Spin-echo decay in a stochastic field environment

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We derive a general formalism with which it is possible to obtain the time (τ) dependence of the echo size for a spin in a stochastic field environment. Our model is based on ''strong collisions.'' We examine in detail two examples. In the first one the field distribution has a finite second moment, and in the second one (a Lorentzian) it does not. We find that the echo decay in the first case is exponential in τ^3 as $\tau\rightarrow 0$, and in the second case can be approximated by the phenomenological expression $\exp(-[2\tau/T_2]^{\beta})$ with $1<\beta<2$; in the $\tau\rightarrow 0$ limit $\beta=2$. In addition, only the first case shows a T_2 minimum effect. [S0163-1829(99)02937-9]

Spin-echo decay (SED) measurements, also known as T_2, are conducted by a variety of experimental techniques, such as radio-frequency–muon-spin resonance (rf-μSR,[1] ESR,[2] nuclear qradrupole resonance (NQR), and NMR.[3] With the recent explosion of high-Tc superconductivity research, NMR-T_2 measurements in particular are receiving renewed attention, since they are very successful in probing both the normal[4,5] and superconducting states[6] of cuprates. These experiments lead to a revival of theoretical activity, focusing on the calculation of the shape of the SED relaxation function (wave form) for different sources of interactions such as spin lattice coupling, spin-spin coupling, and stochastic fluctuations. For this purpose, a variety of analytical[7] and numerical[8] models were applied. However, several dynamical features, observed experimentally, have not been accounted for. In this paper we provide insight into these features by re-examining the echo decay wave form of a spin in a stochastic field environment, and use an analytical approach based on the ''strong collision'' model (see below) to yield quantitative understanding of SED.

An earlier exact treatment of the stochastic problem, based on a diffusionlike model, was presented by Klauder and Anderson (KA).[9] They found that for Lorentzian diffusion the wave form is Gaussian, and for Gaussian diffusion the wave form is exponential in τ^3. Although the KA approach is physically more intuitive, the final result lacks three features: (I) the SED rate depends monotonically on the diffusion rate, although it is natural to expect that when the diffusion is either very fast or extremely slow, the echo does not decay, (II) the wave form does not depend on the diffusion rate, and, therefore, it cannot change continuously (for example, as a function of temperature), and (III) they could not account for stretched exponential relaxation $\exp(-[2\tau/T_2]^{\beta})$ with $\beta<2$. As we shall see, our derivation allows for all these phenomena, and, therefore, might be applicable to some cases to which the diffusion model is not.

In echo NMR, NQR, and ESR transverse relaxation measurements, a $\pi/2$ pulse is applied to a system of spins polarized along the z direction. As a result, a net polarization (M_x) along the x direction in the rotating reference frame (RRF) is obtained. In rf-μSR the muons enter the sample with their spin already polarized along the RRF x direction. After the pulse (or muon arrival), the spins evolve with time, each one in its local field B_z, until time τ when a π pulse is applied, sending the x component (in the RRF) of each spin S_x to $-S_x$ (and S_z to $-S_z$). The spins then continue to evolve, and if B_z is static, an echo is formed at time 2τ. If, however, the local field is dynamic, the phase acquired by the spin before the π pulse is not necessarily equal to the phase lost after it, and the echo size diminishes as a function of τ. This situation can be quantified by

$$M_x(2\tau)=M_x(0)\left\langle \cos\left[\int_0^{\tau}\omega(t)dt-\int_{\tau}^{2\tau}\omega(t)dt\right]\right\rangle, \quad (1)$$

where $\omega(t)=\gamma B_z(t)$, γ is the spin's gyromagnetic ratio, and $\langle\rangle$ is an average over all possible frequency trajectories.

First we would like to evaluate Eq. (1) to lowest order in τ. Assuming that the argument of the cosine is small, we can expand it to second order, and then evaluate terms such as $\int_0^{\tau}\int_0^{\tau}dt'dt''\langle\omega(t')\omega(t'')\rangle$ and $\int_0^{\tau}\int_{\tau}^{2\tau}dt'dt''\langle\omega(t')\omega(t'')\rangle$. Assuming a correlation function of the form

$$\begin{aligned}\langle\omega(t')\omega(t'')\rangle&=\langle\omega^2\rangle\exp(-\nu|t''-t'|)\\&=\langle\omega^2\rangle(1-\nu|t''-t'|+\cdots),\end{aligned} \quad (2)$$

where $\langle\omega^2\rangle$ is the second moment of the instantaneous frequency distribution, we find

$$M_x(2\tau)=M_x(0)\left(1-\frac{2}{3}\langle\omega^2\rangle\nu\tau^3+\cdots\right). \quad (3)$$

Equation 3 is well known[3] and will serve as a test of our derivation.

Next we shall evaluate Eq. (1) to all orders in τ by making some assumptions concerning $\omega(t)$. We quantify the dynamical fluctuation using ''indirect echo'' and the strong collision model. Indirect echo is equivalent to the situation described by Eq. (1) but instead of $S_x\rightarrow -S_x$ at the π pulse, the frequency is reversed ($\omega\rightarrow-\omega$); in Fig. 1(a) we demonstrate indirect echo by showing that a reversal of ω at τ leads to $S_x(2\tau)=S_x(0)\equiv 1$. The strong collision model accounts for $\omega(t)$ by allowing frequency changes only at specific times $t_1,t_2\ldots t_n$. The probability density of finding the frequency ω at any time interval is taken to be the internal frequency distribution $\rho(\omega)$. A demonstration of this situation for a particular spin is presented in Fig. 1(b). Here the spin has experienced two frequency changes at times t_1 and

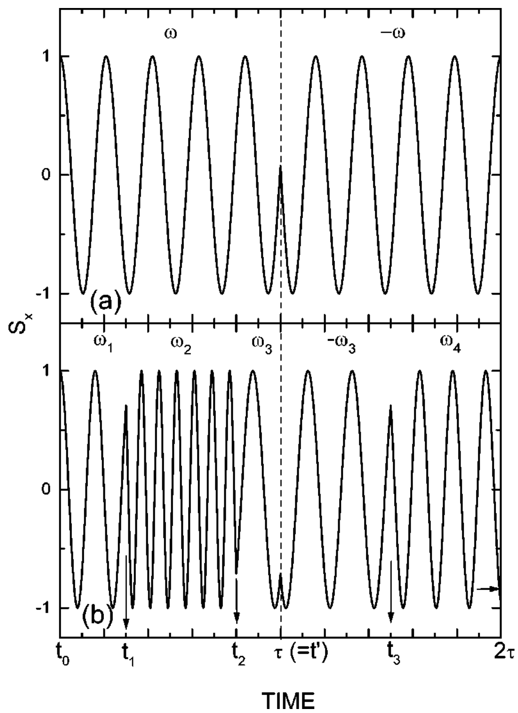

FIG. 1. A demonstration of the indirect echo when there are no local field fluctuations (a), and when the field is dynamical (b) and changes instantaneously.

t_2 before the π pulse and one change after the π pulse at t_3. As a result $S_x(2\tau)\neq S_x(0)$ and on average the echo size will decrease as a function of τ. In this type of dynamical process the spin environment after each jump is not correlated with the spin environment before the jump, and the correlation function is in the form of Eq. (2). By comparison, in the model of KA the frequency after each change depends on the frequency before the change.

We shall now treat the case of an ensemble of spins and average over all possible field changes, the times at which they take place, and all possible fields in each time interval. If there are n hops at times $t_1,\ldots,t_n$ before the π pulse and m hops at times $t_{n+1},\ldots,t_{m+n}$ between the π and the observation time $t=2\tau$, the phase acquired by the spin ($\theta_{n,m}$) is

$$\theta_{n,m}=\omega_{n+m+1}(t-t_{n+m})+\sum_{j=2}^{m}\omega_{j+n}(t_{n+j}-t_{n+j-1})-\omega_{n+1}(t_{n+1}-\tau)+\omega_{n+1}(\tau-t_n)+\sum_{i=1}^{n}\omega_i(t_i-t_{i-1}),\tag{4}$$

where ω_i is the frequency in the ith time interval. The polarization along the RRF x axis is, therefore,

$$M_x(\omega_1,\ldots,\omega_{n+m+1};t,\tau;t_1,\ldots,t_{n+m})\equiv \mathrm{Re}\exp(i\theta_{n,m}),$$

where Re stands for the real part; we shall omit it from now on. We first average over all possible frequencies ω_i in the time segment $[t_{i-1},t_i]$ and define

$$M_x(t,\tau;t_1,\ldots,t_{n+m})\equiv\int\rho(\omega_1)d\omega_1\ldots\int\rho(\omega_{n+m+1})d\omega_{n+m+1}\times M_x(\omega_1,\ldots,\omega_{n+m+1};t,\tau;t_1,\ldots,t_{n+m+1}).$$

This results in

$$M_x(t,\tau;t_1,\ldots,t_{n+m})=g(t-t_{n+m})\left[\prod_{j=2}^{m}g(t_{j+n}-t_{j+n-1})\right]\times g(2\tau-t_{n+1}-t_{n-1})\left[\prod_{i=1}^{n}g(t_i-t_{i-1})\right],$$

where $g(t)$ is given by

$$g(t)=\int_{-\infty}^{\infty}\rho(\omega)\exp(i\omega t)d\omega.\tag{5}$$

The probability density of finding exactly $n+m$ hops at times $t_1,\ldots,t_{n+m}$ is

$$\exp[-\nu(t-t_{n+m})]\prod_{i=1}^{n+m}\exp[-\nu(t_i-t_{i-1})]\nu\,dt_i=\nu^{n+m}\exp(-\nu t)\prod_{i=1}^{n+m}dt_i,$$

where ν is the field hopping rate. Thus, the averaged spin polarization at time t is given by

$$M_x(t)=\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\nu^{n+m}\exp(-\nu t)I_{n,m}(t,\tau),\tag{6}$$

where

$$I_{n,m}(t,\tau)=\int_{\tau}^{t}dt_{n+m}\cdots\int_{\tau}^{t_{n+2}}dt_{n+1}\int_{0}^{\tau}dt_n\cdots\times\int_{0}^{t_2}dt_1M_x(t,\tau;t_1,\ldots,t_{n+m}).\tag{7}$$

The integration limits guarantee that $t_{i+1}>t_i$.

We can simplify Eq. (7) by turning the time at which the π pulse is applied (τ) into a running variable (t') whose value is fixed with a δ function. The δ function should force the sum of time segments from zero until τ to be equal to the sum of time segments from the τ until 2τ, namely,

$$\delta(t'-\tau)=2\delta\left((t'-t_n)+\sum_{i=1}^{n}(t_i-t_{i-1})-\sum_{j=2}^{m+1}(t_{n+j}-t_{n+j-1})-(t_{n+1}-t')\right),$$

where t_{n+m+1} stands for 2τ. As a result

$$I_{n,m}(2\tau,\tau)=\int_0^{2\tau}dt_{n+m}\cdots\int_0^{t_{n+2}}dt_{n+1}\int_0^{t_{n+1}}dt'\int_0^{t'}dt_n\cdots$$
$$\times\int_0^{t_2}dt_1 M_x(2\tau,t';t_1\ldots t_{n+m})\,\delta(t'-\tau), \quad (8)$$

and the integrand in Eq. (8) is a function of time differences only.

We now introduce the integral representation of the δ function

$$\delta(x)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(i\Omega x)d\Omega, \quad (9)$$

and the Laplace transform of M_x:

$$\bar{M}_x(s)=2\int_0^{\infty}M_x(2\tau)\exp(-2s\tau)d\tau. \quad (10)$$

By inserting Eq. (9) into Eq. (8), Eq. (8) into Eq. (6), and substituting this in Eq. (10) we find that all the integrals decouple and

$$\bar{M}_x(s)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\Omega\, f_2(z_-,z_+)$$
$$\times\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}[\nu f_1(z_-)]^n[\nu f_1(z_+)]^m, \quad (11)$$

where

$$z_\pm=s+\nu\pm i\Omega/2, \quad (12)$$

$$f_1(z_\pm)=\int_0^{\infty}du\,\exp(-z_\pm u)g(u), \quad (13)$$

and

$$f_2(z_-,z_+)=\frac{f_1(z_-)+f_1(z_+)}{z_-+z_+}. \quad (14)$$

Finally, $|\nu f(z)|<1$, and performing the sums in Eq. (11) gives

$$\bar{M}_x(s)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\Omega\frac{f_2(z_-,z_+)}{[1-\nu f_1(z_-)][1-\nu f_1(z_+)]}, \quad (15)$$

from which we obtain the time-dependent nuclear magnetization by

$$M_x(2\tau)=\mathcal{L}^{-1}(\bar{M}_x(s))_{t=2\tau}, \quad (16)$$

where $\mathcal{L}^{-1}$ is the inverse Laplace transform operator. Using Eq. (5) and Eqs. (12)–(16) one can obtain the echo decay knowing only the frequency distribution $\rho(\omega)$. Now let us examine two simple cases:

A distribution with a second moment. It is useful to examine a field distribution with a finite second moment so as to compare with Eq. (3). One such distribution is

$$\rho(\omega)=\frac{2\sigma^3}{\pi(\sigma^4+4\omega^4)}, \quad (17)$$

and its second moment is given by $\langle\omega^2\rangle=\sigma^2/2$. This leads to

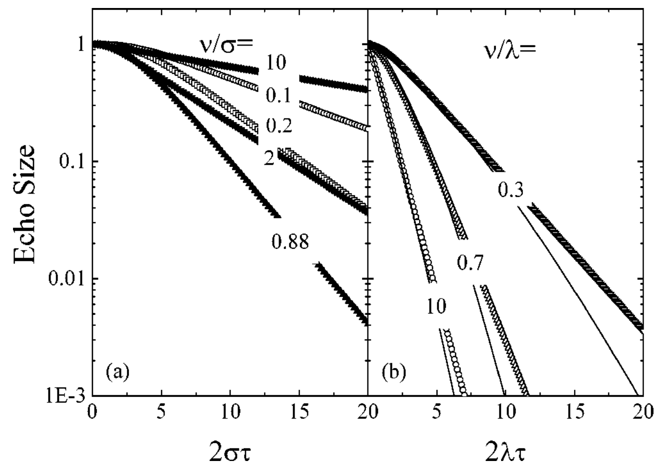

FIG. 2. The echo decay for (a) a distribution with a second moment [Eq. (18)] vs $2\sigma\tau$, and (b) Lorentzian field distribution [Eq. (20)] as a function of $2\lambda\tau$. The solid line in panel (b) represents a fit to Eq. (21) as described in the text.

$$M_x(2\tau)=\frac{\sigma^2 e^{-2\nu\tau}}{(\sigma-\nu)(\sigma-2\nu)}-\frac{\nu\sigma^2 e^{-(\sigma+\nu)\tau}}{2(\sigma-\nu)f_\sigma^2}$$
$$-\frac{\nu(\sigma^2-3\nu\sigma-2\nu^2)e^{-(\sigma+\nu)\tau}}{4(\sigma-2\nu)f_\sigma^2}\cos(2f_\sigma\tau)$$
$$-\frac{\nu(\sigma+2\nu)e^{-(\sigma+\nu)\tau}}{2f_\sigma(\sigma-2\nu)}\sin(2f_\sigma\tau), \quad (18)$$

where $f_\sigma^2\equiv(\sigma^2-2\sigma\nu-\nu^2)/4$. For $f_\sigma^2<0$ the result is the same, except that $f_\sigma\to i|f_\sigma|$. An expansion of Eq. (18) around $\tau=0$ agrees with Eq. (3), thus reinforcing the validity of our derivation. In Fig. 2(a) we depict Eq. (18) for various values of ν/σ. It is clear from this figure that when either $\nu/\sigma\ll 1$ or $\nu/\sigma\gg 1$ the echo decay rate is weak compared to $\nu/\sigma\simeq 1$. To quantify this phenomenon we define T_2 as the time at which the echo size decreases to $1/e$. We find that T_2 is shortest for $\nu=0.88\sigma$, and at this value of ν $T_2=5.75/\sigma$.

Lorentzian distribution. In this case the equilibrium distribution is taken to be

$$\rho(\omega)=\frac{\lambda}{\pi(\lambda^2+\omega^2)}, \quad (19)$$

and we find

$$M_x^{\mathrm{L}}(2\tau)=\frac{\lambda\exp(-2\nu\tau)-\nu\exp(-2\lambda\tau)}{\lambda-\nu}, \quad (20)$$

where L stands for Lorentzian. This expression has interesting properties. An expansion of Eq. (20) around $\tau=0$ gives

$$M_x^{\mathrm{L}}(2\tau)=1-\frac{1}{2}\lambda\nu(2\tau)^2+O(\tau^3),$$

which means that at early enough times the relaxation shape is Gaussian. This result was put to use in NMR data analysis in Ref. 5. One should note that this expansion does not contradict Eq. (3) since a Lorentzian does not have a second moment. However, for $\lambda\gg\nu$ the relaxation is exponential for $\lambda\tau\gg 1$ with the relaxation rate ν. Similarly, when $\lambda\ll\nu$ the relaxation is exponential for $\nu\tau \gg 1$ with the relaxation rate λ. This suggests that experimental data which stem from Eq. (20) can be well fitted to a stretched exponential

$$M_x(2\tau) = \exp\left(-\left[\frac{2\tau}{T_2}\right]^{\beta}\right) \tag{21}$$

with $1<\beta<2$. In Fig. 2(b) we depict three data sets of $M_x^{\mathrm{L}}(2\tau)$ obtained from Eq. (20) for various values of ν/λ. Unlike in the previous cases, the Lorentzian case shows a continuous increase in relaxation rate with increasing ν. In this figure we also depict the best fit of the data sets to Eq. (21). The fits are quite good over more than an order of magnitude in echo size, and when experimental data are fitted, Eq. (20) can easily be confused with Eq. (21). In Fig. 3 we show the parameters β and $1/(\lambda T_2)$ as a function of ν/λ. While T_2 decreases monotonically with increasing fluctuation rate, the power β goes through a maximum at $\nu/\lambda = 1$. However, it should be mentioned that the value of β depends on the range which is used for the fit.

It is interesting to compare our Lorentzian result with that of KA. In the KA model the field dynamics at the site of the observed nuclei is generated by flipping some other unobserved individual spins. Therefore, in their model, it is more likely to undergo small field changes than large ones. The situation KA tried to describe could still be approximated by the strong collision model if $\nu \gg \lambda$, since then many unobserved spins are flipped before the observed nuclei evolve considerably with time. This suggests that in reality, for $\nu \gg \lambda$, we should expect $\beta = 1$, as found here, and for $\nu \simeq \lambda$ we should expect $\beta = 2$ as found by KA. Between these two limits β should change continuously.

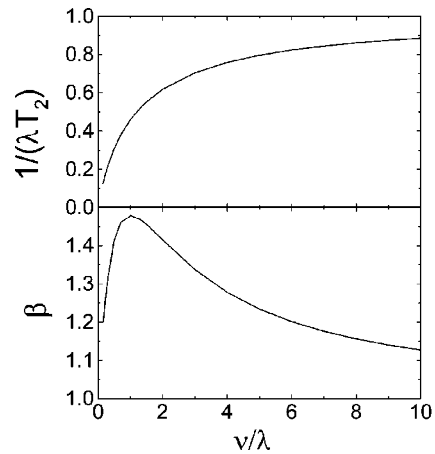

FIG. 3. The parameters $1/(\lambda T_2)$ and β which allow the best approximation of Eq. (20) with Eq. (21).

We thus provide a recipe for obtaining the time dependence of the echo size for a given frequency distribution. We examined two particular cases and found a natural explanation for experimental and conceptual features, such as stretched-exponential relaxation and T_2 minima, which have not been explained quantitatively before.

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