Spin-Echo Decay of Spins Diffusing in a Bounded Region*

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An approximate expression for the spin-echo-decay envelope is obtained from Torrey's equation for spins diffusing in a magnetic field gradient G and in a region that is small compared with $(D/\gamma G)^{1/3}$ in the direction of the large uniform magnetic field, and large in the directions perpendicular to the field. (Here D is the diffusion constant and γ the nuclear gyromagnetic ratio.) In a preceding paper, Wayne and Cotts compare this expression with experiment for regions that are large compared with $(D/\gamma G)^{1/3}$ but small enough that the simple spin-echo-decay envelope for an infinitely large region does not apply.

THE equation of motion for the magnetization of spins diffusing in a magnetic field gradient G has been derived by Torrey. In the rotating frame and with the exponential relaxation factored out of the magnetization, it is[1]

$$\partial M/\partial t = -i\gamma GzM + D\nabla^2 M\,, \tag{1}$$

where γ is the magnetogyric ratio, D is the diffusion constant, and

$$M = M_x + iM_y. \tag{2}$$

Assuming that the boundary surface produces no magnetic fields that can cause the magnetization to relax and since the diffusion currents normal to the boundary must be zero, M satisfies[2]

$$\nabla_n M = 0 \quad \text{on the boundary}, \tag{3}$$

where ∇_n is the component of the gradient operator normal to the boundary surface.

Wayne and Cotts[3] have measured the relaxation of the nuclear spins of gas molecules diffusing in a small compartment. In this paper, we obtain an approximate expression for the spin-echo-decay envelope from Eqs. (1) and (3) for spins in a small compartment. In the Appendix, we discuss the possibility of adding another term to Eq. (1), and we show that its effect is negligible for their experiment.

We assume that the spins are diffusing in a compartment which is infinite in size in the x and y directions but has a size a in the z direction with walls at $z=0$ and at $z=a$. In order to simplify our equations, we measure distances in multiples of a, times in multiples of

$$t_D = a^2/D\,, \tag{4}$$

and the magnetization as a multiple of the constant initial magnitude of the magnetization. Then, in terms of the only dimensionless constant in the problem,

$$\alpha = a^3\gamma G/D\,, \tag{5}$$

the equation of motion (1) becomes

$$\partial M/\partial t = -i\alpha zM + \partial^2 M/\partial z^2\,, \tag{6}$$

the boundary condition (3) becomes

$$\partial M(z,t)/\partial z = 0 \quad \text{at} \quad z = 0, 1\,, \tag{7}$$

and the initial condition after a 90° pulse is

$$M(z,0) = 1\,. \tag{8}$$

Finally, from Eq. (2), the effect of a 180° pulse at time $t=\tau$ is

$$M(z, \tau+) = M(z, \tau-)^*\,, \tag{9}$$

and the envelope of the spin-echo decay is

$$F(2\tau) = \frac{1}{2}\int_0^1 [M(z,2\tau) + M(z,2\tau)^*]dz\,, \tag{10}$$

which is 1 for $\tau = 0$.

We now have a complete statement of the problem that we are to solve. We must integrate Eq. (6) subject to the boundary condition (7) from the initial condition (8) up to time $t=\tau$, then apply Eq. (9), integrate up to time $t=2\tau$, and finally calculate F from Eq. (10). At first glance, it might appear that all that is necessary is to use a solution of the form

$$M(z,t) = \exp[(-i\alpha z + \partial^2/\partial z^2)(t-t_0)]M(z,t_0) \tag{11}$$

with Eqs. (8)–(10). However, although Eq. (11) is a solution to the equation of motion (6), it does not satisfy the boundary condition (7), and so is incorrect.

We may be sure that the boundary condition will be satisfied by expanding the magnetization

$$M(z,t) = \sum a_n(t)\psi_n(z)\,, \tag{12}$$

where the sum is over $n = 0, 1, 2, \cdots$, and where the functions

$$\psi_n(z) = (2-\delta_{n0})^{1/2}\cos(n\pi z) \tag{13}$$

satisfy the boundary condition (7) and are complete and orthonormal on the interval 0 to 1. In terms of the

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[1] H. C. Torrey, Phys. Rev. **104**, 563 (1956).
[2] J. I. Kaplan, Phys. Rev. **115**, 575 (1959).
[3] R. C. Wayne and R. M. Cotts, preceding paper, Phys. Rev. **151**, 264 (1966).

matrix elements

$$Z_{nn'}=\int_0^1 \psi_n z\psi_{n'}dz=Z_{n'n}, \tag{14}$$

$$D_{nn'}=\int_0^1 \psi_n(\partial^2/\partial z^2)\psi_{n'}dz=-\delta_{nn'}n^2\pi^2, \tag{15}$$

the expansion coefficients satisfy the equation of motion

$$\dot{a}_n=\sum(-i\alpha Z_{nn'}+D_{nn'})a_{n'}. \tag{16}$$

Finally, the initial condition becomes

$$a_n(0)=\delta_{n0}, \tag{17}$$

the effect of the 180° pulse becomes

$$a_n(\tau+)=a_n(\tau-)^*, \tag{18}$$

and the envelope becomes

$$F(2\tau)=\tfrac{1}{2}[a_0(2\tau)+a_0(2\tau)^*]. \tag{19}$$

Our problem has been reformulated in such a way that it appears similar to a problem in quantum mechanics. It is not identical since an i does not appear in front of the last term on the right of Eq. (16), since the observed quantity F is the real part of a_0, and since the normal derivative of ψ_n and not ψ_n itself is zero on the boundaries.

A formal solution to the problem is obtained by inserting

$$a(t)=\exp[(-i\alpha Z+D)(t-t_0)]a(t_0) \tag{20}$$

into Eqs. (17)–(19). Here Z and D are matrices operating on the column vector $a(t_0)$ yielding the column vector $a(t)$, which is a solution to Eq. (16). The operators Z and D must be expressed by the representation (14) and (15) or its equivalent and not by the representation in Eq. (11). The two representations are not equivalent as may be seen by comparing the matrix elements of $[\partial^2/\partial z^2,z]=2\partial/\partial z$ with $[D,Z]$ using Eqs. (13)–(15).

Since the matrix $D-i\alpha Z$ does not commute with its Hermitian conjugate, it cannot be diagonalized, but this will not prevent us from using Eq. (20) to express F in a more convenient form than in Eq. (19). Observe that, because the operators (14) and (15) are symmetrical in n and n', the n, n' matrix element of the exponential operator in Eq. (20) is also symmetrical in n and n'. By using this observation with Eqs. (17)–(20), we obtain

$$F(2\tau)=\sum a_n(\tau-)a_n(\tau-)^*. \tag{21}$$

The form of this expression suggests that the problem now defined by Eqs. (16), (17), and (21) may be conveniently reformulated in terms of the density matrix

$$\rho_{nm}(t)=a_n(t)a_m(t)^*, \tag{22}$$

which has the initial condition

$$\rho_{nm}(0)=\delta_{n0}\delta_{m0}. \tag{23}$$

In terms of ρ, the expression for the envelope becomes

$$F(2\tau)=\mathrm{Tr}[\rho(\tau)], \tag{24}$$

where the Tr indicates a sum over $n=m$ from 0 to ∞.

To express the equation of motion for ρ, we define a generalized Liouville operator[4]

$$L=L'+L'', \tag{25}$$

where the matrix elements of L' and L'' are

$$L'_{nm,n'm'}=\alpha(Z_{nn'}\delta_{mm'}-\delta_{nn'}Z_{mm'}), \tag{26}$$

$$L''_{nm,n'm'}=-i\delta_{nn'}\delta_{mm'}(n^2+m^2)\pi^2. \tag{27}$$

The equation of motion then has the form of the Liouville equation

$$\dot{\rho}_{nm}(t)=-i\sum L_{nm,n'm'}\rho_{n'm'}(t). \tag{28}$$

The operator L' gives a commutator of αZ with the operators to the right of itself, and the operator L'' gives an anticommutator of iD with the operators to the right of itself. Only the anticommutator, which arises because the corresponding term in Eq. (16) is real, makes the trace in Eq. (24) not constant in time.

We now use a method due to Nakajima[5] and Zwanzig[6] on Eqs. (23)–(28) to obtain an integrodifferential equation for F. To do so, we introduce the operator

$$P_{nm,n'm'}=\delta_{n0}\delta_{m0}\delta_{n'm'}, \tag{29}$$

which when operating to the right on any operator A gives

$$PA=\rho(0)\,\mathrm{Tr}(A), \tag{30}$$

where A must include all of the operators to the right of P. It follows immediately that

$$\mathrm{Tr}(PA)=\mathrm{Tr}(A), \tag{31}$$

and therefore that

$$P^2=P. \tag{32}$$

The result of P operating on ρ is

$$\sigma(t)\equiv P\rho(t)=\rho(0)F(2t), \tag{33}$$

and therefore ρ and σ have the same initial condition (23). Finally,

$$F(2t)=\mathrm{Tr}[\sigma(t)]. \tag{34}$$

Since P is linear and time-independent, σ must satisfy Zwanzig's linear integrodifferential equation[7]

$$\dot{\sigma}(t)=-iPL\sigma(t)-\int_0^t PLe^{-it'(1-P)L}(1-P)L\sigma(t-t')dt'. \tag{35}$$

[4] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).
[5] S. Nakajima, Progr. Theoret. Phys. (Kyoto) **20**, 948 (1958).
[6] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960).
[7] Equation (11) of Ref. 6 with $f=\rho$ and $f_1=\sigma$.

Now for any operator A

$$\mathrm{Tr}[L'A]=0,\quad PL'A=0, \tag{36}$$

$$L''\rho(0)=0,\quad L''PA=0, \tag{37}$$

so the trace of Eq. (35) becomes

$$dF(2t)/dt=-\int_0^t K(t')F(2t-2t')dt', \tag{38}$$

$$K(t)\equiv \mathrm{Tr}[L''e^{-t(1-P)L}L'\rho(0)]. \tag{39}$$

The integrodifferential equation (38) with the kernel (39) follows exactly from Eqs. (6)–(10) without any assumptions.

The integrodifferential equation (38) can be solved exactly for F in terms of K by use of Laplace transforms. Nevertheless, it will be sufficient for our purposes to assume either that t is small so that F has changed very little or that F varies slowly compared with the time required for K to become small. Then F may be taken out of the integral in Eq. (38), which becomes the ordinary differential equation

$$dF(2t)/dt=-F(2t)\int_0^t K(t')dt'. \tag{40}$$

The exact solution satisfying the initial condition is

$$F(2t)=\exp\left[-\int_0^t dt_1\int_0^{t_1} dt_2 K(t_2)\right]. \tag{41}$$

Since K becomes small after a short time, the first integral will become a constant for large t_1, and the spin-echo-decay envelope F will relax exponentially for large t. Exponential relaxation is also described in a similar way for the magnetization itself but in a different system where diffusion is not taking place but instead there are strong exchange interactions or rapid lattice motion.

To get an approximate expression for K, we expand the exponential in Eq. (39) for small α leaving $i(1-P)L''$ in the exponential and keeping $i(1-P)L'$ to first order.[8] This expansion can be simplified by use of

$$e^{-it(1-P)L''}(1-P)=(1-P)e^{-itL''}, \tag{42}$$

which can be proved by expanding the left side in powers of t and using Eq. (37). When Eq. (42) is used on the perturbation expansion, the result is

$$e^{-it(1-P)L}(1-P)=(1-P)e^{-itL''} -\int_0^t (1-P)e^{-it'L''}iL'(1-P)e^{-i(t-t')L''}dt'+\cdots. \tag{43}$$

When this is inserted into Eq. (39), the result can be simplified by use of Eq. (37) and the following observation. Since F is real and since i and α appear only in the product $i\alpha$, it follows that terms with α to an odd power are zero. By use of this and Eq. (30), we get

$$K(t)=4\alpha^2\sum Z_{n0}^2[\exp(-n^2\pi^2t)-\exp(-n^2\pi^2 2t)], \tag{44}$$

which is correct to second order in α.

Notice that the matrix elements Z_{00} do not appear in the expression for K. This happens because subtracting a constant times the unit matrix from the matrix Z_{nm} in Eq. (26) can have no effect. For $n>0$, the only nonzero matrix elements Z_{n0} are

$$Z_{n0}=-2\sqrt{2}/n^2\pi^2,\quad n=1,3,5,\cdots. \tag{45}$$

Combining Eqs. (41), (44), and (45), we get

$$F(t)=\exp\left\{-\frac{8\alpha^2}{\pi^6}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^6}\left[t-\frac{3-4\exp[-(2n+1)^2\pi^2t/2]+\exp[-(2n+1)^2\pi^2t]}{(2n+1)^2\pi^2}\right]\right\}, \tag{46}$$

which for $t\ll 1/\pi^2$ becomes

$$F(t)=\exp(-\alpha^2t^3/12), \tag{47}$$

and for $t\gg 2/\pi^2$ becomes

$$F(t)=\exp\left[-\frac{\alpha^2}{120}\left(t-\frac{17}{56}\right)\right]. \tag{48}$$

This function is graphed in Fig. 1 for three values of α^2. The rather remarkable coefficients 1/12, 1/120, and 17/56 result from an exact calculation of the sums over n. Finally, we use Eqs. (4) and (5) to put the dimensions back into F, which for $t\ll a^2/\pi^2D$ becomes

$$F(t)=\exp(-\gamma^2G^2Dt^3/12), \tag{49}$$

and for $t\gg 2a^2/\pi^2D$ becomes

$$F(t)=\exp\left[-\frac{a^4\gamma^2G^2}{120D}\left(t-\frac{17}{56}\frac{a^2}{D}\right)\right]. \tag{50}$$

The condition for the validity of the approximations made in deriving Eq. (46) is either that t is so small that F has not yet changed very much or that α is small so that F varies slowly compared with K. Regardless of the size of α but for $t\ll(12/\gamma^2G^2D)^{1/3}$ and $t\ll a^2/\pi^2D$, then, F is a cubic as in the expansion of Eq. (49) in powers of t. On the other hand, for t not small, it is difficult to determine how small α must be for Eq. (43) to be sufficient, but we can easily determine the condition for

[8] See, for example, B. Robertson, Phys. Rev. **144**, 151 (1966), Eq. (A2).

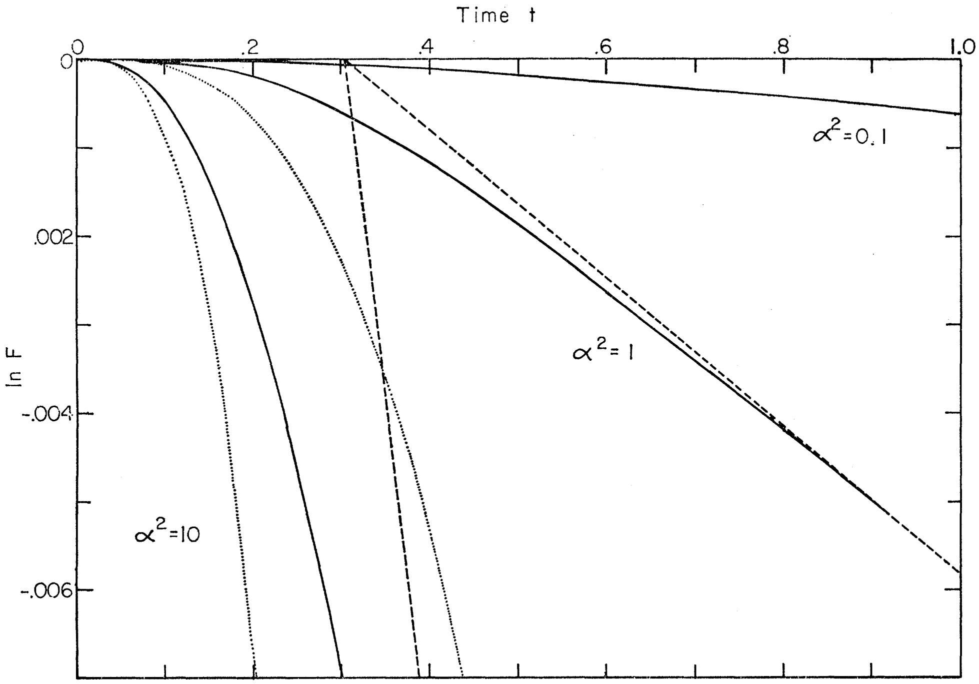

FIG. 1. The solid curves are graphs of the logarithm of the spin-echo-decay envelope F versus time t for $\alpha^2=10$, 1, and 0.1, where $\alpha=a^3\gamma G/D$ and a is the compartment width. The dashed straight lines are the corresponding asymptotes for large t, and the dotted curves are the cubics that $\ln F$ approaches for small t. The asymptote for $\alpha^2=0.1$ is nearly indistinguishable from the solid curve, and it and the corresponding cubic are not drawn. Time t is measured in multiples of $t_D=a^2/D$. The curves are computed from Eqs. (46)–(48).

Eq. (40) to be valid. The kernel (44) has a relaxation time of order $2/\pi^2$, and the envelope (48) has a relaxation time of order $120/\alpha^2$, and so the condition is $2/\pi^2 \ll 120/\alpha^2$ or $\alpha^2 \ll 60\pi^2$. In practice, α^2 can be about 10 at most. This condition limits the range of validity of our derivation so that F will appear to have only the form (50) if we view the relaxation on a scale for which we can see F decay to 0.05.

In spite of our restriction on α, the well-known[9] expression (49) has been shown by Torrey to be correct in the limit of large α even for large t provided α becomes large before t does. This suggests that Eq. (46) is correct over a broader range of α than that for which our two approximations are valid. Perhaps errors introduced by one approximation are partially canceled by the other. If so, we may use our results to obtain a limit on the range of validity for assuming the compartment width a is large. For Eq. (49) to be correct $t \ll a^2/\pi^2 D$, and for F to have decreased appreciably $t > (12/\gamma^2 G^2 D)^{1/3}$, and so the condition is $\alpha \gg 2\sqrt{3}\pi^3$.

Because the dependence of F in Eq. (46) on α^2 is so simple, curves for $\alpha^2 \neq 1$ have the same shape as the curve for $\alpha^2=1$ with only the vertical scale changed. For example, although F in Fig. 1 decreases only to 0.993 at the bottom of the graph, we can multiply the vertical scale and the values of α^2 by 500 without changing the curves, and then F will decrease to about 0.005.

[9] Reference 1 and references cited therein.

Wayne and Cotts[3] compare Eq. (46) with the results of their experiment for α^2 very much larger than 10, but not so large that Eq. (49) is correct throughout the observed relaxation.

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APPENDIX

Besides leading to the boundary condition (3), the boundary walls have another effect on the motion of molecules near them, and this causes $1/T_2$ near the walls to depend upon position. This happens as follows: Because of the rapid randomizing motion of the molecules in the bulk of the fluid, the effective magnetic dipole-dipole interaction between the nuclei is reduced considerably so that $1/T_1$ is much larger and $1/T_2$ is much smaller than they would be if there were little molecular motion. Our case is that of extreme motional narrowing so that in the bulk of the fluid $T_1=T_2$. Near the walls, however, the randomizing motion is slowed down considerably. Partitioning the sample into many compartments will have a negligible effect on the value of $1/T_1$ observed for the whole sample since the layer near the walls has a very small volume and since $1/T_1$ is smaller there than in the bulk of the fluid. But, partitioning will effect the value of $1/T_2$ observed for the whole sample since $1/T_2$ is several orders of magnitude larger there than in the bulk of the fluid.

Since $1/T_2$ depends upon position, the exponential relaxation with rate equal to the spatial average $\langle 1/T_2 \rangle$ should be factored out of the magnetization in deriving Eq. (1). Then Eqs. (1) and (6) would have an additional term $-M/T_2'$ where

$$1/T_2' = 1/T_2 - \langle 1/T_2 \rangle.$$

Since the boundary condition (3) remains the same, all of Eqs. (12)–(43) remain the same except Eqs. (16), (20), and (26) have the matrix element of $1/T_2'$ added, and Eq. (36) must be modified. The additional term in Eq. (26) gives an anticommutator. To second order in $(1-P)L'$, the kernel (44) has an additional term in the square of the matrix element of $1/T_2'$, but contains no terms linear in that matrix element and no cross terms between that matrix element and Z_{nm}. Because there are no cross terms, the effect of the spatial dependence of $1/T_2'$ can be considered separately from the effect of the magnetic field gradient, and F will be a product of two functions corresponding to the two effects.

With the field gradient zero, the second function is 1, and the change in F is due to $1/T_2'$. For the experiment of Wayne and Cotts,[3] however, the effect of the second-order term in $1/T_2'$ is negligible, and therefore the first function is nearly constant and so is also 1. We can see this as follows. Although we do not know the shape of the function $1/T_2(z)$, we can use a rough model in order to get an order of magnitude estimate. Say that $1/T_2(z)$ has the constant magnitude $1/T_{2b}$ everywhere but within a distance λ from the walls where it has the constant magnitude $1/T_{2w}$. Then, for $\lambda \ll a$,

$$\langle 1/T_2 \rangle = 1/T_{2b} + (2\lambda/a) 1/T_{2w},$$

and, for $t \gg 1/4\pi^2$,

$$F(t) = \exp\left[\frac{\lambda^2}{24DT_{2w}^2}\left(t - \frac{a^2}{60D}\right)\right].$$

The function F increases in time because the exponential relaxation factored out at the beginning of the calculation is slightly faster than the exact exponential relaxation for large t. Since the function F obtained without assuming $t \gg 1/4\pi^2$ increases monotonically from 1 at $t=0$, the over-all relaxation proceeds rapidly at first, but then settles down to a slower pure exponential relaxation with rate $1/T_2 - \lambda^2/24DT_{2w}^2$.

For an infinite compartment, the observed relaxation is exponential with relaxation time

$$T_{2b} \approx 1.00 \text{ sec},$$

and, for the smallest compartment, the observed relaxation for large time is asymptotic to an exponential with relaxation time approximately given by

$$\langle 1/T_2 \rangle^{-1} \approx 0.63 \text{ sec}.$$

Furthermore, for this smallest compartment

$$t_D \approx 0.0256 \text{ sec},$$

and so

$$2\lambda t_D / a T_{2w} \approx 0.015.$$

The square of half this number is to be divided by 24 and so is completely negligible. Therefore, assuming all compartments are the same size, the boundary-wall relaxation mechanism does not explain the shape of the observed[3] relaxation with $G=0$.