

Spin-lattice and spin-spin relaxation

Sequence of events in the NMR experiment: (i) application of a 90° pulse alters the population ratios, and creates transverse magnetic field components ($M_{x(y)}$); (ii) the magnetization vector M recovers until it reaches its equilibrium value M_0 . The components of M decay exponentially with time constants T_1 and T_2 :

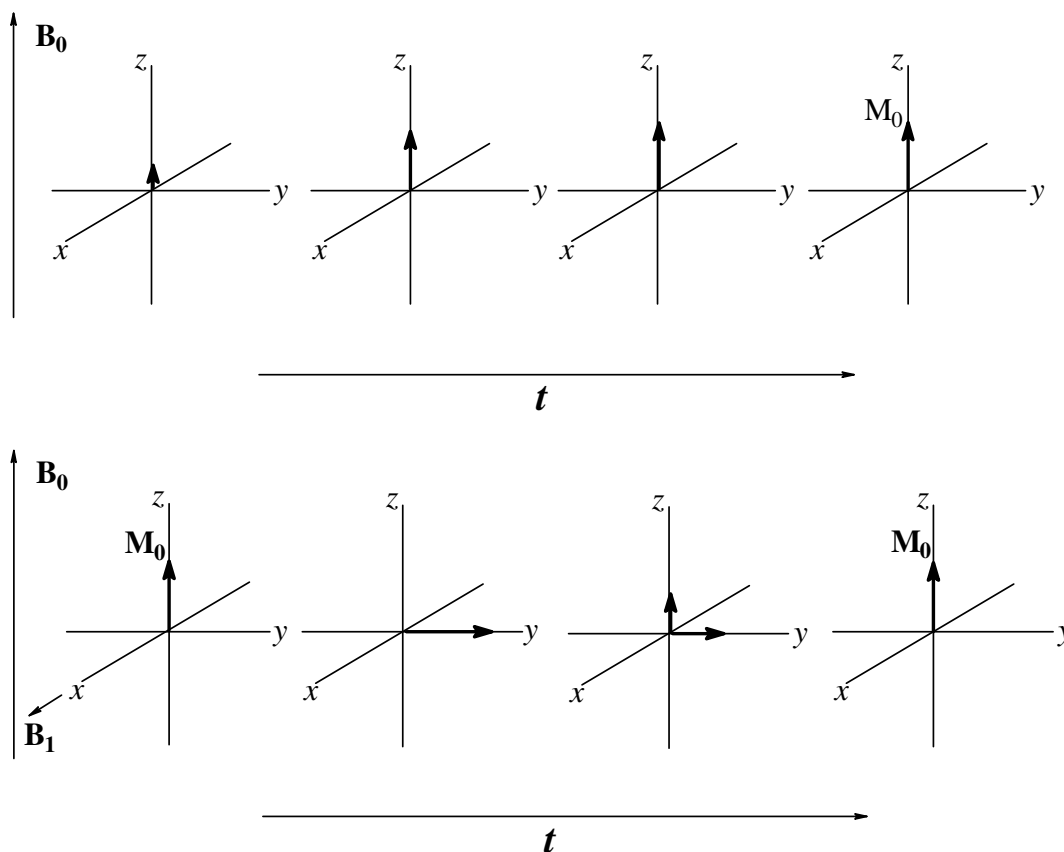
$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1} \quad (1)$$

$$\frac{dM_{x(y)}}{dt} = -\frac{M_{x(y)}}{T_2} \quad (2)$$

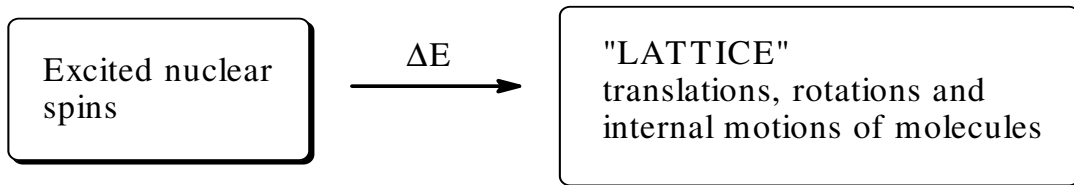
The approach of the system to thermal equilibrium is known as *relaxation* and T_1 and T_2 are *relaxation times* (*relaxation rates* $R_{1(2)}=1/T_{1(2)}$ are also used). Both relaxation times are time constants used to characterize what are assumed to be first order rate processes.

Spin-lattice relaxation mechanisms

The *spin-lattice* (or *longitudinal*) relaxation time T_1 quantifies the rate of transfer of energy from the nuclear spin system to the neighboring molecules (the lattice). This is relaxation in the z -direction and leads to restoration of Boltzmann equilibrium.



Closely spaced energy levels \Rightarrow the rate of spontaneous emission is negligible ($\sim 10^{-25}$ per second)



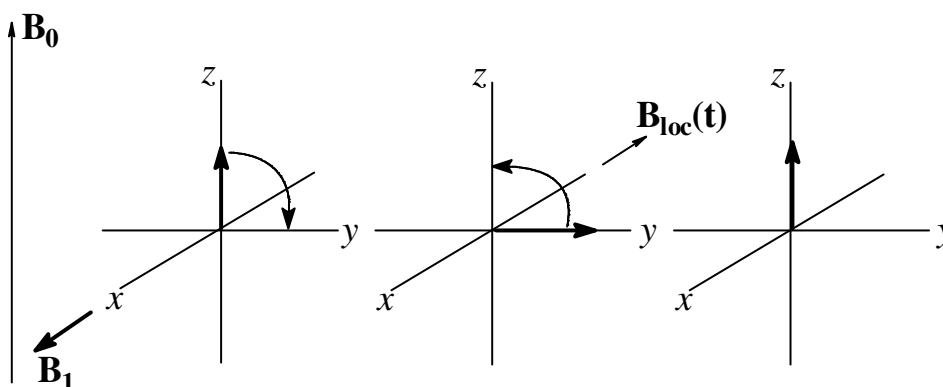
For any given NMR transition, there will be some possible change within the lattice involving the same quantity of energy.

A downward flip of a nuclear spin \Rightarrow An acceleration of some motion of the molecule in which the flip occurred

T_1 values are relatively long due to the lack of means to transfer energies of NMR transitions into thermal energy.

Requirements for the energy transfer:

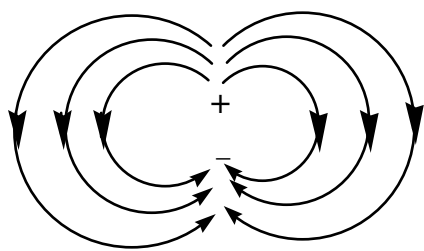
- (i) the motion in the lattice (which is expected to gain or lose the energy from the nuclear spin transition) must cause a *fluctuating magnetic field* (effectively acting as a “local pulse”) at the site of the nuclear spin involved.
- (ii) as for the observe rf pulse, the local fluctuating field must have a component at the Larmor frequency, ν_0 , of the nucleus under consideration.
- (iii) only x and y components of the local field can cause T_1 -relaxation.



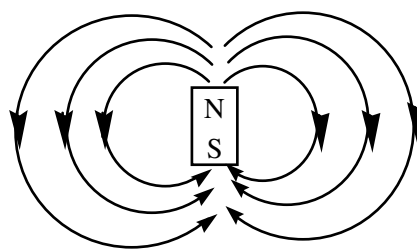
The rf field B_1 affects all the spins similarly and in a concerted way (i.e., the rf pulse is *coherent*).

The local field B_{loc} is randomly different at the site of each spin at any instant (i.e, the local field is *incoherent*).

The most common source of the local fluctuating field for spin-1/2 nuclei is direct *dipolar interaction*.

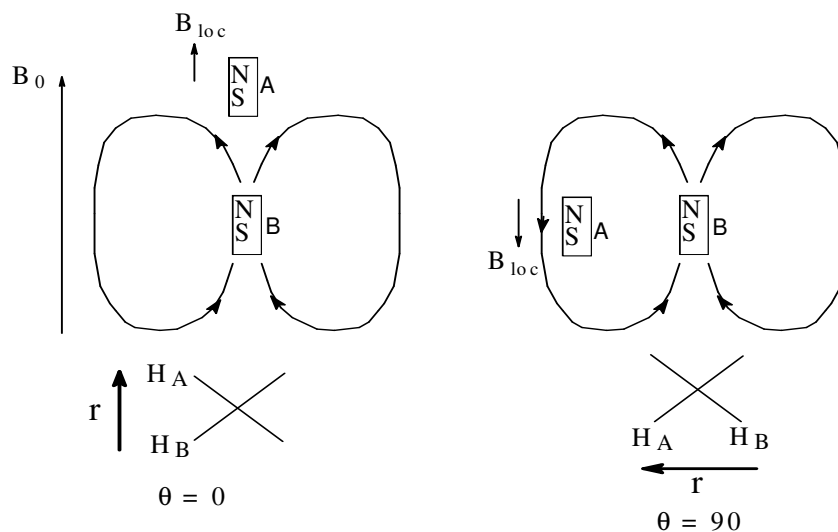


Electric dipole



Magnetic dipole

In single crystals:



In solution *the rapid reorientation of the dipolar interaction* due to molecular motions provides fluctuating fields. This relaxation mechanism depends on the rate of molecular motion. Thus, T_1 is temperature dependent.

Molecular dynamics

The correlation time τ_c – the time taken for the (spherical) molecule to rotate by roughly 1 radian. For typical values of the viscosity in organic solvents:

$$\tau_c \approx 10^{-12} M_w$$

where M_w is the molecular mass (in Daltons).

In the solid state, where the motion is hindered, τ_c is large and there are only weak frequency components near $\omega_0 (= 2\pi\nu_0)$:

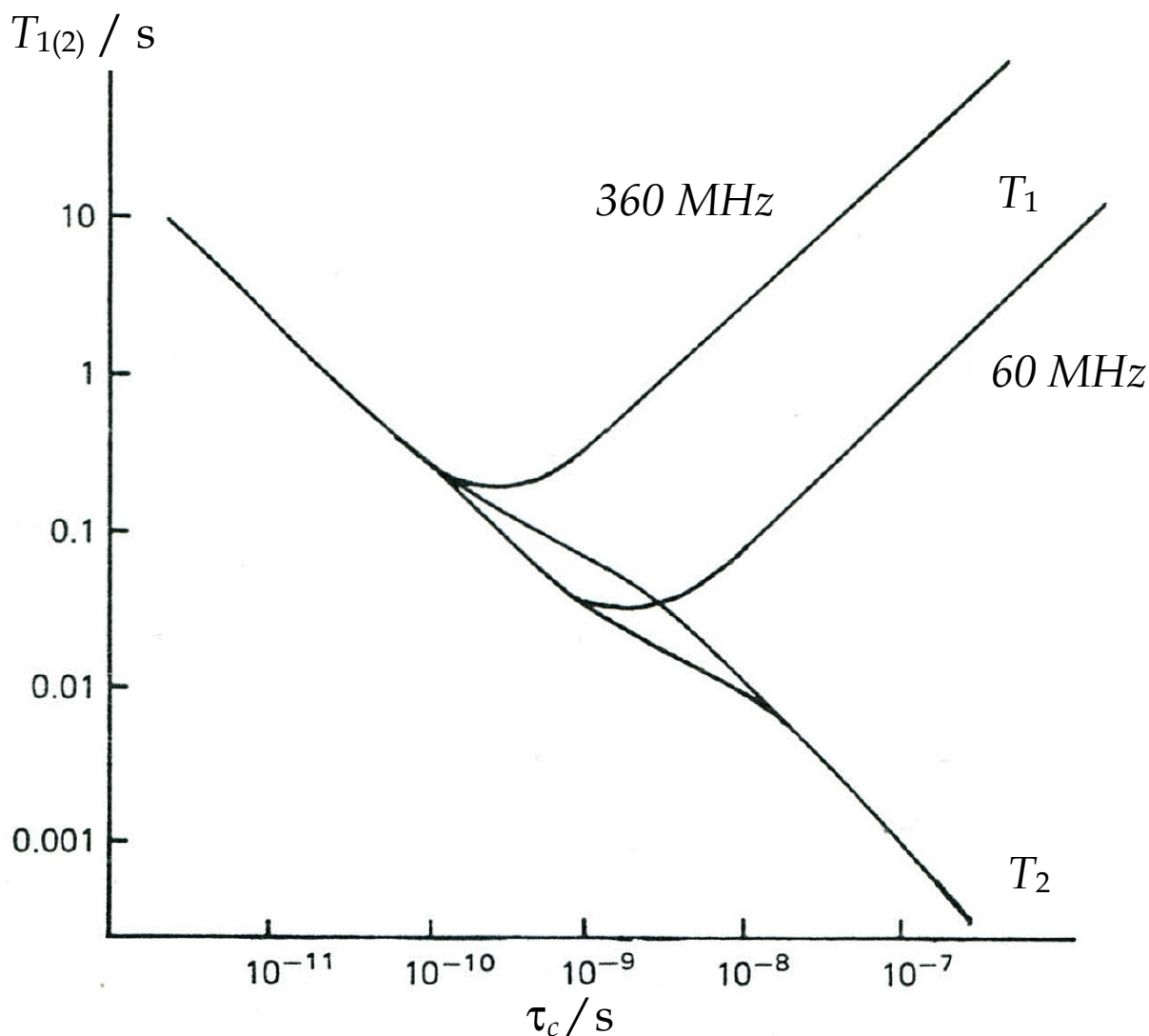
$$\omega_0 \tau_c \gg 1 \quad \Rightarrow \quad T_1 \text{ is long}$$

Rapid motion, associated with short τ_c , does not possess much intensity at ω_0 .

The extreme narrowing limit: $\omega_0 \tau_c \ll 1 \quad \Rightarrow \quad T_1 \text{ is long}$

The frequency distribution is optimum for T_1 relaxation in the intermediate region where $1/\tau_c \sim \omega_0$:

$$\omega_0 \tau_c \approx 1 \quad \Rightarrow \quad T_1 \text{ minimum}$$



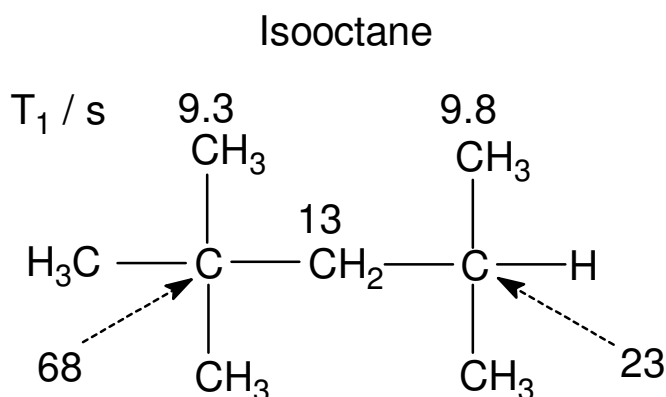
Other mechanisms for spin-lattice relaxation:

- (i) interaction with unpaired electrons (e.g., in paramagnetic substances). This can be very efficient and can lead to featureless broad lines. Sometimes it can be beneficial to add a small amount of paramagnetic impurity if the relaxation times are very long.
- (ii) interaction with electric field gradients for quadrupolar nuclei (with spin $I > 1/2$). This usually leads to short relaxation times and often featureless broad lines are observed.

The spin-lattice relaxation time determines what recycle delay between pulses should be used. The nuclear spin system must be allowed to relax back to equilibrium before the next pulse is applied and this time period is determined by T_1 .

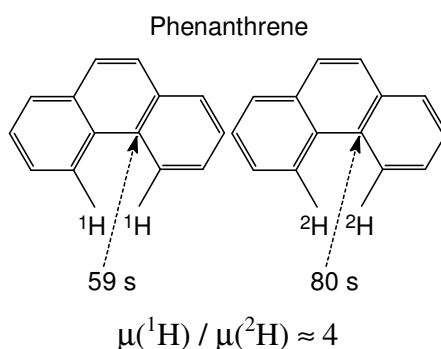
Relationship between T_1 and chemical structure

The T_1 values for ^{13}C nuclei directly bonded to protons vary between 0.1 - 10 s. Longer values (10 - 300 s) are observed for quaternary carbons. This is due to the fact that the main contribution to T_1 -relaxation comes from ^1H - ^{13}C dipole-dipole interactions. In the absence of the motional effects, directly bonded protons have the largest effect on the T_1 values of corresponding ^{13}C nuclei: the more hydrogen atoms are attached to a carbon the shorter T_1 is.



For the dipole-dipole relaxation, there is a strong dependence of the relaxation rate on the distance between interacting nuclei $T_1^{-1} \sim r_{\text{CH}}^{-6}$. In isooctane there are many spin-pairs to consider in order to estimate the contribution of the ^1H - ^{13}C dipole-dipole interaction and the above relationship needs to be modified: $T_1^{-1} \sim \sum_i r_{\text{CH}(i)}^{-6}$. As a first approximation, we can include into consideration only directly-bonded protons: $T_1(\text{CH})/T_1(\text{CH}_2)=2$. This is in agreement with the experimental values: $23/13=1.77$. Possible reasons for the small deviation from the predicted ratio are that the dipolar relaxation is additionally affected by more distant protons [e.g., there are 8 and 1 geminal protons for the CH_2 and CH groups, respectively, in isooctane], and that relaxation mechanisms other than the dipole-dipole interaction may also be present. In the case of the CH_3 groups, T_1 is greater than $T_1(\text{CH})/3$, showing that the *methyl rotation* slows down considerably the ^1H - ^{13}C dipole-dipole relaxation by shortening the effective correlation time τ_c .

Dependence on the magnitude of the nuclear magnetic moment



Spin-lattice relaxation time measurements

The standard method for measuring T_1 is known as *inversion-recovery*. First, a 180°_x pulse inverts the magnetization along the $-z$ axis. A time period, τ , is allowed, during which spin-lattice relaxation occurs causing M_z to go from the value of $-M_0$ through zero to its equilibrium value of M_0 . A 90°_x pulse is then applied and the FID is recorded. The experiment is repeated with different τ delays, allowing determination of the T_1 value.

Quantitatively, the decay of M_z is given by the Bloch equation (1). Integration of Eq (1) with $M_z = -M_0$ at $t = 0$ gives:

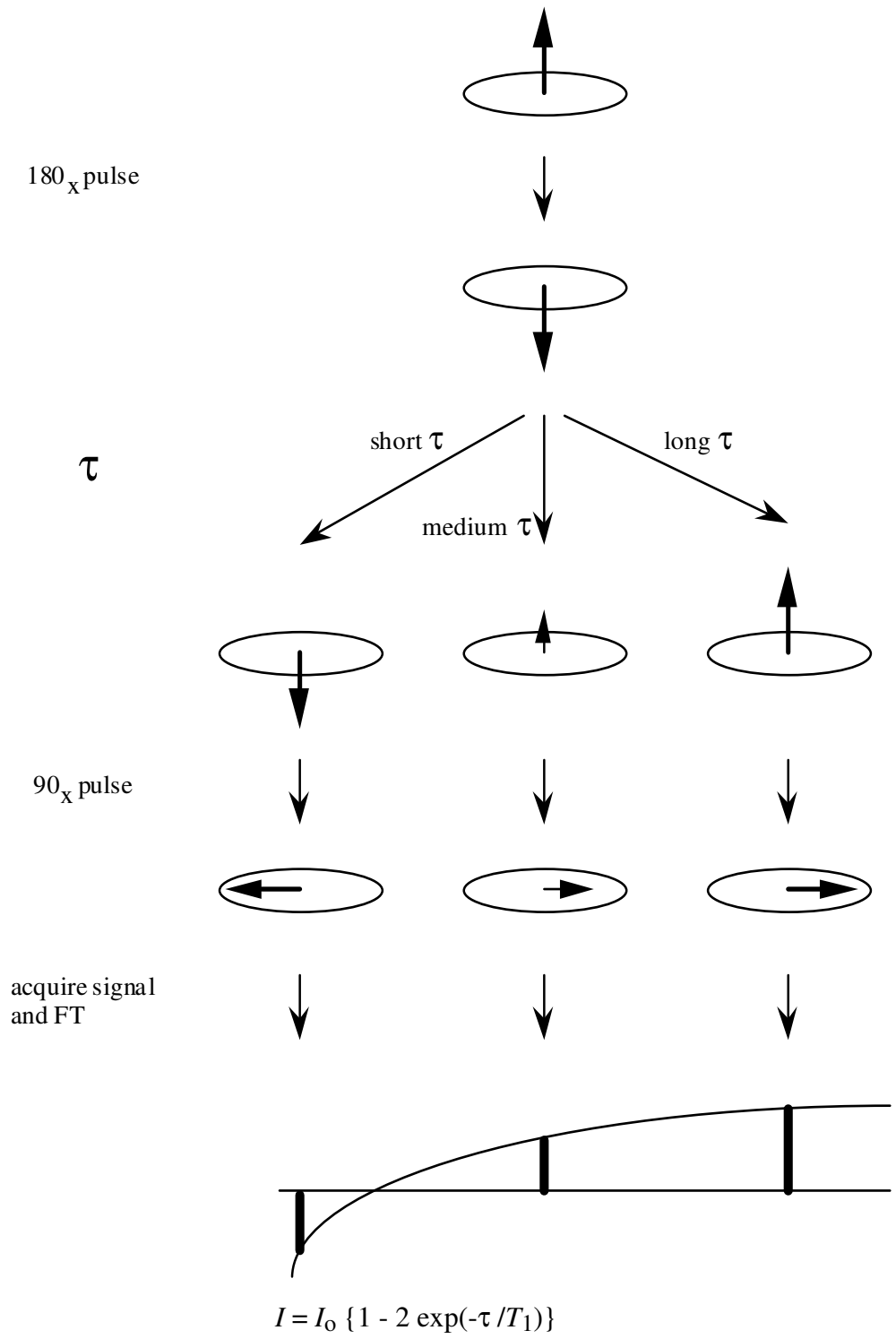
$$M_z = M_0 [1 - 2 \exp(-t/T_1)]$$

In practice, the following equation is used:

$$\ln (I_\infty - I_\tau) = \ln 2I_\infty - \tau / T_1$$

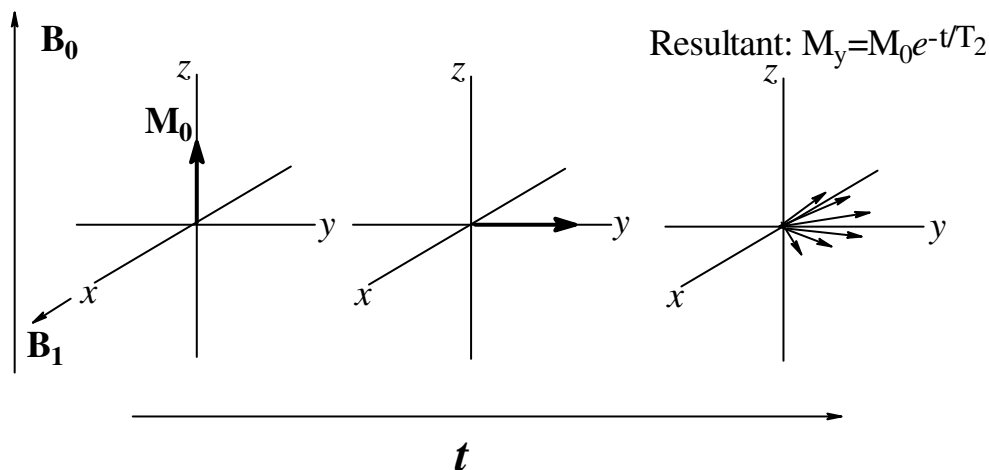
where I_τ is the initial intensity of the signal after the 90°_x pulse at time τ , and I_∞ is the limiting value of I_τ for a very long interval τ . T_1 is determined from the slope of a plot of $\ln (I_\infty - I_\tau)$ vs. τ .

For $\tau = T_1 \ln 2 = 0.69 T_1 \Rightarrow I_\tau = 0$, i.e., T_1 can be estimated from the pulse spacing τ that shows no signal after the 90° pulse.



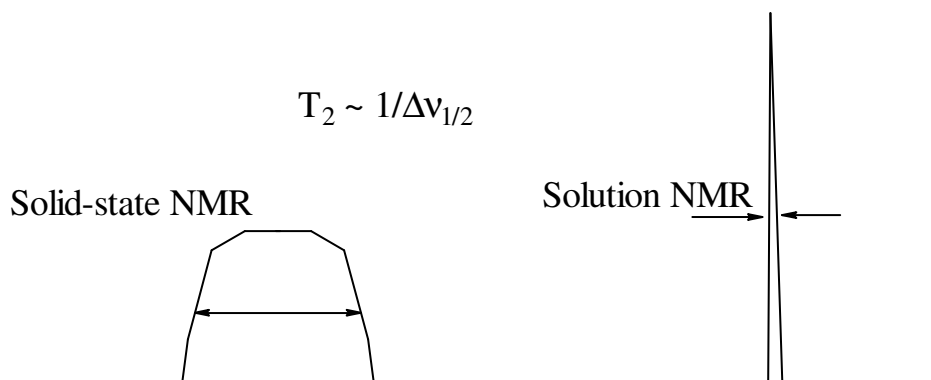
Spin-spin relaxation mechanisms

Spin-spin (or *transverse*) relaxation time T_2 is used to quantify the rate of the decay of the magnetization within the xy plane. After a 90° pulse the nuclear spins are aligned in one direction (are said to be phase coherent), but this arrangement is gradually lost (e.g., due to field inhomogeneities and/or direct interactions between the spins *without energy transfer to the lattice*).



T_2 relaxation does not affect the total amount of z -magnetization, but the degree of synchronization of the transverse magnetization components.

T_2 is related to the linewidth at half-height ($\Delta\nu_{1/2}$) of the NMR signal.



The spin-spin relaxation is related to spin-lattice relaxation, since an increase in z -magnetization without a decrease in the magnetization in the xy plane is not possible:

$$T_2 \leq T_1 \text{ (in solutions } T_2 \approx T_1 \text{ and in solids } T_2 \ll T_1)$$

The static dipolar fields created by neighbouring dipoles:

$$B_{loc} \sim \mu / r^3$$

The static dipolar fields created by neighbouring dipoles are very large in solids. Thus, the spin-spin mechanism is very efficient $\Rightarrow T_2 \sim 1$ ms in solids and polymers.

In non-viscous solutions, the static dipolar fields average out as a result of random molecular motion, leading to $T_2 \approx T_1$.

When extreme narrowing condition breaks down: $T_2 < T_1$

Spin-spin relaxation time measurements

After a 90° pulse the net magnetization in the xy plane gradually decays. The decay is of the form $\exp(-t/T_2^*)$, and is due to two factors: (i) magnetic field inhomogeneity and (ii) spin-spin relaxation. An NMR signal in the time domain decaying according to $\exp(-t/T_2^*)$ gives a Lorentzian peak of half-height linewidth $1/\pi T_2^*$ after Fourier transformation. The time constant T_2^* includes both factors (i) and (ii). In order to eliminate the field inhomogeneity contribution and to measure true T_2 relaxation, a *spin-echo* pulse sequence is used. The modification of the spin-echo pulse sequence developed by Carr and Purcell:

$$90^\circ_x - \tau - 180^\circ_x - \tau \text{ (1st echo)} - \tau - 180^\circ_x - \tau \text{ (2nd echo)} - \dots$$

To determine T_2 we start from equation (2), which can be solved for M_y to give:

$$M_y = M_0 \exp(-t/T_2)$$

$$\ln M_y = \ln M_0 - t/T_2$$

Since intensity of the echo is proportional to M_y :

$$\ln I(t) = \ln I_0 - t/T_2$$

where $t = 2\tau, 4\tau, \dots$. T_2 is determined from the slope of a plot of $\ln I(t)$ vs. t .

