Nuclear Magnetic Relaxation and Diffusion in Paraffin Oil

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NUCLEAR MAGNETIC RELAXATION
AND DIFFUSION IN PARAFFIN OIL

by

David E. Parker

A thesis presented to the
Faculty of the School of Graduate
Studies in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
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INTRODUCTION

Since the introduction of the spin echoes technique by E. L. Hahn¹ many studies have been made in the determination of the spin relaxation \( T_2 \), spin-lattice relaxation \( T_1 \), and the diffusion rates in gases, liquids²⁻⁵, and solids⁶⁻¹⁰. Hahn's methods were later improved by Carr and Purcell¹¹. The Carr-Purcell method serves as the basic technique for this study.

Several studies have been published on the relaxation and

---

diffusion rates in hydrocarbons$^{12}$. These studies have shown:

1. The spin relaxation time $T_2$, is independent of the temperature.

2. The coefficient of self-diffusion is logarithmic in reciprocal temperature.

3. The dependence of the coefficients of self-diffusion on temperature becomes more pronounced as the molecular weight is increased.

Because of its high signal to noise ratio and its broad line width, paraffin oil was chosen as the sample for this study. Because of paraffin oil's chemical properties the following behavior would be expected:

1. Paraffin oil is a hydrocarbon; $T_2$ relaxation time should be temperature independent.

2. The coefficient of self-diffusion should be logarithmic in reciprocal temperature.

3. Because of the high molecular weight of the paraffin oil the temperature dependence of the self-diffusion should be highly pronounced.

---

THEORY

Static Magnetic Field

Most materials containing nuclei which possess a magnetic moment and angular momentum can be studied by the pulse technique in nuclear magnetic resonance. When a static magnetic field is applied to the sample, a macroscopic equilibrium magnetization is created in the direction of the static magnetic field according to the Boltzman law. The individual nuclear spins are space quantized by the static magnetic field with a slightly higher population in the spin state aligned in a direction more nearly that of the static magnetic field. The magnetization that is created by the static magnetic field is expressed by:

\[ M_0 = \chi_0 H_0 \]

where \( M_0 \) is the equilibrium magnetization, \( \chi_0 \) is the magnetic susceptibility and \( H_0 \) is the magnitude of the static magnetic field.

Effect of an Alternating Magnetic Field

In pulse experiments in nuclear magnetic resonance, another smaller alternating magnetic field in a direction perpendicular to the static magnetic field is applied periodically to the sample. This technique is unlike absorption experiments in
nuclear magnetic resonance which employs a continuous alternating magnetic field perpendicular to the static magnetic field. Commonly the direction of the static magnetic field is called the z direction and the direction of the alternating magnetic field is called the x direction. The alternating magnetic field:

\[ \vec{H}(t) = 2H_1 \hat{\cos}\omega t \]

can be broken up into two components:

\[ \vec{H}_R = H_1[\hat{\cos}\omega t + \hat{j}\sin\omega t] \]

and

\[ \vec{H}_L = H_1[\hat{\cos}\omega t - \hat{j}\sin\omega t] \]

The two components can be visualized as being two counter rotating fields \( \vec{H}_R \) and \( \vec{H}_L \) whose magnitudes are \( H_1 \), and rotating

![Diagram](image)

Figure 1. The two components of the alternating magnetic field rotating in opposite directions in phase around the z axis.
in opposite directions in phase around the z axis in the x, y plane. Figure 1 is a diagram of the composition.

If only the component which rotates in the same sense as the precession of the magnetic moment is considered, the effective magnetic field is given by:

$$\mathbf{H}_{\text{eff}} = \hat{k}H_0 + H_1[\hat{i}\cos \omega t + \hat{j}\sin \omega t]$$

The theory involved may be simplified by consideration of a rotating coordinate system x', y', z' which rotates with the angular velocity $\omega$ about the z axis. Observed from the rotating coordinate system, $H_1$ appears to be static and the resultant field appears to be:

$$\mathbf{H}'_{\text{eff}} = \hat{k}(H_0 - \frac{\omega}{\gamma}) + H_1'$$

where $\gamma$ is the gyromagnetic ratio.

---

Figure 3. $\vec{H}_{\text{eff}}$ in the rotating coordinate system.

When $\frac{\omega}{\gamma} = H_0$ or the alternating field has the same frequency as the gyroscopic precession of the individual nuclei, the Larmor frequency,

$$\text{(7)} \quad \vec{H}_{\text{eff}} = H_1 \hat{i}'. $$

Figure 4. When $H_0 = \frac{\omega}{\gamma}$, $H_1$ becomes $H_{\text{eff}}$.

When $\omega$ is not equal to $2\pi$ times the Larmor frequency the magnetization $\vec{M}$ which was originally in the $z$ direction precesses around $\vec{H}_{\text{eff}}$ of equation (6) in the rotating coordinate system. When $H = \frac{\omega}{\gamma}$, of equation (7), $M$ may precess around the $x'$ axis.
in the $y', z'$ plane.

Thus when $H_0 > \frac{\omega}{\gamma}$ the magnetization vector can be reoriented to any direction with respect to the static magnetic field by the correct timing of the duration of the alternating field. Most commonly used are reorientations by $90^\circ$ (90° pulse) which rotate the magnetization vector into the $x, y$ plane, and reorientations by $180^\circ$ (180° pulse) which rotate the magnetization vector into the negative $z$ direction. The angle of reorientation is given by:

\[
\theta = \gamma H_1 t_\omega
\]

where $\theta$ is the angle of reorientation, $\gamma$ the gyromagnetic ratio, $H_1$ the maximum magnitude of the alternating field, and $t_\omega$ is the pulse duration.

The Tail

Following the turn off of $H_1$ after a $90^\circ$ pulse, the magnetization vector diminishes in magnitude due to the diffusion of the individual spins. This diffusion is in part caused by the
different precession rates of the various nuclei and is brought about by the inhomogeneous magnetic field which are inevitably present at the nuclear sites. This phenomenon when observed on an oscilloscope is called the "tail".

The Echo

If the magnetic fields at the nuclear sites are time independent, the precessional rate of each spin will be constant in time. After the application of a $90^\circ$ pulse followed by the appearance of its tail, the spins which were originally aligned creating the magnetization in the $z$ direction are in complete random phase in the $x, y$ plane. Thus the magnetization has been destroyed; it can be recreated by using a $180^\circ$ pulse sometime after the $90^\circ$ pulse.

Figure 7 illustrates the production of an echo. Before the application of the $90^\circ$ pulse a magnetization has been created by the static magnetic field. The $90^\circ$ pulse rotates the magnetization vector into a plane which is perpendicular to the static magnetic
field. After the 90° pulse is over the individual spins precess about the z axis at a rate proportional to the strength of the magnetic field to which each nuclei is exposed. Because of the inhomogeneity of the static magnetic field and the variation in the magnetic field due to neighboring nuclei and electrons, the nuclei are at sites of different magnetic fields. Each spin therefore precesses at a different rate. The spins that are originally in phase with each other become out of phase thus causing the magnitude of the magnetization, which is now rotating in the x, y plane at the Lamor frequency, to diminish in magnitude.

Since it has been assumed that the local nuclear magnetic fields are time independent, each spin will continue to precess at a rate characteristic of its position. At a time \( \tau \) after the 90° pulse a 180° pulse is applied. The 180° pulse reflects each spin with respect to the y', z' plane since they precess 180° about \( H_1 \) of the 180° pulse. After the 180° pulse is over the spins continue to precess around the z axis in the same direction as they did before the 180° pulse. If the magnetic field is time independent, the rate of the precession of each nucleus before and after the 180° pulse will be the same. Thus at a time \( \tau \) after the 180° pulse the spins will come back into phase recreating the magnetization. This phenomenon when observed on an oscilloscope called an "echo".

This sequence of events is illustrated by Figure 8.
Figure 8. Sequence of events leading to the recreation of the magnetization. (A) The magnetization is created by the large static magnetic field. (B) A 90° pulse rotates the magnetization vector into the x', y' plane. (C) The magnetization vector diminishes in magnitude due to the diffusion of the spins. (D) A 180° pulse reflects the diffused spins with respect to the y', z' plane. (E) The regrouping of the spins recreating the magnetization vector. (F) The magnetization vector diminishes again.

After this sequence the magnetization can be recreated many more times by successive 180° pulses.
RELAXATIONS

$T_2$ Relaxation

The magnetic fields at the nuclear sites are time dependent, for the nuclei are constantly moving with respect to each other and with respect to the external magnetic field. Since the time dependent components of the magnetic field are not homogeneous, the phase memory of the spins decreases as the $180^\circ$ pulse gets progressively later in time from the $90^\circ$ pulse. Thus the echo amplitude will decrease with increasing $\tau$, the time interval between the $90^\circ$ pulse and the $180^\circ$ pulse.

If the external magnetic field is extremely homogeneous, the only inhomogeneity of the magnetic field the nuclei experiences is due to other nuclei and electrons. The inhomogeneity due to the nuclei and electrons is due to the exchange interactions and the chemical shift. Calculations show that in this case $T_2$ should be temperature independent.\(^\text{14}\)

Under the conditions of an extremely homogeneous external magnetic field and nuclear movement, the echo envelope is given by:

$$V = V_0 \exp(-t/T_2)$$

where \( V \) is the echo amplitude, \( V_0 \) is the maximum echo amplitude and \( t \) is time. \( t \) is equal to \( 2\tau \) plus the width of the \( 90^\circ \) pulse plus the width of the \( 180^\circ \) pulse. Since the width of the \( 90^\circ \) pulse and \( 180^\circ \) pulse is short (20 microseconds) as compared to \( \tau \) (2-20 milliseconds), \( t \) is approximately equal to \( 2\tau \).

In this experiment an extremely homogeneous magnetic field was not available. Carr and Purcell\(^{11} \) were successful in eliminating the effect of the static magnetic field inhomogeneity by a multiple \( 180^\circ \) pulse method. The pulse sequence is initiated by a \( 90^\circ \) pulse, then after \( \tau \) seconds a \( 180^\circ \) pulse is applied, which is followed by a number of \( 180^\circ \) pulses that are separated by \( 2\tau \) seconds. Figure 9 illustrates this sequence.

![Figure 9. The multiple \( 180^\circ \) pulse method.](image)

For \( n \) pulses,

\[
(10) \quad V = V_0 \exp\left(\frac{-t}{T_2}\right) + \left(-\frac{\gamma^2 G^2 D t^3}{12 n^3}\right)
\]

where \( D \) is the diffusion constant and \( G \) is the magnetic field gradient. For a large \( n \), \( V \) essentially equals \( V_0 \exp(-t/T_2) \).
By this method the effects of the static magnetic field inhomogeneity can be decreased sufficiently, so that the effects can be considered to be cancelled out.

To prove equation (10) reduces to equation (9) when the multiple pulse method is used, Carr and Purcell considered the change in the magnetic field each nuclei experienced as it moved through a liquid. Then by using a random walk method they set the solution up in terms of a series. Later Douglass and McCall proved that the same result could be obtained with the use of integration. The effect the multiple pulse method has on the phase memory of nuclear spins in an inhomogeneous magnetic field as compared to the effect that a single $180^\circ$ pulse has on the phase memory of nuclear spins in an inhomogeneous magnetic field is illustrated in Figure 10.
Figure 10. The effect the multiple pulse method has on the phase memory of nuclear spins in an inhomogeneous magnetic field as compared to the effect that a single 180° pulse has on the phase memory of nuclear spins in an inhomogeneous magnetic field. Two spins which originally have the same phase start from the same reference point in a liquid and move in different directions, (A) one into a region where the static magnetic field is stronger and the other into a region where the static magnetic field is weaker. The spin that is exposed to the larger magnetic field precesses at a faster rate than the one exposed to the weaker magnetic field.

(B, C, D, E, F, G, H, I) The multiple 180° pulse method averages out the effect of the inhomogeneous static magnetic field. (J) The phase memory of the spins acting under the influence of the multiple 180° pulse method is primarily effected by the magnetic fields due to the protons and electrons in the liquid. Whereas, (J'), the phase memory of the spins acting under the influence of the single 180° pulse method is influenced by both the inhomogeneous static magnetic field and the magnetic fields due to the protons and electrons in the liquid.

**T₁ Relaxation**

After a sample is placed in a static magnetic field, some time is required for the nuclear magnetization to be created and approach its equilibrium value. The decay constant of the magnetization's growth is given by T₁, the relaxation time. Since this process gives up energy to the static magnetic field, some mechanism must provide energy to the individual spins making up the magnetization vector. The source of the energy is the lattice. Thus the name "spin-lattice relaxation" (T₁ relaxation).

The T₁ relaxation time can be obtained by the null method. A 180° pulse is applied and is followed by a single 90° pulse which can be applied after a variable time interval. The sequence is illustrated by Figure 11.
Figure 11. The null method. (A) The magnetization is created by the static magnetic field. (B) The 180° pulse is applied reorientating the magnetization vector into a direction opposite to the static magnetic field direction. (C) As time progresses the magnetization decays and regrows in the direction of the static magnetic field. At various time intervals during the cycle a single 90° pulse is applied. (D) The envelope described by the maximum tail heights depicts the growth and decay of the magnetization vector.

$T_1$ can be evaluated directly from the tail envelope.

$$T_1 = \tau_1 \ln 2$$

where $\tau_1$ is the time interval from the 180° pulse to the minimum of the envelope that describes the tail amplitudes.

The concept of $T_1$ relaxation is complicated because of the
movement of the molecules. These motions include rotational tumbling of the individual molecules, relative translational motion of molecules and even, because of the chemical exchange, migration of atoms and groups of atoms from one molecule to another. 15

$T_1$ is usually considered to be due to two relaxation processes, whose rates are:

$$\frac{1}{T_1} = \frac{1}{T_{1,\text{rot}}} + \frac{1}{T_{1,\text{trans}}}$$

$(1/T_1)_{\text{rot}}$ being due to the fluctuating local magnetic field induced by the spins in the same molecule in which the nuclei under consideration is located, and $(1/T_1)_{\text{trans}}$ being due to the spins attached to different molecules. Moniz, Steele and Dixon 16 found that in many cases the relaxation theory predicted relaxation times which were shorter than experiments showed they must be. Moniz, Steele and Dixon also observed that the error was most likely in the $(1/T_1)_{\text{rot}}$ term. From calculations due to Bloembergen, Purcell and Pound 17 of identical nuclei with spin $1/2$,

$$\frac{1}{T_{1,\text{trans}}} = \frac{3\pi^2 \gamma^4 h^2 p_n}{2kT}$$

---

where $\rho$ is the number density of the nuclear spins, $\eta$ is the viscosity of the fluid, and

$$\begin{align*}
(14) \quad (1/T_1)_{\text{rot}} &= 3\gamma h^2/4b^2 J_2^m(0) \\
(15) \quad J_2^m(0) &= \zeta/3kT \\
(16) \quad \zeta &= 8\pi a^3 \eta
\end{align*}$$

where $b$ is the distance separating the spins, and $a$ is the molecular radius. Moniz, Steele and Dixon then proposed a new expression for $(1/T_1)_{\text{rot}}$ for spherical molecules.

$$\begin{align*}
(17) \quad (1/T_1)_{\text{rot}}^I &= (3\gamma h^2/4b^2)(\pi I/3kT)^{1/2}
\end{align*}$$

where $I$ is the moment of inertia of the imaginary top involved. This theory proved to fit the results in their experimental work better than that of Bloembergen, Purcell and Pound.
Diffusion of the molecules within a liquid sample can be calculated if the inhomogeneity of the static external magnetic field is known. By creating a field gradient by the use of opposing magnetic coils with their axis parallel to the static magnetic field, the variations of $H_0$ that each molecule experiences throughout its diffusion path can be predicted. The decay curve due to $T_2$ plus diffusion is:

$$V = V_0 \exp\left(\frac{-t}{T_2} + \left(-\gamma^2G^2Dt^3/12n^3\right)\right)$$

where $D$ is the diffusion constant and $G$ is the field gradient. When $n$ is equal to one then equation (10) becomes:

$$V = V_0 \exp\left(\frac{-t}{T_2} + \left(-\gamma^2G^2t^3/12\right)\right)$$

Then

$$\gamma G = 7.664/a\Delta t$$

where $a$ is the diameter of the sample tube and $\Delta t$ is one half of the echo width.

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EXPERIMENTAL APPARATUS

Pulsing Equipment

General description

The overall repetition rate of the pulsing equipment was controlled by a multivibrator whose differentiated output was fed simultaneously to a pulse former and a delay generator (Figure 12). The delay generator's output was then fed to a second pulse former. The rectangular pulses from the pulse formers were then mixed and used to gate a 30 megacycle oscillator, whose output was amplified and used to drive the transmitter coil producing the transverse pulsed alternating magnetic field.

Pulse train generator

The multivibrator consisted of a single 12AU7 whose RC circuits were adjusted so the repetition rate was approximately ten pulses per second (Figure 13). The trigger output pulse then was fed to a Dumont Type 326 Time Delay Generator which had a delay range from zero to ten milliseconds. The two pulse formers were 6DJ8's. The 6DJ8 was used because of its extremely high transconductance. The width of the rectangular pulses could be adjusted by changing the resistance in the plate circuit of one section of the 6DJ8 or by changing the
grid circuit resistance in the other section. The 6DJ8's were followed by 12AU7's which amplified the pulses. One half of a 6DJ8 was used as a mixer. The output pulses were 7 volts in amplitude and could be adjusted in width from zero to 45 microseconds.

In many places in the circuitry, diodes were used to prevent the reflection of the pulses from one stage to another.

**Oscillator**

The 30 megacycle oscillator was patterned after one described by J. Schartz (Figure 14)\(^{19}\), the main difference being that one-half of a 6DJ8 was used to amplify the incoming pulses*.

**Transmitter**

The transmitter consisted of two 6AG7's followed by a single 6146. Each tank circuit could be adjusted by means of a variable capacitor so that each amplifying stage could be tuned for a maximum output (Figure 15). Special care was taken in construction to eliminate undesirable oscillation. Shielding plates were used to separate each stage and the plate circuit of the 6146 was mounted entirely above the chassis thus shielding it from all the grid circuits. It was also found desirable to be

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* Note that in the original article that a capacitor is missing in the 404A plate circuit and the 50 µf capacitor in the first oscillating circuit is incorrectly labeled.

able to adjust the bias and screen voltage of the 6146 for maximum output.

Transmitter probe

The transmitter probe consisted of the necessary LC circuitry and a short piece of coaxial cable which had been stripped of its shielding and braiding and then replaced by a copper pipe which acted in the place of the braid (Figure 16). One end of the transmitter probe was terminated with two loops 3/4 inch in diameter, of number 18 copper wire. The other end of the transmitter probe was terminated with output tank which consisted of a coil 1-1/2 inches long and one inch in diameter constructed from 15 turns of number 10 copper wire, and a tuning capacitor. The two loops of the transmitting probe could be adjusted in distance from the final inductance coil of the 6146 tube in the transmitter, for maximum power output to the transmitter tank. The copper pipe made the probe more rigid and reduced the noise that might result from the probe moving in the static magnetic field. The transmitter coil was wound around the glass tube which extended from the dry ice chamber (Figure 17).

Multiple pulse trigger

In order to produce the sequence of 180° pulses needed for a $T_2$ plot, the delay generator was replaced by a multiple pulse trigger (Figure 18). The requirements placed on this apparatus
is that it must trigger the oscillator so that a $180^\circ$ pulse is produced at a time $\tau$ after the $90^\circ$ pulse and then produce a finite number of $180^\circ$ pulses separated by a time $2\tau$ after that. $2\tau$ for this experiment was approximately two to twenty milliseconds.

The apparatus was triggered by the differentiated pulse from the multivibrator which was first delayed by the Dumont Type 326 Time Delay Generator for $\tau$ milliseconds. The delayed trigger was used to trigger the B time base of a Tektronix Type 545 Oscilloscope. The gate from this time base then activated a ringing oscillating circuit which consisted of the primary of a small transformer and a 2000 pf capacitor. The ringing output of the secondary winding was used to trigger the B time base of a Tektronix Type 535A Oscilloscope. The B gate then was used to trigger the sequence of $180^\circ$ pulses. Thus $\tau$ is determined by the delay generator and the correct LC values were chosen for the transformer and capacitor so that the rest of the $180^\circ$ pulses were separated by $2\tau$.

\begin{equation}
2\tau = 2\pi\sqrt{LC}
\end{equation}

The number of $180^\circ$ pulses that are produced will depend upon how fast the ringing is damped or upon the Q of the tank circuit formed by the transformer and capacitor.
where $X$ is the reactance of the transformer coil and $R$ is the resistance of the tank circuit. A high $Q$ would provide a large number of $180^\circ$ pulses. The triggering level of the B time base on the Tektronix Type 535A Oscilloscope was used to select the number of $180^\circ$ pulses within the range provided for by the ringing trigger.

Observation Equipment

Observation probe

The observation coil was 5 cm long and had a diameter of 0.5 cm. It consisted of 17 turns of number 32 copper wire. The observation coil was supported and connected to the rest of the observation tank circuit by a piece of coaxial cable that had in place of its shielding and braiding a copper pipe (Figure 16). The observation tank circuit then was coupled directly to the receiver with a coupling capacitor.

Receiver

The receiver was a surplus radar IF strip with a broad band pass at 30 megacycles. Receiver saturation was reduced by the use of diodes in the grid circuits. In each grid circuit two diodes were connected in parallel with one diode reversed with respect to the other. The pair then was connected from the grid
to ground. The number of grid circuits in which the diodes were used depended upon the amount of power produced in the observation coil by the flux of the transmitting pulses.

**Oscilloscope**

The A time base of the Tektronix Type 545 Oscilloscope with a Type 53/54L Plug-in Unit was used to observe the signals produced.

**Camera**

A Tektronix C-19 Polaroid Oscilloscope Camera was used to photograph the signals produced on the oscilloscope screen.

**Static Magnetic Field**

**Magnet**

The electro-magnet used to create the static magnetic field had been constructed by using soft iron as a core and thin copper strips as the windings. The flat cylindrical pole faces were 7 inches in diameter and 2 inches apart.

**Direct current power supply**

The magnet power supply was constructed using 220 volt alternating current. It was current regulated giving an output of zero to 20 amperes at zero to 80 volts (Figure 19). 2N174 transistors were used as the regulating transistors and IN249A
diodes as the rectifier diodes. Both the diodes and transistors were mounted on heat sinks which were ventilated by an air blower. A Philbrick chopper stabilized amplifier was used as the operational amplifier in the regulating circuit.

Temperature Variation and Measurement

The air stream from a hair dryer was passed through a wooden chamber and then through a one inch glass tube which directed the air past the experimental sample (Figure 17). By turning the heater in the dryer off and filling the wooden chamber with dry ice, the air blast cooled the sample down to \(-5^\circ\) centigrade. Then by turning the heater on and allowing the dry ice to sublime, a gradual increase in temperature took place. The highest temperature obtained was \(80^\circ\) centigrade.

Frequency Calibration

A National NC-100 Radio Receiver and a BC-221 Signal Generator was used to adjust the frequency of the oscillator.

Magnetic Field Gradient Coils

Two coils mounted on the electro-magnet pole pieces were used to create the magnetic field gradient needed to measure the diffusion constant. These coils were one inch wide, 9 inches outside diameter and 7 inches inside diameter and constructed from number 10 copper wire. Two six volt batteries connected
in series were used as a source of current (Figure 17).
EXPERIMENTAL PROCEDURE

Temperature Dependence of $T_2$

The temperature dependence of $T_2$ was investigated by using the multiple $180^\circ$ pulse method. At various temperatures pictures were taken of the pulse echo signal which was displayed on the oscilloscope screen (Figure 22). $T_2$ for these various temperatures was determined by the evaluation of the slope of a semi-logarithmic plot of the echo decay curve described by the pictures (Figure 24). The values for the temperature and $T_2$ were then used to make a $T_2$ vs. temperature plot (Figure 25).

Determination of $T_2$

$T_2$ was determined in the temperature dependence study and by interpretation of the echo envelope obtained by using the single $180^\circ$ pulse method. At temperatures below $35^\circ$ centigrade it was noted that effects due to diffusion disappeared (Figure 26 and 27). Thus for temperatures below $35^\circ$ centigrade $T_2$ could be determined from the slope of the semi-logarithmic plot of the decay envelope found by using the single $180^\circ$ pulse method. $T_2$ could also be approximated by noting that the diffusion is the dominate factor only when $t$ is large. By constructing a straight line tangent to the semi-logarithmic plot of the decay curve near the echo amplitude axis the measurements can be made.
Determination of $T_1$

$T_1$ was determined by the null method as indicated in the section on the theory of $T_1$ relaxation. Figure 23 shows the tail produced by the $180^\circ$-$90^\circ$ pulse method.

Determination of the Diffusion Constants

The diffusion constants were determined by the method described by Douglass and McCall\textsuperscript{12}, however, $T_2$ in this experiment was determined from the multiple pulse method and approximated from the single $180^\circ$ pulse method instead of using the single $180^\circ$ pulse method directly. (Douglass and McCall used an extremely homogeneous external static magnetic field and then introduced a magnetic field gradient by using a pair of opposing magnetic coils along the axis of the static magnetic field. The static magnetic field used in this experiment was always inhomogeneous.) A plot of the $T_2$ curve at a particular temperature was compared to a diffusion curve at that temperature and then a plot of the logarithm of the ratio of the two decay functions vs. $(2T)^{3}$ was made (Figure 28 and 29). The slope of this curve is equal to $-(\gamma G)^2D/12$.

In order to determine, $D$, the diffusion constant, $\gamma$ the gyromagnetic ratio and $G$ the static magnetic field gradient must be known. $\gamma G$ was determined by the use of equation (19).
Determination of $H_1$

Many times during the experiment it was convenient to know $H_1$. A short piece of coaxial cable terminated with a single loop and connected to the vertical input of a Tektronix Type 545 Oscilloscope with a Type 53/54L Plug-in Unit, allowed the visual observation of the voltage induced in the loop by the changing flux within the sample coil.

\[(22) \quad E = \frac{d\phi}{dt}\]

$E$ being the induced voltage and $\phi$ the flux. Also

\[(23) \quad E = E_0 \cos\omega t\]

where $\omega$ is the angular velocity. Then

\[(24) \quad d\phi = E dt.\]

Substituting equation (23) into equation (24) and integrating through one quarter cycle

\[(25) \quad \phi = \frac{E}{\omega} \sin(1/2)\pi.\]

Also

\[(26) \quad 2H_1 = \phi/A\]

where $A$ is the area of the loop. Then substituting equation (26) into equation (25) for $\phi$
(27) \[ 2H_1 = \left( \frac{E_o}{A\omega} \right) \sin\left( \frac{1}{2} \right) \pi. \]

In this experiment \( \omega = 2 \cdot 30 \cdot 10^6 \) cycles per second and

(28) \[ A = \left( \frac{1}{4} \right) \pi d^2 \]

where \( d \) is the diameter of the loop, then

(29) \[ H_1 = 0.6775 \left( \frac{E_o}{d^2} \right) \text{ Gauss}. \]
CONCLUSIONS

Temperature Dependence of $T_2$

Since paraffin oil is a mixture of hydrocarbons rather than a pure hydrocarbon no definite melting point is observed, instead the oil gradually softens. From $35^0$ to $80^0$ centigrade, which is above the softening range, $T_2$ seems to be temperature independent. However, in the softening range ($-10^0$ to $35^0$ centigrade) $T_2$ gradually increases as the oil makes the transition from a solid to a liquid. Thus between $-10^0$ and $35^0$ centigrade $T_2$ is temperature dependent.

$T_2$ - Spin Relaxation

From Figure 25, $T_2$ seems to be $10^\pm 3$ milliseconds for the temperature range from $35^0$ to $80^0$ centigrade. However, if this value is compared to values obtained for other hydrocarbons this value seems to be much too small. If $T_2$ is calculated from the echo envelope obtained by the single $180^0$ pulse method, $T_2$ seems to be $225^\pm 100$ milliseconds. This value is more resonable and compares favorably with values for $T_2$ obtained for other hydrocarbons\textsuperscript{20}.

The main cause for the discrepancy when using the multiple 180° pulse method was most likely due to the instability of the static magnetic field's power supply.

\[ T_1 - \text{Spin Lattice Relaxation} \]

\[ T_1 \] for this experiment was greater than 2 seconds which was the largest value for \( T_1 \) that could have been measured with the equipment used in this experiment.

**Diffusion**

The diffusion constants did not follow the predicted pattern. Just above the softening range at 39.2° centigrade, the diffusion constant had a value of \( 14 \times 10^{-5} \text{ cm}^2/\text{sec} \). Above the softening temperature the diffusion decreased with increasing temperature. At 69.4° centigrade the diffusion constant had decreased to a value of \( 4.4 \times 10^{-5} \text{ cm}^2/\text{sec} \). Thus the logarithm of the diffusion constant is not directly proportional to the reciprocal temperature of the paraffin oil. This may be due to the fact that paraffin oil is a mixture of hydrocarbons. At higher temperatures it is possible that the hydrocarbon components combine in such a way to produce a more viscous liquid.

**Another Observation**

It was noted that when using the single 180° pulse method that the echoes which immediately followed the 90° pulse in the
sequence decreased in amplitude as the temperature was increased. By extrapolation the echo amplitude at \( t \) equal to zero could be found. This gives the tail amplitude which is directly proportional to the magnetization of the sample at that time. By plotting the tail amplitudes vs. the temperature it was found that the magnitude of the magnetization at \( t = 0 \) was inversely proportional to the temperature, the behavior predicted by Curie's law.

Summary

1. \( T_2 \) for paraffin oil is \( 225 \pm 100 \) milliseconds and is independent of the temperature between 35° and 80° centigrade.

2. \( T_1 \) for paraffin oil is greater than 2 seconds.

3. The coefficient of self-diffusion is not logarithmic in reciprocal temperature.

4. Self-diffusion is highly pronounced.

5. The magnitude of the magnetization produced in paraffin oil by a static magnetic field is inversely proportional to the temperature.
Figure 12.

BLOCK DIAGRAM

Figure 12.
Figure 13. **PULSE TRAIN GENERATOR**
Figure 14. OSCILLATOR

6DJ8

417A

2C51/396A

404A

+200V

1K

20K

100µf

0.1µf

243K

300Ω

100K

20Ω

CARBON

1K

680Ω

100µf

20Ω

100K

5K

12Ω

0.1µf

20µf

56µf

0.002µf OUT

0.01µf

* ADJUSTED EMPIRICALLY TO RESONATE AT 30 MC
† MOUNTED ON INSULATOR
*ADJUSTED EMPIRICALLY
TO RESONATE AT 30 MC
ALL TANK CIRCUITS ADJUSTED EMPIRICALLY TO RESONATE AT 30 MC
MULTIPLE PULSE TRIGGER

Figure 18.

MULTIVIBRATOR

90° PULSE

180° PULSE

DELAY

MIXER

TO OSCILLATOR

545 OSCILLOSCOPE

535A OSCILLOSCOPE

2000 pf

2 K

4700 μuf

A

B

C

D

E

F

G

H

90° 180° 90°
Figure 20. The single $180^\circ$ pulse method. The $90^\circ$ pulse is followed immediately by the tail, $\tau$ seconds later the $180^\circ$ pulse is applied and is followed after $\tau$ seconds by the echo.

Figure 21. The echo for paraffin oil at $30^\circ$ centigrade.
Figure 22. The multiple $180^\circ$ pulse method. The sequence starts with a $90^\circ$ pulse then is followed by many $180^\circ$ pulses with their corresponding echos.

Figure 23. The tail. The top picture shows the $90^\circ$ pulse when the frequency of $H_1$ is off resonance, then when the frequency is on resonance. The middle and bottom pictures show the tail produced by the $180^\circ-90^\circ$ pulse method.
Figure 24. Echo amplitude vs. time. The echo decay curve found by the multiple 180° pulse method for paraffin oil at 41.6° centigrade.
Figure 25. $T_2$ vs. Temperature
Figure 26. Logarithm of the echo amplitude vs. time at 12° centigrade.
Figure 27. Logarithm of the echo amplitude vs. time at 52° centigrade
Figure 28. Logarithm of the echo amplitude vs. time
Figure 29. Logarithm ($V_{\text{max}}/A$) vs. $t^3$
BIBLIOGRAPHY


