The Memory-Function Technique for the Calculation of Pulsed-Gradient NMR Signals in Confined Geometries

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An approximation technique for the calculation of pulsed-gradient NMR signals in confined spaces is introduced on the basis of a memory-function formalism and compared to the well-known cumulant expansion technique. The validity of the technique is investigated for the cases of a time-independent field gradient and a gradient consisting of two pulses of finite duration. It is found that the validity is governed by the ratio of two characteristic times: the time for the spins to traverse the dimensions of the confining space through diffusion and the reciprocal of the extreme difference between values of the precession frequency of the spin. Oscillations in the time evolution of the signal for the constant gradient, as well as oscillations in the (gradient) field dependence for the two-pulse gradient, which are both characteristic of the exact signals, are predicted by the new technique but not by the cumulant technique. The cumulant results are shown to arise as an approximate consequence of the memory results. © 1996 Academic Press, Inc.

INTRODUCTION

The diffusion of particles possessing a nuclear spin in confined geometries as studied with pulsed-gradient spin-echo NMR has been reviewed in (*1*) and reconsidered in (*2–6*). Many of these studies make use of short gradient pulses (SGP) during which the diffusion of the particles can be taken to be negligible. The signal in the SGP experiment can be shown to be given by the modulus of a structure factor for the confining geometry. However, the SGP limit is not always physically realizable in practice. A few recent articles have been concerned with extending our understanding of the use of NMR as a confining geometry probe in the case of finite-width pulses (*1, 7–12*).

The fact that, during such finite-width pulses, the diffusion of the particles cannot be neglected introduces considerable complication in analytical investigations. Blees and others (*8–10*) have performed numerical calculations which take into account the effect of the finite-width pulse on the typical NMR microscopy experiment. Mitra and Halperin (*7*), Wang *et al.* (*12*), and Caprihan *et al.* (*13*) have proposed and studied the use of various approximation schemes to study the finite-pulse width effects on the NMR microscopy

experiment. We have also recently initiated a study of the theoretical description of these issues with the help of a new approach based on equations which are nonlocal in time. We begin a report on this study in the present paper by analyzing two typical experiments. The first involves the use of a time-independent applied magnetic-field gradient and the second involves the use of two gradient pulses.

Our approach, which may be called the memory approach, is based on the application of projection operators (*14, 15*) to the evolution equation of the system density matrix. Although projection operators have been applied to the problem of spins diffusing in a constant magnetic-field gradient previously (*16*), a Markoffian approximation, which destroys the memory-function nature of the equation, has been made. Retaining the memory-function character of evolution equations has been found to be very useful in a number of other contexts such as in exciton dynamics (*17*), vibrational relaxation (*18*), and polaron evolution (*19*). Because of the considerable practical success of the memory technique in these other contexts, we introduce it in this paper for NMR calculations. We compare the validity of the memory technique with that of another common approximation procedure (*11, 12*) by comparing the approximate results to numerically exact calculations. The paper is outlined as follows. In the remainder of this section, we set out the evolution equations for the system and indicate the exact starting point of the calculations. In the next sections, we introduce the memory-function approach, mention the cumulant expansion technique and show that it can be obtained from our memory result through a partial time-local approximation, consider a simple example of constrained geometry and compare the various results for the time-independent gradient as well as for the two-pulse gradient, and present concluding remarks.

The system comprises a large number of particles, each possessing a nuclear spin diffusing in the presence of a strong homogeneous static magnetic field $\mathbf{B}_0$ and a weak inhomogeneous static magnetic field. Both the homogeneous and inhomogeneous fields are taken to point along the *z* axis. The inhomogeneous field is due to a linear gradient $\mathbf{g}(t) =$

$gx\hat{\mathbf{x}}f(t)$, where $\hat{\mathbf{x}}$ is the unit vector in the x direction. The spins are excited at $t = 0$ by a $\pi/2$ pulse about the y axis.

The equation of motion for the spin and spatial variables of a single diffusing particle is given by

$$\frac{\partial \rho(t)}{\partial t} = -i[\mathcal{H}_{\mathbf{r}} + H_I + H_{xI}, \rho(t)], \qquad [1]$$

where

$$H_I = \omega_0 I_z$$
$$H_{xI} = -f(t)\gamma g x I_z. \qquad [2]$$

Here $\omega_0 = -\gamma B_0$, γ is the gyromagnetic ratio of the particle, $f(t)$ is a shape function for the gradient pulse, and $\mathcal{H}_{\mathbf{r}}$ is the Hamiltonian for the spatial coordinates in the absence of coupling to the spin variables. While $\mathcal{H}_{\mathbf{r}}$ will generally contain the complexities of the kinetic energy of the particles and the collisional potential energy due to interactions among particles and interactions between particles and the confining walls, its essential effects are taken into account in the standard manner through the introduction of a stochastic term to the Liouville equation,

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = -i[H_I + H_{Ix}, \rho(\mathbf{r}, t)] + D\nabla^2 \rho(\mathbf{r}, t), \quad [3]$$

where D is the diffusion coefficient. To take account of the particle interactions with the walls, one must include appropriate boundary conditions for $\rho(\mathbf{r}, t)$. Notice that ρ is now a function of $\mathbf{r}$ as well as t, the operator $\mathbf{r}$ having been replaced by the c-number parameter $\mathbf{r}$. The validity of the replacement of the fully quantum-mechanical starting point by Eq. [3] requires study. However, we will not comment on that issue in the present paper and will take, along with most workers in this area (*8, 12, 13, 16*), Eq. [3] to be the starting point.

A conversion to the interaction picture and use of $\langle I^+ \rangle = \langle I_x + iI_y \rangle = \mathrm{Tr}\{I^+ \rho(\mathbf{r}, t)\}$ leads one from Eq. [3] to

$$\frac{\partial \langle I^+(\mathbf{r}, t) \rangle}{\partial t}$$
$$= -i\gamma g x f(t)\langle I^+(\mathbf{r}, t) \rangle + D\nabla^2 \langle I^+(\mathbf{r}, t) \rangle. \quad [4]$$

Equation [4], known as the Torrey–Bloch equation (*20*) in the magnetic resonance literature, can be solved numerically through standard discretization procedures. Those solutions of Eq. [4] integrated over the confining geometry will be referred to as the numerically exact solutions in this paper, in keeping with standard usage in the recent NMR literature (*8, 12, 13*).

PROJECTION OPERATORS AND THE MEMORY-FUNCTION TECHNIQUE

The application of the projection-operator approach (*14, 15*) to the NMR problem (*16*) proceeds as follows. One defines a projection operator P through

$$PO(\mathbf{r}) = \sigma(\mathbf{r}, 0) \int d\mathbf{r}'^3 O(\mathbf{r}), \qquad [5]$$

where $\sigma(\mathbf{r}, 0)$ is the initial spatial distribution of the spins and $O(\mathbf{r})$ is an arbitrary operator. As an exact consequence of the Liouville Eq. [3], one obtains:

$$\frac{dP\rho(\mathbf{r}, t)}{dt}$$
$$= -iPL(t)P\rho(\mathbf{r}, t) - \int_{-\infty}^{\infty}\int_0^t PL(t)(1 - P)$$
$$\times U(\mathbf{r}, t, \mathbf{r}', t')(1 - P)L(t')P\rho(\mathbf{r}, t')d\mathbf{r}'^3 dt', \quad [6]$$

$$\mathrm{L}(t) = L_I + L_{Ix} + L_{\mathbf{r}},$$

$$L_I O(\mathbf{r}) = [H_I, O(\mathbf{r})]$$
$$L_{Ix} = [H_{Ix}, O(\mathbf{r})]$$
$$L_{\mathbf{r}} = iD\nabla^2 O(\mathbf{r}) \qquad [7]$$

and $U(\mathbf{r}, t, \mathbf{r}'t')$ satisfies

$$\frac{\partial U(\mathbf{r}, t, \mathbf{r}', t')}{\partial t} = -i(1 - P)L(t)U(\mathbf{r}, t, \mathbf{r}', t') \quad [8]$$

along with the boundary conditions of the confining geometry and the initial condition $U(\mathbf{r}, t', \mathbf{r}', t') = \delta(\mathbf{r} - \mathbf{r}')$. In writing Eq. [6], use has been made of the fact (see Eq. [5]) that $P\rho(\mathbf{r}_0, 0) = \rho(\mathbf{r}_0, 0)$. This property is obvious since initially the gradient is off and the spatial and spin variables are uncorrelated with $\rho(\mathbf{r}, 0) = \sigma(\mathbf{r}, 0)\sigma_I(0)$, where $\sigma(\mathbf{r}, t) = \int d\mathbf{r}^3 \rho(\mathbf{r}, t)$ is the reduced density operator for the spin variables.

To obtain useful results from Eqs. [7] and [8] it is usually necessary to perform an expansion in L_{xI}. The lowest order or Born approximation is obtained by neglecting a comparatively small L_{xI} in Eq. [8]. In this case $U(\mathbf{r}, t, \mathbf{r}', t')$ satisfies

$$\frac{\partial U(\mathbf{r}, t, \mathbf{r}', t')}{\partial t}$$
$$= -i\{(1 - P)L_I(t) + L_{\mathbf{r}}\}U(\mathbf{r}, t, \mathbf{r}', t'). \quad [9]$$

Working in the interaction picture and using $M(t) = \langle I^+(t) \rangle$ $= \mathrm{Tr}\{I^+ \sigma(t)\}$, we obtain, with the Liouville superoperator given by Eq. [7],

$$\dot{M}(t)$$
$$= -i\gamma g f(t)\langle x_0\rangle M(t) - \gamma^2 g^2 f(t) \int_0^t dt' f(t')$$
$$\times \langle xx(t-t')\rangle M(t) + \gamma^2 g^2 f(t)\langle x_0\rangle^2$$
$$\times \int_0^t dt' f(t') M(t), \qquad [10]$$

where the dot denotes a time derivative, $\langle x_0\rangle$ and $\langle xx(t - t')\rangle$ are given by

$$\langle x_0\rangle = \int x U(\mathbf{r}_0, t_0) d\mathbf{r}^3$$

$$\langle xx(\tau)\rangle = \iint x_0 x U(\mathbf{r}_0, t_0) U(\mathbf{r}, \tau, \mathbf{r}_0, t_0)$$
$$\times d\mathbf{r}_0^3 d\mathbf{r}^3, \qquad [11]$$

and $U(\mathbf{r}_0, 0)$ is the probability of the particle being between $\mathbf{r}_0$ and $\mathbf{r}_0 + d\mathbf{r}_0$ at $t = 0$. $U(\mathbf{r}, t, \mathbf{r}_0, 0)$ is the solution to

$$D\nabla^2 U(\mathbf{r}, t, \mathbf{r}_0, 0) = \frac{\partial U(\mathbf{r}, t, \mathbf{r}_0, 0)}{\partial t} \qquad [12]$$

with the initial condition $U(\mathbf{r}, 0, \mathbf{r}_0, 0) = \delta(\mathbf{r} - \mathbf{r}_0)$ and boundary condition appropriate to the confining walls.

The origin of the coordinate system can always be chosen in such a way that $\langle x_0\rangle = 0$. Equation [10] then becomes

$$\dot{M}(t) + f(t) \int_0^t dt' f(t')\phi(t - t') M(t') = 0, \quad [13]$$

where $\phi(t) = \gamma^2 g^2 \langle xx(t)\rangle$ is the memory function. Equation [13] is the primary result of the memory technique we introduce and whose validity we study in the following.

CUMULANT EXPANSION TECHNIQUE

The (truncated) cumulant expansion technique, whose validity we will investigate along with that of the memory result of Eq. [13], is well known in the NMR literature (1, 12, 13). Its results can be summarized as follows:

$$M(t) = \exp\{i\langle\varphi(t)\rangle\}\exp\{-\alpha(t)\} \qquad [14]$$

$$\alpha(t) = \frac{1}{2}\gamma^2 g^2 \int_0^t \int_0^t f(t_1) f(t_2)$$
$$\times \langle x(t_1)x(t_2)\rangle dt_1 dt_2 - \frac{1}{2}\langle\varphi(t)\rangle^2 \qquad [15]$$

$$\langle\varphi(t)\rangle = \gamma g \int_0^t f(t')\langle x(t')\rangle dt'. \qquad [16]$$

Choosing the origin so that $\langle x(t')\rangle = 0$, one obtains $\langle\varphi(t)\rangle = 0$, and

$$\alpha(t) = \frac{1}{2}\gamma^2 g^2 \int_0^t \int_0^t f(t_1) f(t_2)\langle x(t_1 - t_2)x\rangle dt_1 dt_2. \quad [17]$$

The cumulant expansion result for the signal $M(t)$ is

$$M(t) = \exp\left\{-\frac{1}{2}\gamma^2 g^2 \int_0^t \int_0^t f(t_1) f(t_2)\right.$$
$$\left.\times \langle x(t_1 - t_2)x\rangle dt_1 dt_2\right\}. \qquad [18]$$

We now show that Eq. [18], which is well known in the NMR literature, can be obtained as a particular case of the memory result, Eq. [13]. If the memory function $\phi(t)$ in Eq. [13] decays very rapidly, $M(t)$ may be removed from the integral, yielding

$$\dot{M}(t) = -\gamma^2 g^2 f(t) M(t) \int_0^t dt' f(t')\langle x(t - t')x\rangle. \quad [19]$$

Integrating Eq. [19] results in

$$M(t) = \exp\left\{-\gamma^2 g^2 \int_0^t dt'' \int_0^{t''} dt' f(t'') f(t')\right.$$
$$\left.\times \langle x(t'' - t')x\rangle\right\}. \qquad [20]$$

For a stationary process, $f(t'')f(t')\langle x(t'' - t')x\rangle$ is symmetric under an exchange of t' and t''. One may, therefore, replace the double integral of Eq. [20] over a triangular region in t' and t'' by $\frac{1}{2}$ the double integral over the corresponding square region. Then Eq. [20] becomes identical to the cumulant result Eq. [18].

This demonstration shows explicitly that the (truncated) cumulant expansion result is a further approximation to the memory result, and that it tends to the latter for those situations in which the memory function decays rapidly in time. Similar connections between the cumulant technique and memory functions have been given in Ref. (18) in the context of vibrational relaxation. It is im-

portant to understand that a significant difference exists between Robertson's earlier projection technique analysis in the NMR context (*16*) and our present treatment. Robertson made the partial time-local approximation referred to above, his results being consequently identical to those of the truncated cumulant technique. By contrast, our interest in introducing the memory technique into NMR calculations is precisely to refrain from making the time-local approximation so that one can go beyond the cumulant results. This is in keeping with the philosophy pursued in the contexts of exciton dynamics and vibrational relaxation (*17, 18*).

TIME-INDEPENDENT GRADIENT

The essential features of the applicability of the memory and cumulant techniques can be understood from the relatively simple case of a time-independent gradient which we treat in this section. We start with the simplest possible case of confining geometry: a line segment of length a. We mention generalizations to cylindrical and spherical confining geometries in the concluding section. If the particle diffuses between $x = -a/2$ and $x = a/2$, we have

$$
\begin{aligned}
U(x, &\, t \,|\, x_0, 0) \\
&= \frac{1}{a} + \frac{2}{a} \sum_{n=1}^{\infty} \cos\left(\frac{n\pi}{a}\left[x_0 + \frac{a}{2}\right]\right) \\
&\quad \times \cos\left(\frac{n\pi}{a}\left[x + \frac{a}{2}\right]\right) \exp\left\{-\frac{n^2\pi^2 D|t|}{a^2}\right\}
\end{aligned} \quad [21]
$$

so that, with $\langle x_0 \rangle = 0$, the autocorrelation of x is

$$
\begin{aligned}
\langle x(t)x \rangle &\\
= \frac{8a^2}{\pi^4} &\sum_{n=1}^{\infty} \frac{1}{(2n-1)^4} \exp\left\{-\frac{(2n-1)^2\pi^2 Dt}{a^2}\right\}. \quad [22]
\end{aligned}
$$

Memory-Function Results

The memory result is obtained in the Laplace domain from Eq. [13] as

$$
\tilde{M}(\epsilon) = \frac{M(0)}{\epsilon + 8\left(\dfrac{\gamma g a}{\pi^2}\right)^2 \Sigma_{n=1}^{\infty}(2n-1)^{-4}}, \quad [23]
$$

$$
[\epsilon + (2n-1)^2\pi^2 Da^{-2}]^{-1}
$$

where ϵ is the Laplace variable and the tilde denotes the transform. The Laplace inversion of this result can be done only numerically. However, it is possible to use an excellent approximation to represent the sum of exponentials in Eq. [23] as a single exponential term whose initial value and time integral (from 0 to ∞) are respectively equal to the corresponding quantities calculated from Eq. [22]. Using the relationship between sums of the form $\Sigma_{n=1}^{\infty}(2n-1)^{-2k}$ and Bernoulli numbers B_{2k}, specifically the results $\Sigma_{n=1}^{\infty}(2n-1)^{-4} = \pi^4/96$ and $\Sigma_{n=1}^{\infty}(2n-1)^{-6} = \pi^6/960$, we obtain the memory function $\phi(t) = \gamma^2 g^2 \langle x(t)x \rangle$ in Eq. [13] as

$$
\phi(t) = C^2 e^{-2\lambda t}, \quad [24]
$$

where $C^2 = (\gamma g a)^2/12$ and $\lambda = 5D/a^2$. Equation [23] now becomes

$$
M(\epsilon) = \frac{M(0)(\epsilon + 2\lambda)}{\epsilon^2 + 2\lambda\epsilon + C^2} \quad [25]
$$

and leads, in the time domain, to

$$
\begin{aligned}
M(t) = \exp(-\lambda t)\Bigg[&\cosh(t\sqrt{\lambda^2 - C^2}) \\
&+ \frac{\lambda}{\sqrt{\lambda^2 - C^2}}\sinh(t\sqrt{\lambda^2 - C^2})\Bigg]. \quad [26]
\end{aligned}
$$

This is the NMR signal predicted by our memory technique for the case of the time-independent gradient. We notice that the signal is formally identical to the displacement of a damped harmonic oscillator, the damping being controlled by the diffusion time a^2/D required to cover the extent of the confining space.

Numerical Comparison

The cumulant result corresponding to the memory result Eq. [26] is obtained from Eqs. [18] and [22],

$$
\begin{aligned}
\ln M(t) = &-\left(\frac{K\gamma g a^3}{D}\right)^2 \\
&\times \sum_{n=1}^{\infty} \frac{(2n-1)^2\pi^2 t Da^{-2} + \exp[-(2n-1)^2\pi^2 t Da^{-2}] - 1}{(2n-1)^8},
\end{aligned}
$$

$$
[27]
$$

where K is the numerical constant $192\sqrt{2}/\pi^8$. We plot the cumulant result along with the memory result, as well as the exact result, in Fig. 1 for a number of values of the characteristic parameter $\zeta = C/\lambda$: (a) 0.5, (b) 1, (c) 2, (d) 10. The signifi-
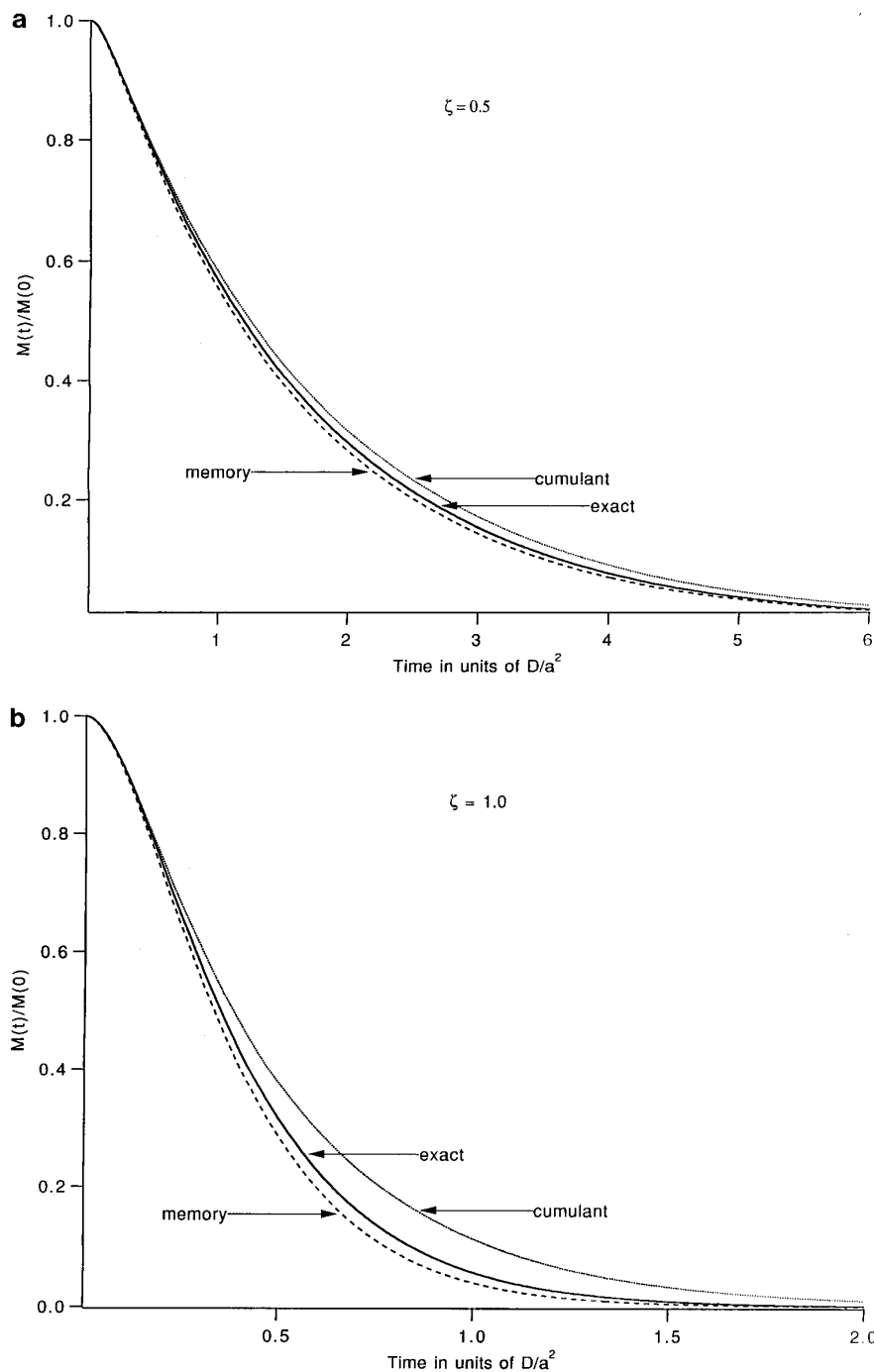
FIG. 1. The NMR signal $M(t)$ as a function of the dimensionless time tD/a^2 in the continual-gradient case showing a comparison of the numerically obtained exact result (solid line), the memory result (dashed line), and the cumulant result (dotted line). The value of ζ (see text) is taken to be (a) 0.5, (b) 1, (c) 2, and (d) 10, respectively.

cance of this parameter ζ, which equals $\gamma g a^3 / 10\sqrt{3}D$, is that, except for a numerical proportionality constant, it is the ratio of the extreme difference between the precessional frequencies in the confining space, viz., $\gamma g a$, to the reciprocal of the time

it would take the spin particle to diffuse from one end of the confining segment to the other, viz., D/a^2.

For small values of ζ, the memory-function results are seen to be quantitatively better than the cumulant results
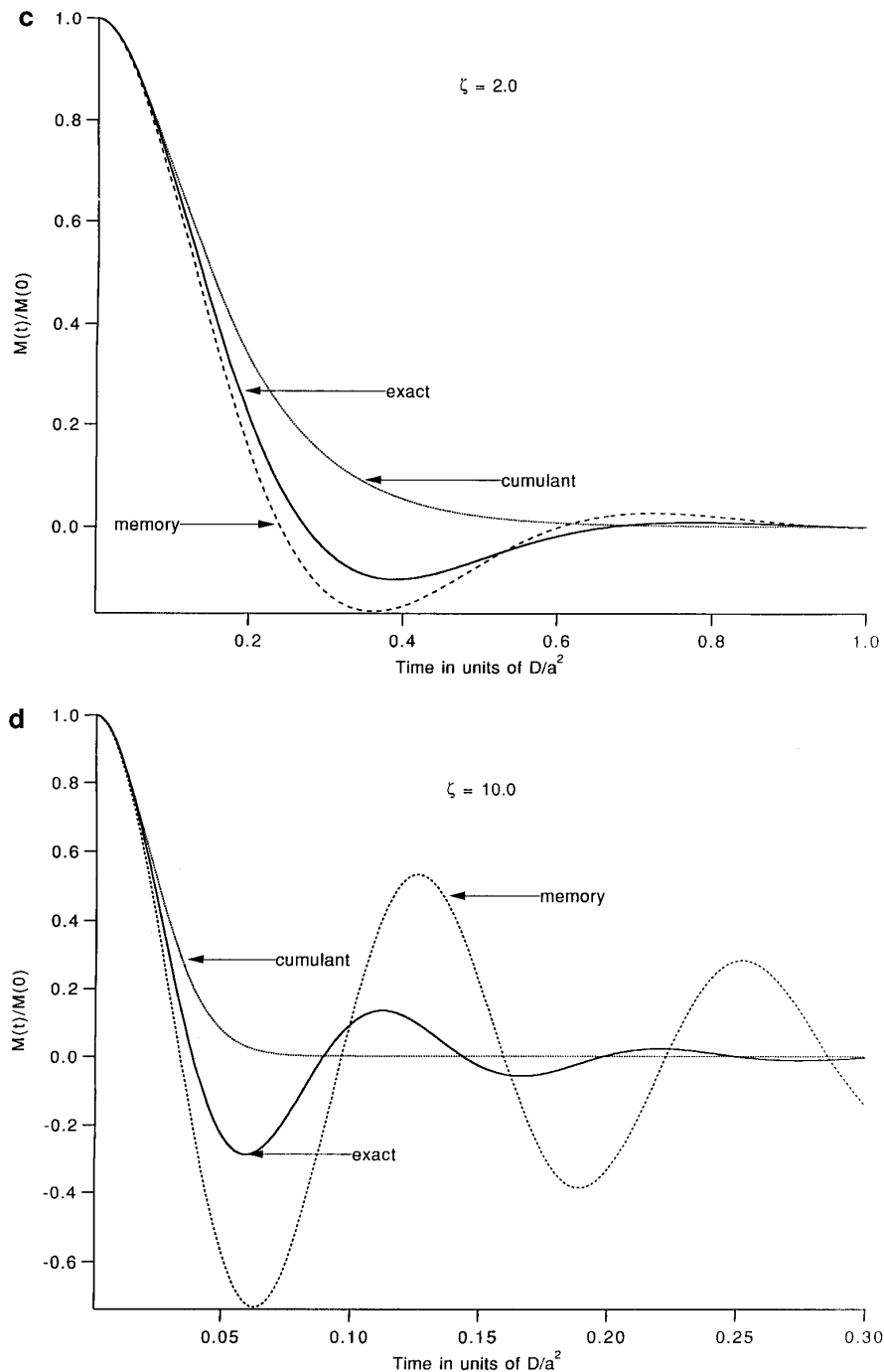
FIG. 1—*Continued*

as Figs. 1a and 1b show. As ζ is increased further, we see from Fig. 1c that a qualitative feature of the exact results, viz., the oscillations with respect to time, are reproduced by the memory technique but not by the cumulant result. As ζ is increased still further, this qualitative superiority of the memory technique persists but the oscillations pre-dicted are overly pronounced. This seen in Fig. 1d. The comparison thus establishes that the memory technique is generally preferable to the cumulant technique, that it produces oscillations characteristic of the exact evolution unlike the cumulant result, and that its quantitative differ-ence from the exact result becomes larger as ζ increases.

Larger ζ corresponds to larger field strengths, larger confinement lengths, and smaller diffusion constants.

TWO-PULSE GRADIENT

While the constant-gradient case treated above facilitates the analysis of the applicability of the approximation technique, it is of interest to examine also a realistic case encountered in NMR observations, viz., the two-pulse experiment known commonly as PGSE (pulsed-gradient spin echo) (*1*).

Memory-Function Results

The two-pulse experiment consists of the application of two gradient pulses of strength *g* and duration δ, and separated by an interval of time Δ. The second pulse is preceded by a π pulse about the *x* axis. This is, however, mathematically equivalent to changing the direction of the field associated with the second pulse and omitting the rotation due to the π pulse. The gradient shape function $f(t)$ is then given by

$$f(t) = \Theta(t) - \Theta(t - \delta) - \Theta(t - \Delta) + \Theta(t - [\Delta + \delta]), \qquad [28]$$

where $\Theta(t)$ is the Heaviside step function. In this case the magnetization is measured at the peak of the echo produced by the $\pi/2$ radiofrequency pulse. The general memory equation now becomes

$$\dot{M}(t)$$

$$= \begin{cases} -\int_0^t dt' \phi(t - t') M(t') & 0 \le t < \delta \\ 0 & \delta \le t < \Delta \\ \int_0^\delta dt' \phi(t - t') M(t') - \int_\Delta^t dt' \phi(t - t') M(t') \\ & \Delta \le t < \delta + \Delta \\ 0 & \delta + \Delta \le t. \end{cases}$$

$$[29]$$

The exponential form of the memory function $\phi(t - t')$ allows the simplification of the above evolution into

$$\ddot{M}(t) + 2\lambda \dot{M}(t) + C^2 M(t) = 0. \qquad [30]$$

For the region $0 \le t < \delta$, we use the solution of Eq. [30] with the initial conditions

$$M(t) = 1$$
$$\dot{M}(t) = 0, \qquad [31]$$

whereas, in the region $\Delta \le t < \delta + \Delta$, the initial conditions become

$$M(\Delta) = M(\delta)$$
$$\dot{M}(\Delta) = -\int_0^\delta \phi(\Delta - t') M(t') dt'. \qquad [32]$$

These initial conditions are found by solution of the problem in region 1 and by using Eq. [29]. The final memory result for the signal strength at the echo is

$$M(2\Delta)$$
$$= e^{-2\lambda\delta} \cos^2(\delta\sqrt{C^2 - \lambda^2}) + e^{-2\lambda\delta} \frac{\lambda}{\sqrt{C^2 - \lambda^2}}$$
$$\times \sin(2\delta\sqrt{C^2 - \lambda^2}) + \frac{1}{C^2 - \lambda^2}(\lambda^2 e^{-2\lambda\delta} + C^2 e^{-2\lambda\Delta})$$
$$\times \sin^2(\delta\sqrt{C^2 - \lambda^2}). \qquad [33]$$

Numerical Comparison

The memory result of Eq. [33] relevant to the two-pulse case has as its cumulant counterpart the following (*11*):

$$\ln M(2\Delta) = -\frac{8}{\pi^8}\left(\frac{\gamma g a}{D}\right)^2$$
$$\times \sum_{n=1}^\infty \frac{1}{(2n-1)^8}\{2[(2n-1)^2\pi^2 D\delta a^{-2}$$
$$+ \exp[-(2n-1)^2\pi^2 D\delta a^{-2}]]$$
$$+ \exp[-(2n-1)^2\pi^2 D\Delta a^{-2}]$$
$$\times \{\exp[-(2n-1)^2\pi^2 D\delta a^{-2}] - 1\}$$
$$\times \{\exp[(2n-1)^2\pi^2 D\delta a^{-2}] - 1\}\}. \qquad [34]$$

The PGSE experiment often allows Δ to be sufficiently large for the diffusing particles to interact with the boundaries of a confining geometry ($\Delta D/a^2 \ge 1$) and strives to make the pulse short ($\delta D/a^2 \ll 1$). A diffraction pattern then results when the echo strength is plotted as a function of the gradient strength, the location of the minima of the diffraction pattern being simply related to the characteristic length of the confining geometry (*1*). One of the serious shortcomings of the (truncated) cumulant technique is that it is unable to predict such diffraction patterns. Our memory result, however, does show the existence of these patterns and is thus particularly

suited to the investigation of the effect of pulses during which significant diffusion occurs.

The times $1/\lambda$ and $1/C$ introduced above for the case of the time-independent gradient are also important for this case. They appear here in comparison to the duration δ and the interval Δ. The relevant quantities are thus $\lambda\delta = \delta D/a^2$ and $\lambda\Delta = \Delta D/a^2$ as well as $C\delta$ and $C\Delta$. The quantity $\Delta D/a^2$, which is a measure of how much the particle diffuses during the interval between the pulses relative to the confining length, has been taken to equal 1.0 in (a), (b), and (c) and 0.2 in (d) of Fig. 2. The confinement is thus sampled much less in (d) than in the other cases. The quantity $\delta D/a^2$, which measures the extent of diffusion during the duration of the pulse, also relative to the confining length, is taken to be 0.001 in Fig. 2a, increased by a factor of 50 to the value 0.05 in Fig. 2b, and increased further to 0.25 in Fig. 2c, and to 0.001 in Fig. 2d. The pulses thus become progressively longer as one goes from (a) to (d).

Wang *et al.* (*12*) introduced the two-parameter space spanned by $\delta D/a^2$ and $\Delta D/a^2$ into the analysis of the two-pulse experiment, and clarified with its help a number of features of the NMR signal. They also mentioned an extension of their two-parameter space into a third dimension spanned by $\gamma g\delta a$ and examined the attenuation behavior for nonzero $\gamma g\delta a$ at specific points of interest in the $\delta D/a^2 - \Delta D/a^2$ plane. Our analysis in the present paper is not restricted to vanishing $\gamma g\delta a$ but has a different domain of validity. Roughly stated, our treatment is valid for $\Delta D/a^2 > 1$ and thus covers only part of the vanishing $\gamma g\delta a$ region that the cumulant analysis is able to treat. However, unlike the cumulant technique, our analysis can provide a description of the diffraction patterns referred to above, which arise for nonzero $\gamma g\delta a$. Although experimental observation of these patterns is difficult except at high gradients, they have been attracting attention recently in the NMR community (*2, 3, 7*).

Our prediction of the patterns is clear in Fig. 2, where we see that increasing the field g yields minima in the signal. In addition to the fact that the very existence of the minima is a feature of the exact result that the memory technique does, while the cumulant technique cannot, reproduce, we see that the memory result is more accurate than the cumulant technique below the first minimum. This is more apparent as the pulse is made wider. Figure 2 also shows that, as $\Delta D/a^2$ is made small so that the particle has insufficient time to sample the boundaries of the confining geometry, a shortcoming of the memory technique emerges: it predicts an exaggerated lifting of the minima from the horizontal axis.

CONCLUDING REMARKS

The purpose of the present paper has been to introduce a new technique for the computation of NMR signals in confining geometries. It is based on a memory formalism as in Refs. (*15–17*), and is represented by Eq. [13]. Through a comparison of numerically obtained exact results (*8*) from the Torrey–Bloch evolution (see Eq. [4]), we have found that the new technique is generally preferable to the truncated cumulant technique used in the NMR field and represented by Eq. [18]. Indeed, we have shown that the cumulant result can be obtained from the memory result through a partial time-local approximation. We have seen that oscillations in the signal, whether as a function of time for the constant gradient case (see Fig. 1) or as a function of the gradient field strength for PGSE, more precisely of the dimensionless wavevector $\gamma g\delta a$ (see Fig. 2), are denied to the cumulant technique but are reproduced by the memory technique. On the other hand, we have seen that the memory technique loses in validity whenever the confinement is not very effective. Thus, for instance, it is inadvisable to use the memory technique near the limit of no confinement. We have discussed the dimensionless ratios $\zeta = \gamma g a^3/10\sqrt{3}D$, as well as $\delta D/a^2$ and $\Delta D/a^2$, in delineating the various limits of validity. Figures 1 and 2 make our findings clear in this context.

The single-exponential approximation in our memory treatment has been made only for simplicity but is indeed excellent as can be seen by plotting the actual memory function $\phi(t)$ as given by the right-hand side of Eq. [22], and comparing it to the approximate single-exponential form. Indeed, a monoexponential approximation which is simpler than the one we have used above is also excellent. It consists of dropping all but the first term in the summation in Eq. [22]. The second and successive terms are at least a factor of 80 smaller than the first one independently of system parameters.

While we have based our analysis above on confinement in a one-dimensional linear segment, it is straightforward to show that, in the case of cylindrical and spherical confining geometries, the analysis is unchanged in essentials. As in Eq. [22], the autocorrelation function $\langle x(t)x \rangle$ has the form of a sum of exponentials,
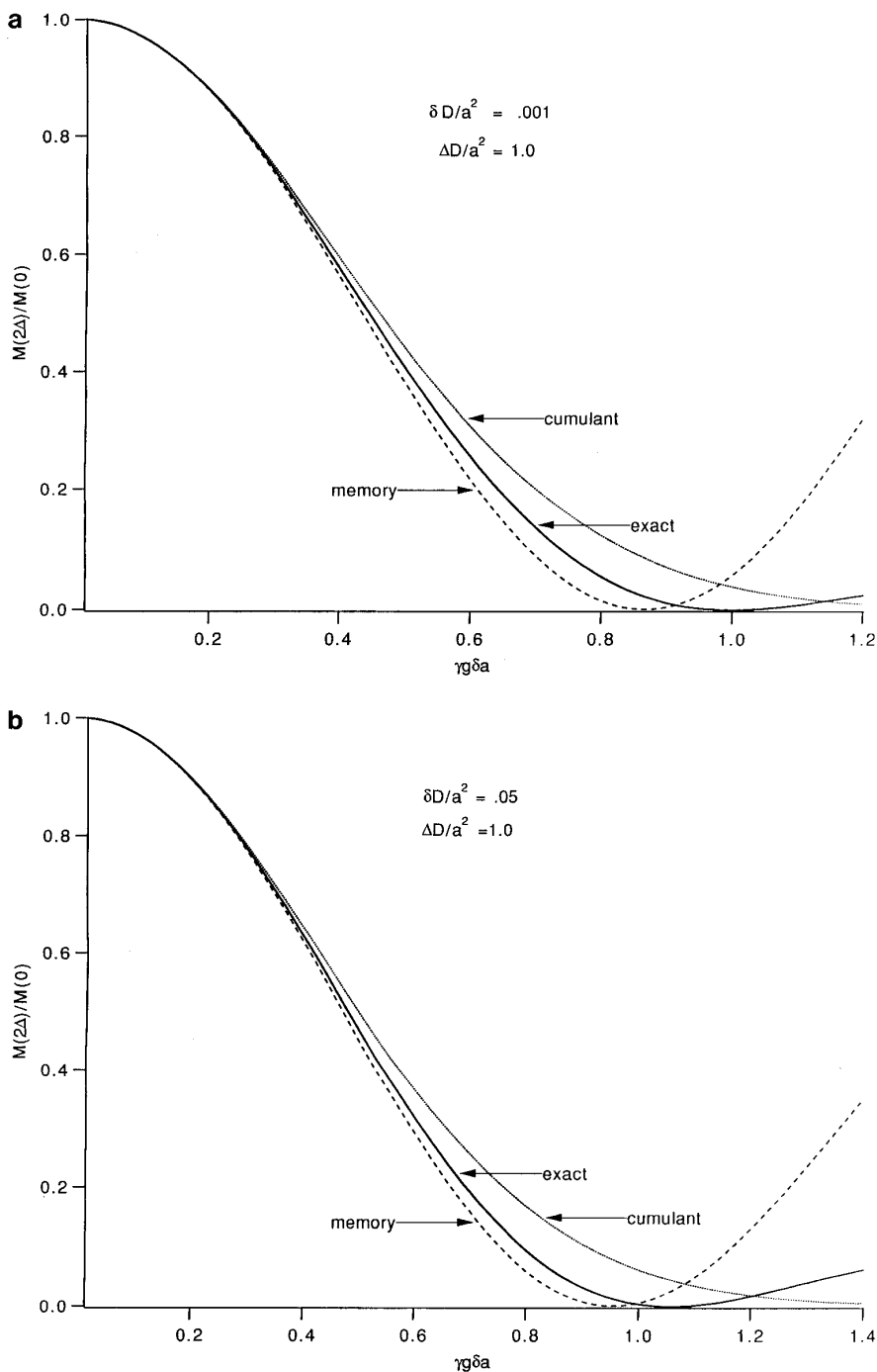
$$\langle x(t)x \rangle = \frac{(\gamma g a)^2}{2} \sum_{k=1}^{\infty} \frac{1}{\beta_k^2(\beta_k^2 - 1)} \exp(-\beta_k^2 D/a^2),$$

[35]

the first term in the k summation being considerably larger than subsequent terms as in Eq. [22]. Approximating the sum by the first term, we find that the memory function $\phi(t)$ is given once again by Eq. [24] with the modification that C and λ are now

$$C^2 = \frac{(\gamma g a)^2}{2\beta_1^2(\beta_1^2 - 1)}$$

[36]

$$\lambda = \frac{\beta_1^2 D}{2a^2}.$$

[37]

FIG. 2. The normalized NMR signal $M(2\Delta)/M(0)$ as a function of the dimensionless wavevector $\gamma g \delta a$ for the PGSE experiment showing a comparison of the exact (solid line), memory (dashed line), and cumulant results (dotted line). The value of the quantities $\delta D/a^2$ and $\Delta D/a^2$ are respectively (a) 0.001, 1.0; (b) 0.05, 1.0; (c) 0.25, 1.0; and (d) 0.001, 0.2.

Here β_1 is the smallest zero determined from $J_1'(\beta) = 0$ for the cylinder and $\beta J_{3/2}'(\beta) - (1/2)J_{3/2}(\beta) = 0$ for the sphere, and a is the radius of the cylinder or sphere. Specifically, β_1 equals 1.84 for the cylinder and 2.08 for the sphere.

The primary virtue of the memory technique is that, unlike the cumulant technique, it predicts oscillations (w.r.t. time and w.r.t. field strength) present in the exact evolution. Its primary shortcoming is that for large gradient strengths,
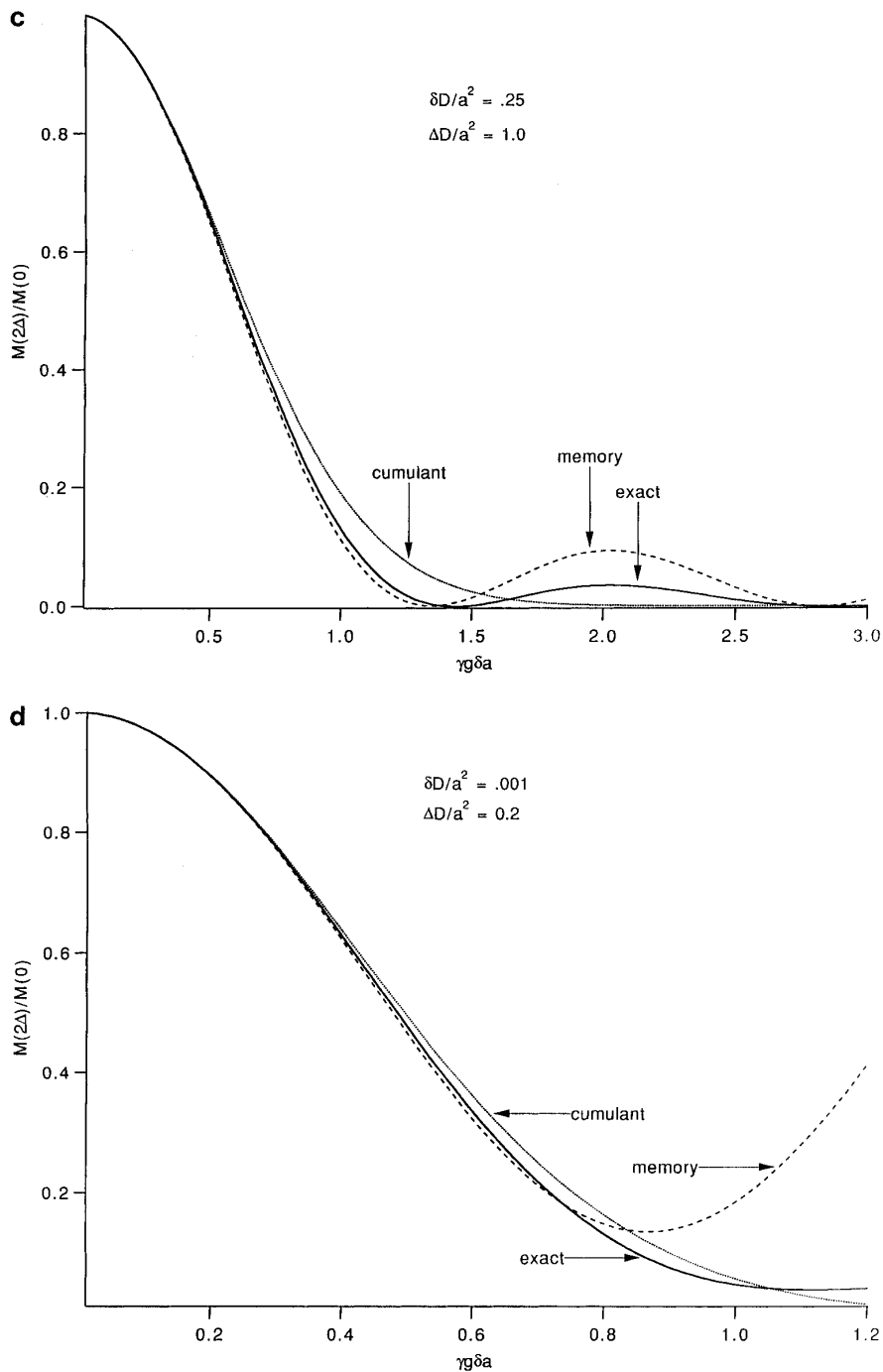
c

$\delta D/a^2 = .25$

$\Delta D/a^2 = 1.0$

cumulant

memory

exact

$\gamma g \delta a$

$M(2\Delta)/M(0)$

d

$\delta D/a^2 = .001$

$\Delta D/a^2 = 0.2$

cumulant

memory

exact

$\gamma g \delta a$

$M(2\Delta)/M(0)$

FIG. 2—*Continued*

large confining lengths, and small diffusion constants, the oscillations it predicts have larger amplitudes than in the exact evolution. We also point out that neither the memory function nor the cumulant expansion approach gives the proper SGP limit as $\delta \to 0$, $g \to \infty$, such that $g\delta = $ constant. Ongoing work addresses this issue as well as the analysis of the motion of spins with special boundary conditions and

potentials of physical interest carried out with the help of the memory and cumulant techniques.

ACKNOWLEDGMENTS

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