Pulsed Nuclear Magnetic Resonance for measuring T_1 and T_2 for light mineral oil

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The spin-lattice (T_1) and spin-spin (T_2) relaxation times were measured for a sample of light mineral oil using pulsed nuclear magnetic resonance (NMR). T_1 was measured by tipping the net magnetization of the sample by 180° so that it aligns with the -z direction and then measuring the magnetization along the z-axis (M_z) as a function of time. M_z was measured through the maximum free induction decay (FID) signal of the sample. T_2 was measured with the spin-echo technique in three different ways: manually varying the time delay between the spin-echo two pulse sequence, the Carr-Purcell method, and the Meiboom-Gill method. We obtained $T_1 = (54 \pm 5)$ ms for the spin-latttice relaxation time of a light mineral oil sample. We also obtained $T_2 = (95 \pm 2)$ ms for the manual method, $T_2 = (117 \pm 2)$ ms for the Carr-Purcell method, and $T_2 = (108 \pm 5)$ ms for the Meiboom-Gill method.

I. INTRODUCTION

Nuclear Magnetic Resonance (NMR) is a technique used to characterize materials using magnetic fields. The nuclei of the sample is placed in a static magnetic field and is perturbed by a time varying RF magnetic field, which leads to a magnetic RF response signal which can characterize the nucleus. NMR has grown useful in chemistry and physics due to the ability to probe local magnetic fields around nuclei. NMR relies on the non zero spin of nuclei, so this experiment focuses on measuring hydrogen nuclei (spin $\frac{1}{2}$).

Pulse NMR involves sending the RF magnetic field out in pulses. Depending on the pulse characteristics and time delays, transient effects can be observed. One of these is the spin-echo effect, which is a signal that occurs after sending a two pulse sequence. The spin-echo effect allows for the measurement of the spin-spin relaxation time (T_2).

The two-pulse sequence utilizes a 90° pulse followed by a 180° pulse. The 90° pulse changes the magnetization of the sample by 90° while the 180° pulse changes the magnetization by 180°. The time delay between these pulses is varied and the maximum voltage of the response pulse is recorded. The response pulse is due to the changing magnetization of the sample and is measured as the EMF through pickup coils. We record the maximum voltage of the EMF signal since this gives the outline of the exponential decay used to characterize T_2.

The Carr-Purcell method is later used since it automates the above process of manually recording the results of two-pulse sequences with varying time delays. This method involves sending one 90° pulse followed by N 180° pulses.

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If the delay between the 90° pulse is τ, then the delay between the consecutive 180° pulses is 2τ for the Carr-Purcell method. In this experiment we choose $N = 25$, since we found that gives enough resolution. Finally, the Meiboom-Gill method is used since it allows for compensation for slight errors in the pulses. For example, if each 180° pulse had an error and instead was a 182° pulse, this would lead to an accumulation of errors after N pulses. However, the Meiboom-Gill method corrects for this by adding a 90° phase delay between the 90° pulse and 180° pulses, which prevents accumulated error. The pulse sequence is the same as the Carr-Purcell method.

T_1 is measured by sending a 180° pulse and measuring the magnetization along the direction parallel to the magnetic field produced by the permanent magnet (z-axis). However, the pickup coils in this experiment can only read signals and magnetization in the x-y plane (perpendicular to permanent magnet axis). So after the 180° pulse, we send a 90° pulse after a time delay to obtain the magnetization in the x-y plane (M_{xy}) corresponding to the magnetization that was along the z-axis (M_z). Similar to the above T_2 measurement, the magnetization is measured as the peak voltage of the response EMF signal from Faraday's Law: $\varepsilon = -\frac{d\phi}{dt}$.

Both T_1 and T_2 are important quantities to measure since they characterize different materials and in this experiment is related to the hydrogen density. This applicable in the medical field where NMR is used to obtain density measurements of tissue and bone samples [1].

II. THEORY

A. Nuclear Magnetic Resonance (NMR)

NMR utilizes two magnetic fields: a static magnetic field (B_0) and a time varying RF field transverse to the permanent magnet. If B_0 is along the z-axis, then the RF field is along the y-axis (See Fig. 1 for the experimental setup). The sample is placed in between the poles of the permanent magnet and inside the coil producing the RF field. At equilibrium, when there is no RF field applied, the sample has a magnetization of M_0 along the z-axis, parallel to B_0. The RF field pushes the sample out of equilibrium so that the magnetization lies in the x-y plane. To get a magnetic RF response signal that can be read as the EMF in the pickup coils, the frequency of the RF driving field must be equal to the Larmor frequency, ω_L

$$\hbar\omega_L = \mu B \tag{1}$$

where $\hbar$ is the reduced Planck's constant, μ is the proton magnetic moment, and B is the applied magnetic field.

Pulse NMR applies the driving RF field in pulses rather as a continuous field. With the right pulse occurring for a set duration, the magnetization can be driven into different states. For example, a 90° pulse will rotate the initial magnetization in the z-axis to the x-axis. The 180° pulse will make the magnetization in the -z direction. Pulse NMR becomes powerful when combining pulses, which we use to measure both T_1 and T_2.

B. Spin-Spin Relaxation Time (T_1)

The Spin-Spin Relaxation Time (T_1) is also known as the longitudinal relaxation time, since it measures the relaxation time of the magnetization of the sample along the longitudinal axis, where the longitudinal axis is the axis along magnetic field of the permanent magnet. In this experiment, the longitudinal axis was labeled as the z-axis. After the sample was moved out of equilibrium, the relaxation time gave a measure of how fast the sample reaches equilibrium. In this experiment, a static magnetic field allowed the sample magnetization to align with the z-axis (See Figure 1 for the experimental setup). The RF driving magnetic field was used to perturb the sample so that the magnetization was out of equilibrium. Then by measuring how fast the sample's magnetization returns back, we can get the relaxation time. The magnetization in the z-axis, M_z, is known to follow the following differential equation:

$$\frac{dM_z(t)}{dt} = \frac{M_0 - M_z}{T_1} \tag{2}$$

where M_0 is the initial magnetization, which in this experiment is along the z-axis.

If we set $M_z(t = 0) = 0$, we find the M_z grows exponentially:

$$M_z(t) = M_0 \left(1 - e^{-\frac{t}{T_1}}\right) \tag{3}$$

M_z would be zero when the magnetization is solely in the x-y plane. We use Eq. (3) to obtain T_1 by fitting the equation to measurements of $M_z(t)$ after a 180° pulse.

C. Spin-Lattice Relaxation Time (T_2)

The Spin-Spin Relaxation Time (T_2) is also known as the transverse relaxation time, since it measures the relaxation time of the magnetization of the sample perpendicular to the longitudinal axis, where the longitudinal axis is the axis along magnetic field of the permanent magnet.

To measure T_2 we used the spin-echo technique described in Section I. A 90° pulse was used to move the magnetization out of equilibrium into the x-y plane (M_{xy}). Since the magnetization was in the x-y plane, it started precessing at the Larmor frequency. M_{xy} decayed after this pulse due to random local fluctuations in the frequency of the nuclei. This lead to a loss of phase between the nuclei. This decay due to the random local fluctuations was what T_2 measures. However, there is another source of dephasing that can lead to inaccurate T_2 results. There are minor differences in the chemical environment (e.g. due to impurities), which can lead to different resonance frequencies for the different nuceli, leading to dephasing sooner than what the local T_2 fluctuations would lead to. The dephasing due to the different nuclei uses the T_2^* relaxation time as a measure of the decay in M_{xy}. Thus T_2^* is always less than T_2. In order to measure the true T_2 instead of T_2^*, the spin echo technique was used. After the initial 90° pulse, a 180°

pulse was sent after a delay of τ. This lead to the magnetization of the nuclei precessing in the opposite direction. Eventually, τ after the 180° pulse, the magnetization vectors of all the nuclei returned to being in phase like it was right after the 90° pulse. With the nuclei in phase, a magnetic signal was produced by the nuclei, which is called the "echo." The echo occured 2τ after the initial 90° pulse. The peak of the echo corresponds to the M_{xy} after a time of 2τ. The M_{xy} at the echo pulse will be less the initial $M_{xy}(t = 0)$ due to the local random fluctuations that T_2 describes. Thus by taking various measurements of M_{xy} via the echo pulse at different τ, we found the T_2 relaxation time. After the 180° pulse, the magnetization vectors started dephasing again due to the T_2^* fluctuations. The signal due to this dephasing is called the Free Induction Decay (FID) signal.

The magnetization in the x-y plane (M_{xy}) follows [1]

$$M_{xy}(\tau) = M_{xy}(0)e^{-2\tau/T_2} \tag{4}$$

where τ is the delay between the 90° pulse and 180° pulse.

Both the Carr-Purcell and Meiboom-Gil methods use the 90° pulse and 180° pulse with a τ time delay, but also send 180° pulses with a delay of 2τ in between. These 180° pulses cause the nuceli to rephase after 2τ, leading to more data points of M_{xy}, which can be used to find T_2.

III. EXPERIMENTAL METHOD

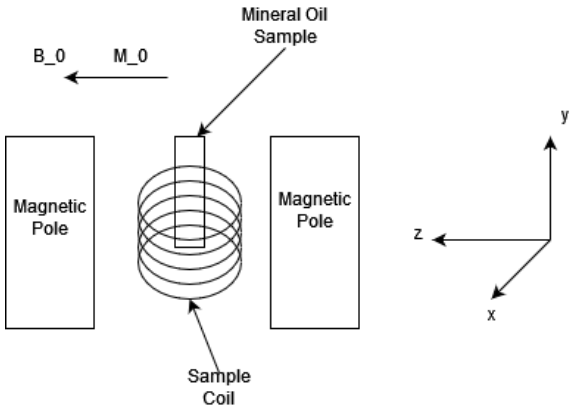

FIG. 1: Setup of apparatus. The magnetic poles of the permanent magnet create a static field while the sample coil is used to create an RF field. The sample coil also acts as a pickup coil to measure the signal coming from the nuclei.

The setup of the experiment is shown in Fig. 1. To produce an NMR signal, a static permanent magnet was used to align the sample magnetization in a state of equilibrium. Then a time varying field was applied to the sample perpendicular to the static field. This lead to a magnetic signal produced by the sample nuclei. This signal was measured as the EMF produced in a coil due to Faraday's Law.

The magnetic poles are from a permanent magnet that produces a field in the z-direction. This static permanent magnetic field produced a field, B_0, and aligned the sample magnetization, M_0 in the z-direction. The sample coil was

used to produce the RF driving field in the y-direction. It was also used as a pickup coil to read the signal produced by the nuclei of the sample.

A. Pulse Programmer

The pulse programmer allows for setting pulse duration, pulse delay time, and pulse number for the RF driving pulses. The programmer can create two different pulse *types*, denoted by **A** and **B**. The programmer chains together a series of pulses into a *sequence*. A sequence can have only one **A** pulse, but up to 100 **B** pulses are allowed. N_B denotes the number of **B** pulses in a sequence. A sequence always starts with an **A** pulse and can have anywhere from 0 to 100 **B** pulses. A_{len} and B_{len} give the individual length of the **A** pulse and **B** pulse, respectively. τ is the delay between the **A** and **B** pulses. The programmer sets the delay between consecutive B pulses to 2τ. P is the period or duration of the entire sequence. P must be greater than the sum of all the pulse durations and delays. Finally, the RF frequency of the pulses can be set to a fixed frequency. We set this value to match closely with the Larmor frequency of the sample's hydrogen nuclei. Each sequence is repeatedly sent to the sample coil by the pulse programmer with period of P.

B. Calibration

The RF driving frequency of the RF pulses must be tuned to match the Larmor frequency of the hydrogen nuclei. The Larmor frequency depends on the applied magnetic field as seen in Eq. (1). The NMR spectrometer manufacturer lists an approximate Larmor frequency that comes from the permanent magnet and hydrogen magnetic moment. However, the true RF driving frequency will differ due to the weak RF driving magnetic field, which will add to the applied magnetic field. The Larmor/precession and RF driving frequencies must also match the pickup coil resonant frequency. In order for the pickup coil to measure the signal coming from the nuclei correctly, the pickup coil must be tuned via tuning capacitors.

To start the calibration of the pickup coil, an RF probe was placed in place of the mineral oil sample inside the sample/pickup coil. A pulse with $A_{len} = 2.5$ μs, $N_B = 0$, and $P = 100$ ms was produced. The RF probe was used to measure this pulse. We maximized the pulse amplitude close to 40 V using the tuning capacitors in order to get the best signal.

Then we replaced the RF probe with a sample of light mineral oil with the same settings as the pickup probe. The frequency of the response signal coming from the precession of the sample nuclei is denoted as ω_{spins}. We multiplied this ω_{spins} signal (also called the FID signal) with the RF pulse signal to get a signal called **I**:

$$I = \sin(\omega_{\text{ref}}\, t) \cdot \sin(\omega_{\text{spins}}\, t) = \frac{1}{2}\cos(\omega_{\text{ref}} - \omega_{\text{spins}})\, t - \frac{1}{2}\cos(\omega_{\text{ref}} + \omega_{\text{spins}})\, t \tag{5}$$

where ω_{ref} is the frequency of the reference signal from the RF pulse.

The **I** signal is used to find beat frequencies to tune the RF magnetic driving frequency so that the pickup coil resonant frequency matches the RF magnetic driving frequency. In Eq. (5), we see that the **I** signal is made up of the $\omega_{\text{spins}} + \omega\text{ref}$ signal and the $\omega_{\text{spins}} - \omega\text{ref}$ signal. The $\omega_{\text{spins}} + \omega\text{ref}$ signal is filtered out since it has a high frequency of around 40 MHz while the $\omega_{\text{spins}} - \omega\text{ref}$ signal is displayed as a signal with a beat frequency.

The RF driving frequency was first set to the approximate Larmor frequency given by the manufacturer and then tuned so that the beat frequencies in the **I** signal were gone. We found this to be between $f = 21.47022$ and $f = 21.47052$ MHz.

C. T1 Measurement

As described in Section II and I, T_1 was measured using a pulse sequence consisting of a 180° pulse followed by a 90° pulse. The delay, τ, was varied and the corresponding maximum spin signal FID voltage was recorded.

In order to find the right pulse length A_{len} and B_{len} for the 180° and 90° pulse, respectively, we set $N_B = 0$ and $P = 100$ ms with only the **A** pulse in the sequence. We increased A_{len} until we saw a maximum in peak of the FID signal. This corresponded to a 90° pulse since the pickup coil and FID signal measure the magnetization in the x-y plane. The maximum magnetization in the x-y plane is achieved when magnetization is completely perpendicular to the z-axis. Next we increased A_{len} until we found a minimum in the signal. This corresponded to a 180° pulse, since there is no component of the magnetization in the x-y plane.

We found that the length of the RF driving pulse for the 90° pulse was 3.24 μs and 6.40 μs for the 180° pulse. We then set the pulse sequence for measuring T_1 by setting the first pulse for 180° and the second pulse for 90°. The settings for this are shown in Table I.

D. T2 Measurement

Similar to the T_1 measurement, we first found the pulse lengths for the 90° pulse and 180° pulse. We made these measurements on a different day from the T_1 measurements, which may impact the resonant frequency, f, as well due to changes in magnetic field. The permanent magnet may change due to slight variations in temperature. Thus the pulse lengths were remeasured as well. For the manual method of measuring T_2, we created a pulse sequence with the first pulse being the 90° pulse and the second being the 180° pulse. We varied the delay between these pulses, τ, and measured the corresponding maximum FID voltage as proxy for M_{xy}. The pulse programmer settings for this are in Table I.

For the Carr-Purcell and Meiboom-Gill methods, the settings were similar to the manual method we used a total of 25 **B** pulses after the **A** pulse. The period was also reduced to 1.0 ms since the measurements for light mineral oil did not work well for long periods. The parameters for these are in Table I.

TABLE I: Pulse and NMR spectrometer settings for T_1 and T_2 measurements

	A_{len} (μs)	B_{len} (μs)	P (ms)	N_B	F (MHz)
T_1	6.40	3.24	300.0	1	21.47022
T_2 Manual	4.04	7.64	320.0	1	21.47052
T_2 Carr-Purcell	4.04	7.64	1.0	25	21.47052
T_2 Meiboom-Gill	4.04	7.64	1.0	25	21.47052

IV. RESULTS AND ANALYSIS

A. T1 Measurement

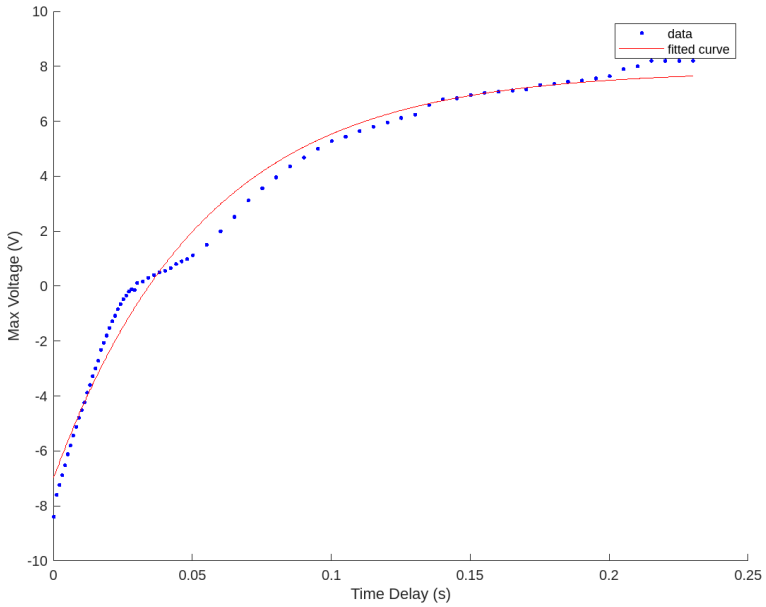

FIG. 2: Maximum FID voltage vs. time delay for the T_1 experiment. Fit parameters are found in Table II.

TABLE II: Fit parameters found for the T_1 experiment. The model follows the form of $a(1-\exp(-(x-b)/c))$ where a, b, and c are fit parameters determined by Matlab's fit function. The uncertainty in fit parameter indicates the 95% confidence interval.

a	b	c
7.9 ± 0.4	0.0344 ± 0.0014	0.054 ± 0.005

In Fig. 2 we plotted the adjusted maximum FID voltage as a function of the time delay (τ). Since the maximum FID voltage just gives the magnitude of M_z, we negated the values before $M_z = 0$ since we know that M_z is in the opposite direction of what it is after it reaches equilibrium.

Table II gives the fit parameters for the curve in Fig. 2 fitted using Matlab's fit function. From Eq.(3), we find that

$$c = T_1 = (54 \pm 5) \text{ ms} \tag{6}$$

.

A significant amount of uncertainty comes from the measurement of FID and thus M_z at $\tau = 0$. In theory, $M_z(t = 0) = 0$, but in our experiment, we measured a non zero FID voltage of 2 V. Thus we subtracted the maximum FID voltage by this floor to get the curve to fit. This still leads some uncertainty around $\tau = 0$ in Fig. 2.

B. T2 Measurement

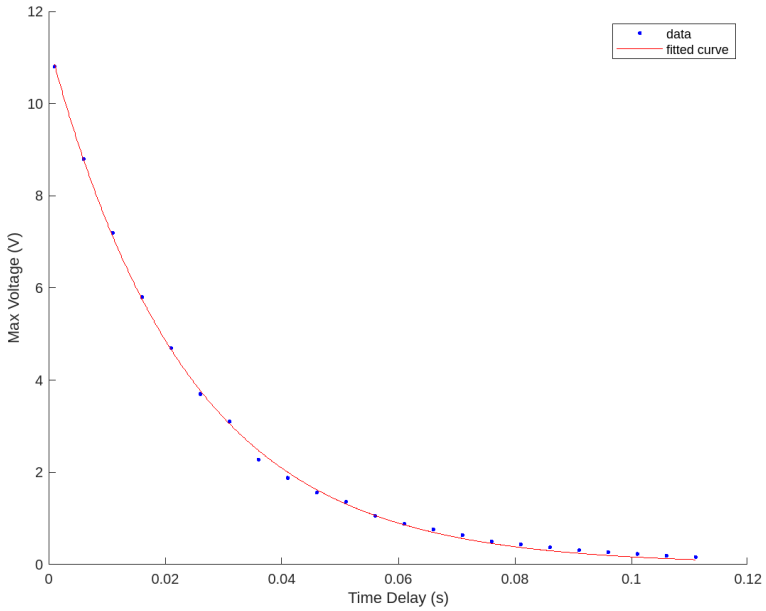

FIG. 3: Maximum FID voltage vs. time delay for the manual two-pulse spin echo experiment. Fit parameters are found in Table III.

TABLE III: Fit parameters found for the manual two-pusle T_2 experiment. The model follows the form of $a\exp(-2x/b)$ where a and b are fit parameters determined by Matlab's fit function. The uncertainty in fit parameter indicates the 95% confidence interval.

a	b
11.31 ± 0.13	0.095 ± 0.002

TABLE IV: Fit parameters found for the T_2 Carr-Purcell experiment. The model follows the form of $a\exp(-2x/b)$ where a and b are fit parameters determined by Matlab's fit function. The uncertainty in fit parameter indicates the 95% confidence interval.

a	b
$(1.3 \pm 0.4) \times 10^5$	0.117 ± 0.004

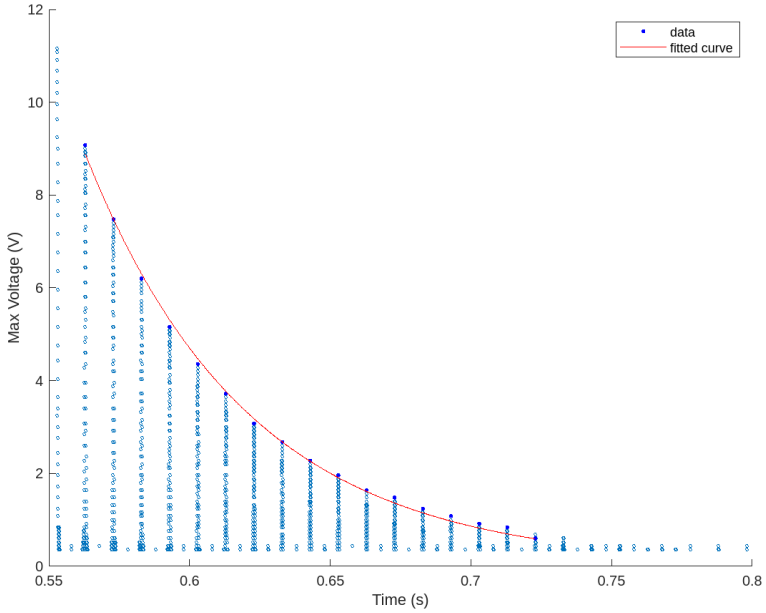

FIG. 4: Maximum voltage vs. time delay for the Carr-Purcell spin echo experiment. Fit parameters are found in Table IV.

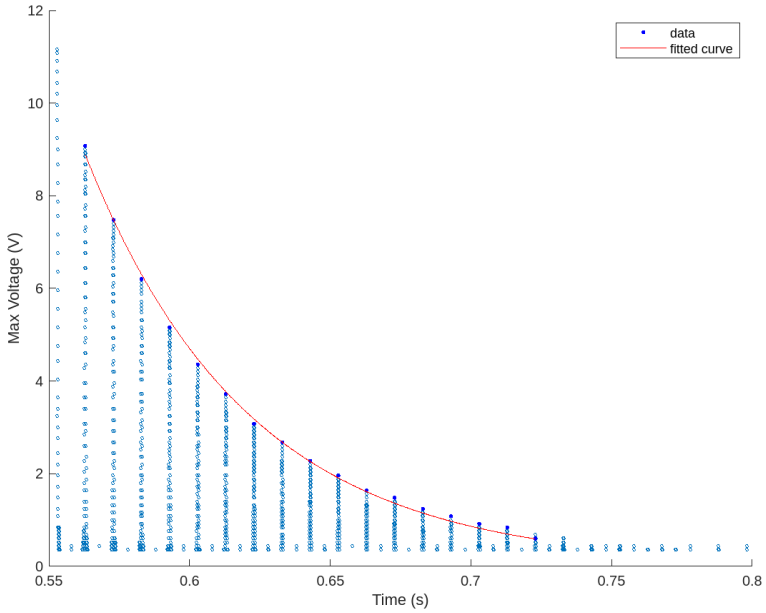

FIG. 5: Maximum voltage vs. time delay for the Meiboom-Gill spin echo experiment. Fit parameters are found in Table V.

TABLE V: Fit parameters found for the T_2 Meiboom-Gill experiment. The model follows the form of $a(\exp(-2x/b)+c)$ where a, b, and c are fit parameters determined by Matlab's fit function. The uncertainty in fit parameter indicates the 95% confidence interval.

a	b	c
1900 ± 800	0.108 ± 0.005	$(1.8 \pm 0.5) \times 10^{-4}$

Figures 3, 4, and 5 give the plot of the peak FID voltage vs. time for the manual, Carr-Purcell, and Meiboom-Gill methods of finding T_2, respectively. Similarly, Tables III, IV, and V give the fit parameters using Matlab's fit function for the data shown in the figures for the manual, Carr-Purcell, and Meiboom-Gill methods of finding T_2, respectively.

From the fit parameters we found $T_2 = (95 \pm 2)$ ms for the manual method, $T_2 = (117 \pm 2)$ ms for the Carr-Purcell method, and $T_2 = (108 \pm 5)$ ms for the Meiboom-Gill method.

Although the uncertainties in all three T_2 measurements are less than 5% of the measured values, the actual measured values between the three methods differs somewhat. This may be due to the inaccurate pulse lengths for the 90° and 180° pulses. The Meiboom-Gill method corrects for incorrect pulse lengths, while the other two methods do not.

A direct comparison with literature values cannot be made, since there are no published results using the exact permanent magnet and equipment used in this experiment ($B = 0.5$ T and Larmor precession frequency of 21.5 MHz). However, T_1 and T_2 are both between 60 and 200 ms in the literature, when magnetic field strengths are between $B = 0.35$ T and $B = 3$ T [2]. This is around the same order of magnitude as the values measured in this experiment.

V. CONCLUSIONS

We measured $T_1 = (54 \pm 5)$ ms by measuring M_z through the maximum FID voltage signal response from the mineral oil sample. We measured $T_2 = (95 \pm 2)$ ms for the manual method, $T_2 = (117 \pm 2)$ ms for the Carr-Purcell method, and $T_2 = (108 \pm 5)$ ms for the Meiboom-Gill method using the spin-echo technique. Both T_1 and T_2 fell within the same order of magnitude of literature values. The theoretical models for the relaxation times were also used to fit the data with low uncertainties for the model parameters, showing that the relaxation for T_1 and T_2 follow exponential models.

[1] *PULSED/CW NMR SPECTROMETER*, TeachSpin, Inc., Buffalo, NY, rev 1.1 4/09 ed. (2009).

[2] H. M. Gach, Technical note: T1 and t2 and complex permittivities of mineral oil, silicone oil, and glycerol at 0.35, 1.5, and 3 t, Medical Physics **46**, 1785 (2019), https://aapm.onlinelibrary.wiley.com/doi/pdf/10.1002/mp.13429.

[3] *Physics 4796 Lab Writeup Pulsed Nuclear Magnetic Resonance*.