I. THEORY

A. Spin-Lattice Relaxation Time

According to quantum mechanics, protons possess intrinsic spin $\mathbf{s}$, and hence a magnetic moment

$$\boldsymbol{\mu} = \gamma \mathbf{s} \tag{1}$$

where γ is the gyromagnetic ratio of the proton. When a material is subjected to a constant external magnetic field $\mathbf{B_0}$, the protons split into two energy levels, given by

$$E = -\boldsymbol{\mu} \cdot \mathbf{B_0} \tag{2}$$

Over time, the magnetic moments of the protons align with the magnetic field; this decay towards the lower energy state is governed by the equation

$$\frac{dM}{dt} = \frac{M_0 - M_z}{T_1} \tag{3}$$

where M_z is the magnitude of the magnetic moment of the material, M_0 is its magnitude when the spins are all aligned with the field $\mathbf{B_0}$, and T_1 is the spin-lattice relaxation time. This equation is a scalar equation: Before the magnetic field is turned on, the spins are oriented randomly, so $\mathbf{M_z} = \mathbf{0}$. When $\mathbf{B_0}$ is turned on, the individual protons eventually align with $\mathbf{B_0}$, but the net magnetic moment $\mathbf{M_z}$ is always parallel to $\mathbf{B_0}$.

To measure T_1 for a material, one must be able to measure the net magnetic moment $\mathbf{M_z}$ of the material. This is achieved by applying a pulsed magnetic field.

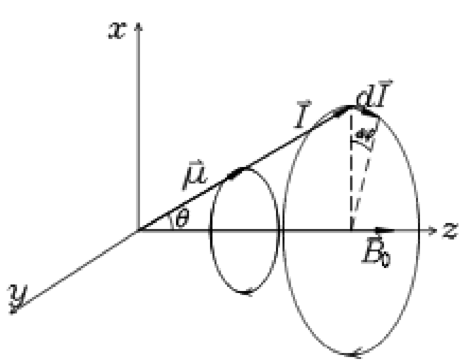

FIG. 1. Larmor precession of a magnetic moment $\boldsymbol{\mu}$ in a constant magnetic field $\mathbf{B_0}$ [2].

B. Pulses

If the magnetic moment $\boldsymbol{\mu}$ of a proton is not parallel to the constant magnetic field $\mathbf{B_0}$, then it will precess according to the equation

$$\boldsymbol{\tau} = \boldsymbol{\mu} \times \mathbf{B_0} = \frac{1}{\gamma}\frac{d\boldsymbol{\mu}}{dt} \tag{4}$$

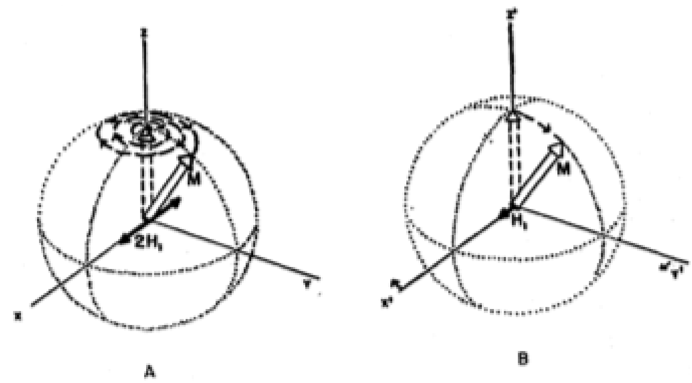

FIG. 2. Image from Carr and Purcell's 1954 paper, explaining how a rotating pulsed magnetic field (here $\mathbf{H}_1$) perpendicular to $\mathbf{B_0}$ can be used to detect the net magnetic moment of a material. On the left, the net magnetic moment is shown precessing about both fields in the lab frame. The image on the right depicts the rotating reference frame, in which the pulsed rotating magnetic field is constant. The net magnetic moment then rotates into the xy-plane. [1].

the equation for Larmor precession. The frequency of precession is $\omega_0 = \gamma B_0$. If the material is exposed to a magnetic field

$$\mathbf{B_1} = B_1 \cos(\omega_0 t)\hat{\mathbf{i}} + B_1 \sin(\omega_0 t)\hat{\mathbf{j}} \tag{5}$$

then the net magnetic moment $\mathbf{M_z}$ will begin to precess about this field as well (see Figure 2). In a reference frame that rotates along with $\mathbf{B_1}$, one can see that, with a pulsed field $\mathbf{B}_1$ of the proper duration, it is possible to rotate $\mathbf{M_z}$ so that it lies entirely in the xy-plane. Then $\mathbf{M_z}$ will begin to precess about the z-axis due to $\mathbf{B_0}$. Pulsed NMR devices contain pickup coils around the sample material, so that the precessing magnetic moment $\mathbf{M_z}$ induces a voltage proportional to M in the pickup coils.

Such an experimental setup makes it possible to measure the T_1 of materials using the following process: First, tune the frequency of the rotating magnetic field $\mathbf{B}_1$ to the Larmor frequency corresponding to the magnetic field $\mathbf{B}_0$. Then, tune the length of the pulse so that it rotates the net magnetic moment $\mathbf{M_z}$ by 180° (such a pulse is called a π-pulse); this rotates the net magnetic moment so that it points along the negative z-axis. The system then obeys the initial value problem in equation (3), with initial condition $M_z(0) = M_0$. The solution is

$$M_z(t) = M_0(1 - 2e^{-t/T_1}) \tag{6}$$

If, at a time t' after the π-pulse, one applies another pulse, this time rotating the net magnetic moment 90° (called a $\pi/2$-pulse), the net magnetic moment will lie in the xy-plane. The magnetic moment will precess due to $\mathbf{B_0}$, inducing a voltage proportional to $M_z(t')$ in the pickup coils. Thus the peak induced voltage as a function of time will be proportional to $M_z(t)$, which means that

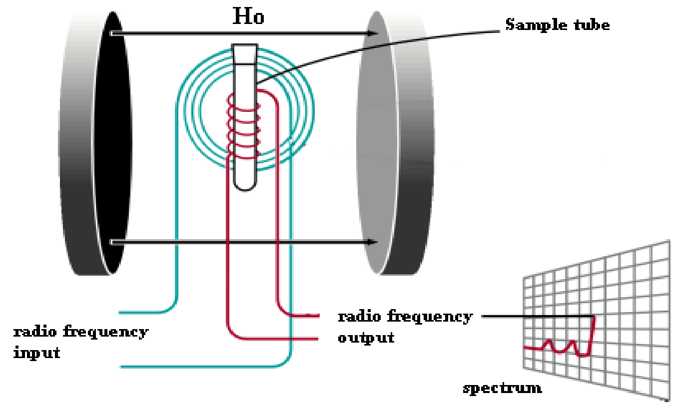

FIG. 3. Schematic of a pulsed NMR device. The sample sits inside a constant magnetic field $\mathbf{H_0}$. One set of coils produces the rotating magnetic field $\mathbf{B_1}$, and a second set (wound around the sample tube) detects the change in flux due to the rotating magnetic moment [3].

the characteristic decay time of a plot of the peak voltage with respect to time between pulses is exactly T_1.

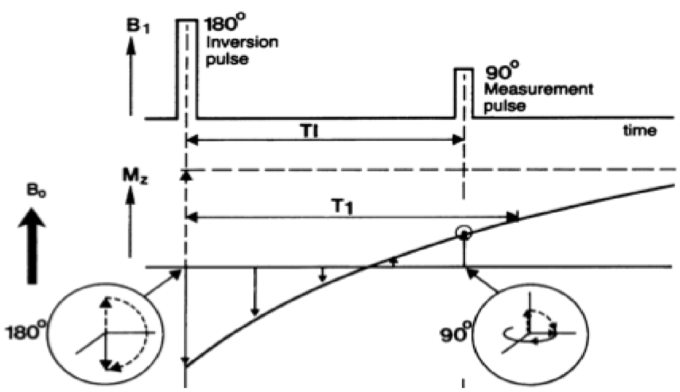

FIG. 4. Method of measuring T_1. A π-pulse first flips $\mathbf{M_z}$; after a time TI, a $\pi/2$-pulse rotates $\mathbf{M_z}$ into the xy-plane. The resulting precession induces a voltage proportional to $M_z(TI)$ in the pickup coils [2].

C. Spin-Spin Relaxation Time

As $\mathbf{M_z}$ precesses about the z-axis, two more effects come into play: Inhomogeneities in the magnetic field $\mathbf{B_0}$ cause the magnetic moments of protons in different parts of the sample to rotate at different frequencies. This is the primary cause of the decay in the voltage signal from the pickup coils. Also, interactions between the protons' moments causes them to drift out of phase with the net magnetic moment. The characteristic time T_2 of this interaction is called the spin-spin relaxation time, and it can be measured using another sequence of pulses:

Suppose $\mathbf{B_1}$ lies along the positive x-axis in the rotating coordinate frame. First, apply a $\pi/2$-pulse to the material; this rotates its net magnetic moment into the xy-plane. Since $\mathbf{B_1} = B_1\hat{\mathbf{i}}$, the net magnetic moment will lie along the positive y-axis.

$\mathbf{B_0}$ causes the net magnetic moment to precess about the z-axis. As this happens, the spins will dephase due to inhomogeneities in $\mathbf{B_0}$ across the material. In the rotating coordinate fraome, the magnetic moments of protons rotating with frequency higher than ω_0 will lie in the first quadrant, and the magnetic moments of protons rotating with frequency less than ω_0 will lie in the second quadrant.

Before all the magnetic moments of the protons become realigned with $\mathbf{B_0}$, apply a π-pulse to the material. This reflects the magnetic moment of each atom about the axis parallel to $\mathbf{B_1}$ in the rotating coordinate frame. So the protons with moments rotating at frequencies greater than ω_0 will end up in the fourth quadrant, and protons with moments rotating at frequencies lower than ω_0 will end up in the third quadrant. (Of course, the spins could dephase more than 90°, but their moments will still be reflected about the x-axis.) Since the "fast" moments are now "behind" the "slow" moments, the moments will realign at the negative y-axis. The magnitude of the net magnetic moment is then large enough to produce a voltage signal again; this signal is called a "spin echo."

However, the peak voltage induced by this echo is smaller than the peak voltage induced directly after the $\pi/2$ pulse. This is because the magnetic moments of the protons interact with each other, causing them to dephase. This dephasing can be modeled as an exponential decay:

$$M_z(t) = M_0 e^{-t/T_2} \tag{7}$$

Since the peak voltage induced in the pickup coils is proportional to $M_z(t)$, the characteristic decay time of the voltage curve is T_2.

In practice, it is more advantageous to apply multiple π-pulses after the initial $\pi/2$-pulse. Each π-pulse produces an echo, and the height of the echoes decays with characteristic time T_2.

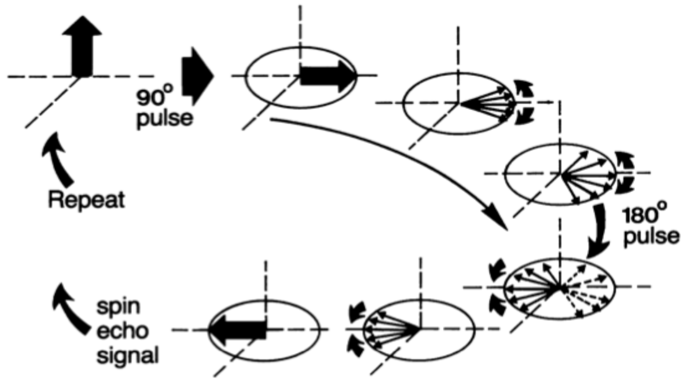

FIG. 5. Method of measuring T_2. A $\pi/2$-pulse first rotates $\mathbf{M_z}$ into the xy-plane, and the individual spins dephase due to inhomogeneities in $\mathbf{B_0}$. A π-pulse reflects the individual moments across the x-axis, causing a spin echo [2].

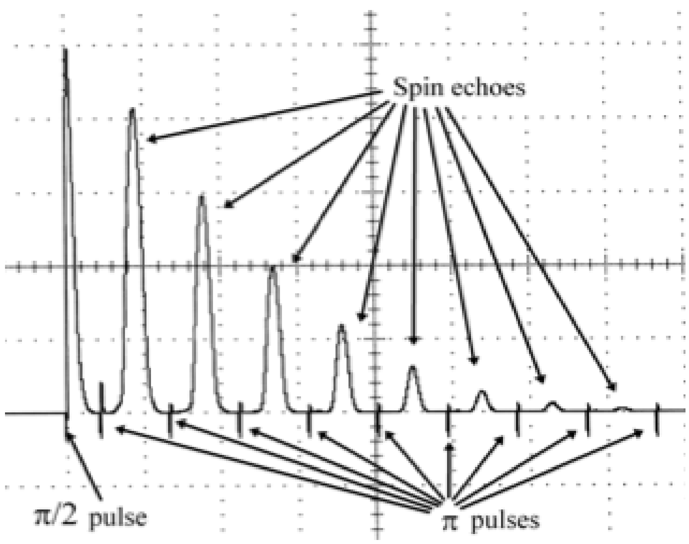

FIG. 6. Typical oscilloscope output of induced voltage in a measurement of T_2. A $\pi/2$-pulse is followed by many evenly-spaced π-pulses, and the resulting echoes decay exponentially with characteristic time T_2 [2].

[1] Carr, H. Y. and Purcell, E. M., "Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments". *Physical Review* **94**, 630-638 (1954). http://prola.aps.org/abstract/PR/v94/i3/p630_1

[2] University of Washington pulsed NMR lab manual: http://courses.washington.edu/phys431/PNMR/Pulsed_NMR.pdf

[3] NMR machine schematic: http://www.mhhe.com/physsci/chemistry/carey/student/olc/ch13nmr.html