PHYSICAL REVIEW B **82**, 100413(R) (2010)

Nonlinear magnetization relaxation of superparamagnetic nanoparticles in superimposed ac and dc magnetic bias fields

Serguey V. Titov,[1] Pierre-Michel Déjardin,[2] Halim El Mrabti,[2] and Yuri P. Kalmykov[2]
[1]*Institute of Radio Engineering and Electronics, Russian Academy of Sciences, 1, Vvedenskii Square, Fryazino 141190, Russia*
[2]*LAMPS, Université de Perpignan Via Domitia, 52, Avenue de Paul Alduy, 66860 Perpignan Cedex, France*
(Received 9 July 2010; revised manuscript received 9 August 2010; published 24 September 2010)

The nonlinear ac response of the magnetization $\mathbf{M}(t)$ of a uniaxially anisotropic superparamagnetic nanoparticle subjected to both ac and dc bias magnetic fields of arbitrary strengths and orientations is determined by averaging Gilbert's equation augmented by a random field with Gaussian white-noise properties in order to calculate exactly the relevant statistical averages. It is shown that the magnetization dynamics of the uniaxial particle driven by a strong ac field applied at an angle to the easy axis of the particle (so that the axial symmetry is broken) alters drastically leading to different nonlinear effects due to coupling of the thermally activated magnetization reversal mode with the precessional modes of $\mathbf{M}(t)$ via the driving ac field.

DOI: 10.1103/PhysRevB.82.100413 PACS number(s): 75.40.Gb, 05.40.Jc, 75.50.Tt, 76.20.+q

Fine ferromagnetic particles are characterized by thermal instability of their magnetization $\mathbf{M}(t)$ resulting in spontaneous change in their orientation from one metastable state to another by surmounting energy barriers, giving rise to superparamagnetism which is very important in information storage and rock magnetism as well as in biomedical applications.[1,2] Due to the large magnitude of the magnetic dipole moment ($\sim 10^4$–10^5 μ_B) giving rise to a relatively large Zeeman energy even in moderate external magnetic fields, the magnetization reversal process has a strong-field dependence causing nonlinear effects in the dynamic susceptibility and field-induced birefringence,[2,3] stochastic resonance,[4–6] dynamic hysteresis,[7,8] etc. However, nonlinear response to an external field represents an extremely difficult task even for dilute systems because it always depends on the precise nature of the stimulus. Thus no *unique* response function valid for all stimuli exists unlike in linear response.[9]

The nonlinear magnetic response of an individual superparamagnetic nanoparticle in the presence of the thermal agitation can be evaluated[2,3,9] by calculating the relevant statistical averages from Gilbert's (or Landau-Lifshitz) equation augmented by a random field $\mathbf{h}(t)$ with Gaussian white-noise properties, accounting for thermal fluctuations of $\mathbf{M}(t)$ due to the heat bath, viz.,[10]

$$\partial_t \mathbf{M}(t) = \gamma\{\mathbf{M}(t) \times [-\partial_{\mathbf{M}} V(t) - \eta \dot{\mathbf{M}}(t) + \mathbf{h}(t)]\}. \qquad (1)$$

Here γ is the gyromagnetic ratio, η is the damping parameter, and $V(\mathbf{M},t)$ is the free energy per unit volume. This is made up of the *nonseparable* Hamiltonian of the magnetic anisotropy $U(\mathbf{M})$ and Zeeman energy densities, the latter arising from external magnetic dc and ac fields $\mathbf{H}_0+\mathbf{H}\cos\omega t$ of arbitrary strengths and orientations. Now the nonlinear ac stationary response has hitherto been calculated for *uniaxial* superparamagnets either (i) by assuming the energy of a particle in external fields is much less than the thermal energy kT so that the response may be evaluated via *perturbation theory* (e.g., Refs. 3 and 11) or (ii) by assuming that strong external fields are directed along the easy axis of the particle so that *axial symmetry* is preserved (e.g., Refs. 2 and 12). Thus the results are very restricted. In particular, the conventional assumption of axial symmetry is hardly realizable in nanoparticle systems under experimental conditions because the easy axes of the particles are randomly oriented in space. Furthermore, many interesting nonlinear phenomena (such as damping dependence of the response and interplay between precession and thermoactivation[3]) cannot be included because in axial symmetry no dynamical coupling between the longitudinal and transverse (or precessional) modes of motion exists. In contrast, discarding the above assumptions we shall now present an exact *nonperturbative* method for the nonlinear magnetization relaxation of superparamagnetic particles with an *arbitrary* anisotropy potential U in a strong ac driving field superimposed on a strong dc bias field of arbitrary orientations. Moreover, taking as example *uniaxial superparamagnets*, we shall demonstrate that for arbitrary orientations of ac and dc bias fields (so breaking the axial symmetry), the magnetization dynamics changes substantially leading to different nonlinear effects which cannot be treated via perturbation theory. We remark in passing that nonlinear effects in relaxation processes of superparamagnetic nanoparticles are closely related to those in nonlinear dielectric relaxation and the dynamic Kerr effect in molecular liquids and liquid crystals,[11,13] harmonic mixing in a cosine potential,[14] the nonlinear impedance of Josephson junctions,[15] ac-driven vortices in superconductors,[16] etc. Thus our approach can also be applied to nonlinear effects in these.

When the magnitude of the ac field $\mathbf{H}(t)$ is so large that the Zeeman energy of a particle is comparable to or higher than kT, one is faced with an intrinsically nonlinear problem which of course cannot be treated by perturbation theory and which we solve as follows. First we transform the stochastic Gilbert Eq. (1) to an infinite hierarchy of stochastic differential-recurrence relations which on averaging over their realizations using the properties of white noise yield differential-recurrence relations for the statistical moments $\langle Y_{l,m}\rangle(t)$ (the expectation values of the spherical harmonics $Y_{l,m}$), viz.,[9,17]

$$\tau_N \partial_t \langle Y_{l,m}\rangle(t) = \sum_{s,r} e_{l,m,l+r,m+s}(t)\langle Y_{l+r,m+s}\rangle(t), \qquad (2)$$

where $\tau_N = \tau_0(\alpha+\alpha^{-1})$, $\alpha = \gamma\eta M_s$ is a dimensionless damping constant, $\tau_0 = \beta M_S/(2\gamma)$ is the free-rotational diffusion time

of $\mathbf{M}(t)$, M_S is the saturation magnetization, $\beta=v/(kT)$, and v is the volume of the particle. Equation (2) was derived in Ref. 16 and we may now solve it exactly as follows.

By introducing column vectors $\mathbf{c}_n(t)$ $(n=1,2,3,\ldots)$ with $\mathbf{c}_0=\langle Y_{00}\rangle=1/\sqrt{4\pi}$, which are formed from the statistical moments $c_{l,m}(t)=\langle Y_{l,m}\rangle(t)$, Eq. (2) becomes the matrix recurrence equation

$$\tau_N\partial_t\mathbf{c}_n(t)=\mathbf{q}_n^-\mathbf{c}_{n-1}(t)+\mathbf{q}_n\mathbf{c}_n(t)+\mathbf{q}_n^+\mathbf{c}_{n+1}(t)+[\mathbf{p}_n^-\mathbf{c}_{n-1}(t)+\mathbf{p}_n\mathbf{c}_n(t)+\mathbf{p}_n^+\mathbf{c}_{n+1}(t)](e^{i\omega t}+e^{-i\omega t}), \tag{3}$$

where the supermatrices $\mathbf{q}_n,\mathbf{q}_n^\pm$ and $\mathbf{p}_n,\mathbf{p}_n^\pm$ are generated from the coefficients $e_{l,m,l+r,m+s}(t)$. We remark in passing that the explicit form of the vectors $\mathbf{c}_n(t)$ depends on the type of the free-energy density $V(\vartheta,\varphi)$; for uniaxial superparamagnets, $\mathbf{c}_n(t)$ are given by Eq. (7) below. Since we are solely concerned with the stationary ac response, which is independent of the initial conditions, we require the steady-state solution of Eq. (3) only. In the steady-state response, symmetry under time translation is retained under the discrete time transformation $t\to t+2\pi/\omega$. Thus we may seek all the $\mathbf{c}_n(t)$ in the form of the time Fourier series $\mathbf{c}_n(t)=\Sigma_{k=-\infty}^{\infty}\mathbf{c}_n^k(\omega)e^{ik\omega t}$. On substituting this series into Eq. (3), we have the recurrence relations for the Fourier amplitudes $\mathbf{c}_n^k(\omega)$, namely,

$$\mathbf{q}_n^k(k\omega)\mathbf{c}_n^k(\omega)+\mathbf{q}_n^+\mathbf{c}_{n+1}^k(\omega)+\mathbf{q}_n^-\mathbf{c}_{n-1}^k(\omega)+\mathbf{p}_n^-[\mathbf{c}_{n-1}^{k-1}(\omega)+\mathbf{c}_{n-1}^{k+1}(\omega)]+\mathbf{p}_n[\mathbf{c}_n^{k-1}(\omega)+\mathbf{c}_n^{k+1}(\omega)]+\mathbf{p}_n^+[\mathbf{c}_{n+1}^{k-1}(\omega)+\mathbf{c}_{n+1}^{k+1}(\omega)]=0, \tag{4}$$

where $\mathbf{q}_n(k\omega)=-ik\tau_N\omega\mathbf{I}+\mathbf{q}_n$ and $\mathbf{I}$ is the identity matrix. Now Eq. (4) can be transformed into the matrix recurrence relations

$$\mathbf{Q}_1\mathbf{C}_1+\mathbf{Q}_1^+\mathbf{C}_2=\mathbf{R},$$

$$\mathbf{Q}_n^-\mathbf{C}_{n-1}+\mathbf{Q}_n\mathbf{C}_n+\mathbf{Q}_n^+\mathbf{C}_{n+1}=\mathbf{0}\quad(n>1), \tag{5}$$

where the column vectors $\mathbf{R}$ and $\mathbf{C}_n$ and the tridiagonal supermatrices $\mathbf{Q}_n$ and $\mathbf{Q}_n^\pm$ are defined as

$$\mathbf{C}_n(\omega)=\begin{pmatrix}\vdots\\ \mathbf{c}_n^{-2}(\omega)\\ \mathbf{c}_n^{-1}(\omega)\\ \mathbf{c}_n^{0}(\omega)\\ \mathbf{c}_n^{1}(\omega)\\ \mathbf{c}_n^{2}(\omega)\\ \vdots\end{pmatrix},\quad \mathbf{R}=\frac{-1}{\sqrt{4\pi}}\begin{pmatrix}\vdots\\ \mathbf{0}\\ \mathbf{p}_1^-\\ \mathbf{q}_1^-\\ \mathbf{p}_1^-\\ \mathbf{0}\\ \vdots\end{pmatrix},$$

$$[\mathbf{Q}_n]_{l,m}=\delta_{l-1,m}\mathbf{p}_n+\delta_{l,m}\mathbf{q}_n(m\omega)+\delta_{l+1,m}\mathbf{p}_n,$$

$$[\mathbf{Q}_n^\pm]_{l,m}=\delta_{l-1,m}\mathbf{p}_n^\pm+\delta_{l,m}\mathbf{q}_n^\pm+\delta_{l+1,m}\mathbf{p}_n^\pm.$$

The exact solution of Eq. (5) for $\mathbf{C}_1$ can be now given using matrix continued fractions, viz.,

$$\mathbf{C}_1=\mathbf{S}_1\cdot\mathbf{R}, \tag{6}$$

where the matrix continued fraction $\mathbf{S}_1$ is defined by the recurrence equation

$$\mathbf{S}_n=-[\mathbf{Q}_n+\mathbf{Q}_n^+\mathbf{S}_{n+1}\mathbf{Q}_{n+1}^-]^{-1}.$$

The vector $\mathbf{C}_1$ contains all the Fourier amplitudes required for the nonlinear stationary response. We emphasize that so far our matrix continued fraction solution, Eq. (6), is valid for an arbitrary anisotropy potential U.

Next we shall apply the above general method to the particular case of uniaxial superparamagnets subjected to the ac and dc bias ac fields $\mathbf{H}_0+\mathbf{H}\cos\omega t$ applied in arbitrary directions, where the free energy can be written in dimensionless form as

$$\beta V=\sigma\sin^2\theta-\xi_0(\gamma_1\sin\vartheta\cos\varphi+\gamma_2\sin\vartheta\sin\varphi+\gamma_3\cos\vartheta)-\xi\cos\omega t(\gamma_1'\sin\vartheta\cos\varphi+\gamma_2'\sin\vartheta\sin\varphi+\gamma_3'\cos\vartheta).$$

Here $\gamma_1,\gamma_2,\gamma_3$ and $\gamma_1',\gamma_2',\gamma_3'$ are the direction cosines of the vectors $\mathbf{H}_0$ and $\mathbf{H}$, respectively, K is the anisotropy constant, $\sigma=\beta K$, $\xi_0=\beta H_0M_S$, and $\xi=\beta HM_S$. Now the vectors $\mathbf{c}_n(t)$ and the supermatrices $\mathbf{q}_n,\mathbf{q}_n^\pm$ and $\mathbf{p}_n,\mathbf{p}_n^\pm$ are given by

$$\mathbf{c}_n(t)=\begin{pmatrix}\langle Y_{2n,-2n}\rangle(t)\\ \vdots\\ \langle Y_{2n,2n}\rangle(t)\\ \langle Y_{2n-1,-2n+1}\rangle(t)\\ \vdots\\ \langle Y_{2n-1,2n-1}\rangle(t)\end{pmatrix},$$

$$\mathbf{p}_n^-=\begin{pmatrix}\mathbf{o}&\mathbf{o}\\ \mathbf{b}_{2n-1}&\mathbf{o}\end{pmatrix},\quad \mathbf{p}_n=\begin{pmatrix}\mathbf{a}_{2n}&\mathbf{b}_{2n}\\ \mathbf{d}_{2n-1}&\mathbf{a}_{2n-1}\end{pmatrix},$$

$$\mathbf{p}_n^+=\begin{pmatrix}\mathbf{o}&\mathbf{d}_{2n}\\ \mathbf{o}&\mathbf{o}\end{pmatrix},\quad \mathbf{q}_n^-=\begin{pmatrix}\mathbf{V}_{2n}&\mathbf{o}\\ \mathbf{W}_{2n-1}&\mathbf{V}_{2n-1}\end{pmatrix},$$

$$\mathbf{q}_n^+=\begin{pmatrix}\mathbf{Z}_{2n}&\mathbf{Y}_{2n}\\ \mathbf{o}&\mathbf{Z}_{2n-1}\end{pmatrix},\quad \mathbf{q}_n=\begin{pmatrix}\mathbf{X}_{2n}&\mathbf{W}_{2n}\\ \mathbf{Y}_{2n-1}&\mathbf{X}_{2n-1}\end{pmatrix}. \tag{7}$$

Here $\mathbf{o}$ and $\mathbf{0}$ are zero matrices and vectors of appropriate dimensions, respectively. The tridiagonal submatrices $\mathbf{a}_l$, $\mathbf{b}_l$, and $\mathbf{d}_l$ have the dimensions $(2l+1)\times(2l+1)$, $(2l+1)\times(2l+3)$, and $(2l+1)\times(2l-1)$, respectively. Their matrix elements are given by

$$(\mathbf{a}_l)_{n,m}=\delta_{n-1,m}a_{l,-l+m}^-+\delta_{n,m}a_{l,-l+m-1}+\delta_{n+1,m}a_{l,-l+m-2}^+,$$

$$(\mathbf{b}_l)_{n,m}=\delta_{n,m}b_{l,-l+m-1}^-+\delta_{n+1,m}b_{l,-l+m-2}+\delta_{n+2,m}b_{l,-l+m-3}^+,$$

$$(\mathbf{d}_l)_{n,m}=\delta_{n-2,m}d_{l,-l+m+1}^-+\delta_{n-1,m}d_{l,-l+m}+\delta_{n,m}d_{l,-l+m-1}^+,$$

where

$$a_{n,m}=-i\frac{m\xi\gamma_3'}{4\alpha},\quad b_{n,m}=-\frac{\xi\gamma_3'n}{4}\sqrt{\frac{(n+1)^2-m^2}{(2n+1)(2n+3)}},$$

$$a^{+}_{n,m} = -i\frac{\xi(\gamma_1' - i\gamma_2')}{8\alpha}\sqrt{(n+m+1)(n-m)},$$

$$b^{+}_{n,m} = \frac{\xi(\gamma_1' - i\gamma_2')n}{8}\sqrt{\frac{(n+m+1)(n+m+2)}{(2n+1)(2n+3)}},$$

$$d_{n,m} = \frac{\xi\gamma_3'(n+1)}{4}\sqrt{\frac{n^2-m^2}{(2n+1)(2n-1)}},$$

$$d^{+}_{n,m} = \frac{\xi(\gamma_1' - i\gamma_2')(n+1)}{8}\sqrt{\frac{(n-m)(n-m-1)}{(2n+1)(2n-1)}}$$

$a^{-}_{n,m}=-(a^{+}_{n,-m})^*$, $b^{-}_{n,m}=-(b^{+}_{n,-m})^*$, and $d^{-}_{n,m}=-(d^{+}_{n,-m})^*$. The matrices $\mathbf{q}_n, \mathbf{q}_n^{\pm}$ consist of the five submatrices $\mathbf{V}_l$, $\mathbf{W}_l$, $\mathbf{X}_l$, $\mathbf{Y}_l$, and $\mathbf{Z}_l$ (they also appear in the linear response and are defined explicitly, e.g., in Ref. 9, Chap. 9). Having determined the amplitudes $c^k_{l,m}(\omega)$ from Eq. (6), we can evaluate the magnetization $M_H(t)=vM_S\Sigma_{k=1}^{\infty}\mathrm{Re}[m^k_1(\omega)e^{ik\omega t}]$, where

$$m^k_1(\omega) = 4\sqrt{\frac{\pi}{3}}\left[\gamma_3' c^k_{10}(\omega) + \frac{(\gamma_1' + i\gamma_2')c^k_{1-1}(\omega) - (\gamma_1' - i\gamma_2')c^k_{11}(\omega)}{\sqrt{2}}\right]. \quad (8)$$

Here we shall assume from now on that the vectors $\mathbf{H}_0$ and $\mathbf{H}$ are parallel and they lie in the XZ plane of the laboratory coordinate system so that $\gamma_1=\gamma_1'=\sin\psi$, $\gamma_2=\gamma_2'=0$, and $\gamma_3=\gamma_3'=\cos\psi$, where ψ is the angle between $\mathbf{H}_0$ and the Z axis is taken as the easy axis of the particle. For nonparallel ac and dc fields, results will be presented elsewhere.

For a weak ac field, $\xi\to 0$, $\chi^1_1(\omega)=3m^1_1(\omega)/\xi$ defines the normalized linear dynamic susceptibility and our results agree in all respects with the benchmark linear-response solution.[18] The plots of the magnetic loss spectrum $-\mathrm{Im}[\chi^1_1(\omega)]$ vs $\omega\tau_N$ are shown in Fig. 1. Here the low-frequency behavior of $\chi^1_1(\omega)$ can be described by a *single* Lorentzian, viz.,

$$\frac{\chi^1_1(\omega)}{\chi^1_1(0)} \approx \frac{1-\delta}{1+i\omega\tau} + \delta, \quad (9)$$

where τ is the longest relaxation time in the absence of an ac external field and δ is a parameter (here τ is associated with the reversal time of the magnetization;[19] simple analytic equations for τ and δ are given in Refs. 9 and 20). Equation (9) is also plotted in Fig. 1. Now τ is related to the characteristic frequency $\omega_{\max}$, where $-\mathrm{Im}[\chi^1_1(\omega)]$ reaches a maximum, and/or the half-width $\Delta\omega$ of $\mathrm{Re}[\chi^1_1(\omega)]$ of the Lorentzian as

$$\tau \approx \omega^{-1}_{\max} \approx \Delta\omega^{-1}. \quad (10)$$

For zero dc bias field, $\xi_0=0$, τ is independent of the angle ψ while in a strong dc field, e.g., for $\xi_0=3$, τ substantially depends on ψ [Fig. 1(b)]. In addition, a far weaker second relaxation peak appears at high frequencies. This relaxation band is due to the "intrawell" modes which are virtually indistinguishable in the frequency spectrum appearing as a single high-frequency Lorentzian band. The third or ferromagnetic resonance (FMR) peak (due to excitation of transverse modes with frequencies close to the precession frequency ω_{pr} of the magnetization) appears only at low damping and strongly manifest itself at high frequencies. Moreover, for $\psi=0$, when the axial symmetry is restored, the FMR peak disappears [curves 1 in Fig. 1(a)] because the transverse modes no longer take part in the relaxation process so that this peak is a signature of the symmetry-breaking action of the applied field.

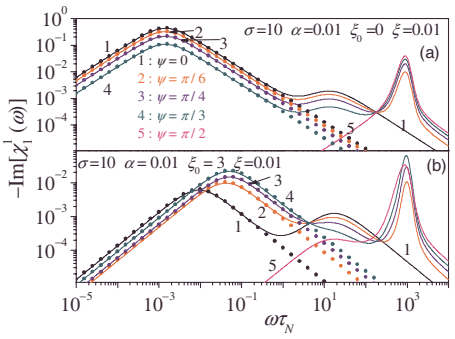

FIG. 1. (Color online) $-\mathrm{Im}[\chi^1_1(\omega)]$ vs $\omega\tau_N$ for various values of the angle ψ and (a) $\xi_0=0$ (no dc bias field) and (b) $\xi_0=3$ (strong dc bias field). Solid lines: matrix continued fraction solution; filled circles: Eq. (9) with τ calculated using the method of Ref. 20.

In strong ac fields, $\xi>1$, pronounced nonlinear effects occur (see Fig. 2). In particular, the low-frequency band of $-\mathrm{Im}[\chi^1_1(\omega)]$ can no longer be approximated by a single Lorentzian. Nevertheless, Eq. (10) may still be used in order to estimate an effective reversal time of the magnetization τ. (We remark that τ may also be evaluated from the spectra of the higher order harmonics[12] because the low-frequency parts of their spectra are *also* dominated by the magnetization reversal). The behavior of $\omega_{\max}$ (and, hence, τ) as functions of the ac field amplitude depends on whether or not a dc field is applied. For a strong dc bias, $\xi_0>1$, the low-frequency peak shifts to lower frequencies reaching a maximum at $\xi\sim\xi_0$ thereafter decreasing exponentially with increasing ξ. In other words, as the dc field increases, the reversal time of the magnetization *initially increases* and then having attained its maximum at some critical value $\xi\sim\xi_0$ decreases exponentially (see Fig. 2). For weak dc bias $0\le\xi_0<1$, the low-frequency peak shifts monotonically to higher frequencies. As seen in Fig. 2(a), as the ac field am-

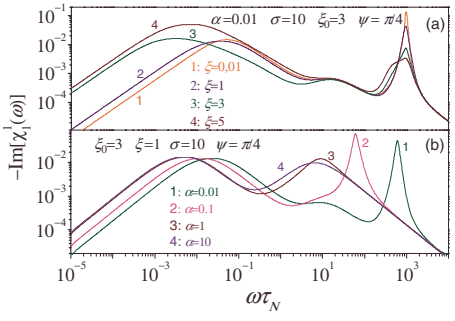

FIG. 2. (Color online) $-\mathrm{Im}[\chi^1_1(\omega)]$ vs $\omega\tau_N$ (a) for various values of the ac field parameter ξ and (b) for various values of damping α.

plitude increases, the FMR peak decreases and also broadens showing pronounced nonlinear saturation effects characteristic for a soft spring. This effect is very similar to that already known in atomic and molecular spectroscopy.[21] Thus we see that the intrinsic damping dependence of the ac nonlinear response for the oblique field configuration [see Fig. 2(b)] serves as a signature of the coupling between the longitudinal and precessional modes of the magnetization. Hence, it should be possible to determine the damping coefficient α from measurements of nonlinear response characteristics,[2] e.g., by fitting the theory to the experimental dependence of $\chi_1^1(\omega)$ on the angle ψ and the ac and dc bias field strengths, so that the sole fitting parameter is α, which can be determined at different temperatures T, yielding its temperature dependence. This is important because a knowledge of α and its T dependence allows for the separation of the various relaxation mechanisms.[9]

We now estimate the parameter range, where the nonlinear effects appear. For cobalt nanoparticles with mean diameter $a \sim 10$ nm and saturation magnetization $M_S \sim 1460$ G, the field parameter ξ for $T \sim 30$ K is on the order of unity for $H \sim 6\ kT/(\pi a^3 M_S) \sim 5$ Oe. Furthermore, an ac field of this order of magnitude is easily attained in measurements of the nonlinear response of magnetic nanoparticles; e.g., Bitoh *et al.*[22] have measured the nonlinear susceptibility of cobalt nanoparticles in the temperature range 4.2–280 K using an ac magnetic field $\sim 5-30$ Oe. As far the characteristic time τ_N is concerned, for $\gamma \approx 2 \times 10^7$ rad/Oe s and $\alpha \sim 0.1$, we have at room temperature $\tau_N \sim 10^{-8}$ s.

To conclude we have developed a nonperturbative approach in terms of matrix continued fractions for the nonlinear relaxation of a uniaxial superparamagnetic particle for *arbitrary strengths* and *orientations* of the dc bias and ac driving fields. We have shown that the nonlinear ac stationary response to a strong ac field applied at an angle to the easy axis of the particle (so that the axial symmetry is broken) is very sensitive to both the ac field orientation and amplitude owing to the coupling induced by the symmetry breaking driving field between the precession of the magnetization and its thermally activate reversal over the saddle point. In particular, the pronounced damping and ac field dependence of the nonlinear response $\chi_1^1(\omega)$ can be used to determine the damping coefficient α just as for higher harmonic responses.[3] We emphasize that these nonlinear effects in $\chi_1^1(\omega)$ cannot be treated via perturbation theory. Our calculations, since they are valid for ac fields of arbitrary strengths and orientations, allow one both to predict and interpret quantitatively nonlinear phenomena in magnetic nanoparticles such as nonlinear magnetic susceptibility, nonlinear stochastic resonance and dynamic hysteresis, nonlinear ac field effects on the switching field curves, etc., where perturbation theory and the assumption that axial symmetry is preserved are no longer valid (these results will be published elsewhere). For practical applications (e.g., in magnetic nanoparticle hyperthermia[1]), in order to account for the polydispersity of the particles of a real sample and the fact the easy axes of particles are randomly distributed in space, one must also average the nonlinear response functions $m_1^k(\omega)$ over appropriate distribution functions[2] (averaging of $m_1^k(\omega)$ over particle volumes and orientations can be readily accomplished numerically using Gaussian quadraturs[23]). Here, only uniaxial superparamagnetic particles have been treated. Particles with nonaxially symmetric anisotropies (cubic, biaxial, etc.) can be considered in like manner. Finally, our results can be adapted to other nonlinear phenomena such as nonlinear dielectric relaxation and the dynamic Kerr effect in molecular liquids and liquid crystals.[11,13]

The support of the work by the Agence Nationale de la Recherche, France (Project No. ANR-08-P147-36) and by EGIDE, France (Program ECO-NET, Project No. 21394NH) is gratefully acknowledged.

[1] Q. A. Pankhurst *et al.*, J. Phys. D **42**, 224001 (2009).
[2] Yu. L. Raikher and V. I. Stepanov, Adv. Chem. Phys. **129**, 419 (2004).
[3] J. L. García-Palacios and P. Svedlindh, Phys. Rev. Lett. **85**, 3724 (2000).
[4] L. Gammaitoni *et al.*, Rev. Mod. Phys. **70**, 223 (1998).
[5] Yu. L. Raikher *et al.*, Phys. Rev. E **56**, 6400 (1997).
[6] Yu. L. Raikher and V. I. Stepanov, Phys. Rev. Lett. **86**, 1923 (2001); Yu. L. Raikher *et al.*, J. Magn. Magn. Mater. **258-259**, 369 (2003).
[7] I. Klik and Y. D. Yao, J. Appl. Phys. **89**, 7457 (2001); Yu. L. Raikher and V. I. Stepanov, J. Magn. Magn. Mater. **320**, 2692 (2008).
[8] P. M. Déjardin *et al.*, J. Appl. Phys. **107**, 073914 (2010).
[9] W. T. Coffey *et al.*, *The Langevin Equation*, 2nd ed. (World Scientific, Singapore, 2004).
[10] W. F. Brown Jr., Phys. Rev. **130**, 1677 (1963); IEEE Trans. Magn. **15**, 1196 (1979).
[11] W. T. Coffey *et al.*, Phys. Rev. E **71**, 062102 (2005).
[12] P. M. Déjardin and Yu. P. Kalmykov, J. Appl. Phys. **106**, 123908 (2009); J. Magn. Magn. Mater. **322**, 3112 (2010).
[13] H. Watanabe and A. Morita, Adv. Chem. Phys. **56**, 255 (1984); J. L. Dejardin *et al.*, *ibid.* **117**, 275 (2001).
[14] H. J. Breymayer *et al.*, Appl. Phys. B: Lasers Opt. **28**, 335 (1982).
[15] W. T. Coffey *et al.*, Phys. Rev. B **62**, 3480 (2000); Phys. Rev. E **61**, 4599 (2000).
[16] V. A. Shklovskij and O. V. Dobrovolskiy, Phys. Rev. B **78**, 104526 (2008).
[17] Yu. P. Kalmykov and S. V. Titov, Phys. Rev. Lett. **82**, 2967 (1999).
[18] Yu. P. Kalmykov and S. V. Titov, Fiz. Tverd. Tela (St. Petersburg) **40**, 1642 (1998) [Phys. Solid State **40**, 1492 (1998)]; W. T. Coffey *et al.*, Phys. Rev. B **64**, 012411 (2001).
[19] W. T. Coffey *et al.*, Phys. Rev. Lett. **80**, 5655 (1998).
[20] Yu. P. Kalmykov, J. Appl. Phys. **96**, 1138 (2004).
[21] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).
[22] T. Bitoh *et al.*, J. Phys. Soc. Jpn. **64**, 1311 (1995); J. Magn. Magn. Mater. **154**, 59 (1996).
[23] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. Stegun (Dover, New York, 1972).