Nuclear Magnetic Resonance

Elijan Mastnak

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1 Tasks

- 1. Find the free precession signal of a sample of water containing paramagnetic ions following a pulses of length $\pi/2$.
- 2. Find the spin echo signal of the paramagnetic water sample following a sequence of pulses of length $\pi/2$ and π , respectively.
- 3. Use the widths of the free precession and spin echo signals for the paramagnetic water sample to find the probe position at which the magnetic field in the sample is most homogeneous. Use the two signal widths to measure T_2^* and estimate the magnetic field's un-homogeneity.
- 4. Use the free precession signal between two pulses of length $\pi/2$ to find the relaxation time T_1 of both the paramagnetic and distilled water.
- 5. Use the dependence of the spin echo signal's height on the time separation τ between two pulses of length $\pi/2$ and π to determine the paramagnetic water's spin-spin relaxation time T_2 .

2 Equipment, Procedure and Data

2.1 Equipment

- Samples of distilled water and water with a mixture of paramagnetic ions (in sealed glass containers)
- Electromagnet with a water-based cooling system and mount to hold the water samples.
- Nuclear magnetic resonance spectrometer, oscilloscope and power supply

2.2 Procedure

- 1. Adjust the current through the electromagnet until the free precession signal appears on the oscilloscope. Once you have a strong free precession signal, change the NMR spectrometer to diode mode and set the pulse type to $\pi/2$.
- 2. Adjust the probe position inside the electromagnet to maximize the free precession signal's duration. Use the width of the free precession signal to estimate the time T_2^* .

3. Part 2: Spin Echo

Change spectrometer setting to SE mode. Set the first pulse to $\pi/2$ and the second pulse to π . Adjust the duration of the second pulse to maximize the spin echo signal. Vary the separation between the first and second pulses using spectrometer time dial and measure the dependence of the spin echo signal amplitude on pulse separation.

4. Part 3: Set the NMR spectrometer to use to $\pi/2$ pulses—set the spectrometer trigger so that the oscilloscope displays the free precession signal after the second $\pi/2$ pulse.

Measure the dependence of the free spin precession signal amplitude on the separation τ between the first and second pulses. Use this data to measure the spin-lattice relaxation time. Expect a roughly millisecond-order value.

5. Part 4: Measuring spin-lattice relaxation time with distilled water.

Set spectrometer REPETITION TIME dial to 10 seconds. (previously was set to 0.3 s). Set the amplification of pulse separation time to 100.

Repeat the measurement from part 3, using the dependence of the free spin precession signal on the separation between the first and second pulses to find the distilled water's spin-lattice relaxation time. Roughly second-order value is expected.

2.3 Data

Independent Variable: Time separation between $\pi/2$ and π pulses (when using the spin echo signal to determine T_2) or time separation between $\pi/2$ and $\pi/2$ pulses (when using the free precession signal to determine T_1).

Dependent Variable: Amplitude of spin-echo signal (when finding T_2) or amplitude of the free precession signal (when finding T_1).

3 Analysis

3.1 Calibrating Dial Position to Time

First, I calibrated the NMR spectrometer's TAU dial position to time for both 1x and 100x amplification. The relationship is linear and shown in Figure 1; the equations

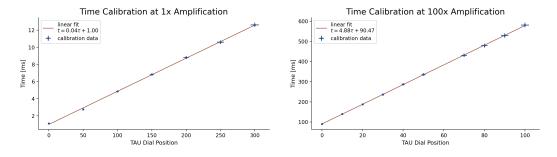


Figure 1: Converting TAU dial position to pulse length at 1x and 100x amplification.

of the best-fit lines are approximately

$$t_{1x}(\tau) = (-0.039 \cdot \tau + 1.003) \text{ms}$$
 and $t_{100x}(\tau) = (-4.88 \cdot \tau + 90.47) \text{ms}$

3.2 Estimating Magnetic Field Non-Homogeneity

Figure 2 show the free precession signal $U_{\rm fp}$ for paramagnetic water at the probe position maximizing magnetic field homogeneity. The signal's full width at half maximum gives an estimate of the non-homogeneous spin-spin decay time T_2^* ; in our case T_2^* is approximately

$$T_2^* \approx \text{FWHM} \left[U_{\text{fp}} \right] \approx 160 \, \mu \text{s}$$

An estimate for the corresponding magnetic field non-homogeneity ΔB_z is

$$\Delta B_z \approx \frac{\pi}{2\gamma T_2^*} = \frac{\pi}{2\cdot 2.675\times 10^8\,{\rm Hz}\,{\rm T}^{-1}\cdot 160\times 10^{-6}\,{\rm s}} \approx 4\,{\rm \mu T}$$

where $\gamma = 2.675 \times 10^8 \, \mathrm{Hz} \, \mathrm{T}^{-1}$ or is the nuclear gyromagnetic ratio.

3.3 Determining Spin-Latice Relaxation Time T_1

We determine the samples; spin-lattice relaxation times T_1 from the dependence of free-precession signal amplitude $U_{\rm fp}$ on the separation τ between the $\pi/2$ pulses applied to the sample. The amplitude should decay with τ as

$$U_{\rm fp} = U_0 \left(1 - e^{-\frac{\tau}{T_1}} \right)$$

where U_0 is the asymptotic value $U_{\rm fp}$ approaches for $\tau \gg T_1$. The above relationship implies plotting the quantity

$$Q_{\mathrm{fp}}(\tau) \equiv -\ln\left(1 - \frac{U_{\mathrm{fp}}}{U_0}\right) = \frac{\tau}{T_1}$$

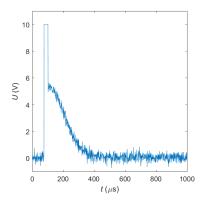


Figure 2: Free precession signal.

on the ordinate axes and pulse separation τ on the abscissa should yield a line whose slope is $\frac{1}{T_1}$. Figures 3 and 4 show the plot of $\mathcal{Q}_{\mathrm{fp}}$ versus τ and the corresponding linear fit used to find T_1 for the paramagnetic and distilled water samples, respectively. I approximate U_0 with the value of U_{fp} at the largest available value of τ .

3.4 Spin-Spin Relaxation Time T_2

We determine the paramagnetic water's spin-spin relaxation time T_2 using the dependence of spin-echo amplitude $U_{\rm se}$ on the separation τ between the $\pi/2$ and π pulses applied to the water sample. $U_{\rm se}$, τ and T_2 are related by

$$U_{\rm se} = U_0 e^{-\frac{2\tau}{T_2}}$$

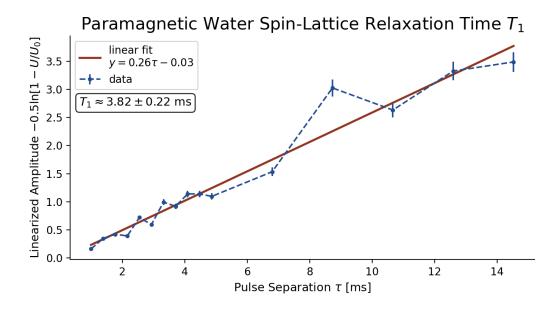


Figure 3: Finding the paramagnetic water's spin-lattice relaxation time T_1 from the linearized free-precession amplitude.

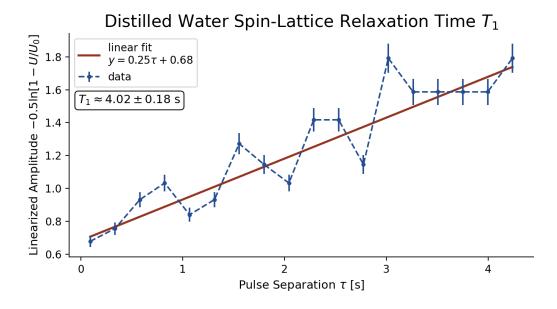


Figure 4: Finding the distilled water's spin-lattice relaxation time T_1 from the linearized free-precession amplitude. Note the distilled water's T_1 is of second order, while the paramagnetic water's T_1 is of millisecond order.

where U_0 is a constant. The above relationship implies plotting the quantity

$$Q_{\rm se}(au) \equiv -\frac{1}{2} \ln U_{\rm se} = \frac{ au}{T_2}$$

on the ordinate axes and pulse separation τ on the abscissa should yield a line whose slope is $\frac{1}{T_2}$. Figure 5 shows the plot of \mathcal{Q}_{se} versus τ and the corresponding linear fit used to find T_2 .

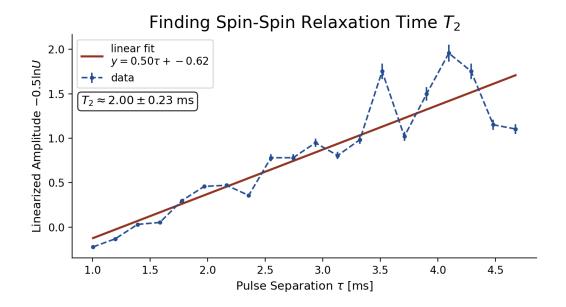


Figure 5: Finding the paramagnetic water's spin-spin time T_2 from the linearized spin-echo amplitude.

4 Error Analysis

4.1 Time Calibration

Pulse time t is found from TAU dial position τ via

$$t_{1x}(\tau) = (-0.039 \cdot \tau + 1.003) \text{ms}$$
 and $t_{100x}(\tau) = (-4.88 \cdot \tau + 90.47) \text{ms}$

Input data is dial position τ ; I assume an uncertainty of one percent for τ . A first-order Taylor approximation gives an estimate for the corresponding uncertainty δt in time:

$$t(\tau + \delta \tau) \approx t(\tau) + \delta \tau \cdot t'(\tau) \implies \delta t \approx |\delta u \cdot t(\tau)|$$

4.2 Spin-Lattice Relaxation Time T_1

Spin-lattice relaxation time T_1 is found by plotting the quantity

$$Q_{\rm fp} = -\ln\left(1 - \frac{U_{\rm fp}}{U_0}\right)$$

versus pulse duration τ . The input quantities are the free precession signal amplitude $U_{\rm fp}$ and the value of asymptotic approach U_0 . Since uncertainties are not given with the simulated data, I assumed both quantities carry an uncertainty of one percent. The sensitivity coefficients are

$$c_{\mathrm{fp}} = \frac{\partial \mathcal{Q}}{\partial U_{\mathrm{fp}}} = \frac{U_0 - 1}{U_0 - U_{\mathrm{fp}}}$$
 and $c_0 = \frac{\partial \mathcal{Q}}{\partial U_0} = \frac{U_0^2 - U_{\mathrm{fp}}}{U_0(U_0 - U_{\mathrm{fp}})}$

and the corresponding error in Q_{fp} is

$$\delta_{\mathrm{Q}} = \sqrt{(c_{\mathrm{fp}}\delta_{\mathrm{fp}})^2 + (c_0\delta_0)^2}$$

I use the error in \mathcal{Q} , together with linear regression software, to find the error $\delta \mathcal{S}$ in the slopes \mathcal{S} of the best-fit lines in Figures 3 and 4. I calculate T_1 using

$$T_1 = \frac{1}{\mathcal{S}},$$

from which I use a first order Taylor approximation to estimate the error in T_1 via

$$\delta T_1 \approx \left| \delta S \cdot T_1'(\mathcal{S}) \right| = \frac{\delta \mathcal{S}}{\mathcal{S}^2}$$

4.3 Spin-Lattice Relaxation Time T_1

Spin-spin relaxation time T_2 is found by plotting the quantity

$$Q_{\rm se} = -\frac{1}{2} \ln U_{\rm se}$$

versus pulse duration τ . The input quantity is the spin echo signal amplitude $U_{\rm se}$. Since no uncertainty is given with the simulated data, I assumed $U_{\rm se}$ carries an uncertainty of one percent. A first-order Taylor approximation of the error in $\mathcal{Q}_{\rm se}$ is

$$\delta_{\mathrm{Q}} pprox \delta U_{\mathrm{se}} \cdot \mathcal{Q}_{\mathrm{se}}'(U_{\mathrm{se}}) = rac{\delta U_{\mathrm{se}}}{2U_{\mathrm{se}}}$$

I use the error in \mathcal{Q} , together with linear regression software, to find the error $\delta \mathcal{S}$ in the slopes \mathcal{S} of the best-fit line in Figure 5. I calculate spin-spin relaxation time T_2 using

$$T_2 = \frac{1}{\mathcal{S}},$$

from which I use a first order Taylor approximation to estimate the error in T_2 via

$$\delta T_2 \approx \left| \delta S \cdot T_2'(\mathcal{S}) \right| = \frac{\delta \mathcal{S}}{\mathcal{S}^2}$$

5 Results

I estimated paramagnetic water's non-homogeneous spin-spin relaxation time T_2^* as

$$T_2^* \approx 160 \, \mu \mathrm{s}$$

I estimated the magnetic field's non-homogeneity ΔB_z inside the paramagnetic water sample as

$$\Delta B_z \approx 4 \, \mu \mathrm{T}$$

The spin-lattice relaxation times of the paramagnetic and distilled water samples, respectively, were

$$T_{1_{\rm p}} = (3.8 \pm 0.2) \,\mathrm{ms}$$
 and $T_{1_{\rm d}} = (4.0 \pm 0.2) \,\mathrm{s}$

Note the difference of three orders of magnitude between the two quantities. Finally, the paramagnetic water's spin-spin relaxation time T_2 was

$$T_2 = (2.0 \pm 0.2) \,\mathrm{ms}$$

A Plots of Spin Echo Data and Free Precession Data

For the sake of completeness, Figures 6 and 7 shows the raw (non-linearized) dependence of the water samples' spin echo and free precession signal amplitude on the separation τ between pulse application.

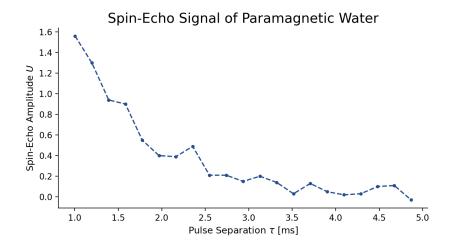
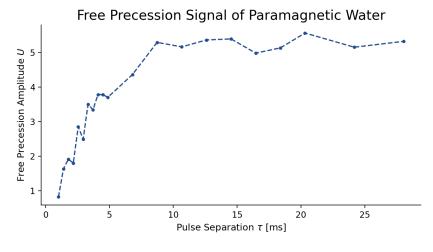


Figure 6: Raw dependence of the paramagnetic water's spin-echo signal amplitude on separation τ between application of $\pi/2$ and π pulses. This data is linearized and used in Figure 5 to find the sample's spin-spin relaxation time T_2 .



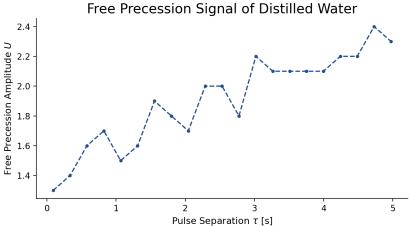


Figure 7: The paramagnetic (top) and distilled water (bottom) samples' free precession signal amplitude on the separation τ between application of $\pi/2$ pulses. This data is linearized and used in Figures 3 and 4 to find the sample's spin-lattice relaxation time T_1 .

B Background Theory

Numerical Value

- The proportionality between nuclear angular momentum and magnetic moment is $\gamma=2.675\times10^8\,{\rm Hz\,T^{-1}}$ or $\frac{\gamma}{2\pi}=42.576\,{\rm MHz\,T^{-1}}$
- Nucleus with spin S and magnetic moment μ related by

$$\mu = \gamma S$$

where γ is the gyromagnetic ratio.

• In an external magnetic field B_0 we have the torque

$$\tau = \mu \times B_0 = \gamma S \times B_0$$

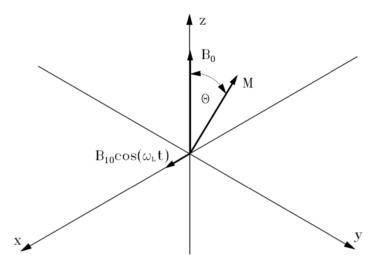


Figure 8: Sketch of the static magnetic field B_0 and pulsed magnetic field B_1 in the lab coordinate system xyz.

from which we get

$$\frac{\mathrm{d}\boldsymbol{S}}{\mathrm{d}t} \equiv \boldsymbol{\tau} = \gamma \boldsymbol{S} \times \boldsymbol{B}_0$$

The change in angular momentum is perpendicular to both the angular velocity and magnetic field, so the nuclear spin (and thus the parallel magnetic moment) precesses about the magnetic field. The precession frequency is the Larmor frequency

$$\omega_L = \gamma B_0$$

• Place a substance with nonzero nuclear spins and magnetic moments in a field $\mathbf{B}_0 = (0, 0, B_0)$. The magnetic moment per unit volume is called volume magnetization \mathbf{M}

$$M = \frac{1}{V} \sum_{i} \mu_{i} \implies \frac{\mathrm{d}M}{\mathrm{d}t} = \gamma M \times B_{0}$$

Lesson: magnetization also precesses about the external magnetic field with the Larmor frequency as long as M and B_0 are not parallel. At equilibrium, though, M and B_0 are parallel.

B.1 Effect of a Pulsed Second Field

- For a short time T we turn on a second magnetic field \mathbf{B}_1 , which points in the x direction, perpendicular to the static external field \mathbf{B}_0 and oscillates at the Larmor frequency $\omega_L = \gamma B_0$.
- Introduce angle θ between magnetization M and static external field B_0 . When B_1 is turned on, θ increases, M and B_0 are no longer parallel, and M begins to precess about B_0 .
- The size of θ depends amplitude and duration of B_1 . We consider such combinations of amplitude B_1 and duration T such that θ changes by π or $\pi/2$.

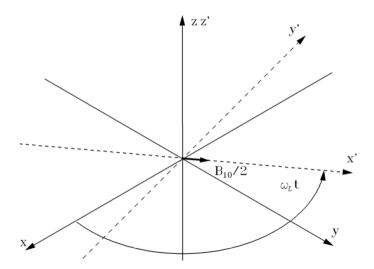


Figure 9: The rotating coordinate system best suited to analyzing the NMR experiment.

• Transition from laboratory coordinate system to a system rotating about the magnetic field at the Larmor frequency; the z' axis of the rotating system points in the direction of \mathbf{B}_0 and $\hat{\mathbf{z}}$. The new coordinates are

$$x' = x \cos \omega_L t + y \sin \omega_L t$$

$$y' = y \cos \omega_L t - x \sin \omega_L t$$

$$z' = z$$

ullet In the lab system write linearly polarized radio-frequency magnetic field is a sum of two circularly polarized components. We write the oscillating field $oldsymbol{B}_1$ as

$$\boldsymbol{B}_1 = B_1(\cos\omega_L t, 0, 0) = \frac{B_1}{2} \left(\cos\omega_L t, \sin\omega_L t, 0\right) + \frac{B_1}{2} \left(\cos\omega_L t, -\sin\omega_L t, 0\right)$$

The first component rotates with the rotating system, and appears as a static field pointing in the x' axis in the rotating system. In the rotating system, the second component rotates about the z' axis at frequency $2\omega_L$.

The second component does not contribute appreciably to the direction of M because of its large frequency $2\omega_L$. The first component causes precession of M about the x' axis.

In the rotating system, magnetization makes an angle θ with the z' axis but does not precess about \hat{z}' , since the system itself rotates at the Larmor frequency. In effect, the original external static field B_0 does not contribute in the rotating coordinate system—it is "built in" to the rotating system because of the system's rotation at the Larmor frequency.

• The $\pi/2$ pulse shifts the magnetization direction from z' (equilibrium position) to y', after which the rotating system's magnetic moment does not experience an external field.

• Introduce a spherical coordinate system. Write the direction of μ with the azimuthal angle ϕ_i and polar angle θ_i .

After a $\pi/2$ pulse, the magnetic moments of individual nuclei spread across the azimuthal angle ϕ_i faster than θ_i returns to zero (corresponding to μ_i aligning with \hat{z}').

Because of the faster spread of μ_i about the azimuthal angle, the projection of the substance's magnetization M onto the x'y' plane exponentially decays with decay constant T_2 , called the *spin-spin relaxation time*.

Meanwhile, the projection of μ_i onto \hat{z}' after a disturbance grows with characteristic time T_1 , called the *spin-lattice relaxation time*. We have

$$M_{z'} = M \left(1 - e^{-t/T_1} \right)$$

B.2 Spin System in a Non-Homogeneous Magnetic Field

• Assume the external field B_0 is non-homogeneous and takes the form

$$\boldsymbol{B}_0(\boldsymbol{r}) = (0, 0, B_z(\boldsymbol{r}))$$

Define the generalized Larmor frequency $\omega_L = \gamma \langle B_z \rangle$.

Remain in the coordinate system rotating about the \hat{z} axis. A given nuclear magnetic moment now feels two interactions: the usual internal magnetic interactions and an additional interaction due to the difference between the magnetic field at the nucleus's position and the average magnetic field $\langle B_z \rangle$. The average magnetic field $\langle B_z \rangle$ is "built in" to the rotating system and doesn't affect the magnetic moments, just like for the previously homogeneous B_0 .

• The difference in magnetic field at at the *i*th nucleus is

$$\Delta B_z(\mathbf{r}_i) = B_z(\mathbf{r}_i) - \langle B_z \rangle$$

These difference at each nucleon cause the individual nuclear magnetic moments to precess the z' axis with different frequencies and in different directions.

Because of this additional precession of the individual magnetic moments, the total magnetization is even more randomly distributed in the x'y' plane about the azimuthal angle than for a homogeneous field.

• In a non-homogeneous external field, the projection of magnetization onto the x'y' plane no longer falls exponentially with characteristic time T_2 , but with a more complicated characteristic that depends on T_2 , the magnetic field's non-homogeneity, and the shape of the sample. We denote the new characteristic decay time by T_2^* .

In practice, non-homogeneity makes it impossible to directly measure T_2 from the time dependence of the free precession signal, which is proportional to the projection of magnetization onto the x'y' plane.

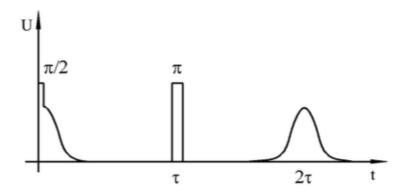


Figure 10: Signals used to measure the relaxation time T_2 . The leftmost signal is a $\pi/2$ pulse followed immediately by the free precession signal, the middle signal is a π pulse, and the rightmost signal is the spin echo signal.

• Let ΔB_z be the average of $\Delta B_z(r_i)$ over all nuclei in the sample. Assume $T_2 \gg T_2^*$, meaning magnetization scatters about ϕ largely because of magnetic field non-homogeneity.

Magnetization in the x'y' plane disappears when the average μ_i is perpendicular to the y' direction (recall y' is the direction of M just after a $\pi/2$ pulse). Magnetic moment μ is perpendicular to y' when μ rotates through an angle $\approx \frac{\pi}{2}$ in the x'y' plane about the z' axis. We have:

$$\omega_z T_2^* = \gamma \Delta B_z T_2^* \approx \frac{\pi}{2} \implies T_2^* \sim \frac{1}{\gamma \Delta B_z}$$

• To find T_2 , we want to eliminate the spread of M about the angle ϕ .

Consider an individual magnetic moment μ_i in a non-homogeneous external field. Just after a $\pi/2$ pulse, μ_i points along y' and then precesses about z' with frequency $\omega_i = \gamma \Delta B_z(\mathbf{r}_i)$. The μ_i rotates by $\phi_i(\tau) = \omega_i \tau$ in the time τ .

A π pulse turns the sample's magnetic moments by an angle π about the x' axis. This rotation about the x' axis by π maps $\phi_i(\tau)$ to $\pi - \phi_i(\tau)$.

Process: Apply a $\pi/2$ pulse. After time τ , after which a given μ_i rotates by $\phi_i(\tau)$, apply a π pulse. At time τ after the π pulse (a time 2τ after the initial $\pi/2$ pulse) the magnetic moments point in the direction -y'.

This rotation of nuclear magnetic moments to -y' generates the so-called *spin-echo signal*.

• The application of the π pulse after the initial $\pi/2$ eliminates the spread of magnetization in the x'y' plane due to the non-homogeneity of the external field.

It does not eliminate the spread of M due to internal field interactions, which exist even in a homogeneous magnetic field. This spread causes the spin-echo signal to fall as e^{-t/T_2}

- The width of the spin-echo signal depends on how quickly the individual nuclear magnetic moments align in the -y' direction after a π pulse, which in turn depends on the non-homogeneity of the external magnetic field—the less homogeneous the magnetic field, the faster the μ_i rotate in the x'y' plane, and the faster the μ_i return to -y'.
- A π pulse effectively reverses the direction of nuclear magnetic moment precession. This means the alignment of nuclear magnetic moments in the y' direction corresponds to a time-reversed scattering of magnetic moments in the x'y' plane. To construct the spin echo signal, combine two free precession signals, where the first is reverse in time via $t \to -t$.

Assuming $T_2 \gg T_2^*$, the width of the spin-echo signal is then $2T_2^*$.

C My Notes

Summary of What Happens

- Nuclear angular momentum, nuclear magnetic moment and a substance's magnetization precess about the static external magnetic field B_0 . Angle between M and B_0 is θ ; M points along B_0 in equilibrium.
- Turn on a pulsed field B_1 in the x direction and oscillating at the Larmor frequency. Increase angle θ between M and B_0 to some nonzero value, and M begins precessing about B_0 .

We choose pulses so that θ changes to $\pi/2$ or π .

- Transition to coordinate system rotating about \hat{z} at Larmor frequency; remain in this system for the rest of the report.
- A $\pi/2$ pulse shifts M from \hat{z}' to \hat{y}' . After a $\pi/2$ pulse, the magnetic moments of individual nuclei spread across the azimuthal angle ϕ_i faster than θ_i returns to zero (corresponding to μ_i aligning with \hat{z}').

Non-Homogeneous Field

- Remain in rotating coordinate system. Each μ_i now feels an interaction because of difference between local and average magnetic field. This causes additional distribution of the μ_i about the x'y' plane.
- Assume $T_2 \gg T_2^*$, meaning scattering of μ_i about ϕ is largely due to magnetic field non-homogeneity.
- Process: Apply a $\pi/2$ pulse, causing the μ_i to point along y'. After time τ , after which a given μ_i rotates by $\phi_i(\tau)$ in the x'y' plane, apply a π pulse, shifting μ_i from $\phi_i(\tau)$ to $\pi \phi_i(\tau)$. At time τ after the π pulse (a time 2τ after the initial $\pi/2$ pulse), μ_i has rotated by another $\phi_i(\tau)$, makes an angle π with y', and thus points in the direction -y'.

Glossary

• Spin-lattice relaxation time T_1 : characterizes the increasing projection of magnetization M onto the z' axis after a disturbance as θ approaches zero, which obeys

$$M_{z'} = M\left(1 - e^{-\frac{t}{T_1}}\right)$$

- Free precession signal: proportional to the projection of magnetization M onto the x'y' plane, which (in a homogeneous magnetic field only) falls exponentially with characteristic time T_2 .
- Spin-spin relaxation time T_2 : characterizes the exponentially decaying projection of M onto the x'y' plane after a $\pi/2$ pulse as θ approaches zero. Result of spreading μ_i about the x'y' plane.
- Spin-spin relaxation time T_2^* : Generalization of T_2 in a non-homogeneous field, where decay is no longer exponential. We assume $T_2^* \ll T_2$.
- Spin echo signal: Corresponds to rotation of nuclear magnetic moments to -y' for a $\pi/2$ pulse followed by a π pulse. Spin-echo signal decreases with time as

$$S \sim S_0 e^{-\frac{2\tau}{T_2}}$$

where τ is the time interval between the $\pi/2$ and π pulses.

• A π pulse effectively reverses the direction of nuclear magnetic moment precession. This means the alignment of nuclear magnetic moments in the y' and -y' directions corresponds to a time-reversed scattering of magnetic moments in the x'y' plane. To construct the spin echo signal, we combine combine two free precession signals, where the first signal is reversed in time via $t \to -t$.