Spin Echo Decay in a Stochastic Field Environment

Amit Keren and Ophir M. Auslaender

Department of Physics, Technion - Israel Institute of Technology,
Haifa 32000, Israel.

Abstract

We derive a general formalism with which it is possible to obtain the time ($\tau$) dependence of the echo size for a spin in a stochastic field environment. Our model is based on “strong collisions”. We examine in detail three cases where: (I) the local field is $\pm \omega_0$, (II) the field distribution is continuous and has a finite second moment, and (III) the distribution is Lorentzian. The first two cases show a $T_2$ minimum effect and are exponential in $\tau^3$ as $\tau \to 0$. The last case can be approximated by the phenomenological expression $\exp(-[2\tau/T_2]^\beta)$ with $1 < \beta < 2$, where in the $\tau \to 0$ limit $\beta = 2$. 
Spin echo decay (SED) measurements, also known as $T_2$, are conducted by a variety of experimental techniques, such as RF-$\mu$SR [3], ESR [4], NQR, and NMR [1]. With the recent explosion of high-$T_c$ superconductivity research, NMR-$T_2$ measurements in particular are receiving renewed attention, since they are very successful in probing both the normal [4] and superconducting states [3] of cuprates. These experiments lead to a revival of theoretical activity, focusing on the calculation of the SED waveform for different sources of interactions such as spin lattice coupling, spin-spin coupling, and stochastic fluctuations. For this purpose, a variety of analytical [3] and numerical [7] models were applied. However, several dynamical features, observed experimentally, have not been accounted for. In this paper we provide new insight into these features by re-examining the echo decay waveform 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 diffusion like model, was presented by Klauder and Anderson (KA) [8]. They found that for Lorentzian diffusion the waveform is Gaussian, and for Gaussian diffusion the waveform is exponential in $\tau^3$ (see bellow). Although the KA approach is physically more intuitive, the final result lacks three features: (I) the waveform does not depend on the diffusion rate, and therefore it cannot change continuously (for example, as a function of temperature), (II) they could not account for stretched exponential relaxation $\exp(-[2\tau/T_2]^\beta)$ with $\beta < 2$, and (III) the SED 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. 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 addition, we examine one case which was not considered by KA, namely, the local field is $\pm \omega_0$. For this case our derivation is exact.

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 along the $x$ direction ($M_x$) is obtained. In RF-$\mu$SR the muons enter the sample with their spin already polarized along the $x$ direction. After the pulse (or muon arrival), the spins evolve
with time, each one in its local field $B_z$, until time $\tau$ when a $\pi$ pulse is applied, sending the $x$ component 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 $2\tau$. If, however, the local field is dynamic, the phase acquired by the spin before the $\pi$ pulse is not necessarily equal to the phase lost after it, and the echo size diminishes as a function of $\tau$. This situation can be quantified by

$$M_x(2\tau) = M_x(0) \left\langle \cos \left[ \int_0^\tau \omega(t)dt - \int_2^{2\tau} \omega(t)dt \right] \right\rangle,$$  \hspace{1cm} (1)

where $\omega(t) = \gamma B_z(t)$, $\gamma$ 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 $\tau$. Assuming that the argument of the cosine is small, we can expand it to second order, and then evaluate terms such as $\int_0^\tau \int_0^\tau \langle \omega(t') \omega(t'') \rangle$ and $\int_0^\tau \int_2^{2\tau} \langle \omega(t') \omega(t'') \rangle$. Assuming a correlation function of the form

$$\langle \omega(t') \omega(t'') \rangle = \left\langle \omega^2 \right\rangle \exp \left( -\nu |t'' - t'| \right) = \left\langle \omega^2 \right\rangle \left( 1 - \nu |t'' - t'| + \ldots \right),$$  \hspace{1cm} (2)

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

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

Equation (3) is well known \cite{1} and will serve as a test of our derivation.

Next we shall evaluate Eq. (1) to all orders in $\tau$ 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 $\pi$ pulse, the frequency is reversed ($\omega \rightarrow -\omega$); in Fig. 1a we demonstrate indirect echo by showing that a reversal of $\omega$ at $\tau$ 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 $\omega$ at any time interval is taken to be the line shape $\rho(\omega)$. A demonstration of this situation for a particular spin is presented in Fig. 1b. Here the spin has experienced two frequency changes at times $t_1$ and $t_2$ before the $\pi$ pulse.
and one change after the $\pi$ 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 $\tau$. This type of dynamical process results in a correlation function in the form of Eq. 2. By comparison, in KA’s model 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 $\pi$ pulse and $m$ hops at times $t_{n+1}, \ldots, t_{n+m}$ between the $\pi$ and the observation time $t = 2\tau$, the phase acquired by the spin $(\theta_{n,m})$ is

$$\theta_{n,m} = \omega_{n+m+1}(t - t_{n+m}) + \sum_{j=2}^{m} \omega_{j+n}(t_{n+j} - t_{n+j-1})$$

$$- \omega_{n+1}(t_{n+1} - \tau) + \omega_{n+1}(\tau - t_n) + \sum_{i=1}^{n} \omega_i(t_i - t_{i-1}).$$

The polarization along the $x$ axis is therefore

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

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

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

This results in

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

where $g(t)$, also known as the free induction decay (FID) function, is given by

$$g(t) = \int_{-\infty}^{\infty} \rho(\omega) \exp(i\omega t) d\omega.$$
\[ M_x(t) = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \nu^{n+m} \exp(-\nu t) I_{n,m}(t, \tau), \]  

where

\[ I_{n,m}(t, \tau) = \int_{t}^{\tau} dt_{n+m} \cdots \int_{t}^{t_{n+2}} dt_{n+1} \int_{t}^{\tau} dt_{n} \cdots \int_{0}^{t_{2}} dt_{1} M_x(t, \tau; t, t_{1}, \ldots, t_{n+m}). \]  

The integration limits guarantee that \( t_{i+1} > t_i \).

We can simplify Eq. 6 by turning the time at which the \( \pi \) pulse is applied (\( \tau \)) into a running variable (\( t' \)) whose value is fixed with a \( \delta \) function. The \( \delta \) function should force the sum of time segments from zero until \( \tau \) to be equal to the sum of time segments from the \( \tau \) until 2\( \tau \), 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 2\( \tau \). As a result

\[
I_{n,m}(2\tau, \tau) = \int_{0}^{2\tau} dt_{n+m} \cdots \int_{0}^{t_{n+2}} dt_{n+1} \int_{0}^{t_{n+1}} dt' \int_{0}^{t'} dt_{n} \cdots \int_{0}^{t_{2}} dt_{1} M_x(2\tau, t'; t, t_{1}, \ldots, t_{n+m}) \delta(t' - \tau),
\]

and the integrand in Eq. 7 is a function of time differences only.

We now introduce the integral representation of the \( \delta \) function

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

and the Laplace transform of \( M_x \):

\[
\overline{M}_x(s) = 2 \int_{0}^{\infty} M_x(2\tau) \exp(-2s\tau) d\tau.
\]

By inserting Eq. 8 into Eq. 7, Eq. 7 into Eq. 5 and substituting this in Eq. 9 we find that all the integrals decouple and

\[
\overline{M}_x(s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\Omega f_{2}(z_{-}, z_{+}) \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} (\nu f_{1}(z_{-}))^{n} (\nu f_{1}(z_{+}))^{m}
\]

where
\[ z_\pm = s + \nu \pm i\Omega/2, \]  
\[ f_1(z_\pm) = \int_0^\infty du \exp(-z_\pm u) g(u), \]  
and
\[ f_2(z_-, z_+) = \frac{f_1(z_-) + f_1(z_+)}{z_- + z_+}. \]

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

\[ \overline{M}_x(s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\Omega \frac{f_2(z_-, z_+)}{[1 - \nu f_1(z_-)][1 - \nu f_1(z_+)])} \]  
from which we obtain the time dependent nuclear magnetization by

\[ M_x(2\tau) = \mathcal{L}^{-1}\left(\overline{M}_x(s)\right)_{t=2\tau}, \]  
where \(\mathcal{L}^{-1}\) is the inverse Laplace transform operator. Using Eqs. 11 to 15 one can obtain the echo decay knowing only the line shape or the FID function. Now let us examine three simple cases:

**Ising field** - this case materializes when the observed spin is coupled only to one unobserved spin 1/2 which fluctuates stochastically, leading to either field up or down at the observed site. In this case the field distribution is given by

\[ \rho(\omega) = \frac{1}{2} \delta(\omega - \omega_0) + \frac{1}{2} \delta(\omega + \omega_0), \]

and its second moment is \(\langle \omega^2 \rangle = \omega_0^2\). Here we have to be careful about the definition of \(\nu\) since the field selection rate \(\nu\), which appears in Eq. 2, is twice the rate \(\nu_\pm\) at which there are actual field changes. It is \(\nu_\pm\) that counts in our derivation, and we find

\[ M_1^I(2\tau) = \frac{\exp(-2\nu_\pm \tau)}{f_1^2} \left(\omega_0^2 + \nu_\pm f_1 \sin(2f_1 \tau) - \nu_\pm^2 \cos(2f_1 \tau)\right), \]

where \(f_1^2 \equiv \omega_0^2 - \nu_\pm^2\), and the superscript \(I\) stands for Ising. For \(f^2 < 0\) the result is the same except that \(f_1 \rightarrow i |f_1|\). The expansion of Eq. 16 to lowest order in \(\tau\) agrees with Eq. 3. In Fig. 2a we present \(\overline{M}_x^I\) on a semi-log scale as a function of \(2\omega_0 \tau\) for various values of \(\nu/\omega_0\).
It is clear from this figure that when either $\nu/\omega_0 \ll 1$ or $\nu/\omega_0 \gg 1$ the echo decay rate is weak compared to $\nu/\omega_0 \simeq 1$. To quantify this phenomena we define $T_2$ as the time at which the echo size decreases to $1/e$. In the Ising case we find that $T_2$ reaches its minimal value of $3.146/\omega_0$ when $\nu/\omega_0 = 0.69$.

In the inset of Fig. 3 we depict $M^I_x$ vs. $(2\omega_0\tau)^2$ for $\nu/\omega_0 = 0.69$. This presentation emphasizes a surprising fact that when $\nu/\omega_0 \simeq 1$ the waveform looks Gaussian over 2 orders of magnitude in echo size, even though at early time it is exponential in $\tau^3$. When fitting this Gaussian to $M^I_x(2\tau) = \exp(-2\omega_0\tau/T_{2G})^2/2$ we find $T_{2G} = 2.17$.

A distribution with a second moment - It is useful to examine a continuous 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

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

where $f_\sigma^2 \equiv (\sigma^2 - 2\sigma\nu - \nu^2)/4$. Again, for $f_\sigma^2 < 0$ the result is the same, except that $f_\sigma \rightarrow i|f_\sigma|$. An expansion of Eq. 18 around $\tau = 0$ agrees with Eq. 3, thus demonstrating the validity of our derivation once again. In Fig. 2b we depict Eq. 18 for various values of $\nu/\sigma$.

It is clear that the echo decay is strongest for $\nu = 0.88\sigma \simeq \sqrt{\langle \omega^2 \rangle}$. In fact, at this value of $\nu$, $T_2$ is minimal and equals $5.75/\sigma$.

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

$$
M^L_x(2\tau) = \frac{\lambda \exp(-2\nu\tau) - \nu \exp(-2\lambda\tau)}{\lambda - \nu}, \quad (20)
$$

where L stands for Lorentzian. This expression has interesting properties. An expansion of Eq. 20 around $\tau = 0$ gives
\[ M_x^L(2\tau) = 1 - \frac{1}{2} \lambda \nu (2\tau)^2 + O(\tau^3) \]

which means that at early enough times the relaxation shape is Gaussian. 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 \( \nu \). Similarly, when \( \lambda \ll \nu \) the relaxation is exponential for \( \nu \tau \gg 1 \) with the relaxation rate \( \lambda \). This suggests that experimental data which stem from Eq. 20 can be well fitted to a stretched exponential

\[ M_x(2\tau) = \exp \left( -\frac{2\tau}{T_2} \right) \]

with \( 1 < \beta < 2 \). In Fig. 2c we depict three data sets of \( M_x^L(2\tau) \) obtained from Eq. 20 for various values of \( \nu/\lambda \). Unlike in the previous cases, the Lorentzian case shows a continuous increase in relaxation rate with increasing \( \nu \). In this figure we also demonstrate 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 \( \beta \), \( 1/(\lambda T_2) \) as a function of \( \nu/\lambda \). While \( T_2 \) decreases monotonically with increasing fluctuation rate, the power \( \beta \) goes through a maximum at \( \nu/\lambda = 1 \). However, it should be mentioned that the value of \( \beta \) 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 \( \beta \) should change continuously.

We thus provide a recipe for obtaining the time dependence of the echo size for a given field distribution. We examined three 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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FIGURES

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.

FIG. 2. The echo decay for: (a) the Ising field (Eq. 16) plotted against $2\omega_0\tau$, (b) A continuous distribution with a second moment (Eq. 18) vs. $2\sigma\tau$, and (c) Lorentzian field distribution (Eq. 20) as a function of $2\lambda\tau$. The solid line in panel (c) represents a fit to Eq. 21 as described in the text.

FIG. 3. The parameters $1/(\lambda T_2)$ and $\beta$ which allow the best approximation of Eq. 20 with Eq. 21. In the inset, the Echo decay for the Lorentzian case with $\nu/\lambda = 0.7$ is shown.
A. Keren Fig. 2
