Thermally Activated Relaxation Time of a Single Domain Ferromagnetic Particle Subjected to a Uniform Field at an Oblique Angle to the Easy Axis: Comparison with Experimental Observations

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New asymptotes of the relaxation time of the magnetic moment of a single domain particle with a uniform magnetic field applied at an oblique angle to the easy axis (in excellent agreement with exact numerical results from the Fokker-Planck equation for the Néel-Brown model) are used to model the experimental angular variation of the switching field for individual Co and BaFeCoTiO particles. Good agreement is obtained, justifying the Néel-Brown (in effect, the Kramers) conception of the superparamagnetic relaxation process and allowing one to deduce the value of the damping constant (hitherto almost unknown). [S0031-9007(98)06341-8]

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An accurate analytical expression for the prefactor of the greatest relaxation time τ due to thermal agitation of the magnetic moment $\mathbf{m}$ of single domain nanoparticles subjected to a uniform external field $\mathbf{H}$ is necessary for modeling experiments and deducing other experimental parameters [1].

This problem is important in long term stability [2,3] of stored information and in [4] macroscopic quantum tunneling (MQT) of $\mathbf{m}$ (a mechanism of magnetization reversal suggested in [5]), as a knowledge of τ allows the separation of the different relaxation mechanisms. In all common particle assemblies, the easy directions $\mathbf{n}$ of the particles are randomized so that asymptotic τ for $\mathbf{H}$ at an arbitrary angle to $\mathbf{n}$ is required; this differs from the Brown (1963) [6] asymptote for axial symmetry; i.e., $\mathbf{H} \parallel \mathbf{n}$ because breaking the axial symmetry couples the transverse and longitudinal relaxation modes. Here we compare experimental and calculated τ as (i) the theory permits direct comparison with experiment (hitherto impossible), and (ii) accurate experiments on *individual* small particles are now available. Concerning the theory [7–11] we have already presented exact numerical solutions and asymptotes of τ for a particle with uniaxial anisotropy with $\mathbf{H}$ in the x-z plane at an angle ψ to the easy direction z so that

$$\nu V(\vartheta) = \nu K \sin^2\vartheta - \nu M_s H \times (\cos\vartheta\cos\psi + \sin\vartheta\cos\phi\sin\psi). \quad (1)$$

ϑ and φ are the polar angles of $\mathbf{m}$, K is the anisotropy constant, and M_s denotes the magnetization of a nonrelaxing particle of volume v.

Equation (1) is a *particular* nonaxially symmetric potential. In Refs. [8–11], we have shown that, for a *general* asymmetric bistable potential of free energy density $V = V(\mathbf{r})$ ($\mathbf{r} = \mathbf{M}/M_s$), with minima at $\mathbf{n}_1$ and $\mathbf{n}_2$ separated by a potential barrier containing a saddle point at $\mathbf{n}_0$ (with the $\mathbf{n}_i$ coplanar) that

$$\tau \approx \frac{2\tau_N}{\lambda_1}, \quad (2)$$

where

$$\lambda_1 \approx \beta\left(\sqrt{c_1^{(1)}c_2^{(1)}}\, e^{-\beta(V_0-V_1)} + \sqrt{c_1^{(2)}c_2^{(2)}}\, e^{-\beta(V_0-V_2)}\right)\left[\frac{-c_1^{(0)} - c_2^{(0)} + \sqrt{(c_2^{(0)} - c_1^{(0)})^2 - 4\alpha^{-2}c_1^{(0)}c_2^{(0)}}}{4\pi\sqrt{-c_1^{(0)}c_2^{(0)}}}\right], \quad (3)$$

verifying Brown's later (1979) calculation [8,10]

$$\tau_N = \frac{\beta M_s(1+\alpha^2)}{2\gamma\alpha}. \quad (4)$$

γ is the gyromagnetic ratio, $\beta = \nu/kT$.

$$\alpha = \eta\gamma M_s \quad (5)$$

is the dimensionless damping factor (η is the friction in Gilbert's equation [8]). Equation (3) is [11]

$$\tau^{-1} \approx \frac{\lambda_1}{2\tau_N} \approx \frac{\Omega_0}{2\pi\omega_0}\{\omega_1 \exp[-\beta(V_0 - V_1)] + \omega_2 \exp[-\beta(V_0 - V_2)]\}. \quad (6)$$

ω_1 and ω_2 are the well angular frequencies; ω_0 and Ω_0 are the saddle and the damped saddle angular frequencies (V at the minima is denoted by $i = 1, 2$, respectively, and at the saddle point by 0). Equation (3) is the leading term in the asymptotic expansion of the smallest nonvanishing eigenvalue λ_1 of the Fokker-Planck equation (FPE) for magnetic moment orientations; $c_1^{(i)}, c_2^{(i)}, i = 0, 1, 2$ in Eq. (3) are the coefficients in the truncated Taylor series [8,9] of the potential at the well and saddle points. The α values for which Eq. (3) is valid are discussed in [10–12], where Eq. (3) is compared with the exact λ_1. Equation (3) approximates λ_1 if [10,11]

$$\alpha\beta(V_0 - V_i) > 1, \qquad \beta(V_0 - V_i) \gg 1 \tag{7}$$

and is called the intermediate to high damping (IHD) formula. Conversely, if α satisfies

$$\alpha\beta(V_0 - V_i) \ll 1, \qquad \beta(V_0 - V_i) \gg 1 \tag{8}$$

so that the energy dissipated in one cycle of the motion is very small ($\ll kT$), then [11,12]

$$\tau^{-1} \approx \frac{\alpha}{2\pi}\{\omega_1\beta(V_0 - V_1)\exp[-\beta(V_0 - V_1)] + \omega_2\beta(V_0 - V_2)\exp[-\beta(V_0 - V_2)]\}. \tag{9}$$

This is the low damping (LD) limit. The evaluation of Ω_0, ω_i $(i = 0, 1, 2)$ for Eq. (1) (involving numerical solution of a quartic equation) is described in [8,9]. Experimentally, relaxation is observed only if τ is of the order of the measuring time of the experiment implying that $\beta(V_0 - V_2) \gg 1$ always (taking V_2 as the shallow minimum). Because of Eqs. (7) and (8), we remark that little information about α for small particles is available so that α between 0.05 and 1 [13] is usually postulated; other values cannot be ruled out, however, meaning that in practice $\alpha\beta(V_0 - V_2)$ can be $\gg 1$, $\ll 1$, or ≈ 1; thus the distinction between Eqs. (6) and (9) becomes important. Here, τ as a function of the field angle ψ is required. Such measurements can be made either on oriented particle assemblies where the easy axes are parallel or on an *individual* particle. We understand that data have not hitherto been available on an individual particle; however, accurate individual particle measurements are now available [3,4] facilitating the comparison of theory and experiment.

In verifying Eqs. (6) and (9) for the IHD and LD limits, we selected metallic Co particles synthesized by arc discharge [14] and insulating $BaFe_{10.4}Co_{0.8}Ti_{0.8}O_{19}$ particles fabricated by a glass crystallization method [15]; each possesses strong uniaxial magnetocrystalline anisotropy. We used the results for a 20 nm sized Co particle [3] and a 10 nm sized BaFeO particle [4] gained by using planar Nb micro-SQUIDS allowing the study of the magnetization reversal of individual nanoparticles by waiting time and switching field experiments. The waiting time measurements yield the switching probability. At a given temperature, the magnetic field **H** is increased to a waiting field near the switching field. Next, the time elapsed until the magnetization switches is measured. This process is repeated several hundred times, yielding a waiting time histogram. The integral of this histogram yields the switching probability. Regarding the switching field measurements, **H** is ramped at a given rate and the value stored when the sample magnetization switches. Next, the field ramp is reversed and the process repeated. After several hundred cycles, switching field histograms are established, yielding the mean switching fields $\langle H_{SW}\rangle$ and the width σ_{SW} (rms deviation). Both measurements can be studied as a function of ψ (the **H** direction). The number of decades for τ values is limited for waiting time experiments; short-time (milliseconds) experiments are limited by the inductance of the field coils and long-time (minutes) studies by the stability of the experimental setup. Furthermore, the total acquisition time is about a week; thus the more convenient switching field measurement is usually employed. Switching field measurements are equivalent to waiting time measurements as the time scale for the sweeping rates is more than 8 orders of magnitude greater than the time scale of the prefactor. We shall demonstrate that the experimental results are in good agreement with the asymptotes, Eqs. (6) and (9) above [written as Eq. (16) below]; moreover, one may determine α.

Thus $\langle H_{SW}\rangle$ may be expressed [16] as

$$\langle H_{SW}\rangle = H_c\left\{1 - \left[A^{-1}\ln\left(\frac{H_cB}{a(dH/dt)A^{1+b/e}}\right)\right]^{1/e}\right\}, \tag{10}$$

and

$$\tau^{-1} = B\varepsilon^{a+b-1}e^{-A\varepsilon^a}, \tag{11}$$

with

$$\varepsilon = 1 - \frac{H}{H_c}, \tag{12}$$

where $H = |\mathbf{H}|$ and dH/dt is the rate of field ramping. For uniaxial anisotropy [7,8],

$$H_c = \frac{2K}{M_s}h_c = \frac{2K}{M_s}(\sin^{2/3}\psi + \cos^{2/3}\psi)^{3/2}, \qquad h_c = \frac{M_sH_c}{2K}, \tag{13}$$

where K is the total anisotropy constant, and h_c is the reduced critical field where the bistable V structure vanishes. The particles have a large volume leading to high anisotropy barriers at low temperatures; thus, to observe relaxation, $\beta(V_0 - V_2)$ must be about 25. The large volume implies small ε leading to $\beta(V_0 - V_1) \gg \beta(V_0 - V_2)$. Thus we neglect $\exp[-\beta(V_0 - V_1)]$ in τ^{-1} and approximate $V_0 - V_2$ for $\varepsilon \ll 1$ by [17]

$$\frac{V_0 - V_2}{K} = 4\left(\frac{2}{3}\varepsilon\right)^{3/2}\frac{|\cot\psi|^{1/3}}{1 + |\cot\psi|^{2/3}}. \tag{14}$$

[We checked Eq. (14) numerically against the exact solution [17,18]; it is an excellent approximation for $5° < \psi < 85°$ and $\varepsilon < 0.05$.] To determine the parameters in Eqs. (10) and (11), let

$$\tau^{-1} = \frac{K\gamma}{M_s} P \exp[-\beta(V_0 - V_2)], \tag{15}$$

where in IHD

$$P = P_{\rm IHD} = \frac{M_s}{K\gamma}\frac{\Omega_0}{2\pi}\frac{\omega_2}{\omega_0} = \frac{\alpha}{4\pi(1+\alpha^2)} \times \left(\frac{\sqrt{c_1^{(2)}c_2^{(2)}}}{\sqrt{-c_1^{(0)}c_2^{(0)}}}\right)\Big[-c_1^{(0)} + c_2^{(0)} + \sqrt{(c_2^{(0)} - c_2^{(0)})^2 - 4\alpha^{-2}c_1^{(0)}c_2^{(0)}}\,\Big], \tag{16}$$

while in LD

$$P = P_{\rm LD} = \frac{M_s}{K\gamma}\frac{\alpha}{2\pi}\,\omega_2\beta(V_0 - V_2) = \frac{\alpha}{2\pi}\sqrt{c_1^{(2)}c_2^{(2)}}\,\beta(V_0 - V_2)\,. \tag{17}$$

These can be fitted to

$$P_{\rm IHD} = f_{\rm IHD}(\psi,\alpha)\varepsilon^{\delta_{\rm IHD}}, \tag{18}$$

and

$$P_{\rm LD} = \alpha f_{\rm LD}(\psi)\beta(V_0 - V_2)\varepsilon^{\delta_{\rm LD}-3/2} = \alpha f_{\rm LD}(\psi) \times \left[4\beta K\left(\frac{2}{3}\right)^{3/2}\frac{|\cot\psi|^{1/3}}{1 + |\cot\psi|^{2/3}}\right]\varepsilon^{\delta_{\rm LD}}, \tag{19}$$

with ε given by Eq. (12). Equations (14)–(19) yield

$$a = \frac{3}{2}, \qquad b = \delta - \frac{1}{2}, \qquad B = \frac{K\gamma}{M_s}\frac{P}{\varepsilon^{\delta}}, \qquad A = 4\beta K\left(\frac{2}{3}\right)^{3/2}\frac{|\cot\psi|^{1/3}}{1 + |\cot\psi|^{2/3}}\,. \tag{20}$$

In adjusting the theory to switching field measurements of individual nanoparticles, several conditions must be fulfilled: (i) The angular dependence of the switching field must obey the model of magnetization reversal by uniform rotation [19], Eq. (13), and (ii) the switching probability determined by waiting time measurements must be an exponential function of the time ($\approx \exp[-t/\tau]$). These are satisfied by the metallic Co particle of Ref. [3] and the insulating BaFeCoTiO particle of Ref. [4].

Our comparison was accomplished as follows: (i) We chose IHD and guessed α. (ii) We adjusted the theory to the switching field measurements [3] at various ψ, knowing ν from scanning electron microscopy, γ and M_s from Refs. [14,15], and K from H_c at $\psi = 90°$ and Eq. (13). (iii) We compared the observed ψ of $f_{\rm IHD}(\psi,\alpha)$ with the IHD formula [Eq. (18)]. (iv) We altered the assumed α and repeated the adjustment of step (iii) until optimum agreement between theory and experiment is achieved. (v) Finally, where Eq. (7) is violated, we repeated the process using LD; i.e., we compared the results to $f_{\rm LD}(\psi)$ of Eq. (19).

Results for Co and BaFeCoTiO are presented in Figs. 1(a) and 1(b). $f_{\rm IHD}(\psi,\alpha)$ of the Co particle provides a good fit to IHD using $\alpha = 0.5 \pm 0.2$; likewise, $f_{\rm LD}(\psi)$ of the BaFeCoTiO particle to LD with $\alpha = 0.035 \pm 0.005$. Both α fits are reasonable because (i) the damping in metallic particles is expected to be higher than in insulating particles in agreement with our experimental results and (ii) the values are close to the results of Refs. [1,13]. Nevertheless, more detailed measurements should be carried out to substantiate these preliminary measurements. We emphasize that α is the *sole* fitting parameter causing us to reiterate that little information is available on α for fine particles; for γFe_2O_3 particles in a polymer, α ranges between 0.05 and 1 depending on the interparticle interaction strength [13]; again for interacting Fe particles in an alumina matrix [1] $\alpha \approx 1$ while, for bulk Fe, $\alpha \approx 0.01$. Furthermore, very low α values are observed for particular compounds such as yttrium garnet. Also, in fine particles, α is a phenomenological constant in the Gilbert equation for the *entire* particle including *all* defects, in particular, the

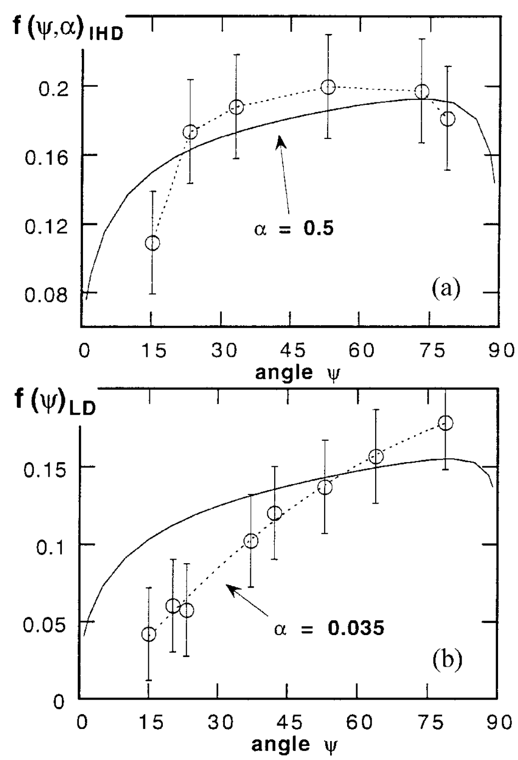

FIG. 1. Comparison of the (a) IHD and the (b) LD formulas with measurements obtained on (a) a metallic Co particle [3] and (b) an insulating BaFeCoTiO particle [4]; $K\gamma/M_s = 5 \times 10^{10}\ \mathrm{s}^{-1}$ and $K\gamma/M_s = 6.9 \times 10^{10}\ \mathrm{s}^{-1}$, respectively, were used.

surface defects; thus one expects that, the *smaller* the particle, the more pronounced will be the increase of α over its bulk value. The damping problem also plays an important role in the MQT of $\mathbf{m}$. In general, dissipation due to, for example, conduction electrons strongly reduces quantum effects. This agrees with our measurements in that, for metallic Co particles, no quantum effects were found at low temperatures [3] whereas, for insulating BaFeCoTiO particles [4], strong deviations from the classical model exist below 0.4 K which are quantitatively in agreement with the predictions of the MQT theory in the low dissipation regime [4].

We conclude that new asymptotes of τ of $\mathbf{m}$ of a nanoparticle with $\mathbf{H}$ at angle ψ with respect to $\mathbf{n}$ (in numerical agreement with the FPE [9,11,18]) reproduce the angular variation of the switching field of *individual* particles to a reasonable degree of accuracy, justifying the Néel-Brown (in effect, the Kramers) conception of the thermal relaxation process. Equations (6) and (9) are also valid for *any* nonaxially symmetric bistable potential with coplanar minima and saddle points allowing extension to other potentials, i.e., taking into account higher terms of the magnetocrystalline anisotropy. These asymptotes also pertain to the memoryless (white noise) limit (Ohmic damping). Nevertheless, as conjectured in [20] in the presence of long-time memory, they should hold with a reduced effective dissipation constant which influences, in particular [21], the LD prefactor.

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