Pulsed Nuclear Magnetic Resonance

Experiment NMR

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References


A. C. Melissinos, Experiments in Modern Physics,

Theory

Recall that the hydrogen nucleus consists of a single proton and no neutrons. The precession of a bare proton in a magnetic field is a simple consequence of the proton’s intrinsic angular momentum and associated magnetic dipole moment. A classical analog would be a gyroscope having a bar magnet along its rotational axis. Having a magnetic moment, the proton experiences a torque in a static magnetic field. Having angular momentum, it responds to the torque by precessing about the field direction. This behavior is called Larmor precession.

The model of a proton as a spinning positive charge predicts a proton magnetic dipole moment $\mu$ that is aligned with and proportional to its spin angular momentum $s$

$$\mu = \gamma s$$  \hspace{1cm} (1)

where $\gamma$, called the gyromagnetic ratio, would depend on how the mass and charge is distributed within the proton. Determined by various magnetic resonance experiments to better than 1 ppm, to four figures $\gamma = 2.675 \times 10^8 \text{ rad/(sec tesla)}$.

Note that different nuclei will have different spin angular momentum, different magnetic moments, and different gyromagnetic ratios. The gyromagnetic ratio given above is only for the hydrogen nucleus. In NMR, the word proton generally only refers to the nucleus of the
$^1$H hydrogen isotope (a bare proton), not protons in other nuclei. For example, the nucleus of $^{16}$O has eight protons, but no nuclear spin or magnetic dipole moment. While it is possible to study NMR in other nuclei, such measurements require different experimental settings and can not be performed at the same time that protons are under investigation.

Exercise 1  
Show that the classical value for the proton gyromagnetic ratio (the ratio of the classical magnetic moment to the classical angular momentum) is $e/2m$ (a) assuming the proton is a point particle of mass $m$ and charge $e$ moving at constant speed in a circular orbit, and (b) assuming the proton is a solid sphere with a uniform mass and charge density rotating at a constant angular velocity. (c) Using the proton mass $m = 1.67 \times 10^{-27}$ kg, and charge $e = 1.60 \times 10^{-19}$ C, find the ratio of the true gyromagnetic ratio of the proton given above to this classical value (called the proton $g$-factor). (d) Why might different nuclei be expected to have different gyromagnetic ratios?

The proton has two energy eigenstates in a magnetic field $B_0$: spin-up and spin-down. The eigenenergies are governed by the Hamiltonian

$$\mathcal{H} = -\mu \cdot B_0 \tag{2}$$

Defining the z-axis along $B_0$

$$B_0 = B_0 \hat{z} \tag{3}$$

and with $\mu = \gamma s$, the Hamiltonian becomes

$$\mathcal{H} = -\gamma B_0 s_z \tag{4}$$

where $s_z$ is the z-component of the spin. Since $s_z$ has eigenvalues $\hbar/2$ for the spin-up state and $-\hbar/2$ for the spin-down state, $\mathcal{H}$ has eigenenergies

$$E_{\pm} = \pm \frac{\hbar \omega_0}{2} \tag{5}$$

where $\omega_0 = \gamma B_0$ is called the Larmor frequency.

NMR signals arise from the collective behavior of a large number of nuclei in a macroscopic sample. The net nuclear angular momentum $S_{\text{tot}}$ is the sum of the individual spin angular momenta

$$S_{\text{tot}} = \sum s \tag{6}$$

The net dipole moment becomes

$$\mu_{\text{tot}} = \sum \mu = \sum \gamma s = \gamma S_{\text{tot}} \tag{7}$$

The dipole moment per unit volume is called the magnetization and is given the symbol $M$. Depending on experimental conditions $M$ may vary at different points within a sample. Here we will assume $M$ is uniform throughout the sample volume $V$ so that $M = \mu_{\text{tot}}/V$. (However, keep in mind there may be effects associated with a non-uniform sample magnetization.) In the jargon of NMR, it is more common to refer to the sample magnetization rather than the dipole moment, and we will adopt this language in this writeup. In most instances, the term magnetization and dipole moment can be substituted for one another without confusion.

It is important to note that Eqs. 6 and 7 are vector sums, so if the individual proton moments are randomly oriented—as is often the case in the absence of any applied magnetic field—the net angular momentum (and net dipole moment) will sum to zero. In a magnetic field, however, a sample of protons at an absolute temperature $T$ will come to thermal equilibrium with more spins in the lower energy (spin-up) state. The ratio of the number of protons in the higher energy state $N_+$ to the lower energy state $N_-$ is given by the
Boltzmann factor:
\[
\frac{N_-}{N_+} = e^{-\Delta E/kT}
\]  
(8)

where \(k\) is Boltzmann’s constant and \(\Delta E = \hbar \omega_0\) is the energy difference between the spin-up and spin-down states.

The excess of protons in spin-up states results in a net equilibrium magnetization \(M_0\) in the direction of \(B_0\). That is, \(M_0 = M_0\hat{z}\), where
\[
M_0 = \mu (N_+ - N_-) / V
\]  
(9)

and \(\mu = \gamma \hbar / 2\) is the magnitude of the \(z\) component of an individual proton magnetic moment. \(M_0\) can be calculated from the Boltzmann factor with \((N_+ + N_-)/V\) being the density of protons in the sample.

Exercise 2  
(a) The ratio of excess spin-up protons to the total number of protons would be expressed: \((N_+ - N_-)/(N_+ + N_-)\). Evaluate this expression in the weak field or high temperature limit: \(kT \gg \hbar \omega_0\) to lowest order in the small parameter \(\hbar \omega / kT\).  
(b) Calculate the value of \(M_0\) for water at room temperature in a 2 kG field.  
(c) Why must you determine the density of hydrogen atoms in the sample, but not include any protons inside the water’s oxygen nuclei?  
(d) The dipole moment of a simple wire loop of area \(A\) carrying a current \(I\) is \(\mu = IA\). So how big is the dipole moment of a 1 cm\(^3\) sample of water in a 2 kG field? Express your answer in SI units and also as the current needed in a 1 cm\(^2\) loop that would give it the same dipole moment.

We will later show how the nuclear magnetization \(M\) can be turned away from its equilibrium alignment with the \(z\)-axis. For the present discussion we assume the configuration shown in Fig. 1 has been achieved and \(M\) (and \(\mu_{\text{tot}}\) and \(S_{\text{tot}}\)) make a non-zero angle with the \(z\)-axis. The resulting torque \(\tau = \mu_{\text{tot}} \times B_0\) causes the angular momentum \(S_{\text{tot}}\) to change according to the equation of motion:
\[
\tau = dS_{\text{tot}}/dt
\]  
(10)

By substituting Eq. 7 for \(S_{\text{tot}}\) and dividing through by \(V\), this equation can be rewritten
\[
\frac{dM}{dt} = \gamma M \times B_0
\]  
(11)

With \(B_0 = B_0\hat{z}\) and \(\omega_0 = \gamma B_0\) this equation further simplifies to
\[
\frac{dM}{dt} = \omega_0 M \times \hat{z}
\]  
(12)

By components
\[
\frac{dM_z}{dt} = 0
\]  
(13)
\[
\frac{dM_x}{dt} = \omega_0 M_y
\]
\[
\frac{dM_y}{dt} = -\omega_0 M_x
\]

These are the equations for the clockwise precession of \(M\) on a cone that maintains a con-
stant polar angle with the \( z \)-axis. This behavior is called Larmor precession and the frequency of the precession is \( \omega_0 \), the Larmor frequency defined after Eq. 5.

As \( \mathbf{M} \) precesses, its dipole field precesses with it. The precession can be detected by the alternating voltage it induces in a receiver coil surrounding the sample. The voltage arises from Faraday’s law \( V = -d\phi/dt \) and thus the coil axis is oriented perpendicular to \( B_0 \) to maximize the change in the magnetic flux \( \phi \) through the coil as \( \mathbf{M} \) precesses.

To get a precession and an induced coil voltage (signal), \( \mathbf{M} \) must make a non-zero angle with \( B_0 \), i.e., the \( z \)-axis. So we define the transverse magnetization \( \mathbf{M}_r \)

\[
\mathbf{M}_r = M_x \hat{x} + M_y \hat{y}
\]

and the longitudinal magnetization \( \mathbf{M}_z \)

\[
\mathbf{M}_z = M_z \hat{z}
\]

The amplitude of the precession-induced coil signal is proportional to the magnitude \( M_r \) of \( \mathbf{M}_r \) and is independent of \( M_z \). Note that \( M_r \) is zero or positive, while \( M_z \) can be positive, negative, or zero.

In thermal equilibrium, the magnetization is entirely longitudinal: \( \mathbf{M}_0 = M_0 \hat{z} \) or \( M_z = M_0 \) and \( M_x = 0 \). With no transverse magnetization, there is no precession and no induced coil voltage. To observe Larmor precession we need a way to create transverse magnetization. We will show how an oscillating magnetic field can tip the equilibrium longitudinal magnetization away from the \( z \)-axis so that precessional motion will occur. To this end, the protons are placed inside a drive coil oriented with its axis perpendicular to \( B_0 \). The coil axis will be taken to define the laboratory \( x \)-direction. In some apparatuses the drive coil is separate from the receiver coil used to pick up the Larmor precession. In our apparatus one coil performs both jobs.

The oscillating field is produced by applying an ac voltage to the coil at a frequency \( \omega \) near the Larmor frequency \( \omega_0 \) causing an alternating current to flow in the coil. Near the coil center, a linearly polarized magnetic field is created which oscillates back and forth along the coil axis. Choosing an arbitrary initial phase and taking the amplitude of this field as \( 2B_1 \), the linearly oscillating \( \mathbf{B} \)-field can be written

\[
\mathbf{B}_1' = 2B_1 \cos \omega t \ \hat{x}
\]

The field has been named \( \mathbf{B}_1' \) and the amplitude has been chosen as \( 2B_1 \) because this linearly polarized field will next be decomposed into two counter-rotating, circularly polarized components each with half the amplitude of the linearly polarized field. That is, we can add and subtract the term \( B_1 \sin \omega t \ \hat{y} \) to write

\[
\mathbf{B}_1' = B_1 (\cos \omega t \ \hat{x} - \sin \omega t \ \hat{y}) + B_1 (\cos \omega t \ \hat{x} + \sin \omega t \ \hat{y})
\]

Each component now represents a vector of constant amplitude \( B_1 \) rotating in the \( xy \)-plane at an angular frequency \( \omega \). These two circularly polarized components rotate in opposite directions and when added together produce the linearly polarized field of amplitude \( 2B_1 \).

The first component rotates in the same sense as the Larmor precession and is responsible for tipping the magnetization away from the \( z \)-axis as will be described next. The second, rotating opposite the Larmor precession, has little effect on the protons and can be neglected. Neglecting the counter-rotating component is called the rotating-wave approximation and allows us to write what will be called the \( \mathbf{B}_1 \) field as

\[
\mathbf{B}_1 = B_1 (\cos \omega t \ \hat{x} - \sin \omega t \ \hat{y})
\]
The equation of motion for the magnetization $\mathbf{M}$ is still given by Eq. 11
\[
\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B}
\]  
(19)
with the replacement of $\mathbf{B}_0$ by $\mathbf{B}$, the vector sum of $\mathbf{B}_0$ and the rotating field $\mathbf{B}_1$ given by Eq. 18.

However, it will be mathematically convenient to work in a frame rotating clockwise about the $z$-axis at the frequency $\omega$. In this frame, the unit vectors are time dependent
\[
\begin{align*}
\hat{x}' &= \cos\omega t \hat{x} - \sin\omega t \hat{y} \\
\hat{y}' &= \sin\omega t \hat{x} + \cos\omega t \hat{y} \\
\hat{z}' &= \hat{z}
\end{align*}
\]  
(20)
and the $\mathbf{B}_1$ field is constant
\[
\mathbf{B}_1 = B_1 \hat{x}'
\]  
(21)
The $\mathbf{B}_0$ field—lying along the rotation axis—is the same in both the laboratory and rotating frames.

A time dependent vector $\mathbf{v}$ in the laboratory frame could be expressed
\[
\mathbf{v} = v_x \hat{x} + v_y \hat{y} + v_z \hat{z}
\]  
(22)
where $v_x$, $v_y$, and $v_z$ are functions of time. This same vector in a rotating reference frame would be expressed
\[
\mathbf{v} = v'_x \hat{x}' + v'_y \hat{y}' + v'_z \hat{z}'
\]  
(23)
where $v'_x$, $v'_y$, and $v'_z$ are new functions of time determined by $v_x$, $v_y$ and $v_z$ and the unit vector transformations describing the rotating frame.

Differentiating Eq. 23 gives
\[
\frac{d\mathbf{v}}{dt} = \frac{dv'_x}{dt} \hat{x}' + \frac{dv'_y}{dt} \hat{y}' + \frac{dv'_z}{dt} \hat{z}' + v'_x \frac{dx'}{dt} + v'_y \frac{dy'}{dt} + v'_z \frac{dz'}{dt}
\]  
(24)

The first three terms give the time derivative of $\mathbf{v}$ as it would appear in the rotating frame and will be written $(d\mathbf{v}/dt)'$. The final three terms are equal to the expression $\omega \times \mathbf{v}$ where $\omega$ is the vector angular velocity of the rotating frame.
\[
\frac{d\mathbf{v}}{dt} = \left(\frac{d\mathbf{v}}{dt}\right)' + \omega \times \mathbf{v}
\]  
(26)
For a frame rotating clockwise about the $z$-axis at a frequency $\omega$ the transformation is given by Eqs. 26 with $\omega = -\omega \hat{z}$.

Eq. 19 then becomes
\[
\left(\frac{d\mathbf{M}}{dt}\right)' + \omega \times \mathbf{M} = \gamma \mathbf{M} \times (\mathbf{B}_0 + \mathbf{B}_1)
\]  
(27)
or
\[
\left(\frac{d\mathbf{M}}{dt}\right)' = \gamma \mathbf{M} \times \left(\mathbf{B}_0 + \frac{\omega}{\gamma} + \mathbf{B}_1\right)
\]  
(28)
With $\mathbf{B}_0 = B_0 \hat{z}$ and $\omega = -\omega \hat{z}$ we can define an effective field along the $z$-axis
\[
\mathbf{B}'_0 = B'_0 \hat{z}
\]  
(29)
where
\[
B'_0 = B_0 - \frac{\omega}{\gamma}
\]  
(30)
With $\mathbf{B}_1 = B_1 \hat{x}'$, the total effective field in the rotating frame becomes
\[
\mathbf{B}' = B'_0 \hat{z} + B_1 \hat{x}'
\]  
(31)
The “on resonance” condition is $\omega = \omega_0 = \gamma B_0$, and is achieved by adjusting either the static field strength $B_0$ (thereby changing the Larmor frequency $\omega_0$) or the frequency $\omega$ of the voltage applied to the coil. On resonance, the effective field along the $z$-axis is zero ($B'_0 = 0$) and the net effective field lies entirely along the rotating $x$-axis. ($\mathbf{B}' = B_1 \hat{x}'$).

But on resonance or not, the net effective field $\mathbf{B}'$ is a constant, and the equation of motion for $\mathbf{M}$ in the rotating frame becomes
\[
\left(\frac{d\mathbf{M}}{dt}\right)' = \gamma \mathbf{M} \times \mathbf{B}'
\]  
(32)
This equation is analogous to Eq. 11, and its solution is also analogous. $M$ precesses clockwise about the effective field at a frequency $\omega' = \gamma B'$ where $B'$ is the magnitude of $B'$. $\omega'$ is called the Rabi frequency in analogy with the first treatment of this effect in atomic physics by I.I. Rabi.

On or near the resonance condition, $B_1 \gg B_0$, the net effective field lies along or nearly along the rotating $x'$-axis. Then, if $B_1$ is pulsed on and off just long enough to cause $1/4$ of a Rabi cycle, $M$ will Rabi-precess to the rotating $y'$-axis. This kind of pulse is called a $90^\circ$ or $\pi/2$ pulse. After the $\pi/2$ pulse ends, it should be clear that in the laboratory frame the magnetization will lie in the $xy$-plane and it will be Larmor-precessing flat out like one blade of a propeller. Were $B_1$ left on for a longer time, $M$ would Rabi-precess further than $90^\circ$ and the Larmor precession cone would start to close around the negative $z$-axis. If the $B_1$ field is pulsed on just long enough to cause $1/2$ of a full precession cycle (such a pulse is called a $180^\circ$ or $\pi$ pulse), the magnetization becomes inverted and points opposite the external magnetic field.

**Relaxation**

Relaxation in NMR refers to processes that restore the equilibrium magnetization after a perturbation, such as a $B_1$ pulse, has created a non-equilibrium population of nuclear spin states. The breadth of possible relaxation studies and the wealth of information regarding the nuclear environment and the nuclear motion that becomes available through those studies is why NMR has become such an important experimental/analytical technique. The sections to follow focus on a small subset of those studies which highlight the most general features of relaxation.

Figure 2a shows the magnetization $M$ (solid arrow) immediately following a $\pi/2$-pulse. The pulse has Rabi-precessed the equilibrium magnetization (dashed arrow) to the $y'$-axis. At the end of the $B_1$ pulse, the now transverse magnetization induces an observable Larmor precession signal.

After the $\pi/2$-pulse, the relaxation of the transverse and longitudinal magnetization from their perturbed values $M_r = M_0$ and $M_z = 0$ back to their equilibrium values of $M_r = 0$ and $M_z = M_0$, respectively, can occur on quite different time scales.

**Free Induction Decay**

Figures 2b and c show a case where the transverse magnetization (and thus the signal) decays away quickly, before there is any significant change in the longitudinal magnetization. As in our apparatus, this is often the case, and is a result of the inhomogeneities in the $B_0$ field. Spins in different parts of the sample experience slightly different $B_0$ field strengths and thus precess at slightly different Larmor
frequencies. As shown in Fig. 2b, the individual dipole moments begin to spread out in the xy-plane. In Figs. 2b and c, the \( x' \)- and \( y' \)-axes rotate at the average Larmor frequency, corresponding to the average \( B_0 \) field strength. Some spins precess at this frequency and stay aligned with the \( y' \)-axis. However, those spins in regions of higher field strength precess faster than the average and get ahead of the \( y' \)-axis, and those in lower fields fall behind. The vector sum of the individual spins, and therefore the net transverse magnetization, decreases. As the spins completely spread out over the xy-plane as in Fig. 2c, the transverse magnetization, and therefore the signal, decays to zero. The decay of the transverse magnetization is called free induction decay (FID). We will also refer to the signal picked up by the receiver coil as a FID.

The relaxation of the transverse magnetization \( M_r \) from an initial value \( M_i \) to its equilibrium value of zero is often modeled by an exponential

\[
M_r(t) = M_i e^{-t/T_2}
\]

(33)

where \( T_2 \) is called the transverse relaxation time. While most real FID signals decay non-exponentially, the concept of a time constant associated with the decay of transverse magnetization is nonetheless useful.

Inhomogeneities in the \( B_0 \) field are not the only reason the spins fan out. There are also randomly fluctuating magnetic fields from other sources in the sample, e.g., the dipole field of one proton moving past another. These random fields vary over the sample volume and thus also cause proton precession rates to vary. Were the \( B_0 \) field perfectly uniform, the random fields (and other processes) would become the dominant source for the decay of the FID. The decay of transverse magnetization would then occur on a longer time scale, called the spin-spin relaxation time, and given the symbol \( T_2 \). The spin echo (described later) is an interesting phenomenon which largely cancels the effect of field inhomogeneities and makes measurements of \( T_2 \) possible even when \( T_2^* \) is much shorter.

Longitudinal Relaxation

As described in the previous section, any transverse magnetization decays to zero as the individual spins fan out. What happens to longitudinal magnetization \( M_z \) after it is perturbed from equilibrium? Recall (Eq. 9) that the value of \( M_z \) is directly proportional to the difference between the populations of protons in the spin-up and spin-down states. Also recall that these states differ in energy by the amount \( h\omega_0 \). In a sample, individual spins make transitions from spin-up to spin-down and vice versa, absorbing and releasing energy depending on the transition direction. At equilibrium, although the populations of the two states are unequal (more spins are in the lower energy spin-down state), the transition rates in the two directions are equal and there is no net energy transfer into or out of the spin degrees of freedom.

If the longitudinal magnetization \( M_z \) is not at its equilibrium value \( M_0 \), the transition rates in the two directions will not be equal, and there will be a net energy transfer into or out of the spin degrees of freedom. For isolated spins, spontaneous photon emission and stimulated emission and absorption from the background radiation field would reestablish the Boltzmann populations, though it might take quite some time to come to equilibrium. In a real sample, the spins are not isolated. While stimulated emission and absorption are still the major mechanisms by which transitions occur, the radiation field experienced by the spins includes contributions from the motion of the electrons and nuclei in the sample.
In effect, the spins exchange energy with the electrons and other nuclei causing the transition rates to be much higher than for isolated spins and the approach to equilibrium is much faster.

An exponential approach to equilibrium is often a satisfactory model. If the initial perturbed longitudinal magnetization is taken as $M_i$, $M_z(t)$ would be expressed

$$M_z(t) = M_0 + (M_i - M_0)e^{-t/T_1}$$

where $T_1$ is called the longitudinal relaxation time. $T_1$ is also called the spin-lattice relaxation time in reference to NMR in solids where the constituents of the lattice (nuclei and electrons) provide for the exchange of energy necessary for the relaxation process.

**Spin Echo**

The basic spin echo technique, used to measure the spin-spin relaxation time $T_2$, is to apply a $\pi/2$-pulse, wait a bit, and then apply a $\pi$-pulse, as illustrated in Fig. 3. In (a) the magnetization $M$ is shown already rotated to the $y'$-axis by an initial $\pi/2$-pulse. With no field inhomogeneities and no $T_2$ processes, all spins would precess at the same rate and there would be no decay of the transverse magnetization. If we now allow for field inhomogeneities, then some spins will precess faster than average and some slower. As in Fig. 2, the spins eventually fan out into a uniform pancake covering the $xy$-plane and the FID decays to zero. Figure 3b shows the situation at some time $t/2$ when the spins are completely fanned out, though in the figure only three spins are shown. One spin is precessing at the average Larmor frequency, another is precessing faster than the average, and the third is precessing slower.

Figure 3b also shows the application of a second $B_1$ pulse, this one a $\pi$-pulse. The $\pi$-pulse flips the pancake of spins over, $180^\circ$ about the $x'$-axis. The three illustrated spins end up as shown in Fig. 3c. The proton that was ahead is now behind the average and the proton that was behind is now ahead. In addition to no $T_2$ processes, let’s also temporarily assume that the spins don’t move around within the field during the pulse sequence. A spin in a stronger-than-average field stays in that field, continually precessing at a constant, faster-than-average rate from the beginning of the $\pi/2$-pulse to well after the end of the $\pi$-pulse. Similarly, a spin in a lower-than-average field continually precesses at a constant, slower-than-average rate. The faster precessing proton in Fig. 3c, now behind, begins to catch up to the average. The slower, now ahead, begins to lose ground to the average. If it took a time $t/2$ to get to the configuration in Fig. 3b/c, then after an additional time $t/2$ (i.e., at the time $t$), the three spins (in fact, all the spins) would be realigned along the $-y'$-axis as shown in Fig. 3d. The transverse magnetization created by the original $\pi/2$-pulse would be completely restored and the amplitude of the FID would be as large as it was at Fig. 3a. This is the echo FID. Afterward, the spins again fan out and again the FID decays away.

The magnetization at $t$ (Fig. 3d) will be smaller than the original magnetization because spins don’t only fan out due to the $B_0$ field inhomogeneities. As mentioned previously, the spin-spin relaxation time $T_2$ arises because there are other random fields in the sample which make individual spins precess at different rates. For liquids, the diffusion of protons within the sample provides an additional reason the spin echo signal will be smaller than the original FID. During the interval from the initial $\pi/2$-pulse to the appearance of the echo, the spins move within the sample. Consequently, if there is any in-
homogeneity in the $B_0$-field, all spins will not precess at the same rate for the whole time $t$ as was assumed, and the echo will not reconstitute perfectly.

The amplitude of the echo pulse, as a function of the time $t$ when it is made to appear, decays according to the relation

$$M(t) = M_0 \exp \left[-\left(\frac{t}{T_2} + \frac{\gamma^2 G^2 D t^3}{12}\right)\right] \quad (35)$$

The first term in the exponential describes the spin-spin relaxation processes. The second term arises from the diffusive motion. $G$ is the $B_0$-field gradient, i.e. the maximum rate of change of $B_0$ with position (units of $G$ are thus tesla per meter) and $D$ is the diffusion coefficient which has units of square meters per second.

Equation 35 illustrates how spin echo measurements provide information about parameters of physical interest by unmasking the effects of field inhomogeneities responsible for the quick and relatively uninteresting $T_2^*$ decay of the FID. Fits to the data can be used to determine $T_2$ as well as the diffusion constant $D$ (under the right conditions such as a known field gradient and sufficiently long $T_2$). Whereas the $T_2^*$ decay of the FID depends on the field inhomogeneity over the whole length of the sample, field inhomogeneity in the diffusion term involves the smaller distances spins diffuse during the measurement time $t$.

**Inversion Recovery**

We next consider the inversion recovery sequence used to measure $T_1$ and illustrated in Fig. 4. Recall that $T_1$ gives the time scale for relaxation of longitudinal magnetization toward the equilibrium value $M_0$. The inversion recovery sequence starts with a $\pi$-pulse applied to a sample initially aligned in the $z$-direction. In Fig. 4a, the initial magnetization (dashed arrow) is inverted by the $\pi$-pulse, and ends up pointing along the negative $z$-axis: $M_z = -M_0$. In Fig. 4b, the inverted $\mathbf{M}$ becomes smaller as it relaxes back toward equilibrium. $\mathbf{M}$ continues shrinking,
Figure 4: The $\pi - \pi/2$ inversion recovery sequence.

passes through zero, and then increases until it reaches the equilibrium value $M_0$.

An exponential decay of the longitudinal magnetization from a perfectly inverted value $M_z = -M_0$ to the equilibrium value $M_z = M_0$ is modeled

$$M_z(t) = M_0 \left(1 - 2e^{-t/T_1}\right) \quad (36)$$

Because the perturbed magnetization has no component in the $xy$-plane after it is inverted by the $\pi$-pulse (nor while it is relaxing toward equilibrium), there is no transverse magnetization to produce a FID. To observe the changing $M_z(t)$, the magnetization is tipped over to the $xy$-plane by applying a second pulse, this time a $\pi/2$-pulse, at the desired observation time $t$. This is illustrated in Fig 4b. The FID will decay with the $T_2^*$ time constant, but its initial size will be proportional to $M_z(t)$. By varying the time $t$ at which the second $\pi/2$ pulse is applied, the behavior of $M_z(t)$ can be measured.

**Exercise 3** Make a plot of $M_z(t)$ (assuming exponential decay) and describe what effect the second $\pi/2$-pulse will have on $M$ if it is applied at $t = 0$, $t = T_1 \ln 2$, and $t = \infty$?

**Spectral Density Function**

An important concept in NMR relates to the intensity of the random electromagnetic fields experienced by spins in different frequency intervals. This spectral density function is strongly related to the motion of the spins and therefore depends indirectly on the temperature and (for liquid samples) the viscosity of the sample. At low temperatures and high viscosities the mean time $t_c$ between molecular collisions is long and the spectrum is dominated by low frequency fluctuations. At high temperatures and low viscosities, $t_c$ is short and the spectrum spreads out to higher frequencies. Figure 5 shows how the frequency...
distribution spreads out as the collision time decreases.

Recall that the $B_1$-field must oscillate near the resonant frequency $\omega_0$ to cause a Rabi-precession of $M$ away from its equilibrium alignment with the $z$-axis, and thus effect a change in the relative populations of the two spin states. So, too, must the random fields have intensities in the frequency interval near $\omega_0$ to stimulate transitions and reestablish the equilibrium longitudinal magnetization $M_z = M_0$. Thus at low temperatures (long $t_c$) where low frequencies dominate the spectrum, $T_1$ is long. While at very high temperatures (short $t_c$) the spectrum is spread so thin that again the intensity near $\omega_0$ is small and $T_1$ is long. At intermediate collision times one expects to find a minimum in $T_1$. Theory predicts the shortest $T_1$ when $t_c$ is of order $1/\omega_0$.

$T_2$ is also affected by these “resonant” field fluctuations but in addition, field fluctuations along the $z$-axis at any frequency will cause the individual spins to fan out; just as they fan out due to field inhomogeneities. It is these fluctuations that can cause $T_2$ to be appreciably shorter than $T_1$.

Besides varying the sample temperature or viscosity to influence the relaxation times, adding small amounts of paramagnetic ions to the sample will change the amplitude of the frequency fluctuations. These ions have large magnetic moments, which when whizzing by the protons, cause very large fluctuations. Their importance can be investigated by varying the concentration of the ions.

Apparatus

A schematic of the experimental apparatus is shown in Fig. 6.

The RF signal generator should be set to produce a 9.5 MHz, continuous RF signal at an amplitude of 10 dBm$^1$ (0.707 V$_{\text{rms}}$, 2.00 V$_{\text{pp}}$). This value is chosen because the 50-50 splitter reduces the voltage at its two outputs by 3 dBm and 7 dBm is the recommended amplitude for the local oscillator (LO) input of the doubly balance mixer.

This RF is reduced another 10 dB by the attenuator to about -3 dBm so that it will be at the appropriate level before being fed to the RF gate. The gating signal for the RF gate is not shown in the schematic. It is derived from a TTL circuit in a separate interface box which is driven by timing signals from a National Instruments 6601 timer/counter board inside the computer. The output of the RF

\[^1\text{dBm is a unit of absolute power and is defined by the expression } 10\log_{10}(V^2/V_0^2) \text{ where } V_0 = \sqrt{0.05} = 0.224 \text{ volts is the rms voltage across a } R = 50 \Omega \text{ resistor that will dissipate energy at a rate of } V_0^2/R = 1 \text{ mW.} \]
gate then consists of short RF pulses whose amplitude and frequency are set by the signal generator amplitude and the attenuator settings and whose durations are set by the computer generated gating signal.

The gated RF pulses are amplified to about 50 Vrms by the power amplifier. However, the RF gate is not perfect and even while the computer gating signal is off, a small amount of RF still passes through. After amplification, this gate-off RF signal has an amplitude around 1 V and is largely eliminated by the two sets of diode pairs.

The pulsed RF is delivered to the coil through a hybrid junction which when properly balanced, sends half the incident power to the coil and half to the 50 Ω terminator. The receiver circuity (RF amplifier and doubly balanced mixer) thus sees very little of the transmitter power driving the $B_1$-field.

The sample coil and the two capacitors $C_s$ and $C_p$ form a resonance circuit, called a tank circuit. $C_s$ and $C_p$, called the series and parallel capacitors, are variable and must both be properly tuned (1) to get the resonance frequency of the tank circuit—approximately $1/\sqrt{L(C_p + C_s)}$—equal to the drive frequency of the signal generator and (2) to make the overall impedance of the tank circuit equal to 50 Ω. Satisfying these two conditions ensures that the current oscillations in the coil will be maximized (giving the largest possible amplitude of the rotating $B_1$ field). Matching the total impedance to 50 Ω (with no imaginary, i.e., reactive component) is also needed for proper operation of the hybrid junction.

The hybrid junction also routes the FID to the receiver circuity. The first component of the receiver is a low noise RF amplifier protected from large signals by a diode pair to ground. The amplified RF signal is frequency “mixed” with the steady 9.5 MHz signal from the other output of the splitter. The frequency of the signal at the mixer output will be the difference between the FID frequency (at the Larmor frequency $\omega_0$) and the signal generator frequency $\omega$. The $B_0$ field strength will be adjusted so that the “beat” frequency $\omega - \omega_0$ is around 1 kHz.

The signal from the mixer is filtered and amplified by a voltage preamp before being measured with a digital oscilloscope.

**Experiment**

The magnet is field regulated using a Hall probe attached to one pole face. The instructor will show you how to bring up the magnet. Remember to open the cooling water supply and drain line. While it is important to have the water running while the magnet supply is on it is even more important to **turn off the water lines when the magnet supply is turned off**. If the water is left running for more than a few hours while the supply is not running, humidity in the air will condense all over the internal cooled parts of the supply. If you think the water has been left on for more than a few hours with the supply off, do not turn the supply back on without first asking an instructor to check it for condensation.

**Tuning the tank circuit**

Make sure the RF power amplifier is off or that its output is temporarily disconnected. If the gate signal from the computer stays high (as it may when starting or shutting down the computer), the high (50 W) output power will be on continuously instead of only for short bursts and the components downstream will fry in no time at all.

Check the sample coil and remove any sample vial that may have been left in it from the previous experimenters. It is easily pushed out the top of the mounting tube with a pencil in-
sported from the coil end at the bottom. Do not try to push it out the bottom of the tube. Place a glycerin sample in the coil taking care to center the glycerin near the center of the coil and then place the coil near the center of the magnet.

Set the signal generator for a 10 dBm output (0.7 $V_{\text{rms}}$, 2 $V_{\text{pp}}$) and a frequency of 9.5 MHz. This signal goes to the splitter which provides two equal RF voltages of 7 dBm amplitude at its outputs.

Temporarily disconnect one of the 7 dBm continuous signals from the splitter, say the one that normally goes to the LO input of the doubly balanced mixer, and connect it instead to the hybrid junction “A” input. Disconnect the “B” output from the RF amp and monitor it with an oscilloscope. Be sure to use a BNC tee and 50 Ω terminator at the oscilloscope input. Get a clear stable trace showing the 9.5 MHz waveform. The basic idea in tuning the tank circuit capacitors is that when the impedance of the branch connected to the “C” output matches the 50 Ω impedance attached to the “D” output, the “B” output will be as small as possible. When the “C” and “D” outputs are not balanced, more of the “A” input will pass through to the “B” output.

Adjust the series capacitor knob for a minimum signal on the oscilloscope and note its amplitude. Next adjust the back-most knob for the parallel capacitors\(^2\) by about 1/20 of a turn at first (you may need to go in even smaller steps as you get close to the correct setting) and note whether you are turning the knob clockwise or counterclockwise. Either is OK at first. Because your hand on this knob seems to significantly affect the tuning, don’t worry about how it affects the oscilloscope signal, but move your hand away and then again adjust the series capacitance for a minimum on the oscilloscope. If the voltage at the minimum goes down after adjusting the series capacitance, you are changing the parallel capacitance in the correct direction. If it goes up, you are going the wrong way; change the parallel capacitance in the opposite direction. Continue this two-step procedure until the oscilloscope signal becomes fairly non-sinusoidal and has an amplitude under 50 mV. The perfectly balanced circuit would show a doubled frequency around 19 MHz.

Check with the instructor if this tuning process is taking more than 15 minutes or so.

When balanced, note how the balance is affected when you move the sample coil a few centimeters farther or closer to the pole faces. The balancing is important, but getting it perfect is not critical.

When you are finished tuning, return the 7 dBm splitter output to the “LO” input of the mixer and the “B” output to the RF amp.

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Learning the NMR pulse sequencer

Temporarily, rout the gating signal from the computer interface to an oscilloscope input and rout the trigger signal from the computer interface to the oscilloscope trigger source. Launch the NMR pulser program and viewing the gating pulses on the oscilloscope, learn how to externally trigger the oscilloscope and see the gating pulses. Also learn how to operate the program to produce gating pulse-pairs. You can adjust the width of each pulse, the separation between them, and the pulse sequence repetition rate. The separation between the start of the (first) $A$-pulse and the start of the (second) $B$-pulse is labeled $T_d$. Between the start of one $A$-pulse and the next is the repeat time $T_r$. Try turning the $A$- and $B$-pulses on and off by clicking on the appro-

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\(^2\)The parallel capacitors are two capacitors in series that are in parallel with the coil (go to ground). The series capacitor is a single capacitor in series with the coil.
appropriate buttons. The rising edge of the trigger output can be set to transition at the end of the A-pulse, the B-pulse or at the temporal position of a spin echo. It can also be offset from these positions with the pretrigger control, which should be kept at zero. Play around with the buttons and controls to get familiar with their workings. Check that the gating pulse durations and the separations between them agree with the values as specified on the program control panel. Check with an instructor if they don’t.

Creating the RF pulses

Now, reconnect the gating signal from the computer interface to the gating input on the RF gate and rout the pulsed RF from the output of the RF gate to the input of the RF power amplifier. Disconnect the output from the power amplifier and turn it on. The power level meter on the front panel should barely move because it measures average output power (into a 50 Ω load) and is only on for short pulsed periods. If you ever see the amplifier output meter rise above zero while the output is connected to anything, turn it off immediately. Something will likely be cooking.

Look at the amplified RF pulses using a 10× oscilloscope probe. (The pulse amplitude is too big for a direct connection to the oscilloscope.) Pull off the 10× probe’s clip lead and push the straight tip end into the BNC jack. The fit is a bit loose. Just rest the probe on the bench top with the tip connected. Look at the RF pulses straight out of the power amplifier Set the oscilloscope for the 10× probe, and adjust the time base and volts/division (gain) so you can see the amplitude and duration of the RF pulses. Then zoom in time to see the turn on and the waveform for the 9.5 MHz oscillations inside the RF pulse. While looking at the RF pulses with the oscilloscope, adjust the attenuator around the suggested value of 10 dB. This adjustment changes the amplitude to the input (and output) of the gate and thus it also changes the input to the RF amplifier. Then, because the RF amplifier has a fixed gain, changing the attenuator will also change the amplitude of its RF output. If the attenuation is reduced too much, the input to the amplifier will become too big and the output waveform will become distorted. If the attenuation is raised too much, the RF amplitude out will become unnecessarily small, requiring unnecessarily long $T_a$ and $T_b$ to get the desired $\pi/2$ or $\pi$ pulses. The attenuator should be set so that the amplitude of the output RF pulse is right about 50 V$_{rms}$ and is not distorted significantly.

Exercise 4 Show that this amplitude would produce 50 W of rms power into a 50 Ω load, the power limit for this amplifier. What would the peak-to-peak RF voltage (as measured on the oscilloscope waveform) be for this 50 W condition?

Now further zoom in to see the amplitude of the 9.5 MHz signal in the region where the gate should be turning it off, say, in the region before the gating turns on. Because the gate is not perfect, some small amplitude RF leaks through to its output even when the RF is supposed to be gated off. This leakage is amplified by the RF amplifier and shows up in its output. How big is this leakage compared to the 50 V$_{rms}$ that it outputs when the RF is gated on?

Connect the RF amplifier output to the crossed diode circuit and move the 10× probe to the BNC connector after the diodes. Again look at the amplitude of the RF pulses when the gate is on and off and describe the changes in these two regions compared to the direct output from the RF amplifier. The attenua-
tion during the gated on period is mostly due to the 50 Ω resistor to ground in the crossed diode circuit. The diodes are responsible for attenuating the leakage RF during the gated off period. Explain how the diodes attenuate the leakage nearly perfectly without doing much attenuation during the gated on period.

Set the pulser program for $A$-pulses only (turn $B$ off). Make the $A$-pulse width 8 μs, and set the repetition time to 250 ms. Rout the amplified RF pulses from the power amplifier through the series diodes to the hybrid junction “A” terminal and rout the “B” terminal to the diode-protected input of the RF signal amplifier (not the power amplifier). Connect the output of the RF signal amplifier to the RF input of the mixer. The mixer’s LO (local oscillator) input is taken from one of the two RF splitter outputs driven directly by the function generator. The mixer’s IF (intermediate frequency) output is then routed to the voltage preamp input. View the output from the preamp on the oscilloscope. Start with this preamp set to AC coupling, high-pass filtering to 100 Hz, low-pass filtering to 10 kHz, and gain to 1000. Set the oscilloscope to a time base around 2 ms/div and the gain to around 50 mV/div. You are now ready to find a resonance.

Finding the FID

Now it’s time to adjust the $B_0$ field strength to find the free induction decay. Put the glycerin sample into the sample coil (from the top) taking care to get the 5 mm or so of glycerin centered in the 1 cm coil. You can put a small piece of tape on the sample if it slides around too easily in the coil.

Make sure the screw marked LOCK located below the coarse dial on the magnet power supply is loosened. Then slowly vary the magnetic field around 2-2.5 kG until you see a FID. Keep your eye on the oscilloscope because decaying oscillations at the beat frequency (the FID) will appear at resonance. Once you have a signal, finger tighten the coarse control locking screw and adjust the fine control to get the FID beat frequency around 1 kHz. Check that its locking mechanism—a sliding lever at the base of the dial—is also loose (pushed left) during adjustments.

The FID decays with the time constant $T_2^*$, which will vary if the sample is moved around in the field. Move the sample up/down, back/forth, and left/right trying to find the most uniform field region characterized by the longest decay.

If the $B_0$ field varies—even by a little—the FID frequency varies by a lot. If your FID frequency is not very stable, the problem may lie with the potentiometers connected to the fine and coarse adjustment knobs. They may be a little noisy (have a varying resistance) depending on where they are set and whether they are locked in position. We have found less problems when the coarse control knob is in the locked position. The fine control knob can be left in the unlocked position. If the FID frequency is still unstable, try finding a better spot for the potentiometers—moving both dials to keep the beat frequency around 1 kHz. Remember to unlock both before making adjustments and to lock down the coarse control afterward.

Another cause of field instability seems to be associated with the cooling water. We have found that changing a dirty filter in the water line sometimes improves the magnet stability.

If your efforts to get a stable $B_0$ fail and the beat frequency continues to vary, you can still get good data. This is because mostly you will make measurements of the starting amplitude of the FID envelope. As long as the envelope is stable, this measurement is independent of the beat frequency.

December 17, 2015
If necessary, you can hit the stop button on the oscilloscope to hold a good-looking FID from which to make measurements.

Whether or not you are having $B_0$-field stability problems, purposely vary the magnetic field fine control setting to see how the FID changes as the beat frequency changes. What role do the the preamp filter settings play in this regard? Adjust those as well. Report on your observations and describe the issues associated with the preamp settings and the FID beat frequency and the field instabilities. Return the preamp filters to the recommended 100 Hz and 10 kHz settings.

**Measurements**

In general, pulse sequences should not be repeated at intervals faster than $5T_1$. It takes at least this long for the sample to return to thermal equilibrium after being perturbed.

With only $A$-pulses on, vary $T_a$ to find pulses which rotate the magnetization by $\pi/2$, $\pi$, $3\pi/2$, $2\pi$, and $5\pi/2$. The $\pi/2$-pulse is at the first maximum in the FID signal. The $\pi$-pulse is at the first minimum, etc. Use the duration of the $A$-pulses relative to the rotation of the magnetization they cause to determine the Rabi frequency and then use it to estimate the amplitude of your $B_1$-field. You can assume you are exactly on resonance (where $\omega' = \gamma B_1$) for the calculation.

Applying $\pi/2$ $A$-pulses, adjust the $B_0$-field slightly and notice the change in frequency of the detected signal. Describe how the signal changes as you go through the zero beat frequency.

The true transverse magnetization $M_r(t)$ precesses at the Larmor frequency and decays quickly due to field inhomogeneities. The precessing $M_r(t)$ induces a pickup in the sample coil at the Larmor frequency with an amplitude proportional to $M_r(t)$. After amplifying that signal, mixing it, and amplifying it again, the signal measured by the oscilloscope, now oscillates at the beat frequency, (around 1 kHz), but its amplitude should be proportional to $M_r(t)$. That is, the envelope of the decaying oscilloscope signal should be proportional to the magnitude $M_r(t)$.

As the theory is usually concerned with the starting amplitude $M_r(0)$, the starting amplitude of the envelope should provide the desired measure. You should measure a peak-to-peak amplitude using the oscilloscope cursors—a measure that should be proportional to $M_r(0)$. Typical oscilloscope traces of FIDs and a spin echo are shown in Fig. 7 and demonstrate several issues that arise when trying to determine a peak-to-peak amplitudes as the separation of two horizontal oscilloscope cursors. Keep in mind that the envelope is that of the oscillations and there will be noise riding on top of those oscillations. You should try to set the cursors as if the noise were absent.

The leftmost trace shows a fairly strong FID where the noise component is small. In this case, the cursors have been “eyeballed” a bit above and below the trace to try to take into account where the envelope amplitude would be at $t = 0$ ($t = 0$ is at the external trigger or at the sharp spike arising from the strong RF drive pulse leaking into the detection system). For the weaker FID in the middle, significant noise rides on top of the signal. The cursor separation has been set to provide the desired measure. You should try to set the cursors as if the noise were absent.

The third figure is from a spin echo with a small noisy signal. For a spin echo, one is trying to measure the envelope amplitude at the middle of the signal. For the case shown in the figure, the noise is fairly large and has components on the same time scale as that of the signal. The cursor separation has been set to
try to match the size of the oscillations at the middle of the trace as if the noise were absent. In any case, be careful not to measure amplitudes when the oscillations are not clearly bigger than the noise.

\(T_2^*\)
Look at the FID envelope for a \(\pi/2\)-pulse. Does it appear exponential? Make a rough estimate of \(T_2^*\). Estimate the dimensions of your sample and assuming \(T_2^*\) is entirely due to \(B_0\)-field inhomogeneities, estimate the gradient of the \(B_0\)-field. For the estimate, you may assume \(T_2^*\) represents the time for protons at one end of the sample to make one more Larmor precession than those at the other end.

\(T_1\)
Set the \(A\)-pulse to a \(\pi\)-pulse by adjusting \(T_a\). Then turn the \(A\)-pulse off and set the \(B\)-pulse to a \(\pi/2\)-pulse. Then turn the \(A\)-pulse back on. Starting at \(T_d\) small, as you increase \(T_d\), you should see the FID decrease in size until it is nearly zero as \(M_z\) increases from around \(-M_0\) towards zero, and then it will increase again as \(M_z\) increases to its equilibrium value \(M_0\). The point where the signal goes to zero, the crossover, occurs at \(t = 0.693 T_1\). Measure the amplitude of the FID as a function of \(T_d\). Check if your decay is exponential by computer fitting the amplitude of the FID as a function of \(t = T_d\) in Eq. 34 with \(M_0\), \(M_i\) and \(T_1\) as fitting parameters. Do not fit to Eq. 36, which is Eq. 34 with \(M_i = -M_0\). The fitted value for \(M_i\) should come out close to \(-M_0\), but if the \(A\)-pulse is not a good \(\pi\)-pulse, the longitudinal magnetization following this pulse will not be perfectly inverted and \(M_i\) will be smaller (in magnitude) than \(M_0\). Fitting the data to a formula with \(M_i\) fixed at \(-M_0\) can then lead to systematic errors in the fitted \(T_1\).

For the fit, you must treat the FID amplitude as negative for signals before the crossover and positive for those afterward. Near the crossover you may want to throw out data points as it may be difficult to determine...
their correct sign. Does the fitted time constant agree with the crossover time? Determine the uncertainty in the fitted time constant.

$T_2$

Set up the necessary $A$- and $B$-pulse widths and find the spin echo. Measure the FID amplitude of the echo as a function of $T_d$. Perform a fit to Eq. 35 with $t = 2T_d$ (why $t = 2T_d$, not $t = T_d$?) and determine a value and uncertainty for $T_2$. Perform fits both with and without the $t^3$ term in the exponential. Can you see the effects of diffusion and field inhomogeneities? Why would the effects of diffusion be difficult or impossible to measure if $T_2$ is too short? Comment on the relative sizes of $T_2^*$, $T_1$, and $T_2$. What should be their predicted ordering and why?

CHECKPOINT: Measurements for the glycerin sample and the determinations of its $T_2^*$, $T_1$, and $T_2$ should be complete.

Distilled Water

Change to the distilled water sample. Push the glycerin sample vial out of the sample holder with a pencil eraser from the bottom so the vial comes out the top of the mounting tube. Then push the distilled water vial in from the top of the tube so the liquid inside is in the center of the coil.

The time constants $T_1$ and $T_2$ for distilled water will be much longer—on the order of seconds. This means data acquisition for inversion recovery and echo sequences will take much longer. (Recall that $T_r$ needs to be at least $5T_1$ to let the spins reestablish equilibrium populations.) For long $T_1$, the oscilloscope trigger must be set for normal (not auto) so the FIDs will not disappear between pulses.

A good way to determine how big $T_r$ needs to be is to measure the zero-crossing time for the inversion recovery sequence, increasing $T_r$ until the crossover time stops changing. This also lets you check the $T_r > 5T_1$ rule of thumb. Report on the results of this experiment and the validity of this rule.

Because of the long $T_2$, the spin echo measurements in distilled water clearly show the the effect of diffusion. Unfortunately, the field gradient $G$ is not well determined in the present apparatus. So use your measurements and the fitted coefficient of the $t^3$ term (in the argument of the exponential) with the known value of $D$ (about $2.3 \times 10^{-9}$ m$^2$/s at 25°C) to determine $G$ and compare with the cruder determination based on $T_2^*$.

Finally, measure $T_1$ using an alternative method that is sometimes used when $T_1$ is long. This method applies a single $A$-pulse repeatedly at fixed time intervals $T_r$. This one pulse (with its repeat time $T_r$) is then used for both preparation and probing. For an $A$-pulse that causes a precession through an angle $\theta$ ($\theta = \pi/2$ is typically used) the steady state amplitude of the magnetization immediately following each $A$-pulse can be shown to be:

$$M = M_0 \sin \theta \cdot \frac{1 - \exp(-T_r/T_1)}{1 - \cos \theta \exp(-T_r/T_1)}$$

(You might want to try to derive this equation yourself.)

To use Eq. 37, measure the size of the FID using a $\pi/2$ $A$-pulse (leave the $B$-pulse off) as you vary the pulse repeat time $T_r$. Start off by fitting your results to Eq. 37 with $M_0$ and $T_1$ as fit parameters but with $\theta$ fixed at the nominal value of $\pi/2$ (1.57). The reason that fitting $\theta$ is problematic should become clearer if you try the fit with $\theta$ still fixed but off the nominal value (at, say, 1.47 and 1.67). What happens to $T_1$ for these conditions? What happens to $T_1$ if you let $\theta$ be a third fitting parameter? Is
the fitted value of $\theta$ reasonable? Discuss the results.

**Special projects**

There are many studies that can be performed with this apparatus. Here are three you might consider.

1. Measure the gyromagnetic ratio of the $^{19}$F (fluorine) nucleus in the liquid Fluorinert (perfluorotributylamine or FC-43) or in the solid teflon (tetrafluoroethylene). Only try the solid sample after finding a FID with the liquid. Solids, in general, have short $T_1$ and $T_2$. Thus, in order to see enough beats within the FID, you may need to go with a higher beat frequency and higher band pass filtering. You may also have to increase the amplifier gain to see the weak FID.

   The Fluorinert FID should show a beating pattern. Learn enough about chemical shifts to relate them to the (at least two) Larmor frequencies that must be present in the sample in order to create a beating FID. (See auxiliary material for chemical shifts in FC-43.) How can you determine the very small difference in the two Larmor frequencies from the beat pattern? Express the difference in ppm of the mean Larmor frequency.

2. Add small amounts of CuSO$_4$ (copper sulfate) to distilled water samples to determine how the time constants depend on the concentrations of paramagnetic ions.

3. Make mixtures with varying ratios of glycerin and water, which changes the viscosity of the mixture. Measure how the time constants depend on the viscosity.