Diffusion with Pulsed NMR

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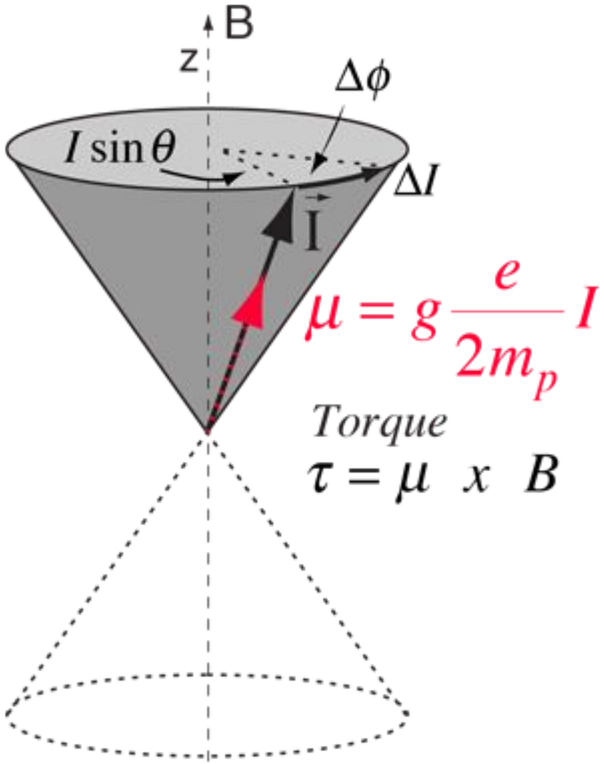
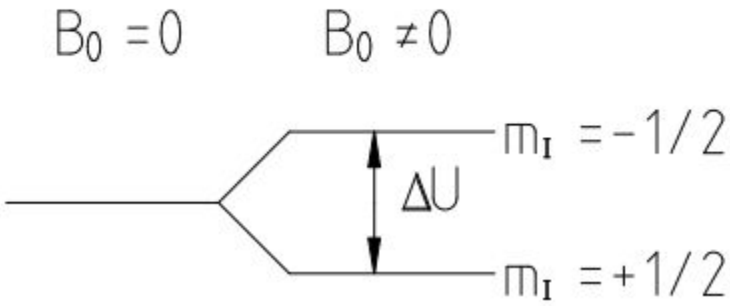
Introduction

- Nuclear Magnetic Resonance (NMR)
  - Place atomic nuclei into background magnetic field B_0
  - Apply circularly polarized perturbation field B_1
  - On resonance, nuclei precess around B_1
- Applications of this phenomenon
  - Magnetic Resonance Imaging (MRI)
  - Material properties
    - Rate of alignment with background magnetic field (T_1)
    - Rate of magnetization decay (T_2)
    - Diffusion coefficient (D) of material
  - Spectroscopy to reveal molecular structure

Protons in B_o





$$\mu_z = \gamma m_I = \pm\gamma\hbar/2$$

$$U = -\boldsymbol{\mu} \cdot \boldsymbol{B}$$

$$\Delta U = \gamma\hbar B_0$$

$$\Delta U = \hbar\omega_0$$

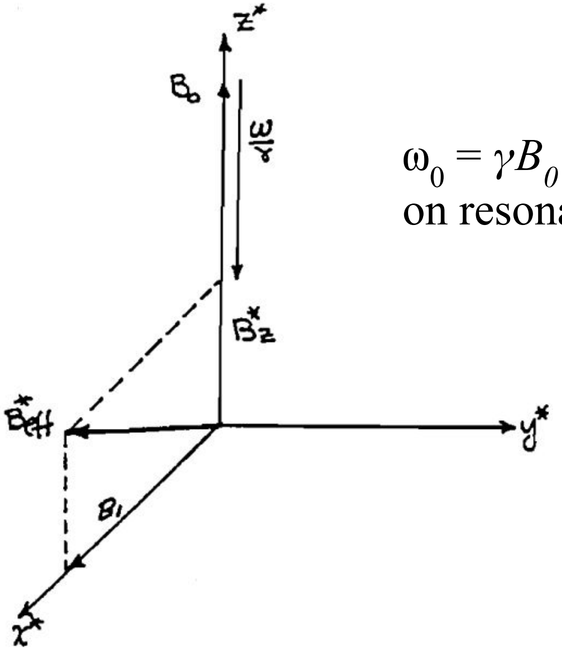
$$\omega_0 = \gamma B_0$$

http://hyperphysics.phy-astr.gsu.edu/hbase/Nuclear/larmor.html

NMR Apply Perturbation Field B_1

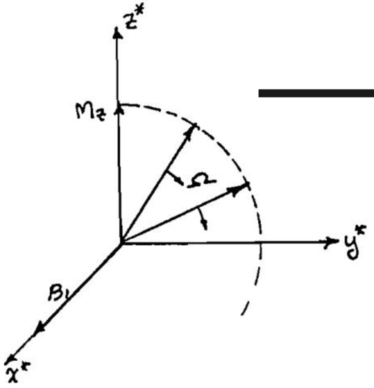
- Perpendicular to B_0
- Circularly polarized
- Oscillating at ω

$$\mathbf{B^*}_{\mathbf{eff}} = B_1\,\hat{\imath}^* + (B_0 - \omega/\gamma)\,\hat{k}^*$$

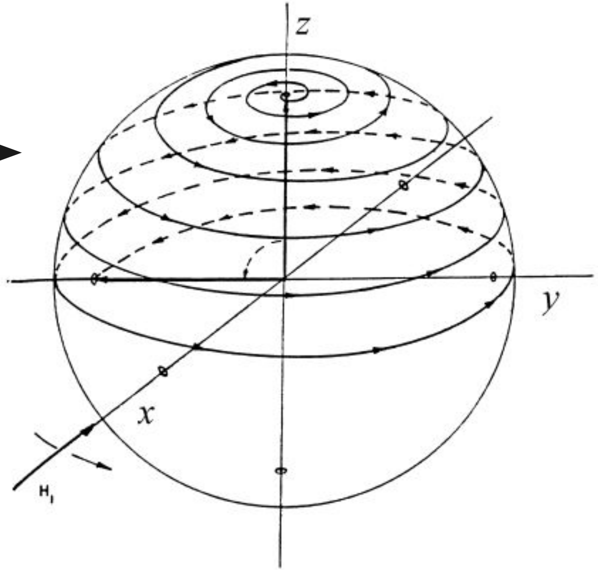


$\omega_0 = \gamma B_0 = \omega$
on resonance

In rotating frame



In stationary frame



$$\pi/2 \text{ pulse} \rightarrow M_z \rightarrow M_{x,y}$$
$$\pi \text{ pulse} \rightarrow M_z \rightarrow -M_z$$
$$2\pi \text{ pulse} \rightarrow M_z \rightarrow M_z$$

Measuring T_2 and D

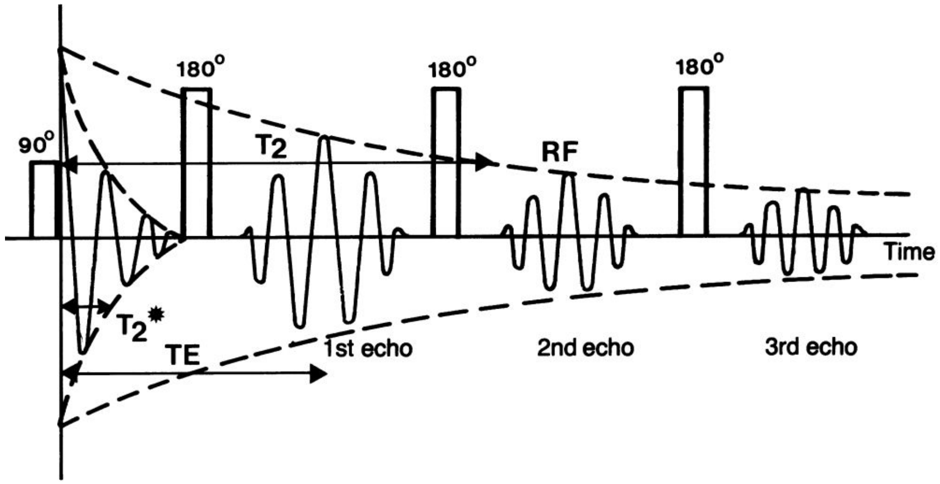
Measuring the decay of spin echoes

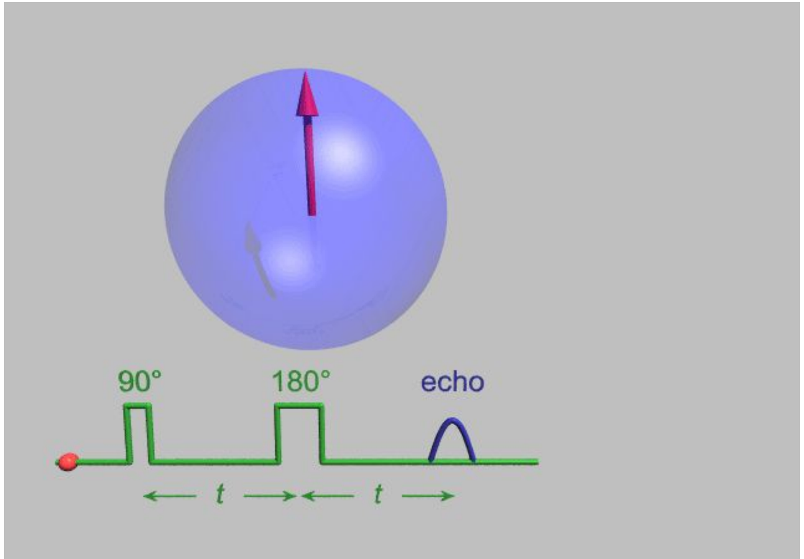
$$M_{x,y}(t) = M_0 e^{-\left(\frac{1}{T_2} - \frac{\gamma^2 (\frac{\partial B_{0,z}}{\partial x,y})^2 D t^2}{12 n^2}\right)t}$$

In rotating frame

Employ the following pulse sequence:

- Flip the spins into the x-y plane with **$\pi/2$ pulse**
- Retain spins in x-y plane with **n** number of **π pulses**



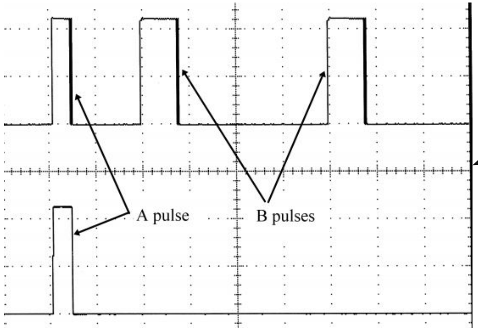


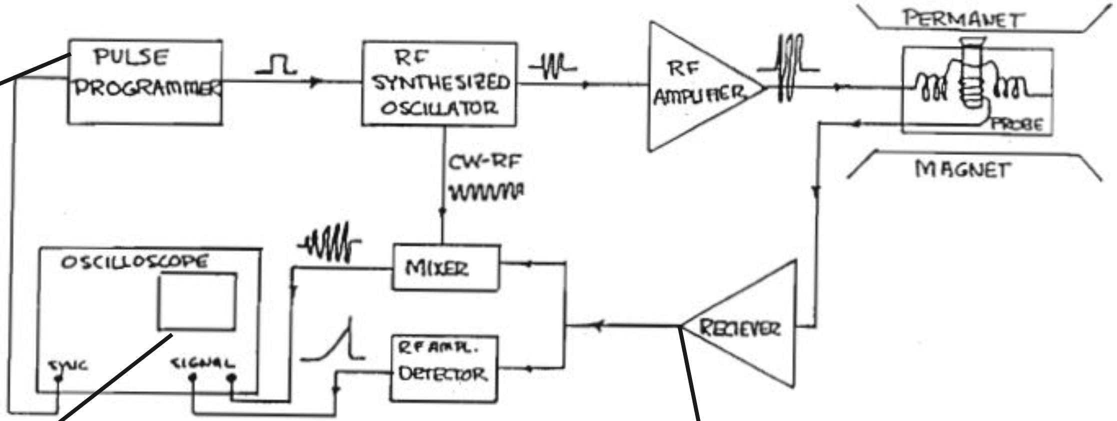
https://en.wikipedia.org/wiki/Spin_echo

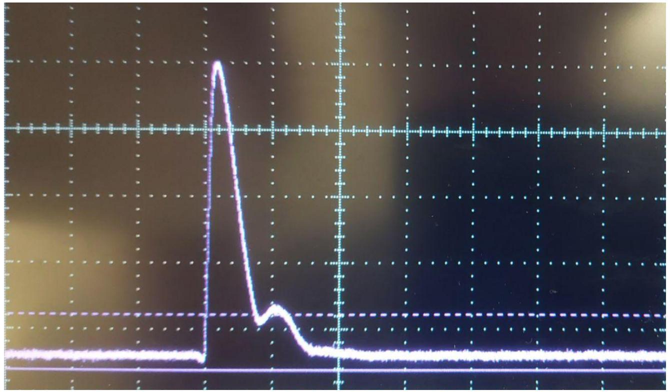
Limitations of Experiment/Apparatus

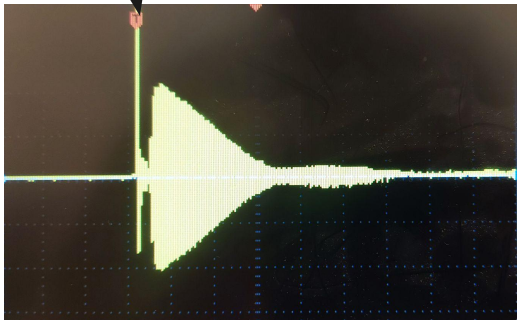
- Highly non-uniform magnetic field
  - Accurate T_2 measurements require suppression of Diffusion term
  - Gradient changes across width of sample
- Apparatus constraints
  - Maximum number of π pulses (99)
  - Limited frequency range of detector coil

Experimental Apparatus







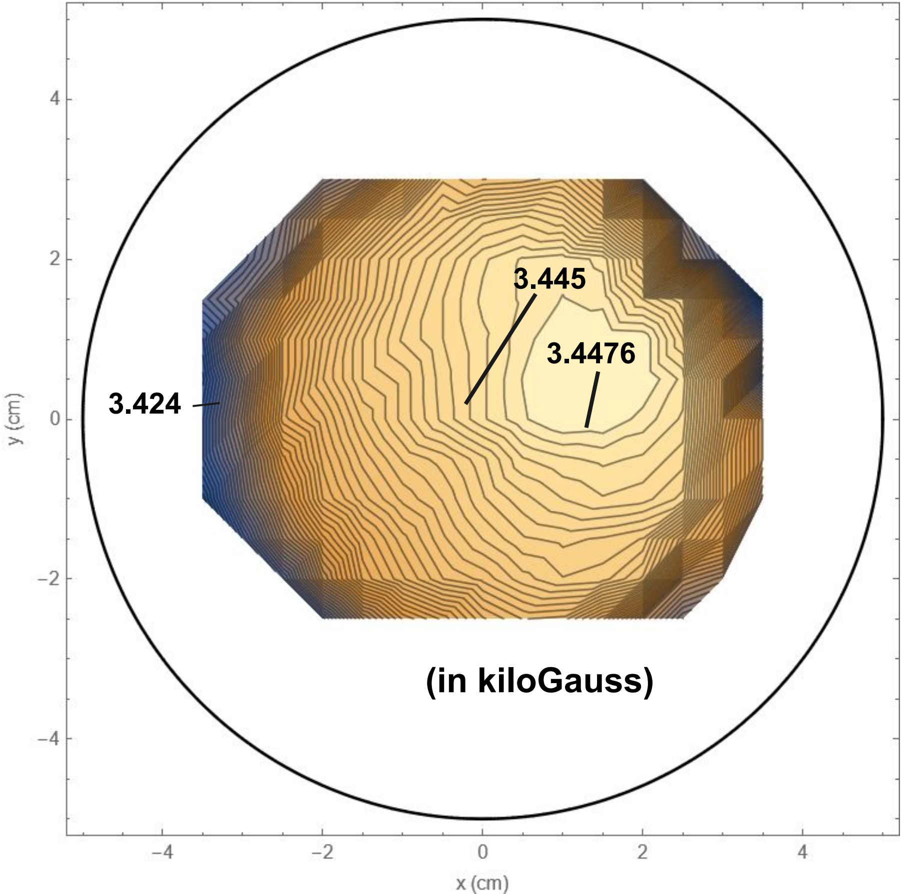


Exploring Permanent Magnet

On resonance: $\omega = \gamma B_0$

- Tune TeachSpin NMR apparatus to this frequency
    - Use this frequency to derive B_0

- What is the utility of this?
    - Identify low-gradient regions
    - Identify regions of near-linear gradient



What does tuning to resonance mean?

Aliased frequency between larmor and applied frequencies

vs.

Aliased frequency approaches 0Hz on resonance

Measuring Decay (T_2)

Measurements made of echo peaks (V)

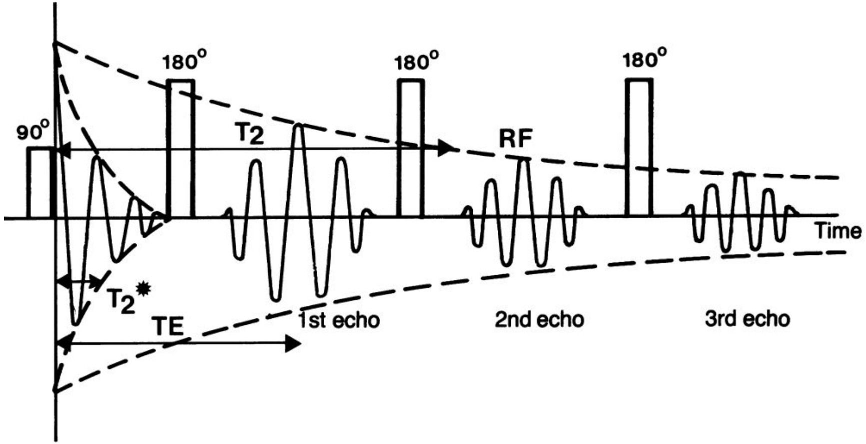
Delay time between peaks gives time (t)

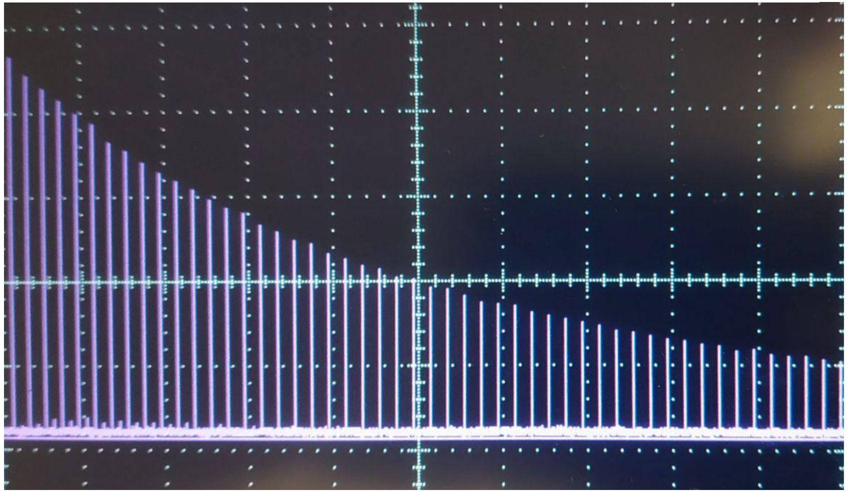
Using a π-pulse sequence with many pulses, we can measure T_2 by assuming:

$$M_{x,y}(t) = M_0 e^{-t/T_2}$$

- Requires that Diffusion is suppressed
  - Low gradient region
  - High density of pulses

$$M_{x,y}(t) = M_0 e^{-(\frac{1}{T_2} - \cancel{\frac{\gamma^2 (\frac{\partial B_{0,z}}{\partial x,y})^2 D t^2}{12 n^2}})t}$$

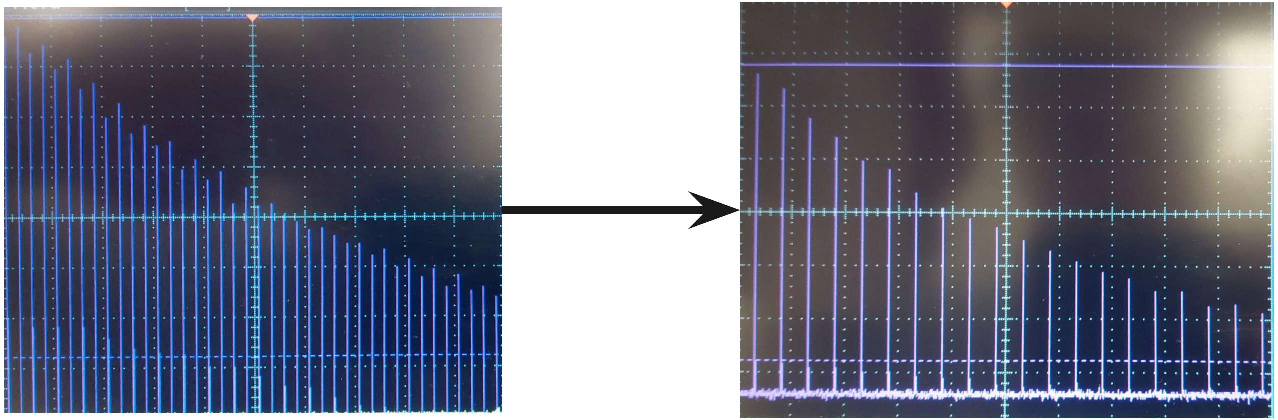




Measuring Diffusion Coefficient (D)

- Similar pulse sequence
  - Fewer π-pulses
  - Larger gradient
- With known T_2 we can fit with D as the only unknown parameter

$$M_{x,y}(t) = M_0 e^{-\left(\frac{1}{T_2} - \frac{\gamma^2 \left(\frac{\partial B_{0,z}}{\partial x,y}\right)^2 D t^2}{12 n^2}\right)t}$$



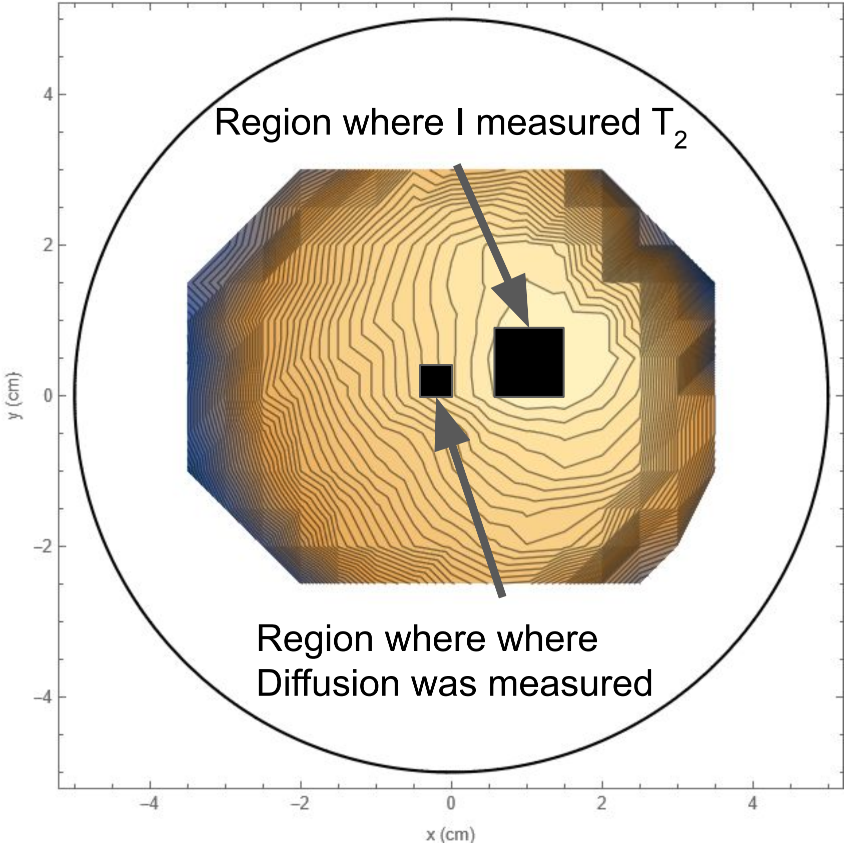
Magnetic Field Gradient Measurement

Assume T_2 measurement region has gradient of 0.

Gradient in diffusion region:

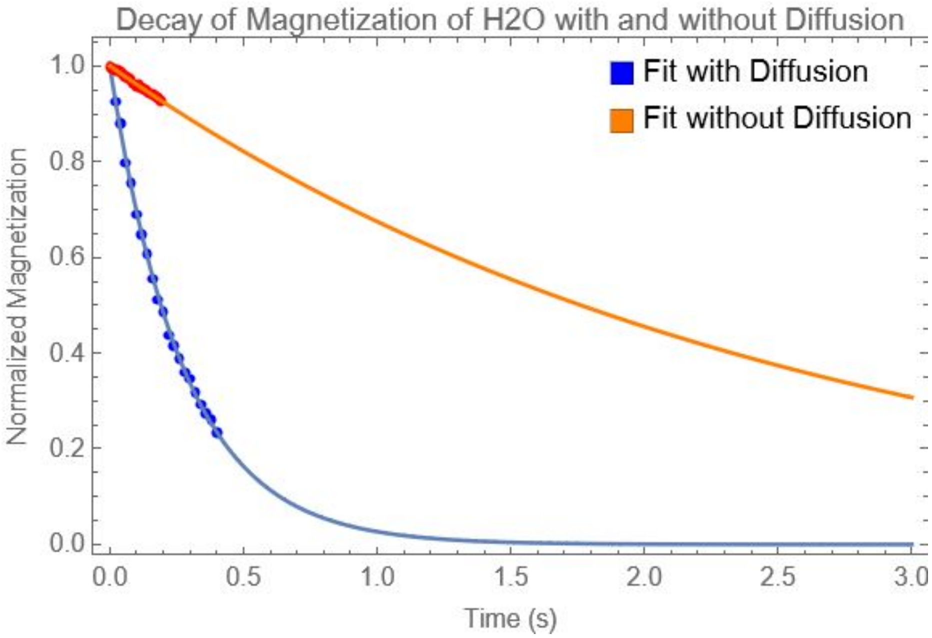
$$\left|\frac{\partial B_{0,z}}{\partial x,y}\right| = 2.6 \pm 0.2\ gauss/cm$$

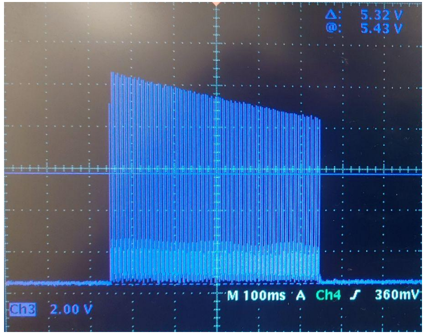
This value is used for all future diffusion measurements



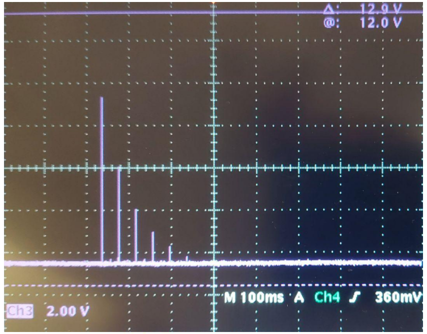
T_2 and D of Water

Water has both a long T_2 and high D





vs.



$$M_{x,y}(t) = M_0 e^{-\left(\frac{1}{T_2} - \frac{\gamma^2 \left(\frac{\partial B_{0,z}}{\partial x,y}\right)^2 D t^2}{12 n^2}\right) t}$$

$T_2 = 2.58 \pm 0.03$ s

D = $(2.0 \pm 0.3) * 10^{-5}$ $cm^2\, s^{-1}$

(at 21℃)

Most of the uncertainty in D comes from uncertainty in the gradient

Substances of Complex Molecules

- Much thicker than water or isopropanol.
  - High viscosity means it is harder for molecules to diffuse through to regions of different magnetic field
- Decays are more complex
  - Biexponential*

$$M_{x,y}(t) = M_0 e^{-t/T_2}$$

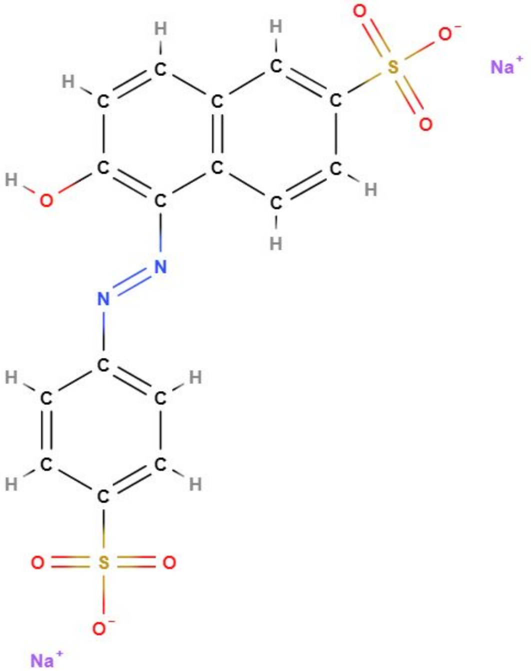
$$\downarrow$$

$$M_{x,y}(t) = M_{0,1} e^{-t/T_{2,1}} + M_{0,2} e^{-t/T_{2,2}}$$

$$where\ M_{0,1} + M_{0,2} = M_0$$

*May be additional terms that are less prevalent

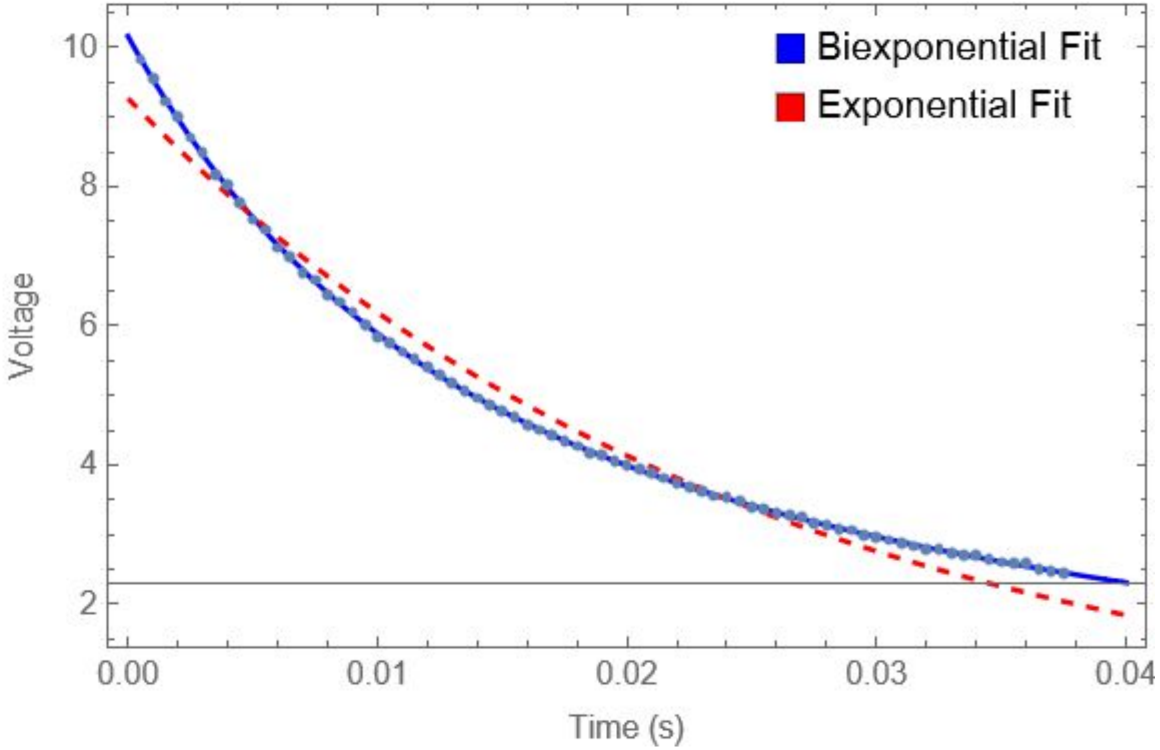
3 in 1 Household Oil



Light Mineral Oil

Mineral Oil T_2 and D

$$M_{x,y}(t) = (M_{0,1}e^{-\frac{t}{T_{2,1}}} + M_{0,2}e^{-\frac{t}{T_{2,2}}})e^{-\frac{\gamma^2(\frac{\partial B_{0,z}}{\partial x,y})^2 D t^3}{12n^2}}$$



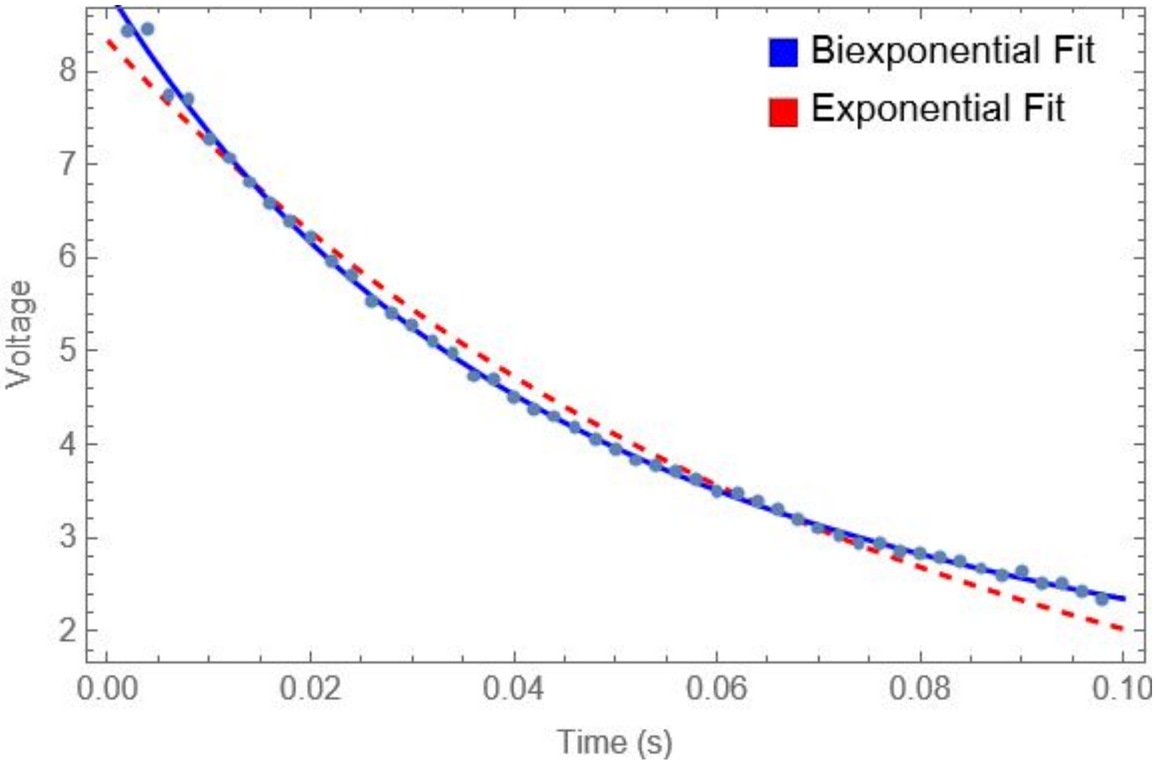
$T_{2,1}$ = 9.4 ± 0.1 ms
$T_{2,2}$ = 49.1 ± 0.5 ms

D = (2.5 ± 0.6) * 10^{-7} $cm^2 s^{-1}$

D is much smaller than that of water.

3 in 1 T_2 and D

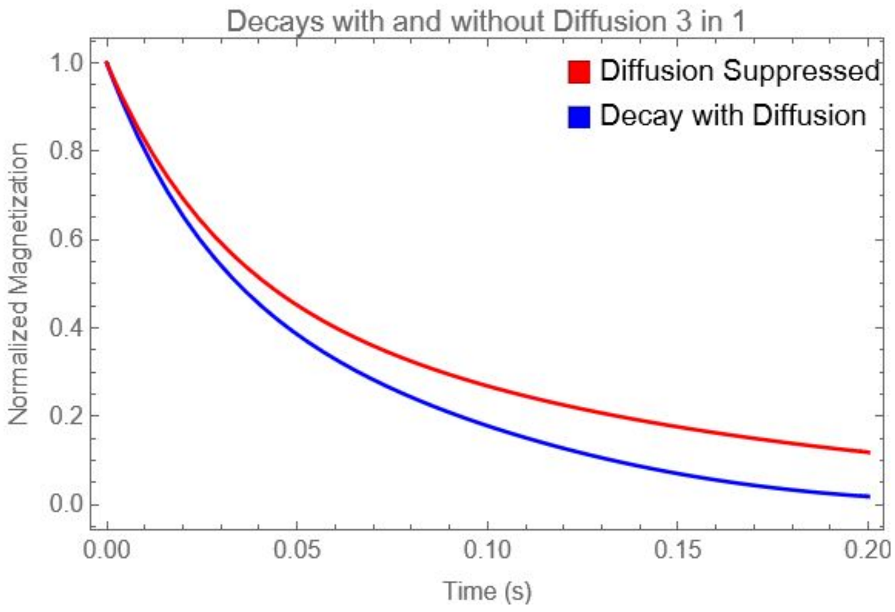
$$M_{x,y}(t) = (M_{0,1}e^{-\frac{t}{T_{2,1}}} + M_{0,2}e^{-\frac{t}{T_{2,2}}})e^{-\frac{\gamma^2(\frac{\partial B_{0,z}}{\partial x,y})^2 D t^3}{12n^2}}$$



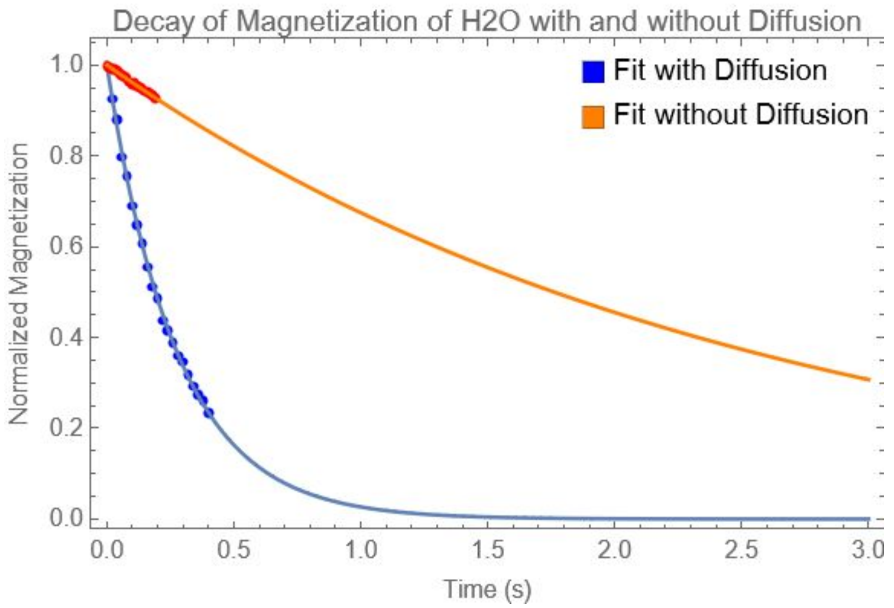
$T_{2,1}$ = 29 ± 1 ms
$T_{2,2}$ = 131 ± 5 ms

D = (4.8 ± 0.8) * 10^{-7} cm^2 s^{-1}

Effect of Diffusion



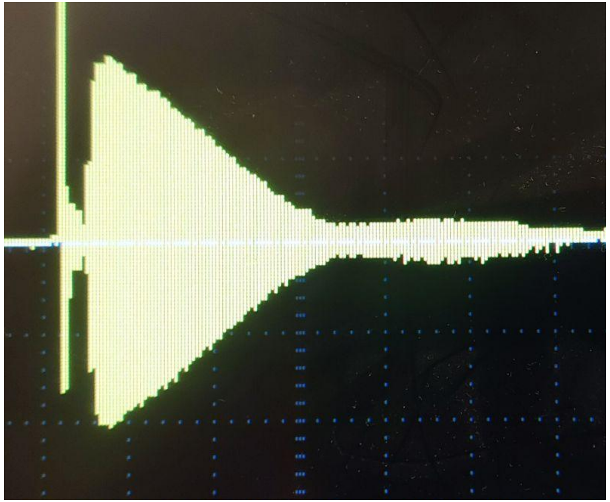
$D = (4.8 \pm 0.8) * 10^{-7}\ cm^2\ s^{-1}$



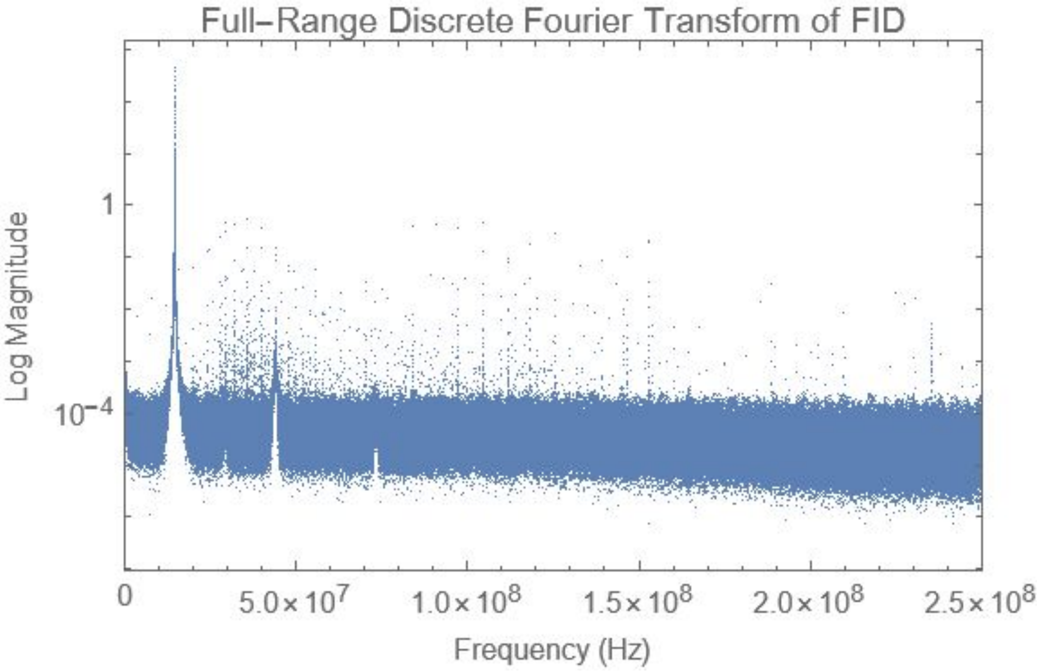
$D = (2.0 \pm 0.3) * 10^{-5}\ cm^2\ s^{-1}$

NMR Spectroscopy on Mineral Oil

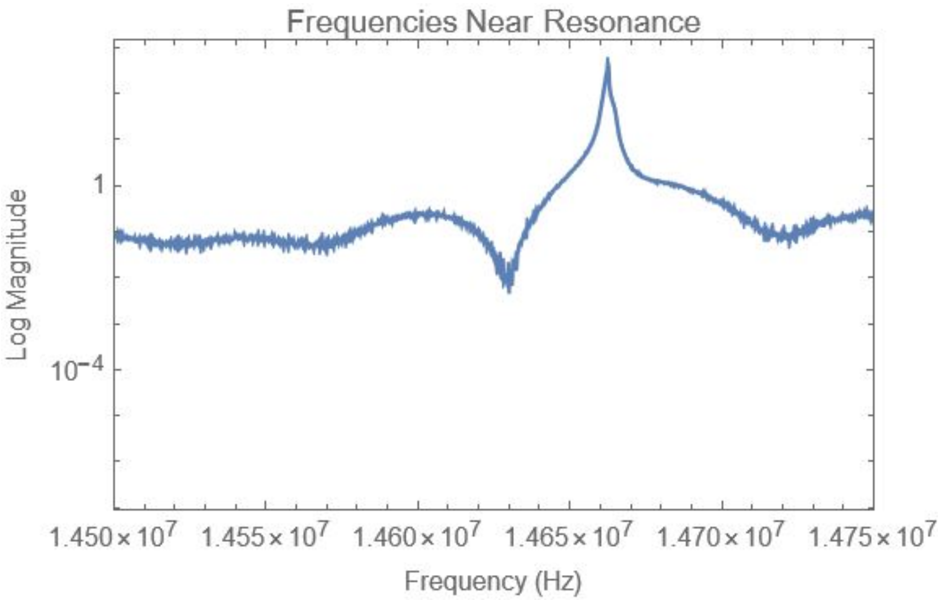
Free-Induction Decay

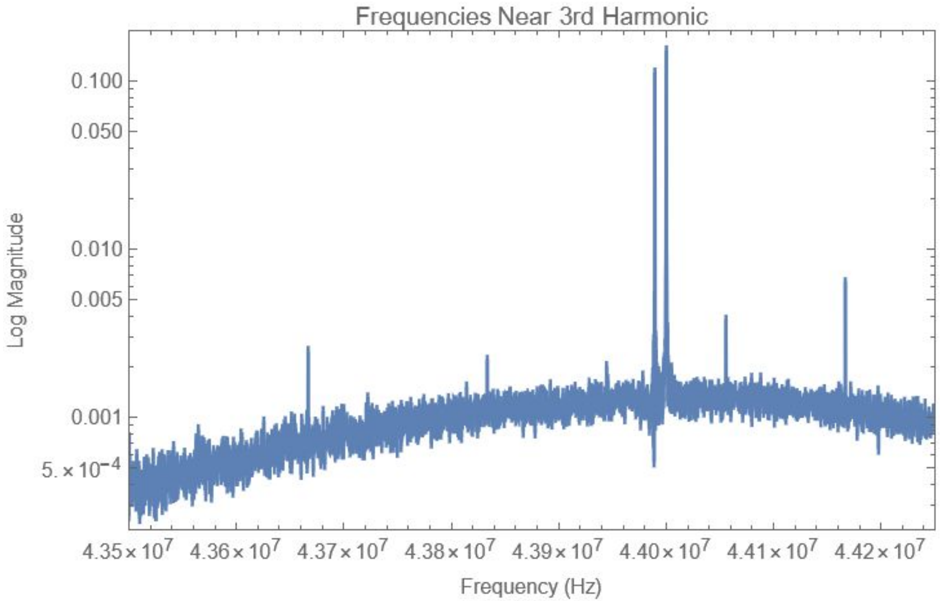


Discrete Fourier Transform



Existence of Distinct Peaks





NMR as a Method of Measuring Diffusion

- From the results of this experiment, we can broadly say that NMR provides an effective means of measuring D
  - D of water was consistent
  - Low D -> less stark effect of diffusion
- Not all protons are the same
  - Need for bi-exponential fit for mineral oil and household oil
  - Local environments change interaction
    - Smaller molecules have longer T_2 from molecular tumbling

Further Work

- Identify exactly which protons in mineral oil contribute to each decay
- Explore broader range of materials
- Refine measurements of T_2 by reducing size of sample and find region of near-zero gradient
- Reduced sample size allows for linear gradient approximation to be more accurate as well
- Isopropanol is complex and may be characterized by more than one T_2
- D changes with temperature