

# Pulsed NMR

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Pulsed NMR has become a widely-practiced tool used to characterize small homogenous samples. Since 1950, Erwin Hahn's discovery has rapidly grown in popularity in standard science laboratories around the world. In this experiment, we attempt to find two critical time constants,  $T_1$  and  $T_2$  which characterize the spin relaxation times, for a mineral oil sample. Although our data provides precise results, the accuracy of our experiment is subject to small calibrations that seem to have shifted our experimental conclusions.

Pulsed NMR technology utilizes radio frequency (rf) electronic waves to manipulate an electromagnet in the NMR chamber. The sample is subject to this magnetic field along with a constant field in the  $+z$  direction, orthogonal to the alternating magnetic field. The response of the field on the spin states of the sample is measured, and two critical time constants are found. The  $T_1$  time is referred to as the spin-lattice relaxation time, and the  $T_2$  time is the spin-spin relaxation time. We know that the time dependence of a population in an agitated state is an exponential decay. Both of these times refer to an amount of time to change the population by  $\frac{1}{e}$ .

## BACKGROUND

Although NMR technology was first established by Edward Purcell and Felix Bloch using continuous wave (cw) rf magnetic fields, the ease of calculating characteristic time qualities of a sample were very difficult from the original setup. Nonetheless, Purcell and Bloch were awarded the 1952 Nobel Prize in Physics for their discoveries of how molecules react to rf magnetic fields. However, in 1950, Erwin Hahn developed a more straightforward approach that took advantage of specifically-long wave pulses that changed the thermodynamic state of a solution. The theory of quantized spin and angular momentum were critical in understanding the population distribution at a given temperature. The decay rate for any state to return to its thermodynamic equilibrium goes like an exponential function. Just so, Boltzman's statistical physics theory tell us that at a given energy level, the population distribution also goes like an exponential of  $\frac{-E}{kT}$ .

There is a constant magnetic field pointing in the  $+z$  direction in our experimental setup. Thus, the thermodynamic equilibrium for a solution in the chamber exists with a net magnetic spin pointing in the  $z$  direction - without this field, the net spin would be zero for all three directions, but in this case, the  $x$  and  $y$  directions have no net spin magnetization because of the constant field. We can apply an alternating field in the  $x$ - $y$  plane that creates precession of the magnetic spin around the  $z$

axis. Thus, we can rotate the net spin of the solution by well-timed pulses of magnetic field, and we can measure the net magnetization in the  $x$ - $y$  plane by our experimental setup. Thus, we can find a resonant rf frequency to which the solution has a maximal response (no beats are produced and the amplitude is maximized) - that is, a pulse that rotates the net spin magnetization by  $90^\circ$ . Roughly, the pulse that will rotate the spin by  $180^\circ$  will be twice as long as the prior pulse, but the exact time width of the pulses can be determined experimentally.

There are two different equilibriums that the proton particle can be in. One is a thermodynamic equilibrium in the  $z$  direction of only  $z$ -directed spin magnetic moments. The distribution of particles at a given temperature will tend to favor more particles in the lower energy state, which is the spin state aligned with the magnetic field. However, if we apply a  $180^\circ$  pulse, we'll flip the distributions in each state by adding a certain amount of energy. To recover, energy dissipates from the system into the surrounding lattice structure so that the original equilibrium distribution is regained. The  $-z$  magnetization will go like  $M = M_o e^{-\frac{\tau}{T_1}}$ , and the  $+z$  like  $M = M_o(1 - e^{-\frac{\tau}{T_1}})$ , and thus the total magnetization goes like  $M = M_o(1 - 2e^{-\frac{\tau}{T_1}})$ . The time  $T_1$  is characteristic of the rate at which magnetization is flipped as each particle in the agitated state releases energy to the lattice, thus it is called the spin-lattice relaxation time. In our setup, we'll rotate the net magnetization in the  $z$  direction into the  $x$ - $y$  plane and then immediately measure it. If we repeat the process for different times  $\tau$ , we can find the  $T_1$  time from the magnetization data set.

The second equilibrium refers to another type of artificial thermodynamic stimulus we can make. If we add a  $90^\circ$  pulse, we change the net magnetization from the  $+z$  direction to the  $x$ - $y$  plane. Because the constant  $+z$  magnetic field still exists, the net magnetization precesses in the  $x$ - $y$  plane and scatters as different particle precess with different speeds. We consider two different facets of this setup: first, the net magnetization in the  $x$ - $y$  plane will slowly decay as the magnetic spins align with the  $z$  axis, according to the decay  $M_{xy} = M_o e^{-\frac{\tau}{T_2}}$ , where  $T_2$  is called the spin-spin relaxation time, or the Free Induction

Decay (FID) if it's observed as a straight decay (which is not true in the case of pulsed NMR). Eventually, the net +z spin magnetic moment will be regained in order for equilibrium. Second, since we can only measure the x-y magnetization, but the particles' spin magnetization scatter with different speeds of precession and thus measuring it at any given time would not give us the correct net magnetization, we apply a  $180^\circ$  pulse at a certain time  $\tau$ , and then wait  $2\tau$  for the spins to converge at as an echo. This allows the precessing spins to double back the distance they moved away from the original  $90^\circ$  rotation off the z-axis, and gives us a correct value for the  $T_2$  time.

These two characteristic times are the forte of pulsed NMR equipment. Because we could either take  $90^\circ$  and multiple  $180^\circ$  rotations, or a  $180^\circ$  and a time dependent  $90^\circ$  rotation, we can measure both critical constants by controlling how we give energy and stimulate the net magnetization.

## EXPERIMENT DESIGN

In this lab, we utilize the TeachSpin PS1-A, a full pulsed NMR spectrometer. It uses a powerful magnetic and a rf generator to create the basic tools for the NMR. It's also connected to two oscilloscopes: one for reviewing the rf pulse bands, and the other to see the net x-y magnetization as represented by the voltage. We'll use the mineral oil sample provided to calculate our  $T_1$  and  $T_2$  times.

We can control the delay between A and B pulses, set multiple B pulses, control the time length of A and B pulses, change the voltage gain on the magnetization oscilloscope, set the repetition time between successive pulse trains, and change the frequency of the rf pulses. There are other subtle adjustments to be made. Most importantly, our data set is affected by the exact homogeneity of the magnetic field near the sample vial. Because of imperfections in the magnet construction itself, we are limited to FID values of .4 ms, but the ingenuity of the pulsed NMR design still allows us to calculate a  $T_2$  value. Our mineral oil has a  $T_1$  near 12 ms, so we should wait about 3-4 times longer for each pulse train repetition in order to get an accurate reading on the oscilloscope. Thus, we'll set the repetition time to 100 ms to give adequate time.

## RESULTS AND CONCLUSION

After performing the experiment, we have calculated highly precise measurements for the  $T_1$  and  $T_2$  times. The  $T_2$  time is near a value of 16.5 ms, and the  $T_1$ , calculated two different ways, is near 25.5 ms. Roughly, we see that the  $T_1$  is about double what we expected from

the literature (12 ms). Nonetheless, our exponential fits for each of the data sets seems to be precise, but systematic errors in the inhomogeneity of the magnetic field disturbed our calculated values.

The  $T_1$  experiment was calculated two different ways. We can find the zero crossing point, where  $M_z(\tau) = 0$  so that we can calculate  $T_1$  straight from the formula given above. We also know the shape of the curve once the zero crossing point is passed, which is the same function used just above. The first half of the data set is a reflection about the z axis immediately following the precession about the z axis immediately following the original  $180^\circ$  pulse, and decays quickly as a function of the magnet or  $T_2$ , the normal spin-spin relaxation time. Only the data from the zero crossing point and onwards is significant in determining a  $T_1$  value. We have also estimated a  $M(\infty)$  value of 7.36, which is near the fit function's value of 6.37. Thus, our data set is reasonable, and measurements from both calculations match.

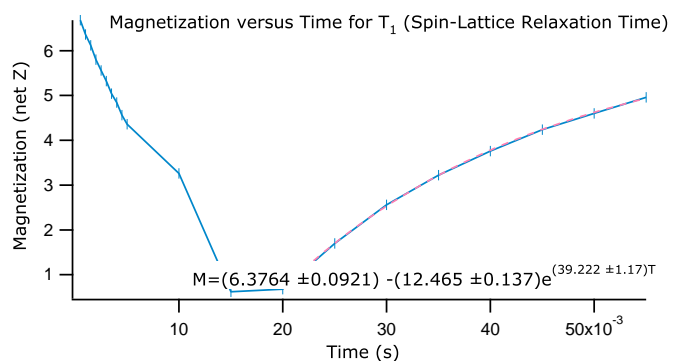


FIG. 1: Graph of  $T_1$  experiment, where  $M = M_o(1 - 2e^{-\frac{\tau}{T_1}})$ . A log fit was calculated for points after the zero crossing point at 17.4 ms.  $M(\infty) = 7.36$  from experimental data.

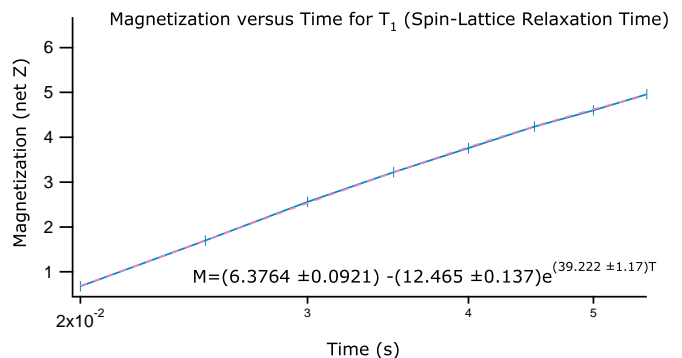


FIG. 2: Log graph of  $T_1$  experiment for times after the zero crossing point. The relationship between  $\text{Log}(t)$  and  $M$  is linear on this graph.

The  $T_2$  experiment is much more straight forward. Ten  $90^\circ$  pulses were used applied at 2.0 ms intervals, with echoes every 4.0 ms. The experimental fit gives us a  $T_2$  about twice that expected from the literature, however.

Nonetheless, our exponential fit works well, and the relationship between  $M$  and  $e^{\tau}$  is nearly linear with a small M-axis offset.

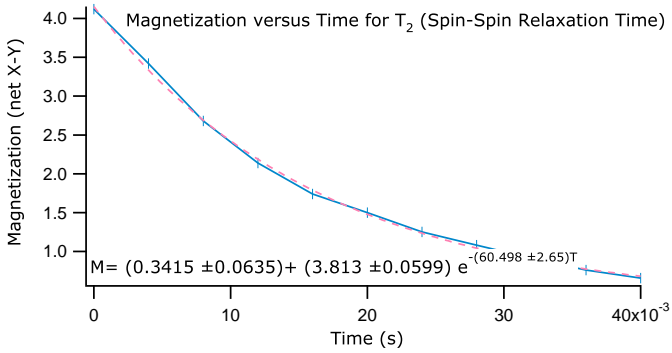


FIG. 3: Graph of  $T_2$  experiment, where  $M = M_0 e^{-\frac{2\tau}{T_2}}$ .

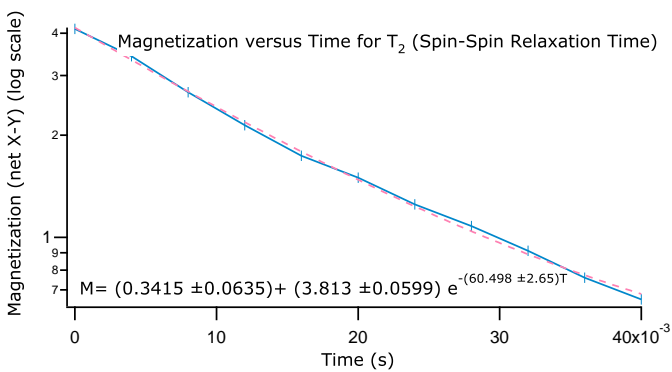


FIG. 4: Log graph of  $T_2$  experiment. The relationship between  $\text{Log}(M)$  and  $t$  is most nearly linear because of the small M-intercept value. A more appropriate log graph would show  $M$  versus  $\text{Log}(t)$  with an offset on the x-axis.

90° band	6.4 $\mu\text{s}$
180° band	11.4 $\mu\text{s}$
Voltage	2.96 V
Frequency	15.35700 Mhz
T2 (Spin-Spin Relaxation Time)	0.016529 $\pm$ 0.377358 s
Zero Crossing Point	17.4 ms
T1 (Spin-Lattice Relaxation Time)	0.02510 s
Exact T1	0.0255 $\pm$ 0.8547 s

FIG. 5: Major statistics gathered from the NMR experiment. The resonance frequency was tuned to produce zero beats and maximum amplitude for 90° pulse. The approximate  $T_1$  value is calculated from the zero crossing point, and the second, more specific value is derived from the exponential fit on the graph.

The table summarizes all the pertinent data accumulated from the pulsed NMR experiment on a mineral oil sample. We have well-defined values of  $T_1$  and  $T_2$ , yet our data set seems to be off. First off, should we expect a larger  $T_1$  or  $T_2$ ? The thermodynamic equilibrium with the net magnetic spin should be slower to attain than the spin-spin equilibrium, which can be attained quite rapidly. Indeed, some materials have well defined  $T_2$  values less than .4 ms. Our data suggests that mineral oil has a spin-spin relaxation time about 4 times as long. Nonetheless, we know our  $T_1$  is about twice as long as it should be, but it makes sense that  $T_1$  should be longer as  $T_2$  becomes longer for a solution, since thermodynamic equilibrium takes place at the heel of spin equilibrium. The only two sources of error are in the sample preparation itself: either, there is too much sample and the magnetic fields aren't adequately concentrated, or the magnetic fields aren't calibrated correctly to be adequately homogenous near the solution vial. These are two of the major systematic errors that would alter our measured values, yet still give us data sets that fit the correct form. A sensitive teslameter should be used to calibrate the machine before use for best results.

Applications of pulsed NMR technology are widespread. Identification and characterization of most any sample can be attained with general ease. As long as the machine is calibrated correctly, data samples will be accurate in addition to being quite precise. Chemicals with similar hydrogen characteristics, however, might be difficult to differentiate in an NMR spectrometer. For example, long hydrocarbons such as mineral oil have very similar hydrogen features, but hydrogens attached to oxygens as alcohols, aldehydes, and acids can have quite characteristic features. These properties allow for good measurements of  $T_1$  and  $T_2$ , which is the seat that pulsed NMR is based off of.