# Physics 180C: Pulsed NMR of Mineral Oils and Aqueous $Cu_2SO_4$ Solutions

Spenser Talkington,* Madeline Gullen, Joshua Lee, Teresa Le, and Stuart Brown
*Department of Physics and Astronomy, University of California at Los Angeles, 405 Hilgard Avenue, Los Angeles, California 90095, USA*
(Dated: February 16, 2020)

Nuclear Magnetic Resonance (NMR) of protons and other nuclei is a common analytical technique used in physics, chemistry, and medicine. While Larmor precession and Rabi oscillations describe basic spin behaviors, they do not account for relaxation, and relaxation times can be used to characterize materials. Here, we determine the $T_1$ and $T_2$ relaxation times of light and heavy mineral oil using inversion recovery and Meiboom-Gill pulse techniques as $T_1(\text{light}) = 66.1 \pm 2.4$ ms, $T_1(\text{heavy}) = 34.5 \pm 2.0$ ms, $T_2(\text{light}) = 31.6 \pm 2.0$ ms, and $T_2(\text{heavy}) = 12.16 \pm 0.95$ ms respectively. Additionally, we determined the $T_1$ relaxation times of aqueous $Cu_2SO_4$ solutions at different molar concentrations using inversion recovery pulse techniques as $T_1(0) = 780 \pm 160$ ms, $T_1(0.063) = 19.99 \pm 0.77$ ms, and $T_1(0.125) = 13.77 \pm 0.93$ ms. These results indicate that heavy mineral oil has stronger spin-lattice and dephasing interactions than light mineral oil, and that introducing magnetic impurities is an effective way to reach equilibrium more quickly.

## INTRODUCTION

Particles with spin respond to magnetic fields according to their gyromagnetic ratio $\gamma$. In particular in a static field $B_0$, by Zeeman splitting, energy levels $E$ are broken into $E + \gamma m\hbar B_0$ and $E - \gamma m\hbar B_0$. This splitting introduces a frequency of oscillation $\omega_0 = \gamma B_0$, corresponding to the Larmor precession of the spin in the field. This frequency happens to be in the radiofrequency (RF) band for protons and neutrons, and their composite nuclei. When driven at this resonant frequency, nuclear spin states can be flipped and rotated by carefully selecting the duration of RF pulses.

The precise measurement of nuclear responses to applied RF fields has enabled accurate imaging that yields precise structural and density characteristics of materials, including humans for medical diagnostic purposes.

For a spin, the state $|\psi(t)\rangle = a(t)|\uparrow\rangle + b(t)|\downarrow\rangle$, where $a$ and $b$ are complex coefficients, evolves according to the Schrödinger Equation:

$$H(t)|\psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle \tag{1}$$

Where the Hamiltonian in the presence of a magnetic field $\boldsymbol{B}$ in terms of the spin matrices $\boldsymbol{\sigma}$ is:

$$H(t) = -\gamma \boldsymbol{B}(t)\cdot\boldsymbol{\sigma} \tag{2}$$

Here we consider a specific form where $B_1 \ll B_0$ and the total field experienced by the spins depends on what the RF field is and whether it is on or off:

$$\boldsymbol{B}(t) = B_0\hat{\boldsymbol{z}} + \begin{cases} B_1[\cos(\omega_0 t+\phi)\hat{\boldsymbol{x}} + \sin(\omega_0 t+\phi)\hat{\boldsymbol{y}}] \\ 0 \end{cases} \tag{3}$$

As mentioned above, the solution for the evolution of the wavefunction in the presence of a uniform magnetic field is Larmor precession. However, applying an RF field on top of the constant field leads to Rabi Oscillations. Mathematically, the Bloch Equations describe the macroscopic nuclear magnetization, $M_i = N\langle S_i\rangle$, in the rotating frame of the spins:

$$\frac{dM_x(t)}{dt} = \gamma(\boldsymbol{M}(t)\times\boldsymbol{B}(t))_x - \frac{M_x(t)}{T_2} \tag{4}$$

$$\frac{dM_y(t)}{dt} = \gamma(\boldsymbol{M}(t)\times\boldsymbol{B}(t))_y - \frac{M_y(t)}{T_2} \tag{5}$$

$$\frac{dM_z(t)}{dt} = \gamma(\boldsymbol{M}(t)\times\boldsymbol{B}(t))_z - \frac{M_z(t)}{T_1} + \frac{M_0}{T_1} \tag{6}$$

Here we note the appearance of two relaxation times: $T_1$ and $T_2$. $T_1$ is the time scale on which equilibrium is reestablished after the spin system is exposed to the RF field. In particular, following exposure to an RF field that flips the spins, a $t_\pi$ pulse, the spins relax as:

$$M_z(t) = M_0(2e^{-t/T_1} - 1) \tag{7}$$

$T_2$ is the time scale on which the phases of the spins decohere due to inhomogeneities in the field and environment, resulting in a decreased spin echo amplitude. In particular, following exposure to an RF field that flips the spins into the $xy$ plane, a $t_{\pi/2}$ pulse, the spins relax as:

$$M_{xy}(t) = M_0 e^{-t/T_2} \tag{8}$$

We subjected light and heavy mineral oils to RF field pulses and measured the $T_1$ and $T_2$ relaxation behaviors using $t_\pi$ and $t_{\pi/2}$ pulses and Meiboom-Gill pulse patterns respectively. We found that the $T_1$ and $T_2$ times are shorter in the heavy oil than in the light oil, indicating that heavy mineral oil has stronger spin-lattice and dephasing interactions than light mineral oil. Additionally, we considered the effect of the magnetic impurity $Cu_2SO_4$ on the $T_1$ relaxation time, and found that increasing impurities hastened relaxation.

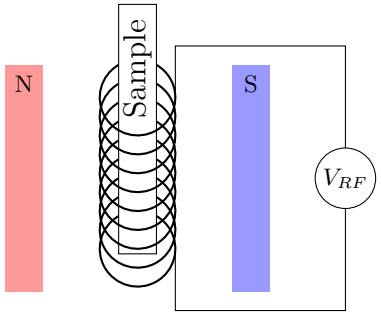


FIG. 1. Experimental setup showing sample, and fields. The sample is placed inside a solenoid between two permanent magnets. The permanent magnets provide $B_0 \approx 0.5$ T and $V_{RF}$ provides either $B_1 = 0$ or a $B_1 \approx 0.01$ T radiofrequency field at $\omega_0 = 21.47$ MHz. The signal detector is next to the solenoid.

## EXPERIMENTAL METHODS

We used four pieces of equipment to measure the NMR response of liquid samples to pulsed RF magnetic fields. Specifically, they are a Pulsed NMR Spectrometer, Correction Box, Permanent Magnet/Sample Enclosure, and Oscilloscope. The NMR Spectrometer was used to generate RF pulsed signals as described below, and to divide the response into in-phase and quadrature signals. The correction box was used to correct for non-uniformities in the field of the permanent magnet, which Stuart did, and could have been used to introduce a gradient to measure the free induction decay (FID) time $T_2^*$. The enclosure held the samples, permanent magnet, RF solenoid, and signal detector. The input signals and output signals were measured on a digital oscilloscope.

We first determined the fields generated by the permanent magnet, the strength RF field, the Rabi Flopping frequency, and consequently the time for $\pi$ and $\pi/2$ pulses. Then through measurement of the NMR response of protons in light and heavy mineral oil, and water with varying concentrations of $Cu_2SO_4$ magnetic impurities to pulsed RF fields, we determined the spin-lattice relaxation time $T_1$, and the decoherence time $T_2$.

### Field Strengths

In a constant magnetic field, spins precess at the Larmor frequency:

$$\omega_0 = \gamma B_0 \tag{9}$$

Equivalently:

$$B_0 = \frac{\omega_0}{\gamma} \tag{10}$$

We determined the static field $B_0$ by determining resonant frequency of our samples. We measured the response to pulses of different frequencies and found the largest response at $21.4768 \pm 0.0051$ MHz, which for $\gamma_{\text{proton}} = 42.5781$ MHz/T corresponds to:

$$B_0 = 0.50441 \pm 0.00012 \text{ T} \tag{11}$$

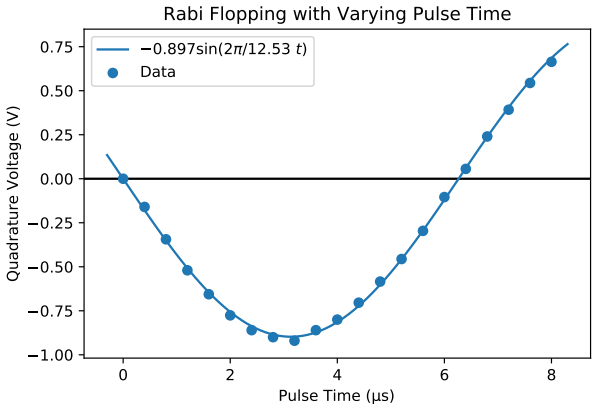


FIG. 2. We measured the in-phase voltage response directly following RF pulses with durations that varied from 0 $\mu$s to 8 $\mu$s. Theoretically voltages are sinusoidal in time with angular frequency Rabi Frequency $\omega_1 = \gamma B_1$. We fitted our data with a sinusoidal curve and determined that $t_{2\pi} = 1/2\pi\omega_1 = 12.531 \pm 0.025$ $\mu$s.

In an RF field, spins precess at the Rabi Frequency:

$$\omega_1 = \gamma B_1 \tag{12}$$

Equivalently, the RF field strength is given by:

$$B_1 = \frac{2\pi}{\gamma\, t_{2\pi}} \tag{13}$$

We then measured the Rabi Flopping frequency by varying pulse time from 0 to 8 $\mu$s, and measuring the in-phase response directly following the pulse (we adjusted the phase so that the quadrature response was zero). Substituting for the gyromagnetic ratio of the proton and determining $t_{2\pi} = 12.531 \pm 0.025$ $\mu$s by fitting our data as shown in Fig. 2, we find:

$$B_1 = 0.011777 \pm 0.000023 \text{ T} \tag{14}$$

### RF Pulses and Data Acquisition

From the strength of the RF field that we determined above, we found the period of Rabi Flopping $t_{2\pi}$, and now define the following RF pulse durations:

$$t_\pi = 6.30 \ \mu\text{s} \tag{15}$$

$$t_{\pi/2} = 3.14 \ \mu\text{s} \tag{16}$$

For each measurement, the data acquisition scheme was the same: Madeline adjusted the relaxation time $\tau$,

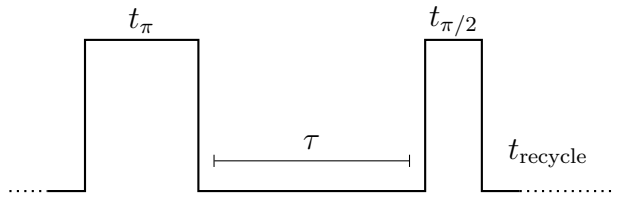


FIG. 3. RF pulse sequence for $T_1$ measurements. We varied $\tau$ from 1 ms to 500 ms and used $t_\pi = 6.30\ \mu$s, $t_{\pi/2} = 3.14\ \mu$s, and $t_{\text{recycle}} = 1000$ ms. We measured the in-phase and quadrature voltages directly following $t_{\pi/2}$ to determine $T_1$.

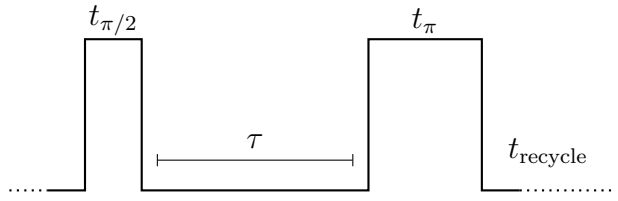


FIG. 4. RF pulse sequence for $T_2$ measurements. We varied $\tau$ from 10 ms to 90 ms and used $t_{\pi/2} = 3.14\ \mu$s, $t_\pi = 6.30\ \mu$s, and $t_{\text{recycle}} = 500$ ms. We measured the in-phase and quadrature voltages directly following $t_\pi$ to determine $T_2$.

Spenser measured the pulse amplitudes using the oscilliscope, and Joshua recorded the times and amplitudes.

To measure $T_1$ we used a $t_\pi$ pulse to flip the spins, then waited variable relaxation times $\tau$, then measured their amplitude after a $t_{\pi/2}$ pulse. We then recycled the signal. This pulse is shown in Fig. 3.

To measure $T_2$ we used a $t_{\pi/2}$ pulse to rotate the spins from the $z$-axis into the $xy$ plane, measured the amplitude of the spin-echo, and recycled the signal. This pulse is shown in Fig. 4. Since this method of measurement for $T_2$ is not very efficient, we only used it for the light mineral oil. In general, we measured $T_2$ by using a Meiboom-Gill pulse pattern. This involves an initial $t_{\pi/2}$ pulse, and a relaxation time of $\tau$ followed by multiple (in our case, 10) $t_\pi$ pulses to regroup the dephased spins followed by relaxation times of $2\tau$, and measured the decreasing amplitude of spin echos. This pulse is shown in Fig. 5.

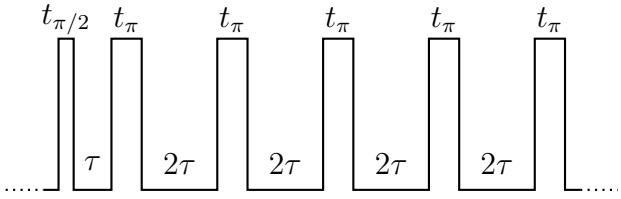


FIG. 5. RF pulse sequence for Meiboom-Gill $T_2$ measurements. We used $\tau = 10$ ms and $\tau = 4$ ms and used $t_{\pi/2} = 3.14\ \mu$s, $t_\pi = 6.30\ \mu$s. We measured the amplitude of each spin echo (in between each) $t_\pi$ pulse to determine $T_2$.

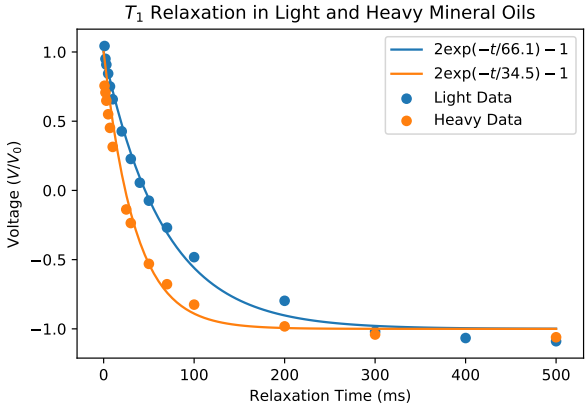


FIG. 6. $T_1$ relaxation is faster for heavy oil than for light oil, where we have $T_1(\text{light}) = 66.1 \pm 2.4$ ms, and $T_1(\text{heavy}) = 34.5 \pm 2.0$ ms. This indicates that heavy oil has a stronger spin-lattice interaction than light oil. Error bars are of order the marker size.

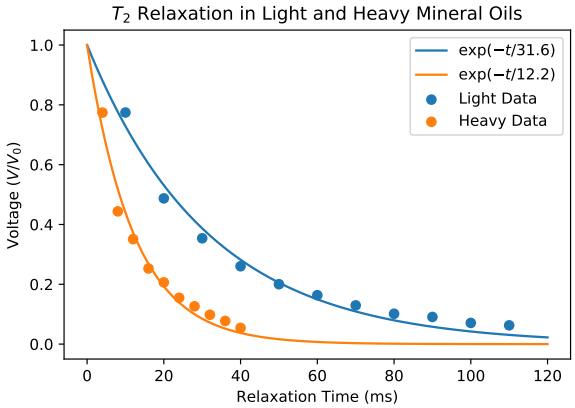


FIG. 7. $T_2$ relaxation is faster for heavy oil than for light oil, where we have $T_2(\text{light}) = 31.6 \pm 2.0$ ms, and $T_2(\text{heavy}) = 12.16 \pm 0.95$ ms. This indicates that heavy oil has a stronger dephasing interactions than light oil. Additionally, we note that spin decoherence is faster than spin-lattice relaxation, $T_2 < T_1$. Error bars are of order the marker size.

### Samples and Measurements

We used a light mineral oil sample, a heavy mineral oil sample, a distilled water sample, a 0.0625 molar aqueous $Cu_2SO_4$ solution, and a 0.125 molar aqueous $Cu_2SO_4$ solution. We determined the optimal insertion depth for the maximum signal in the sample enclosure and held them in place using rubber o-rings.

We then used RF field pulses to manipulate the spins using $t_\pi$ and $t_{\pi/2}$ pulses and then measured the relaxation behavior as described above and in Figs. 3-5. Note that we adjusted the phase of the RF pulse so that the voltage was entirely in-phase and quadrature was 0.

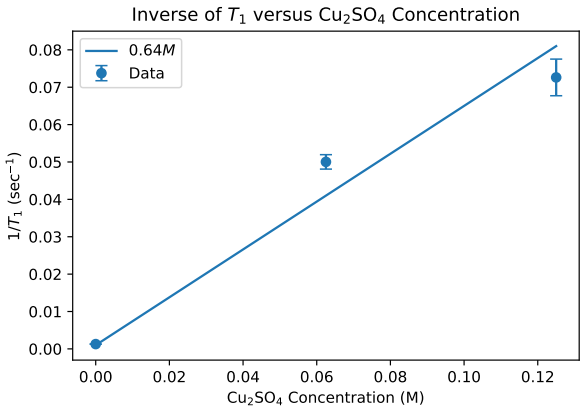


FIG. 8. We observe a fairly linear relationship between the inverse of $T_1$ and the molar concentration of the magnetic impurity $Cu_2SO_4$. As expected, with increasing impurity concentration, equilibrium is reached more quickly.

Following a $t_\pi$ pulse and a decay time of $\tau$, we expect to measure a probe voltage of:

$$V(\tau) = V_0(2e^{-\tau/T_1} - 1) \tag{17}$$

Following a $t_{\pi/2}$ pulse and a decay time of $\tau$, we expect to measure a probe voltage of:

$$V(\tau) = V_0 e^{-\tau/T_2} \tag{18}$$

We then fit the data to these functions using least squares fits as shown in Fig. 6 and Fig. 7. Using a similar fit, we determined $T_1$ for the aqueous solutions and plotted the inverses in Fig. 8.

## RESULTS

We determined the $T_1$ and $T_2$ relaxation times of light and heavy mineral oil using inversion recovery and Meiboom-Gill pulse techniques as $T_1(\text{light}) = 66.1 \pm 2.4$ ms, $T_1(\text{heavy}) = 34.5 \pm 2.0$ ms, $T_2(\text{light}) = 31.6 \pm 2.0$ ms, and $T_2(\text{heavy}) = 12.16 \pm 0.95$ ms respectively. Additionally, we determined the $T_1$ relaxation times of aqueous $Cu_2SO_4$ solutions at different molar concentrations using inversion recovery pulse techniques as $T_1(0) = 780 \pm 160$ ms, $T_1(0.063) = 19.99 \pm 0.77$ ms, and $T_1(0.125) = 13.77 \pm 0.93$ ms. The uncertainties reported represent those of least squares fits and do not incorporate possible systematic or additional random errors.

### Error Analysis

We set the driving (resonant) frequency to six significant figures, and set pulse times to three significant figures. Additionally, we determined $B_0$ and $B_1$ to four significant figures. We believe that the biggest source of error in the experiment was the measurement of voltages using the oscilloscope, where measurements were accurate to at most two significant figures, but the first peaks following the pulses were often unclear. We believe that if we had repeated the experiment with a different phase shift, this might have made the peaks clearer.

### Discussion

We observe good agreement between the theory of relaxation and our experimental measurements. In particular, following a $t_\pi$ pulse, voltages range from $+V_0$ to $-V_0$, and following a $t_{\pi/2}$ pulse voltages range from $+V_0$ to 0, in correspondence with the expectations, Eq. (7) and Eq. (8), for $T_1$ and $T_2$ relaxations respectively. We observe that $T_2 < T_1$ for all samples. Additionally, we find that $T_1$ relaxation time varies inversely with concentration of magnetic impurities, in agreement with the theory of concentration gradients from fluctuations.

## CONCLUSIONS

Following manipulation, nuclear spins relax to align with a net magnetization in the direction of a permanent field. The rate at which they do so depends on density/viscosity as we measured that heavy mineral oil reequilibrates faster than light mineral oil. Additionally, the presence of magnetic impurities, such as $Cu_2SO_4$ greatly speeds up reequilibration. If we were to repeat the experiment, we would like to have determined whether the difference between light and heavy mineral oil was due to their density or viscosity. We could compare these by measuring $T_1$ and $T_2$ for a variety of light-heavy mixtures at a variety of temperatures-viscosities.

* stalkington@ucla.edu

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