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Nonlinear longitudinal relaxation of a quantum superparamagnet with arbitrary spin value *S*: Phase space and density matrix formulations

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The nonlinear relaxation of quantum spins interacting with a thermal bath is treated via the respective evolution equations for the reduced density matrix and phase space distribution function in the high temperature and weak spin-bath coupling limits using the methods already available for classical spins. The solution of each evolution equation is written as a finite series of the polarization operators and spherical harmonics, respectively, where the coefficients of the series (statistical averages of the polarization operators and spherical harmonics) are found from entirely equivalent differential-recurrence relations. Each system matrix has an identical set of eigenvalues and eigenfunctions. For illustration, the time behavior of the longitudinal component of the magnetization and its characteristic relaxation times are evaluated for a uniaxial paramagnet of arbitrary spin *S* in an external constant magnetic field applied along the axis of symmetry. In the large spin limit, the quantum solutions reduce to those of the Fokker-Planck equation for a classical uniaxial superparamagnet. For linear response, the results entirely agree with existing solutions.

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I. INTRODUCTION

Phase-space representations of quantum mechanical evolution equations [via the coherent state representation of the density matrix $\hat{\rho}(t)$ introduced by Glauber and Sudarshan long familiar in quantum optics[1–3]] when applied to spin systems characterized by a Hamiltonian $\hat{H}_S$ allow one to analyze spin relaxation using a master equation for a *quasiprobability distribution function* $W_S^{(s)}(\vartheta,\varphi,t)$ of spin orientations in a phase (here configuration) space (ϑ,φ). Here ϑ and φ are the polar and azimuthal angles constituting the canonical variables[4–9] and the master equation is

$$\frac{\partial W_S^{(s)}}{\partial t} = L_S W_S^{(s)}, \tag{1}$$

where S is the spin size and L_S is a differential operator depending on the particular spin system. Equation (1) is derived by mapping onto phase space the evolution equation for the reduced density matrix $\hat{\rho}$, namely,

$$\frac{\partial\hat{\rho}}{\partial t} + \frac{i}{\hbar}[\hat{H}_S,\hat{\rho}] = \hat{Q}(\hat{\rho}), \tag{2}$$

where $\hat{Q}(\hat{\rho})$ is the collision kernel operator. The transformation may be accomplished because $W_S^{(s)}(\vartheta,\varphi,t)$ and $\hat{\rho}$ are related via the bijective map[2]

$$W_S^{(s)}(\vartheta,\varphi,t) = \mathrm{Tr}\{\hat{\rho}(t)\hat{w}_s(\vartheta,\varphi)\},$$

$$\hat{\rho}(t) = \frac{2S+1}{4\pi}\int_{\vartheta,\varphi} \hat{w}_s(\vartheta,\varphi)W_S^{(-s)}(\vartheta,\varphi,t)\sin\vartheta d\vartheta d\varphi.$$

The Wigner-Stratonovich operator (or kernel of the transformation) $\hat{w}_s(\vartheta,\varphi)$ is defined as

$$\hat{w}_s(\vartheta,\varphi) = \sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}(C_{S,S,L,0}^{S,S})^{-s}Y_{L,M}^{*}(\vartheta,\varphi)\hat{T}_{L,M}^{(S)}.$$

Here $\mathrm{Tr}\{\hat{w}_s\}=1$ and $[(2S+1)/4\pi]\int_{\vartheta,\varphi}\hat{w}_s \sin\vartheta d\vartheta d\varphi = \hat{I}^{(S)}$ ($\hat{I}^{(S)}$ is the identity matrix), the asterisk denotes the complex conjugate, $Y_{L,M}(\vartheta,\varphi)$ are the spherical harmonics,[10] $\hat{T}_{L,M}^{(S)}$ are the polarization operators,[10] and $C_{S,S,L,0}^{S,S}$ are the Clebsch-Gordan coefficients.[10] Either $W_S^{(s)}(\vartheta,\varphi,t)$ or $\hat{\rho}$ allow one to calculate the *average* value of an arbitrary spin operator $\hat{A}$ as

$$\langle\hat{A}\rangle = \mathrm{Tr}\{\hat{\rho}\hat{A}\}$$

or

$$\langle\hat{A}\rangle = \frac{2S+1}{4\pi}\int_{\vartheta,\varphi} A^{(s)}(\vartheta,\varphi)W_S^{(-s)}(\vartheta,\varphi,t)\sin\vartheta d\vartheta d\varphi,$$

respectively, where $A^{(s)}(\vartheta,\varphi)=\mathrm{Tr}\{\hat{A}\hat{w}_s(\vartheta,\varphi)\}$ is the Weyl symbol of $\hat{A}$. The symbol s characterizes quasiprobability functions of spins belonging to the SU(2) dynamical symmetry group. The parameter values $s=0$ and $s=\pm 1$ correspond to the Stratonovich[11] and Berezin[12] contravariant and covariant functions, respectively (the latter are directly related to the P and Q symbols appearing naturally in the coherent state representation[2]). We consider below only $W_S^{(-1)}(\vartheta,\varphi)$ [omitting everywhere the superscript −1 in $W_S^{(-1)}(\vartheta,\varphi)$] because it alone satisfies the non-negativity condition required of a true probability density function, viz., $W^{(-1)}(\vartheta,\varphi)\geq 0$.[13]

The phase space distribution (Wigner) function for spins having been originally introduced by Stratonovich[11] for closed systems was further developed for both closed and open spin systems.[7–9,14–18] In the present context phase space methods are highly relevant because they allow one to map quantum mechanical evolution equations for the (reduced) density matrix for spins onto a classically meaningful c-number space, which has an obvious advantage over the operator equations in the consideration of the classical limit.[17] In particular, the mapping of the quantum spin dynamics onto c-number quasiprobability density evolution equations transparently shows how evolution equation (1) reduces in that limit to the Fokker-Planck equation describing the stochastic dynamics of a classical spin.[5,6,9,17,18] Moreover, the formalism is relatively easy to implement in practice because the existence of phase space master equations for spins enables existing powerful computational techniques for Fokker-Planck equations (e.g., statistical moments, continued fractions, mean first passage times, etc.[19,20]) to be seamlessly carried over into the quantum domain.[7–9]

Now, although the phase space and spin density matrix representations have outwardly very different forms, they must yield exactly the same results. However, use of one or the other representation may provide a more transparent method of obtaining the desired result depending on the problem at hand. In particular the phase space representation, because it is closely allied to the classical representation, is very convenient for the study of the passage to the classical limit. This feature has been amply demonstrated in Ref. 9 for the simple model of a spin in a dc magnetic field. Here, as another explicit example, which now involves the magnetocrystalline anisotropy, we consider a uniaxial paramagnet of arbitrary spin value S in an external *constant* magnetic field $\mathbf{H}_0$ applied along the Z axis, i.e., the axis of symmetry. Thus, the Hamiltonian has the form

$$\hat{H} = \hat{H}_S + \hat{H}_{SB} + \hat{H}_B,$$

where

$$\beta\hat{H}_S = -\frac{\sigma}{S^2}\hat{S}_Z^2 - \frac{\xi}{S}\hat{S}_Z, \tag{3}$$

$\hat{S}_Z$ is the Z component of the spin operator $\mathbf{S}$, σ is the anisotropy constant, $\xi = \beta S\hbar\gamma H_0$ is the field parameter, γ is the gyromagnetic ratio, and $\beta = 1/(kT)$ is the inverse thermal energy, the term $\hat{H}_{SB}$ describes interaction of the spin with the thermostat, and $\hat{H}_B$ characterizes the thermostat. This Hamiltonian includes a uniaxial anisotropy term plus the Zeeman coupling to the external field, comprising a generic model for the study of quantum relaxation phenomena in uniaxial spin systems such as molecular magnets, nanoclusters, etc. (see, e.g., Refs. 26 and 27 and references cited therein). Recently Garanin[26] and García-Palacios *et al.*[27] using the spin density matrix in the second order of perturbation theory in the spin-bath coupling considered the longitudinal relaxation of quantum superparamagnets with Hamiltonian (3) for arbitrary S. They gave a concise treatment of the spin dynamics by proceeding from the quantum Hubbard operator representation of the evolution equation for the spin density matrix. However, they limited themselves to the linear response so that their solution pertains to a small perturbation in the dc field and is not valid for *arbitrary* changes. Here we shall present solutions for the *nonlinear* relaxation of the averaged longitudinal component of the spin $\langle\hat{S}_Z\rangle(t)$ as a function of the spin value S using both the density matrix and phase space formulation. As far as the phase space approach is concerned, the master equation corresponding to Hamiltonian (3) has been derived already in Ref. 18 but has not yet been solved. Here we shall demonstrate how the solution of the corresponding classical problem[21–25] carries over into the quantum domain illustrating how the magnetization, its reversal, and integral relaxation times for an *arbitrarily strong* change in the uniform field may be evaluated. Furthermore, we shall show that the long time behavior of $\langle\hat{S}_Z\rangle(t)$ comprising $2S$ exponentials may be accurately approximated by a *single* exponential with a definite relaxation time T_1 for arbitrary S. In other words, even for a giant spin ($S \gg 1$), $\langle\hat{S}_Z\rangle(t)$ still obeys the Bloch equation

$$\frac{d}{dt}\langle\hat{S}_Z\rangle(t) + [\langle\hat{S}_Z\rangle(t) - \langle\hat{S}_Z\rangle_{eq}]/T_1 = 0, \tag{4}$$

where $\langle\hat{S}_Z\rangle_{eq}$ is the equilibrium average of the operator $\hat{S}_Z$. In the *linear-response approximation*, the solution reduces to that previously given by Garanin[26] and García-Palacios and Zueco.[27]

The paper is arranged as follows. In Sec. II, the method of statistical moments in the context of the density matrix and phase space formalism is presented. In Sec. III, the differential-recurrence equations for relaxation functions (statistical moments) of a uniaxial quantum paramagnet are derived. In Sec. IV, by solving these equations, the nonlinear transient response of a uniaxial quantum paramagnet is treated. The characteristic relaxation times of nonlinear transients are calculated in Sec. V. The results are presented in Sec. VI. Section VII contains their discussion and conclusions. Various useful formulas for a classical superparamagnet are summarized in Appendix A. The detailed calculation of the integral relaxation time is given in Appendix B.

II. METHOD OF STATISTICAL MOMENTS

A very efficient method of solution of the Fokker-Planck equation governing the stochastic dynamics of classical spin systems comprises the determination of the statistical moments[19,20,28] which in general satisfy differential-recurrence relations. This method can also be applied to the quantum problem. The reason is that the phase-space distribution $W_S(\vartheta,\varphi,t)$ may be presented for arbitrary S in terms of a finite linear combination of the spherical harmonics, namely,[2]

$$\frac{2S+1}{4\pi}W_S(\vartheta,\varphi,t) = \sum_{L=0}^{2S}\sum_{M=-L}^{L}\langle Y_{L,M}^*\rangle(t)Y_{L,M}(\vartheta,\varphi), \tag{5}$$

where

$$\langle Y_{L,M}^*\rangle(t) = \frac{2S+1}{4\pi}\int_{\vartheta,\varphi} Y_{L,M}^*(\vartheta,\varphi)W_S(\vartheta,\varphi,t)\sin\vartheta\, d\vartheta\, d\varphi$$

and $Y_{L,M}^* = (-1)^M Y_{L,-M}$. Equation (5) obviously emphasizes the relationship with the conventional infinite series representation of the relevant classical Boltzmann distribution.

The formal solution of the reduced density evolution equation (2) can also be written in analogous fashion using the polarization operators $\hat{T}_{L,M}^{(S)}$ as the linear combination[2,10,28]

$$\hat{\rho}(t) = \sum_{L=0}^{2S} \sum_{M=-L}^{L} (-1)^M a_{L,-M}(t) \hat{T}_{L,M}^{(S)}, \tag{6}$$

where the coefficients $a_{L,M}$ (representing the expectation values of the $\hat{T}_{L,M}^{(S)}$ in a state described by $\hat{\rho}$) are[10]

$$a_{L,M}(t) = \langle \hat{T}_{L,M}^{(S)} \rangle(t) = \mathrm{Tr}\{\hat{\rho}(t)\hat{T}_{L,M}^{(S)}\}. \tag{7}$$

In general, the scalar coefficients $\langle \hat{T}_{L,M}^{(S)} \rangle$ are related to the expectation values of the spherical harmonics $\langle Y_{L,M} \rangle$ (statistical moments) by the equation[18]

$$\begin{aligned}\langle Y_{L,M} \rangle &= \sqrt{\frac{2S+1}{4\pi}} C_{S,S,L,0}^{S,S} \langle \hat{T}_{L,M}^{(S)} \rangle \\ &= \frac{(2S)!(2S+1)}{\sqrt{4\pi(2S-L)!(2S+L+1)!}} \langle \hat{T}_{L,M}^{(S)} \rangle. \end{aligned} \tag{8}$$

Thus, knowing $\langle Y_{L,M} \rangle(t)$ from phase space equations (1) and (5), we can also determine $\hat{\rho}$ from Eqs. (6) and (8) without formally solving its evolution equation (2). Vice versa, having calculated $\langle \hat{T}_{L,M}^{(S)} \rangle(t)$ from the density matrix Eqs. (2) and (6), we can also find $W_S(\vartheta,\varphi,t)$ from Eqs. (5) and (8) without formally solving the phase space evolution equation (1).

The finite series Eq. (5) is valid for an *arbitrary* spin system with states described by $\hat{\rho}$ given by Eq. (6). In general, either expansion of the phase-space distribution as a linear combination of the spherical harmonics or expansion of the density matrix in polarization operators permits direct calculation of the observables $\langle \hat{S}_X \rangle$, $\langle \hat{S}_Z \rangle$, etc. For example, noting the correspondence rules of the operator $\hat{S}_Z$ and its Weyl symbol (c number) $S_Z(\vartheta,\varphi)$ in the phase space, we have in the phase space representation[18]

$$\langle \hat{S}_Z \rangle(t) = \sqrt{4\pi/3}(S+1)\langle Y_{1,0} \rangle(t).$$

While in terms of the polarization operators, we have

$$\langle \hat{S}_Z \rangle(t) = \sqrt{S(S+1)(2S+1)/3}\langle \hat{T}_{1,0}^{(S)} \rangle(t).$$

The differential-recurrence relations for $\langle Y_{L,M} \rangle(t)$ can be obtained by substituting the distribution function $W_S(\vartheta,\varphi,t)$ from Eq. (5) into master equation (1) so that the latter becomes

$$\frac{d}{dt}\langle Y_{L,M} \rangle(t) = \sum_{L',M'} b_{L,M}^{L',M'} \langle Y_{L',M'} \rangle(t), \tag{9}$$

where $b_{L,M}^{L',M'}$ are the Fourier coefficients which depend on the precise form of the Hamiltonian. The corresponding equation for $\langle \hat{T}_{L,M}^{(S)} \rangle(t)$, viz.,

$$\begin{aligned}\frac{d}{dt}\langle \hat{T}_{L,M}^{(S)} \rangle(t) = \sum_{L',M'} &\sqrt{\frac{(2S-L)!(2S+L+1)!}{(2S-L')!(2S+L'+1)!}} \\ &\times b_{L,M}^{L',M'} \langle \hat{T}_{L',M'}^{(S)} \rangle(t), \end{aligned} \tag{10}$$

can be obtained either by substituting the polarization operator series representation of the reduced density matrix $\hat{\rho}$ from Eq. (6) into Eq. (2) or directly from the Fourier series Eq. (9) by noting Eq. (8). Equations (9) and (10) are entirely equivalent and can be solved either by direct matrix diagonalization, involving the calculation of the eigenvalues and eigenvectors of the system matrix, or by the computationally efficient (matrix) continued fraction method[19,20] so yielding the magnetization as a function of S, etc.

III. DIFFERENTIAL-RECURRENCE RELATION FOR STATISTICAL MOMENTS FOR A UNIAXIAL PARAMAGNET

The density matrix evolution equation for the reduced density matrix $\hat{\rho}$ describing the longitudinal relaxation of a uniaxial spin system with Hamiltonian (3) is in the weak coupling and high temperature limit[18]

$$\frac{\partial \hat{\rho}}{\partial t} = \mathrm{St}(\hat{\rho}), \tag{11}$$

where

$$\mathrm{St}(\hat{\rho}) = 2D_{\perp}\{[\hat{S}_-\hat{\rho},\hat{S}_+] + [\hat{S}_+ e^{(\sigma/S^2)(2\hat{S}_Z+\hat{I}^{(S)})+(\xi/S)\hat{I}^{(S)}}\rho(t),\hat{S}_-]\}, \tag{12}$$

$\hat{S}_\pm = \hat{S}_X \pm i\hat{S}_Y$; $\hat{S}_X$ and $\hat{S}_Y$ are the X and Y components of the spin operator $\hat{\mathbf{S}}$, respectively. The collision kernel operator $\mathrm{St}(\hat{\rho})$ in Eq. (12) is explicitly determined via the ansatz that the equilibrium spin density matrix $\hat{\rho}_{eq} = e^{-\beta \hat{H}_S}/\mathrm{Tr}\{e^{-\beta \hat{H}_S}\}$ renders it zero, i.e., $\mathrm{St}(\hat{\rho}_{eq}) = 0$. Conditions for the validity of Eq. (11) are discussed in detail elsewhere.[18] Essentially, that equation follows from the equation of motion of the reduced density matrix in the rotating-wave approximation (familiar in quantum optics, where counter-rotating, rapidly oscillating terms are averaged out[27]). Moreover the spin-bath interactions are taken in the weak coupling limit and for Ohmic damping. Thus, the correlation time characterizing the bath is short enough to allow one to approximate the stochastic process originating in it by a Markov process. These approximations may be used in the high temperature limit, $\beta(\varepsilon_m - \varepsilon_{m\pm1}) \ll 1$, where $\varepsilon_m, \varepsilon_{m\pm1}$ are the energy eigenvalues. In the parameter range, where the approximation fails (e.g., throughout the very low temperature region), more general forms of the phase space and density matrix equations must be used (such as treated, e.g., in Refs. 26 and 27). Nevertheless, we still use the model based on the above approximation because despite many drawbacks[26,27] it can qualitatively describe the relaxation in spin systems. Moreover, the model can be regarded as the direct quantum generalization of the Langevin formalism used by Brown in his theory of relaxation of classical superparamagnetic particles.[21]

The phase space evolution equation for $W_S(\vartheta,t)$ corresponding to Eq. (11) is (because in longitudinal relaxation the azimuthal angle dependence of W_S may be ignored)[18]

$$\frac{\partial W_S}{\partial t} = \frac{D_\perp}{2}\frac{\partial}{\partial z}\left\{(1-z^2)\left[\frac{\partial}{\partial z}\{\bar{P}^{(S)}+1+z(\bar{P}^{(S)}-1)\}W_S - (2S+1)(\bar{P}^{(S)}-1)W_S\right]\right\}, \qquad (13)$$

where $D_\perp$ is the "diffusion" coefficient, $z=\cos\vartheta$, and the operator $\bar{P}^{(S)}$ has a complicated differential form, given explicitly in Ref. 18. For $\sigma=0$, i.e., for a spin in a dc magnetic field, we have simply $\bar{P}^{(S)}=e^{\xi/S}$ and Eq. (13) reduces to the Fokker-Planck equation treated in Ref. 9. In the classical limit, Eq. (13) further reduces to the Fokker-Planck equation for a classical uniaxial paramagnet in a dc magnetic field, viz.,[20–25]

$$\frac{\partial}{\partial t}W = D_\perp\frac{\partial}{\partial z}\left[(1-z^2)\left(\frac{\partial}{\partial z}W + W\frac{\partial}{\partial z}V\right)\right], \qquad (14)$$

where $V(z)=-\sigma z^2-\xi z$ is the normalized classical free energy.

The formal solutions of the axially symmetric Eqs. (13) and (11) can now be written as

$$\hat{\rho}(t) = \sum_{L=0}^{2S} a_L(t)\hat{T}^{(S)}_{L,0}, \qquad (15)$$

$$\frac{2S+1}{4\pi}W_S(\vartheta,\varphi,t) = \sum_{L=0}^{2S} b_L(t)Y_{L,0}(\vartheta,\varphi). \qquad (16)$$

The coefficients $a_L(t)$ and $b_L(t)$ are of course [cf. Eqs. (5) and (7)] the averages of the polarization operators $\hat{T}^{(S)}_{L,0}$ and spherical harmonics $Y_{L,0}$, viz.,

$$a_L(t) = \langle \hat{T}^{(S)}_{L,0}\rangle(t), \quad b_L(t) = \langle Y_{L,0}\rangle(t). \qquad (17)$$

By substituting Eqs. (15) and (16) into Eqs. (11) and (13), respectively, we have the *finite* hierarchy of differential-recurrence equations for the statistical moments (in contrast to the classical case, where the corresponding hierarchy is *infinite*).

Since either approach presented above yields similar hierarchies, we give the derivation using the density matrix. This is accomplished as follows. First, the matrix exponent $e^{(\sigma/S^2)(2\hat{S}_Z+\hat{I}^{(S)})+(\xi/S)\hat{I}^{(S)}}$ in Eq. (12) can be expanded in terms of the polarization operators $\hat{T}^{(S)}_{L,0}$ as

$$e^{(\sigma/S^2)(2\hat{S}_Z+\hat{I}^{(S)})+(\xi/S)\hat{I}^{(S)}} = e^{(\sigma/S^2)+(\xi/S)}\sum_{l=0}^{2S} d_l\hat{T}^{(S)}_{l,0}, \qquad (18)$$

where

$$d_l(\sigma) = \mathrm{Tr}\{e^{(2\sigma/S^2)\hat{S}_0}\hat{T}^{(S)}_{l,0}\} = \sqrt{\frac{2l+1}{2S+1}}\sum_{m=-S}^{S} C^{S,m}_{S,m,l,0}e^{(2\sigma/S^2)m}. \qquad (19)$$

Here the expansion coefficients d_l have been found by using the orthogonality property

$$\mathrm{Tr}\{\hat{T}^{(S)}_{L_1,M_1}\hat{T}^{(S)}_{L_2,M_2}\} = (-1)^{M_1}\delta_{L_1,L_2}\delta_{M_1,-M_2} \qquad (20)$$

and the explicit form of the matrix elements, viz., $[\hat{T}^{(S)}_{L,M}]_{m',m}=[(2L+1)/(2S+1)]^{1/2}C^{S,m'}_{S,m,L,M}$. By substituting Eq. (15) into the explicit evolution Eq. (11), noting Eq. (18), and the product formula[10]

$$\hat{T}^{(S)}_{l,0}\hat{T}^{(S)}_{L,0} = \sum_{L'=|L-l|}^{L+l}(-1)^{2S+L'}\sqrt{(2l+1)(2L+1)} \times \begin{Bmatrix} l,L,L' \\ S,S,S \end{Bmatrix} C^{L',0}_{l,0,L,0}\hat{T}^{(S)}_{L',0}, \qquad (21)$$

($\begin{Bmatrix} l,L,L' \\ S,S,S \end{Bmatrix}$ is Wigner's $6j$-symbol[10]) we have the hierarchy of multiterm differential-recurrence equations for the averages $a_L(t)$, namely,

$$\tau_N\frac{\partial a_L(t)}{\partial t} = \sum_{L'=0}^{2S} g^S_{L,L'}a_{L'}(t), \qquad (22)$$

where $\tau_N=(2D_\perp)^{-1}$ is the characteristic (free diffusion) time and

$$\begin{aligned} g^S_{L,L'} = {} & \frac{L(L+1)}{4}\sqrt{\frac{(2S-L)(2S+L+2)}{(2L+1)(2L+3)}}\delta_{L,L'+1} \\ & - \frac{L(L+1)}{4}\delta_{L,L'} - \frac{L(L+1)}{4} \\ & \times\sqrt{\frac{(2S-L+1)(2S+L+1)}{(2L+1)(2L-1)}}\delta_{L,L'-1} - e^{(\sigma/S^2)+(\xi/S)} \\ & \times(-1)^{2S+L}\frac{L(L+1)}{4}\sqrt{2L'+1} \\ & \times\left[\sum_{l=|L'-L|}^{L'+L} d_l(\sigma)\sqrt{2l+1}\begin{Bmatrix} l,L',L \\ S,S,S \end{Bmatrix}C^{L,0}_{l,0,L',0}\right. \\ & + \frac{\sqrt{(2S-L+1)(2S+L+1)}}{\sqrt{(2L-1)(2L+1)}}\sum_{l=|L'-L+1|}^{L'+L-1} d_l(\sigma)\sqrt{2l+1} \\ & \times\begin{Bmatrix} l,L',L-1 \\ S,S,S \end{Bmatrix}C^{L-1,0}_{l,0,L',0} \\ & - \frac{\sqrt{(2S-L)(2S+L+2)}}{\sqrt{(2L+3)(2L+1)}}\sum_{l=|L'-L-1|}^{L'+L+1} d_l(\sigma)\sqrt{2l+1} \\ & \left.\times\begin{Bmatrix} l,L',L+1 \\ S,S,S \end{Bmatrix}C^{L+1,0}_{l,0,L',0}\right] \end{aligned} \qquad (23)$$

with $a_0=\langle T^{(S)}_{0,0}\rangle=(2S+1)^{-1/2}$. We remark that the built-in functions ClebschGordan[$\{a,\alpha\},\{b,\beta\},\{c,\gamma\}$] and SixJSymbol[$\{j_1,j_2,j_3\},\{j_4,j_5,j_6\}$] of the MATHEMATICA program facilitate calculation of the Clebsch-Gordan coefficients and the Wigner $6j$ symbols in Eq. (23). On the other hand, in the phase space representation, we have formally the relevant system of differential-recurrence equations for the averaged spherical harmonics $\langle Y_{l,0}\rangle(t)$ from Eqs. (9), (10), and (22). Alternatively the differential-recurrence equations can be directly derived by substituting Eq. (16) into Eq. (13) and using the recurrence relations[10]

$$\begin{pmatrix} \cos\vartheta Y_{l,m} \\ \sin\vartheta\partial_\vartheta Y_{l,m} \end{pmatrix} = \begin{pmatrix} 1 \\ l \end{pmatrix} \sqrt{\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}} Y_{l+1,m} - \begin{pmatrix} -1 \\ l+1 \end{pmatrix} \sqrt{\frac{l^2-m^2}{4l^2-1}} Y_{l-1,m},$$

$$\partial_\vartheta^2 Y_{l,m} = [m^2\csc^2\vartheta - l(l+1)]Y_{l,m} - \cot\vartheta\partial_\vartheta Y_{l,m}.$$

The details have been given in Ref. 9 for $\sigma=0$.

In the classical limit, $S\to\infty$, Eq. (22) reduces to the differential-recurrence equation for a classical uniaxial paramagnet treated in Refs. 20, 29, and 30 (see Appendix A). In the limiting case $\sigma=0$, Eqs. (19) and (23) simplify yielding $d_l(0)=\sqrt{2S+1}\,\delta_{l,0}$ and $g^S_{L,L'}=0$ with the exceptions $g^S_{L,L}=e^{\xi/S}q_L$ and $g^S_{L,L\pm1}=-e^{\xi/S}q_L^{\pm}$, where

$$q_L = -\frac{L(L+1)}{4}, \quad q_L^{\pm} = \pm\frac{1}{4}L(L+1)\frac{2S\pm L+3/2\pm 1/2}{2L+1},$$

so that with the replacement

$$c_L(t) \to \frac{\sqrt{(2S-L)!(2S+L+1)!(2L+1)}}{4\pi(2S)!}a_L(t),$$

we have from Eq. (22)

$$\tau_N\frac{\partial c_L(t)}{\partial t} = (1+e^{\xi/S})q_L c_L(t) + (1-e^{\xi/S})q_L^- c_{L-1}(t) + (1-e^{\xi/S})q_L^+ c_{L+1}(t). \tag{24}$$

This result exactly corresponds to the spin relaxation in a uniform field treated comprehensively in Ref. 9.

IV. CALCULATION OF THE OBSERVABLES

We suppose that the magnitude of an external uniform dc magnetic field is suddenly altered at time $t=0$ from $\mathbf{H}_\mathrm{I}$ to $\mathbf{H}_\mathrm{II}$ (the magnetic fields $\mathbf{H}_\mathrm{I}$ and $\mathbf{H}_\mathrm{II}$ are applied parallel to the Z axis of the laboratory coordinate system in order to preserve axial symmetry). Thus, we study as in the classical case,[20] the nonlinear transient longitudinal relaxation of a system of spins starting from an equilibrium state I with density matrix $\hat\rho^\mathrm{I}_{eq}$ $(t\le 0)$ to a new equilibrium state II with density matrix $\hat\rho^\mathrm{II}_{eq}$ $(t\to\infty)$. Here the longitudinal component of the spin $\langle\hat S_Z\rangle(t)$ relaxes from the equilibrium value $\langle\hat S_Z\rangle_\mathrm{I}$ to the value $\langle\hat S_Z\rangle_\mathrm{II}$, the transient being described by an appropriate relaxation function. The transient response so formulated is truly *nonlinear* because the change in amplitude $H_\mathrm{I}-H_\mathrm{II}$ of the external dc magnetic field is *arbitrary* (the linear response is the particular case $|H_\mathrm{I}-H_\mathrm{II}|\to 0$). We remark in passing that the equilibrium phase space distributions W^I_{eq} and W^II_{eq} corresponding to the equilibrium spin density matrices $\hat\rho^\mathrm{I}_{eq}$ and $\hat\rho^\mathrm{II}_{eq}$ comprise the appropriate stationary (time independent) solutions of Eq. (13). These distributions have been extensively studied in Ref. 31 and are given by

$$W_S^i(\vartheta) = \sum_{L=0}^{2S}\frac{2L+1}{2S+1}\langle P_L\rangle_i P_L(\cos\vartheta), \tag{25}$$

where $\langle P_L\rangle_i=(S+1/2)\int_{-1}^{1}P_L(z)W_S^i(z)dz$ are the equilibrium values of the Legendre polynomials P_L given explicitly by[31]

$$\langle P_L\rangle_i = Z_S^{-1}C^{S,S}_{S,S,L,0}\sum_{m=-S}^{S}C^{S,m}_{S,m,L,0}e^{\sigma(m/S)^2+\xi_i(m/S)}$$

and $Z_S=\mathrm{Tr}\{e^{-\beta\hat H_S}\}=\sum_{m=-S}^{S}e^{\sigma(m/S)^2+\xi_i(m/S)}$ is the partition function.

According to Eq. (22), the behavior of any selected average is coupled to that of all the others so forming a *finite* hierarchy (because the index L ranges only between 0 and $2S$) of averages. The solution of such a multiterm recurrence relation may always be obtained by rewriting it as a first-order linear matrix differential equation with constant coefficients. In order to accomplish this, we first construct a column vector $\mathbf{C}(t)$ such that

$$\mathbf{C}(t) = \begin{pmatrix} c_1(t) \\ c_2(t) \\ \vdots \\ c_{2S}(t) \end{pmatrix}, \tag{26}$$

with elements $c_L(t)=\langle\hat T^{(S)}_{L,0}\rangle(t)-\langle\hat T^{(S)}_{L,0}\rangle_\mathrm{II}$. Now the after-effect functions $c_L(t)$ satisfy the same recurrence relations Eq. (22) as the $a_L(t)$ with the initial conditions

$$c_L(0) = \langle\hat T^{(S)}_{L,0}\rangle_\mathrm{I} - \langle\hat T^{(S)}_{L,0}\rangle_\mathrm{II}. \tag{27}$$

However, vector (26) now contains just $2S$ elements (the index L ranges between 1 and $2S$) as the evolution equation for the function $c_0(t)$ is simply $\partial_t c_0(t)=0$ with the trivial solution $c_0(t)=\mathrm{const}$. Hence, the matrix representation of the recurrence equations for the $c_L(t)$ has the form of the linear matrix differential equation

$$\dot{\mathbf{C}}(t) + \mathbf{X}\cdot\mathbf{C}(t) = 0, \tag{28}$$

where $\mathbf{X}$ is the $2S\times 2S$ system matrix with matrix elements given by

$$(\mathbf{X})_{n,m} = -\tau_N^{-1}g^S_{n,m}. \tag{29}$$

For example, for $S=1$, the matrix $\mathbf{X}$ is given by

$$\mathbf{X} = \frac{1}{2\tau_N}\begin{pmatrix} 1+e^{\xi-\sigma} & 3^{-1/2}(2e^{\xi+\sigma}-1-e^{\xi-\sigma}) \\ 3^{1/2}(1-e^{\xi-\sigma}) & 2e^{\xi+\sigma}+3+e^{\xi-\sigma} \end{pmatrix}. \tag{30}$$

The solution of the homogeneous matrix Eq. (28) is[32]

$$\mathbf{C}(t) = e^{-\mathbf{X}t}\mathbf{C}(0). \tag{31}$$

The one-sided Fourier transform of Eq. (31) yields the spectrum $\tilde{\mathbf{C}}(\omega)=\int_0^\infty\mathbf{C}(t)e^{-i\omega t}dt$, viz.,

$$\tilde{\mathbf{C}}(\omega) = (\mathbf{X}+i\omega\mathbf{I})^{-1}\mathbf{C}(0). \tag{32}$$

Matrix solutions (31) and (32) may now be used to calculate the longitudinal component of the magnetization spin operator

$$\langle\hat{S}_Z\rangle(t) - \langle\hat{S}_Z\rangle_{\mathrm{II}} = \sqrt{S(S+1)(2S+1)/3}\,c_1(t) \tag{33}$$

and its spectrum as well as the integral relaxation time defined as the area under the relaxation curve of the relevant observable so that

$$\tau_{\mathrm{int}} = \frac{1}{\langle\hat{S}_Z\rangle_{\mathrm{I}} - \langle\hat{S}_Z\rangle_{\mathrm{II}}}\int_0^t [\langle\hat{S}_Z\rangle(t) - \langle\hat{S}_Z\rangle_{\mathrm{II}}]dt. \tag{34}$$

Equation (34) can now be written[20] using the final value theorem of Fourier-Laplace transforms as

$$\tau_{\mathrm{int}} = \tilde{c}_1(0)/c_1(0), \tag{35}$$

where $\tilde{c}_1(\omega)=\int_0^\infty c_1(t)e^{-i\omega t}dt$. The function $\tilde{c}_1(0)$ is the first element of the vector $\tilde{\mathbf{C}}(0)$ which in accordance with Eq. (32) is

$$\tilde{\mathbf{C}}(0) = (\mathbf{X})^{-1}\mathbf{C}(0). \tag{36}$$

The general solution (31) can be written as[32]

$$\mathbf{C}(t) = \mathbf{U}e^{-\mathbf{\Lambda}t}\mathbf{U}^{-1}\mathbf{C}(0), \tag{37}$$

where $\mathbf{\Lambda}$ is a diagonal matrix containing the eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_{2S}$ of the system matrix $\mathbf{X}$ and $\mathbf{U}$ is a right eigenvector matrix composed of all the eigenvectors of the system matrix $\mathbf{X}$, namely, $\mathbf{U}^{-1}\mathbf{X}\mathbf{U}=\mathbf{\Lambda}$. *All* the λ_k are real and positive. In accordance with Eqs. (35) and (36), the relaxation function $c_1(t)$ and the integral relaxation time are given by

$$c_1(t) = \sum_{k=1}^{2S} u_{1,k}g_k e^{-\lambda_k t}, \tag{38}$$

$$\tau_{\mathrm{int}} = \sum_{k=1}^{2S} u_{1,k}g_k\lambda_k^{-1} \Big/ \sum_{k=1}^{2S} u_{1,k}g_k, \tag{39}$$

where $u_{l,k}$ are the matrix elements of $\mathbf{U}$ and g_k are the elements of the vector $\mathbf{U}^{-1}\mathbf{C}(0)$. Thus, the integral relaxation time contains contributions from *all* the eigenvalues λ_k and so characterizes the overall relaxation behavior. The other important characteristic of the relaxation process is the smallest nonvanishing eigenvalue λ_1. This is the reciprocal time constant associated with the *long time behavior* of the relaxation function $c_1(t)$ comprising the slowest (lowest frequency) relaxation mode. A knowledge of λ_1 is essential because it characterizes the reversal time of the magnetization. Furthermore, because the influence of the high-frequency relaxation modes on the low-frequency relaxation may often be ignored, λ_1 provides sufficient information concerning the low-frequency dynamics of the system (see Sec. VI).

Our matrix method also allows us to evaluate the *linear response* of a spin system due to infinitesimally small changes in the magnitude of the dc field, which we stress has already been evaluated[26,27] using the spin density matrix. Thus, we again suppose that the uniform dc field $\mathbf{H}_{\mathrm{II}}$ is directed along the Z axis of the laboratory coordinate system and that a small probing field $\mathbf{H}_1$ ($\mathbf{H}_1 \parallel \mathbf{H}_{\mathrm{II}}$) having been applied to the assembly of spins in the distant past ($t=-\infty$) so that equilibrium conditions obtain at time $t=0$ is switched off at $t=0$. The only difference here is in the initial conditions. Instead of the general Eq. (27), in linear response, $\xi_{\mathrm{I}}-\xi_{\mathrm{II}}=\varepsilon \ll 1$, they become

$$c_L(0) = \langle\hat{T}_{L,0}^{(S)}\rangle(0) - \langle\hat{T}_{L,0}^{(S)}\rangle_{\mathrm{II}} \approx \frac{\varepsilon}{S}\,\mathrm{Tr}\{\hat{\rho}_{eq}^{\mathrm{II}}\hat{S}_Z(\hat{T}_{L,0}^{(S)} - \langle\hat{T}_{L,0}^{(S)}\rangle_{\mathrm{II}}\hat{I}^{(S)})\}. \tag{40}$$

Furthermore, $c_1(t)/c_1(0)$ reduces to the normalized longitudinal dipole equilibrium correlation function $C_\parallel(t)$,[33] that is,

$$C_\parallel(t) = \lim_{\varepsilon\to 0}\frac{c_1(t)}{c_1(0)} = \frac{1}{\chi_\parallel}\left[\beta^{-1}\left\langle\int_0^\beta \hat{S}_Z(0)\hat{S}_Z(t+i\lambda\hbar)d\lambda\right\rangle_{\mathrm{II}} - \langle\hat{S}_Z\rangle_{\mathrm{II}}^2\right] \approx \frac{1}{\chi_\parallel}\left[\frac{1}{2}\langle\hat{S}_Z(0)\hat{S}_Z(t) + \hat{S}_Z(t)\hat{S}_Z(0)\rangle_{\mathrm{II}} - \langle\hat{S}_Z\rangle_{\mathrm{II}}^2\right], \tag{41}$$

where

$$\chi_\parallel = \beta^{-1}\left\langle\int_0^\beta \hat{S}_Z(0)\hat{S}_Z(i\lambda\hbar)d\lambda\right\rangle_{\mathrm{II}} - \langle\hat{S}_Z\rangle_{\mathrm{II}}^2 \approx \langle\hat{S}_Z^2\rangle_{\mathrm{II}} - \langle\hat{S}_Z\rangle_{\mathrm{II}}^2 \tag{42}$$

is the normalized static susceptibility. According to linear-response theory,[33] having determined the one-sided Fourier transform $\tilde{C}_\parallel(\omega)=\int_0^\infty C_\parallel(t)e^{-i\omega t}dt$, we have the dynamic susceptibility $\chi_\parallel(\omega)=\chi'_\parallel(\omega)-i\chi''_\parallel(\omega)$ via[33]

$$\chi_\parallel(\omega)/\chi_\parallel = 1 - i\omega\tilde{C}_\parallel(\omega). \tag{43}$$

We have also the integral relaxation time, which is now the correlation time of $C_\parallel(t)$, viz.,[20]

$$\tau_{cor} = \tilde{C}_\parallel(0). \tag{44}$$

Yet another time constant characterizing the time behavior of $C_\parallel(t)$ is the effective relaxation time τ_{ef} defined by[20,34]

$$\tau_{ef} = -1/\dot{C}_\parallel(0) \tag{45}$$

[yielding precise information on the initial decay of $C_\parallel(t)$ in the time domain]. Just as the correlation time τ_{cor}, τ_{ef} may equivalently be defined in terms of the eigenvalues λ_k as

$$\tau_{ef} = \sum_{k=1}^{2S} u_{1,k}g_k \Big/ \sum_{k=1}^{2S} u_{1,k}g_k\lambda_k. \tag{46}$$

According to Eqs. (38) and (43), the dynamic susceptibility is a finite sum of Lorentzians, viz.,

$$\frac{\chi(\omega)}{\chi_\parallel} = \sum_{p=1}^{2S}\frac{c_p}{1+i\omega/\lambda_p}, \tag{47}$$

where $c_p=u_{1,p}g_p$. In the low- ($\omega\to 0$) and high- ($\omega\to\infty$) frequency limits, its behavior can be easily evaluated. Noting Eqs. (39) and (46), we have from Eq. (47), respectively, for $\omega\to 0$ and for $\omega\to\infty$,

$$\chi(\omega) \approx \chi_\parallel(1 - i\omega\tau_{cor} + \cdots), \quad \omega\to 0, \tag{48}$$

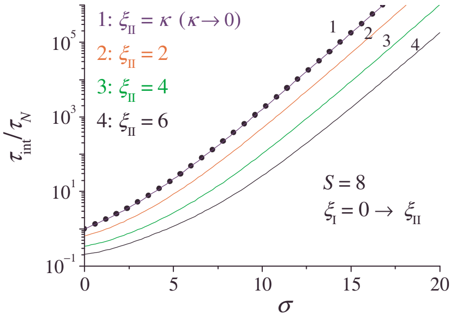

FIG. 1. (Color online) Nonlinear integral relaxation time $\tau_{\rm int}/\tau_N$ for the rise transient response as a function of the barrier parameter σ for the spin value $S=8$, $\xi_{\rm I}=0$, and various values of $\xi_{\rm II}=\kappa\to 0,2,4,6$. Solid lines: calculations from Eq. (58); circles: Eq. (60).

$$\chi(\omega)\sim\chi_{\parallel}(i\omega\tau_{ef})^{-1}+\cdots,\qquad \omega\to\infty. \tag{49}$$

We remark that the equilibrium averages $\langle\hat{S}_Z\rangle_{\rm I}$, $\langle\hat{S}_Z\rangle_{\rm II}$, and $\langle\hat{S}_Z^2\rangle_{\rm II}$ appearing in the above expressions can be expressed in terms of both the density matrix and phase space distribution as

$$\langle\hat{S}_Z\rangle_i=\sum_{m=-S}^{S}m\rho_m^i,\quad \langle\hat{S}_Z^2\rangle_i=\sum_{m=-S}^{S}m^2\rho_m^i, \tag{50}$$

$$\langle\hat{S}_Z\rangle_i=\left(S+\frac{1}{2}\right)(S+1)\int_{-1}^{1}zW_S^i(z)dz, \tag{51}$$

$$\langle\hat{S}_Z^2\rangle_{\rm II}=\left(S+\frac{1}{2}\right)(S+1)\int_{-1}^{1}\left[\left(S+\frac{3}{2}\right)z^2-\frac{1}{2}\right]W_S^{\rm II}(z)dz. \tag{52}$$

Here we have noted that the corresponding Weyl symbols of the operators $\hat{S}_Z$ and $\hat{S}_Z^2$ are $S_Z=(S+1)\cos\vartheta$ and $S_Z^2=(S+1)[(S+\frac{3}{2})\cos^2\vartheta-\frac{1}{2}]$, respectively.

V. ANALYTIC SOLUTIONS FOR THE RELAXATION TIMES

The matrix solution outlined above can be radically simplified for axially symmetric Hamiltonian (3) because the diagonal terms of the density matrix decouple from the nondiagonal ones. Hence, only the former partake in the time evolution. In order to see this we first transform the density matrix evolution equation into an evolution equation for its individual matrix elements. We have from Eq. (11) the following three-term differential-recurrence equation for the *diagonal* elements $\rho_m=\rho_{m,m}$ $(m=-S,-S+1,\ldots,S)$

$$\tau_N\frac{\partial\rho_m(t)}{\partial t}=p_m^-\rho_{m-1}(t)+p_m\rho_m(t)+p_m^+\rho_{m+1}(t), \tag{53}$$

where

$$p_m=S_{m,m-1}^+S_{m-1,m}^-+S_{m,m+1}^-S_{m+1,m}^+e^{(2m+1)(\sigma/S^2)+(\xi_{\rm II}/S)},$$

$$p_m^+=-S_{m,m+1}^-S_{m+1,m}^+,$$

$$p_m^-=-S_{m,m-1}^+S_{m-1,m}^-e^{(2m-1)(\sigma/S^2)+(\xi_{\rm II}/S)},$$

and

$$S_{m\pm 1,m}^{\pm}=\mp\sqrt{(S\mp m)(S\pm m+1)/2}.$$

Substitution of the equilibrium matrix element $\rho_m^{\rm II}=e^{(\sigma/S^2)m^2+(\xi_{\rm II}/S)m}/Z_S^{\rm II}$ with $Z_S^{\rm II}=\Sigma_{m=-S}^{S}e^{(\sigma/S^2)m^2+(\xi_{\rm II}/S)m}$ into the right-hand side of Eq. (53) renders it zero, namely,

$$p_m^-\rho_{m-1}^{\rm II}+p_m\rho_m^{\rm II}+p_m^+\rho_{m+1}^{\rm II}=0,$$

because of our ansatz that the equilibrium spin density matrix $\hat{\rho}_{eq}$ must render the collision kernel zero. Consequently, $\rho_m^{\rm II}$ is the stationary solution of Eq. (53).

In order to calculate the integral relaxation time defined by Eq. (34), we now introduce the functions $f_m(t)$ defined as

$$f_m(t)=\rho_m(t)-\rho_m^{\rm II}. \tag{54}$$

The $f_m(t)$ also satisfy Eq. (53). The initial conditions for $f_m(t)$, i.e., at $t=0$, are

$$f_m(0)=\rho_m^{\rm I}-\rho_m^{\rm II}. \tag{55}$$

Noting that

$$\langle\hat{S}_Z\rangle(t)-\langle\hat{S}_Z\rangle_{\rm II}=\sum_{m=-S}^{S}mf_m(t)$$

and

$$\langle\hat{S}_Z\rangle(0)-\langle\hat{S}_Z\rangle_{\rm II}=\langle\hat{S}_Z\rangle_{\rm I}-\langle\hat{S}_Z\rangle_{\rm II},$$

the normalized spectra of the relaxation function $\tilde{c}_1(\omega)/c_1(0)$ and the integral relaxation time are now given by [cf. Eq. (34)]

$$\frac{\tilde{c}_1(\omega)}{c_1(0)}=\frac{1}{\langle\hat{S}_Z\rangle_{\rm I}-\langle\hat{S}_Z\rangle_{\rm II}}\sum_{m=-S}^{S}m\tilde{f}_m(\omega), \tag{56}$$

$$\tau_{\rm int}=\frac{1}{\langle\hat{S}_Z\rangle_{\rm I}-\langle\hat{S}_Z\rangle_{\rm II}}\sum_{m=-S}^{S}m\tilde{f}_m(0), \tag{57}$$

where $\langle\hat{S}_Z\rangle_i=\Sigma_{m=-S}^{S}m\rho_m^i$. As shown in Appendix B, $\tilde{c}_1(\omega)/c_1(0)$ and $\tau_{\rm int}$ can be calculated analytically using continued fractions. In particular, we have

$$\tau_{\rm int}=\frac{2\tau_N}{\langle\hat{S}_Z\rangle_{\rm I}-\langle\hat{S}_Z\rangle_{\rm II}}\sum_{k=1-S}^{S}\frac{\sum_{m=k}^{S}(\rho_m^{\rm I}-\rho_m^{\rm II})\sum_{m'=k}^{S}(m'-\langle\hat{S}_Z\rangle_{\rm II})\rho_{m'}^{\rm II}}{[S(S+1)-k(k-1)]\rho_k^{\rm II}}. \tag{58}$$

Both the eigensolution Eq. (39) and the explicit Eq. (58) yield exactly the same numerical result. Thus, $\tau_{\rm int}$ for various nonlinear transient responses (such as the rise, decay, and rapidly reversing field transients) may be easily evaluated from Eq. (58). In linear response, i.e., transient relaxation between the states I and II with

$$\hat{H}_S^{\mathrm{I}} = \frac{\sigma}{S^2}\hat{S}_Z^2 + \frac{\xi_{\mathrm{II}}+\varepsilon}{S}\hat{S}_Z \quad \text{and} \quad \hat{H}_S^{\mathrm{II}} = \frac{\sigma}{S^2}\hat{S}_Z^2 + \frac{\xi_{\mathrm{II}}}{S}\hat{S}_Z$$

(ε is a small external field parameter), the initial condition for $f_m(t)$ becomes

$$f_m(0) = e^{(\sigma/S^2)m^2+[(\xi_{\mathrm{II}}+\varepsilon)/S]m}/Z_S^{\mathrm{I}} - e^{(\sigma/S^2)m^2+(\xi_{\mathrm{II}}/S)m}/Z_S^{\mathrm{II}} \approx \frac{\varepsilon}{S}(m - \langle\hat{S}_Z\rangle_{\mathrm{II}})\rho_m^{\mathrm{II}}. \tag{59}$$

Thus, Eq. (58) yields the correlation time τ_{cor} as

$$\tau_{cor} = \frac{2\tau_N}{\chi_\parallel}\sum_{k=1-S}^{S}\frac{\left[\sum_{m=k}^{S}(m-\langle\hat{S}_Z\rangle_{\mathrm{II}})\rho_m^{\mathrm{II}}\right]^2}{[S(S+1)-k(k-1)]\rho_k^{\mathrm{II}}}. \tag{60}$$

Equations (58) and (60) are valid for an *arbitrary* axially symmetrical potential $\hat{H}_S(\hat{S}_Z)$. The *particular* form of the potential is contained *only* in the equilibrium matrix elements of the density operator ρ_m^{II} and in the constants $\chi_\parallel$ and $\langle\hat{S}_Z\rangle_{\mathrm{II}}$.

We remarked above that the linear response has been previously studied by Garanin[26] and García-Palacios and Zueco[27] using the spin density matrix in the second order of perturbation theory. In that context they also gave analytic expressions for the linear-response integral relaxation time τ_{cor}, effective relaxation time τ_{ef}, and the longest relaxation time $\tau_\Delta \approx \lambda_1^{-1}$ for more general models of a quantum superparamagnet interacting with phonons, e.g., superimposed linear and bilinear spin-bath interactions with super-Ohmic damping. However, for the collision kernel given by Eq. (12) pertaining to the high temperature and weak coupling limit their results for τ_{cor} reduce to ours. Hence, we can also apply the general results for τ_{ef} and λ_1^{-1} given in Ref. 27. Thus, the effective relaxation time τ_{ef} defined as

$$\tau_{ef} = -\varepsilon S\partial_\varepsilon\langle\hat{S}_Z\rangle_{\mathrm{I}}|_{\varepsilon=0}\Big/\sum_{m=-S}^{S} m\dot{f}_m(0) \tag{61}$$

is

$$\tau_{ef} = \frac{2\chi_\parallel\tau_N}{\sum_{k=1-S}^{S}[S(S+1)-k(k-1)]\rho_k^{\mathrm{II}}}. \tag{62}$$

Furthermore, the approximate equation for the longest relaxation time $\tau_\Delta \approx \lambda_1^{-1}$ is

$$\tau_\Delta = \frac{2\tau_N}{\chi_\Delta}\sum_{k=1-S}^{S}\frac{\left[\sum_{m=k}^{S}(m-\langle\hat{S}_Z\rangle_{\mathrm{II}})\rho_m^{\mathrm{II}}\right]\left\{\sum_{m=-S}^{k-1}[\Delta - \mathrm{sgn}(m-m_b)]\rho_m^{\mathrm{II}}\right\}}{[S(S+1)-k(k-1)]\rho_k^{\mathrm{II}}}, \tag{63}$$

where m_b is the quantum number corresponding to the top of the barrier, $\Delta = \sum_{m=-S}^{S}\mathrm{sgn}(m-m_b)\rho_m^{\mathrm{II}}$, and

$$\chi_\Delta = \sum_{m=-S}^{S} m\,\mathrm{sgn}(m-m_b)\rho_m^{\mathrm{II}} - \left(\sum_{m=-S}^{S} m\rho_m^{\mathrm{II}}\right) \times \left[\sum_{m=-S}^{S}\mathrm{sgn}(m-m_b)\rho_m^{\mathrm{II}}\right].$$

For values of the field $\xi < \sigma$, the relative deviation of τ_Δ from λ_1^{-1} does not exceed 1%.[27]

The foregoing equations have been derived using the density matrix method. They can also be obtained using the phase space formalism.[9] For example, the effective relaxation time τ_{ef} from Eq. (62) can be written as

$$\tau_{ef} = 2\tau_N\frac{\langle\hat{S}_Z^2\rangle_{\mathrm{II}} - \langle\hat{S}_Z\rangle_{\mathrm{II}}^2}{\langle\hat{\mathbf{S}}^2 - \hat{S}_Z^2 + \hat{S}_Z\rangle_{\mathrm{II}}}, \tag{64}$$

where $\langle\hat{S}_Z\rangle_{\mathrm{II}}$ and $\langle\hat{S}_Z^2\rangle_{\mathrm{II}}$ are given by Eqs. (51) and (52) and

$$\langle\hat{\mathbf{S}}^2 - \hat{S}_Z^2 + \hat{S}_Z\rangle_{\mathrm{II}} = (S+1)\left(S+\frac{1}{2}\right)\int_{-1}^{1} \times\left[S(1-z^2)+\frac{1}{2}+z-\frac{3}{2}z^2\right]W_S^{\mathrm{II}}(z)dz. \tag{65}$$

Equation (64) is simply a quantum analog of the known equation for the effective relaxation time τ_{ef} of a classical superparamagnet[20]

$$\tau_{ef} = 2\tau_N\frac{\langle\cos^2\vartheta\rangle_{\mathrm{II}} - \langle\cos\vartheta\rangle_{\mathrm{II}}^2}{1-\langle\cos^2\vartheta\rangle_{\mathrm{II}}}. \tag{66}$$

VI. RESULTS

The nonlinear relaxation time τ_{int} for the rise transient response as a function of the anisotropy parameter σ and the spin value S is plotted in Figs. 1 and 2. They indicate a strong dependence of this time on the field (ξ_{II}), anisotropy (σ), and spin (S) parameters; in particular it decreases with increasing field strength ξ_{II}. For linear response, the correlation time τ_{cor} from Eq. (60) and the inverse smallest nonva-

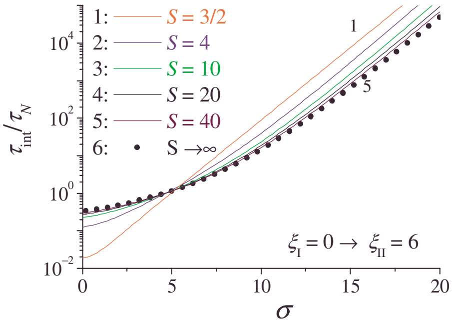

FIG. 2. (Color online) Nonlinear relaxation time τ_{int}/τ_N for the rise transient response as a function of the barrier parameter σ for $\xi_I=0$ and $\xi_{II}=6$ and various values of spin S. Solid lines: Eq. (58); circles: classical equation (A5).

nishing eigenvalue, $1/\lambda_1$, are plotted in Figs. 3 and 4 as a function of ξ_{II} and σ, respectively, for various values of S. Furthermore, τ_{cor} and $1/\lambda_1$ are also plotted in Figs. 5 and 6 as a function of S for various values of ξ_{II} and σ. It is apparent from Figs. 1–6 that for large S, the quantum solutions reduce to the corresponding classical ones but the quantum and classical solutions can disagree substantially for small S. Typical values of S for the quantum-classical crossover are ~10–40. The smaller the anisotropy σ the smaller the S required for convergence of the quantum equations to the classical ones. The behavior of τ_{cor} and $1/\lambda_1$ is similar only for small external fields. In a strong external field, $1/\lambda_1$ can diverge exponentially from τ_{cor} as for a classical uniaxial paramagnet.[20] This effect was discovered numerically by Coffey *et al.*[23] and later explained quantitatively by Garanin[24] (see also Ref. 20, Chap. 1 for details). He showed analytically that the contribution of relaxation modes other

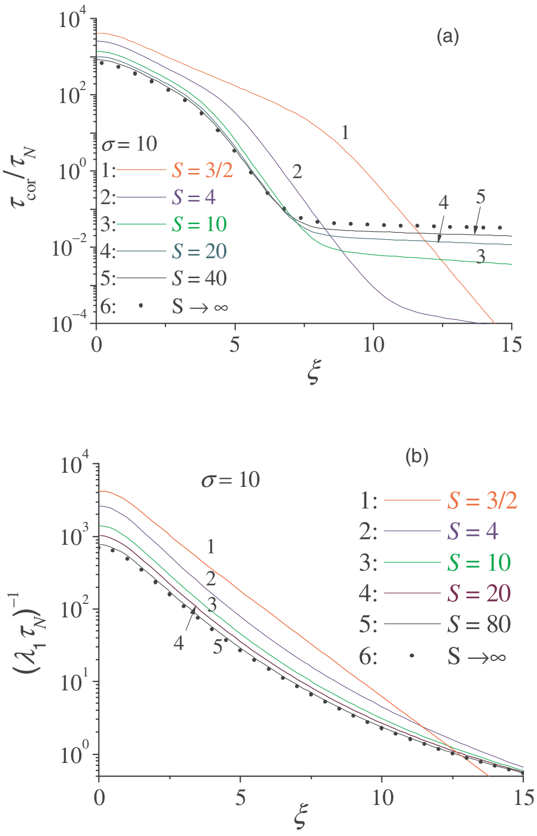

FIG. 3. (Color online) Correlation time τ_{cor}/τ_N (a) and inverse smallest nonvanishing eigenvalue, $1/\lambda_1$, of the system matrix **X** (b) vs the field parameter ξ for the barrier parameter $\sigma=10$ and various values of S. Filled circles: the classical limit.

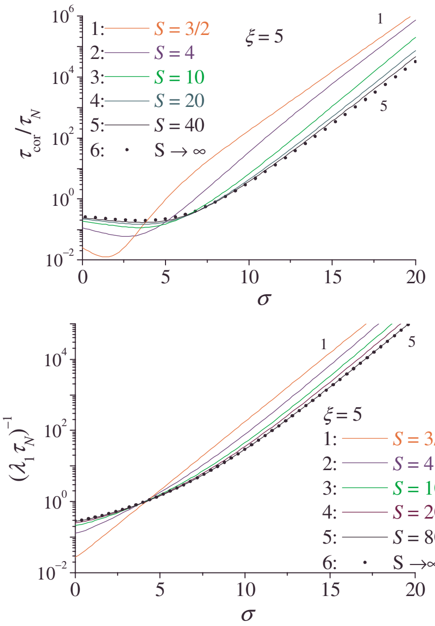

FIG. 4. (Color online) Correlation time τ_{cor}/τ_N (a) and inverse smallest nonvanishing eigenvalue, $1/\lambda_1$, (b) vs the barrier parameter σ for the field parameter $\xi=5$ and various values of S. Filled circles: the classical limit.

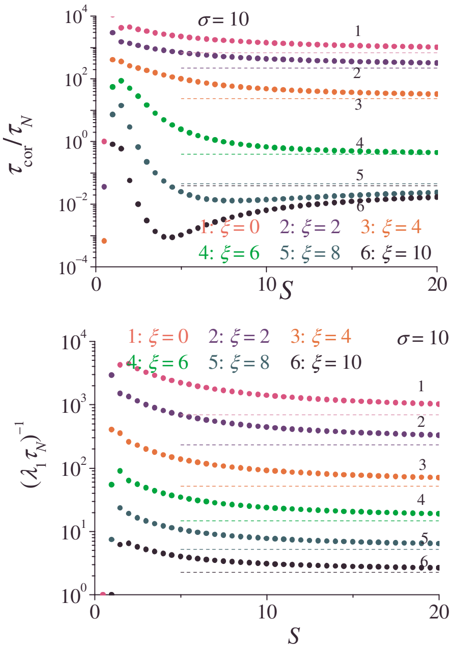

FIG. 5. (Color online) Correlation time τ_{cor}/τ_N (a) and inverse smallest nonvanishing eigenvalue, $1/\lambda_1$, vs the spin value S for barrier parameter $\sigma=10$ and different field parameter ξ. Dashed lines: the classical limit.

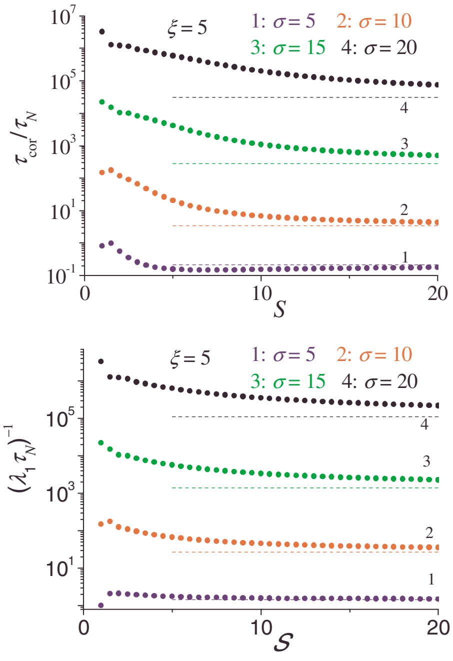

FIG. 6. (Color online) Correlation time τ_{cor}/τ_N (a) and inverse smallest nonvanishing eigenvalue, $1/\lambda_1$, vs the spin value S for field parameter $\xi=5$ and various values of the barrier parameter σ. Dashed lines: the classical limit.

than the overbarrier one becomes significant for high external fields due to population depletion of the shallower of the two potential wells of a bistable potential under the action of an external applied field.

In Figs. 7 and 8, we have plotted the real part of $\tilde{c}_1(\omega)/c_1(0)$ vs the normalized frequency $\omega\tau_N$ for the rise transient response, $\xi_{\mathrm{I}}=0\to\xi_{\mathrm{II}}\neq 0$. Here the Lorentzian

$$\frac{\tilde{c}_1(\omega)}{c_1(0)}\approx\frac{\tau_{\mathrm{int}}}{1+i\omega/\lambda_1} \tag{67}$$

is shown for comparison. These figures indicate that τ_{int} and λ_1 allow one to comprehensively describe the low-frequency behavior of the spectrum $\tilde{c}_1(\omega)/c_1(0)$. In the time domain, the single-mode approximation Eq. (67) amounts to assuming that the relaxation function $c_1(t)$ as determined by Eq. (38) (comprising $2S$ exponentials) may be approximated for $t>0$ by a *single* exponential. Consequently, the long time relaxation behavior of $\langle\hat{S}_Z\rangle(t)$ may be accurately approximated by a single exponential with relaxation time $T_1=1/\lambda_1$ and thus is governed by Bloch equation (4).

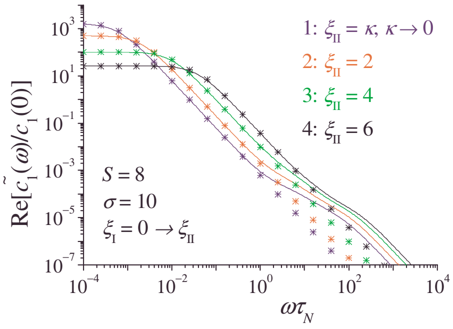

FIG. 7. (Color online) $\tilde{c}_1(\omega)/c_1(0)$ vs the normalized frequency $\omega\tau_N$ for the rise transient response for $S=8$, $\sigma=10$, $\xi_{\mathrm{I}}=0$, and various values of $\xi_{\mathrm{II}}=\kappa\to 0,2,4,6$. Solid lines: calculations from Eq. (32); stars: Eq. (67).

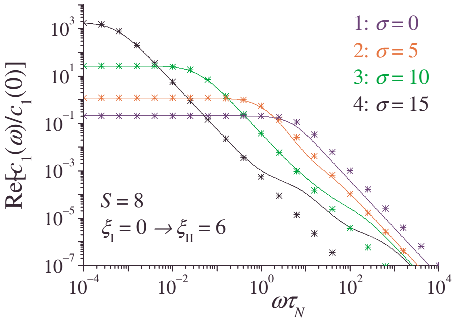

FIG. 8. (Color online) $\tilde{c}_1(\omega)/c_1(0)$ vs $\omega\tau_N$ for the rise transient response for $\xi_{\mathrm{I}}=0$, $\xi_{\mathrm{II}}=6$, $S=8$, and various values of the anisotropy parameter σ. Solid lines: calculations from Eq. (32); stars: Eq. (67).

In Figs. 9–11 we have plotted the real and imaginary parts of the dynamic susceptibility $\chi(\omega)$. Clearly two bands appear in the spectrum of the imaginary part $\chi''(\omega)$. The low-frequency band is due to the slowest ("overbarrier") relaxation mode. The characteristic frequency and the half-width of this band are determined by λ_1. The high-frequency band of $\chi''(\omega)$ is due to high-frequency modes corresponding to the eigenvalues λ_k $(k\geq 2)$. These individual "intrawell" modes are indistinguishable in the spectrum of $\chi''(\omega)$ appearing merely as a single high-frequency Lorentzian band. Just as the classical case,[20] λ_1 is sufficient to accurately predict the low-frequency part of $\chi(\omega)$ as well as the long time behavior of the equilibrium correlation function $C(t)$. Thus, if one is interested solely in the low-frequency region $(w\tau\leq 1)$, where the effect of the high-frequency modes may be ignored, the dynamic susceptibility $\chi(\omega)$ may be approximated as

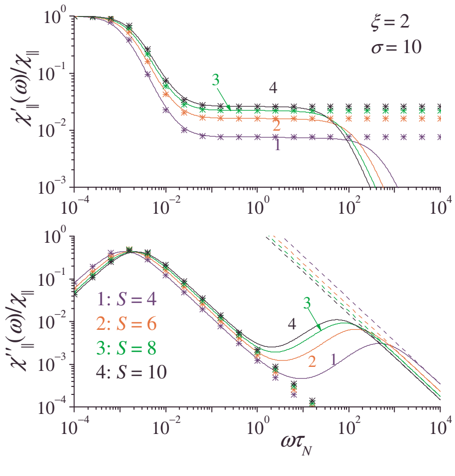

FIG. 9. (Color online) Real and imaginary parts of $\chi(\omega)$ vs $\omega\tau_N$ for field parameter $\xi=2$, the anisotropy parameter $\sigma=10$, and various values of spin S. Crosses are the single Lorentzian approximation, Eq. (68), while straight dashed lines are the high-frequency asymptote, Eq. (49).

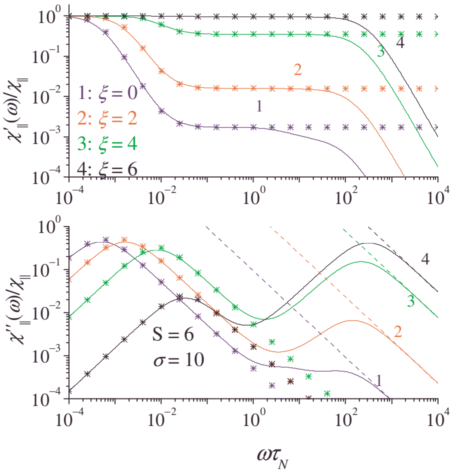

FIG. 10. (Color online) Real and imaginary parts of $\chi(\omega)$ vs $\omega\tau_N$ for the barrier parameter $\sigma=10$, $S=6$, and various values of field parameter ξ. Crosses are the single Lorentzian approximation, Eq. (68), while the straight dashed lines are the high-frequency asymptote, Eq. (49).

$$\frac{\chi(\omega)}{\chi} \approx \frac{1-\delta}{1+i\omega/\lambda_1} + \delta, \tag{68}$$

where δ is a parameter characterizing the contribution of the high-frequency modes which can be evaluated as[20,25]

$$\delta = \frac{\lambda_1\tau_{cor} - 1 - \tau_{cor}/\tau_{ef} + 1/(\lambda_1\tau_{ef})}{\lambda_1\tau_{cor} - 2 + 1/(\lambda_1\tau_{ef})}. \tag{69}$$

In order to verify the single Lorentzian approximation, we plot in Figs. 7–9 the real and imaginary parts of $\chi(\omega)$ calculated from the matrix solution and the approximate Eq. (68). It is apparent from Figs. 7–9 that at low frequencies no practical difference exists between the numerical solution and the single-mode approximation (the maximum relative deviation between the corresponding curves does not exceed a few percent). We remark in passing that García-Palacios and Zueco[27] have shown that a two mode approximation originally developed for classical systems[20,25] accurately describes the linear response of quantum superparamagnets at all frequencies of interest.

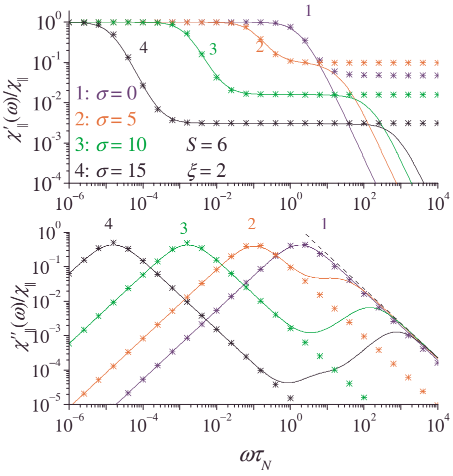

FIG. 11. (Color online) Real and imaginary parts of $\chi(\omega)$ vs $\omega\tau_N$ for $S=6$, for field parameter $\xi=2$, and various values of the barrier parameter σ. Crosses are the single Lorentzian approximation, Eq. (68), while straight dashed lines are the high-frequency asymptote, Eq. (49).

VII. CONCLUDING REMARKS

We have studied the transient nonlinear longitudinal relaxation of a quantum uniaxial superparamagnet of arbitrary spin S in the high temperature and weak spin-bath coupling limit. The principal result is that one may determine the transition from quantum elementary spin relaxation to the classical superparamagnetic relaxation pertaining to a giant spin as a function of the spin size S. Hence, one may accurately estimate the value of S (typically in the range 20–40) at which the crossover to classical superparamagnetic behavior takes place. Thus, one may assign a range of validity as a function of the spin size to the classical Néel-Brown treatment of a superparamagnetic particle with the simplest uniaxial anisotropy and Zeeman energy given in Appendix A. The relatively elementary calculation outlined above is of particular interest as a basis for future understanding of relaxation of spin systems characterized by nonaxially symmetrical Hamiltonians. For example, by extending it to nonaxially symmetric potentials one could study the transition of the relaxation from that of an elementary spin to molecular magnets ($S\sim 10$) to nanoclusters ($S\sim 100$), and to classical superparamagnetic particles ($S\geq 1000$). The extension to particular nonaxially symmetric spin systems such as biaxial, cubic, etc. would also allow one to include spin size effects in important technological applications of magnetic relaxation such as the reversal time of the magnetization, the switching and hysteresis curves, etc. In particular one could evaluate the temperature dependence of the switching fields and corresponding hysteresis loops via obvious spin size corrected generalizations of the known classical methods used in the analysis of the classical spin dynamics.

We have treated the longitudinal relaxation in two superficially distinct ways, viz., the phase space formalism embodied in the Wigner-Stratonovich bijective transformation and the density matrix in the second order of perturbation theory, with the high temperature and weak spin coupling limit being understood in each case. Thus, we have provided an essential check on the validity of both methods by explicitly demonstrating their equivalence. We emphasize that a very useful feature of the phase space representation is that existing powerful computational techniques for the Fokker-Planck equation may be extended to the quantum domain which also suggest new closed form quantum results via corresponding classical ones. For example, the integral and effective relaxation times, Eqs. (58) and (64), are clearly quantum analogs of the corresponding classical expressions (66) and (A5).

The relaxation function, its spectrum, and characteristic relaxation times as evaluated explicit pronounced nonlinear and quantum effects. The exact continued fraction solution yields in closed form the dependence of the longitudinal spin relaxation function on the spin size S, which is dominated by a single exponential having as time constant the longest relaxation time $1/\lambda_1$. Thus, a simple description of the long time behavior of the longitudinal relaxation function as Bloch equation (4) holds for the nonlinear response of a quantum superparamagnet for arbitrary spin S. In linear response, the approach so developed reproduces the results previously obtained by Garanin[26] and García-Palacios and Zueco.[27] We remark in passing that our approach can also be applied to the calculation of nonlinear ac stationary responses of quantum superparamagnets by generalizing the matrix continued fraction method of solution of the Fokker-Planck equation for classical spins driven by a strong ac field.[35] This will allow to treat quantum effects in the ac nonlinear response of quantum superparamagnets.[36] It has been shown experimentally[36] for the molecular magnet Mn_{12} characterized by $S=10$ that the behavior of the nonlinear susceptibility of quantum superparamagnets is qualitatively different from that of classical spin systems with $S \gg 1$.

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APPENDIX A: CLASSICAL LIMIT

In the classical limit, $S \to \infty$, Hamiltonian (3) corresponds to a free energy V of the form

$$\beta V(\vartheta) = -\sigma \cos^2 \vartheta - \xi \cos \vartheta. \tag{A1}$$

The distribution functions in the equilibrium states I and II are given by

$$W_i(z) = e^{\sigma z^2 + \xi_i z}/Z_i \quad (i = \mathrm{I}, \mathrm{II}),$$

where $z = \cos \vartheta$,

$$Z_i = \frac{1}{2}\sqrt{\frac{\pi}{\sigma}} e^{-\sigma h_i^2} \{\mathrm{erf}\, i[(1+h_i)\sqrt{\sigma}] + \mathrm{erf}\, i[(1-h_i)\sqrt{\sigma}]\}$$

is the partition function, $h_i = \xi_i/(2\sigma)$, and $\mathrm{erf}\, i(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{t^2} dt$ is the error function of imaginary argument. For arbitrary σ, Eq. (22) becomes in the classical limit, $S \to \infty$,

$$\tau_N \frac{\partial c_L(t)}{\partial t} = q_L c_L(t) + q_L^- c_{L-1}(t) + q_L^+ c_{L+1}(t) + q_L^{--} c_{L-2}(t) + q_L^{++} c_{L+2}(t), \tag{A2}$$

where $c_L(t) = \langle P_L(\cos \vartheta)\rangle(t) - \langle P_L(\cos \vartheta)\rangle_{\mathrm{II}}$, P_L are the Legendre polynomials,

$$q_L = -\frac{L(L+1)}{2}\left(1 - \frac{2\sigma}{(2L-1)(2L+3)}\right),$$

$$q_L^{\pm} = \mp \xi \frac{L(L+1)}{2(2L+1)},$$

$$q_L^{--} = -q_{L-1}^{++} = \frac{\sigma L(L+1)(L-1)}{(2L-1)(2L+1)}.$$

The detailed solution of Eq. (A2) is given in Ref. 20, Ch. 8. For $\sigma=0$, we have from Eq. (A2)

$$\frac{2\tau_N}{L(L+1)}\frac{\partial}{\partial t} c_L(t) + c_L(t) = \frac{\xi}{2L+1}[c_{L-1}(t) - c_{L+1}(t)], \tag{A3}$$

which is the known result for relaxation of a classical spin in a uniform field.[20,37] Recurrence equations (A2) can also be presented in the homogeneous matrix form

$$\dot{\mathbf{C}}(t) + \mathbf{X}_c \cdot \mathbf{C}(t) = 0, \tag{A4}$$

where the system matrix $\mathbf{X}_c$ is now infinite and five diagonal.

In the classical limit, the nonlinear integral relaxation time τ_{int} of the dipole relaxation function $c_1(t) = \langle \cos \vartheta \rangle(t) - \langle \cos \vartheta \rangle_{\mathrm{II}}$ is given by[20,29,30]

$$\tau_{\mathrm{int}} = \frac{2\tau_N}{\langle \cos \vartheta \rangle_{\mathrm{I}} - \langle \cos \vartheta \rangle_{\mathrm{II}}} \int_{-1}^{1} \frac{\Phi(z)\Psi(z) e^{-\sigma z^2 - \xi_{\mathrm{II}} z}}{1 - z^2} dz, \tag{A5}$$

where

$$\begin{aligned}\Phi(z) &= \int_{-1}^{z} [W_{\mathrm{I}}(z') - W_{\mathrm{II}}(z')] dz' \\ &= \frac{\pi^{1/2} e^{-\sigma h_{\mathrm{II}}^2}}{2\sigma^{1/2} Z_{\mathrm{II}}} \{\mathrm{erf}\, i[(z + h_{\mathrm{II}})\sqrt{\sigma}] + \mathrm{erf}\, i[(1 - h_{\mathrm{II}})\sqrt{\sigma}]\} \\ &\quad - \frac{\pi^{1/2} e^{-\sigma h_{\mathrm{I}}^2}}{2\sigma^{1/2} Z_{\mathrm{I}}} \{\mathrm{erf}\, i[(z + h_{\mathrm{I}})\sqrt{\sigma}] + \mathrm{erf}\, i[(1 - h_{\mathrm{I}})\sqrt{\sigma}]\},\end{aligned}$$

$$\begin{aligned}\Psi(z) &= \int_{-1}^{z} (z' - \langle z \rangle_{\mathrm{II}}) e^{\sigma(z'^2 + 2h_{\mathrm{II}} z')} dz' \\ &= \frac{1}{2\sigma}[e^{\sigma(z^2 + 2h_{\mathrm{II}} z)} - e^{\sigma(1 - 2h_{\mathrm{II}})}] \\ &\quad - e^{\sigma(1 - h_{\mathrm{II}}^2)} \frac{\pi^{1/2} \sinh(2\sigma h_{\mathrm{II}})}{2\sigma^{3/2} Z_{\mathrm{II}}} \{\mathrm{erf}\, i[(z + h_{\mathrm{II}})\sqrt{\sigma}] \\ &\quad + \mathrm{erf}\, i[(1 - h_{\mathrm{II}})\sqrt{\sigma}]\},\end{aligned}$$

$$\langle \cos \vartheta \rangle_i = \frac{e^{\sigma} \sinh(2\sigma h_i)}{\sigma Z_i} - h_i.$$

In linear response, the correlation time τ_{cor} can be expressed in the closed form as[20,25]

$$\tau_{cor} = \frac{2\tau_N}{Z_{\mathrm{II}}(\langle \cos^2 \vartheta\rangle_{\mathrm{II}} - \langle \cos \vartheta\rangle_{\mathrm{II}}^2)}\int_{-1}^{1} \times \left[\int_{-1}^{z} (z' - \langle \cos \vartheta\rangle_{\mathrm{II}}) e^{\sigma z'^2 + \xi_{\mathrm{II}} z'} dz'\right]^2 \times \frac{e^{-\sigma z^2 - \xi_{\mathrm{II}} z}}{1 - z^2} dz, \tag{A6}$$

which is in complete agreement with Eq. (60) in the limit $S \to \infty$.

APPENDIX B: CALCULATION OF THE INTEGRAL RELAXATION TIME

In algebraic transformations, it is more convenient to work with indexes ranging from 0 to $2S$. Hence, we introduce a new index n defined as $n = m + S$. Equation (53) can now be rearranged as

$$\tau_N \frac{\partial f_n}{\partial t} = p_n^- f_{n-1} + p_n f_n + p_n^+ f_{n+1}, \tag{B1}$$

where

$$p_n = -\frac{1}{2}(2S - n + 1)n - \frac{1}{2}(2S - n)(n + 1)e^{(2n - 2S + 1)(\sigma/S^2) + (\xi_{\mathrm{II}}/S)},$$

$$p_n^+ = \frac{1}{2}(2S - n)(n + 1),$$

$$p_n^- = \frac{1}{2}(2S - n + 1)n e^{(2n - 2S - 1)(\sigma/S^2) + (\xi_{\mathrm{II}}/S)}.$$

Now recurrence equations (B1) can also be presented in the homogeneous matrix form

$$\tau_N \dot{\mathbf{F}}(t) = \mathbf{\Pi} \cdot \mathbf{F}(t), \tag{B2}$$

where the vector $\mathbf{F}(t)$ and the system matrix $\mathbf{\Pi}$ are

$$\mathbf{F}(t) = \begin{pmatrix} f_0(t) \\ f_1(t) \\ f_2(t) \\ f_3(t) \\ \vdots \\ f_{2S}(t) \end{pmatrix},$$

$$\mathbf{\Pi} = \begin{pmatrix} p_0 & p_0^+ & 0 & 0 & \cdots & 0 \\ p_1^- & p_1 & p_1^+ & 0 & \cdots & 0 \\ 0 & p_2^- & p_2 & p_2^+ & \cdots & 0 \\ 0 & 0 & p_3^- & p_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & p_{2S} \end{pmatrix}. \tag{B3}$$

We remark that the system matrix $\mathbf{\Pi}$ has exactly the same eigenvalues as the system matrix $\mathbf{X}$ given by Eq. (29) plus an additional zero eigenvalue $\lambda_0 = 0$ corresponding to the thermal equilibrium state.

Clearly Eq. (B2) can be solved by the matrix methods described in Sec. III. However, we shall present an exact analytic solution in terms of continued fractions. Applying the general method of solution of inhomogeneous three term recurrence relations to the Fourier-Laplace transform of Eq. (B1),[20] we have

$$\tilde{f}_n(\omega) = \Delta_n(\omega) p_n^- \tilde{f}_{n-1}(\omega) + \tau_N (p_{n-1}^+)^{-1} \sum_{l=n}^{2S} \prod_{k=n}^{l} [p_{k-1}^+ \Delta_k(\omega)] f_l(0). \tag{B4}$$

Here $\Delta_n(\omega)$ are the continued fractions defined by the recurrence equation

$$\Delta_n(\omega) = [i\omega\tau_N - p_n - p_n^+ p_{n+1}^- \Delta_{n+1}(\omega)]^{-1}$$

for $0 \leq n \leq 2S$ and $\Delta_{2S+1}(\omega) = 0$. For $\omega = 0$, Eq. (B4) can be considerably simplified

$$\tilde{f}_n(0) = e^{[2(n-S)-1](\sigma/S^2) + (\xi/S)} \tilde{f}_{n-1}(0) - \frac{2\tau_N}{n(2S - n + 1)} \sum_{m=n-S}^{S} f_m(0), \tag{B5}$$

where we have noticed that $\Delta_n(0) = (p_{n-1}^+)^{-1}$. Because recurrence equations (B1) are not linearly independent, the determinant of the matrix $\mathbf{\Pi}$ from Eq. (B1) is zero ($\det \mathbf{\Pi} = 0$). Thus, the functions $\tilde{f}_n(0)$ can be determined only in terms of $\tilde{f}_0(0)$. In order to find $\tilde{f}_0(0)$, we can utilize the normalization properties of the density matrix, namely,

$$\sum_{m=-S}^{S} f_m(t) = \sum_{m=-S}^{S} (\rho_m(t) - \rho_m^{\mathrm{II}}) = 0,$$

so that

$$\sum_{m=-S}^{S} \tilde{f}_m(0) = 0. \tag{B6}$$

Consequently, Eqs. (B4) and (B6) yield the closed-form expression

$$\tilde{f}_0(0) = \frac{2\tau_N e^{\sigma - \xi_{\mathrm{II}}}}{Z} \sum_{k=1-S}^{S} \frac{\sum_{m=k}^{S} (\rho_m^{\mathrm{I}} - \rho_m^{\mathrm{II}}) \sum_{m'=k}^{S} \rho_{m'}^{\mathrm{II}}}{(S - k + 1)(k + S)\rho_k^{eq}}. \tag{B7}$$

By substituting Eqs. (B5) and (B7) into Eq. (56), we have the integral relaxation time as

$$\tau_{\mathrm{int}} = \frac{1}{\langle \hat{S}_Z\rangle_{\mathrm{I}} - \langle \hat{S}_Z\rangle_{\mathrm{II}}} \sum_{n=1}^{2S} n \tilde{f}_n(0). \tag{B8}$$

Equation (B8) can be written in the analytic form of Eq. (58). The spectrum $\tilde{c}_1(\omega)$ is

$$\frac{\tilde{c}_1(\omega)}{c_1(0)} = \frac{1}{\langle \hat{S}_Z\rangle_{\mathrm{I}} - \langle \hat{S}_Z\rangle_{\mathrm{II}}} \sum_{n=1}^{2S} n \tilde{f}_n(\omega). \tag{B9}$$

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