RICE UNIVERSITY

MEASUREMENT OF DIFFUSION

BY

THE SPIN-ECHO METHOD

By

Donald Choy Chang

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ABSTRACT

A convenient and accurate method to measure the diffusion coefficient in a liquid is provided by nuclear magnetic resonance. It is called the "Spin-echo" method. Experimental apparatus has been built to observe spin-echos in samples of water. The results of these experiments agree with the theory of the method. An extended discussion of experimental details is given in this thesis.
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I. INTRODUCTION

In the past two decades, a powerful technique to study the nuclear motion in bulk material has been developed. It is called "Nuclear Magnetic Resonance (NMR)." This technique is widely used nowadays, especially in measurements of relaxation time. Through the work of Hahn, NMR also provides a very convenient method to measure the diffusion coefficient of a liquid. Hahn applied intense radio-frequency power in the form of pulses to an ensemble of spins in a liquid placed in a large static magnetic field. The pulses have a special duration and timing order: they are called a sequence of 90°-90° pulses. Through the excitation of these pulses, a transverse nuclear magnetization signal is induced after a time delay. This signal is called an "echo." The amplitude of the echo is determined by the relaxation times $T_1$ and $T_2$, and the diffusion coefficient $D$, so that by measuring the amplitude of the echo we can measure $T_1$, $T_2$ and $D$. Later Carr and Purcell extended Hahn's spin-echo method and suggested another pulse sequence (called a 90°-180° sequence) and an improved result was obtained. This method is now recognized to be the most accurate way for the measurement of diffusion.

This thesis will discuss the experiments needed to measure the diffusion coefficient by the spin-echo method.
In order to perform this experiment, a pulsed nuclear magnetic resonance spectrometer was built. A temperature control system and a gas handling system are also available for use with this spectrometer. The whole device will enable us to measure the diffusion coefficient of various liquids in a wide temperature range (from room temperature to about 1°K). However, since the main interest of this thesis is to demonstrate the method, only the experiments at room temperature with water samples and Fe(NO₃)₃ solution samples are described. The possibility to use the device to measure the diffusion coefficient in liquid helium will be discussed in the fifth section.
II. METHOD

A compact description of the principle of the spin-echo method is given in the following:

1. 90 Degree and 180 Degree Pulses

Suppose a system of spins is placed in a static magnetic field $\vec{H}$. The motion of the nuclear magnetization $M$ will be described by the equation

$$\frac{d \vec{M}}{dt} = \gamma \vec{M} \times \vec{H}$$

(1)

where $\gamma$ is the gyromagnetic ratio. Equation (1) is a result both of quantum mechanics and of the classical theory of electromagnetism. Now let $S'$ be a frame of reference rotating with respect to the laboratory frame $S$ with an angular velocity $\omega_z$ along the $z$ axis. According to the general law of relative motion, the time derivative of a vector $\vec{V}$ in the Lab frame $S$ ($\frac{d \vec{V}}{dt}$), and its derivative computed in frame $S'$ ($\frac{d \vec{V}}{dt} (s')$), will be related by

$$\frac{d \vec{V}}{dt} = \frac{d \vec{V}}{dt} (s') + \vec{\omega}_z \times \vec{V}$$

where $\vec{\omega}_z = \omega_z \hat{z}$

Replace $\vec{V}$ by $\vec{M}$, and make use of equation (1).
As both $H$ and $\omega_z$ are parallel to $\hat{z}$, if $\omega_z = -\gamma H$, then

$$\frac{d\vec{M}}{dt}(S') = 0$$

which implies $\vec{M} = $ constant in the $S'$ frame. So we see that $\vec{M}$ is precessing around the static field with a frequency equal to $-\gamma H$.

Now, if a small rotating field $\vec{H}_1$ perpendicular to $\vec{H}_0$ is applied, then the motion of the magnetic moment in the S frame is

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times (\vec{H}_0 + \vec{H}_1)$$

Here we choose $\vec{H}_0$ along z axis, i.e. $\vec{H}_0 = H_0 \hat{z}$. $H_1$ has an angular velocity $\omega_z$. In the Lab frame S

$$\vec{H} = \vec{H}_0 + \vec{H}_1 = H_0 \hat{z} + H_1 \cos \omega_z t \hat{x} + H_1 \sin \omega_z t \hat{y}$$
In rotating frame $S'$, $\overrightarrow{H}_1 = H_1 \hat{x}'$ is stationary. Therefore,

$$\overrightarrow{H} = H_0 \hat{z}' + H_1 \hat{x}'$$

(Note: $z = z'$)

So if we write equation (3) in frame $S'$

$$\frac{d\overrightarrow{M}}{dt} (s') = \overrightarrow{M} \times [(\gamma H_0 + \omega_z) \hat{z}' + H_1 \hat{x}']$$

For convenience, let $\omega_z = -\omega$

then

$$\frac{d\overrightarrow{M}}{dt} (s') = \overrightarrow{M} \times [(\gamma H_0 - \omega) \hat{z}' + H_1 \hat{x}']$$

Denote $\omega_0 = \gamma H_0$ = Larmor frequency. Since $H_1$ satisfies the resonance condition, i.e. $\omega = \omega_0$,

then

$$\frac{d\overrightarrow{M}}{dt} (s') = \gamma \overrightarrow{M} \times \overrightarrow{H}_1$$

Comparing equation (4) with equation (1), we see that the magnetic moment $\overrightarrow{M}$ will precess around $\overrightarrow{H}_1$ with angular frequency $\omega_1 = -\gamma H_1$ in the rotating frame $S'$. 
Now, suppose $H_1$ is not turned on continuously, but applied in the form of pulses. Denoting the pulse duration by $\Delta t$, then the angle that $\vec{M}$ precesses around $\hat{x}'$ during the time when $H_1$ turned on is given by

$$\theta = \omega, \Delta t$$

If we only care for the absolute value, then

$$\theta = \gamma H_1 \Delta t$$

If a pulse has a $\Delta t$ that makes $\theta = \frac{\pi}{2}$

i.e.

$$\Delta t = \frac{\pi}{2 \gamma H_1}$$

The pulse is called a "90 degree pulse."

If $\theta = \pi$

i.e.

$$\Delta t = \frac{\pi}{\gamma H_1}$$

then it is called a "180 degree pulse."

Thus a 90 degree pulse would rotate a magnetic moment along the $z$ axis into the $x$-$y$ plane, and a 180 degree pulse would reverse the projection of a magnetic moment along the static field $\vec{H}_0$. These two pulses are very important in the spin-echo method.
2. Relaxation Times----Bloch Equation

We should notice that equation (1) is true only when there is no appreciable influence to the nuclei other than the external field. But in real material the coupling between spins and other systems cannot be avoided. F. Bloch considered the influence of thermal agitation and nuclear interaction and proposed the three relations

\begin{align*}
\dot{M}_z &= - \frac{M_e - M_z}{T_1} \quad (5) \\
\dot{M}_x &= - \frac{M_x}{T_2} \quad (6) \\
\dot{M}_y &= - \frac{M_y}{T_2} \quad (7)
\end{align*}

based on the fact that in thermal equilibrium the magnetization is parallel to the magnetic field. Combining equations (5), (6), (7) with equation (1), a set of phenomenological equations is obtained. The vector form of these equations is

\begin{equation}
\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H} - \frac{M_x}{T_2} \hat{x} + \frac{M_y}{T_2} \hat{y} - \frac{M_e - M_0}{T_1} \quad (8)
\end{equation}
This is called the "Bloch Equation."

3. Description of Spin-Echo from Basic Equations

If we look from a rotating frame $S'$, and denote by $M'_x, M'_y, M'_z$ the three components of $\vec{M}$ in that frame, and if

$$\vec{H} = H_0 \hat{z},$$

then equation (8) becomes

$$\frac{d\vec{M}}{dt}(S') = \gamma \vec{M} \times (\vec{H}_0 - \frac{\omega}{\gamma}) - \frac{M'_x \hat{x}' + M'_y \hat{y}'}{T_2} - \frac{M'_z - M_0}{T_1} \hat{z}.'$$

at resonance $\omega = \omega_0 = \gamma H_0$, and

$$\frac{d\vec{M}}{dt}(S') = - \frac{M'_x \hat{x}' + M'_y \hat{y}'}{T_2} - \frac{M'_z - M_0}{T_1}$$

From this equation, we can solve for the magnetization:

$$M'_x(t) = M'_x(0) e^{-\frac{t}{T_2}}$$

$$M'_y(t) = M'_y(0) e^{-\frac{t}{T_2}}$$

$$M'_z = M'_z(t) = M_0 (1 - e^{-\frac{t}{T_1}})$$
We see as the system approaches thermal equilibrium, the magnetic moment will approach the \( \hat{z} \) direction. Now, suppose at \( t = 0 \), \( M \) is along the \( z \) axis. If we apply a 90° pulse, the magnetic moment will be rotated into the \( x-y \) plane. Since the magnetic field inside the sample is not exactly homogeneous, some of the spins would have a faster precessing rate than the others. As the time goes on, the magnetic moment of the individual nuclei would spread out like a fan because of the difference in precession rate. This would have a net effect to reduce the total magnetic moment. If after a time \( \tau \), \( (\Delta T \leq \tau < T_1, T_2) \), we applied a 180° pulse, the order of different spins in the \( x-y \) plane will be reversed. Now the spins with faster precessing rate would lag behind the spins with slower precessing rate. (This will reverse the process because now the faster one is chasing the slower one.) Then after the same time period \( \tau \) (remember now \( t = 2\tau \)) the faster spins will just catch up to the slower spins; so all the spins will be in phase again. The total magnetic moment, therefore, becomes a maximum. This would induce a signal in a coil whose axis lies in the \( x-y \) plane. This signal is called an "echo." If we apply another 180 degree pulse at \( t = 3\tau, 5\tau, \ldots, (2n+1)\tau, \ldots \), by a similar argument, we would see echos at \( t = 4\tau, 6\tau, \ldots \). From equation (8) we can show that the amplitude of the echo appearing at \( t = 2n\tau \) is proportional
$k(n) = \exp \left\{ -\frac{2\pi n v}{T_2} \right\}$

4. Diffusion

For a liquid sample, if the viscosity is not too high, at the time interval $2\tau$, the diffusion would contribute an extra damping to the transverse magnetization. This damping can be evaluated by adding a diffusion term to the Bloch equation. Then instead of equation (8), the nuclear magnetization now is given by a modified Bloch equation

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H} - \frac{M_x x + M_y y}{T_2} - \frac{M_z - M_0}{T_1} + D \nabla^2 \vec{M}$$

(9)

where $D$ is the diffusion coefficient.

Between the 90° and 180° pulses, $H_1 = 0$, but we need to consider that the magnetic field may have some inhomogeneity. Let $\hat{G} = \nabla H$. Then

$$H_x = H_0 + \hat{r} \cdot \hat{G}$$

(10)
Substitute equation (10) into equation (9) and define

\[ m = M_x + i M_y \]

If \( t \) is the time when the first echo appears, then the solution to equation (9) has the form:\(^4\)

\[ m(t) = m_0 \exp \left\{ i \omega_0 t - \frac{t}{T_2} - \frac{1}{12} D g^2 G^2 t^3 \right\} \] (11)

If \( t \) is the time when the \( n^\text{th} \) echo appears, (i.e. \( t = 2n\tau \)) then the solution is\(^8\)

\[ m(t) = m_0 \exp \left\{ i \omega_0 t - \frac{t}{T_2} - \frac{1}{3} D g^2 G^2 \tau^2 t \right\} \] (12)

We may measure either the decay of the amplitude of the first echo with different \( \tau \), or measure the exponential decay of the echos in a sequence of \( 90^\circ - 180^\circ - 180^\circ - \cdots \) pulses. Since the amplitude of echo is proportional to \( m \), the diffusion coefficient \( D \) can then be calculated from equation (11) or (12).
III. APPARATUS

The main apparatus is a Pulsed Nuclear Magnetic Resonance Spectrometer. It contains five principal basic units:

1. Timing Pulse sequence generator
2. Transmitter
3. Sample circuit
4. Receiver
5. Magnet

The block diagram of the spectrometer is shown in Figure III-1. Other units are: recording device, sample container and holder, temperature control system, and gas handling system.

1. PULSE TIMING AND SEQUENCING CIRCUITRY

This circuit includes three Tektronix 161 pulse generators, two Tektronix 161 waveform generators, and a cathode follower mixer. The block diagram is shown in Figure III-2.

A sequence of a sawtooth wave and a rectangular positive pulse with the same phase are generated from the 162 (A) waveform generator. The positive pulse is sent to trigger 161 (A) which produces a rectangular pulse with variable width $\Delta T_1$. The sawtooth voltage is sent to 161 (B), which produces another pulse with width $T_w$ after a time delay $\tau$. This rectangular pulse then goes to the gate input of 162 (B). At the time when the pulse is on, the waveform generator will generate a train of positive pulses with separation $T'$. Each
Fig. III-1
Fig. III-2
of these pulses then triggers the 161 (C) pulse generator and generates a pulse of amplitude $V_2$ and width $\Delta T_2$. The output from both 161 (A) and 161 (C) will be sent to the mixer, and a combined pulse sequence is then obtained. The mixer has two identical outputs: one goes through the d.c. amplifier to gate the transmitter and another serves to trigger the oscilloscope.

All the parameters mentioned above can be adjusted by the front panel controls of the 161 and 162 generators. The repetition period can be set manually or by internal triggering of the 162 generator in a range from 0.1 millisecond to 10 seconds. The delay $\tau$ is adjusted by varying the triggering level of 161 (B), it can be set at any value between 0 and $T$. The ranges of the other parameters are:

- $\Delta T_1$: From 5 micro-second to 0.1 sec
- $\Delta T_2$: ditto
- $T_w$: ditto
- $T'$: From 0.1 milli-second to 10 sec
- $V_1$: From 0 to 50 volts
- $V_2$: ditto

The number of pulses following the first pulse is determined by $T_w$ and $T'$. The relation is

$$n = \left\lceil \frac{T_w}{T'} \right\rceil + 1$$
where \([X]\) is the step function

\[
[X] = \begin{cases} 
0 & (0 \leq X < 1) \\
1 & (1 \leq X < 2) \\
2 & (2 \leq X < 3) \\
\ldots & 
\end{cases}
\]

In the illustration of Figure 2, \(n\) is taken as 2.

2. TRANSMITTER

The purpose of the transmitter is to produce pulsed radio-frequency power with negligible r-f leakage between pulses. The principal part is an r-f gated amplifier. The circuit diagram of it is shown in Figure III-3. Radio-frequency power from a General Radio Type 1211B 0.5-50 mc/sec unit oscillator is coupled to the control grid of the first 7788 vacuum tube which is normally cut off by negative grid bias. The negative output of the d.c. amplifier is coupled to the cathode resistor of the same tube. When a negative pulse is sent from the Timing Pulse Sequence Generator, the potential of the cathode drops suddenly, and the grid signal is no longer cut off. Then the radio-frequency power appearing at the plate is amplified by a push-pull amplifier and again by a 3E29 power tube. Finally, the output is coupled to the transmitter coil around the sample. The maximum voltage output is about 1000 volts (peak to peak).

The transmitter is tuned to a radio-frequency of about 6 mc/sec. The proper output wave form is obtained by
adjusting the three variable capacitors. The magnitude of the r-f pulse is controlled by the $B^+$ voltage from the power supply, the circuit diagram of which is not shown here.

3. SAMPLE CIRCUIT

The sample circuit includes the transmitter coil and the receiver coil. They are arranged perpendicular to each other, and the latter is inside the former, as shown in Figure III-4 (a) and (b). When they are placed in the air gap of the magnet, both coils are perpendicular to the static magnetic field.

The transmitter coil and receiver coil are made by winding copper wire on a lucite coil and a teflon coil, respectively. Their specifications are:

A. Transmitter coil
   Conductor: #16 copper wire
   Turns : 17
   Length : 1"
   Inside diameter: 13/16"

B. Receiver coil
   Conductor: #26 copper wire
   Turns : 27
   Length : 1/2"
   Inside diameter: 5/16"
Fig. III-4 (a)
Sample holder

Fig. III-4 (b)
Both coils are tuned to resonance at $f = 6\text{ mc/sec}$. (The resonance was tested by a Heathkit grid dip meter Model GD-1B.) The transmitter coil is tuned by adjusting the output coupling capacitor of the gated amplifier, while the receiver coil is tuned by a parallel condenser. (Actually the major part of the parallel capacitance to tune the receiver coil is contributed by the coaxial cable. The cable used in this experiment is RG-58A/U, which has a capacitance 29.5pf per foot. The length of the cable connecting the coil and receiver is about 4.5 feet; the total capacitance is about 140 pf. That is almost enough to tune the receiver coil.)

In the spin-echo experiment the transmitter coil and receiver coil must have the following characteristics:

**A.** The r-f voltage across the transmitter coil should decay to zero rapidly after the driving pulse from the transmitter is removed.

**B.** The voltage induced in the receiver coil by the transmitter signal should be nearly zero or decay to zero very rapidly.

**C.** The voltage induced in the receiver coil by the nuclear magnetization of the sample must be as large as possible. The decay of the r-f voltage across an inductive element in the absence of a driving emf is given by
\[ v(t) = v_0 e^{-\frac{\omega t}{2a}} \]

where \( Q \) is the "Quality Factor" of the coil. From the above equation we see that requirement A. can be fulfilled by using a low \( Q \) transmitter coil. However, requirement B. and C. demand an opposite value for the \( Q \) of the receiver coil. To solve this problem we have to use a variable \( Q \) device. This is furnished by connecting two T8G semi-conductor diodes back to back across the receiver coil. For large voltage (greater than 1 volt) these diodes look like small resistors in parallel thus lowering the \( Q \) value. For a small voltage, these diodes look like large parallel resistors, and thus, the value \( Q \) becomes higher. Since the transmitting pulse is much larger than the signal induced from the sample, the receiver coil has low \( Q \) for the transmitting pulse and high \( Q \) for the NMR signal, so that both desired characteristics B. and C. are obtained.

4. RECEIVER

The receiver is a six stage high gain radio-frequency amplifier. The circuit diagram is shown in Figure III-5.

The input level is designed to be very low since the induced NMR signal has a very low voltage (less than 0.1 milli-volt). The receiver has the following characteristics:
A. Gain is high, up to approximately $10^6$.

B. It is tuned to operate at 6 mc/sec, but has a sufficiently broad bandwidth (about 1.5 mc). This makes it linear enough to amplify the nuclear resonance signals without distortion.

C. The recovery time is short. It will recover from complete saturation in about 5 micro-seconds.

The power for this receiver is supplied by a Hamner H-107 regulated d-c power supply.

5. MAGNET

A Varian model V-4012A 12" electromagnet is used. The magnet is water cooled. It has an air gap of 1.75". The maximum magnetic field between poles is 10 kilogausses. (In this Experiment the field is set to be about 1.4 kilogausses.) The current of the electromagnet is supplied by a Varian V-2200 regulated magnet power supply.

6. RECORDING DEVICE

The signal from the receiver is displayed on the screen of a Hewlett Packard 175A oscilloscope. Then, photographs are taken. The trace of the signal thus is recorded on Polaroid film. Two kinds of scopecameras have been used. One is a Hewlett Packard 196B oscilloscope camera, another is a Du Mont type 353-2620 scopecamera.
Another way of recording was tried. The signal in the scope can be sent to a Moseley 2D-2 X-Y recorder through a Hewlett Packard 1782A display scanner. However, the result is not so satisfactory as the photographs.

7. SAMPLE CONTAINER AND HOLDER

The fluid sample is contained in a small pyrex glass cup, which has an outside diameter 9 mm and is 16 mm in length. The mouth of the cup is stopped by a thin cork and sealed by paraffin.

The sample holder is made with lucite. It supports the sample and the sample circuit. The orientation of this holder is adjustable. The side view of it is shown in Figure III-4(a).

8. TEMPERATURE CONTROL SYSTEM

A double jacketed dewar system sits between the poles of the magnet. The outside dewar is made of metal. It is used to contain liquid nitrogen. The inside dewar which is made with pyrex glass is for liquid helium. A powerful pumping system is connected to the helium dewar, so that a temperature of 1°K can be reached by decreasing the vapor pressure of helium.
9. GAS HANDLING SYSTEM

This system consists of a sample storage container, a helium trap, a glass manometer, Hoke valve controls, and a glass chamber at the end of a filling capillary. This system will enable us to study liquid He$^3$-He$^4$ solutions.

For the experiment described in this thesis, water samples have been prepared and studied at room temperature. Therefore, neither the cryogenic system nor the gas handling system has been used.
IV. EXPERIMENTAL METHOD

1. Sample

Samples of pure H₂O and Fe(NO₃)₃ solution of different concentration—-0.05 m, 0.02 m, 0.003 m and 0.001 m, were used. Their relaxation times $T_1$ and $T_2$ vary in a large range. Thus their echos are very different in appearance. The results are given in the next section.

2. Method of Observing Echo

There are many parameters to control in the spin-echo experiment. It is a nerve-breaking job to search for an echo when one does not know where it is. The following procedure may be found to be practical and helpful:

A). Tune the transmitter coil and receiver coil to the same frequency. (In this setup, $f = 6 \text{ mc/sec}$).

B). Produce a two pulses sequence from the Timing Pulse Sequence Generator. Both pulses must be rectangular and have independent duration control.

C). Adjust the r-f oscillator so that the r-f wave produced is at the frequency to which the transmitter coil and receiver coil are tuned.

D). Adjust the three variable capacitors of the transmitter from the front panel controls, so that the envelope of the output waves is very close to
rectangular form. The tail of the pulse should decay as fast as possible.

E). Using the formulas

\[ \gamma H_1 \Delta T_1 = \frac{\pi}{2} \]

\[ \gamma H_1 \Delta T_2 = \pi \]

calculate the approximate values of \( \Delta T_1 \) and \( \Delta T_2 \).

(We can estimate \( H_1 \) from the inductance of the transmitter coil and pulse amplitude.) Then set the duration of the 90° and 180° pulses at the calculated value.

F). Adjust the gain level of the receiver by observing the amplification of a modulated r-f wave at 6 mc/sec from an r-f signal generator.

G). Apply the static magnetic field \( H_0 \). For \( \omega_0 = 6 \) mc/sec, \( H_0 \) is set to 1.4 kilogauss. Wait for awhile to let the field become stable.

H). Now if everything is all right, we should see a small echo when the output of the receiver is displayed on the screen of an oscilloscope; or, at least a tail after the 90° pulse should appear. If such a signal does exist, then, the following things can be done to improve the signal:
a) Change the $B^+$ voltage of the transmitter to adjust the voltage amplitude of the pulses. See if the magnitude of the signal is enlarged.

b) Adjust the magnetic field very slowly around $H_0$ and fix it at a value for which the largest echo and the smallest tail after the 180° pulse is seen.

c) Since the calculated value of $\Delta T_1$ and $\Delta T_2$ is only approximate, and the reading on the dials of the equipment is not very reliable, we should try to adjust the duration of the two pulses to optimize the signal. Especially when the minimum tail after the 180° pulse is not zero, we can conclude that the two pulses are not exactly 90° and 180°.

d) The echo decays almost exponentially with a time constant $T_2$. Shortening the pulse interval $\tau$ may thus help to increase the echo amplitude. (This is shown in Figure IV-1.)

e) In a spin echo experiment, the repetition period is subjected to the requirement that it must be several times $T_1$. Reducing the repetition rate may improve the signal. (See Figure IV-2.)
Fig. IV-2 b.
Fig. IV-2 a.

T = 4 sec.

T = 8 sec.
I). If we did not see any signal at all, then something might be wrong in the equipment. Check the various parts of the spectrometer, especially the receiver and the coils. After we have made sure that all the equipment is working all right, then follow all the procedures a), b), c), d), e) described in H). If we still have no signal, then the following possibilities should be considered:

a') As pointed out in e) of the last subsection, $T$ must always be larger than $T_1$ of the sample. The maximum $T$ that can be set on this spectrometer is 10 seconds. We will not see any signal if the sample used has a $T_1$ much larger than our maximum $T$. Also, if a tail is seen after $90^\circ$ pulse but no echo, then it is probably because the sample has a $T_2$ shorter than the minimum $\tau$ we can set. In this case it will be wise to change to a sample with shorter $T_1$ or longer $T_2$.

b') The signal picked up from the sample may be too weak, and then make the amplified signal lower than the noise level of the output from the receiver. The calculated maximum nuclear resonance signal is given by $^{12}$
\[ V = 4\pi \frac{I+1}{I} \frac{n \mu^2}{(l^2+L^2)^{3/2}} \frac{\omega \gamma \lambda}{k T} \ N \ V \]

\[ \times 10^{-9} \text{ volt} \]

where

- \( I \): nuclear spin
- \( n \): number of atoms per unit volume of sample
- \( \mu \): nuclear magnetic moment
- \( V \): volume of sample
- \( d, l, N \) and \( Q \) are descriptions of the receiver coil:
  - \( d \): diameter
  - \( l \): length
  - \( N \): number of turns
  - \( Q \): quality factor

So we see if we can make \( V \) and \( N \) larger, the amplitude of the signal would be enlarged proportionally. Thus the sample used should be as large as possible. (\( N \) is limited by the resonance condition.)

The noise can be reduced by using coaxial cables and trying different methods of grounding. In these experiments the noise level is about 20 millivolt.
After satisfactory echos have been produced, we can go ahead to measure the echo amplitude as a function of pulse separation $\tau$. From those measurements we will get the information about the diffusion coefficient and the spin-spin relaxation time. The data and results will be discussed in the next section.

3. Magnetic Field Gradient

From equation (11) and (12) of Section II, we see if we measure the diffusion coefficient $D$ we must know the field gradient $G$. Fortunately, there is a simple way to determine $G$ from the shape of an echo. The width of an echo is measured by the lifetime of the signal $T_2^*$. The variation of field over the whole sample is related to $T_2^*$ by

$$\Delta H \approx \frac{2\pi}{\gamma T_2^*}$$

From this relation $G$ can be estimated.

The preceding relation shows that if the field were more inhomogeneous, the width of the echo would be narrower. Figure IV-3 is an illustration of this effect. When those pictures were taken, the field gradient had been produced by placing an iron bar parallel to the transmitter coil between the two poles of the electromagnet. By adjusting the
position of the iron bar, different field gradients could be produced.
Very small field gradient

A little field gradient

Fig. IV-3 a.
A little more field gradient

More field gradient

Fig. IV-3 b.
V. RESULTS AND DISCUSSION

1. Result of Method A

In this method a 90°-180° pulse sequence is used. (A 90° pulse is followed by a 180° pulse after time τ.) The echoes which are produced by different settings of τ are recorded on Polaroid film by multiple exposure. Some of these pictures are shown on the following pages.

Figure V-1 shows the decay of the echo for a sample consisting of 0.001 molar Fe(NO₃)₃ solution (in water). The repetition period is one second. The sweep time is 10 m sec per division, τ varies from 4 to 45 millisec. T₂ of this solution is about 46 millisec. The decay is very close to an exponential form.

Figure V-2 shows the amplitude of the echo as a function of τ for a pure water sample. Now the decay is much slower in comparison with the Fe(NO₃)₃ solution sample. The repetition period is 2 seconds. The sweep time is 100 millisec per division. τ varies from 50 millisec to 450 millisec.

From the result for these two samples, we see very clearly that if T₂ is short enough, the decay of the echo is characterized by the spin-spin relaxation only. As pointed out in Section II, when T₂ dominates the damping, the magnitude of the echo is given by
Fig. V-2 (a)

Fig. V-2 (b)
\[ h = h_0 \exp \left\{ -\frac{t}{T_2} \right\} \]

The exponential decay in Figure V-1 agrees perfectly with the theory. If \( T_2 \) is not so short, the damping effect contributed by diffusion cannot be neglected. According to the discussion in Section II, the magnitude of the echo should be governed by a factor

\[ \exp \left\{ -\frac{t}{T_2} - D \gamma G^2 t^{3/2} \right\} \]

and that is what we actually see in Figure V-2. The curve in Figure V-2(b) is well fitted by an equation

\[ \ln h = A - B t - C t^3 \]

The constants \( A, B, \) and \( C \) can be calculated by computer using a least-square analysis. This thesis, however, will not go through this calculation because the purpose of this thesis is to show the method rather than to get a numerical result.

As we discussed before, in the case when diffusion is important, the magnitude of the echo is given by
From this equation we may predict that if the magnetic field gradient $G$ increases sufficiently, the $t^3$ term would become dominant and would make the echo decay faster. To show this effect, the following experiment was performed. The sample was pure water. All the conditions were equivalent to those of the experiment which gave the result shown in Figure V-2, except a magnetic field gradient is added. The result is shown in Figure V-3. The decay of the echo has changed. The curvature is larger and the damping is faster. This result gives a beautiful confirmation of the theory. (Note: the sweep times in Figure V-2 and Figure V-3 are the same.)

2. **Result of Method B**

In this method a $90^\circ$ pulse is followed by a sequence of $180^\circ$ pulses with constant separation $2\tau$. According to the discussion in Section II, the amplitude of the echo appearing at the time $t = 2n\tau$ is given by

$$h(t) = h_0 \exp \left\{ - \frac{t}{T_2} - \frac{1}{3} D \gamma^2 G^2 \tau^2 t^3 \right\}$$
Fig. V-3

Method A with adding magnetic field gradient
\[ h(t) = h_0 \exp\left\{ -\frac{t}{T_2'} \right\} \]

\[
\frac{1}{T_2'} = \frac{1}{T_2} + \frac{1}{3} D \gamma^2 G^2 T^2
\]

Therefore, no matter how large the diffusion and field gradient is, the echo would still decay exponentially with the time constant \( T_2' \). Figure V-4 shows the echo decay of a pure water sample by this method. The sweep time is 20 millisecond per division. The repetition period is 4 sec, \( t \) is set equal to 12.5 millisecond. The picture shows that the decay of the echo is really governed by an exponential form. Figure V-5 is another picture taken for the same sample with the same pulse, sequence, and the same repetition rate. But now a field gradient is applied. The echo decays in the same manner although the echo shape is changed. In these two pictures, \( T_2' \) is estimated to be about 90 millisecond.

The spin-spin relaxation times of other samples (0.05 m, 0.02 m, 0.03 m Fe(NO_3)_3 solution) are too short to show the decay of the echo by diffusion. Therefore, their pictures are not given here.
Fig. V-4 (a)

Fig. V-4 (b)
Fig. V-5
Method B with adding magnetic field gradient
3. Discussion of Application to He³-He⁴ Solution

From the preceding discussions in this thesis we see that the spin-echo method does provide a convenient and accurate way to measure the diffusion coefficient. The only requirement to use the spin-echo method is that the condition $\Delta t \leq \tau < T_1, T_2$ must be satisfied. For protons or helium 3, the order of $\Delta t$ is about 10 microsec, for the value of $H_1$ used in this NMR spectrometer. So, if we use this spectrometer to measure the diffusion coefficient of He³-He⁴ solutions by the spin-echo method, we will have no trouble to fulfill the condition $\Delta t \leq \tau < T_1, T_2$ because $T_1$ and $T_2$ of He³ are of the order of several minutes. We, however, will not be able to use the internal triggering to control the repetition rate because $T$ in this spectrometer is limited to 10 seconds. But if we use the manual triggering this trouble will be solved.

As mentioned in Section III, a temperature control system and a gas handling system are already available for use with this spectrometer. We thus can handle the helium mixture and operate at liquid helium temperatures. The only trouble left may be the sample holder, since a separate transmitter and receiver coil are used in the preceding experiments. If we are going to use He³-He⁴ solution sample, we may have to use one coil to serve as both transmitter coil and receiver coil, since the sample is now connected
with a filling capillary making two perpendicular coils difficult to arrange. This might raise a minor tuning problem. But it will not be hard to solve because the one coil method has been successful in other work.

The gyromagnetic ratio of $\text{He}^3$ is different from that of the protons so far observed in $\text{H}_2\text{O}$,

$$\gamma(\text{He}^3) = 2.038 \times 10^4 \sec^{-1} \text{gauss}^{-1}$$

Since our spectrometer is tuned at 6 mc/sec, the static field must be set at 1.85 kilogauss for the He$^3$ sample. A magnetic field with such magnitude can be produced in the magnet used in this spectrometer. Every requirement to run a He$^3$-He$^4$ solution sample with this spectrometer can thus be fulfilled.
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