Determining the relaxation times, T_1, T_2, and T_2^*, in glycerin using pulsed magnetic resonance.

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We use pulsed magnetic resonance to determine the multiple relaxation times in glycerin and mineral oil. For mineral oil we find $T_1 = 57.7 \pm .3ms$, $T_2 = 37.6 \pm .2ms$, and $T_2^* = .35 \pm .03ms$. The corresponding values for glycerin are $T_1 = 45.6 \pm .2ms$, $T_2 = 22.2 \pm .1ms$, and $T_2^* = .35 \pm .03ms$

I. INTRODUCTION

Nuclear magnetic resonance is the phenomenon where an atomic nuclei will absorb and re-emit electromagnetic radiation. There are two main techniques used in NMR experiments: continous wave and pulsed NMR. In both types of NMR a sample is placed in a magnetic field to align the nuclear spins and then perturbed with an outside source. Continuous wave NMR, as can be implied from its name, uses a continuous source to perturb a material. This technique involves an indirect measurement of the important relaxation times in the system because the magnet producing the B-field will have some spatial inhomogeneity. It is the genius of Erwin Hahn who in 1950 developed the technique of pulsed NMR. This technique uses a series of pulses to perturb the system rather than a continuous wave.

Nuclear magnetic resonance has many practical applications such as nuclear magnetic resonance imaging which allows us to probe human bodies without harmful radiation. In this paper we use pulsed NMR to determine the spin-lattice and the spin-spin relaxation times in glycerin and mineral oil samples. Section II will present the theory of pulsed NMR, section III details the methods used in our experiments, section IV presents our findings, and section V is left for final remarks.

II. THEORY

Magnetic resonance is experienced in any atom that has both a magnetic moment and angular momentum. The magnetic moment is determined by the following equation:

$$\vec{\mu} = \gamma \vec{J}. \tag{1}$$

In this equation $\vec{\mu}$ is the magnetic moment γ is defined to be the gyromagnetic ratio, the ratio of the dipole moment to the angular momentum, and $\vec{J}$ is the angular momentum. Because of the quantization inherent in quantum mechanics we know that the angular momentum is quantized in units of $\hbar$ to be

$$\vec{J} = \hbar \vec{I}, \tag{2}$$

where I is the spin of the nucleus. In our work we choose to study hydrogen nuclei with spin states, $I = \pm \frac{1}{2}$.

Suppose we have a collection of hydrogen nuclei that are in thermal equilibrium without an applied external magnetic field. Then classically the magnetization vectors of these atoms will be randomly oriented and the magnetic energy will sum to zero. If we then apply a magnetic field to this ensemble we can develop a new thermal equilibrium for the system. With an applied magnetic field there now exists a total magnetic energy:

$$U = -\vec{\mu} \cdot \vec{B}. \tag{3}$$

If our coordinate system is such that the B-field is aligned along the z axis the energy is:

$$U = -\gamma \hbar I_z B_0, \tag{4}$$

where I_z is the spin component along the z-axis and B_o is the magnitude of the magnetic field. As stated previously, the hydrogen atom has only two values for I_z, namely, $I_z = \pm \frac{1}{2}$. If we apply this magnetic field to an ensemble of protons then we have a simple two state system with $U_{-\frac{1}{2}} = \frac{\gamma \hbar B_0}{2}$ and $U_{\frac{1}{2}} = -\frac{\gamma \hbar B_0}{2}$.

Because nature tends to minimize the energy of an ensemble the spins of these protons will tend to align parallel with the magnetic field, but, as with any physical process, this process does not take place instantaneously. This process is described in the following equation:

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}. \tag{5}$$

In equation 5, M_0 is the magnetization when all the spins are aligned with the B-field and T_1 is referred to as the spin-lattice relaxation time. Equation 5 can be solved to give:

$$M_z(t) = M_0(1 - exp(-\frac{t}{T1})). \tag{6}$$

It is equation 6 that explains why T_1 is considered a relaxation time– it is the characteristic time of when the exponential reaches $\frac{1}{e}$ of its initial value. In our case, the magnetization reaches $\frac{e-1}{e}$ of its maximum value. After a sufficiently long time the population of each state can be determined from a basic Boltzmann statistics in the following equation:

$$\frac{N2}{N1} = exp(-\frac{\Delta U}{kT}) = exp(-\frac{\hbar \omega_0}{kT}), \tag{7}$$

where ΔU is the energy difference in energies where the energy of each state is defined in Equation 4 and ω_0 is the frequency of light required to produce a transition between the two states.

It is now only natural to question what happened to the net magnetizations in the magnetic field. This can be resolved through the classical model of magnetic fields. If we consider the protons to be loops of current we can define the torque due to the B field to be:

$$\vec{\mu} x \vec{B} = \frac{1}{\gamma} \frac{d\vec{u}}{dt}. \tag{8}$$

Equation 8 can be solved to show that the magnetic moment will precess about the applied magnetic field with a frequency ω_0 which is the transition frequency from equation 7. This then implies that the total magnetization in the x and y directions will sum to 0.

Suppose we wish to achieve a magnetization in the x-y plane. We can do this by by blasting our sample of protons with a radio frequency perpendicular to the applied B-field with a frequency ω_0 as set in equation 7. A pulse that is kept on long enough such that the resulting magnetization ends up in the x-y plane is called a $\frac{\pi}{2}$ pulse because it rotates the magnetization through $\frac{\pi}{2}$ radians. A pulse kept on such that the magnetization is ends up along the -z axis is called a π pulse. These pulses will be important in describing the methods used to determine the multiple relaxation times.

If we use a $\frac{\pi}{2}$ pulse we can quantify the remaining magnetization in either the x or y direction by the following equation:

$$\frac{dM_i}{dt} = -\frac{M_i}{T_2}, \tag{9}$$

where the index i stands for either the x or y direction and T_2 is another relaxation time which results from the local magnetic fields produced by neighboring nuclei.

The previous paragraphs were a very classical interpretation. In terms of quantum mechanics, what the radio frequency does is converts the magnetization from a complete $|+z>$ state to a superposition of $|+z>$ and $|-z>$. The corresponding coefficients for this superposition are such that the probability of being in either of these states is $\frac{1}{2}$ and the total probability sums to 1.

III.   METHODS

We completed 3 different experiments that all use the same equipment set up as seen in Figure 1. Notice that in the figure, the sample and the coil are drawn incorrectly. If we consider the schematic to be seen from above then then sample will be going into the page with the coil wrapped around it.
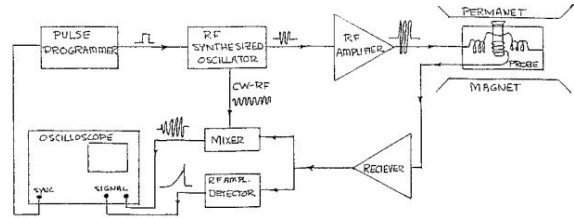

FIG. 1. A schematic of the nmr apparatus. The pulse programmer sets the pulse amplitude and time between pulses and triggers the oscilloscope for the proper burst. The RF synthesizer creates RF that is then amplified before hitting the sample. The receiver amplifies the EMF and the current is sent to two detectors. The amplitude detector measures the FID amplitude. The mixer amplifies the signal and checks that the RF frequency matches the frequency of the energy levels within our sample. The oscilloscope is used to collect both signals.

A.   Determination of T_1

To determine T_1 we first hit our relevant sample, glycerin or mineral oil, with a π pulse, wait a specific delay time, and then apply our $\frac{\pi}{2}$ pulse. The reason we must apply this second pulse is because we can only measure spins in the x-y direction. This second pulse puts the spins in the x-y direction and the magnetization we measure here is proportional to the magnetization right before this pulse. By varying the delay time we can find the magnetization as a function of delay time. Fitting our amplitudes with exponential fitting algorithms then determines the spin-lattice relaxation time.

B.   Determination of T_2

Determining T_2 involves applying a $\frac{\pi}{2}$ pulse followed by a specific delay time and then a π pulse. This second π pulse is necessary because of the inhomogenities in the static B-field. This means that some of the spins will be in a higher magnetic field and this leads to a decoherence of the magnetization in the x-y plane. The π pulse flips these magnetizations by π radians allowing the slower spins to "catch up" and recohere with the faster moving spins. After the π pulse we observe what is known as the spin-echo. This echo is the result of all the spins recohering and giving a measurable voltage that occurs at a time 2τ where τ is our delay time. We repeat these π pulses multiple times and measure the amplitudes of the decaying spin-echo as a function of time to determine T_2, the spin-spin relaxation time, for our sample.

C. Determination of T_2^*

The experimental procedure outlined in subsection B appears to be slightly complicated. If T_2 is the decay time associated from flipping the magnetization into the x-y plane, which occurs after a $\frac{\pi}{2}$ pulse, why can we not just use this single pulse and measure the decay of the signal it produces? In fact, we do measure this signal and determine a new decay constant, T_2^*, but since the inhomogenities in the static B field exist, the decoherence of the magnetization will lead to a false value for T_2. T_2^* is a useful physical quantity in two particular cases: (1) if the spin-spin relaxation time is less than 0.3ms then T_2^* is the true T_2 and (2) we can relate the value of T_2^* to the variation in the magnetic field through either of the following two equations[1]:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_1} + \gamma \Delta B, \qquad (10)$$

or

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta B, \qquad (11)$$

where equation 11 applies for T_1 values significantly larger than T_2 values.

D. Measuring the gyromagnetic ratio

To measure the gyromagnetic ratio we used a guass-meter that was placed in the center of the magnet which produces the static field. We then recorded the frequecny and can determine the gyromagnetic ratio through the following relation:

$$\gamma = \frac{\omega}{B} \qquad (12)$$

IV. RESULTS AND DISCUSSION

We find that mineral oil has a spin-lattice relaxation time of $T_1 = 57.3 \pm 0.3ms$ and a spin-spin relaxation time of $T_2 = 37.6 \pm 0.2ms$. The corresponding values for glycerin are $T_1 = 45.6 \pm 0.2ms$ and $T_2 = 22.2 \pm 0.1ms$. The T_2^* for both materials comes out to be $T_2^* = 0.35 \pm 0.03ms$. The gyromagnetic ratio is determined to be $\gamma = 2.8 * 10^4 \pm 0.1 \frac{rad}{s*gauss}$. The plots describing these values are seen in figures 2-5

The higher value of T_1 in mineral oil when compared to glycerin means that it takes longer to establish equilibrium in this system. This is due to the interactions with the lattice, the backbone structure, of the mineral oil liquid. This occurs because when the nuclei are transitioning to this equilibrium state they must give off some of their energy to the surrounding lattice as obeying the conservation of angular momentum where the lattice

must have the proper angular momentum states available for the nucleus to transition between its two spin states.

We also see that the T_2 value for mineral oil is larger than that in glycerin. The T_2 value has to do with interactions between the local magnetic fields, which in a classical sense are produced from the nearby spinning nuclei. A larger decay time here implies that there is less of an effect from these nearby nuclei.

The fact that both T_2^* values are the same because, as mentioned before, if $T_2^* > 0.3$ms, it is not an accurate measurement of the true spin-spin relaxation time. We can use this value to determine the importance of T_1 in equation 10 and 11. For mineral oil we measure ΔB including and excluding T_1 to be $1.0047 * 10^{-4}$ and $1.0109 * 10^{-4}$ respectively. This gives a percent difference of 0.6152 which means that T_1 is large enough to ignore in these calculations. A similar thing can be said about glycerin with ΔB equal to $9.96 * 10^{-5}$ and $1.0043 * 10^{-4}$ with percent difference 0.83.
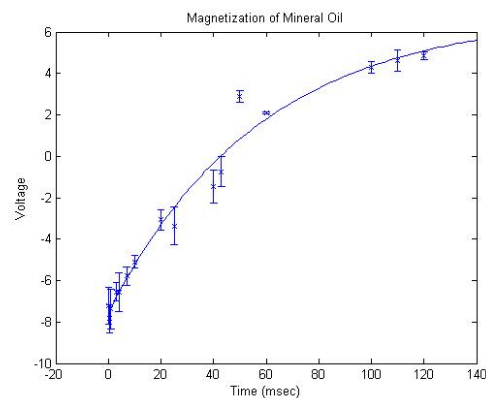

FIG. 2. A plot of the voltage, which is proportional to the magnetization, as a function of time for mineral oil. Fitting this curve determines the spin-lattice relaxation time to be $57.3 \pm 0.3ms$.
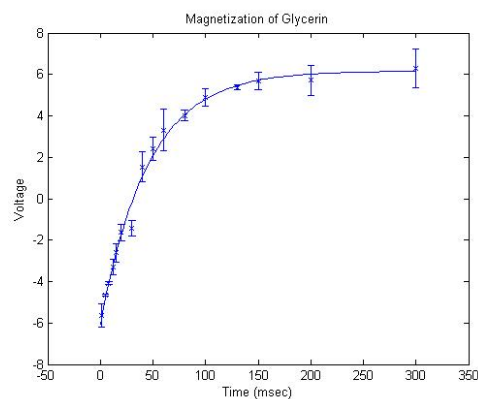

FIG. 3. A plot of the magnetization as a function of time for glycerin from which we determine T_1 to be $22.2 \pm 0.1ms$.
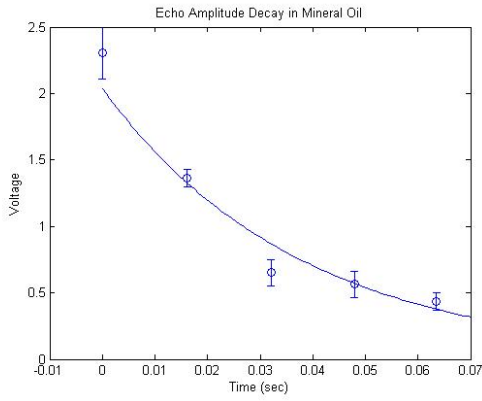
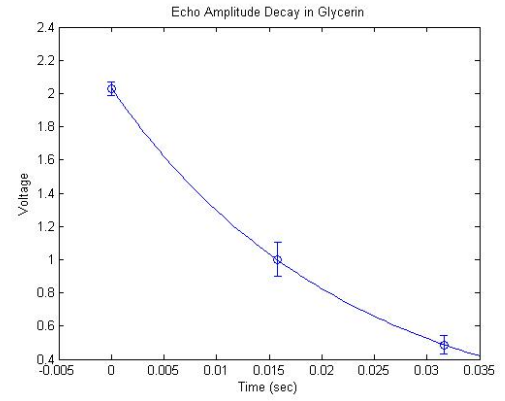FIG. 4. Decay of the spin echos in mineral oil. The spin-spin relaxation time is $37.6 \pm 0.2ms$.

FIG. 5. Spin echo decays in glycerin. Here we find T_2 to be $22.2 \pm 0.1ms$.

V. CONCLUSIONS

Through the use of pulsed NMR we were able to determine the different interactions present in glycerin and mineral oil. We determined both the spin-spin and spin-lattice relaxation times in both of these materials. We also showed that the effect of T_1 is negligible in determining the spatial inhomogeneity of the magnet. With these factors in mind we have a better understand of how pulsed NMR can be used to probe material properties on a small scale.

[1] A.C. Melissinos. *Experiments in Modern Physics*. (Elsevier Science, USA, 2003)p.270.