

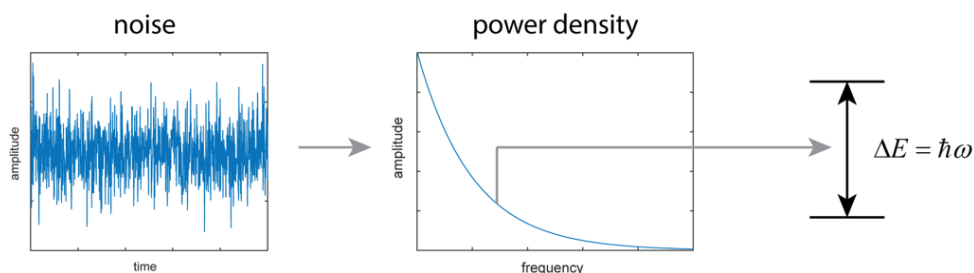
Lecture 07: Spin echoes and relaxation

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

Relaxation is the gradual return of the spin system to thermal equilibrium. It happens because the system is not isolated – it interacts with the environment. In liquid state magnetic resonance, the primary environmental process that leads to spin relaxation is Brownian motion of molecules, both translational and rotational. It introduces noise into the Hamiltonian; some frequencies in that noise match transition frequencies between system energy levels and cause random transitions to occur.



Because the noise experienced by different molecules is different, and the environment has a temperature, this gradually drives the average values of the observables to their thermal equilibrium values.

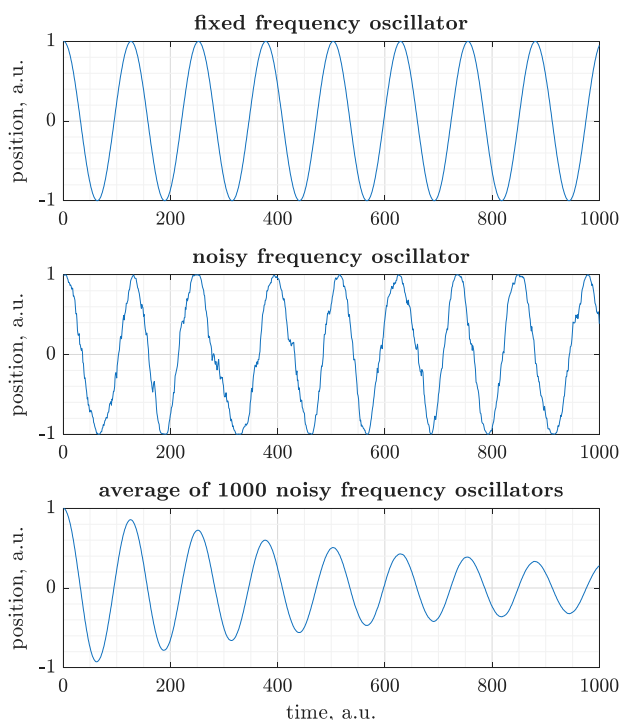


Figure 1. An illustration of the fact that spin ensemble dephasing proceeds from the noise in the interaction parameters. The top trace is the coordinate of a fixed frequency oscillator. The middle trace is the coordinate of an oscillator that has a randomly varying component in its frequency. The bottom 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 primarily 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.

2. Longitudinal and transverse relaxation times

In strong magnetic fields, the magnetisation of the NMR sample decays at different rates in the direction parallel and perpendicular to the field. The characteristic time for longitudinal relaxation is historically called *spin-lattice relaxation time* T_1 , the characteristic time of transverse relaxation is called *spin-spin relaxation time* T_2 . In the absence of spin precession, the following empirical equations approximately describe the relaxation process:

$$\begin{cases} \frac{d}{dt}\mu_x = -\frac{1}{T_2}\mu_x \\ \frac{d}{dt}\mu_y = -\frac{1}{T_2}\mu_y \\ \frac{d}{dt}\mu_z = -\frac{1}{T_1}[\mu_z - \mu_{eq}] \end{cases} \Rightarrow \begin{cases} \mu_x(t) = \mu_x(0)\exp(-t/T_2) \\ \mu_y(t) = \mu_y(0)\exp(-t/T_2) \\ \mu_z(t) = \mu_{eq} + (\mu_z(0) - \mu_{eq})\exp(-t/T_1) \end{cases} \quad (1)$$

where μ_{eq} is the equilibrium longitudinal magnetisation. Within the classical physics framework, spin precession is described by the equations that we have derived in the previous lecture:

$$\begin{cases} \frac{d}{dt}\mu_x = -\omega\mu_y \\ \frac{d}{dt}\mu_y = +\omega\mu_x \\ \frac{d}{dt}\mu_z(t) = 0 \end{cases} \Rightarrow \begin{cases} \mu_x(t) = \mu_{\perp} \cos(\omega_0 t + \varphi) \\ \mu_y(t) = \mu_{\perp} \sin(\omega_0 t + \varphi) \\ \mu_z(t) = \mu_{\parallel} \end{cases} \quad (2)$$

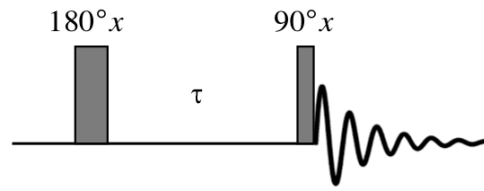
where the constants are replaced by the physically meaningful initial longitudinal magnetisation $\mu_{\parallel}$ and the initial transverse magnetisation $\mu_{\perp}$. Eqs (1) and (2) may be combined to yield *Bloch equations*:

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

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

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

The *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 (3) for the case when $\mu_z(0) = -\mu_{\text{eq}}$ is:

$$\mu_z(\tau) = \mu_{\text{eq}} (1 - 2e^{-\tau/T_1}) \quad (4)$$

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

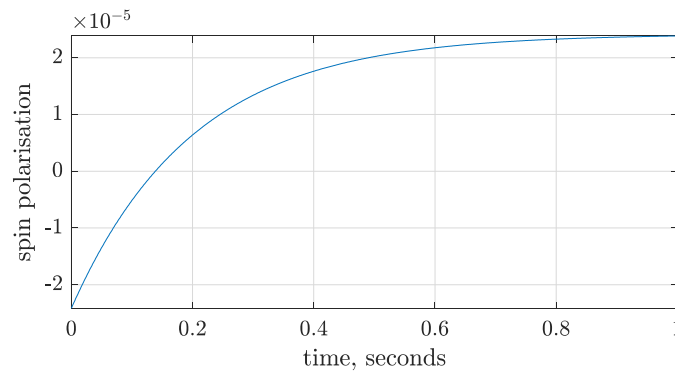


Figure 2. A simulated (for source code see Spinach example set) inversion-recovery experiment for an ensemble of protons in a 600 MHz magnet at 298 K with the longitudinal relaxation time of 0.2 seconds.

Another experiment 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 magnetic field that destroys the magnetisation; the recovery begins from zero (Figure 3):

$$\mu_z(\tau) = \mu_{\text{eq}} (1 - e^{-\tau/T_1}) \quad (5)$$

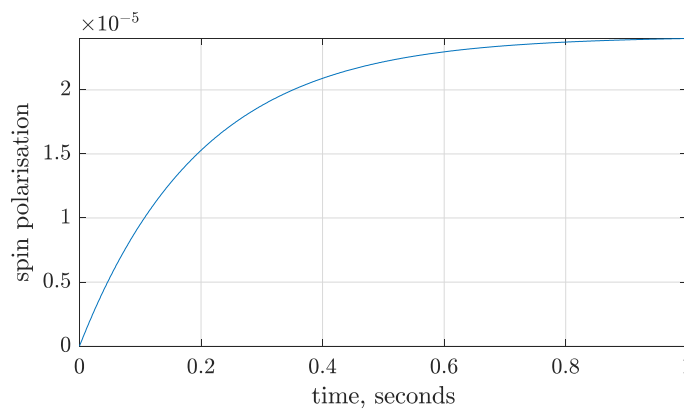


Figure 3. A simulated (for source code see Spinach example set) saturation-recovery experiment for an ensemble of protons in a 600 MHz magnet at 298 K with the longitudinal relaxation time of 0.2 seconds.

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.

4. Measuring T_2 time: spin echoes and CPMG pulse sequence

The complication in the case of transverse relaxation is the presence of spin precession. Nuclear spins of the same type can have different precession frequencies for the following 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.

In such circumstances, the magnetisation would not only relax, but also dephase (Figure 4).

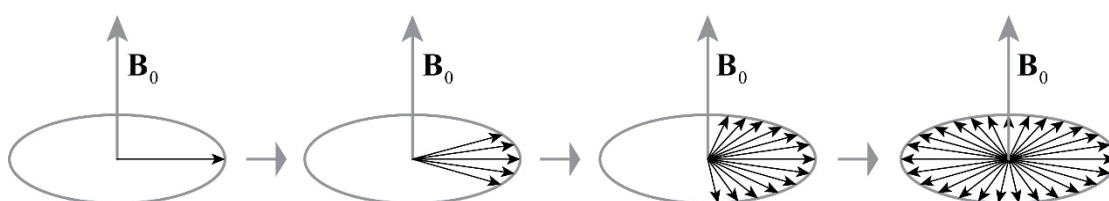


Figure 4. A schematic illustration of the dephasing process. When different spins precess at different frequencies, they eventually spread out uniformly in the XY plane. The average magnetisation is then reduced to zero.

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).

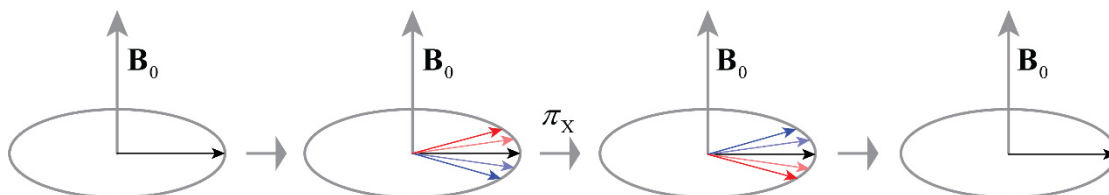
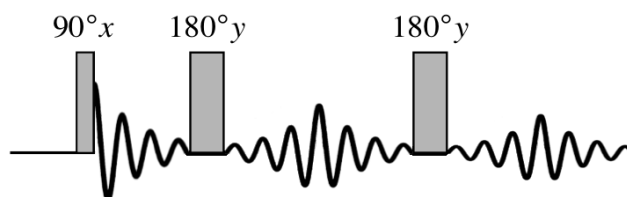


Figure 5. The effect of the 180° pulse on the position of the magnetisation vectors in the transverse plane. After the 180° -degree pulse, the vectors that were ahead are moved behind, and the vectors that were behind are moved ahead. After a period of time, the vector bunch is refocussed and the average magnetisation is restored to its original value.

This process is called **refocussing**, and phenomenon of the transverse magnetisation first disappearing and then reappearing after a 180° pulse is called **spin echo**. To prevent coherent dephasing from interfering with transverse relaxation measurements, T_2 times are measured using a series of echoes, proposed by Carr, Purcell, Meiboom and Gill (hence the CPMG 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:

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

is fitted to that data. A simulated example of a CPMG echo train is shown in Figure 6.

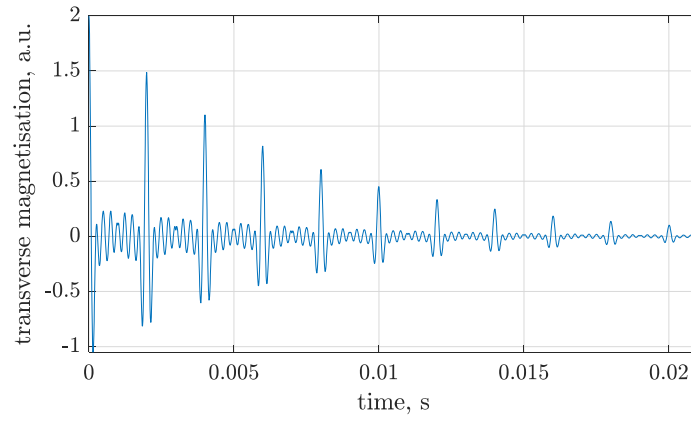


Figure 6. A simulated (for source code see *Spinach* example set) CPMG echo train for a powder sample of a two-spin system with anisotropic chemical shifts and a transverse relaxation time of 1/150 seconds. The inversion pulses are placed 2 ms apart.