Spectral Diffusion Decay in Spin Resonance Experiments

J. R. KLAUDER AND P. W. ANDERSON
Bell Telephone Laboratories, Murray Hill, New Jersey

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In spin resonance experiments random flipping by T_1 or T_2 processes of nearby, nonresonant spins introduces fluctuations into the precessional frequency of the observed spins. These fluctuations may be described by means of a stochastic model, and for wide classes of both Markoffian and non-Markoffian distributions we make predictions for the line shape, for the free induction decay, and for various spin-echo signals. If the homogeneous broadening of the line is due to a dipolar interaction term, then we find that the conditional distribution for the precessional frequency has the shape of a Lorentzian with a cutoff on the wings, rather than a Gaussian shape as commonly assumed. The causes and consequences of Lorentzian diffusion are analyzed in detail for samples in which T_1 processes control the source of local frequency fluctuations and for samples in which T_2 processes dominate. Recent two- and three-pulse spin-echo experiments of Mims *et al.* dramatically confirm the predictions of Lorentzian diffusion for electron paramagnetic resonances in samples with temperature-dependent diffusion, as well as with temperature-independent diffusion. "Instantaneous" diffusion caused by the action of the applied pulses is predicted by our model and explains features of Mims' data. The generality of our principal results still permits the outcome of various resonance experiments to be predicted, even when a simple dipolar interaction is no longer an adequate model.

I. INTRODUCTION

In a solid, or in a liquid suspension, there are a variety of perturbing effects that will modify the elementary behavior of isolated moments which would otherwise precess at a constant rate proportional to the applied magnetic field. The resultant spread in precessional frequencies, whose distribution is studied in resonance experiments, can be separated into two classes[1]: (i) Homogeneous broadening, a dynamic broadening due commonly to spin-spin interactions (dipolar and exchange) and to spin-lattice interactions, and (ii) inhomogeneous broadening, an essentially static broadening due frequently to spatial inhomogenities in the applied external field, to crystal defects, or to hyperfine interactions with nuclei, etc. When the inhomogeneous broadening is dominant, we may speak of homogeneously broadened "packets" of spins, each packet having the same inhomogeneous part of the frequency. In particular, spin-lattice interactions tend to flip spins at random and therefore give rise to random fluctuations in the local magnetic field at neighboring spin sites. Spin-spin flips also introduce local field fluctuations and thus precessional frequency fluctuations at nearby sites. The frequencies of the individual spins in each of the homogeneously broadened "packets" are therefore in a complex state of turmoil. However, viewed collectively, the spins in each packet have certain useful equilibrium properties. Because of the static nature of the inhomogeneous broadening, the communication is quite small between spins in different packets, and thus each packet may more or less be treated as dynamically independent.[1]

On the other hand, for many purposes, and particularly for a study of spectral diffusion, it is necessary to consider the physics of what goes on inside the spin-packets; perhaps it is even more accurate to say that one must discard the "packet" concept entirely and attempt to treat the motion of the individual spins in some kind of detail. While some progress has been made in solving, under rather restricted circumstances and with assumptions which are not by any means always valid, the exact quantum-mechanical equations of motion,[2] there is little hope of real progress in that direction on such immensely complicated questions as spectral diffusion.

Alternatively, one may attempt to set up a model with properties similar to those of the real system, for which more or less exact conclusions can be drawn. Such a model is the random frequency-modulation or stochastic model, which was first introduced in line-breadth theory.[3] The basic approximation is to separate the spin interactions into two parts, a part which causes broadening and is treated as essentially diagonal, i.e., as having the form $\sum_{jk} B_{jk}\mu_j^z\mu_k^z$, and a part which is basically off-diagonal and causes spin flips, i.e., changes in the value of μ_j^z. This latter part of the interaction is then replaced by a stochastic process—in many cases, simply by a random Markoff flipping process of rate $1/T_2$, where T_2 is taken as a given parameter. Various attempts have been made to estimate T_2 from first principles (see, e.g., reference 1) but no rigorous theory exists. (We will discuss later in this paper the possibility of an approach from the present point of view.)

It may be emphasized that the above assumptions are much more closely related to the actual problem in the case of strong inhomogeneous broadening with which we concern ourselves primarily in this paper. For the great majority of spin pairs, the frequencies of the two spins will be so different that only the diagonal, $\mu_j^z\mu_k^z$ terms will be secular perturbations, the off-diagonal terms being simply treatable by perturbation theory. Thus the broadening effect is mainly diagonal in nature. The only assumption—and even this need only be made where $T_1 > T_2$—is that the remaining off-diagonal interactions, those between spins of accidentally equal frequencies, may be replaced by a stochastic process. We shall find that the description

[1] A. M. Portis, Phys. Rev. **91**, 1070 (1953).

[2] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

[3] P. W. Anderson and P. R. Weiss, Revs. Modern Phys. **25**, 269 (1953).

of this stochastic process can be made so general that in fact we believe that from a phenomenological point of view the remainder of the work, given the nature of this stochastic process, is essentially rigorous in the inhomogeneous broadening range.

The interesting question of the approach to the other limit, of concentrated materials with less inhomogeneous broadening, can be considered as one of the convergence of a kind of perturbation theory. As the interactions become stronger, the "individual spins" μ_j^z which we treat, take on much more of a "quasiparticle" status, as being a kind of "effective" spin, which is not in fact the spin of a single electron but an elementary excitation of energy $\hbar\omega_j$, obtained by some perturbation procedure. The lifetime of such an "effective" spin is presumably what is meant by T_2, and thus its frequency can be determined only to within $1/T_2$. We can then meaningfully ask only about motions of the frequency ω_j over distances greater than $1/T_2$; this may in fact be the correct meaning of the concept of spin packet. But when $1/T_2$ becomes close to the width of the line, the concept of spectral diffusion has clearly lost any conceivable meaning. Perhaps a second way to define $1/T_2$, or the width of the spin packet, is to say that it is in fact impossible to meaningfully excite, by any experimental arrangement, a group of frequencies with structure narrower than $1/T_2$.

In spite of these difficulties the model is certainly good for the region of our primary interest, and has been used successfully to study various other resonance phenomena: resonance absorption line shapes,[3–5] free induction signals,[2,6,7] and various spin-echo experiments.[7–9] The predictions based on this stochastic model of frequency fluctuations have been in accord with the few rigorous quantum-mechanical results thus far obtained.[10–12]

In this paper we employ the stochastic model for a study of the line shape, free induction signal, and spin-echoes for a wide class of diffusion processes, not necessarily Gaussian, that include both Markoffian and non-Markoffian distributions. Our work is motivated by recent two- and three-pulse spin-echo experiments of Mims and Nassau,[13] which exhibit a two-pulse τ^2-decay law [i.e., $\exp(-\text{const.}\tau^2)$] rather than the τ^3-decay law previously derived[6,8] on the basis of Gaussian diffusion. Herein we prove that the τ^2-decay law is characteristic of a Lorentzian diffusion, and furthermore that Lorentzian diffusion is to be widely expected in solids, particularly in electron paramagnetic resonance, whenever the relaxing spins are a small fraction of the total spins. Our discussion is strongly oriented towards spin-echo experiments. However, since the free induction signal $F(t)$ is a special case of spin-echo signals (only one applied rf pulse), and since the line shape $I(\omega)$ is the Fourier transform of $F(t)$,[2,12] the inclusion of these two experiments in our discussion is quite straightforward.

Stochastic Model

Before summarizing our principal results, let us make some general remarks about the mathematical model that is appropriate to describe the frequency fluctuations of spins. We assume there is a constant external magnetic field H_0 along the z axis. At any time t, the distribution of spin frequencies in the whole sample is given by $g(\omega)$, independent of t. Not all of these spins will be affected by external rf fields of a small range of frequencies and of strength H_1 much less than the total linewidth, but only a narrow resonant subset given say by $P_1(\omega)$, which like g we choose normalized to unity. This divides the spins into a small group "A" of essentially independent spins that are under study [within $P_1(\omega)$], and a group "B" [outside $P_1(\omega)$] that are relevant because they cause fluctuations in the local field of the A spins. Each A-spin frequency undergoes a certain history in time. The collection of all such histories represents the relevant ensemble of functions for the random variable $\omega(t)$ that characterizes the group of A spins. For observations of spins in crystals it appears essential to assume only that this process is stationary, i.e., the final distribution of spins is independent of time. In most cases the final distribution is the observed breadth; in others, it may be useful to suppose that the line is divided into parts which cannot exchange excitation. Only the stationary assumption is necessary for the following reason. Any experimental outcome involves an average over an enormous number of spins and moreover these observations are *reproducible.* Hence a sum over individual moments is no longer a random variable, and this sum is therefore equivalent to carrying out ensemble averages.[14] In view of this fact all we assume about the spin-frequency distribution is that it is stationary.[15]

A common measure of the constancy of the frequency

[4] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).
[5] R. Kubo, J. Phys. Soc. Japan **9**, 935 (1954).
[6] E. L. Hahn, Phys. Rev. **80**, 580 (1950).
[7] B. Herzog and E. L. Hahn, Phys. Rev. **103**, 148 (1956).
[8] H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954).
[9] T. P. Das and A. K. Saha, Phys. Rev. **93**, 749 (1954).
[10] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).
[11] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238 (1953).
[12] I. J. Lowe and R. E. Norberg, Phys. Rev. **107**, 46 (1957).
[13] W. B. Mims and K. Nassau, Bull. Am. Phys. Soc. **5**, 419 (1960); W. B. Mims, K. Nassau, and J. D. McGee, Phys. Rev. **123**, 2059 (1961).

[14] It is of interest to contrast this behavior with the usual viewpoint for noise in a receiver. While the noise voltage is likewise the sum of a myriad of small effects, the resultant signal is *not* reproducible, even if we restrict attention to those voltages which satisfy a specific initial condition, and thus the total noise voltage must still be represented by a random variable. The decisive distinction between these two cases lies in the fact that a long-time coherence exists for individual spin frequencies, while in the noise example only a short-time coherence exists in the voltage of each source.

[15] The stationarity assumption is no longer physically necessary when rf pulses are applied, since the pulses serve to distinguish certain points of time. In Sec. V we ascribe an extraneous diffusion observed in several two-pulse spin-echo experiments to the influence of the applied rf pulses.

variable is the covariance function

$$\rho_c(t) \equiv \langle \Delta\omega(t+t')\Delta\omega(t')\rangle, \tag{1.1}$$

where angular brackets $\langle\ \rangle$ denote an ensemble average, and $\Delta\omega(t)=\omega(t)-\langle\omega(t)\rangle$. Equation (1.1) is both independent of t' and even in t because of the stationarity of the ensemble. Of course to evaluate (1.1) it is necessary to know, in addition to $P_1(\omega_0)$, only $P(\omega,t;\omega_0)$, the conditional probability distribution for finding the frequency ω at time t given that the frequency was ω_0 at $t=0$.

In line-shape experiments one studies the ability of the system to absorb a weak continuous-wave signal at a fixed frequency ω. A spin will absorb power when it is at resonance. If each spin acts incoherently from its neighbors, then the rate of power absorption $I_i(\omega) \propto |\tilde{\mu}_i(\omega)|^2$, where for a typical spin history $\mu_i(t)$,[16]

$$\tilde{\mu}_i(\omega) \equiv \int \mu_i(t)e^{-i\omega t}dt.$$

The total absorption $I(\omega)$ is then given by the sum over all spins. By the argument given above, this sum just reduces to the ensemble average. For this average we introduce the complex random variable $\mu(t)$, whose real part is identified as the total moment, where

$$\mu(t) \equiv \exp\left[i\int_{-\infty}^{t} \omega(t'')dt''\right]. \tag{1.2}$$

For simplicity $\mu(t)$ is chosen to have a constant modulo, which is taken as unity. The Fourier transform $\varphi(t)$ of the line shape $I(\omega)$ is then

$$\varphi(t) = \{\text{Average over } t'\}\langle\mu(t+t')\mu^*(t')\rangle, \tag{1.3}$$

based on well-known Fourier transform theorems. The stationarity of the ω distribution makes the ensemble average in (1.3) independent of t' so that the average over t' is no longer necessary. Thus, with (1.2), Eq. (1.3) becomes

$$\varphi(t) = \left\langle \exp\left[i\int_0^t \omega(t'')dt''\right]\right\rangle, \tag{1.4}$$

where we have arbitrarily set $t'=0$.

In a free-induction experiment, a short rf pulse, of pulsewidth t_w and strength H_1, is applied at time 0 to the sample. This pulse is designed to rotate the resonant spins by 90° (i.e., $t_w\gamma H_1 \equiv \pi/2$) from the z axis into the x axis, say. Ignoring amplitude (but not phase) modulations brought about by T_1 processes, which tend to restore the spins to the z axis, we again adopt Eq. (1.2) for $\mu(t)$ but impose the condition that $\omega(t'')\equiv 0$ for $t''<0$. Thus the free-induction signal $F(t)$ is

$$F(t) = \langle\mu(t)\rangle_{\omega=0 \text{ for } t''<0}$$
$$= \left\langle \exp\left[i\int_0^t \omega(t'')dt''\right]\right\rangle, \tag{1.5}$$

and $F(t)$ is identical with $\varphi(t)$, Eq. (1.4), as has been frequently observed.[2,12,17]

In spin-echo experiments, two or more short rf pulses are used. Consider the two-pulse experiment in which, as before, a 90° pulse is applied at $t=0$ (about the y axis), and subsequently a 180° pulse is applied about the third axis (the x axis) at $t=\tau$. The effect of the second pulse is to flip each resonant spin by 180° in the z plane, and thus to negate the phase that each of these spins has acquired in the interval τ. For times $t>\tau$ the phase is given by

$$\int_\tau^t \omega(t'')dt'' - \int_0^\tau \omega(t'')dt''.$$

Since we are only interested in the real part of equations such as (1.5), we can equally well, from a mathematical point of view, negate the frequency $\omega(t')$ after τ rather than negate the phase acquired before τ. Thus the sum of the individual moments can be expressed in the general form

$$M(t) = \left\langle \exp\left[i\int_0^t s(t'')\omega(t'')dt''\right]\right\rangle, \tag{1.6}$$

where, for the two-pulse spin-echo experiment just described,

$$\begin{aligned} s(t') &= 1, \quad 0<t<\tau; \\ s(t') &= -1, \quad \tau<t. \end{aligned} \tag{1.7}$$

Various other spin-echo experiments can also be described by (1.6) if we choose different "echo functions," $s(t')$. For example, the three-pulse stimulated echo signal (based on three 90° pulses) is characterized by

$$\begin{aligned} s(t') &= 1, \quad 0<t<\tau; \\ s(t') &= 0, \quad \tau<t<T; \\ s(t') &= -1, \quad T<t; \end{aligned} \tag{1.8}$$

where T is the time at which the third pulse is applied.[18] Between τ and T, $s=0$ because in this experiment the moments are stored along the z axis during that time interval, and no additional phase is acquired. In general, a spin-echo signal has a peak at a time t [and

[16] All integrals with unspecified limits extend from $-\infty$ to $+\infty$.

[17] N. G. Koloskova and U. Kh. Kopvillem, Fiz. Tverd. Tela 2, 1368 (1960) [translation: Soviet Phys.—Solid State 2, 1243 (1961)].

[18] Our definition for T conforms with Hahn,[6] but differs from that of Mims and Nassau,[13] who choose T to be the time between the third and *second* rf pulse.

only for those functions $s(t')$] such that

$$\int_0^t s(t')dt'=0, \tag{1.9}$$

a relation we establish in the next section. Thus the two-pulse signal Eq. (1.7) peaks at $t=2\tau$, while the three-pulse stimulated echo peaks at $t=T+\tau$, as is well known.[6]

Clearly, a study of the general form (1.6) for arbitrary $s(t')$ includes both $F(t)$, the free-induction signal [$s(t')\equiv 1$], and $\varphi(t)$[$=F(t)$], the Fourier transform of the line shape, as well as the various possible spin-echo signals.

Summary of Principal Results

In the next section we explicitly evaluate Eq. (1.6) for a large class of probability distributions each member of which we call "homogeneous." For these distributions the random process is Markoffian and furthermore the conditional distribution satisfies

$$P(\omega,t;\omega_0)=P(\omega-\omega_0;t).$$

Combining the Markoffian assumption and the homogeneous requirement, we are led to require

$$\int P(\omega_3-\omega_2;t_a)d\omega_2 P(\omega_2-\omega_1;t_b) = P(\omega_3-\omega_1;t_a+t_b). \tag{1.10}$$

The Fourier transform of (1.10) taken over the frequency variables shows that

$$\tilde{P}(y;t_a)\tilde{P}(y;t_b)=\tilde{P}(y;t_a+t_b).$$

Hence $\tilde{P}(y;t)$ must be a representation of the semigroup of additive real numbers, and the desired solution is simply $\tilde{P}(y;t)=\exp[-tf(y)]$. It follows by an inverse Fourier transform that the most general form for P is

$$P(\omega,t;\omega_0)=(2\pi)^{-1}\int e^{iy(\omega-\omega_0)-tf(y)}dy, \tag{1.11}$$

where in order that P represent a probability we must have

$$f^*(-y)=f(y), \quad (P \text{ is real}); \tag{1.12a}$$

$$f(0)=0, \quad (P \text{ is normalized}); \tag{1.12b}$$

$$\mathrm{Re} f(y)\geq 0, \quad (P \text{ is non-negative}). \tag{1.12c}$$

If $f(y)=ky^2$, then P describes Gaussian diffusion; if $f(y)=m|y|$, then P describes Lorentzian diffusion. The general results of the ensemble average in Eq. (1.6) for arbitrary spin-echoes, and in particular the general predictions for the two-pulse and three-pulse stimulated echo experiments, are summarized in the first three rows of Table I (the proof of these expressions being given in Sec. II).

It is clear from Table I that the two-pulse decay for Gaussian diffusion [$f(y)=ky^2$] is $\exp(-2k\tau^3/3)$,[8] while it is $\exp(-m\tau^2)$ for Lorentzian diffusion [$f(y)=m|y|$], the latter result agreeing very well with several recent

TABLE I. Predictions for the time evolution of various spin-resonance effects based on homogeneous Markoffian diffusion and its generalizations with an arbitrary characteristic function f.

Resonance effect under consideration	Initial frequency distribution	Evolution in time of relative signal amplitude
Two-pulse spin-echo peak decay	Initial spectrum much broader than diffusion interval (peak $t=2\tau$)	$\exp\left\{-2\int_0^\tau f(t')dt'\right\}$
Three-pulse stimulated echo peak decay	Initial spectrum much broader than diffusion interval (peak $t=T+\tau$)	$\exp\left\{-(T-\tau)f(\tau)-2\int_0^\tau f(t')dt'\right\}$
General spin-echo peak for arbitrary pulse sequence	Initial spectrum much broader than diffusion interval (peak at t such that $\int_0^t s(t')dt'=0$)[a]	$\exp\left\{-\int_0^t f\left[\int_0^{t'} s(t'')dt''\right]dt'\right\}$
Time dependence of free induction or echo signal with arbitrary spin response function $G(t')$[a]	Equilibrium distribution of the stationary random frequency ensemble	$\exp\left\{-\int_{-\infty}^t f\left[-\int_{-\infty}^t G(t''-t')s(t'')dt''\right]dt'\right\}$
Attenuation factor due to instantaneous diffusion brought about by the rf pulses[b]	(not applicable)	$\begin{cases}\exp\left\{-(\delta/r)\sum_p f\left[\int_0^{t_p} s(t'')dt''\right]\right\} \\ \exp\left\{-\sum_p F\left[\int_0^{t_p} s(t'')dt''\right]\right\}^{\text{c}}\end{cases}$

[a] The echo function $s(t')$, equal to $+1$, 0, or -1, changes only when a pulse is applied and characterizes a given echo by: (i) $s=0$ for $t'<0$ and during those intervals in which the spin is "stored" parallel to the static field, (ii) $s=\pm 1$ during those intervals in which the spin precesses, and (iii) s changes sign whenever an applied 180° rf pulse is effective.

[b] t_p is the time of the pth 90° pulse interval, δ the fraction of spins affected, and r a representative relaxation rate.

[c] This form applies if the pulses cause an arbitrary frequency spread characterized by F, as for example through affecting nuclear spins,

experiments of Mims.[13] Apparently, Gaussian diffusion is not taking place in these experiments.

It may be noted that (1.11) does not in fact represent a stationary distribution since no limiting distribution is approached as $t\rightarrow\infty$. However, as long as the range of diffusion in an experiment is small compared to the width of the actual final distribution, no significant error is made by adopting a wider final distribution. The criterion for a small diffusion is simply a long-time coherence in the frequency, a condition generally satisfied. A rigorous justification of the simpler, nonstationary form (1.11) will be given in Sec. II. There we outline the results for a proper stationary distribution whose covariance function ρ_c is proportional to $\exp(-Rt)$. If R is very small the equilibrium distribution is approached very slowly in time simulating the nonstationary model.

In Sec. III we present a microscopic theory that relates the fluctuations in local frequency to local field fluctuations which arise from the random flipping of independent spins interacting through the dipole-dipole interaction. It is established with this model that a Lorentzian diffusion process is to be generally expected if only the number of resonant A spins is small compared to the number of B spins. The argument of this proof is largely "dimensional," and therefore is quite general. The physical reason for a Lorentzian spreading of the conditional distribution can be readily seen. Imagine at one instant the spins to be aligned in a certain manner. A short time t later, T_1 processes, say, will have flipped at random a small fraction of the total spins, a fraction proportional to t itself. We can ignore any flipping that takes place in the already assumed small number of observed A spins. Consequently, the frequency distribution at the A sites will correspond to the frequency distribution of a low density of randomly oriented spins with a dipolar interaction. As is well known the distribution is just a Lorentzian with a suitable cutoff on the wings.[11,19] The width of this Lorentzian is roughly $\mu\gamma n_{\mathrm{eff}}$, where in the present case if r is some suitable rate ($\approx 1/T_1$) then $n_{\mathrm{eff}}=nrt$. Since the parameter mt of the Lorentzian diffusion is proportional to the Lorentzian linewidth, it is thus plausible that

$$m=2\pi^2\mu\gamma nr/3, \tag{1.13}$$

the numerical factors following from the detailed proof in Sec. III. Substantial agreement with this prediction for m is found in the experiments of Mims. This is especially so when it is recognized that the rate r which enters m is related to the fastest T_1 process available should there be a distribution of relaxation rates.

However, as soon as we admit a distribution of relaxation rates we are describing a fundamentally different stochastic process that is no longer Markoffian. The subject of Sec. IV is thus to extend the analysis of Sec. II to apply to a wide class of stationary non-Markoffian distributions. This discussion has a double benefit. First, it provides a general description for covariance functions (1.1) with an initially fast falloff in time, characteristic of the desired spread in relaxation rates. Second, it gives a proper formalism with which to discuss a second class of experiments where T_1 is long and T_2 processes determine the homogeneous broadening. Our approach to this alternate broadening mechanism is as follows. Adopting a conditional distribution representing the fluctuations of the individual moments, we first calculate a conditional frequency distribution at the A sites. For purely kinematical reasons, this again turns out to be essentially a Lorentzian in frequency, but it differs in an unknown way with respect to its *time* dependence. This uncertainty in the time dependence forces us to consider non-Markoffian distributions and in this paper we evaluate the desired ensemble average (1.6) in exceptional generality. The second aspect of our calculation will appear in a subsequent paper. In that part we shall attempt to determine the basic time dependence of the conditional frequency distribution by a self-consistency requirement, namely, that the frequency fluctuations calculated from the assumed moment fluctuations are in turn responsible for the moment fluctuations themselves.

The results of our general non-Markoffian analysis of Sec. IV can also be readily summarized. For this purpose it is convenient to introduce a causal function $G(t')$ vanishing for negative arguments. Physically this function accounts for the fact that the random resonant rf fields (coming from the $\mu_j^+\mu_k^-$ terms in the dipolar interaction), which are responsible for the motions of the spins that we represent by the T_2 process, are not infinitely large. Thus the spins cannot flip at an infinitely rapid rate, but must precess from the $+z$ to $-z$ direction at a finite rate, given by γ times some average of the random resonant field precessing in the xy plane. The G function may be defined as proportional to the unbalance in the z direction of an average spin vector following a pulse of field applied in the z direction. Since the spins must return to equilibrium, $G(t')\rightarrow 0$ as $t'\rightarrow\infty$. On the other hand, a spin system with a long T_1 exhibits a certain "inertia" or resistance to change, so that just after the impulse, G remains near zero; i.e., the system has no step function response. It is the characteristic class of functions G which remain small near $t'=0$ that we associate with samples controlled by T_2 processes. The various effects that different spin response functions introduce, particularly into echo signals, is discussed from a general point of view in Sec. IV. For reference we have tabulated in Table I the basic formula of that section, namely, the evaluation of the general ensemble average $M(t)$, Eq. (1.6), including the effect of the spin response function $G(t')$. This formula is applicable to free induction signals as

[19] P. W. Anderson, Phys. Rev. 82, 342 (1951).

well as to spin echoes. Some of the electron spin resonance measurements of Mims on Ce- and Er-doped $CaWO_4$ exhibit the effects of a nonconstant spin response function, consistent with the general modifications made in Sec. IV of the elementary predictions of Sec. II. A brief discussion of these experiments in terms of our theory is presented in Sec. V.

In addition to the above-mentioned effects, we also discuss in Sec. IV an "instantaneous" diffusion induced by the rf pulses themselves. Such a diffusion can also be put into the general form of Eq. (1.11). In particular, a sharp distribution at frequency ω_0 is spread into

$$\mathcal{P}(\omega)=(2\pi)^{-1}\int \exp[iy(\omega-\omega_0)-F(y)]dy \quad (1.14)$$

by the forced precession of a fraction δ of the spins. This can occur either because the spins actually flipped by the pulse interact with each other, or by the spins' reaction on nearby B spins which in turn flip and react back on the A spins. The instantaneous diffusion introduces an additional decay factor $\exp[-2F(\tau)]$ for either the two-pulse or three-pulse stimulated echo. Since the frequency spread in (1.14) is physically only an artificially accelerated form of the normal diffusion, it also is Lorentzian. Thus this diffusion leads to a linear decay with τ, quite characteristic and easily distinguishable from the normal diffusion effects. Indeed, spin reactions with nuclear spins of neighboring nonmagnetic atoms appear to be controlling in the tungstate samples at very low doping densities, according to recent measurements of Mims. The attenuation factor for an arbitrary echo is given in the last row of Table I, where t_p represents the time of the pth 90° pulse interval (for this purpose a 180° pulse enters twice as two 90° pulses), δ is the fraction, assumed small, of spins flipped by the pulse, and r is the same rate as in (1.13).

Finally, in Appendix A we analyze in detail a diffusion model of some interest that has been partially discussed by other authors. In this example the time dependence of the covariance function is taken simply as $\exp(-Rt)$. When R is a large parameter, the frequency fluctuations become rapid and coherence is quickly lost. Such rapid fluctuations lead to line narrowing[3] and herein we discuss their effects on spin echoes, clarifying some aspects of an earlier discussion by Herzog and Hahn.[7] Generally, such echo signals are characterized by high free-induction "backgrounds," by a broadness of the echo, and by a time shift of the echo peak, due essentially to the attenuation of a more usual echo by a rapidly decaying envelope.

II. FREE-INDUCTION SIGNAL, LINE SHAPE, AND SPIN-ECHO DECAY

A. Ensemble Average

Those readers familiar with functional methods or path integral techniques will appreciate that it is possible to work directly with the expression for $M(t)$ given in Eq. (1.6). However, it is operationally much more clear if we first expand the integral appearing in (1.6) as a Riemann sum, and then pass to the limit of this sum after the analysis is completed. We therefore study the "skeletonized" expression

$$\begin{aligned} M(t)&=\langle\exp(i\epsilon\sum_{l=0}^{M} s_l\omega_l)\rangle \\ &=\int\langle\exp(i\epsilon\sum s_l\omega_l)\rangle_{\omega_0}P_1(\omega_0)d\omega_0, \quad (2.1)\end{aligned}$$

where ϵ is the uniform time interval, $(M+1)\epsilon\equiv t$, and where in the second form of (2.1) we divide the ensemble average into those frequency "histories" which pass through ω_0 at $t=0$, and then average over ω_0 subsequently in the distribution P_1. Let

$$P(\omega_{M+1},\cdots,\omega_2,\omega_1|\omega_0;t)$$

denote the joint probability density that the skeletonized frequency history successively passes through the series of frequency values ω_1, ω_2, $\cdots$, ω_{M+1} at the appropriate time intervals subject to the requirement that all histories pass through ω_0 at $t=0$. Then the conditional average in Eq. (2.1) becomes

$$M(t,\omega_0)=\int \exp(i\epsilon\sum s_l\omega_l)P(\omega_{M+1},\cdots,\omega_1|\omega_0;t) \times\prod_{1}^{M+1}d\omega_l. \quad (2.2)$$

Because of our Markoffian assumption in this section the necessary joint probability distribution is readily expressed by

$$P(\omega_{M+1},\cdots,\omega_1|\omega_0;t)=\prod_{l=0}^{M}P(\omega_{l+1},\epsilon;\omega_l). \quad (2.3)$$

We shall carry out the analysis in detail only for the simple distribution given in Eq. (1.11), and in our subsequent calculations we shall indicate the necessary modification in the present calculation that would be necessary to find $M(t)$ for more complex distributions. Based on (1.11), therefore, each factor on the right side of (2.3) becomes

$$P(\omega_{l+1},\epsilon;\omega_l)=\frac{1}{2\pi}\int\exp[iy_{l+\frac{1}{2}}(\omega_{l+1}-\omega_l) -\epsilon f(y_{l+\frac{1}{2}})]dy_{l+\frac{1}{2}}. \quad (2.4)$$

When Eqs. (2.2)–(2.4) are made use of, $M(t,\omega_0)$ is given by the limit of the expression

$$\frac{1}{(2\pi)^{M+1}}\int\cdots\int\exp[i\sum_{0}^{M}y_{l+\frac{1}{2}}(\omega_{l+1}-\omega_l) +i\epsilon\sum_{1}^{M}s_l\omega_l-\epsilon\sum_{0}^{M}f(y_{l+\frac{1}{2}})]\prod_{0}^{M}dy_{l+\frac{1}{2}}\prod_{1}^{M+1}d\omega_l. \quad (2.5)$$

Let us first carry out the $M+1$ integrations over ω_l called for by (2.5). An $(M+1)$-fold product of delta functions will result and all of the inverse 2π factors will be cancelled. Hence, Eq. (2.5) leads to

$$\int\cdots\int \exp[-iy_{\frac{1}{2}}\omega_0-\epsilon\sum_0^M f(y_{l+\frac{1}{2}})]\delta(y_{M+\frac{1}{2}}) \times\prod_1^M \delta(y_{l-\frac{1}{2}}-y_{l+\frac{1}{2}}+\epsilon s_l)\prod_0^M dy_{l+\frac{1}{2}}. \quad (2.6)$$

Next we carry out the $M+1$ integrations over $y_{l+\frac{1}{2}}$. These integrations just "use up" all the delta functions and generate the sequence of identities,

$$y_{l+\frac{1}{2}}=y_{l-\frac{1}{2}}+\epsilon s_l, \quad (2.7a)$$

together with the boundary condition

$$y_{M+\frac{1}{2}}=0. \quad (2.7b)$$

These two relations simply state that

$$y_{l+\frac{1}{2}}=-\epsilon\sum_{l+1}^M s_m. \quad (2.8)$$

When this result is substituted back into (2.6) we find that

$$M(t,\omega_0)=\exp[i\omega_0\epsilon\sum_1^M s_m-\epsilon\sum_0^M f(-\epsilon\sum_{l+1}^M s_m)]. \quad (2.9)$$

Now it is a simple matter to pass to the limit $M\rightarrow\infty$, $\epsilon\rightarrow 0$ so that (2.9) becomes rigorously

$$M(t,\omega_0)=\exp\left\{i\omega_0\int_0^t s(t')dt' -\int_0^t f\left[-\int_{t'}^t s(t'')dt''\right]dt'\right\}, \quad (2.10)$$

which gives the final expression for $M(t,\omega_0)$, the ensemble average with a fixed initial frequency ω_0.

Equation (2.10) is now averaged over the stationary distribution $P_1(\omega_0)$, and the final result for $M(t)$ is

$$M(t)=\tilde{P}_1\left[-\int_0^t s(t')dt'\right] \times\exp\left\{-\int_0^t f\left[-\int_{t'}^t s(t'')dt''\right]dt'\right\}, \quad (2.11)$$

where $\tilde{P}_1$ denotes the Fourier transform of P_1. In the free-induction signal experiment [for which we let $M(t)=F(t)$] Eq. (2.11) predicts that

$$F(t)=\tilde{P}_1(-t)\exp\left\{-\int_0^t f(-t')dt'\right\}. \quad (2.12)$$

Thus $F(t)$ is a product of two terms, the first factor due completely to a spread in the initial distribution of frequencies without regard to any diffusion, while the second factor represents the smearing introduced by diffusion into a pure spectral component. Equation (2.12) differs from more conventional results for the Fourier transform of the line shape[2,3] that are based on the more restrictive assumption of a stationary ergodic ensemble. (We shall make contact with these previous results in Appendix A when we study the consequences of rapid decay in a simple stationary ergodic ensemble for which P_1 and f are related.) Equation (2.12) has physical validity as the expected shape of the free-induction signal when, for example, f describes diffusion within spin-packets and $P_1(\omega)$ characterizes the spin distribution that is effectively rotated 90° by the rf field H_1.

On the other hand, the application of (2.11) in the case of spin echoes is somewhat different. Since the initial distribution $P_1(\omega_0)$ is non-negative and is normalized, its Fourier transform $\tilde{P}_1(y)$ has its maximum value of one at $y=0$. If the initial distribution is sufficiently broad, then the maximum of M occurs at the maximum of $\tilde{P}_1$, namely, when

$$\int_0^t s(t')dt'=0. \quad (2.13)$$

This relation assumes, of course, a comparatively slow decay due to the second factor in (2.11), an assumption which is correct whenever the diffusion is slow. In this case, the simple formula that applies to the attenuation of spin-echo peaks is expressed by

$$M_{\text{peak}}(t)=\exp\left\{-\int_0^t f\left[\int_0^{t'} s(t'')dt''\right]dt'\right\}, \quad (2.14)$$

where we have made use of Eq. (2.13) to simplify the argument of f.[20] By concentrating attention on the behavior of the peak of the output signal, the well-known advantage of spin-echo studies shows up directly in (2.14), namely, that all reference to the initial distribution $P_1(\omega_0)$ disappears and only diffusion effects remain.

For the two-pulse spin-echo experiment [$s(t')$ given in Eq. (1.7)], it follows with $M_{\text{peak}}\equiv E$ that

$$E(2\tau)=\exp\left[-2\int_0^\tau f(t')dt'\right], \quad (2.15)$$

which leads to the τ^3-decay law, $\exp(-2k\tau^3/3)$, for Gaussian diffusion [$f(y)=ky^2$],[6,8] while for Lorentzian diffusion [$f(y)=m|y|$] a τ^2-decay law results: $\exp(-m\tau^2)$. The familiar three-pulse stimulated echo

[20] This decay law is equivalent to the result given previously apart from the sign of s: J. R. Klauder, Bull. Am. Phys. Soc. **6**, 103 (1961).

decay, $M_{\text{peak}}\equiv S$, is given by

$$S(T+\tau)=\exp\left[-(T-\tau)f(\tau)-2\int_0^\tau f(t')dt'\right], \quad (2.16)$$

an expression which decays exponentially with T for any characteristic function f.

Equation (2.11), and its special cases (2.12), (2.14), (2.15), and (2.16), represent the results of our ensemble average, and the last two results for spin-echoes, Eqs. (2.15) and (2.16), will be compared to some experimental results in Sec. V.

Let us point out, however, that our entire calculation has been based on the use of a *non*stationary distribution (1.11), since as t increases this distribution provides no limitation to the diffusion whatsoever. It is useful at this point to introduce the proper stationary Markoffian distribution to which (1.11) represents a small-time approximation and, leaving most of the details to Appendix A, to show under what conditions the simpler nonstationary model applies.

B. The Stationary Markoffian Distribution. Justification for the Nonstationary Model

We seek a modification of our Markoffian conditional distribution law (1.11) for the spreading of the excited frequencies such that it eventually tends to an equilibrium distribution, independent of the initial frequency ω_0. The appropriate modification, which maintains as much as possible of the homogeneous character of the original distribution, is well known in the case of Markoff-Gaussian diffusion.[21] From this special case we learn that, in the proper coordinate system, the initial alteration we must make in Eq. (1.11) takes the form of replacing the variable $\omega-\omega_0$ by $\omega-\exp(-Rt)\omega_0$; here R represents the "rate" at which the final distribution is approached. It is not difficult to show that $\exp(-Rt)$ is in fact the only function of time compatible with the homogeneous Markoffian requirement. It follows further that the covariance function will have the same time dependence,

$$\langle\Delta\omega(t)\Delta\omega(0)\rangle=e^{-Rt}\langle\Delta\omega(0)^2\rangle, \quad (2.17)$$

where as usual $\Delta\omega(t)=\omega(t)-\langle\omega(t)\rangle$. The final modification of (1.11) is uniquely determined by the requirement that a Markoffian distribution results, and as a consequence we find that

$$P(\omega,t;\omega_0)=(2\pi)^{-1}\int\exp\left[iy(\omega-\omega_0e^{-Rt})-\int_0^t f(ye^{-Rt'})dt'\right]dy. \quad (2.18)$$

[21] M. C. Wang and G. E. Uhlenbeck, Revs. Modern Phys. **17**, 323 (1945), reprinted in *Selected Papers on Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, New York, 1954).

For t small, i.e., more precisely $Rt\ll 1$, Eq. (2.18) reduces to (1.11), but as $t\rightarrow\infty$, Eq. (2.18) passes over to a final, equilibrium distribution

$$P(\omega)=(2\pi)^{-1}\int\exp\left[iy\omega-\int_0^\infty f(ye^{-Rt'})dt'\right]dy, \quad (2.19)$$

independent of ω_0.

The mean frequency in the equilibrium distribution $P(\omega)$ is, of course, governed by the function f. Suppose we add to $f(y)$ the term $i\bar{\omega}Ry$. This additional term introduces a factor $-i\bar{\omega}[1-\exp(-Rt)]$ into the exponent of (2.18) which leads back to the original distribution (2.18) expressed in the new variable $\omega'-\omega_0'\exp(-Rt)$, where $\omega_i'\equiv\omega_i-\bar{\omega}$. Hence $\bar{\omega}$ introduces a linear frequency translation, as would arise in transforming to a rotating coordinate system. Indeed, it follows directly from (2.18) that quite generally

$$\langle\omega\rangle=-if'(0)/R. \quad (2.20)$$

The mean-square fluctuation in $P(\omega)$ is given quite generally by a similar formula:

$$\langle\Delta\omega^2\rangle=f''(0)/2R. \quad (2.21)$$

It is clear from Eqs. (2.19)–(2.21) that the presence of a nonzero decay R enables meaning to be given the limit of the conditional distribution, and thus enables the various moments of that distribution to be defined. It is physically reasonable to associate the equilibrium distribution $P(\omega)$ with the spins in a particular spin packet, whose mean frequency is given by (2.20). The initial distribution $P_1(\omega)$ then can either be taken equal to $P(\omega)$, if the rf field H_1 is so weak as to excite only a single or just a few packets, or alternatively, $P_1(\omega)$ can be interpreted as the distribution of spin-packet center frequencies, if H_1 is strong enough to excite a large number of packets. Both of these cases are discussed in Appendix A and $M(t)$ is calculated for an arbitrary value of the decay rate R. In either case, however, whenever the parameter $Rt\ll 1$, (where t represents the experimental time interval), then the results for $M(t)$ are in accord with the simple calculation presented initially based on the nonstationary distribution, differing from the latter calculation only by terms of order Rt. Physically, a very small value for R implies, according to (2.17), a long-time frequency stability, i.e., a tendency to diffuse slowly. Over a moderate time interval t, each frequency diffuses comparatively very little, and thus the diffusion is influenced negligibly by the bounds imposed by the equilibrium distribution $P(\omega)$.

When, as we shall assume, the relaxation rate R is small, $P(\omega)$ equals the intrinsic absorption line shape $I(\omega)$ of an individual, homogeneously broadened spin packet. Consider the common case of an homogeneous, dipolar broadened Lorentzian line shape arbitrarily

centered at $\omega=0$:

$$I(\omega)=[2/\pi(\Delta\omega)_{\frac{1}{2}}]\{1+[2\omega/(\Delta\omega)_{\frac{1}{2}}]^2\}^{-1},$$

where $(\Delta\omega)_{\frac{1}{2}}$ represents the intrinsic half-power linewidth. The same functional form for $P(\omega)$ follows from (2.19) if we let $f(y)=m|y|$ and choose the parameter $m=R(\Delta\omega)_{\frac{1}{2}}/2$. For samples where T_1 processes control the frequency fluctuations in the "B" or unobserved, group of spins, we have $R=T_1^{-1}$, while in other samples, where T_2 processes dominate the "B" spin fluctuations, $R=T_2'^{-1}$.[22] Thus it appears reasonable that

$$R=1/T_2\approx 1/T_2'+1/T_1, \tag{2.22}$$

where T_2, as usual, represents the cumulative effect of spin-spin and spin-lattice relaxation effects on the "B" group of spins. It follows from (2.22) that R will be small—and thus the ensemble average leading to Eq. (2.11) is applicable—whenever T_2 is large. A discussion of the line shape, free-induction signal, and spin-echo signals for which Rt is not small is reserved for Appendix A.

III. DIPOLAR MODEL FOR NEARLY LORENTZIAN DIFFUSION

As remarked in Sec. I, the fluctuations of the precessional frequencies of the A spins have their physical origin in local magnetic field changes brought about by the random flipping of the (numerically superior) B spins. In this section, we analyze a model (i) in which the spins interact through the dipolar interaction Hamiltonian

$$\mathcal{H}=\sum_{i\neq j}{}'\left(\frac{\boldsymbol{\mu}_i\cdot\boldsymbol{\mu}_j}{r_{ij}^3}-\frac{3(\boldsymbol{\mu}_i\cdot\mathbf{r}_{ij})(\boldsymbol{\mu}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5}\right), \tag{3.1}$$

and (ii) in which each B moment $\mu_i^z(t)$ is treated as an independent stochastic variable capable of either of two values, say $\pm\mu$, which flips on the average with a rate r. The dipolar interaction Hamiltonian involves: terms $\mu_i^+\mu_j^-$ responsible for transitions, etc.; terms $\mu_i^z\mu_j^z$, which determine the local field; and mixed terms that involve angular momentum exchange with the lattice. Only the $\mu_i^z\mu_j^z$ terms in (3.1) need be retained to define the instantaneous local field. For the random spin components $\mu_j^z(t)$ we simply write $\mu_j(t)$. Thus, the local frequency variable $\omega_i\equiv\omega$ at a typical A spin is

$$\omega(t)=\gamma\sum{}'\mu_j(t)r_{ij}^{-3}, \tag{3.2}$$

where γ is the common gyromagnetic ratio of the A spins.

We now assume that μ_j, $j=1, 2, \cdots, N$, represent a set of statistically independent random variables for which $\rho(\mu_l)$ represents the distribution of the lth spin.

[22] The identification of R with $1/T_2'$ in the latter case is based simply on an analogy with the former identification of R and involves only the *large*-time behavior of the covariance function (for a proof, see Appendix B). In no way does this identification require the applicability of any of the other temporal results of Sec. II when T_2 processes dominate.

Equation (3.2) clearly defines a new stochastic variable $\omega(t)$ as the linear sum of other, independent variables. The specification of the distribution $p(\omega)$ can be readily found in terms of the distribution $\rho(\mu)$ by standard techniques that we reproduce below.

By means of the integral representation for the δ function, the distribution $p(\omega)$ is defined by

$$p(\omega)=\frac{1}{2\pi}\sum\int dy\,\exp[iy(\omega-\gamma\sum{}'\mu_jr_{ij}^{-3})]\times\prod_{l=1}^{N}\rho(\mu_l), \tag{3.3}$$

where the external summation sign calls for a sum over all possible spin combinations. Since each of the independent moments in (3.3) appear in separate multiplicative factors, Eq. (3.3) may be written as

$$p(\omega)=\frac{1}{2\pi}\int dy\,e^{iy\omega}\prod_j{}'\langle\exp(-iy\gamma\mu r_{ij}^{-3})\rangle, \tag{3.4}$$

where the average of μ is taken with respect to the distribution $\rho(\mu)$.

Since we are interested in studying a time-dependent Markoffian conditional probability, we define

$$\rho(\mu)=P(\mu,t;\mu_0)=\delta_{\mu\mu_0}e^{-rt}+(1-e^{-rt})\sigma(\mu), \tag{3.5}$$

where $\sigma(\mu)$ represents the normalized final distribution, which we assume satisfies $\sigma(\uparrow)=\sigma(\downarrow)=\frac{1}{2}$. In terms of the distribution (3.5), the required average needed in (3.4) becomes

$$\langle e^{-iz\mu}\rangle=e^{-iz\mu_0-rt}+(1-e^{-rt})\sum e^{-iz\mu}\sigma(\mu),$$

where z stands for $y\gamma r_{ij}^{-3}$. After rearrangement we find

$$\langle e^{-iz\mu}\rangle=e^{-iz\mu_0}[1-(1-e^{-rt})J(z)], \tag{3.6}$$

where

$$\begin{aligned}J(z)&=\sum[1-e^{-iz(\mu-\mu_0)}]\sigma(\mu)\\&=(1-\cos z\mu),\end{aligned} \tag{3.7}$$

the latter result following because of our assumption that $\sigma(\mu)$ is uniformly distributed. Thus $J(z)$ is independent of the initial value μ_0, as we have anticipated by our notation. For small t to which we now pass (or equally well for small values of z) the second factor in the square brackets in (3.6) is much less than one so that

$$\langle e^{-iz\mu}\rangle\approx\exp[-iz\mu_0-rtJ(z)], \tag{3.8}$$

our final form for the average over an individual moment.

We next let $z\to y\gamma r_{ij}^{-3}$ and $\mu_0\to\mu_{0j}$ in (3.8) and take the necessary product over j as called for by Eq. (3.4). Thus the distribution in ω becomes

$$p(\omega)=(2\pi)^{-1}\int dy\,\exp[iy(\omega-\omega_0)-rtK(y)], \tag{3.9}$$

where

$$\omega_0 \equiv \gamma \sum_j{}' \mu_{0j} r_{ij}^{-3}, \tag{3.10}$$

and

$$K(y) \equiv \sum_j{}' J(y\gamma r_{ij}^{-3}) = \sum_j{}' (1-\cos\mu y\gamma r_{ij}^{-3}). \tag{3.11}$$

The right-hand side of (3.11) is a familiar expression that arises in line-shape studies and which is commonly approximated by an integral form:

$$K(y) = 4\pi n \int_{r_{\min}}^{r_{\max}} r^2 dr (1-\cos\mu y\gamma r^{-3}), \tag{3.12}$$

where n is the density of B spins.

With no significant error, $r_{\max}$ in Eq. (3.12) can be taken as infinity; this we shall assume to be done. Furthermore, if $\mu\gamma|y| \gtrsim 2\pi r_{\min}^3$, then we may set the lower limit equal to zero, and

$$K(y) \approx 4\pi n \int_0^\infty r^2 dr (1-\cos\mu y\gamma r^{-3}) = \tfrac{2}{3}\pi^2 n\mu\gamma|y|. \tag{3.13}$$

The term $\mu\gamma|y|$ arises simply from a change of variable, while the remaining integral only modifies the numerical coefficient. On the other hand, for $\mu y\gamma$ extremely small we expand the cosine in (3.12) and find

$$K \approx \frac{4\pi n}{2}(\mu y\gamma)^2 \int_{r_{\min}}^\infty \frac{dr}{r^4} = \tfrac{2}{3}\pi n(\mu y\gamma)^2/r_{\min}^3. \tag{3.14}$$

As a result of Eqs. (3.13) and (3.14), $K \propto |y|$, except when y is very small where $K \propto y^2$. When this functional form for K is reinserted into (3.9) and a comparison is made with Eq. (1.11), we find that the dipolar interaction does indeed lead to a nearly Lorentzian diffusion process for the frequency ω, as was claimed.

The two asymptotic forms for $K(y)$ may be incorporated if we let

$$K(y) = m[(y^2+\rho^2)^{\frac{1}{2}} - \rho], \tag{3.15}$$

where the parameters m and ρ are defined by

$$m = \tfrac{2}{3}\pi^2 \mu\gamma n r, \tag{3.16a}$$

$$\rho = \pi r_{\min}^3/2\mu\gamma. \tag{3.16b}$$

The deviation from the pure Lorentzian form $m|y|$ suggested by (3.15) is precisely of the kind found experimentally by Mims. This slight deviation provides a physically desirable cutoff on the wings of the Lorentzian that suffices to make the second moment converge, since, according to (2.21), $\langle\Delta\omega^2\rangle = m/2R\rho$. The cutoff frequency can be estimated from $\omega_c \approx \rho^{-1}$, i.e.,

$$\omega_c \approx \mu\gamma r_{\min}^{-3}, \tag{3.17}$$

which equals the change in local frequency caused by a single nearest neighbor flip. Just such a limitation on instantaneous frequency excursions is to be expected, and the cutoff on the Lorentzian wings is therefore entirely reasonable.

It remains for us to discuss the rate r at which the A spins lose their spin sense. In "T_1 samples," i.e., samples for which $T_2' \gg T_1$, with a single relaxation rate it is plausible that

$$r = R = 1/T_1, \tag{3.18}$$

the rate of loss of frequency memory introduced in Sec. II. With this assignment for r we can compare the relation $m = 2\pi^2\mu\gamma nR/3$, derived in this section with the relation $m = R(\Delta\omega)_{\frac{1}{2}}/2$ derived in the last section. It follows that for these two relations to be equal

$$(\Delta\omega)_{\frac{1}{2}} = \tfrac{4}{3}\pi^2\mu\gamma n,$$

which, apart from a factor of order 1, is just the result derived earlier by Anderson.[19]

On the other hand, for T_2 samples (i.e., $T_1 \gg T_2'$), there is no basis for identifying the short-time relaxation rate r with the long-time rate R since in this case the assumed dependence of (3.5) cannot be justified. Only the kinematical part of the present analysis applies, which therefore predicts a nearly Lorentzian frequency diffusion model for T_2 samples as well. Further analysis of this case is presented in the next section.

Generalized Spin-Flip Distributions

There are just three fundamental reasons why $K(y)$ exhibited the asymptotic behavior given in (3.13) and (3.14). Two of these reasons have to do with elementary properties of the function $J(z)$ by which K is defined. Let us assume $J(z)$ to be a rather general function and investigate the general $K(y)$ based on (3.11) and (3.12), namely,

$$K(y) = 4\pi n \int_{r_{\min}}^{r_{\max}} r^2 dr J(y\gamma r^{-3}). \tag{3.19}$$

If $J(z) \propto z^2$ for small z—which is necessary to make $\langle\Delta\mu^2\rangle$ finite—then without error we can extend $r_{\max}$ to infinity. This same requirement tells us that $K(y) \propto y^2$ for very small y, so that $\langle\Delta\omega^2\rangle$ is also finite. On the other hand, to set $r_{\min}$ equal to zero when y is of reasonable size means we must study $J(z)$ for large argument. It is clear that we need

$$\lim_{r\to 0} r^2 J(y\gamma r^{-3}) = 0, \tag{3.20}$$

which even precludes J from having a linear term for large argument. In order to satisfy (3.20) we shall assume J to be bounded for large z. This is of course just the property of the particular $J(z)$ in (3.7). So long as J leads off as z^2 and for large z obeys (3.20), it follows by a simple change of variable that $K(y) \propto |y|$, and hence Lorentzian frequency diffusion results.

All of this generality means that the derivation carried out above to derive $p(\omega)$ can be extended to a

generalized class of spin distributions, analogous in form to (1.11), and given by

$$\rho(\mu)=(2\pi)^{-1}\int \exp[i\alpha(\mu-\mu_0)-th(\alpha)]d\alpha, \quad (3.21)$$

where $h(\alpha)$ is any function that satisfies the two requirements on $J(z)$ just discussed, in addition to the general requirements expressed in (1.12). If we substitute (3.21) for the distribution $\rho(\mu)$ required in Eq. (3.4) and repeat the derivation through Eq. (3.9), we find now that

$$p(\omega)=(2\pi)^{-1}\int \exp[iy(\omega-\omega_0)-tH(y)]dy, \quad (3.22)$$

where again

$$\omega_0\equiv\gamma \textstyle\sum_j{}' \mu_{0j}r_{ij}^{-3},$$

while

$$H(y)\equiv\textstyle\sum_j{}' h(y\gamma r_{ij}^{-3}). \quad (3.23)$$

Based on the requirements imposed on h it follows that

$$H(y)\approx 4\pi n\int_0^\infty r^2dr\, h(y\gamma r^{-3})$$

$$=n\gamma|y|\frac{4\pi}{3}\int_0^\infty dx\, h(x^{-1}), \quad (3.24)$$

save for y very small, where $H(y)\propto y^2$. As a consequence of (3.24), a nearly Lorentzian frequency diffusion follows from a very broad class of spin distributions interacting through a dipolar term.

We seek now to interpret qualitatively the necessary large argument behavior of h in order to justify (3.24). We can, in analogy to Eq. (2.19), write down a final, equilibrium spin distribution

$$p(\mu)=(2\pi)^{-1}\int \exp[i\alpha\mu-B(\alpha)]d\alpha, \quad (3.25)$$

where

$$B(\alpha)\equiv\frac{1}{R}\int_0^\alpha \frac{h(x)dx}{x}. \quad (3.26)$$

This equilibrium distribution is based on the small-time conditional spin distribution $\rho(\mu)$ given in Eq. (3.21). Since the spin variable is clearly *bounded*, it follows that $p(\mu)$ should vanish for $|\mu|>\mu'$. A necessary condition that the distribution $p(\mu)$ have the desired finite range is that its Fourier transform

$$\tilde{p}(\alpha)=\exp[-B(\alpha)]$$

should fall off for large α as a power, i.e.,

$$|\tilde{p}(\alpha)|\underset{\alpha\to\infty}{\longrightarrow}\alpha^{-L}, \quad 0<L<\infty.$$

To secure the desired asymptotic behavior of $\tilde{p}(\alpha)$ it suffices to have

$$B(\alpha)=L\ \ln\alpha+(\text{lower order terms}),$$

or because of (3.26)

$$h(x)=LR+(\text{lower order terms}),$$

when x is large. Thus when h is bounded for large arguments, a Lorentzian diffusion for the precessional frequency follows from (3.24), while with some additional restrictions on h, which need not concern us, the equilibrium distribution of the spins is nonzero only over a finite range. Although it is true for small times that the conditional spin distribution (3.21) is not similarly bounded, it is nevertheless approximately true since very little diffusion to the wings occurs in a small time interval. Clearly, a continuous distribution of spins, as might be described by (3.21), could represent a cooperative effect in which groups or clusters of spins tend to flip together. It is rewarding that in spite of such generality in the spin distribution only one form of frequency diffusion is to be expected.

IV. EXTENSION TO VARIOUS NON-MARKOFFIAN DIFFUSION PROCESSES

The frequency fluctuation model discussed in Secs. II and III is deficient in one important respect, namely, in their adoption of the Markoffian assumption. Suppose, for example, there are several T_1 processes with differing relaxation rates. In this case the conditional frequency distribution will rapidly spread out to an initial "equilibrium" distribution governed by the fastest rate; next, it will spread more slowly towards a second "equilibrium" distribution governed by the next fastest rate, etc. Such a very physical example can be characterized by a covariance function—the measure of frequency memory—that initially falls off very rapidly but eventually decays more slowly at a rate controlled by the slowest T_1 process. Such a process is no longer described by a Markoffian variable.

The second case of interest occurs when T_2 processes control the frequency fluctuations. The characteristic behavior in this case is one of "inertia": Spin-spin flips exhibit inertia in that once initiated they tend to continue to completion. Thus this case too is non-Markoffian, since a Markoffian variable could equally likely "turn around" at any time. Characteristically, the variable of a random process possessing inertia resists instantaneous changes so that the covariance function decays initially not linearly with time but at least quadratically, i.e., $\rho_c(t)=\rho_c(0)+(t^2/2!)(\partial^2\rho_c/\partial t^2)_{t=0}+\cdots$. Therefore, we adopt

$$\partial\rho_c(t)/\partial t|_{t=0}=0 \quad (4.1)$$

as our basic requirement for random frequency processes with "inertial diffusion" suitable to describe T_2 samples. We must associate with (4.1) the qualitative require-

ment that $(\partial^2\rho_c/\partial t^2)_{t=0}$ is small, otherwise the inertia-stabilization of the frequency will not be retained for a long enough interval of time to be of significance.

At the end of this section we extend our analysis in another direction to include an instantaneous frequency diffusion brought about by the rf pulses themselves. Such a diffusion is neither Markoffian nor is it stationary.

Diffusion in the Presence of a General Spin-Response Function

Our first task is to reevaluate the basic ensemble average

$$M(t)=\left\langle \exp\left[i\int_0^t s(t')\omega(t')dt'\right]\right\rangle$$

for more general diffusion processes. In this reevaluation, the term

$$\sum_0^M y_{l+\frac{1}{2}}(\omega_{l+1}-\omega_l) \tag{4.2}$$

appearing in the exponent of Eq. (2.5), or for brevity the term

$$\int_0^t y(t')\dot{\omega}(t')dt', \tag{4.3a}$$

is replaced by a more general expression in which, for example, higher order derivatives appear in the integrand, i.e., terms such as $y\partial^2\omega/\partial t^2$, $y\partial^3\omega/\partial t^3$, etc. To be specific we replace (4.3a) by the general bilinear expression

$$\int_{-\infty}^t\int_{-\infty}^t dt'dt''y(t')K(t'-t'')\omega(t''), \tag{4.3b}$$

which of course includes (4.3a) as a special case. Note that the lower limit of the integrals has been extended to $-\infty$; this is a necessary consequence of introducing possible long-term memory effects via the kernel K. In the reevaluation of the ensemble average $M(t)$, which we carry out in Appendix B, it is necessary to integrate over all histories for y and ω from $t'=-\infty$ up to $t'=t$, rather than just those from $t'=0$ to $t'=t$.

To facilitate writing the expression for M, we introduce a causal Green's function $G(t')$—causal because $G(t')\equiv 0$ for $t'<0$—that satisfies

$$\int K(t'-t'')dt''\,G(t''-t''')=\delta(t'-t''').$$

We shall shortly determine the physical meaning of G, but in order to gain this insight it is first convenient to find $M(t)$.

In terms of the Green's function G, it follows from the analysis presented in Appendix B that

$$\left\langle \exp\left[i\int_0^t s(t')\omega(t')dt'\right]\right\rangle$$
$$=\exp\left\{-\int_{-\infty}^t f\left[-\int_{-\infty}^t G(t''-t')s(t'')dt''\right]dt'\right\}. \tag{4.4}$$

In Eq. (4.4), $s(t'')\equiv 0$ for $t''<0$; furthermore, the particular expression given there is based on the assumption that the initial distribution $P_1(\omega_0)$ equals the equilibrium distribution; if this is not the case, $f(y)$ may be given a term proportional to $i\bar{\omega}\hbar y$, and then a subsequent average over $P_1(\bar{\omega})$ may be carried out (compare Appendix A). It follows directly from a power series expansion of (4.4) in powers of s that

$$\langle\omega(t)\rangle=-if'(0)\int_0^\infty G(t')dt', \tag{4.5}$$

and

$$\langle\Delta\omega(t)\Delta\omega(0)\rangle=f''(0)\int_0^\infty G(t')G(t+t')dt', \tag{4.6}$$

which are obvious generalizations of Eqs. (2.17), (2.20), and (2.21).

In order to satisfy (4.1), our "criterion of suitability" for T_2 samples, it is necessary according to (4.6) that

$$0=\int_0^\infty G(t')\dot{G}(t')dt'=\tfrac{1}{2}[G^2(\infty)-G^2(0)].$$

Hence, since physically G must fall to zero at infinite time in order that (4.5) and (4.6) can be finite, we can satisfy (4.1) simply by choosing

$$G(0)=G(\infty)=0. \tag{4.7}$$

Such conditions on the Green's function are obtained automatically as soon as one introduces a second derivative term, i.e., $y\partial^2\omega/\partial t^2$, into (4.3a) (along with the ever-present term $Ry\omega$, which provides the necessary damping at $t=\infty$). Kernels with still higher order derivatives also permit (4.7) to be satisfied.

In order to interpret G let us *temporarily* specialize to a diffusion*less* process where $f(y)\equiv iA_0y$. Let $s=1$; then (4.4) becomes

$$\left\langle \exp\left[i\int_0^t \omega(t')dt'\right]\right\rangle$$
$$=\exp\left\{i\int_{-\infty}^t A_0dt'\int_0^t G(t''-t')dt''\right\}$$
$$=\exp\left\{i\left[A_0\int_0^\infty G(t')dt'\right]t\right\}, \tag{4.8}$$

which states that the phase is acquired at a constant rate $\bar{\omega}=A_0\int_0^\infty G(t')dt'$, in accord with (4.5). Let us now imagine that at $t=0$ an additional localized field $H_0'(t)$ is applied along the z axis. This field is to simulate a field fluctuation at a neighboring B spin which leads on the average to an unbalanced spin population. Ever present, random rf fields in the z plane enable the unbalanced spins to flip and thus to finally cause a frequency fluctuation at the A-spin sites. The response of the precessional frequency to the field $H_0'(t)$ is a measure of the response of an average spin to fluctuations in H_z.

The constant A_0 in (4.8), being proportional to the local magnetic field will now become $A_0+A_0'(t)$, where $A_0'(t)\propto H_0'(t)$. Repeating the derivation of (4.8) with the added term we find that the phase is no longer acquired at a constant rate but at the variable rate

$$\omega'(t)=\bar{\omega}+\int_0^t G(t-t')A_0'(t')dt'. \tag{4.9}$$

Equation (4.9) shows that the precessional frequency of A spins, hence the moment orientation of the B spins, is not responsive to the instantaneous magnetic field. In particular if $H_0'(t)\propto\delta(t)$, an impulsive field, then

$$\omega'(t)=\bar{\omega}+\lambda G(t),$$

where λ is some constant. We shall refer to G as the spin response function. Note that the interpretation of G in no way involves the properties of any real diffusion process for which $f''(0)>0$. We now return to our general discussion assuming that an arbitrary diffusion is actually present.

Let us examine Eq. (4.4) for the case of various spin-echo experiments. Although G must eventually fall to zero, we shall assume this falloff to be very slow (the analog of a small R in Sec. II). This corresponds to the physically important cases with slow diffusion. To determine the instant of peak response, we break the integral on the right side of (4.4) into two parts:

$$M(t)=\exp\left\{-\int_0^t f\left[-\int_{t'}^t G(t''-t')s(t'')dt''\right]dt' -\int_0^\infty f\left[-\int_0^t G(t''+t')s(t'')dt''\right]dt'\right\}. \tag{4.10}$$

Due to the infinite range in the second integral and the assumed slow falloff of G, the maximum of $M(t)$ occurs when the latter integral is minimum. Because of the time-entanglement within $G(t''+t')$ we cannot in general pick a *single* value of t that will reduce the integrand to zero for all values of t'. Hence the minimum of the second integral is generally nonzero in contrast to the case discussed in Sec. II. Nevertheless, the slow falloff of G, i.e., we assume that G eventually becomes constant in an interval t, will force the minimum of the second integral, and thus the maximum of $M(t)$, to occur when

$$\int_0^t s(t')dt'=0. \tag{4.11}$$

Therefore, we have the important result that the echo will peak at the customary time even in the "presence" of G, whenever the spin response function falls off very slowly for large times. The value of M_{peak} then follows from (4.10) and (4.11).

We next take up the question of the decay of the echo peak for Lorentzian and near-Lorentzian diffusion. (A corresponding discussion for Gaussian diffusion can be easily carried out following the lines developed in Appendix A; however, we shall omit it.) For pure Lorentzian diffusion the exponent $A(t)$ of Eq. (4.10) becomes

$$A(t)=-m\int_0^t dt'\left|\int_{t'}^t G(t''-t')s(t'')dt''\right| -m\int_{-\infty}^0 dt'\left|\int_0^t G(t''-t')s(t'')dt''\right|, \tag{4.12}$$

whose minimum $A_{\min}$ occurs essentially when Eq. (4.11) is satisfied. The value of $A_{\min}$ must be virtually insensitive to the precise rate of falloff of G so long as it is very slow. In order to evaluate $A_{\min}$ we can idealize G so that asymptotically G approaches *one*, not zero; then (4.11) holds rigorously. With this device we can initially investigate monotonic G's for which, e.g., for the two-pulse and three-pulse stimulated echo experiments, Eq. (4.12) is equivalent to [sign convention on s similar to that in Eqs. (1.7) and (1.8)]

$$A_{\min}=m\int_{-L}^t dt'\int_0^t G(t''-t')s(t'')dt'', \tag{4.13}$$

when $L\to\infty$. (It is necessary to let $L\to\infty$ as the last step; otherwise $A_{\min}=0\times\infty$.)

From Eqs. (4.13) it follows that

$$A_{\min}=m\int_0^t s(t'')dt''\int_{-L}^{t''}[G(t''-t')-1]dt' +m\int_0^t s(t'')(t''+L)dt''. \tag{4.14}$$

The coefficient of L vanishes in the last term because of (4.11), while in the other term which contains L we can now pass to the limit since for large arguments the modified G approaches one. After this limit is taken and a change of variables made, the integral involving $G-1$ also vanishes because of (4.11). We are left with only the expression $m\int_0^t s(t'')t''dt''$, which by integration by parts [and (4.11) again] shows that the final

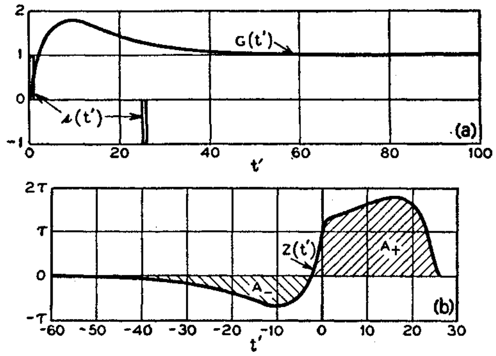

FIG. 1. Illustration of the graphical estimation of a possible stimulated echo peak decay when $T_2' \ll T_1$. (a) The echo function $s(t')$ which characterizes the stimulated echo, and also a non-monotonic Green's function or spin response function G. For large t, G falls to zero very slowly. (b) The convolution product of $G(t')$ and $s(-t')$ defines $Z(t')$. The signed area under Z, $A_+ - A_-$, is constrained to equal $T\tau$, independent of G. The absolute area under Z, $A_+ + A_-$, determines the true peak decay of the stimulated echo. In this example $A_- \approx \frac{1}{3}A_+$.

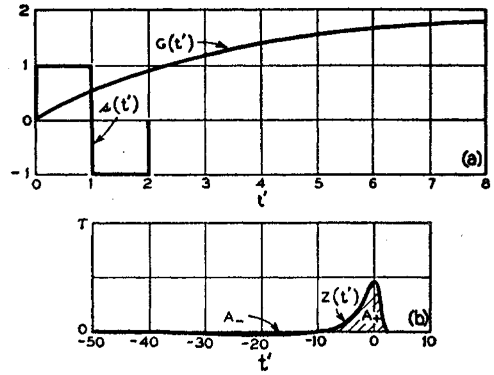

FIG. 2. Illustration of the graphical estimation of a possible two-pulse echo peak decay when $T_2' \ll T_1$. (a) The echo function $s(t')$ which characterizes the two-pulse echo, and the same Green's function as in Fig. 1, illustrated on an expanded time scale. (b) The convolution product of $G(t')$ and $s(-t')$ defines $Z(t')$. The signed area under Z, $A_+ - A_-$, is constrained to equal τ^2 independent of G. The true peak decay factor of the two-pulse echo is no longer proportional to the absolute area under Z because for small arguments the characteristic function f ceases to be linear.

exponent of M_{peak} is just

$$A_{\min} = -m\int_0^t dt' \int_0^{t'} s(t'')dt''. \qquad (4.15)$$

Thus we find a remarkable result: For suitable echo functions and if G is monotonic, so that (4.12) can be written as (4.13), the decay of the echo peak is independent of G and identical to the result derived in Sec. II. For all practical purposes the results of Sec. II still remain correct when we permit $G(t')$ to fall to zero as $t' \to \infty$ so long as this falloff is slow. The real departures from the results of Sec. II arise (i) if $G(t')$ is not monotonic (save for the very slow falloff), and (ii) if f deviates from the pure Lorentzian form of $m|y|$. Let us take up the modifications introduced by these two effects in order.

Equations (4.13) and (4.15) state that the area under the curve

$$Z(t') = -\int_0^t G(t''-t')s(t'')dt''$$

has the same value independent of G. However, if for some t', $Z(t') < 0$, then the integrand of (4.13) does not represent the integrand of (4.12), which must always be positive. To correct for the negative area erroneously introduced in (4.13) we must add twice its magnitude to the simple result of (4.13) to correctly obtain $A_{\min}$. The simple sketch in Fig. 1 for a three-pulse stimulated echo experiment should illustrate the manner in which (4.12) can be graphically estimated when $Z(t')$ becomes negative. It is clear that a greater attenuation of the peak occurs when Z goes negative than that predicted by the analysis of Sec. II. We shall exploit this mechanism in Sec. V to explain an anomalously large attenuation in a set of three-pulse experiments.

The deviation of f from a pure Lorentzian represents another way in which the presence of G can affect spin-echo experiments. Let us consider the two-pulse experiment depicted in Fig. 2. While it is quite true that the area under the curve $Z(t')$ equals τ^2, this area is distributed over an extremely long time interval during which Z remains *small*. Now it becomes important to re-examine the behavior of the characteristic function f. While we have tacitly assumed that f was "linear," i.e., $f(y) = m|y|$, we have shown on general grounds in Sec. III that this is not expected to hold true for small arguments. Instead, based on (3.15), $f(y) \approx my^2/2\rho$ when $y < \rho$, and thus f can be significantly reduced from $m|y|$. To calculate the two-pulse attenuation for the case illustrated in Fig. 2, we should not use $m\int_{-\infty}^t dt' \times |Z(t')|$, but, as an extreme, we should use

$$A_{\min} = (m/2\rho)\int_{-\infty}^t Z^2(t')dt'. \qquad (4.16)$$

As a crude estimate of the effect of (4.16) we let $Z(t') = \alpha\tau$, $\alpha \ll 1$, which must therefore extend over a time interval τ/α. From (4.16) it follows that

$$A_{\min} \approx m\tau^2(\alpha\tau/2\rho). \qquad (4.17)$$

The τ dependence of this result is not necessarily significant, rather it is the fact that less attenuation of the echo peak may actually take place than otherwise expected whenever $(\alpha\tau/2\rho) < 1$. An estimate of this parameter for an example discussed in the next section is about 0.1, and thus explains the unusually small attenuation actually observed.

Without a detailed knowledge of what function to assume for G, it is difficult to make any further remarks about expected echo behavior other than the qualitative ones that we have already mentioned.

Instantaneous Diffusion by the rf Pulses

The application of an rf pulse flips a small fraction δ of spins, the A spins, which causes essentially an instantaneous unbalance of frequencies at the A and B spins alike. A rapid B-spin reaction to this unbalance introduces what we shall term an instantaneous diffusion at the A sites. Clearly, an initial delta function of frequency $\delta(\omega-\omega_0)$ is spread by the pulse into a Lorentzian,

$$(\pi/\Omega)/[1+(\omega-\omega_0)^2/\Omega^2]^{\frac{1}{2}}, \tag{4.18}$$

because a Lorentzian is the frequency distribution of a low density of spins—as the A spins are—with a dipolar interaction. Equation (4.18) is derived in detail in Appendix C (for the same model as in Sec. III), where we show further that

$$\Omega=2\pi^2\delta n\gamma\mu/3(=\delta m/r). \tag{4.19}$$

Each time a pulse is applied we should expect an instantaneous spreading of the instantaneous spin distribution by the distribution (4.18), or more generally by

$$\mathcal{P}(\omega)=(2\pi)^{-1}\int \exp[iy(\omega-\omega_0)-(\delta/r)f(y)]dy. \tag{4.20}$$

It is not difficult to include this effect into the formal analysis of Sec. II. In particular, each time a pulse is applied we must compress into a very short time Δt the natural diffusion that would take place in a longer time interval δ/r. Thus at each pulse $f\rightarrow(\delta/r\Delta t)f$, and in the limit $\Delta t\rightarrow 0$ we replace f by

$$f(y;t')=[1+\textstyle\sum_p(\delta/r)\delta(t'-t_p)]f(y), \tag{4.21}$$

where t_p is the time of the pth 90° pulse interval. For simplicity we ignore any correlation between the effects of each 90° pulse. Thus we consider one 180° pulse as the limit of two independent 90° pulses.

To find the influence of instantaneous diffusion on spin-echo peaks we substitute the time-dependent f of (4.21) into the general formula Eq. (2.14). (If $\delta\ll 1$ then no shift of the echo peak should occur.) The modified peak amplitude $\bar{M}_{\text{peak}}$ can be expressed in the form NM_{peak}, where M_{peak} is given in (2.14), and

$$\begin{aligned}N&=\exp\left\{-\sum_p(\delta/r)\int_0^t dt'\,\delta(t'-t_p)f\left[\int_0^{t'}s(t'')dt''\right]\right\}\\&=\exp\left\{-(\delta/r)\sum_p f\left[\int_0^{t_p}s(t'')dt''\right]\right\}.\end{aligned} \tag{4.22}$$

For Lorentzian diffusion, Eq. (4.22) becomes

$$N=\exp\left\{-\Omega\sum_p\left|\int_0^{t_p}s(t'')dt''\right|\right\}. \tag{4.23}$$

If (4.23) is specialized to a two-pulse echo then

$$N=\exp(-2\Omega\tau), \tag{4.24}$$

which gives rise to a linear decay law.

The general characteristics of the more realistic diffusion models discussed in this section—the effects of the spin-response function and of the instantaneous diffusion—will now be used in interpreting several experimental results.

V. COMPARISON WITH EXPERIMENT

Mims *et al.*[13] have observed various electron spin resonance lines in either the Ce or Er ions with which they have lightly doped ($n\approx10^{18}$/cc) $CaWO_4$ crystals. The presence of Er in the crystal was generally decisive in determining the diffusion rate in a manner such that a T_1 sample resulted. This behavior still persisted even when roughly the same amount of Ce was present, and also when the resonance of the Ce ions was being studied. It is data from just such a "mixed" sample that we study as our "T_1 example." However, when Ce was the only doping then the diffusion rate was insensitive to temperature (for $T\leq4.2$°K). Data from such a sample (Ce density$\approx10^{18}$/cc) are the data we study for our "T_2 example."

By means of a series of three-pulse stimulated echo experiments in which τ is held fixed while T is varied, a study can be made of the exponential decay property of the peak with T since, according to Eq. (2.16),

$$M_{\text{peak}}\propto\exp[-Tf(\tau)].$$

From the decay constant of such a curve, $f(\tau)$ directly follows. Similar series of three-pulse experiments for different values of τ give sufficient information to determine $f(\tau)$. With $f(\tau)$ so determined, the theory developed in this paper can be tested in a variety of ways since the predictions for many experiments, e.g., free-induction and other spin-echo experiments, are in principle determined. We shall discuss only the two- and three-pulse spin-echo experiments and relate their predicted decay, given in Eq. (2.15), to the observed behavior.

For the T_1 sample that we shall discuss the necessary data appear in Figs. 3(a), 4(a), 5(a), and 6(a) in the cited work of Mims. Exceptionally good exponential decay with T of the three-pulse stimulated echo experiments is found in this sample. In the interval 5 μsec $\leq\tau\leq20$ μsec, $f(\tau)$ follows closely a displaced straight line $f(\tau)=m(\tau-\rho)$, or, equally well, the data fit a curve of the form

$$f(\tau)=m[(\tau^2+\rho^2)^{\frac{1}{2}}-\rho], \tag{5.1}$$

where

$$m=3\times10^9\ \text{sec}^{-2}, \tag{5.2a}$$

$$\rho=2\ \mu\text{sec}. \tag{5.2b}$$

Such an analytical form for f was discussed earlier in Sec. III and Eq. (3.16) relates both m and ρ to more fundamental quantities. For an estimate of m, we take $g_{\mathrm{Er}}\approx 8$, $g_{\mathrm{Ce}}\approx 1.4$, and we assume $r\approx 1/T_1=10^2$.[13] It follows from (3.16a) that $m\approx 1.7\times 10^8$, which is to be compared with the observed value 3×10^9. The discrepancy between the predicted and observed values for m strongly suggests that T_1 processes faster by an order of magnitude than those ordinarily measured enter into the echo diffusion. This is plausible since the echo measurements on this sample take place in about one millisecond, a time insufficient for 10-msec T_1 processes to have become important. For an estimate of ρ we assume that $r_{\min}$ represents the average distance between particles in a random array with average density n. This assertion leads[23] to the relationship that $r_{\min}{}^3\approx 1/8n$. Thus using (3.16b) we find $\rho\approx 1$ μsec, in accord with (5.2b)

There remains to discuss for this sample the behavior of the two-pulse spin-echo experiments. Roughly speaking, the time integral of f in Eq. (5.1) is very nearly a parabola. If we adopt the experimental values of m and ρ, then excellent agreement with Mims' experimental two-pulse data is obtained, which is well within the experimental accuracy. The good agreement with theory given by this sample encourages one to look for other materials to study that have similar properties.[24] It seems likely that our understanding of such "ideal" T_1 samples is quite high.

Unfortunately, not all samples appear to be so simple. In the other sample—a T_2 sample—for which Mims presents extensive data there appear to be additional complications. In the first place, the three-pulse stimulated echo does not decay as a simple exponential in T. As a function of T this echo has a region with an initially fast falloff followed by a region with a simple exponential decay. It is suggestive that there may be two (or more) independent modes of decay. Suppose, for example, there were fluctuations in the density of B spins around the sites of the various observed A spins. Then there could be several different spin-spin relaxation rates, which give rise to decays with different m factors. Roughly speaking, the three-pulse peak might then be described by an equation of the form

$$A_1e^{-m_1T\tau}+A_2e^{-m_2T\tau},$$

where $A_1>A_2$ and $m_1>m_2$.

A more appropriate description of this apparent three-pulse anomaly involves a nonconstant spin response function $G(t')$ similar in general character to that shown in Fig. 1. It is clear from this figure that if T were increased practically no change in the negative area A_- would occur. Thus the change in total area would be strictly proportional to the change in T, and the echo would decay as a simple exponential. On the other hand, if T were reduced from the value illustrated in Fig. 1 a point would be reached at which A_- itself would begin to reduce. Since A_- contributes a constant loss factor to the echo for large T, the *reduction* of A_- for smaller T would be manifested as an initially fast decay of the stimulated echo. That the transition to a simple exponential decay should occur when $T\approx 1$ msec is consistent with the estimated value of T_2,[13] which, of course, is also the time-scale of the spin response function.

From the simple exponential portion of the three-pulse experiments in this T_2 sample, a fit to the law $\exp[-Tf(\tau)]$ determines $f(\tau)$. Here, too, the result for f [Fig. 4(b), and reference 13] is strikingly linear in τ, again fitting (5.1) quite well. Since the paramagnetic ion density is essentially unchanged, the prediction of 1 μsec for ρ is retained, which is consistent in order of magnitude with the observed value of 4 μsec. The observed $m=1.7\times 10^8$ sec^{-2} but, unfortunately, we cannot make an accurate estimate of m since we have no independent determination of the rate R, i.e., $1/T_2'$; clearly, though, the order of magnitude for m is consistent with our expectations for T_2'.

With $f(\tau)$ again determined to be nearly a straight line, it follows from (2.15) that the two-pulse decay should be proportional to $\exp(-m\tau^2)$. The observed data [Fig. 6(b), and reference 13] differs from this behavior in two important respects. First, there is distinctly a tendency for the two-pulse echo to fall initially as a simple exponential $\exp(-a\tau)$, where $a\approx 2\times 10^4$ sec^{-1}. Second, there is only a weak "τ^2 decay," only approximately quadratic, given by $\exp(-m'\tau^2)$ where $m'\approx m/10$. Although the linear term in the exponent makes the two-pulse echo fall faster initially than $\exp(-m\tau^2)$, within 100 μsec this elementary prediction "catches up" and thereafter predicts a greater attenuation than the combined effect of the linear and reduced "quadratic" term (m') actually indicate. We must explain the origin of both the reduced effective m value and the origin of the linear term $a\tau$.

We take up the question of the reduced m value first, for which Fig. 2 and the related discussion in Sec. IV apply. Because of the assumed long time-coherence of G the argument of f remains small. The argument of f may, for long times, be so small as to lie in the initial quadratic region of f so that the echo attenuation becomes significantly reduced. Very crudely, the reduction parameter for m is of order $a\tau/2\rho\approx 5\alpha$ for reasonable τ, where α is the fraction of τ actually reached by the variable Z: $\alpha\approx\tau/T_2$ for small τ (as τ approaches to within order of magnitude of T_2, such a linear approximation is inaccurate and α is probably much less than τ/T_2). At any rate, we estimate that $\alpha\approx 20/10^3$ so that $m'\approx m/10$. While this calculation is understandably very crude, it does make plausible the

[23] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943), reprinted in *Selected Papers on Noise and Stochastic Processes*, edited by N. Wax (Dover Publications, New York, 1954).

[24] Evidence for similar behavior for donors in silicon has been given by J. P. Gordon and K. D. Bowers, Phys. Rev. Letters **1**, 368 (1958).

reduction of the "normal" quadratic effect to some lesser value, as was observed.

Lastly, we study the initial decay of the echo peak as $\exp(-a\tau)$. This decay we attribute to the instantaneous diffusion brought about by the rf pulses. Since the characteristic function f is virtually linear in this sample we identify a with Ω in Eq. (4.19). Adopting $R=1/T_2\approx 10^3$, we find $\Omega\approx 10^4$ sec^{-1} in good agreement with the observed value 2×10^4. It is clear that the linear effect is apparent principally because of the reduced quadratic effect. The reduced quadratic effect is in turn a consequence of the slow initial rise in the spin response function. Thus, a linear two-pulse echo decay may very likely be common to many T_2 samples. Recent measurements of Mims have shown that at even lower Ce dopings an auxiliary linear decay appears, which to a first approximation is insensitive to the paramagnetic ion density. This decay is similar to other instantaneous diffusion decays, but is probably due to nuclear spins of nonmagnetic ions that are close to A sites.

It appears that all features of the observed echo decays for both of the T_1 and T_2 samples discussed in this section can be accounted for by the theory developed in this paper.

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APPENDIX A

In this Appendix we calculate and discuss in detail the result of the ensemble average $M(t)$ for stationary Markoff processes when the conditional probability (2.18) applies.

In order to calculate the modified value of $M(t)$ it is necessary to repeat a calculation similar to that carried out in Sec. II. Since the modified distribution (2.18) is also Markoffian, the evaluation is similar in many respects, and we shall only indicate the necessary modifications to be made in the major steps of the earlier derivation. Equations (2.2) and (2.3) still apply, but Eq. (2.4) is slightly altered by a term in R:

$$P(\omega_{l+1},\epsilon;\omega_l)=(2\pi)^{-1}\int \exp[iy_{l+\frac{1}{2}}(\omega_{l+1}-\omega_l)+i\epsilon R\omega_l y_{l+\frac{1}{2}}-\epsilon f(y_{l+\frac{1}{2}})]dy_{l+\frac{1}{2}}. \quad \text{(A1)}$$

While this equation does not agree with (2.18) for all ϵ, this is an adequate representation for infinitesimal time intervals. If the conditional distribution (A1) is substituted in (2.5) then the series of identities analogous to (2.7) become

$$y_{l+\frac{1}{2}}=y_{l-\frac{1}{2}}+\epsilon R y_{l+\frac{1}{2}}+\epsilon s_l, \quad \text{(A2a)}$$

together with the boundary condition

$$y_{M+\frac{1}{2}}=0. \quad \text{(A2b)}$$

The solution to this pair of equations is just

$$y_{l+\frac{1}{2}}=-\epsilon\gamma^{l+1}\sum_{m=l+1}^{M}\gamma^{-m}s_m, \quad \text{(A3)}$$

where

$$\gamma=(1-\epsilon R)^{-1}.$$

If Eq. (A3) for $y_{l+\frac{1}{2}}$ is substituted into the integrand of (2.6), and further the limit $M\to\infty$, $\epsilon\to 0$, and $(M+1)\epsilon=t$ is taken it follows that

$$M(t,\omega_0)=\exp\left\{i\omega_0\int_0^t e^{-Rt'}s(t')dt' -\int_0^t f\left[-e^{Rt'}\int_{t'}^t e^{-Rt''}s(t'')dt''\right]dt'\right\}, \quad \text{(A4)}$$

which reduces to the previously derived expression, Eq. (2.10), when $R\to 0$.

It is next necessary to average $M(t,\omega_0)$ with the initial distribution $P_1(\omega_0)$. Two particular cases will be considered: The first assumes that a narrow distribution of spins are affected by H_1 and thus $P_1(\omega_0)$ can be taken equal in form to the equilibrium distribution $P(\omega)$ in Eq. (2.19). After discussing this case we analyze a model for which H_1 is assumed large [relative to $P(\omega)$] and it is therefore necessary to make a subsequent average over a broad distribution of "spin-packet" center frequencies. It should be remarked that it is only the former case which represents an ergodic ensemble and thus includes the Markoff-Gaussian ergodic analyses discussed elsewhere.[3,7]

Single Spin Packet Excited

For our first example, the average of (A4) in the distribution (2.19) is easily found to be

$$M(t)=\exp\left\{-\int_0^t f\left[-e^{Rt'}\int_{t'}^t e^{-Rt''}s(t'')dt''\right]dt' -\int_0^\infty f\left[-e^{-Rt'}\int_0^t e^{-Rt''}s(t'')dt''\right]dt'\right\}; \quad \text{(A5)}$$

this result applies quite generally both to free induction and to spin-echoes whenever the initial distribution is given by the equilibrium distribution. Equation (A5) is of course a special case of (B10) when $G(t)=\exp(-Rt)$.

In the free induction case ($M\equiv F$) $s(t')=1$, and (A5)

can be somewhat simplified:

$$F(t)=\exp\left\{-\int_0^t f[-R^{-1}(1-e^{-Rt'})]dt' -\int_0^\infty f[-R^{-1}(1-e^{-Rt})e^{-Rt'}]dt'\right\}. \quad \text{(A6)}$$

For Gaussian diffusion, where $f(y)=ky^2$, it follows directly from (A6) that

$$F(t)=\exp\{-(k/R^3)[Rt-(1-e^{-Rt})]\}, \quad \text{(A7)}$$

an expression obtained, for example, by Anderson as the Fourier transform of the corresponding line shape, and discussed also by Herzog and Hahn. If R is sufficiently large, say through exchange mechanisms, the free induction signal decays approximately as $\exp(-kt/R^2)$, characteristic of a significantly narrowed, Lorentzian line shape.

Interestingly, these are not the only conditions which lead to a simple exponential falloff for the free-induction signal. Let us consider the predictions based on (A6) for a Lorentzian distribution where $f(y)=m|y|$. In this case we obtain the free-induction decay

$$F(t)=\exp(-mt/R), \quad \text{(A8)}$$

which is strictly exponential in t for *all* ranges of Rt. Observe that here the line shape $I(\omega)$ is a Lorentzian, which happens to be identical with the equilibrium distribution $P(\omega)$. It can be shown that only for Lorentzian-Markoffian, homogeneous diffusion is $I(\omega)=P(\omega)$; however, if R is small—and thus the diffusion is slow—$I(\omega)\approx P(\omega)$ quite generally.

An approximately exponential falloff of the free induction signal would be also expected if $f(y)$ were given by a more "realistic" form (say, as $m[(y^2+\rho^2)^{\frac{1}{2}}-\rho]$) rather than $m|y|$. If $\rho R\ll 1$, then Eq. (A8) should represent $F(t)$ closely for the modified characteristic function. Hence existing free-induction data consistent with (A7), wherein $Rt\gg 1$, are also consistent with a nearly Lorentzian diffusion model as well.

We now turn to a discussion of Eq. (A5) for spin-echo experiments. Let us analyze two specific cases in detail, Gaussian and Lorentzian, to see the effect of a significant R value on various spin-echoes.

For Gaussian diffusion, Eq. (A5) quite generally takes on a particularly simple analytical form,

$$M(t)=\exp\left[-\frac{1}{R}\int_0^t dt'\int_0^{t'} dt''\, e^{-R(t'-t'')}s(t')s(t'')\right], \quad \text{(A9)}$$

which is a special case of the more general formula,

$$\exp\left[-\int_0^t dt'\int_0^{t'} dt''\, \hat{\rho}_c(t'-t'')s(t')s(t'')\right],$$

where $\hat{\rho}_c$ is the normalized covariance function, not necessarily representing a Markoffian process. The maximum of (A9) for echo experiments occurs generally at a time t such that

$$\int_0^t e^{Rt''}s(t'')dt''=0, \quad \text{(A10)}$$

which, e.g., states that $t<2\tau$ for two-pulse experiments in contrast to the result stated by Herzog and Hahn.[7]

The specific evaluation of (A9) for two-pulse spin-echo experiments is

$$M(t)=\exp\{-(k/R^3)[Rt-3-e^{-Rt}+2e^{-R\tau}+2e^{-R(t-\tau)}]\}, \quad \text{(A11)}$$

while the attenuation at the peak [which occurs when $Rt=\ln(2e^{R\tau}-1)$] is expressed by

$$M_{\text{peak}}=\exp\{-(k/R^3)[\ln(2e^{R\tau}-1)-2+2e^{-R\tau}]\}. \quad \text{(A12)}$$

Both Eqs. (A11) and (A12) differ from previous results.[7] To illustrate the modification that (A12) introduces, we plot in Fig. 3 the ratio of the exponents of (A12) and the exponent of the "normal" two-pulse Gaussian decay, $2k\tau^3/3$, as given by (2.15). If we let $R\tau=x$, then

$$y=3[\ln(2e^x-1)-2+2e^{-x}]/2x^3 \quad \text{(A13)}$$

is the curve marked "Gaussian" in Fig. 3. The variable plotted is related to that in Fig. 1 of reference 7. We wish to emphasize that spin-echo signals with sizeable R values *and* small H_1 fields are generally characterized by the unusual times at which they peak [see (A10)]. This feature alone should signal the presence of rapid fluctuations taking place, i.e., a large R.

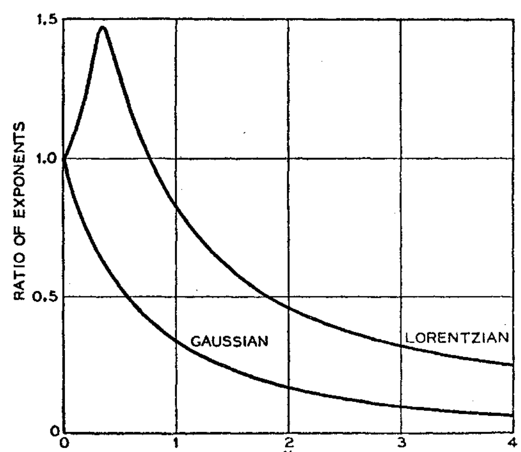

FIG. 3. Ratio of exponents in the decay of the peak for two-pulse experiments when only a narrow distribution of spins is excited. The variable $x=R\tau$, the Markoffian decay rate times the pulse interval. A ratio less than one signifies less attenuation of the peak when the decay rate R is significant than when R can be neglected. For Gaussian diffusion, the relative attenuation is always reduced when R is included; for Lorentzian diffusion the decay first increases then decreases. In both cases the peak of the pulse does not occur when $t=2\tau$.

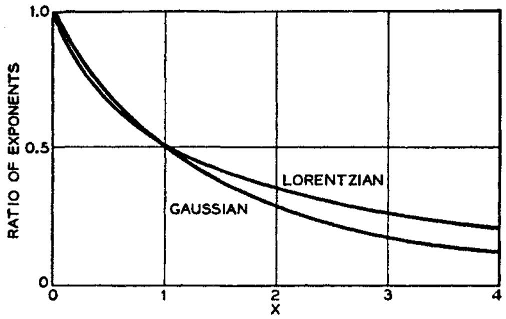

FIG. 4. Ratio exponents in the decay of the peak for two-pulse experiments when a broad distribution of spins are excited. The variable $x = R\tau$. For both Gaussian and Lorentzian diffusion the relative attenuation is always reduced when R is included. In both cases the peak of the pulse occurs when $t = 2\tau$.

The qualitative features of the preceding argument are retained in the case of Lorentzian diffusion based on Eq. (A5). Unfortunately, no general simplification such as (A9) takes place here and each case must be treated individually. For the two-pulse spin-echo, for example,

$$M(t) = \exp\left(-\frac{m}{R^2}\{R(t-\tau) - \ln[2 - e^{-R(t-\tau)}] + |R\tau - \ln[2 - e^{-R(t-\tau)}]|\}\right). \quad \text{(A14)}$$

By maximizing (A14) we find the peak occurs at a time t such that

$$\begin{aligned} Rt &= -\ln(2e^{-R\tau} - 1); \quad R\tau < \ln(4/3), \\ Rt &= R\tau + \ln(3/2); \quad R\tau \geq \ln(4/3), \end{aligned} \quad \text{(A15)}$$

and the peak value of M is then

$$\begin{aligned} M_{\text{peak}} &= \exp[(m/R^2)\ln(2e^{R\tau} - e^{2R\tau})]; \\ &\qquad R\tau < \ln(4/3), \\ M_{\text{peak}} &= \exp\{-(m/R^2)[R\tau - \ln(32/27)]\}; \\ &\qquad R\tau \geq \ln(4/3). \end{aligned} \quad \text{(A16)}$$

The exponent of M_{peak}, normalized by the factor $m\tau^2$, is plotted in Fig. 3; this curve, labeled by the word "Lorentzian," illustrates the influence of rapid frequency fluctuations on the peak of two-pulse spin-echo signals which undergo Lorentzian diffusion. As in the Gaussian case, the two pulse spin echoes are distinguished by the fact that they no longer peak at $t = 2\tau$. However, whenever $Rt \ll 1$ all of the results of Gaussian, Lorentzian, or any other form of diffusion, reduce to the results already derived in Sec. II as can readily be checked.

Many Spin Packets Excited

When many packets are excited it is necessary to consider the variation in individual spin-packet center frequencies. Recall from Eq. (2.20) that it is the linear term in $f(y)$ that governs $\langle\omega\rangle$ according to

$$\langle\omega\rangle = -if'(0)/R. \quad \text{(A17)}$$

Let us take Eq. (A5) and give to $f(y)$ a linear term by explicitly adding the term $i\bar{\omega}yR$. One of the two time integrals that result can be directly carried out and we find that

$$M(t;\bar{\omega}) = \exp\left[i\bar{\omega}\int_0^t s(t'')dt''\right]M(t), \quad \text{(A18)}$$

where $M(t)$ is identical to (A5). No R dependence appears in the $\bar{\omega}$ term because the spin-packet *center* frequency is not forced to diffuse preferentially in either direction. If only one packet is excited, $M(t;\bar{\omega})$ contains a rapidly changing phase factor ($\bar{\omega} \propto H_0$) which is masked by signal detection. However, if a broad distribution of spin packets is excited, we must average $M(t;\bar{\omega})$ further in $P_c(\bar{\omega})$, a spin-packet center frequency distribution. As a result (assuming R, f, etc., to be independent of $\bar{\omega}$)

$$\begin{aligned} \bar{M}(t) &\equiv \int M(t;\bar{\omega})P_c(\bar{\omega})d\bar{\omega} \\ &= \tilde{P}_c\left[-\int_0^t s(t')dt'\right]M(t), \end{aligned} \quad \text{(A19)}$$

where $\tilde{P}_c$ is the Fourier transform of P_c.

For free-induction signals the effect of P_c is to introduce a new multiplicative time dependence to the decay over and above the result of $M(t)$ alone. To be more specific than this would require detailed knowledge of what expression to assume for $\tilde{P}_c$; the question of free-induction decay we do not pursue further.

For spin-echo signals we assume that the peak point of time and the signal shape are determined by $\tilde{P}_c$, as would be so if P_c were sufficiently broad. Since P_c is normalized and non-negative the maximum of $\tilde{P}_c$, and by our assumption $\bar{M}$, occurs at a time t such that

$$\int_0^t s(t')dt' = 0, \quad \text{(A20)}$$

a relation independent of R and reminiscent of the condition derived in Sec. II. Furthermore, narrow echo signals will also result if P_c is broad enough. Hence the introduction of a broad distribution of spin-packet center frequencies leads to a narrow echo, and has restored the echo peak to the moment predicted by the elementary theory.

But the peak amplitude need not be identical to that derived in Sec. II. Rather

$$M_{\text{peak}} = M(t),$$

where t satisfies (A20). For particular examples we can study the two cases for which $M(t)$ was determined above. For example, for Gaussian diffusion in a two-

pulse experiment we simply substitute $t=2\tau$ in (A11):

$$M_{\text{peak}}=\exp\{-(k/R^3)[2R\tau-3+4e^{-R\tau}-e^{-2R\tau}]\}. \quad \text{(A21)}$$

On the other hand, for Lorentzian diffusion in a two-pulse experiment it follows from (A14) that

$$M_{\text{peak}}=\exp\{-(2m/R^2)[R\tau-\ln(2-e^{-R\tau})]\}. \quad \text{(A22)}$$

In Fig. 4 we plot, as in Fig. 3, normalized forms of the exponents of (A21) and (A22) as functions of $x=R\tau$. If many packets are excited and if Markoffian decay with a nontrivial R is expected, then Eq. (A22), or perhaps (A21), represents the expected behavior. Of course, if $R\tau\ll 1$, (A21) and (A22) also reduce to the predictions of Sec. II.

Other echo functions can be studied with the formulas presented above to determine the behavior for either a narrow or a broad distribution of excited spins.

APPENDIX B

Herein we calculate the ensemble average $M(t)$ for a general class of non-Markoffian distributions so as to establish Eq. (4.4) in terms of the kernal K in Eq. (4.3b). We follow closely the type of derivation discussed in Sec. II. However, because of the non-Markoffian character of the ensemble we choose not to break up $M(t)$ as in (2.1) but rather to "prepare the initial state" by integrating over all skeletonized frequency histories from $-\infty$ to t. To maintain clear and meaningful results at all stages we continue to resist the temptation to employ continuous integration techniques, and instead define initially

$$M_{M,L}=\frac{1}{(2\pi)^{M+L+2}}\int\cdots\int \exp[i\epsilon^2 \textstyle\sum_{l,m} y_{l+\frac{1}{2}}K_{l-m}\omega_m + i\epsilon\sum_m s_m\omega_m - \epsilon\sum_l f(y_{l+\frac{1}{2}})]\displaystyle\prod_{-L}^{M} dy_{l+\frac{1}{2}} \prod_{-L}^{M+1} d\omega_m, \quad \text{(B1)}$$

where all sums in the exponent cover all variables; in the limit $L\to\infty$, $M\to\infty$, $\epsilon\to 0$, $L\epsilon\to\infty$, $M\epsilon\to t$, Eq. (B1) defines the desired ensemble average $M(t)$. We first carry out the $M+L+2$ integrations over ω_m, which lead to

$$M_{M,L}=\int\cdots\int \exp[-\epsilon\textstyle\sum_l f(y_{l+\frac{1}{2}})] \displaystyle\times\prod_{-L}^{M+1}\delta(\epsilon^2\textstyle\sum_l y_{l+\frac{1}{2}}K_{l-m}+\epsilon s_m)\displaystyle\prod_{-L}^{M} dy_{l+\frac{1}{2}}. \quad \text{(B2)}$$

The y integrations generate the constraints

$$\epsilon\textstyle\sum_l y_{l+\frac{1}{2}}K_{l-m}+s_m=0, \quad \text{(B3)}$$

the solution of which, say $\hat{y}_{l+\frac{1}{2}}$, is then substituted into $\exp[-\epsilon\sum f(\hat{y}_{l+\frac{1}{2}})]$ to give $M_{M,L}$.

What are some properties of K_{l-m}? For the (Markoffian) example analyzed in Sec. II

$$K_{l-m}=\epsilon^{-2}(\delta_{l+1,m}-\delta_{l,m}),$$

so that K represents the difference analog of $\delta'(t'-t'')$. With this particular K the $m=M+1$ equation for (B3) reduces to

$$\epsilon^{-1}y_{M+\frac{1}{2}}+s_{M+1}=0, \quad \text{(B4)}$$

since $y_{M+\frac{3}{2}}$ does not exist. For $m<M+1$ a standard difference equation results from Eq. (B3). The interpretation given to (B4) as $\epsilon\to 0$ is that of a boundary condition, namely, $y_{M+\frac{1}{2}}=0$.

A similar investigation may be carried out for other possible K kernels, such as, for example,

$$\epsilon^{-3}(\delta_{l+1,m}-2\delta_{l,m}+\delta_{l-1,m}),$$

which corresponds to the second derivative kernel $\delta''(t'-t'')$. In this example we would find two boundary conditions contained in the set of Eqs. (B3), namely, $y_{M+\frac{1}{2}}=0$ and $(y_{M+\frac{1}{2}}-y_{M-\frac{1}{2}})/\epsilon=0$.

The general picture of what (B3) signifies should be fairly clear now on the basis of the study of these two skeletonized cases. Let us first rewrite (B3) in the limit $\epsilon\to 0$ as an integral equation:

$$\int_{-\infty}^{t} y(t')K(t'-t'')dt'+s(t'')=0. \quad \text{(B5)}$$

According to our interpretation of Eq. (B3), the desired solution to Eq. (B5) must satisfy certain boundary conditions at $t'=t$, which are

$$y(t)=y'(t)=\cdots=y^p(t)=0, \quad \text{(B6)}$$

where p is one less than the highest order differential operator contained in K.

Let us define a Green's function G according to the relation

$$\int G(t'-t'')dt''K(t''-t''')=\delta(t'-t'''), \quad \text{(B7)}$$

whose solution we require to be causal in the sense that $G(t')\equiv 0$ if $t'<0$. The demand for causality puts a standard requirement on the location of zeros of $\tilde{K}(\omega)$ that we shall assume to be satisfied. If the highest derivative represented by K is of the $(p+1)$th order, then it follows from (B7) that

$$(d/dt')^l G(t')\,|_{t'=0}=0 \quad \text{(B8)}$$

for $l=0, 1, 2, \cdots, p-1$. In terms of G the solution to (B5) is expressed by

$$y(t')=-\int G(t''-t')s(t'')dt''; \quad \text{(B9)}$$

the upper limit in (B9) is effectively t because $s\equiv 0$ if $t''>t$; likewise, the lower limit is effectively zero if $t'<0$ since $s\equiv 0$ if $t''<0$, otherwise causality imposes t' as the lower limit. It is easy to see that the conditions

(B8) on G combined with the one additional integral in (B9) suffice to insure that all the necessary boundary conditions on $y(t')$ are satisfied.

Having determined the pertinent solution to Eq. (B5), we return to the analog of (B2) and substitute the result (B9) into the appropriate exponential factor. It follows that the desired ensemble average finally becomes

$$M(t)=\exp\left\{-\int_{-\infty}^{t} f\left[-\int_{-\infty}^{t} G(t''-t')s(t'')dt''\right]\times dt'\right\}, \quad \text{(B10)}$$

which is just the form adopted in (4.4), thus establishing its validity.

Another quite different use of Eq. (B10) is also worth illustrating. Let us calculate the final equilibrium distribution $P(\omega)$ for the present ensemble of frequency histories. Clearly

$$P(\omega)=\langle\delta[\omega-\omega(0)]\rangle,$$

which can be written in the form

$$P(\omega)=\frac{1}{2\pi}\int e^{ia\omega}\langle e^{-ia\omega(0)}\rangle da. \quad \text{(B11)}$$

It follows from the definition of $M(t)$ that we can formally evaluate the necessary average in (B11) simply by setting $s(t'')=-a\delta(t'')$ in Eq. (B10). Thus

$$P(\omega)=(2\pi)^{-1}\int \exp\left\{ia\omega-\int_0^\infty f[aG(t')]dt'\right\}da, \quad \text{(B12)}$$

which is just the appropriate extension of (2.19). If eventually G falls to zero at a very slow rate R, whose precise functional form is not too important, i.e., whether it is $\exp(-Rt)$ or $\exp(-R^2t^2)$, or whatever, then the integral over G in (B12) will be proportional to R^{-1}. If for T_2 samples R is identified as $1/T_2'$, then the present analysis provides the justification for footnote 22.

While we have proceeded in this appendix as if K contained only a finite number of differential operators, it is probably true that (B10) is still correct if K contained infinite-order differential operators, and thus perhaps differential operators of nonintegral order. Equation (B10) represents, therefore, a result of extreme generality that may have various uses outside our present application.

APPENDIX C

The determination of the "instantaneous" diffusion introduced by the pulses themselves can be readily found for the dipolar interaction model analyzed in Sec. III. The distribution in frequency is expressible in terms of the distributions of the independent moments:

$$\mathcal{P}(\omega)=(2\pi)^{-1}\sum\int dy\,\exp\{iy[\omega-\textstyle\sum_j{}'\,\gamma\mu_j/r_{ij}^3]\}\times\prod_k\mathcal{P}(\mu_k). \quad \text{(C1)}$$

Before the rf pulse, let us say, each μ_k has zero spread so that $\mathcal{P}(\omega)=\delta(\omega-\omega_0)$, where ω_0 is determined by the initial spin configuration. The application of a pulse flips a fraction δ of the spins whose positions we do not know a priori. The uncertainty in just which spins were flipped by the pulse introduces the uncertainty into $\mathcal{P}(\omega)$. A sum over the various possible sets of flipped spins is then equivalent to an average over positions for each of the flipped spins. With a fixed change of each μ_j, Eq. (C1) becomes

$$\mathcal{P}(\omega)=(2\pi)^{-1}\int dy\,e^{iy(\omega-\omega_0)}\textstyle\prod^*\langle\exp(-iy\gamma\mu/r_{ij}^3)\rangle_r, \quad \text{(C2)}$$

where the brackets denote an average over positions and where the starred product is only over flipped spins. The position average we carry out by assuming the flipped spins to be uniformly and independently distributed. Letting V represent the volume of space, we find

$$\langle\exp(-iz/r^3)\rangle_r=1-V^{-1}\int[1-\exp(-iz/r^3)]d\mathbf{r}; \quad \text{(C3)}$$

raising this expression to the (δN)th power, and passing to the limit $N\to\infty$, $V\to\infty$, $N/V=n$, Eq. (C2) becomes

$$\mathcal{P}(\omega)=(2\pi)^{-1}\int dy\,e^{iy(\omega-\omega_0)}e^{-\delta K(y)}, \quad \text{(C4)}$$

where $K(y)$ is defined and evaluated in Eq. (3.13). Any imaginary part present in (C3) just corresponds to a shift of the center frequency and has been ignored since that need not concern us.

It is clear that $\delta K(y)=\Omega|y|$ will lead to a Lorentzian diffusion, for which Eq. (4.19) Ω follows directly from (3.13). For nondipolar interactions it is natural to generalize (C4) to an arbitrary characteristic function f, which thus leads directly to (4.20).