Longitudinal relaxation induced by colored noise

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Following the analytical results presented in our recent paper [Phys. Rev. A **46**, 6222 (1992)], we clarify the conditions leading to a single exponential decay of the longitudinal magnetization in a multilevel system. A direct expression of the longitudinal relaxation time is provided in terms of the transition rates induced by colored noise.

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Very recently, there has been a renewed interest in the topic of relaxation behavior of two-level systems [1–9] and, more generally, multilevel systems [1] induced by colored noise. The central issue has been represented by investigating the conditions under which a set of relaxation times can be defined. A remarkable limit is represented by the case in which a *dominant* relaxation time T^d exists, fairly exceeding the other ones, so that for long times a single exponential decay is found. A correct approach to the matter cannot have as a starting point the familiar treatment of second-order cumulant due to Redfield [10], since it *assumes* a time-scale separation between the microscopic time scale represented by the correlation time τ_c and the macroscopic time scale T_A (T_A is the time in which the observable A appreciably changes in the interaction representation). For short τ_c (white noise) the above assumption follows from the well known *sufficient* condition $H_1\tau_c \ll 1$ (H_1 is the fluctuating part of the total hamiltonian H) and the relaxation of any observable exhibits a Markovian behavior accounted for by the Redfield equations [10]. By increasing τ_c (colored noise), the breakdown of the time-scale separation *depends on the selected observable* and for some observables does not even occur [1]. Since the time evolution of the different observables of the system are usually intertwined, this regime of fluctuation cannot be conveniently handled by cumulant theory. The identification of the weakest conditions under which relaxation times exist is of remarkable interest for applications and some analysis avoiding the cumulant theory has been reported for cases of interest [1,7]. Here we consider the field of magnetic resonance where the subject of relaxation induced by microscopic fluctuations has been investigated extensively. Nonetheless, to the authors' best knowledge, identifying the weakest conditions under which relaxation times may exist seems to be an overlooked issue. In NMR in many cases the extreme weakness of the interactions warrants the condition $H_1\tau_c \ll 1$, so that the Redfield theory holds. We simply quote the case of quadrupolar relaxation of nuclei with $I=1$, e.g., ^{2}H, ^{6}Li, and ^{14}N, leading to monoexponential decay [11,12] and $I=\frac{3}{2}$, e.g., ^{23}Na, leading to biexponential decay if $\omega_0\tau_c \gg 1$, ω_0 being the Larmor frequency [13]. The Redfield theory is extensively employed also in cases such as the nuclear relaxation induced by paramagnetic centers, where the strong dipolar coupling can make the time-scale separation questionable [14]. From the standpoint of electron spin resonance the topic of relaxation times has been limited for a long time to the evaluation of the transverse relaxation time T_2, since the longitudinal relaxation time T_1 was hardly accessible due to technical limitations. However, more recently, techniques able to detect relaxation phenomena partly [15] or fully [16] governed by spin-lattice relaxation have been developed. The character of T_2 is not robust, since its rigorous definition becomes doubtful for $H_1\tau_c \gg 1$. Instead, it has been recently proven under general conditions that the time-scale separation between the longitudinal relaxation and τ_c holds for arbitrary fluctuation regime provided that the mild condition $H_1/\omega_0 < 0.1$ holds [1]. The development of T_1-oriented techniques discloses new opportunities. It allows studies of extended time scales, T_1 usually being longer than T_2, and allows the investigation of the correlation functions $C(t)$ for times $t \approx \omega_0^{-1}$ whereas T_2-oriented techniques look at the *area* of $C(t)$ [10]. One interesting case is represented by complex systems with *multiple microscopic time scales,* e.g., polymers, where cooperativity is believed to play a major role, deviations of $C(t)$ from exponentiality are usually found and the separation of microscopic and macroscopic time scales must be examined carefully [17].

The above discussion points out that in magnetic resonance in the regime $H_1\tau_c \gg 1$ *little is known* about the weakest constraints under which selected observables of the system of interest relax with Markovian behavior, whereas the long correlation times found in cases of current interest (undercooled phases and glasses, polymers, biomaterials) demand the development of spectroscopies with extended observation time.

These remarks motivate the present Brief Report, the purpose of which is twofold: to further pursue the analysis of [1] on longitudinal relaxation of multiple level systems to identify the weakest conditions under which longitudinal relaxation times can be defined with possibly a dominant term $T_1 \equiv T^d$, and to provide practical expressions for cases of wide interest in the electron-spin-

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resonance (ESR) case.

In [1] the system of interest was modeled as an electron spin $S=\frac{1}{2}$ interacting with a nuclear spin I. The study was concerned with the characterization of the separation between the time scales of the relaxation of the electron magnetization (T) and the correlation time of the fluctuations causing the relaxation (τ_c). For large time-scale separation explicit expressions of the relaxation times were derived by developing a proper coarse-graining procedure on a scale Δt such as $T \gg \Delta t \gg \tau_c$.

For the transverse part of the magnetization, the time-scale separation is dictated by

$$H_1 \tau_c \ll 1 \ . \tag{1}$$

Differently, for the longitudinal component of the magnetization, the time-scale separation is governed by the inequality

$$H_1/\omega_0 \ll 1 \ . \tag{2}$$

The latter condition is much weaker than Eq. (1), since it is independent of the correlation time τ_c.

In [1] a general expression for the longitudinal relaxation time T_1 has been given. The model Hamiltonian takes the form

$$H = H_0 + H_1(\Omega) \ , \tag{3}$$

where H_0 is the part of the Hamiltonian independent of the fluctuating variable Ω. Its explicit form is

$$H_0 = \omega_0 S_z + \omega_I S_z I_z \tag{4a}$$

and it is appropriate for a magnetic species with electron spins S (we assume $S=\frac{1}{2}$) interacting with a nucleus with arbitrary spin I. ω_0 and ω_I are the Zeeman and hyperfine frequencies, respectively. The coupling with the fluctuating variable is expressed by

$$H_1(\Omega) = \boldsymbol{\omega}_0(\Omega)\cdot\mathbf{S} + \mathbf{S}\cdot\underline{\omega}_I(\Omega)\cdot\mathbf{I} = \sum_{\substack{\mu=-1,0,1 \\ \alpha=-1,0,00,1}} \omega_{\mu\alpha}(\Omega) S_\mu I_\alpha \ . \tag{4b}$$

$\boldsymbol{\omega}_0(\Omega)$ and $\underline{\omega}_I(\Omega)$ are a vector and a matrix, respectively, with elements depending on the stochastic variable Ω. No particular forms for $\boldsymbol{\omega}_0(\Omega)$ and $\underline{\omega}_I(\Omega)$ are assumed. In the second line of Eq. (4b) the following definitions have been introduced:

$$S_0 = S_z \ , \qquad S_{\pm 1} = S_x \pm i S_y \ , \tag{5a}$$

$$I_0 = I_z \ , \qquad I_{\pm 1} = I_x \pm i I_y \ . \tag{5b}$$

The symbol 00 labels the identity in the space of the nuclear states. It is assumed that

$$\langle \boldsymbol{\omega}_0(\Omega) \rangle = \langle \underline{\omega}_I(\Omega) \rangle = 0 \ , \tag{6}$$

where the angular brackets denote an average on the values of the stochastic variable Ω. We can always reduce the problem at hand to the form of Eq. (6), by including in H_0 the average value $\langle H_1(\Omega) \rangle$.

In [1] it is assumed

$$\omega_0 > \omega_I, [\boldsymbol{\omega}_0(\Omega)]_i, [\underline{\omega}_I(\Omega)]_{ij} \ , \tag{7a}$$

$$\beta\omega_0, \beta\omega_I \ll 1 \ , \tag{7b}$$

where $[\boldsymbol{\omega}_0(\Omega)]_i$ and $[\underline{\omega}_I(\Omega)]_{ij}$ are the generic elements of $\boldsymbol{\omega}_0(\Omega)$ and $\underline{\omega}_I(\Omega)$, respectively, and $\beta = \hbar/kT$; $\hbar$ is the Planck constant divided by 2π, k is the Boltzmann factor, and T is the absolute temperature.

In [1] the averaged longitudinal magnetization was studied:

$$\bar{S}_z(t) = \mathrm{Tr}_{\{S,I\}}\{\rho_0 \langle S_z(t) \rangle\} \ , \tag{8}$$

where a trace operation on the electron and nuclear states is performed weighted by ρ_0. ρ_0 characterizes the initial nonequilibrium state of the spin system, being represented in [1] by the rotated magnetization of π radians with respect to the thermal equilibrium value. On the coarse-grained scale $\Delta t > \omega_0^{-1}$, $\bar{S}_z(t)$ was found to decay with a single relaxation time T_1 given by

$$\frac{1}{T_1} = \frac{1}{2I+1} \sum_{\substack{m=-I,I \\ \mu_1=\pm 1}} \mathrm{Tr}_{\{I\}} \Bigg\{ 2 \sum_{\alpha,\beta=0,00} C_{-\mu_1\alpha;\mu_1\beta}\{\mu_1[\omega_0 + (m\omega_1)]\} I_\alpha I_\beta P_m + \sum_{\alpha_1=\pm 1} \big(C_{-\mu_1-\alpha_1;\mu_1\alpha_1}\{\mu_1[\omega_0 + (m-\alpha_1/2)\omega_1]\} I_{-\alpha_1} P_m I_{\alpha_1} + C_{-\mu_1-\alpha_1;\mu_1\alpha_1}\{\mu_1[\omega_0 + (m+\alpha_1/2)\omega_1]\} I_{\alpha_1} P_m L_{\alpha_1} \big) \Bigg\} \ , \tag{9}$$

where

$$C_{\alpha,\beta;\gamma,\delta}(s) = \int_0^\infty ds \exp[is\tau] \langle \omega_{\alpha,\beta}(t+\tau) \omega_{\gamma,\delta}(t) \rangle \ . \tag{10}$$

Equation (9) is based on Eqs. (7) and is correct at second order with respect to the amplitude of the fluctuating fields.

The inequalities expressed by Eqs. (7) need some comment. In Eq. (7a) the small amplitude of the fluctuating fields $[\boldsymbol{\omega}_0(\Omega)]_i$ and $[\underline{\omega}_I(\Omega)]_{ij}$ with respect to ω_0 ensures

the separation between the time scale T_1, on which $\bar{S}_z(t)$ relaxes, and the microscopic time scale denoted by the correlation time τ_c [see Eq. (2)]. Furthermore, the condition $\omega_0 > \omega_I$ and the assumed high temperature [Eq. (7b)] were enough to guarantee a single exponential decay of $\bar{S}_z(t)$. In [1] the different roles of these latter positions were not investigated.

In this Brief Report we prove that the relaxation of $\bar{S}_z(t)$ may be described at long times by a single exponential with time constant T_1 under two distinct premises: case A finite temperature, $\omega_0 > \omega_I$; case B high temperature, more precisely $\beta\omega_I \ll 1$ and initial thermal equilibrium of the nuclear multiplet.

It is understood that the time-scale separation condition [Eq. (2)] is valid. The derivation is based only on quantum-mechanical arguments, proving that our conclusions are independent of stochastic assumptions. As in [1], we are interested in slow fluctuations, i.e., those with correlation time τ_c longer than ω_0^{-1}.

It is found that the complex expression Eq. (9), derived by using stochastic arguments, may be replaced by the simpler form

$$\frac{1}{T_1} = \sum_{m_1, m_2 = -I}^{I} \rho_{+m_1} \Gamma_{+m_1 \to -m_2} + \rho_{-m_2} \Gamma_{-m_2 \to +m_1} , \tag{11}$$

where $\Gamma_{+m_1 \to -m_2}$ is the transition rate from the level characterized by $S_z = +\frac{1}{2}$, $I_z = m_1$ to the level $S_z = -\frac{1}{2}$, $I_z = m_2$ [10] and $\rho_{\pm m}$ is a Boltzmann weight factor appropriate for levels belonging to the same multiplet, namely, levels with the same electron spin number:

$$\rho_{\pm m} = \begin{cases} \dfrac{\exp[\mp \beta m \omega_I / 2]}{\displaystyle\sum_{n=-I}^{I} \exp[\mp \beta n \omega_I / 2]} , & \text{case A} \\ \dfrac{1}{2I+1} , & \text{case B} . \end{cases} \tag{12}$$

With a view to evaluating Eq. (11) in practical cases, stochastics must be reintroduced and one finds for the semiclassical Hamiltonian $H_1(\Omega)$ [Eq. (4b)] the following expression for the transition rate:

$$\begin{aligned} \Gamma^{SC}_{+m_1 \to -m_2} = {} & \delta_{m_1, m_2 - 1} [[I(I+1) - m_2^2 + m_2](C_{+,-;,-,+}\{-[\omega_0 + (m_2 - \tfrac{1}{2})\omega_I]\} + C_{+,+;,-,-}\{-[\omega_0 + (m_2 - \tfrac{1}{2})\omega_I]\})] \\ & + \delta_{m_1, m_2 + 1} [[I(I+1) - m_2^2 - m_2](C_{+,-;-,+}\{-[\omega_0 + (m_2 + \tfrac{1}{2})\omega_I]\} + C_{+,+;-,-}\{-[\omega_0 + (m_2 + \tfrac{1}{2})\omega_I]\})] \\ & + 2\delta_{m_1, m_2} [m_2^2 C_{+,0;-,0}\{\omega_0 + m_2\omega_I\} + C_{+,00;-,00}\{\omega_0 + m_2\omega_I\} \\ & + m_2 (C_{+,0;-,00}\{\omega_0 + m_2\omega_I\} + C_{+,00;-,0}\{\omega_0 + m_2\omega_I\})] . \end{aligned} \tag{13}$$

For high temperatures ($\beta\omega_I \ll 1$) and $\omega_0 > \omega_I$, replacing the above expression in Eq. (11) recovers Eq. (9). For finite temperatures, the semiclassical, stochastic character of $H_1(\Omega)$ implies $\Gamma^{SC}_{p \to q} = \Gamma^{SC}_{q \to p}$, namely, $T \to \infty$. This makes questionable the direct replacement of $\Gamma_{p \to q}$ with $\Gamma^{SC}_{p \to q}$ in Eq. (11). This flaw is usually removed by identifying the quantum spectral densities $C(\omega)$ appearing in $\Gamma_{p \to q}$ with $C(\omega)^{SC} \exp[\hbar\omega / 2kT]$, leading to the detailed balance condition and therefore to the correct thermal equilibrium [10].

To prove Eq. (11), we consider $[\omega_0(\Omega)]_i$ $[\underline{\omega}_I(\Omega)]_{ij}$ as quantum bath variables so that H_1 describes a quantum coupling between the spin system and a thermal bath accounted for by the Hamiltonian H_b. In this frame the average $\langle\ \rangle$ is interpreted as a trace over the degrees of freedom of the bath weighted by its equilibrium density matrix ρ_b. Equation (8) can be rewritten as

$$\begin{aligned} \bar{S}_z(t) &= \mathrm{Tr}_{\{S,I\}}\{\rho_0 \langle S_z(t) \rangle\} \\ &= r_+ \mathrm{Tr}_{\{I\}}\{\rho_+ \langle S_z^+(t) \rangle\} \\ &\quad + r_- \mathrm{Tr}_{\{I\}}\{\rho_- \langle S_z^-(t) \rangle\} , \end{aligned} \tag{14}$$

where $X^{\pm} = \langle \pm | X | \pm \rangle$ and $|\pm\rangle$ are the two eigenvectors of S_z with eigenvalues $\pm\frac{1}{2}$ and

$$\begin{aligned} r_\pm &= \frac{\mathrm{Tr}_{\{I\}}\{\langle \pm | \rho_0 | \pm \rangle\}}{\mathrm{Tr}_{\{S,I\}}\{\rho_0\}} , \\ r_+ + r_- &= 1 , \end{aligned} \tag{15}$$

and

$$\rho_\pm = \frac{\langle \pm | \rho_0 | \pm \rangle}{\mathrm{Tr}_{\{I\}}\{\langle \pm | \rho_0 | \pm \rangle\}} . \tag{16a}$$

Let us assume for the moment

$$\rho_\pm = \frac{\exp\left[\mp \dfrac{\beta\omega_I}{2} I_z\right]}{\displaystyle\sum_{m=-I}^{I} \exp\left[-\frac{\beta\omega_I}{2} m\right]} , \tag{16b}$$

namely, initial internal equilibrium of the multiplet. Let us define the projector operators $P_\pm$ as

$$P_\pm X = \mathrm{Tr}_{\{I\}}\{\rho_\pm \langle X \rangle\} \tag{17}$$

so that Eq. (14) becomes

$$\bar{S}_z(t) = = r_+ P_+ S_z^+(t) + r_- P_- S_z^-(t) . \tag{18}$$

At second order in H_1, the cumulant expansion, outlined

in [1], delivers the equations of motion for $P_{\pm}S_z^{\pm}(t)$. In the cases of interest A and B they take the form

$$\frac{\partial}{\partial t}P_{\pm}S_z^{\pm}=\mathcal{R}P_{\pm}S_z^{\pm}\ , \tag{19}$$

where

$$\mathcal{R}=\int_0^{\infty}d\tau P_{\pm}\{H_1^{(0)\times}(t)H_1^{(0)\times}(t-\tau)\}\ , \tag{20}$$

$A^{\times}B=AB-BA$; the superscript (0) denotes the interaction representation with respect to H_0 (see [1] for details). Equation (19) states that $P_+S_z^+(t)$ and $P_-S_z^-(t)$ exhibit the same relaxation behavior. From Eqs. (18)–(20), it is found that the relaxation of $\bar{S}_z(t)$ is described by

$$\frac{\partial}{\partial t}\bar{S}_z(t)=-\frac{1}{T_1}[\bar{S}_z(t)-\bar{S}_z(\infty)]\ , \tag{21}$$

where T_1 is given by Eq. (11) and $\Gamma_{p\to q}$ by the familiar Fermi golden rule [10].

For the case A the above results can be extended to arbitrary initial conditions, i.e., it is not required that the nuclear multiplet be in initial internal equilibrium. In fact, the thermalization of the multiplet takes place with rates

$$\Gamma_{\pm m_1\to\pm m_2}\approx\Delta^2\tau_c/(\omega_1^2\tau_c^2+1)$$

much higher than the rates between the multiplets

$$\Gamma_{\mp m_1\to\pm m_2}\approx\Delta^2\tau_c/(\omega_0^2\tau_c^2+1)\ ,$$

being $\omega_I,\Delta,\tau_c^{-1}<\omega_0$, where Δ is the order of magnitude of H_1. So, for $t\gg 1/\Gamma_{\pm m_1\to\pm m_2}$, during the long-time relaxation regime of $\bar{S}_z(t)$, the nuclear multiplet is thermalized.

The above results point out that, in the regime of slow fluctuations, i.e., $\omega_0\tau_c>1$, a single exponential decay of $\bar{S}_z(t)$ is expected for either small hyperfine coupling ($\omega_I\ll\omega_0$) (implying rapid thermalization within the nuclear multiplet), or high temperature (implying equal transition rates within the nuclear multiplet), or both. For finite temperature *and* hyperfine splitting ω_I comparable to the Larmor frequency ω_0, a single exponential decay cannot be expected, even if the time-scale separation, dictated by Eq. (2), allows one to resort to the cumulant expansion. The multiexponential decay of $\bar{S}_z(t)$ must be ascribed to the comparable rates of the relaxation processes involving states with the same electron spin state (intramultiplet relaxation) and the relaxation processes involving states with different electron spin state (intermultiplet relaxation). In the case of finite temperature and $\omega_0>\omega_I$ (case A) the former are faster than the latter, provided that $\omega_0\tau_c>1$.

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