Determining Relaxation Times of Mineral Oil using Pulsed Nuclear Magnetic Resonance

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Pulsed Nuclear Magnetic Resonance (NMR) is a spectroscopy technique that study material properties by placing the material in uniform magnetic field and applying pulse bursts of external magnetic fields at certain radio frequency to create resonance with nuclei in the material. We applied this technique in an experiment to investigate properties of mineral oil. Based on NMR theories, we measured the spin-lattice relaxation time of our mineral oil sample to be 31.3 ms ± 0.2 ms and its spin-spin relaxation time to be 20.7 ms ± 0.5 ms.

I. INTRODUCTION

Nuclear magnetic resonance (NMR) was discovered in 1946 by Edward Purcell and Felix Bloch independently. They investigated the behavior of nuclei when they are placed in an external uniform magnetic field and subject to a continuous (cw) radio frequency (RF) magnetic field oriented perpendicular to the external field [1]. The nuclei resonated with the RF magnetic field at certain frequency. This discovery introduced a new kind of spectroscopy that can be used to determine material properties, especially for liquid [2]. This spectroscopy has been extensively used in the field of physics, chemistry, biology, and geology.

In 1950, instead of applying continuous RF fields indefinitely to the sample, Erwin Hahn applied pulse bursts of these same RF magnetic field and investigated its effects on the nuclei [3]. He discovered a new form of signal, called spin echo signal, from the magnetic nuclei after applying a two-pulse sequence. His discovery and analysis on the spin echo signal introduced a new technique for analyzing NMR, and eventually led to the popularity of pulsed NMR technique, which we used in this experiment.

NMR spectroscopy also made significant contribution to the medical field. The most notable example is the Magnetic Resonance Imaging (MRI) technique [4]. This technique can non-invasively provide detailed three-dimensional images within living organisms and reveal their inner mechanisms. To a certain extent, MRI has the potential to revolutionize the radiology since it avoids the injection of radioactive isotopes for scanning.

This paper discusses an experiment in which we used the technique of pulsed NMR to investigate properties of mineral oil. In specific, we investigated two kinds of relaxation time of mineral oil, one is the spin-lattice relaxation time, \( T_1 \), and the other is the spin-spin relaxation time, \( T_2 \).

II. THEORY

Magnetic resonance can be observed in systems that have both a magnetic moment and an angular momentum. This is the characteristic of most stable nuclei of ordinary matter. In our experiment, we only concerned about nucleus of hydrogen, which is a single proton. The magnetic moment, \( \mu \), of a proton is related to its angular momentum (spin) \( S \) by

\[ \mu = \gamma S \]

where \( \gamma \) is the gyromagnetic ratio. For proton [5],

\[ \gamma = 2.675 \times 10^4 \text{ rad/(s \cdot gauss)} \]

When placed in an external uniform magnetic field, \( B \), a proton processes at the Larmor frequency,

\[ \omega_L = \gamma B, \]

This associates with a potential energy of

\[ U = - \mathbf{\mu} \cdot \mathbf{B} = - \mu_z B = - \gamma S_z B \]

if the magnetic field \( B \) is pointing in the \( z \)-direction. Since

\[ S_z = \pm \frac{\hbar}{2} \]

for proton and \( \hbar \) is the reduced Planck constant, the energy difference of the two states is

\[ \Delta U = \gamma hB. \]

This corresponds to a resonant frequency of

\[ \omega_0 = \frac{\Delta U}{\hbar} = \gamma B. \]

In our experiment, this resonant frequency would be the frequency of the RF magnetic field that we tuned to, and it was closed to 15 MHz for mineral oil.

When the sample material, which has zero net magnetization initially, is placed in an external magnetic field in the \( z \)-direction, the protons, which have magnetic moments, tend to orient themselves toward the \( z \)-direction. Over time, an equilibrium with a net magnetization \( M_1 \) in the \( z \)-direction will be established in the sample. During this process, the sample net magnetization in the \( z \)-direction as a function of time is described by the equation.

\[ M_z(t) = M_1 + (M_0 - M_1) e^{-t/T_1} \tag{1} \]

where \( M_0 \) is the initial net magnetization and the time constant \( T_1 \) is called spin-lattice relaxation time [3]. This relaxation time varies for different materials.

In our experiment, we were able to manipulate the nuclei orientation by generating an RF magnetic field in the \( x \)-direction. We generated them in pulse sequences. Each pulse lasts for a certain time interval, ranging from 1 to 36 \( \mu s \), which can be controlled and is called the pulse width, denoted by \( t_\mu \). Since these pulses consist of sinusoidal magnetic fields that oscillate in resonance with the nuclei, we were able to rotate their orientations by a certain angle,
depending on the pulse width. For example, as illustrated in Figure 1, if the net magnetization is initially in the z-direction, a RF pulse with width $t_W = t_{90}$, a 90° pulse, can rotate the magnetization in to the x-y plane and create a temporary non-zero $M_x$ and $M_y$ [2]. A RF pulse with width $t_{180} = 2 \cdot t_{90}$, called a 180° pulse, can rotate each nuclear to its opposite direction [3]. These manipulations are important due to two reasons. First, since our detector can only measure the net magnetization in the y-direction, $M_y$, it is necessary to do the rotation when we want to measure $M_z$. Second, these rotations create conditions that allow measurements of relaxation times, as detailed below.

To measure $T_1$, we first let the sample establish thermal equilibrium with net magnetization $\vec{M} = M_1 \vec{z}$ when placed in a uniform magnetic field in the z-direction. Then, a 180° pulse is applied and rotate the sample magnetization to be $\vec{M} = -M_1 \vec{z}$. The sample starts to reestablish its equilibrium in z-direction as described by Equation (1). After a certain time, a 90° pulse is applied to rotate the magnetization from z-direction into x-y plane some that the magnetization in y-direction can be picked up by the detector. If we take the measurement of $M_x$ immediately after the second pulse is applied, it should equal the absolute magnitude of $M_z$ before the second pulse. Thus, according to Equation (1), $M_x$ as a function of the time interval between the two pulses, $\tau$, called the delay time, is:

$$M_x(\tau) = M_y(1 - 2 e^{-\tau/T_1})$$

and its absolute value equals $M_y$ as measured by our detector.

When a net magnetization in the x-y plane is established, it does not last forever and decays exponentially:

$$M_x(t) = M_0 e^{-t/T_2}$$
$$M_y(t) = M_0 e^{-t/T_2}$$

where $M_0$ are the initial magnetization and the characteristic decay time $T_2$ is called spin-spin relaxation time. The decay of $M_y$ produces signal called free induction decay (FID). Measuring $T_2$ through FID is possible but inconvenient. Instead we used the spin echo signals.

A spin echo signal is produced by first applying a 90° pulse to a sample in equilibrium and then after a delay time $\tau$ applying a 180° pulse. The effect of this pulse sequence on the spin orientation is illustrated in Figure 1. This pulse sequence generates a spin echo signal which reaches its maximum at 2$\tau$ after the first pulse is sent out, as shown in Figure 2 [6]. The maximum height of spin echo signal as a function of $\tau$ is [3]:

$$M_{x,y}(\tau) = M_0 e^{-2\tau/T_2}.$$  

We base on this to determine $T_2$.

**III. APPARATUS**

We used a TeachSpin’s PS1-A Pulsed Nuclear Magnetic Spectrometer, which generates programmable RF magnetic field pulses in the x-direction, uses a set of permanent magnets to generate uniform magnetic field in the z-direction, and includes a receiver coil that detects sample net magnetization in the y-direction [3].

We used a TDS 1012B Two Channel Digital Storage Oscilloscope to monitor the signals and used its cursors to take measurements [7].

We used CVS mineral oil (lubricant laxative) for our sample and used a plastic vial to contain the sample.

We also used a Walker Scientific MG-5D Gaussmeter to measure the magnetic field of the permanent magnets [8].

**IV. EXPERIMENTAL PROCEDURE**

My collaborator first carefully cleaned up a plastic vial and ensured that it was dry before we placed sample in it. Then we injected about 0.5 mL of mineral oil into the vial, sealed it, and properly labeled it.
Then, we measured the extent to which the magnetic field produced by the permanent magnets is uniform using the gaussmeter. Due to time limit, we chose to rely on measurements by our predecessors and verified their results at several points. Then we chose a position around which the magnetic field is uniform and placed our sample there.

Then we set up the apparatus as shown in Figure 3. We used the oscilloscope to monitor signals in two channels. Channel 1 received signals from the detector, and the signal heights, measured in volts, are linearly proportional to the absolute value of the sample net magnetization in y-direction. Channel 2 received signals from the mixer.

We first adjusted the frequency of the RF magnetic field to achieve resonance with the nuclei. This was achieved by monitoring Channel 2 and ensuring that the mixer output signal did not oscillate like a sinusoidal wave, or in other words, it showed no beats. We recorded down a range of this tuning frequency and left it in resonance.

Since we were going to repeatedly generate sequences of RF pulses, we need to ensure that the sample net magnetization had returned to thermal equilibrium state before each pulse sequence started. Conventionally this pulse sequence repetition time needs to be at least 10 times longer than the sample’s $T_1$. We eventually set a repetition time to be $490 \pm 10$ ms.

We first performed measurements for $T_1$ by generating a $180^\circ$ pulse followed by a $90^\circ$ pulse. This was done by adjusting the pulse width so that, on Channel 1, the first signal pulse height was minimized and the second pulse height was maximized. Then we changed the delay time between these two pulses, $\tau$. We used the oscilloscope cursors to measure and record the height of the second pulse signal in Channel 1 at different values of $\tau$, ranging from 1 ms to 300 ms. These data contain information on $T_1$.

Here, it is worth noting that the signals displayed on the oscilloscope was subject to random fluctuations in addition to fluctuation caused by the RF pulses. These random fluctuations introduced some difficulties for us when we tried to determine where the pulse peak was, especially when the pulse height was closed to 0 and random fluctuations dominated. After some debates, we settled down on a set of measurement criteria that stayed consistent when we took measurements for different pulse height in the presence of random fluctuations. The criteria are stated as follow: given a certain $\tau$, we determined that the signal pulse peak occurred at a voltage level such that roughly half of the time the maximum of the fluctuating signal exceeded this level and the other half the time it didn’t. Under this set of criteria, the error bars on our measurements corresponded to statistical uncertainties in determining the average pulse height due to random fluctuations.

After this, we started measuring $T_2$ by generating a different pulse sequence. To produce a $90^\circ$ pulse followed by a $180^\circ$ pulse, we adjusted the pulse width so that, on Channel 1, the first signal pulse height was maximized and the second pulse height was minimized, as shown in Figure 2. When this was done properly, we observed a spin echo signal at $t = 2\tau$ as expected. We took measurements for this spin echo signal height for different values of $\tau$, ranging from 1 ms to 50 ms, in a similar way as we did for $T_1$ using the same pulse height measurement criteria.

V. DATA ANALYSIS

We processed and analyzed the data using CERN ROOT. We first analyzed data for $T_1$. When we took this set of data, the resonant RF magnetic field was:

$$v_0 = \frac{\omega_0}{2\pi} = 14.980 \pm 0.002 \text{ MHz}$$

Figure 4 (a) shows the recorded signal pulse heights plotted against delay time $\tau$. The recorded pulse heights are measurements of the absolute values of $M_y$, which equals $M_2$ before the $90^\circ$ pulses. According to Equation (2), as $\tau$ increases from 0, $M_2$ starts out as a negative value and gradually increases. Theoretically, $M_2$ passes 0 and becomes positive at a certain point of $\tau$. At this point, the absolute value of $M_2$ drops to 0 and bounces back. According to our experimental data in Figure 4 (a), we determined that this point of $\tau$ occurred between 21 ms and 22 ms. Thus, we processed the original signal data by multiplying the pulse height voltage by $-1$ for measurements with $\tau < 22$ ms. Then, we performed a least-square best fit to the processed data using the following fitting equation, which is in the same form as Equation (2):

$$V(\tau) = V_0(1 - 2 e^{-\tau/T_1})$$

and the fitting results are shown in Figure 4 (b). According to the fitting, the spin-lattice relaxation time is measured to be

$$T_1 = 31.3 \pm 0.2 \text{ ms}$$

with a corresponding Chi-square of

$$\chi^2 = 122.1 \text{ for } ndf = 48 \pm 9.8$$

in which $ndf$ denotes “number of degrees of freedom”. The error bars in the measurement represent statistical errors.

There are rooms for improvement for this fitting because equation (2) does not fully explain the data we observed. First, our measured pulse heights in Figure 4 (a) does not go
to 0 or cover 0 at $\tau$ near 21 ms and 22 ms, which deviates from the prediction of Equation (2). This discrepancy between experimental data and theory may be a result of the measurement criteria we set, or it may due to reasons unknown to us as researchers. Second, the ratio of $\chi^2/ndf$ is larger than 2 in the fit, indicating that either we underestimated our errors or we used an improper fitting equation. According to the fitting pattern in Figure 4 (b), the latter is more likely. Thus, we used another equation to fit the data, which introduces three more parameters:

$$V(\tau) = -V_1 e^{-\tau/T_1.1} - V_2 e^{-\tau/T_1.2} + V_3$$

and the fitting results are shown in Figure 4 (c) with an improved Chi-square of

$$\chi^2 = 82.2 \text{ for } ndf = 45 \pm 9.5.$$  

This represents a model that better explains the data, but as researchers we admit our incapability of explaining the physical implications behind this fitting equation.

We then analyzed data for $T_2$. The resonant RF magnetic field frequency for this set of data was:

$$v_0 = \frac{\omega_0}{2\pi} = 14.967 \pm 0.002 \text{ MHz}$$

Figure 5 (a) shows the recorded pulse heights plotted against delay time $\tau$. The recorded pulse heights are measurements of the peak height of spin echo signal. The data are least-square fitted with the following equation:

$$V(\tau) = V_1 e^{-2\tau/T_2} + V_2,$$

which is similar to Equation (3) but introduces an additional constant parameter to account for background signals and potential effects of our choice of measurement criteria. According to the fitting results in Figure 5 (a), the spin-spin relaxation time is measured to be

$$T_2 = 20.7 \pm 0.5 \text{ ms}$$

with a corresponding Chi-square of

$$\chi^2 = 75.9 \text{ for } ndf = 29 \pm 7.6.$$  

The error bars in the measurement represent statistical errors.

In this fit, the ratio of $\chi^2/ndf$ is also larger than 2, indicating that either we have underestimated our errors or we used an improper fitting equation. Again, according to the fitting pattern in Figure 5 (a), the latter is more likely. Thus, we used another equation to fit the data:

$$V(\tau) = V_1 e^{-2\tau/T_2.1} + V_2 e^{2\tau/T_2.2} + V_3$$

and the fitting results are shown in Figure 5 (b) with an Chi-square of

$$\chi^2 = 1.3 \text{ for } ndf = 27 \pm 7.3.$$  

This ratio of $\chi^2/ndf$ is much less than 1, indicating that we have a model that fits the data too well and we have overestimated the statistical errors of our measurements. Besides, although the equation greatly explains the data, we again cannot explain the physical implications behind it.

There are several systematic errors that potentially affect our measurements. One of them is the fluctuation of room temperature in our laboratory, which may affect our sample property. Another systematic error might occur when we produced a 90° or 180° pulse by either minimizing or maximizing the pulse heights shown on oscilloscope. Since we performed this step by eyeballing them, we might not produce pulses that exactly had the width of 90° or 180°, and this uncertainty in the pulse width introduced systematic errors. Other systematic errors include the fluctuation of the resonant frequency over time, the non-uniformity of the magnetic field of the permanent magnets, and many systematic errors related to taking measurements on an oscilloscope.

We tested the effect of the systematic error introduced by the presence of Earth’s magnetic field. When we horizontally rotated our apparatus, including the sample and the permanent magnets, into different directions, we
observed that the resonant RF frequency fluctuated by 0.0015 MHz. We performed a quick run of data acquisition for $T_2$, but we observed no significant changes in the decay characteristic time due to this fluctuation in resonant frequency. Thus, the magnitude of this systematic error is estimated to be smaller than our statistical errors.

VI. CONCLUSION

By applying pulsed NMR spectroscopy technique, we were able to investigate the relaxation times of a mineral oil sample. After least-square fitting the data with equations based on pulsed NMR theories, we measured the spin-lattice relaxation time to be $T_1 = 31.3 \pm 0.2$ ms and measured the spin-spin relaxation time to be $T_2 = 20.7 \pm 0.5$ ms. There exists room for improvements for our fitting equations.

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FIG. 5. Plots of signal pulse heights (in Volts) against delay time $\tau$ (in ms) for measuring $T_2$. Data in (a) and (b) are fitted with different equations.