

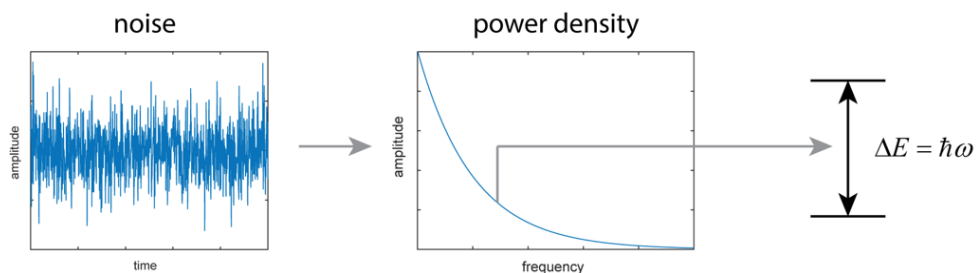
CHEM6154 - Week 20 - Lecture 2: Spin echoes and relaxation

P.J. Hore, "NMR: The Toolkit", 1st edition - Chapter 1.

J. Keeler, "Understanding NMR Spectroscopy" - Chapter 4.

1. Physical origins of the relaxation process in spin ensembles

The primary reason why spin relaxation happens is the presence of noise in the system. The noise can have a variety of origins (random molecular rotation, crystal lattice vibration, conformational flexibility, and so on). The important factor is that some frequencies in this noise would match the transition frequencies between the energy levels.



Because the noise experienced by different molecules is different, this would gradually drive the average values of the observables to their thermal equilibrium values.

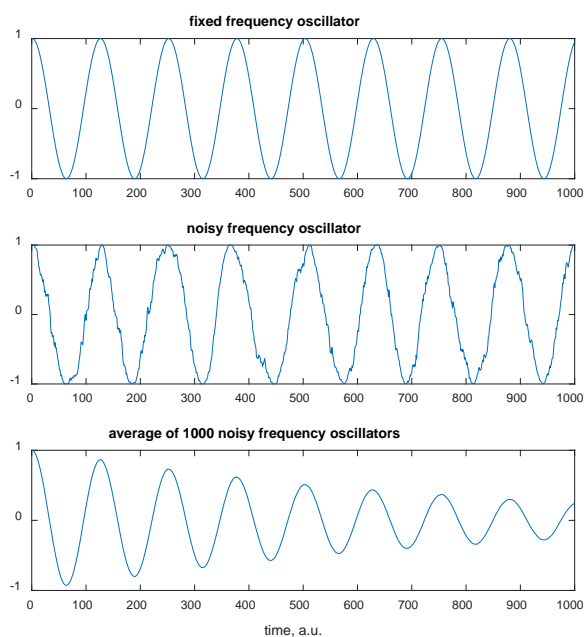


Figure 1. An illustration of the fact that spin ensemble relaxation proceeds from the noise in the interaction parameters. The top trace is the coordinate of a fixed frequency oscillator. The middle trace is the coordinate of an oscillator that has a randomly varying component in its frequency. The bottom trace is the average of coordinates of 1000 oscillators, each with its own random component in the frequency.

In solution state NMR spectroscopy, relaxation is caused by the random rotational motion of the molecules, called *rotational diffusion*. Many interactions (dipolar, chemical shift, etc.) are anisotropic, and rotation makes the corresponding frequencies noisy. The result, illustrated in Figure 1 above, is the slow decay of the magnetisation to the thermodynamic equilibrium.

Longitudinal and transverse relaxation times

Magnetisation in the NMR sample decays at different rates in the direction parallel and perpendicular to the applied magnetic field. The characteristic time for longitudinal relaxation is historically called T_1 , the transverse relaxation time is called T_2 . In the absence of precession, the following equations approximately describe the relaxation process:

$$\begin{cases} \frac{d}{dt} M_x(t) = -\frac{1}{T_2} M_x(t) \\ \frac{d}{dt} M_y(t) = -\frac{1}{T_2} M_y(t) \\ \frac{d}{dt} M_z(t) = -\frac{1}{T_1} [M_z(t) - M_{eq}] \end{cases} \Rightarrow \begin{cases} M_x(t) = M_x(0) \exp(-t/T_2) \\ M_y(t) = M_y(0) \exp(-t/T_2) \\ M_z(t) = M_{eq} + (M_z(0) - M_{eq}) \exp(-t/T_1) \end{cases} \quad (1)$$

where M_0 is the equilibrium longitudinal magnetisation. Precession is described by Bloch equations:

$$\begin{cases} \frac{d}{dt} M_x(t) = -\omega M_y(t) \\ \frac{d}{dt} M_y(t) = +\omega M_x(t) \\ \frac{d}{dt} M_z(t) = 0 \end{cases} \Rightarrow \begin{cases} M_x(t) = M_{\perp} \cos(\omega_0 t + \varphi) \\ M_y(t) = M_{\perp} \sin(\omega_0 t + \varphi) \\ M_z(t) = M_{\parallel} \end{cases} \quad (2)$$

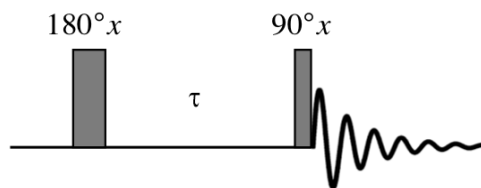
The two sets of equations may be combined to yield:

$$\begin{cases} \frac{d}{dt} M_x(t) = -\omega M_y(t) - \frac{1}{T_2} M_x(t) \\ \frac{d}{dt} M_y(t) = +\omega M_x(t) - \frac{1}{T_2} M_y(t) \\ \frac{d}{dt} M_z(t) = -\frac{1}{T_1} (M_z - M_{eq}) \end{cases} \Rightarrow \begin{cases} M_x(t) = M_{\perp} \cos(\omega_0 t + \varphi) \exp(-t/T_2) \\ M_y(t) = M_{\perp} \sin(\omega_0 t + \varphi) \exp(-t/T_2) \\ M_z(t) = M_{eq} + (M_{\parallel} - M_{eq}) \exp(-t/T_1) \end{cases} \quad (3)$$

The solutions to these equations are an exponentially decaying oscillation in the transverse plane and an exponential process returning the magnetization to its thermal equilibrium value on the Z axis.

Measuring T_1 time: inversion-recovery and saturation-recovery experiments

An inversion-recovery experiment consists of a 180-degree pulse, an evolution period, and a 90-degree pulse followed by signal acquisition:



The solution of the last equation in the system (4) for the case when $M_z(0) = -M_{eq}$ is:

$$M_z(t) = M_{eq} (1 - 2e^{-t/T_1}) \quad (4)$$

In practice this equation is fitted to the experimental data using the least squares method. An examples of simulated inversion-recovery relaxation curve is shown in Figure 2.

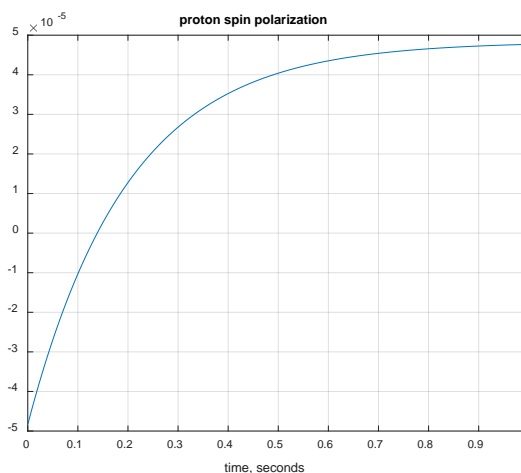


Figure 2. A simulated inversion-recovery experiment for an ensemble of protons in a 600 MHz magnet at 298 K with the longitudinal relaxation time of 0.2 seconds.

Another experiment that may be used to measure T_1 time is saturation-recovery. The difference is that the inversion pulse is replaced by a long blast of strong radiofrequency irradiation that destroys the magnetisation. The recovery begins from zero:

$$M_z(t) = M_{eq} (1 - e^{-t/T_1}) \quad (5)$$

An example is shown in Figure 3.

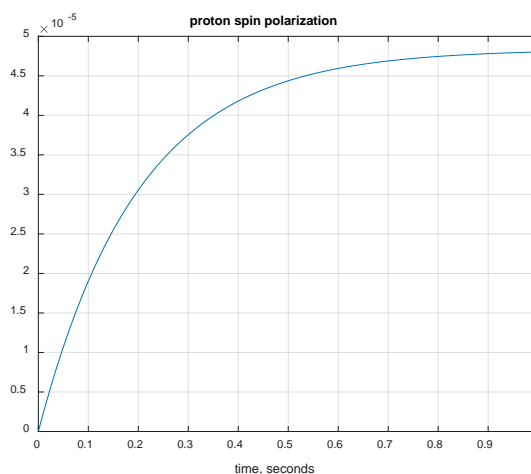


Figure 3. A simulated saturation-recovery experiment for an ensemble of protons in a 600 MHz magnet at 298 K with the longitudinal relaxation time of 0.2 seconds.

Longitudinal relaxation times are used in structural biology research, where the extent of local mobility of protein backbone atoms may be estimated from their relaxation parameters.

Measuring T_2 time: CPMG pulse sequence

The complication in the case of transverse relaxation is the presence of spin precession. The spins can have different precession frequencies for a variety of reasons:

- (a) different chemical shifts for different nuclei of the same molecule;
- (b) low quality magnet or an imaging system where the primary magnetic field is different at different points of the sample;
- (c) a heterogeneous sample where the parameters of the spin system, including the precession frequency are different in different parts;
- (d) presence of external interactions that influence different spins differently.

The magnetisation would not only relax, but also dephase as a function of time (Figure 4).

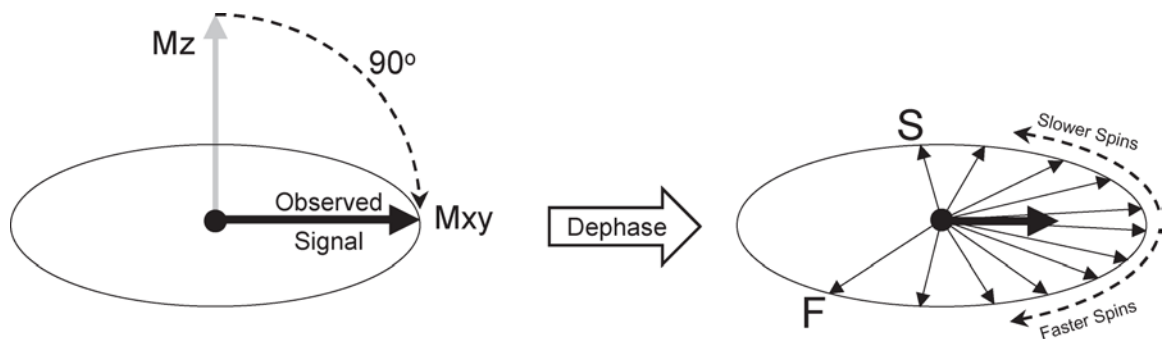


Figure 4. A schematic illustration of the dephasing process. When different spins precess at different frequencies, they would eventually spread out in the XY plane. The average magnetisation would be reduced to zero.

This complicates the measurement of the transverse relaxation time because the dephasing process is not actually relaxation. However, dephasing may be reversed by applying a 180° pulse (Figure 5).

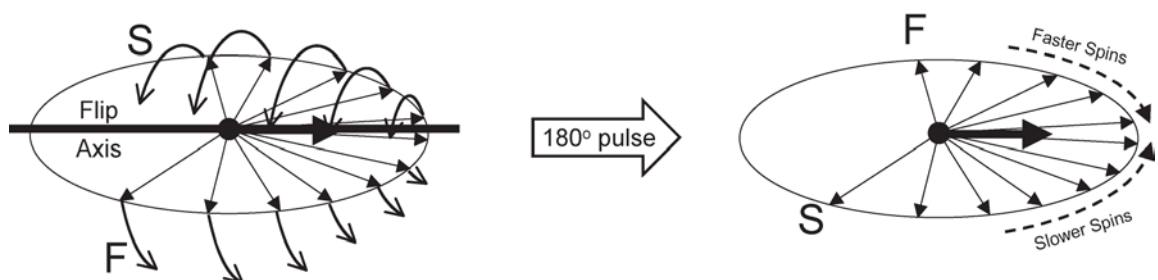


Figure 5. The effect of the 180° pulse on the position of the magnetisation vectors in the transverse plane. The vectors that were ahead are now behind, and the vectors that were behind are now ahead.

As Figure 5 illustrates, after the 180° pulse, the faster vectors are put behind the slower ones. If the spins are allowed to evolve for an identical period of time, the magnetization vectors would re-collect into a tight group (Figure 6). This process is called refocusing. It causes the observable magnetisation to reappear. The whole phenomenon of the magnetisation first disappearing and then reappearing after a 180°

pulse is called spin echo. Situations like this are very common, and the spin echo technique for re-collecting the lost magnetisation is therefore very popular.

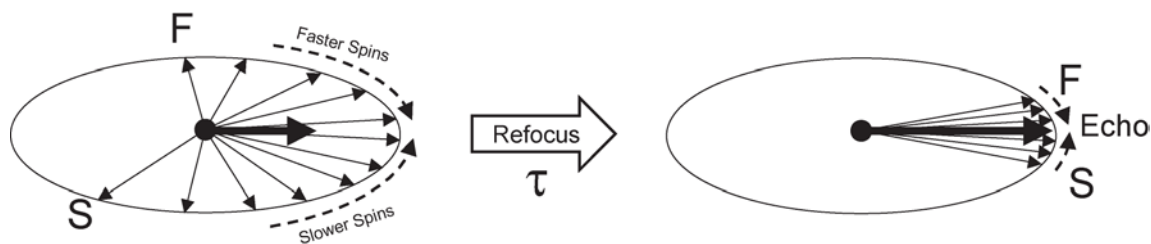
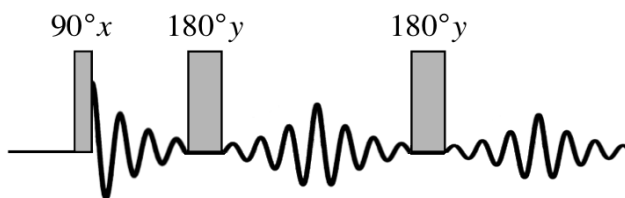


Figure 6. An illustration of the refocusing process that happens after the 180° pulse in the spin echo experiment.

To prevent dephasing from interfering with transverse relaxation measurements, T_2 times are measured using a series of echo trains, proposed by Carr, Purcell, Meiboom and Gill (hence the abbreviation):



At the peak of each echo, coherent interactions are refocused, and only the genuine spin relaxation remains. The intensities of the echo peaks are then plotted against time and an exponential function

$$M_{\perp}(t) = M_{\text{eq}} e^{-t/T_2} \quad (6)$$

is fitted to that data. A simulated example of a CPMG echo train is shown in Figure 7.

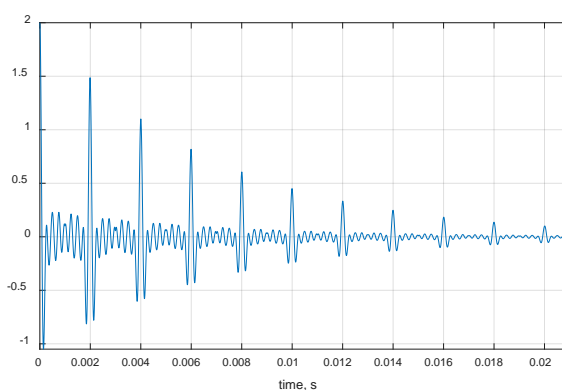


Figure 7. A simulated CPMG echo train for a powder sample of a two-spin system with anisotropic chemical shifts and a transverse relaxation time of 1/150 seconds. The inversion pulses are placed 2 ms apart.