

Measuring Material Properties With Pulsed NMR

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We measure various properties of the Hydrogen nucleus in different environments using pulsed NMR. We find the gyromagnetic moment of ^1H to be $42.48 \pm 0.001 \text{ MHz T}^{-1}$. We measure the spin-spin and spin-lattice relaxation times of ^1H in glycerin solutions of varying viscosity and find an power law relationship ($v^{-2/3}$) between viscosity and T_2 , and an inverse square root relationship between viscosity and T_1 . We explore the use of the Carr-Purcell pulse sequence and begin preliminary investigations into the effect of paramagnetic ions on the spin-spin relaxation time.

I. INTRODUCTION

NMR was first developed in the late 1940s by Felix Bloch and Edward Purcell[8] to measure the magnetic moments and other properties of nuclei and molecules. Since then, it has become an incredibly powerful tool used to image the human body and brain, identify hazardous substances, and discover the structure of complex proteins. This paper develops the foundations of the field with experiments similar to those carried out by Bloch and Purcell.

II. THEORY

NMR relies on two principles: that particles with spin carry a magnetic moment, and that magnetic moments precess in an external magnetic field.

In general, an ensemble of quantum spins can be treated classically, due to the Bloch theorem. Each spin can be modeled as a current loop, which will align itself in the direction of a permanent magnetic field. Then, an oscillating perpendicular magnetic field will cause the loop to precess at a frequency $\omega = \gamma B$, where γ is the gyromagnetic ratio of magnetic moment to angular momentum. This frequency is the Larmor precession frequency.

Theoretically, the particle would keep on precessing forever, but in reality, it interacts with other elements in its neighborhood. These interactions that each spin undergoes lead to a reestablishment of the original polarization. This happens exponentially according to $M_z(t) = M_z^{eq} + (M_z(0) - M_z^{eq})e^{-t/T_1}$. where $M_z(t)$ is the polarization at time t and M_z^{eq} is the polarization at equilibrium.

This cannot be measured with a single pulse, since the NMR probe can only measure polarization in the $x - y$ plane. Thus, a two pulse sequence is used: first, a 180° pulse inverts the population, then after some time τ , a 90° pulse rotates the spins that are still polarized in the z direction into the $x - y$ plane where they can be measured.

The equilibration of the z spins is not the only relaxation that takes place. In fact, the most immediately visible effect is the decoherence of the spins. The local magnetic fields vary across the sample because the permanent magnet is imperfect, and because the spins influence one another with their own magnetic fields. Measuring the strength of these couplings can reveal significant information about the bond structure of the elements being studied.

The first place this relaxation is visible is in the decay of the induced signal immediately following a pulse, known as free induction decay (FID). However, this decay results from the permanent magnet inhomogeneity and from the intrinsic spins - so measuring this does not actually reveal interesting things. Of course, there are pulse sequences that can mitigate these effects.

The primary technique discussed here is spin echoes[5]. First, a 90° pulse rotates the spins into the $x - y$ plane such that they are all coherent. Then, the local magnetic fields make them all rotate at slightly different rates. After some time τ , a 180° pulse is applied, keeping the spins in the $x - y$ plane, but making it so that the spins that rotated the least are now far ahead of the spins that rotated the most. So after another period of time τ , the spins line up again and a “spin echo” is observed.

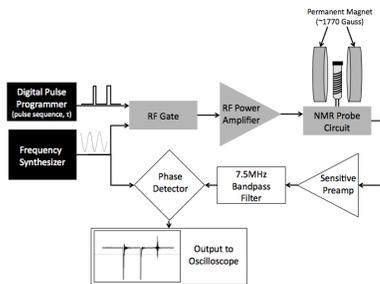
The spin echo technique suffers from some second-order diffusion and magnetic field gradient effects, so the Carr-Purcell technique[4][7] is used to further mitigate these. This consists of a single 90° pulse followed by a train of 180° pulses. This allows for a short τ , which reduces the effects of diffusion, but still allows the decay to be observed.

III. EQUIPMENT AND APPARATUS

The signal path is shown in Figure III. A pulse of RF energy is gated through to the probe by the switch, which is controlled by the digital pulse programmer. On the receiving end, the signal is mixed back with the driving signal to produce a beat frequency of the difference between the driving signal and the Larmor frequency, which can be brought down to a few kilohertz and easily examined on an oscilloscope.

The NMR probe consists of an inductor and a pair

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of tuning capacitors. There are two constraints on the probe: its impedance must match the impedance of the RF amplifier that powers it, and its resonant frequency must match the Larmor frequency of the sample to optimize its use as an antenna. These can both be satisfied by manipulating the tuning capacitors.

IV. RESULTS

To measure the gyromagnetic moment of hydrogen, a sample of 100% glycerin was placed in the NMR probe and the driving frequency was varied until an FID signal was observed. The magnitude of the FID decreased, then increased around the Larmor frequency, which meant that the FID could not be observed when the driving frequency was closer than 2 kHz to the Larmor frequency. However, as discussed earlier, the frequency of the FID at the output of the signal chain is equal to the difference between the driving frequency and the Larmor frequency, so the Larmor frequency is determined to be 7.5193 ± 0.0002 MHz based on the intersection of the best-fit lines above and below the Larmor frequency (Fig IV).

The gyromagnetic ratio is given by $\frac{\omega_0}{B_0}$. A hall effect probe was inserted into the sample holder to measure the permanent magnet strength as 1.83 ± 0.04 kilogauss, resulting in a gyromagnetic ratio of 41.08 ± 0.89 MHz T^{-1} , which deviates by 3.5% from the known value of 43.576 MHz T^{-1} . However, if the provided permanent magnetic field of 1.77 kilogauss is used, the gyromagnetic ratio is 42.48 ± 0.001 MHz T^{-1} , which is within 0.22 % of the known value[9].

We got the value of ω_0 for ^{19}F from Baumgartner and Christensen[1], who found a spin echo at $\omega = 7.100 \pm 0.001$ MHz, yielding $\gamma = 40.113 \pm 0.005$ MHz T^{-1} for the provided B_0 and $\gamma = 38.80 \pm 0.08$ MHz T^{-1} for the measured B_0 , compared to the known value of 40.053 MHz T^{-1} [9].

The spin-lattice relaxation time (T_1) was measured by applying a $180^\circ - 90^\circ$ pulse sequence ($34 \mu s$ and $17 \mu s$), as described previously. Measuring the amplitude of the free induction decay as a function of τ , the separation between the pulses, allowed for a measurement of T_1 .

Since we measured only the amplitude of the free induction decay, and not its phase, we observed a function that looked almost like the absolute value of an inverse exponential. However, since we ignored the phase, the

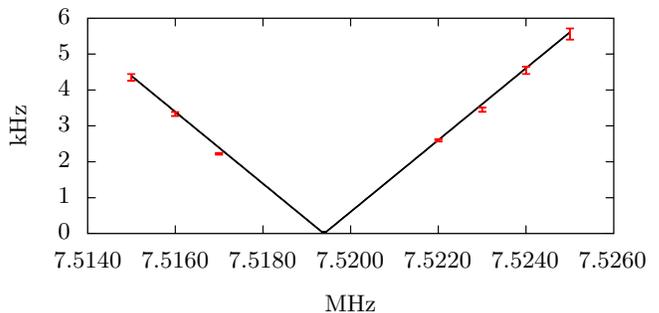


FIG. 1. Varying the driving frequency about the Larmor frequency determines that $\omega_0 = 7.5194$ MHz

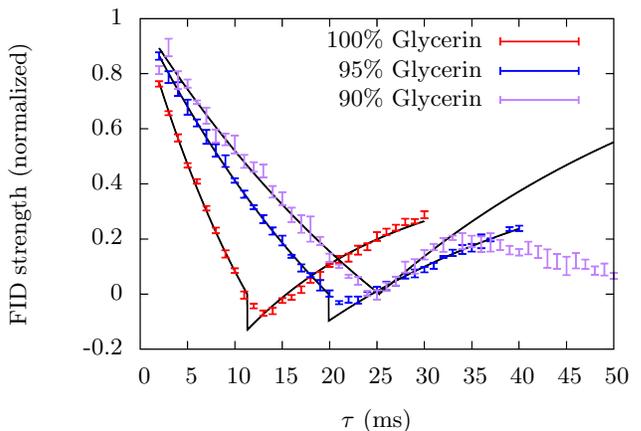


FIG. 2. The FID strengths of glycerin at various concentrations and τ are compared to determine the spin-lattice relaxation times of 100%, 95%, and 90% glycerin a 15.9, 28.8, and 36.6 μs respectively, with χ^2 values of 4.66, 0.53, and 3.55.

points after the zero-crossing were attenuated by a factor of between 0.5 and 2.0. The FID responses as a function of τ are given for several concentrations of glycerin in Figure 2.

The T_1 relaxation time of glycerin follows an inverse power law as shown in Figure 3. These figures are generally in agreement with Bloembergen [3], who finds a similar relationship between viscosity and T_1 .

The spin-spin relaxation time (T_2) was measured by applying a $90^\circ - 180^\circ$ pulse sequence. This created a response like that shown in Figure 4. The oscilloscope peak detection function was used to measure the magnitude of the spin echo, which was plotted against τ . These relationships for various concentrations of glycerin are shown in Figure 5.

While measuring the spin echo magnitudes, a fast repeat rate (100 ms) was initially used, meaning that the pulse sequence fired every 100 ms. However, we found that this caused a suppression in the observed T_2 times, so this data could not be used to accurately determine T_2 .

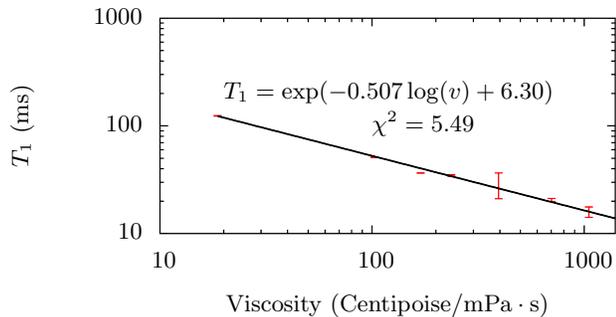


FIG. 3. Measuring T_1 for various viscosities of glycerin shows that T_1 varies as the inverse square root of viscosity

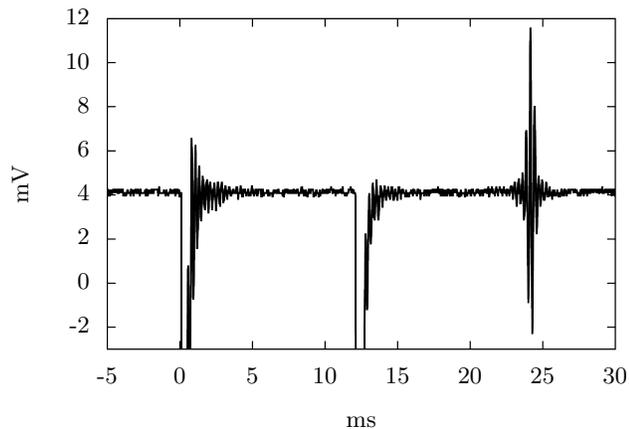


FIG. 4. A strong spin echo resulting from a $90^\circ - 180^\circ$ pulse sequence

As with T_1 , a log-log plot (Figure 6) shows a decreasing power law relationship between viscosity and T_2 . This plot clearly shows the increased effect of the short repeat time as τ becomes larger.

The Carr-Purcell technique was applied to the 100% glycerin sample in order to measure T_2 . The raw scope output for $\tau = 4$ ms is shown in Figure 7. The data was collected for up to 8 ms, and the general trend is for the value of T_2 to increase with τ , as shown in Figure 8.

We measured the T_2 of water doped with Fe ions to test the effect of paramagnetic ions on relaxation times. The procedure was identical to that of the glycerin T_2 measurement, and the results are summarized in Figure 9. The relationship appears to be roughly linear, though more data is needed to establish a conclusion.

V. ERROR ANALYSIS

In general, the statistical error for most of the measurements described above was quite low. For most data points, three separate measurements were averaged, and it was not unusual for all three measurements to be iden-

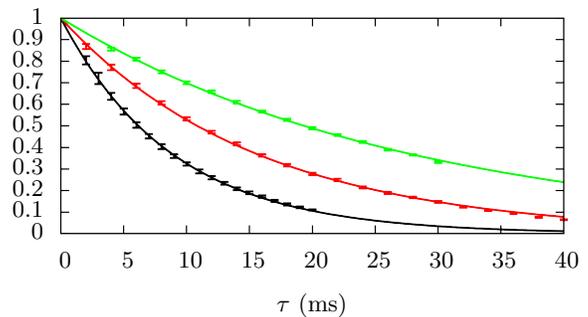


FIG. 5. T_2 tends to decrease with viscosity, with values for 90%, 95%, 100% glycerin being 8.90 ± 0.13 ms, 15.65 ± 0.15 ms, and 27.9 ± 0.18 ms, with χ^2 values of 0.35, 4.95, and 1.07 respectively

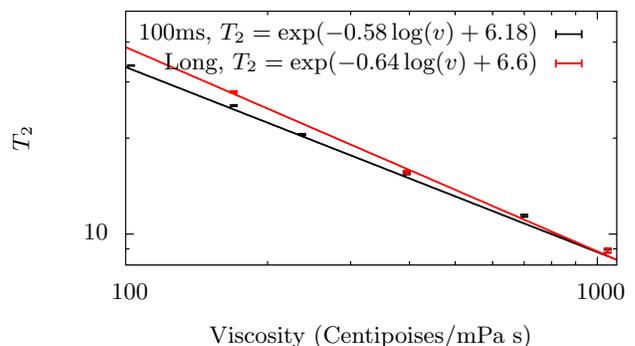


FIG. 6. Comparing the measured T_2 with long and short repeat times shows an increased discrepancy at lower viscosities, and a 10% error in the power. χ^2 for 100 ms and long repeat times are 4.43 and 16.9, respectively.

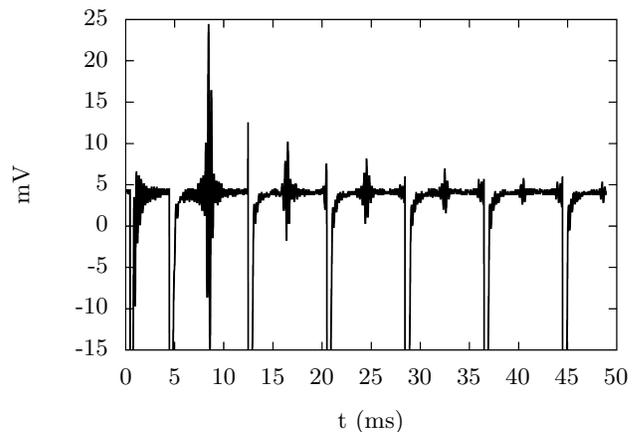


FIG. 7. The Carr-Purcell experiment creates a train of pulses that decays exponentially with T_2 .

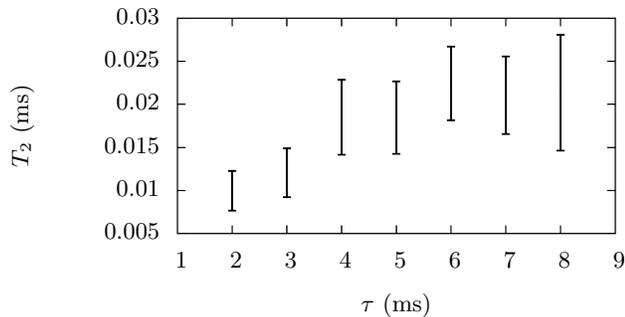


FIG. 8. The Carr-Purcell experiment shows that T_2 appears to increase with τ .

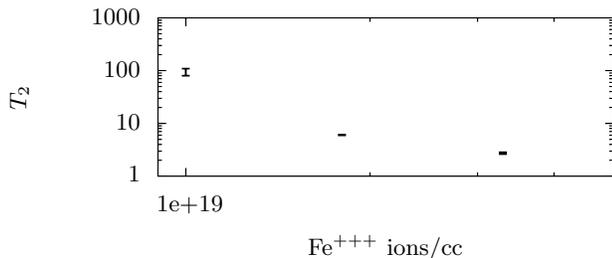


FIG. 9. The T_2 time of water decreases dramatically with the addition of paramagnetic ions

tical down to the precision of the oscilloscope. Thus, the primary sources of error were systematic, rather than statistical.

A significant source of error in many of the measurements comes from gradients in the permanent magnetic field. The maximum magnetic field strength inside the magnet was measured to be 1.880 ± 0.010 kilogauss, but the field near the center of the magnet was measured to be only 1.79 ± 0.002 kilogauss. The stated value of the magnet is 1.77 kilogauss. Much of the error comes from the fact that the material being probed samples from a range of these values.

The most obvious effects of this are on the gyromagnetic ratio measurements. An inaccuracy in the magnetic field measurement will result in a shift in the measured

gyromagnetic ratio, and a gradient over the sample will result in a smeared peak.

The less obvious effect is on the measurement of T_2 . The spin-echo measurement requires that the magnetic field on individual particles stay constant, otherwise the 180° pulse will not put them in a place corresponding to their Larmor frequency. The echo amplitude is therefore given not by $\exp(-\frac{2\tau}{T_2})$, but rather by $\exp(-\frac{2\tau}{T_2} - \frac{2}{3}\gamma^2 G^2 D\tau^3)$, where G is the field gradient and D is the diffusion constant of the material. Through this mechanism, magnetic field inhomogeneities suppress T_2 for large τ and non-viscous materials.

The largest source of error in this experiment came from discretization errors and equipment response. The slow rate of the RF signal chain was $0.1 \mu\text{s}$, meaning that the switch took that long to fully turn on. This turned out to be the dominating error for most of the measurements. However, it is possible to mitigate the effects of this error. Since measurements are always taken with τ as the independent variable, the error in the dependent variable is $\frac{dy}{d\tau}\delta\tau$. By taking measurements at points where y varies slowly with τ , this error can be minimized, but at the cost of having to take more measurements at higher equipment sensitivities.

In addition, the oscilloscope used was limited at 0.1 mV, and the frequency generator was set in increments of 1 Hz.

VI. SUMMARY

We have quantified several important relationships here. First, we find the gyromagnetic ratio of ^1H - that is, the ratio of its magnetic moment to its angular momentum - to be $42.48 \pm 0.001 \text{ MHz T}^{-1}$, which is within 0.3% of the known value. Then, we find a power law relationship between the viscosity of glycerin and its T_2 with exponent $-2/3$, and an inverse square root relationship between the viscosity of glycerin and its T_1 . We also make preliminary measurements of the effect of paramagnetic ion doping, which appears to sharply lower T_2 , and use the Carr-Purcell technique to better eliminate diffusion and magnetic field gradient artifacts in the measurement of T_2 .

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