NMR Techniques Applied to Mineral Oil, Water, and Ethanol

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Using a TeachSpin PS1-A pulsed NMR device, we performed experiments to determine the spin-lattic relaxation times, T_1, of mineral oil, water, and ethanol. We also found the spin-spin dephasing time, T_2, of mineral oil and water. Using a known diffusion constant of water we estimated the magnetic field gradient.

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I. THEORY

From quantum mechanics we know that the magnetic moment, $\vec{\mu}$, of a nucleon is given by

$$\vec{\mu} = \gamma\hbar\vec{I}, \tag{1}$$

where $\vec{I}$ is the nuclear spin in units of $\hbar$ and for a proton, $\gamma_{\mathrm{p}^+} = 2.675 \times 10^8\ \mathrm{s}^{-1}\ \mathrm{T}^{-1}$[1].

Particles with magnetic moments placed in an external magnetic field, $\vec{B}$, have a change in potential energy given by

$$U = -\vec{\mu} \cdot \vec{B} = \gamma\hbar m_I B_0 \tag{2}$$

for $\vec{B} = B_0\hat{z}$, and $m_I = I, I-1, I-2, \ldots, -I$ [2].

For hydrogen, the only nucleon is a proton and its only spin states are $m_I = \pm 1/2$. The transition energy between these two states is given by

$$\Delta E = \gamma\hbar B_0. \tag{3}$$

This energy is electromagnetic in nature, so we may view it as a photon with energy $E = hf$. Upon equating these energies, the resultant resonance frequency is given by

$$f = \frac{\gamma B_0}{2\pi}. \tag{4}$$

To deal with macroscopic samples, we define $\vec{M} \equiv \Sigma_i \vec{\mu}_i$ to be the total magnetization. When placed in a strong external magnetic field, $\vec{B} = B_0\hat{z}$, the magnetization will be

$$\vec{M} = M_0\hat{z} = \chi_0 B_0 \hat{z}, \tag{5}$$

where χ_0 is the magnetic susceptibility of the material [1].

However, when the magnetization is not in equilibrium we assume that it approaches equilibrium at a rate proportional to the difference from equilibrium [1]. This yields the relation

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}, \tag{6}$$

where T_1 is referred to as the spin-lattice relaxation time.

If at $t = 0$ we have $M_z = -M_0$, then integration of the previous equation yields

$$M_z(t) = M_0\left(1 - 2e^{-t/T_1}\right). \tag{7}$$

With the condition $M_z(t=0) = 0$, we obtain

$$M_z(t) = M_0\left(1 - e^{-t/T_1}\right). \tag{8}$$

The transverse component, M_x, M_y are described by the equation

$$\frac{dM_{x,y}}{dt} = -\frac{M_{x,y}}{T_2}, \tag{9}$$

where T_2 is the spin-spin relaxation time or the dephasing time. The solution to these equations are simple exponentials, i.e.,

$$M_{x,y} = M_0 e^{-t/T_2}. \tag{10}$$

In addition, if the magnetic moment vector were to be aligned along the y-direction in the presence of a permanent magnetic field, $B_0\hat{z}$, Carr and Purcell [3] showed that there is self-diffusion of the magnetic moment in addition to the previous equation. Their result is

$$M_y(t) = M_0 \exp\left[(-t/T_2) - \left(\gamma^2 G^2 D t^3 / 12 n^2\right)\right], \tag{11}$$

where G is the magnetic field gradient, $\partial B/\partial z$ for an inhomogenous permanent magnet in the z direction, D is the self-diffusion constant and n is the number of 180° pulses applied which we explain in Section II.

II. EQUIPMENT

We used a TeachSpin PS1-A pulsed NMR device, which uses a permanent magnet with a field strength of $B_0 \simeq 0.36$ T and an RF coil which induces a magnetic field of $B_1 = 12$ Gauss. This RF coil is oriented along the y direction; a second coil acts as a receiver and is oriented in the x direction. The RF coil is controlled by a pulse programmer, which produces square waves. The first wave it produces is controlled by the "A pulse" and

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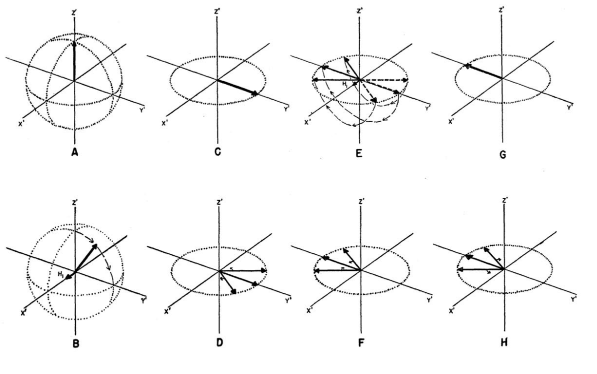

FIG. 1: The formation of a spin echo. (A) shows the original magnetic moment in the z direction. In (B), the field B_1 is applied giving a 90° pulse which rotates the magnetic moment into the $x - y$ plane, shown in (C). This will then dephase as depicted in (D). A 180° pulse is applied in (E), causing the spins to rephase in (F) yielding the final echo in (G); the process repeats itself as the spins then dephase in (H). This image is from Carr-Purcell [3].

all subsequent pulses are controlled by the "B pulse." The delay time, τ, between the A pulse and the first B pulse is controllable to one part in 10^3. Once the first B pulse is applied, an additional B pulse is applied every 2τ until the number of B pulses specified has been applied.

The pulses are fundamentally specifying how long to leave the field B_1 on; conventionally we do not refer to it in terms of seconds but in degrees. Since the applied field is orthogonal to the permanent magnet, the action of the field is to rotate the magnetic moment about the x-axis. If one can apply the field for a length of time such that the magnetic moment, starting in equilibrium, becomes $M_z = 0$ then we know that the magnetic moment lies entirely in the $x - y$ plane, specifically in the y-direction. This pulse would be referred to as a 90° pulse. Similarly, if one applies a pulse long enough to rotate the magnetic moment such that $M_z = -M_0$, then this is a 180° pulse. Pulses of 270° may also be applied but are equivelant to 90° pulses in all experiments we performed. In addition, pulses of arbitrary angle are achievable which is part of the difficulty in performing experiments.

In order for the RF pulses to interact with the nuclear spins it must be set to the precise frequency, or energy, that corresponds to a nuclear spin flip. For our equipment this frequency is 15.5MHz and is tunable in 10Hz increments. The exact frequency is given in Eq. 4, however for it to be of any use we need to know the magnetic field strength with similar precision; instead, this equation is used to estimate the field strength.

The signal from the receiver coil is first run through a pre-amp, as the signal is on the order of μV. This signal is then mixed with a signal at the user-tuned frequency. From elementary wave analysis, we expect the signals to interfere and cause a beat pattern. The frequency of this pattern is the difference between the precession frequency and our tuned frequency. The proper tuning should result in no beating; we are able to determine this with an oscilloscope.

The receiver coil signal is also sent to a Tektronix TDS-1002 digital oscilloscope. The amplitude of the signal is directly proportional to the magnetic moment of the sample in the $x - y$ plane. This important fact allows us to obtain decay amplitude data and treat it as magnetization. The exact conversion from voltage back to magnetization is therefore unimportant; knowing what the value of M_0 is of no real benefit. In the case of a single 90° pulse, the signal is referred to a Free Induction Decay (FID).

By varying the pulse widths, or times, we are able to determine that a 90° pulse is obtained when the FID amplitude is at a maximum. Similarly, a 180° corresponsd to a FID which is technically zero; practically speaking the FID will simply be indistinguishable from background noise. This fact causes an experimental problem in that a very similar pulse may be applied which is not 180° but we are unable to determine the actual angle of rotation. As such, if we are off by an angle δ in the pulse then if we perform an experiment which requires a large number, n, of pulses the final result is off by a cumulative angle of $n\delta$ which in general is significant.

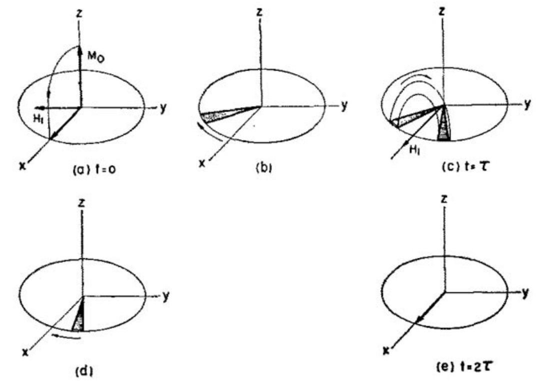

FIG. 2: Meiboom-Gill modification to the 90° pulse. The effect is spin echoes form along a single direction. This image is from Meiboom and Gill [4].

The NMR device we used has implemented the Meiboom-Gill (MG) modification [4], which eliminates most of this error as we can not be off by more than δ even for arbitrarily large n. This modification consists of changing the phase of the 90° pulse by 90° (pulse A) with respect to a 180° pulse (pulse B). The unmodified sequence is shown in Fig. 1, and described in Section III B. The result of this is that instead of echoes being formed along alternating $+y, -y$ axes we find that the echoes are formed along the $+y$ axis only. This is illustrated in Fig. 2.

III. PROCEDURE

A. Measuring T_1

The process we used to measure T_1 is called spin inversion. We set the A pulse to 180°, and the B pulse to 90°. After the A pulse, the magnetic moment is inverted and will decay due to the permanent magnetic field according to Eq 7. Immediately after the 90° pulse the magnetization amplitude is $M_z(\tau)$, but now in the $x-y$ plane where it will be recorded as a FID. We performed this experiment at multiple values of τ, recording the FID amplitude after the 90° pulse. We then fit this data to Eq. 7 in Mathematica to find T_1.

B. Measuring T_2

There are two methods to obtain T_2, which have a similar setup. In either case, we set the A pulse to correspond to a 90° pulse and the B pulse to 180°. With the magnetic moment in the $x-y$ plane after the A pulse, each spin begins to precess about the z axis as well as dephasing, a motion called nutation [3]. However, due to field inhomogenity as well as local effects with interactions of nearby spins each spin precess at a different frequency which is approximately the Larmor Frequency [3, 5]. As such, we see that the magnetic moment begins to "spread out" in the $x-y$ plane and the FID recorded reflects this as a decay to zero amplitude, which indicates the spins have no net alignment. At a time τ the 180° is applied which causes all the spins to reverse direction. The spins that had a frequency greater than the Larmor frequency still do, but they now move e.g. counterclockwise instead of clockwise. Similarly, the slower spins are still slow but moving clockwise rather than counterclockwise. As such, after a further time 2τ has elapsed the spins have re-aligned to their original positions, merely reversed by 180°, and produce a peak, called a spin-echo. This is shown in Fig. 1. The amplitude of this peak is governed by diffusion effects and the spin-spin dephasing time, T_2. The actual equation obeyed is given in Eq. 11, however we have techniques to separate out the two exponentials.

Carr and Purcell describe two methods to measure T_2, and we adopt their naming convention [3].

1. *Method A*

This method generally is sensitive to diffusion effects and as such may be used to determine D or G in materials where the diffusion effects dominate, such as water. With this method, we set the number of B pulses to one and vary the delay time similar to the procedure for measuring T_1. We will then have data that corresponds to $M_y(0)$, and $M_y(2\tau)$ and we know that $n = 1$ in Eq. 11.

For simpler material, such as mineral oil, the diffusion effects are minimal and may be ignored such that the data obtained is essentially given by

$$M_y(t) = M_0 \exp\left(-t/T_2\right), \qquad (12)$$

whereas for diffusion dominated materials such as water we have, approximately, only the diffusion term

$$M_y(t) = M_0 \exp\left(-\gamma^2 G^2 D t^3/12n^2\right). \qquad (13)$$

2. *Method B*

In contrast, this method was developed by Carr and Purcell [3] and allows us to make a direct measurement of T_2 in one shot instead of the multiple data points required by Method A.

By setting the number of B pulses high, we are able to increase n in Eq. 11 and thus minimize the effect of diffusion. This yields a closer measurement to T_2, but will not aid in determining G or D. For materials like water that are diffusion dominated, it is important to set the delay time smaller than the characteristic time scale of diffusion. We fit the spin-echo peaks to an exponential of the form in Eq. 12.

C. Measuring the Field Gradient, G

It is not possible to measure both G and D simultaneously. Instead, we must first know D in order to obtain G. Carr and Purcell have already shown that for water $D = 2.5 \times 10^{-5}\text{cm}^2\ \text{s}^{-1}$, which they accomplished by appling a second magnetic field with known gradient [3].

Using the data from Method A for measuring T_2, since we have $n = 1$ the decay is particularly sensitive to diffusion effects. Water is a particularly good candidate for this measurement, as the diffusion effects dominate such that the decay time due to diffusion alone is an order of magnitude lower than the value of T_2. In this case, we found that the data is, approximately, fit to the curve given by Eq. 13.

1. *Determining T_2 for Water*

Due to the large role diffusion has for water, it is not straight-forward to apply Method B to this system. Instead, to determine the actual value of T_2, we first found the magnetic field gradient from Method A data. We then performed a series of Method B experiments. The important feature here is that we are always investigating a constant time. By varying the number of pulses, n, to arrive at the specific time value we can alter the significance of the diffusion term in Eq. 11. Furthermore, since t has a fixed value when we fit the data to a curve, we are allowed to substitute in the known time value and the constant obtained previously for the entire expression $\gamma^2 G^2 D$ and obtain a reasonable value for T_2 in this rather complicated system [5].

IV. EXPERIMENTS

A. Mineral Oil

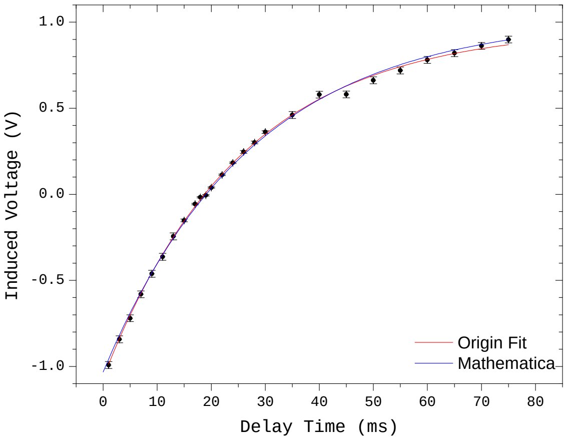

FIG. 3: The results of a series of spin inversion experiments with fitting routines performed by Origin and Mathematica. The value of T_1 obtained is 25.4 ± 0.7 ms from Origin and 27.5 ms from Mathematica.

We began with experiments on mineral oil, as it is one of the easier systems to study. Due to the low value of $T_1 = 27.5$ ms, we are free to set the repetition time to ≈ 200 ms which allows a fairly quick reaction on the oscilloscope to our settings. This makes it extremely easy to establish 90° and 180° pulses as well as set the tuning frequency.

In Fig. 3, we show the final result of this experiment. The two lines correspond to the fitting routines provided by Origin as well as a fit that we performed manually with Mathematica. The fit from Mathematica is forced to fit the theory, Eq. 7, whereas the Origin fit is merely of the form $y_0 + A\exp\left(-t/T_1\right)$ where $A/y_0 \neq -2$ as our theory demands. It is for this reason that the Origin result while clearly well-fitted to the data, with $R^2 = 0.999$, is not believed to be as accurate as the Mathematica result. However, the Origin fit does provide us with some estimate of the error in the fitting parameter, T_1. Our result is on the same order of magnitude as those obtained by Purcell and Pound [6]; our value is approximately twice as high, however we are not certain which mineral oil they used so the results are not directly comparable.

Furthermore, the error bars present in Fig. 3 change depending on how close we are to a FID amplitude of zero. To obtain the values and errors present, we first averaged the amplitude of all the data recorded before the FID. This gave us an estimate of the noise, which was then subtracted from the amplitude of the FID obtained after the B pulse was applied. Since the amplitude determines what the setting on the oscilloscope was, this limits our precision in measuring the voltage. Therefore, the error indicated is that of the smallest division our oscilloscope was capable of recording. The error in time is estimated to be 0.2 ms, which is the time division of the oscilloscope. While the NMR delay time has an experimental error attributed to it as well, with the smallest setting at 10 ms and the largest at 10 s we believe that the precision is fairly high such that the oscilloscope is the limiting factor.

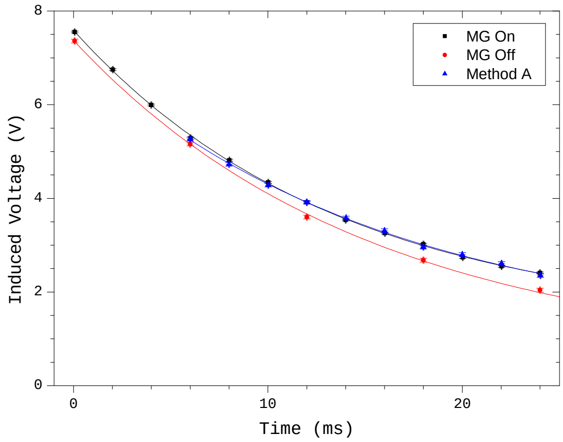

FIG. 4: We obtained T_2 data for mineral oil using Methods A and B, with and without the Meiboom-Gill modification. Though the Method A and MG off data compare well, we believe the MG on data provides a more probable value of T_2. All three methods agree to within 15%.

We performed both a Method A and Method B experiment on mineral oil, however with the Method B experiment we performed it both with the MG) modification on and off. This illustrates the effect that the MG modification truly has, as we can see the red curve in Fig. 4 would suggest $T_2 = 15.2$ ms, which compares well with Method A which is best fit with $T_2 = 15.7 \pm 0.1$ ms. This indicates that in performing Method B we did not have the B pulse set to 180°, but with the MG modification turned on we obtain $T_2 = 13.6$ ms. The error listed is from the fitting routine of Origin, and we should note that such routines provided us with error estimates for the Method B data of under 0.1 ms in both cases whereas the error for Method A is higher at 0.1 ms.

As in the T_1 data for mineral oil, the errors indicated on the graph are those derived from the oscilloscope settings which in this case we did not observe FIDs whose amplitude were approaching zero so the errors are constant.

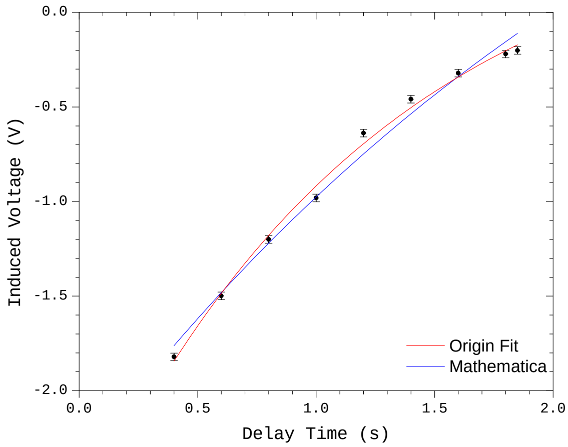

FIG. 5: We obtained a value of $T_1 = 2.9$ s for water by fitting the data with Mathematica to Eq. 7.

B. Water

We performed the same experiment as we did for mineral oil to obtain T_1. The difference with water is the data fit. Allowing Origin to fit to our data yielded $T_1 = 1.27 \pm 0.22$ s, which is not correct. The problem here is that Origin is, as before, using a fitting function of $y_0 + A\exp\left(-t/T_1\right)$, whereas the theory demands $A/y_0 = -2$. The result is that Origin obtains a value of $A = -3.4$ and $y_0 = 0.6$, a ratio of -5.5. When we force this ratio to be -2, via Mathematica, we obtain $T_1 = 2.9$ s, which agrees with known data [6]. However, the error indicated by Origin of 17% is likely appropriate, which makes our result $T_1 = 2.9 \pm 0.5$ s for water.

From Fig. 6 we can see the Method A data and Method B data do not agree at all, quite unlike the mineral oil. The reason is simple and fundamental to our study. The diffusion effects in mineral oil are minimal, so by inspection of Eq. 11, we see that Method A has $n = 1$ whereas for each peak in Method B n increases, meaning the contribution to the decrease from peak-to-peak at large n is due more to the spin dephasing than from diffusion. Also, the Method A data provides us with a hint at the time scale over which diffusion effects become significant, approximately 50 ms.

To obtain the fit to the Method A data in Fig. 6, we used Eq. 13. Origin and Mathematica both agreed on the fit parameter, as we performed a fit to the equation $A\exp\left(-Ct^3\right)$. The value of C obtained was $C = \gamma^2 G^2 D/12 = 1700\ \mathrm{s}^{-3}$. Using the known value of γ and D, we determined that the magnetic field gradient in our experiments is

$$G = \frac{\partial B}{\partial z} = 0.31 \frac{\mathrm{Gauss}}{\mathrm{cm}}. \tag{14}$$

The manufacturer states that the permanent magnet has a field uniformity of 0.01% over a distance of 1 cm. Our data agrees with this, given that the magnetic field strength is 3600 Gauss.

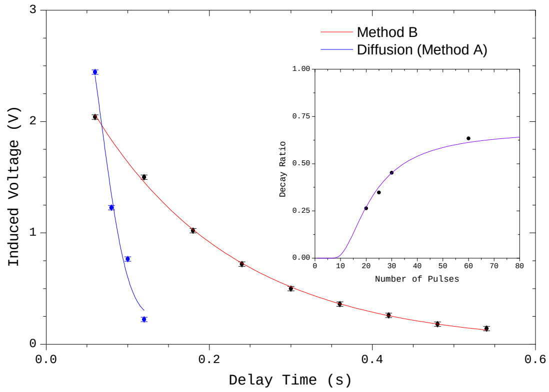

FIG. 6: We used the method A data fit by the blue line as it represents a system decaying due almost purely due to diffusion. With the diffusion term known, we can then perform multiple Method B experiments and investigate a single fixed time. We chose to investigate $t = 600$ ms and used 20, 25, 30 and 60 pulse sequences to obtain the spin-echo data. The purple line is then a fit where the fitting parameter is $T_2 = 1.1$ s. A single Method B curve is also provided to illustrate that the diffusion term is truly dominant in the Method A data.

With this information we are then free to design an experiment outlined in section III C 1. We chose an arbitrary time that could be factored into integers several ways, specifically 600 ms. Recall that it requires a time of 2τ to form an echo, so this means we are able to use a 20 pulse sequence at $\tau = 15$ ms, a 25 pulse sequency at $\tau = 12$ ms, a 30 pulse sequency at $\tau = 10$ ms and a 60 pulse sequency at $\tau = 5$ ms. Each of these pulse trains will feature a peak at 600 ms, which we then fit to the full function of the form given in Eq. 11. Specifically, since we previously found that $\gamma^2 G^2 D/12 = 1700\ \mathrm{s}^{-3}$, we used Mathematica to fit our data obtained from the four Method B experiments as

$$V\left(n\right) = A\exp\left(\frac{-1700\tau^3}{n^2} - \frac{\tau}{T_2}\right), \tag{15}$$

where we substituted for $\tau = 0.6$ s. The result of this fit is show in the inset graph of Fig. 6. With this method we found that $T_2 = 0.71$ s.

As a comparison, if one were to not realize the effect of diffusion on water and blindly apply the approach taken for mineral oil by simply fitting the spin-echo peaks to $M_0 \exp\left(-t/T_2\right)$, the value of T_2 obtained would be 0.18 s, a significant difference which justifies the approach we have taken.

C. Ethanol

We also began a study of ethanol. Using the same method as for mineral oil and water to obtain T_1 data, we

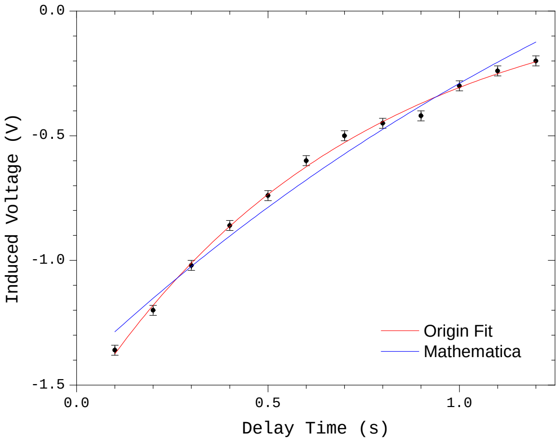

FIG. 7: Upon fitting our spin inversion data for ethanol to Eq. 7, we found that $T_1 = 2.0$ s.

found that $T_1 = 2.0$ s, which agrees with known results [6]. As before, the Mathematica and Origin fits yielded different values and for the same reasons, we believe the Mathematica fit is more appropriate.

V. CONCLUSION

We were able to determine $T_1 = 27.5$ ms and $T_2 = 15.7 \pm 0.1$ ms for mineral oil. We found that for water, $T_1 = 2.9 \pm 0.5$ s and $T_2 = 0.71$ s by considering the effects of diffusion and using delay times shorter than the time scale on which diffusion has a meaningful effect. In the process, we determined that the magnetic field gradient of the permanent magnet is $G = 0.31$ Gauss/cm. A study of ethanol was started and we were able to obtain $T_1 = 2.0$ s. Furthermore, we find that the data collected agrees with known values from previous experiments.

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