Spin relaxation with bistable precession

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We study the effects of the reaction field on the spin relaxation. We find that they are not only responsible for a nonlinear frction process, as recently pointed out by several authors, but, in the case of sufficiently strong coupling, they also result in a bistable precession process. This implies that at weak temperatures the rate of the spin relaxation is expected to exhibit an Arrhenius-like dependence on temperature.

I. INTRODUCTION

The theoretical interpretation of the data of resonance spectroscopy widely rests on the Kubo stochastic theory of line shape,[1,2] called stochastic Liouville equation (SLE) theory. The SLE theory is very popular especially in the field of spin relaxation,[2] where slow molecular processes, the so-called slow motion,[2] give the spin probe highly non-Markovian properties.

It is well known that, within the SLE approach,[1,2] the magnetization does not relax towards its equilibrium value corresponding to the given external field but towards the zero value. Kubo and Hashitsume[3] showed that if a frictional resistance is assumed to accompany the random field causing Brownian motion, the random equation of the spin motion leads to a Fokker-Planck equation that guarantees approach to equilibrium. It is remarkable that these authors found the friction associated with random fluctuations to result in a nonlinear relaxation process. Seshadri and Lindenberg[4] found the same result from a rigorous microscopic picture. A more phenomenological approach was followed by Stillman and Freed.[5] These authors studied the rotational dynamics of a molecule within the theoretical framework of the SLE. They made the assumption that the rotator reaches a canonical equilibrium distribution, and using the detailed balance method illustrated by Haken,[6] supplemented the SLE picture with a convenient reaction field. More recently, an approach of the same kind was adopted and applied by Grigolini and Roncaglia[7] to the field of magnetic resonance spectroscopy. With this technique, these authors found the same nonlinear fluctuation-dissipation process as did Kubo and Hashitsume[3] and Seshadri and Lindenberg.[4]

In all these papers the system of interest reaches a canonical equilibrium distribution either as a consequence of a rigorous microscopic description[4] or of explicit constraints stemming from statistical mechanics.[3,5,7] However, it must be noted that, both in quantum and classical physics, the requirement for the equilibrium distribution of the system to be canonical in the unperturbed Hamiltonian may be incorrect. In the case of a classical oscillator coupled to a bath simulated by another stochastic and dissipative oscillator, it has been pointed out[8] that the system of interest reaches an equilibrium distribution that happens to be canonical with respect to a renormalized potential rather than to the bare potential. The same effect is present in quantum mechanics when the weak-coupling assumption leading to the canonical equilibrium distribution is rejected.[9,10]

The main purpose of the present paper is to study the effects of the reaction field, i.e., the bath motion induced by the coupling with the system, which is neglected in the current SLE approaches. Moreover, we shall not impose any constraint on the equilibrium distribution of the spin system, but only the canonical equilibrium condition for the initial state of the bath. For the sake of simplicity, we shall limit ourselves to adopt a procedure that will permit us to show the effects associated with the presence of the reaction field within a conventional second-order cumulant expansion.

We will find that the bare Hamiltonian must be replaced by a renormalized one, which will result in a nonstandard precessional motion. This means that, in addition to the external static field along the z axis, a component orthogonal to it, which depends on the mean value of the x component of the dipole, appears. In the strong-coupling regime this renormalized Hamiltonian results in a bistable precession motion, schematically illustrated in Fig. 1.

The problem of spin relaxation, as originally imagined by Kubo,[1] is still the object of current interest due to its

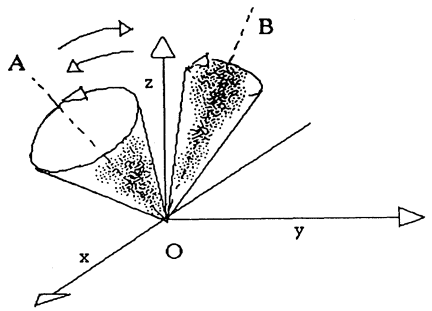

FIG. 1. Scheme of the bistable precession motion resulting from a strong coupling of the magnetic dipole with its bath. In addition to the magnetic field along the z axis a component along the x axis appears, the intensity of which depends on the x component of the dipole itself. As a result, the spin executes a sort of precession around the axis OA. A symmetric trapped state exists, illustrated here by the precessional cone around the axis OB. Because of thermal fluctuations the spin can also jump from one to the other precessional cone. The axes OA and OB are not fixed and their actual direction depends on the state of the spin system. In the adiabatic limit the precessional motion illustrated by this figure corresponds to the mathematical picture of Eq. (3.8).

close connection with the problem of colored noise.[11,12] In our paper we are not concerned with memory effects, but only with the role of the reaction field, which is neglected in these recent papers, too.

In Sec. II we illustrate how to make the semiclassical approximation without neglecting the reaction field. In Sec. III we adopt a convenient reference framework that allows us to reproduce all the relevant effects of the reaction field within a second perturbation order. The interesting physical predictions will be discussed in Sec. IV.

II. THE MICROSCOPIC HAMILTONIAN

As is well known, the Kubo theory[13] has essentially a phenomenological foundation. This is made especially clear by the so-called Kubo stochastic oscillator.[1] This is a stochastic model, written as

$$\dot{\mu}(t)=i[\omega(t)+\omega_0]\mu(t) \ . \tag{2.1}$$

This means that, due to the influence of the environment, the dipole $\mu(t)$ is driven by a stochastic process as well as by the time-independent Larmor frequency ω_0. Within the Kubo picture, the random frequency $\omega(t)$ is assumed to be a colored Gaussian noise, whose dynamics is described by

$$\dot{\omega}(t)=-\gamma\omega(t)+f(t) \ , \tag{2.2}$$

where $f(t)$ is a white Gaussian noise, with vanishing mean value, defined by

$$\langle f(0)f(t)\rangle=2\gamma\langle\omega^2\rangle_{\rm eq}\delta(t) \ . \tag{2.3}$$

The imaginary frequency mimicks a precession process that actually takes place in a three-dimensional space. Thus a more realistic description is

$$\dot{\boldsymbol{\mu}}(t)=\boldsymbol{\mu}(t)\times\boldsymbol{\Omega}_0+\boldsymbol{\mu}(t)\times\boldsymbol{\Omega}(t) \ , \tag{2.4}$$

where Ω_0 is the time-independent contribution to the Larmor frequency, assumed throughout the remaining part of this paper to be directed along the z axis, and $\Omega(t)$, a fluctuation resulting from the interaction with a bath. The multidimensional character of the system of equations (2.4) makes it necessary to have recourse to higher than the second-order cumulants for a satisfactory solution of the colored-noise problem to be obtained.[14] We focus here on the problem of the reaction field, rather than on that of the color of noise.

The theoretical investigation of this paper rests on the following microscopic Hamiltonian:

$$\mathcal{H}=-\frac{\omega_0}{2}\sigma_z+\frac{\alpha}{2}\sigma_x x+\mathcal{H}_B \ . \tag{2.5}$$

This means that we restrict ourselves to studying a strongly nonisotropic model in which the interaction along the x direction prevails over that along the y direction. The nonisotropic relaxation case has also been studied by Faid and Fox.[15] Here we focus our attention on the nonisotropic case with no fluctuations along the y direction. This is done, first of all, for the sake of simplicity. We do not aim to reproduce quantitatively a true spin-relaxation process. Rather, we aim at a general discussion of the problems involved by the presence of the reaction field within a model that has the essential aspects of a genuine problem of spin relaxation. The variable x in Eq. (2.5) represents the thermal bath degrees of freedom interacting with the spin system and $\mathcal{H}_B$ drives the free motion of x. We also assume that the magnetic dipole has a $\frac{1}{2}$ spin, so that the σ_i's are the Pauli matrices.

We study the time evolution of the following "polarization vector:"

$$\mu\equiv(\langle\sigma_x\rangle_S,\langle\sigma_y\rangle_S,\langle\sigma_z\rangle_S) \ , \tag{2.6}$$

which univocally describes the spin-$\frac{1}{2}$ density matrix ($\langle\ \rangle_S$ means the average over the spin degrees of freedom). To write the equation of motion of μ, we proceed as follows. First, from the Hamiltonian of Eq. (2.5), we derive the Heisenberg picture providing the time evolution of $\sigma_x(t)$, $\sigma_y(t)$, $\sigma_z(t)$, and $x(t)$. This picture also involves terms such as $x(t)\sigma_y(t)$ and $x(t)\sigma_z(t)$, the mean values of which in principle cannot be factorized into a system and a bath part. By application of the semiclassical approximation, according to which x is regarded as being a fluctuating c number, it is natural to make this factorization assumption. We thus obtain

$$\begin{aligned}
&\dot{\mu}_x=\omega_0\mu_y \ , \\
&\dot{\mu}_y=-\omega_0\mu_x-\alpha\mu_z x \ , \\
&\dot{\mu}_z=\alpha x\mu_y \ , \\
&\dot{x}=-\Gamma x+\Gamma\mu_x+F(t) \ ,
\end{aligned} \tag{2.7}$$

where the friction Γ and the white Gaussian noise F, with vanishing mean value, are related to each other by the standard fluctuation-dissipation relation

$$\langle F(t_1)F(t_2)\rangle = 2\Gamma\langle x^2\rangle\delta(t_1-t_2) , \tag{2.8}$$

with

$$\langle x^2\rangle = \frac{2k_BT}{\alpha} . \tag{2.9}$$

The fourth term of Eqs. (2.7) means that the bath variable x is thought of as the coordinate of an overdamped oscillator, driven by the white and Gaussian stochastic force $F(t)$.

Note that the quantum-mechanical variable x has dissipative properties due to the interaction with a virtually infinite number of degrees of freedom. All this is taken into account by Hamiltonian of Eq. (2.5). The semiclassical approximation allows us to simplify the problem, by replacing the quantum-mechanical dissipation process with the standard classical fluctuation-dissipation process of Eq. (2.8). On the contrary, in the last equation of the set of equations (2.7), the reaction term $\Gamma\mu_x$ has precisely the same structure as that of a rigorous Hamiltonian description. Equations (2.7) are equivalent to those derived from the discrete nonlinear Schrödinger equation applied to the case of the nonlinear nonadiabatic dimer. This fact will make us benefit from the results known in this research field.[16]

The Fokker-Planck equation corresponding to Eqs. (2.7) reads

$$\frac{\partial}{\partial t}\pi(\mu,x;t) = \mathcal{L}\pi(\mu,x;t) \equiv (\mathcal{L}_a' + \Lambda + \mathcal{L}_1')\pi(\mu,x;t) , \tag{2.10}$$

where

$$\mathcal{L}_a' \equiv -\omega_0\mu_y\frac{\partial}{\partial\mu_x} + \omega_0\mu_x\frac{\partial}{\partial\mu_y} , \tag{2.11}$$

$$\Lambda \equiv \Gamma\left[\frac{\partial}{\partial x}x + \langle x^2\rangle\frac{\partial^2}{\partial x^2}\right] , \tag{2.12}$$

$$\mathcal{L}_I' \equiv \alpha x\mu_z\frac{\partial}{\partial\mu_y} - \alpha x\mu_y\frac{\partial}{\partial\mu_z} - \Gamma\mu_x\frac{\partial}{\partial x} . \tag{2.13}$$

We have chosen to consider μ_x,μ_y,μ_z as three independent variables, ranging over the whole real axis; in this way, the constraint on the norm of the vector μ turns out to be simply a consequence of the dynamics originated by Eqs. (2.7). Note that Eqs. (2.10)–(2.13) must be regarded as being an exact description of the dynamics of the whole system, system of interest, and bath. This is due to the fact that we use the standard fluctuation-dissipation process of Eq. (2.8), which makes exact the corresponding multidimensional Fokker-Planck equation.

If we apply the projection method to Eq. (2.10),[17] we obtain a generalized master equation fully equivalent to it, depending on the moments[18]

$$M_n \equiv \langle\mathcal{L}_I'(t)Q\mathcal{L}_I'(t_1)Q\mathcal{L}_I'(t_2)\cdots Q\mathcal{L}_I'(t_{n-1})\mathcal{L}_I'(t_n)\rangle_B . \tag{2.14}$$

Let us now make the assumption that the last term on the right-hand side (rhs) of Eq. (2.13) can be neglected. This means that the bath is not influenced by the effect of the reaction term and the moments M_n are replaced by approximated expressions, denoted by M_n'. If we apply the Zwanzig projection technique[19] to the quantum-mechanical Liouville equation associated to the Hamiltonian of Eq. (2.5) and we then evaluate the resulting moments with the semiclassical approximation, these turn out to be identical to the approximated moments M_n'. Since the Zwanzig approach supplemented by the semiclassical approximation is known[20] to be equivalent to the SLE, we conclude that Eq. (2.10), with the last term on the rhs of Eq. (2.13) neglected, is equivalent to the SLE.

The fact that the operator $\mathcal{L}$ of Eq. (2.10) turns out to be equivalent to the SLE if the reaction term is neglected is extremely important. Reference 2 shows how to express the absorption spectrum in terms of an infinite continued fraction, with truncation carried out at an arbitrarily high order so as to guarantee a satisfactory convergence to the "exact" result. The same approach can be used without neglecting the reaction term. This will make it possible to study the effects induced by the reaction field in the so-called slow-motion regime. This continued-fraction procedure is virtually equivalent to a resummation over all the cumulants and will be adopted in a subsequent paper.[21] In Sec. III we shall show how to derive the bistable precession of Fig. 1 in a straightforward manner, without using this sophisticated calculation technique.

III. RENORMALIZATION OF THE SYSTEM OF INTEREST

We have now to approach the problem of replacing the equation of motion of Eq. (2.10) with a reduced description concerning only the system of interest, i.e., the dipole μ in this case. This must be done in such a way as to properly take into account the role of the reaction force. In principle this might be done with the version of the projection-operator approach established by Willis and Picard[22] to put the system of interest and the bath on the same footing. As already mentioned, in Sec. II, a further technique to adopt might be the cumulant expansion,[23–29] and especially the resummation at infinite order recently developed by Der[28] and Der and Schumacher.[29] It is easy to prove, in close agreement with the point of view of Chaturvedi and Shibata,[27] that the perturbation expansion[17,30] of the Zwanzig master equation[19] is equivalent to the standard cumulant expansion. Thus the second-order treatment of the Zwanzig master equation[17,30] is equivalent to the second cumulant. Our view is that, instead of looking for a resummation over all the cumulants, a repartition of the total dynamical operator $\mathcal{L}$ can be found that allows the corresponding second cumulant to account properly for the relevant physical properties of the system. This problem has been studied in the recent past in the case of a classical oscillator of interest nonlinearly coupled to another classical oscillator,[8] and it was shown that the second-order expansion corresponding to the proper repartition results in the correct

equilibrium distribution, whereas the more conventional repartition was shown[8] to produce the same result only after resummation over all the perturbation contributions. The big advantage of the recipe illustrated in Sec. II is that, after making the semiclassical approximation, we set the dynamics of the system under the form of a process of nonlinear stochastic physics. The latter has the same form as that of Ref. 8, thereby allowing us to use all the procedures proved to be effective in that case.

First, the oscillator is driven to a canonical equilibrium distribution by the standard fluctuation-dissipation relation of Eqs. (2.9) and (2.10), and via the spin-bath interaction, transmits its own canonical properties to the system. As a result of this, the whole system is driven towards the following equilibrium distribution:

$$\pi_{\rm eq}(\mu_x,\mu_y,\mu_z,\tilde{x}) \propto \exp\left[-\frac{1}{2k_BT}\left[\omega_0\mu_z-\alpha\mu_x x+\frac{\alpha}{2}x^2\right]\right] \times\delta(\mu_x^2+\mu_y^2+\mu_z^2-1)\ . \tag{3.1}$$

It is indeed straightforward to verify that this is the stationary solution of Eq. (2.10).

Equation (3.1) naturally leads one to describe the thermal bath in terms of a new coordinate,

$$\tilde{x}=x-\mu_x\ , \tag{3.2}$$

so that the total equilibrium distribution of Eq. (3.1) appears to be factorized into a system and a bath part, with no interference term:

$$\pi_{\rm eq}(\mu_x,\mu_y,\mu_z,\tilde{x}) \propto \exp\left[-\frac{1}{2k_BT}\left[\omega_0\mu_z-\frac{\alpha}{2}\mu_x^2+\frac{\alpha}{2}\tilde{x}^2\right]\right] \times\delta(\mu_x^2+\mu_y^2+\mu_z^2-1)\ . \tag{3.3}$$

Integrating over $\tilde{x}$, we get that the spin part happens to be canonical with respect to the effective Hamiltonian

$$\mathcal{H}_{\rm ren}=\frac{1}{2}\left[\omega_0\mu_z-\frac{\alpha}{2}\mu_x^2\right]\ . \tag{3.4}$$

This means that the weak-coupling prediction of usual statistical mechanics

$$p_{\rm eq}(\mu) \propto \exp\left[-\frac{1}{2k_BT}\omega_0\mu_z\right]\delta(\mu_x^2+\mu_y^2+\mu_z^2-1)\ , \tag{3.5}$$

must be replaced by the following more reliable prediction:

$$p_{\rm eq}(\mu) \propto \exp\left[-\frac{1}{2k_BT}\left[\omega_0\mu_z-\frac{\alpha}{2}\mu_x^2\right]\right] \times\delta(\mu_x^2+\mu_y^2+\mu_z^2-1)\ . \tag{3.6}$$

This explains why an approach using the assumption of Eq. (3.5) must be avoided.

Note that, in the weak-coupling case, the two equilibrium distributions, Eqs. (3.5) and (3.6), almost coincide. In the strong-coupling case, on the contrary, we have a quite significant discrepancy, due to the term that is quadratic in the x component of the dipole that ultimately comes from our proper treatment of the reaction term.

Equation (3.6) gives a complete description of the equilibrium properties of the spin system for arbitrary values of the coupling α, as is shown in Ref. 31. For example, in the weak-coupling limit, the equilibrium value of the z component of the dipole is expressed by the "canonical" Langevin function as a function of temperature. In the large-coupling case, on the contrary, Eq. (3.6) results in a strong departure from this behavior, and this striking effect is completely confirmed by the computer simulation of Ref. 31.

It is also interesting to briefly analyze the dynamical behavior of the system. By applying the transformation of Eq. (3.2), the set of equations (2.7) is replaced by

$$\begin{aligned}
&\dot{\mu}_x=\omega_0\mu_y\ ,\\
&\dot{\mu}_y(t)=-\omega_0\mu_x(t)-\alpha\mu_x(t)\mu_z(t)-\alpha\mu_z(t)\tilde{x}(t)\ ,\\
&\dot{\mu}_z(t)=\alpha\mu_x(t)\mu_y(t)+\alpha\tilde{x}(t)\mu_y(t)\ ,\\
&\dot{\tilde{x}}(t)=-\Gamma\tilde{x}(t)+f(t)-\omega_0\mu_y(t)
\end{aligned} \tag{3.7}$$

[in this new "reference frame" the reaction field is given by the term $\omega_0\mu_y(t)$]. In the adiabatic limit we can regard the variable $\tilde{x}$ as being so fast fluctuating as to make it possible to replace it with its vanishing mean value. In this way we get the "systematic" motion of the spin system, which is described by the renormalized Hamiltonian of Eq. (3.4) and whose equations of motion are

$$\begin{aligned}
&\dot{\mu}_x=\omega_0\mu_y\ ,\\
&\dot{\mu}_y(t)=-\omega_0\mu_x(t)-\alpha\mu_x(t)\mu_z(t)\ ,\\
&\dot{\mu}_z(t)=\alpha\mu_x(t)\mu_y(t)\ .
\end{aligned} \tag{3.8}$$

In the large-coupling regime, this set of equations is proved[16] to result in the bistable precessional motion illustrated in Fig. 1. This is so because a systematic x component of the "magnetic" field appears. When this x component is large enough with respect to the original component along the z axis, the dipole is prevented from executing a full precession around the z axis. The analysis of this deterministic motion and the corresponding predictions for the transition from the "untrapped" (one precessional cone around the z direction) to the "trapped" behavior (two distinct precessional cones) can be carried out precisely as done by Kenkre and coworkers to study the adiabatic nonlinear dimer,[16,32] and we refer the interested reader to those references for details. Using this analysis it is also possible to show that, upon increasing the coupling α, the transition from two distinct precessional cones into a single one takes place abruptly at the threshold value $\alpha_c=2\omega_0$. This behavior depends on the nonlinear structure of the systematic part of Eq. (3.8).

The transition from a trapped precessional motion to the other one implies the existence of an activation process, i.e., a very precise energy level has to be reached. It is easy to predict from this fact that, at small temperatures, the relaxation process has a dependence on temperature of the Arrhenius type. This temperature behavior in the field of spin relaxation is exhaustively studied in

Ref. 33. In Ref. 33 the Arrhenius-like law at small temperature is totally confirmed by computer simulation.

The new reference system of Eq. (3.2) suggests an efficient way of dividing the dynamical operator $\mathcal{L}$ of Eq. (2.10). The Fokker-Planck equation for the probability distribution $\pi(\mu_x,\mu_y,\mu_z,\tilde{x};t)$ corresponding to the set of equations (3.7) reads

$$\frac{\partial}{\partial t}\pi(\mu_x,\mu_y,\mu_z,\tilde{x};t)=\mathcal{L}\pi(\mu_x,\mu_y,\mu_z,\tilde{x};t)\ , \tag{3.9}$$

where

$$\mathcal{L}=\mathcal{L}_A+\mathcal{L}_B+\mathcal{L}_I\ , \tag{3.10}$$

$$\mathcal{L}_A\equiv-\omega_0\mu_y\frac{\partial}{\partial\mu_x}+\omega_0\mu_x\frac{\partial}{\partial\mu_y}+\alpha\mu_x\mu_z\frac{\partial}{\partial\mu_y}-\alpha\mu_x\mu_y\frac{\partial}{\partial\mu_z}\ , \tag{3.11}$$

$$\mathcal{L}_I\equiv\alpha\tilde{x}\mu_z\frac{\partial}{\partial\mu_y}-\alpha\tilde{x}\mu_y\frac{\partial}{\partial\mu_z}+\omega_0\mu_y\frac{\partial}{\partial\tilde{x}}\ , \tag{3.12}$$

$$\mathcal{L}_B\equiv\Gamma\left[\frac{\partial}{\partial\tilde{x}}\tilde{x}+\langle x^2\rangle\frac{\partial^2}{\partial\tilde{x}^2}\right]\ . \tag{3.13}$$

Note that if we express Eqs. (3.9)–(3.13) in terms of x, then we recover the model of Eqs. (2.10)–(2.13). In other words, the latter set of equations is still an exact model.

The calculation of the second cumulant involves some technical difficulties that have been the object of recent investigation.[17] We want to avoid the complicated calculations necessary to take into account the interplay between the "color"[17] of the stochastic variable $\tilde{x}$ and the unperturbed dynamics of the system. Thus, under the basic assumption that $\mathcal{L}_A\ll\mathcal{L}_B$, we limit ourselves to the first order in the ratios α/Γ and ω_0/Γ, thereby immediately obtaining

$$D_2(t)=C(t)\left[\alpha\mu_z\frac{\partial}{\partial\mu_y}-\alpha\mu_y\frac{\partial}{\partial\mu_z}\right]\times\left[\alpha\mu_z\frac{\partial}{\partial\mu_y}-\alpha\mu_y\frac{\partial}{\partial\mu_z}-\frac{\omega_0}{\langle x^2\rangle}\mu_y\right]\ , \tag{3.14}$$

where

$$C(t)\equiv\int_0^t ds\,\langle\tilde{x}^{(0)}(s)\tilde{x}^{(0)}(0)\rangle=\frac{\langle x^2\rangle}{\Gamma}(1-e^{-\Gamma t})\ . \tag{3.15}$$

$\tilde{x}^{(0)}(t)$ is the unperturbed motion of the oscillator and so it is a colored Gaussian stochastic process with zero mean value [see Eqs. (2.7) and (2.8)]. In conclusion we get for the reduced probability distribution $\sigma(\mu;t)$ the following equation of motion:

$$\frac{\partial\sigma(\mu;t)}{\partial t}=[\mathcal{L}_A+D_2(t)]\sigma(\mu;t)\ , \tag{3.16}$$

where

$$\mathcal{L}_A+D_2(t)\equiv-\omega_0\mu_y\frac{\partial}{\partial\mu_x}+\omega_0\mu_x\frac{\partial}{\partial\mu_y}+\alpha\mu_x\mu_z\frac{\partial}{\partial\mu_y}-\alpha\mu_x\mu_y\frac{\partial}{\partial\mu_z}+\frac{\langle x^2\rangle\alpha^2}{\Gamma}(1-e^{-\Gamma t})\left[\mu_y^2\frac{\partial}{\partial\mu_z^2}+\mu_z^2\frac{\partial}{\partial\mu_y^2}-\mu_z\frac{\partial}{\partial\mu_y}\mu_y\frac{\partial}{\partial\mu_z}-\mu_y\frac{\partial}{\partial\mu_z}\mu_z\frac{\partial}{\partial\mu_y}\right]+\frac{\omega_0\alpha}{\Gamma}(1-e^{-\Gamma t})\left[\mu_y^2\frac{\partial}{\partial\mu_z}-\mu_z\frac{\partial}{\partial\mu_y}\mu_y\right]\ . \tag{3.17}$$

The first important property of this reduced Fokker-Planck equation is that it results in the *exact* equilibrium distribution, i.e., Eq. (3.6). This is an advantage of the repartition of the total Liouvillian $\mathcal{L}$ induced by the new "reference frame" of Eq. (3.2), which permits one to recover the correct equilibrium properties within a straightforward second-order treatment.

To fully appreciate the elements of our approach compared with the predictions of the other theories,[3–5,7] let us evaluate the time evolution of the first moments of the dipole μ. We obtain

$$\begin{aligned}
&\langle\dot{\mu}_x(t)\rangle=\omega_0\langle\mu_y(t)\rangle\ ,\\
&\langle\dot{\mu}_y(t)\rangle=-\omega_0\langle\mu_x(t)\rangle-\alpha\langle\mu_x(t)\mu_z(t)\rangle+\alpha\frac{\omega_0}{\Gamma}(1-e^{-\Gamma t})\langle\mu_y(t)\mu_z(t)\rangle-\frac{2k_BT\alpha}{\Gamma}(1-e^{-\Gamma t})\langle\mu_y(t)\rangle\ ,\\
&\langle\dot{\mu}_z(t)\rangle=\alpha\langle\mu_x(t)\mu_y(t)\rangle-\alpha\frac{\omega_0}{\Gamma}(1-e^{-\Gamma t})\langle\mu_y^2(t)\rangle-\frac{2k_BT\alpha}{\Gamma}(1-e^{-\Gamma t})\langle\mu_z(t)\rangle\ .
\end{aligned} \tag{3.18}$$

If we consider macroscopic times, that is, $\Gamma t \gg 1$, we get from Eqs. (3.18) the following set of differential equations with time-independent coefficients:

$$\langle \dot{\mu}_x(t) \rangle = \omega_0 \langle \mu_y(t) \rangle ,$$

$$\langle \dot{\mu}_y(t) \rangle = -\omega_0 \langle \mu_x(t) \rangle - \alpha \langle \mu_x(t) \mu_z(t) \rangle + \alpha \frac{\omega_0}{\Gamma} \langle \mu_y(t) \mu_z(t) \rangle - \frac{2k_B T \alpha}{\Gamma} \langle \mu_y(t) \rangle , \quad (3.19)$$

$$\langle \dot{\mu}_z(t) \rangle = \alpha \langle \mu_x(t) \mu_y(t) \rangle - \alpha \frac{\omega_0}{\Gamma} \langle \mu_y^2(t) \rangle - \frac{2k_B T \alpha}{\Gamma} \langle \mu_z(t) \rangle .$$

We note that the relaxation terms $2k_B T \alpha \langle \mu_y(t) \rangle / \Gamma$ and $2k_B T \alpha \langle \mu_z(t) \rangle / \Gamma$ are those predicted by the standard Bloch theory. The terms $\alpha \omega_0 \langle \mu_y(t) \mu_z(t) \rangle / \Gamma$ and $\alpha \omega_0 \langle \mu_y(t)^2 \rangle / \Gamma$ are nonlinear friction processes coinciding with the predictions of Kubo and Hashitsume[3] and Seshadri and Lindenberg.[4] More recently the same nonlinear dissipation process has been independently derived by Kenkre and Wu.[32] The novelty within the field of spin relaxation is given by the second term of the second equation and by the first term of the third equations. These terms correspond to the bistable precession illustrated in Fig. 1 and are an effect of the renormalization of the Hamiltonian of interest, which, in turn, is a consequence of the presence of the reaction term, which is neglected by the current treatments of the spin-relaxation problem. According to the arguments of Ref. 8, we should have had recourse to a resummation up to infinite order to derive this bistable process if we had used the original reference framework.

IV. CONCLUDING REMARKS

The interesting results of this paper are the following ones:

(i) A procedure is adopted that allows us to carry out the semiclassical approximation without losing the influence of the reaction field. The Zwanzig projection approach[19] applied to the quantum-mechanical Liouville equation corresponding to the Hamiltonian of Eq. (2.5), supplemented with the semiclassical approximation in the evaluation of the moments and carried out to all perturbation orders would be unable to reproduce the effect of the reaction field.[30] It must also be stressed that this procedure has the advantageous property of fully recovering the SLE when the reaction term is neglected. Notice that to determine the spectra according to the prediction of the SLE it is necessary to use a recursion method, which determines the spectrum in terms of its moments.[2(a)] The moments evaluated with our procedure reduce to the moments provided by the SLE when the reaction field is neglected. The iterative evaluation[2(a)] of the new moments should not pose serious technical difficulties and it should be possible to determine the effect of the reaction field also in the highly non-Markovian cases of Ref. 2(a) with a minor additional computational effort. This is a work in preparation.[21]

(ii) We have found interesting phenomena due to the presence of the reaction field.

(a) Different equilibrium properties. In the weak-coupling limit the equilibrium distribution is given by Eq. (3.5). This means that the average value of the magnetic dipole with spin $\frac{1}{2}$ is given by the Langevin equation rather than by the hyperbolic tangent, as it should be in a rigorous quantum-mechanical process. It is not yet completely clear to us whether this is a consequence of neglecting the quantum fluctuations of the angular momentum $\frac{1}{2}$ within its uncertainty cone, or that it stems from the semiclassical approximation. If the weak-coupling approximation is not made, then the system distribution turns out to be canonical with respect to the renormalized Hamiltonian of Eq. (3.4). This produces deviations from the predictions of the standard statistical mechanics that are much more significant than the discrepancies between the Langevin function and the quantum hyperbolic tangent.[31] All this is supported by the results of computer simulation of Ref. 31.

(b) Bistable precession. The main effect of the reaction field is the renormalization of the Hamiltonian of the system of interest, whose direct consequence is the bistable precession process described in Fig. 1. We must acknowledge, however, that our understanding of this effect highly benefited from the results known from studies of the nonlinear dimer.[16] Moreover, the transition from one to the other unstable precessional process of Fig. 1 implies an energy activation process, so that it is easy to predict that at weak temperatures the spin relaxation must take place with a rate following an Arrhenius-like law. This important prediction of the theory of the present paper has been recently confirmed by computer simulation.[33] Of course this property is absent from the relaxation theories developed so far,[1-5,7,11-15] because even in the few cases where attention is focused on the important role of the reaction field,[3,4,7] the important renormalization of the spin system has not been taken into account.

It is also possible to make another prediction, stemming from the fact that the process of transition from a precessional cone to another has a rate which depends on temperature via an Arrhenius-like expression. The transition from one configuration to another is an incoherent process with a mean transition time that is the inverse of such a rate. It is then expected that a stochastic resonance effect takes place when an external coherent excitation is tuned to the mean frequency of this process.[34] Computer simulation fully confirms this prediction.[34]

From a theoretical point of view the significant results of this paper stem from the idea of considering the density matrix elements of the spin system as fluctuating quantities. The idea is derived from the previous research work of Grigolini, Wu, and Kenkre.[35] It must be stressed that a similar procedure, can also be found in the semiclassical laser theory.[36] However, in these theories, the system of interest is the oscillator instead of the spin system and the stochastic force is introduced after contraction over the spin system and not before. Within the context of spin relaxation, our approach not only takes the friction generated by the reaction term into account, but remarkably results in the bistable precession illustrated in Fig. 1.

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