Pulsed Nuclear Magnetic Resonance

Molly S. Peeples*
MIT Department of Physics
(Dated: October 16, 2003)

Nuclear Magnetic Resonance is an important tool in modern science, greatly because of it's discernably different effects on materials of different molecular composition or viscosity. One of these effects is the relaxation time of the coherence of nuclear spins after an applied $\vec{B}$ field is removed. In these laboratory experiments, we found that the relaxation times decreased as expected with increases in either paramagnetic ion doping or viscosity.

1. INTRODUCTION

Advances in Nuclear Magnetic Resonance, or NMR, technology have led to several Nobel Prizes. NMR has revolutionized scientific technique, ranging from brain research to determining the structures of complex molecules.

NMR technology is based on the properties of spin. Spin, a quantum mechanical phenomenon arising from the intrinsic angular momemtum of a particle, forms the canonical two-state system. The particle's equation of motion is given by

$$\frac{\mathrm{d}\vec{I}}{\mathrm{d}t} = \gamma\vec{I} \times \vec{B}, \tag{1}$$

where $\vec{I}$ is the angular momentum, γ is the gyromagnetic ratio, a quantity unique to each particle, and $\vec{B}$ is the external magnetic field. In our case, i.e., that of NMR, the applied magnetic field is given by $\vec{B} = B_0\hat{z} + B_1 \sin(\omega t)\hat{x}$, where $B_1 \ll B_0$. For our experiments, B_0 is a constant field of about 1770 gauss, whereas B_1 could be applied for a variable amount of time. In the presence of just B_0, the spins of the atomic nuclei will precess about the $\hat{z}$ axis like a top. The resonant frequency for the system is given by $\omega_0 = \gamma B_0$. When B_1 is applied, they will then begin to precess about the $\hat{x}$ direction while simultaneously still rotating about the $\hat{z}$ axis at a very high frequency, thus sweeping out over the surface of a sphere. The duration of the B_1 field can be set so that the spins precess to a predictable and useful place, i.e., the xy plane. The time that it takes for the spins to precess to the xy plane is known as a 90°pulse.

Once the B_1 field is removed, the spins will not continue to oscillate exactly as they had done when the B_1 field was applied. They will gradually relax back to their initial state due to inhomogenities in the $\vec{B}$ field (both B_0 and the random contributions of nearby molecules) and natural thermal (Boltzmann) relaxation. The overall relaxation time is known as T_2, and the relaxation time due to just field inhomogenities (energy exchange between particles) is known as T_1. It is obvious that T_1 should always be greater than T_2. Furthermore, for nonviscous materials, T_1 and T_2 should be approximately equal because there is very little molecular interaction. On the other hand, both T_1 and T_2 should decrease with an increase in viscosity. Similarly, if a sample is doped with paramagnetic ions, T_1 should decrease because there is a greater molecular interaction [1].

2. PURPOSE

The purpose of this experiment was to learn about and verify the relations between T_1, T_2, paramagnetic ion doping, and viscosity.

3. EXPERIMENTAL SETUP

The experimental setup is given in Figure 1. The wave-

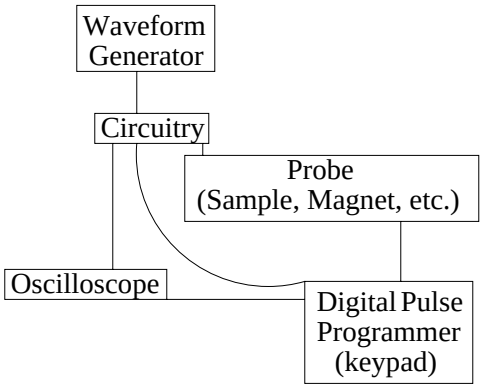

FIG. 1: Experimental Setup

form generator was set near ω_0 for the proton (i.e., hydrogen). Using a 100% glycerine sample and a 90°–180°pulse (as described in §4), we found that our signal was the largest when ω was set to 7.535MHz with a 90°pulse of 21μs. For reference, this gives us, with the measured B_0 of 1786 gauss, a γ_{proton} of 4.219MHz/kgauss, as compared to the actual value of 4.26MHz/kgauss. Similarly, we found γ for flourine from a tri-flouric acetic acid sample to be 3.997MHz/kgauss.

As the hydrogen ion was the relevant particle in the experiments described below, the rf was always set at

*Electronic address: molly@mit.edu

7.535MHz, the first pulse was set to be 21μs, and the second pulse to be 42μs.

4. PARAMAGNETIC ION DOPING

In order to determine the effects of Fe^{3+} concentration, as an example of paramagnetic ion doping, on the relaxation times, we measured T_1 for eight different concentrations of iron ions. (T_1 and T_2 should be approximately equal in this case because the samples are not very viscous; see §5 for an analysis of the effects of viscosity on the relaxation times[1].) We determined T_1 for each sample by using what is known as a 90°–180° echo sequence. First, a 90°pulse, i.e., a pulse lasting 21ms, was applied,

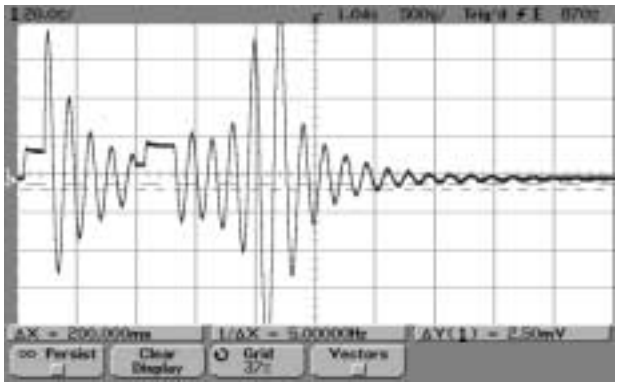

FIG. 2: A sample 90°–180° echo sequence (100% glycerine)

exactly enough time for the spins to precess down into the xy-plane. Due to inhomgenities in the magnetic field (differing molecular environments), the spins begin to slowly decohere; that is, they have slightly different frequencies than their neighbors as they rotate in the xy-plane. This is mostly a thermal relaxation[1]. A 180°pulse, lasting twice as long, then rotates all of the spins such that they are once again in the xy-plane, but now going in the opposite direction about the z axis. This causes them to recohere as the ones with lower frequencies catch up to the ones with higher, but now decreasing, frequencies. The overall effect is a large echo peak, which can be clearly seen in Figure 2. The height of this echo was expected to depend on the repeat time, t, between sucessive pulse sequences. The echo amplitude was expected to increase like $-a\exp[-t/T_1]+c$, where a and c are constants. Sample data and the subsequent plot, for distilled water, are given in Table I and Figure 3.

We calculated T_1 using this method for eight concentrations of Fe^{3+}, as summarized in Table II and Figure 4.

5. VISCOSITY

As explained in §1, T_1 and T_2 vary differently for viscous materials. In order to study this effect, we determined T_1 and T_2 for five samples of different concentrations of viscosity, and thus different viscosities. T_1 was found in the same manner as described in §4. We found T_2 using the Carr-Purcell method, as programmed into the Digital Pulse Programmer. First used by Carr and Purcell [1], a 90°pulse is followed by 180°pulses at times τ, 3τ, 5τ, etc. The echos, which have amplitudes given

Repeat Time (ms)	Echo Amplitude (mV)	Error (mV)
100	3.62	.05
150	4.92	.05
200	6.18	.05
250	7.38	.05
300	8.52	.1
350	9.6	.1
400	10.68	.1

TABLE I: Sample data for determining T_1 for distilled water using the 90°–180° pulse method. The error is systematic and due to the "jumping" of the signal on the oscilloscope.

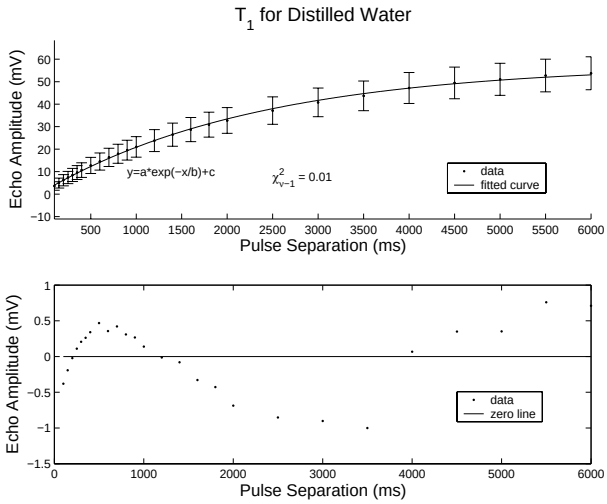

FIG. 3: T_1 plot for Distilled Water [2], $T_1 = 2241$ms.

Concentration (ions/L)	T_1 (ms)	Error (ms)
0	2241	50
3×10^{18}	1725	50
6×10^{18}	1626	50
1×10^{19}	1733	50
3×10^{19}	1298	40
6×10^{19}	1148	24
1×10^{20}	1203	30
3×10^{20}	636	10
6×10^{20}	753	10

TABLE II: T_1 for different concentrations of Fe^{3+}. Errors are given by about one standard deviation from the value for T_1 obtained from the fitted curves.

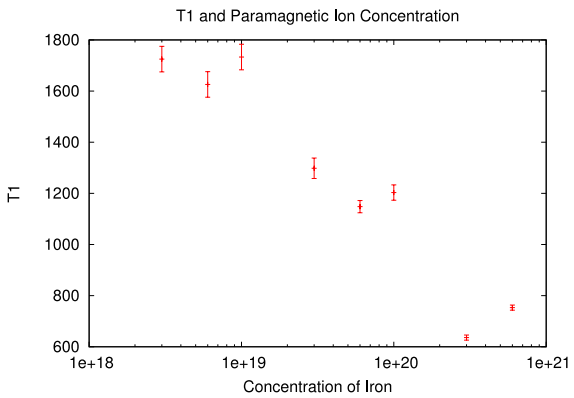

FIG. 4: T_1 as a function of iron ion concentration.

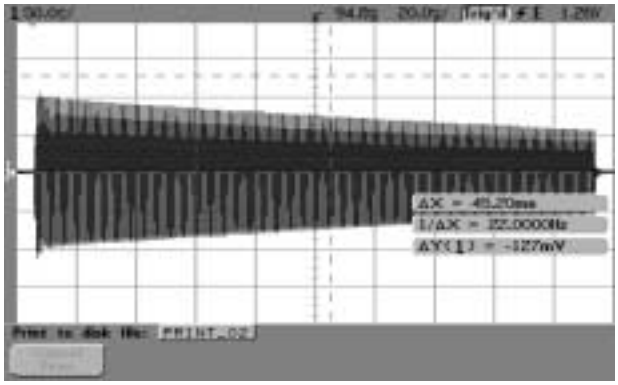

FIG. 5: Screenshot from Carr-Purcell method for determining T_2 for 50% glycerine.

by

$$E(2\tau) = E(0)\exp[-(2\tau/T_2) - \left(\frac{2}{3}\right)\gamma^2 G^2 D\tau^3], \quad (2)$$

will then be observed at times that are multiples of 2τ. Because the only relevant part of Eq. (2) is the rate of decay, we can model this as a simple decaying exponential, $\exp(-t/T_2)$.

Using a small τ (1ms) and a large repeat time ($\sim$ 10s) with the Carr-Purcell function, we were able to obtain signals like that shown in Figure 5. The echo amplitudes were then read off of a computer, generating data like that shown in Table III. This data was then fitted to an exponential to find T_2, as shown in Figure 6.

T_1 and T_2 were determined using these methods for five different concentrations of glycerine, as summarized in Table IV and Figure 7.

6. DISCUSSION AND CONCLUSIONS

As expected, T_1 decreased as Fe^{3+} concentration was increased, and both T_1 and T_2 decreased with an increase

Time (ms)	Amplitude (mV)	Error (mV)
9.13E1	6.59E1	2.5
9.52E1	6.35E1	2.5
9.89E1	6.29E1	2.5
1.03E2	6.05E1	2.5
1.07E2	5.82E1	2.5
1.11E2	5.75E1	2.5
1.15E2	5.52E1	2.5
1.19E2	5.44E1	2.5

TABLE III: Sample data for determining T_2 by the Carr-Purcell method. The errors are systematic, given by 1/20 of a division (in this case, 50mV), and are due mostly to a limit of screen resolution.

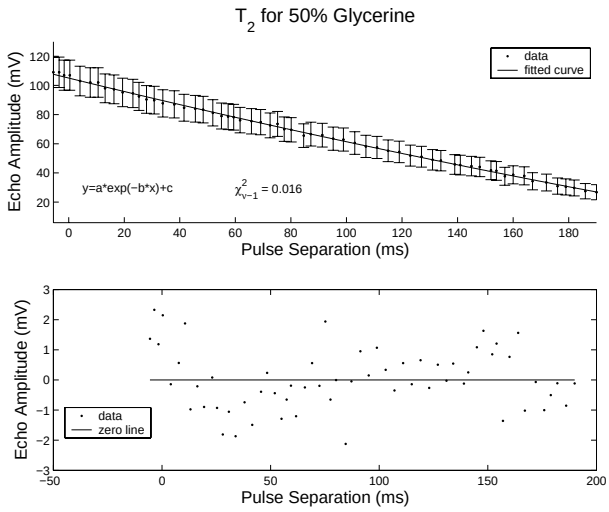

FIG. 6: T_2 plot for 50% Glycerine [2]. The errors are systematic, given by 1/20 of a division (in this case, 50mV), and are due mostly to a limit of screen resolution.

in viscosity. However, the T_1s for iron were more scattered than expected, even though the regressions for each data set were extremely good. We believe this is because the samples were inhomogenous; there were noticeable precipitates and dissolved air bubbles in most samples, lowering the measured T_1. Similarly, it was expected that T_1 and T_2 be close for lower viscosity samples, i.e., distilled water and 25% glycerine. For the 25% glycerine, this is clearly the case. Again, we believe that the measured T_1 was too low due to possible contamination from

Percent of Glycerine	Viscosity (C/mPas)	T_1 (ms)	T_2 (ms)
0	1.005	2241	3077
25	2.13	1026	1000
50	6.0	489.9	726.8
75	35.5	180.6	76.81
100	1410	46.63	30.23

TABLE IV: T_1 and T_2 for different viscosities.

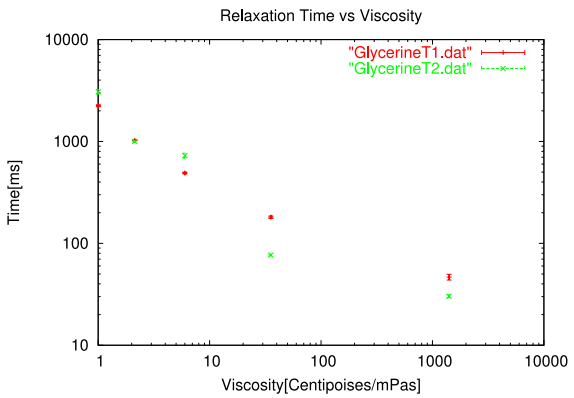

FIG. 7: T_1 and T_2 for different viscosities. Errors are given by one standard deviation from the values given by the fitted curves.

the cork on the test tube. However, T_2 did decrease more rapidly than T_1 as viscosity increased, as expected.

[1] MIT Physics Department, *Junior Lab Reader* (2003)
[2] http://web.mit.edu/8.13/matlab/

Acknowledgments

I would like to thank my lab partner, Austin Roach, for his help with performing and understanding the experiments, as well as for Figures 4 and 7. I would also like to thank Prof. Jay Kirsch for explaining the theory to us.