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Gaussian Phase Approximation for Evaluating the Decay of NMR Spin Echoes

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Gaussian-approximation formalism for evaluating decay of NMR spin echoes

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We present a formalism for evaluating the amplitude of the NMR spin echo and stimulated echo as a function of pulse spacings, for situations in which the nuclear spins experience an effective longitudinal magnetic field $h_z(t)$ resulting from an arbitrary number of independent sources, each characterized by its own arbitrary time correlation function. The distribution of accumulated phase angles for the ensemble of nuclear spins at the time of the echo is approximated as a Gaussian. The development of the formalism is motivated by the need to understand the transverse relaxation of ^{89}Y in $YBa_2Cu_3O_7$, in which the ^{89}Y experiences $^{63,65}Cu$ dipolar fields which fluctuate due to $^{63,65}Cu$ T_1 processes. The formalism is applied successfully to this example, and to the case of nuclei diffusing in a spatially varying magnetic field. Then we examine a situation in which the approximation fails—the classic problem of chemical exchange in dimethylformamide, where the methyl protons experience a chemical shift which fluctuates between two discrete values. In this case the Gaussian approximation yields a monotonic decay of the echo amplitude with increasing pulse spacing, while the exact solution yields distinct ''beats'' in the echo height, which we confirm experimentally. In light of this final example the limits of validity of the approximation are discussed. [S0163-1829(96)05630-5]

I. INTRODUCTION

The problem of nuclear spins which experience a fluctuating effective local magnetic field is ubiquitous in NMR. Often situations arise in which only the z component h_z of the local field **h** plays an important role (where z is also the direction of the applied static field), affecting the transverse relaxation process (T_2) only. One classic example is the dipolar coupling of nuclear species ''*B*'' to an unlike species ''*A*'' which is being observed. Only the secular terms in the ''*A*-*B*'' dipolar Hamiltonian, whereby the ''*A*'' spins experience an effective z component of magnetic field emanating from the B spins, are important. Herzog and Hahn[1] treat situations in which this dipolar coupling field is modulated, either through dipolar interactions within the B spin system or through the application of radio-frequency magnetic fields at the B Larmor frequency. More recently Walstedt and Cheong[2] have demonstrated the importance of ^{63}Cu-^{17}O dipolar interactions in their ^{17}O T_2 data for high-T_c superconductors. In their case the dipolar field fluctuations experienced by ^{17}O result from very rapid $^{63,65}Cu$ spin-lattice relaxation (T_1) processes. Another such situation is the problem of spins diffusing in a magnetic-field gradient;[3–5] in this case the magnetic fields are uniform in time, yet the field experienced by the nuclear spins is modulated due to their motion within the gradient.

In our research on vortex fluctuations in $YBa_2Cu_3O_7$ we find that the ^{89}Y T_2 is effected by the $^{63,65}Cu$-^{89}Y dipolar interactions in a manner identical to that described by Walstedt and Cheong. They performed numerical Monte Carlo simulations of the $^{63,65}Cu$ T_1 process, and its effect upon the ^{17}O T_2, and obtained results which agreed quantitatively with experiment. In order to understand our own ^{89}Y T_2 data, and to obviate the need for numerical simulation, we have sought and obtained an approximate analytical method which can be used to model T_2 behavior resulting when spins experience fluctuating longitudinal fields.

At the outset we must distinguish between transverse relaxation as measured by the envelope of the free-induction decay (FID) (T_2^*), and the decay of the amplitude of the spin echo as a function of 2τ, where τ is the spacing between the 90 and 180° pulses. In many cases, especially for solids and quadrupolar nuclei, there exist static (inhomogeneous) broadening mechanisms in addition to the dynamic processes which are of interest, and in these cases the dynamical behavior is accessible *only* through the spin-echo peak height, since the spin echo refocuses the inhomogeneous effects. Treatments of the free-induction decay are relatively plentiful in standard textbooks,[6–8] while treatments of transverse relaxation for the spin echo are somewhat less common.[9,10,1,8] Anderson and Weiss[11] approached the problem taking a Gaussian distribution of instantaneous fields h_z, fluctuating with an arbitrary correlation function. Their approach has also been generalized to treat the spin-echo amplitude.[8] There is a distinction, however, between the Anderson-Weiss approach, and a subsequent approximation taken by Neumann,[12] and later by Tarczon and Halperin,[9] in treating transverse relaxation of spins undergoing restricted diffusion in a magnetic-field gradient. In this situation the distribution of instantaneous fields h_z is clearly non-Gaussian. The Neumann approximation, however, is to take the distribution of accumulated *phases* at the time of the spin echo to be Gaussian distributed. It is reasonable to expect that this is a less stringent condition.

The approach which we take is identical in physical content to that of Neumann.[12] We generalize the approach, however, to allow for an arbitrary number of independent sources field h_z, each having its own arbitrary correlation function. This generalization yields an expression which is convenient and transparent for our application of the method to the calculation of the ^{89}Y T_2 in $YBa_2Cu_3O_7$, which experiences dipolar fields from both ''plane'' and ''chain'' ^{63}Cu and ^{65}Cu, each producing dipolar fields with differing correlation functions. We show that our approach also yields transverse

relaxation results obtained by Tarczon and Halperin[9] for spins diffusing in an arbitrary magnetic-field profile, but with a simple physical interpretation for their results: that each spatial Fourier component of the magnetic field distribution acts as an independent source of fluctuating field with an exponential correlation time related to the Fourier wave vector and the diffusion coefficient D.

Finally we apply our expression (in this case with only a single source of h_z) to a classic problem: that of chemical exchange, specifically for the molecule dimethylformamide. Here the methyl protons experience a chemical shift which fluctuates between two discrete values on a time scale which shortens with increasing temperature. The transverse relaxation in this case can be derived *exactly*, and we show, both experimentally and theoretically, that in the limit of long correlation times the echo height (as a function of pulse spacing) contains ''beats'' which are not predicted in our approximation. In light of this final example we discuss the limits of validity of the model.

II. GENERAL FORMALISM

We consider an ensemble of spins, initially pointing along the z axis, and the trajectories of their magnetic moment vectors during the time following a 90° and then a 180° pulse. [Implicitly we are taking an average over a set of *sub*ensembles of nuclear spins such that within each subensemble the spins experience the same fluctuating magnetic field with z component $h_z(t)$.] We operate in a rotating frame such that ensemble average $\langle h_z(t)\rangle$ of the fluctuating-field vanishes. Immediately following a 90° pulse the spins are oriented along what we define to be the x direction. Subsequently spins respond to their local field $h_z(t)$ and rotate within the xy plane, accumulating a phase (measured from the initial x axis) $\phi(t)$:

$$\phi(t)=\gamma\int_0^t h_z(t')dt', \tag{1}$$

where γ is the gyromagnetic ratio of the processing nuclear spins. A 180° pulse (about the x axis) at time τ then changes the sign of the phase, so that the phase at the time of the echo is given by

$$\phi(2\tau)=\gamma\int_\tau^{2\tau} h_z(t'')dt''-\gamma\int_0^\tau h_z(t')dt'. \tag{2}$$

Since the time dependence of the fluctuating field is random, the phase is also a random variable.

The NMR signal size at time 2τ is given by the product of M_0 (the signal size for $\tau=0$) and the average of $\cos\phi$:

$$M(2\tau)=M_0\frac{\int(\cos\phi)P(\phi)d\phi}{\int P(\phi)d\phi}, \tag{3}$$

where $P(\phi)$ is the probability distribution function for the accumulated phase ϕ. We see immediately from Eqs. (2) and (3) that for *time-independent* magnetic fields h_z the spin-echo height is undiminished; ϕ will be zero both at $t=0$ and at $t=2\tau$. For time dependent fields, however, ϕ may average to zero over the full ensemble, yet typical values for the subensemble are nonzero.

In the event that $P(\phi)$ should be a Gaussian with second moment $\langle\phi^2\rangle$, the signal $M(2\tau)$ from expression (3) is given by

$$M(2\tau)=M_0\exp\left[-\frac{1}{2}\langle\phi^2\rangle\right]. \tag{4}$$

Our approach uses one essential approximation taken by Neuman,[12] that $P(\phi)$ is a Gaussian, or, in the event that it is not Gaussian, that expression (4), incorporating the *second moment* of the phase probability distribution, provides an adequate approximation of the signal size. The problem of finding the echo signal amplitude then reduces to that of finding the second moment. We now proceed to find the *second moment* of the actual probability distribution $P(\phi)$. We find that the calculation is not very difficult for many cases of interest.

First it is convenient to write the z component of magnetic field h_z acting on a spin as a sum of any number of *independently* fluctuating contributions $h_z^{(i)}$

$$h_z(t)=\sum_i h_z^{(i)}(t). \tag{5}$$

Now we compute $\langle\phi^2\rangle$ at the time $t=2\tau$, the peak of the spin echo where τ is the 90–180° pulse spacing. First we calculate ϕ^2 for an individual spin experiencing a field $h_z(t)$ by using expression (2) above:

$$\phi^2=\gamma^2\left(\int_\tau^{2\tau}\int_\tau^{2\tau}-\int_\tau^{2\tau}\int_0^{\tau}-\int_0^{\tau}\int_\tau^{2\tau}+\int_0^{\tau}\int_0^{\tau}\right)\times\sum_{i=1}^{V}\sum_{q=1}^{V}h_z^{(i)}(t)h_z^{(q)}(t')dt\,dt', \tag{6}$$

where the leftmost and rightmost integrations in each term apply to t and t', respectively. Now we need the ensemble average $\langle\phi^2\rangle$ of this quantity ϕ^2, given above. First, the fluctuators h_i and h_q are assumed to be independent; thus, in the ensemble average their products for i not equal to q will vanish. The ensemble average of $h^i(t)h^i(t')$ can be reexpressed in terms of the field autocorrelation function $g_i(t)$ (Refs. 6 and 7) for the ith independent fluctuator:

$$\langle h_z^{(i)}(t)h_z^{(q)}(t')\rangle\equiv g_i(t-t')\,\delta_{iq}, \tag{7}$$

thus yielding

$$\langle\phi^2\rangle=\gamma^2\left(\int_\tau^{2\tau}\int_\tau^{2\tau}-\int_\tau^{2\tau}\int_0^{\tau}-\int_0^{\tau}\int_\tau^{2\tau}+\int_0^{\tau}\int_0^{\tau}\right)\times\sum_{i=1}^{V}g_i(t-t')dt\,dt'. \tag{8}$$

The correlation functions $g_i(t)$ satisfy the conditions that $g_i(0)=\langle(h_0^{(i)})^2\rangle$, that $g_i(-t)=g_i(t)$, and that $g_i(t)$ vanishes in the limit as t approaches infinity. We now introduce the spectral density $J_i(\omega)$, the Fourier transform of $g_i(t)$:

$$J_i(\omega)=\int_{-\infty}^{\infty} g_i(t)\exp(i\omega t)dt;$$
$$g_i(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty} J_i(\omega)\exp(-i\omega t)d\omega. \tag{9}$$

Combining the previous two equations and performing the integration, we obtain for the mean-square precession phase at the time $t=2\tau$ of the echo

$$\langle\phi^2\rangle_{\substack{\text{spirit}\\ \text{echo}}}=-\frac{\gamma^2}{\pi}\sum_{i=1}^{V}\int_{-\infty}^{\infty}d\omega\,\frac{J_i(\omega)}{\omega^2}\times\{4\cos\omega\tau-\cos2\omega\tau-3\}. \tag{10}$$

The size of the echo signal can be determined within the Gaussian approximation from $\langle\phi^2\rangle$ via expression (4).

An analogous result can be derived for the *stimulated echo* (Ref. 3) consisting of the sequence 90-τ-90-T-90-τ-*acquire*. Phase is only accumulated during the times τ, and not during the T interval when the spins are along the z axis. The mean-square phase is evaluated by replacing the $(\tau,2\tau)$ limits of integration by $(\tau+T,2\tau+T)$ in Eq. (8):

$$\langle\phi^2\rangle_{\substack{\text{stim.}\\ \text{echo}}}=-\frac{\gamma^2}{\pi}\sum_{i=1}^{V}\int_{-\infty}^{\infty}d\omega\,\frac{J_i(\omega)}{\omega^2}(2\cos\omega\tau+2\cos\omega(\tau+T)-\cos\omega(2\tau+T)-\cos\omega T-2). \tag{11}$$

III. FLUCTUATING FIELDS WITH EXPONENTIAL CORRELATION FUNCTIONS

The expressions derived above have an advantage of generality in that they are written in terms of an unspecified, general correlation function. As they stand, however, they are rather unwieldy; it is desirable to demonstrate their application for a specific case. The exponential correlation function has wide applicability, and in fact the expressions given above reduce to much simpler expressions if the exponential function is taken.

The exponential correlation function $g(t)$ is given by

$$g_i(t)=\langle(h_0)^2\rangle\exp\left(-\frac{|t|}{\tau_c}\right) \tag{12}$$

with correlation time τ_c. The spectral density in this case is Lorentzian. For this particular correlation function the expressions for $\langle\phi^2\rangle$ evaluated at the echo peaks become

$$\langle\phi^2\rangle_{\substack{\text{spin}\\ \text{echo}}}=2\gamma^2\sum_{i=1}^{V}\langle(h_0^{(i)})^2\rangle(\tau_c^{(i)})^2\{[(2\tau)/\tau_c^{(i)}]+4e^{-(2\tau)/2\tau_c^{(i)}}-e^{-(2\tau)/\tau_c^{(i)}}-3\}, \tag{13a}$$

$$\langle\phi^2\rangle_{\substack{\text{stim.}\\ \text{echo}}}=2\gamma^2\sum_{i=1}^{V}\langle(h_0^{(i)})^2\rangle(\tau_c^{(i)})^2\left\{\begin{array}{l}(2\tau)/\tau_c^{(i)}+2\exp(-\tau/2\tau_c^{(i)})+2\exp[-(\tau+T)/\tau_c^{(i)}]\\ -\exp[-(2\tau+T)/\tau_c^{(i)}]-\exp(-T/\tau_c^{(i)})-2\end{array}\right\}. \tag{13b}$$

Again taking the Gaussian approximation we can determine the height of the echo peaks:

$$M_{\substack{\text{spin}\\ \text{echo}}}=M_0\exp\left[-\gamma^2\sum_{i=1}^{V}\langle(h_0^{(i)})^2\rangle(\tau_c^{(i)})^2\times\{(2\tau)/\tau_c^{(i)}+4e^{-(2\tau)/2\tau_c^{(i)}}-e^{-(2\tau)/\tau_c^{(i)}}-3\}\right], \tag{14a}$$

$$M_{\substack{\text{stim.}\\ \text{echo}}}=\frac{M_0}{2}\exp\left[-\gamma^2\sum_{i=1}^{V}\langle(h_0^{(i)})^2\rangle(\tau_c^{(i)})^2\{2\tau/\tau_c^{(i)}+2e^{-\tau/\tau_c^{(i)}}+2e^{-(\tau+T)/\tau_c^{(i)}}-e^{-(2\tau+T)/\tau_c^{(i)}}-e^{-T/\tau_c^{(i)}}-2\}\right]. \tag{14b}$$

If only one source of fluctuating field is present [so that the summation symbol in expression (14a) is unnecessary], then expression (14a) is identical to an expression given by Herzog and Hahn[1] and by Abragam,[8] using the approach of Anderson and Weiss[21] in which the instantaneous *field* distribution is taken to be Gaussian distributed. It is important to note, however, that the above results are obtained using the less stringent condition that the *phase* distribution at the time of the echo maximum is approximated as Gaussian. It is also important that Eq. (14) and the more general expressions (4), (10), and (11), do allow the possibility of multiple sources of fluctuating field, each with its own distinct correlation function. This feature of our result makes application of the Gaussian approximation more transparent. For the case of the ^{89}Y T_2 in $YBa_2Cu_3O_7$, for example, we will show that this approach can accurately duplicate the results of numerical simulations.

IV. LIMITING BEHAVIOR AND THE EFFECTIVE TRANSVERSE RELAXATION TIME $T_{2\text{eff}}$

We now consider limiting behaviors for the case of a single fluctuating field source $h(t)$ with mean-square z component h_0^2 and correlation time τ_c. For this special case results are well known,[8] but we summarize them here for convenience:

$$M\approx M_0\exp\left[-\frac{1}{12}\gamma^2h_0^2\tau_c^{-1}(2\tau)^3\right]\quad\text{for }\tau/\tau_c\ll1, \tag{15a}$$

$$M\approx M_0\exp[-\gamma^2h_0^2\tau_c(2\tau)]\quad\text{for }\tau/\tau_c\gg1. \tag{15b}$$

For the short correlation time limit the signal follows a simple exponential decay with T_2 given by Redfield theory predictions, while for the opposite limit the behavior is exponential in the quantity $(2\tau)^3$.

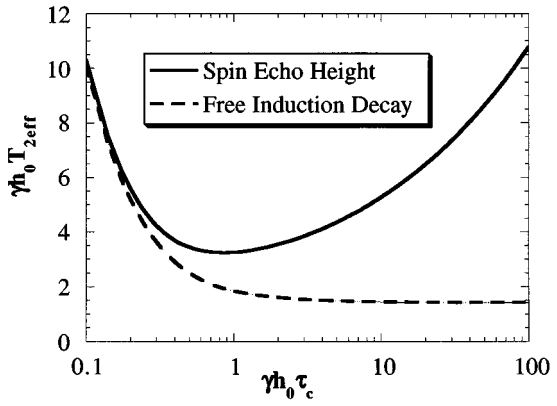

FIG. 1. Effective transverse relaxation time $T_{2\text{eff}}$, as derived from the Gaussian-approximation method described in the text, for the decay of the spin-echo height with 2τ, where τ is the spacing between the 90° and 180° pulses (solid curve), and for the free induction decay (Refs. 1 and 8) (dashed curve), both plotted as a function of the dimensionless parameter $\gamma h_0 \tau_c$. Here $\gamma h0$ characterizes the low-temperature (long correlation time) NMR linewidth, and τ_c is a correlation time (see text for more rigorous definitions). $T_{2\text{eff}}$ is defined as the time required for the signal to fall to $1/e$ times its initial value. The minimum in $T_{2\text{eff}}$ for the spin echo occurs when $\gamma h_0 \tau_c \sim 1$, reminiscent of the well-known minimum in T_1,[7,8] which occurs when $\gamma H_0 \tau_c \sim 1$, where τ_c is a similarly defined correlation time, and γH_0 is the Larmor frequency. Note that $T_{2\text{eff}}$ for the spin echo is always greater than or equal to that of the free-induction decay, reflecting the refocusing effect of the 180° pulse.

Expression (14a) for the echo size certainly does not predict simple exponential behavior. Nevertheless the practical spectroscopist may wish to estimate an ''effective T_2'' defined as the time when the signal drops to $1/e$ times its full value. Such an effective T_2 we call ''$T_{2\text{eff}}$.'' $T_{2\text{eff}}$ can be obtained from Eq. (13a) by solving for the roots of a transcendental equation. The results for a single fluctuator are shown in Fig. 1. (Also shown is the $T_{2\text{eff}}$ for a free-induction decay, discussed below.) The qualitative features of Fig. 1 are as expected: For very long correlation times $T_{2\text{eff}}$ for the spin echo becomes long, since some frequency jump is certainly required in order to prevent the echo from refocusing perfectly. For very short correlation times motional narrowing occurs, and again $T_{2\text{eff}}$ becomes long. For intermediate correlation times, where $1/\tau_c$ is of the order of γh_0, however, $T_{2\text{eff}}$ has a minimum of $3.78\tau_c$ [equal to $3.25(\gamma h_0)^{-1}$], occurring when $\gamma h_0 \tau_c = 0.86$. The minimum in $T_{2\text{eff}}$, occurring for $1/\tau_c$ of order of the *spread* in instantaneous frequencies, is reminiscent of the well-known minimum in T_1,[7] which occurs when a similarly defined correlation rate $1/\tau_c$ matches the Larmor frequency ω_0.

It is illustrative to compare the behavior of the spin echo with that of the free-induction decay (FID).[6,1,8] Here we must make assumptions about the static (long τ_c limit) line shape. We take it to be a Gaussian with a second moment $(\gamma h_0)^2$.[1,8] Taking the same correlation time $\gamma h_0 \tau_c = 0.86$, we find that the $1/e$ time for the FID is 2.2 τ_c [equal to $1.9(\gamma h_0)^{-1}$], substantially shorter than the echo decay time, reflecting the expected (partial) ''refocusing'' effect of the 180° pulse. The $T_{2\text{eff}}$ minimum for the free-induction decay occurs in the limit of τ_c approaching infinity, and is equal to $\sqrt{2}(\gamma h_0)^{-1}$.

V. SPECIFIC APPLICATIONS

Now having presented the general results for the method, we turn to two specific examples illustrating its application. We first consider the transverse decay of ^{89}Y in the high-T_c superconductor $YBa_2Cu_3O_7$, as it experiences fluctuating dipolar fields from neighboring ^{63}Cu and ^{65}Cu nuclei. The results are shown to agree with numerical calculations which do not employ the Gaussian approximation, and with experiment. Then we address the problem of diffusion of spins in an arbitrary field profile, and show that our approach reproduces results obtained by Tarczon and Halperin[9] and by Robertson.[10] Subsequently in Sec. VI we explore the limits of the model by applying it to the problem of proton NMR in the presence of chemical exchange in the molecule dimethylformamide.

A. The T_2 of ^{89}Y in $YBa_2Cu_3O_7$ as influenced by ^{63}Cu T_1

We initiated these calculations of spin-echo heights during our investigations of vortex dynamics in the high-T_c superconductor $YBa_2Cu_3O_7$ using ^{89}Y NMR. Suh, Torgenson, and Borsa[13] reported extensive T_2 measurements on ^{89}Y and found a substantial vortex contribution to the transverse relaxation rate $(1/T_2)$; yet $1/T_2$ effects were present and also substantial in the normal state, and by our estimates much faster than could be explained through spin-spin coupling between the ^{89}Y themselves.

We considered the ^{89}Y-^{63,65}Cu dipolar coupling effect. With a resonance frequency of 2.1 MHz/T for ^{89}Y and 11.3 MHz/T for ^{63}Cu, these nuclei are clearly ''unlike'' in the sense that mutual spin flips do not conserve energy and hence do not occur. The ^{89}Y-^{63}Cu effective dipolar coupling then consists of only the Hamiltonian term containing the ^{89}Y spin z component I_z (z points along the applied, static field, which in our case is along the crystal c axis) and ^{63}Cu spin S_z:

$$^{89-63}H_{\text{dip.}} = \frac{^{89}\gamma\,^{63}\gamma\hbar^2}{r^3}(1-3\cos^2\theta)I_z S_z \qquad (16)$$

where r is the magnitude of the position vector connecting the nuclei and θ is the angle made between it and the z axis. For the ^{89}Y this Hamiltonian gives an effective magnetic field h_z:

$$h_z = \frac{^{63}\gamma\hbar}{r^3}(1-3\cos^2\theta)m_z, \qquad (17)$$

where m_z is the z component of spin for the ^{63}Cu. Of course, the ^{89}Y has many ^{63}Cu neighbors, and thus it experiences magnetic fields from many sources. ^{63}Cu is a spin 3/2 nucleus, and thus m_z can take on values $-3/2, -1/2, 1/2, 3/2$.

Upon first consideration it would seem that the effective field h_z as given in expression (17) would have no effect upon the amplitude of the ^{89}Y spin echo—the effects of such a static magnetic field should be *refocused* in a spin-echo experiment. As Walstedt and Cheong[2] have noted, however, this field is *not* static on the time scale of the ^{89}Y T_2 ($\sim$10 ms) (or the ^{17}O T_2, as in their measurement), because the ^{63}Cu T_1 is quite fast ($\sim$1 ms). Walstedt and Cheong simulate

the fluctuating ^{63}Cu dipolar field using known T_1 values and accurately calculate the ^{17}O T_2 in the lanthanum cuprate superconductors.

Of course, if the ^{89}Y-^{63}Cu dipolar interaction does indeed determine the ^{89}Y T_2, then one must be quite careful in interpreting the ^{89}Y T_2 temperature dependence in terms of vortex dynamics; the ^{63}Cu T_1 varies dramatically as one lowers temperature below T_c, and thus one must be concerned that the ^{89}Y T_2 variation may result from ^{63}Cu T_1 variation rather than the properties of the vortex system.

Thus, we have performed calculations that are analogous to those of Walstedt and Cheong for ^{89}Y in $YBa_2Cu_3O_7$. The great advantage of the calculation is that there are *no adjustable parameters*. ^{63}Cu and ^{65}Cu T_1's are known,[14] as are the position vectors of Cu neighbors with respect to the ^{89}Y nucleus. We have shown that, in order to attain accurate results one must include dipolar fields from the nearest-neighbor planar Cu nuclei (of which there are eight), the nearest-neighbor chain Cu nuclei (eight), and the next-nearest-neighbor planar Cu (16). In the numerical calculation we consider an ensemble of 1000 ^{89}Y spins, and of course for each we must simulate the independently fluctuating behavior of the 32 near-neighbor Cu atoms. The results of this numerical calculation in the normal state for $T=95$ K are shown in Fig. 2. Also shown are the experimental data and the *analytic* formula, which we discuss below. It is clear that the numerical calculation provides an excellent match with the experimental data with *no adjustable parameters*. This confirms that at 95 K ^{89}Y-^{63}Cu dipolar interactions dominate the ^{89}Y T_2. (We have also found that in the superconducting state an extra contribution, presumably from vortex dynamics effects, is required. We will describe these results in a future publication.)

Now we turn to a comparison of the *numerical* and *analytical* calculation results, again shown in Fig. 2. While the numerical result requires detailed, stochastic simulations of large ensembles, the analytic result is quite simple. The application of Eq. (14a) to the problem is a straightforward procedure. The independent fluctuators $h_i(t)$ are the various ^{63}Cu and ^{65}Cu neighbors of the ^{89}Y, and the correlation times $\tau_c^{(i)}$ are precisely the ^{63,65}Cu T_1's, as T_1 characterizes the exponential decay of the autocorrelation function $\langle m_z(0)m_z(t)\rangle$ for magnetic relaxation processes. It would at first appear that a complication arises from the random occupations of the naturally abundant ^{63}Cu (69% abundant) and ^{65}Cu (31%). But in fact this presents no problem: the mean-square dipolar field of the ith Cu neighbor is given with an added abundance weighting factor:

$$^{63}h_0^2 = 0.69(^{63}\gamma\hbar(1-3\cos^2\theta)/r^3)^2 I(I+1)/3,$$

$$^{65}h_0^2 = 0.31(^{65}\gamma\hbar(1-3\cos^2\theta)/r^3)^2 I(I+1)/3, \qquad (18)$$

where $I=3/2$ for both ^{63}Cu and ^{65}Cu. For each atomic site both of the terms listed above for ^{63}Cu and ^{65}Cu, respectively, must be included, along with their accompanying factors that appear in Eq. (14a). In essence, at each Cu site, we think of there being *two* independent fluctuators with weightings 0.69 and 0.31 and having correlation times given by the ^{63}Cu and ^{65}Cu T_1's. This is *not* any additional approximation beyond the Gaussian approximation that has been used all along.

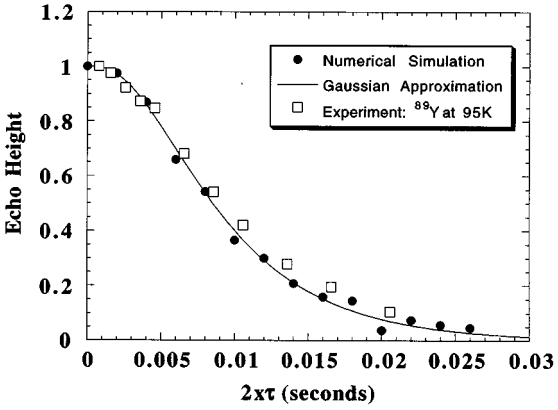

FIG. 2. Spin-echo height vs 2τ (where τ is the spacing between the 90° and 180° pulses) for ^{89}Y in the normal state of $YBa_2Cu_3O_7$, with an applied field of 9 T and temperature 95 K. The hollow diamonds (◇) are experimental data. The solid dots (●) are the results of a computerized numerical simulation, which contains *no adjustable parameters*. This simulation is fully analogous to work of Walstedt and Cheong (Ref. 2), who use this method to analyze the T_2 of ^{17}O in high-T_c cuprates. In the simulation the echo decay is assumed to be the result of the fluctuating dipolar field produced by the neighboring ^{63}Cu and ^{65}Cu spins. The dipolar field fluctuations are the result of ^{63}Cu and ^{65}Cu T_1 processes, and the T_1 values are well known from experiment. The simulation uses an ensemble of 1000 ^{89}Y spins (implying approximately 3% statistical error for the early times), each under the influence of fluctuating dipolar fields of 32 Cu near neighbors (including both plane and chain Cu's, and with appropriate statistical populations of ^{63}Cu and ^{65}Cu). The simulation is in excellent agreement with experiment. Finally the solid line uses the Gaussian approximation formalism described in the text. There are 32 sources h_i of fluctuating field, corresponding to the 32 Cu near neighbors. The field strength of each of these sources is easily calculated from their known distances from the ^{89}Y spin, and their correlation times are equal to their T_1's (which are different for ^{63}Cu and ^{65}Cu, and for plane and chain Cu's). The Gaussian approximation, which yields a relatively simple analytical expression, is in excellent agreement with the numerical simulation.

The analytical result for the decay of the ^{89}Y spin echo with 2τ is shown together with the numerical calculation in Fig. 2. The agreement is quite remarkable. This might be as expected in this case—with 32 near neighbors each contributing one of 24 possible different local fields at the yttrium site it seems likely that the phase distribution $P(\phi)$ would approach a Gaussian for most parameter times. We return to this point later.

B. Diffusion in arbitrary magnetic-field profiles

Hahn[3] addressed the problem of finding the spin-echo height in the presence of spatial diffusion of the nuclei within a nonuniform magnetic field. For the case of an effectively infinite sample dimension with a constant applied magnetic field gradient G, Hahn showed that the echo amplitude as a function of twice the pulse spacing τ could be written as

$$M(2\tau) \propto \exp[-\gamma^2 G^2 D(2\tau)^3/12], \tag{19}$$

where D is the molecular diffusion coefficient and γ is the nuclear gyromagnetic ratio. NMR studies of diffusion have historically been of great interest, and currently applications in biomedical physics make the subject even more timely. The idealized case considered by Hahn of infinite sample length and uniform gradient, however, is not adequate for many situations of interest. For example, the water trapped inside a biological cell will experience ''restricted'' diffusion. Equation (19) may be valid for early times, but not for times greater than τ such that $\sqrt{D\tau}$ is greater than or comparable to the sample dimension. Robertson[10] used the Bloch equations to treat the case of a finite cylindrical sample in a uniform field gradient. Subsequently Neuman[12] used the Gaussian approximation to extend the calculations to samples of noncylindrical shape. Finally Tarczon and Halperin[9] again used the Gaussian approximation to address the problem of an arbitrary magnetic-field distribution. The Gaussian-approximation formalism which we use here is a generalization of these approaches, and thus naturally their results also follow as a consequence of the formalism.

We consider a one-dimensional sample of length L aligned along the z axis, extending from $z=0$ to L, and experiencing a magnetic field $h_z(z)$. Following Wayne and Cotts,[15] we artificially extend the sample in the following way: First, we extend the sample to include the range for 0 to $-L$ using the condition $h_z(-z)=h_z(z)$. Now this structure of length $2L$ is periodically repeated (with period $2L$) to extend the sample from $-\infty$ to $+\infty$. While in reality a nuclear spin approaching the sample boundary at $z=L$ would be reflected back, we consider instead that it instead moves forward, but experiences the field profile which it would have had, had it been reflected. In this way the finite sample may be thought of as infinite, with a periodic magnetic field, and the effective field may be written as a Fourier series $h_z(z)=\Sigma_k \tilde{h}(k)e^{ikz}$ with $k=2n\pi/2L$.

Now, in order to apply the formalism we must calculate the correlation function experienced by the nuclear spins diffusing in this magnetic field profile of infinite length. Consider first a *sub*ensemble of nuclei which are assumed to begin at position z_0 at time t, and which experience a field of $h_z(z_0)$. The correlation function a time t' later for this subensemble is given by

$$\overline{h_z(t)h_z(t+t')} = h_z(z_0)\frac{\int dz\, h_z(z)e^{-(z-z_0)^2/4Dt'}}{\int dy\, e^{-y^2/4Dt'}}, \tag{20}$$

where the range of integrations is $-\infty$ to $+\infty$. Then, to find the ensemble average for the whole system we average over the equally probable starting positions z_0:

$$\overline{h_z(t)h_z(t+t')} = \frac{\int dz_0 h_z(z_0)\int dz\, h_z(z)e^{-(z-z_0)^2/4Dt'}}{\int dz_0 \int dy\, e^{-y^2/4Dt'}}. \tag{21}$$

This expression is evaluated to yield

$$\overline{h_z(t)h_z(t+t')} = \sum_k \tilde{h}(k)\tilde{h}(-k)e^{-k^2Dt'}. \tag{22}$$

Remarkably, this result expresses the field autocorrelation function as the sum of contributions from independent fluctuators, here indexed by the wave vector k, with mean-square fields and correlation times given by the following expressions:

$$\langle (h_0^{(k)})^2 \rangle = \tilde{h}(k)\tilde{h}(-k),$$

$$1/\tau_c^{(k)} = k^2 D. \tag{23}$$

Thus we can identify each spatial Fourier component as an independent fluctuator, and apply the Gaussian-approximation formalism, using Eq. (14). This yields the results obtained by Tarczon and Halperin[9] for the spin-echo height resulting from diffusion in an arbitrary field profile. Again this result is exact apart from the assumption that the phase distribution at the time of the echo can be approximated as a Gaussian.

VI. LIMITS OF APPLICABILITY, AND APPLICATION TO A SIMPLE MODEL OF CHEMICAL EXCHANGE

The Gaussian-approximation method which we have presented provides a simple recipe for understanding spin-echo heights in many cases. The *only* approximation that we have taken is that the distribution of phase angles is taken to be Gaussian. Our exact calculation of the second moment of the phase distribution then fully specifies the distribution and enables us to compute the signal. There are, however, realistic and realizable experimental situations in which the phase distribution at the time of the echo is distinctly *non*-Gaussian. We consider such a situation, which is also a classic problem of NMR—the simplest form of chemical exchange, whereby a nucleus experiences a chemical shift which can randomly alternate between two discrete values, each occurring half the time on average. This kind of system was considered by Gutowsky, McCall, and Slichter,[16] and is also treated by Slichter,[7] and others.[17–20]

A. Two-site chemical exchange model

The results for the continuous wave absorption curve (or, equivalently, the Fourier transform of the free-induction-decay signal) of the two-site chemical exchange model introduced above are well known:[7] the low-temperature line shape consists of two sharp peaks of equal area, located at frequencies $+\omega_0$ and $-\omega_0$ (where we measure frequencies from the center of mass of the line shape). At high temperature, however, these peaks collapse into one narrow peak at zero frequency. As the temperature is raised from the low to high, the peaks gradually broaden and shift towards zero, and then collapse to zero frequency at temperatures such that the molecular jumping rate becomes comparable to or faster than the low-temperature frequency splitting.

Although it has previously been calculated theoretically,[20] the behavior of the spin-echo height as a function of pulse

spacing for this system is not widely known. We will derive an exact expression for this quantity and then compare and contrast it with the prediction based on the Gaussian-phase approximation, which gives the following:

$$M_{\substack{\text{spin}\\\text{echo}}} = M_0 \exp[-\omega_0^2 \tau_c^2 \{(2\tau)/\tau_c + 4e^{-(2\tau)/2\tau_c} - e^{-(2\tau)/\tau_c} - 3\}], \tag{24}$$

where 2τ is twice the pulse spacing, and the quantity τ_c is the correlation time for ''jumps'' of the NMR frequency between the values of plus and minus ω_0. More precisely, if the frequency is initially $+\omega_0$, then the probability per unit time for a jump to $-\omega_0$ is $1/(2\tau_c)$. We will show that Eq. (24) is highly accurate for short correlation times ($\omega_0\tau_c \ll 1$), but very inaccurate for the opposite limit. In fact, for the case of longer correlation times the echo height as a function of 2τ is found theoretically, and observed experimentally, to have *beats*.

We follow the approach given by Slichter[7,16,21] to calculate the free-induction decay, and extend it to calculate the spin-echo height. We denote the two alternate sites for the nuclei as sites A (having resonance frequency $+\omega_0$) and B ($-\omega_0$). We may also define the quantities M_A^+ and M_B^+ in terms of the instantaneous nuclear magnetization vectors associated with the A and B sites, respectively: $M_A^+ = M_{Ax} + iM_{Ay}$ (henceforth we will omit the ''+'' superscript). Now, with a jumping rate $1/2\tau_c$ between the A and B sites, the differential equations governing the behavior of the magnetization are as follows:

$$\frac{d}{dt}(M_A) = i\omega_0 M_A - \frac{1}{2\tau_c}(M_A - M_B),$$

$$\frac{d}{dt}(M_B) = -i\omega_0 M_B + \frac{1}{2\tau_c}(M_A - M_B). \tag{25}$$

It is helpful to reexpress these equations in terms of the variables

$$X \equiv M_A + M_B; \quad Y \equiv M_A - M_B. \tag{26}$$

Following the initial pulse, the quantity X, which gives the signal size, can be taken as one. We assume that the initial pulse orients the magnetization along the x axis. The evolution of X and Y at a time t following the initial 90° pulse (but before the 180° pulse) can be shown to be

$$X = \exp(-t/2\tau_c)\left[\cos\omega t + \frac{1}{2\omega\tau_c}\sin\omega t\right],$$

$$Y = \exp(-t/2\tau_c)\left[\frac{i}{\omega/\omega_0}\sin\omega t\right], \tag{27}$$

where

$$\omega \equiv \omega_0\left[1 - \left(\frac{1}{2\omega_0\tau_c}\right)^2\right]^{1/2}.$$

ω is the effective oscillation frequency which is reduced by a damping term. (We shall also consider the cases of *critical* damping [$\omega = 0$] and *over*damping [ω is imaginary].) Now, it is clear by symmetry that the x components of the M_A and M_B vectors will remain equal as time evolves, while their y components will remain of equal magnitude but opposite sign. Following a time τ a 180° pulse is applied about the x axis, and the effect is to *reverse* instantaneously the sign of the quantity Y while leaving X unchanged. This creates a new initial condition, and the time evolution may recommence. One can show that the echo height at a time 2τ following the initial 90° pulse is given by

$$M(2\tau) = M(0)\exp(-2\tau/2\tau_c)\left[\cos^2\frac{\omega}{2}(2\tau) + \left(\frac{1+1/Q^2}{1-1/Q^2}\right)\sin^2\frac{\omega}{2}(2\tau) + \frac{1}{2\omega\tau_c}\sin[\omega(2\tau)]\right], \tag{28}$$

where

$$Q \equiv 2\omega_0\tau_c.$$

Equation (28) is formally correct even for imaginary frequencies ω. It is interesting, however, to consider the *long correlation time* case, where Q is large, and to keep only terms up to first order in $1/Q$. That yields the following simple approximate result, valid for large Q, and for *all* values of the parameter τ/τ_c:

$$M(2\tau) \approx M(0)\exp(-2\tau/2\tau_c)\left[1 + \frac{1}{2\omega\tau_c}\sin[\omega(2\tau)]\right]. \tag{29}$$

This expression demonstrates that the echo has ''beats'' in the long correlation time regime. Although the ''beats'' in the echo height vs 2τ which are discussed here have previously been demonstrated theoretically,[18,20] the present authors are unaware of any experimental verifications. The molecule dimethylformamide provides a realization.[17] Figure 3 illustrates the two molecular orientations leading to the two discrete chemical shift values experienced by the methyl protons. The C-N bond has partial double bond character, which tends to maintain the molecule in a planar configuration. The methyl protons experience a different instantaneous chemical

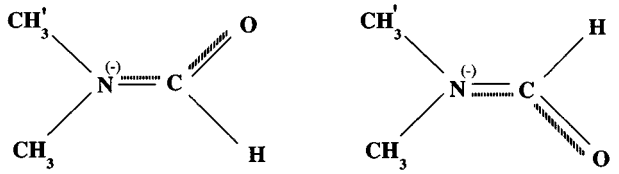

FIG. 3. The molecule dimethylformamide. The figure illustrates the two possible configurations of the molecule with respect to the methyl protons which we label with a prime ($'$). The C-N bond has partial double bond character, partially hindering ''twisting'' motions of the molecule about this axis. In the left panel the formyl oxygen is opposite the primed methyl protons, but in the right panel the formyl hydrogen is opposite. These two configurations result in different chemical shifts for the primed methyl protons. Jumps between these two configurations then cause the chemical shift of the methyl proton to be modulated, and this modulation serves to diminish the height of the spin echo with increasing 90–180° pulse spacing.

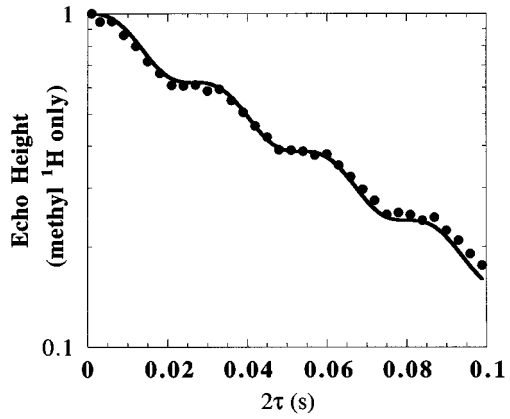

FIG. 4. Spin-echo height vs 2τ of the methyl protons in dimethylformamide. τ is the spacing between the 90° and 180° pulses. The echo height clearly shows a beat structure which is predicted in the text, but which is not consistent with the Gaussian approximation formalism. Also shown is a fit to Eq. (29), a solution of the Bloch equations supplemented with the chemical exchange process as detailed in the text. The damped frequency parameter $\omega=234.36$ radians/s is obtained directly from the Fourier transform of the free-induction-decay signal (not shown). The one remaining adjustable parameter is τ_c. The fit shown above yields $\tau_c=28.1$ ms. Note that a single parameter τ_c determines both the overall decay rate *and* the amplitude of the sinusoidal term.

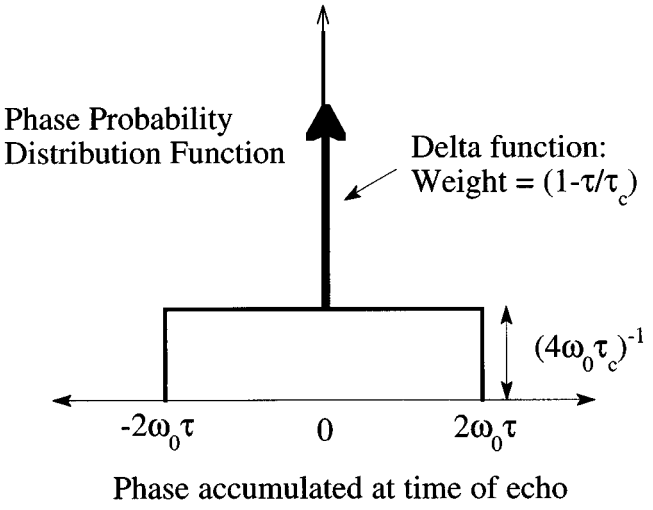

FIG. 5. Schematic diagram to explain the ''beats'' which occur in the spin-echo height vs 2τ (where τ is the pulse spacing) for the two site chemical exchange problem in the long correlation time limit. The instantaneous NMR frequency of an ensemble spin can take on one of two discrete values, $+\omega_0$ or $-\omega_0$. The frequency jumps between these values randomly with a probability per unit time $1/(2\tau_c)$. This figure shows the probability distribution of the accumulated phase at the time of the echo (at a time 2τ following the initial 90° pulse, and assume the long correlation time regime $\tau_c \gg \tau$ and $\tau_c \gg 1/\omega_0$. The fraction of spins which will experience one frequency jump is $\varepsilon=2\tau/2\tau_c$. The spins which experience *no* jump will be refocussed at the time of the echo, and accumulate zero phase. They contribute a δ function of weight $1-\varepsilon$ at $\phi=0$. The phase accumulated by the spins experiencing one jump is uniformly distributed between zero (for spins which have jumps occurring immediately following the 90° pulse or immediately prior to the echo) and $\pm 2\omega_0\tau$ and contributes a total area ε. The signal contribution from the spins experiencing one jump is obtained by integrating the probability distribution times $\cos\phi$, which yields a contribution containing beats: $(1/2\omega_0\tau_c)\sin\omega_0(2\tau)$.

shift (differing by some 0.16 ppm) depending upon whether they are located opposite the formyl group oxygen or the formyl hydrogen; however, if the molecule ''twists'' as shown in the figure, these shift assignments are reversed. Gutowsky and Holm[17] measure correlation times for the twist of order of 10–100 ms near and above room temperature with an activation barrier of ~3500 K.

Figure 4 shows the spin-echo height of the methyl protons vs 2τ at a temperature of 393 K. (The echo height is obtained as follows: We Fourier transform the spin echo, taking the zero of time to be located at 2τ following the initial 90° pulse. Then to obtain the echo height associated only with the methyl protons, we measure the area under their absorption curve, which is easily resolved from the formyl proton peak which is also present.) The echo clearly shows the predicted beat structure. Also shown is a fit to Eq. (29). We obtain the damped frequency parameter $\omega=234.36$ radians/s directly from the Fourier transform of the free-induction-decay signal (not shown). The one remaining adjustable parameter τ_c can be obtained by fitting the echo height vs 2τ. Figure 4 shows the fit with $\tau_c=28.1$ ms. Note that a single parameter τ_c determines both the overall decay rate *and* the amplitude of the sinusoidal term; thus the excellent fit obtained is an impressive demonstration of the concept.

B. Limits of validity of the Gaussian approximation

How might these beats be understood, given that they do not occur in the Gaussian approximation? As it happens, the result can be easily understood for the case of large *Q and* small values of τ/τ_c, which we now consider. Figure 5 gives a semiquantitative illustration, in terms of the expected probability distribution function for the phase accumulated by a nuclear spin at the time of the echo. (The Appendix gives a thorough, systematic approach to calculating the phase probability distribution for this problem.) The figure shows the probability distribution of the accumulated phase at the time of the echo (at a time 2τ following the initial 90° pulse, assuming the long correlation time regime $\tau_c \gg \tau$ and $\tau_c \gg 1/\omega_0$. The former restriction assures that each spin will experience few, if any, frequency jumps during the echo sequence. The fraction of spins which will experience *no* frequency jumps is $\sim 1-\tau/\tau_c$. These spins will refocus perfectly at the time of the spin echo. Thus, they contribute to the phase probability distribution a δ function at $\phi=0$ of weight $1-\tau/\tau_c$. The phase accumulated by the spins experiencing *one* jump is uniformly distributed between zero (for spins which experience jumps occurring immediately following the 90° pulse or immediately prior to the echo) and $\pm 2\omega_0\tau$ (for jumps occurring at the same time as the 180° pulse) and contributes a total area τ/τ_c. The signal contribution from the spins experiencing one jump is obtained by integrating the phase probability distribution times $\cos\phi$, which yields the contribution containing beats: $(1/2\omega_0\tau_c)\sin\omega_0(2\tau)$. This ap-

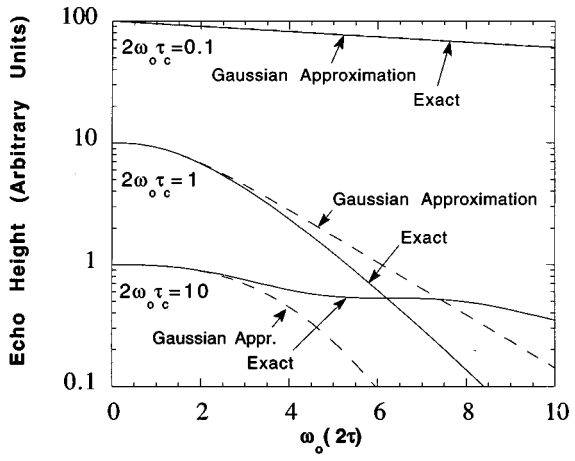

FIG. 6. Spin-echo heights vs $\omega_0(2\tau)$ where τ is the spacing between the 90 and 180° pulses, for a model in which the nuclei experience an instantaneous resonance frequency of either $+\omega_0$ or $-\omega_0$. Jumping between these two discrete frequencies occurs randomly with a probability per unit time $1/(2\tau_c)$. The echo height is calculated using two theoretical methods: the Gaussian approximation method, and the exact solution, both described in the text. The figure shows that the Gaussian approximation method is quite good for small values of the parameter $\omega_0(2\tau_c)$, but not good at all for larger values. For large values of $\omega_0(2\tau_c)$ the phase probability distribution deviates strongly from a Gaussian form, as illustrated in Fig. 5; thus it is not surprising that in this case the Gaussian approximation fails.

proximate expression is quite similar to the second term in Eq. (29), except that it involves the undamped frequency ω_0 instead of ω. Clearly the approximation is quite good for $\tau \ll \tau_c$ and for $\omega_0\tau_c$ large.

Although we can understand Eq. (29) for $\tau \ll \tau_c$ and for $\omega_0\tau_c$ large, it is much more difficult to understand Eq. (29), in terms of the anticipated phase probability distributions, for the case of $\tau \gg \tau_c$ (and, again, $\omega_0\tau_c \gg 1$). In that case the typical spin has experienced many frequency jumps, and thus the simple argument given in the preceding paragraph is not valid. One can at least understand the *first* term in Eq. (29). It results from the dwindling supply of spins which have experienced *no* frequency jumps, despite the fact that $\tau \gg \tau_c$. Note that this term decays as $\exp(-2\tau/2\tau_c)$, which is *dramatically slower* than the decay predicted by the Gaussian approximation for the same limit ($\tau \gg \tau_c$ and $\omega_0\tau_c \gg 1$): $\exp[-\omega_0^2\tau_c(2\tau)]$. It is clear that *even for* $\tau \gg \tau_c$, the phase probability distribution retains important deviations from the Gaussian form, notably including a δ function at zero phase, which cause the Gaussian-approximation method to fail dramatically.

Overall, how adequate is the Gaussian-phase distribution approximation to treat this system? Figure 6 shows spin-echo heights vs $\omega_0(2\tau)$ calculated using both the Gaussian-approximation method and the exact solution. The figure shows that the Gaussian-approximation method is quite good for small values of the parameter $\omega_0(2\tau_c)$, but not good at all for larger values, as discussed above.

For small values of $\omega_0(2\tau_c)$, and for $\tau \gg \tau_c$, the typical spin has experienced approximately τ/τ_c frequency jumps, accumulating a phase of order $\pm\omega_0(2\tau_c)$ each time. This is a classic ''random-walk'' situation, and in this limit the phase probability distribution should indeed approach a Gaussian with second moment $2\omega_0^2\tau_c(2\tau)$; thus, it is not surprising that the Gaussian approximation is successful.

Even for large values of $\omega_0(2\tau_c)$, Fig. 6 demonstrates that the Gaussian approximation is accurate for small values of $\omega_0(2\tau)$. This is also easily understood. In this limit the phase distribution is highly non-Gaussian; however, its full width is quite small, since the largest values of accumulated phase are $\pm\omega_0(2\tau)$. In this limit the average value $\langle\cos\phi\rangle$ can be approximated as $(1-\langle\phi^2\rangle/2)$, which is in agreement with the expression obtained from the Gaussian approximation, $\exp(-\langle\phi^2\rangle/2)$.

The model of chemical exchange presented here might be considered a ''worst case scenario'' for application of the Gaussian approximation, and yet the approximation remains adequate in most limits. The limit which gives trouble is $\omega_0(2\tau_c) \gg 1$, where the phase distribution becomes highly non-Gaussian. This does *not* indicate, however, that the Gaussian approximation is invalid for all problems in which τ_c much greater than the reciprocal of the low-temperature linewidth. τ_c characterizes the amount of time required for a field change of magnitude comparable to the total linewidth. In many situations, however, smaller field changes occur on much smaller time scales. For example, for the case of diffusion in a field gradient, the instantaneous frequency is a continuous function of time. For any nonzero time interval each spin experiences continuous range of frequencies with some random character. It certainly appears more plausible in this case that the phase distribution would take on a near-Gaussian form. (Nevertheless, deviations from the Gaussian approximation in these situations are predicted.[22–24]) Similarly, for the case of ^{89}Y experiencing dipolar fields from ^{63,65}Cu—in a time τ_c (which is equal to the Cu T_1), *all* the neighboring Cu's experience typically one T_1 transition, so again the field experienced by the ^{89}Y is more nearly a continuous function of time, and thus one expects approximately Gaussian-phase distributions.

VII. CONCLUSIONS

We have presented a simple and fairly general approximate formalism which enables one to evaluate spin echo and stimulated echo heights. The formalism approximates the phase distribution $P(\phi)$ at the time of the echo as a Gaussian, and presents a mathematical method for calculating the width of the Gaussian, and hence the signal, for situations in which the spins experience fluctuating longitudinal magnetic fields having arbitrary time correlation functions. The approximation is applied successfully (and shown to be in agreement with numerical calculations not incorporating the approximation) to the problem of the transverse relaxation of ^{89}Y in the high-T_c superconductor $YBa_2Cu_3O_7$, where the ^{89}Y experiences fluctuating dipolar fields from ^{63,65}Cu neighbors which undergo rapid T_1 transitions. Results obtained by Tarczon and Halperin[9] for transverse relaxation of spins which diffuse in an arbitrary field profile are also shown to follow from the formalism—not surprisingly, since the formalism which we have presented is a generalization of the approach which they applied to that specific problem. Finally, we discuss a situation in which the formalism is not appropriate—the two-site chemical exchange problem,

where a nucleus experiences an instantaneous frequency of either $+\omega_0$ or $-\omega_0$, and over time also experiences transitions between these frequencies occurring with a correlation time τ_c. In that situation, we find, both experimentally and through an exact theoretical solution, that for $\omega_0\tau_c \gg 1$, oscillations occur in the height of the echo as a function of 2τ, where τ is the spacing between the 90° and 180° pulses. These oscillations are clearly not expected from the Gaussian-approximation formalism. We discuss the highly non-Gaussian-phase distribution which is obtained in this problem. Finally, we discuss the limits of validity of the approximation; the approximation is expected to be reasonably good for all cases in which *either* $\Delta\omega\tau_c \ll 1$ *or* $\Delta\omega\tau \ll 1$ (or both), where $\Delta\omega$ characterizes the *instantaneous* distribution of NMR frequencies. Finally, the approximation may be reasonably good even for $\Delta\omega\tau_c \gg 1$ *and* $\Delta\omega\tau \gg 1$ if the instantaneous frequencies are nearly continuous functions of time, and do not experience the large (of order $\Delta\omega$) and effectively instantaneous (occurring in times much faster than $1/\Delta\omega$) frequency ''jumps'' which occur in the two-site chemical exchange problem.

ACKNOWLEDGMENTS

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APPENDIX

In this appendix we present an approach to calculate the probability distribution for the phase angle accumulated by a nuclear spin at the time of the spin echo for the two-site chemical exchange model discussed in Sec. VI. We calculate the distribution including the effects of up to seven frequency jumps; hence the calculation should yield accurate results for small values of the parameter τ/τ_c, which characterizes the typical number of frequency jumps experienced by a nuclear spin. The methodology of the calculation can, in principle, be used to calculate the distribution to an arbitrary number of jumps and arbitrarily large τ/τ_c.

We first define the function $n(\Delta t)=(1-e^{-\Delta t/2\tau_c})$, the average *fraction* of spins whose precession frequency switches at least once during any time interval Δt. Consider a subensemble of spins whose precession frequencies jump j times before the 180° pulse (with the first jump occurring at time t_1, the second jump at time $t_2, \ldots$ and the jth jump at t_j where $0<t_1<t_2<\cdots<t_j<\tau$) and an additional k times (at times $\tau<t_{j+1}<t_{j+2}, \ldots, t_{j+k}<2\tau$) after the 180° but prior to the time of the echo. We label this subensemble as B^jA^k, where B stands for ''before'' and A stands for ''after.'' If the spin has an initial frequency of $\pm\omega_0$ then its accumulated phase at the time of the echo is $\pm\phi_{B^jA^k}$, where $\phi_{B^jA^k}$ is given by

$$\phi_{B^jA^k}(\{t_i\})=2\omega_0\sum_{i=1}^{j}(-1)^i t_i-2\omega_0\sum_{i=j+1}^{j+k}(-1)^i t_i - 2\omega_0\tau(-1)^j[1-(-1)^k]. \tag{A1}$$

Note that the accumulated phase is a function of the random set of transitions times $\{t_i\}$. Below we list a few examples:

$$\phi_0=0,$$

$$\phi_A=2\omega_0 t_1-4\omega_0\tau, \quad \phi_B=-2\omega_0 t_1,$$

$$\phi_{AA}=2\omega_0 t_1-2\omega_0 t_2, \quad \phi_{BA}=-2\omega_0 t_1-2\omega_0 t_2+4\omega_0\tau,$$

$$\phi_{BB}=-2\omega_0 t_1+2\omega_0 t_2,$$

$$\phi_{AAA}=2\omega_0 t_1-2\omega_0 t_2+2\omega_0 t_3-4\omega_0\tau. \tag{A2}$$

One can show that the average differential number of spins $dN_{B^jA^j}(t_1,t_2,\ldots,t_{j+k-1},t_{j+k})$ in the subensemble B^jA^k at the time of the echo is given by

$$\begin{aligned} dN_{B^jA^k}(t_1,t_2,\ldots,t_{j+k-1},t_{j+k}) &= dt_1\dot{n}(t_1)\times dt_2\dot{n}(t_2-t_1)\times dt_3\dot{n}(t_3-t_2)\times\cdots dt_{j+k-1}\dot{n}(t_{j+k-1}-t_{j+k-2})\times dt_{j+k}\dot{n}(t_{j+k}-t_{j+k-1})\times\{1-n(2\tau-t_{j+k})\} \\ &= (2\tau_c)^{-(j+k)}dt_1dt_2\cdots dt_{j+k-1}dt_{j+k}e^{-2\tau/2\tau_c}, \end{aligned} \tag{A3}$$

where $\dot{n}(\Delta t)=(2\tau_c)^{-1}\exp(-\Delta t/2\tau_c)$ is the derivative of $n(\Delta t)$. The differential $dN_{B^jA^j}(t_1,t_2,\ldots,t_{j+k-1},t_{j+k})$ contributes to the phase probability distribution, δ functions of weight $(1/2)(2\tau_c)^{-(j+k)}dt_1dt_2\cdots dt_{j+k-1}dt_{j+k}e^{-2\tau/2\tau_c}$ occurring at the phases $\pm\phi_{B^jA^k}(\{t_i\})$, where $\phi_{B^jA^k}(\{t_i\})$ is given in Eq. (A1). The phase distribution for the entire subensemble B^jA^k is then given by

$$P_{B^jA^k}(\phi)=\frac{1}{2(2\tau_c)^{j+k}}\int_0^\tau dt_1\int_{t_1}^\tau dt_2\cdots\int_{t_{j-1}}^\tau dt_j\int_\tau^{2\tau}dt_{j+1}\int_{t_{j+1}}^{2\tau}dt_{j+2}\cdots\int_{t_{j+k-1}}^{2\tau}dt_{j+k}\{\delta(\phi-\phi_{B^jA^k}\{t_i\}) + \delta(\phi+\phi_{B^jA^k}\{t_i\})\}e^{-2\tau/2\tau_c}. \tag{A4}$$

By summing the phase distribution functions $P_{B^jA^k}(\phi)$ for all the subensembles B^jA^k which have $j+k=n$, we obtain the contribution to the phase probability distribution function $P_n(\phi)$ of the subensemble of spins which execute exactly n jumps during the spin-echo sequence (without regard to the *timing* of the jumps). One can verify that the $P_n(\phi)$ are appropriately normalized in that their integrals yield the Poisson distribution functions N_n, the fraction of spins which experience n jumps within the time interval 2τ (with jumps occurring with probability per unit time of $1/2\tau_c$). N_n is given by the following relation:

$$N_n=\frac{e^{-2\tau/2\tau_c}(2\tau/2\tau_c)^n}{n!}. \tag{A5}$$

Equation (A6) gives the appropriately normalized subensemble phase distribution functions up to $n=7$, all of which are nonzero only in the range $-2\omega_0\tau<\phi<2\omega_0\tau$:

$$\begin{aligned}
P_0(\phi)&=e^{-2\tau/2\tau_c}\delta(\phi),\\
P_4(\phi)&=\frac{e^{-2\tau/2\tau_c}}{12(2\omega_0\tau_c)^4}\,(4\omega_0^3\tau^3-3\omega_0\tau\phi^2+|\phi|^3),\\
P_1(\phi)&=\frac{e^{-2\tau/2\tau_c}}{4\omega_0\tau_c},\\
P_5(\phi)&=\frac{e^{-2\tau/2\tau_c}}{128(2\omega_0\tau_c)^5}\,(16\omega_0^4\tau^4-8\omega_0^2\tau^2\phi^2+\phi^4),\\
P_2(\phi)&=\frac{e^{-2\tau/2\tau_c}}{2(2\omega_0\tau_c)^2}\,(2\omega_0\tau-|\phi|),\\
P_6(\phi)&=\frac{e^{-2\tau/2\tau_c}}{960(2\omega_0\tau_c)^6}\,(48\omega_0^5\tau^5-40\omega_0^3\tau^3\phi^2\\
&\quad+15\omega_0\tau\phi^4-4|\phi|^5),\\
P_3(\phi)&=\frac{e^{-2\tau/2\tau_c}}{8(2\omega_0\tau_c)^3}\,(4\omega_0^2\tau^2-\phi^2),\\
P_7(\phi)&=\frac{e^{-2\tau/2\tau_c}}{4608(2\omega_0\tau_c)^7}\,(64\omega_0^6\tau^6-48\omega_0^4\tau^4\phi^2\\
&\quad+12\omega_0^2\tau^2\phi^4-\phi^6).
\end{aligned} \tag{A6}$$

Summing these functions yields the phase probability distribution function, accounting for the effects up to seven jumps. The expression should be accurate for situations in which the parameter τ/τ_c is small.

$P_0(\phi)$ is a δ function containing $\exp(-2\tau/2\tau_c)$ spins, while the function $P_1(\phi)$ is a box of height $\exp(-2\tau/2\tau_c)/4\omega_0\tau_c$; each of these terms are discussed in Sec. VI in the main body of this paper. These terms alone would lead to a signal given by Eq. (28) (but with ω replaced by ω_0). It is certainly not easy to understand why inclusion of the remaining terms in phase probability distribution expansion [as they appear up to $n=7$ in Eq. (A1)] should result in the very simple (and exact) expression for the signal size which is given in Eq. (28).

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