where a_j represents the annihilation operator at site j. In spin language a_j flips a down spin up, or

$$a_j=[\tfrac{1}{2}(\sigma_x+i\sigma_y)]_j. \qquad \text{(A24)}$$

We can also calculate $\langle a_j^\dagger a_i\rangle$, which is the probability that at site j the spin is up and at site i it is down:

$$\langle a_j^\dagger a_i\rangle=\frac{m(\mathfrak{N}-m)}{\mathfrak{N}(\mathfrak{N}-1)}. \qquad \text{(A25)}$$

Equations (A23) and (A25) give the elements of the reduced density matrix ρ_1 in coordinate representation:

$$\begin{aligned}\langle j|\rho_1|j\rangle&=m/\mathfrak{N},\\ \langle i|\rho_1|j\rangle&=m(\mathfrak{N}-m)\mathfrak{N}^{-1}(\mathfrak{N}-1)^{-1}. \qquad \text{(A26)}\end{aligned}$$

ρ_1 is a cyclic matrix which is diagonal in the momentum (which is discrete) representation:

$$\begin{aligned}\langle k'|\rho_1|k\rangle&=0 \quad \text{if} \quad k\neq k',\\ \langle k|\rho_1|k\rangle&=m\mathfrak{N}^{-1}-m(\mathfrak{N}-m)\mathfrak{N}^{-1}(\mathfrak{N}-1)^{-1}\\ &=m(m-1)\mathfrak{N}^{-1}(\mathfrak{N}-1)^{-1}\leq 1, \qquad \text{(A27)}\\ \langle k|\rho_1|k\rangle&=m\mathfrak{N}^{-1}+m(\mathfrak{N}-m)\mathfrak{N}^{-1}\\ &=m\mathfrak{N}^{-1}(\mathfrak{N}-m+1) \quad \text{if} \quad k=0.\end{aligned}$$

These equations show that there is condensation of particles in *one* "single-particle state" characterized by $k=0$. In other "single-particle states" ($k\neq 0$) the occupation number is $\leqq 1$. This is an explicit example where the speculation of Girardeau[5] does not hold. [Girardeau's speculation is that, e.g., $\sim(m)^{2/5}$ states are multiply occupied each with $\sim(m)^{3/5}$ particles.] We suspect that it also does not hold in a physical system.

[5] M. D. Girardeau, J. Math. Phys. 6, 1083 (1965).

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Nuclear-Magnetic-Resonance Study of Self-Diffusion in a Bounded Medium*

R. C. WAYNE† AND R. M. COTTS
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

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The investigation of the effects of diffusion in a magnetic field gradient on the spin-echo experiment in nuclear magnetic resonance (NMR) is extended to small samples in which the diffusion is bounded, or restricted. From the point of view of NMR, bounded diffusion means that the spin dephasing time $T_2 \gg t_x$, the average time for a molecule to diffuse once across a sample width a. A more realistic criterion is that a is small enough or that the diffusion coefficient D is large enough that the quantity $\gamma G a^3/D$ is about equal to or less than 1, where G is a linear magnetic field gradient and γ is the nuclear gyromagnetic ratio. An effective self-diffusion coefficient $D'(t)=-12\ln[M(t,G)/M(t,0)]/\gamma^2G^2t^3$ is defined from the Hahn spin-echo experiment, where $t=2\tau$ is the time of the echo, and $M(t,G)$ is the echo amplitude. For infinite samples, $D'=D$, the true self-diffusion coefficient. However, when $t_x \ll T_2$, then $D'/D<1$ and D' depends on t. The measurement of D' is made by holding the times of an echo, $t=2\tau$, constant and varying G. Experimental data are presented on $D'(t)$ for four values of a and values of $\gamma G a^3/D$ which range from being much greater than unity to less than unity. Results of the Carr-Purcell experiment are also presented and briefly discussed. A comparison of data from the spin-echo experiment is made with a theoretical calculation of $D'(t)$ which uses Torrey's modification of the Bloch equations and requires that boundary conditions be satisfied. Results are compared with the theory developed by Robertson. A universal curve for D'/D versus t/t_x is plotted, illustrating that D' is independent of G. It is shown that the reduced rate of decay of the echo envelope in the case of bounded diffusion is, in effect, a motional-narrowing phenomenon.

I. INTRODUCTION

THIS paper is concerned with the effect of diffusion in a *noninfinite* sample on the Hahn spin-echo experiment[1] and the Carr-Purcell experiment.[2] In previous studies[1–4] known to the authors the assumption has been made that the sample is infinite in size. For many experiments this assumption is perfectly valid; however, there exists a group of experiments for which the diffusion coefficient D is so large and/or the sample size a is so small that the infinite-sample assumption breaks down. In particular, two such experiments have motivated the present work. Measurements of the spin-lattice relaxation time T_1 and the spin dephasing time T_2 were made on small particles of liquid lithium[5] and on rapidly self-diffusing protons[6] in powdered NbH$_x$ under

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† Present address: Sandia Corporation, Albuquerque, New Mexico.

[1] E. L. Hahn, Phys. Rev. 80, 580 (1950).

[2] H. Y. Carr and E. M. Purcell, Phys. Rev. 94, 630 (1954).

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[4] D. C. Douglass and D. W. McCall, J. Phys. Chem. 62, 1102 (1958).

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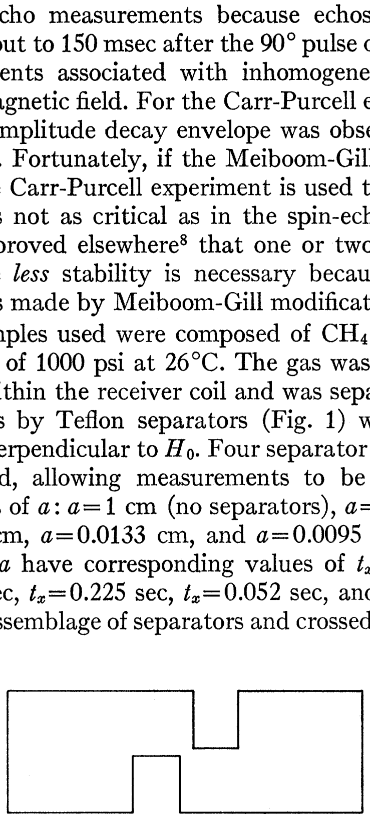
conditions where D is very large and a very small. In both cases the average time $t_x=a^2/2D$ for a nucleus to cross the sample was less than T_2. One of the measurements made in these experiments was a Carr-Purcell[2] measurement of T_2 in which the decay time of the echo amplitude envelope, $(T_2)_m$, was observed as a function of τ, the spacing between the 90° pulse and the 180° pulse. In an infinite medium the dependence of $(T_2)_m^{-1}$ on τ^2 is known to be linear since the transverse magnetization can be expressed as $M(t)=M_0\exp[-(1/T_2+\gamma^2G^2D\tau^2/3)t]$, where G is a linear magnetic field gradient and γ is the nuclear gyromagnetic ratio. In the case of the bounded media encountered,[5,6] the dependence of $(T_2)_m^{-1}$ on τ^2 was distinctly nonlinear with the slope of $(T_2)_m^{-1}$ versus τ^2 becoming smaller with increasing τ. An exact analysis of the reasons for this behavior could not be made at the time because of the variety of shapes and sizes of the small metal particles which comprised the samples. A further complication existed owing to the distribution of magnetic field gradients arising from the volume magnetic susceptibility.

The purpose of the experiment described here is to study the effect of bounded self-diffusion on the pulsed NMR measurements of T_1 and T_2 where there are a well-defined sample geometry, a well-defined linear external magnetic field gradient, and a known coefficient of self-diffusion. There is a clear experimental advantage in having the sample as large as possible in order to facilitate construction and definition of sample dimensions. Since the requirement for "bounding" is that $t_x<T_2$, T_1, a large D was sought to make t_x small. This led to the selection of a gas, methane, which at a pressure of 1000 psi has $t_x<T_2$ if $a<0.068$ cm. A range of sample sizes down to $a=0.0095$ cm provided values of t_x/T_2 down to 0.02. The samples used are noninfinite in one only dimension which is parallel to the magnetic field H_0. The other two dimensions perpendicular to H_0 are made essentially infinite (1 cm) in order to reduce the complexity of the theoretical analysis. It is found, as expected, that the dephasing of the transverse magnetization caused by the bounded diffusion in an inhomogeneous field is far less than occurs in an infinite medium. The reduction becomes greater as τ is increased in both the spin-echo and Carr-Purcell experiments. The reduction in dephasing is shown to be partly due to the limitation in the range of field imposed by the boundaries and partly due to an effective averaging of the gradient by the motion of the spins between their "reflecting" boundaries.

II. EXPERIMENTAL EQUIPMENT AND SAMPLES

A phase-coherent pulsed NMR spectrometer was used to measure T_1 and T_2. The spectrometer operated at 11.67 mcps and was modified in order to use Meiboom and Gill's pulse error correction technique[7] in the Carr-Purcell T_2 measurements. Spin-echo data were recorded directly from an oscilloscope and the Carr-Purcell data were measured from photographs of the oscilloscope trace. Since T_1 and T_2 are longer than 1 sec, the short-term stability requirements of H_0 and the rf frequency were rather stringent. The stability of the magnetic field was the critical factor. A measurement of the longer term stability yielded a drift of 0.1 G/h or 30 μG/sec. Short-term (less than 1 sec) stability measurements showed that the field drifted in a discontinuous fashion, but at a rate which never exceeded 200 μG/sec. This amount was too small to affect the echo amplitude in the spin-echo measurements because echos could be seen only out to 150 msec after the 90° pulse due to nonzero gradients associated with inhomogeneity of the applied magnetic field. For the Carr-Purcell experiment the echo-amplitude decay envelope was observable for over 2 sec. Fortunately, if the Meiboom-Gill modification of the Carr-Purcell experiment is used the magnet stability is not as critical as in the spin-echo case. It has been proved elsewhere[8] that one or two orders of magnitude *less* stability is necessary because of self-corrections made by Meiboom-Gill modification.

The samples used were composed of CH_4 gas under a pressure of 1000 psi at 26°C. The gas was contained entirely within the receiver coil and was separated into thin layers by Teflon separators (Fig. 1) which were oriented perpendicular to H_0. Four separator units were constructed, allowing measurements to be made for five values of a: $a=1$ cm (no separators), $a=0.040$ cm, $a=0.027$ cm, $a=0.0133$ cm, and $a=0.0095$ cm. These values of a have corresponding values of $t_x=300$ sec, $t_x=0.48$ sec, $t_x=0.225$ sec, $t_x=0.052$ sec, and $t_x=0.026$ sec. The assemblage of separators and crossed-coil probe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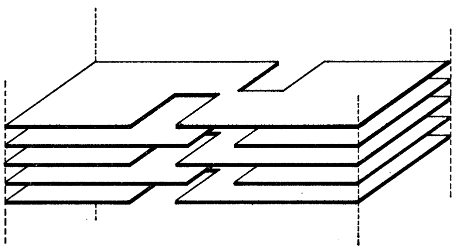
Means of stacking the elements of an insert

FIG. 1. Expanded view of Teflon separator sandwich. H_0 and G are oriented perpendicular to the Teflon sheets.

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[7] S. Meiboom and D. Gill, Rev. Sci. Instr. 29, 688 (1958).

[8] R. C. Wayne, Ph.D. thesis, Cornell University, 1966 (unpublished).

fitted snugly into a beryllium-copper pressure vessel. A linear field gradient was produced using two circular coils for which the square of the diameter was $\frac{4}{3}$ the square of their separation. Values of G over 3 G/cm were obtainable.

III. MEASUREMENTS

Measurements were made in an infinite sample ($a = 1$ cm) as a test of the equipment and as standards for the bounded medium measurements. T_1 is 1.35 ± 0.05 sec, in agreement with the published work of Bloom *et al.*[9] Carr-Purcell measurements of T_2 with $G \approx 0$ and $\tau = 1$ msec yielded a value of 1.3 ± 0.1 sec agreeing with T_1. The self-diffusion coefficient D was determined to be $1.70 \pm 0.05 \times 10^{-3}$ cm^2/sec at 1000 psi, which is in agreement with the published values.[10]

A. Surface Relaxation

T_1 was measured each day an experiment was performed and for each separator used on any one day. No T_1 dependence on separator or on G was seen. However, Carr-Purcell T_2 measurements made using $\tau = 1$ msec and $G \approx 0$ showed a strong dependence, with the decay of the transverse magnetization becoming more rapid with smaller a. These measurements indicate that a source of transverse relaxation other than the diffusion in a field gradient is present. It is "surface relaxation" due to the contact of the molecules with the surface of the separator walls.

Since the thermal relaxation time T_1 is unaffected by the presence of the separators, it is evident that the increase in relaxation rate of the transverse magnetization must be due to dipole-dipole interactions. The only possibilities are dipole-dipole interactions between intramolecular hydrogens, or between the hydrogens and the fluorine in the Teflon. If a dipole-dipole interaction is to be an effective source of relaxation then the molecule cannot be undergoing rapid random translational and rotational motion. It must behave as if it were in a rigid or semirigid lattice. Extreme precautions[8] were taken to clean the separators and to prevent any impurity from entering the sample so that the only difference in sample condition due to the presence of a separator is in the amount of surface area. It must then be concluded that the methane at the surfaces is not a fluid, at least so far as NMR is concerned. This means that the molecules in the surface layer have both their translational and rotational degrees of freedom hindered.

The translational motion of CH_4 molecules is, of course, hindered if the molecules are physically adsorbed. By using infrared spectroscopy, Shepard and Yates[11] have shown that methane physically adsorbed on glass has either one or no rotational degrees of freedom excited. If there is *one* excited, they conclude that its axis of rotation is perpendicular to the surface. In either case, the intramolecular dipole-dipole interaction between hydrogens in the CH_4 molecules would not be well averaged. Completely random motion does not occur and the relaxation rate approaches some value within an order of magnitude of that for solid CH_4 (which is 14 μsec[12]). This provides one mechanism for surface relaxation which could have little or no effect on T_1; the dipole-dipole interaction causes a mutual spin exchange between two intramolecular hydrogens and there is no resulting change in M_z.

If the adsorbed CH_4 molecules are close together (possibly several layers deep on the surface), the intermolecular hydrogens can interact causing a loss in the phase coherence of the transverse magnetization. Finally, there is the possibility that the hydrogen in molecules directly on the surface of the Teflon experience strong dipole-dipole interactions with fluorine. To test the role of the fluorine, separators with the same a were made from Teflon, Mylar, and glass. The decay rate of the transverse magnetization was the same in all three cases, indicating that the role of the fluorine in the surface relaxation is small.

To summarize this argument, surface relaxation occurs and is mainly due to the physical adsorption of the gas molecules. Each molecule remains near the separator wall only a short time in comparison to T_2 and τ, and a large fraction of the sample has an opportunity to sample the wall environment. The size of this fraction depends on a, D, and the time. This relaxation mechanism does not depend on the wall material.

B. Spin-Echo, Self-Diffusion Coefficient Measurements

Because of the effect of the surface relaxation when separators were used, the self-diffusion coefficient could not be measured for the bounded samples by examining the time dependence of $M(2\tau)$. However, the contribution of the surface relaxation is independent of G. Thus, the spin-echo amplitude was measured at a fixed time, but for various values of G. This method of measurement allows determination of those transverse relaxation processes which *do* depend on G without interference from G-independent processes. Since neither T_2 nor the surface relaxation rate depend on G, the only process measured is that due to the diffusion.

In the case of an infinite medium the echo amplitude is described by[2–4]

$$M(t,G) = M_0 \exp(-\gamma^2 G^2 D t^3/12), \qquad (1)$$

and D can be determined from the slope of a graph of $\ln[M(t,G)/M(t,0)]$ versus G^2. The value measured for D is independent of G and was found to be (1.70 ± 0.05)

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[9] M. Bloom, M. Lipsicas, and B. H. Muller, Can. J. Phys. **39**, 1093 (1961).

[10] Q. R. Jeffries and H. G. Drickamer, J. Chem. Phys. **21**, 1358 (1953).

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[12] M. Bloom and H. Sandhu, Can. J. Phys. **40**, 292 (1962).

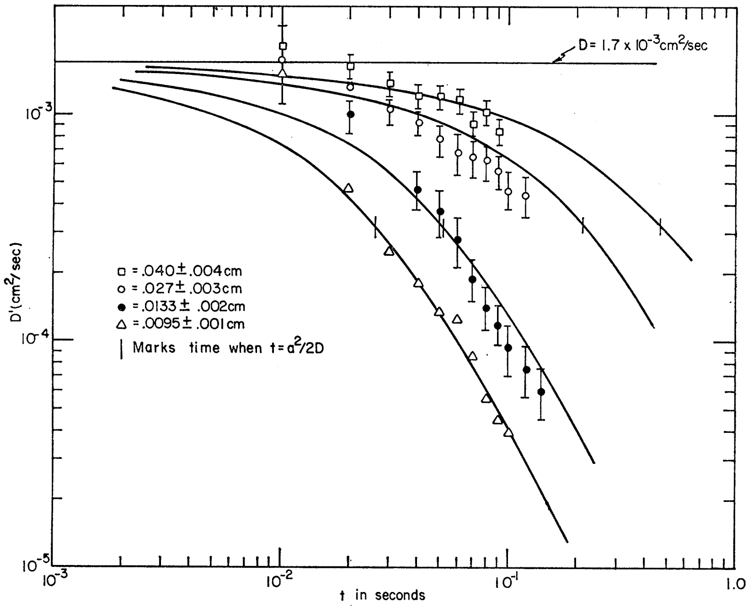

FIG. 2. Experimental data for $D'(t)$. The solid lines represent $D'(t)$ from the computer calculation. Robertson's theory, Eq. (6), provides identical curves.

$\times 10^{-3}$ cm²/sec. However, when this same measurement is made in a bounded sample, the self-diffusion coefficient so derived depends on τ. An "effective coefficient of self-diffusion" D' is obtained from experimentally determined values of the ratio $\{M(t,G)/M(t,0)\}$ by use of the equation

$$D'(t)=\frac{-12[\ln\{M(t,G)/M(t,0)\}_{\text{expt}}]}{\gamma^2G^2t^3}. \tag{2}$$

The experiment indicates that $D'=D$ for an infinite sample and $D'<D$ for a bounded sample. This does not imply that the real self-diffusion coefficient depends in any way on sample size, but that the functional dependence for $M(t,G)$ given in Eq. (1) does not apply to a bounded medium. D' was measured for four sample sizes, and the results are shown in Fig. 2 and discussed in the next section.

One correction had to be made on the raw data for the D' measurements. Bulk Teflon is porous and when it is under (methane) gas pressure it absorbs some of the gas. This gas can then contribute to the NMR signal. There is also a possibility for methane gas to flow between layers of Teflon in the separator since the layers are not glued together but simply clamped together firmly. (Glue could not be used for fear of contaminating the proton resonance of the gas sample.) Both the interlayer spaces and the pores are very small. Any signal from methane in these places is undesired and must be corrected for by subtracting the proper amount from each echo. Fortunately, "the proper amount" could be well determined experimentally. Taking advantage of the smallness of the pores and spaces, the contribution to the echo signal from these sources could be found by making G sufficiently large. Since these molecules cannot self-diffuse very far, if at all, D' for them is very small. G was increased until the echo amplitude was no longer reduced as G was further increased. This G-independent part of the echo signal amounted to between 10 and 20% of the total echo signal observed at $G=0$; the exact percentage depended upon the particular separator. It is assumed that when the remaining signal is G-independent, the *desired* signal from the gas between the walls has completely decayed and the remainder is due solely to absorbed and interlayer gas.

An experimental check supports this assumption. The gas pressure was released so that most of the methane (all but 1 atm) was removed from the sample cell. The spin-echo amplitude was observed immediately (1 sec after releasing pressure) for a large value of τ and *no* dependence on G was seen. This signal, from absorbed CH_4, then slowly lost amplitude as the absorbed gas escaped with a time constant of roughly 15 min. The effective diffusion constant D' for the absorbed gas is so small that no effect of the field gradient can be seen with G as large as 3.4 G/cm and $\tau=50$ msec. The relaxation from the surface of the Teflon surrounding the pore is great enough due to the small size that the signal from this source completely decays in less than 200 msec.

The above procedure allowed the contribution from the absorbed and interlayer methane to be accurately eliminated from the experimental results. When this was done the dependence of $\ln M(t,G)$ on G^2 was linear.

C. Carr-Purcell, $(T_2)_m^{-1}$ versus τ^2 Dependence

The Carr-Purcell[2] modification of the spin-echo experiment was studied in order to compare the measurements on methane in a bounded region to those made

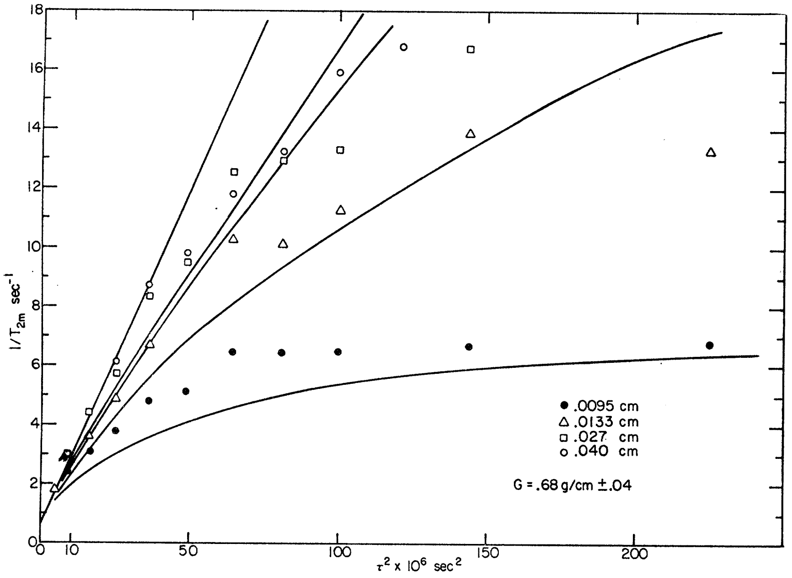

FIG. 3. The $1/T_{2m}$ versus τ^2 for the Carr-Purcell experiment shows the same curvature as in the case of Li^7. A theoretical calculation made (solid lines) by computer verifies this behavior.

on lithium[5] in small particles. In an infinite medium the decay rate of the transverse magnetization depends on D, τ, G, and T_2 in such a way that the measured decay constant is

$$(T_2)_m^{-1} = (1/T_2 + \gamma^2 G^2 D \tau^2/3)\,. \tag{3}$$

From Eq. (3) the linear dependence of $(T_2)_m^{-1}$ on τ^2 mentioned in Sec. I can be seen. If, now, D is replaced by $D'(t=2\tau)$ obtained from the spin-echo data the linear dependence is no longer predicted and the slope of a graph of $(T_2)_m^{-1}$ versus τ^2 changes directly with $D'(2\tau)$. Figure 3 shows the result of measurements made with $G=0.68$ G/cm; clearly this change in slope occurs.

The effect of the surface relaxation is prominent in the Carr-Purcell measurement of T_2 and cannot be handily avoided as in the D' measurement. Signals from the absorbed and interlayer gas add to the uncertainty caused by the surface relaxation because they represent a superposition of many separate signals of differing amplitude and T_2. Contrary to the case of the D' experiment, the time dependence of all contributions must be directly known in order to make a direct correction.

Because of this, a technique was used which measured the dependence of the decay on G *only* by comparing echo trains with $G\neq 0$ to one with $G=0$ for each set of Teflon spacers. First the Carr-Purcell echo train was observed for a given 180° pulse spacing (2τ) at $G=0$. An echo envelope is obtained, $M_{\text{CP}}(t,0)$, where echos occur at $t=2n\tau$. With G applied, the echo envelope $M_{\text{CP}}(t,G)$ is recorded for the same value of τ. It is assumed that both $M_{\text{CP}}(t,0)$ and $M_{\text{CP}}(t,G)$ are similarly affected by surface relaxation and "interlayer" gas.

A normalized decay envelope is then defined as

$$f_{\text{CP}}(t,G) = \frac{M_{\text{CP}}(t,G)}{M_{\text{CP}}(t,0)}\,. \tag{4}$$

In all cases, the corrected decay envelope, $f_{\text{CP}}(t,G)$ for Carr-Purcell (Meiboom-Gill) pulse trains were simple exponentials. The decay rate of the exponential fitted to $f_{\text{CP}}(t,G)$ is defined as $(1/T_2)_m'$, and values of $(1/T_2)_m'$ are plotted against τ^2, as in Fig. 3. (In Fig. 3 the contribution from $1/T_2$ is included as a non-τ-dependent shift of the base line.)

Since the real T_2 has been eliminated by this method $(T_{2m})'$ represents only that decay due to diffusion $(1/T_2)_m = 1/T_2 + (1/T_2)_m'$. As stated earlier, in an infinite medium, the plot of $(1/T_2)_m$ versus τ^2 would have constant slope. The observed decrease in slope with increase in τ corresponds, as in the spin-echo (single pulse), to a decrease in an effective diffusion constant at large values of τ.

IV. THEORY

In addition to the usual intrinsic magnetic dipolar contributions to the transverse relaxation rate of the sample, there is in this experiment an increased relaxation rate near the boundary surfaces as well as the dephasing due to the restricted diffusion of spins in a field gradient between the boundaries. In the following paper, Robertson[13] proves that the transverse relaxation due to surfaces and that due to the magnetic field gradient are independent to second order and may be treated separately to a very good approximation. We have taken this position throughout this study. The analysis of the field-gradient–dependent relaxation will be presented independently of consideration of wall, or surface, relaxation.

A. Magnetic-Field-Gradient–Dependent Relaxation

The main purpose of this experiment, as mentioned earlier, is the study of restricted diffusion in a field

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[13] B. Robertson, following paper, Phys. Rev. **151**, 273 (1966).

gradient. A necessary condition for observation of effects of bounded diffusion is that $T_2 \gg t_x$. There are also limitations on the value of G applied. The gradient G must be small enough that the dephasing due to diffusion (even in the unbounded sample) is not appreciable for times $t < t_x$. This means that $(\gamma^2 G^2 D t_x^3) \leq 1$, or that $(\gamma G a^3/D) \lesssim 1$. The experimental results are compared with solutions to Torrey's modified Bloch equations[3] containing a boundary condition. Torrey's equation is written for $M = M_x + iM_y$ where M_x and M_y are transverse components of the magnetization in the frame of reference rotating at the Larmor frequency:

$$\frac{\partial M}{\partial t} = i\gamma G z M + D\frac{\partial^2 M}{\partial z^2}. \tag{5}$$

(T_2 is assumed to be infinite for the purpose of the calculation.)

In Eq. (5), γ is the nuclear gyromagnetic ratio, G is the applied magnetic field gradient $(\partial H_z/\partial z)$ and D is the self-diffusion coefficient. Since the wall relaxation is mathematically independent of the reflection effects of the wall,[13] the boundary condition is written for perfect reflection;

$$\frac{\partial M}{\partial z} = 0, \quad \text{at} \quad z = 0, a,$$

where a is the spacing between boundaries perpendicular to z. The large applied magnetic field H_0 is in the z direction. In the spin-echo experiment the initial condition, following the 90° pulse, is

$$M(z, t=0) = M_0,$$

where $M_0 = \chi H_0$ is the equilibrium magnetization of the sample.

Equation (5) with boundary conditions has been solved numerically for $(a^3\gamma G/D) \leq 1$ on the Cornell Computing Center CDC 1604-160A computer. Robertson[13] has obtained an approximate solution of Torrey's equation for $(a^3\gamma G/D) \leq 1$ and he obtains the following expression for the spin-echo decay envelope:

$$M(t,G) = M_0 \exp\left\{\frac{8a^6\gamma^2 G^2}{\pi^6 D^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^6} \left[t - \frac{\left(3 - 4\exp\left[\frac{-(2n+1)^2\pi^2 D t}{2a^2}\right] + \exp\left[\frac{-(2n+1)^2\pi^2 D t}{a^2}\right]\right)}{(2n+1)^2\pi^2}\right]\right\}, \tag{6}$$

which for $t \ll a^2/\pi^2 D$ becomes

$$M(t,G) \approx M_0 \exp(-\gamma^2 G^2 D t^3/12), \tag{7}$$

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

$$M(t,G) \approx M_0 \exp\left[\frac{-\gamma^2 G^2 a^4}{120 D}\left(t - \frac{17a^2}{56D}\right)\right], \tag{8}$$

where $t = 2\tau$ is the time of the echo in the spin-echo experiment.

In the presence of some wall relaxation, the effects of restricted diffusion are obtained by determining the dependence of $M(t)$ on G^2 at fixed values of t. From Eq. (6) it follows that

$$\ln\left[\frac{M(t,G)}{M(t,0)}\right] \propto (-G^2),$$

for all values of t. Thus the comparison of the experimental value $\ln[M(t,G)/M(t,0)]_a$ with the familiar Torrey solution for unbounded diffusion, $\ln[M(t,G)/M(t,0)]_\infty = -(\gamma^2 G^2 D t^3/12)$, to give a value of effective diffusion coefficient D' as in Eq. (2) is clearly justified.

Robertson's solutions, Eqs. (7) and (8), predict $D' \approx D$ in the limit $t \ll a^2/\pi^2 D$, and

$$D' \approx \frac{a^4}{10D}\left(\frac{1}{t^2} - \frac{17}{56}\frac{a^2}{Dt^3}\right), \tag{9}$$

in the limit $t \gg 2a^2/\pi^2 D$. For large times the second term in the parenthesis in Eq. (9) is negligible, and to a good approximation,

$$D' \approx \frac{a^4}{10Dt^2}. \tag{10}$$

As the echo time t is increased, the effective diffusion coefficient decreases as t^{-2}. In the time domain where $t \gg (2a^2/\pi^2 D)$ the root-mean-squared displacement of a spin during time t is several times the cell width, a. The random walk of one spin back and forth across the cell partially averages out the dephasing effects of the gradient. This effect is much like the motional narrowing phenomena encountered in other magnetic-resonance experiments (see Appendix).

In the time domain where $t \ll (a^2/\pi^2 D)$, t is so small that most spins in the cell never encounter the wall. The sample is, in effect, an infinite medium, so that $D' \approx D$ for small values of t.

The values of D' calculated by using the value of $M(t,G)$ from Eq. (6) are plotted with the measurements in Fig. 2. The agreement is good within experimental uncertainty.

When Eq. (2) is written in dimensionless form, a universal curve for (D'/D) can be found for any set of values of time, cell width a, and gradient G. By defining $t' = (Dt/a^2)$ and $\alpha = (a^3\gamma G/D)$ then, from Eq. (2),

$$\frac{D'}{D} = -\frac{12\ln[M(t',G)/M(t',0)]_a}{\alpha^2 (t')^3}. \tag{11}$$

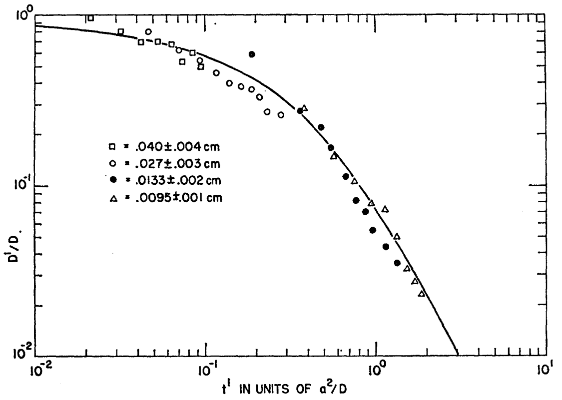

FIG. 4. Universal curve for D'/D versus t' where $t'=tD/a^2$. Data for all values of a are shown.

Values of $\ln[M(t',G)/M(t',0)]_a$ are calculated from Eq. (6) and the corresponding D'/D are plotted in Fig. 4. The experimental data from Fig. 2 also appear on Fig. 4 and can be compared with the theoretical values of D'/D.

B. Surface-Relaxation Effects

With a transverse spin-relaxation rate (T_2 process) at the surface of the cell that is greater than that in the volume in the cell, the expression for the magnetization in Eq. (6) must be multiplied by an additional function, $W(t)$. An approximate form of $W(t)$ has been determined by Robertson[13] to be

$$W(t)=\exp-\left[(1/T_2)_b+\left(\frac{2\lambda}{a}\right)(1/T_2)_w\right]t, \qquad (12)$$

where $(1/T_2)_b$ is the transverse relaxation rate in the bulk of the sample, $(1/T_2)_w$ is the transverse relaxation rate in the surface layers each of which has a characteristic width λ.

The smaller the cell width, the greater is the effect of the surface (wall) relaxation term in Eq. (12) for $W(t)$. The form of $W(t)$ should be obtainable from a spin-echo or a Carr-Purcell experiment with $G=0$. The observed form of the relaxation in this experiment is not a single exponential as predicted by Eq. (12). Instead, the rate of decay observed in a Carr-Purcell experiment at short times is greater than at long times. Some of the reasons for this are discussed in Sec. II. A distribution in values of a and $(T_2)_w$ cause this observed effect.

The nature of the surface relaxation is not fully understood. Since its effects are independent of the gradient-induced effects the subject will not be pursued further here. Where corrections for surface relaxation were necessary, these corrections were made empirically.

V. SUMMARY

The presence of boundaries can have a marked effect on the rate of relaxation caused by diffusion in a field gradient. The effect of boundaries will not be apparent in the shape of the spin-echo decay envelope unless the time t between the 90° pulse and the echo is longer than t_x, the rms time for a diffusing molecule to cross the sample from one boundary to another. When $t \ll t_x$, the usual (infinite sample) case holds and the echo envelope decay is proportional to $\exp(-t^3)$. As t approaches t_x the decay rate decreases until at $t \gg t_x$ the echo envelope becomes a simple exponential proportional to $\exp(-\gamma^2G^2a^4t/120D)$. The dephasing effects of the field gradient are partially "averaged out" when $t \gg t_x$, in a motional narrowing type of phenomena, which is discussed in the Appendix.

The boundary effects are also expressible in terms of an effective diffusion constant D'. For $t \ll t_x$, measured values of $D' \approx D$. At $t \gg t_x$, $D' < D$ and $(D'/D) \approx (\frac{2}{5})(t_x/t)^2$.

In the observation of spin-echos in fluids confined to small cavities or in small volumes, the effects of diffusion in a magnetic field gradient can occur. Even though no external gradient is applied, gradients associated with normal magnetization over the small scale of small particles or cavities can exist.[5,6] The gradients can be large even though the total inhomogeneous broadening of the usual NMR line may be small. The amount of spin dephasing produced by diffusion in these gradients will depend upon the combination of the size of the cavity as well as the gradient G.

Although the present understanding of these effects is for slab-shaped samples, we will apply the theory here, as an approximation, to spherical samples, since only the direction parallel to the magnetic field is of importance.

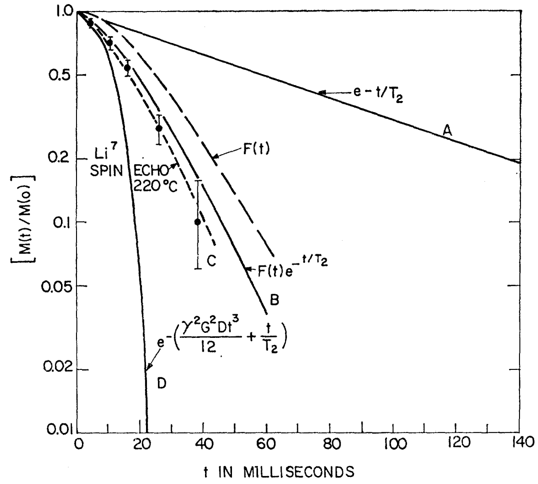

FIG. 5. Effect of limited diffusion on the measurement of the spin-echo envelope of Li^7 in liquid lithium particles. Curve A: Theoretical normalized echo envelope for $T_2=T_1=83$ msec (no diffusion). Curve B: Normalized echo envelope including the effects of bounded diffusion as predicted by Eq. (6) and $T_2=83$ msec. Values of $a=2\times10^{-3}$ cm and $G=20$ G/cm were used. Curve C: (dotted curve) Experimental data from Fig. 3 of Ref. 5. Curve D: Normalized echo envelope for an unbounded medium ($G=20$ G/cm, $a=\infty$).

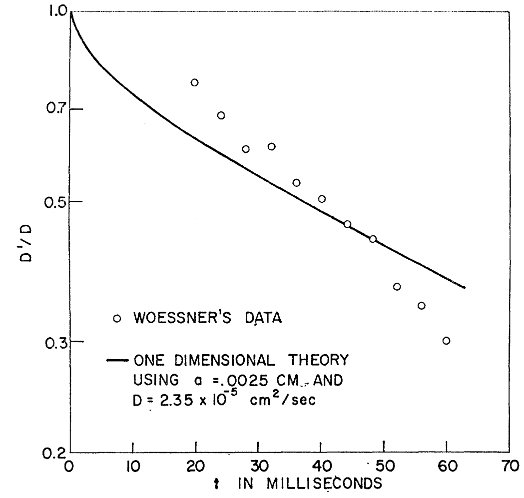

FIG. 6. Comparison of D'/D data of D. E. Woessner with the one-dimensional theory. The data are from Ref. 14.

The *apparent* value of T_2 in such systems will be less than the true value. The amount of error in T_2 caused by this spin dephasing mechanism will depend upon whether or not the echo time t is greater than t_x, the approximate random-walk time from one side of the particle or cavity to the other.

If the echo time is much less than t_x, and if diffusion effects due to magnetic field gradients exist, the spin-echo decay will be nonexponential with the t^3 dependence of Eq. (7). If the echo time is greater than t_x then the diffusion contribution to echo decay is exponential or nearly exponential and its presence as an additional transverse relaxation process may not be so obvious.

It is apparent that diffusion effects are present in the spin-echo experiments in liquid lithium. In the experiments reported[5] the lithium particles are small enough that $t > t_x$ (a is taken as a particle diameter). The diffusion contribution to the transverse decay is almost exponential and measured values of T_2 are less than T_1. That T_2 could be less than T_1 in liquid lithium was considered for some time to be anomalous but this anomaly is resolved by the recognition of the diffusion mechanism.

For a full understanding of the T_2 data in liquid lithium the effects of particle boundaries on restricted diffusion must be included. In Ref. 5 it was estimated that in a dispersion of lithium in oil with particles of 10-μ radius, that G is about 20 G/cm. By using the following values listed in Ref. 5: $a = 2\times10^{-3}$ cm, $G = 20$ G/cm, $\gamma = 1.035$ (sec G)$^{-1}$, and $D \approx 10^{-4}$ cm^2/sec, the spin-echo decay envelope has been calculated from Eq. (5). Since $(2a^2)/(\pi^2 D) = 8$ msec and echo times are about 30 msec, $t > (2a^2)/(\pi^2 D)$ and a nearly exponential decay is predicted. It is assumed that the one-dimensional theory of Eq. (6) yields a reasonably good approximation to the spin-echo decay for the spherical particles.

The prediction of Eq. (6) is plotted in Fig. 5 against experimental data for the spin-echo decay published as Fig. 3 in Ref. 5, assuming that the natural $T_2 = T_1 = 83$ msec. No surface relaxation is included. The agreement with Eq. (6) is much better than for the unbounded medium theory. Further, the qualitative behavior of the Carr-Purcell experiment data in the Li^7 is the same as predicted as shown in Fig. 3.

Woessner[14] has reported the proton resonance of water in a sandstone with a porosity of 33% and a 22- to 28-μ median pore size. He measured D'/D and his results are shown in Fig. 6. Assuming $a = 25\ \mu$, $a^2/D = 260$ msec. From these values the theoretical (one-dimensional model) curve for D'/D has been calculated and is also plotted in Fig. 6. The agreement between the model and Woessner's data is good considering the approximations made.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Baldwin Robertson for valuable aid in developing an efficient computer program, for his continued interest in this work, and for his subsequent analytical analysis (following paper) of the spin-echo problem.

APPENDIX

This bounded-medium problem can also be viewed, in the limiting case of $t > t_x$, and $t < (D/\gamma^2 G^2 a^4)$, as a motional-narrowing problem. This motional-narrowing argument is not rigorous, but it does provide a useful physical picture of how restricted diffusion affects the transverse relaxation time. Although the applied field gradient is time-independent, a diffusing spin experiences the field of the applied gradient as though it were time-dependent due to the diffusive motion of the molecule carrying the spin. In effect, we imagine we move along with the spin and calculate the relaxation rate resulting from the time-dependent magnetic field.

In this model, subject to the usual assumptions,[15] the transverse relaxation rate is given by the spectral density, at zero frequency, of the correlation function of the random variation in the z component of the field. That is, the contribution to the relaxation rate due to diffusion would be

$$\left(\frac{1}{T_2}\right)_D = \gamma^2 \int_{-\infty}^{\infty} \langle H_z(0) H_z(t) \rangle dt, \tag{13}$$

where H_z is the value of the gradient field at some particular value of z.

Equation (13) is valid[15] for times t such that $t \gg \tau_c$, where τ_c is the correlation time for the motion. In this

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[14] D. E. Woessner, J. Phys. Chem. **67**, 1365 (1963).

[15] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), p. 276; and C. P. Slichter, *Principles of Magnetic Resonance* (Harper & Row, New York, 1963), pp. 146–153.

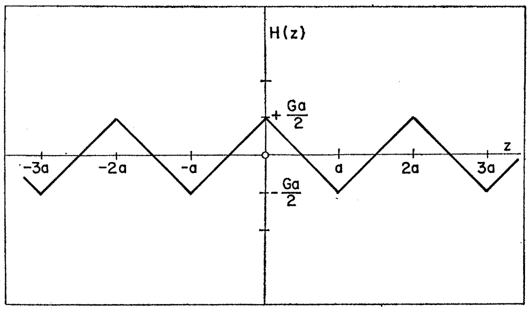

FIG. 7. A model of the field having a uniform gradient G across the cell of width a. The random walk of molecules within one cell is assumed to be equivalent to unbounded diffusion (no walls) in a field with z dependence as shown.

problem τ_c will be no greater than $t_x=(a^2/2D)$. Another condition which this theory[15] places on t is that $t\ll(T_2)_D$. By usual motional narrowing arguments, $(T_2)_D$ will be approximately $(T_2)_D^{-1}\approx\gamma^2\langle H_z^2\rangle_{\text{av}}\tau_c$ in the short-time limit of τ_c, where $\langle H_z^2\rangle_{\text{av}}$ is the mean-squared local field in the cell. For the problem under consideration the gradient field is

$$H_z(z)=\tfrac{1}{2}Ga(1-2z/a)$$

and

$$\langle H_z^2\rangle_{\text{av}}=G^2a^2/12.$$

The condition on t then becomes, $t\ll 12/(\gamma^2G^2a^2\tau_c)$. By using the upper limit on τ_c given above, the two inequalities can be written as $(a^2/2D)\ll t\ll(24D/\gamma^2G^2a^4)$. The outer terms give $(\gamma^2G^2a^6/D^2)\ll 48$. This last condition is the one mentioned in Sec. IVA, that states that the spins are not appreciably dephased before the spins are likely to encounter the walls, and it is equivalent to Robertson's[13] assumption that $\alpha<1$ where $\alpha=(\gamma Ga^3/D)$.

The correlation function is found from

$$\langle H_z(0)H_z(t)\rangle=\frac{1}{a}\int_0^a dz_0H_z(z_0)\int_{-\infty}^{\infty}dz\,H_z(z)P(z,t)\,,\tag{14}$$

where

$$P(z,t)=(4\pi Dt)^{-1/2}\exp[-(z-z_0)^2/4Dt]\,,\tag{15}$$
$$H_z(z_0)=\tfrac{1}{2}Ga(1-2z_0/a)\,,$$

and

$$H_z(z)=\frac{4Ga}{\pi^2}\sum_{n=0}^{\infty}\frac{\cos[(2n+1)\pi z/a]}{(2n+1)^2}\,.\tag{16}$$

In making an evaluation of $\langle H_z(0)H_z(t)\rangle$ it has been assumed in writing Eq. (14) that at $t=0$, the spins have a uniformly spatial distribution in the region $0<z<a$. For purposes of calculation, the effects of diffusion (in the gradient G between the walls at $z=0$, a) are found by allowing the diffusion to occur beyond the range $0<z<a$ in an unbounded space but with a field gradient which is alternating in slope as shown in Fig. 7. Equation (16) is the Fourier series representation of this field.

Equations (14)–(16) give

$$\langle H_z(0)H_z(t)\rangle=\frac{8G^2a^2}{\pi^4}\sum_{n=0}^{\infty}\frac{\exp[-2(n+1)^2\pi^2Dt/a^2]}{(2n+1)^4}\,.\tag{17}$$

Equations (13) and (17) give

$$\left(\frac{1}{T_2}\right)_D=\frac{\gamma^2G^2a^4}{120D}\,,\tag{18}$$

which agrees with the long-time-limit result of the more complete treatment of Robertson.[13] Equation (18) will hold only in the extreme motional narrowing limit of $t<t_x$. The dependence of the relaxation rate on the fourth power of a can be understood from (1) the dependence upon a^2 resulting from the mean squared value of H_z, and (2) the dependence upon a^2 resulting from τ_c which is proportional to the mean random-walk time from one wall to the other.