

# Analysis of Mineral Oil and Glycerin through pNMR

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(Dated: 27 March 2011)

The experiment consisted of using pulsed nuclear magnetic resonance to determine characteristic properties of mineral oil and glycerin. The properties measured in this experiment were spin-lattice relaxation time ( $T_1$ ) and spin-spin relaxation time ( $T_2$ ).  $T_1$  times were found to be  $20 \pm 2$  ms and  $40 \pm 2$  ms for mineral oil and glycerin respectively.  $T_2$  times were found to be  $15 \pm 2$  ms and  $35 \pm 2$  ms for mineral oil and glycerin, respectively.

## I. INTRODUCTION

In 1946, Carl Purcell and Felix Bloch independently observed nuclear magnetic resonance in magnetic nuclei. In the past half century, technology that exploits nuclear magnetic resonance has pervaded modern society. Its most common use is for medical purposes, where doctors are able to take non-invasive scans of sensitive areas of the body through magnetic resonance imaging (MRI). It is also a very powerful spectroscopic tool. Nuclear magnetic resonance is able to identify many substances based off their characteristic relaxation times,  $T_1$  and  $T_2$ . Our objective in this experiment was to measure these characteristic relaxation times for two substances, mineral oil and glycerin. These times are unique for each substance and can become tools that contribute to determining and unknown. This paper will begin by explaining the theory behind the characteristic relaxation times in addition general NMR theory. This will be followed by a description of the experiment that was carried out. This section will be divided into parts explaining the technique used to obtain each characteristic relaxation times as well as the result in each case.

## II. THEORY

Nuclear magnetic resonance is a phenomena that can be observed in magnetic materials have a magnetic moment and angular momentum. This property is held by most nuclei of everyday matter, so it is very useful as a spectroscopic tool. Understanding NMR is requires both classical and quantum mechanics. Classically, one can think of the mentioned nuclei as spinning bar magnets. The magnetic moment associated with the magnetic is  $\mu$  and the angular momentum is given by  $\mathbf{J}$ . These two properties are not independent and are in fact related by the equation

$$\mu = \gamma \mathbf{J}, \quad (1)$$

where  $\gamma$  is known as the gyromagnetic ratio. The magnetic moment has a linear dependence on the nuclear angular momentum  $\mathbf{J}$ , which takes on quantized values restricted by quantum mechanics to be

$$\mathbf{J} = \hbar \mathbf{I}, \quad (2)$$

where  $\mathbf{I}$  is the nuclear spin.

If there is no external magnetic field present, there is no energetically preferred orientation along a given axis. If there is an external homogeneous magnetic field present along one axis,  $z$ , the energy of the nucleus is given by

$$U = -\mu_z \mathbf{B}_0 = -\gamma \hbar I_z B_0. \quad (3)$$

In the case of our experiment, we are concerned with the nucleus of hydrogen, which is simply one proton. The proton has an  $\mathbf{I}$  value of  $I=1/2$ . Quantum mechanics restricts the orientation of the nuclear spin to only two cases. There is one state parallel to the magnetic field while the other is anti parallel.  $M_I=1/2$  refers to the parallel state while  $M_I=-1/2$  refers to the antiparallel state. A visual representation is shown in Figure 1. The energy separation between the two states is given by

$$\Delta U = \omega_0 \hbar = \gamma B_0 \hbar, \quad (4)$$

from which

$$\omega_0 = \gamma B_0, \quad (5)$$

can be obtained.  $\omega_0$  is an angular frequency known as the Larmour frequency. Using the gyromagnetic ratio value for the proton  $\gamma_{proton}=2.675 \times 10^4$  rad/(sec gauss), the resonance condition for stimulated absorption of radiation is given by

$$f_0(MHz) = 4.258 B_0(kilogauss), \quad (6)$$

where  $f_0$  is the required frequency of radiation. Due to the energy difference between the states, the parallel (low energy) state is preferred at room temperature due to Boltzmann statistics. This causes the population to have a net magnetic moment parallel to the external magnetic field.

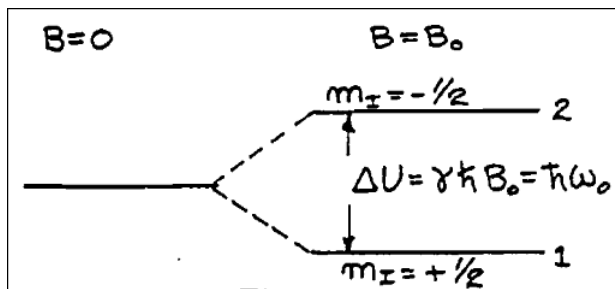


FIG. 1. A diagram showing the splitting in energy between the up and down states in a magnetic field.

Given a population of protons in a homogeneous magnetic field, one could use an orthogonal RF driven magnetic field at the Larmor frequency to cause transitions between the two states. Depending on the length of time of that the population is exposed to the RF field, the net magnetic field of the population will shift. A pulse that completely inverts the spin up population, known as a  $\pi$  pulse, lasts for a time given by

$$\tau_{\pi} = \frac{\pi}{\gamma B_1}. \quad (7)$$

where  $B_1$  represents the perturbing magnetic field. A pulse that rotates the net magnetic moment only 90 degrees, known as a  $\pi/2$  pulse, last for half the time of a  $\pi$  pulse, and lasts for a time given by

$$\tau_{\pi/2} = \frac{\pi}{2\gamma B_1}. \quad (8)$$

### A. Spin-Lattice Time, $T_1$

There is a characteristic time for a population to equilibrate its magnetization once placed in a magnetic field. In the process of reaching equilibrium, energy and angular momentum are exchanged between the nuclei and the lattice. This process can be described by the differential equation

$$\frac{dM_z}{dt} = -\frac{M_0 - M_z}{T_1}, \quad (9)$$

where  $M_0$  is the equilibrium magnetization and  $M_z$  is the magnetization along the z-axis.  $T_1$  is the characteristic spin lattice relaxation time. In the instance where  $M_z$  and  $t=0$ , Equation 9 becomes

$$M_z(t) = M_0(1 - e^{-\frac{t}{T_1}}), \quad (10)$$

which describes the rate at which a sample reaches its equilibrium value.

### B. Spin-Spin Time, $T_2$

There is a characteristic time for the spins of a population to dephase from each other. If a population is subjected to a  $\pi/2$  pulse, the spins of each nucleus precess according to the Larmor frequency in phase. However, due to local variations in magnetic field on a nuclear level, the spins dephase from each other. The rate at which they do so is given by the differential equation

$$\frac{dM_z}{dt} = -\frac{M_z}{T_2}, \quad (11)$$

Once again, given  $M_z$  and  $t=0$ , Equation 11 becomes

$$M_z(t) = M_0 e^{-\frac{2t}{T_2}}, \quad (12)$$

which describes the rate at which the spins dephase from each other.

## III. EXPERIMENT

### A. Apparatus

For this experiment, a teachspin PS1-A pulsed NMR spectrometer was used. A simple block diagram is displayed in Figure 2. The pulse programmer generates RF pulses at a frequency given by user input. One can also vary the number, duration, and delay time between the pulses. The RF signal from the programmer is sent through a transmitter coil that is wrapped around the

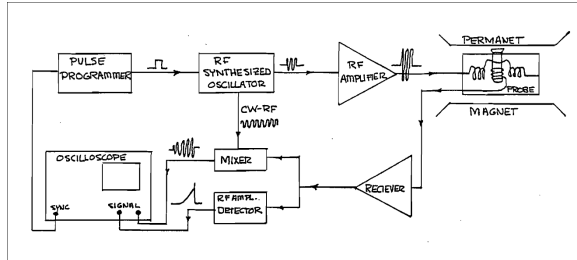


FIG. 2. A block diagram of the pNMR apparatus.

sample. The sample is also placed between two permanent magnets such that the field acting on the sample is as homogeneous as possible. Also around the sample is a pickup coil. It must be noted that the permanent magnets, the transmitter coil, and the pickup coil are orthogonal to each other. In this way, the pickup coils are sensitive only to the precession of the nuclei in the plane orthogonal to static magnetic field. The RF programmer signal is also sent to a mixer where it is mixed with the signal coming from the pickup coil. The pickup coil signal is also sent straight to the oscilloscope. The mixed signal is sent to the oscilloscope. If the input signal is resonant with the signal from the pickup coil, the reading on the oscilloscope will be smooth. If not, the signal will have beats. As the output RF becomes closer to resonance, the beats will lessen.

### B. Spin-Lattice Time, $T_1$

The spin-lattice relaxation time is found by exposing the sample to a  $\pi$  pulse followed by a  $\pi/2$  pulse. The  $\pi$  pulse completely flips the magnetization. Then, the  $\pi/2$  pulse flips the spin 90 degrees. This was repeated for increasing delay times between the  $\pi$  and  $\pi/2$  pulses. For no delay between the two pulses, the precession begins in the x-y plane, and therefore the signal in the pickup coils is greatest. As delay time is increased the signal will decrease until reaching 0. At this point, the  $\pi/2$  pulse is hitting the sample when the magnetization is in the x-y plane, where a  $\pi/2$  pulse would create no output signal. After this zero point, the signal will increase with increased delay time. It will asymptotically approach the same value as with no delay time when the  $\pi/2$  pulse hits the sample after it has already reached equilibrium magnetization. For both mineral oil and glycerin, the signal output was recorded vs the delay time. The output for the values before 0 are absolute values and represent magnetization in the -Z direction. The graph of the data, seen for mineral oil in Figure 3, can be fitted to Equation 10.  $T_1$  can then be calculated from the exponent.  $T_1$  times were found to be  $20 \pm 2$  ms and  $40 \pm 2$  ms for mineral oil and glycerin respectively.

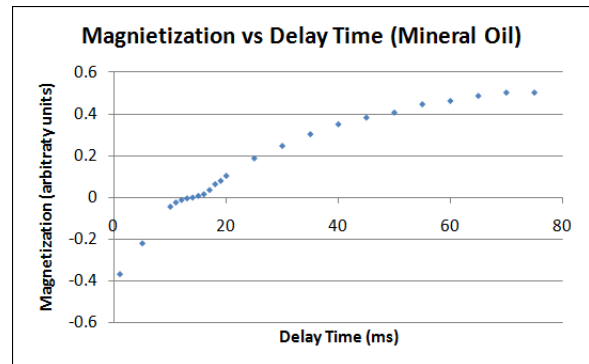


FIG. 3. A graph of arbitrary magnetization vs the time delay between the  $\pi$  pulse  $\pi/2$  pulse for mineral oil.

### C. Spin-Spin Time, $T_2$

The spin-spin relaxation time was found through spin echo. This was done because local inhomogeneity in the static magnetic field changes the free induction decay (FID), which is the relaxation time after a simple  $\pi/2$  pulse. The FID time  $T_2^*$ , was found to be  $1.1 \pm .1$  ms and  $1.2 \pm .1$  ms for mineral oil and glycerin respectively. The sample is exposed to a  $\pi/2$  pulse followed by a  $\pi$  pulse. The  $\pi/2$  pulse rotates the magnetization where the individual magnetizations of the nuclei dephase at different rates because of the inhomogeneity in the magnetic field. However, the following  $\pi$  pulse flips both the magnetic moments and the direction of the dephasing. The result is that the individual moments rephase to a second local maximum that is seen on the output signal. The height of this maximum is dependent on the delay time between the pulses. The height of the second maximum vs delay time was recorded for both mineral oil and glycerin. The heights were then graphed vs twice the delay time, because the dephasing and rephasing times are equal and each equal to the delay time. The data, shown in Figure 4, was fitted to a curve of the same form as Equation 12. From the exponent of the curve equation,  $T_2$  was calculated.  $T_2$  times were found to be  $15 \pm 2$  ms and  $35 \pm 2$  ms for mineral oil and glycerin, respectively.

#### IV. CONCLUSION

$T_1$  times were found to be  $20 \pm 2$  ms and  $40 \pm 2$  ms for mineral oil and glycerin respectively.  $T_2$  times were found to be  $15 \pm 2$  ms and  $35 \pm 2$  ms for mineral oil and glycerin, respectively. In both cases, we found  $T_1$  times to be larger than  $T_2$  times. The experiment approximately verified literature values for mineral oil and glycerin. However, several sources of error are inherent to this experiment. The first is the dependence of the experiment on the value of the B field on the sample. This has a direct affect on the resonance frequency of the sample, as can be seen from Equation 5. It was noted that the resonance frequency change over the course of a data taking run an average of 150 Hz. This may have been due to heating of the permanent magnet by an external source of perhaps the transmitter coils of the apparatus. Another source of error is the resolution of the oscilloscope, which only allowed for readings accurate to two significant figures. Even with the error, the characteristic times of the two substances as well as an understanding of the concepts and method to obtaining the times were gained. This could allow for future experiments to determine the spin-lattice and spin-spin relaxation times of other substances for which these have not yet been measured. This experiment also begs the question of how one might be able to perform this spectroscopy on larger nuclei, instead of covalently bonded hydrogen, which acts closely to a free proton.

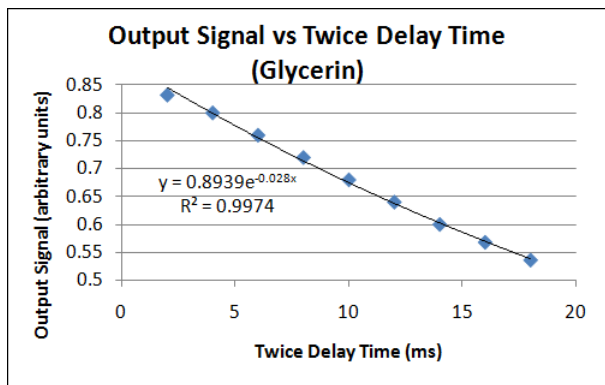


FIG. 4. A graph of output signal vs twice the time delay between the  $\pi/2$  pulse  $\pi$  pulse for glycerin.