PHYS 309 Final Report: The effect of table salt and methanol on the spin-lattice relaxation time of water

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The effect of table salt and methanol on the spin lattice relaxation time of tap water was investigated using Earth's field nuclear magnetic resonance. The concentration of table salt in the water was found to be linearly related to the spin lattice relaxation time by $T_1 = (14.0 \pm 0.93)s[g/ml]^{-1} \times [\mathrm{NaCl}] + (2.19 \pm 0.04)s$. The data collected on methanol was inconclusive, but suggests that methanol might decrease the spin lattice relaxation time.

In nuclear magnetic resonance, spin lattice relaxation is the mechanism by which the nuclear magnetic spins of the protons align with a static external magnetic field, eventually reaching thermal equilibrium with its environment (the lattice). Understanding how this relaxation occurs, and in particular, measuring the time scale of the relaxation in different situations is important in many related fields.

For example, in magnetic resonance imaging (MRI), the protons in different tissues relax at different rates and thus provide a method for contrasting the various tissues in the body. It is possible to increase the contrast of MRI images by introducing paramagnetic contrast agents into the tissues. These contrast agents work by changing the spin-lattice relaxation time of the tissues in which they accumulate[1].

Another example is in physical chemistry where techniques such as fast field cycling NMR relaxometry[2] is used to investigate the molecular dynamics of a wide variety of liquids and polymers. These techniques depend on being able to accurately measure and vary the spin-lattice relaxation times of many different samples.[3]

It is thus of great interest to further understand the methods of measuring and changing this spin-lattice relaxation time. In my experiment, I used Earth's field nuclear magnetic imaging (EFNMR) to measure the spin-lattice relaxation times of the five different samples listed in TABLE II.

The alignment of proton spins to a magnetic field is well described by an exponential model. In the case of this experiment where the magnetic spins have been tilted 90^o from the external Earth's field (in the z direction) onto the xy plane (see FIG. 1), the equation is of the form

$$M_z(t) = M_{z,0}(1 - e^{-t/T_1}) \tag{1}$$

where $M_z(t)$ is the magnetization of the spins in the direction of the external field, $M_{z,0}$ is the thermal equilibrium magnetization of the spins and T_1 is the spin-lattice relaxation time. From EQN. 1, it is evident that T_1 is the time it takes the spins to recover $1 - 1/e \approx 63\%$ of its initial magnetization after being tilted by a 90^o pulse.

The most common method used to measure T_1 is the inversion recovery technique. However, since I can easily change the polarization time in my set-up (FIG. 2), there is an easier way to make the measurement. The idea is to measure how the signal changes as I vary polarization time. It is expected that for longer polarization times, the signal will increase as spins become more aligned with the Earth's field following EQN. 1. The signal detected is the AC voltage generated by a change in magnetic flux caused by the precession of the protons' spin at the Larmor frequency ($\omega = \gamma B$, where γ is the gyromagnetic ratio and B is the strength of the magnetic field) around the z axis. Note that the signal strength is proportional to the magnetization of the spins. Therefore, there is no need to measure the magnetization directly, but simply the strength of the signal. This should give the same time constant T_1 when fitting the data.

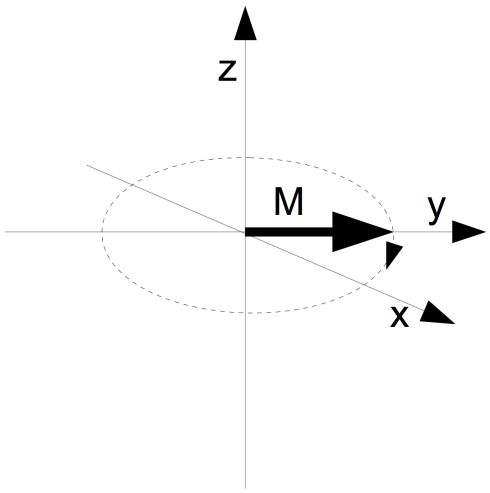


FIG. 1. The proton's magnetic spin vector (M) tilted by a 90^o pulse onto the xy plane. The Earth's magnetic field points in the z direction. Spin-lattice relaxation will cause the spin to realign in the z direction.

I considered two alternative estimators of the signal strength based on the signal peak seen in the frequency space of my data (FIG. 5):

1. The maximum of the peak

2. The integrated area under the peak

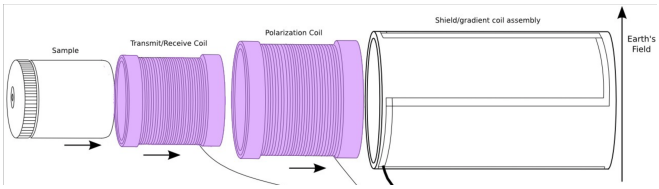


FIG. 2. My EFNMR set-up. The sample (550ml plastic water bottle) is placed inside the transmit/receiver coil, which is placed inside the polarization coil. Finally, a shield/gradient assembly surrounds both coils and the sample. The coils are controlled by an Arduino, while a black box with adjustable gradient knobs controls the shield/gradient assembly and powers the coils. The NMR signal is picked up by the smaller transmit/receiver coil and is then filtered and amplified before being detected by the Arduino. The Earth's magnetic field points perpendicular to the coil axis.

I first tried the idea of measuring the maximum of the peak because that was the easiest measurement to make. It was also intuitive that the strength of the signal will depend on the maximum of the peak, and I could clearly see the maximum increasing with polarization time. After getting the spectrum of the signal, I was able to use the tools installed in the lab computer to make very quick measurements simply by selecting the peak limits around the peak; I did not have to worry about keeping my peak limits consistent between measurements as the maximum will be the same provided that the peak is somewhere within my select range and that I did not select another noise peak within that range. The results did somewhat fit the model given in EQN. 1, but after discussions with Professor Folk, as well as with Yoko and Shawna, who were also measuring T_1, I decided that it was a better idea to measure the integrated area under the peak. I found that the fit to the peak areas was better than the fit to the peak maximums.

This makes sense because there is some spread to the precession frequencies due to inhomogeneities in the Earth's magnetic field. This effect where the spins start precessing at slightly different frequencies due to inhomogeneities in the field is well known as the T_2 time. It is important to account for all of the polarized spins in our measurement, and so it makes sense that the area under the peak is a better indicator of signal strength.

However, this did raise the issue of what to use for the peak limits. Initially, I thought that different peak limits would give slightly different T_1 from the fit, and this was observed when I tried a small range of peak widths around the observed peak limits. But then after discussions with Professor Folk, I realized that any extra area that I integrated outside the signal peak could be absorbed by adding a vertical displacement term d in EQN. 1, as long as I kept the peak limits the same for each polarization time. This extra area would therefore not have affected the T_1 times I calculated from my fits to the model. In fact, I wanted to make my peak limits as wide as possible to make sure that I included all of the signal peak. Then, using the same peak limits for each polarization time should have allowed me to measure the increase in the signal strength very accurately. An example of the peak limits I used is shown in FIG. 3.

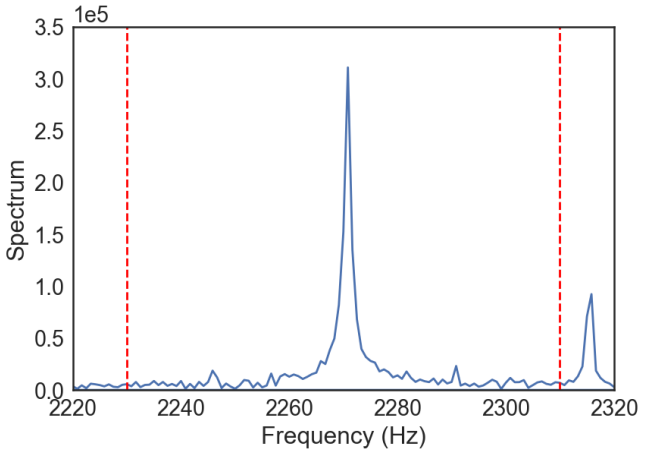


FIG. 3. The dashed red lines show an example of the peak limits used to calculate the area under the peak. The limits were set as wide as possible to make sure all of the peak is included without including any of the noise spikes. The same peak limits were used at each polarization time.

As discussed above, the model used to fit the data is a modified version of EQN. 1 which includes a vertical offset d:

$$M_z(t) = M_{z,0}(1 - e^{-t/T_1}) + d \tag{2}$$

Using my set-up (see FIG. 2) and the *OnePulseNoSync.prog* program on the computer, I was able to detect and measure the precession of the protons in the H atoms of water molecules. The settings used for the program are listed in TABLE I.

Setting	Value
frequency	2050 Hz
polarization time	variable
90 half cycles	10
receiver delay	5 ms
repetition delay	3000 ms
num points	12000
num runs	4

TABLE I. The settings used for the *OnePulseNoSync.prog* program.

One of the unprocessed time domain signals received by the Arduino is shown in the first panel of FIG. 4. (They all looked essentially the same in the time domain.) In order to analyse the signal, I took the discrete Fourier transform using SciPy's fast Fourier transform routine. The absolute magnitude of the Fourier transform of the signal is shown in the second panel of FIG. 4. The plot of the measured signal strength vs. the polarization time can then be fitted to the model of EQN. 2 to find T_1.

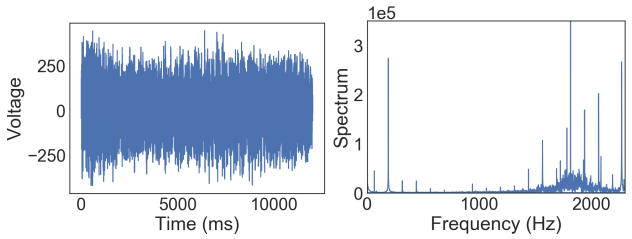


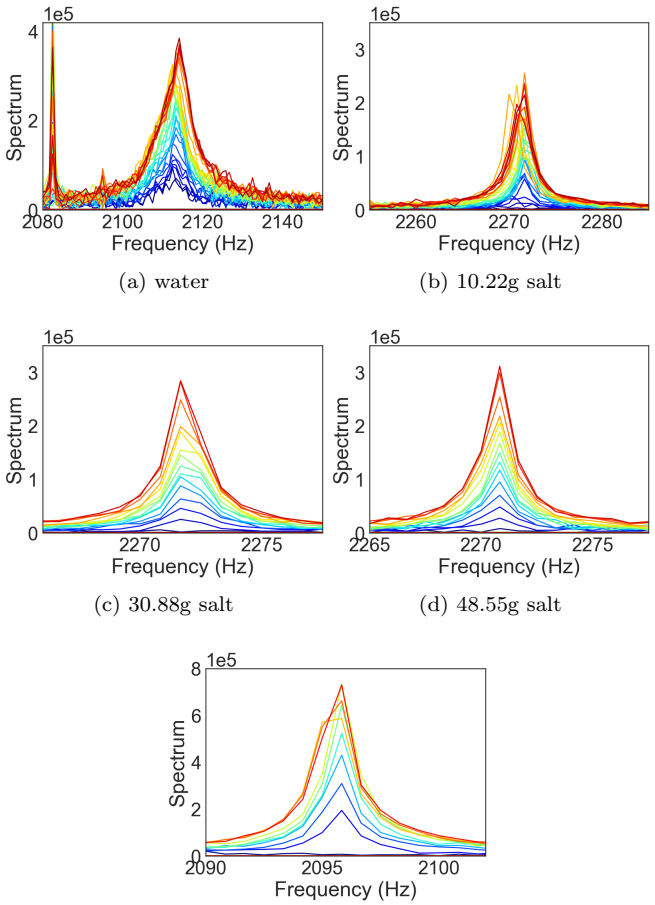
FIG. 4. An example of a time domain signal and its discrete Fourier transform. The signal peak is hard to see among the many other noise peaks, but it is clear when you zoom in as shown in FIG. 5

To measure the signal strength at multiple polarization times in one run, I used the *Arrayed Acquire* function of the *OnePulseNoSync.prog* program. The general steps occurring in the coils after I click the *Arrayed Acquire* button are:

1. Polarize the sample for the specified polarization time.
2. Apply a 90^o pulse to tilt the spins into the xy plane
3. Detect the NMR signal
4. Repeat steps 1-3 four times (the num_runs setting in the program) for the same polarization time.
5. Repeat steps 1-4 for the next polarization time specified in the array

The spectra of my data zoomed in on the signal peaks is shown in FIG. 5. Obviously, I got better at collecting the data as time went on. (You can see the peaks becoming much better separated and the noise becoming much smaller in the later samples I measured.) There are several changes I made that helped improve the signal:

1. Thanks to the group working beside me (Yoko and Shawna), I discovered the *shim* program installed on the computer. This program helped improve the sharpness of my signal by helping me adjust the gradient coils to their optimal positions. I was able to improve the FWQM of the signal from $\sim$ 10Hz to $\sim$ 2Hz.
2. I eventually figured out that the set-ups created large magnetic fields that interfered with each other, and that running my coils at the same time as the group behind me had a large detrimental effect on both of our signals. I noticed that my single peaks oddly split into two separate peaks when another coil is running nearby. Although I could not figure out why this "peak splitting" effect happens, I agreed to stagger my runs with the group behind me to avoid the interference. I also started taking data later into the lab when some groups have already left.



(a) water (b) 10.22g salt

(c) 30.88g salt (d) 48.55g salt

(e) methanol

FIG. 5. Examples of the spectra at the signal peak for each sample at various polarization times. The bluer lines show the signal at shorter polarization times while the redder lines show the signal at longer polarization times. The signal received is clearly stronger for longer polarization times. The polarization times go from 0s to 10s.

3. I increased the repetition delay between each polaraization sequence from 1000ms to 3000ms ($3000ms \approx T_1$).

Unfortunately, due to time constraints, I could not take as many data points for my later samples, which is reflected in the slightly larger uncertainties of my later T_1 measurements despite the better quality measurement at each polarization time. (see FIG. 8)

As I noted above, spin-lattice relaxation results from the interaction between the protons' magnetic spins and its environment. Therefore, it is reasonable to expect that altering the water's environment by dissolving various solutes into the water might affect this interaction and change the measured T_1 time. In particular, paramagnetic ions will certainly have a great effect on T_1 as they are already used routinely in hospitals to enhance contrast in MRIs. Unfortunately, despite substantial efforts to detect a signal from a copper sulfate ($CuSO_4$)

solution (where the ions are paramagnetic), I was unable to do so, and therefore could not measure its T_1.

Instead, I was able to measure the T_1 of table salt solutions (where the ions are diamagnetic). The salt water samples were prepared using the water from the water fountain found directly outside Hebb 42. The table salt used was Windsor brand iodized table salt which contains mainly NaCl, but also small amounts of calcium silicate, sugar, and potassium iodide. The amount of salt added was measured by differences using an AWS-100 portable digital scale. After adding each sample of salt using a funnel made of a sheet of lined paper, I shook the bottle for approximately 30s to dissolve the salt before inserting it back into the coils. Each run was repeated 3 times to get an average at each polarization time. (Only 2 times for plain water because I ran out of time during the lab. See TABLE II.)

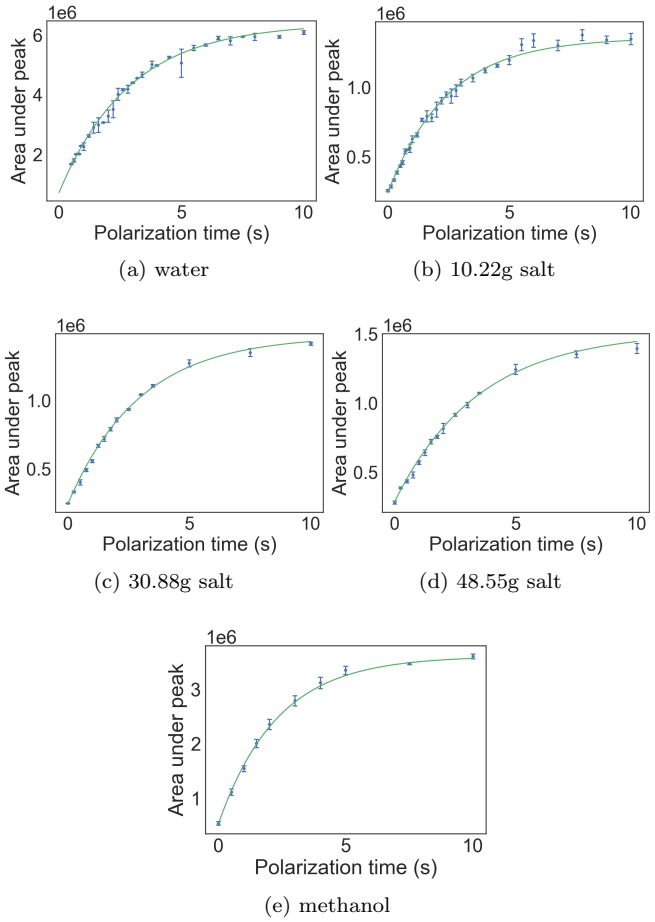
The methanol solution was prepared using a large beaker found in the front of the room and may not be too accurately measured. In addition, only one concentration of methanol was examined because I did not have enough time to do more measurements.

The polarization time was the independent variable in the experiment and I was careful to choose an array of polarization times that covered the entire range allowed by the program, from the minimum of 0s to the maximum of 10s. More points were taken at shorter polarization times because that is when the signal strength increases the fastest. A few points were always taken at longer polarization times to constrain the asymptotic behaviour. Looking at the plots in FIG. 6, the range and number of polarization times used appear to have been well chosen to constrain the model (EQN. 2). Notice that for plain water, 30 points were taken, but none below a polarization time of 500ms. This was because I could not visually see a peak below 500ms and I did not yet develop my data analysis code to analyse the small peaks at the lower polarization times. For the lowest concentration of salt water, 30 points were also taken, but the range was extended down to include 0 polarization time. For the next two concentrations of salt measured, data was only taken at 15 different polarization times because time was running out in that lab section. Finally, the data for methanol was taken near the end of the last lab section after a long frustrating two hours trying to find the signal peak for the copper sulfate solution. As a result, there was only time for taking data at 10 different polarization times. The above discussion is summarized in the *N polarization times* column of TABLE II.

The error bars plotted in in FIG. 6 and FIG. 7 show the standard error in the mean of the repeated measurements at each polarization time.

The results of the experiment are shown in FIG. 6, 7, 8, 9, and TABLE II. The data for each sample was fitted to the exponential model given by EQN. 2 using the minimized χ^2 fitting routine scipy.optimize.curve_fit. The residuals plotted in FIG. 7 and the reduced χ^2 for each plot shown in TABLE II indicate a good fit to the data for all of the five samples.

The error bars plotted in FIG. 9 and FIG. 8 represent one standard deviation errors on the optimized parameters returned by the SciPy curve_fit function.



(a) water (b) 10.22g salt

(c) 30.88g salt (d) 48.55g salt

(e) methanol

FIG. 6. The minimized χ^2 fits for each sample. Error bars show the standard error in the mean for repeated measurements at each polarization time.

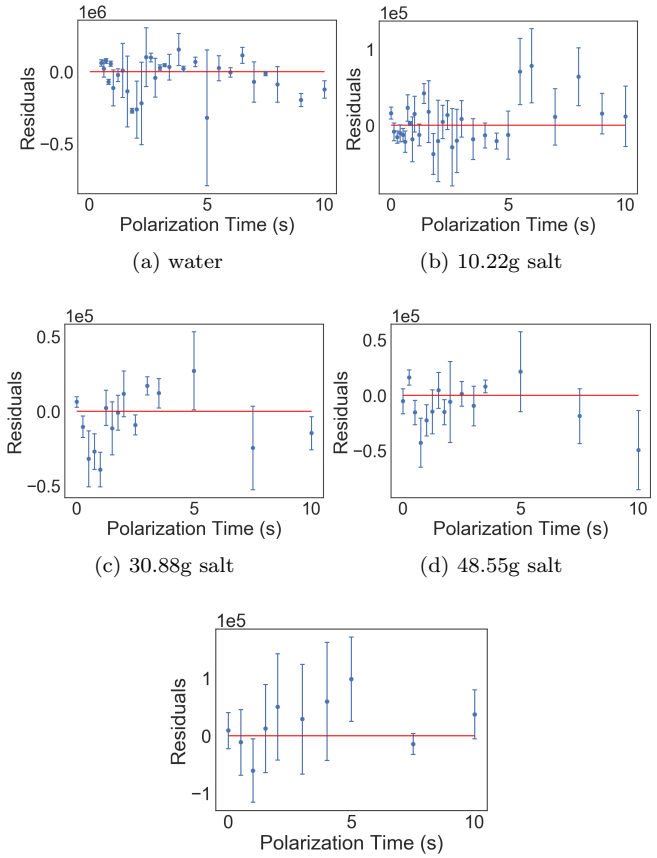
In FIG. 9, the three different concentrations of salt is plotted and fitted with a linear model. These data points were all measured on the same day using the same set-up in the same position in the lab. The plot shows a statistically significant difference between the T_1 times of the samples. A minimized χ^2 linear fit is given by $T_1 = (14.0 \pm 0.93)s[g/ml]^{-1} \times [\mathrm{NaCl}] + (2.19 \pm 0.04)s$.

Comparing with the T_1 measurement for plain water I made two weeks prior however, showed that the two measurements do not agree. Extrapolating from the salt water data gives a T_1 of 2.19 ± 0.04 s for water with no salt dissolved, which is clearly in tension with the measurement of 2.90 ± 0.13 s made earlier.

A potential explanation for this discrepancy is that the water itself might be slightly different. The plain water sample was taken as is from the front of the lab and may have been left there for some time. It is uncertain as to whether or not there has been anything accidentally or

Amount of water	Solute added	Concentration [NaCl]	T_1	Reduced χ^2 of the fit	N polarization times	N trials per polarization time
550 ml	None	0 g/ml	2.90 ± 0.13 s	15.34	30	2
550 ml	10.22g salt	0.019 g/ml	2.46 ± 0.09 s	0.84	30	3
550 ml	30.88g salt	0.056 g/ml	2.96 ± 0.11 s	1.68	15	3
550 ml	48.55g salt	0.088 g/ml	3.48 ± 0.22 s	0.91	15	3
450 ml	100 ml methanol	–	2.32 ± 0.09 s	0.38	10	3

TABLE II. Final results for each of the five samples. The data is plotted in FIG. 8.



(a) water (b) 10.22g salt (c) 30.88g salt (d) 48.55g salt (e) methanol

FIG. 7. The residuals for each fit in FIG. 6 respectively. Error bars show the standard error in the mean for repeated measurements at each polarization time.

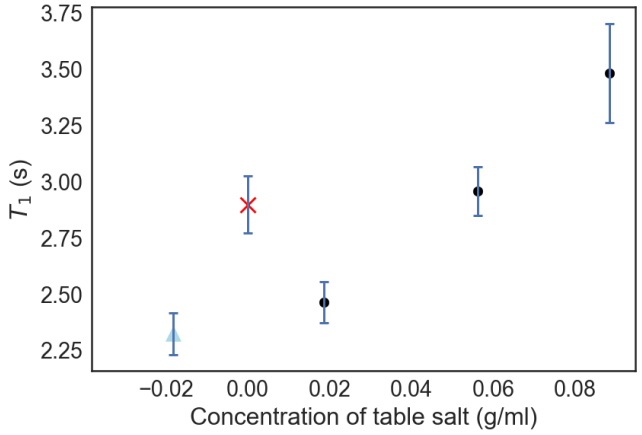


FIG. 8. The measured T_1 for the 5 different samples. The light blue triangle is the water and methanol mixture and is arbitrarily placed on the x axis. The red x is the potentially contaminated unsalted water. The black dots are the water and salt mixtures. Error bars represent one standard deviation errors on the optimized parameters returned by the minimized χ^2 fitting routine. The values plotted are listed in TABLE II.

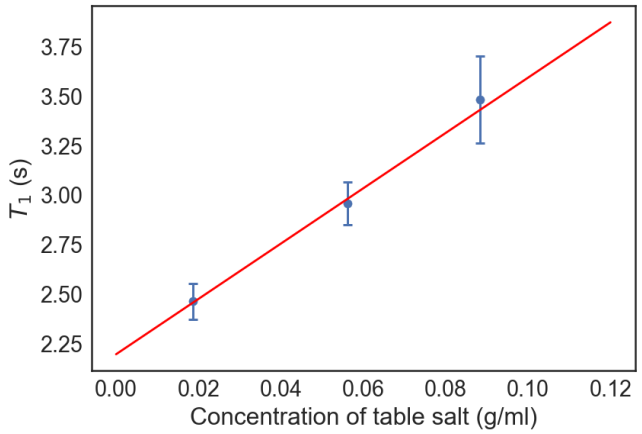


FIG. 9. Increasing the concentration of table salt increases the T_1 time. A linear fit to the three data points is given by $T_1 = (14.0 \pm 0.93)s[g/ml]^{-1} \times [\mathrm{NaCl}] + (2.19 \pm 0.04)s$. Error bars represent one standard deviation errors on the optimized parameters returned by the minimized χ^2 fitting routine.

purposefully dissolved in the water. Even dissolved gases might affect the spin-lattice relaxation time. The water used for the salt water experiments was taken fresh from the water fountain outside the lab at the start of the lab section.

Another possible explanation might be that the temperature of the water did not reach thermal equilibrium with the room when I started taking data. Although I did spend around 30 minutes getting a signal and shimming the gradients before making the measurements, the water from the fountain was substantially colder than

room temperature; it may still have been warming up during the experiments. The plain water sample on the other hand, was definitely at room temperature because it was sitting in that room for a very long time. I believe that increasing temperature does increase T_1, but I am not sure by how much. In hindsight, temperature is something I should have monitored better.

Interestingly, both the Na^+ and Cl^- ions dissolved in the salt water are diamagnetic species, which respond weakly to magnetic fields, and were not expected to have a large effect on T_1.

Contrast agents such as gadolinium ions used in MRI decreases T_1 because unpaired electrons in their valence shells allow the ions to align with the external field and also generate their own magnetic fields that interact with the protons in the water molecules. This amplifies the effect of the external field and causes the spin-lattice relaxation process to proceed more quickly.

In contrast to paramagnetic contrast agents, the magnetic fields induced in diamagnetic ions oppose the applied magnetic field and might reduce the effect of the external field on the protons in the water. This may have caused the increase in T_1 observed in this experiment. However, diamagnetism is generally known as a weak effect and I was surprised that I may have detected this in my experiment.

Again, it is possible that I did not control well for the temperature of the water, and that it is the gradual warming of the water throughout the experiment that caused the measured increase in T_1, and not the added salt ions. Further experiments should be performed to check if diamagnetic ions really do increase the spin-lattice relaxation time.

As for methanol, I did expect it to decrease T_1 because it is paramagnetic, similar to the contrast agents used in MRI. Referring to FIG. 8, the decrease in T_1 due to methanol is observed, but may not be statistically significant compared to the T_1 measured for the lowest concentration of salt. Further experiments are required to determine if methanol does indeed decrease the T_1 of water.

In conclusion, adding table salt to water was found to increase the spin-lattice relaxation time by $T_1 = (14.0 \pm 0.93) s[g/ml]^{-1} \times [\mathrm{NaCl}] + (2.19 \pm 0.04) s$. However, this result should be checked because in retrospect, temperature may not have been well controlled. Methanol may decrease the T_1 of water, but insufficient data was gathered to make a statistically significant claim.

All of my data and Jupyter notebooks used for data analysis can be found at `https://github.com/jackhong6/PHYS309`.

[1] Y. Cao, L. Xu, Y. Kuang, D. Xiong, and R. Pei, J. Mater. Chem. B **5**, 3431 (2017).

[2] V. Zampetoulas, D. J. Lurie, and L. M. Broche, Journal of Magnetic Resonance **282**, 38 (2017).

[3] R. Meier, D. Kruk, and E. A. Rössler, ChemPhysChem **14**, 3071 (2013).