# Spin Echo Nuclear Magnetic Resonance

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This experiment was performed in collaboration with Daniel Martin

**Abstract**

The phenomenon of spin echo was observed from a sample of glycerine, which was presumed as being pure, using the continuous wave method. The effect of different concentrations of water in glycerine upon the spin-spin and spin-lattice relaxation times was observed. Finally, these relaxation times were observed for a solution containing paramagnetic ions and a separate solution containing Flutex; a fluorine based chemical.

The spin – spin relaxation time for a sample of pure glycerine was found to be $8.07 \pm 1.06$ ms and the spin – lattice relaxation time was found to be $26.11 \pm 4.79$ ms. It was found that both the spin-spin and spin-lattice relaxation times increased with concentration of water. Also it was observed that increasing the concentration of paramagnetic ions reduced the amplitude of the spin echo acquired and so decreased the associated relaxation times. Finally it was found that Flutex gave similar results as for glycerine.

## 1. Introduction

Nuclear Magnetic Resonance techniques provide an efficient and reliable method of identifying unknown substances. The phenomenon of spin echo is a particularly well used technique – it is currently used throughout industry and medical services across the world to identify unknown samples. The best example of this is the use of spin echo technology in Magnetic Resonance Imaging in hospitals, which provides detailed information through a non-invasive scan.

As its name suggests, a spin echo experiment is concerned with the intrinsic spin angular momentum[1] of the particles under inspection. These spins are forced into a particular alignment via a particular series of magnetic field pulses, after which the behaviour of the spins can be monitored and compared to previous observations, thereby allowing the substance to be identified.

Two different methods were used during this experiment. Both methods involved the use of similar equipment; the main difference was the series of magnetic field pulses that was used.

This first method was a series of two pulses. Using this method, the sample is placed in a strong, almost homogeneous, fixed magnetic field. This fixed field had the affect of aligning the spins in the same direction as the magnetic field.

A radio frequency primary magnetic pulse was then used to displace the spins by $\frac{\pi}{2}$ radians. The spins were then able to precess in a somewhat similar fashion to a common gyroscope in the plane which is perpendicular to the fixed magnetic field.

However, inhomogenities in the fixed magnetic field cause the spins to become misaligned during this precession (as individual spins precess at different rates). This collection of coplanar spins is sometimes referred to as the 'pancake' for obvious reasons.

A secondary magnetic pulse rotates the spins by $\pi$ radians, the effect of which is to force precession in the opposite sense to previously; thereby allowing the spins to coalesce and almost realign. It is this realignment which is detected as being the spin echo and it is the average time taken for the spins to realign with the fixed magnetic field that is known as the spin – spin relaxation time, $T_2$.

The second method used was to use two secondary magnetic pulses to 'flip' the plane of the spins by $\frac{\pi}{2}$ radians twice, this causes the spins of the protons to cyclically misalign and coalesce. This method was used to measure the spin – lattice relaxation time, $T_1$.

## 2. Theory[2]

For a nucleus with intrinsic spin quantum number $I$ and gyromagnetic ratio $\gamma$, the magnetic moment, $\bar{\mu}$, is:

$$\bar{\mu} = \gamma \hbar \bar{I} \qquad [1]$$

If a nucleus is subject to a magnetic field, $\bar{B}_0$, at some angle, $\theta$, to the magnetic moment, then the magnetic moment will precess about the magnetic field.

The torque that the nucleus is subject to will be equal to the rate of change of the angular momentum:

$$d_t\left(\hbar \bar{I}\right) = \bar{\mu} \times \bar{B}_0 \qquad [2]$$

Substitution of Equation 1 into Equation 2 yields:

$$d_t\left(\bar{\mu}\right) = \gamma \bar{\mu} \times \bar{B}_0 \equiv \bar{\mu} \times \gamma \bar{B}_0 . \qquad [3]$$

If the magnetic moment vector, $\bar{\mu}$, is rotated at an angular velocity and direction are denoted by $\bar{\omega}_0$ then the rate of change of the magnetic moment is given by:

$$d_t\left(\bar{\mu}\right) = \bar{\omega}_0 \times \bar{\mu} . \qquad [4]$$

Comparing equations 3 and 4 gives:

$$\bar{\omega}_0 = -\gamma \bar{B}_0 \qquad [5]$$

This angular frequency is of specific interest and is called the Larmour frequency.

If the previously discussed magnetic field pulse, of amplitude $B_1$, is rotated in the $z - x$ plane is rotated about the $z$ axis, at an angular frequency denoted by $\omega$, then a resonant condition will occur at the Larmour frequency, i.e. when $\bar{\omega} = \bar{\omega}_0$. The effect of such interactions will be to increase the angle between the magnetic moment, $\bar{\mu}$, and the fixed magnetic field, $\bar{B}_0$.

By moving into a rotating reference frame where the $x' - y'$ plane is coplanar to the $x - y$ plane and rotates about $z$ at angular frequency $\bar{\omega}$, the magnetic field pulse, $\bar{B}_1$, may be aligned along the $x'$ axis in this rotating frame.

If $\bar{B}_1 = \bar{0}$, then the coordinate transformation links the time variation of $\bar{\mu}$ and $\bar{\mu}'$ in their respective reference frames by:

$$d_t \bar{\mu} = \partial_t\left(\bar{\mu}'\right) + \bar{\omega} \times \bar{\mu} = \gamma \bar{\mu} \times \bar{B}_0 . \qquad [6]$$

Rearranging equation 7 gives

$$\partial_t(\overline{\mu}') = \gamma\overline{\mu}\times\overline{B}_0 - \overline{\varpi}\times\overline{\mu} \equiv \gamma\overline{\mu}\times\left(\overline{B}_0 + \frac{\overline{\varpi}}{\gamma}\right) \qquad [7]$$

This indicates that $\overline{\mu}'$ precesses around a magnetic field, $\overline{b}$, in the $\overline{z}'$ direction where;

$$\overline{b} = \overline{B}_0 + \frac{\overline{\varpi}}{\gamma} \qquad [8]$$

If $\overline{\varpi} = -\gamma\overline{B}_0$, then $\overline{\mu}'$ is stationary in this frame, which is now rotating at the Larmour frequency. If $\overline{B}_1 \neq 0$, but is still rotating about the $z'$ axis and is rotating at $\varpi$ such that $\overline{B}_1$ lies along the $x'$ axis, then the total effective field in this frame is

$$\overline{b}_{\text{eff}} = \overline{B}_0 + \frac{\overline{\varpi}}{\gamma} + \overline{B}_1 \qquad [9]$$

The interaction $\overline{\mu}'\times\overline{b}_{\text{eff}}$ causes $\overline{\mu}'$ to precess about $\overline{b}_{\text{eff}}$.

If an ensemble of spins is subjected to these conditions then a net magnetisation per unit volume, $\overline{M}$, is obtained. In the absence of $\overline{B}_1$, this net magnetisation per unit volume will be aligned with $\overline{B}_0$ in the $\overline{z}'$ direction. The effect of $\overline{B}_1$ is to force the net magnetisation per unit volume in the rotating reference frame, $\overline{M}'$, where it will trace out a cone. At the Larmour frequency $(\overline{\varpi} = \overline{\varpi}_0 = -\gamma\overline{B}_0)$, the net magnetisation in the rotating frame, $\overline{M}'$, will trace out a flat disc in the $z'-y'$ plane. If the spins precess at different rates then this vector rotating to trace out a flat disc will ‘spread out’ to form a pancake as discussed earlier.

## 3. Experimental Procedure

Initially the continuous wave method[2] was used to identify the optimum magnetic field strength. Theoretical calculation gave this value to be $0.423T$ rotating at a Larmour frequency of $18.00MHz$.

Once the required magnetic field strength had been established, the required primary and secondary pulse duration times were investigated. This was done by observing the variation of the magnitude of the echo produced as the primary pulse duration was varied for a fixed value of the secondary pulse. This process was then repeated whilst varying the secondary pulse duration for the previously found optimum value of the primary pulse duration.

After these parameters had been acquired, the spin – spin relaxation time of distilled water was measured. This was done by measuring the exponential decay of the spin echo amplitude, $H$, as the delay between the primary and secondary pulses, $d$, varied (see Figure 1 for an example of such a plot). For completeness this process was repeated to obtain concurrent results. It can be shown[2] that the exponent of this exponential decay can be used to find the spin – spin relaxation time;

$$H = A\exp(Bd) \qquad B = \frac{-2}{T_2} \qquad \Rightarrow T_2 = \frac{-2}{B} \qquad [10]$$

Using the standard methods[3], the error associated with the spin-spin relaxation time can easily be found;

$$\sigma_{T_2} = \frac{\sigma_B T_2}{B} \qquad [11]$$

Finally, the spin – lattice relaxation time was found by using a primary pulse and two secondary pulses. To find this relaxation time, the amplitude of the spin echo, $H$, was observed as the delay between the secondary pulses, $D$, varied. It was found that the spin echo decayed exponentially as the delay between the secondary pulses increased, and by using the same methods as for the spin-spin relaxation time;

$$H = C\exp(De) \qquad D = \frac{-2}{T_1} \qquad \Rightarrow T_1 = \frac{-2}{D} \qquad \sigma_{T_1} = \frac{\sigma_D T_1}{D} \qquad [12]$$

Both of these methods were used for a variety of different concentrations of water in glycerine, paramagnetic ions in water and Flutex in water.

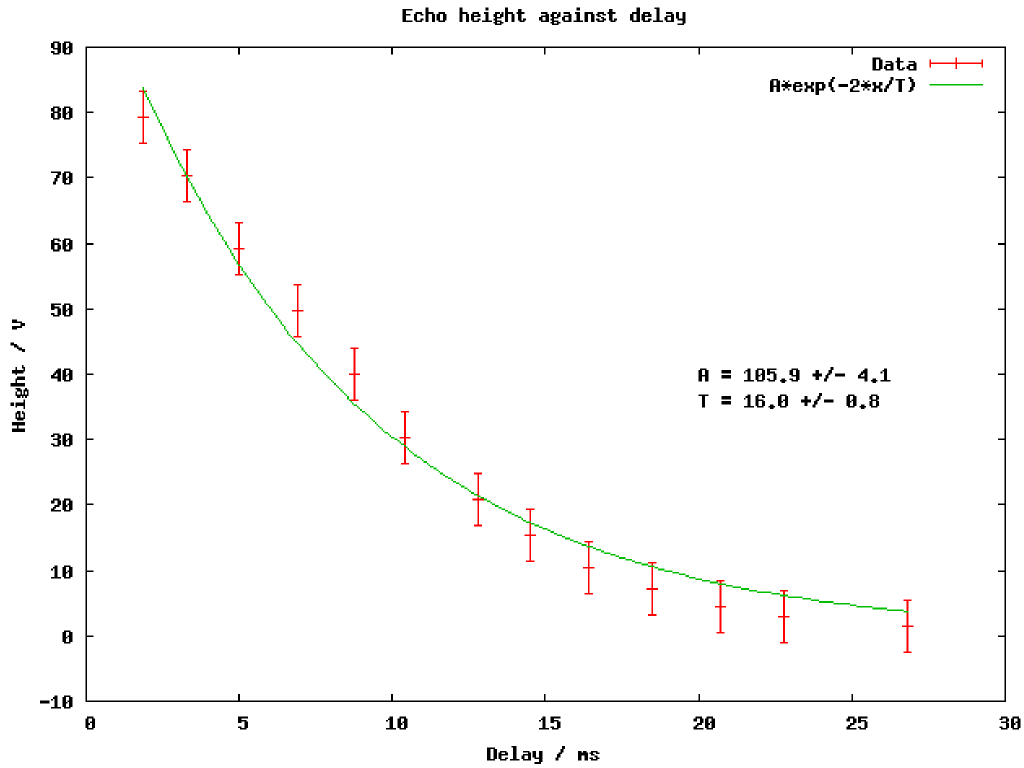


Figure 1: Variation of amplitude of spin echo with delay between primary and secondary pulses (for a mixture of 20% water in 80% glycerine)

## 4. Results

Using the methods described above and the standard methods for combining measurements[3], the spin-spin relaxation time for pure glycerine was found to be $8.07 \pm 1.06\ \text{ms}$ and the spin – lattice relaxation time was found to be $26.11 \pm 4.79\ \text{ms}$.

Figure 2 displays the measured variation of the spin – spin relaxation time with the concentration of water in glycerine. The data is not sufficient to provide a meaningful fit, however it is observed that the relaxation time increases as the concentration of water present in the mixture increases.

In a similar fashion Figure 3 displays the variation of the spin – lattice relaxation time with the concentration of water. Again, this data is not sufficient to provide a reliable fit, however it is observed that the spin – lattice relaxation time also increases with concentration of water.

The presence of paramagnetic ions was observed to reduce the amplitude of the spin echo when compared to that of pure distilled water. To make these observations Ferric Nitrate dissolved in distilled water was used.

Finally, a sample of 10% Flutex in distilled water was compared to pure distilled water. It was found that the fluorine containing solution gave a greatly reduced amplitude of spin echo and also that this echo was produced at a slightly different magnetic field strength.

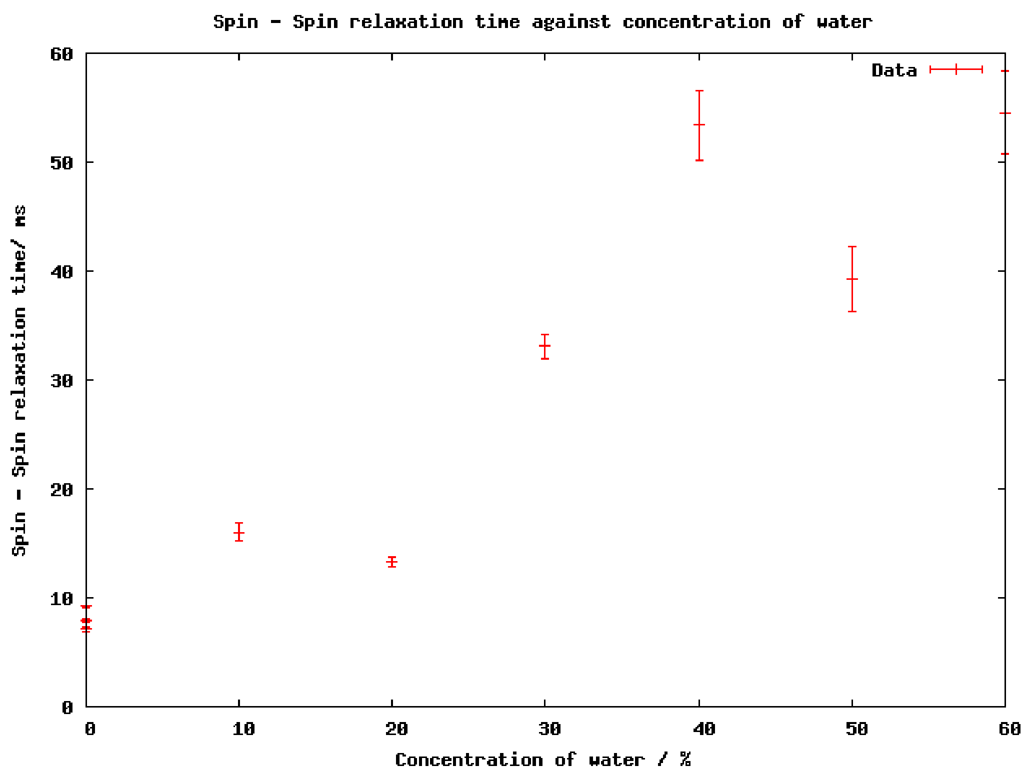


Figure 2: Variation of Spin – Spin Relaxation time with concentration of water in glycerine sample

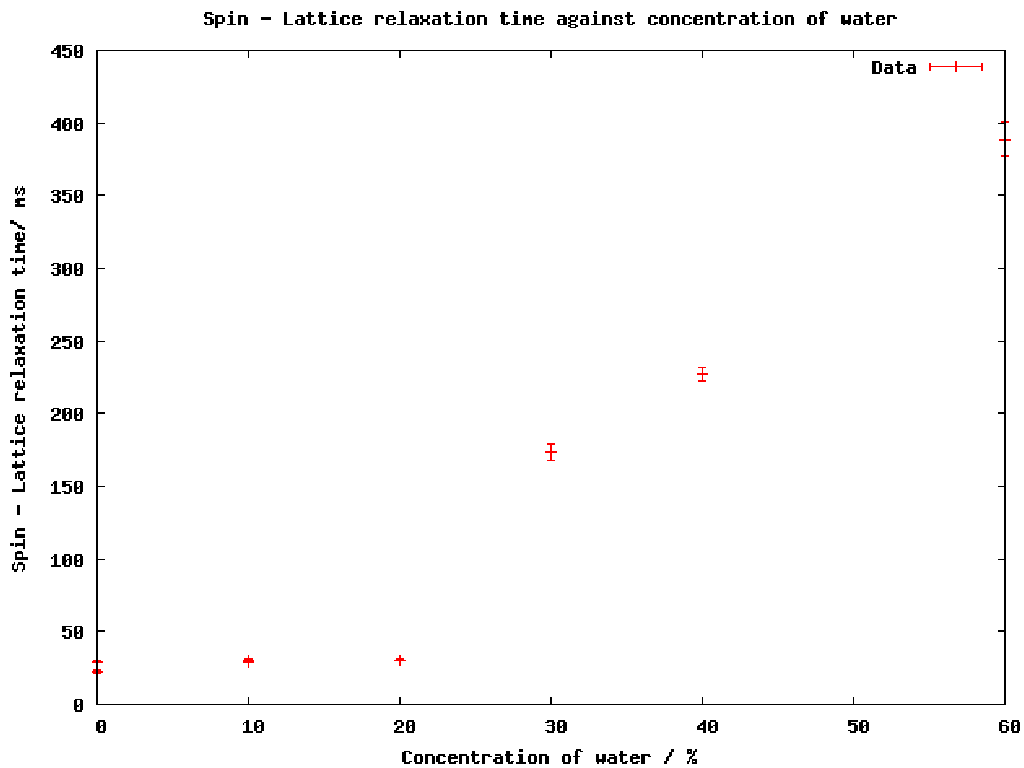


Figure 3: Variation of Spin – Lattice Relaxation time with concentration of water in glycerine sample

## 5. Discussion

This experiment proved very difficult to provide meaningful results; this is highlighted by the fact that a fit of the final data is not worthwhile. The reasons for this lie within the nature of the experiment.

Research[4] showed that that both the spin-spin and spin-lattice relaxation times varied drastically as temperature varied. A solution to this problem would be to perform the experiment under more controlled temperatures, perhaps by placing the experiment in a heat bath of some description; however the obvious logistical problems of this would have to be overcome.

The second issue which caused particular difficulties was caused by changes in the magnetic field. Once the spin echo of a sample had been acquired, one would expect the echo to remain unchanged throughout the course of the day. However, it became apparent that this was not the case. As part of the procedure, the relaxation times of samples were measured more than once. It was found that particularly in the first few hours of the experiment being turned on, the values obtained varied dramatically. It is believed that the cause of this lies with heating the electrical apparatus. It is known that the current (and therefore the magnetic field produced) that flows through a wire depends upon temperature and so, when one considers that an electromagnet was used to produce both our fixed and oscillating field, this would explain the 'drifting' spin echo. To rectify this issue, a permanent magnet could be used to produce the fixed field.

Alternatively, a Carr-Purcell Sequence could be used instead of the method previously detailed. This method would be similar to the method used to measure the spin – lattice relaxation time, however instead of just one secondary pulse, many are used. The effect of this is to continuously 'flip the pancake', which gives a series of decreasing echoes which can be measured within minutes. Therefore, this method would limit the issue of drift affecting an individual measurement.

A third issue was that of interference. In the vicinity of this experiment, there were a number of other magnetic resonance experiments operating. Some of these were performing the same experiment as detailed in this report and so occasionally two experiments would operate at the same frequency which would be observed in the measurements taken. There are a number of ways to resolve this issue, the simplest of which is to make a conscious effort to avoid the frequency at which other experiments are using. A more complex method of resolving this would be to shield the experiment from electromagnetic radiation with an appropriate metal 'cage'.

The affect of a magnetic field upon paramagnetic ions is to create a net excess of electrons with their spins parallel to the field (as this is energetically favourable). The result of this is a slightly reduced effective magnetic field acting upon the protons of the sample and so produce a reduced amplitude of spin echo. This is in accordance with our observations.

As previously shown in the theoretical explanation, the calculation of the relaxation times is dependant upon the gyromagnetic ratio, $\gamma$. This ratio is similar for protons within hydrogen $\left(\mu\left(H^{1}\right)=0.235\right)$ as for protons within Flutex $\left(\mu\left(F^{19}\right)=0.249\right)$ and so the observed spin echoes produced are quite similar in nature.

The purity of the samples used would obviously affect all of the results acquired, and so further investigation into the purity of the samples used could be undertaken to ensure the most reliable results possible.

## 6. Summary

The phenomenon of nuclear magnetic resonance spin echo was observed, relaxation times were found for a variety of concentrations of water in glycerine, the affect of paramagnetic ions and fluorine was observed. This experiment proved difficult to understand and to obtain reliable results for, however it also proved interesting and provided an insight into a practical branch of physics which has proved invaluable many times over.

## 7. References


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Word Count; 1986 words (excluding subheadings, captions and references).