Relaxation induced by colored noise. II. Homogeneous and heterogeneous correlation loss

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The relaxation of a two-level system under the influence of multiple stochastic fields with finite correlation time τ_c is investigated. Both dichotomic and Gaussian noises are considered with strong or negligible mutual correlations. The fluctuation regimes of the noises are not assumed to be equal, as is customarily done. By extending our previous findings [Phys. Rev. A **46**, 6222 (1992)] the dominance of a single longitudinal relaxation time T_1 is proven for most of the fluctuation regimes, provided that the fluctuating fields have smaller amplitudes Δ_i than the Larmor frequency ω_0. The key role of the ratio $\sum_i \Delta_i^2/\omega_0^2$ to provide an upper bound of the relative error between the exact value of T_1 and its second-order cumulant expansion is shown. The crossover between the heterogeneous and the homogeneous relaxation, depending on the observation time, is investigated. In the case of a continuous distribution of relaxation times the generalized Langevin equation yields the correct behavior in terms of a *finite* number of exponential decays. Finally, a counterexample to the usual belief concerning the independence of T_1 from fluctuations occurring along the direction of the static magnetic field is presented.

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I. INTRODUCTION

The relaxation phenomena induced by stochastic fluctuations on atomic systems have attracted renewed interest in recent years [1–18]. The question in hand is a paradigm of the most general case dealing with the time evolution of a system of interest, the "atom," coupled to a thermal bath. Stochastic models depict the bath by introducing a suitable set of classical random variables, which are "colored" if their correlation time τ_c is finite. Customarily, the attention is directed to the time dependence of atomic populations and coherences (Schrödinger picture) or ensemble averaged atomic observables (Heisenberg picture). These quantities are often associated with the stochastic theory of spectroscopic lines [18–22] and a thorough discussion of the relationship between the nonlinear response of a multilevel atom and the relaxation induced by colored noise has been recently reported [20].

With a view to working out tractable models, the atom is often assumed to be a simple two-level system or, equivalently, a fictitious spin $S=\frac{1}{2}$ precessing in a static magnetic field $\mathcal{H}_0$ with Larmor frequency $\omega_0=\gamma\mathcal{H}_0$ (γ is the magnetogyric factor). Nonetheless, the more realistic case of multilevel atoms has also been discussed [16,17,20].

The drastic simplifications introduced in the description of the atomic system allow one to investigate the relaxation governed by complex stochastic perturbations often modeled by multiple random fields. Studies have been reported dealing with uncorrelated Gaussian noise [3–6,9,11], uncorrelated dichotomic noise [8,9,11], and correlated dichotomic noise [16]. Several papers [2,4,5,9,12,13,16] have been devoted to the possible violation of the standard inequality $T_2 \le 2T_1$, which is well known from textbooks [21]. An analysis of this intriguing topic will be presented elsewhere [23].

Relaxation regimes, which are deprived of the "natural" motion of the observable, i.e., the motion in the absence of any external disturbances, are usually expressed in terms of a sum of exponentials with a spread of decay constants. Identifying the weakest conditions, which ensure at long times the dominance of a *single* decay constant, is a crucial issue in many spectroscopic schemes [20]. This topic, which seems to be overlooked in the current literature, has been reported in Refs. [16,17]. It is usually stated that, if the amplitudes of the random fields Δ_i are smaller than the fluctuation rate γ, the relaxation of an atomic variable A occurs on a time scale T_A, which is longer than $\tau_c=1/\gamma$. This establishes a separation between the microscopic time scale (τ_c) and the macroscopic one (T_A). According to Ref. [20], the A variable will be called a *slow* variable.

In Refs. [16,17] the relaxation of a spin $S=\frac{1}{2}$ coupled both to the static magnetic field and to one unlike spin I is discussed. The coupling includes random components of amplitudes Δ_i, characterized by equal fluctuation rates γ. In [16] in the high temperature limit ($\omega_I<\omega_0 \ll \hbar^{-1}kT$, where ω_I is the hyperfine coupling constant, k the Boltzmann constant, and T the temperature) it is shown that (i) the inequality $\Delta \ll \gamma$ is only a *sufficient* condition to ensure that a variable is slow and (ii) slow variables of both two-level and *multilevels* systems may be explicitly identified provided that the weak condition

$$\frac{\sum_i \Delta_i^2}{\max\{\omega_0^2,\gamma^2\}} \ll 1 \tag{1.1}$$

is fulfilled. The sum is performed on all the random fields

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Δ_i acting on the atom. Equation (1.1) is worth noting in that for slow fluctuations ($\gamma < \omega_0$) it becomes independent of the fluctuation rate and depends only on the ratio $(\Delta/\omega_0)^2$. In [16] particular attention was paid to the comparison between T_1 and its second-order cumulant expansion T_1'' ($T_1'' \propto \Delta_i^{-2}$). The relative error between T_1 and T_1'' was bounded by

$$\left| \frac{T_1''^{-1} - T_1^{-1}}{T_1^{-1}} \right| < 2 \frac{\sum_i \Delta_i^2}{\max\{\omega_0^2, \gamma^2\}} \tag{1.2}$$

for $\Delta_i < \omega_0$.

With a view to generalizing the results of [16], the slow character of $\bar{S}_z$, the averaged projection of the fictitious spin along the static magnetic field $\mathcal{H}_0$, was investigated in [17]. By writing proper master equations ensuring detailed balance, a single relaxation time T_1 was found at a long time, provided that Eq. (1.1) is supplemented with one of the following assumptions: case (a), finite temperature and $\omega_0 > \omega_I$; case (b): $\hbar\omega_I/KT \ll 1$ and initial internal equilibrium of the hyperfine multiplet. As in [16], the discussion in [17] was limited to the case of random fields with equal or comparable fluctuation rates. For multilevel atoms ($\omega_I \neq 0$) case (a) holds only in the region $\gamma < \omega_0$. A minor constraint assumed in [16,17] is the inequality $T_1 \min\{\omega_0, \omega_I\} \gg 1$. In the special case $\omega_I = 0$ the above inequality reduces to $T_1\omega_0 \gg 1$.

The present paper deals with two-level systems ($\omega_I = 0$) and case (a) follows immediately in the presence of random fields with equal fluctuation rates. Having defined a set of mild conditions ensuring both the existence of a *single* relaxation time T_1 and *the correct thermodynamical equilibrium,* we evaluate the relaxation behavior in a number of cases in the framework of stochastic theory. This choice is motivated by the remark that stochastics provides an effective tool to evaluate T_1 in practical cases. The price to pay is that the temperature dependence of the parameters describing the stochastic "bath" is absent and, most important, that the correct thermodynamic destination is not ensured. However, these two remarks are not influential in the present work since (i) as usually done in virtually all the related literature, we will content ourselves with describing the stochastic bath in terms of phenomenological parameters and (ii) our calculations include only the relaxation times and not the equilibrium state.

The task of the present paper is to present in an integrated way a thorough analysis of the range of validity of Eqs. (1.1) and (1.2), by discussing four different kinds of fluctuations, namely, uncorrelated Gaussian, uncorrelated dichotomic, correlated Gaussian, and correlated dichotomic noise. The fluctuations will be thought of as random fields ω_i ($i = x,y,z$) acting along the three Cartesian axes on a two-level system. The z axis is along the static magnetic field $\mathcal{H}_0$. Particular attention will be given to the case of uncorrelated fields ω_i ($i = x,y,z$), where the time scale separation will be investigated in the general case $\gamma_x \neq \gamma_y \neq \gamma_z$ to test Eqs. (1.1) and (1.2) beyond their assessed range of validity ($\gamma_x = \gamma_y = \gamma_z$).

The above models are richer than the usual ones, which assume either $\omega_z = 0$ (transverse fluctuations) [3,6,9] or, more frequently, $\gamma_x = \gamma_y = \gamma_z$ [3–6,9]. Releasing the condition $\gamma_x = \gamma_y = \gamma_z$ is a central point of this paper. It discloses a path to investigate the nonergodic, heterogeneous relaxation of the atomic variable. In the present context "nonergodic" means that, on the time scale of the relaxation time T_A, the representative point of the observable of interest A is not able to explore all the space spanned by the atom-bath states. In particular, the limit $\gamma_z \ll \gamma_x, \gamma_y$ takes into account the case of a slow random modulation of the level spacing of the atom $\omega_0 + \omega_z$ in the presence of rapid transverse fluctuations [24]. This model mimics some features of the relaxation behavior of particles embedded in environments which are slowly fluctuating, such as supercooled fluids, glasses, or macromolecules. For such systems during the observation time T_A, some degrees of freedom of the bath are frozen in (ω_z if $\gamma_z \ll 1/T_A$), whereas others are still active ($\omega_{x,y}$ if $\gamma_{x,y} \gg 1/T_A \gg \gamma_z$) [25]. Loosely speaking, ω_z models the so-called slow α relaxation, whereas $\omega_{x,y}$ the fast β relaxation [26]. Disorder resulting from fluctuations of the site energy is the dominant type of disorder in random organic media composed of a single molecular species. The case of a walker hopping across a lattice whose sites have Gaussian-distributed energies has been considered by Bassler and co-workers to study both viscous flow and charge transport [27]. In this respect our models dealing with *uncorrelated* fluctuations explore the spin relaxation of a walker with spin $S = \frac{1}{2}$ jumping with a rate γ_z between sites with energies that are either Gaussian or dichotomic distributed. The problem is of direct interest for experimentalists working in the field of electron spin resonance who are concerned with the brownian motion of radicals in simple or complex fluids (see Ref. [20] and references cited therein).

The paper is organized as follows.

In Sec. II the relevant theory is presented. General relaxation regimes are investigated by generalized Langevin equations leading to continued fraction expansions of the spectra of the averaged observables [16]. Time scale separation is dealt with in terms of cumulant expansions [28–30]. In Sec. III the models of the atom and the bath are detailed. The results are presented and discussed in Sec. IV. Finally, in Sec. V the main conclusions of the work are summarized.

II. THEORY

In the Heisenberg picture the observable of interest $A(t)$ obeys the equation of motion

$$\dot{A}(t) = \mathcal{L} A(t) , \tag{2.1}$$

where $\mathcal{L}$ is the Liouville operator. For closed systems with Hamiltonian H the Liouvillian is defined by the commutator

$$\mathcal{L} A \equiv i[H, A] , \tag{2.2}$$

where $i^2 = -1$. We suppose that $A(t)$ is coupled with both the stochastic variable Ω and the set of quantum variables $\{\mathbf{a}\} = \{a_1, a_2, \ldots\}$. Let $\rho\{\mathbf{a}\}$ and $\rho(\Omega)$ be the density matrices of $\{\mathbf{a}\}$ and Ω, respectively. The average value $\overline{A}(t)$ can be expressed in different fashions:

$$\overline{A}(t)=\sum_{\Omega}\mathrm{Tr}_{\{\alpha\}}[\rho(\Omega)\rho\{\mathbf{a}\}A(t)\} \tag{2.3a}$$

$$=\mathrm{Tr}_{\{\alpha\}}\{\langle\rho\{\mathbf{a}\}A(t)\rangle\} \tag{2.3b}$$

$$=\mathrm{Tr}_{\{\alpha\}}\{\rho\{\mathbf{a}\}\langle A(t)\rangle\} . \tag{2.3c}$$

$\mathrm{Tr}_{\{\alpha\}}\{X\}$ defines the trace operation over the space spanned by the set $\{\mathbf{a}\}$. $\langle X\rangle=\sum_{\Omega}\rho(\Omega)X$ defines the average over the discrete determinations of Ω. Obvious changes are understood if Ω is a continuous variable. Equations (2.3) assume that $\mathbf{a}$ and Ω are uncorrelated.

Equations (2.3b) and (2.3c) point out that $\overline{A}(t)$ can be derived equally either from the cross correlation of $\rho\{\mathbf{a}\}$ and $A(t)$ or form the stochastic average $\langle A(t)\rangle$, respectively. Starting from Eq. (2.1), the time evolution of the cross correlations can be derived rigorously in terms of generalized Langevin equations [16]. Instead, an equation of motion of $\langle A(t)\rangle$ is provided by the cumulant expansion for stochastic equations [28,29]. The former is a more general approach than the latter, which is convergent only when good separation between macroscopic and microscopic time scales takes place. Nonetheless, in this case the cumulant expansion delivers a systematic procedure for the elimination of fast variables.

The following consists of a short derivation of both methods.

A. Generalized Langevin equation

Let us consider the quantity $\Psi_{BA}(t)$ defined as

$$\Psi_{BA}(t)=(B,A(t)) , \tag{2.4}$$

where (B,C) denotes a suitable scalar product [Eq. (2.3) shows the usual case of a weighted trace operation]. The approach based on the generalized Langevin equation expresses the Laplace transform $\hat{\Psi}_{BA}(z)$ of the correlation function $\Psi_{BA}(t)$ as a continued fraction

$$\hat{\Psi}_{BA}(z)=\cfrac{(B,A)}{z-a_0-\cfrac{b_1^2}{z-a_1-\cfrac{b_2^2}{z-a_2-\cdots}}} \quad (B,A)\neq 0 . \tag{2.5}$$

If the correlations vanish at the initial time, i.e., $(B,A)=0$, one resorts to the modified expansion

$$\hat{\Psi}_{BA}(z)=\cfrac{(B,\mathcal{L}^n A)z^{-n}}{z-a_0'-\cfrac{b_1'^2}{z-a_1'-\cfrac{b_2'^2}{z-a_2'-\cdots}}}$$

$$(B,\mathcal{L}^m A)=0,\ 0\le m<n , \tag{2.6}$$

where n is the first integer for which $(B,\mathcal{L}^n A)$ does not vanish, a, a', b, b' are complex numbers.

An analytical expansion of the Laplace transform of $\Psi_{BA}(t)$ is provided by introducing a proper biorthogonal basis set. The set is generated by starting with two seed states $f_0=A$ and $\tilde{f}_0=B$ and iterating for the right states according to

$$f_1=\mathcal{L}f_0-a_0f_0 ,\qquad f_{n+1}=\mathcal{L}f_n-a_nf_n-b_n^2f_{n-1} \tag{2.7a}$$

and for the left states according to

$$\tilde{f}_1=\tilde{f}_0\mathcal{L}-a_0\tilde{f}_0 ,\qquad \tilde{f}_{n+1}=\tilde{f}_n\mathcal{L}-a_n\tilde{f}_n-b_n^2\tilde{f}_{n-1} , \tag{2.7b}$$

where

$$a_n=\frac{(\tilde{f}_n,\mathcal{L}f_n)}{(\tilde{f}_n,f_n)},\quad b_n^2=\frac{(\tilde{f}_n,f_n)}{(\tilde{f}_{n-1},f_{n-1})} . \tag{2.8}$$

Further details are given elsewhere [16,20].

B. Cumulant expansion method

Let us decompose the operator $\mathcal{L}$ as

$$\mathcal{L}=\mathcal{L}_0+\mathcal{L}_1 \tag{2.9}$$

with $\mathcal{L}_0=\langle\mathcal{L}\rangle$ and $\mathcal{L}_1=\mathcal{L}-\mathcal{L}_0$. To deprive the dynamics of $A(t)$ of the "free" motion due to $\mathcal{L}_0$, one defines the interaction representation

$$A^{(0)}(t)=\exp(-\mathcal{L}_0t)A(t) ,\qquad \mathcal{L}_1^{(0)}(t)=\exp(-\mathcal{L}_0t)\mathcal{L}_1\exp(\mathcal{L}_0t) \tag{2.10}$$

so that Eq. (2.1) becomes

$$\dot{A}^{(0)}(t)=\mathcal{L}_1^{(0)}(t)A^{(0)}(t) . \tag{2.11}$$

Starting from Eq. (2.11) an exact equation of motion for the average value of $A^{(0)}(t)$ follows, which takes the form

$$\frac{\partial}{\partial t}\langle A^{(0)}(t)\rangle=\mathcal{K}^{(0)}(t)\langle A^{(0)}(t)\rangle \tag{2.12}$$

with

$$\mathcal{K}^{(0)}(t)=\sum_{m=2}^{\infty}\mathcal{K}_m^{(0)}(t) . \tag{2.13}$$

The detailed derivation of Eq. (2.12) is presented elsewhere [16]. The terms $\mathcal{K}_n^{(0)}(t)$ are usually named *ordered cumulants* and rules have been derived for building them up [28–30].

For Eq. (2.12) to become of practical interest, we must distinguish between two time scales. The first is the time scale T_A on which $\langle A^{(0)}(t)\rangle$ varies appreciably. The second time scale is determined by the autocorrelation time τ_c of $\mathcal{L}_1^{(0)}(t)$. As soon as $\tau_c\ll T_A$, the properties of ordered cumulants lead to successive Markovian approximated forms of Eq. (2.12) of higher and higher order with respect to $\mathcal{L}_1^{(0)}(t)$, which are effective on the coarse-grained time scale Δt such as $\tau_c\ll\Delta t\ll T_A$. On this scale $\mathcal{K}^{(0)}(t)$ can be replaced by $\mathcal{K}^{(0)}(\infty)$.

At second order Eq. (2.12) reduces to

$$\frac{\partial}{\partial t}\langle A^{(0)}(t)\rangle=\mathcal{K}_2^{(0)}(\infty)\langle A^{(0)}(t)\rangle \tag{2.14}$$

with

$$\mathcal{K}_2^{(0)}(\infty)=\int_0^\infty d\tau_1 k_2^{(0)}(t|t-\tau_1) , \quad (2.15)$$

where

$$k_2^{(0)}(t|t-\tau)=\langle \mathcal{L}_1^{(0)}(t)\mathcal{L}_1^{(0)}(t-\tau)\rangle . \quad (2.16)$$

The second-order cumulant $\mathcal{K}_2^{(0)}(\infty)$ can be separated into a Hermitian and anti-Hermitian part $\mathcal{K}_{+2}^{(0)}(\infty)$ and $\mathcal{K}_{-2}^{(0)}(\infty)$, respectively,

$$\mathcal{K}_2^{(0)}(\infty)=\mathcal{K}_{+2}^{(0)}(\infty)+\mathcal{K}_{-2}^{(0)}(\infty) ,$$
$$\mathcal{K}_{\pm 2}^{(0)}(\infty)=\tfrac{1}{2}\int_0^\infty d\tau_1 \langle [\mathcal{L}_1^{(0)}(t),\mathcal{L}_1^{(0)}(t-\tau_1)]_\pm \rangle , \quad (2.17)$$

where $[X,Y]_\pm=XY\pm YX$. The integrand function of $\mathcal{K}_{+2}^{(0)}(\infty)[\mathcal{K}_{-2}^{(0)}(\infty)]$ is an *even* [odd] function of τ_1.

This second-order approximation in $\mathcal{L}_1^{(0)}(t)$ can be pursued further. The fourth-order approximation to Eq. (2.12) is

$$\frac{\partial}{\partial t}\langle A^{(0)}(t)\rangle=[\mathcal{K}_2^{(0)}(\infty)+\mathcal{K}_4^{(0)}(\infty)]\langle A^{(0)}(t)\rangle \quad (2.18)$$

with

$$\mathcal{K}_4^{(0)}(\infty)=\int_0^\infty d\tau_1 k_4^{(0)}(t|t-\tau_1)-\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3\{k_2^{(0)}(t|t-\tau_1-\tau_2)k_2^{(0)}(t-\tau_1|t-\tau_1-\tau_2-\tau_3)$$
$$+k_2^{(0)}(t|t-\tau_1-\tau_2-\tau_3)k_2^{(0)}(t-\tau_1|t-\tau_1-\tau_2)\} , \quad (2.19)$$

where

$$k_4^{(0)}(t_1|t_4)=\int_{t_4}^{t_1}dt_2\int_{t_4}^{t_2}dt_3\langle \mathcal{L}_1^{(0)}(t_1)\mathcal{L}_1^{(0)}(t_2)\mathcal{L}_1^{(0)}(t_3)\mathcal{L}_1^{(0)}(t_4)\rangle-\langle \mathcal{L}_1^{(0)}(t_1)\mathcal{L}_1^{(0)}(t_2)\rangle\langle \mathcal{L}_1^{(0)}(t_3)\mathcal{L}_1^{(0)}(t_4)\rangle . \quad (2.20)$$

The Markovian form of Eq. (2.12) deserves some comments. The ordered-cumulant expansion (2.13) of $\mathcal{K}^{(0)}(t)$ is often employed in the limit of short correlation times τ_c. In fact, it can be proven that the order of magnitude of $\mathcal{K}_m^{(0)}(t)$ is $\mathcal{L}_1^{(0)}(t)^m\tau_c^m$ and the series (2.13) is expected to converge rapidly for small values of the expansion parameter $\mathcal{L}_1^{(0)}(t)\tau_c$. However, it must be pointed out that the smallness of the parameter $\mathcal{L}_1^{(0)}(t)\tau_c$ is *sufficient but not necessary* to guarantee meaningfulness to the Eq. (2.12). The basic requirement is the time scale separation between the dynamics of $\langle A^{(0)}(t)\rangle$ and $\mathcal{L}_1^{(0)}(t)$. In Ref. [16] cases have been given where the expansion (2.13) has been extended to the region $\mathcal{L}_1^{(0)}\tau_c \gg 1$.

For later use we specialize $\mathcal{K}_2^{(0)}(\infty)$ in Eq. (2.15) to the usual case

$$H_1(\Omega)=\sum_i \omega_i(\Omega)A_i , \quad (2.21)$$

where A_i and $\omega_i(\Omega)$ are a quantum operator and a classical function of the stochastic variable Ω, respectively. Let $|a\rangle,|b\rangle,\ldots$ the eigenstates of H_0 with energies $\omega_a,\omega_b,\ldots$. Equation (2.14) becomes

$$\frac{\partial}{\partial t}\langle A_{ab}^{(0)}(t)=\sum_{cd}\mathcal{K}_{2\,abcd}^{(0)}(\infty)\langle A_{cd}^{(0)}(t)\rangle , \quad (2.22)$$

where $X_{ab}=\langle a|X|b\rangle$. By inspection it is seen that

$$\mathcal{K}_{2\,abcd}^{(0)}(\infty)=\exp[i(\omega_{cd}-\omega_{ab})t]\mathcal{R}_{2\,abcd}^{*} , \quad (2.23)$$

where $\omega_{nm}=\omega_n-\omega_m$ and $\mathcal{R}_{2_{abcd}}$ is a constant quantity for stationary stochastic processes (X^* is the complex conjugate of X). From Eq. (2.15), disentangling the double commutator in Eq. (2.16) gives

$$\mathcal{R}_{2_{abcd}}=-\sum_{\alpha\beta}\int_0^\infty ds\, C_{\alpha\beta}(s)\left[\delta_{bd}\sum_n A_{an}^{\alpha}A_{nc}^{\beta}e^{i\omega_{cn}S}-A_{ac}^{\beta}A_{db}^{\alpha}e^{i\omega_{ca}s}\right.$$
$$\left.+C_{\beta\alpha}(-s)\left[\delta_{ac}\sum_n A_{dn}^{\beta}A_{nb}^{\alpha}e^{i\omega_{nd}s}-A_{ac}^{\alpha}A_{db}^{\beta}e^{i\omega_{bd}s}\right]\right] . \quad (2.24)$$

$C_{\alpha\beta}$ is the correlation function defined as

$$C_{\alpha\beta}(s)=\langle \omega_\alpha[\Omega(\tau+s)]\omega_\beta[\Omega(t)]\rangle . \quad (2.25)$$

In Eq. (2.22) only the terms $\langle A_{ab}^{(0)}(t)\rangle$ and $\langle A_{cd}^{(0)}(t)\rangle$, for which the inequality

$$|\omega_{ab}-\omega_{cd}| \ll 1/\Delta t \quad (2.26)$$

holds, are significantly coupled to each other. This secular approximation reduces Eq. (2.22) to

$$\frac{\partial}{\partial t}\langle A_{ab}^{(0)}(t)\rangle=\sum_{cd}^{(\mathrm{sec})}\exp[i(\omega_{cd}-\omega_{ab})t]$$
$$\times\mathcal{R}_{2\,abcd}^{*}\langle A_{cd}^{(0)}(t)\rangle , \quad (2.27)$$

where the sum is now limited to terms which obey Eq. (2.26). Returning back to the original representation yields

$$\frac{\partial}{\partial t}\langle A_{ab}(t)\rangle = i\omega_{ab}\langle A_{ab}(t)\rangle + \sum_{cd}^{(\mathrm{sec})} \mathcal{R}^{*}_{2\,abcd}\langle A_{cd}(t)\rangle \ . \tag{2.28}$$

Equation (2.28) shows that the time evolution of the quantum system is described on the coarse-grained scale Δt by a linear differential system with constant coefficients.

III. BASIC EQUATIONS OF THE MODEL

We focus on a two-level system represented by a particle with spin $S=\frac{1}{2}$ precessing around a static magnetic field $\mathcal{H}_0$ with Larmor frequency $\omega_0=\gamma_e\mathcal{H}_0$. $\mathcal{H}_0$ defines the z axis of the reference frame. We assume that the precession is affected by three random fields aligned with the axis of the reference frame. The fields, with Gaussian or dichotomic character, will be taken with strong or vanishingly small mutual correlations. The spin Hamiltonian can be separated as

$$H=H_0+H_1(\Omega) \ , \tag{3.1}$$

where $H_0=H-\langle H\rangle$ is the part of the total Hamiltonian H independent of the stochastic process and $H_1(\Omega)$ is the "fluctuating" part, respectively, $\Omega=\{\Omega_1,\ldots,\Omega_N\}$ represents an N-dimensional stationary stochastic process. The general expressions of H_0 and $H_1(\Omega)$ are

$$H_0=\omega_0 S_z \ , \tag{3.2a}$$

$$H_1(\Omega)=\omega_x(\Omega)S_x+\omega_y(\Omega)S_y+\omega_z(\Omega)S_z \ . \tag{3.2b}$$

$\omega_i(\Omega)$ are scalar functions of the stochastic process Ω. For the case of correlated fields, the amplitudes $\omega_i(\Omega)$ are modeled as

$$\omega_i(\Omega)=\Delta_i\Omega, \quad i=x,y,z \quad \text{(correlated fields)} \ , \tag{3.3}$$

where Δ_i is the noise amplitude and Ω is a scalar random variable. For either Gaussian or dichotomic Ω, one finds $(t\geq t')$

$$\begin{aligned}&\langle\Omega\rangle=0 \ ,\\&\langle\Omega(t)\Omega(t')\rangle=\exp[-\gamma(t-t')] \ .\end{aligned} \tag{3.4}$$

For the case of uncorrelated fields we assume

$$\omega_i(\Omega)=\Delta_i\Omega_i, \quad i=x,y,z \quad \text{(uncorrelated fields)} \ , \tag{3.5}$$

where Ω_i $(i=x,y,z)$ are either Gaussian or dichotomic random variables characterized by $(t\geq t')$

$$\begin{aligned}&\langle\Omega_i\rangle=0 \ ,\\&\langle\Omega_i(t)\Omega_j(t')\rangle=\delta_{ij}\exp[-\gamma_i(t-t')] \ .\end{aligned} \tag{3.6}$$

If the fluctuating field along the x and y axes are correlated, one takes advantage of some simplifications. First, a suitable rotation recasts Eq. (3.2b) into the simpler form

$$H_1(\Omega)=\tilde{\Delta}_x\Omega S_x+\Delta_z\Omega S_z \ , \tag{3.7}$$

where

$$\tilde{\Delta}_x=\sqrt{\Delta_x^2+\Delta_y^2} \ . \tag{3.8}$$

Furthermore, $H_1(\Omega)$ can be factorized into the product of quantum and stochastic parts

$$H_1(\Omega)=h\Omega \tag{3.9}$$

with

$$h=\tilde{\Delta}_x S_x+\Delta_z S_z \ , \tag{3.10}$$

so that each averaged term in Eq. (2.19) may be factorized in quantum and averaged stochastic parts. For completeness, the basic properties of dichotomic and Gaussian Markov processes are briefly summarized.

A. Dichotomic Markov process

The dichotomic Markov process (DMP) Ω has only two possible realizations ± 1. The singlet equilibrium distribution is expressed by the two component vector $P(\Omega)=\{\frac{1}{2},\frac{1}{2}\}$ and the transition probability obeys the equation

$$\frac{\partial}{\partial t}P(\Omega,t|\Omega_0,t_0)=\Gamma P(\Omega,t|\Omega_0,t_0) \ , \tag{3.11}$$

where Γ is the 2×2 matrix

$$\Gamma=\tfrac{1}{2}\gamma\begin{bmatrix}-1 & 1\\ 1 & -1\end{bmatrix} . \tag{3.12}$$

The DMP exhibits an exponential correlation decay [Eq. (3.4)]. The higher-order correlations functions of the DMP can be expressed in term of the two-time correlations functions with the aid of the following property. If $\Psi[\Omega(\cdots)]$ is a functional involving only times prior to t_1, then for $t>t_1$ [31],

$$\langle\Omega(t)\Omega(t_1)\Psi[\Omega(\cdots)]\rangle=\langle\Omega(t)\Omega(t_1)\rangle\langle\Psi[\Omega(\cdots)]\rangle \ . \tag{3.13}$$

This result allows a strong reduction of the terms required to evaluate the higher-order cumulants. In particular, for the correlated DMP it follows that

$$k_4^{(0)}(t_1|t_4)=0 \tag{3.14}$$

and the fourth-order cumulant $\mathcal{K}_4^{(0)}(t)$ reduces to

$$\mathcal{K}_4^{(0)}(\infty)=-\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3\{k_2^{(0)}(t|t-\tau_1-\tau_2)k_2^{(0)}(t-\tau_1|t-\tau_1-\tau_2-\tau_3) + k_2^{(0)}(t|t-\tau_1-\tau_2-\tau_3)k_2^{(0)}(t-\tau_1|t-\tau_1-\tau_2)\} \ . \tag{3.15}$$

B. Gaussian Markov processes

For a Gaussian Markov Process (GMP), Doob's theorem states that the correlation function is exponential [32]. The equilibrium distribution is

$$P(\Omega)=\frac{1}{\sqrt{2\pi}}\exp\left[-\frac{\Omega^2}{2}\right] \quad (3.16)$$

and the transition probability obeys Eq. (3.11) with

$$\Gamma=\gamma\frac{\partial}{\partial\Omega}\left[\Omega+\frac{\partial}{\partial\Omega}\right] . \quad (3.17)$$

As in the case of the DMP, the higher-order correlation functions of the GMP can be expressed in terms of two-time correlation functions according to

$$\langle\Omega(t_1)\Omega(t_2)\cdots\Omega(t_n)\rangle = \begin{cases} 0 & \text{odd } n \\ \sum\limits_{\substack{\text{all}\\ \text{pairings}}}\prod\limits_{\text{pairs}}\langle\Omega(t_i)\Omega(t_j)\rangle & \text{even } n \end{cases} . \quad (3.18)$$

In Eq. (3.18) the summation means that the set $t_1,t_2,\ldots,t_n$ must be divided into pairs preserving the time ordering to construct the product of quantities $\langle\Omega(t_i)\Omega(t_j)\rangle$ for this pairing and then sum up such terms for all possible ways of pairings. Equation (3.18) reduces the terms involved in the explicit calculations of the higher-order cumulants. We note that in the case of correlated Gaussian noise the fluctuating Hamiltonian $H_1(\Omega)$ assumes the form Eq. (3.9). In such a case, if $[h(t),h(t')]=0$ for $t\neq t'$, the fourth-order cumulant $\mathcal{K}_4^{(0)}(\infty)$ vanishes and the second-order approximation becomes exact.

The observable of interest A evolves under the joint influence of the spin Hamiltonian [Eq. (3.1)] and the stochastic bath whose dynamics is determined by the transition matrix Γ [Eqs. (3.12) and (3.17)]. The overall effect is accounted for by the stochastic Liouville equation, which introduces an effective *non-Hermitian* Liouvillian $\mathcal{L}$ of the form [32]

$$\mathcal{L}=i[H,\ldots]+\Gamma . \quad (3.19)$$

The effective Liouvillian will be used in the calculations involving the generalized Langevin equation. Cumulant expansions will be evaluated by resorting to Eqs. (3.4) and (3.6) and the reduction formulas (3.13) and (3.18).

IV. RESULTS

We focus on the relaxation behavior of $\bar{S}_y$ and $\bar{S}_z$, namely, the components of the magnetization transverse and parallel to the static magnetic field $\mathcal{H}_0$. According to Eq. (2.3), the problem will be completely posed after having defined a suitable preparation of the quantum system in terms of $\rho\{\mathbf{a}\}$. In order to make contact with the usual experimental protocol the decay of $\bar{S}_z$ will follow the prepared state

$$\rho\{\mathbf{a}\}=\exp(\beta\omega_0 S_z)/\mathrm{Tr}_{\{S\}}\{\exp(-\beta\omega_0 S_z)\}$$
$$\cong\tfrac{1}{2}(1+\beta\omega_0 S_z) . \quad (4.1a)$$

For $\bar{S}_y$ the prepared state is

$$\rho\{\mathbf{a}\}=\exp(\beta\omega_0 S_y)/\mathrm{Tr}_{\{S\}}\{\exp(-\beta\omega_0 S_z)\}$$
$$\cong\tfrac{1}{2}(1+\beta\omega_0 S_y) . \quad (4.1b)$$

In Eqs. (4.1) $\beta=1/kT$ (k is the Boltzmann constant and T is the temperature). In the second lines of Eqs. (4.1) high temperature is assumed. Equation (4.1a) is the nonequilibrium state created by a so-called π pulse, which rotates the equilibrium magnetization π rad from its direction along $\mathcal{H}_0$. Equation (4.1b) describes the state prepared by a $\pi/2$ pulse [21]. From Eqs. (2.3) and (4.1) it follows that

$$\bar{S}_y(t)=\frac{\beta\omega_0}{2}\mathrm{Tr}_{\{S\}}\{\langle S_y S_y(t)\rangle\} , \quad (4.2a)$$

$$\bar{S}_z(t)=\frac{\beta\omega_0}{2}\mathrm{Tr}_{\{S\}}\{\langle S_z S_z(t)\rangle\} . \quad (4.2b)$$

The above forms are particularly suitable for calculations using the generalized Langevin equation since they relate the average quantities to particular correlation functions.

The expansion of the relaxation times in terms of cumulant theory will be outlined in the next section. The predictions will be compared with the exact results about $\bar{S}_y$ and $\bar{S}_z$ drawn from the generalized Langevin equations. The discussion will be limited to fluctuating fields with amplitudes smaller than the Larmor frequency ($\Delta<\omega_0$), which is the relevant range for application purposes [21].

A. Relaxation rates

Let us define

$$S_0=S_z,\quad S_{\pm1}=S_x\pm iS_y . \quad (4.3)$$

Owing to Eqs. (2.10) and (3.2), in the interaction representation the fluctuating Liouvillian $\mathcal{L}_1$ assumes the form

$$\mathcal{L}_1^{(0)}(t)=i\{\omega_z(\Omega)[S_0,\ldots] + \tfrac{1}{2}[\omega_x(\Omega)-i\omega_y(\Omega)]e^{-i\omega_0 t}[S_+,\cdots] + \tfrac{1}{2}[\omega_x(\Omega)+i\omega_y(\Omega)]e^{+i\omega_0 t}[S_-,\ldots]\} , \quad (4.4)$$

where $S_0\equiv S_0(0)=S_0^{(0)}(0)$ and $S_{\pm1}\equiv S_{\pm1}(0)=S_{\pm1}^{(0)}(0)$.

Relaxation rates correct up to $[\mathcal{L}_1^{(0)}]^4$ can be derived by resorting to Eq. (2.18). $\mathcal{K}_2^{(0)}$ is expanded according to Eq. (2.23). The final form of Eq. (2.18) for the relevant averaged values is

$$\frac{\partial}{\partial t}\langle S_1^{(0)}(t)\rangle=(\mathcal{R}^*_{2_{11}}+\mathcal{R}^*_{4_{11}})\langle S_1^{(0)}(t)\rangle + \exp[-2i\omega_0 t]\mathcal{R}^*_{2_{1-1}}\langle S_{-1}^{(0)}(t)\rangle + \exp[-i\omega_0 t]\mathcal{R}^*_{2_{10}}\langle S_0^{(0)}(t)\rangle , \quad (4.5a)$$

$$\frac{\partial}{\partial t}\langle S_0^{(0)}(t)\rangle=(\mathcal{R}^*_{2_{00}}+\mathcal{R}^*_{4_{00}})\langle S_0^{(0)}(t)\rangle + \exp[+i\omega_0 t]\mathcal{R}^*_{2_{01}}\langle S_1^{(0)}(t)\rangle + \exp[-i\omega_0 t]\mathcal{R}_{2_{01}}\langle S_{-1}^{(0)}(t)\rangle , \quad (4.5b)$$

where $\mathcal{R}_{4_{nn}} \equiv \mathcal{K}^{(0)}_{4_{nn}}$. The equation for $\langle S^{(0)}_{-1}(t)\rangle$ is the complex conjugate of Eq. (4.5a). The explicit expressions of the matrix elements of $\mathcal{R}_2$ and $\mathcal{R}_4$ are found by using Eqs. (2.24) and (2.19), respectively.

The dynamic shift and the longitudinal and transverse relaxation times including terms up to Δ^4 are found by solving Eqs. (4.5). The procedure, which is detailed in Appendix A, yields the equation of motion

$$\frac{\partial}{\partial t}\langle S_{\pm}(t)\rangle = \left[\pm i(\omega_0+\Delta\omega'''')-\frac{1}{T_2''''}\right]\langle S_{\pm}(t)\rangle \ , \tag{4.6}$$

where

$$\frac{1}{T_2''''} = -\mathrm{Re}\left\{\mathcal{R}_{2_{11}}+\mathcal{R}_{4_{11}}+i\frac{\mathcal{R}_{2_{01}}\mathcal{R}_{2_{10}}}{\omega_0}\right\} \tag{4.7a}$$

and for the dephasing

$$\Delta\omega'''' = -\mathrm{Im}\left\{\mathcal{R}_{2_{11}}+\mathcal{R}_{4_{11}}+i\frac{\mathcal{R}_{2_{01}}\mathcal{R}_{2_{10}}}{\omega_0}\right\}-\frac{|\mathcal{R}_{2_{1-1}}|^2}{2\omega_0} \ , \tag{4.7b}$$

where Re(z) and Im(z) mean the real and the imaginary parts of z, respectively, T_2'''' and $\Delta\omega''''$ are correct up to $[\mathcal{L}_1^{(0)}]^4$. By similar manipulations one finds up to $[\mathcal{L}_1^{(0)}]^4$

$$\frac{\partial}{\partial t}\langle S_0(t)\rangle = -\frac{1}{T_1''''}\langle S_0(t)\rangle \ , \tag{4.8}$$

with

$$\frac{1}{T_1''''} = -\mathcal{R}_{2_{00}}-\mathcal{R}_{4_{00}}-2\,\mathrm{Im}\left\{\frac{\mathcal{R}_{2_{01}}\mathcal{R}_{2_{10}}}{\omega_0}\right\} . \tag{4.9}$$

Equations (4.6) and (4.8) hold if the averaged quantities $\langle S_0^{(0)}\rangle$ and $\langle S_{\pm 1}^{(0)}\rangle$ relax on time scales longer than both the correlation times of the fluctuating fields and ω_0^{-1}. In the particular case of uncorrelated noise Eqs. (4.7) and (4.9) benefit from $\mathcal{R}_{2_{01}}=\mathcal{R}_{2_{10}}=0$ and, if $\gamma_x=\gamma_y$ and $\Delta_x=\Delta_y$, from $\mathcal{R}_{2_{1-1}}=0$. In the general case and beyond the second-order approximation, Eqs. (4.7) and (4.9) clearly state that it is *not* correct to neglect $\mathcal{R}_{2_{01}}$, $\mathcal{R}_{2_{10}}$, and $\mathcal{R}_{2_{1-1}}$, by invoking the oscillatory character of the related terms in Eqs. (4.5). The explicit expressions of the coefficients $\mathcal{R}$ for the different models under study are rather involved and are omitted. However, they are listed in Appendix A for the case of correlated dichotomic noise.

According to Eqs. (2.3c) and (4.1), one finds for the Laplace transform of the average values of the magnetization component $\bar{S}_y(z)$ and $\bar{S}_z(z)$

$$\bar{S}_y(i\omega) = \frac{\beta\omega_0}{8}\frac{1}{i[\omega-(\omega_0+\Delta\omega'''')]+1/T_2''''}+\text{c.c.} \ , \tag{4.10a}$$

$$\bar{S}_z(i\omega) = \frac{\beta\omega_0}{4}\frac{1}{i\omega+1/T_1''''} \ . \tag{4.10b}$$

Owing to the relations (4.2), the theory developed in Sec. II A provides us with an alternative approach to evaluate the spectrum of the relaxation times. The most general form of $\bar{S}_y(z)$ and $\bar{S}_z(z)$, as derived via Eqs. (2.5) and (4.2), is a ratio between two polynomials

$$\bar{S}_z(z) = \frac{N_1^{(n-1)}(z)}{D_1^{(n)}(z)}, \quad \bar{S}_y(z) = \frac{N_2^{(n-1)}(z)}{D_2^{(n)}(z)} \ , \tag{4.11}$$

where $N^{(n-1)}(z)$ and $D^{(n)}(z)$ are polynomials of degree $n-1$ and n, respectively. n depends on the particular model in hand. For correlated dichotomic noise $n=6$. For uncorrelated dichotomic noise $n=24$. For Gaussian noises $n\to\infty$, but in practical cases the continued fraction can be safely truncated at $n_t<100$. To characterize completely the relaxation behavior of $\bar{S}_y$ and $\bar{S}_z$, the complete set of the roots of $D_1^{(n)}(z)$ and $D_2^{(n)}(z)$ must be identified. A straightforward procedure to perform this task numerically is the Laguerre algorithm [34], which has been extensively used in this paper. The dominance of a single relaxation time at long times is signaled by single, well isolated roots of $D_1^{(n)}(z)$ and $D_2^{(n)}(z)$ with real parts smaller than the fluctuation rates. In this case $1/T_1$ and $1/T_2+i\Delta\omega$ can be defined as

$$\alpha=\frac{1}{T_1}, \quad \alpha=\min[\alpha_i|\alpha_i \text{ real}, D_1^{(n)}(-\alpha_i)=0\} \ , \tag{4.12a}$$

$$\beta=\frac{1}{T_2}+i\Delta\omega, \quad \mathrm{Re}\beta=\min\{\mathrm{Re}\beta_i|D_2^{(n)}(-i\omega_0-\beta_i)=0\} \ , \tag{4.12b}$$

The explicit, analytical expressions of $1/T_1$ and $1/T_2+i\Delta\omega$ have been evaluated in two different ways. For Gaussian noise we resorted to the cumulant expansions Eqs. (4.7) and (4.9). For the dichotomic noise we evaluated α and β directly, according to Eq. (4.12). The search of the roots of the polynomials $D_1^{(n)}(z)$ and $D_2^{(n)}(z)$ with the smallest real part has been carried out by algebraic manipulations performed by MATHEMATICA on a Macintosh computer SE/30. With two iterations of the Newton-Raphson method [34], $1/T_1$ and $1/T_2+i\Delta\omega$ become correct at fourth order with respect to Δ. The resulting expressions coincide with $1/T_1''''$ and $1/T_2''''+\Delta\omega''''$, derived by the cumulant expansions. A point worth noting is that the analytical root-search procedure proves to be fairly more efficient than the cumulant expansions.

The analytical expressions of both the relaxation times and the dynamic shifts for our models of fluctuations are listed in Appendix B, T_1'''', T_2'''', and $\Delta\omega''''$ are correct at fourth order in Δ^4. The same expressions truncated at second order will be denoted as T_1'', T_2'', and $\Delta\omega''$ henceforth. Special cases of these expressions for the case of uncorrelated Gaussian fluctuations were also reported elsewhere [3–6,9,11].

In [16] it was noted that for the correlated dichotomic noise the relation

$$\frac{1}{T_2}=\frac{1}{2T_1}+\frac{1}{T_2^{\text{adiabatic}}} \tag{4.13}$$

holds beyond the usual second-order approximation [see Eq. (B5)] [21]. It is worth noting that Eq. (4.13) is not recovered beyond second order for correlated Gaussian noise. Equation (4.13) is also not recovered for either Gaussian or dichotomic *uncorrelated* noise (see Appendix B). These results indicate that recovering Eq. (4.13) at fourth order is model dependent and is not related to statistical correlations. A direct consequence of Eq. (4.13) is the well known inequality $T_2 \leq 2T_1$, which for correlated dichotomic noise is satisfied up to fourth order in Δ. This inequality is a constraint between T_1 and T_2, weaker than Eq. (4.13), and cases have been reported for which $T_2 \leq 2T_1$ is always satisfied even if Eq. (4.13) is never satisfied [5]. A more complete discussion on the inequality $T_2 \leq 2T_1$ will be presented elsewhere [23].

In the next section the analytical predictions on the relaxation behavior of $\bar{S}_y(z)$ and $\bar{S}_z(z)$ will be compared with the exact results derived by the generalized Langevin equation.

B. Relaxation behavior

The discussion on the relaxation behavior of the two-level system subjected to colored noise will be divided in two parts. The first part will be concerned with correlated fluctuations and uncorrelated fluctuations with equal rates, namely, $\gamma_x = \gamma_y = \gamma_z$. The second part will illustrate relaxation in the presence of uncorrelated fluctuations with different rates.

1. *Equal fluctuation regimes* $\gamma_z = \gamma_x = \gamma_y = \gamma$

Figure 1 illustrates the general features of the spectrum of $\bar{S}_y$ for uncorrelated Gaussian and dichotomic noises. If the fluctuations are fast, i.e., $\gamma \to \infty$, in both cases the line is a Lorentzian, according to Eq. (4.10a). Slowing down the fluctuations broadens the spectrum, which approaches a form given by the statistical distribution of the eigenfrequencies of the Hamiltonian H [Eqs. (3.1) and (3.2)]. This effect is well known and was pointed out by R. Kubo a long time ago [32]. If Ω is Gaussian, since $H_1(\Omega)$ is linear in Ω, $\bar{S}_y(i\omega)$ has a Gaussian profile. If Ω is dichotomic $\bar{S}_y(i\omega)$ exhibits two narrow resonances located at $\omega_\pm \approx \omega_0 \pm \Delta_z$. For correlated fields, the spectra of $\bar{S}_y(i\omega)$ exhibit similar features [16].

Figure 2 shows the spectrum of $\bar{S}_z$ for both Gaussian and dichotomic uncorrelated noises (for correlated noise see Ref. [16]). $\bar{S}_x(i\omega)$ is characterized by a strong component at low frequency, extending less and less when the fluctuations become slower and slower. In contrast to $\bar{S}_y(i\omega)$, there are no remarkable modifications in the shape of $\bar{S}_z(i\omega)$ when the regime of fluctuation changes. This feature is a clue to the special character of the relaxation of $\bar{S}_z(i\omega)$. In Ref. [16] it was pointed out that, for correlated dichotomic fields with amplitudes Δ smaller than ω_0, $\bar{S}_z(i\omega)$ is well described by Eq. (4.10b). In other words, $\bar{S}_z(t)$ decays at long times with a single, dominant relaxation time T_1. In particular, T_1 exists for slow fluctuations ($\mathcal{L}_1^{(0)}\tau_c \gg 1$, i.e., $\Delta \gg \gamma$). On the contrary, T_2 cannot even be defined for $\gamma \ll \Delta$. We state in advance that the robustness of T_1 does not depend on the charac-

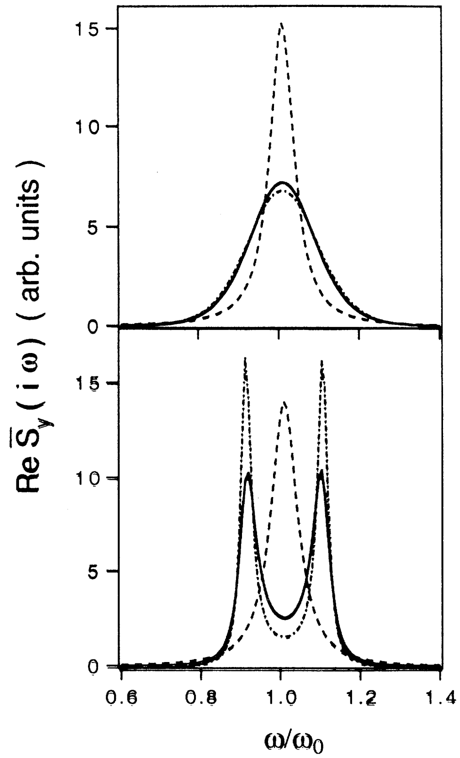

FIG. 1. Spectrum of the real part of $\bar{S}_y(\omega)$ for uncorrelated Gaussian (top) and dichotomic (bottom) noise. $\omega_0 = 1$, $\Delta_x = \Delta_y = \Delta_z = 0.1$, and $\gamma_x = \gamma_y = \gamma_z = 0.03$ (dot-dashed line), 0.05 (continuous line), and 0.3 (dashed line).

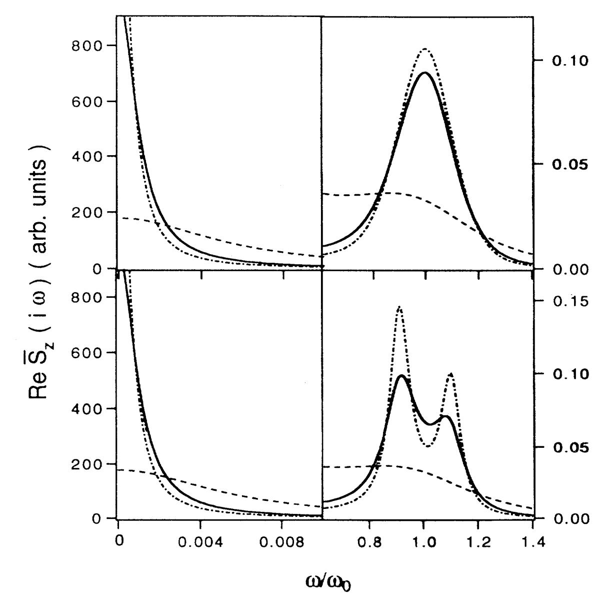

FIG. 2. Spectrum of the real part of $\bar{S}_z(i\omega)$ for uncorrelated Gaussian (top) and dichotomic (bottom) noise. $\omega_0 = 1$, $\Delta_x = \Delta_y = \Delta_x = 0.1$, and $\gamma_x = \gamma_y = \gamma_z = 0.03$ (dot-dashed line), 0.05 (continuous line), and 0.3 (dashed line).

ter of the fluctuations as long as the fluctuation regimes of the multiple noises acting on the spin are comparable. This assertion will be substantiated in the following.

Figure 2 also shows the portion of the spectrum of $\bar{S}_z(i\omega)$ close to the Larmor frequency ω_0. This weak structure resembling a "replica" of the spectrum of $\bar{S}_y(i\omega)$ is due to a remnant of the deterministic motion of the spin system. For $t \ll 1/\gamma$ the evolution is governed by Eq. (3.2), where $\omega_{x,y,z}$ do not fluctuate appreciably during the time evolution. If the precession around the total field is not disturbed by fluctuations over times longer than the precession period $2\pi[\omega_x^2+\omega_y^2+(\omega_0+\omega_z)^2]^{-1/2} \cong 2\pi/\omega_0$, the coherences $(S_{x,y})$ and the populations (S_z) are quite correlated. By making the rate of the fluctuation γ larger than ω_0 the correlations weaken and the replica vanishes. By a comparison with the results of Ref. [16], it is seen that uncorrelated fluctuations broaden the replica with respect to the spectrum of $\bar{S}_y(i\omega)$ more than the correlated fluctuations do (e.g., compare Figs. 2 and 3 of [16] and Figs. 1 and 2 of the present work).

Figure 3 and 4 dealing with the dichotomic and Gaussian cases, respectively, compare the relaxation time T_2 derived by Eq. (4.12b) with the second- and fourth-order cumulant expansions. The following features appear: (i) the fourth order always improves the second-order approximation; (ii) for fast fluctuations T_2'', $T_2'''' \rightarrow T_2$; and (iii) for $\gamma > \Delta$ the cumulant expansion fails to estimate T_2 (in fact, Fig. 1 reveals that T_2 cannot even be defined for $\gamma > \Delta$).

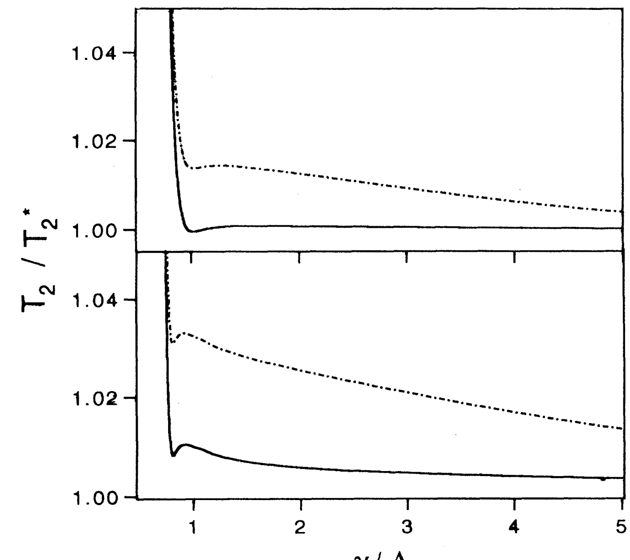

FIG. 4. Same as Fig. 3, but for Gaussian noise.

Figures 5–8 compare the relaxation time T_1 derived by Eq. (4.12a) and the second- and fourth-order cumulant expansions. Figures 5 and 6 deal with uncorrelated and correlated dichotomic noise, respectively. Figures 7 and 8 deal with uncorrelated and correlated Gaussian noise, respectively. The following common features are ap-

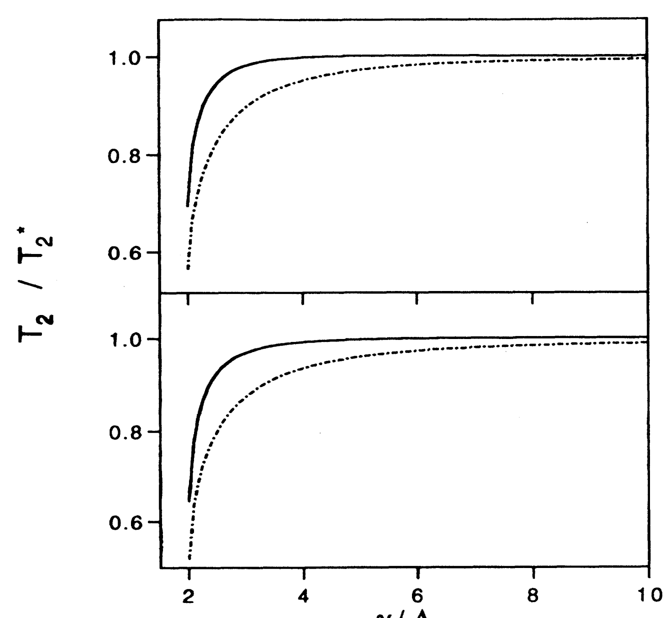

FIG. 3. Dichotomic noise. Dependence on the fluctuation rate of the ratio of the transverse relaxation time T_2 and the second-order T_2'' (dot-dashed line) or fourth-order T_2'''' (continuous line) approximation. $\omega_0=1$. Top: uncorrelated noise, $\Delta=\Delta_x=\Delta_y=\Delta_z=0.1$ and $\gamma=\gamma_x=\gamma_y=\gamma_z$. Bottom: correlated noise, $\Delta=\Delta_x=\Delta_z=0.1$.

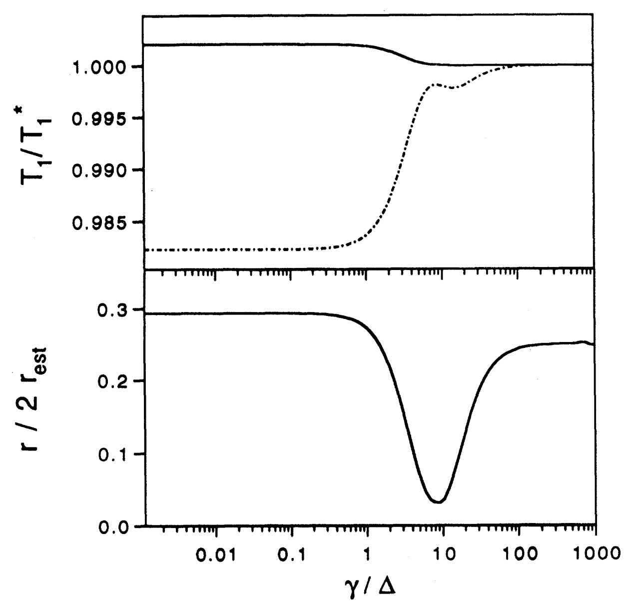

FIG. 5. Uncorrelated dichotomic noise. Top: dependence on the fluctuation rates of the ratio of the transverse relaxation time T_1 and the second-order T_1'' (dot-dashed line) or fourth-order T_1'''' (continuous line) approximation. Bottom: comparison of the relative error r between T_1^{-1} and $T_1''^{-1}$ and the estimated upper bound $2r_{\text{est}}$. $\omega_0=1$, $\Delta=\Delta_x=\Delta y=\Delta z=0.1$, and $\gamma=\gamma_x=\gamma_y=\gamma_z$.

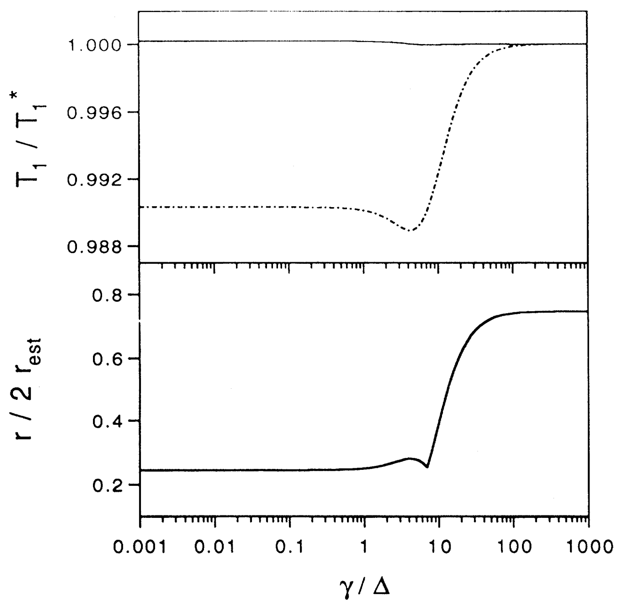

FIG. 6. Same as Fig. 5, but for correlated dichotomic noise. $\omega_0 = 1$ and $\Delta = \tilde{\Delta}_x = \Delta_z = 0.1$.

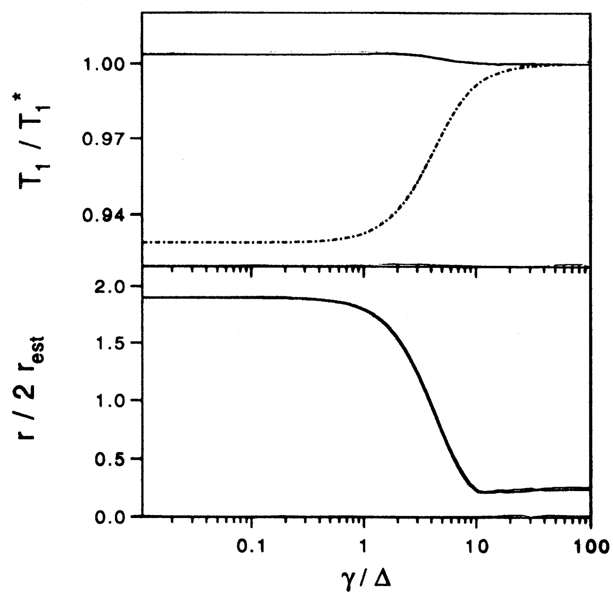

FIG. 8. Same as Fig. 6, but for correlated Gaussian noise.

parent: (i) the fourth order always fairly improves the second-order approximation; (ii) for fast fluctuations both T_1'' and $T_1'''' \to T_1$ and (iii) T_1 *exists* also for $\gamma > \Delta$ and the cumulant expansion lead to *good* estimates of T_1. The deviation of the second-order approximation T_1'' from the exact result T_1 is limited. It becomes negligible by extending the approximation to fourth order (T_1''''), even for $\Delta = 0.1\omega_0$ (in magnetic resonance $\Delta \approx 0.01\omega_0$).

The relative error r between T_1^{-1} and the second-order approximation $T_1''^{-1}$ is defined as

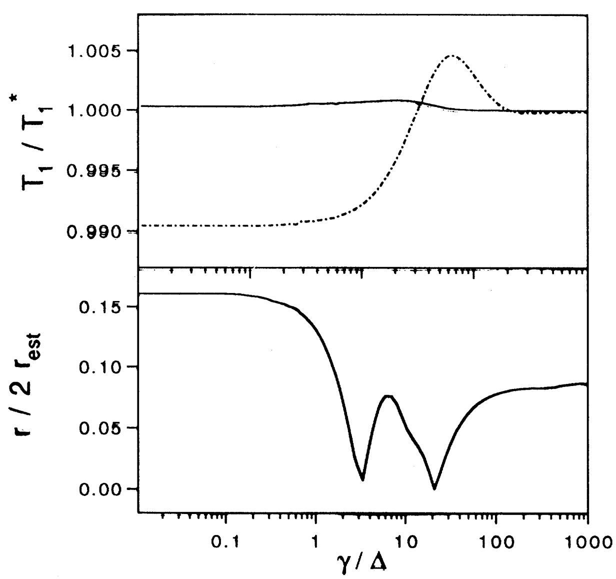

FIG. 7. Same as Fig. 5, but for uncorrelated Gaussian noise.

$$r \equiv \left| 1 - \frac{T_1}{T_1''} \right| . \tag{4.14}$$

In [16] it was estimated that r is bound according to

$$r < 2r^{(\mathrm{est})}, \quad r^{(\mathrm{est})} \equiv \frac{\Delta_x^2 + \Delta_y^2 + \Delta_z^2}{\max\{\omega_0^2, \gamma^2\}} . \tag{4.15}$$

Equation (4.15) was tested extensively for two-level systems in the presence of correlated dichotomic fluctuations and extended also to multilevel systems. It was likewise confirmed by examining the literature on the uncorrelated Gaussian noise. By recalling the discussion on the cumulant expansions (Sec. II B), one can easily convince oneself of Eq. (4.15) for $\gamma \gg \omega_0$, but for $\gamma \leq \omega_0$ its rigorous proof is not known.

With a view to testing in depth the inequality (4.15), in Figs. 5–8 the relative error r is plotted. r is found to be less than $2r^{(est)}$ for both correlated and uncorrelated dichotomic noise (Fig. 5 and 6) and for Gaussian uncorrelated noises (Fig. 7). For correlated Gaussian noise we found (Fig. 8)

$$r < 4r^{(\mathrm{est})} . \tag{4.16}$$

For this model and $\gamma > \omega_0$ the dependence of the relative error r on the amplitude of the random fields is shown in Fig. 9. The best-fit curve is

$$r = 4\frac{\Delta_x^2 + \Delta_y^2 + \Delta_z^2}{\omega_0^2} . \tag{4.17}$$

The results support the conclusion that, also for Gaussian correlated fluctuations, r is still proportional to the sum of the *squared* amplitudes of the fluctuating fields, even if the numerical prefactor is different from other models.

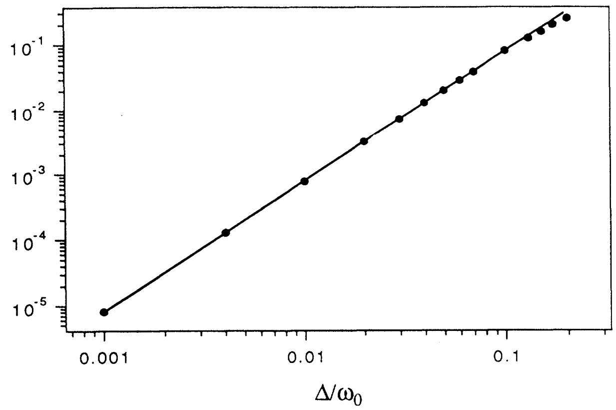

FIG. 9. Correlated Gaussian noise. Dependence of the relative error r between T_1^{-1} and $T_1''^{-1}$ on the amplitude of the noise. $\omega_0=1, \Delta=\tilde{\Delta}_x=\Delta_z$, and $\gamma=10^{-4}$. The equation of the superimposed line is $r=8(\Delta/\omega_0)^2$.

We can encompass all the results concerning the Gaussian and dichotomic noises (correlated or uncorrelated) by correcting Eq. (4.15) as

$$r<4r^{(\text{est})} . \tag{4.18}$$

2. *Different fluctuation regimes* $\gamma_z \neq \gamma_x = \gamma_y$

Our model assumes that the random fields are aligned along the three orthogonal axes x,y,z [Eqs. (3.2)]. The case of comparable fluctuation regimes provides a reasonable picture of an isotropic environment affecting the spin relaxation. However, a wide class of situations of current interest draws the attention to the regime of different fluctuation rates. As an example, we quote the case of complex systems, such as polymeric materials or supercooled fluids where the paramagnetic site is influenced simultaneously both by fast, local perturbations and by slow, cooperative dynamic processes [26]. Radicals diffusing in anisotropic fluids, e.g., liquid crystals or membranes, are also of interest [33]. Finally, the limit of well separated fluctuation regimes is well suited to clarify the basic spectroscopic concepts of "inhomogeneous" and "homogeneous" broadening.

In the present work we will address the case of longitudinal fluctuations slower than the transverse ones, namely, $\gamma_z<\gamma_x,\gamma_y$ [24]. Figure 10 shows the dependence of the ratio T_1/T_1'' on γ_z and $\gamma_x=\gamma_y=\gamma_\perp$. The contour plots drawn in the $\{\gamma_z,\gamma_\perp\}$ plane bound the region where the inequality

$$\left|\frac{T_1''^{-1}-T_1^{-1}}{T_1^{-1}}\right|<2\frac{\sum_i \Delta_i^2}{\max\{\omega_0^2,\gamma_\perp^2\}} \tag{4.19}$$

holds. Equation (4.19) is an obvious generalization of Eq. (1.2). In the "phase diagram" $\{\gamma_z,\gamma_\perp\}$ the region of validity of Eq. (4.19) includes the line $\gamma_z=\gamma_\perp$ and the half plane $\gamma_\perp \geq \omega_0$. The presence of a "path" close to the line $\gamma_z \cong \gamma_\perp \leq \omega_0$ is remarkable and makes it possible to extend Eq. (1.2) also to *uncorrelated* dichotomic fluctuations with *comparable* rates.

The breakdown of Eq. (4.19) occurs in two distinct regions of the half plane $\gamma_\perp \leq \omega_0$, which are separated by the line $\gamma_z=\gamma_\perp$ and indicated henceforth as the "well" (located at $\gamma_z \geq \gamma_\perp$) and the "mesa" (located at $\gamma_z \leq \gamma_\perp \leq \omega_0$). Let us first discuss the well.

The well originates by an unpleasant feature of the cumulant expansion, which neglects at second order any contribution to T_1 by the longitudinal random fields [Eq. (4.13)]. If $\gamma_\perp \gg \omega_0$ this contribution is fairly small. If $\gamma_\perp \ll \omega_0$, the spin system precesses around a field with amplitude $\mathcal{H}_0=\gamma^{-1}\sqrt{\omega_0^2+\omega_x^2+\omega_y^2}$, which is *not* parallel to the z axis. If γ_z is comparable to $\gamma\mathcal{H}_0 \simeq \omega_0$, the random fields directed along the z axis affect $\bar{S}_z$ very efficiently, since they have a component *normal* to $\mathcal{H}_0$ with amplitude about $\omega_{x,y}\omega_z/\omega_0$. A second-order treatment of this component leads to a correction to T_1 that is proportional to $(\omega_{x,y}\omega_z/\omega_0)^2$. This is the origin of the fourth-order terms proportional to $\omega_{x,y}^2\omega_z^2$ in T_1'' [Eq. (B1)]. These conclusions are readily confirmed by inspecting Fig. 10. The discrepancy between T_1 and T_1'''' increases by decreasing $\gamma_\perp$ below ω_0 with γ_z constant $(\gamma_z>\gamma_\perp)$. The onset of the discrepancy is found at the highest $\gamma_\perp$ value for $\gamma_z=\omega_0$, in agreement with the above discussion.

Our view is confirmed by Fig. 11, where T_1 and T_1'''' are compared and the well disappears. This confirms that the well is *not* a manifestation of the breakdown of the time scale separation, but it is due to an accidental information loss fully recovered by the next higher approximation T_1''''. One verifies that the terms in $(\omega_{x,y}\omega_z/\omega_0)^2$ are small in T_1'''' when $\gamma_z=\gamma_\perp$ and therefore $T_1 \cong T_1''$ on the line $\gamma_z=\gamma_\perp$.

Let us discuss now the mesa, namely, the region with $\gamma_z<\gamma_\perp<\omega_0$. In Fig. 11 the mesa is unchanged with respect to Fig. 10 and this indicates that the structure is not related to the misconvergence of the cumulant expansion. We will show that the mesa is a consequence of the breakdown of the time scale separation between the relaxation times of $\bar{S}_z$ and $1/\gamma_z$. The long-time relaxation of $\bar{S}_z(t)$ is in general described by a sum of exponentials whose rates α_i are given by the roots of $D_1^{(n)}(z)$ [Eq. (4.12a)]. The roots are usually simple, but multiple roots may be found for particular choices of the model parameters [6]. The minimum of the set $\{\alpha_i\}$, α, is identified with T_1^{-1}. For z close to $z=0$, i.e., far from $z=i\omega_0$, the Laplace transform of $\bar{S}_z$, $\bar{S}_z(z)$ takes the form

$$\bar{S}_z(z)=\sum_i \frac{c_i}{z+\alpha_i} . \tag{4.20}$$

The weight c_i is determined by

$$c_i=\lim_{\varepsilon\to 0}\varepsilon\bar{S}_z(\varepsilon-\alpha_i) . \tag{4.21}$$

The dependence on $\gamma_\perp$ of the decay rates of $\bar{S}_z(t)$, i.e., α_i, and the quantity $(\alpha_i T_1'')^{-1}$ is examined in Fig. 12. $\bar{S}_z(t)$ is characterized by two different rates (upper part of Fig. 12). The first one is close to $T_1''^{-1}$. The other one is close to γ_z for $T_1''^{-1}<\gamma_z$. In this region $\bar{S}_z(t)$ decays at long

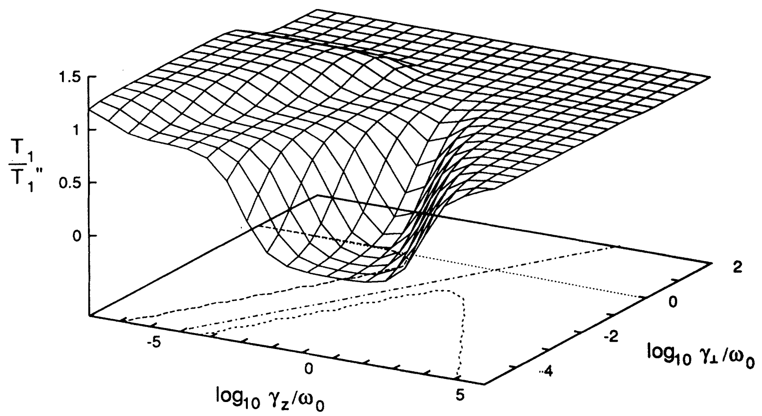

FIG. 10. Uncorrelated dichotomic noise. Dependence of the ratio T_1/T_1'' on the fluctuation rates γ_z and $\gamma_\perp$. Contour plots bound the region where Eq. (4.19) is fulfilled. The dot-dashed line is the locus $\gamma_\perp=\gamma_z$. $\omega_0=1$ and $\Delta_x=\Delta_y=\Delta_z=0.1$.

times with a single relaxation rate $T_1''^{-1}$. When $T_1''^{-1}>\gamma_z$ the two rates merge. In the lower part of Fig. 12 the region where $T_1''^{-1}>\gamma_z$ is examined in more detail. The highest curve gives the ratio T_1/T_1'' and coincides with a cross section along the $\gamma_\perp$ axis of the surface drawn in Fig. 10. The cross section of the mesa in Fig. 10 looks like a bump, whereas the well is signaled by the slight decrease of the ratio T_1/T_1'' for low values of $\gamma_\perp$.

As noted above, for short and long values of $\gamma_\perp$, $T_1^{-1}\equiv\alpha$ is well isolated. Then, $\bar{S}_z(t)$ decays with a single exponential with rate T_1^{-1} well estimated by $T_1''^{-1}$. Bounds for the fluctuation regimes ensuring the time scale separation between the relaxation time and the correlation times of the noise may be given. Let us evaluate for which values of $\gamma_\perp$ the time scale separation condition

$$T_1''\gamma_z>1 \tag{4.22}$$

is fulfilled. By replacing Eq. (B1) truncated at second order in Eq. (4.22) with $\gamma_x=\gamma_y=\gamma_\perp$ and $\Delta_x=\Delta_y=\Delta_\perp$ we found that Eq. (4.22) is fulfilled if

$$\gamma_\perp>\frac{\Delta_\perp^2+\sqrt{\Delta_\perp^4-\gamma_z^2\omega_0^2}}{\gamma_z} \quad\text{or}\quad \gamma_\perp<\frac{\Delta_\perp^2-\sqrt{\Delta_\perp^4-\gamma_z^2\omega_0^2}}{\gamma_z}\,. \tag{4.23}$$

In the case shown in Fig. 12, $\gamma_z\omega_0/\Delta_\perp^2\ll 1$, so that the inequalities (4.23) reduce to

$$\gamma_\perp>\frac{2\Delta_\perp^2}{\gamma_z} \quad\text{or}\quad \gamma_\perp<\frac{\gamma_z\omega_0^2}{2\Delta_\perp^2}\,. \tag{4.24}$$

The particular choice of parameters used in Fig. 12 leads to the chain of inequalities $2\Delta_\perp^2/\gamma_z>\omega_0>\gamma_z\omega_0^2/(2\Delta_\perp^2)$. With this choice Fig. 12 displays all the relevant features of the model. By replacing the numerical values, we find that the time scale separation takes place (and then a single exponential decay must be expected) for $\gamma_\perp/\omega_0>400$ or $\gamma_\perp/\omega_0<2.5\times10^{-3}$, in agreement with the numerical results.

When Eq. (4.22) breaks down, the fluctuations along the z axis are so slow that the transverse noise relaxes $\bar{S}_z$ *before* a fluctuation of the field along z takes place. $\bar{S}_z$ decays with two relaxation rates α' and α'', which, for $\gamma_x=\gamma_y=\gamma_\perp$ and $\Delta_x=\Delta_y=\Delta_\perp$ are given by

$$\alpha'=\frac{2\Delta_\perp^2\gamma_\perp}{(\omega_0+\Delta_z)^2+\gamma_\perp^2}\,,\quad \alpha''=\frac{2\Delta_\perp^2\gamma_\perp}{(\omega_0-\Delta_z)^2+\gamma_\perp^2}\,. \tag{4.25}$$

α' and α'' describe the spin relaxation induced by the transverse noises in the effective static field $\omega_0\pm\Delta_z$. One notes that, in the region of values of $\gamma_\perp$ where Eq. (4.22) breaks down (in Fig. 12 for $400>\gamma_\perp/\omega_0>2.5\times10^{-3}$),

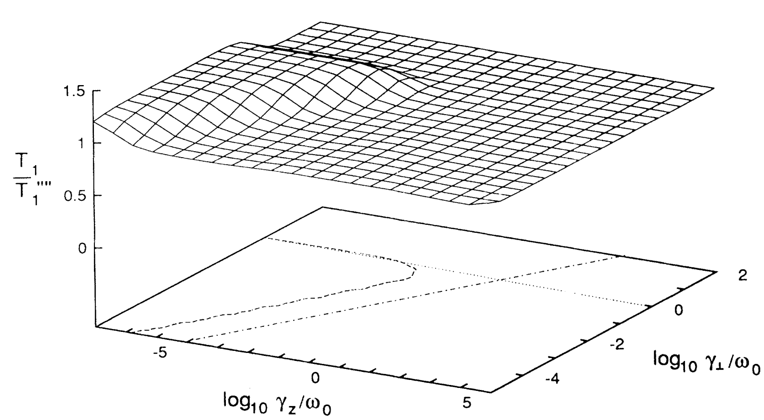

FIG. 11. Same as in Fig. 10, but for the ratio T_1/T_1''''.

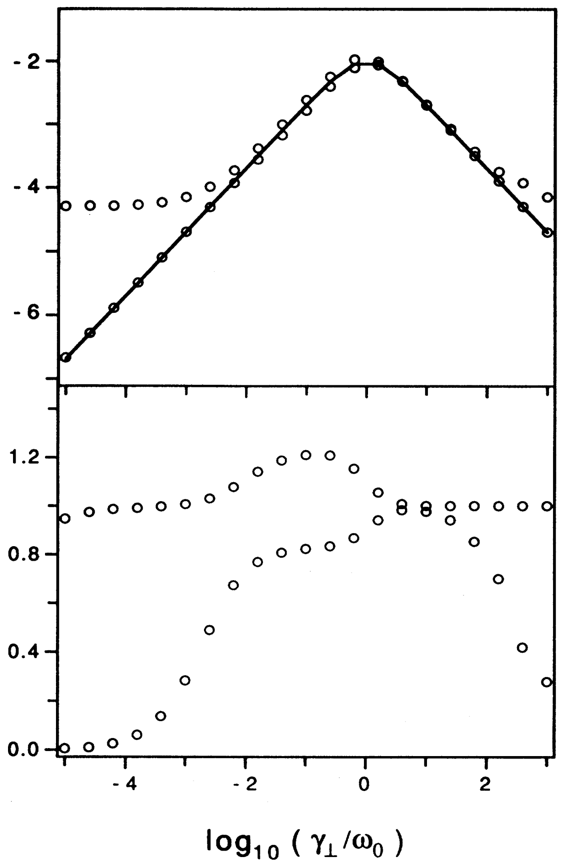

FIG. 12. Uncorrelated dichotomic noise. Dependence of the decay rates of $\bar{S}_z, \alpha_i$ (top), and the ratio $(\alpha_i T_1'')^{-1}$ (bottom), on the transverse fluctuation rate $\gamma_\perp = \gamma_x = \gamma_y$. In the top graph the superimposed line plots $T_1''^{-1}(\gamma_\perp)$, $\omega_0 = 1$, $\gamma_z = 5\times 10^{-5}$, and $\Delta_x = \Delta_y = \Delta_z = 0.1$.

$$(\alpha' T_1'')^{-1} \cong 1 + \frac{2\Delta_z}{\omega_0}, \quad (\alpha'' T_1'')^{-1} \cong 1 - \frac{2\Delta_z}{\omega_0}, \quad \gamma_\perp < \omega_0$$
$$(\alpha' T_1'')^{-1} \cong 1 + \left[\frac{\omega_0 + \Delta_z}{\gamma_\perp}\right]^2, \tag{4.26}$$
$$(\alpha'' T_1'')^{-1} \cong 1 + \left[\frac{\omega_0 - \Delta_z}{\gamma_\perp}\right]^2, \quad \gamma_\perp > \omega_0 .$$

In particular, in the region $2\Delta_\perp^2/\gamma_z > \gamma_\perp > \omega_0$, the two rates α' and α'' are very close to each other: the relaxation of $\bar{S}_z$ still cannot be described by a single relaxation time. For $\gamma_z \omega_0^2/2\Delta_\perp^2 < \gamma_\perp < \omega_0$, α' and α'' are further separated, but still faster than γ_z.

Figure 12 can be read from a different standpoint. If the spin system is observed via $\bar{S}_z$, it appears to be *homogeneous* for $\gamma_\perp/\omega_0 > 400$ or $\gamma_\perp/\omega_0 < 2.5\times 10^{-3}$, whereas it appears to be *inhomogeneous* for $400 > \gamma_\perp/\omega_0 > 2.5\times 10^{-3}$. In the phase diagram $\{\gamma_\perp, \gamma_z\}$, the crossover from the homogeneous (ergodic) decay of $\bar{S}_z(t)$ with a single decay constant to the inhomogeneous (nonergodic) decay with multiple decay constants takes place when the observation time T_1 becomes shorter than $1/\gamma_z$.

The role of the longitudinal fluctuations to determine the homogeneous or inhomogeneous character of $\bar{S}_z$ is shown in Fig. 13, where the quantity $(\alpha_i T_1'')^{-1}$ is plotted against γ_z. The top curve coincides with the ratio T_1/T_1'' and is a cross section along the γ_z axis of the surface drawn in Fig. 10 (note that the well observed in Fig. 10 is signaled in Fig. 13 by a dip). $\bar{S}_z$ is homogeneous if $1/\gamma_z$ is longer than the observation time $T_1 \cong T_1''$. If $\gamma_z \ll T_1^{-1}$, the decay of $\bar{S}_z$ is described by a sum of decaying exponentials.

If ω_z is discrete, the limit case $\gamma_z = 0$ may be described by

$$\bar{S}_z(t) = \bar{S}_z(0) \sum_{\omega_z} p(\omega_z) \exp[-t/T_1(\omega_z)], \quad \gamma_z = 0 . \tag{4.27a}$$

$p(\omega_z)$ is the equilibrium distribution of the random variable ω_z. $T_1(\omega_z)$ is defined as the "residual" longitudinal relaxation time, which one finds by keeping ω_z constant and making only $\omega_{x,y}$ fluctuate. The second-order expression of $T_1(\omega_z)$ is ($\Delta_x = \Delta_y = \Delta_\perp$ and $\gamma_x = \gamma_y = \gamma_\perp$)

$$T_1''^{-1}(\omega_z) = \frac{2\Delta_\perp^2 \gamma_\perp}{(\omega_0 + \omega_z)^2 + \gamma_\perp^2} . \tag{4.27b}$$

For the dichotomic noise $\omega_z = \pm\Delta_z$. Only two residual rates $1/T_1(\omega_z)$ with equal weight $p(\omega_z) = 0.5$ are found, namely, α' and α'' [Eq. (4.25)].

Let us consider now the longitudinal relaxation of a particle with spin $S = \frac{1}{2}$ in the presence of the three uncorrelated, Gaussian random fields directed along the three orthogonal axes. For this model the ratio T_1/T_1'' is plotted in Fig. 14. Once again, we limit the discussion to the region $\gamma_x = \gamma_y = \gamma_\perp$ and $\Delta_x = \Delta_y = \Delta_\perp$. The pattern of Fig. 14 is similar to the one found in the dichotomic case (Fig. 10). The region where the inequality

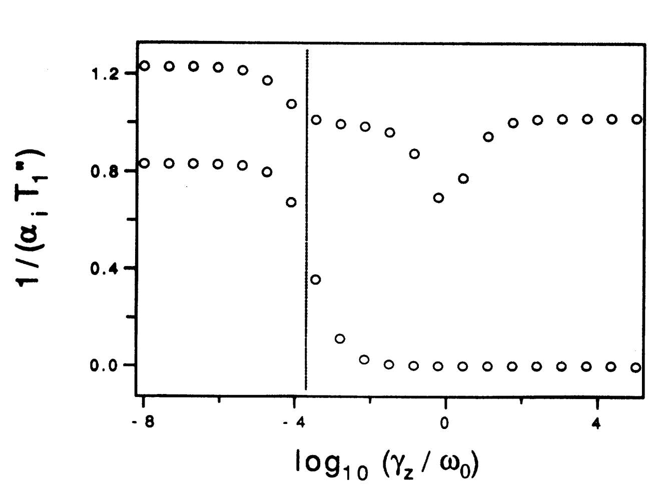

FIG. 13. Uncorrelated dichotomic noise. Dependence of the ratio $(\alpha_i T_1'')^{-1}$ on the longitudinal fluctuation rate γ_z. $\omega_0 = 1$, $\gamma_\perp = 0.01$, and $\Delta_x = \Delta_y = \Delta_z = 0.1$.

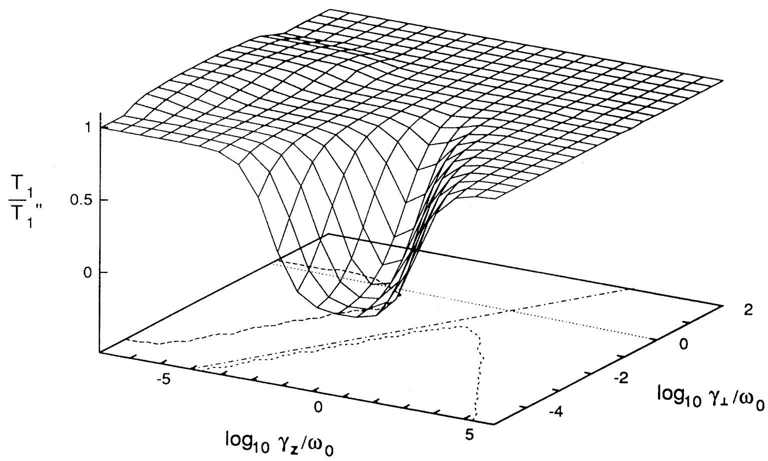

FIG. 14. Uncorrelated Gaussian noise. Dependence of the ratio T_1/T_1'' on the fluctuation rates γ_z and $\gamma_\perp$. Contour plots bound the region where Eq. (4.19) is fulfilled. The dot-dashed line is the locus $\gamma_\perp=\gamma_z$. $\omega_0=1$, $\Delta_x=\Delta_z=0.05$, and $\Delta_y=0$.

$$\left|\frac{T_1''^{-1}-T_1^{-1}}{T_1^{-1}}\right|<2\frac{\sum_i \Delta_i^2}{\max\{\omega_0^2,\gamma_\perp^2\}} \tag{4.28}$$

is fulfilled is bound by contour plots. As in the dichotomic case, the region includes the line $\gamma_\perp=\gamma_z$. The fact that for $\gamma_\perp=\gamma_z$ the Gaussian, uncorrelated fluctuations obey Eq. (4.28) was already noted elsewhere [16], by analyzing the existing treatments, which assume $\gamma_\perp=\gamma_z$ [3–6,9]. As in the dichotomic case, the well in Fig. 14 stems from neglecting at second order the contribution of ω_z to the longitudinal relaxation rate. This is confirmed by Fig. 15, where the ratio T_1/T_1'''' is plotted [Eq. (4.28)] and the well has virtually disappeared.

Finally, let us discuss the hills appearing in Figs. 14 and 15 for $\gamma_z\leq\gamma_\perp\leq\omega_0$. We anticipate that, as in the dichotomic case, this structure signals the breakdown of the time scale separation between T_1 and $1/\gamma_z$. In this region the signal is well approximated by a form analogous to Eq. (4.27), namely,

$$\bar{S}_z(t)=\bar{S}_z(0)\int d\omega_z p(\omega_z)\exp[-t/T_1(\omega_z)] \,. \tag{4.29}$$

There is an important difference between Eqs. (4.27) and (4.29). The former has a discrete spectrum of relaxation rates, the latter a continuous one. The generalized Langevin equation replaces the space spanned by the states of the quantum system and the bath with an effective one of *finite* dimension whose basis is given by Eqs. (2.7). The dimension N of this effective space is set by truncating the recursion at a definite step $n_t=N$. If the original phase space is finite itself, the replacement corresponds to a change of representation. In that case (e.g., our dichotomic model) the rates of $\bar{S}_z(t)$ derived from Eqs. (4.12a) in the old representation and the new one coincide. If the old phase space has *infinite* dimension (e.g., our Gaussian model), the new *finite* representation is only approximate. In particular, in the limit $\gamma_z=0$, Eq. (4.29) states that the spectrum of relaxation rates $\bar{S}_z(t)$ is *continuous,* whereas the approximate representation yields only a finite number of decay rates.

To gain insight in the distribution of approximate decay rates provided by the generalized Langevin equation, we have plotted it in Fig. 16. WIth respect to the dichotomic case (Fig. 12), some similarities are apparent, namely, the coincidence of the smallest relaxation rate with $T_1''^{-1}$ and the presence of a band of rates close to γ_z, merging with the smallest one in the heterogeneous

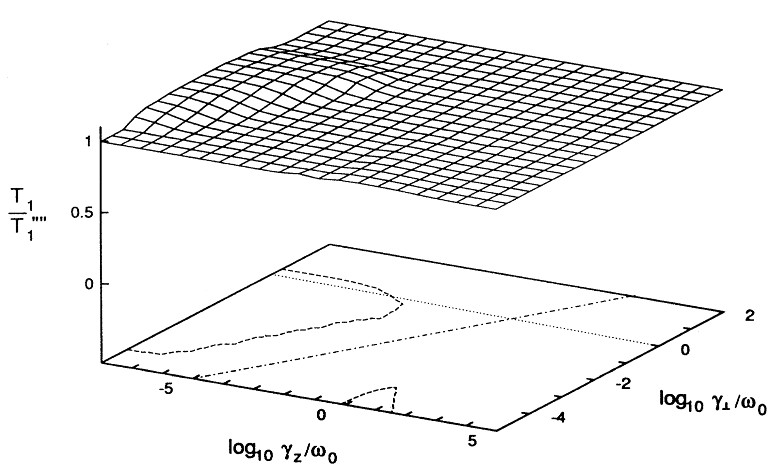

FIG. 15. Same as in Fig. 14, but for the ratio T_1/T_1''''.

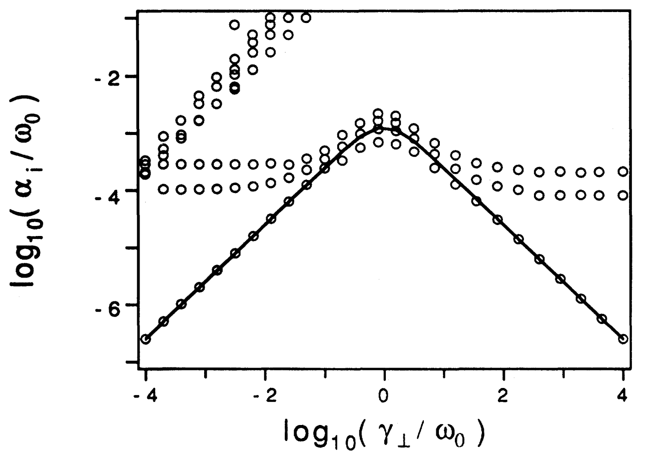

FIG. 16. Uncorrelated Gaussian noise. Dependence of the decay rates of $\bar{S}_z, \alpha$, on the fluctuation rate $\gamma_\perp$. The superimposed line plots $T_1''^{-1}(\gamma_\perp)$, $\omega_0=1$, $\Delta_x=\Delta_z=0.05$, $\Delta_y=0$, and $\gamma_z=10^{-4}$.

region ($T_1''^{-1}>\gamma_z$). In addition, the Gaussian model shows a band of rates close to $\gamma_\perp$. In the heterogeneous region ($\gamma_\perp \simeq \omega_0$), where Eq. (4.29) applies, only four relaxation rates are found close to $T_1''^{-1}$, even if the continued fraction is truncated at $n_t=100$. By inspection, it is found that (i) most poles of $D_1^{(100)}(z)$ [Eq. (4.12a)] crowd in $z \approx -\gamma_z, -\gamma_\perp, \pm i\omega_0$ and (ii) by increasing n_t, the poles close to $T_1''^{-1}$ are generated slowly. This is in contrast to the opinion that the generalized Langevin equation, which is equivalent to the Mori approach (see Ref. [16] and references cited therein), generates, by iterating Eq. (2.7), first slowly relaxing basis vectors and then fast relaxing ones.

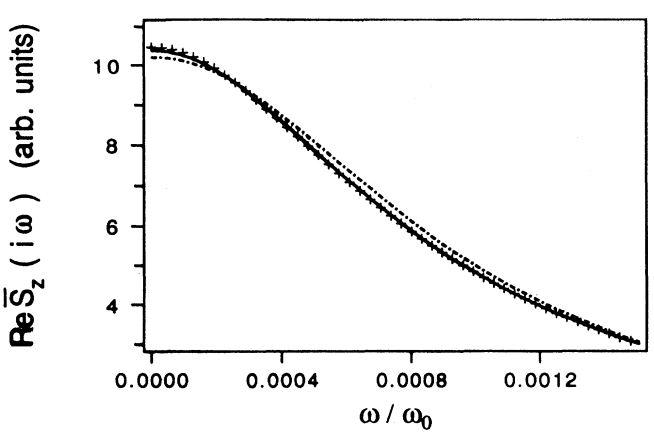

FIG. 17. Uncorrelated Gaussian noise. Spectrum of $\bar{S}_z(i\omega)$ for slow fluctuations of ω_z. Comparison of the numerical results [Eq. (4.20)] (crosses) with the asymptotic form [Eq. (4.27)] (continuous line), and the single relaxation time approximation (dot-dashed line). $\omega_0=1$, $\Delta_x=0.05$, $\Delta_y=0, \Delta_z=0.7$, $\gamma_z=10^{-8}$, and $\gamma_\perp=1.77$. The parameters of Eq. (4.20) are $c_1=0.407$, $c_2=0.593$, $\alpha_1=1.592\times10^{-3}$, and $\alpha_2=9.044\times10^{-4}$.

Remarkably, the few poles close to $T_1''^{-1}$ are enough to recover the spectrum of $\bar{S}_z(i\omega)$ close to $\omega=0$. In Fig. 17 the spectrum of $\bar{S}_z(i\omega)$ is drawn according to Eq. (4.20), by considering only the two rates α_t with the largest weights c_i. The result is compared with the limit from Eq. (4.29). The good agreement indicates that, even in the case of a continuous distribution of relaxation rates, the generalized Langevin equation provides a good approximation of the exact behavior. It is worth noting that in Fig. 17 the high value of Δ_z ($\Delta_z=0.7\omega_0$) broadens the distribution of residual $T_1''^{-1}(\omega_z)$ [$T_1''^{-1}(\omega_0-\Delta_z)/T_1''^{-1}(\omega_0+\Delta_z)=1.9$] [35].

In Fig. 17 the spectrum expected for a *single* relaxation time, i.e., $p(\omega_z)=\delta(\omega_z-\bar{\omega})$ in Eq. (4.29), was fitted to the spectrum of $\bar{S}_z(i\omega)$. It is apparent that the fit is not as good as the one using Eq. (4.20). Nonetheless, the discrepancy is small and one may conclude that $\bar{S}_z(i\omega)$ and $\bar{S}_z(t)$ are not sensitive quantities to the local heterogeneities. This remark parallels similar findings concerning the dependence on the distribution of the decay times of correlation, response, or relaxation functions. Some authors have pointed out that even complex distributions

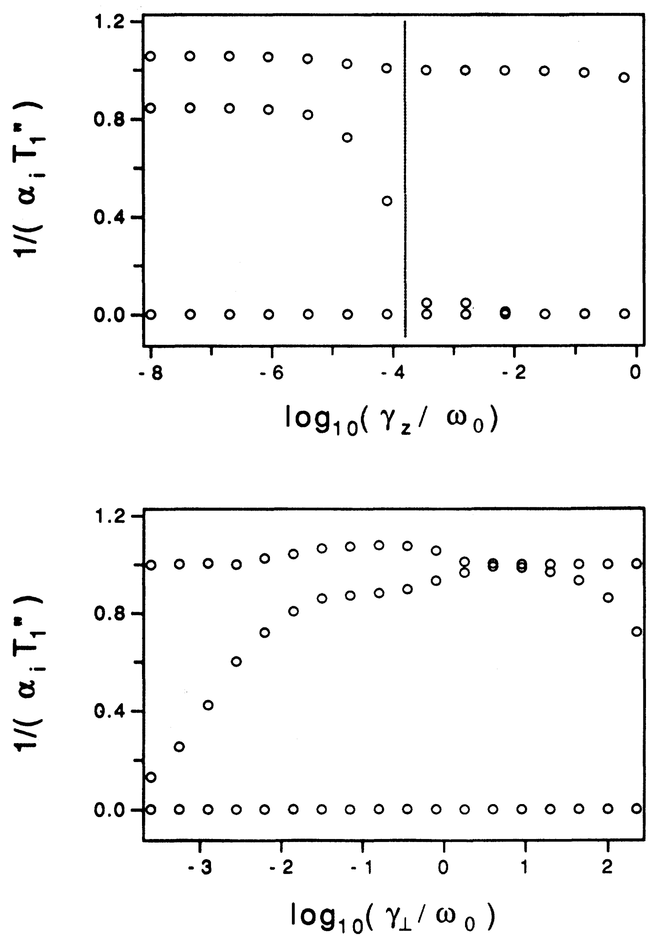

FIG. 18. Uncorrelated Gaussian noise. Dependence of the ratio $(\alpha_i T_1'')^{-1}$ on the fluctuation rate γ_z (top: $\gamma_\perp=3.16\times10^{-2}$) and $\gamma_\perp$ (bottom; $\gamma_z=3.98\times10^{-6}$). $\omega_0=1$, $\Delta_x=\Delta_z=0.05$, and $\Delta_y=0$.

lead in many cases to behaviors which are well reproduced by few exponentials (e.g., see the paper by Gotze in [26]) or that very different distributions yield virtually identical results [36].

Finally, in Fig. 18 the dependence of the spectrum of relaxation rates of $\bar{S}_z(t),\alpha_i$, on γ_z and $\gamma_\perp$ is shown. The general pattern is similar to the one shown by the dichotomic case (Figs. 12 and 13), apart from a narrow distribution of fast relaxation rates close to γ_z and $\gamma_\perp$. If $T_1''^{-1} \ll \gamma_z$, Eq. (4.24) holds ($T_1''^{-1}$ is the same for both the dichotomic and the Gaussian case) and $\bar{S}_z(t)$ relaxes at long times with a single, dominant rate T_1^{-1} well approximated by $T_1''^{-1}$. If Eqs. (4.24) are not fulfilled, namely, γ_z is small, the long time behavior of $\bar{S}_z(t)$ approaches the limit form given by Eq. (4.29). In this region, Fig. 18 shows that two rates get close to each other. In the dichotomic case the two close rates are the residual rates $T_1(\omega_z)$ defined by Eq. (4.27b). As discussed above, in the Gaussian case the residual rates are in principle infinite, so that the two close rates do not have a direct physical interpretation. They may be seen as "effective" rates to approximate Eq. (4.29) in terms of Eq. (4.20) (Fig. 17).

V. CONCLUSIONS

We have presented a thorough discussion of the relaxation behavior of a two-level system influenced by colored fluctuations. Even though several papers recently reported on this issue [1–18], they limited the discussion to specific models with some restrictions on the model parameters. Studies have dealt with uncorrelated Gaussian noise [3–6,9,11], uncorrelated dichotomic noise [8,9,11], and correlated dichotomic noise [16]. For the case of uncorrelated fluctuations, it has often been assumed that either they are transverse (i.e., $\omega_z=0$) [3,6,9] or their rates are equal $\gamma_x=\gamma_y=\gamma_z$ [3–6,9].

The present paper extends the above discussions and illustrates the topic of the relaxation of a two-level system from a unified point of view. Four models of noise have been studied, i.e., dichotomic and Gaussian fluctuations with strong or vanishing correlations.

This paper has been motivated by two previous papers [16,17], which addressed the question of the weakest conditions ensuring the presence of a single (dominant) relaxation time at long times. In particular, in [16] a careful investigation of the case of correlated dichotomic noise and an analysis of some sparse results in the open literature for the uncorrelated Gaussian noise with equal fluctuation rates $\gamma_x=\gamma_y=\gamma_z$ have been presented. For these cases it was proven that the averaged longitudinal magnetization $\bar{S}_z$ relaxes with a dominant relaxation time T_1, provided that the mild constraint of Eq. (1.1) is fulfilled. Furthermore, an upper bound of the relative error between T_1 and his second-order approximation T_1'' was given [Eq. (1.2)].

One of the main results of the present paper is to confirm the basic result of Refs. [16,17] by proving on a firmer basis the robustness of Eqs. (1.1) and (1.2), provided that the random fields are strongly correlated or uncorrelated, but with similar fluctuation rates. Interestingly, for the latter case the region of the phase space $\{\gamma_\perp,\gamma_z\}$, where Eq. (1.2) holds, includes for $\gamma_\perp \le \omega_0$ only a narrow strip around the locus $\gamma_\perp=\gamma_z$ (Figs. 10 and 14).

Extending other studies, general expressions of the relaxation times when the fluctuations have different rates, i.e., $\gamma_x\neq\gamma_y\neq\gamma_z$, have been derived. The expressions are correct at fourth order in the amplitude of the random fields. It is found that the well known rule $1/T_2=1/T_2^{\text{adiabatic}}+1/(2T_1)$ is recovered at fourth order only for correlated dichotomic noise [16]. We focused our attention on the case $\gamma_x=\gamma_y\neq\gamma_z$. The general features of the phase diagram of both the dichotomic and the Gaussian model are summarized in Fig. 19. Three different regions may be identified ($\gamma_\perp=\gamma_x=\gamma_y$).

The HOM region. In this zone the relaxation is homogeneous and is characterized by a single relaxation rate T_1^{-1} well approximated by $T_1''^{-1}$. The relative error between T_1^{-1} and $T_1''^{-1}$ is given by a form analogous to Eq. (1.2), given by Eq. (4.19).

The IV region. In this zone T_1 differs markedly from T_1''. The discrepancy is due to the lack of any second-order contribution to the longitudinal relaxation coming from ω_z. By replacing T_1'' with T_1'''', Eq. (4.19) is fully recovered (Figs. 11, and 15).

The HET region. In this region the homogeneous relaxation is replaced by the heterogeneous relaxation. The former is expected if the observation time T_1 exceeds the microscopic time scales, the latter in the reverse case, which is typical in slowly fluctuating environments such as undercooled liquids and polymers. The HET region is located at $\omega_0>\gamma_\perp>\gamma_z$ and corresponds to a slow fluctuation of the energy spacing ($\gamma_z\to 0$) [24,27]. A single longitudinal relaxation time is not observed at long times. Far from the boundaries of the HET region $\bar{S}_z(t)$ decays according to Eqs. (4.27) or (4.29). We have shown that the generalized Langevin equation reproduces well the heterogeneous decay with a few exponentials, even if the residual relaxation times $T_1^{-1}(\omega_z)$ are fairly distributed in a *continuous* way (Fig. 17).

Finally, we remark on the low sensitivity of spectroscopic schemes which try to detect local heterogeneities

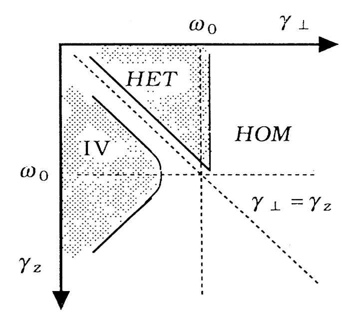

FIG. 19. Relevant regions in the phase space of the stochastic bath modeled by uncorrelated noise. HOM region homogeneous relaxation of $\bar{S}_z(t)$ with a dominant relaxation time $T_1 \cong T_1''$; IV region, homogeneous relaxation of $\bar{S}_z(t)$ with a dominant relaxation time $T_1 \cong T_1''''$; HET region; heterogeneous relaxation of $\bar{S}_z(t)$ with a distribution of relaxation times.

via *linear* susceptibilities in the frequency domain or, equivalently, response or relaxation functions in the time domain. Work is in progress to show that a *nonlinear* response may dramatically increase that sensitivity.

We plan in a forthcoming paper to extend the results presented here and in [16,17] to include the case of strongly nonexponential correlation loss in the time domain, as usually found in supercooled fluids [26] or critical phenomena.

ACKNOWLEDGMENTS

The authors are indebted to Professor M. Giordano for many helpful discussions during the present work.

APPENDIX A

Equations (4.5) describe the dynamics of the magnetization $\mathbf{S}$ up to the fourth order in the amplitude of the fluctuating fields Δ. Their Laplace transform is

$$z\langle S_1^{(0)}(z)\rangle-\langle S_1^{(0)}(t=0)\rangle$$
$$=(\mathcal{R}^*_{2_{11}}+\mathcal{R}^*_{4_{11}})\langle S_1^{(0)}(z)\rangle+\mathcal{R}^*_{2_{1-1}}\langle S_{-1}^{(0)}(z+2i\omega_0)\rangle$$
$$+\mathcal{R}^*_{2_{10}}\langle S_0^{(0)}(z+i\omega_0)\rangle\ , \qquad \text{(A1a)}$$

$$z\langle S_{-1}^{(0)}(z)\rangle-\langle S_{-1}^{(0)}(t=0)\rangle$$
$$=(\mathcal{R}_{2_{11}}+\mathcal{R}_{4_{11}})\langle S_{-1}^{(0)}(z)\rangle+\mathcal{R}_{2_{1-1}}\langle S_1^{(0)}(z-2i\omega_0)\rangle$$
$$+\mathcal{R}_{2_{10}}\langle S_0^{(0)}(z-i\omega_0)\rangle\ , \qquad \text{(A1b)}$$

$$z\langle S_0^{(0)}(z)\rangle-\langle S_0^{(0)}(t=0)\rangle$$
$$=(\mathcal{R}^*_{2_{00}}+\mathcal{R}^*_{4_{00}})\langle S_0^{(0)}(z)\rangle+\mathcal{R}^*_{2_{01}}\langle S_1^{(0)}(z-i\omega_0)\rangle$$
$$+\mathcal{R}_{2_{01}}\langle S_{-1}^{(0)}(z+i\omega_0)\rangle\ , \qquad \text{(A1c)}$$

where the asterisk indicates the complex conjugate. In the limit of fluctuating fields with amplitudes $\Delta\ll\omega_0$ $\langle S_{\pm1}^{(0)}(z)\rangle$ and $\langle S_0^{(0)}(z)\rangle$ for $|z|=\omega_0$, or multiples are small. This fact allows the explicit evaluation of $\langle S_0^{(0)}(z)\rangle$ and $\langle S_{\pm1}^{(0)}(z)\rangle$ when $z=i\omega$ and $\omega\ll\omega_0$.

Let us consider $\langle S_{+1}^{(0)}(z)\rangle$. In the absence of the coupling between the transverse and the longitudinal magnetization (i.e., $\mathcal{R}_{2_{10}}=0$) and by neglecting $\langle S_{-1}^{(0)}(-2i\omega_0)\rangle$, Eq. (A1a) yields the explicit expression of the transverse relaxation time T_2 as

$$\frac{1}{T_2}=-\mathrm{Re}\{\mathcal{R}_{2_{11}}+\mathcal{R}_{4_{11}}\}\ . \qquad \text{(A2)}$$

If $\mathcal{R}_{2_{10}}\neq0$, the complete expression for the transverse relaxation time is

$$\frac{1}{T_2''''}=-\mathrm{Re}\left\{\mathcal{R}_{2_{11}}+\mathcal{R}_{4_{11}}+i\frac{\mathcal{R}_{2_{01}}\mathcal{R}_{2_{10}}}{\omega_0}\right\} \qquad \text{(A3)}$$

and for the dephasing

$$\Delta\omega''''=-\mathrm{Im}\left\{\mathcal{R}_{2_{11}}+\mathcal{R}_{4_{11}}+i\frac{\mathcal{R}_{2_{01}}\mathcal{R}_{2_{10}}}{\omega_0}\right\}-\frac{|\mathcal{R}_{2_{1-1}}|^2}{2\omega_0}\ . \qquad \text{(A4)}$$

The corrections are evaluated by replacing in Eq. (A1a) the expression of $\langle S_0^{(0)}(-i\omega_0)\rangle$, derived from Eq. (A1c) by setting $z=-i\omega_0$ and neglecting $\langle S_{-1}^{(0)}(-2i\omega_0)\rangle$. Analogously, one finds for the longitudinal relaxation time

$$\frac{1}{T_1''''}=-\mathcal{R}_{2_{00}}-\mathcal{R}_{4_{00}}-2\,\mathrm{Im}\left\{\frac{\mathcal{R}_{2_{01}}\mathcal{R}_{2_{10}}}{\omega_0}\right\} \qquad \text{(A5)}$$

since $\mathcal{R}_{2_{00}}$ and $\mathcal{R}_{4_{00}}$ are real.

For the reader's convenience we write explicitly the relevant elements of the $\mathcal{R}$ matrix for the case of correlated dichotomic noise:

$$\mathcal{R}_{2_{11}}=\mathcal{R}^*_{2_{-1-1}}=-\frac{\tilde{\Delta}_x^2}{2}\frac{1}{-i\omega_0+\gamma}-\frac{\Delta z^2}{\gamma}\ , \qquad \text{(A6)}$$

$$\mathcal{R}_{2_{00}}=-\tilde{\Delta}_x^2\frac{\gamma}{\omega_0^2+\gamma^2}\ , \qquad \text{(A7)}$$

$$\mathcal{R}_{2_{1-1}}=\mathcal{R}^*_{2_{-11}}=\frac{\tilde{\Delta}_x^2}{2}\frac{1}{i\omega_0+\gamma}\ , \qquad \text{(A8)}$$

$$\mathcal{R}_{2_{0\pm1}}=\frac{\tilde{\Delta}_x\Delta_z}{\gamma}\ , \qquad \text{(A9)}$$

$$\mathcal{R}_{2_{10}}=\mathcal{R}^*_{2_{-10}}=\frac{\tilde{\Delta}_x\Delta_z}{2}\frac{1}{i\omega_0+\gamma}\ , \qquad \text{(A10)}$$

$$\mathrm{Re}\{\mathcal{R}_{4_{11}}\}=-\frac{\Delta_z^4}{\gamma^3}-\frac{\tilde{\Delta}_x^4\gamma(\gamma^2-\omega_0^2)}{2(\gamma^2+\omega_0^2)^3}-\frac{\tilde{\Delta}_x^2\Delta_z^2(3\gamma^2+\omega_0^2)}{2\gamma(\gamma^2+\omega_0^2)^2}\ , \qquad \text{(A11)}$$

$$\mathrm{Im}\{\mathcal{R}_{4_{11}}\}=-\frac{\tilde{\Delta}_x^4\gamma^2\omega_0}{(\gamma^2+\omega_0^2)^3}-\frac{\tilde{\Delta}_x^2\Delta_z^2\omega_0}{(\gamma^2+\omega_0^2)^2}\ , \qquad \text{(A12)}$$

$$\mathcal{R}_{4_{00}}=-\frac{\tilde{\Delta}_x^4\gamma(\gamma^2-\omega_0^2)}{(\gamma^2+\omega_0^2)^3}-\frac{\tilde{\Delta}_x^2\Delta_z^2(\gamma^2-\omega_0^2)}{\gamma(\gamma^2+\omega_0^2)^2}\ . \qquad \text{(A13)}$$

Replacing the above expressions in Eqs. (A3)–(A5) yields Eqs. (B4)–(B6) of Appendix B.

APPENDIX B

We list the fourth-order dynamic shifts and relaxation times for the four models of the fluctuation studied in the paper. For uncorrelated dichotomic noise

$$\frac{1}{T_1''''}=\frac{\Delta_x^2\gamma_x}{\omega_0^2+\gamma_x^2}+\frac{\Delta_y^2\gamma_y}{\omega_0^2+\gamma_y^2}+\frac{\Delta_x^4\gamma_x(\gamma_x^2-\omega_0^2)}{(\omega_0^2+\gamma_x^2)^3}+\frac{\Delta_y^4\gamma_y(\gamma_y^2-\omega_0^2)}{(\omega_0^2+\gamma_y^2)^3}+\frac{\Delta_x^2\Delta_y^2(\gamma_x+\gamma_y)(\gamma_x^2\gamma_y^2-\omega_0^4)}{(\omega_0^2+\gamma_x^2)^2(\omega_0^2+\gamma_y^2)^2}$$
$$-\frac{\Delta_x^2\Delta_z^2[\gamma_x(\gamma_x^2-3\omega_0^2)+\gamma_z(\gamma_x^2-\omega_0^2)]}{(\omega_0^2+\gamma_x^2)^2[\omega_0^2+(\gamma_x+\gamma_z)^2]}-\frac{\Delta_y^2\Delta_z^2[\gamma_y(\gamma_y^2-3\omega_0^2)+\gamma_z(\gamma_y^2-\omega_0^2)]}{(\omega_0^2+\gamma_y^2)^2[\omega_0^2+(\gamma_y+\gamma_z)^2]}\;, \tag{B1}$$

$$\frac{1}{T_2''''}=\frac{\Delta_x^2\gamma_x}{2(\omega_0^2+\gamma_x^2)}+\frac{\Delta_y^2\gamma_y}{2(\omega_0^2+\gamma_y^2)}+\frac{\Delta_z^2}{\gamma_z}+\frac{\Delta_x^4\gamma_x(\gamma_x^2-\omega_0^2)}{2(\omega_0^2+\gamma_x^2)^3}+\frac{\Delta_y^4\gamma_y(\gamma_y^2-\omega_0^2)}{2(\omega_0^2+\gamma_y^2)^3}+\frac{\Delta_z^4}{\gamma_z^3}$$
$$-\frac{\Delta_x^2\Delta_y^2[(\gamma_x^2+\gamma_y^2)[(\omega_0^4+\gamma_x^2\gamma_y^2)+4\gamma_x^2\gamma_y^2\omega_0^2]}{2(\omega_0^2+\gamma_x^2)^2(\omega_0^2+\gamma_y^2)^2(\gamma_x+\gamma_y)}-\frac{\Delta_x^2\Delta_z^2[2(\omega_0^4-\gamma_x^4)+\gamma_x\gamma_z(\omega_0^2-3\gamma_x^2)+\gamma_z^2(\omega_0^2-\gamma_x^2)]}{2(\omega_0^2+\gamma_x^2)^2[\omega_0^2+(\gamma_x+\gamma_z)^2]\gamma_z}$$
$$-\frac{\Delta_y^2\Delta_z^2[2(\omega_0^4-\gamma_y^4)+\gamma_y\gamma_z(\omega_0^2-3\gamma_y^2)+\gamma_z^2(\omega_0^2-\gamma_y^2)]}{2(\omega_0^2+\gamma_y^2)[\omega_0^2+(\gamma_y+\gamma_z)^2]\gamma_z}\;, \tag{B2}$$

$$\Delta\omega''''=\frac{\Delta_x^2\omega_0}{2(\omega_0^2+\gamma_x^2)}+\frac{\Delta_y^2\omega_0}{2(\omega_0^2+\gamma_y^2)}-\frac{\Delta_x^4[(\omega_0^2-\gamma_x^2)^2-4\omega_0^2\gamma_x^2]}{8\omega_0(\omega_0^2+\gamma_x^2)^3}-\frac{\Delta_y^4[(\omega_0^2-\gamma_y^2)^2-4\omega_0^2\gamma_y^2]}{8\omega_0(\omega_0^2+\gamma_y^2)^3}$$
$$-\frac{\Delta_x^2\Delta_y^2[(\omega_0^2-\gamma_x\gamma_y)[(\omega_0^2+\gamma_x\gamma_y)^2-\omega_0^2(\gamma_x-\gamma_y)^2]}{4\omega_0(\omega_0^2+\gamma_x^2)^2(\omega_0^2+\gamma_y^2)^2}+\frac{\Delta_x^2\Delta_z^2\omega_0[4\gamma_x(\omega_0^2+\gamma_x^2)+\gamma_z(\omega_0^2+5\gamma_x^2+2\gamma_x\gamma_z)]}{2(\omega_0^2+\gamma_x^2)^2[\omega_0^2+(\gamma_x+\gamma_z)^2]\gamma_z}$$
$$+\frac{\Delta_y^2\Delta_z^2\omega_0[4\gamma_y(\omega_0^2+\gamma_y^2)+\gamma_z(\omega_0^2+5\gamma_y^2+2\gamma_y\gamma_z)]}{2(\omega_0^2+\gamma_y^2)^2[\omega_0^2+(\gamma_y+\gamma_z)^2]\gamma_z}\;. \tag{B3}$$

For correlated dichotomic noise

$$\frac{1}{T_1''''}=\frac{\tilde\Delta_x^2\gamma}{\omega_0^2+\gamma^2}+\tilde\Delta_x^4\frac{\gamma(\gamma^2-\omega_0^2)}{(\omega_0^2+\gamma^2)^3}+\tilde\Delta_x^2\Delta_z^2\frac{2\gamma}{(\omega_0^2+\gamma^2)^2}\;, \tag{B4}$$

$$\frac{1}{T_2''''}=\Delta_z^2\frac{1}{\gamma}+\Delta_z^4\frac{1}{\gamma^3}+\frac{1}{2T_1''''}\;, \tag{B5}$$

$$\Delta\omega''''=\frac{1}{2}\frac{\tilde\Delta_x^2\omega_0}{\omega_0^2+\gamma^2}+\frac{\tilde\Delta_x^2\Delta_z^2(\omega_0^2-\gamma^2)}{[2\omega_0(\omega_0^2+\gamma^2)^2]}-\frac{\tilde\Delta_x^4[(\omega_0^2-\gamma^2)^2-4\gamma^2\omega_0^2]}{[8\omega_0(\omega_0^2+\gamma^2)^3]}\;. \tag{B6}$$

For uncorrelated Gaussian noise

$$\frac{1}{T_1''''}=\frac{\Delta_x^2\gamma_x}{\omega_0^2+\gamma_x^2}+\frac{\Delta_y^2\gamma_y}{\omega_0^2+\gamma_y^2}-\frac{2\Delta_x^4\omega_0^2\gamma_x}{(\omega_0^2+\gamma_x^2)^3}-\frac{2\Delta_y^4\omega_0^2\gamma_y}{(\omega_0^2+\gamma_y^2)^3}-\frac{\Delta_x^2\Delta_y^2(\gamma_x+\gamma_y)(\omega_0^4-\gamma_x^2\gamma_y^2)}{(\omega_0^2+\gamma_x^2)^2(\omega_0^2+\gamma_y^2)^2}$$
$$-\frac{\Delta_x^2\Delta_z^2[\gamma_x^2(\gamma_x+\gamma_z)-\omega_0^2(3\gamma_x+\gamma_z)]}{(\omega_0^2+\gamma_x^2)^2(\omega_0^2+(\gamma_x+\gamma_z)^2)}-\frac{\Delta_y^2\Delta_z^2[\gamma_y^2(\gamma_y+\gamma_z)-\omega_0^2(3\gamma_y+\gamma_z)]}{(\omega_0^2+\gamma_y^2)^2(\omega_0^2+(\gamma_y+\gamma_z)^2)}\;, \tag{B7}$$

$$\frac{1}{T_2''''}=\frac{\Delta_z^2}{\gamma z}+\frac{\Delta_x^2\gamma_x}{2(\omega_0^2+\gamma_x^2)}+\frac{\Delta_y^2\gamma_y}{2(\omega_0^2+\gamma_y^2)}+\frac{\Delta_x^4\omega_0^2}{4\gamma_x(\omega_0^2+\gamma_x^2)^2}+\frac{\Delta_y^4\omega_0^2}{4\gamma_y(\omega_0^2+\gamma_y^2)^2}$$
$$-\frac{\Delta_x^2\Delta_y^2[(\gamma_x^2\gamma_y^2+\omega_0^4)(\gamma_x^2+\gamma_y^2)+4\gamma_x^2\gamma_y^2\omega_0^2]}{2(\gamma_x+\gamma_y)(\omega_0^2+\gamma_x^2)^2(\omega_0^2+\gamma_x^2)^2}+\frac{\Delta_x^2\Delta_z^2[2\gamma_x^4+\gamma_x^2\gamma_z(3\gamma_x+\gamma_z)-\omega_0^2\gamma_z(\gamma_x+\gamma_z)-2\omega_0^4]}{2\gamma_z(\omega_0^2+\gamma_x^2)^2[\omega_0^2+(\gamma_x+\gamma_z)^2]}$$
$$+\frac{\Delta_y^2\Delta_z^2[2\gamma_y^4+\gamma_y^2\gamma_z(3\gamma_y+\gamma_z)-\omega_0^2\gamma_z(\gamma_y+\gamma_z)-2\omega_0^4]}{2\gamma_z(\omega_0^2+\gamma_y^2)^2[\omega_0^2+(\gamma_y+\gamma_z)^2]}\;, \tag{B8}$$

$$\Delta\omega''''=\frac{\Delta_x^2\omega_0}{2(\omega_0^2+\gamma_x^2)}+\frac{\Delta_y^2\omega_0}{2(\omega_0^2+\gamma_y^2)}-\frac{\Delta_x^4(\gamma_x^2+3\omega_0^2)}{8\omega_0(\omega_0^2+\gamma_x^2)^2}-\frac{\Delta_y^4(\gamma_y^2+3\omega_0^2)}{8\omega_0(\omega_0^2+\gamma_y^2)^2}-\frac{\Delta_x^2\Delta_y^2(\omega_0^2-\gamma_x\gamma_y)[(\omega_0^2+\gamma_x\gamma_y)^2-\omega_0^2(\gamma_x-\gamma_y)^2]}{4\omega_0(\omega_0^2+\gamma_x^2)^2(\omega_0^2+\gamma_y^2)^2}$$
$$+\frac{\Delta_x^2\Delta_z^2\omega_0[\gamma_x(4\gamma_x^2+5\gamma_x\gamma_z+2\gamma_z^2)+\omega_0^2(4\gamma_x+\gamma_z)]}{2\gamma_z(\omega_0^2+\gamma_x^2)^2[\omega_0^2+(\gamma_x+\gamma_z)^2]}+\frac{\Delta_y^2\Delta_z^2\omega_0[\gamma_y(4\gamma_y^2+5\gamma_y\gamma_z+2\gamma_z^2)+\omega_0^2(4\gamma_y+\gamma_z)]}{2\gamma_z(\omega_0^2+\gamma_y^2)^2[\omega_0^2+(\gamma_y+\gamma_z)^2]}\;. \tag{B9}$$

For correlated Gaussian noise

$$\frac{1}{T_1''''}=\frac{\tilde{\Delta}_x^2\gamma}{\omega_0^2+\gamma^2}-\frac{2\tilde{\Delta}_x^4\omega_0^2\gamma}{(\omega_0^2+\gamma^2)^3}+\frac{2\tilde{\Delta}_x^2\Delta_z^2(2\gamma^2+5\omega_0^2)\gamma}{(\omega_0^2+\gamma^2)^2(\omega_0^2+4\gamma^2)}\,, \tag{B10}$$

$$\frac{1}{T_2''''}=\frac{\tilde{\Delta}_x^2\gamma}{2(\omega_0^2+\gamma^2)}+\frac{\Delta_z^2}{\gamma}+\frac{\tilde{\Delta}_x^4\omega_0^2}{4\gamma(\omega_0^2+\gamma^2)^2}+\frac{\tilde{\Delta}_x^2\Delta_z^2(3\omega_0^4+8\omega_0^2\gamma^2+2\gamma^4)}{\gamma(\omega_0^2+\gamma^2)^2(\omega_0^2+4\gamma^2)}\,, \tag{B11}$$

$$\Delta\omega''''=\frac{1}{2}\frac{\tilde{\Delta}_x^2\omega_0}{\omega_0^2+\gamma^2}-\frac{\tilde{\Delta}_x^4(\gamma^2+3\omega_0^2)}{8\omega_0(\omega_0^2+\gamma^2)}-\frac{\tilde{\Delta}_x^2\Delta_z^2(4\gamma^6+7\omega_0^2\gamma^4+13\omega_0^4\gamma^2+4\omega_0^6)}{2\gamma^2\omega_0(\omega_0^2+\gamma^2)^2(\omega_0^2+4\gamma^2)}\,. \tag{B12}$$

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