Pulsed NMR

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Abstract:

Introduction:

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[1], 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),

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

where t_2 is the fitting parameter and is either equal to τ_2 or τ_2, depending on the experiment.This implies that $\Delta\tau_2$ is equal to either Δt_2 or $\frac{\Delta t_2}{2}$, where Δt_2 is derived in the "Uncertainty Relations" section in the Appendix.

Procedure:

[1] hence t_q for quadratic

Results:

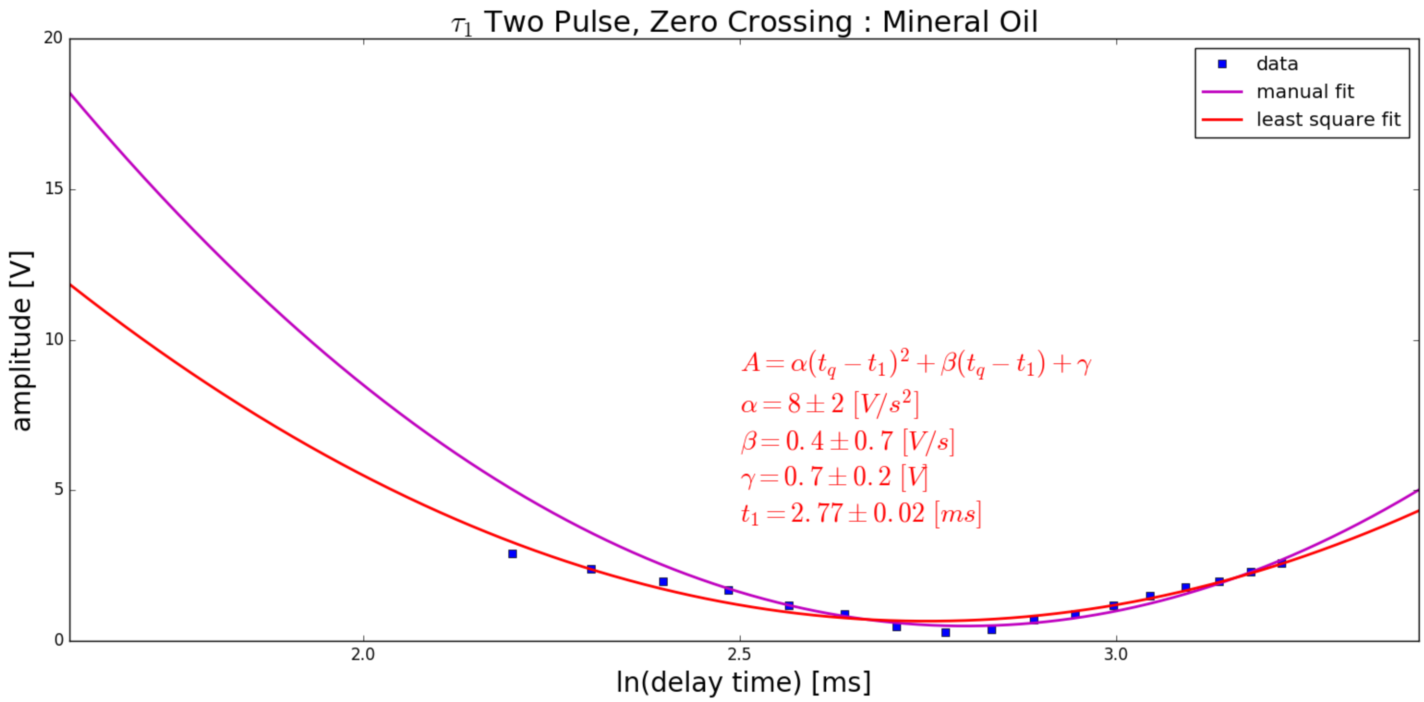

Figure 1: After converting the time measurements to natural log, the data is plotted. A manual curve is found using Equation 1 and finding some initial parameters that approximate the data. The manual fit is shown in magenta. Equation 3 is then used again, along with a least squares fitting algorithm, to produce the fitted curve (shown in red). The uncertainty is found by manually adjusting the fitted parameters until a noticeable difference is seen. The parameters and their associated uncertainty are shown in the figure as well as in Table 1 below. The uncertainty for τ_1 found using this method is also included in Table 1 and is compared with an analytical uncertainty for τ_1 in Table 7 (in the Discussion section).

Table 1: Two Pulse, Zero Crossing Fitting Parameters and τ_1

	q_i	Δq_i
α $[V/ms^2]$	8	2
β $[V/ms]$	0.4	0.7
A_0 $[V]$	0.7	0.2
$\ln(t_0)$ $[ms]$	2.77	0.02
τ_1 $[ms]$	16.0	0.3

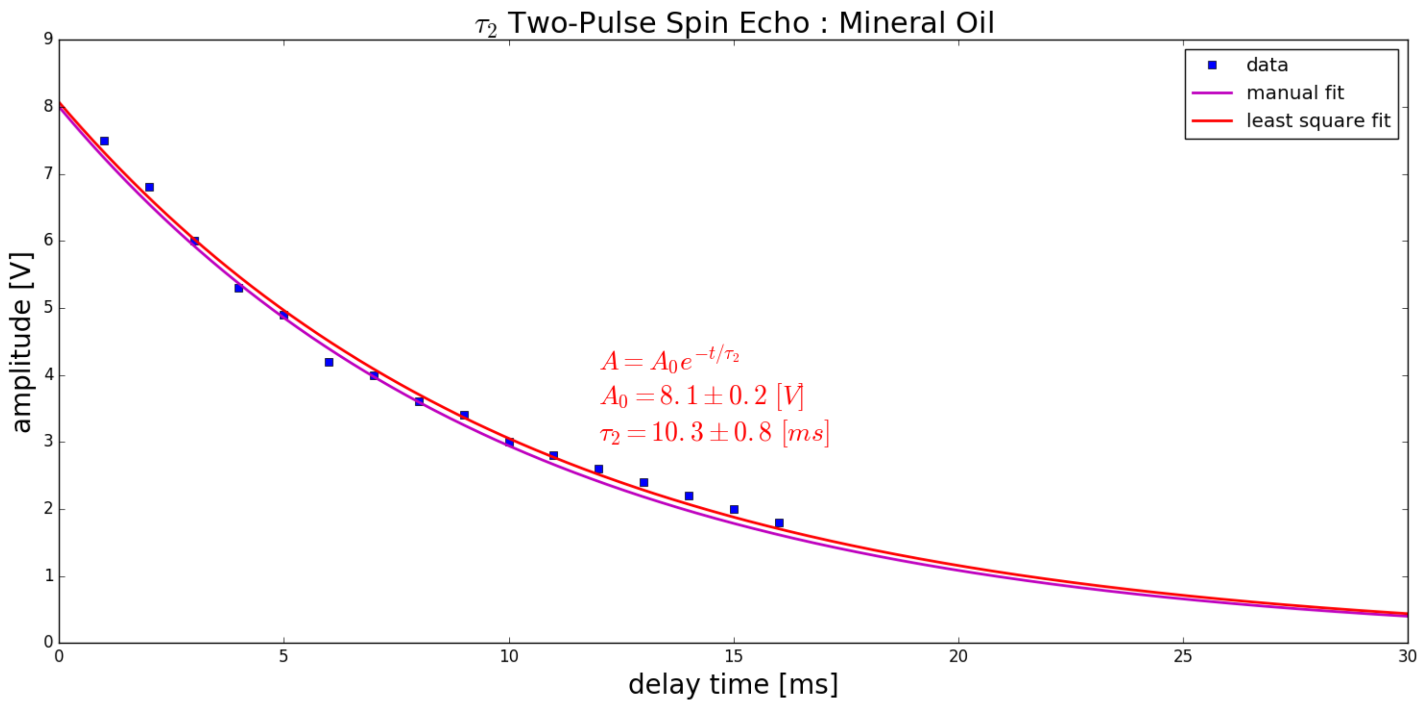

Figure 2: After the data is plotted (shown in blue), Equation 3 is used, along with some initial parameters that approximate the data, is used to find a manual fit (shown in magenta). A least squares algorithm is then used to find the fitted parameters and the fitted curve is plotted (shown in red). The uncertainty of these parameters is found by slightly varying the fitted parameters until a noticeable difference is seen in the fitted curve. The parameters and their associated uncertainty are shown in Table 2 below. An analytical value for the uncertainty of τ_2 is also found using Equation 6 (Uncertainty Relations) and is compared in Table 7 (Discussion)

Table 2: Two-Pulse Spin Echo Fitting Parameters and τ_2

	q_i	Δq_i
$A_0[V]$	8.1	0.2
$\tau_2[ms]$	10.3	0.8

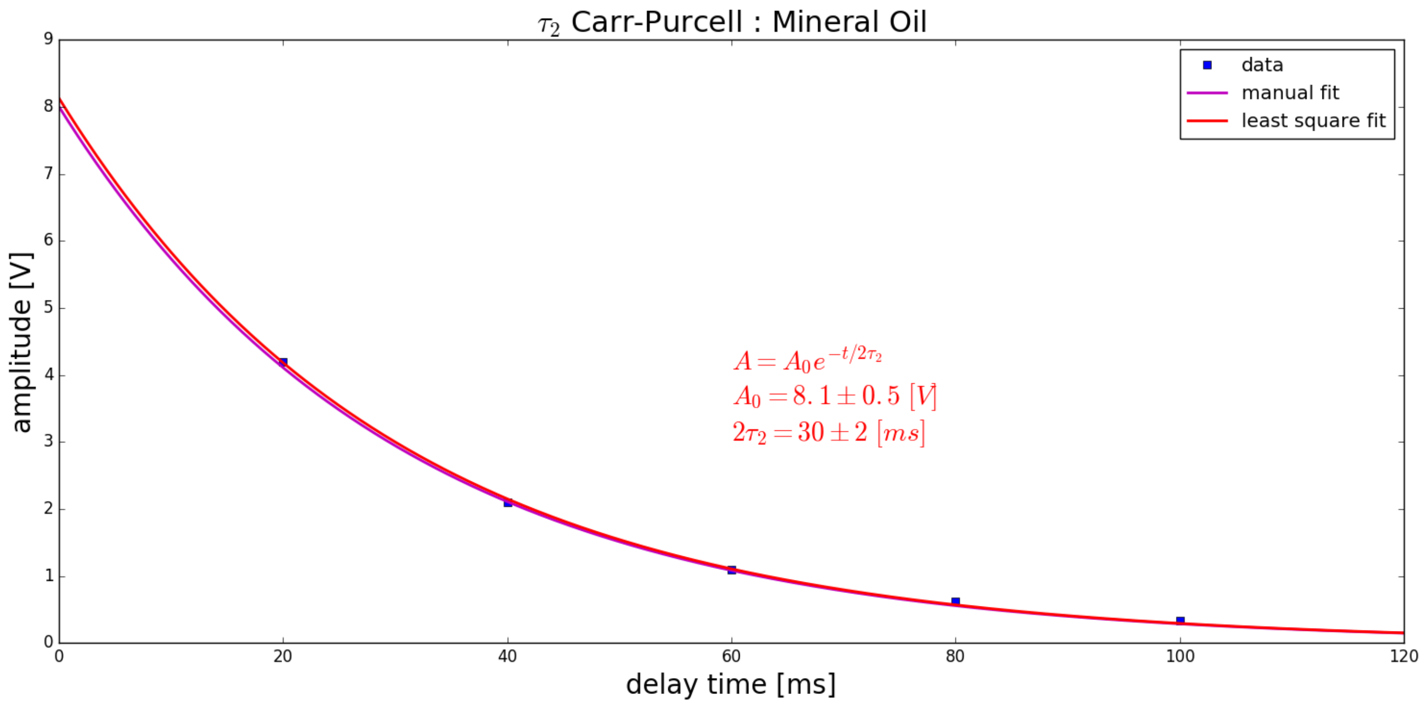

Figure 3: After the data is plotted (shown in blue), Equation 3 is used, along with some initial parameters that approximate the data, is used to find a manual fit (shown in magenta). A least squares algorithm is then used to find the fitted parameters and the fitted curve is plotted (shown in red). The uncertainty of these parameters is found by slightly varying the fitted parameters until a noticeable difference is seen in the fitted curve. The parameters and their associated uncertainty are shown in Table 3 below. An analytical value for the uncertainty of τ_2 is also found using Equation 6 (Uncertainty Relations) and is compared in Table 7 (Discussion)

Table 3: Carr-Purcell Fitting Parameters and τ_2

	q_i	Δq_i
$A_0[V]$	8.1	0.5
$\tau_2[ms]$	15	1

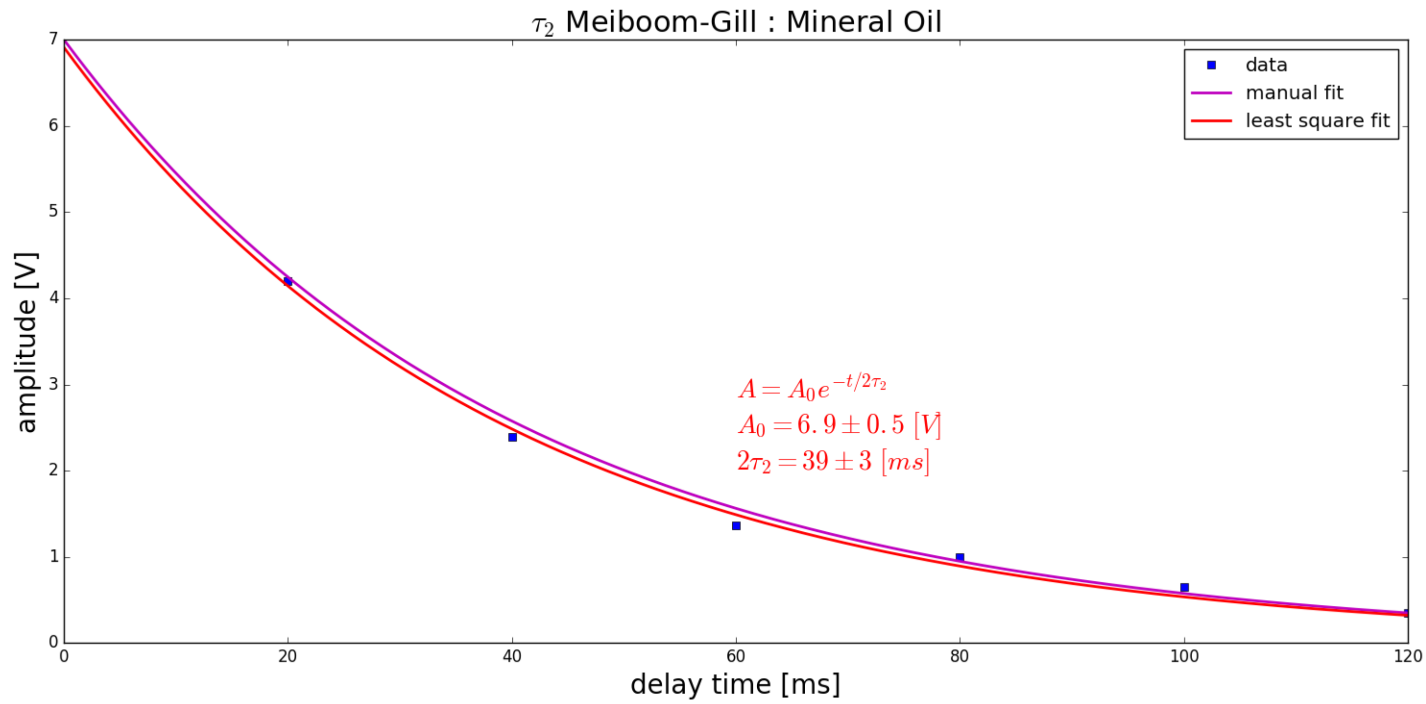

Figure 4: After the data is plotted (shown in blue), Equation 3 is used, along with some initial parameters that approximate the data, is used to find a manual fit (shown in magenta). A least squares algorithm is then used to find the fitted parameters and the fitted curve is plotted (shown in red). The uncertainty of these parameters is found by slightly varying the fitted parameters until a noticeable difference is seen in the fitted curve. The parameters and their associated uncertainty are shown in Table 4 below. An analytical value for the uncertainty of τ_2 is also found using Equation 6 (Uncertainty Relations) and is compared in Table 7 (Discussion)

Table 4: Meiboom-Gill Fitting Parameters and τ_2

	q_i	Δq_i
$A_0[V]$	6.9	0.5
$\tau_2[ms]$	19	1

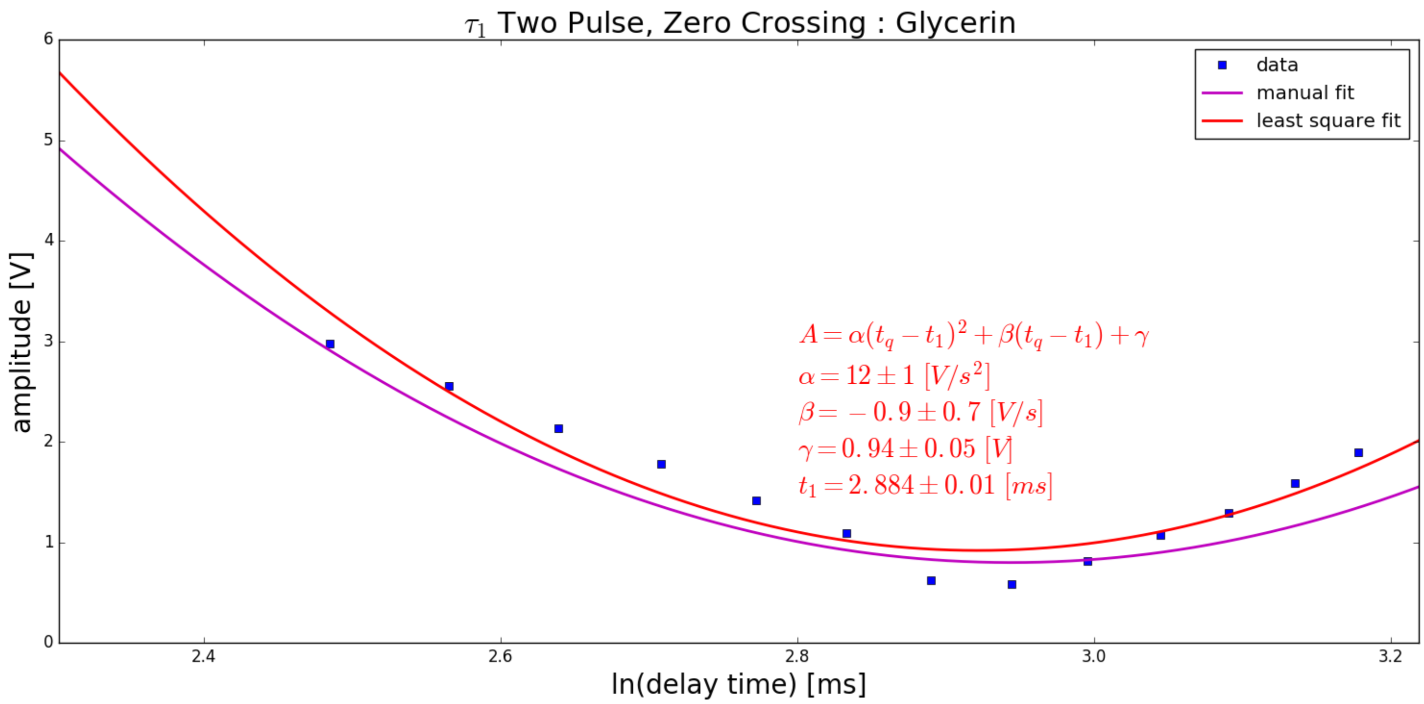

Figure 5: The Two Pulse, Zero crossing experiment in mineral oil is repeated using a sample of Glycerin. After converting the time measurements to natural log, the data is plotted. A manual curve is found using Equation 1 and finding some initial parameters that approximate the data. The manual fit is shown in magenta. Equation 3 is then used again, along with a least squares fitting algorithm, to produce the fitted curve (shown in red). The uncertainty is found by manually adjusting the fitted parameters until a noticeable difference is seen. The parameters and their associated uncertainty are shown in the figure as well as in Table 5 below. The uncertainty for τ_1 found using this method is also included in Table 5 and is compared with an analytical uncertainty for τ_1 in Table 8 (in the Discussion section).

Table 5: Two Pulse, Zero Crossing Fitting Parameters and τ_1 for Glycerin

	q_i	Δq_i
α $[V/ms^2]$	12	1
β $[V/ms]$	-0.9	0.7
A_0 $[V]$	0.94	0.05
$\ln(t_0)$ $[ms]$	2.88	0.01
τ_1 $[ms]$	17.9	0.2

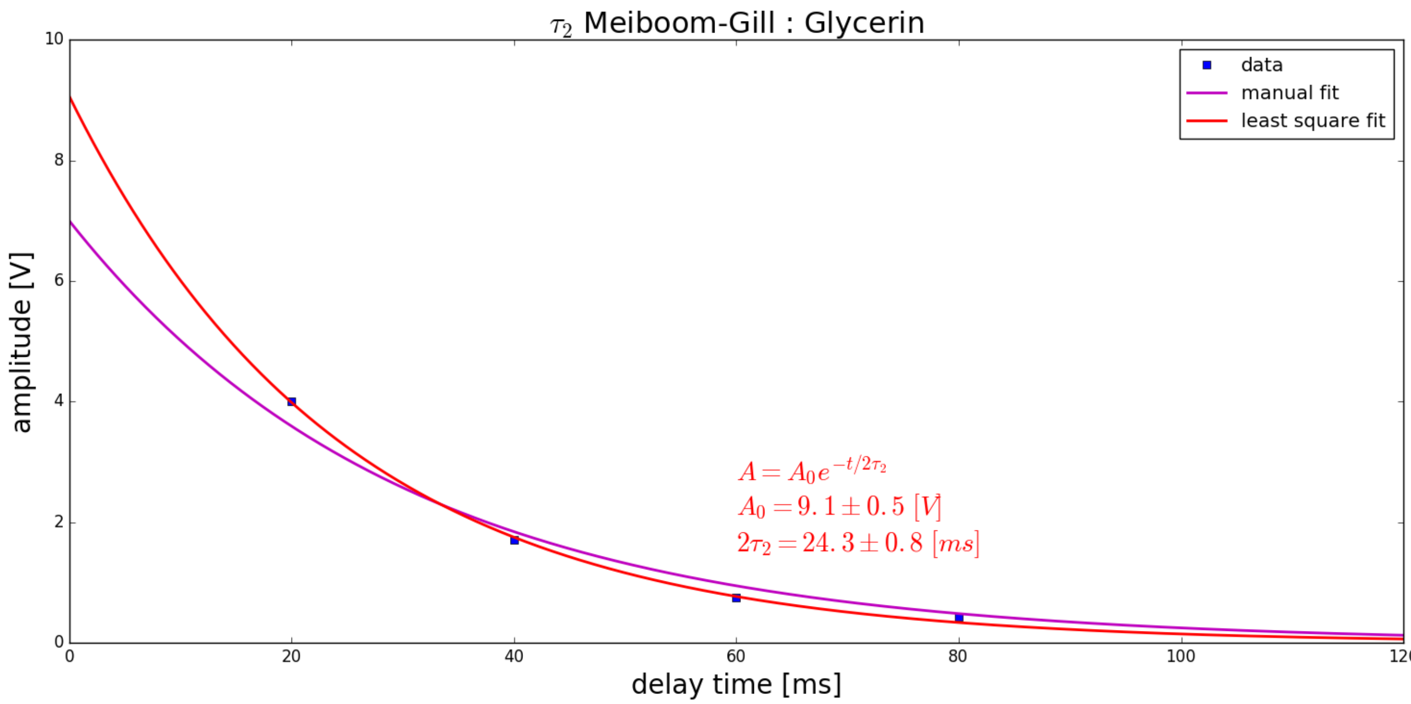

Figure 6: The Meiboom-Gill experiment with mineral oil is repeated using a sample of Glycerin. After the data is plotted (shown in blue), Equation 3 is used, along with some initial parameters that approximate the data, is used to find a manual fit (shown in magenta). A least squares algorithm is then used to find the fitted parameters and the fitted curve is plotted (shown in red). The uncertainty of these parameters is found by slightly varying the fitted parameters until a noticeable difference is seen in the fitted curve. The parameters and their associated uncertainty are shown in Table 6 below. An analytical value for the uncertainty of τ_2 is also found using Equation 6 (Uncertainty Relations) and is compared in Table 8 (Discussion)

Table 6: Meiboom-Gill Fitting Parameters and τ_2 for Glycerin

	q_i	Δq_i
$A_0[V]$	9.1	0.5
$\tau_2[ms]$	12.2	0.4

Discussion:

Table 7: τ_1 and τ_2 for Mineral Oil

	variation method	**analytic method**	**type**
τ_2 $[ms]$			free induction decay, 90^o pulse
τ_1 $[ms]$			spin lattice relaxation, single pulse
τ_1 $[ms]$	16.0 ± 0.3	12.2 ± 0.6	spin lattice relaxation, two pulse-zero crossing
τ_2 $[ms]$	10.3 ± 0.8	10.5 ± 0.5	spin-spin relaxation, two pulse-spin echo
τ_2 $[ms]$	15 ± 1	15 ± 1	spin-spin relaxation, Carr-Purcell
τ_2 $[ms]$	19 ± 1	19 ± 1	spin-spin relaxation, Meiboom-Gill

Table 8: τ_1 and τ_2 for Glycerin

	variation method	**analytic method**	**type**
τ_1 $[ms]$	17.9 ± 0.2	13.6 ± 0.6	spin lattice relaxation, two pulse-zero crossing
τ_2 $[ms]$	12.2 ± 0.4	12 ± 1	spin-spin relaxation, Meiboom-Gill

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),

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

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

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

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)