Nonlinear response of superparamagnets with finite damping: An analytical approach

J. L. García-Palacios
*Dep. de Física de la Materia Condensada e Instituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, E-50009 Zaragoza, Spain
and Department of Materials Science, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden*

D. A. Garanin
Institut für Physik, Johannes-Gutenberg-Universität, D-55099 Mainz, Germany
(Received 31 October 2003; revised manuscript received 19 April 2004; published 23 August 2004)

The strongly damping-dependent nonlinear dynamical response of classical superparamagnets is investigated by means of an analytical approach. Using rigorous balance equations for the spin occupation numbers a simple approximate expression is derived for the nonlinear susceptibility. The results are in good agreement with those obtained from the exact (continued-fraction) solution of the Fokker-Planck equation. The formula obtained could be of assistance in the modeling of the experimental data and the determination of the damping coefficient in superparamagnets.

DOI: 10.1103/PhysRevB.70.064415 PACS number(s): 75.50.Tt

I. INTRODUCTION

Superparamagnets are nanoscale solids or clusters with a large net spin ($S \sim 10^1 - 10^4$). Due to the coupling to the environmental degrees of freedom (lattice vibrations, electromagnetic fields, nuclear spins, conduction electrons, etc.), the spin is subjected to thermal fluctuations and may undergo a Brownian-type rotation, surmounting the potential barriers created by the magnetic anisotropy. This relaxation mechanism was proposed by Néel in the late 1940's (Ref. 1) and subsequently reexamined by Brown[2] by means of the theory of stochastic processes (see also Ref. 3), establishing the basis of the modern study of these systems.

Classical spins with nonaxially symmetric Hamiltonians can exhibit[4] a large dependence of the thermoactivation escape rate Γ on the Landau-Lifshitz damping coefficient λ in the medium-to-weak damping regime. λ measures the relative importance of the relaxation and the precession in the dynamics. Experiments on individual magnetic nanoparticles,[5] analyzed with accurate expressions for the relaxation rate, gave damping coefficients in that regime $\lambda \approx 0.05 - 0.5$.[6]

Uniaxial spins are supposed not to show important effects of the damping except in high-frequency conditions (such as FMR experiments). Somewhat unexpectedly, noninteracting spins with uniaxial anisotropy, but subjected to alternate forcing, exhibit a large nonlinear response very sensitive to λ,[7] which has no analog in the low-frequency linear response. This effect was interpreted in terms of the coupling, via the driving field, of the precession of the spin and its thermoactivation over the anisotropy barrier. On the other hand, using micromagnetic Langevin simulations,[8] Berkov and Gorn[9] found that uniaxial spins coupled via dipole-dipole interaction also exhibit damping effects such as enhanced shifts of the blocking temperature and nonmonotonic behavior of the linear susceptibility peaks with the coupling strength. In Ref. 10 it was shown that these effects can be interpreted on the basis of the expression derived for Γ in the mentioned Ref. 4, which is valid for weak transversal fields but arbitrary damping. Plugging heuristically into that relaxation rate the average dipolar fields obtained with thermodynamic perturbation theory,[11] the dynamical effects of the damping on the linear response of dipole-dipole coupled systems could be qualitatively reproduced.[10]

In this article we use a similar analytical approach to study the low-frequency nonlinear dynamical response of noninteracting classical superparamagnets. We derive an approximate expression for the nonlinear susceptibility which is in good agreement with the exact (continued-fraction) solution of the Fokker-Planck equation. The formula obtained is quite simple and may be used to model experimental data of the nonlinear response. Exploiting its nontrivial damping dependence, the equation could assist in obtaining the damping coefficient in these systems. The determination of the intrinsic dependences of this parameter (on temperature, pressure, etc.) could shed some light on the microscopic mechanisms of spin-environment coupling in superparamagnets.

II. BROWN AND KUBO-HASHITSUME MODEL

Let us briefly consider the dynamics of a (sub)system accounting for its interaction with the surrounding "medium." This interaction, after the elimination of the environmental degrees of freedom, can usually be separated into a time-dependent modulation of the system by the proper modes of the environment (fluctuating term), and the back reaction on the system of its action on the surrounding medium (relaxation or damping term).

This approach was particularized phenomenologically by Brown[2] and Kubo and Hashitsume[3] to classical spins, by introducing the stochastic partner of the Landau-Lifshitz equation. The associated Fokker-Planck equation governing the time evolution of the probability density of spin orientations $P(\vec{s})$ can be written as[12]

$$2\tau_{\mathrm{D}}\partial_t P = i\vec{\mathcal{J}}\cdot\left[\frac{1}{\lambda}\vec{B}_{\mathrm{e}} - (\vec{s}\wedge\vec{B}_{\mathrm{e}}) + i\vec{\mathcal{J}}\right]P. \tag{1}$$

Here $\vec{\mathcal{J}}=-i\vec{s}\wedge(\partial/\partial\vec{s})$ is the generator of infinitesimal rotations and $\vec{B}_{\mathrm{e}}=-\beta(\partial\mathcal{H}/\partial\vec{s})$ is an effective field. The Landau-Lifshitz relaxation parameter λ (dimensionless) measures the relative importance of the damping and precession terms. Finally, τ_{D} is the relaxation time of isotropic spins (the counterpart of the Debye time in dielectrics)

$$\tau_{\mathrm{D}} = \frac{1}{\lambda}\frac{m}{2\gamma k_{\mathrm{B}}T}, \tag{2}$$

where m is the spin magnitude and γ the gyromagnetic ratio. For generalizations of the Brown and Kubo-Hashitsume model, see, for instance, Refs. 13 and 14.

III. GENERIC BALANCE EQUATIONS

Before proceeding from the Fokker-Planck equation to study the nonlinear dynamics, let us consider some generic expressions for systems describable by a set of kinetic balance equations for some occupation numbers N_+ and N_-

$$\dot{N}_+ = -A^+N_+ + A^-N_-,$$

$$\dot{N}_- = A^+N_+ - A^-N_-. \tag{3}$$

Here the $A^{\pm}$ are some transition amplitudes which depend on the external forcing or control parameter ξ. The occupation numbers satisfy the "constrain" $N_+ + N_- = 1$, which indicates the conservation of the number of representative points ($\dot{N}_+ = -\dot{N}_-$). The response of the system is characterized by the difference in populations $\Delta N = N_+ - N_-$, which obeys

$$\frac{d}{dt}\Delta N = -(A^+ + A^-)\Delta N - (A^+ - A^-). \tag{4}$$

Thus, $(A^+ + A^-)$ plays the role of a relaxation rate while the inhomogeneous term $(A^+ - A^-)$ is to be related to the external forcing.

To get the linear and first nonlinear susceptibilities (or corrections to the linear susceptibility due to a weak static forcing) we expand $A^{\pm}$ in a series of powers of ξ to the third order

$$A^{\pm} \simeq A_0^{\pm} + \xi A_1^{\pm} + \xi^2 A_2^{\pm} + \xi^3 A_3^{\pm}. \tag{5}$$

Let us consider in detail the case of harmonic forcing $\Delta\xi(t) = \frac{1}{2}\Delta\xi(e^{+i\omega t} + e^{-i\omega t})$. First, we replace ξ by $\Delta\xi(t)$ in the above expansion. Next, we plug into the dynamical equation for ΔN both the resulting $A^{\pm}(t)$ and the Fourier expansion of the population difference, namely,

$$\Delta N \simeq \Delta N_0 + \left(\frac{\Delta\xi}{2}\right)\Delta N_1\, e^{i\omega t} + \left(\frac{\Delta\xi}{2}\right)^2\Delta N_2\, e^{2i\omega t} + \left(\frac{\Delta\xi}{2}\right)^3\Delta N_3\, e^{3i\omega t} + \text{c.c.} \tag{6}$$

Equating the coefficients with the same oscillating factor $\exp(ki\omega t)$ one gets the ΔN_k, which are directly related with the susceptibilities. We keep at each order k only the leading term in $\Delta\xi$ (if required, the next order terms can be obtained along the same lines).

Let us assume that in the absence of perturbation the two states (wells) are equivalent (symmetric). Taking into account that $(A^+ + A^-)$ is a relaxation rate (and hence even in ξ) and that $(A^+ - A^-)$ is related to the forcing (odd in ξ), the response will depend only on the sum of the $A_k^+ + A_k^-$ for even k and the difference $A_k^+ - A_k^-$ for odd k [see Eq. (5)]. Taking this into account, the amplitudes of the response read ($\Delta N_0 = 0$ and $\Delta N_2 = 0$)

$$\Delta N_1 = -\frac{A_1^+ - A_1^-}{\Gamma_0 + i\omega}, \tag{7}$$

$$\Delta N_3 = -\frac{A_3^+ - A_3^-}{\Gamma_0 + 3i\omega} + \frac{(A_1^+ - A_1^-)(A_2^+ + A_2^-)}{(\Gamma_0 + i\omega)(\Gamma_0 + 3i\omega)}, \tag{8}$$

where we have introduced the relaxation rate in the absence of forcing

$$\Gamma_0 = A_0^+ + A_0^-. \tag{9}$$

These results are quite generic. In particular cases the $A_k^{\pm}$ will be constructed from the specific details of the model.

IV. BALANCE EQUATIONS: SPIN DYNAMICS

For a spin with the simplest uniaxial anisotropy in a field (chosen by convenience to lay in the XZ plane), the Hamiltonian can be written as ($\vec{s}=\vec{m}/m$)

$$-\beta\mathcal{H} = \sigma s_z^2 + \xi_{\parallel}s_z + \xi_{\perp}s_x. \tag{10}$$

The anisotropy term has two minima at $s_z = \pm 1$ (the "poles") with a barrier between them at $s_z = 0$ (the "equator"). The spin-Hamiltonian parameters are introduced in temperature units $\sigma = D/k_{\mathrm{B}}T$ is the anisotropy barrier while $\xi_{\parallel}$ and $\xi_{\perp}$ are the longitudinal and transverse components of the field $\xi = mB/k_{\mathrm{B}}T$, with respect to the anisotropy axis.

A. Balance equations

Garanin *et al.*[4] rigorously derived from the Fokker-Planck equation a set of balance equations for the occupation numbers in the upper $s_z > 0$ well (our N_+) and the lower $s_z < 0$ well (N_-), namely,

$$\dot{N}_+ = \Gamma(N_+^{\mathrm{eq}}N_- - N_-^{\mathrm{eq}}N_+),$$

$$\dot{N}_- = -\Gamma(N_+^{\mathrm{eq}}N_- - N_-^{\mathrm{eq}}N_+). \tag{11}$$

Here $N_{\pm}^{\mathrm{eq}} = \mathcal{Z}_{\pm}/\mathcal{Z}$ are the equilibrium occupation numbers with $\mathcal{Z}_{\pm}$ the partition function restricted to the upper and lower wells, respectively. On comparing with the generic Eq. (3), we find for the transition amplitudes (note the sign reversal)

$$A^{\pm} = \Gamma N_{\mp}^{\mathrm{eq}}. \tag{12}$$

The relaxation rate Γ is given by[4]

$$\Gamma = \left(\frac{1}{\mathcal{Z}_+} + \frac{1}{\mathcal{Z}_-}\right)\frac{k_B T}{m/\gamma}\int_0^{2\pi} d\varphi\, e^{-\beta\mathcal{H}}\left[\frac{\partial\zeta}{\partial\varphi} + \lambda(1-s_z^2)\frac{\partial\zeta}{\partial s_z}\right], \tag{13}$$

where s_z and φ (the azimuthal angle) are the canonical variables of the spin. The function $\zeta(s_z,\varphi)$ is determined by the quasistationary solution of the Fokker-Planck equation

$$0 = \frac{\partial\mathcal{H}}{\partial\varphi}\frac{\partial\zeta}{\partial s_z} - \frac{\partial\mathcal{H}}{\partial s_z}\frac{\partial\zeta}{\partial\varphi} + \lambda\left[\left(-\frac{\partial\mathcal{H}}{\partial s_z} + k_B T\frac{\partial}{\partial s_z}\right)(1-s_z^2)\frac{\partial\zeta}{\partial s_z} + \frac{1}{1-s_z^2}\left(-\frac{\partial\mathcal{H}}{\partial\varphi} + k_B T\frac{\partial}{\partial\varphi}\right)\frac{\partial\zeta}{\partial\varphi}\right],$$

subjected to the boundary conditions $\zeta=1$ and $\zeta=0$ at the bottom of the lower and upper wells, respectively.

B. The transition amplitudes $A^{\pm}$ at low fields

In order to get the field expansion of the transition amplitudes $A^{\pm}=\Gamma N_{\mp}^{\mathrm{eq}}$, we need the corresponding expansions of the equilibrium occupation numbers and the relaxation rate.

1. The low-field equilibrium occupation numbers

The partition function corresponding to the Hamiltonian (10) can be written as

$$\mathcal{Z} = \int_{-1}^{1} ds_z \int_0^{2\pi}\frac{d\varphi}{2\pi}\exp(-\beta\mathcal{H}). \tag{14}$$

The one-well partition functions $\mathcal{Z}_{\pm}$ correspond to integrate s_z over $[0,1]$ and $[-1,0]$, respectively. Writing $s_x=\sqrt{1-s_z^2}\cos\varphi$ and following Shcherbakova[15] in doing first the integrals over φ, we get the unified expression

$$Z_{\pm} = \int_0^1 ds_z\, \exp(\sigma s_z^2 \pm \xi_{\parallel}s_z)I_0(\xi_{\perp}\sqrt{1-s_z^2}), \tag{15}$$

where we have made the change of variable $s_z\to -s_z$ in $\mathcal{Z}_-$ and I_0 is the modified Bessel function of the first kind of order 0 (Ref. 16, Sec. 11.5). Thus, $\mathcal{Z}_{\pm}$ can be written in terms of an integral over s_z only [compare Eq. (11) in Ref. 17].

Calling $a=\pm\xi_{\parallel}s_z$ and $b=\xi_{\perp}\sqrt{1-s_z^2}$ and using the expansion (to third order) $I_0(b)\simeq 1+\frac{1}{4}b^2$, we obtain for the field-dependent part of the integrand of $\mathcal{Z}_{\pm}$

$$e^a I_0(b) \simeq 1 + a + \frac{1}{2}a^2 + \frac{1}{4}b^2 + \frac{1}{6}a^3 + \frac{1}{4}a\, b^2. \tag{16}$$

Now we introduce the zero-field averages in one well

$$\langle s_z^l\rangle_w = \frac{\int_0^1 ds_z\, s_z^l e^{\sigma s_z^2}}{\int_0^1 ds_z\, e^{\sigma s_z^2}}, \tag{17}$$

where the denominator is proportional to the zero-field partition function $\mathcal{Z}_0=\int_{-1}^{1}ds_z\, e^{\sigma s_z^2}$. Introducing the expansion of $e^a I_0(b)$ in Eq. (15) we get the field expansions of $\mathcal{Z}_{\pm}$ and, by adding them, that of $\mathcal{Z}$ itself. Using the binomial formula to get the corresponding expansion of $1/\mathcal{Z}$, and multiplying this by those of $\mathcal{Z}_{\pm}$, we finally obtain the equilibrium occupation numbers $N_{\pm}^{\mathrm{eq}}=\mathcal{Z}_{\pm}/\mathcal{Z}$. These can be written as (note that $N_+^{\mathrm{eq}}+N_-^{\mathrm{eq}}=1$)

$$N_{\pm}^{\mathrm{eq}} = \frac{1}{2}(1 \pm z_1\xi_{\parallel} \pm z_3\xi_{\parallel}^3 \pm z_{1,2}\xi_{\parallel}\xi_{\perp}^2), \tag{18}$$

with the coefficients $z_{j,k}$ given by

$$z_1 = \langle s_z\rangle_w, \tag{19}$$

$$z_3 = \frac{1}{6}(\langle s_z^3\rangle_w - 3\langle s_z\rangle_w\langle s_z^2\rangle_w), \tag{20}$$

$$z_{1,2} = -\frac{1}{4}(\langle s_z^3\rangle_w - \langle s_z\rangle_w\langle s_z^2\rangle_w). \tag{21}$$

In the coefficients $z_{j,k}$ the first index is the power of $\xi_{\parallel}$ and the second (omitted when zero) the power of $\xi_{\perp}$. Note that the expressions for $N_{\pm}^{\mathrm{eq}}$ are valid for an arbitrary uniaxial potential.

2. The low-field relaxation rate

As the spins have inversion symmetry in the absence of the field, the total relaxation rate should be an even function of the field (Γ accounts for jumps over the energy barrier in both directions). For spins with uniaxial anisotropy we can write[10]

$$\Gamma \simeq \Gamma_0(1 + g_{\parallel}\xi_{\parallel}^2 + g_{\perp}\xi_{\perp}^2), \tag{22}$$

where Γ_0 is the zero-field relaxation rate and the expansion is valid to third order. The vanishing of the term $\propto\xi_{\parallel}\xi_{\perp}$ follows from the invariance of the relaxation rate upon field reflection through the barrier plane in uniaxial spins.

3. Generic expression for the transition amplitudes

Plugging the expansions (18) and (22) in the expression for the relaxation amplitudes $A^{\pm}=\Gamma N_{\mp}^{\mathrm{eq}}$, we arrive at

$$\frac{2}{\Gamma_0}A^{\mp} = 1 \pm (z_1 b_{\parallel})\xi + (g_{\parallel}b_{\parallel}^2 + g_{\perp}b_{\perp}^2)\xi^2 \pm [(z_3 + z_1 g_{\parallel})b_{\parallel}^3 + (z_{1,2} + z_1 g_{\perp})b_{\parallel}b_{\perp}^2]\xi^3, \tag{23}$$

where we have introduced the direction cosines of the field

$$b_{\parallel} = \xi_{\parallel}/\xi, \quad b_{\perp} = \xi_{\perp}/\xi.$$

Let us write the components $A_k^+ \pm A_k^-$ that enter the equations for the response [Eqs. (7) and (8)]. Note first that the obtained result fulfills the consequences of the well-symmetry mentioned above $A_0^+-A_0^-=0$ and $A_2^+-A_2^-=0$, along with $A_1^+ + A_1^-=0$ and $A_3^+ + A_3^-=0$. The combinations entering in the response are given by

$$\tilde{A}_0^+ + \tilde{A}_0^- = 1,$$

$$-(\tilde{A}_1^+ - \tilde{A}_1^-) = z_1 b_{\parallel},$$

$$\tilde{A}_2^+ + \tilde{A}_2^- = g_\parallel b_\parallel^2 + g_\perp b_\perp^2,$$

$$-(\tilde{A}_3^+ - \tilde{A}_3^-) = (z_3 + z_1 g_\parallel) b_\parallel^3 + (z_{1,2} + z_1 g_\perp) b_\parallel b_\perp^2,$$

where we have introduced the notation $\tilde{A} = A/\Gamma_0$.

V. EXPRESSIONS FOR THE DYNAMICAL SUSCEPTIBILITIES

A. Generic expressions

Let us divide numerator and denominator of the ΔN_k by Γ_0 and introduce the relaxation time

$$\tau = \Gamma_0^{-1}. \tag{24}$$

Then, Eqs. (7) and (8) appear with $\tilde{A}$'s $(=A/\Gamma_0)$ in the numerator and factors $1+ki\omega\tau$ in the denominator. The response is the projection of the average spin onto the field direction. This projection is obtained by multiplying the difference in the populations of both wells ΔN by $b_\parallel$ and the spin magnitude m.

In order to get the susceptibilities, recall that we used the field in temperature units, $\xi = mB/k_B T$, which yields factors $(m/k_B T)^k$. Thus, $\chi^{(k)} = (m/k_B T)^k \Delta N_k \times (m b_\parallel)$, and the linear susceptibility reads

$$\chi^{(1)} = \frac{m^2\, b_\parallel^2}{k_B T} \frac{z_1}{1 + i\omega\tau}. \tag{25}$$

For the first nonlinear susceptibility we obtain

$$\chi^{(3)} = \frac{m^4\, b_\parallel^4}{(k_B T)^3} \frac{z_3 + (z_3 + z_1 g_\parallel) i\omega\tau}{(1 + i\omega\tau)(1 + 3i\omega\tau)} + \frac{m^4\, b_\parallel^2 b_\perp^2}{(k_B T)^3} \frac{z_{1,2} + (z_{1,2} + z_1 g_\perp) i\omega\tau}{(1 + i\omega\tau)(1 + 3i\omega\tau)}, \tag{26}$$

where we have grouped terms with the same powers of $b_\parallel^j b_\perp^k$, so that the angular dependence (tensor structure) is better recognized.

Note that the expressions for the response are quite generic and depend only on the coefficients of the expansion of the equilibrium occupation numbers and the relaxation rate. Specific formulas will be obtained depending on the features of the uniaxial potential and the approximations done in calculating the coefficients $z_{j,k}$ and $g_{\parallel,\perp}$.

B. The case of low temperatures

Let us now specialize the above formulas to the case of low temperatures, where the superparamagnetic blocking takes place for long measurement times (or equivalently low frequencies, as those of ordinary magnetic experiments).

The coefficients $z_{j,k}$ are determined by the one-well averages of low-order powers of s_z [Eqs. (19)–(21)]. For anisotropy energy $\propto s_z^2$, these can be obtained along the lines of the calculation of Ref. 18 (Appendix A). Thus, using the asymptotic expansion of the confluent hypergeometric (Kummer) functions,[16] one finds the following low-T expansion:

$$\langle s_z^l \rangle_w \simeq 1 - \frac{l}{2\sigma} + \frac{l(l-3)}{4\sigma^2}, \tag{27}$$

where $\sigma = D/k_B T$. With this result, we immediately obtain the coefficients of the field-expansion of the equilibrium occupation numbers

$$z_1 = 1 - \frac{1}{2\sigma} - \frac{1}{2\sigma^2}, \tag{28}$$

$$z_3 = -\frac{1}{3} + \frac{1}{2\sigma} + \frac{1}{4\sigma^2}, \tag{29}$$

$$z_{1,2} = -\frac{1}{8\sigma^2}. \tag{30}$$

For the relaxation rates we shall only obtain the leading order term in $1/\sigma$; for consistency, the above $z_{j,k}$ will only be used up to such order (we shall return to this point below).

To get the coefficients $g_\parallel$ and $g_\perp$ appearing on the field expansion of the relaxation rate [Eq. (22)], one can choose special configurations in which they are known (strictly longitudinal and transversal fields).[10] Expanding the formula for Γ in the presence of a longitudinal field $\xi_\parallel$ (Refs. 2 and 19) one finds

$$\Gamma(\xi_\parallel, \xi_\perp = 0) \simeq \Gamma_0\left(1 + \frac{1}{2}\xi_\parallel^2\right), \quad \Gamma_0 = \frac{1}{\tau_D}\frac{2}{\sqrt{\pi}}\sigma^{3/2}e^{-\sigma},$$

where Γ_0 is Brown's zero-field result for the relaxation rate. Comparison with the general expansion (22) gives the longitudinal coefficient $g_\parallel = 1/2$. Note that in a longitudinal field the damping parameter λ only enters through τ_D [Eq. (2)] and hence λ only matters to establish a global time scale. In other words, results for different damping parameters presented in units of τ_D show complete dynamical scaling, and in this sense the λ dependence is said to be trivial.

Nontrivial effects of the damping arise in an oblique field. Nevertheless, there is no general expression for the relaxation time in the presence of transverse fields. In Ref. 4, however, a low-temperature formula valid for weak transversal fields was derived, which is perfectly suited for the purpose of determining $g_\perp$, namely,

$$\Gamma(\xi_\parallel = 0, \xi_\perp) \simeq \Gamma_0\left[1 + \frac{1}{4}F(\alpha)\xi_\perp^2\right], \quad \alpha = \lambda\ \sigma^{1/2}. \tag{31}$$

The function $F(\alpha)$ takes into account, without further approximations, the effects of the damping and is given in terms of the incomplete gamma function $\gamma(a;z) = \int_0^z dt\ t^{a-1}e^{-t}$ by

$$F(\alpha) = 1 + 2(2\alpha^2 e)^{1/(2\alpha^2)}\ \gamma\left(1 + \frac{1}{2\alpha^2}; \frac{1}{2\alpha^2}\right). \tag{32}$$

Comparing with the expansion (22) one gets the transversal coefficient $g_\perp = F/4$.

Summarizing, the low-temperature coefficients in the field expansion of the relaxation rate [Eq. (22)] are given by

$$g_{\parallel} = \frac{1}{2}, \quad g_{\perp} = \frac{1}{4}F(\alpha). \tag{33}$$

The function F decreases towards 1 for strong damping [see Eq. (41) below]. Then, $g_{\parallel}$ and $g_{\perp}$ are of the same order of magnitude. However, F grows as $1/\lambda$ for weak damping, where the relaxation time turns to be very sensitive to the damping (or to transversal fields).

Before giving the corresponding expressions for the susceptibilities, we write the complete formulas for the transition amplitudes $A^{\pm} = \Gamma N_{\mp}^{\mathrm{eq}}$ at low temperatures (including only the leading order in the $1/\sigma$ expansions)

$$A^{\mp} = \frac{1}{2}\Gamma_0\left[1 \pm b_{\parallel}\xi + \frac{1}{2}\left(b_{\parallel}^2 + \frac{1}{2}Fb_{\perp}^2\right)\xi^2 \pm \frac{1}{6}b_{\parallel}\left(b_{\parallel}^2 + \frac{3}{2}Fb_{\perp}^2\right)\xi^3\right]. \tag{34}$$

This expression can also be of use in other problems like the obtaining of the linear susceptibility in weak bias fields.

The linear susceptibility arising from Eq. (25) simply reads

$$\chi^{(1)} = \frac{m^2\, b_{\parallel}^2}{k_{\mathrm{B}}T}\frac{1}{1 + i\omega\tau}, \tag{35}$$

while the nonlinear susceptibility obtained from Eq. (26) is given by

$$\chi^{(3)} = -\frac{1}{3}\frac{m^4\, b_{\parallel}^4}{(k_{\mathrm{B}}T)^3}\frac{1 - \frac{1}{2}i\omega\tau}{(1 + i\omega\tau)(1 + 3i\omega\tau)} + \frac{1}{4}\frac{m^4\, b_{\parallel}^2 b_{\perp}^2}{(k_{\mathrm{B}}T)^3}F(\alpha)\frac{i\omega\tau}{(1 + i\omega\tau)(1 + 3i\omega\tau)}. \tag{36}$$

This is one of the main results of this article. As special cases we consider the response to a strict longitudinal probing field ($b_{\parallel}=1$ and $b_{\perp}=0$)

$$\chi_{\parallel}^{(3)} = -\frac{1}{3}\frac{m^4}{(k_{\mathrm{B}}T)^3}\frac{1 - \frac{1}{2}i\omega\tau}{(1 + i\omega\tau)(1 + 3i\omega\tau)}, \tag{37}$$

and the response of an ensemble of identical spins with axes distributed at random ($\overline{b_{\parallel}^4}=1/5$ and $\overline{b_{\parallel}^2 b_{\perp}^2}=2/15$)

$$\overline{\chi^{(3)}} = -\frac{1}{15}\frac{m^4}{(k_{\mathrm{B}}T)^3}\frac{1 - \left(\frac{1+F}{2}\right)i\omega\tau}{(1 + i\omega\tau)(1 + 3i\omega\tau)}. \tag{38}$$

Recall now that for *overdamped* spins one has $F \to 1$. Therefore, the formula derived reduces in this case to

$$\overline{\chi^{(3)}}\big|_{\lambda \gg 1} = -\frac{1}{15}\frac{m^4}{(k_{\mathrm{B}}T)^3}\frac{1 - i\omega\tau}{(1 + i\omega\tau)(1 + 3i\omega\tau)}. \tag{39}$$

This particular case (with $1/\sigma$ corrections) was derived in Ref. 20 from an analytical treatment of the Fokker-Planck equation disregarding the precession terms.

C. Practicalities implementing the analytical expressions

To compensate for disregarding $1/\sigma$ corrections, we can heuristically replace the low-T equilibrium linear and nonlinear susceptibilities by their exact expressions.[18,21,22] Further, for axes at random, we can simply use the leading correction for the equilibrium nonlinear susceptibility

$$\overline{\chi_{\mathrm{eq}}^{(3)}} = -\frac{1}{15}\frac{m^4}{(k_{\mathrm{B}}T)^3}\left(1 - \frac{2}{\sigma}\right). \tag{40}$$

As for the function $F(\alpha)$, we can use the approximate forms[4]

$$F(\alpha) \simeq \begin{cases} 1 + 1/\alpha^2 - 1/(2\alpha^2)^2, & \alpha > 1, \\ \sqrt{\pi}/\alpha - 1/3 + \sqrt{\pi}\ \alpha/6, & \alpha < 1. \end{cases} \tag{41}$$

Finally, for the relaxation time at zero field, we use the accurate interpolation formula of Cregg, Crothers, and Wickstead[23]

$$\Gamma_0 = \frac{1}{\tau_{\mathrm{D}}}\left(\frac{2}{\sqrt{\pi}}\frac{\sigma^{3/2}}{1 + 1/\sigma} + \sigma 2^{-\sigma}\right)\frac{1}{\exp(\sigma) - 1}. \tag{42}$$

With these prescriptions, no special functions appear in the analytical formulas, which are expressed in terms of simple functions and polynomials. We shall see below that the agreement of the resulting formulas with the exact continued-fraction results is quite good.

VI. RESULTS FOR THE NONLINEAR SUSCEPTIBILITY

Numerically exact results for the nonlinear susceptibility can be obtained by solving the Fokker-Planck equation by continued-fraction methods. In this approach, one considers the equations for the spherical harmonics $Y_l^m(s_z,\varphi)$ averaged with respect to the nonequilibrium distribution $P(\vec{s})$ obeying Eq. (1). The equations for the Y_l^m (Refs. 24 and 25) (see Ref. 12 for an alternative derivation) can be solved perturbatively in the forcing $\Delta\xi(t)$.[7] At each perturbative level, on introducing appropriate 2-vectors and 2×2 matrices[7,24] the equations for the Y_l^m can be cast into the form of a three-term recurrence relation (in the index l with fixed m). This recurrence can be solved efficiently and accurately by using *matrix* continued fraction methods.[26] Eventually, the average response of the system is obtained with help from the relations $s_z = \sqrt{4\pi/3}\ Y_1^0$ and $s_x + is_y = -\sqrt{8\pi/3}\ Y_1^1$.

The features of the nonlinear susceptibility spectra of classical superparamagnets in the experimentally most common case of anisotropy axes distributed at random are displayed in Fig. 1. The nonlinear susceptibility $\chi^{(3)}$ shows a large dependence on λ,[7] dependence that is absent in the *linear* susceptibility for the same axes distribution and in the longitudinal and strict transverse *nonlinear* susceptibilities. The sensitivity to the damping was interpreted in terms of the dynamical saddle point created by the oblique driving field in the uniaxial potential barrier. This saddle favors interpotential-well jumps that would be unlikely if the field were in the linear range (weakly deformed barrier), and hence leads to an increase of the magnitude of the low-T response.

To illustrate this interpretation, consider one spin that after a "favorable" sequence of fluctuations, approaches the top

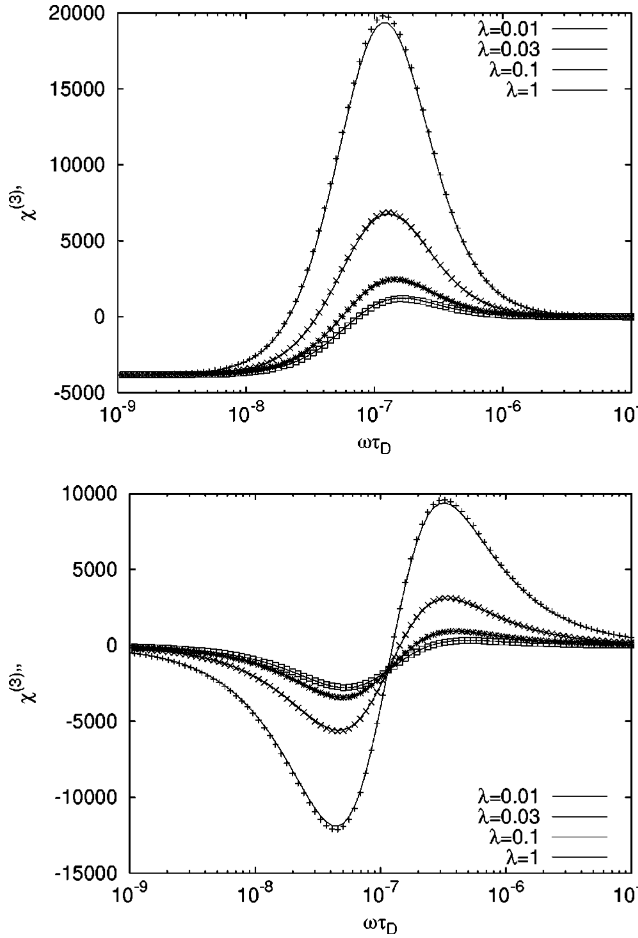

FIG. 1. Nonlinear susceptibility $\chi^{(3)}$ of classical spins with randomly distributed anisotropy axes vs frequency. The temperature is $k_{\mathrm{B}}T/D=0.05$ ($\sigma=20$) and $\lambda=1, 0.1, 0.03$, and 0.01 (bottom to top). The lines are the approximate formula (38) and the symbols the exact continued-fraction solution (Ref. 7). The upper and lower panels display, respectively, the real and imaginary parts of $\chi^{(3)}(\omega)$.

of the barrier but does not surmount it. In the subsequent spiraling down back to the bottom of the well, a strongly damped spin descends almost straightly, whereas a weakly damped spin executes several rotations ($\sim 1/\lambda$) about the anisotropy axis. This allows the weakly damped spin to pass close to the saddle area, where it will have additional opportunities, not available for the damped spin, to cross the barrier, enhancing its relaxation rate. Naturally, this mechanism will make a difference at low temperatures, where reaching the barrier region is a rare event.

The analytical expression derived in Sec. V is displayed for comparison in Fig. 1. The agreement with the exact results is notable. The maximum relative error occurs when $\lambda=0.01$ at the peak of $\chi^{(3)\prime}(\omega)$, and it is only a 2%; going to much higher temperatures, $\sigma=10$, where the approach should start to fail, that error is still less than a 4% (recall that typical experimental conditions correspond to $\sigma\sim 20-25$). This agreement, in turn, supports the interpretation discussed above of the damping dependence. The reason is that our analytical expression includes at its heart the formula for Γ in a weak transverse field,[4] which accounts for the effects of the corresponding saddle point on the relaxation rate.

VII. DISCUSSION

With help from the expression for the relaxation rate of Garanin *et al.*,[4] it has been shown that effects apparently different as the damping dependence of Γ in transverse fields, the damping sensitivity of the *nonlinear* susceptibility,[7] and the effects of the damping on the *linear* response of dipole-dipole coupled systems,[9,10] have a common origin, which is the strong sensitivity of the relaxation rate to the damping in transverse fields.

The damping parameter λ carries information of the coupling with the environmental degrees of freedom causing the relaxation in superparamagnets. In Ref. 7 it was suggested that the large λ dependence of $\chi^{(3)}$ could be exploited to determine λ experimentally. This would by-pass its determination from the preexponential factor τ_0 in the relaxation time ($\propto\tau_{\mathrm{D}}$), which usually only gives an order-of-magnitude estimate. In addition, one does not need high frequencies to explore the effects of λ, in contrast to magnetic resonance experiments (avoiding the associated technical difficulties). Clearly, the availability of a simple analytical expression to model the $\chi^{(3)}$ data should be of great assistance to determine λ.

Coffey *et al.*[27] suggested that a method based on the linear susceptibility with superimposed bias fields would make the resort to the nonlinear response unnecessary. However, in their case the fittings should be done to a formula involving more complicated expressions, both for the equilibrium parts (numerically obtained) and the relaxation times (involving the different Kramers' regimes). In addition, their results have to be eventually integrated over the distribution of anisotropy axis orientations.

Our expression is free from those complications (basically involves the simple zero-field τ of Brown and equilibrium susceptitibilities known analytically). In addition, the measurement of $\chi^{(3)}$ is becoming standard (see, for instance, Ref. 28). In the modeling of real experiments the incorporation of the particle-size distribution can be done by simple integration of our equation. For these reasons, we consider the method based on $\chi^{(3)}$ more suited for the experimental determination of the important, and hitherto quite evasive, dissipation parameter in superparamagnets. Finally, the genericity of the intermediate expressions derived could allow the incorporation of quantum effects, by taking them into account in the field-expansion coefficients of the equilibrium quantities and the relaxation rate.

ACKNOWLEDGMENTS

This work was partially supported by DGES (Spain), Project No. BFM2002-00113 and the Swedish Foundation for Strategic Research (SSF). Discussions with P. Svedlindh, P. Jönsson, and F. Luis are warmly acknowledged.

[1] L. Néel, Ann. Geophys. (C.N.R.S.) **5**, 99 (1949).
[2] W. F. Brown, Jr., Phys. Rev. **130**, 1677 (1963).
[3] R. Kubo and N. Hashitsume, Suppl. Prog. Theor. Phys. **46**, 210 (1970).
[4] D. A. Garanin, E. C. Kennedy, D. S. F. Crothers, and W. T. Coffey, Phys. Rev. E **60**, 6499 (1999).
[5] W. Wernsdorfer *et al.*, Phys. Rev. Lett. **78**, 1791 (1997).
[6] W. T. Coffey *et al.*, Phys. Rev. Lett. **80**, 5655 (1998).
[7] J. L. García-Palacios and P. Svedlindh, Phys. Rev. Lett. **85**, 3724 (2000).
[8] A. Lyberatos, D. V. Berkov, and R. W. Chantrell, J. Phys.: Condens. Matter **5**, 8911 (1993); J. L. García-Palacios and F. J. Lázaro, Phys. Rev. B **58**, 14 937 (1998).
[9] D. V. Berkov and N. L. Gorn, J. Phys.: Condens. Matter **13**, 9369 (2001).
[10] P. E. Jönsson and J. L. García-Palacios, Europhys. Lett. **55**, 418 (2001).
[11] P. E. Jönsson and J. L. García-Palacios, Phys. Rev. B **64**, 174416 (2001).
[12] J. L. García-Palacios and P. Svedlindh, Phys. Rev. B **63**, 172417 (2001).
[13] D. A. Garanin, V. V. Ishchenko, and L. V. Panina, Teor. Mat. Fiz. **82**, 242 (1990) [Theor. Math. Phys. **82**, 169 (1990)].
[14] J. L. García-Palacios, Eur. Phys. J. B **11**, 293 (1999).
[15] V. V. Shcherbakova, Izv., Acad. Sci., USSR, Phys. Solid Earth **14**, 308 (1978).
[16] G. Arfken, *Mathematical Methods for Physicists*, 3rd ed. (Academic Press, Boston, 1985).
[17] P. J. Cregg and L. Bessais, J. Magn. Magn. Mater. **203**, 265 (1999).
[18] J. L. García-Palacios, Adv. Chem. Phys. **112**, 1 (2000).
[19] A. Aharoni, Phys. Rev. **177**, 793 (1969).
[20] Y. L. Raĭkher and V. I. Stepanov, Phys. Rev. B **66**, 214406 (2002).
[21] J. L. García-Palacios and F. J. Lázaro, Phys. Rev. B **55**, 1006 (1997).
[22] J. L. García-Palacios, P. Jönsson, and P. Svedlindh, Phys. Rev. B **61**, 6726 (2000).
[23] P. J. Cregg, D. S. F. Crothers, and A. W. Wickstead, J. Appl. Phys. **76**, 4900 (1994).
[24] Y. P. Kalmykov and W. T. Coffey, Phys. Rev. B **56**, 3325 (1997).
[25] Y. P. Kalmykov and S. V. Titov, Phys. Rev. Lett. **82**, 2967 (1999).
[26] H. Risken, *The Fokker-Planck Equation*, 2nd ed. (Springer, Berlin, 1989).
[27] W. T. Coffey, D. S. F. Crothers, Y. P. Kalmykov, and S. V. Titov, Phys. Rev. B **64**, 012411 (2001).
[28] P. Jönsson, T. Jonsson, J. L. García-Palacios, and P. Svedlindh, J. Magn. Magn. Mater. **222**, 219 (2000).