Spin-lattice relaxation, T_1

Time constant describing the approach of the magnetisation to thermal equilibrium that is the Boltzmann distribution

Exponential process:

$$\frac{d\,M_z}{dt}=\frac{-(M_z-M_0)}{T_1}$$

Determines
- initial polarisation in the pulse NMR experiment
- pulse repetition rate
  - optimum sensitivity
  - quantitative analysis

Requirement for relaxation

Fluctuating magnetic field at the Larmor frequency

Brownian motion of molecules in solution modulates the dipole-dipole coupling

Effect of the correlation time

Distribution of frequencies associated with the fluctuating field.

- spectral density, J(ω)

Correlation time, τ_c, average time between molecular collisions

Spectral density changes with the correlation time

$$J(\omega)=\frac{2}{5}\frac{\tau_c}{1+(\omega\tau_c)^2}$$

Area under curve of J(ω) against ω constant

Consequences

- **slow motion**, fluctuating field does not generate significant components at Larmor frequency. ***T_1* long**

- $\omega = \tau_c^{-1}$, maximise frequency component at Larmor frequency. ***T_1* short**

- **fast motion**, spectral density more spread out decreasing component at the Larmor frequency. ***T_1* long**

Effect of the correlation time

Spin-lattice relaxation as a function of τ_c

$$\frac{1}{T_1}=\gamma^2\left[B_{xl}\right]^2\left(J(\omega)+J(2\omega)\right)$$

First term

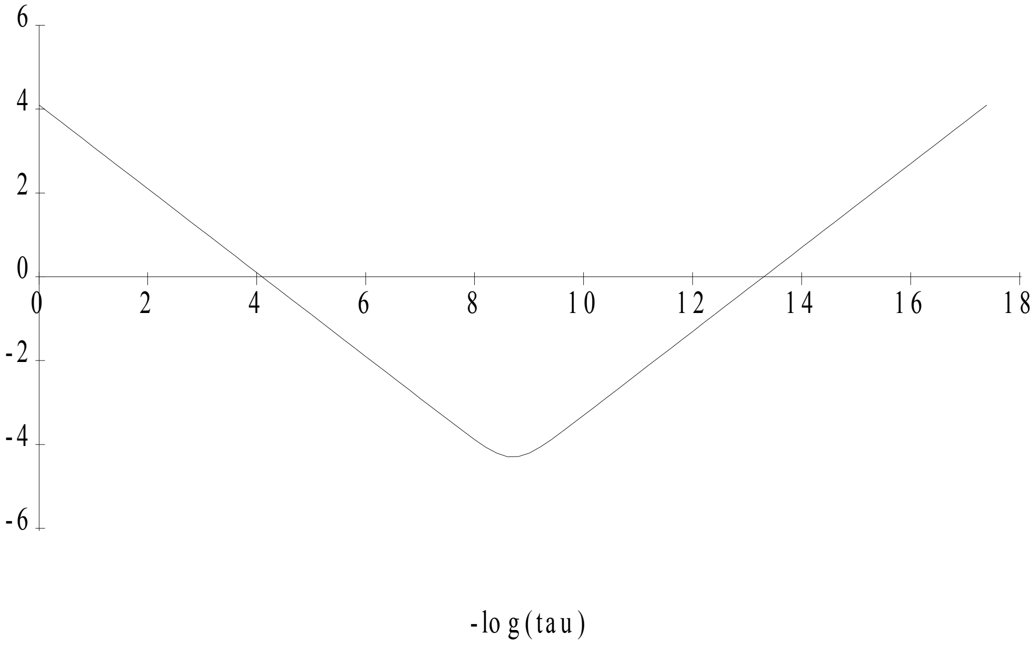
- magnitude of the local fields generated by the molecular motion

Second term

- frequency distribution based on J(ω)

Overall we see:

Variation of T1 with correlation time



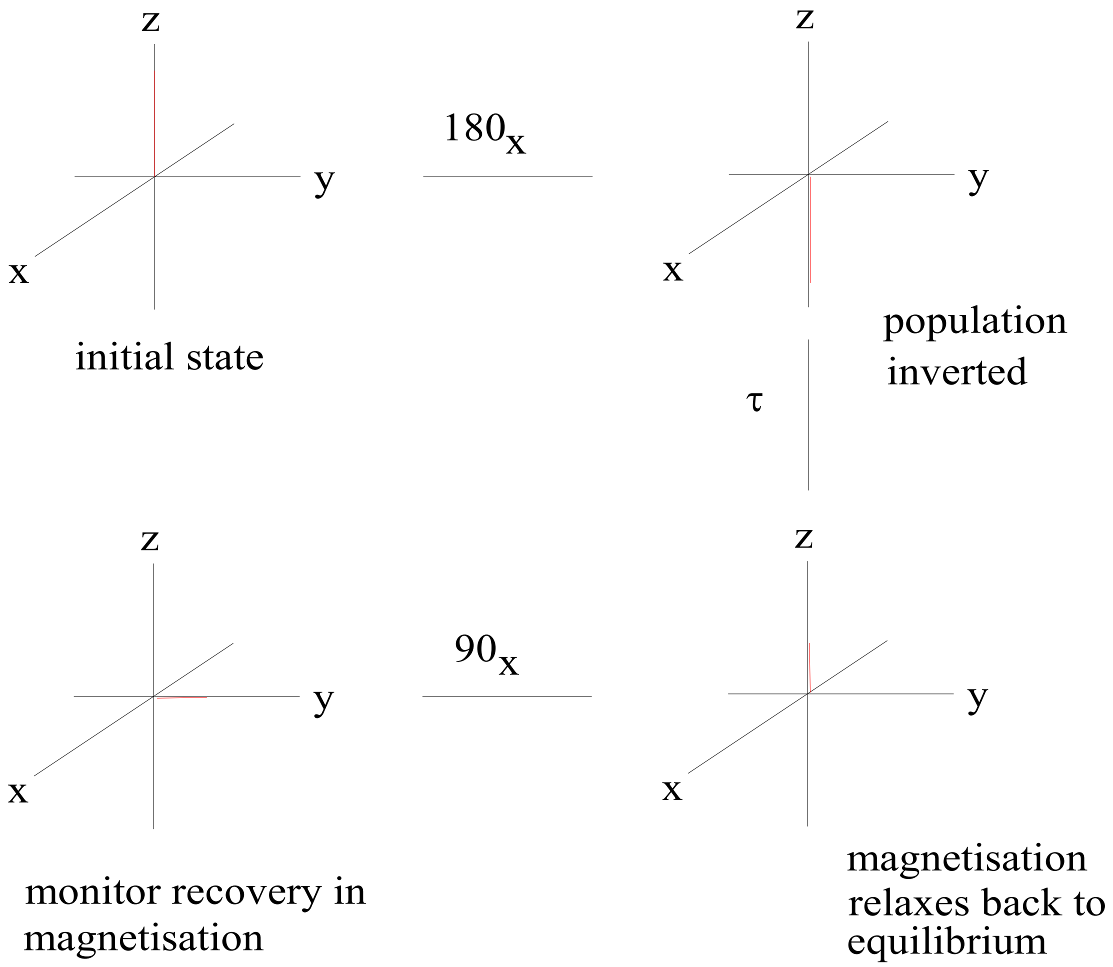
Measurement of the spin-lattice relaxation time

1. Inversion-recovery

A. Pulse sequence:

$[\ 180_x - t - 90_x - (\mathrm{FID}) - \text{recycle delay}\ (\ 5\mathrm{x}T_1)]$

B. Vector diagram description:



Measurement of the spin-lattice relaxation time

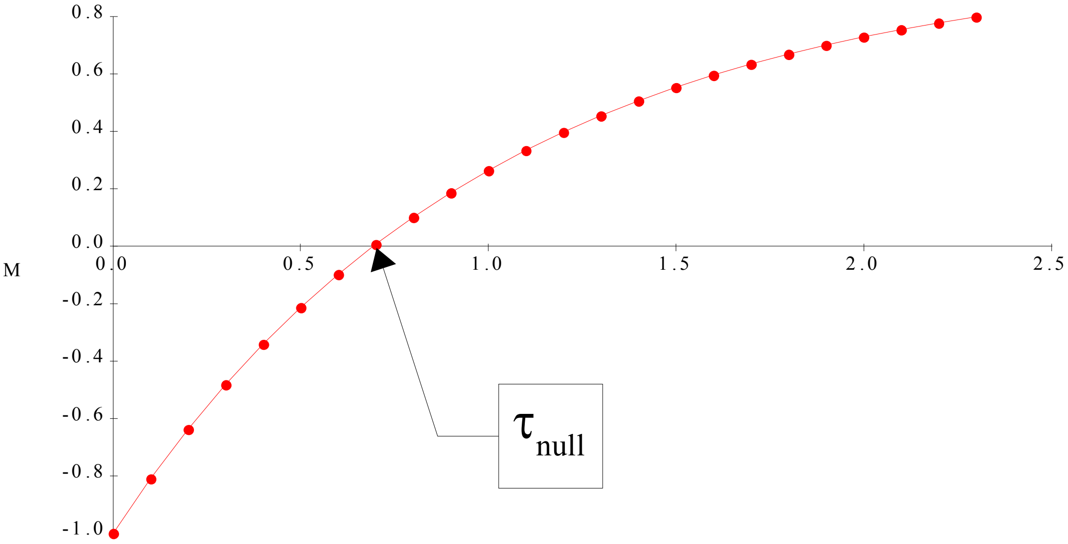
1. Inversion-recovery

C. Data analysis

Magnetisation after a time, τ, is given by:

$$M(\tau) = M(\infty)[\,1 - 2\exp(-\tau/T_1)]$$

Typical set of data:



Estimate of T_1 from τ_{null}

$$T_1 = \frac{\tau_{null}}{\ln 2}$$

Spin-spin relaxation time ,T_2

Time constant for the decay of the magnetisation components in the xy plane

Exponential process:

$$\frac{d\,M_{x,y}}{dt} = \frac{-M_{x,y}}{T_2}$$

N.B. At thermal equilibrium there are no magnetisation components in the xy plane

Determines

- the rate of decay of the FID

- the linewidth in the NMR spectrum
  for a lorentzian line
  $\nu_{1/2} = 1/\pi T_2$

Two components

1. T_1 lifetime

    magnetisation component in the xy plane must at least as fast as T_1.

Mechanism for relaxation the same as T_1, fluctuating field at the Larmor frequency

Implies a linewidth, $\nu_{1/2} > 1/T_1$

2. Nuclear spins exchange magnetisation
   Flip-flop transitions. Magnetisation vectors in the xy plane fan out, loss of phase coherence.

Requires two coupled spins with the same transition energy. Energy conserving so occurs at zero frequency. No motion is necessary

Two limiting cases:

1. Extreme narrowing: $T_1 = T_2$
   Dominated by the first term
    For molecules reorienting very rapidly;
    $\omega_o \tau_c << 1$

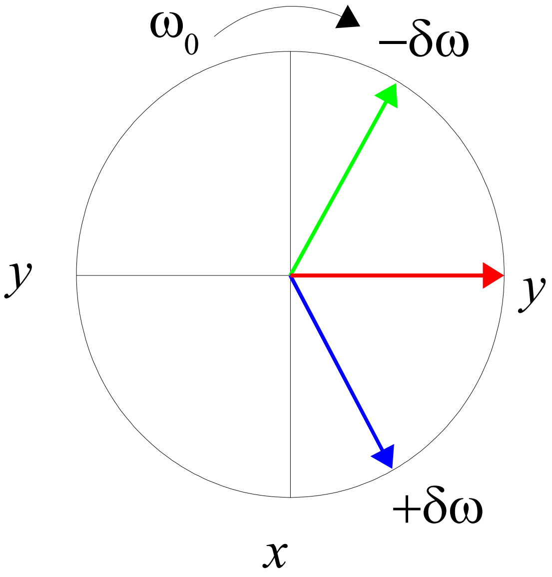
2. In a rigid solid: $T_1 >> T_2 \sim 20\ \mu s$
   Dominated by the zero frequency term
   No motion

Effect of magnetic inhomogeneity on T_2

- Homogeneity of the applied field B_0 better than 1 part in 10^{10}

- Small differences in B_0, δB, slightly alter the resonance condition

$$\omega_0 + \delta\omega = \gamma\,(\,B_0 + \delta B)$$



- Net magnetisation along x or y axis reduced, hence signal decays faster than the real T_2

- Effective T_2 in the presence of magnet inhomogeneity known as T_2*

- Linewidth in the NMR spectrum now

$$\nu_{1/2} = 1/\pi T_2^*$$

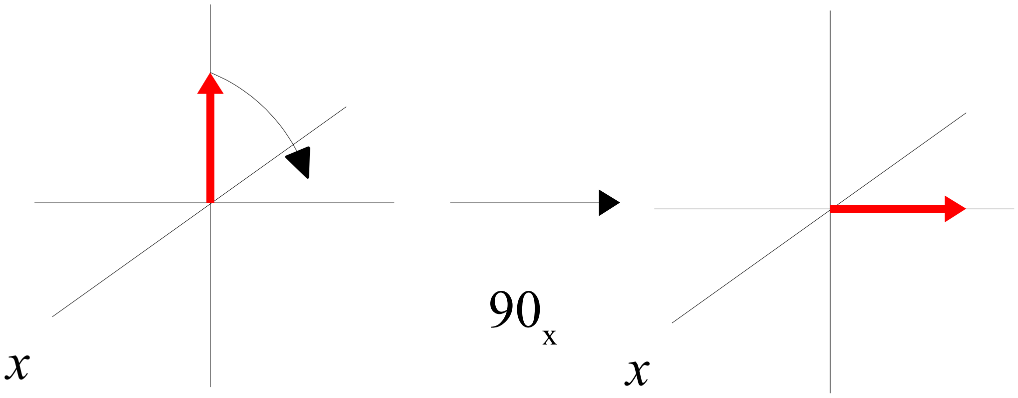
Spin echoes

- Refocus the dephasing caused by δB
- No chemical shift evolution after the full period of the spin echo
- Basis of the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence for measuring T_2
- Pulse sequence

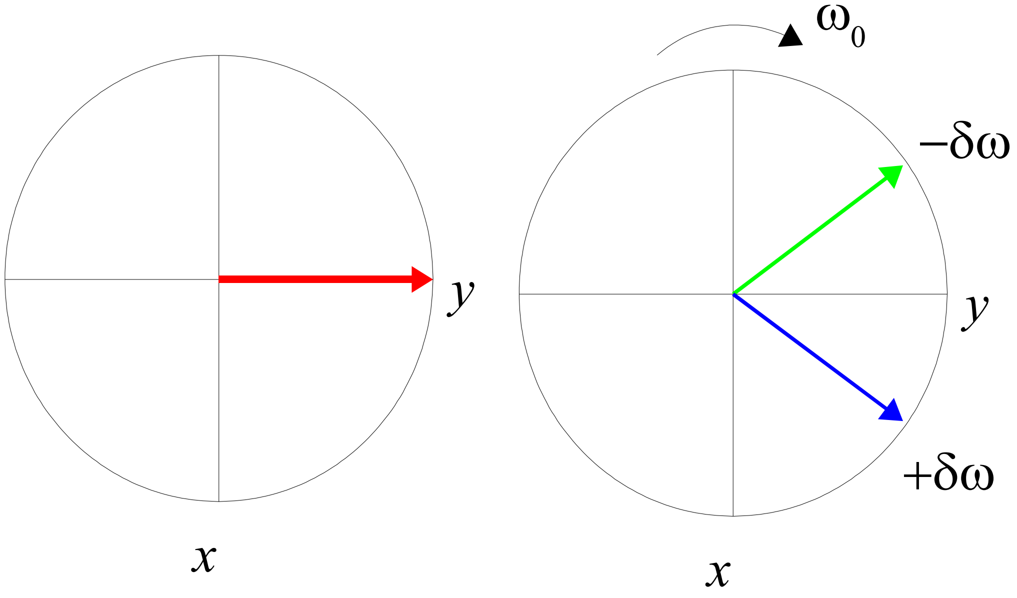
$$90_x - \tau - 180_y - \tau - \text{Echo}$$

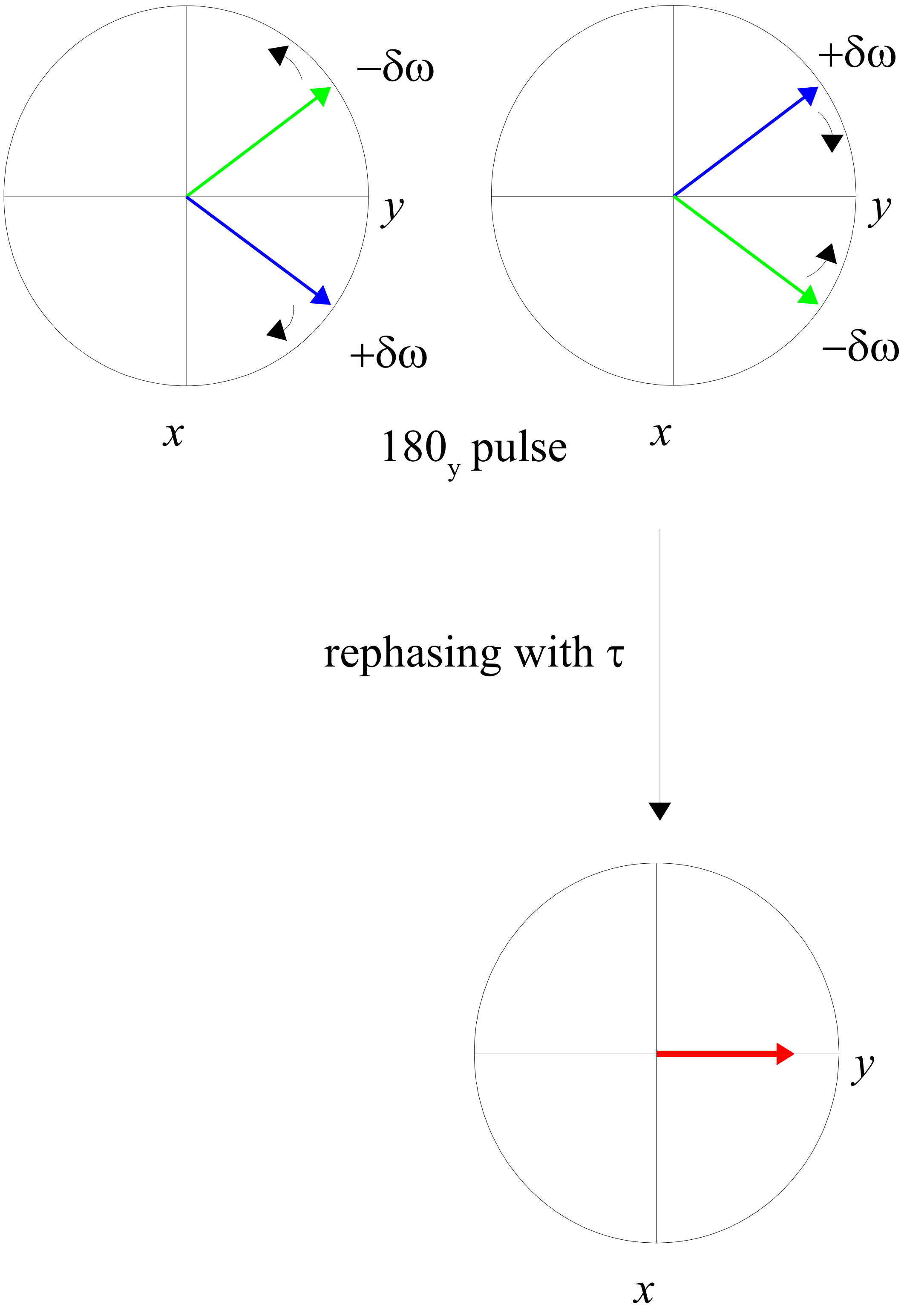
- Vector diagram

Spin echoes



dephasing with τ





- Signal decays by T_2