April 13, 2000

Experiment G7a

Pulsed NMR: Spin Echoes

A horizontal (z axis) magnetic field is used to polarize the proton spins in a liquid sample. These spins are then tipped 90 degrees into the xy plane. This is done with an rf magnetic field which is perpendicular to the dc field. The rf frequency is fixed at the resonance frequency. The resonance is tuned by tweaking the dc field. After the spins are tipped into the plane, they become out of phase with each other due to "relaxation"—random molecular fields due to the other molecules. As a result, the signal, which is due to all the spins acting in concert together, quickly disappears [†] After they have spread out in the xy plane, they are reversed by tipping them 180 degrees. They will then precess until they are back together. The spin relaxation reduces the magnitude of the "spin echo" observed. Varying the time delay between the 90 degree and 180 tipping pulses allows you to measure the relaxation time T_2 by observing the decay of the echo.

1. Set up the apparatus according to the instructions in the next section. Ask the instructor or Nick if there are any questions about this. You should be able to observe a spin echo in the glycerine sample. Use the Hall probe to measure the magnetic field. Estimate the rf frequency and calculate the proton magnetic moment. Insert (carefully!) a small amount of magnetic material into the magnet, and observe the effect on the signal. Explain. Read the introductory article on NMR by Pake.

2. Measure T_2 and T_2^* for glycerine. This will involve taking a number of data points on the spin echo amplitude vs. delay time between the 90 degree pulse and the echo (2τ).

3. Find a pure water sample. T_1 is very long for pure water– it is hard for the spins to exchange energy with the other degrees of freedom in water. Also measure T_2 and T_2^*. Compare the values you get for T_2^* with the value you get for glycerine. Why are the proton spin relaxation times different for water and glycerine? Could you measure the self-diffusion constant in water? (See Carr and Purcell, page 636ff.)

4. The light blue tubes contain a solution of copper sulphate in water, with the various concentrations, ranging from 10^{17} to 10^{20} ions/cc labelled. Copper is a paramagnetic ion, so the water protons "feel" different fluctuating magnetic fields. Measure T_1 and T_2 for several different concentrations and plot T_2 vs concentration on a log-log plot. What can you conclude from this? (Instead of copper ions you can use iron ions. The yellow colored solutions are ferric nitrate. Try some of these, and see if you agree with the data plotted on page 586 of the 1950 article by Hahn. Also compare with equation (54) on page 705 of the article by Bloembergen, Purcell and Pound. Explain.

[†] This is called the "free induction decay".

5. Viscosity has a large effect on the relaxation times. Measure T_1 and T_2 in epoxy while it is curing. Plot the relaxation rates vs. curing time, as the viscosity increases. Explain why the relaxation time decreases as the epoxy becomes more viscous.

References For Experiment G7a

1. **Nuclear Magnetic Resonance**, G.E. Pake, reprinted from *Solid State Physics*, vol 2, Academic Press 1956 (QC173.S68). This is a general introduction to the subject of NMR.

2. **Simple, Spin-Echo Spectrometer**, B.H. Muller, et al, *American Journal of Physics*, vol 42, p58 (1974). A description of a spectrometer very similiar to ours.

3. **Spin Echoes**, E.L. Hahn, *Physical Review*, vol 80, p580 (1950). This is the original article detailing the method of spin echoes. It includes a theoretical formula ((21), page 586) for the time dependence of the signal you observe.

4. **Effect of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments**, H.Y.Carr, E.M. Purcell, *Physical Review*, vol 94, p630(1954). Explains how diffusion affects the T_2 measurement. A procedure is invented to avoid the non- exponential decay (we do this in experiment G7b).

5. **Relaxation Effects in Nuclear Magnetic Resonance Absorption**, N.Bloembergen, E.M.Purcell, R.V.Pound, *Physical Review*, vol 73, p679 (1948). A general discussion of relaxation, including the effect of viscosity on T_2, and the relation between T_1 and T_2 in some interesting cases.

6. **Nuclear Induction**, F. Bloch, *Physical Review*, vol 70, p460(1946). This is one of the original articles following the discovery of NMR by Bloch at Stanford and Purcell at Harvard. It is included here because it contains the description of the famous Bloch equations used everywhere in NMR studies. It also has historical interest. Bloch and Purcell made the discovery independently, and were given the Nobel Prize for it.

1. Setup Notes

These setup notes were written by Nick Szabo to help you get started. Please follow the procedure below when turning on the experiment

1. Turn on the AC line regulator (on the floor, to the right of the table).

2. Make sure the magnet variac (large block knob on the magnet power supply) is turned down. Then turn on the magnet power supply.

3. Adjust the variac to approximately 21 (2.7 Amps in the magnet). Turn on the regulator, and adjust the coarse knob to make the needle appear in the center of the meter on the regulator. The current is NOT regulated properly unless this is set correctly. Sometimes you have to start with lower variac setting, turn up the coarse knob until the needle is midscale, then advance the variac, again advance the coarse knob, etc until two conditions are simultaneously satisfied: a) the current is close to 2.7 A , b) the regulator meter is in the center of the scale. Settings which worked for us were: coarse setting = 8.5, fine setting = 6.1, but you should find the proper operating points independently, since they can change.

4. Now turn on the +12 volt power supply(home made box). This powers the transmitter amplifier and receiver.

5. Get familiar with the controls on the Tek scope. Set the scope according to the following: CH1=2 volts/cm, CH2=500 mV/cm, hor sweep (M) 2.5 millisec/cm, trigger on Ext(normal, not auto), level 0.5 volts. Set "Acquire" menu on "sample" initially to tune for the resonance, then for data taking on "average=4 or 16". Learn to use the cursors (there are 2) to measure the intervals (delta) in time and voltage. Do not "eyeball" these, but make accurate measurements with the cursors. *Note: we have observed a glitch in which the cursor reading does not give the correct voltage after the scale is changed. So check that the cursor reading does agree with the number of centimeters on the scale. The cursor may have to be reset after the voltage scale is changed.*

There are 3 connections to the scope: a trigger from the ramp, the signal to monitor the pulse sequence, and (CH2) the signal from the receiver.

6. The diagram below shows the correct settings for the 4 pulse generators. From left to right, they are 1) ramp generator, which sets the repetition rate for the pulse sequence (important for the T_1 measurement), 2) the delay between pulse 1 and pulse 2 (this is what you change to make the T_2 measurement, 3) the length and magnitude of pulse 1 (90° pulse), and 4) the length and magnitude of pulse 2 (180° pulse. Please check that all settings are correct, since the last experimenter might have changed them.

PULSE GENERATOR SETUP   G7a

| Repetition rate | Delay Pulse 2-Pulse 1 | Pulse 1 (90 deg.) | Pulse 2 (180 deg.) |
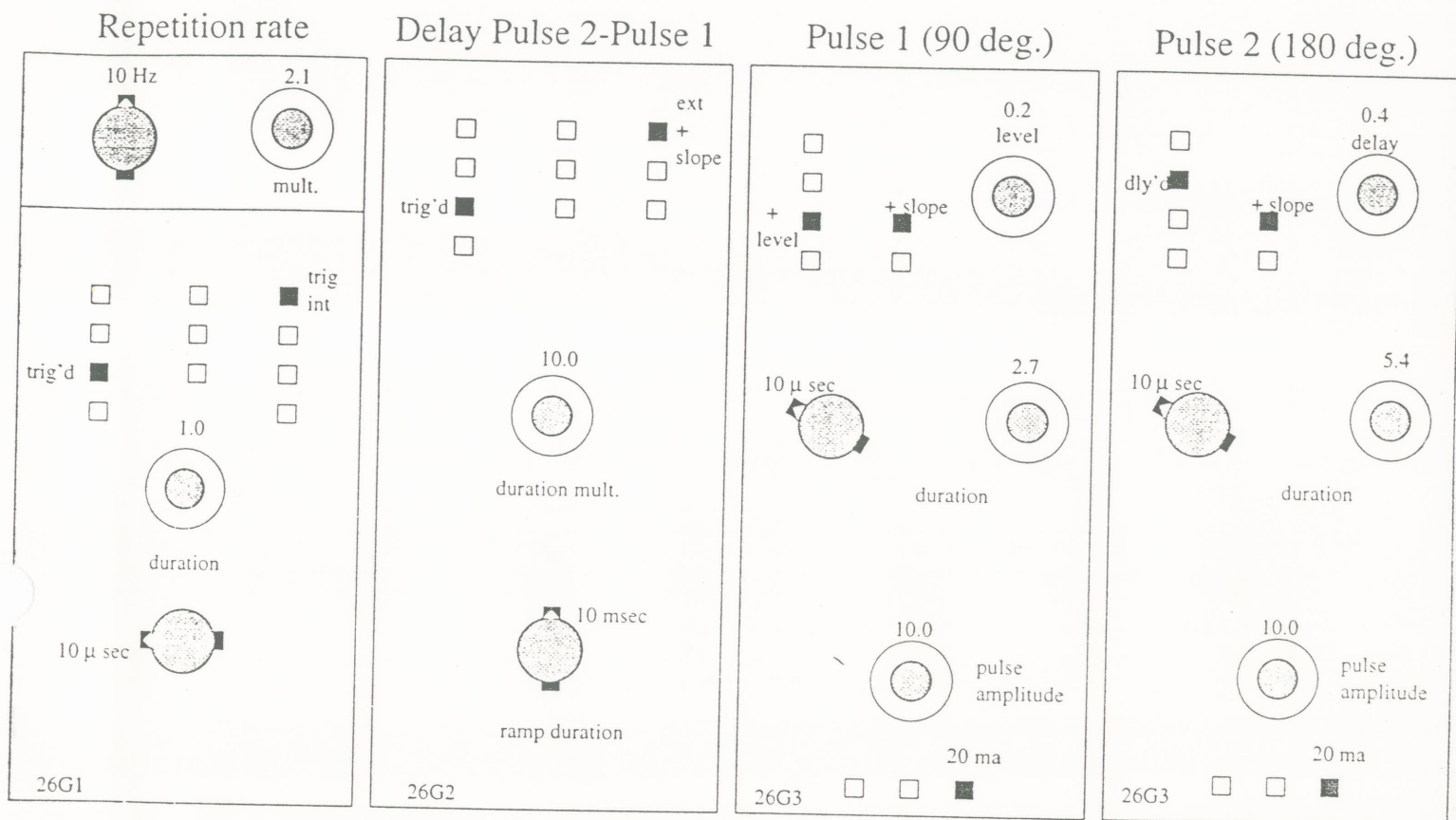
J101 ⟶ Scope ext. trigger   J103 ⟶ Scope CH1   J104 ⟶ transmitter input

Receiver out ⟶   Scope CH2   (timing pulse)

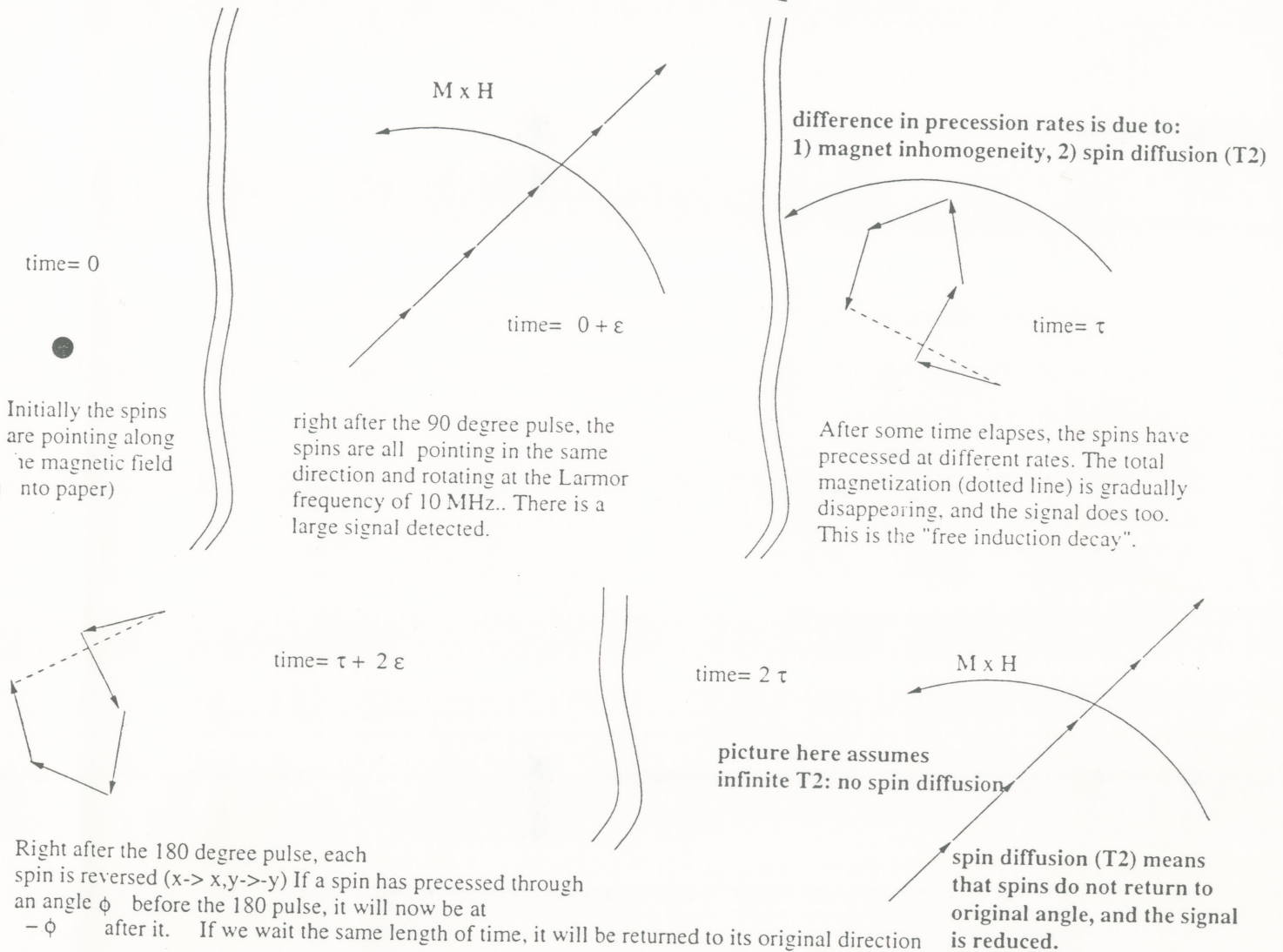### Starting the experiment: first observation of the spin echo

Install the glycerine sample (it says "Glyc" on the rubber stopper. This is the easiest to measure. Unfortunately, T_1 is too short to measure with this sample, but can be very roughly measured with the other samples provided.

Tune the fine or coarse controls on the regulator until you see a third pulse. This is the spin echo. It should be spaced the same distance in time from pulse 2 as the delay between pulse 1 and 2. When the magnetic field is close to the resonance value, you will see the signal after pulse 1 "fatten" up and look like an exponential decay. This is the so-called "free induction decay" (FID). The spin echo should appear at the same time. Adjust the fine control to maximize the spin echo magnitude.

Use the cursor to measure the spin echo magnitude. You will want to take the differencee between

the top and bottom of the pulse to avoid errors due to a possible base-line shift when looking at short delays between pulse 1 and pulse 2. Also, when tuning the magnetic field to look for the echo, don't do any averaging, but when measuring the echo pulse, average over at least 16, and if the noise is large, 64 or more.

EFFECT ON SPINS OF THE PULSE SEQUENCE

M x H

difference in precession rates is due to:
1) magnet inhomogeneity, 2) spin diffusion (T2)

time= 0

time= 0 + ε

time= τ

Initially the spins are pointing along the magnetic field (into paper)

right after the 90 degree pulse, the spins are all pointing in the same direction and rotating at the Larmor frequency of 10 MHz.. There is a large signal detected.

After some time elapses, the spins have precessed at different rates. The total magnetization (dotted line) is gradually disappearing, and the signal does too. This is the "free induction decay".

time= τ + 2 ε

time= 2 τ

M x H

picture here assumes infinite T2: no spin diffusion

Right after the 180 degree pulse, each spin is reversed (x-> x,y->-y) If a spin has precessed through an angle φ before the 180 pulse, it will now be at
− φ after it. If we wait the same length of time, it will be returned to its original direction

spin diffusion (T2) means that spins do not return to original angle, and the signal is reduced.

2. First measurement: glycerine sample

Begin by understanding why the spin echo occurs. There is a nice description and figure on page 632 of the 1954 article by Carr and Purcell. The different kinds of relaxation: exchange of energy between the spins and the "lattice" characterized by the time T_1, random dephasing of a group of spins in time T_2, and the phase spread due to magnetic field inhomogenity in time T_2^*. To understand these better, you should read the articles by Carr and Purcell, and the 1950 article by Hahn, the inventor of the spin echo technique. T_1 is the time in which the spins are reoriented along the horizontal magnetic field axis. This must occur in

the interval between 90 degree pulses. It is a very short time for glycerine, and a very long time for water. Other samples you will measure lie in between. The physics behind these different relaxation times will be discussed later.

We start with glycerine because it is one of the easiest samples to measure, and has a relatively long T_2. The sample illustrates the power of the spin echo method in being able to measure a long value of T_2 (weak relaxation) in the presence of a short value of T_2^*, due to large magnetic field inhomogenities, which would otherwise dominate the spin diffusion.

Use the TIME and VOLTS cursors on the TeK scope to make accurate measurements of the time delay and and amplitude of the spin echo. Try to peak it up with the fine control on the regulator, and use the AVERAGE feature of the scope to average out fluctuations. (I suggest averaging 16 samples.) The power supply should be warmed up at least $\frac{1}{2}$ hour. Even so, drift can be a problem. The smallest change in the magnet current can reduce the spin echo signal and ruin the measurement. Keep it peaked up. Use both cursors when measuring the amplitude, and put the first one on the baseline to the right of the signal.

Take data from 1 millisecond to over 30 milliseconds delay between the first pulse and the spin echo signal. Plot the log of the signal amplitude, and find the best fit. (See the graphs below, and the discussion after the graphs.) Discuss your results with the instructor before going on to do the rest of the experiment.

The plots below are both $Y=Log_e[volts]$ vs. $X=time = 2\tau$ in milliseconds. The same experimental data is plotted in both graphs.

Linear fit to glycerine data: A t
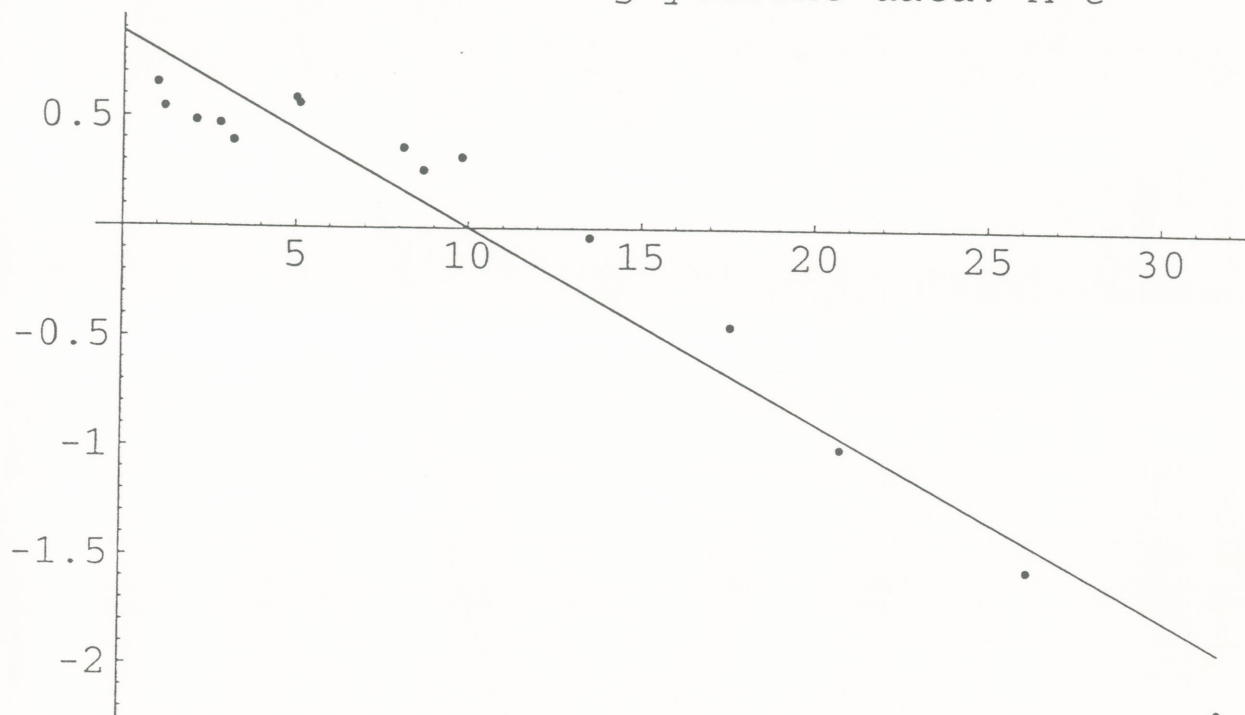
Cubic fit to glycerine data: A t + B t^3
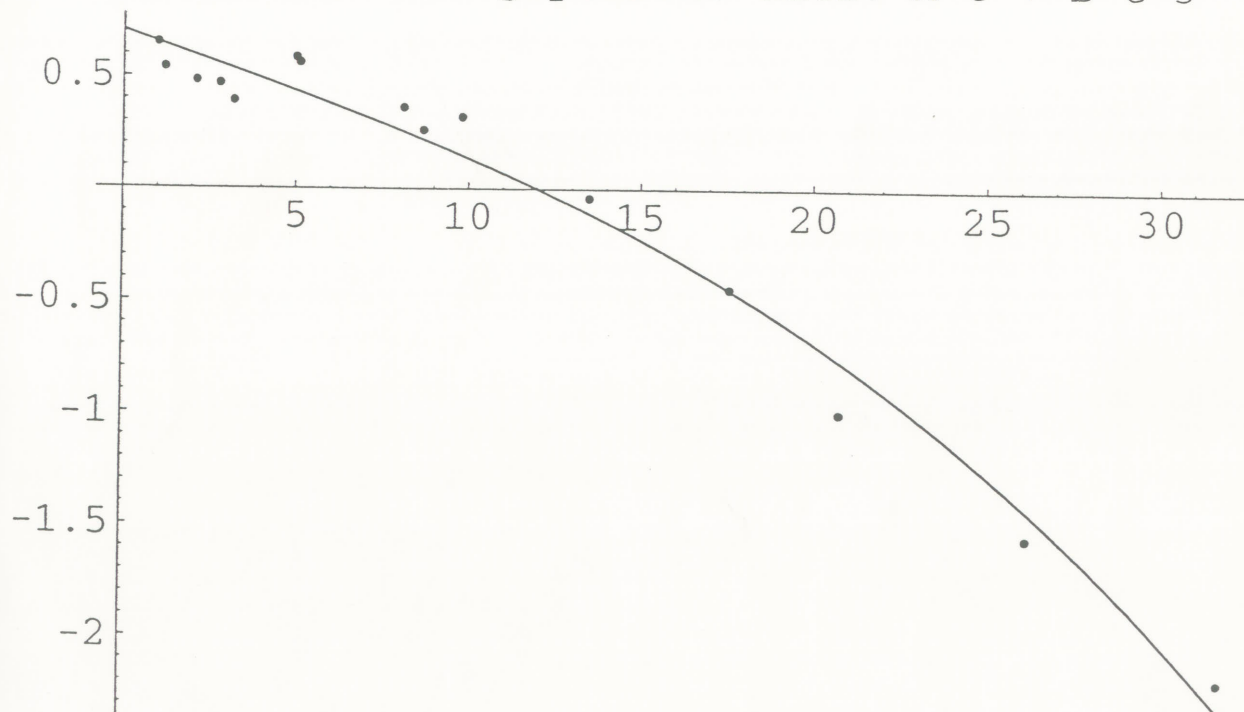
On page 586 of the article by E.L. Hahn, formula (21) gives a theoretical formula for the spin echo. The first term gives the echo at $t = 2\tau$. The key factor is $e^{\left(-\frac{kt^3}{3} - \frac{t}{T_2}\right)}$. The time t is measured from the start of the 90 degree pulse. k takes into account self-diffusion of the molecules. From the gaussian prefactor, $e^{-\frac{(t-2\tau)^2}{2T_2^{*2}}}$, we see that T_2^* is obtained from the width of the spin echo pulse. In this case, we obtained, using the cursors, a full width at half max of 440 μseconds, giving a $T_2^* \approx 190$ μseconds. This is a measure of how (in)homogeneous the magnetic field is over the sample volume.

From linear or cubic fits to the log of the amplitude from the spin echo data, we obtain:

$$T_2 = 18.96 \text{ msec.} \qquad \text{Cubic fit}$$

$$T_2 = 11.33 \text{ msec.} \qquad \text{Linear fit}$$

These are very different! Not including the cubic term for diffusion can cause a significant error in T_2. The fit is better for $Log[amplitude] = At + Bt^3$, with a χ^2 of 1.9 as opposed to fitting $Log[amplitude] = At$, which gives a different value for "A", and a χ^2 of 4.6. (χ^2 is computed by arbitrarily assuming a 10% statistical error, summing the squares of the deviations from the fit, and dividing by the number of degrees of freedom, which, for 15 data points is 13 for the linear fit and 12 for the cubic fit.) Of course, the errors are mainly due to drift, and are thus systematic errors rather than random errors, so χ^2 is only a rough guide to the "goodness of fit".

T_1 for glycerine is too short to measure with this setup. The cubic self-diffusion term is expected to be important in liquids of low viscosity with long spin-spin (T_2) relaxation times.

With very careful measurements, a curious effect is observed for very short time delays t. The echo amplitude decreases slightly to a minimum and then increases a few percent before dropping on the "exponential + cubic exponential" curve as predicted by the Hahn formula. The effect appears to be real, not an artifact of the data taking. The Hahn formula (21) is actually more complicated than a single gaussian envelope centered at $t = 2\tau$. Could this be the cause of the "dip" at small t? See if you can observe and explain this effect, but don't spend too much time on looking for it.

There is a way to avoid the diffusion effect experimentally. That is to make a sequence of 180 degree pulses and thus multiple spin echos. (Carr-Purcell sequence) It can be shown that the envelope of successive echos decays as a pure exponential: $e^{-\frac{t}{T_2}}$ without the complicating diffusion term. This kind of measurement is possible in the computer-controlled NMR experiment, G7b, but cannot be done here.

3. Relaxation times for a water sample

You will need to find a pure water sample to get a good handle on the relaxation times. Since T_1 in water is on the order of seconds rather than milliseconds, a rep rate for the pulses of 10 Hz is too fast for the spins to reorient along the dc field. You will have to use a rep rate (26G1) of .1 times 1 Hz or something similiar. Only a crude measurement of T_1 is possible with this apparatus.

For low viscosity liquids, it is true that $T_1 = T_2$. You can therefore expect T_2 to be a time on the order of several seconds. If you find a much shorter time, your "pure" water may be contaminated with a small amount of paramagnetic ions. Try getting some water which is "low conductivity" water. Some of the labs in the basement of Clark have this. Or we can get some from the Chem stockroom. You could also try some "deionized" water and check it out.

4. Paramagnetic ions: effect on T_2

Ions of this type have large local magnetic fields. Since the ions are not oriented in any particular direction, there is no average field from them felt by the protons in the water, but the fluctuations in the field cause the proton spin to randomly be reoriented, thus destroying any phase coherence between the spins on a time scale determined by the concentration of the ions in the solution.

Check this out by measuring T_2 for a range of concentrations varying from 10^{17} ions/cc to 10^{21} ions/cc. Plot the log of T_2 vs. the log of the concentration to find out if the dephasing rate ($\frac{1}{T_2}$) is really proportional to the concentration of the ions.

On the average, how far is a proton in the water from an ion in terms of the concentration?

One more thing to check quickly: do 10^{17} copper ions/cc have the same effect on the spin-spin relaxation (T_2) as the same concentration of iron ions/cc? Just compare one sample of each for T_2.

Paul Hartman's Original Preliminary Notes On G7a

These remarks give some of the flavor of Prof. Hartman's style. He developed many of the experiments in the P410-510 Lab over the years, including this one. Some of his specific instructions refer to obsolete apparatus, so should not be taken literally.

This is a very pretty experiment, the understanding of which involves as much or more physics than the simpler NMR experiment G7. It is particularly useful for the determination of the transverse relaxation time T_2. The electronics is considerably more complicated than in the marginal oscillator experiment.

The idea is described in the xeroxed literature of Hahn, the protons are polarized with an excess in one direction of the DC magnetic field, along the z-axis. A short RF pulse is applied to the sample, as in the usual NMR experiment except this is of amplitude and duration long enough only to wind the precessing excess spins down into the x-y plane: the so called 90° pulse. And there they precess in free induction decay, the decay coming about mostly because of the poor magnetic field uniformity— the reason one doesn't determine the true T_2 in the other experiments on NMR we have. Because of the non-uniformity they get out of step and soon interfere so no signal is observed. Still they remember the phase with which they started out. After some time, another pulse flips the whole plane of spins over through 180° . Spins precessing fast are now <u>behind</u> spins precessing slowly. At a time later, equal to the time between the two pulses, the spins all coalesce to give a nice big signal—the echo. This could be repeated in suitable apparatus until the true T_2 has destroyed the phase memories. Purcell and Carr report many echoes; diffusion also enters into the decay. If Brownian motion carries protons from one point to another, the phase memory is lost. In the ideal situation the protons sit at the point at which their phase relationship to all the others was established at time t=0.

So the apparatus should have a variable time between the two pulses, it should be able to separately adjust the duration of the first pulse and the second pulse, and it might be nice if the repetition rate of the whole occurence could be varied. These functions our apparatus attempts to do; the repetition rate and the pulse separation seem to behave OK. The two pulse shapes are not particularly pretty and square topped—at least as viewed through the received RF signal. At the output of the transmitter they seem quite good. However, the duration of the first pulse is not entirely independent of that of the second pulse, particularly as the duration of the latter approaches the red region of its adjustment dial. In general, stay out of the red regions on the adjustment dials. For the RATE dial, this means only when the upper switch is on F(for fast). The whole range is OK when this switch is on S(ffor slow—and it can be made very slow—like ten seconds between repeats). Things go amok when the dials are extended into the red regions or when the power supply voltage exceeds 12 volts, so don't exceed these dial settings.

Now to the apparatus. <u>DO NOT DIDDLE WITH THE SCREW ADJUSTMENTS ON ANYTHING.</u> And: <u>DO NOT SWITCH CABLES AROUND.</u> The tuning is critical and has been done, at what cost in patience you will never know. Nick spent one very long time on the thing. With that admonition, the small

power supply can be turned on, with the voltage dial setting put at the 12v mark. For starters, set the RATE at about 50 with the upper switch set on F(for fast), set $R\tau$ at about 30 (this puts the pulse separation such that the echo will appear on the scope set on .5 ms(that's millisecond) per division; set Rt_1 on about 15; and set Rt_2 on about 20. With the current control on the magnet supply at zero, bring the Variac control up to a current reading of about an ampere. Bring up the current control until the regulator RANGE needle is within its limits and slowly adjust the current control knob. The needle should stay within llimits and resonance found at about a current of about 1.6 plus amperes(withour magnet gap and oscillator frequency of about 10.7 mc). At the resonant condition, a free induction decay will be seen trailing the first pulse, and probably the second. <u>Slowly</u> scanning the current through the region will see the tail lessen(it really should almost disappear if things were as they should be by the books) and the echo will as far beyond the second pulse as the second is beyond the first. Its amplitude jumps around more than would be nice, this may be magnetic field fluctuations. The echo is very sensitive in height to the field, as can be seen in the field control. Once the echo is found—not too difficult—then one can play with the various times. The effect of τ is clear: the echo decreases as this time increases; all according to Hoyle. For a viscous fluid(little Brownian diffusion effect on T_2) it should go down exponentially. For our water, it is presumably more like the time inverse cube, if we understand Carr and Purcell correctly. It will be noticed we hope that the echo is maximized by making the free induction signal after the second pulse more or less a minimum. If the free decay is gone from the first pulse when we put on the second one and the latter really flips the x-y plane effectively over(about H_1 in the rotating scheme of things) then there should also be no free decay after the second pulse—UNLESS, things have relaxed some by T_1. If they have, then some free induction signal will appear following the second pulse, even with the 180° flip (and maximum consequent echo). Carr and Purcell show how T_1 can be obtained by the growth in the free induction signal after the second pulse as it is moved out and away from the first.

In principle if the first pulse is too large or in our case too long, the excess spins will be turned through more than 90° , say to 180° , and the free decay so go away. It does diminish after a maximum but it doesn't go to zero before things go haywire in the red region of the dial setting. Likewise, given the spins put in the x-y plane, if the second pulse is not 180° , the echo will not be maximum, and a free decay is observed(not sure why).

The effect of a small inhomogeneity in the field is striking. A small iron wire on one pole sharpens up the echo markedly. The free decays also sharpen. The field is now so inhomogeneous that the phases get rapidly out of step and as sharply fall back through the original phased array in the echo and then out again.

One can presumably determine the proton moment with this set up as with the other more usual. We can measure the RF frequency(the radio receiver responds to it—and also greatly disturbs the scope display) and we could determine the magnetic field in the usual way. Because things are rather clamped up in this set up, we probably won't go through that exercise.

Finally(?), in closing things down, simply switch OFF the small 12v power supply and <u>TURN DOWN</u> the controls on the magnetic supply before switching it off (transients from the large L di/dt in the magnet may cream the silicon controlled rectifier otherwise: this is advisable practice in the use of any large electromagnet driven by any type of supply). And turn off the oscilloscope.

OK; let's try it.