Pulsed Nuclear Magnetic Resonance

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(Dated: February 25, 2011)

In this experiment the phenomena of nuclear magnetic resonance is used to determine the magnetic moments of the proton and fluorine nucleus. The magnetic moment of the proton is found to be $\mu = (1.41 \pm 0.14) \times 10^{-23}$erg/gauss and the magnetic moment of the fluorine nucleus is found to be $\mu = (1.33 \pm 0.13) \times 10^{-23}$erg/gauss. To measure the magnetic moments, radio frequency pulses are applied to a sample in a large homogenous magnetic field. By tuning the applied frequency to the resonance frequency of the sample, the magnetic moments can be calculated. Measurements are performed to relate the spin-spin and spin-lattice relaxation times of glycerin to viscosity. Using the same apparatus, the spin-spin and spin-lattice relaxation times are measured by applying sequences of rf pulses to the samples. The relationship found between the viscosity of glycerin samples and their relaxation times is within 2σ of the accepted value from literature.

1. INTRODUCTION

Individual particle spins are related to single particle magnetic moments by a constant factor. Nuclear magnetic resonance is a technique to measure the magnetic moment of nuclei in a sample. Nuclei are made up of protons and neutrons, each of which are spin $\frac{1}{2}$ particles. For a particle with total spin $\frac{1}{2}$, spin in the $+z$ direction can be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

In nuclear magnetic resonance experiments a classical approximation is used to understand the behavior of particle spins.

2. NUCLEAR MAGNETIC RESONANCE AND RELAXATION TIMES

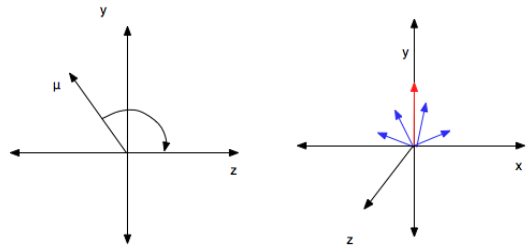
2.1. Theory of NMR and Classical Approximation

By considering an ensemble of spins in a sample we can use the classical understanding of angular momentum to approximate the behavior of many spins.

Each ensemble can be thought of as a total magnetic moment of many spins. In an ensemble there can be spins pointing in any direction, the resulting total magnetic moment vector can have components in any direction. By considering this ensemble of spins, the classical understanding of angular momentum can be used.

The total magnetic moment of an ensemble of spins is $\vec{\mu} = \gamma \vec{I}$, where γ is the gyromagnetic ratio for the relevant nucleus and $\vec{I}$ is the total angular momentum of the ensemble. In the classical approximation, placing a particle with magnetic moment $\vec{\mu}$ in a magnetic field $\vec{B}$ produces a torque τ, causing the magnetic moment to precess about the direction of the applied magnetic field.

$$\tau = \vec{\mu} \times \vec{B_0} \tag{1}$$



(a)Spin-Lattice Relaxation Time (b)Spin-Spin Relaxation Time

FIG. 1: Illustration of effect of Spin-Lattice and Spin-Spin relaxation times.

Since torque is $\frac{d\vec{I}}{dt}$, the Larmor frequency ω_0 can be computed to be

$$\vec{\omega_0} = -\gamma \vec{B_0} = -\frac{g\mu_n \vec{B_0}}{\hbar} \tag{2}$$

$\vec{\omega_0}$ is called the Larmor Frequency and is the resonance frequency of the ensemble of spins in a magnetic field. Finding the Larmor frequency allows the calculation of μ, the magnetic moment of the nucleus. This resonance phenomena also allows the measurement of the spin-lattice relaxation time and the spin-spin relaxation time, called T_1 and T_2 respectively. [1]

2.2. Relaxation Times

Nuclear magnetic resonance involves a sample placed large constant magnetic field in the $+\hat{z}$ direction, and a small oscillating magnetic field applied primarily in the $\hat{x}$ direction. Subsequently, the oscillating field is turned off, and the magnetic moments decay back to a thermal state. The spin-spin and spin-lattice relaxation times are measures of how the magnetic moments decay back into the the xz plane.

The spin-lattice relaxation time is a measure of the time it takes for spins to decay back to alignment with the

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large magnetic field after they have been excited. A large magnetic field in the $+\hat{z}$ direction causes states where the spins are aligned with the field to have a lower energy configuration. As energy dissipates from the protons due to electromagnetic interaction, more spins will become aligned along the large magnetic field, as shown in Fig. 1(a).

The spin-lattice relaxation time, called T_1 is the time constant for this exponential decay.

The decay involved in spin-spin relaxation time does not change the energy of the system. It is local and quantum mechanical; the effect is between protons in nuclei that are slightly out of alignment in the direction transverse to the large magnetic field. The spin-spin interaction of these unaligned particles causes increasing transverse decoherence.

2.3. Relaxation Times and Viscosity

The relationship between viscosity and relaxation times is measured. In viscous materials, to a zeroth order approximation the molecules are closer together than they are in a less viscous material. Both spin-spin and spin lattice relaxation times are determined by the coupling of magnetic fields in protons to magnetic fields in the surrounding environment. Since molecules are closer together in viscous samples, the interactions will be stronger, the stronger interactions will return the sample to equilibrium faster. The spin-spin relaxation time and the spin-lattice relaxation time will decrease as the viscosity increases.

3. EXPERIMENTAL SETUP

The necessary small magnetic field is applied by generating radio frequency pulses that produce a magnetic field. The rf pulses are applied for different durations. The pulse durations correspond to rotating the spins in the sample by a specified angle. Combinations of pulses of different frequency and duration are used to probe characteristics of the sample.

3.1. Experimental Apparatus

This experimental apparatus has five main components: two large permanent magnets, a radio frequency pulse generator, a probe circuit that the sample sits in, and a phase detector that mixes the input signal from the frequency generator and the output Larmor frequency signal from the sample together. An oscilloscope is used to view and collect data.

The permanent magnets are used to produce the large magnetic field, measured to be $(1.768 \pm 0.180) \times 10^3 G$. The error on this measurement takes into account 10% inhomogeneity in the magnetic field. A sample, glycerin, water or flourine, is placed in the probe circuit between the two large magnets. The sample sits in a solenoid that measures the magnitude of the magnetization in the $+z$ direction.

A set of tunable capacitors in the probe circuit are used to ensure a visible signal. The probe circuit is placed under the sample, and connected to the pulse generator and filtering electronics by way of input and output cables. The output signal from the proton spins is mixed with the output signal from the pulse generator. The result is beating between the two signals that is visible on the oscilloscope.

4. DATA AND ANALYSIS

4.1. Method for Measuring Magnetic Moments

To calculate the magnetic moment of a sample, the Larmor frequency of that sample is measured. The Larmor frequency is related to the magnetic moment by equation 2 and $\vec{\mu} = \gamma \vec{I}$. When a magnetic field is applied, the spins in the sample will precess with the said frequency. When the input frequency on the pulse generator is the Larmor frequency, the beating terms vanish.

A sample of glycerin, $C_3H_5(OH)_3$, is placed in the solenoid to measure the magnetic moment of the proton in hydrogen. Once the adjustable capacitors are tuned to see a signal, a series of pulses are applied in order to determine the correct duration for a pulse that rotates the spins in the sample by 180°.

The frequency on the frequency generator is tuned such that there is a large free induction decay (FID) viewed on the oscilloscope. The FID is an exponentially damped sinusoid, due to the mixing of the NMR output signal with the frequency input signal, as described above. The time constant on the exponential damping is T_1, the Spin-Lattice relaxation time. The measurement of T_1 will be discussed in detail in Sec. 4.2. To calculate the magnetic moment of the proton, a so-called 90° pulse is applied. A 90° pulse is a pulse of duration t that rotates the spins in the sample 90° around the z-axis, into the xy plane.

In order to determine t, we sweep through pulse durations, from $1\mu s$ to $100\mu s$. The 180° pulse produces no FID, or a minimal amplitude FID. Under these conditions, the spins of the protons will have no components parallel to the solenoid. Since there is no parallel component, there will be no emf induced in the solenoid, and thus no signal. Once the 180° pulse is found, its duration is halved to find a 90° pulse.

Once a 90° pulse is found, a series of repeating 90° pulses are applied to the sample, producing FIDs. The frequency generator is tuned between each 90° pulse. As the frequency approaches the Larmor frequency, the effect of beating between the mixed input and NMR output signals approaches the resonance condition. The frequency at resonance is recorded to calculate the magnetic moment using Eq. 2.

4.2. Method for Measuring T_1

T_1, the spin-lattice relaxation time is measured using two different methods. The first method is to apply a series of 2-pulse sequences. The first pulse in the sequence has the duration determined previously to produce a 90° rotation. A time τ allows the spin-lattice relaxation to occur, and is followed by a second 90° pulse.

The first pulse moves the spins into the xy plane. The time τ allows the spins to decay back toward the z-axis. Once the pulses have decayed, the second 90° pulse is applied. This second pulse rotates the spins 90° about the $z - axis$, such that the net magnetization vector is positioned as in Fig 1(a). The spins are then allowed to decay again, back to alignment in the z-axis.

Data is collected following the second pulse. This signal is an FID whose magnitude is proportional to the magnitude of the magnetic moment vector that has decayed completely into alignment with the z-axis. As tau is varied, the amplitude of the FID should decrease, since when more time elapses between the first pulse and the second, more magnetization has decayed completely into the $\hat{z}$ direction. The result of this sequence will be a descending decaying exponential, whose time constant is T_1. This pulse sequence is therefore useful for measuring T_1 for samples where T_1 is expected to be short.

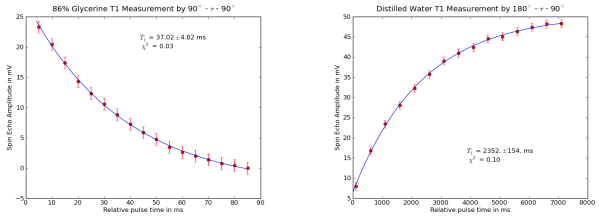
The second method used to measure T_1 employs a 180° pulse, followed by a delay τ, and a 90° pulse. This pulse sequence rotates the spins first 180° producing no FID. The delay τ allows the spins to decay toward the z axis. The 90° pulse rotates spins back toward the xy plane. As in the previous pulse sequence, T_1 is measured by varying τ, and measuring the amplitude of the FID produced after the last pulse. In this method, the amplitude of the FID will be maximal when τ is larger than T_1. In time τ, the magnetization is entirely aligned with the magnetic field, causing the 90° pulse to rotate the spins back to the xy plane. Once τ is sufficiently large the magnitude of the FID stabilizes.

This method lends itself to measuring long T_1s, as spins must decay further, from 180° to 0°, rather than from 90° to 0°.

4.3. Method for Measuring T_2

T_2, the time constant for spin-spin relaxation is measured with one of two methods. The first method is a simple pulse sequence, similar in nature to those used to measure T_1. This pulse sequence is a 90° pulse, followed by a delay τ, followed by a 180° pulse.

A spin-echo occurs a time τ after the 180° pulse in this sequence. The 90° pulse rotates the spins from the $\hat{z}$ axis up to the $\hat{x}$ direction. A time τ passes, letting the spins decay transversely, spreading out in the xy plane. The 180° pulse inverts the spins, but they continue moving in the same direction. The result is that the spins recohere, producing a signal again. As the spins decohere the signal



(a)T_1 Measurement with 90° -τ 90° pulse sequence (b)T_1 Measurement with 180° -τ 90° pulse sequence

FIG. 2: Data collected by the two methods for measuring T_1

induced in the solenoid becomes smaller, since there is less magnetization in the $\hat{z}$ direction. After the 180°, the spins rotate back through the xy plane while recohering. The result is a signal that begins rising τ after the 180° pulse, reaches a maximum and falls again. This rising and falling signal is the spin-echo.[2]

By varying τ and measuring the amplitude of the spin-echo produced, a decaying exponential is plotted. The exponential's decay constant is T_2[3].

The second method for measuring T_2 is the Carr-Purcell sequence. The Carr-Purcell sequence also begins with a 90°-τ-180° pulse sequence. Instead of repeating this pulse sequence manually, varying τ, the Carr-Purcell sequence uses a delay of 2τ, then another 180° pulse, then another delay of 2°, and so on. Each 2τ-180° pulse sequence allows the spins to further decohere in the transverse plane. The result is a decaying exponential that can be fit to produce values for T_2.

4.4. Determining Magnetic Moments

The method for determining the magnetic moment of the proton was described above. By tuning the frequency generator, resonance was found to be $\omega_0 = 7.52196 \times 10^6 \frac{rad}{s}$. Converting this to a frequency and using $\mu = \frac{\omega_0 \hbar}{2B_0}$, $\mu = (1.41 \pm 0.14) \times 10^{-23} \frac{ergs}{gauss}$. For the flourine nucleus, $\omega_0 = 7.0760 \times 10^6 \frac{rad}{s}$, giving $\mu = (1.33 \pm 0.13) \times 10^{-23} \frac{ergs}{gauss}$[4]. Each of these values differ by less than one standard deviation from the accepted values[5].

4.5. Determining T_1 and T_2

T_1 and T_2 were measured for different concentrations of glycerine, ranging from 100% glycerine to distilled water. T_1 and T_2 were measured using the methods above, and fit to the appropriate exponentials. Sample data is shown in Figs. 2(a) and 3. Descending exponentials were fit to $f(x) = Ae^{-\tau/T} + B$. Rising exponentials, like those produced by the 180° - τ - 90° pulse sequence used to measure T_1 as in 2(b) were fit to $f(x) = A(1 - 2e^{-\frac{\tau}{T}}) + B$. The data are shown in Table I. The error bars on

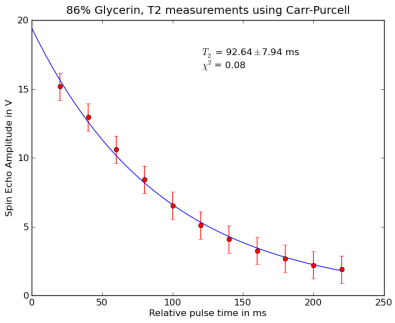


FIG. 3: Sample data collected for measurement of T_2 for 86% Glycerine sample. Data was collected using the Carr-Purcell method for spin-echo measurement.

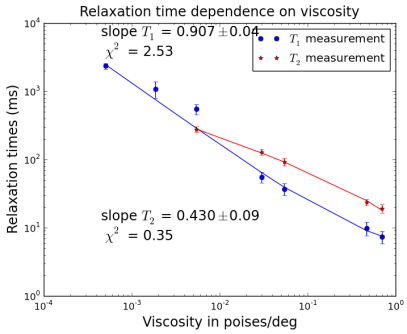


FIG. 4: Results plotted on a log-log scale for different viscosities of glycerine. Blue data points are measurements of T_1, and red data points are measurements of T_2.

both the T_1 and T_2 measurements were calculated by adding in quadrature the standard deviation of each of the three trials for each data point and the uncertainty in the amplitude measurement from the oscilloscope. This uncertainty was .3 mV.

4.6. Relationship between Relaxation Time and Viscosity

By measuring relaxation times for samples of varying viscosity, we establish that within the range measured both T_1 and T_2 decrease as the viscosity of the sample increases.

This plot has Pa per degree on the x axis. In order to probe further range of viscosities, we intended to cool the different concentration glycerine samples. By normalizing this graph by temperature, these samples would be comparable at different temperatures. Due to time constraints we were unable to perform this procedure. By fitting the log of the data for T_1 and T_2 to linear functions, the slope of the power laws were obtained. Error on each data point was taken to be the error produced by the T_1 and T_2 fit functions. The relationship was fit to a power law, as expected. The slope of the T_1 fit was found to be -0.91 ± 0.04, the slope of the T_2 fit was found to be 0.43 ± 0.10. This varies from the Bloembergen and Purcell of -1 measurement by 2σ in the case of T_1. The measurement for T_2 is significantly less accurate because data were unable to be obtained for very low concentrations of glycerine.[6].

Percent Glycerine	T_1 (ms)	T_2 (ms)
Distilled Water	2352.98 ± 154.12	-
40	1087.08 ± 199.90	-
60	549.42 ± 62.43	275.72 ± 17.85
80	55.57 ± 6.70	128.84 ± 8.54
86	37.03 ± 4.82	92.64 ± 7.94
98	9.84 ± 1.44	23.55 ± 1.71
100	7.31 ± 1.02	19.18 ± 1.74

TABLE I: T_1 and T_2 collected for different concentrations of glycerine

5. CONCLUSIONS

In conclusion, the values calculated for the magnetic moment of the proton and flourine nucleus were $\mu = (1.41 \pm 0.14) \times 10^{-23}$erg/gauss and $\mu = (1.33 \pm 0.13) \times 10^{-23}$erg/gauss, respectively. These values are both within σ of the accepted values.

The viscosity relaxation time relationship was found to agree well with the relationship presented by Bloembergen in the 1954 paper[6]. The value for the relationship between T_1 and viscosity was within 2σ of that measured by Bloembergen. The T_2 measurements were less in agreement because fewer measurements were performed.

In order to confirm the behavior of high viscosity T_1 and T_2 relationships, in further experiment the different concentrations of glycerine will be cooled in order to change the viscosity of the samples.

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