-axis alignment to the equilibrium magnetization: the effective cluster moment and the anisotropic magnetopotential difference. We generalize the room-temperature nanocluster dynamics as a semi-rigid dipole system, which provides a practical framework for a spectroscopic magnetoassay based on the selective relaxation of magnetically free-labeled targets or phase-contrast magnetic particle imaging derived from the viscosity-sensitive Brownian relaxation of tracers.

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