Pulsed Nuclear Magnetic Resonance Analysis of Glycerin and Mineral Oil

Janet Chao, Dean Henze, Patrick Smith, Kent Lee

February 27, 2013

Abstract

Pulsed nuclear magnetic resonance was used in order to determine characteristic properties of mineral oil and glycerin by observing the free induction decays (FID). The properties studied included spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2). The spin-lattice relaxation time (T_1) for mineral oil was found to be 21 ±1.9 ms, while T_1 for glycerin was 41 ±2.5 ms. The spin-spin relaxation time (T_2) for mineral oil was found to be 21 ±1.9 ms while T_2 for glycerin was 43.5 ±3.5 ms.

1 INTRODUCTION

In 1946, Carl Purcell and Felix Bloch discovered the response of magnetic nuclei in a constant magnetic field to radio frequency induced magnetism, introducing the world to the now widely utilized spectroscopic tool known as NMR. NMR has not only proven to be an important form of spectroscopy used to study quantum and nuclear phenomena, but also spans various fields of research including chemistry, biology, geology, and medicine [1]. Notably, doctors use NMR through common magnetic resonance imaging (MRI) devices in order to take non-invasive scans of human tissue, allowing them to diagnose medical issues without invasive surgery. In 1950, Erwin Hahn at the University of Illinois observed the response of magnetic nuclei to pulsed bursts of radio frequency magnetic fields. He discovered the spin echo signal that is observed after a two pulse sequence at a time equal to the delay time between the two pulses. This discovery made way for the pulsed NMR technique for studying magnetic resonance [1]. In modern experimental physics, NMR is used to identify certain substances through characteristic properties such as their relaxation times T_1, spin-lattice relaxation time, and T_2, spin-spin relaxation time. In this experiment, pulsed NMR is applied in order to find T_1 and T_2 of mineral oil and glycerin. Since relaxation times are a distinct property of a substance, these times can often be used to reveal certain properties or to determine the identity of an unknown substance. This paper will provide the experimental design and apparatus (Section 2), the theory behind nuclear magnetic resonance (Section 3), a summary of the results Section 4), and a discussion of the conclusion of the experiment (Section 5).

2 EXPERIMENTAL DESIGN

This experiment uses TeachSpin’s PSI-A, the first pulsed NMR spectrometer designed uniquely for teaching purposes. The PSI-A uses new high-energy magnetic materials for high homogeneity and separates the transmitter and receiver functions for users to easily understand each individual function. The pulse programmer shown in Figure 1 generates radio frequency (rf) pulses that are amplified and sent to the transmitter coils, producing homogeneous, time-dependent, rotating B_1 fields that produce the precession of magnetization [1]. These pulses are known as 90° ($\frac{\pi}{2}$) and
180° ($\pi$) pulses. The precessing nuclear magnetization in the x-y plane induces an EMF in a receive coil that can be detected by both the rf amplitude detector (records free induction decays and spin echoes signals) and the mixer (determines the proper resonance frequency of the oscillator). The Helmholtz transmitter coil and the pickup coil are wrapped around the sample so that both coils are orthogonal to the permanent magnets [1]. This way, the pickup coils read the nuclei precessions in the plane perpendicular to the constant magnetic field. Since the RF programmer also sends a signal to the mixer, the mixed signal is a combination of both the signal from the pickup coil and the rf signal being transmitted. When these two signals are in resonance and cancel each other out for a smooth mixer signal on the oscilloscope, the resonant frequency of the sample has been found. The measurement of spin-lattice relaxation time $T_1$ and spin-spin relaxation time $T_2$ will be described in the following theory section.

3 THEORY

Magnetic resonance is observed in systems where the magnetic components have both a magnetic moment and an angular momentum. Classically, magnetic nuclei such as the simple Hydrogen proton can be thought of as a spinning bar magnet where magnetic moment $\mu$ and angular moment $J$ are related so that

$$\mu = \gamma \cdot J,$$

where $\gamma$ is the gyromagnetic ratio ($\gamma_{\text{proton}} = 2.675 \times 10^4 \text{ rad sec}^{-1} \text{ gauss}^{-1}$). The angular momentum of a protons is dependent on the spin of the nucleus (I) so that

$$J = I \hbar,$$

where two spin states exist ($I = +\frac{1}{2}, I = -\frac{1}{2}$) for fermions. The spin up state ($I = +\frac{1}{2}$) is lower in energy than the higher energy spin down state ($I = -\frac{1}{2}$) [1]. When a sample containing magnetic nuclei are placed inside the permanent magnetic field, $B_0$, most of the "spinning bar magnets" align with the magnetic field and occupy the lower energy spin up state, establishing a net magnetization along the external magnetic field in the z-direction. In thermal equilibrium in an external constant magnetic field, the only net magnetization of the sample is $M_z$, where $M_z$ is the sum of all individual $\mu_z$’s, while $M_x$ and $M_y$ are zero (or the sums of individual $\mu_x$ and $\mu_y$ all cancel out). Each spin moment precesses around the axis of the magnetic field as shown in Figure 3 [2].

Figure 1: A simplified block diagram of the most important functions of the apparatus

Figure 2: A sketch of the sample probe showing the permanent magnet and the receiver coil and transmitter Helmholtz coil wrapped around the sample.
The energy difference between the two spin states, $\Delta U$, can be written in terms of the magnetic energy of the nucleus and also in terms of an angular frequency so that

$$\Delta U = \mu B_0 = \hbar \omega_0.$$  \hspace{1cm} (3)

Combining Equation 3 with Equation 1 and Equation 2, we find that

$$\omega_0 = \gamma B_0.$$  \hspace{1cm} (4)

Equation 4 shows that the resonant frequency is related to the external magnetic field by the gyromagnetic ratio $\gamma$ [1]. Resonance occurs when pulsed radio frequencies are applied transverse to the external magnetic field at the precession frequency. This resonant rf pulse rotates the thermal equilibrium magnetization $M_0$ into the x-y plane, creating a temporary $M_x$ and $M_y$. A 90° ($\frac{\pi}{2}$ pulse) is created by turning off the $B_1$ field created by the rf pulse at the instant that the magnetization reaches the x-y plane, while a 180° ($\pi$ pulse) is created if the rotating field is applied for twice as long [1]. Upon application of an rf pulse, the net magnetization is knocked out of the z-axis and is transversed into the x-y plane as shown in Figure 4 [2].

Furthermore, the absorption of the RF energy causes the population of nuclei with mostly spin up states to flip into the higher energy spin down state until most of the nuclei have become spin down and the signal on the oscilloscope has the highest peak possible. This is the 90° pulse. After a pulse is applied on the sample, the magnetization will begin to decay immediately, generating an observable decay on the oscilloscope known as the free induction decay (FID) [2]. There are two different relaxation processes involved in this spin decay, the spin-lattice relaxation and the spin-spin relaxation. After a 90° ($\frac{\pi}{2}$) pulse is applied, a spin-lattice relaxation occurs where the magnetization will begin to decay immediately in the x-y plane where net magnetization relaxes back to its orientation in the z-direction, giving the characteristic time constant $T_1$ or the spin-lattice relaxation time [2]. The differential equation that describes this process is written as

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}.$$  \hspace{1cm} (5)

When we integrate this equation with initial condition $t = 0, M_z = 0$, we find that

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

The spin-spin relaxation refers to the exponential decay of the net magnetization in the x-y plane. The major reason this decay occurs is due to inhomogeneity in the constant external magnet that creates different precessional frequencies based on spatial inequalities in the...
magnetic field. Similar to Equation 4,
\[ \Delta \omega = \gamma \Delta B_0. \] (7)

Equation 7 reveals that the inhomogeneity of the magnetic field would create various resonance frequencies that would cancel out over time, producing the spin-spin relaxation due to dephasing frequencies. The Spin-spin relaxation time, \( T_2 \) can be determined by taking the differential equation
\[ \frac{dM_x}{dt} = -\frac{M_x}{T_2} \quad \text{and} \quad \frac{dM_y}{dt} = -\frac{M_y}{T_2}. \] (8)
and finding its solution to be
\[ M_x(t) = M_0 e^{-t/T_2} \quad \text{and} \quad M_y(t) = M_0 e^{-t/T_2}. \] (9)

PNMR creates a two pulse sequence with an initial 90° pulse followed by an 180° pulse after time \( \tau \). The additional 180° pulse rephases the x-y magnetization so that the signal looks like that of a perfectly homogenous magnet, but the height of this spin echo signal is slightly lower than that of the maximum FID because some random fluctuation in the nuclear sites could not be rephased by the 180° pulse. Therefore, several PNMR two pulse sequences were produced and plotted while varying the delay time \( \tau \) in order to find the spin-spin relaxation time \( T_2 \) [1].

4 RESULTS

4.1 GLYCERIN

\( T_1 \) for glycerol was found to be 41 ±2.5 ms, while \( T_2 \) for glycerol was found to be 43.5 ±3.5 ms. When measuring the peak voltages for the spin echo in \( T_2 \) trials and measuring the peaks of the FIDs in \( T_1 \) trials, we found that uncertainty was ±0.12V.

4.2 MINERAL OIL

\( T_1 \) for mineral oil was found to be 21 ±1.9 ms, while \( T_2 \) for mineral oil was found to be 21 ±1.9 ms. When measuring the peak voltages for the spin echo in \( T_2 \) trials and measuring the peaks of the FIDs in \( T_1 \) trials, we found that uncer-
tainty was $\pm 0.12V$.

Figure 10: Magnetization and delay time plot of mineral oil sample used to calculate spin-lattice relaxation time $T_1$.

Figure 11: Magnetization and delay time plot of mineral oil sample used to calculate spin-spin relaxation time $T_2$.

5 CONCLUSION

For mineral oil, $T_1$ and $T_2$ were the same value at 21 ms. For glycerin, $T_1$ was 41 ms and $T_2$ was 44 ms. According to this data, mineral oil has returns to equilibrium more rapidly than glycerin. The values for mineral oil are inconsistent with those found in literature$^{2,3}$ in which $T_2$ of mineral oil (16 ms) is lower than $T_1$ of mineral oil (27.5 ms) $^{3}$. Our data shows that they are nearly equivalent values. Our data for glycerin follows the trend in which $T_2$ at 44 ms is slightly higher than $T_1$ at 41 ms. In Magat, $T_2$ of glycerin (18 ms) is only slightly higher than $T_1$ of glycerin (17 ms) $^{2}$. However, our uncertainty ranges for both glycerine and mineral oil make it difficult to be conclusive about any of this data since both relaxation time values for both samples are so close in range (where mineral oil’s relaxation times are equal and glycerin’s relaxation times are within 3 ms and all uncertainties range from 1.9 ms to 3.5 ms). One major source of error in this experiment was the apparent systematic shift in resonant frequency over time due to temperature changes when the apparatus was kept on for too long and began to heat up. This is because the frequency is temperature dependent. Furthermore, the oscilloscope’s representation of the pulses were often difficult to read and determine a precise value from, giving an uncertainty of approximately $\pm 0.12V$. The uncertainty values for relaxation times were found by creating best fit lines within the $\pm 0.12V$ range and calculating relaxation time values from these lines. In order to avoid these errors, the experiment must be done quickly as to not overheat the system. The error in measurement due to oscilloscope capabilities could not be avoided.

6 ACKNOWLEDGMENTS

References

[1] Physics 480W (Experimental Modern Physics) Manual. NMR San Echo Lab, Dept. of Physics at the University of San Diego, Spring 2013