Pulsed NMR

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Abstract:
Between the different experiments for determining the spin-lattice relaxation time (τ_1) and the spin-spin relaxation time (τ_2), the most reliable seem to be the two pulse-zero crossing and the Meiboom-Gill. For mineral oil, $\tau_1 = 16.0 \pm 0.2\ ms$ and $\tau_2 = 7.0 \pm 0.1\ ms$; for glycerin, $\tau_1 = 17.9 \pm 0.2\ ms$ and $\tau_2 = 10.8 \pm 0.4\ ms$. These results seem to loosely agree with other experimental results[1,2], although the relaxation times found are a few times smaller than the referenced results.

[1] http://home.sandiego.edu/~severn/p480w/NMRDJM.pdf
[2] http://home.sandiego.edu/~severn/p480w/m2h.pdf

Introduction:

Nuclear Magnetic Resonance (NMR) is an important phenomena that that has many useful applications, the most famous of which is the Magnetic Resonance Imaging (MRI) device used in medical applications which allows sensitive images taken inside a living person without harmful exposure to high energy X-Rays.

In the NMR experiments, there are two kinds of relaxation times. First, there is the spin-lattice relaxation time, τ_1, which describes how long it takes to reach 1/e of the original value. The second is the spin-spin relaxation time, τ_2 which describes the characteristic time for magnetization to be coherent, subject to multiple pulses.

Theory:

There are basically two ways to determine τ in these experiments; finding the minimum amplitude from opposing "A" and "B" pulses, and measuring the decay in Amplitude as a function of delay time (t).

In the first method, the delay time is found which gives the minimum amplitude and then several measurements are taken on either side of the minimum so the data can be fit to a curve. Since the response will decrease with the natural log of the delay time, the time axis (t) is transformed by $t_q = \ln t$ and the data is then fit to a quadratic curve[3], which is shown by Equation (1),

$$\begin{aligned} A(t_q) &= \alpha(t_q - t_1)^2 + \beta(t_q - t_1) + \gamma \\ \Rightarrow t_q - t_1 &= \frac{-\beta \pm \sqrt{\beta^2 - 4\alpha(\gamma - A)}}{2\alpha} \\ \Rightarrow t_1 &= t_q + \frac{1}{2\alpha}\left(\beta \mp \sqrt{\beta^2 - 4\alpha(\gamma - A)}\right), \end{aligned} \tag{1}$$

where α, β, and γ are the coefficients of the quadratic polynomial, t_q is the natural log of the time, and t_1 is the natural log of τ_1. τ_1 is then given by Equation (2),

$$\begin{aligned} \tau_1 &= e^{t_1} \\ \Rightarrow \Delta\tau_1 &= \Delta t_1 e^{t_1}, \end{aligned} \tag{2}$$

where Δt_1 is derived in the "Uncertainty Relations" section of the Appendix.

The second method measures the amplitude decay as a function of t and is given by Equation (3),

$$\begin{aligned} A &= A_0 e^{-t/t_2} + C \\ \Rightarrow t_2 &= t \ln \frac{A - C}{A_0}, \end{aligned} \tag{3}$$

where t_2 is the fitting parameter and is equal to $\frac{1}{2}\tau_2$.This implies that $\Delta\tau_2$ is equal to $\frac{\Delta t_2}{2}$, where Δt_2 is derived in the "Uncertainty Relations" section in the Appendix.

Procedure:

The Free Induction Decay (FID) from a single 90^o pulse consists of finding a frequency that minimizes the beat oscillations and maximizing the pulse strength by tuning the pusle width. The beat oscillations come from two signals with different frequencies, which means that the superposition of both signals causes both destructive and constructive interference at different phase angles. By minimizing the beat oscillations, the two frequencies are better matched up - or in resonance. Two convenient points are picked on the envelope, which should look like a decaying exponential; a point near the maximum and a later point that has a value of 1/e the initial point. the time difference between these two points gives a single rough estimate of τ_2.

For the single pulse measurement of τ_1, the "repetition time" is increased until the pulse is at a maximum. the difference in "repetition time" that takes the max amplitude to 1/e of the max amplitude gives a single rough approximation of τ_1.

A better measurement of τ_1 comes from the two pulse-zero crossing experiment. As the the name suggests, there are two pulses used. The first pulse A is minimized (set to 180^o) while the B pulse is maximized (set to 90^o. The use of multiple pulses provides a better measurement by offsetting the non-uniform effects of the permanent magnet. τ_1 is the value that minimizes the amplitude of the B pulse. A statistical value for τ_1 is found by measuring the amplitude and delay time several points on either side of the expected τ_1 value, taking the natural log of the delay times, and fitting the data to a second order polynomial.

[3] hence t_q for quadratic

For the two pulse-spin echo experiment, pulse A is set to 180^o and pulse B is set to 90^o, which would maximize B. A statistical value for τ_2 is found by adjusting the delay time and recording the echo amplitude for several points and fitting the data to a decaying exponential curve. It is important to remember that the delay times recorded are $2\tau_2$, because the time separation between pulse A and B is $1\tau_2$ and the time separation between pulse B and the echo is another $1\tau_2$.

The Car-Purcell experiment is very similar to the two pulse-spin echo experiment, except that multiple pulses will now be added. It is a good idea to first scale back the view on the oscilloscope in order to see the multiple pulses that will be filling the screen; the view should be scaled so that the pulses look like spikes on the screen, the exponential decay patterns should not be visible. If switching from A, the pulses would read like: A, B, echo, B, echo, B ...; if switching from B, the pulses will read: B, echo, B, echo ... Its also a good idea to reduce the delay time (perhaps 1 ms) so more measurements can be taken; if the delay time is too great, the amplitude will decay too quickly and fewer measurements will be possible. The best practice was found by recording the amplitude of the first echo, add a second pulse and record the amplitude and so on until a sufficient number of measurements are taken. Since each additional pulse will add both a B and an echo, each measurement is separated by two times the delay time; setting the delay time to an easy number - like 1 ms - means each echo is separated by 2 ms. this makes data collection easier for this experiment.

The Meiboom-Gill experiment closely mirrors the Car-Purcell. The experiment is conducted in exactly the same way except the CPMG switch is turned on. This feature allows for a more accurate reading by working around the A and B pulses not being perfectly tuned.

Results:

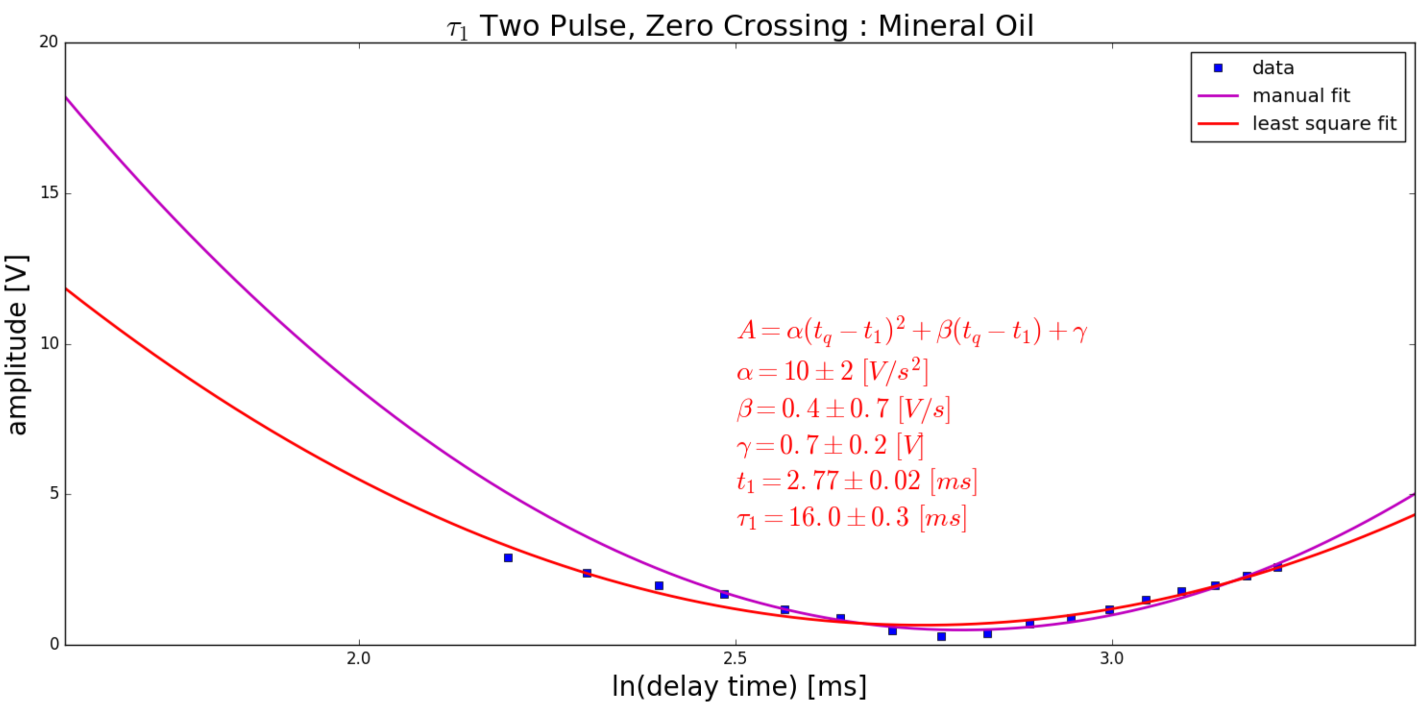

Figure 1: In order to reflect the expected time dependence, the time axis is transformed by its natural log. The data is then plotted (blue). Equation 1 and an initial guess are used to produce a manual fit (magenta) and the initial parameters are used to produce fitted parameters and a fitted curve (red). The uncertainty for the fitted parameters is found by individually adjusting them until a visual deviation from the data is observed.

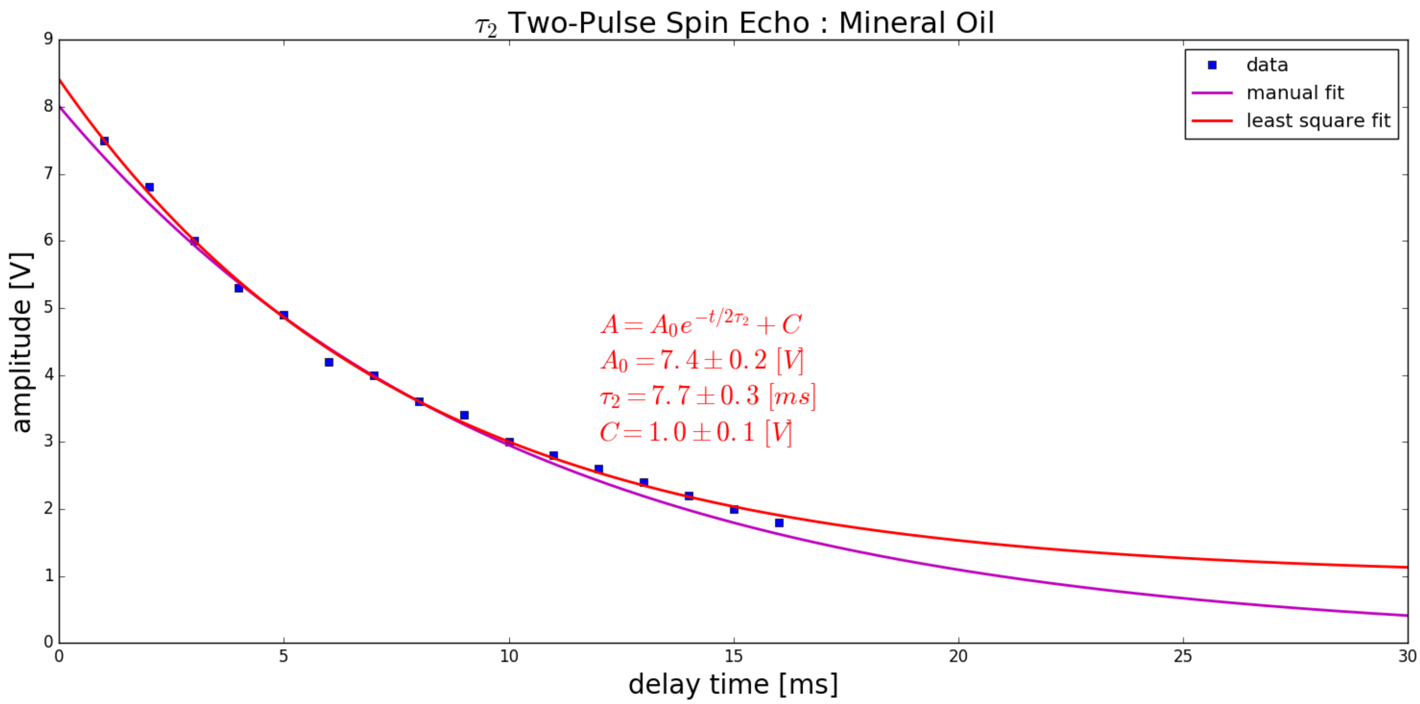

Figure 2: First, the data is plotted (blue). Equation 3 and an initial guess are used to produce a manual fit (magenta) and the initial parameters are used to produce fitted parameters and a fitted curve (red). The uncertainty for the fitted parameters is found by individually adjusting them until a visual deviation from the data is observed.

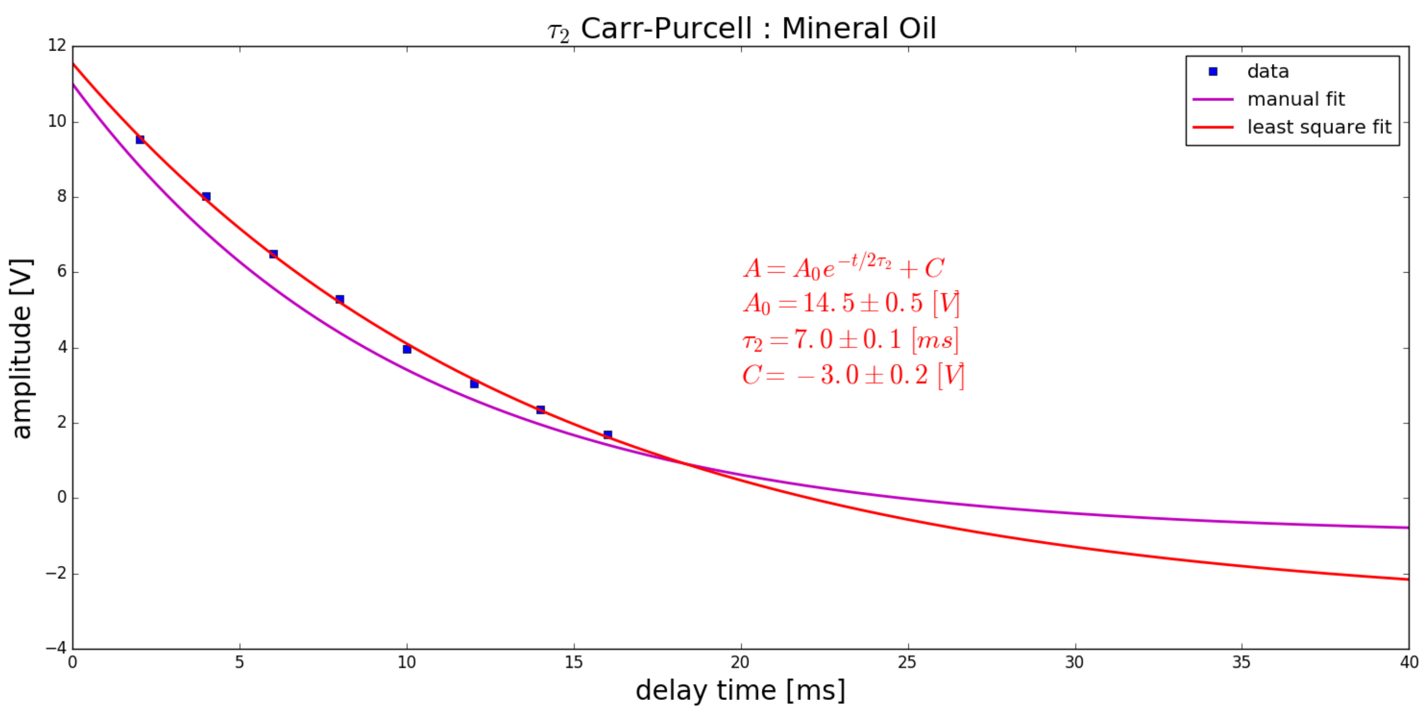

Figure 3: First, the data is plotted (blue). Equation 3 and an initial guess are used to produce a manual fit (magenta) and the initial parameters are used to produce fitted parameters and a fitted curve (red). The uncertainty for the fitted parameters is found by individually adjusting them until a visual deviation from the data is observed.

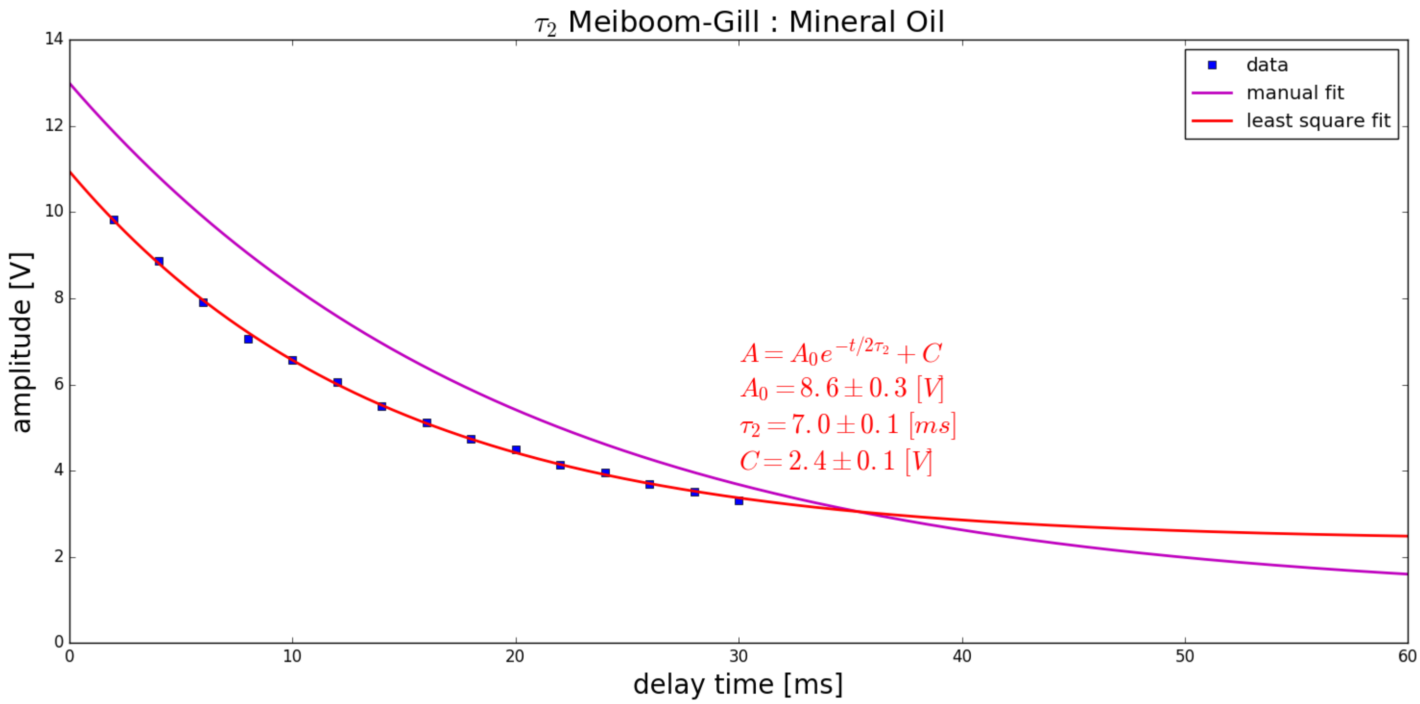

Figure 4: First, the data is plotted (blue). Equation 3 and an initial guess are used to produce a manual fit (magenta) and the initial parameters are used to produce fitted parameters and a fitted curve (red). The uncertainty for the fitted parameters is found by individually adjusting them until a visual deviation from the data is observed.

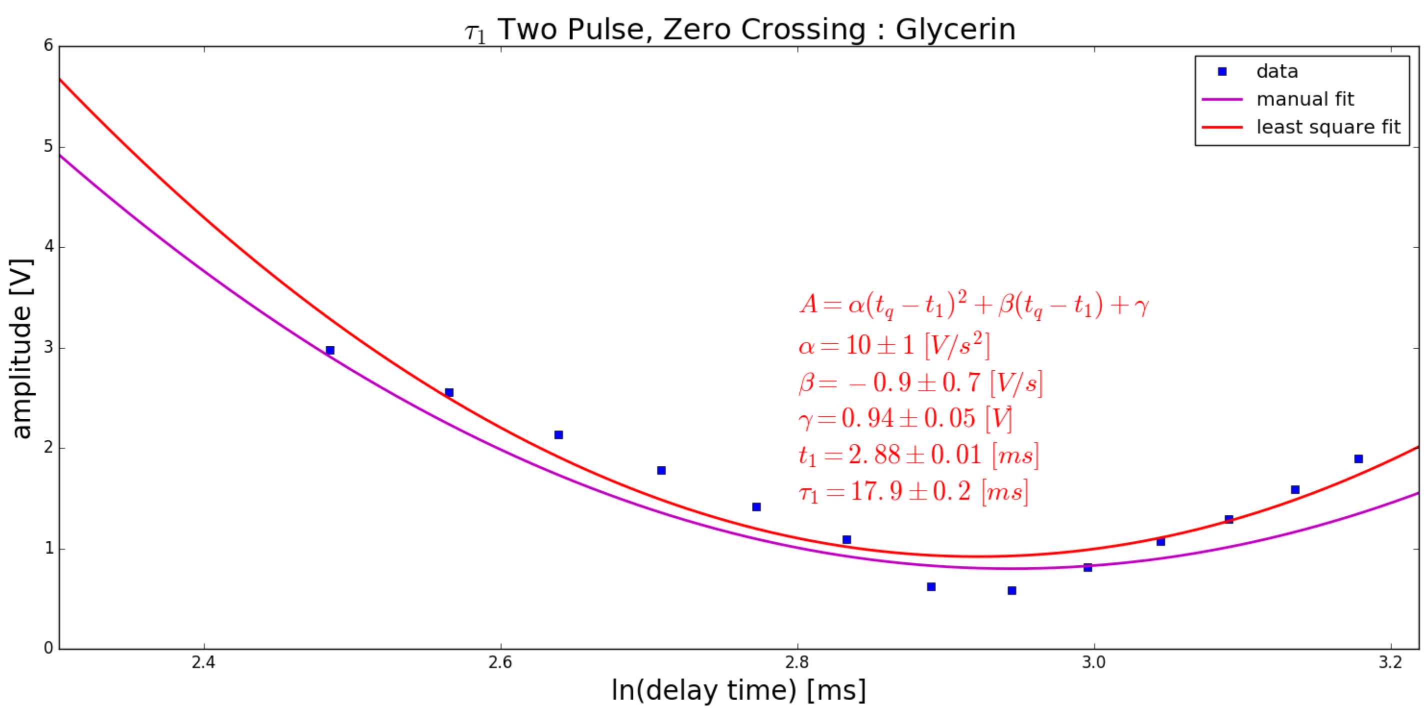

Figure 5: The Two Pulse, Zero crossing experiment in mineral oil is repeated using a sample of Glycerin. In order to reflect the expected time dependence, the time axis is transformed by its natural log. The data is then plotted (blue). Equation 1 and an initial guess are used to produce a manual fit (magenta) and the initial parameters are used to produce fitted parameters and a fitted curve (red). The uncertainty for the fitted parameters is found by individually adjusting them until a visual deviation from the data is observed.

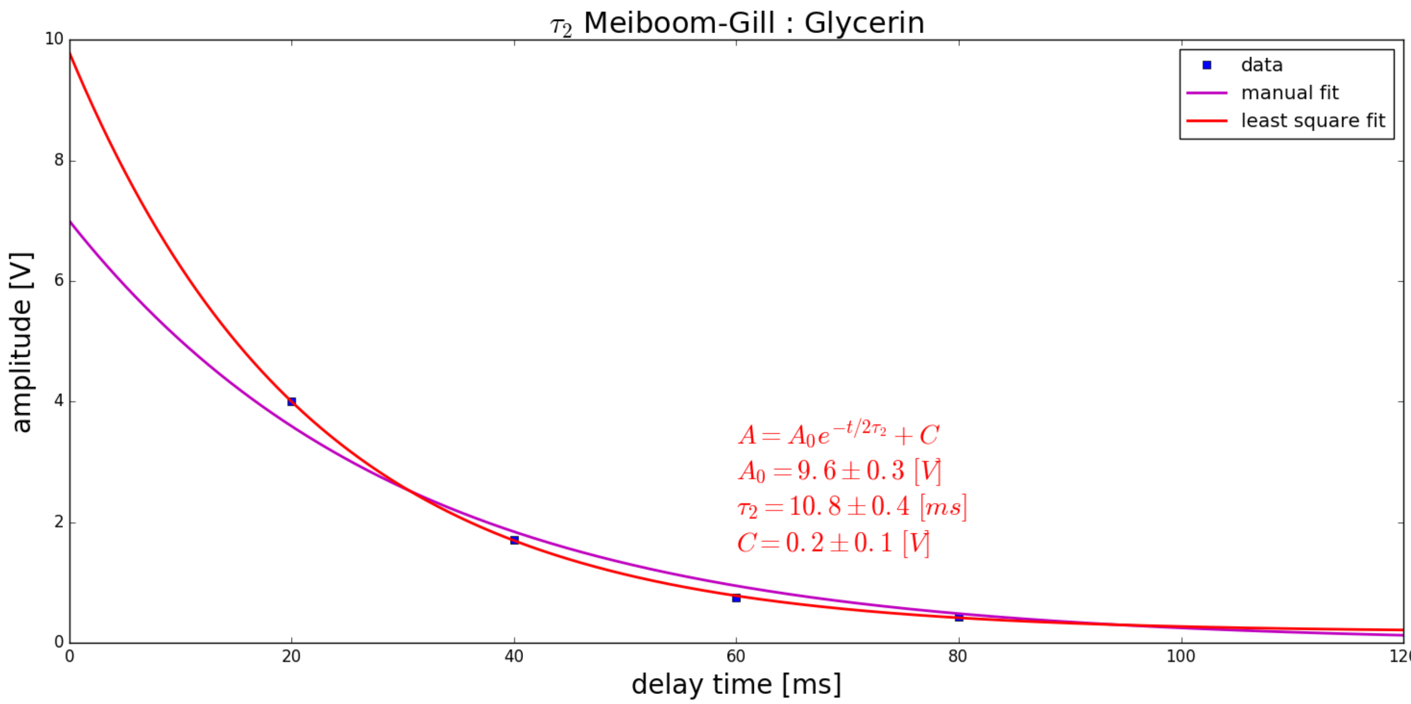

Figure 6: The Meiboom-Gill experiment with mineral oil is repeated using a sample of Glycerin. First, the data is plotted (blue). Equation 3 and an initial guess are used to produce a manual fit (magenta) and the initial parameters are used to produce fitted parameters and a fitted curve (red). The uncertainty for the fitted parameters is found by individually adjusting them until a visual deviation from the data is observed.

Discussion:

Although an analytical solution for the uncertainty is derived in the Appendix, the uncertainty in the fitting parameters is taken by varying the parameter in increments. This is because the uncertainty for τ_1 and τ_2 is more reliable when considering the fit to the data as a whole, rather than the uncertainty of each individual measurement. A better method still would be to use an algorithm that varies the parameters and finds the uncertainty in each that allows the fitted line a maximum overall error with the data. This method should be used in later experiments.

Table 1: τ_1 and τ_2 for Mineral Oil

	$q_i \pm \Delta q_i$	**type**
τ_2 $[ms]$	0.138	free induction decay, 90^o pulse
τ_1 $[ms]$	4	spin lattice relaxation, single pulse
τ_1 $[ms]$	16.0 ± 0.3	spin lattice relaxation, two pulse-zero crossing
τ_2 $[ms]$	7.7 ± 0.3	spin-spin relaxation, two pulse-spin echo
τ_2 $[ms]$	7.0 ± 0.1	spin-spin relaxation, Carr-Purcell
τ_2 $[ms]$	7.0 ± 0.1	spin-spin relaxation, Meiboom-Gill

Table 2: τ_1 and τ_2 for Glycerin

	$q_i \pm \Delta q_i$	**type**
τ_1 $[ms]$	17.9 ± 0.2	spin lattice relaxation, two pulse-zero crossing
τ_2 $[ms]$	10.8 ± 0.4	spin-spin relaxation, Meiboom-Gill

Tables (1) and (2) above show the τ_1 and τ_2 measurements from all the experiments.

The τ_2 measurement from the free induction decay is limited by the non-uniform magnetic field. Theoretically, any value over 0.3 ms would not contribute further, in other words, the maximum value expected to be measured in this experiment is 0.3 ms. The measured value of $\tau_2 = 0.1\ ms$ is in relative agreement with this expectation. This measurement is considered a rough approximation and the uncertainty is not considered.

The single pulse, spin lattice relaxation time of $\tau_1 = 4\ ms$ is another rough approximation. Since it is a single measurement, a statistical uncertainty is not considered.

Between the different experiments, the two pulse-zero crossing and the Meiboom-Gill seem to be the most reliable measurements for τ_1 and τ_2, which is why these two experiments were repeated for with a glycerin sample. For mineral oil, $\tau_1 = 16.0 \pm 0.2\ ms$ and $\tau_2 = 7.0 \pm 0.1\ ms$; for glycerin, $\tau_1 = 17.9 \pm 0.2\ ms$ and $\tau_2 = 10.8 \pm 0.4\ ms$.

Appendix:

Uncertainty Relations:

The fundamental uncertainties from direct measurement, Δt and ΔA, are taken to be 0.5 ms and 0.005 V, respectively.

In the quadratic fitting equation, the standard t-axis is transformed into the natural log of the old t-axis.

$$\begin{aligned} t_q &= \ln(t) \\ \Rightarrow \Delta t_q &= \frac{\Delta t}{t} \end{aligned} \tag{4}$$

The uncertainty for t_1 is found by starting with the result of Equation (1),

$$\begin{aligned} t_1 &= t_q + \frac{1}{2\alpha}\left(\beta \mp \sqrt{\beta^2 - 4\alpha(\gamma - A)}\right) \\ \Rightarrow \Delta t_1 &= \left[\left(\frac{\partial t_1}{\partial t_q}\Delta t_q\right)^2 + \left(\frac{\partial t_0}{\partial \alpha}\Delta \alpha\right)^2 + \left(\frac{\partial t_1}{\partial \beta}\Delta \beta\right)^2 + \left(\frac{\partial t_1}{\partial \gamma}\Delta \gamma\right)^2 + \left(\frac{\partial t_1}{A}\Delta A\right)^2\right]^{1/2} \\ \frac{\partial t_1}{\partial t_q}\Delta t_q &= \Delta t_q \\ \frac{\partial t_1}{\partial \alpha}\Delta \alpha &= \frac{\Delta \alpha}{2\alpha}\left[\frac{1}{\alpha}\left(\beta + \sqrt{\beta^2 - 4\alpha(\gamma - A)}\right) + \frac{2(\gamma - A)}{\sqrt{\beta^2 - 4\alpha(\gamma - A)}}\right] \\ \frac{\partial t_1}{\partial \beta}\Delta \beta &= \frac{\Delta \beta}{2\alpha}\left[1 + \frac{\beta \Delta \beta}{\sqrt{\beta^2 - 4\alpha(\gamma - A)}}\right] \\ \frac{\partial t_1}{\gamma}\Delta \gamma &= \frac{\gamma \Delta \gamma}{\sqrt{\beta^2 - 4\alpha(\gamma - A)}} \\ \frac{\partial t_1}{A}\Delta A &= \frac{A \Delta A}{\sqrt{\beta^2 - 4\alpha(\gamma - A)}} \end{aligned} \tag{5}$$

The uncertainty for t_2 is found by starting with the result of Equation (3),

$$
\begin{aligned}
t_2 &= \frac{t}{\ln \frac{A_0}{A}} \\
\Rightarrow \Delta t_2 &= \left[\left(\frac{\partial t_2}{\partial t} \Delta t \right)^2 + \left(\frac{\partial t_2}{\partial A} \Delta A \right)^2 + \left(\frac{\partial t_2}{\partial A_0} \Delta A_0 \right)^2 \right]^{1/2} \\
\frac{\partial t_2}{\partial t} \Delta t &= \frac{\Delta t}{\ln \frac{A_0}{A}} \\
\frac{\partial t_2}{\partial A} \Delta A &= \frac{A_0 \Delta A}{A^2 \ln^2 \frac{A_0}{A}} \\
\frac{\partial t_2}{\partial A_0} \Delta A_0 &= \frac{\Delta A_0}{A \ln^2 \frac{A_0}{A}}
\end{aligned} \tag{6}
$$

Pre-Lab:

1 **Setup**

2 **Free-Induction Decay (FID)**

A 90^o Pulse FID

i default oscilloscope settings: Time/Div 20 μs, CH1 1 V/cm, CH2 $2V/cm$, Trig: Ext, 1 V, POS.

ii tune the oscilloscope until the FID (detector out, channel 1) is maximized.

iii minimize the beat oscillations (mixer out, channel 2) by using the "Frequency Adjust".

iv adjust "A-width" for 90^o pulse, for maximimum FID.

v ensure optimum values by repeating steps (i), (ii), and (iii - this step).

vi record all settings

vii adjust the "Frequency Adjust" to see the beat oscillations in channel 2, sketch them, describe what causes them, and estimate T_2 - the time it takes for oscillation to reach 1/e of its original amplitude.

B Other Pulse Lengths

i start with the "A-width" and "Frequency Adjust" settings for 90^0 pulse and beat oscillations from part A.

ii increase "A-width" and describe what happens to the oscillation in channel 2.

iii how is a 360^o pulse width identified?

iv scetch oscillations from channel 2 with pulse lengths of 90^0, 180^o, and 360^0 and explain the behavior.

3 **Spin-Lattice Relaxation Time (T_1)**

A Single Pulse

i start with the 90^0 settings found in 2.A.v. Maximize "Detector Out" channel 1 by increasing "Repetition Time".

ii record the "Repetition Time" that gives max amplitude for 90^0 pulse.

iii decrease "Repetition Time" and explain reduction in amplitude.

iv get an estimate for T_1 by the "Repetition Time" that gives about $1/e \approx 1/3$ of the maximum value.

B Two Pulses, Zero Crossing

i Use the settings from 2.A.v for the in-tune 90^o and set the repetition rate to about 100 ms.
ii Turn the B pulses on (B pulses = 1) and start with a small delay - about 0.2 ms.
iii Adjust the settings on the oscilloscope until both A and B pulses can be observed.
iv Adjust the "A-width" to a 180^o pulse (minimized)
v Adjust the "B-width" to a 90^o pulse (maximized)
vi focus on the amplitude of the second pulse by switching "Sync" to B.
vii find T_1 by adjusting the "Delay Time" (τ). T_1 is the time that minimized the amplitude.
viii find a more statistically reliable value for T_1; measure the amplitude of the second pulse as a function of τ and fit the curve to a quadratic function and find the minimum if the curve.

4 **Spin-Spin Relaxation Time (T_2)**

A Two-Pulse Spin Echo

i start with A and B pulses set as in 3.B
ii adjust the "A-width" to maximized 90^o pulse; the initial value of second amplitude should be minimized.
iii adjust the "B-width until it is maximized (180^o pulse).
iv get the second amplitude as a function of total delay time (2τ), using the cursor for Channel 1 to get the best values for the amplitude.
v fit data to an exponential decay to find T_2.

B Carr-Purcell Multiple Pule Spin Echo Sequences

i Start with same settings as 4.A, but start with 3 B pulses and make sure the CPMG switch is turned off.
ii lower the repetition rate to avoid overheating of the rf amplifier.
iii adjust the "Delay Time" and other possible oscilloscope settings until several time separated pulses can be observed.
iv Add more B pulses and tweak the settings until a decay in their amplitudes can be seen.
v obtain a function of the second amplitude as a function of "Delay Time" from the first 90^o pulse).
vi fit the data to an exponential decay to obtain a fitted value for T_2.

C Meiboom-Gill Sequence

i turn on the CPMG (Meiboom-Gill), repeat 4.B.iv - 4.B.vi, and obtain another value of T_2; why would the two numbers differ?

5 **Repeat in New Medium**Find T_1 and T_2 using one of the experiments in a different medium (B glycerin or D petroleum jelly)