Spin dephasing in the extended strong collision approximation

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For Markovian dynamics of field fluctuations we present here an extended strong collision approximation, thereby putting our previous strong collision approach [Phys. Rev. Lett. **83**, 4215 (1999)] into a systematic framework. Our approach provides expressions for the free induction and spin-echo magnetization decays that may be solved analytically or at least numerically. It is tested for the generic cases of dephasing due to an Anderson-Weiss process and due to restricted diffusion in a linear field gradient.

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I. INTRODUCTION

The understanding of spin dephasing is of paramount interest in all fields of nuclear magnetic resonance (NMR) sciences. In NMR spectroscopy it determines the line shape, in NMR imaging it is—besides longitudinal relaxation—the major mechanism determining the contrast and contains morphological as well as functional information.

The processes contributing to spin dephasing are related to the spin environment. In biological tissues, for example, spin dephasing may result from dipole-dipole interaction of water proton spins with paramagnetic ions such as Fe^{2+}. Another cause is diffusion within inhomogeneous magnetic fields generated by native or contrast agent induced susceptibility differences that are related to tissue composition and/or cellular and subcellular compartments. In magnetic resonance imaging, spin dephasing in external gradient fields is exploited to get information about diffusion within biological systems. These diffusion sensitive imaging techniques are applied to study tissue anisotropy and restrictions of diffusion that are given by membranes of cells and subcellular structures.

Essential for dephasing of spins are the field fluctuations that induce the phase modulations. It is important to note that in biological tissues the relevant processes cover almost the whole range of time scales. For example, the dynamics of interactions of water proton spins with paramagnetic macromolecules such as ferritin is so fast that it can be considered to be within the motional narrowing regime. On the other hand, dephasing of spins in magnetic field gradients around larger vessels is almost coherent, i.e., it is in the static dephasing regime [2]. Hence, for biological applications it is important to obtain results from theory that are valid over the whole motion regime. However, in most cases this is not possible analytically.

Therefore, most efforts have focused on limiting cases. The *motional narrowing limit* is well investigated and a number of analytical results were obtained for it [1]. The characteristic of this limit is that the mean phase shift induced by a field realization is much smaller than 1, i.e., $|\delta\varphi| = \tau\langle\Delta\omega^2\rangle^{1/2} \ll 1$, where the correlation time τ gives the mean duration of some field realization, and $\langle\Delta\omega^2\rangle$ is the variance of the inhomogeneous field. The relaxation time is then obtained as $1/T_2 = \tau\langle\Delta\omega^2\rangle$. In the other limiting case, i.e., the *static dephasing regime* $(\tau\langle\Delta\omega^2\rangle^{1/2} \gg 1)$, Yablonski and Haake [2] derived analytical expressions for coherent dephasing of spins in inhomogeneous fields around magnetic centers such as cylinders or spheres. Kiselev and Posse [3] extended Yablonski and Haake's static dephasing approach by considering diffusion of spins within local linear gradients. However, this approach requires that the diffusion length l during dephasing is within the linear approximation of the inhomogeneous fields $\omega(x_0+l) \approx \omega(x_0) + \partial_x\omega(x_0)l$. Note that expansion around the limiting cases by perturbation approaches leads to divergences in the other respective limits. Therefore, the intermediate motion regime, i.e., almost everything between the static dephasing and motional narrowing limit, was in most situations accessible by simulations only [5].

Recently, we used a strong collision (SC) approach to characterize spin dephasing in a particular situation: An inhomogeneous field around regularly arranged parallel cylinders filled with a paramagnetic substance [4], a model reflecting the capillary network of the cardiac muscle. The results agreed well with simulations [5] over the whole dynamic range and with experimental data [6,7].

The basic idea behind the SC approach is to replace the original generator of the Markov process by a simpler one, the SC generator, which conserves particular features of the original process. In particular, by an appropriate choice of its parameter the SC process reproduces the correlation time of the field fluctuations induced by the original Markov process. There are several advantages of the SC approximation. First, it is correct both in the motional narrowing and the static dephasing limits; thereby also the error in the intermediate regime is reduced considerably, when compared to perturbation approaches. And second, it provides a simple expression for the magnetization decay, which may be solved analytically or at least numerically.

However, the drawback of the SC approach was—up to now—that it is not part of a systematic approximation to or an expansion of the original generator. Therefore, it was unclear how results could be improved beyond the SC approxi-

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mation. The aim of this paper is to extend the SC approach and provide a framework for a systematic approximation.

In the following section we will present a formal description of spin dephasing that will be the basis for our analytical analysis. In Sec. III we will introduce the extended strong collision (ESC) approximation proper and show how it is used to describe free induction and spin-echo decay. In Sec. IV we will apply it to two generic cases: spin dephasing induced by an Anderson-Weiss process [8] and by restricted diffusion in a linear field gradient. We will close the paper with a summary and a discussion of our results.

II. FORMAL DESCRIPTION OF SPIN DEPHASING

We assume that dephasing of transversely polarized nuclear spins exposed to an external field is induced by randomly fluctuating magnetic perturbation fields with frequency ω_i, where i is a discrete or continuous variable. The transition dynamics between two distinct states i and j is that of a stationary continuous time Markov process described by rates r_{ji} for the transition $i\rightarrow j$. The matrix $\mathbf{R}=(r_{ji})$ as the generator of the Markov process conserves the probability to find a spin within one state, i.e., $r_{ii}=-\Sigma_{j\neq i}r_{ji}$. The eigenvalues l of $\mathbf{R}$ fulfill the condition $l\leqslant 0$ where $l=0$ corresponds to the equilibrium probability distribution. To simplify the notation we denote the normalized left and right eigenvectors of $\mathbf{R}$ as $\langle l|$ and $|l\rangle$, respectively, with $\langle l'|l\rangle=\delta_{l'l}$.

The time evolution between t and $t+dt$ of the transverse magnetization of spins in the state j (in polar notation $m_j=m_{jx}-im_{jy}$) results from the linear superposition of the transition and the precession dynamics, i.e., $\partial_t m_j(t)=\Sigma_i r_{ji}m_i(t)+i\omega_j m_j(t)$. The precession within the external field was omitted since it only induces a constant offset of the frequency which may be gauged to zero. With the diagonal frequency, matrix $\mathbf{\Omega}=(\delta_{ji}\omega_i)$ one obtains for the magnetization $|m\rangle=(m_j)$,

$$\partial_t|m(t)\rangle=(\mathbf{R}+i\mathbf{\Omega})|m(t)\rangle, \tag{1}$$

which is a generalization of the Bloch-Torrey equation [9] originally formulated for diffusing spins, i.e., $\mathbf{R}\sim\nabla^2$. In most cases it is reasonable to assume that the initial magnetization $|m(0)\rangle$ is proportional to the equilibrium probability distribution $|0\rangle$, e.g., when free diffusion is considered this would imply a homogeneous transverse magnetization. Equation (1) then provides the time evolution of the transverse magnetization (free induction decay) as

$$|m(t)\rangle=\exp[(\mathbf{R}+i\mathbf{\Omega})t]|0\rangle, \tag{2}$$

where the initial magnetization was normalized to 1. The overall magnetization is then determined as

$$M(t)=\langle 0|m(t)\rangle=\langle 0|\exp[(\mathbf{R}+\mathrm{i}\mathbf{\Omega})t]|0\rangle. \tag{3}$$

The free induction decay as determined by Eqs. (2) and (3) results from coherent and incoherent spin dephasing. The incoherent contribution is determined from spin-echo experiments. In-plane polarized spins are rotated by $180°$ (π-pulse) after a time $t/2$. This pulse transforms the original magnetization $|m(t/2)\rangle$ to its complex adjoint $|m^*(t/2)\rangle=\exp[(\mathbf{R}-i\mathbf{\Omega})t/2]|0\rangle$. This procedure cancels the coherent spin dephasing after the time t (echo time), i.e. the decay of magnetization at t is solely due to incoherent spin dephasing. The time course of the magnetization after the pulse, i.e., for times $t'>t/2$, is determined by

$$|m(t')\rangle=\exp[(\mathbf{R}+i\mathbf{\Omega})(t'-t/2)]\exp[(\mathbf{R}-i\mathbf{\Omega})t/2]|0\rangle, \tag{4}$$

i.e., the overall spin-echo magnetization at the echo time t is

$$\begin{aligned}M_{SE}(t)&=\langle 0|\exp[(\mathbf{R}+i\mathbf{\Omega})t/2]\exp[(\mathbf{R}-i\mathbf{\Omega})t/2]|0\rangle\\&=\langle m(t/2)|m^*(t/2)\rangle.\end{aligned} \tag{5}$$

Equation (5) relates the overall spin-echo magnetization to the magnetization of the free induction decay.

III. THE STRONG COLLISION APPROXIMATION AND ITS EXTENSION

The analytical determination of the free induction decay according to Eqs. (3) is restricted to very few cases, e.g., free diffusion in a linear gradient or stochastic fluctuations between two precession frequencies. The idea of the strong collision approach and its extension is to replace the generator of the Markov process $\mathbf{R}$ by a more simple generator $\mathbf{D}$ that conserves specific features of the original dynamics.

A. Strong collision approximation

In many cases the stochastic fluctuations of the perturbation fields occur on a much shorter time scale than spin dephasing, i.e., the correlation time τ of field fluctuations is much shorter than the relaxation time of the magnetization. For ergodic Markov processes one can estimate that after some value of τ a spin has visited almost all relevant states with the equilibrium probability. On the other hand, there is only little change of the magnetization during this time interval. Therefore, spin dephasing in this situation can be described equivalently by a process in which the transition rate between two states $i\rightarrow j$ is independent of the initial state. Consequently, the transition rate for $i\rightarrow j$ is proportional to the equilibrium probability of the final state, $p_{0,j}$. Such a dynamics is referred to as *strong collision dynamics*.

The generator $\mathbf{D}$ of this process has the form

$$\mathbf{D}=-\lambda(\mathbf{id}-\mathbf{\Pi}_0), \tag{6}$$

where $\mathbf{\Pi}_0=|0\rangle\langle 0|$ is the projection operator onto the eigenspace generated by the the equilibrium eigenvector of $\mathbf{R}$, and $\mathbf{id}$ is the identity operator. The factor λ has to be determined self-consistently.

Since the starting point of the strong collision approximation is the observation that—in many cases of interest—the correlation of the stochastic field fluctuations appear on a shorter time scale than that of changes of the magnetization, only the long-time behavior of the field fluctuations is of importance. This long-time behavior is characterized by the correlation time of the two-point autocorrelation function of the field fluctuations (see also Appendix A),

$$C_2(t) = \langle \omega(t)\omega(0)\rangle = \langle 0|\mathbf{\Omega}\,\exp(\mathbf{R}t)\mathbf{\Omega}|0\rangle, \tag{7}$$

which is defined as

$$\tau_2 = \int_0^\infty dt \frac{C_2(t)-C_2(\infty)}{C_2(0)-C_2(\infty)} = \frac{\langle 0|\mathbf{\Omega}[\exp(\mathbf{R}t)-\mathbf{\Pi}_0]\mathbf{\Omega}|0\rangle}{\langle 0|\mathbf{\Omega}^2|0\rangle - \langle 0|\mathbf{\Omega}|0\rangle^2}. \tag{8}$$

Stochastic field fluctuations determined by the SC process should have the same correlation time as the original process, leading to the self-consistency condition

$$\tau_2^{(\mathrm{SC})}(\lambda) = \tau_2. \tag{9}$$

It is easy to determine that the correlation time for the strong collision approximation is $\tau_2^{(\mathrm{SC})}(\lambda) = \lambda^{-1}$, see Eq. (C2), leading to

$$\lambda = \tau_2^{-1}. \tag{10}$$

B. Extended strong collision approximation

The extension of the strong collision approximation is based on a comparison with the spectral expansion of the original operator,

$$\mathbf{R} = \sum_{j=0}^{\infty} l_j \mathbf{\Pi}_j, \tag{11}$$

where $l_0 = 0 > l_1 > \cdots$ are the ordered eigenvalues of $\mathbf{R}$ and $\mathbf{\Pi}_j = |j\rangle\langle j|$ is the projection operator onto the eigenspace corresponding to l_j. Since the time evolution operator is $\exp(\mathbf{R}t) = \Sigma_{j=0}^{\infty} e^{l_j t}\mathbf{\Pi}_j$, it is clear that the low order eigenvalues determine the long-time behavior, while higher orders dominate shorter and shorter time scales. A comparison with a rewriting of Eq. (6),

$$\mathbf{D} = l_0 \mathbf{\Pi}_0 - \lambda(\mathbf{id} - \mathbf{\Pi}_0) \tag{12}$$

(note that $l_0 = 0$), shows that in the strong collision approximation, just the lowest order term of Eq. (11) is taken into account explicitly, while the contribution of the higher eigenvalues is approximated by the self-consistently determined parameter λ.

A natural extension, therefore, would be to take into account more low order eigenvalues explicitly, thereby increasing the accuracy of the description of the long-time behavior:

$$\mathbf{D}_n' = \sum_{j=1}^{n} l_j \mathbf{\Pi}_j - \lambda(\mathbf{id} - \mathbf{\Pi}). \tag{13}$$

with $\mathbf{\Pi} = \Sigma_{j=0}^{n}\mathbf{\Pi}_j$. A stochastic process generated by an operator $\mathbf{D}_n'$ in Eq. (13) will be referred to as a simplified extended strong collision (ESC_n') approximation of order *n*. As before, the contribution of the higher eigenvalues is approximated by the parameter λ, which is determined again self-consistently from condition (9). Here it leads to

$$\lambda = \frac{c_2(0) - \sum_{j=1}^{n} |\omega_{0i}|^2}{c_2(0)\tau_2 + \sum_{j=1}^{n} l_j^{-1}|\omega_{0i}|^2}, \tag{14}$$

with $\omega_{0i} = \langle 0|\mathbf{\Omega}|i\rangle$ and $c_2(0) = \langle 0|\mathbf{\Omega}^2|0\rangle - \omega_{00}^2$. Note that for $n \to 0$ this equation becomes Eq. (10) again.

However, there are several problems involved with an approximation based on Eqs. (13) and (14). Practically, an exact determination of the low order eigenvalues and eigenvectors is possible only in special cases. Therefore, one has to deal with the problem that the eigenvalues and eigenvectors are known either only approximately or not at all. Furthermore, even with eigenvalues and eigenfunctions known, it turns out that the ESC′ approximation may be not applicable at all in certain situations: If the autocorrelation function of the field fluctuations is determined fully by the eigenfunctions included in $\mathbf{D}'$, Eq. (14) is undetermined. In that case additional self-consistency requirements would be necessary for a better description of the intermediate time regime.

Nevertheless, the above approach can be readily adapted to these situations. Equation (13) can be viewed as an optimized reduced description of the relaxation in various subspaces of the original operator $\mathbf{R}$. Such a optimized description should also be possible for subspaces that are not eigenvectors of $\mathbf{R}$. We can, therefore, set

$$\mathbf{D}_n = -\sum_{j=1}^{n} \lambda_j \mathbf{\Pi}_j - \lambda(\mathbf{id} - \mathbf{\Pi}). \tag{15}$$

However, now the rates λ_j, $j = 1, \ldots, n$ are not eigenvalues anymore, but have to be determined by additional self-consistency requirements, see below. Moreover, the $\mathbf{\Pi}_j$ are not projectors onto the eigenspace of a particular eigenvalue, but onto the spaces defined by arbitrarily chosen mutually orthogonal functions $|f_j\rangle$, $j = 1, \ldots, n$, with $\langle f_i|f_j\rangle = \delta_{ij}$ and $\langle f_j|0\rangle = 0$; i.e., the projectors have the form $\mathbf{\Pi}_j = |f_j\rangle\langle f_j|$ and $\mathbf{\Pi} = \mathbf{\Pi}_0 + \Sigma_{j=1}^{n}\mathbf{\Pi}_j$. Naturally, one would try to choose the functions $|f_j\rangle$ close to the eigenfunctions $|j\rangle$, although it is not required for the extension to work. Another natural function space, for example, is based on polynomials in the frequency operator $\mathbf{\Omega}$, i.e.,

$$|f_i\rangle = p_i(\mathbf{\Omega})|0\rangle, \tag{16}$$

where p_i is some polynomial of degree *i*, the coefficients of which are chosen in such a way that the orthonormal relations are fulfilled. In the following we will refer to this base of functions as the Ω base.

In analogy to Eq. (13) a stochastic process generated by an operator $\mathbf{D}_n$ in Eq. (15) will be referred to as an extended strong collision (ESC_n) approximation of order *n*. It is evident that the ESC_0 approximation refers to the strong collision approximation.

We mentioned already that the rates λ_j, $j = 1, \ldots, n$ in Eq. (15) have to be determined now by additional self-consistency requirements. As it was with the SC approximation, the aim of the ESC_n approximation is to approximate more closely the correlation of field fluctuations. This is achieved by considering also higher order correlation functions

$$C_m(t_{m-1},\ldots,t_1)=\left\langle \omega\left(\sum_{j=1}^{m-1} t_j\right)\ldots\omega(t_2+t_1)\omega(t_1)\omega(0)\right\rangle$$
$$=\langle 0|\boldsymbol{\Omega}\exp(\mathbf{R}t_{m-1})\boldsymbol{\Omega}\cdots\exp(\mathbf{R}t_1)\boldsymbol{\Omega}|0\rangle. \tag{17}$$

Following the same arguments as for the strong collision approximation, the long-time behavior of the C_m is of interest. In the same way as for the strong collision approximation this should be characterized by some first order statistical moment, which is obtained by integration of the correlation function over $t_{m-1},\ldots,t_1$. However, direct usage of C_m is hampered by its nonvanishing asymptotic behavior: It is easily seen that from the relation $\lim_{t_\nu\to\infty}\exp(\mathbf{R}t_\nu)=\boldsymbol{\Pi}_0$ follows

$$\lim_{t_\nu\to\infty} C_m(t_{m-1},\ldots,t_1)=C_{m-\nu}(t_{m-1},\ldots,t_{\nu+1})\times C_\nu(t_{\nu-1},\ldots,t_1), \tag{18}$$

which does not necessarily vanish. In the strong collision approximation we avoided this problem by considering the operator $[\exp(\mathbf{R}t)-\boldsymbol{\Pi}_0]$ instead of $\exp(\mathbf{R}t)$ in Eq. (8), i.e., we considered only the relaxational part of the stochastic process. When we perform the same replacement in Eq. (17) we obtain modified correlation functions $c_m(t_{m-1},\ldots,t_1)$ that we will call *quasicumulants* (see Appendix A). They vanish asymptotically for all t_ν. We now require that the generalized correlation times derived from these quasicumulants,

$$\tau_m^{m-1}=\int_0^\infty \Pi_{i=1}^{m-1} dt_i \frac{c_m(t_{m-1},\ldots,t_1)}{c_m(0,\ldots,0)}, \tag{19}$$

are equal for the exact process and for the extended strong collision description. The relaxation rates are, therefore, determined by

$$\tau_m^{(\mathrm{ESC}_n)}(\lambda,\lambda_1,\ldots,\lambda_n)=\tau_m,\quad m=2,4,\ldots,2n+2, \tag{20}$$

which replace the single self-consistency condition (9). Note that in many systems the correlation functions $c_m(t_{m-1},\ldots,t_1)$ vanish for odd values of m due to symmetry. Therefore, we require the equivalence of relaxation times in Eq. (20) for even values of m only. Otherwise one has to determine the correlation times of the first $n+1$ nonvanishing correlation functions.

It is important to emphasize some properties of the ESC approximation. First of all, it usually does not reduce to the ESC′ approximation when eigenfunctions are used for the projection operator; i.e., the $\lambda_1,\ldots,\lambda_n$ do not take on the numerical values of the corresponding eigenvalues, although they usually do approximate them. In the light of the problems with the ESC′ approximations mentioned above, it will turn out that this is an advantage: the self-consistent determination of the relaxation parameters λ and $\lambda_1,\ldots,\lambda_n$ according to Eq. (20) is more balanced than when only Eq. (9) is used, and gives rise to an improved approximation. Moreover, the self-consistency conditions (20) imply that both processes, the ESC process and the original Markov process, have the same motional narrowing expansion of the transverse relaxation, as it is shown in Eq. (B7).

C. Transverse spin relaxation in the extended strong collision approximation

In this section we will exploit the simple structure of the generator $\mathbf{D}_n$ to determine the time course of magnetization. We will consider both: the free induction decay, i.e., the superposition of coherent and incoherent spin dephasing, and the spin-echo decay, i.e., pure incoherent spin dephasing.

1. Free induction decay

In the extended strong collision approximation the generator $\mathbf{R}$ of the free induction decay in the generalized Bloch-Torrey equation (1) is replaced by the generator $\mathbf{D}_n$ of Eq. (15). Instead of solving the propagator $\mathbf{U}(t)=\exp[(\mathbf{D}_n+i\boldsymbol{\Omega})t]$ it is more convenient to solve its Laplace transform $\hat{\mathbf{U}}(s)=(s-\mathbf{D}_n-i\boldsymbol{\Omega})^{-1}$, which may be expanded as

$$\hat{\mathbf{U}}(s)=\hat{\mathbf{U}}_0(s+\lambda)+\hat{\mathbf{U}}_0(s+\lambda)\boldsymbol{\Lambda}\hat{\mathbf{U}}(s). \tag{21}$$

where $\hat{\mathbf{U}}_0(s)=(s-i\boldsymbol{\Omega})^{-1}$ is the Laplace transform in the static dephasing limit ($\mathbf{D}_n=\mathbf{0}$), and the operator $\boldsymbol{\Lambda}$ is defined as

$$\boldsymbol{\Lambda}=\sum_{j=0}^{n}(\lambda-\lambda_j)\boldsymbol{\Pi}_j, \tag{22}$$

where we set $\lambda_0=0$. We will now confine the operators in Eq. (21) onto the subspace defined by the projection operator $\boldsymbol{\Pi}=\Sigma_{j=0}^{n}\boldsymbol{\Pi}_j$. Using the abbreviation $\mathbf{O}^{\Pi}:=\boldsymbol{\Pi}\mathbf{O}\boldsymbol{\Pi}$ for denoting any operator $\mathbf{O}$ confined to that subspace, we obtain

$$\hat{\mathbf{U}}^{\Pi}(s)=\hat{\mathbf{U}}_0^{\Pi}(s+\lambda)+\hat{\mathbf{U}}_0^{\Pi}(s+\lambda)\boldsymbol{\Lambda}^{\Pi}\hat{\mathbf{U}}^{\Pi}(s), \tag{23}$$

where we exploited the fact that $\boldsymbol{\Lambda}=\boldsymbol{\Pi}\boldsymbol{\Lambda}\boldsymbol{\Pi}$ and the idempotency of projection operators, i.e., $\boldsymbol{\Pi}=\boldsymbol{\Pi}^2$. Equation (23) is of fundamental importance. It demonstrates that the relation (21) between the ESC approximation and the static dephasing is also valid in the subspace $[|0\rangle,|f_1\rangle,\ldots,|f_n\rangle]$. This simplifies determination of spin relaxation considerably, since one only has to determine the $(n+1)\times(n+1)$ matrices[1] of the static dephasing limit $\hat{\mathbf{U}}_0^{\Pi}$ and $\boldsymbol{\Lambda}$, i.e.,

$$\hat{\mathbf{U}}^{\Pi}(s)=[\boldsymbol{\Pi}-\hat{\mathbf{U}}_0^{\Pi}(s+\lambda)\boldsymbol{\Lambda}^{\Pi}]^{-1}\hat{\mathbf{U}}_0^{\Pi}(s+\lambda). \tag{24}$$

[1]In case of degeneracy of the eigenvalues the matrix dimension is the sum of the dimensions of the eigenspaces plus 1.

The Laplace transform of the overall magnetization decay $\hat{M}_{[n]}(s)$ in the extended strong collision approximation has the form

$$\hat{M}_{[n]}(s)=\langle 0|\hat{\mathbf{U}}^{\Pi}(s)|0\rangle. \tag{25}$$

For the special case of the strong collision approximation, ESC_0, Eqs. (24) and (25) result in

$$\hat{M}_{[0]}(s)=\frac{\hat{M}_{sd}(s+\lambda)}{1-\hat{M}_{sd}(s+\lambda)\lambda}, \tag{26}$$

with $\hat{M}_{sd}(s)=\langle 0|\hat{\mathbf{U}}_0(s+\lambda)|0\rangle$ as the Laplace transform of the overall magnetization in the static dephasing regime. The time evolution $M(t)$ can be obtained from Eqs. (24) and (25) either by the numerical inverse Laplace transform by or using the generalized moment approach [4,10], which allows a multiexponential approximation.

2. Spin-echo decay

The spin-echo decay is obtained by inserting the generator $\mathbf{D}_n$ into Eq. (5), i.e.,

$$\begin{aligned}\partial_t M_{SE,[n]}(t)&=-\lambda M_{SE,[n]}(t)+\langle m(t/2)|\mathbf{\Lambda}|m^*(t/2)\rangle\\&=-\lambda M_{SE,[n]}(t)+\langle 0|\mathbf{U}(t/2)\mathbf{\Lambda}\mathbf{U}^*(t/2)|0\rangle\\&=-\lambda M_{SE,[n]}(t)+\langle 0|\mathbf{U}^{\Pi}(t/2)\mathbf{\Lambda}\mathbf{U}^{*\Pi}(t/2)|0\rangle,\end{aligned} \tag{27}$$

i.e., the spin-echo decay is expressed as a function of the spin-echo amplitude M_{SE}, and the projection of the free induction decay onto the subspace $[|0\rangle,|f_1\rangle,\dots,|f_n\rangle]$, i.e., $\mathbf{U}^{\Pi}(t)|0\rangle$. This projection of the free induction decay is obtained from Eq. (24) by inverse Laplace transform, i.e., $\mathbf{U}^{\Pi}(t)|0\rangle=\mathcal{L}^{-1}(\hat{\mathbf{U}}^{\Pi}(s)|0\rangle)$. The solution of Eq. (27) is

$$M_{SE,[n]}(t)=e^{-\lambda t}\left[1+2\int_0^{t/2}d\xi e^{2\lambda\xi}\langle 0|\mathbf{U}^{\Pi}(\xi)\mathbf{\Lambda}\mathbf{U}^{*\Pi}(\xi)|0\rangle\right] \tag{28}$$

3. Time constants of transverse relaxation

The free induction and the spin-echo decay are usually described by the time constants T_2^* and T_2. However, there is no unique definition of these parameters. One definition of the relaxation times is

$$1/T_2^*=-\ln[M(t)]/t,$$

$$1/T_2=-\ln(M_{SE})/t. \tag{29}$$

For the ESC decay one has to replace M by $M_{[n]}$ and M_{SE} by $M_{SE,[n]}$. This definition implies a dependence of relaxation times on t, except for single exponential decay.

Another definition of relaxation times is based on the assumption that these constants provide the best single exponential approximation of magnetization decays, i.e., $M(t)\approx e^{-t/T_2^*}, M_{SE}\approx e^{-t/T_2}$. According to the mean relaxation time approximation the relaxation times are then the first long-time moments of the decays [10], i.e.,

$$T_2^*:=\mu_{-1}(M)=\int_0^{\infty}dt\,M(t),$$

$$T_2:=\mu_{-1}(M_{SE})=\int_0^{\infty}dt\,M_{SE}(t). \tag{30}$$

For a single exponential the mean relaxation time definition and the definitions (29) give the same results. According to definition (30) the relaxation times of the ESC decays can be related to their Laplace transforms as

$$T_2^*=\hat{M}_{[n]}(0),$$

$$T_2=\hat{M}_{SE,[n]}(0). \tag{31}$$

The term $\hat{M}_{[n]}(0)$, which provides T_2^*, is obtained from Eq. (25). Applying some rules of Laplace transforms, the term $\hat{M}_{SE,[n]}(0)$ giving T_2 is obtained from Eq. (27) as

$$T_2=\lambda^{-1}+2\sum_{i=0}^{n}(1-\lambda_i/\lambda)\Theta_i, \tag{32}$$

where

$$\begin{aligned}\Theta_0&=\int_0^{\infty}dt|\langle 0|\mathbf{U}^{\Pi}(t)|0\rangle|^2\\&=\frac{1}{2\pi i}\int_{-i\infty}^{i\infty}dz\langle 0|\hat{\mathbf{U}}^{\Pi}(z)|0\rangle\langle 0|\hat{\mathbf{U}}^{*\Pi}(-z)|0\rangle\end{aligned} \tag{33}$$

is the mean relaxation time of the absolute squared overall free induction magnetization $|M_{[n]}(t)|^2=|\langle 0|\mathbf{U}(t)^{\Pi}|0\rangle|^2$, and for $i\geqslant 1$,

$$\begin{aligned}\Theta_i&=\int_0^{\infty}dt\langle 0|\mathbf{U}^{\Pi}(t)|f_i\rangle\langle f_i|\mathbf{U}^{*\Pi}|0\rangle(t)\rangle\\&=\frac{1}{2\pi i}\int_{-i\infty}^{i\infty}dz\langle 0|\hat{\mathbf{U}}^{\Pi}(z)|f_i\rangle\langle f_i|\hat{\mathbf{U}}^{*\Pi}(-z)|0\rangle\end{aligned} \tag{34}$$

are transit times describing the transient occurrence of the nonequilibrium components of the free induction decay $\mathbf{U}(t)|f_i\rangle$. Equation (32) relates T_2, which describes the incoherent, i.e., irreversible, component of spin dephasing to the stochastic field dynamics (λ,λ_i) and time constants of the free induction decay (Θ_i), i.e., Eq. (32) is a dissipation-fluctuation-coherence relation. Note that the Eqs. (33) and (34) directly relate the time constants Θ_i to the Laplace transform of the free induction decay $\hat{\mathbf{U}}^{\Pi}(s)$ given by the fundamental equation (23).

From Eq. (32) one can derive asymptotic relations for very fast and slow stochastic field fluctuations. Let ϵ be some scaling parameter of $\mathbf{D}_n$, i.e., $\lambda,\lambda_i\sim\epsilon$, then Eq. (32) reads in the static dephasing limit $(\epsilon\to 0)$

$$T_2 \approx \lambda^{-1}, \tag{35}$$

where we exploited that $\Theta_i(\epsilon)$ approaches its finite static dephasing limit. For very fast fluctuations i.e., in the motional narrowing limit ($\epsilon \to \infty$) one exploits that $\langle f_i|\hat{\mathbf{U}}(s)|0\rangle / \langle 0|\hat{\mathbf{U}}(s)|0\rangle \sim \epsilon^{-1}$, as a power expansion demonstrates, i.e., one obtains

$$T_2 \approx 2\Theta_0. \tag{36}$$

This implies that the spin-echo relaxation time is almost identical with the relaxation time of the absolute squared magnetization of the free induction decay, or vice versa that the free induction decay is almost irreversible.

The dissipation-fluctuation-coherence relation (32) takes a very simple form in the strong collision approximation, when we assume that the overall magnetization decay is well approximated by a single exponential, i.e., $M_{[0]}(t) \approx e^{-t/T2^*}$. Since $\lambda = \tau_2^{-1}$, see Eq. (10), Eq. (32) reads

$$T_2 = \tau_2 + 2\Theta_0 \approx \tau_2 + T_2^*. \tag{37}$$

From Eqs. (37) follows that in the motional narrowing limit $T_2 \approx T_2^*$ holds whereas in the static dephasing limit of the strong collision approximation the relation $T_2 \approx \tau_2$ holds.

IV. APPLICATIONS

A. Anderson-Weiss model

The Anderson-Weiss model [8] is one of the rare approaches—besides the ESC approximation—which describes spin dephasing over the whole dynamic range of stochastic field fluctuations. The approach is suitable, for example, when dephasing is induced by spin interaction with a great number of independently fluctuating perturbation fields in the spin environment. Then analytical results are obtained for the free induction and the spin-echo magnetization decay as

$$M(t) = \exp\left[-\int_0^t (t-\xi) c_2(\xi) d\xi\right], \tag{38}$$

$$M_{SE}(t) = \exp\left[-4\int_0^{t/2} (t/2-\xi) c_2(\xi) d\xi + \int_0^t (t-\xi) c_2(\xi) d\xi\right], \tag{39}$$

where c_2 is the modified two-point correlation function (see Appendix A). In this section we will first characterize the class of Markovian processes which fulfills the conditions of the Anderson-Weiss model. This leads to a generalized Bloch-Torrey equation according to Eq. (1), which is solved. Finally we compare the Anderson-Weiss model with its ESC_0 and ESC_1 approximation.

1. Markovian and Anderson-Weiss dynamics

The Anderson-Weiss approach is based on a Gaussian distribution of perturbation field frequencies ω. Even more important is the *additional* assumption that the stochastic phase accumulation of a spin $\phi = \int_0^t d\xi \omega(\xi)$ also exhibits a Gaussian distribution. This latter condition implies that the Green's function $G(\omega_j, \omega_i, t)$, i.e., the probability that a spin initially precessing with frequency ω_i precesses at t with ω_j, is also a Gaussian function in ω_j, ω_i with the condition $G(\omega_j, \omega_i, 0) = \delta(\omega_j - \omega_i)$. This implies that only nearest neighbor transitions rates are nonvanishing. Markovian processes in a continuous variable ω with this property are described equivalently by a Fokker-Planck equation [11], i.e., the probability density $p(\omega)$ satisfies

$$\partial_t p(\omega,t) = \mathbf{R} p(\omega,t) = \partial_\omega D(\omega)[\partial_\omega - F(\omega)] p(\omega,t), \tag{40}$$

where $D(\omega)$ is a—possibly ω dependent—diffusion coefficient and $F(\omega)$ is some driving force. Since the equilibrium probability density is a Gaussian function one obtains $F(\omega) = -c\omega$ with $c > 0$. The generalized Bloch-Torrey equation (1), which determines the dynamics of magnetization as a superposition of precession and stochastic transitions, then reads

$$\partial_t m(\omega,t) = [\partial_\omega D(\omega)(\partial_\omega + c\omega) + \mathrm{i}\omega] m(\omega,t). \tag{41}$$

The derivation of the Eqs. (40) and (41) is of fundamental importance, since it states that a Markovian dynamics of a variable ω, which satisfies the Anderson-Weiss conditions, is equivalent to a diffusion process in this variable within a harmonic potential $c\omega^2/2$ and vice versa. Transformation of variables $\omega \to c^{1/2}\omega$ and $t \to c^{-1/2} t$ simplifies Eq. (41) to

$$\partial_t m(\omega,t) = [\partial_\omega \beta(\omega)(\partial_\omega + \omega) + \mathrm{i}\omega] m(\omega,t), \tag{42}$$

where we continue to denote also the transformed variables as ω and t and $\beta = c^{3/2} D$ is the transformed diffusion coefficient. In the following we will restrict consideration to the case of a constant diffusion coefficient β. The left and right sided eigenfunctions of the transition operator $\mathbf{R} = \beta\partial_\omega(\partial_\omega + \omega)$ are the Hermite functions, i.e.,

$$|n\rangle \sim \exp(-\omega^2/2) H_n(\omega),$$
$$\langle n| \sim H_n(\omega) \tag{43}$$

with eigenvalues

$$l_n = -n\beta. \tag{44}$$

From the definition of the Hermite functions and the operator intertwining relation $[\partial_\omega, (\partial_\omega + \omega)] = 1$ follow the recursive equations

$$|n+1\rangle = -\frac{1}{n+1}\partial_\omega |n\rangle, \quad |n-1\rangle = (\partial_\omega + \omega)|n\rangle,$$

$$\langle n+1| = \langle n|(\partial_\omega + \omega), \quad \langle n-1| = -\frac{1}{n}\langle n|\partial_\omega, \tag{45}$$

which also provide the normalization of eigenfunctions. The advantage of the Markovian formulation of the Anderson-

Weiss model is that it does not only provide global parameters but also local ones, e.g., the time course of the magnetization with frequency ω. Straightforward application of Eqs. (45) and some operator algebra provides the solution of Eq. (42) as

$$\begin{aligned} m(\omega,t) &= \exp[\beta\partial_\omega(\partial_\omega+\omega)+\mathrm{i}\omega]|0\rangle \\ &= \exp[-\beta^{-1}t+\beta^{-2}(1-e^{-\beta t})](2\pi)^{-1/2} \\ &\quad\times\exp[-1/2\{\omega-\mathrm{i}\beta^{-1}(e^{\beta t}-1)\}]. \end{aligned} \tag{46}$$

Integration over ω just gives the free induction decay of the overall magnetization

$$M(t)=\exp[-\beta^{-1}t+\beta^{-2}(1-e^{-\beta t})], \tag{47}$$

which is just equivalent to the result of Eq. (38), since the two-point correlation function of Eq. (42) is $c_2(t)=e^{-\beta t}$ [see Eq. (E1)]. Insertion of this two-point correlation function into Eq. (39) provides the spin-echo decay as

$$M_{SE}(t)=M(t/2)^2\exp[\beta^{-2}(e^{-\beta t/2}-1)^2]. \tag{48}$$

Relaxation times of the free induction and spin-echo decay were determined according to Eqs. (30).

2. ESC approximation

The ESC propagator is determined from the propagator in the static dephasing limit $\mathbf{U}_0=\exp(\mathrm{i}\mathbf{\Omega}t)=[\exp(\mathrm{i}\omega t)]$, and the $\mathbf{\Lambda}$ matrix of Eq. (22), both restricted either to the function space $[|0\rangle]$ for the ESC_0 or $[|0\rangle,|f_1\rangle]$ for the ESC_1 approximation Eq. (24). The special structure of the transition rate operator of the Anderson-Weiss model implies that the base of eigenfunctions, Eqs. (43), is identical with the Ω base, Eq. (16), i.e., $p_n(\mathbf{\Omega})|0\rangle=|n\rangle$. Hence, we will set in the following $|f_1\rangle=p_1(\mathbf{\Omega})=|1\rangle$.

ESC_0 approximation. The matrix element of the Laplace transformed propagator in the static dephasing limit required for the ESC_0 approximation is

$$\langle 0|\hat{\mathbf{U}}_0(s)|0\rangle=\sqrt{\pi/2}e^{s^2/2}\,\mathrm{erfc}(s/\sqrt{2}), \tag{49}$$

where $\mathrm{erfc}(z)=1-\mathrm{erf}(z)$ is the complementary error function. The coefficient λ, which guarantees the self-consistency condition Eq. (9), is determined form the Eqs. (C2) and (E2) as

$$\lambda=\beta. \tag{50}$$

ESC_1 approximation. The matrix elements of the Laplace transformed propagator in the static dephasing limit required for the ESC_1 approximation in the Ω base are that of Eq. (49) and

$$\begin{aligned} \langle 0|\hat{\mathbf{U}}_0(s)|1\rangle &= N\mathcal{L}[\langle 0|\exp(\mathrm{i}\mathbf{\Omega}t)\mathbf{\Omega}|0\rangle] \\ &= N(-\mathrm{i})\mathcal{L}[\partial_t\langle 0|\exp(\mathrm{i}\mathbf{\Omega}t)|0\rangle] \\ &= N\mathrm{i}[1-s\langle 0|\hat{U}_0(s)|0\rangle], \end{aligned} \tag{51}$$

where the factor N generally is some normalization factor with $N^2=\langle 0|\mathbf{\Omega}^2|0\rangle$, i.e., in the case of the Anderson-Weiss model it is simply $N=1$. Consequently, using some elementary rules of Laplace transforms, one derives the other matrix elements as

$$\begin{aligned} \langle 1|\hat{\mathbf{U}}_0(s)|0\rangle &= \langle 0|\hat{\mathbf{U}}_0(s)|1\rangle, \\ \langle 1|\hat{\mathbf{U}}_0(s)|1\rangle &= N^2 s[1-s\langle 0|\hat{\mathbf{U}}_0(s)|0\rangle], \end{aligned} \tag{52}$$

It has to be stressed that the Eqs. (51) and (52) are generally valid for all ESC_1 approximations in the Ω base.

The coefficients λ,λ_1 guaranteeing the self-consistency condition Eq. (20) are obtained from Eqs. (D4),(E2) and (D7),(E4)

$$\begin{aligned} \lambda_1 &= \beta, \\ \lambda &= 2\beta. \end{aligned} \tag{53}$$

Relaxation in the ESC_0 and ESC_1 approximation. The matrix $\hat{\mathbf{U}}_0^{\Pi}(s)$ and the coefficients λ and λ_1 determine the Laplace transformed ESC propagator $\hat{\mathbf{U}}^{\Pi}(s)$ in Eq. (24), which itself is the base for all other calculations. It directly provides T_2^* when defined as the first moment, Eq. (31), of the free induction decay Eq. (25). Insertion of $\hat{\mathbf{U}}^{\Pi}(s)$ into Eqs. (33) and (34) provides according to Eq. (32) the relaxation time of the spin-echo decay when defined as its first long-time moment Eq. (31). Inverse Laplace transformation of $\hat{\mathbf{U}}^{\Pi}(s)$ gives the ESC propagator $\mathbf{U}^{\Pi}(t)$, which itself allows determination of the spin-echo decay Eq. (28).

The relaxation time $T_2^*:=\mu_{-1}(M)$ of the Anderson-Weiss process is well approximated by the ESC_0 and ESC_1 approximation over the whole dynamic range of stochastic field fluctuations (Fig. 1). In the static dephasing regime all curves approach $\lim_{\beta\to 0}\mu_{-1}^{-1}=\sqrt{2/\pi}$. The successive approximation of the spin-echo relaxation by the ESC approximation is seen from the magnetization decay curves (Fig. 2) and the curves showing the dependence of T_2 obtained by either definition [Eqs. (29) and (30)] on the diffusion coefficient β as Fig. 3 demonstrates. The latter curves all run parallel in the motional narrowing regime $[\tau_2(\langle 0|\mathbf{\Omega}^2|0\rangle)^{1/2}=\beta^{-1}\ll 1]$ and exhibit a similar location of the maximum relaxation rate. Towards the static dephasing regime ($\beta\to 0$) the rate of the Anderson-Weiss process declines less than the rates of the ESC processes.

B. Spin dephasing by restricted diffusion in a linear gradient field

1. The exact process

Whereas dephasing of free diffusing spins in a linear gradient field can be treated analytically, only numerical solutions exists for the restricted diffusion case [12]. On the one hand restricted diffusion in a linear gradient field provides a simple model to study principle features of spin dephasing by diffusion. On the other hand treatment of this problem is not only of academic interest as already mentioned in the

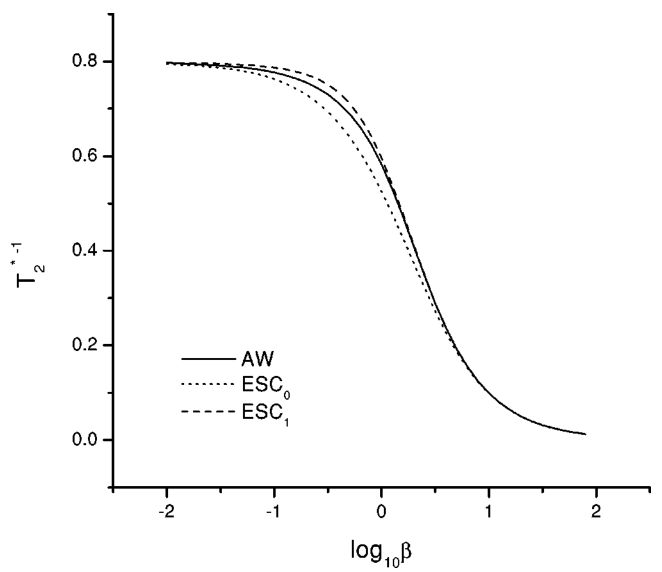

FIG. 1. Relaxation time T_2^* (defined as the first long-time moment μ_{-1}) of the free induction decay in the Anderson-Weiss model (AW) and its ESC_0 and ESC_1 approximation as a function of the diffusion coefficient β.

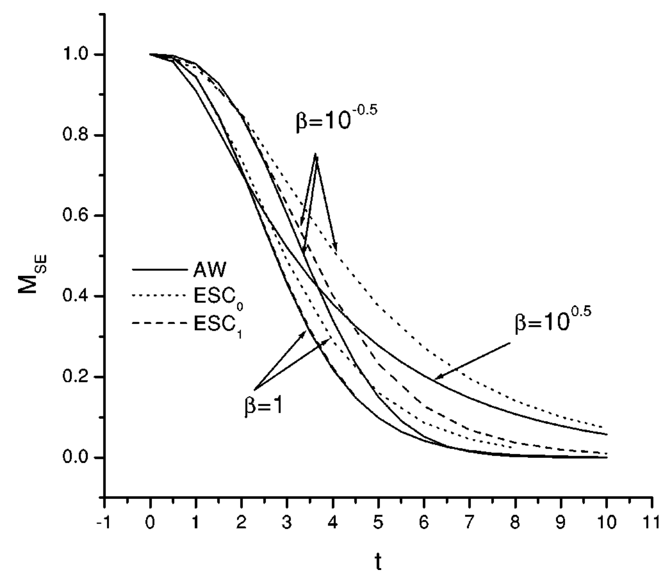

FIG. 2. Spin-echo magnetization decay in the Anderson-Weiss model (AW) and its ESC_0 and ESC_1 approximations for three different diffusion coefficients β. Note: for the diffusion coefficient close to the motional narrowing regime ($\beta=10^{0.5}$) the Anderson-Weiss and the ESC curves almost run parallel. Therefore for the clearness of the figure, only the Anderson-Weiss curve is shown. In the intermediate motion regime $\beta=1$ the original and the ESC_1 curve still run parallel, whereas the ESC_0 approximation already shows a moderate deviation. Towards the static dephasing regime ($\beta=10^{-0.5}$) the successive improved approximation of the Anderson-Weiss curve by the ESC curves is evident.

Introduction. We will approximate the free induction and spin-echo decay of the global magnetization for the case of restricted diffusion by the strong collision approximation (ESC_0) and its first extension (ESC_1). The ESC_1 approximation will be performed for both, in the Ω-polynomial base, i.e., $|f_1\rangle \sim \mathbf{\Omega}|0\rangle$, and in the eigenfunction base, i.e., $|f_1\rangle = |1\rangle$.

We assume that the spins diffuse within an interval of size L in a linear gradient field $\omega(x)=gx$. Reflecting boundary conditions at $x=\pm L/2$ imply that $\partial_x m(\pm L/2,t)\equiv 0$. With D as the diffusion coefficient and $\mathbf{R}=D[\partial_x^2]$ the Bloch-Torrey equation (1) has the form $\partial_t m(x,t)=(D[\partial_x^2]+igx)m(x,t)$, where the brackets [ ] denote that the application of the operator ∂_x^2 is restricted to functions which fulfill the reflecting boundary conditions. Transformation of variables $x\rightarrow x/L$ and $t\rightarrow tgL$ results in

$$\partial_t m(x,t)=(\beta[\partial_x^2]+ix)m(x,t), \tag{54}$$

and vanishing derivatives at the edges of the unit interval

$$\partial_x m(\pm 1/2,t)\equiv 0, \tag{55}$$

with the diffusion coefficient $\beta=D/(gL^3)$. We continue to denote also the transformed variables as x and t to reduce the number of symbols. When the initial magnetization is proportional to the equilibrium probability, i.e., $m(x,0)\equiv 1$, the Laplace transform $\hat{m}(x,s)$ of the local magnetization decay satisfies

$$(\beta[\partial_x^2]+ix)\hat{m}(x,s)=-1. \tag{56}$$

Equation (54) was solved numerically. Integration of the result over the unit interval provided the free induction decay of the overall magnetization, and application of Eq. (5) on the result gave the spin-echo decay. When the spin-echo relaxation time was defined as the first statistical moment of the magnetization decay Eq. (30) was applied. For determination of T_2^*, defined as the first moment of the free induction decay, Eq. (56) was solved numerically, and integration $\int_{-1/2}^{1/2}dx\hat{m}(x,s)=\hat{M}(s)$ gave $T_2^*=\hat{M}(0)=\mu_{-1}(M)$.

2. ESC approximation

The determination of the ESC_0 and ESC_1 approximation is completely analogous to that for the Anderson-Weiss model, except that the Ω polynomial and the eigenfunction base are not identical.

ESC_0 approximation. The equilibrium function for the restricted diffusion within the unit interval is

$$|0\rangle = 1, \tag{57}$$

i.e., one obtains

$$\langle 0|\hat{\mathbf{U}}_0(s)|0\rangle = i\ln\left(\frac{s-i/2}{s+i/2}\right). \tag{58}$$

The self-consistency condition for the strong collision approximation (9) determines the parameter λ as [see Eqs. (C2) and (E11)]

$$\lambda = 10\beta. \tag{59}$$

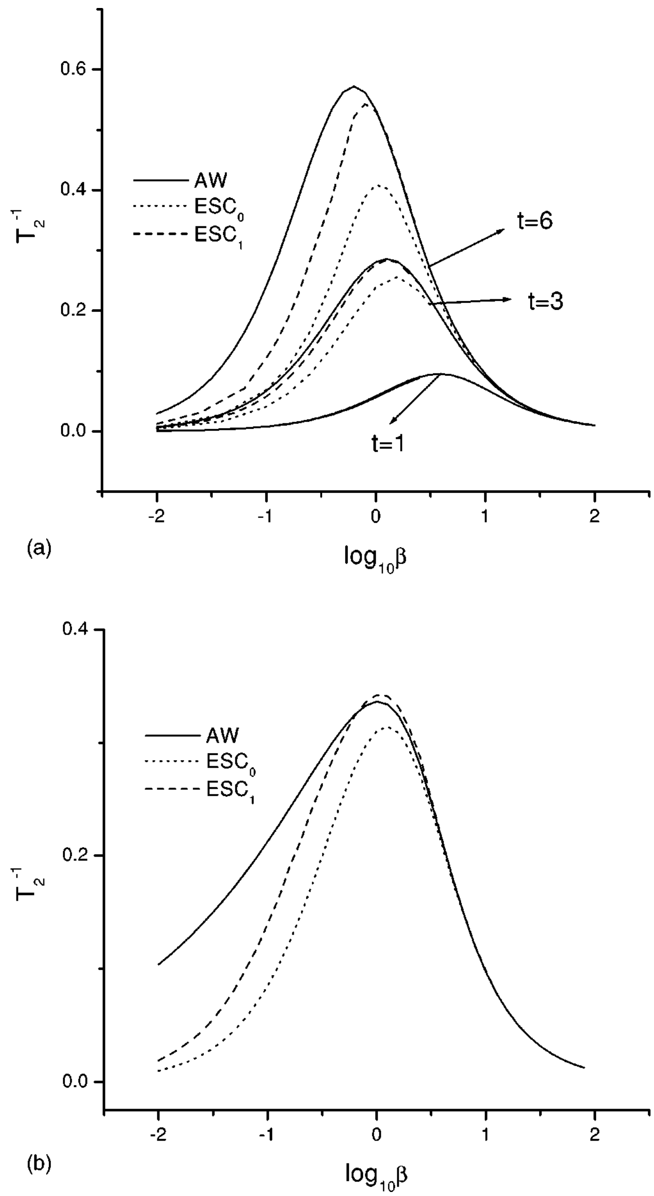

FIG. 3. Dependence of the spin-echo relaxation time T_2 on the diffusion coefficient β for the Anderson-Weiss model (AW) and its ESC_0 and ESC_1 approximation: (a) The relaxation time was defined according to Eq. (29) by the echo time t, and (b) as the first long-time moment μ_{-1} of spin-echo magnetization decay according to Eq. (30). The Anderson-Weiss curves and the corresponding approximations converge as β approaches the motional narrowing regime $\tau_2(\langle 0|\mathbf{\Omega}^2|0\rangle)^{1/2}=\beta^{-1}\ll 1$. When defined by the echo time (a) the T_2 curves of the Anderson-Weiss model and its approximations all run parallel for the short echo time $(t=1)$. With increasing echo time $(t=3,6)$ the successive ESC approximation becomes evident.

Insertion of the results of Eqs. (58) and (59) into Eq. (24) determines the Laplace transformed propagator in the ESC_0 approximation $\langle 0|\hat{\mathbf{U}}(s)|0\rangle$ from which T_2^*, T_2, and spinecho decay curves are obtained.

ESC_1 approximation in the Ω-polynomial base. The lowest order function besides the equilibrium state in the Ω-polynomial base has the form

$$|f_1\rangle=\langle 0|\mathbf{\Omega}^2|0\rangle^{-1/2}\mathbf{\Omega}|0\rangle=2\sqrt{3}x. \tag{60}$$

The matrix element (58) and the Eqs. (51) and (52) then directly provide the static dephasing operator $\hat{\mathbf{U}}_0(s)=(s-ix)^{-1}$ in the $[|0\rangle,|f_1\rangle]$ base. The parameters λ_1,λ of the ESC_1 approximation are determined from the self-consistency condition (20), i.e., with Eqs. (D4), (E11) and Eqs. (D7),(E17), one obtains

$$\lambda_1=10\beta,$$
$$\lambda=\frac{443\,520}{8900}\beta,$$
$$\approx 49.83\beta. \tag{61}$$

Development in the eigenfunction space. The normalized nonequilibrium eigenfunctions of the restricted diffusion operator are

$$|\nu\rangle=\sqrt{2}\sin(\nu\pi x) \quad \text{for } \nu=1,3,\ldots$$
$$=\sqrt{2}\cos(\nu\pi x) \quad \text{for } \nu=2,4,\ldots. \tag{62}$$

Since $[\partial_x^2]$ is a symmetric operator, left and right sided eigenfunctions are identical. With $|f_1\rangle=|1\rangle$ and $z=\pi(1/2+is)$ one obtains

$$\langle 0|\hat{\mathbf{U}}_0(s)|1\rangle=\sqrt{2}[\sinh(\pi s)\mathrm{Ci}(\xi)+i\cosh(\pi s)\mathrm{Si}(\xi)]\Big|_{\xi=-z^*}^{\xi=z},$$
$$\langle 1|\hat{\mathbf{U}}_0(s)|1\rangle=-2\arctan(2s)-[i\cosh(2\pi s)\mathrm{Ci}(\xi)+\sinh(2\pi s)\mathrm{Si}(\xi)]\Big|_{\xi=-2z^*}^{\xi=2z}, \tag{63}$$

where Ci and Si denote the integral cosine and integral sinus function, respectively. The parameters λ_1, λ in the eigenfunction base are determined similarly as in the Ω base (see Appendixes D and E) and one obtains

$$\lambda_1\approx 9.89\beta,$$
$$\lambda\approx 41.6\beta. \tag{64}$$

Relaxation in the ESC_0 and ESC_1 approximation. Figure 4 demonstrates the first long-time moment of the free induction decay, that of the strong collision approximation, and its first extension for both bases as a function of the diffusion coefficient β. All curves show the same asymptotic behavior in the static dephasing $(\beta\to 0)$ and in the motional narrowing limit $[\tau_2(\langle 0|x^2|0\rangle)^{1/2}=1/(20\sqrt{3})\beta^{-1}\ll 1]$. Furthermore, the better approximation by the ESC_1 curves compared to the ESC_0 curve in the intermediate motion regime is evident. There is no significant difference between the ESC_1 approximation in the eigenfunction and in the Ω-polynomial base.

The spin-echo magnetization decay is shown in Fig. 5. Especially in the long-time behavior near the static dephasing regime, the ESC_1 curves either in the eigenfunction space or in the Ω space demonstrate a better approximation

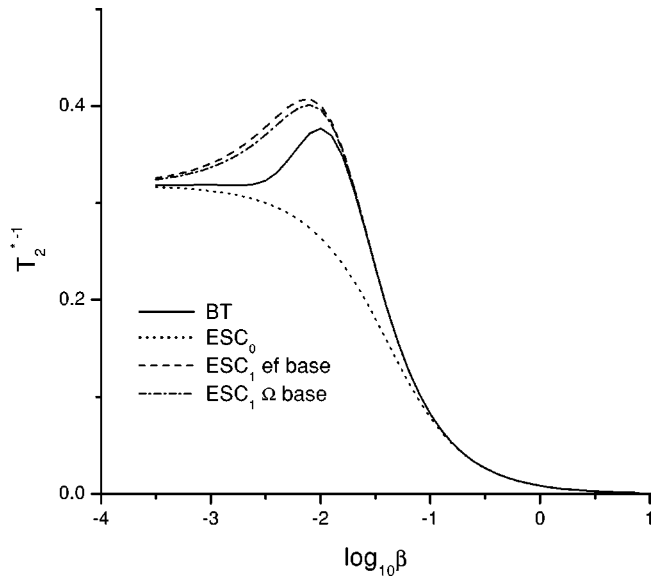

FIG. 4. Relaxation time of the free induction decay T_2^* of spins diffusing within a linear field gradient in the unit interval as a function of the diffusion coefficient β. T_2^* is defined as the first long-time moment μ_{-1} and obtained from the Bloch-Torrey (BT) equation (54). The ESC approximations are shown. The ESC_1 approximation was determined for the eigenfunction (ef) and the Ω base.

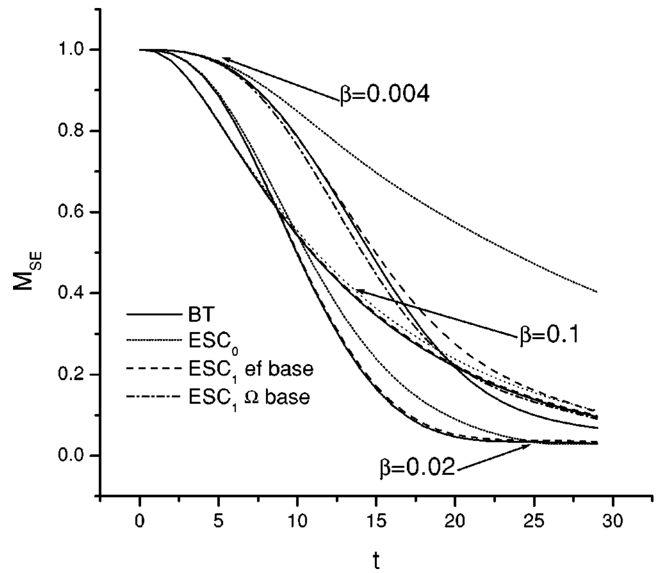

FIG. 5. Spin-echo magnetization decay for restricted diffusion within a linear field gradient in the unit interval as obtained from the Bloch Torrey (BT) equation (54). Three diffusion coefficients β are considered. The ESC approximations in the different diffusion regimes are demonstrated. The ESC_1 approximation was obtained for the eigenfunction (ef) and the Ω base.

than the ESC_0 curve. This is also reflected by the dependence of spin-echo relaxation rate $1/T_2$ on the diffusion coefficient (Figs. 6 and 7). When defined by the echo time [Eq. (29)] the ESC_0 and ESC_1 curves run parallel with the curve obtained for restricted diffusion dynamics for short echo times. For longer echo times and decreasing diffusion coefficients the ESC_1 curve provides a better approximation. Again as for the free induction decay there is no significant difference between ESC_1 approximations in the eigenfunction and that in the Ω base.

V. SUMMARY AND DISCUSSION

Analytical results on transverse spin relaxation due to stochastic phase modulation exist mainly for limiting cases, such as the motional narrowing and the static regime. Perturbation approaches are only valid close to their respective limits, and they diverge as one tries to extend them towards the opposite motion regime. Particularly the intermediate motion regime cannot be described reliably by such a treatment.

We choose a different approach. Our aim was to approximate the dynamics, assumed to be Markovian, by a more simple one that conserves specific features of the original. The starting point was the strong collision approximation [4] that assumes the transition probability between two states being independent from the initial state, an approximation that holds when spin dephasing occurs on a time scale significantly longer than the stochastic phase modulations. Hence, all states perpendicular to the equilibrium state relax with the same exponential factor that is determined self-consistently by comparison with the field fluctuations.

Note that the motional narrowing limit as well as the static dephasing regime are described correctly by this approximation. Consequently, the error in the intermediate motion regime is already less than it would be by perturbation approaches of a comparable low order. Nevertheless, there is still room for improvement. Also, one would like to have higher order approximations that can be used to check the quality of low order descriptions.

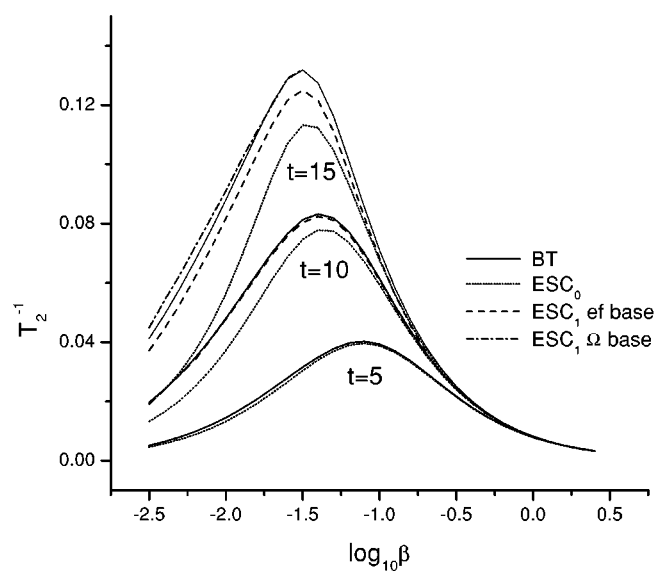

FIG. 6. Spin-echo relaxation time T_2 as a function of the diffusion coefficient β for restricted diffusion in the unit interval and the corresponding ESC approximations. The labeling of the curves is as in Fig. 4. The relaxation time was defined by the echo time t according to Eq. (29).

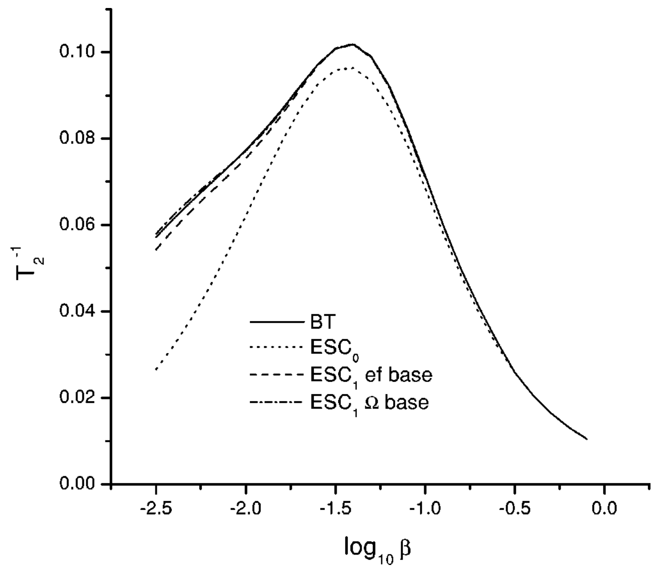

FIG. 7. Spin-echo relaxation time T_2 as a function of the diffusion coefficient β for restricted diffusion in the unit interval and the ESC approximations. Labeling is as in Fig. 4. The relaxation time is defined as the first long-time moment μ_{-1} of the spin-echo decay Eq. (30).

A systematic extension of the strong collision ansatz is to include the relaxation of states of an appropriate finite function base explicitly. We require that correlation times of original and approximate dynamics are identical to a certain order. This self-consistency condition assures that both dynamics have the same motional narrowing expansion of spin dephasing. As it was already in the strong collision ansatz, spin dephasing is asymptotically identical for both dynamics in the limit of the static motion regime.

The finite function base of the ESC_n approximation may be given by the first n ordered eigenfunctions of the generator of the original phase modulations. Obviously, then the ESC generator directly reflects the dynamics of the original generator up to a time scale corresponding to the nth eigenvalue. For practical applications the ESC approach within an eigenfunction space may be a safe way to approximate spin dephasing. However, when the determination of the eigenfunctions is tedious, the application of the Ω base $[|0\rangle,|f_1\rangle \sim \mathbf{\Omega}|0\rangle,|f_2\rangle\sim\mathbf{\Omega}^2|0\rangle,\ldots]$ may be more appropriate, at least for the ESC_1 approximation. Within the Ω base the determination of the two- and four-point correlation times (see Appendix D) and the propagator in the static motion regime, Eq. (52), is considerably simplified.

The mechanism by which the ESC_1 approach in the Ω base works becomes evident by the following consideration: terms of the motional narrowing expansion Eq. (B1) may be interpreted as repetitive interactions of the spin system with the inhomogeneous field $\mathbf{\Omega}$ and intermediate evolution with the free propagator $\exp(\mathbf{R}t_i)$. In the motional narrowing limit, one obtains from Eq. (B7),

$$1/T_2=\hat{c}_2(0)=\int_0^\infty dt\langle 0|\mathbf{\Omega}\exp(\mathbf{R}t)\mathbf{\Omega}|0\rangle$$

$$=\langle 0|\mathbf{\Omega}^2|0\rangle\int_0^\infty dt\langle f_1|\exp(\mathbf{R}t)|f_1\rangle, \qquad (65)$$

where the factor $\langle 0|\mathbf{\Omega}^2|0\rangle$ is due to the normalization of $|f_1\rangle$, $\langle f_1|f_1\rangle=1$. Equation (65) implies that in the motional narrowing limit, the long-time behavior of spin dephasing solely depends on the free propagator related relaxation of the state $|f_1\rangle$, i.e., this state remains the only relevant one. Hence, it is obvious that in the intermediate motion regime an ESC_1 approximation including the state $|f_1\rangle$ in its generator is superior to the ESC_0 approximation.

Within the function base the propagator of spin dephasing is directly related to the propagator of spin dephasing in the absence of stochastic phase modulations. This specific feature of the ESC dynamics tremendously facilitates the actual determination of spin dephasing for the following reasons: (i) in many cases the propagator in the static motion regime (which is an average phase factor) may be determined analytically or at least numerically; (ii) the determination of the propagator from that in the static motion regime is self-contained within the base, i.e., it is obtained from a combination of finite dimensional matrices.

The two lowest order ESC approximations were applied to two generic models: spin dephasing in the Anderson-Weiss model, i.e., Gaussian frequency distribution and Gaussian transition dynamics, and dephasing by restricted diffusion in a linear frequency gradient. The reason for this choice was that—besides their generic character—these models allow either an analytical (Anderson-Weiss) or, at least, a simple numerical treatment (linear gradient) of magnetization decay. These features are helpful to prove the ESC approach. For the Anderson-Weiss model we determined the corresponding Markov generator of the phase modulations, which—to our knowledge—was done here for the first time.

For both generic models the subsequent improvement by ESC_n approximations of dephasing parameters and magnetization decays could be demonstrated. One of our next aims will be the application of the ESC approach to more realistic scenarios.

In closing, we would like to emphasize that the ESC approach is actually not limited to spin dephasing only. It can be applied, in principle, in any situation where the time behavior of complicated observables of stochastic processes is of interest. In each case, however, an appropriate function base has to be chosen, corresponding to the Ω base for spin dephasing.

ACKNOWLEDGMENTS

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APPENDIX A: AUTOCORRELATION FUNCTIONS AND QUASICUMULANTS

The general n-point autocorrelation function of stochastically fluctuating fields ω_j is defined as

$$C_n(t_{n-1},\dots,t_1) := \sum_{j_{n-1},\dots,j_0} p\left(\omega_{j_{n-1}},\sum_{i=1}^{n-1} t_i;\dots;\omega_{j_1},t_1;\omega_{j_0},0\right)\prod_{\nu=0}^{n-1}\omega_{j_\nu}, \tag{A1}$$

where $p(\omega_{j_{n-1}},\Sigma_{i=1}^{n-1}t_i;\dots;\omega_{j_1},t_1;\omega_{j_0},0)$ is the probability to find at $t=0$ the frequency ω_{j_0}, at $t=t_1$ the value $\omega_{j_1},\dots,$ and at $t=\Sigma_{i=1}^{n-1}t_i$ the frequency $\omega_{j_{n-1}}$.When the stochastic dynamics is determined by a Markov process, this probability can be factored into transition probabilities between sequential states $i\rightarrow i+1$ after the interval t_{i+1} and the initial $(t=0)$ probability distribution, i.e.,

$$p\left(\omega_{j_{n-1}},\sum_{i=1}^{n-1} t_i;\dots;\omega_{j_0},0\right) = \prod_{i=1}^{n-1} p(\omega_{j_i}\leftarrow\omega_{j_{i-1}},t_{j_i})p(\omega_{j_0},0). \tag{A2}$$

The transition probabilities after the interval t_i are the matrix elements of evolution operator $\exp(\mathbf{R}t_i)$. Since the dynamics is assumed to be stationary the initial probability $p(\omega_{j_0},0)$ is the equilibrium state probability distribution, i.e., we can rewrite Eq. (A1),

$$C_n=\langle 0|\mathbf{\Omega}\exp(\mathbf{R}t_{n-1})\mathbf{\Omega}\cdots\exp(\mathbf{R}t_1)\mathbf{\Omega}|0\rangle, \tag{A3}$$

where $\mathbf{\Omega}=(\omega_j\delta_{j,k})$ is the diagonal frequency matrix. A modification of the correlation functions occurs if one exchanges the evolution operator $\exp(\mathbf{R}t)$ with the operator $\exp(\mathbf{R}t)-\mathbf{\Pi}_0$, where $\mathbf{\Pi}_0=|0\rangle\langle 0|$ is the projection operator onto the equilibrium state space. This modified evolution operator describes the relaxation of observables minus their equilibrium state values. The modified autocorrelation functions will be denoted as quasicumulants and they are then defined as

$$c_n=\langle 0|\mathbf{\Omega}[\exp(\mathbf{R}t_{n-1})-\mathbf{\Pi}_0]\mathbf{\Omega}\cdots[\exp(\mathbf{R}t_1)-\mathbf{\Pi}_0]\mathbf{\Omega}|0\rangle. \tag{A4}$$

The Laplace transform of the correlation function in Eq. (A4) has the form

$$\hat{c}_n(s_{n-1},\dots,s_1)=\langle 0|\mathbf{\Omega}\left[\frac{1}{s_{n-1}-\mathbf{R}}-\frac{1}{s_{n-1}}\mathbf{\Pi}_0\right]\times\mathbf{\Omega}\cdots\left[\frac{1}{s_1-\mathbf{R}}-\frac{1}{s_1}\mathbf{\Pi}_0\right]\mathbf{\Omega}|0\rangle. \tag{A5}$$

This Laplace transform allows the determination of temporal moments of the normalized autocorrelation function $c_n(t_{n-1},\dots,t_1)/c_n(0,\dots,0)$ as the generalized correlation times

$$\tau_n^{n-1}=\hat{c}_n(0,\dots,0)/c_n(0,\dots,0). \tag{A6}$$

APPENDIX B: MOTIONAL NARROWING EXPANSION

The motional narrowing expansion is a perturbation approach to determine the overall magnetization $M(t)$—or its Laplace transform $\hat{M}(s)$—in terms of powers of the fluctuating fields $\mathbf{\Omega}$. It is based on the assumption that the stochastic fluctuations are more rapid than the precession frequencies of the perturbation fields (motional narrowing limit). We will present a general relation between the relaxation of the magnetization and the correlation of the field fluctuations that contains the motional narrowing limit as a limit case. The first step is to expand the Laplace transform of the overall magnetization, Eq. (3), in $\mathbf{\Omega}$, i.e.,

$$\begin{aligned}\hat{M}(s)&=\left\langle 0\left|\frac{1}{s-\mathbf{R}-i\mathbf{\Omega}}\right|0\right\rangle\\&=\langle 0|(s-\mathbf{R})^{-1}+i(s-\mathbf{R})^{-1}\mathbf{\Omega}(s-\mathbf{R})^{-1}\\&\quad+i^2(s-\mathbf{R})^{-1}\mathbf{\Omega}(s-\mathbf{R})^{-1}\mathbf{\Omega}(s-\mathbf{R})^{-1}+\cdots|0\rangle\\&=s^{-1}+s^{-2}i\langle 0|\mathbf{\Omega}|0\rangle+s^{-2}i^2\langle 0|\mathbf{\Omega}(s-\mathbf{R})^{-1}\mathbf{\Omega}\rangle+\cdots\\&=s^{-1}\left(1+s^{-1}\sum_{\nu=1}^{\infty}i^\nu\hat{C}_\nu(\underbrace{s,s,\dots,s}_{(\nu-1)\times})\right),\end{aligned} \tag{B1}$$

where $\hat{C}_\nu$ are the Laplace transformed n-point correlation functions of Eq. (A3). To avoid singularities at $s=0$ it is better to consider $\hat{M}^{-1}(s)$. When we set $q=s^{-1}\Sigma_{\nu=1}^{\infty}i^\nu\hat{C}_\nu(\underbrace{s,s,\dots,s}_{(\nu-1)\times})$, one obtains

$$\begin{aligned}\hat{M}^{-1}(s)&=s\left(1+\sum_{\rho=1}^{\infty}(-1)^\rho q^\rho\right)\\&=s-\sum_{\nu=1}^{\infty}i^\nu\hat{C}_\nu+s^{-1}\sum_{\nu_1,\nu_2=1}^{\infty}i^{\nu_1+\nu_2}\hat{C}_{\nu_1}\hat{C}_{\nu_2}\\&\quad+\cdots+(-1)^\rho s^{-(\rho-1)}\sum_{\nu_1,\dots,\nu_\rho=1}^{\infty}i^{\nu_1+\nu_\rho}\\&\quad\times\prod_{m=1}^{\rho}\hat{C}_{\nu_m}+\cdots.\end{aligned} \tag{B2}$$

Rearrangement of terms of equal order in $\mathbf{\Omega}$ provides

$$\hat{M}^{-1}(s)=s-\sum_{j=1}^{\infty}i^jK_j, \tag{B3}$$

where the coefficients K_j have the form

$$K_j=\hat{C}_j-s^{-1}\sum_{\nu_1+\nu_2=j}\hat{C}_{\nu_1}\hat{C}_{\nu_2}+\cdots+(-s)^{1-\rho}\times\sum_{\nu_1+\cdots+\nu_\rho=j}\prod_{m=1}^{\rho}\hat{C}_{\nu_m}+\cdots+(-s)^{1-j}\hat{C}_1^j. \tag{B4}$$

A comparison of this sum with the modified correlation functions c_j, Eqs. (A4) and (A5), shows that

$$K_j = \hat{c}_j(\underbrace{s,\ldots,s}_{(j-1)\times}), \tag{B5}$$

i.e., one obtains

$$\hat{M}^{-1}(s) = s - \sum_{j=1}^{\infty} i^j \hat{c}_j(\underbrace{s,s,\ldots,s}_{(j-1)\times}). \tag{B6}$$

Equation (B6) expands the relaxation of the magnetization in terms of correlation functions to an arbitrary order. The long-time behavior of $M(t)$ is determined by the Laplace transform in the limit of small s, i.e., in this range the relation

$$\hat{M}^{-1}(0) = -\sum_{j=1}^{\infty} i^j \hat{c}_j(0,0,\ldots,0) \tag{B7}$$

is valid; see also Eq. (A6). The series in Eq. (B7) contains terms of magnitude $\leqslant \langle 0|\mathbf{\Omega}^\nu|0\rangle/l^\nu$, where l denotes nonvanishing eigenvalues of $\mathbf{R}$. The latter determine the fluctuation frequency. In the motional narrowing limit these fluctuations are much higher than the precessing frequencies $\langle 0|\mathbf{\Omega}^\nu|0\rangle/l^\nu \ll 1$, i.e., after normalization of the average perturbation field $\langle 0|\mathbf{\Omega}|0\rangle$ to zero, i.e., $c_1=0$, $M(t)$ is given a single exponential decay with the well known result for the transverse relaxation rate as $1/T_2 = \hat{c}_2(0) = \tau_2\langle 0|\mathbf{\Omega}^2|0\rangle$.

APPENDIX C: QUASICUMULANTS IN THE STRONG COLLISION APPROXIMATION

In the strong collision (ESC_0) approximation the quasicumulants take a very simple form. Insertion of the generator $\mathbf{D} = -\lambda(\mathbf{id} - \mathbf{\Pi}_0)$ into Eq. (A5) results in

$$\hat{c}_n^{(\mathrm{ESC}_0)}(s_{n-1},\ldots,s_1) = \prod_{i=1}^{n-1} \frac{1}{s_i+\lambda} c_{n-1}(0,\ldots,0), \tag{C1}$$

i.e., the quasicumulant is a product of single exponential functions $e^{-\lambda t_i}$ and the generalized correlation times, Eq. (A6), are all identical, namely,

$$\tau_n^{(SC)} = \lambda^{-1}. \tag{C2}$$

APPENDIX D: QUASICUMULANTS IN THE EXTENDED STRONG COLLISION APPROXIMATION

We restrict ourselves here to the ESC_1 approximation and determine the correlation functions and generalized relaxation times for the Ω-polynomial base only in order to show the principle. Extensions to higher order approximations and to other function bases are straightforward, although they may be more tedious to calculate.

For ESC_1 the generator of the stochastic field fluctuations has the form $\mathbf{D} = -\lambda_1\mathbf{\Pi}_1 - \lambda(\mathbf{id} - \mathbf{\Pi}_0 - \mathbf{\Pi}_1)$. We will determine only the Laplace transforms of the two- and four-point correlation functions, since the three-point correlation functions vanishes in the models we consider. According to Eq. (A5) the determination of the correlation functions requires the operator

$$\frac{1}{s-\mathbf{D}} - \frac{1}{s}\mathbf{\Pi}_0 = \frac{1}{s+\lambda_1}\mathbf{\Pi}_1 + \frac{1}{s+\lambda}(\mathbf{id} - \mathbf{\Pi}_0 - \mathbf{\Pi}_1). \tag{D1}$$

Assuming that the average frequency vanishes, i.e., $\langle\mathbf{\Omega}\rangle = \langle 0|\mathbf{\Omega}|0\rangle = 0$, which can always be achieved by normalization, $|f_1\rangle \sim \mathbf{\Omega}|0\rangle$. Hence, the projector $\mathbf{\Pi}_1 = |f_1\rangle\langle f_1|$ takes the form

$$\mathbf{\Pi}_1 = \frac{\mathbf{\Omega}|0\rangle\langle 0|\mathbf{\Omega}}{\langle 0|\mathbf{\Omega}^2|0\rangle}. \tag{D2}$$

For the Laplace transformed two-point correlation function one obtains then

$$\hat{c}_2^{(\mathrm{ESC}_1)}(s) = (\lambda_1+s)^{-1}\langle 0|\mathbf{\Omega}^2|0\rangle, \tag{D3}$$

i.e., the two-point correlation function exhibits a single exponential decay with relaxation rate

$$\tau_2^{(\mathrm{ESC}_1)} = \lambda_1^{-1}. \tag{D4}$$

The four-point correlation function is

$$\begin{aligned}\hat{c}_4^{(\mathrm{ESC}_1)}(s_3,s_2,s_1) = {} & \frac{1}{(s_3+\lambda_1)(s_1+\lambda_1)} \times \left(\frac{1}{s_2+\lambda_1} - \frac{1}{s_2+\lambda}\right)\frac{\langle 0|\mathbf{\Omega}^3|0\rangle^2}{\langle 0|\mathbf{\Omega}^2|0\rangle} \\ & + \frac{1}{(s_3+\lambda_1)(s_2+\lambda)(s_1+\lambda_1)} \times (\langle 0|\mathbf{\Omega}^4|0\rangle - \langle 0|\mathbf{\Omega}^2|0\rangle^2).\end{aligned} \tag{D5}$$

The four-point correlation time is then determined as

$$\begin{aligned}\tau_4^{(\mathrm{ESC}_1)} &= [\hat{c}_4^{(\mathrm{ESC}_1)}(0)/c_4^{(\mathrm{ESC}_1)}(0)]^{1/3} \\ &= \left[\frac{1}{\lambda_1^2}\left(\frac{1}{\lambda_1} - \frac{1}{\lambda}\right)\frac{\langle 0|\mathbf{\Omega}^3|0\rangle^2}{\langle 0|\mathbf{\Omega}^2|0\rangle(\langle 0|\mathbf{\Omega}^4|0\rangle - \langle 0|\mathbf{\Omega}^2|0\rangle^2)} + \frac{1}{\lambda_1^2\lambda}\right]^{1/3}.\end{aligned} \tag{D6}$$

In the case of the Anderson-Weiss model and for the restricted diffusion linear gradient, one has $\langle 0|\mathbf{\Omega}^3|0\rangle = 0$, i.e., Eq. (D6) simplifies to

$$\tau_4^{(\mathrm{ESC}_1)} = \sqrt[3]{\frac{1}{\lambda_1^2\lambda}}. \tag{D7}$$

APPENDIX E: RELAXATION TIMES OF CORRELATION FUNCTIONS IN THE MODELS

In this final appendix we will determine the generalized relaxation times of stochastic field fluctuations up to the fourth order for the generic models we discuss in the main text.

1. Diffusion in a harmonic potential

When field fluctuations result from diffusion in a harmonic potential according to Eq. (40) and spin dephasing is described by Eq. (42), the corresponding Laplace transformed two-point correlation function, Eq. (A5), is

$$\hat{c}_2(s)=\left\langle 0\left|\omega\frac{1}{s-\beta\partial_\omega(\partial_\omega+\omega)}\omega\right|0\right\rangle =\left\langle 1\left|\frac{1}{s-\beta\partial_\omega(\partial_\omega+\omega)}\right|1\right\rangle =\frac{1}{s+\beta}, \tag{E1}$$

where we applied the operator properties of $\partial_\omega,(\partial\omega+\omega)$ according to Eqs. (45). This result shows that the two-point correlation function exhibits a single exponential decay. Since $c_2(0)=\langle 0|\omega^2|0\rangle=1$, one obtains

$$\tau_2=\beta^{-1}\ . \tag{E2}$$

Since $c_3(t)$ vanishes, the next relevant correlation function is $c_4(t)$. Similarly, one obtains for its Laplace transform

$$\hat{c}_4(s_3,s_2,s_1)=\frac{2}{(s_3+\beta)(s_2+2\beta)(s_1+\beta)}\ . \tag{E3}$$

And since $c_4(0)=\langle 0|\omega^4|0\rangle=2$ the corresponding correlation time is

$$\tau_4=\sqrt[3]{\frac{1}{2}}\beta^{-1}\ . \tag{E4}$$

2. Restricted diffusion in a linear gradient field

In this section we will determine the correlation times τ_n of Eq. (A6) for $n=2,4$ for the one-dimensional restricted diffusion of spins in a unit box in which they are affected by a linear gradient field. In dimensionless parameters one obtains for the generator $\mathbf{R}=\beta[\partial_x^2]$, where β is the dimensionless diffusion coefficient. The brackets denote that the application of the operator ∂_x^2 is restricted to functions with a vanishing derivative at $x=\pm 1/2$ (reflecting boundary conditions). The frequency operator is $\mathbf{\Omega}=x$ and the equilibrium state eigenfunction is $|0\rangle\equiv 1$.

The determination of correlation times τ_n requires the calculation of the Laplace transformed quasicumulants $\hat{c}_n(0,\ldots,0)$, Eq. (A6). The definition of these quasicumulants according to Eq. (A5) shows the need of recurrent determination of terms of the form

$$f=\lim_{s\to 0}[-(s-\mathbf{R})^{-1}+s^{-1}\mathbf{\Pi}_0]g, \tag{E5}$$

with some function g, i.e., f fulfills

$$\mathbf{R}f=(1-\mathbf{\Pi}_0)g, \tag{E6}$$

i.e., with $\mathbf{R}=\beta[\partial_x^2]$ Eq. (E6) becomes a second order differential equation. The application of the inverse second order differential operator leaves, in general two integration constants. One may be determined from the reflective symmetric boundary conditions; however, a further condition is needed to get the second constant. A spectral decomposition $\mathbf{R}$ in Eq. (E5) shows $\Pi_0 f\equiv 0$, i.e., we obtain as a further condition

$$\int_{-1/2}^{1/2}dx\, f(x)=0. \tag{E7}$$

Two-point correlation time. We define

$$f_1(x)=\lim_{s\to 0}[-(s-\mathbf{R})^{-1}+s^{-1}\mathbf{\Pi}_0]x|0\rangle=\beta^{-1}(x^3/6-x/8), \tag{E8}$$

which obviously fulfills the reflecting boundary condition at $x=\pm 1/2$ and Eq. (E7). Hence, the two-point Laplace transformed quasicumulant is

$$\hat{c}_2(0)=-\langle 0|x\lim_{s\to 0}[-(s-\mathbf{R})^{-1}+s^{-1}\mathbf{\Pi}_0]x|0\rangle =\int_{-1/2}^{1/2}dx\, x\, f_1(x)=\beta^{-1}\frac{1}{120}, \tag{E9}$$

and with

$$c_2(0)=\langle 0|x^2|0\rangle=\int_{-1/2}^{1/2}dx\, x^2=1/12, \tag{E10}$$

one obtains

$$\tau_2=\frac{1}{10}\beta^{-1}\ . \tag{E11}$$

Four-point correlation time. Iterative application of Eq. (E5) defines

$$f_2(x)=\lim_{s\to 0}[-(s-\mathbf{R})^{-1}+s^{-1}\mathbf{\Pi}_0]xf_1(x), \tag{E12}$$

which, according to Eq. (E6), fulfills

$$\beta[\partial_x^2]f_2(x)=(1-\mathbf{\Pi}_0)xf_1(x)$$
$$=xf_1(x)-\int_{-1/2}^{1/2}dx\,xf_1(x)$$
$$=xf_1(x)+\frac{1}{120}\beta^{-1}\ . \tag{E13}$$

Insertion of f_1, Eq. (E8), and considering the reflective boundary conditions and the condition (E7) yields

$$f_2(x)=\beta^{-2}\left(\frac{x^6}{180}-\frac{x^4}{96}+\frac{x^2}{240}-\frac{37}{161280}\right). \tag{E14}$$

Similarly to the procedure above we could determine a function $f_3(x)$, but instead we use a different approach which exploits the symmetry of eigenfunctions of the operator $\mathbf{R}=\beta[\partial_x^2]$. The Laplace transformed four-point quasicumulant is

$$\hat{c}_4(0,0,0)=-\Bigg\langle 0\Bigg|\overbrace{x\lim_{s_3\to 0}\left[-\frac{1}{s_3-\mathbf{R}}+\frac{1}{s_3}\mathbf{\Pi}_0\right]x}^{=f_1(x)}$$
$$\times\lim_{s_2\to 0}\left[-\frac{1}{s_2-\mathbf{R}}+\frac{1}{s_2}\mathbf{\Pi}_0\right]x$$
$$\times\lim_{s_1\to 0}\left[-\frac{1}{s_1-\mathbf{R}}+\frac{1}{s_1}\mathbf{\Pi}_0\right]x\Bigg|0\Bigg\rangle$$
$$=-\int_{-1/2}^{1/2}dx\,f_1(x)xf_2(x)$$
$$=\beta^{-3}\frac{89}{79\,833\,600}, \tag{E15}$$

and with

$$c_4(0,0,0)=\langle 0|x^4|0\rangle-\langle 0|x^2|0\rangle^2=\frac{1}{180}, \tag{E16}$$

we finally have

$$\tau_4=\sqrt[3]{\frac{89}{443\,520}}\beta^{-1}. \tag{E17}$$

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