Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient

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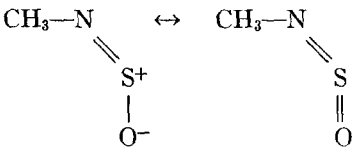
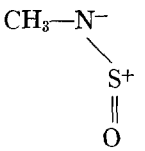


in which the methyl group eclipses the N–S bond and the structure



in which the methyl group staggers the N–S bond. The barrier may also be affected by steric interaction between the CH_3 group and the oxygen atom. For a reasonable structure the closest approach of the methyl H to the O is 2.48 Å.

It may be possible to determine the equilibrium conformation of the methyl group by study of the microwave spectrum of CH_2DNSO or CHD_2NSO.

The apparent structure obtained here shows a slight opening of the HNSO bond angle (116° Ref. 6) on substitution of a methyl group to $\angle CNS = 122°$. This change is smaller than that of HNCO ($\angle HNC = 128.5°$) going to CH_3NCO ($\angle CNC \cong 140°$).

ACKNOWLEDGMENT

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Spin Diffusion Measurements: Spin Echoes in the Presence of a Time-Dependent Field Gradient*

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A derivation is given of the effect of a time-dependent magnetic field gradient on the spin-echo experiment, particularly in the presence of spin diffusion. There are several reasons for preferring certain kinds of time-dependent magnetic field gradients to the more usual steady gradient. If the gradient is reduced during the rf pulses, H_1 need not be particularly large; if the gradient is small at the time of the echo, the echo will be broad and its amplitude easy to measure. Both of these relaxations of restrictions on the measurement of diffusion coefficients by the spin-echo technique serve to extend its range of applicability. Furthermore, a pulsed gradient can be recommended when it is critical to define the precise time period over which diffusion is being measured.

The theoretical expression derived has been verified experimentally for several choices of time dependent magnetic field gradient. An apparatus is described suitable for the production of pulsed gradients with amplitudes as large as 100 G cm^{-1}. The diffusion coefficient of dry glycerol at 26°±1°C has been found to be $(2.5\pm0.2)\times10^{-6}$ cm^2 sec^{-1}, a value smaller than can ordinarily be measured by the steady gradient method.

INTRODUCTION

ONE of the most satisfactory methods for measuring self-diffusion coefficients is the spin-echo method of Hahn,[1] as developed by Carr and Purcell and others,[2,3] particularly so because of the negligible extent to which the diffusing molecules are perturbed by this method. However, there are experimental limitations in the ordinary spin-echo experiment arising from the magnetic field gradient, which must be present at all times. As the gradient is increased to make possible the observation of smaller and smaller values of the diffusion coefficient, the nuclear magnetic resonance linewidth also increases, with a corresponding decrease in the duration of the free induction decay following the first (90°) pulse in the spin-echo sequence and a decrease in the width of the echo following the second (180°) pulse. There is thus a decrease in the information available from the echo. As the gradient is increased further the bandwidth of the detection system will have to be increased in order to improve its transient response, a procedure which will admit more noise. Finally, with increasing linewidth, the power output of the pulse transmitter will have to be increased to keep the rf field amplitude H_1 greater than the line-

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[1] E. L. Hahn, Phys. Rev. **80**, 580 (1950); Phys. Today **6**, No. 11, 4 (1953).

[2] H. Y. Carr and E. M. Purcell, Phys. Rev. **94**, 630 (1954); and, for example, D. E. Woessner, J. Chem. Phys. **34**, 2057 (1961), which includes an extensive bibliography of the theory of the spin-echo experiment.

[3] D. W. McCall, D. C. Douglass, and E. W. Anderson, Ber. Bunsenges. Physik. Chem. **67**, 336 (1963).

width. Furthermore, recent observations on systems in which the diffusion coefficient is spatially dependent (restricted diffusion)[4] have made it desirable that the precise period of time during which diffusion is being observed be clearly defined. It is also desirable to make this time as short as possible.

In an attempt to eliminate some of the experimental limitations mentioned above, we have developed a technique in which the field gradient is considerably reduced during the times at which the rf pulses are being applied and also at the time of appearance of the echo. The line width is thus small at the time of the rf pulses, reducing the requirements on H_1, and small at the time of the echo, providing a broad echo. The gradient may be arbitrarily large at other times. If the gradient at the time of the echo is kept constant as the gradient at other times is varied, the echo will appear to change amplitude (if diffusion is present) but not shape. Although this technique was evolved primarily for the experimental reasons mentioned, if the gradient is applied in short pulses, it will be seen below that the time during which the diffusion process is being observed is precisely defined.

Many features of the experiment described in this paper have been anticipated by the work of Anderson, Garwin, Hahn, Horton, Tucker, and Walker,[5] who demonstrate how spin echoes in the presence of a pulsed field gradient may be used for purposes of information storage. These authors note the effect of diffusion on their experiment but do not further develop the pulsed gradient technique for the measurement of self-diffusion coefficients. McCall, Douglass, and Anderson[3] note the experimental possibilities of this technique in the measurement of self-diffusion coefficients but do not provide a mathematical analysis or experimental test of the method.

THEORY

The spin-echo experiment, in particular the effect on the echo of spin diffusion in a steady magnetic-field gradient, has been described by Hahn,[1] Carr and Purcell, and others.[2,3] In order to compute the effect of varying the field gradient, it is most convenient to develop the approach due to Torrey[6] in the form presented by Abragam.[7] We begin our derivation with Eq. (46) given by Abragam (p. 60 of this reference) and compute the result for the case of one 90° pulse followed by one 180° pulse.

$$\partial\psi/\partial t = -i\gamma(\mathbf{r}\cdot\mathbf{G})\psi + D\nabla^2\psi. \tag{1}$$

Here $\psi(\mathbf{r}, t)$ is defined by

$$M_x + iM_y = \psi \exp[-(i\omega_0 + 1/T_2)t],$$

where M_x+iM_y represents the behavior of the components of the nuclear magnetization $\mathbf{M}$ in the plane perpendicular to the applied magnetic field $\mathbf{H}_0$. The z axis is chosen parallel to $\mathbf{H}_0$ and the gradient $\mathbf{G}(t)$ is defined by $H_z = H_0 + (\mathbf{r}\cdot\mathbf{G})$. The gradient $\mathbf{G}$ is assumed uniform throughout the sample. The function ψ, which is independent of the transverse (T_2) relaxation process, describes the behavior in a coordinate system rotating with angular velocity $\omega_0 = \gamma H_0$ about the z axis and in the same sense as $\mathbf{M}$ precesses. In the above, γ represents the gyromagnetic ratio and H_0 the magnitude of the uniform applied static field; D is the diffusion coefficient.

Consider first the behavior in the absence of the diffusion term. The simplified equation must be solved in two parts. Between the 90° pulse (at $t=0$) and the 180° pulse (at $t=\tau$) ψ is given by

$$\psi = A \exp(-i\gamma\mathbf{r}\cdot\mathbf{F}),$$

where

$$\mathbf{F}(t) = \int_0^t \mathbf{G}(t')\,dt'. \tag{2}$$

We have imposed the boundary condition that $\psi = A$ immediately following the 90° pulse. The effect of the 180° pulse is to set back the phase of ψ by twice the amount which it has advanced. Hence, following the 180° pulse we have

$$\psi = A \exp[-i\gamma\mathbf{r}\cdot(\mathbf{F}-2\mathbf{f}) + i\varphi],$$

where

$$\mathbf{f} = \mathbf{F}(\tau).$$

The phase angle φ depends upon the phase of the 180° pulse relative to that of the 90° pulse and may be set equal to zero without loss of generality. It may be seen that the echo may be expected at $t=\tau'$ such that $\mathbf{F}(\tau') = 2\mathbf{f}$ since then $\psi = A$ for all values of $\mathbf{r}$ as it did immediately following the 90° pulse. Note that depending upon $\mathbf{G}$ this condition may not ever occur; and, if it does, τ' need not equal 2τ as it will when $\mathbf{G}$ is constant. Whether or not this condition does occur, there may be times at which the nuclear signal reaches a maximum for which $\psi \neq A$ everywhere. The occurrence of such echoes will depend to a degree upon the shape of the sample (through the dependence of ψ on $\mathbf{r}$ since the observed nuclear signal is calculated by summing ψ over the sample). We discuss only the situation in which $\psi = A$. See Anderson *et al.*[5] for further discussion of this point. We may use the following single expression to represent the behavior of ψ from the 90° pulse to the echo (and beyond):

$$\psi = A \exp\{-i\gamma\mathbf{r}\cdot[\mathbf{F} + (\xi-1)\mathbf{f}]\}, \tag{3}$$

if

$$\xi = +1 \quad \text{for} \quad 0 < t < \tau,$$

$$\xi = -1 \quad \text{for} \quad t > \tau.$$

We now return the diffusion term to Eq. (1). We

[4] D. E. Woessner, J. Phys. Chem. **67**, 1365 (1963).
[5] A. G. Anderson, R. L. Garwin, E. L. Hahn, J. W. Horton, G. L. Tucker, and R. M. Walker, J. Appl. Phys. **26**, 1324 (1955).
[6] H. C. Torrey, Phys. Rev. **104**, 563 (1956).
[7] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

shall assume a solution to this equation identical with that shown by Eq. (3) except that we permit A to be a function only of t. Substitution into Eq. (1) yields the following equation for $A(t)$:

$$dA/dt=-\gamma^2D[\mathbf{F}+(\xi-1)\mathbf{f}]^2A. \quad (4)$$

Integrating Eq. (4) between $t=0$ and $t=\tau'$ we obtain

$$\ln\left[\frac{A(\tau')}{A(0)}\right]=-\gamma^2D\left[\int_0^{\tau'}F^2dt-4\mathbf{f}\cdot\int_\tau^{\tau'}\mathbf{F}dt+4f^2(\tau'-\tau)\right]. \quad (5)$$

Since $\psi=A(0)$ immediately following the 90° pulse and $\psi=A(\tau')$ at the peak of the echo, $A(\tau')/A(0)$ represents the effect of diffusion on the echo amplitude. Note that the quantity within the brackets is dependent only upon the choice of τ and $\mathbf{G}$. Thus even if $\mathbf{G}$ is not well known it is possible to make measurements relative to a substance with known D.

By way of illustration we choose the following $\mathbf{G}(t)$ and calculate its effect on the echo amplitude. Let $\mathbf{G}(t)$ equal:

$$\begin{aligned}
&\mathbf{g}_0 && \text{when} && 0<t<t_1,\\
&\mathbf{g}_0+\mathbf{g} && \text{when} && t_1<t<t_1+\delta<\tau,\\
&\mathbf{g}_0 && \text{when} && t_1+\delta<t<t_1+\Delta>\tau,\\
&\mathbf{g}_0+\mathbf{g} && \text{when} && t_1+\Delta<t<t_1+\Delta+\delta<2\tau,\\
&\mathbf{g}_0 && \text{when} && t_1+\Delta+\delta<t.
\end{aligned}$$

Thus the nuclei are subjected to a steady gradient $\mathbf{g}_0$, which is due, in part at least, to the inhomogeneities in the laboratory field, and a second gradient $\mathbf{g}$, which may be in a different direction than $\mathbf{g}_0$ and which is turned on for a time δ once between the 90° pulse and the 180° pulse and once again between the 180° pulse and the echo. The first gradient pulse occurs at a time t_1 and the second at a time $t_1+\Delta$. For this choice of $\mathbf{G}(t)$ the echo occurs at $t=2\tau$. The effect on the echo amplitude is given by:

$$\ln[A(2\tau)/A(0)]=-\gamma^2D\{\tfrac{2}{3}\tau^3g_0^2+\delta^2(\Delta-\tfrac{1}{3}\delta)g^2 -\delta[(t_1^2+t_2^2)+\delta(t_1+t_2)+\tfrac{2}{3}\delta^2-2\tau^2]\mathbf{g}\cdot\mathbf{g}_0\}, \quad (6)$$

where $t_2=2\tau-(t_1+\Delta+\delta)$ and is the time between the end of the second gradient pulse and the peak of the echo.[8]

When $\mathbf{g}$ vanishes, only the term in g_0^2 remains and the result is the same as that obtained for the conventional two pulse spin-echo experiment.

As $\mathbf{g}_0$ approaches zero,[9] only the term in g^2 remains and the result is

$$\ln[A(2\tau)/A(0)]=-\gamma^2D\delta^2(\Delta-\tfrac{1}{3}\delta)g^2.$$

If δ is allowed to approach zero, at least until $\frac{1}{3}\delta\ll\Delta$, while increasing $\mathbf{g}$ so as to keep the product $\mathbf{g}\delta$ finite, the result is even simpler:[10]

$$\ln[A(2\tau)/A(0)]=-\gamma^2D\delta^2\Delta g^2.$$

This last experiment is worth visualizing. Following the 90° pulse there is negligible loss of phase coherence until the first gradient pulse. This pulse produces an almost instantaneous phase shift depending upon the position of each nucleus in the direction of the field gradient at that time. Following the gradient pulse the loss of phase coherence is again negligible; but the nuclei, as they diffuse, change position. The 180° pulse inverts the phase shifts, and then the second gradient pulse produces phase shifts equal to those produced by the first gradient pulse. In the absence of diffusion the second gradient pulse, aided by the 180° pulse,[11] would exactly undo the effect of the first. Diffusion causes the refocusing to be incomplete. Note that in this experiment the nuclear positions are recorded by the first gradient pulse, and any change at the time of the second is noted by the incompleteness of the refocusing. Only the changes in position occurring between the two gradient pulses are important and are equally weighted regardless of when they occur within this interval. In the conventional two pulse constant gradient spin-echo experiment a change in position affects the echo amplitude more when it occurs near the 180° pulse than if it occurs near the 90° pulse or just before the echo. Thus the pulsed gradient experiment provides a better definition of the time during which diffusion is being observed and is more easily adaptable to the problem of restricted diffusion.[4,12]

When both $\mathbf{g}_0$ and $\mathbf{g}$ are of significant magnitude, then all three terms in the general equation for the echo amplitude may contribute. It may be noted that to compare the relative importance of the steady gradient and the pulsed gradient one would ordinarily compare the quantities $\tau\mathbf{g}_0$ and $\delta\mathbf{g}$ (so long as Δ is not much smaller than τ).

Another choice of $\mathbf{G}(t)$ which may be of some interest is the following:

$$\mathbf{G}(t)=\mathbf{g}_1+\mathbf{g}_2[1-\cos(2\pi t/\tau)].$$

[8] The method described by Carr and Purcell (Ref. 2) for the calculation of the echo amplitude has been suitably modified and carried through for this particular $\mathbf{G}(t)$. The result is the same as that shown in Eq. (6), although more cumbersome to obtain. We have not succeeded in obtaining Eq. (5) by this method.

[9] Strictly speaking, if $\mathbf{g}_0$ vanishes completely, there is no echo identifiable as such since the nuclei will not lose phase coherence after the 90° pulse until the first gradient pulse appears and will regain complete phase coherence immediately after the end of the second gradient pulse. The expression for $\ln[A(2\tau)/A(0)]$ is still valid, however.

[10] Torrey (Ref. 6) mentions "drift" terms which arise from the space dependence of the equilibrium magnetization $\mathbf{M}_0$ when the gradient is very large and which can complicate the steady gradient experiment. In the pulsed gradient experiment, if $\delta\ll T_1$, the "drift" terms will not have time to develop any importance regardless of the magnitude of $\mathbf{g}$.

[11] The 180° pulse could be dispensed with if the second gradient pulse were applied with reverse polarity. Abragam (Ref. 7, p. 63) explicitly points out the analogous phenomenon for the steady gradient experiment; Anderson *et al.* (Ref. 5, p. 1333) imply as much in their discussion of electron spin echoes.

[12] A discussion of the effect on the spin-echo experiment, particularly the pulsed gradient experiment, of a position dependent, anisotropic diffusion coefficient, molecular forces which modify the diffusional motion, and hydrodynamic flow will be shortly submitted for publication by one of us (E. O. S.).

As before, the 90° pulse occurs when $t=0$ and the 180° pulse when $t=\tau$. The echo will occur when $t=2\tau$.[13] The inhomogeneities inherent in the laboratory field are represented by $\mathbf{g}_1$. This particular gradient should be easier to obtain experimentally than the pulsed gradient described earlier. For one thing, the image currents and eddy currents (see below) will not distort $\mathbf{G}$; they will only shift its phase. However, although the applied gradient (the term involving $\mathbf{g}_2$) is zero during the two pulses and at the time of the peak of the echo, changing $\mathbf{g}_2$ will produce a change in the echo shape, particularly near the baseline. For this choice of $\mathbf{G}(t)$, we obtain the following expression for the echo amplitude:

$$\ln\left[\frac{A(2\tau)}{A(0)}\right]=-\gamma^2 D\tau^3\left[\frac{2}{3}g_1^2+\left(\frac{2}{3}+\frac{5}{4\pi^2}\right)g_2^2+\left(\frac{4}{3}+\frac{1}{\pi^2}\right)\mathbf{g}_1\cdot\mathbf{g}_2\right]. \tag{7}$$

EXPERIMENTAL

By way of verification of the theoretical treatment given above we have made a variety of experimental observations. First, we have tested several different choices of $\mathbf{G}(t)$, including that giving rise to Eq. (6), and found agreement between theory and experiment. Equation (7) has not been tested. Second, we have used this technique in the measurement of the diffusion coefficient in several systems.

The basic nuclear resonance pulse apparatus used in this study has been described elsewhere.[14] It resembles closely that described by Buchta, Gutowsky, and Woessner.[15] Nuclear signal intensities are measured by means of digital techniques.[14] The observations described in this paper were all made on protons; the resonant frequency was 20.00 Mc/sec.

Magnetic field gradients are applied by means of a pair of coils wound on specially tapered forms. The coils are coaxial with their axis parallel to the laboratory field, so that the gradient will be parallel to $\mathbf{H}_0$. The coils are electrically in series but magnetically opposed. The tapered forms are designed to produce as large a region of homogeneous gradient as possible; among the effects taken into account are image currents in the magnet pole caps.[16] Since these image currents and, more important, eddy currents, which develop in any metal near the gradient coils during switching, will affect the transient response of the gradient coils, a compromise must be sought when choosing the magnet air gap geometry and the size and placement of the gradient coils.

The current source consists of 25 Nicad nickel-cadmium alkaline storage cells, approximately 1.3 V and 30 A·h per cell. Currents up to about 6 A are drawn, corresponding to a gradient of about 100 G/cm.[17] The measurement of current is by means of the voltage observed across a calibrated standard resistor in series with the gradient coils. For the pulsed gradient experiments the standard resistors (and the decade resistance boxes, see below) should be noninductively wound to minimize the effect on transient response. Digital techniques are usually employed in the measurement of the voltage across the standard resistor. For steady gradients the current is controlled by means of a decade resistance box in series with the gradient coils. For the pulsed gradients an additional two-stage transistor switching circuit is inserted into the circuit. This switch consists of a 2N1480 and a 2N174 in a Darlington compound (series) connection,[18] modified by the addition of minor circuit elements to improve switching characteristics.[16] The switch is activated by the pulse output of one or more Tektronix Type 163 pulse generators, which are integrated into the pulser which controls the pulse transmitter. Control of the current through the switch is obtained by varying both the amplitude of the switching pulse and the resistance in series with the gradient coils. Leakage current through the switch is about 0.1 mA. The rise and fall times (90%) of the current pulses through the gradient coils are of the order of 40 μsec; the image currents and eddy currents change more slowly. We feel that it should be possible to improve this figure appreciably. If a steady gradient current is desired in addition to a

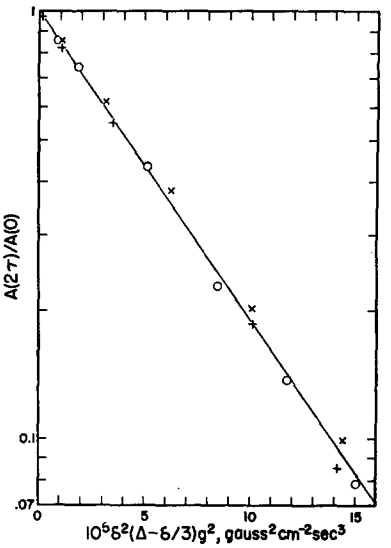

FIG. 1. Effect of the pulsed gradient on the echo amplitude, as observed in several aqueous $CuSO_4$ solutions at 25.5°±0.5°C. (See Table I for an identification of the symbols used.)

[13] Depending upon $\mathbf{g}_1$ and $\mathbf{g}_2$ there may be echoes observed at other times—whenever $\psi=A$, as indicated by Eq. (3). It is also possible that echoes may be observed for which $\psi\neq A$.

[14] E. O. Stejskal, Rev. Sci. Instr. **34**, 971 (1963).

[15] J. C. Buchta, H. S. Gutowsky, and D. E. Woessner, Rev. Sci. Instr. **29**, 55 (1958); D. E. Woessner, Ph.D. thesis, University of Illinois, 1957 (unpublished).

[16] A more detailed discussion will soon be submitted for publication by one of us (J. E. T.); see also the Ph.D. thesis of J. E. Tanner (in preparation).

[17] If allowed to flow steadily, such a current would burn up the gradient coils. Keeping the duty cycle for the pulsed gradient current low minimizes heating of the gradient coils.

[18] *Motorola Power Transistor Handbook*, edited by R. Greenburg (Motorola, Inc., Phoenix, Arizona, 1960), 1st ed., p. 146ff.

TABLE I. Identification of symbols used in Fig. 1.

Symbol	g (G cm^{-1})	Δ (msec)	δ (msec)	τ (msec)
+	varied	20.00	1.002	15.02
○	82.0	varied	0.496	50.05
×	10.7	15.04	varied	15.05

pulsed gradient current, the transistor switch may be shunted.

An extensive series of measurements have been made by way of verification of Eq. (6). In Fig. 1 are shown the results of observations made on several aqueous $CuSO_4$ solutions to check the term involving g^2. With $\mathbf{g}_0$ too small to be significant, a plot of $\log[A(2\tau)/A(0)]$ vs $\delta^2(\Delta-\frac{1}{3}\delta)g^2$ should yield a straight line passing through the origin with slope $=-0.4343\gamma^2D$. In this series of measurements several different concentrations of $CuSO_4$ were chosen so as to result in different values of T_2. A choice of τ was made which was compatible with T_2; and two of the three variables δ, Δ, g were fixed. The remaining variable was then changed, giving rise to the points shown on Fig. 1. Varying t_1 produced no effect not capable of being attributed to imperfections in the shape of the gradient pulses, e.g., putting the first gradient pulse close enough to the 180° pulse to permit the falling edge of the gradient pulse to overlap the 180° pulse. Table I summarizes the choices of g, Δ, δ, and τ used in the preparation of Fig. 1. The slope of this plot indicates the diffusion coefficient for H_2O at 25.5°±0.5°C to be $(2.34\pm0.08)\times10^{-5}$ cm^2 sec^{-1}, which is reasonably good agreement with the value of Simpson and Carr[19] who obtained $(2.13\pm0.15)\times10^{-5}$ cm^2 sec^{-1} at 25°C by means of spin-echo measurements in a steady field gradient and better agreement with our own value of $(2.23\pm0.05)\times10^{-5}$ cm^2 sec^{-1} measured at 25.5°±0.5°C with a steady field gradient.

The terms in Eq. (6) involving $\mathbf{g}\cdot\mathbf{g}_0$ were checked in a series of measurements analogous to those described above but too cumbersome to describe here in detail. Among other points noted was the effect of the angle between $\mathbf{g}_0$ and $\mathbf{g}$. This angle was varied in the following fashion: By shunting the transistor switch it is possible to produce a component of $\mathbf{g}_0$ parallel to $\mathbf{g}$ of any desired magnitude. Moving the probe to the edge of the magnet air gap produces a component of $\mathbf{g}_0$ which is perpendicular to $\mathbf{g}$ (since $\mathbf{g}$ is parallel to $\mathbf{H}_0$ in our apparatus). The component of $\mathbf{g}_0$ perpendicular to $\mathbf{g}$ is calculated from its effect on the echo shape,[2] and hence the angle between $\mathbf{g}_0$ and $\mathbf{g}$ is known. No systematic deviations between theory and experiment were observed which could not be ascribed to imperfections in the shape of the gradient pulses. Ordinarily, as a practical matter, we prefer to make $\mathbf{g}_0$ small enough compared to $\mathbf{g}$ to be able to neglect it in our calculations, especially if $\mathbf{g}_0$ is due to imperfections in the laboratory field since then its directional character may not be well defined. There is at least one situation, however, in which it is desirable to have $\mathbf{g}_0$ (parallel to $\mathbf{g}$) of considerable magnitude. This situation arises when $\mathbf{g}$ is very large and/or δ very short. Then, small fluctuations in either $\mathbf{g}$ or δ from gradient pulse to gradient pulse will produce fluctuations in τ'. The effect of $\mathbf{g}_0$ is to stabilize τ'.

To test the applicability of the pulsed gradient method to a system with a relatively small diffusion coefficient, glycerol was studied at 26°±1°C. The following approximate experimental conditions were used: g up to 96 G cm^{-1}, $\tau=19$ msec, $\Delta=21$ msec, and $\delta=10$ msec. This system, which was thoroughly dried, yielded a diffusion coefficient of $(2.5\pm0.2)\times10^{-8}$ cm^2 sec^{-1}. This value will be seen to be smaller than the lower limit of 10^{-7} cm^2 sec^{-1} placed by McCall, Douglass, and Anderson[3,20,21] on the steady gradient experiment. We concur with them when we estimate that values at least ten times smaller ($\approx10^{-9}$ cm^2 sec^{-1}) should be accessible by means of the pulsed gradient method.

[19] J. H. Simpson and H. Y. Carr, Phys. Rev. **111**, 1201 (1958), see also P. A. Johnson and A. L. Babb, Chem. Rev. **56**, 387 (1956); D. W. McCall, D. C. Douglass, and E. W. Anderson, J. Chem. Phys. **31**, 1555 (1959).

[20] D. W. McCall (private communication) informs us of diffusion coefficients of the order of 10^{-8} cm^2 sec^{-1} being measured using a steady gradient in particularly favorable systems: medium molecular weight silicone fluids having exceptionally long T_2 despite small D. Such systems may be of practical importance in the operation of a spin-echo serial storage memory as described by Anderson *et al.* (Ref. 5) since these are the characteristics (long T_2, small D) which they require.

[21] Anderson *et al.* (Ref. 5) employ a value of $D=2\times10^{-8}$ cm^2 sec^{-1} for glycerol without stating the source. We infer that this represents an order of magnitude estimate derived from the maximum echo storage capacity attainable with glycerol.