TeachSpin's Pulsed NMR
A Conceptual Introduction to the Experiment

Many nuclei, but not all, possess both a magnetic moment, μ, and an angular momentum, L. Such particles are said to have spin. When the angular momentum and magnetic moment are collinear, as they are in protons (hydrogen nuclei) and fluorine nuclei, both the particle and its surroundings can be investigated using various techniques of Nuclear Magnetic Resonance Spectroscopy. For these particles, the quantity μ/L, defined as the gyromagnetic ratio, is an important signature by which the particle can be identified and its behavior predicted or interpreted.

For our "tour" we will consider a specific collection of these magnetic nuclei, the protons in a liquid mineral oil sample. In the absence of a magnetic field, the spin axes of these particles are randomly oriented; there is no **net magnetization, M**, of the sample. We will begin our NMR experiment by placing our sample into a magnetic field, $\mathbf{B_0}$. For PS2-A this is the field of our permanent magnet. There is *no instantaneous* net magnetization. In time, however, a net magnetization does develop which is collinear with the direction of our B_0 field. This is the **thermal-equilibrium condition**. The time constant for the build-up of this **net magnetization, M**, which is almost always exponential, is called the **spin-lattice relaxation time, T_1**. (For certain kinds of MRI, the "image" is nothing more than a grayscale map of the T_1 for the tissue.)

We'll begin our discussion of TeachSpin's Pulsed NMR with the probe head tuned to investigate protons and our proton containing mineral oil sample already located in the field of the magnet and the net magnetization of the spins already in the thermal equilibrium condition.

Figure 1 shows a side view sketch of the basic system. The sample sits in the **Sample coil**, a tightly wound solenoid which has its axis perpendicular to the constant magnetic field, $\mathbf{B_0}$, of the permanent magnet. This coil serves **two** purposes. In the role of **transmitter coil,** it supplies an oscillating RF (radio frequency) field which can change the orientation of the net magnetization. In the vernacular, we say that the RF pulse "tips the spins" away from the $\mathbf{B_0}$ direction. After such an RF pulse, the net magnetization vector will then freely precess around $\mathbf{B_0}$. Once the spins have been tipped, the solenoid switches roles to become a **pickup coil** "sensing" the precession of any component of the magnetization which is in x-y plane. This three-dimensional process is easier to understand with some diagrams.

Figure 1 is a very simplified schematic. Figure 2, shows the relative directions of the magnetic fields we are discussing. The cylinder represents the solenoid/sample coil. The dark arrows represent the field, $\mathbf{B_0}$, created by the permanent magnet. The thermal equilibrium magnetization of the protons is represented by the thinner arrow labeled $\mathbf{M_0}$. The dashed double ended arrow, $\mathbf{B_1}$, shows the direction of the oscillating RF field used to tip the spins

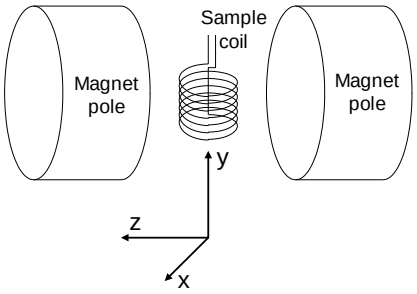

Figure 1 – Artist Sketch of Basic System

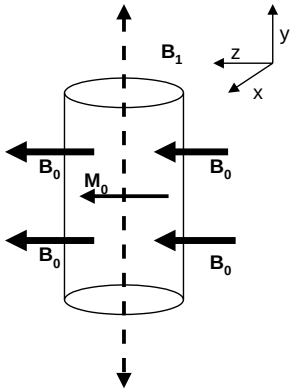

Figure 2 – Vector Fields

The duration of a short burst of the RF field, (a pulse) can be adjusted to cause the magnetization **M** to rotate into the x-y plane. For the pulsed experiments we will be describing, it is important that the frequency of the oscillating RF matches the **Larmor frequency**, the frequency at which protons precess around $\mathbf{B_0}$. In this "on resonance" condition, if a pulse lasting some time t tips the spins into the x-y plane, a pulse lasting twice as long, 2t, will tip the spins until the net magnetization is pointing in a direction, opposite to $\mathbf{B_0}$. In NMR jargon, these are referred to as 90° and 180° pulses. (TeachSpin's Magnetic Torque apparatus provides a hands-on classical analog for this spin-flip mechanism.)

Figure 3a is a top view of the sample before and after a 90° pulse. In this view, the oscillating RF field $\mathbf{B_1}$ is directed perpendicular to the page. The gray line labeled $\mathbf{M_0}$ represents the initial thermal equilibrium magnetization of the spins parallel to $\mathbf{B_0}$. The vector $\mathbf{M_T}$ represents the net magnetization of the sample the instant that the 90° RF pulse has ended. The net magnetization has been rotated into the x-y plane and will now precess, as shown in Figure 3b. This "free" precession creates an alternating emf in the solenoid surrounding the sample. This is clearly a non-equilibrium or transient condition. The rate at which the amplitude of the free precession signal diminishes, and the causes for that decrease, will be discussed later.

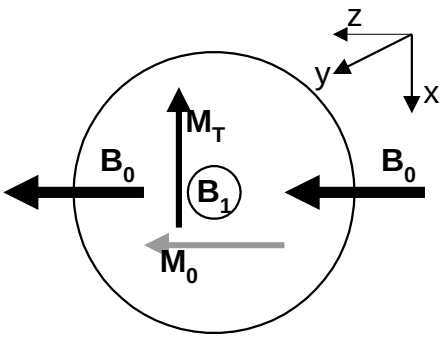

Fig. 3a Top view of the Sample showing the effect of a 90° pulse on the magnetization **M** of the sample. The thermal equilibrium magnetization $\mathbf{M_0}$ has been rotated to the transient $\mathbf{M_T}$.

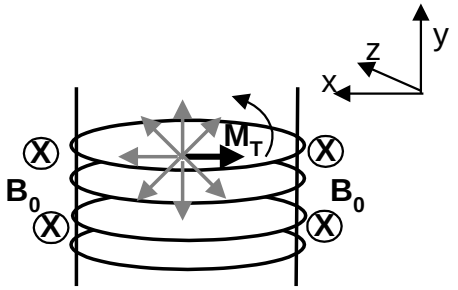

Fig. 3b Side view of the sample with, $\mathbf{B_0}$, the field of the permanent magnet, directed into the page. Following a 90° pulse, the net magnetization, $\mathbf{M_T}$ precesses around $\mathbf{B_0}$.

The PS2-A electronics system is composed of four modules, only three of which are involved in Pulsed NMR. The black knobs on the **Synthesizer** and **Pulse Programmer** are used first to select the aspect of the signal to be changed, and then rotated to change magnitude. The RF signal used to "tip" the spins is created by the **Synthesizer**. The **Pulse Programmer** module is used to determine the duration and spacing of the RF signals produced by the Synthesizer. The **Receiver** plays several roles. The connection labeled **Sample** first transmits the RF pulse to the solenoid surrounding the sample to tip the spins and then receives the resulting signal coming from the free precessing spins.

Let's follow the progression of the signal. The module is in bold; the connector titles are shown in parenthesis. **Pulse Programmer** (*Pulse Out*) ▶ (*Pulse In*) **Synthesizer** (*Pulsed RF Out*) ▶ (*Pulsed RF*) **Receiver** (*Sample*) ▶ Solenoid acts as RF transmitter > Spins "tip" > Solenoid acts as Pickup Coil ▶ (*Sample*) **Receiver** (*Env. Out*) ▶ Oscilloscope, Channel 1

One role of the **Receiver** module is to amplify and "forward" the signal coming from the solenoid/pickup coil. As the spins precess inside the solenoid, they induce a voltage which rises and falls as a sine wave with each rotation. The sinusoidal signal can be observed at the *RF Out* connector. The signal usually associated with NMR, however, and shown in the lower trace of the oscilloscope capture in Figure 4, comes from the connector labeled *Env. Out* (envelope out). In this case, the signal is first "rectified" so that all values become positive and then only the maximum amplitudes for each cycle are selected. It is this rectified envelope which is referred to as the **free induction decay or FID**.

Set on *F*, the **Synthesizer** module displays the frequency in MHz of the RF (radio frequency) pulse being used to tip the spins, and change the direction of the net magnetization of the sample. As we have mentioned, for on resonance operation, this frequency must be adjusted to match, with high precision, the Larmor precession frequency of the protons in the field of the permanent magnet. (In TeachSpin's Magnetic Torque simulation, this is equivalent to the frequency at which the small rotating field accessory is turned by hand.)

The **Receiver** module also houses the electronics which are used monitor the relationship between the **Synthesizer** and Larmor frequencies. As already discussed, the portion of the **Synthesizer** signal coming from the connector labeled *Pulsed RF Out*, enters the **Receiver** via connection *Pulsed RF* and is then used to tip the spins of the sample.

Another portion of the synthesized signal becomes a reference signal that is used to monitor the Synthesizer/Free Precession frequency match. It goes from the **Synthesizer** connector *Ref Out* into the *Ref In* connector of the **Receiver**. An internal connection in the **Receiver** diverts part of the signal coming from the precessing protons to a phase detector system where it is "multiplied" with the reference signal coming from the **Synthesizer**. The output is monitored from either the *I Out* or *Q Out* connector on the **Receiver**. This is the signal shown as the upper trace of Figure 4.

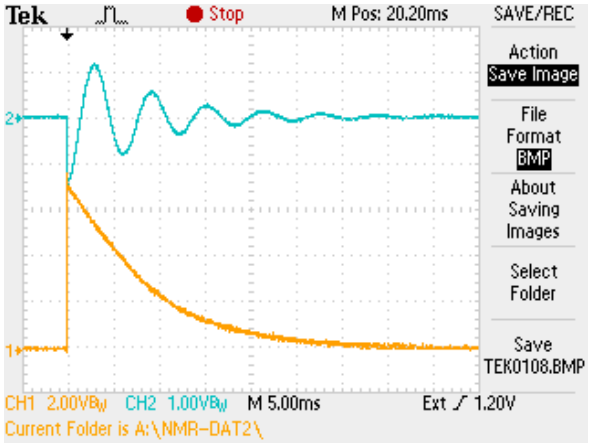

Figure 4 – Upper Trace: Mixer Signal
Lower Trace: FID Envelope

But how does this signal multiplication work; how does tell us if we are on resonance? We get an answer to this by looking at what happens when we "multiply" two sign wave expressions mathematically. If the synthesized frequency is ω_1 and the free precession frequency is ω_2, a bit of trigonometry gives $2 \sin\omega_1 \sin \omega_2 = \cos (\omega_1 - \omega_2) + \cos (\omega_1 + \omega_2)$. A low pass filter inside the **Receiver** allows only difference signals to reach the *I* and *Q* outputs. When the oscillator is properly tuned to the resonant frequency $\omega_1 = \omega_2$ and the signal from either of the phase detector outputs should show no "beats." The upper trace of Figure 4 indicates that when this measurement was made the system was not exactly "on resonance," but is very close and requires only a little tweaking. In many permanent magnet NMR systems, the precession frequency drifts because the temperature of the permanent magnet is not absolutely constant. Any change in magnet temperature causes a change in the magnetic field $\mathbf{B_0}$ and thus in the precession frequency. The PS2-A, however, has a temperature and thus field stability of one part per million over 25 minutes.

The **Pulse Programmer** determines the duration of individual RF pulses as well as the number of pulses in a series, the spacing between pulses, and how often an entire series is repeated. The PS2 pulse programmer provides two different pulses, A and B, both at the same frequency. Duration and number of pulses, however, are independent. The selected pulse pattern is sent from the *Pulse Out* connectors of the **Pulse Programmer** to the *Pulse In* connectors of the **Synthesizer**. For the experiments in this discussion, *Sync Out* connects to the oscilloscope. The *Sync* toggle switch can be set to either pulse. Now let's look at how each of the pulse parameters is controlled by the settings on the **Pulse Programmer**.

A_len and B_len control the length of time each of these RF pulses persists. (In the Magnetic Torque apparatus, this "pulse" time is equivalent to how long you must rotate the horizontal field to get the ball's handle, and thus its magnetic moment, horizontal.)

N indicates the number of pulses to be used. The PS2 provides only one A pulse, but there can be anywhere from 0 to 100 B pulses in a given series.

The τ setting indicates the delay time, the time between the first and second pulses of a series. When more than two pulses are used, the system adjusts subsequent delay times between the second and third, third and fourth etc. to 2τ. We will see why this matters later.

The *P*, or Period setting determines how often an entire pulse sequence is repeated. This is also called the repetition time.

The total time for the pulse series itself, is determined by the combination of *N* and τ. This must be less than the repetition time *P* so that the digital logic does not lock up. In addition, *P* must be long enough so that, after the pulse series had ended, the net magnetization has time to realign with the primary field. If *P* is too short, a pulse sequence will begin before the system has returned to thermal equilibrium and the FID will make little sense. **In fact the repetition time *P*, should be such that the time *after* the last echo or FID is long compared to T_1. To be safe it should be close to $10T_1$.**

Describing Relaxation Time

As we have discussed, the Pulsed NMR experiments we are describing involve the sum of the magnetic moments of many protons, the net magnetization. (By contrast, Magnetic Torque works with the spin of only one "proton" which is represented by the ball.) When the sample is in thermal equilibrium, the net magnetization of the protons of the sample is aligned with the field of the permanent magnet, $\mathbf{B_0}$. Any change in the orientation of the spins decays back to an alignment with this "primary" field. The time constant of this usually exponential return to thermal equilibrium magnetization is the $\mathbf{T_1}$ relaxation time. But TeachSpin's PS2 can actually be used to measure two **different kinds of relaxation times**, referred to as T_1 and T_2. $\mathbf{T_1}$, the **spin-lattice** relaxation time already described, is the time characteristic of establishing thermal-equilibrium magnetization in the $\mathbf{B_0}$ direction. The **spin-spin** relaxation time, $\mathbf{T_2}$, is the time constant for the exponential loss of x-y magnetization due to dephasing of the spins. The variation in the "local" field surrounding individual protons, which is created by magnetic properties of nearby atoms, changes the local precession frequency. This dephasing is thus an indication of important qualities of the sample.

A First Exploration

Once the probe-head of the TeachSpin Pulsed NMR has been tuned to the proton frequency, we can investigate the PNMR signal following a single pulse. The duration of TeachSpin's A and B pulses are set independently. Start with both pulse widths set to 0, the repetition time, P, set to about 0.10 seconds, the A pulse on, the B pulse off and the oscilloscope triggering on A.

Slowly increase the A pulse length and examine the effect. (To be sure the RF pulse is in resonance, check the phase signal on the oscilloscope and tweak the **Synthesizer** frequency until there is a zero beat condition.) Pulse length determines the time allowed for the RF to tip the spins. The longer the RF is on, the farther the spins tip. As the time, A_len, increases, you will notice that the initial height of the FID (the signal on the oscilloscope) first rises to a maximum, indicating a 90° pulse, then decreases to close to 0 at about twice the 90º pulse time. This indicates a 180º rotation. After a 180° rotation there is no x-y magnetization and thus no signal. Continuing to increase the pulse time shows the signal increase to another maximum for a 270º rotation etc.

The repetition time can be used to estimate T_1, the time characteristic of re-establishing thermal equilibrium magnetization in the z-direction. Set the A pulse length for the first maximum. Decrease the repetition time, *P*, until the signal maximum begins to shrink. This decrease in the initial height of the FID occurs because the z-magnetization has not returned to its thermal equilibrium value before the next 90º pulse. We have found a rough measure of T_1. This effect becomes more dramatic as the repetition time decreases.

Measuring T_1, the spin-lattice relaxation time

(Time characteristic of establishing equilibrium magnetization in the z-direction)

A more precise measurement of T_1 requires a two pulse sequence. The net magnetization, M_o, is first tipped by 180º to $-M_o$ or the –z direction. The z-magnetization is then interrogated as it returns to its thermal equilibrium value, M_o. We have a problem however. Our spectrometer cannot directly detect M_z. Only precession in the x-y plane induces an emf in the sample coil. The "trick" we will use is to follow this initial 180º pulse with a 90º B pulse.

To tip the magnetization to $-M_o$, the length of the A pulse is increased until it has passed through the first maximum and returned to a 0 signal on the oscilloscope. This indicates a 180° pulse after which there is no net magnetization in the x-y plane. The A pulse is then turned off and the width of the B pulse is adjusted to the first maximum signal, indicating a 90º pulse.

The key to this experiment is the fact that the B pulse, which tips *any* spin by 90°, is being used to interrogate what has happened to the magnetization along the z axis. This second pulse rotates the z-magnetization into the x-y plane where it can be detected. The maximum amplitude of the Fee Induction decay (FID) signal which follows the B pulse is directly proportional to the magnitude of M_z at the time the B pulse occurs. For example, if the delay time for B, following A, were to be 0, the signal would be at a maximum because the spins would be tipped from -z to the x-y plane.

By changing the delay time between the A and B pulses, the rate at which the net magnetization returns to alignment with the "primary" magnetic field can be investigated. When the delay time results in a 0 signal in the pickup coil, it means that the net magnetization along the z-axis is zero. When the signal again reaches a maximum, the spins have "relaxed" back to alignment along the z-axis. Careful observation of the Q or I phase detector signal will show a 180º phase shift as the z-axis magnetization passes through 0.

If the maximum amplitude, **M**, of the FID following the 90° pulse is plotted against the delay time, the relaxation of the spins from - z to + z can be observed. To extract T_1 correctly, however, the difference between the FID maximum for long delay times, which is a measure of the thermal equilibrium magnetization, and the FID maxima at time t is plotted against delay time. It is this difference, M_0 - M, which changes exponentially. The equation is:

$$\frac{dM_z(t)}{dt} = \frac{M_0 - M_z(t)}{T_1}$$

An arbitrary scale can be used to plot the magnitude of the initial FID signal after the B pulse as a function of delay time. From the shape of this curve, T_1 can be calculated.

Figure 5 shows diagrams of both the actual net magnetization M and the maximum amplitude of the FID just after the 90° pulse as a function of time.

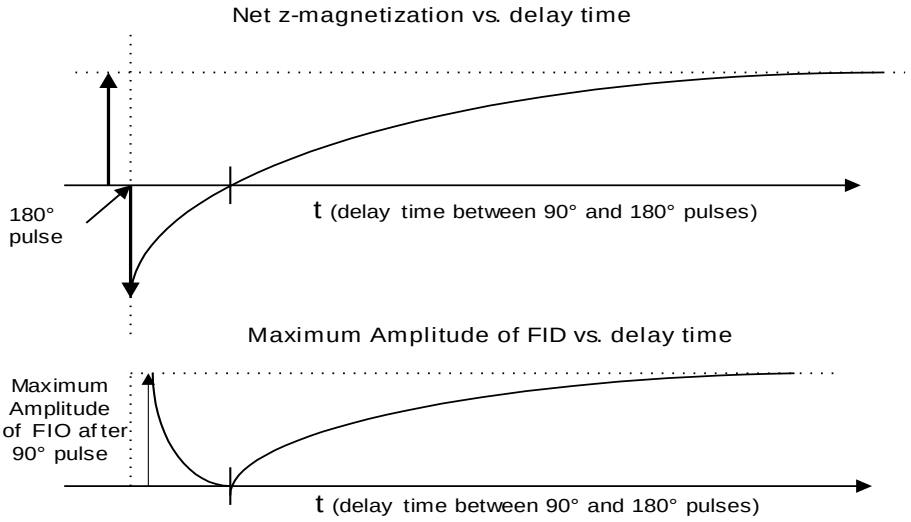

Figure 5 – Upper Diagram: Net z magnetization vs. delay time
Lower Diagram: Maximum Amplitude of FID vs. delay time

Measuring T_2, the spin-spin relaxation time

(The time characteristic of the loss of x-y magnetization)

The characteristic time for the spins to lose a non-thermal equilibrium x-y magnetization, which has been established by a 90º RF pulse, is called T_2. To measure this relaxation time, the width of the A pulse is adjusted to the first maximum signal, indicating a 90° pulse. The oscilloscope must trigger on A.

In the pick-up coil, the precessing spins induce a sinusoidally varying voltage which decays over time. As discussed at the beginning, the detector transmits only the absolute value of the maximum voltages during each precession. The rectified envelope represents the free induction decay or FID. Spin-spin relaxation occurs by two mechanisms:

1. The spins re-orient along the + z axis of the main magnetic field, B_o due to stochastic, T_1, processes.

2 The interaction of the spins themselves creates a variation in the local magnetic field of individual atoms. Because their precession frequency is proportional to the magnitude of the local magnetic field, the precessing spins dephase.

Understanding T2*

If the external magnetic field across the sample is not perfectly homogenous, spins in different physical locations will precess at different rates. This means that the precession of the individual spins is no longer in phase. Over time, the phase difference between the precessions of the individual protons increases and the net voltage induced in the pick-up coil decreases. The time for this loss of signal, which is not due to relaxation processes, is called T_2*. The free induction decay observed after a single 90º pulse is often due primarily to this effect. If, however, the external magnetic field is very homogeneous and T_2* is long compared to T_2, the free induction will represent a true measure of T_2. As good as the PS2 magnet is, it is not perfect. If the T_2 of the ample is less than 0.5 ms, the FID time constant can be used as a good measure of the real T_2. However, if the spin-spin relaxation time of the sample is longer than a few milliseconds we will need to use a spin echo experiment to measure it.

Spin Echo

In 1950, Irwin Hahn found a way to compensate for the apparent decay of the x-y magnetization due to inhomogeneity in an external magnetic field. The external inhomogeneity creates a variation in the proton precession times around an average. The introduction of a 180° pulse, or spin flip, allows the spins to regroup before again dephasing. This creates a *spin echo* which allows us to measure the true T_2.

After our initial 90° pulse, the spins in areas of stronger than average fields precess faster than average and those in weaker fields more slowly. The spins "dephase" and the induced emf fades. After the 180º flip, however, the spins that were "ahead" because they are in a stronger field are now "behind." Because their protons are precessing faster, however, they will now "catch up" to the "average." In the same way, after the 180° pulse, "slow" spins are now "ahead" and the "average" will overtake them. The spins rephase momentarily and dephase again. This is why the oscilloscope trace after the first 180º pulse shows a rise to a maximum and then a decay. The initial dephasing and then the rephasing and dephasing wings of the echo can be seen in the diagram below. The difference between the height of the initial signal and the echo maximum is due to the actual stochastic processes of T_2.

The magnitude T_2 can be investigated two ways. The time between the A and B pulses can be varied and T_2 determined by plotting the resulting echo maximum as a function of time. Another option is to introduce a series of 180° B pulses and look at the decrease of the maxima.

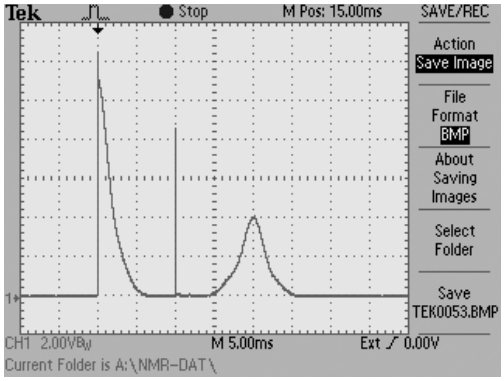

Figure 6a: Oscilloscope trace showing 180° pulse spike and spin echo.

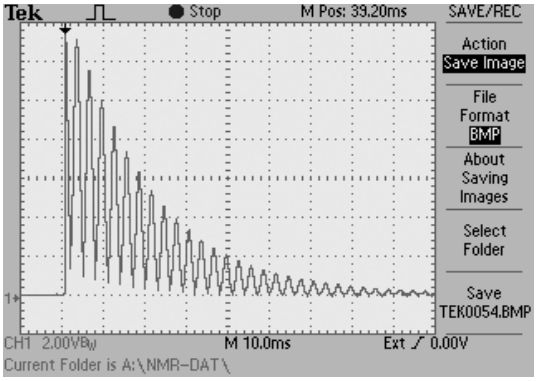

Figure 6 – Oscilloscope Trace of Multiple Echoes

Understanding the effect of the 180º Spin Flip - a Jonathan Reichert analogy

Consider the plight of a kindergarten teacher who must devise a foot race which keeps all children happy, no matter how fast they run. What if the race has the following rules? All children are to line up at the starting line. At the first whistle they are to run as fast at they can down the field. At the second whistle they are to turn around and run back toward the starting line. First person back wins!! Of course, it is a tie, except for the ones who "interfere" with one another or fall down. As the children run away the field spreads out with the fastest ones getting farther and farther ahead. At some point there is no semblance of order. On the trip back, as the faster ones overtake the slow guys now in the lead, the group comes together again "rephasing" as they pass the start line.

This is a good analogy for the effect of the 180° spin flip which creates a spin echo. The effect of the 180º pulse is analogous to that of the kindergarten whistle. After the 180° pulse, the signal increases as the spins rephase, hitting a maximum somewhat lower than the initial height of the FID and decreasing as the spins again dephase. The decay of the maxima shows how the protons are losing the x-y magnetization. In our kindergarten analogy, this tells us the rate at which the children are actually interacting with each other.

The Output of the Mixer as a Phase Indicator

During a T_1 measurement the output of the mixer can be used to determine when the direction of the magnetization changes from the minus to the plus z direction. This cannot be inferred from detector output because it always gives a positive signal on the oscilloscope. By watching the mixer as delay time is changed you can see when the magnetization passes through the x-y plane. The initial signal of the mixer can have its maximum either above or below the time axis on the oscilloscope when the net magnetization of the sample has been driven to $-M_o$ by the A pulse. As the direction of the net magnetization changes from below ($-z$) to above ($+z$) the x-y plane, the mixer signal will reverse its orientation around the time axis of the oscilloscope. If you have truly caught the moment when the net magnetization is in the x-y plane, both the pick up signal and the mixer signal will be 0. The way this time can be used to give a very good estimate of T_1 is discussed in the PNMR manual.

An Interesting Activity

With the pulse series for determining T_2 on the oscilloscope screen, change one of the gradient settings so that the magnetic field at the sample becomes less homogeneous. Notice that although the widths of the individual echo traces narrow, the maximum heights of the peaks do not change. This shows that although the time for the spins to dephase due to inhomogeneity does decrease, the true time for the spins to return to their thermal equilibrium value, as indicated by the decay of the peaks, does not.