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What Are the Conditions for Exponential Time-Cubed Echo Decays?

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Diffusion of precessing spins through a constant field gradient is well-known to produce two distinctive features: an $\exp(-bt^3)$ decay of the echo amplitude in response to two pulses and a much slower decay of the Carr–Purcell echo train. These features will appear whenever the spin *frequency* is described by a continuous random-walk. The present work shows that this may also occur in the presence of motions with long correlation times τ_c—continuous Gaussian frequency noise with an exponential autocorrelation has the correct properties over time durations smaller than τ_c. Thus, time-cubed echo decays will occur in situations other than physical diffusion. The decay rate of the Carr–Purcell echo train is shown to vary with the pulse spacing τ whenever the correlation time τ_c is long; the slower Carr–Purcell decay compared to the two-pulse echo decay is not unique to diffusion. Simulations are presented that display time-cubed decays. The simulations confirm two important criteria: the echo time must be less than τ_c and the frequency noise must consist of nearly continuous variations, as opposed to step-like changes. These criteria define the range of physical parameters for which time-cubed decays will be observable.

Key Words: **diffusion; transverse relaxation; spin–spin relaxation; spin echoes.**

I. INTRODUCTION

From the earliest observations of spin echoes (*1*) in NMR, the case of spins diffusing with coefficient D through a constant field gradient $G = (\partial|H|/\partial x)$ has been discussed. The problem can be treated with Torrey's formalism of the diffusion-modified Bloch equations (*2–4*) or by following the frequency and phase trajectories of the ensemble of spins. The result (*3, 4*) is that the echo amplitude A decays as the exponential of the *cube* of the echo time ($t = 2\tau$, where τ is the pulse spacing). Thus A follows

$$A(t) = \exp(-\gamma^2 G^2 D t^3/12), \qquad [1]$$

where all other sources of decay have been neglected. Furthermore, the damping due to diffusion can be suppressed by refocusing the spins many times during the time t. Thus, the Carr–Purcell–Meiboom–Gill pulse sequence (*5, 6*) (90_y–τ–180_x–τ–echo–τ–180_x–τ–echo–τ, etc.) yields an echo at time t ($t = n2\tau$, where n is the integer echo number at time t) with amplitude A,

$$A(t) = \exp(-\gamma^2 G^2 D \tau^2 t/3). \qquad [2]$$

For a large number of echoes n, τ is much smaller than t. Thus, the CPMG echoes decay exponentially in time t and decay more slowly (*3–5*) than the two-pulse echoes of Eq. [1]. Indeed, in the limit that the pulse spacing τ approaches 0, the diffusive damping is zero, allowing the "true T_2" (neglected here) to be determined; this was an original purpose of the Carr–Purcell pulse sequence (*5, 6*).

Recently, spin echoes have been used to measure the diffusion coefficient of the modulation wave of incommensurately distorted solids (*7–10*). Here the distortion wave couples through the quadrupole interaction to the frequency of a given spin transition. Some of the work has been (*7*) zero-field NQR and some has been (*8–10*) high-field, quadrupole-perturbed NMR. The spin-echo envelope in these systems has a decay $e^{-at}e^{-bt3}$; the linear term is ordinary T_2 damping while the t^3 damping is regarded as a *signature* for diffusion of the distortion wave. Here the role of the field gradient is supplied by the distortion wave's *slope*, linking spin frequency to position. Indeed, the variation of the apparent diffusion coefficient across the inhomogeneously broadened lines is clear evidence for *small variations* of the phase of the modulation wave (*9*).

In the incommensurately distorted systems, the distortion wave is generally pinned to defects or impurities. Thus, one expects thermal agitation to yield *restricted* diffusion of the distortion, at best. Of course, provided the spin echo times are short enough, unbounded diffusion and restricted diffusion of the distortion wave will be indistinguishable.

Our purpose here is not to further examine the incommensurate solids. Instead, the use of the e^{-bt3} decay as a signature of diffusion advances the central questions of the present work: "Are there circumstances other than physical diffusion that result in e^{-bt3} two-pulse echo decays? Under what circumstances do CPMG echoes decay more slowly than two-pulse echoes?"

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II. RESULTS AND DISCUSSION

Time-Cubed Decay

In the presence of a constant gradient G, a spin's frequency ω is linearly related to its position x, with $\omega = \omega_0 + \gamma G x$. Thus, in the case that the spin diffuses, its frequency is a continuously changing variable that executes a random walk (i.e., $\overline{(\Delta\omega)^2}$ is proportional to the time interval). Obviously, *any system* in which the spin frequency is a continuously changing, random-walking variable will produce the same spin echo behavior as in diffusion-through-a-gradient. That is, the two-pulse echo amplitude will decay as e^{-bt^3} and CPMG echo trains will decay more slowly than two-pulse echoes. The key ingredient is that the *spin frequency must be diffusing,* regardless of how this arises.

For a spin diffusing in a box of side L with a constant gradient G, the peak excursions of the frequency ω are $\pm\gamma GL/2$. The frequency has a well-defined correlation time τ_c (if the diffusion were unbounded, this would not be so) which is approximately the time to diffuse across the box: $\tau_c \simeq L^2/2D$. Since the results of Eqs. [1] and [2] refer to unbounded diffusion, they apply only for echo experiments over times $t \ll \tau_c$.

Thus, we are led to examine other sources of continuous spin frequency fluctuations with long correlation times τ_c. Specifically, we consider a spin whose frequency ω is determined by the sum of a very large number N of independent fluctuators,

$$\omega = \omega_0 + \sum_{j=1}^{N} x_j. \qquad [3]$$

The fluctuators could be other spins that couple magnetically to ω or they could be molecules that jump between two or more orientations and couple to ω through quadrupole interaction. The number N is large so that ω fluctuates essentially *continuously,* regardless of whether the individual fluctuations x_j are continuous or discrete. Each fluctuator must couple to ω weakly so that any step-changes in ω are of no consequence; again this says the number N must be large. We assume that the individual fluctuators are all characterized by the same exponential autocorrelation (*3, 4, 11*) function, $\exp(-|t|/\tau_c)$, with the same correlation time τ_c. Thus, as ω is the sum of N independent fluctuators, ω will have the same autocorrelation function and time constant as the individual fluctuators. By the central limit theorem (*12*), the values of ω will have an approximately Gaussian distribution.

Now, the above model does *not* result in ω executing a true random-walk. Indeed, ω will have upper and lower bounds given by the sums over all the fluctuators of the largest and smallest values x_j. But for N very large, these limits are inconsequential over times $t \ll \tau_c$. To show this, we first use a heuristic argument and later use a Langevin model.

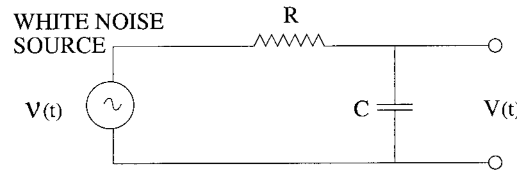

FIG. 1. Circuit for generating continuous, Gaussian noise with an autocorrelation function of $\exp(-|t|/\tau_c)$, with τ_c = RC. The circuit is used to calculate the statistical properties of the output voltage V for times short compared to τ_c. The voltage V is analogous to the spin frequency ω in this Langevin model.

For simplicity, let each fluctuator be a two-state device with allowed values of $x = \pm 1$. We go to the limit of $N \to \infty$. We note that the rms value of $\omega - \omega_0$ is $\sqrt{N}$ and that this rms value corresponds closer and closer to a 50:50 distribution of two-state fluctuators as $N \to \infty$. Thus, for $N \to \infty$, nearly the entire probability distribution of ω involves configurations near 50:50, more and more distant from the upper and lower bounds ($\pm N$). Thus, it is reasonable that the effects of the limits disappear as $N \to \infty$ and the behavior becomes that of an unbounded random-walker for $t \ll \tau_c$.

The continuous, Gaussian noise of our model may be created by the action of an RC-filter on white noise, $\mathcal{V}$. This Langevin model (*12*) is presented in Fig. 1. The output voltage V plays the same role as the spin frequency ω, above. The output voltage V will obey a differential equation,

$$\frac{dV}{dt} = \frac{\mathcal{V} - V}{\mathrm{RC}}. \qquad [4]$$

Integrating from t_0 to $t_0 + t$, one obtains ΔV, the change in output voltage,

$$V_{(t_0+t)} - V_{(t_0)} \equiv \Delta V = \frac{1}{\mathrm{RC}} \int_{t_0}^{t_0+t} \mathcal{V}_{(t')} dt' + \frac{-1}{\mathrm{RC}} \int_{t_0}^{t_0+t} V_{(t')} dt'. \qquad [5]$$

Provided the time duration t obeys $t \ll \tau_c$, $V_{(t')}$ in the second integral may be treated as a constant, $V_{(t_0)}$. Thus, one has

$$\mathrm{RC}(\Delta V) = \int_{t_0}^{t_0+t} \mathcal{V}_{(t')} dt' - V_{(t_0)} t, \qquad [6]$$

where the first term is the result that would be obtained if the white noise were simply integrated, the random-walk case. Taking the mean square of ΔV, and using RC $= \tau_c$, we have

$$\tau_c^2\overline{(\Delta V)^2} = \overline{\left(\int_{t_0}^{t_0+t} \mathcal{V}_{(t')}dt'\right)^2} + V_{(t_0)}^2 t^2 - 2tV_{(t_0)}\int_{t_0}^{t_0+t} \overline{\mathcal{V}_{(t')}}dt'. \quad [7]$$

In this equation $\bar{\mathcal{V}} = 0$, removing the cross-term. The first term is the random walk result and is *linear* in time, because the correlation time *of the white noise* $\mathcal{V}$ is infinitesimal and consequently short compared to t, yielding

$$\tau_c^2\overline{(\Delta V)^2} = 2\overline{V^2}\tau_c t + V_{(t_0)}^2 t^2. \quad [8]$$

The coefficients in front of t are secondary to our argument and result from standard Langevin theory (*12*). [In detail, in terms of the autocorrelation U of the input noise voltage $\mathcal{V}$, the first term F of [7] may be written as a double integral. The end result is $F = t \int U_{(\tau)}d\tau$, where the infinitesimally short correlation time allows the integral limits on τ to be taken to $\pm\infty$. The Green's function solution to [4] is

$$V(t) = \int_{t'=-\infty}^{t} \mathcal{V}_{(t')}e^{-(t-t')/\mathrm{RC}}dt'.$$

From this, the mean squared output voltage $\overline{V^2}$ is found by double integration again, leading to $\overline{V^2} = \int U_{(\tau)}d\tau/2\tau_c$, with integral limits again taken out to $\pm\infty$. Together the result is $F = 2\tau_c\overline{V^2}t$.] Returning to [8], the first term dominates the second one for short times, $t \ll \tau_c$. Thus, for such short times, the change in V (or ω in the spin problem) is just that of a pure random-walk (simple integration of white noise yields only the first term, linear in t). Thus, the spin in the above model will yield an echo amplitude that decays as e^{-bt3}.

We stress that the above scenario of N independent fluctuators is quite distinct from the diffusion problem. For example, in the above scenario, ω has an approximately Gaussian distribution while in the diffusion problem, the distribution of frequencies reflects the size and shape of the sample.

A more formal approach is to use the result of Klauder and Anderson (*13*) for the spin echo amplitude A in the presence of Gaussian noise with an exponential autocorrelation with time constant τ_c. As quoted elsewhere (*14, 15*), for echo time t,

$$A(t) = \exp\left(-M_2\tau_c^2\left\{4e^{-t/2\tau_c} - e^{-t/\tau_c} + \frac{t}{\tau_c} - 3\right\}\right). \quad [9]$$

This expression is valid for all times t, shorter or longer than τ_c. It is derived (*13*) using the relation for Gaussian distributions of spin phase ϕ, $\langle e^{i\phi}\rangle = \exp(-\frac{1}{2}\overline{\phi^2})$. For times $t \ll \tau_c$, the inner brackets of Eq. [9] can be expanded and have a leading term in t^3, resulting in

$$A(t) = \exp(-M_2\tau_c^2(t^3/12\tau_c^3)). \quad [10]$$

Thus, the e^{-bt3} echo decay is a direct result of the assumptions about the fluctuations in the spin frequency.

The above argument used explicitly only the autocorrelation of the spin frequency. Where does the requirement for *continuous* Gaussian noise arise? The calculation assumes (*13*) that, at all times, the distribution of spin phase is Gaussian. Discrete changes in spin frequency (hopping) would give rise to a two-component distribution—a zero-width component for spins with no frequency change and a broader component from those spins whose frequency jumped once or more. Only for $t \gg \tau_c$ (not useful here) does this tend to Gaussian, with all spins experiencing many frequency changes. Thus, Eqs. [9] and [10] refer specifically to continuous frequency variations.

Carr–Purcell Echo Trains

Unlike the T_2 damping of the Bloch equations (*3, 4*), the damping due to diffusion through a field gradient is substantially reduced by using a multiple echo sequence like the Carr–Purcell or CPMG sequence (*5, 6*). But this reduction in transverse damping *cannot* be regarded as a signature of diffusion. Indeed, we show here that the reduction in damping should occur whenever the correlation time τ_c of the fluctuations of ω is long, specifically $\tau \ll \tau_c$ where τ is the pulse spacing of the CP or CPMG sequence.

Karlicek and Lowe (*16*) introduced the widely used notion that the π pulses of a CP or CPMG sequence effectively invert the resonance offset or field gradient at each π pulse (*17*). Thus, the actual resonance offset is to be thought of as multiplied by a square wave of frequency $1/4\tau$. Thus, for any weak field to have a cumulative effect it must contain components at frequency $1/4\tau$ (or, to a lesser extent, any of its odd harmonics, $3/4\tau$, $5/4\tau$, etc.). So approximately, standard relaxation theory (*3, 4, 11*) which is restricted to weak collision cases predicts a decay rate T_2^{-1}

$$T_2^{-1} = M_2 \cdot J_{(\pi/2\tau)}, \quad [11]$$

where M_2 is the second moment (mean-square) of the fluctuations and J is their spectral density; the angular frequency $\pi/2\tau$ corresponds to $1/4\tau$ in cycles per second. An excellent discussion of this viewpoint appears in Callaghan's text (*18*).

Consider a fluctuating frequency ω described by an exponential autocorrelation function, $\exp(-|t|/\tau_c)$, with correlation time τ_c. Here we do not require that ω be a continuously fluctuating variable, so this is much less restrictive than the model proposed above to yield e^{-bt3} two-pulse decays. The spectral density will be

$$J_{(\omega')} = \frac{\tau_c}{1 + \omega'^2 \tau_c^2}, \qquad [12]$$

which reduces to $1/\omega'^2\tau_c$ for $\omega'\tau_c \gg 1$. Here the variable ω' is named to avoid confusion with the fluctuating spin frequency ω. The CPMG decay rate will be, with $\tau \ll \tau_c$,

$$T_2^{-1} = M_2[(\pi/2\tau)^2\tau_c]^{-1} = 4M_2\tau^2/\pi^2\tau_c. \qquad [13]$$

This last result has the usual result of $T_2^{-1} \propto \tau_c^{-1}$ in the slow fluctuation limit. The τ^2 dependence of T_2^{-1} is present in the result of the diffusion case expressed in Eq. [2], but its presence here shows it is more general, resulting simply from the $1/\omega'^2$ tail of the Lorentzian spectral density.

In the case of diffusion (*12*), the particle velocity has a nearly white frequency spectrum (typically out to 10^{11} s^{-1}). Particle position x and velocity v are related by $v = i\omega' x$ (here we adopt a frequency domain viewpoint of the particle motion), or $x = v/i\omega'$. Because power spectra involve *two* powers of the fluctuating variable, the spectrum of particle position (and the directly related spin frequency ω) is $1/\omega'^2$, just as in Eq. [12]. Thus, the well-known τ^2 dependence of Eq. [2] results from the $1/\omega'^2$ spectrum of a diffusing particle's position and spin frequency. Again, this view is developed by Callaghan (*18*).

Ansermet *et al.* considered a Carr–Purcell echo train with a model of a spin coupled to a single (unobserved) other spin (*19*). The other spin makes transitions (from $S_z = +1/2$ to $-1/2$) with a correlation time τ_c. These transitions may result from dipolar-driven flip-flops among the other spins or T_1 processes of the other spin. In a time t, there will be a mean number $m = t/\tau_c$ transitions of the other spin. Each transition gives rise to a dephasing of $\Delta\phi = \delta\omega \cdot$ time. The frequency change $\delta\omega$ is just $2w$, recalling that the other spin has just two states, leading to frequencies $+w$ and $-w$ for the observed spin. The time over which the changed frequency acts is between 0 and τ, depending on the exact time at which the transition of the other spin occurs relative to the RF pulses. Subsequent transitions produce phase changes of either sign, again depending on the timing relative to the RF pulses. Thus, the mean squared phase error is approximately

$$\overline{(\Delta\phi)^2} = m \cdot (2w \cdot \tau/2)^2 = (t/\tau_c)w^2\tau^2. \qquad [14]$$

The linear increase in $\overline{(\Delta\phi)^2}$ with time t indicates that the amplitude of the echoes decays exponentially with time t, with rate

$$T_2^{-1} = w^2\tau^2/2\tau_c; \qquad [15]$$

here we have assumed the weak collision limit in which $\overline{(\Delta\phi)^2}$ for a single transition of the other spin is small compared to one. The above result for the echo train decay rate agrees with that of Ansermet *et al.* (*19*) to within an unimportant small numerical factor. This decay rate is very close to that from relaxation theory, Eq. [13]; the numerical difference between $4/\pi^2$ and 1/2 is likely due to our approximations, including the neglect of the higher harmonics of the square wave in the relaxation theory calculation. The practical importance of the result (*15*) is that the effect of the other spin on the observed spin's transverse decay may be driven to zero by making the pulse spacing very small. Finally, we reiterate that the τ^2 dependence of T_2^{-1} depends only on the $1/\omega'^2$ tail of $J_{(\omega')}$ and can occur widely, anywhere from diffusing systems to two-state models. The τ^2 dependence cannot be taken as a signature of diffusion.

III. SIMULATIONS

Simulations of two-pulse echoes and CPMG echo trains have been performed using a Monte Carlo approach to determine the conditions yielding e^{-bt^3} decays. The frequency of a spin is determined by its interaction with N two-state fluctuators. Each fluctuator is equally likely to be in either state, producing a frequency shift of the spin of $\pm(\Delta\omega)$; the spin's frequency ω is the sum over all N of these. Each of the N fluctuators in the system has a correlation time τ_c. Thus, the time t' to the next jump is chosen from a distribution $P(t') \sim \exp(-t'/(2\tau_c/N))$. At that time, a randomly selected fluctuator is toggled to the opposite state.

The spin's precessional phase ϕ is initially zero, following a $\pi/2$ RF pulse. The phase ϕ is the time integral of the frequency ω, trivially calculated by multiplying ω by the duration of the time interval over which ω is constant. The effect of an RF π pulse is to invert the precessional phase ϕ. The total spin magnetization is computed as $\langle \cos\phi \rangle$, where the averaging is over an ensemble of 4000 spins, typically.

Two-pulse echo decays are shown in Fig. 2. There, the fluctuators' correlation time is $\tau_c = 5$. The normalized echo amplitude A is presented by plotting $-\ln(A)$ vs echo time t on log–log axes so that the slope of any straight-line section indicates the power on the time variable in the exponential. Horizontal lines corresponding to $A = 0.999$, 0.99, 0.9, 0.5, 0.1, and 0.01 are provided. All of these results are well fit by Eq. [9] with no adjustments to parameters. We do not present this fit because our goal is not to verify Eq. [9], but to indicate clearly the conditions under which one finds cubic-exponential decays. In the figure, the cubic-exponential decay is clearly evident for $t < \tau_c$, as shown by the solid lines with slope = 3, while the results for $t > \tau_c$ tend toward slope = 1. For such long times, the theory of motional averaging applies, yielding linear-exponential decays as is well-known (*3, 4, 11*). The cubic-exponential regime appears in simulations of systems with slow rotational diffusion (*20*).

The middle curve in Fig. 2 is a superposition of four sets of results, all with the same value of the mean-squared interaction

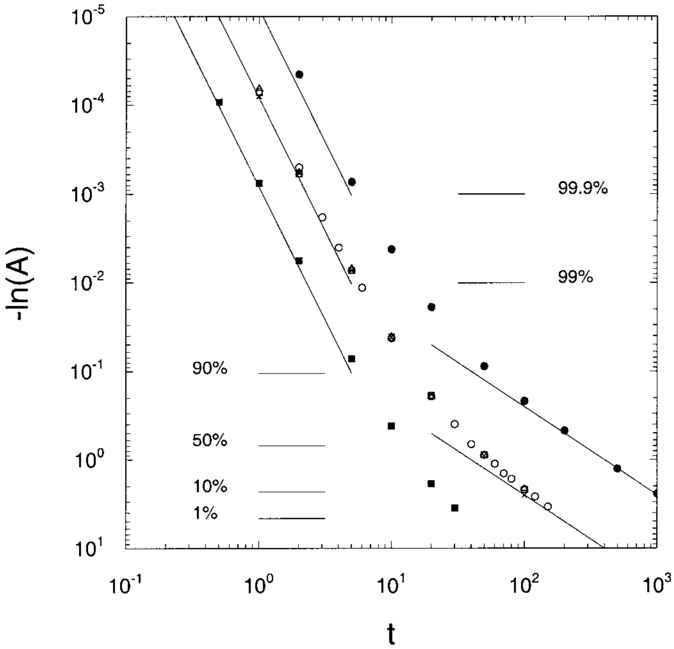

FIG. 2. Decay of the normalized two-pulse echo amplitude A, with the vertical axis displaying $-\ln(A)$, as a function of echo time t. Horizontal lines show the locations of $A = 0.999$, 0.99, 0.9, 0.5, 0.1, and 0.01. The value of τ_c is 5. In the lower, middle, and upper curves, the second moment $N(\Delta\omega)^2$ has values 0.05, 0.005, and 0.0005. In the middle curve, for fixed $N(\Delta\omega)^2 = 0.005$, four values of N and $\Delta\omega$ are used. The primary result is that the e^{-bt3} decay (slope = 3) becomes e^{-kt} (unity slope) for echo time $t > \tau_c$.

strength (second moment), $N(\Delta\omega)^2 = 0.005$. The four sets have $N = 50$, 20, 10, and 5. The observation that the sets fall on the same curve shows that only the second moment matters here, whether in the t^3 or linear region. The upper and lower curves are also for $N = 50$, but with $N(\Delta\omega)^2 = 0.0005$ and 0.05, respectively. The change in second moment results in the offsets of these curves.

For a given set of parameters, one measure of the importance of the $t < \tau_c$ criterion for cubic-exponential decays is the amplitude A of the decay for $t = \tau_c$. From Eq. [10] and substituting $t = \tau_c$,

$$A_{(\tau_c)} = \exp(-N(\Delta\omega)^2\tau_c^2/12) = \exp(-Q^2), \qquad [16]$$

where the dimensionless parameter Q is defined by

$$Q \equiv \Delta\omega\tau_c\sqrt{N}/\sqrt{12}. \qquad [17]$$

Clearly, for $Q \gg 1$, the echo amplitude has already decayed to small values before the regime of motional narrowing is entered. In this case, the time-cubed decay will be evident. For $Q \ll 1$, most of the observable part of the decay (between $A = 0.99$ and 0.01, for example) will occur for $t > \tau_c$ and will be of the form e^{-kt}.

The results in Fig. 3 explore the effect of the noncontinuous, step-like nature of the frequency noise in the present model. This is an important issue, because step-like variations will often be encountered in magnetic resonance—magnetic coupling to unlike spins is quantized through spin quantum mechanics. In the case of incommensurately distorted solids, continuous motion of the (pinned) modulation wave seems unlikely. Rather, discrete small motions should result from distant phase slippages.

In Fig. 3, $\tau_c = 50$ and all the diplayed echo times are smaller than τ_c, avoiding the motional averaging effect apparent in Fig. 2. The second moment is held constant at $N(\Delta\omega)^2 = 50$, with $N = 5$, 20, and 50. The slope = 3 regions of the decay (following e^{-bt3}) all overlap, showing again that it is the second moment that is important here. As t increases, each data set gradually becomes a linear-exponential.

The linear-exponential region is easily understood from strong collision theory. The distribution of precessional phase ϕ in the present model is not Gaussian, as assumed by Klauder and Anderson, for example (*13*). Instead, a fraction $\exp[-t/(2\tau_c/N)]$ of the spins have suffered zero frequency changes from their N fluctuators (note—this is zero changes, not a net change of zero). Thus, the distribution of phase ϕ is roughly a Gaussian with an added delta-spike at $\phi = 0$, corresponding to this fraction of spins. At long enough times, any spin that has suffered a change in frequency will develop a large phase error, effectively removing the spin from the signal. Under these

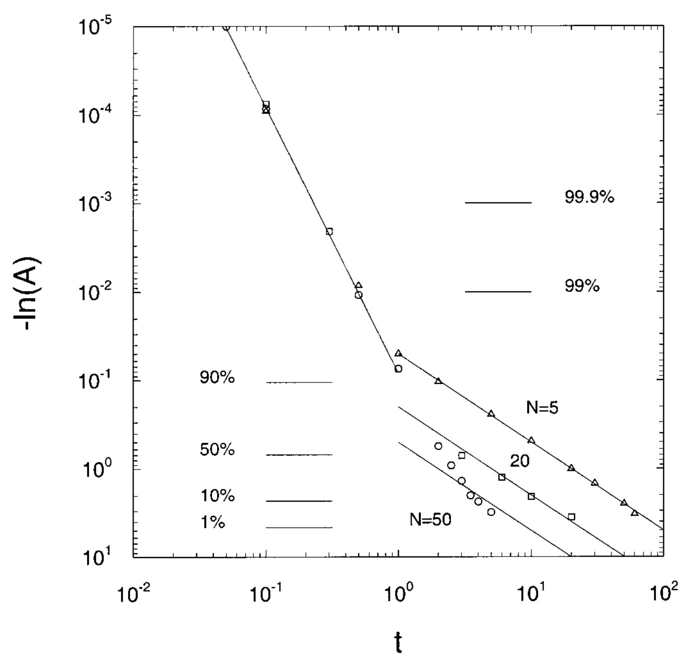

FIG. 3. Decay of two-pulse echoes, all at echo times $t < \tau_c$. Here $\tau_c = 50$ and the second moment $N(\Delta\omega)^2$ is 50 throughout. The echo amplitude A is limited from below by the lines of unity slope corresponding to $\exp(-Nt/2\tau_c)$, from strong collision theory. Three values of N are used: 5, 20, and 50. Thus, the cubic-exponential decay will become linear-exponential at long t, due to the discontinuous, step-like nature of the frequency fluctuations.

conditions, the observed signal is entirely from the spins with zero frequency changes and the amplitude is $A = \exp(-Nt/2\tau_c)$. Solid lines of unity slope appear in Fig. 3, corresponding to the above limiting amplitude for $N = 5$, 20, and 50. Clearly, the unity-slope parts of the decays are well-described by the above formula, $A = \exp(-Nt/2\tau_c)$. This is a "strong collision" model, because it describes the limit in which a single change in any of the N fluctuators is sufficient to totally dephase any spin. Only the spins with no "collisions" (no flips of any of the fluctuators) contribute to the echo. The strong collision limit also describes relaxation by slow molecular reorientations, in the case of large-angle jumps (*21*).

The unity-slope regions of the Fig. 3 decays show the strong-collision effect. As N increases in Fig. 3, the unity-slope lines are moved down on the plot; for large enough N, the slope = 3 region covers all of the measurable portion of the decay (e.g., $A > 0.01$). This dependence on N stems from the fixed second moment: for large N the step-size $2\Delta\omega$ of the individual fluctuations is small and small frequency changes require more time to develop into "fatal" phase errors.

The results of Fig. 3 demonstrate that the echo amplitude decay will always follow e^{-bt3} for small echo times t. It is easy to show analytically that the exponent will be cubic in t whether the distribution of precessional phase ϕ is Gaussian or not, for short time.

The crossover from cubic-exponential to linear-exponential behavior will occur for echo time t such that the cubic-exponential of Eq. [10] approximately equals the limiting form of the amplitude:

$$A = \exp(-N(\Delta\omega)^2 t^3/12\tau_c) = \exp(-Nt/2\tau_c). \quad [18]$$

This occurs for $(\Delta\omega)^2 t^2 = 6$ and will correspond to an echo amplitude of $\exp(-N\sqrt{1.5}/\Delta\omega\tau_c) = e^{-1/P}$, where we define the dimensionless parameter $P \equiv \Delta\omega\tau_c/\sqrt{1.5}N$. P is a measure of the effect of the step-like fluctuations in frequency. For $P \gg 1$, the case of large $\Delta\omega$ and/or small N, the shift from cubic-exponential to linear-exponential decay occurs at large values of the amplitude A. Thus, most of the observable decay will be linear-exponential. On the other hand, for the case of small $\Delta\omega$ and/or large N, $P \ll 1$, the shift will occur at very small amplitudes A. Thus, the observable portion of the decay will be cubic-exponential (unless the motional narrowing region of $t > \tau_c$ is entered).

In short, all the decays will start out cubic-exponential and become linear-exponential at long times, either because t will eventually exceed τ_c or because the decay amplitude is limited from below by $\exp(-Nt/2\tau_c)$. This last limitation will be easily detected provided that $P = \Delta\omega\tau_c/\sqrt{1.5}N \gg 1$.

The curves in Fig. 4 show all of these effects. The number of fluctuators N is fixed at 50 and τ_c is 5. In the region $t > \tau_c$, the region of motional averaging, the decay curves tend to the form e^{-kt}, unity slope in Fig. 4. For $t < \tau_c$, the decay curves

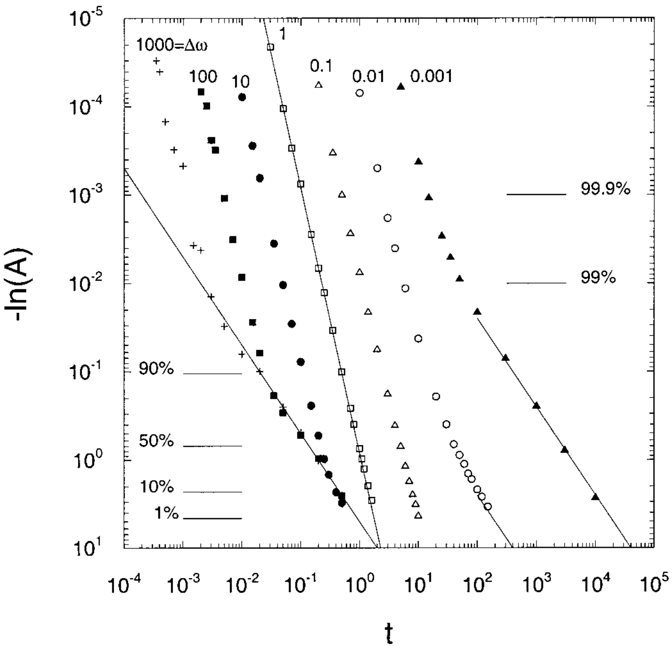

FIG. 4. Plot of two-pulse echo amplitude A over a wide range of interaction strengths $\Delta\omega$, all with $\tau_c = 5$ and $N = 50$. For very small $\Delta\omega$, one must enter the motional averaging region ($t > \tau_c$) for substantial echo attenuation. For very large $\Delta\omega$, most of the observable portion of the decay ($0.99 > A > 0.01$) occurs along the strong collision limit line (unity slope at left) given by $\exp(-Nt/2\tau_c)$. The time-cubed decay is observable for intermediate values of $\Delta\omega$.

all begin as e^{-bt3} until they run into the limiting line given by $\exp(-Nt/2\tau_c)$. The data sets with the largest values of $\Delta\omega$ (and hence P as defined above) follow the limiting line over the entire measurable portion of the decay.

The two criteria for the observability of the e^{-bt3} decay are $Q \gg 1$ and $P \ll 1$. Together these may be written

$$1/\sqrt{N} \ll \Delta\omega\tau_c \ll N. \quad [19]$$

Clearly, the larger the number of fluctuators N, the larger the range of $\Delta\omega\tau_c$ values that yield the cubic-exponential decay.

The simulations were also used to test the CPMG decays. The decays were always exponential, with a decay rate proportional to $N(\Delta\omega)^2\tau^2/\tau_c$ in the relevant conditions, in accord with Eqs. [13] and [15]. Hence, in an experiment on a system with slowly fluctuating spin frequencies, two-pulse cubic exponential-decays that become linear-exponential in CPMG experiments could be observed.

IV. CONCLUSIONS

Diffusion of spins through a constant field gradient results in an e^{-bt3} decay of two-pulse spin-echoes and yields a Carr–Purcell echo train that decays (as e^{-kt}) more slowly than the two-pulse echoes. However, both of these features can result from situations not involving physical diffusion. First, it was noted that the critical ingredient is that the *spin frequency diffuses* (i.e., the spin frequency is a continuous variable and executes a random-walk). Second, it was shown that continuous Gaussian noise may be considered to execute a random-walk over times shorter than the correlation time. Thus, e^{-bt^3} echo decays may occur for situations such as a single spin coupled to a great many fluctuators when the correlation time is long.

The variation of the decay rate T_2^{-1} upon the pulse spacing τ of a CP or CPMG pulse sequence is readily understood by weak collision relaxation theory. The transverse decay rate is essentially proportional to the spectral density of field fluctuations at frequency $1/4\tau$. Thus, any fluctuation with a ω'^{-2} frequency spectrum will result in a τ^2 dependence of T_2^{-1}; this includes diffusion through a constant gradient as well as any fluctuation with an exponential autocorrelation, provided that the experiment involves times short compared to τ_c.

Simulations confirm the e^{-bt^3} decays of two-pulse echoes from an ensemble of spins, each subjected to frequency shifts $\pm\Delta\omega$ from each of N two-state fluctuators. The simulations show that the echo decay becomes e^{-kt} for $t \gtrsim \tau_c$, where motional averaging theory applies. For large interaction strengths $\Delta\omega$ and/or small numbers of fluctuators N, the echo decay is again of the form e^{-kt} because of the noncontinuous, step-like nature of the frequency noise. This limit is well-described by strong collision theory. For large N, there is a range of $\Delta\omega\tau_c$ values that result in observable e^{-bt^3} decays.

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