Relaxation

Relaxation times: T_1 and T_2

Relaxation rate = $1/T_{1,2}$

Relaxation in NMR

Relaxation spin-lattice:

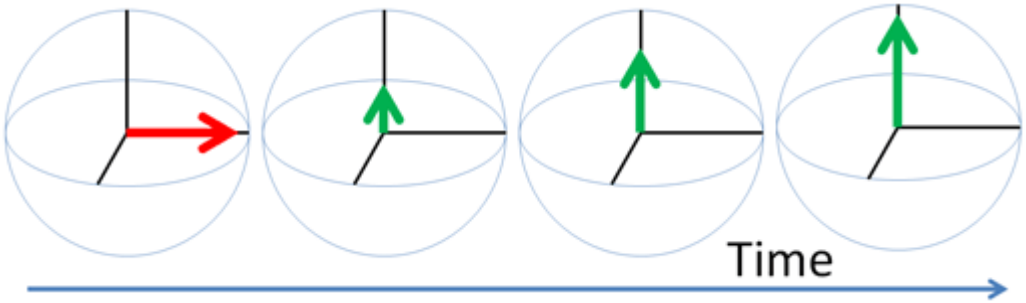
Transfert of energy from the system of spins to an acceptor of the lattice: rotations, translations, vibrations fluctuating in the domain of larmor frequencies

Relaxation spin-spin:

Destruction of the component M_{xY} after a pulse.

Two mechanisms: spin-lattice and spin-spin relaxation

Spin-lattice relaxation (T_1) is the mechanism by which an excited magnetization vector returns to equilibrium along the axis of the static applied magnetic field.



The relaxation process is induced by field fluctuation due to molecular motion. (The local field experienced by a molecule changes when the molecule reorients)

The correlation time -τc (Tau-c): During this time the system does not move

The magnitude of the relaxation time depends highly on:

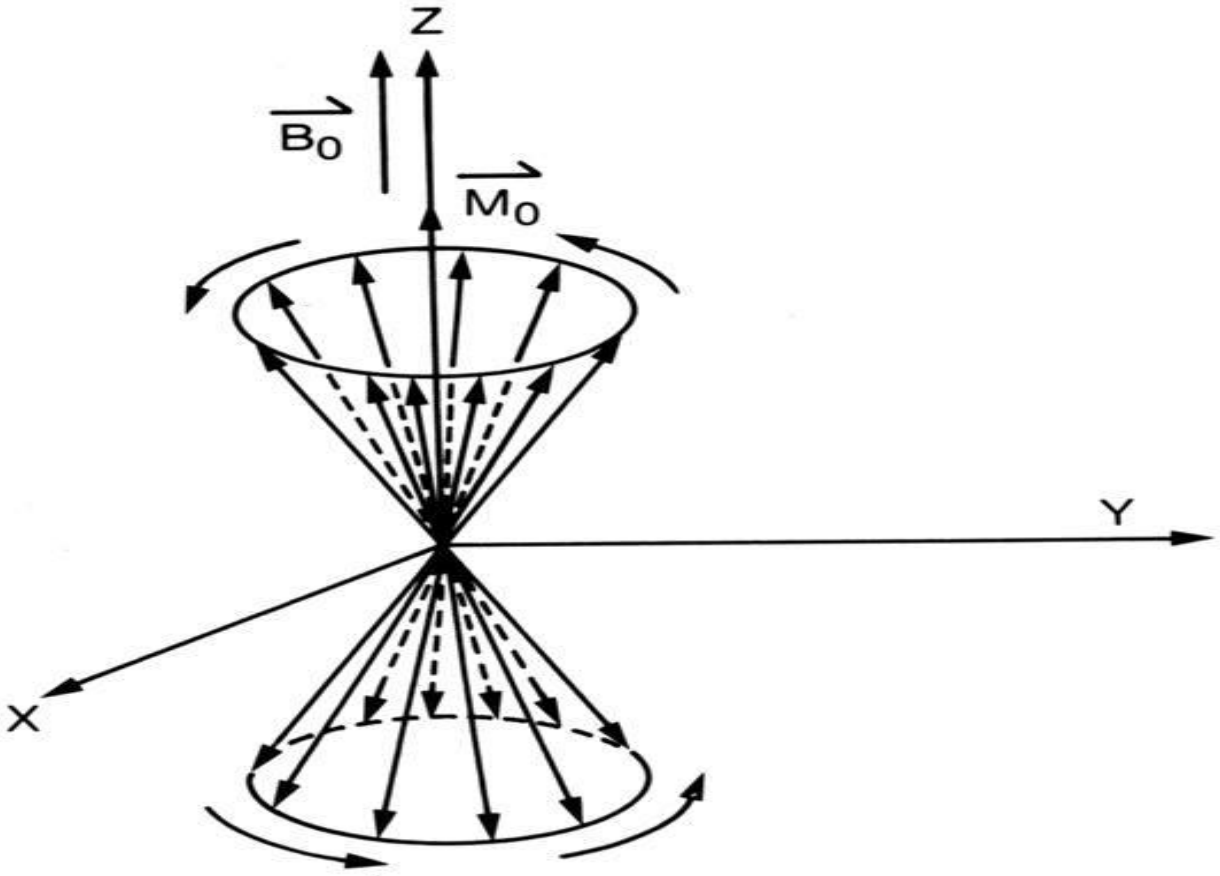
- the type of nuclei (nuclei with spin 1/2 and low magnetogyric ratio have usually long relaxation time whereas nuclei with spin>1/2 have very short relaxation time)
- other factors like the physical state (solid or liquid state), the viscosity of the solution, the temperature ... etc.

In other words the relaxation time depends on the motion of the molecules.

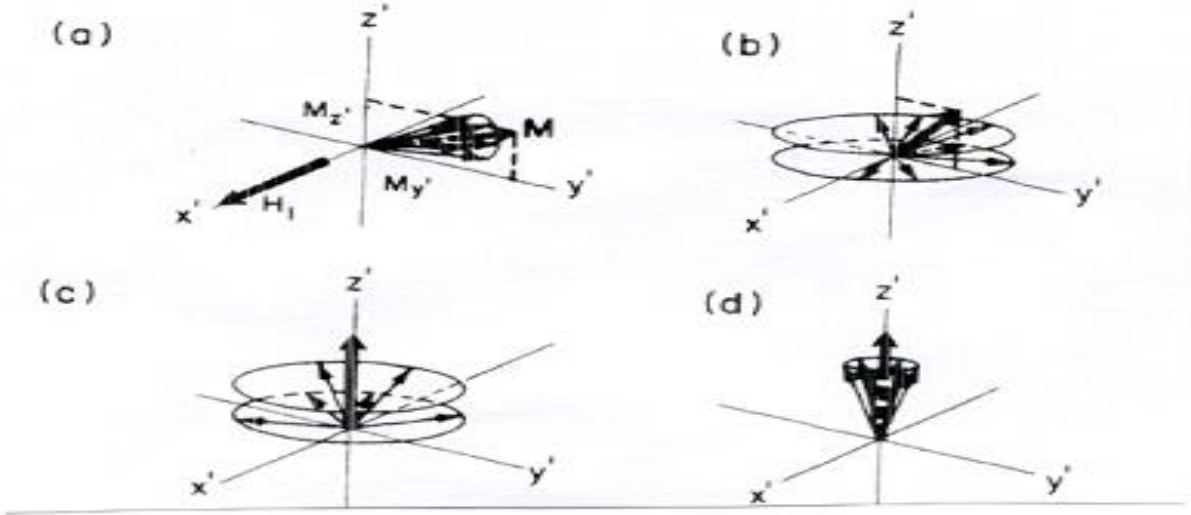
Definitions:

The correlation time -τc (Tau-c): represents the time it takes for a molecule to reorient by 1 degree ("tumbling time").

The spectral density - J(w): describes the ranges of frequency motion that are present. Not all molecules tumble at a unique rate: molecules tumble, collide, change direction... at a range of rates up to the maximum rate of ($1/\tau c$).


Z
$\vec{B_0}$
$\vec{M_0}$
Y
X

Pulsed NMR- Relaxation



The system evolves under two relaxation mechanisms:

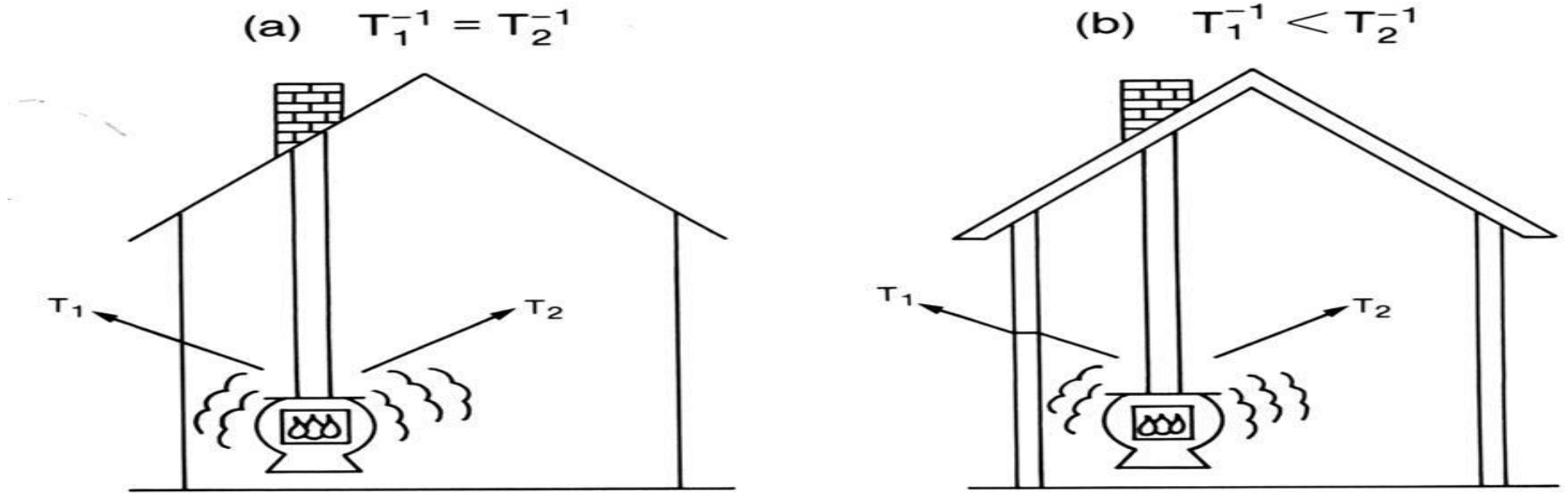
- For a set of spins coupled by interactions, as in a solid, the system can tend very rapidly towards an internal quasi-equilibrium with a time constant, **T_2, named spin-spin relaxation time.** During T_2 there is disappearance of the transversal magnetization by dispersion of the spins in the XOY plane.
- For such a set of spins in contact with the lattice, there is a **spin-lattice relaxation** characterized by the time **T_1,** and then restoration of the magnetization M_0 along B_0.

Generally, and specially for solids, $T_2 << T_1$

Bloch's equations: $dM_Z/dt = -(M_Z - M_0)/T_1$

$dM_X/dt = -M_X/T_2$ $\quad dM_Y/dt = -M_Y/T_2$

Stove-in-a-house analogy to T1 and T2 relaxation. In (a), the house is not insulated. So the energy emitted by the stove is lost to the surrounding environment (lattice) as fast as it is dispersed throughout the house. In (b), the house is insulated so that the energy from the stove is not dissipated to the surroundings nearly as fast as it equilibrates in the house.



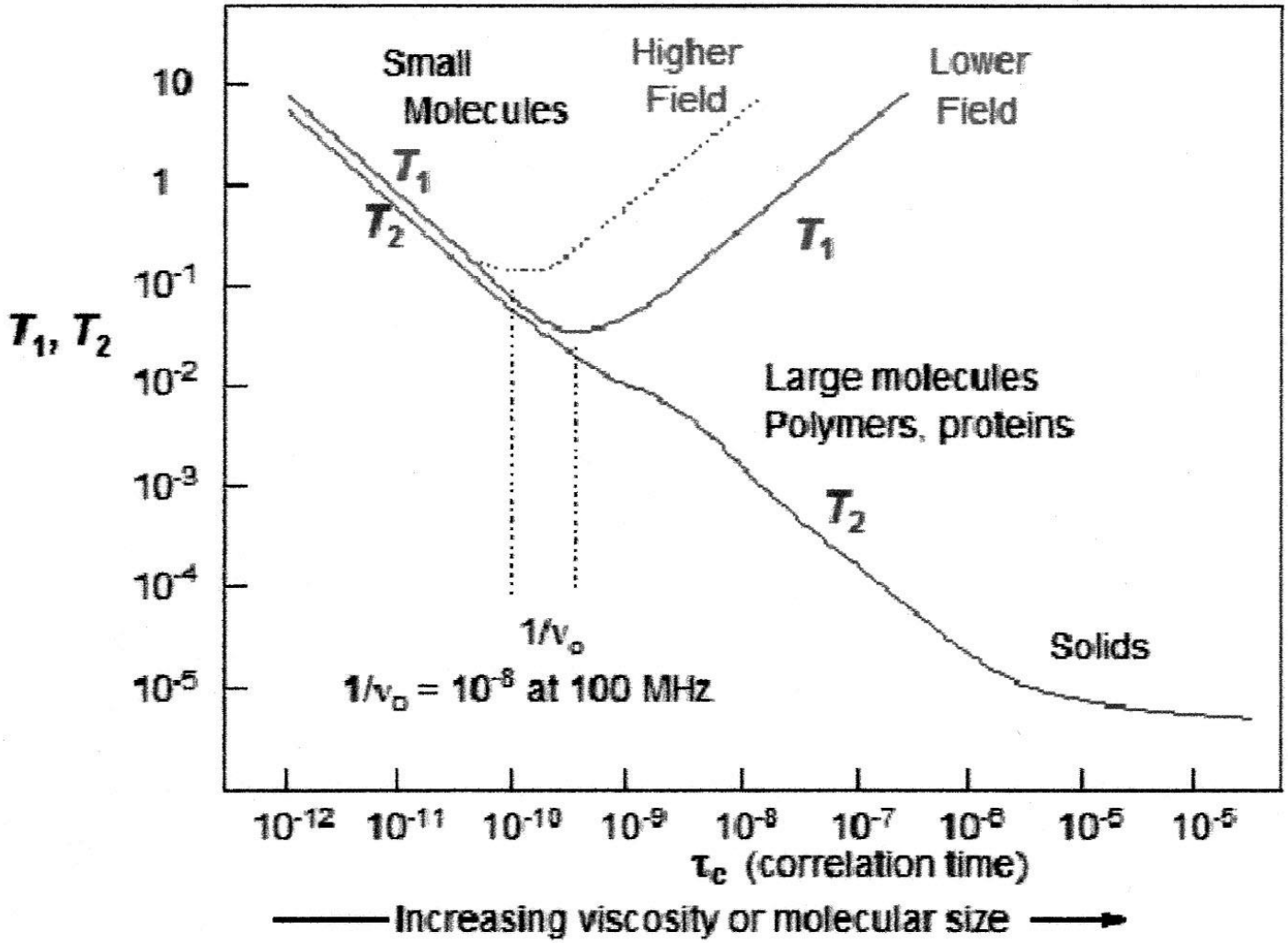
Interaction	Range of interaction (Hz)	Relevant parameters
Dipolar coupling	10^4 - 10^5	- abundance of magnetically active nuclei - size of the magnetogyric ratio $1/T_1 = R_1 = k.\ \gamma_I^2 \ .\ \gamma_S^2 \ .\ (r_{IS})^2 \ .\ f(\tau)$
Quadrupolar coupling	10^6 - 10^9	- size of quadrupolar coupling constant - electric field gradient at the nucleus
Paramagnetic	10^7 -10^8	concentration of unpaired electrons (paramagnetic impurities)
Scalar coupling	10 - 10^3	size of the scalar coupling constant (interacting nuclei with close frequency)
Chemical shift anisotropy (CSA)	10 - 10^4	- size of the chemical shift anisotropy - symmetry at the nuclear site
Spin rotation		Intramolecular dynamic process. Most effective for small, symetrical molecules, or freely rotation methyl groups. $1/T_1 = R_1 \uparrow$ with T $\uparrow$ Coupling of the nuclear spin angular momentum with the molecular rotation angular momentum.

Bloch equations

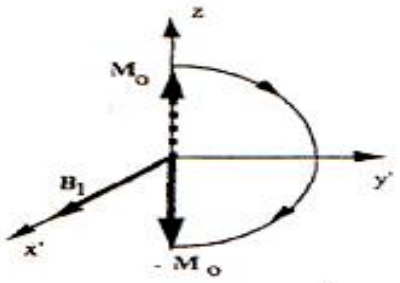
$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}$$

$$\frac{dM_{X(Y)}}{dt} = \frac{M_{X(Y)}}{T_2}$$

Variation of T_1 and T_2 against viscosity or molecular size

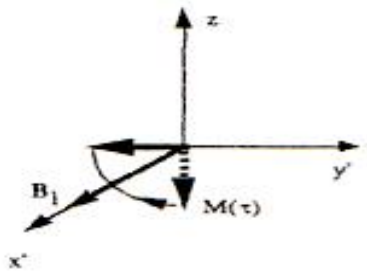


Measurement of T_1 with 180°, τ, 90° sequences



t = 0 + ε

Figure (a)



t = τ

Figure (b)

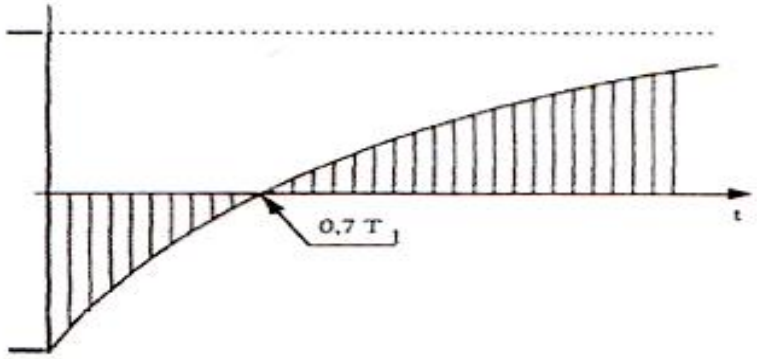
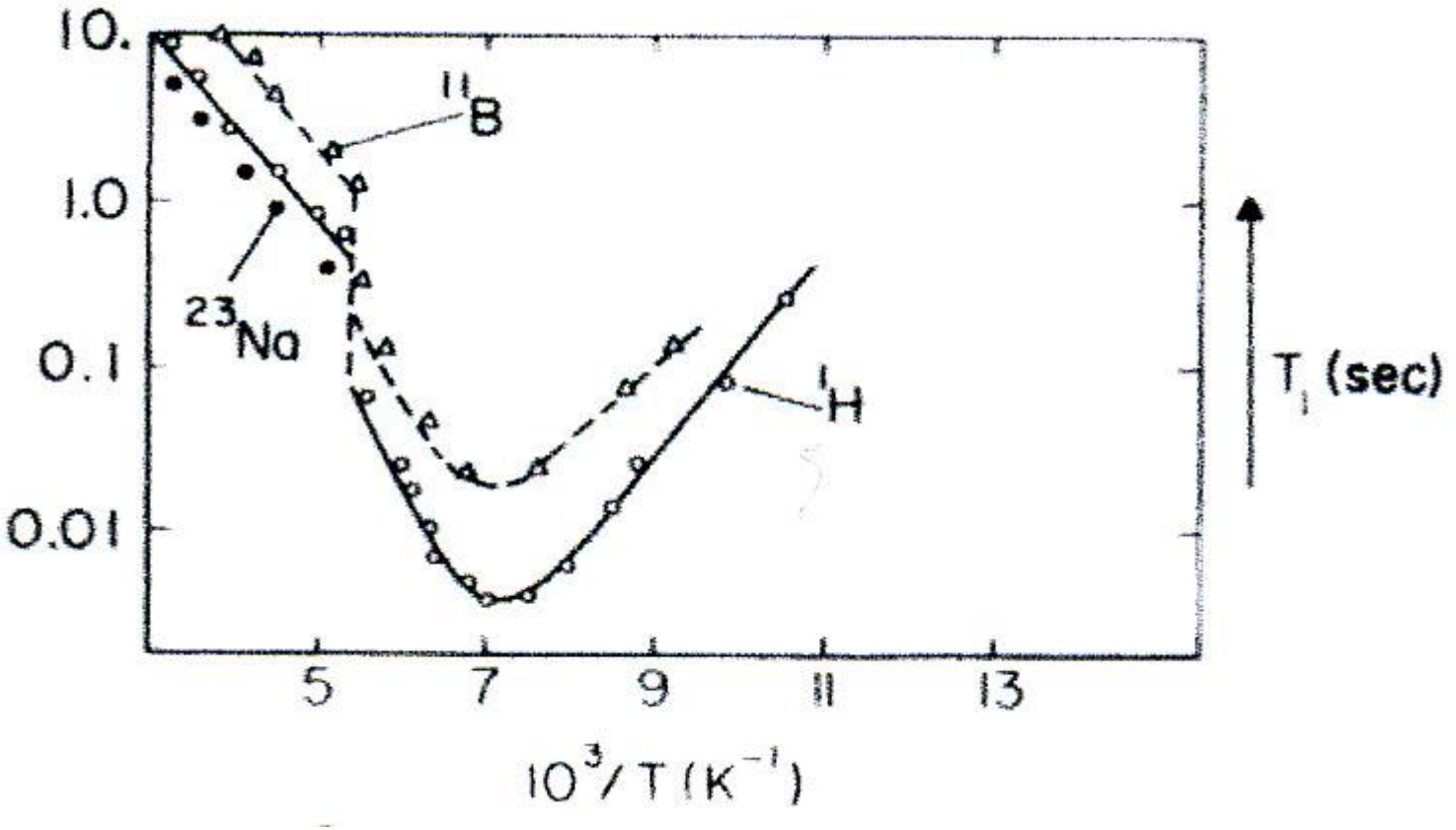


Figure (c)

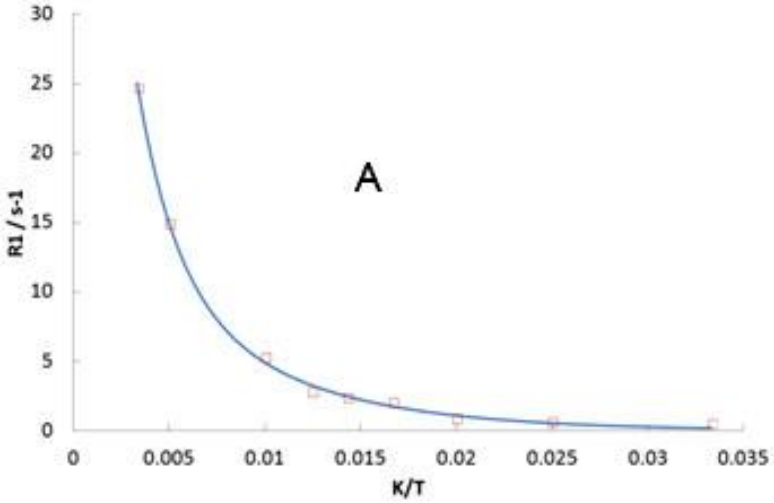
a) M is inverted by a 180° pulse at time 0; b) After a time τ a 90° rotates M to the Y' (or –Y') axis. c) the amplitude of the FID after the 90°pulse, which is proportional to the amplitude of M at time τ, is plotted as a function of τ.

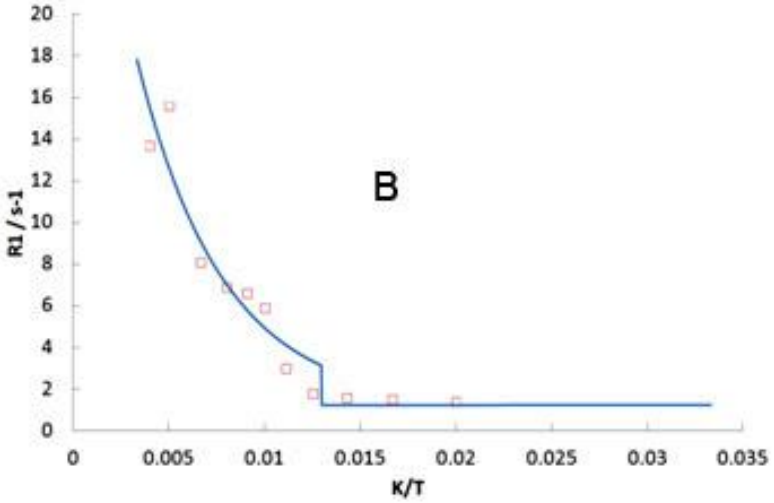
$$dM_z/dt = -(M_z - M_0)/T_1 \quad \Rightarrow M_z = M_0(1 - 2\exp - t/T_1)$$

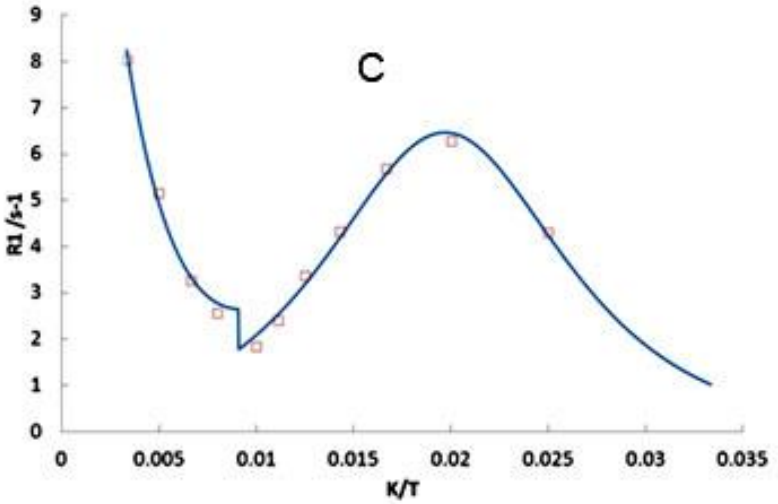
Spin-lattice T_1 in $NaBH_4$ *vs* 1/T showing a phase transition at about 190°K

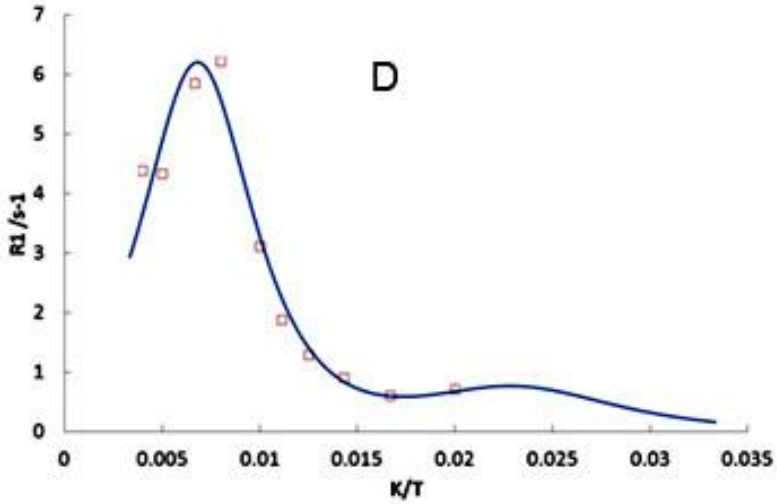


Relaxation rate R1 *versus* T-1. A- SBA-80: spin-rotation;
B- Zeolite Omega:spin-rotation + dipolar contribution (cut-off 77K)
C- Zeolite ZSM5: spin-rotation + dipolar contribution (cut-off 110K) ;
D- Zeolite Rho: two dipolar contributions









Relaxation due to dipolar interaction (spins ½)

$$\frac{1}{T_1} = K\left[\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right]$$

$$\frac{1}{T_2} = \frac{K}{2}\left[3\tau_c + \frac{5\tau_c}{1+\omega_0^2\tau_c^2} + \frac{2\tau_c}{1+4\omega_0^2\tau_c^2}\right]$$

$K = f(\tau_c, \gamma, \omega_0, r^{-6})$

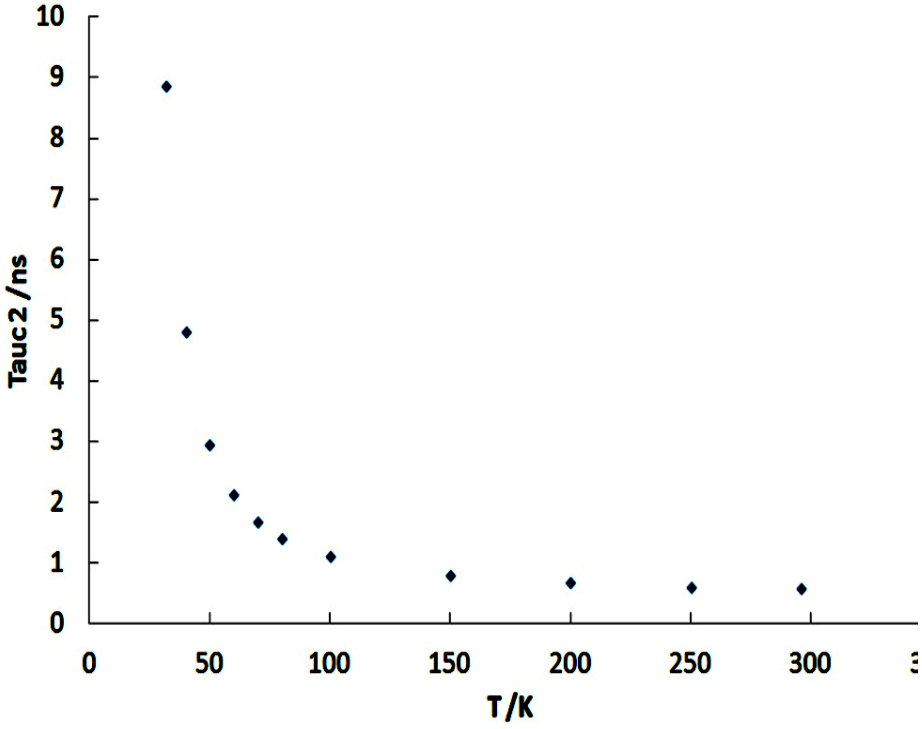
ω_0 = Larmor frequency

τ_c = correlation time of the tumbling motion

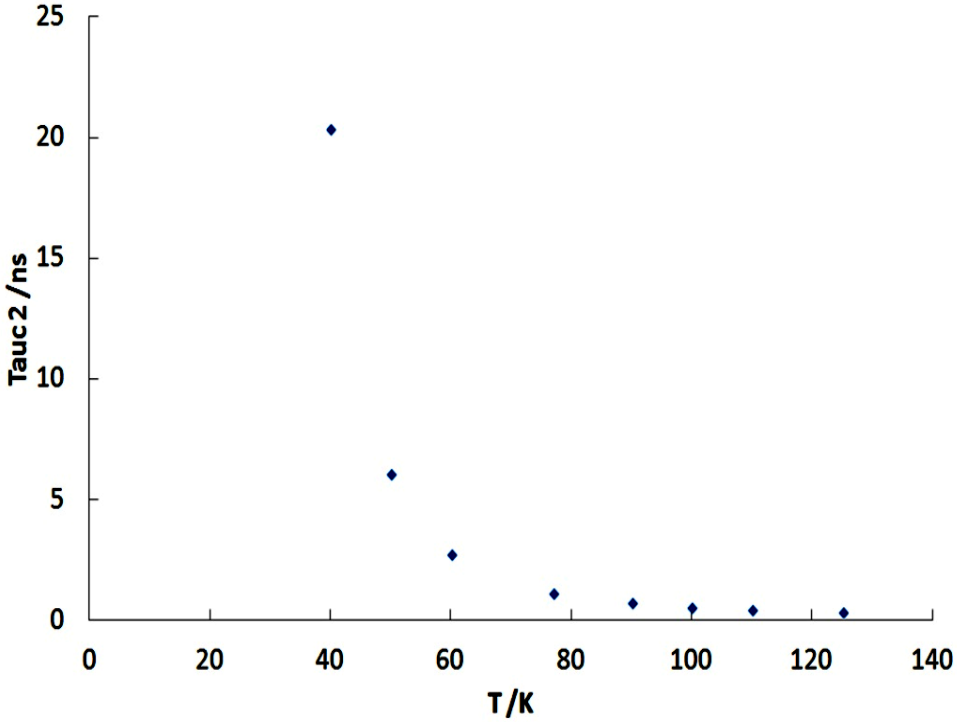
γ = gyromagnetic ratio

The dipolar correlation time of the N_2 molecule *versus* T within

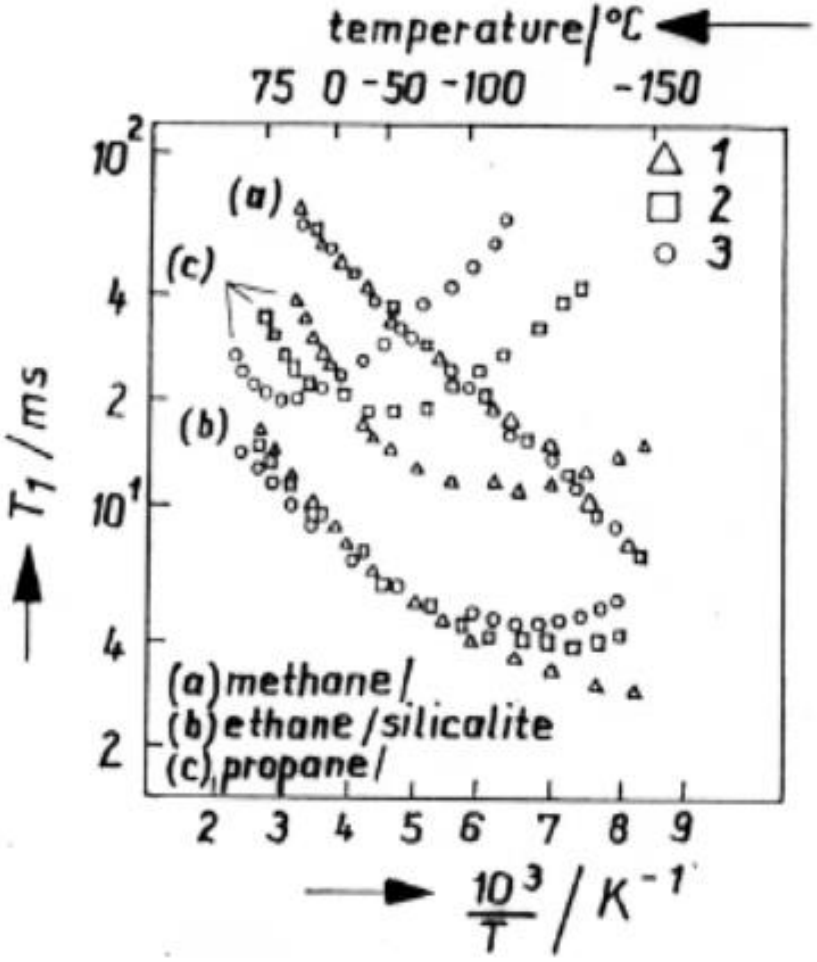
Y

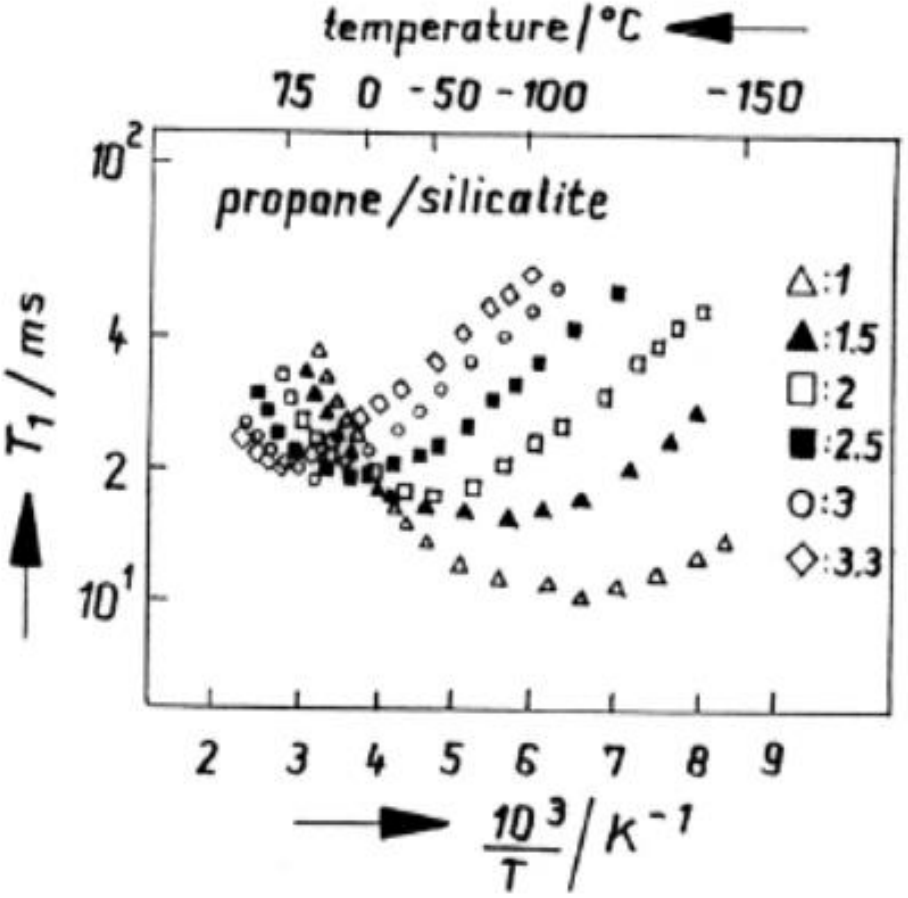


mordenite



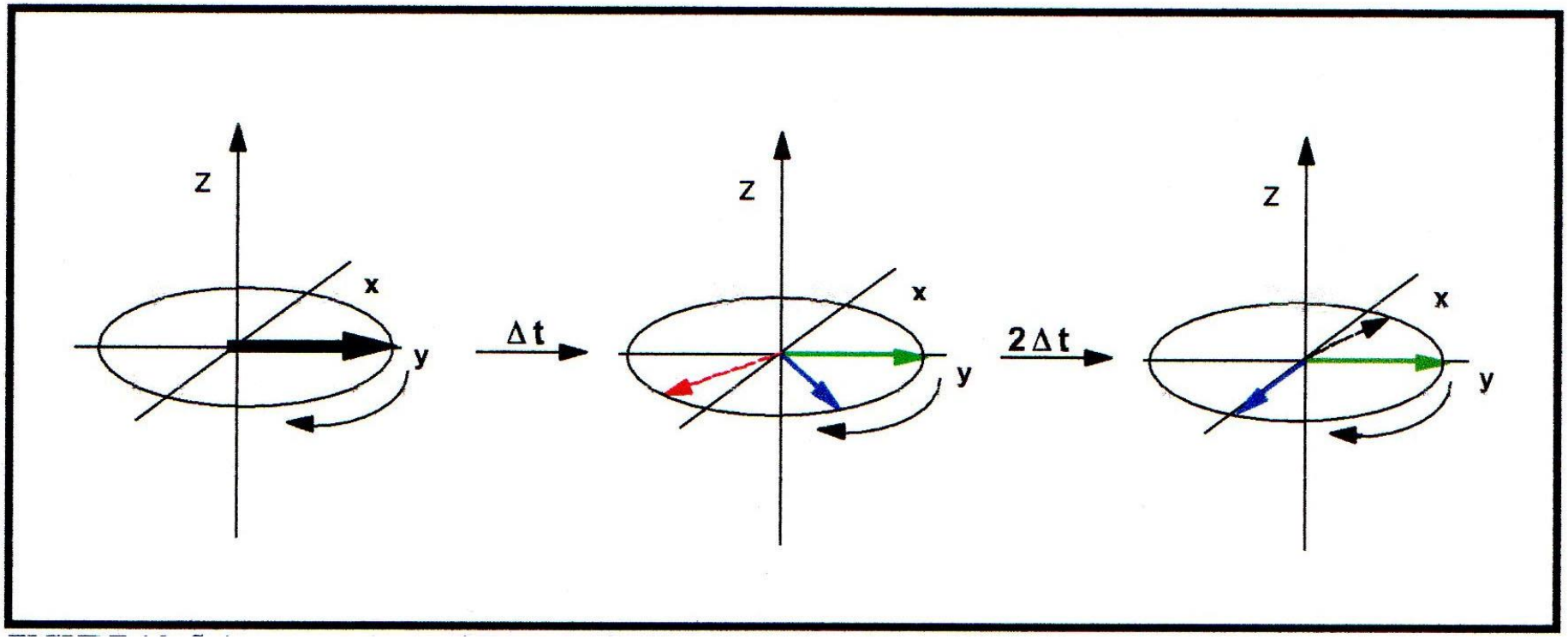
Variation of T1 versus 1/T of adsorbed molecules
a:methane; b:ethane; c:propane
1Δ, 2□, 3 o molecules / channel interaction





- Hahn Spin-echo

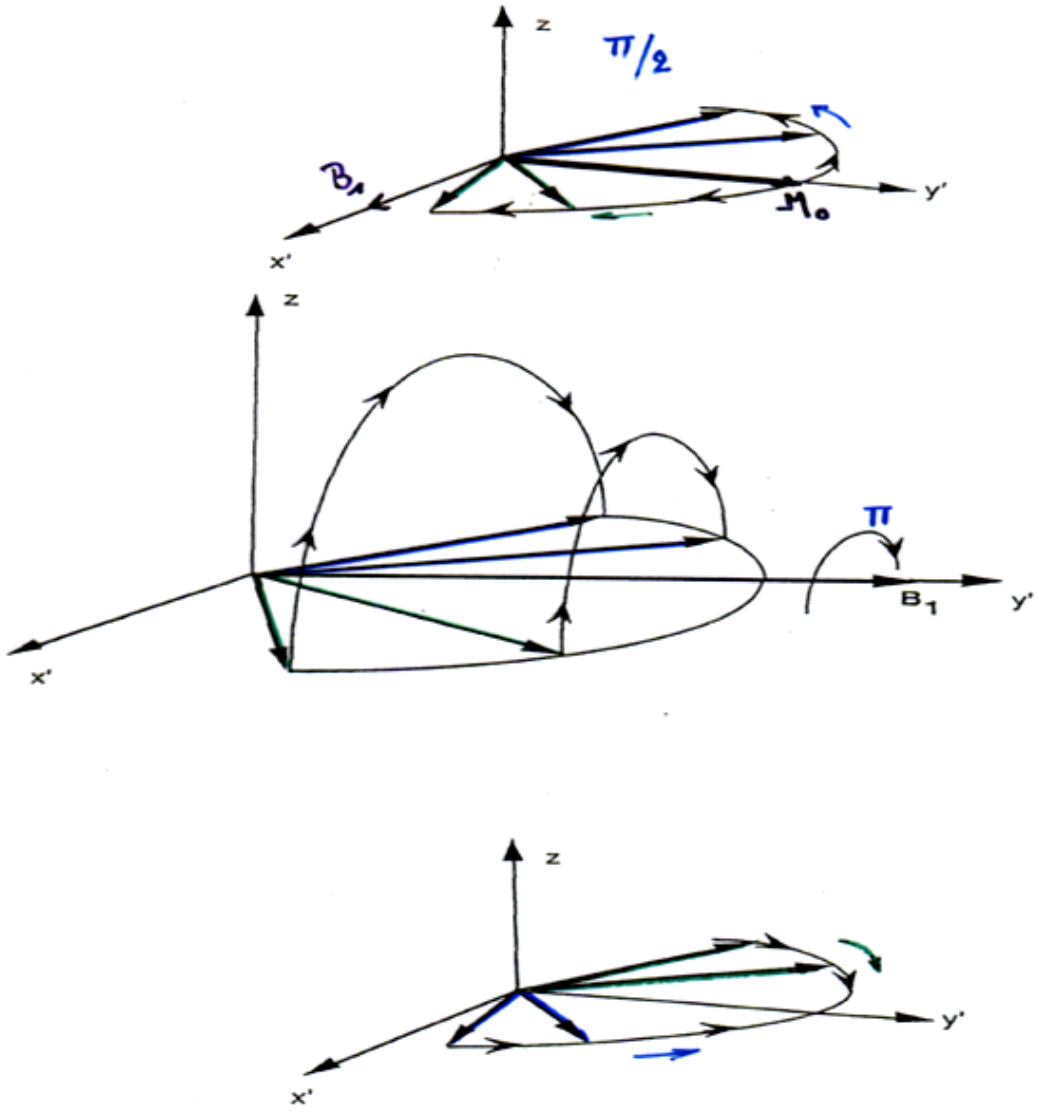
Spins processing at different velocities because of different chemical shits are color coded



When a rabbit and a turtle run in one direction for a certaine time, then turn around and run in the opposite direction with the same speed for the same time they will arrive at the starting point at the same time.

VID_20170517_151507_815.mp4

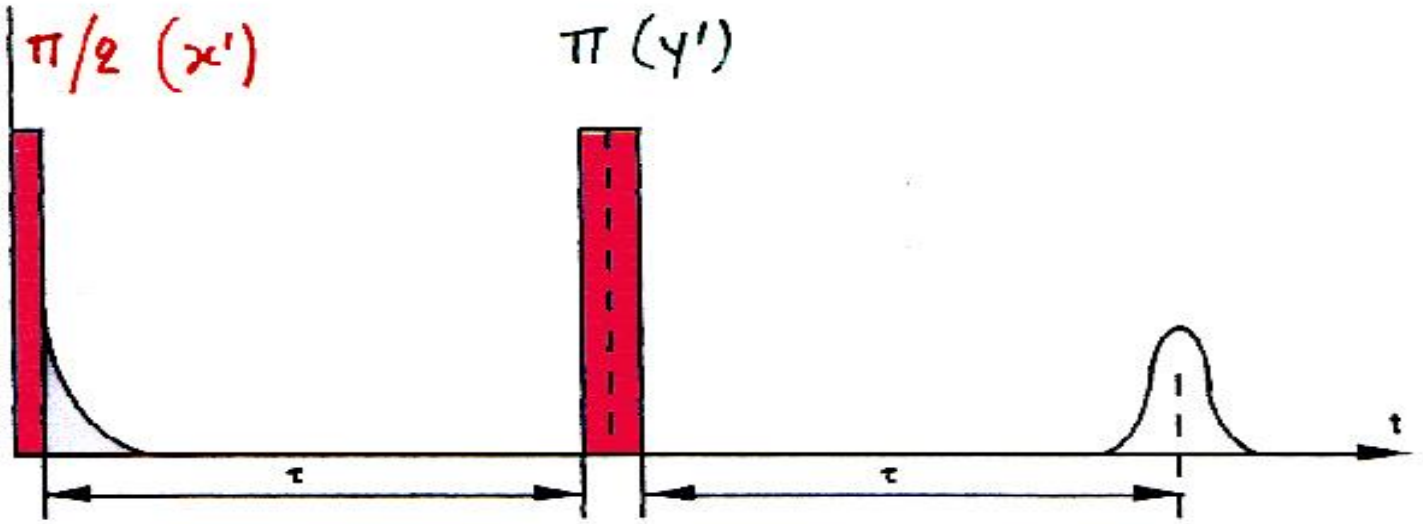
Hahn spin-echo experiment



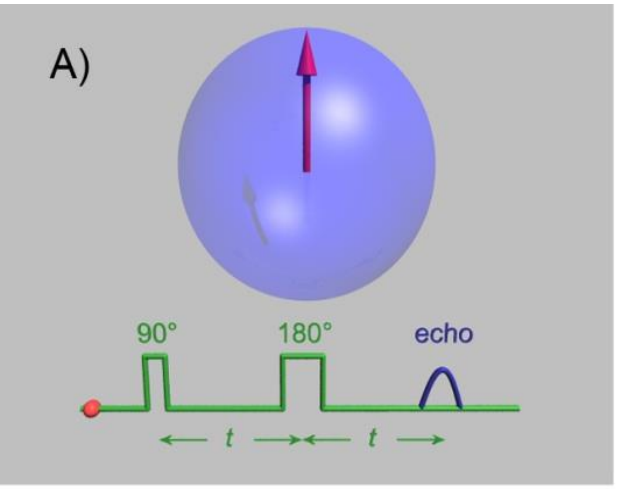
Hahn spin-echo experiment

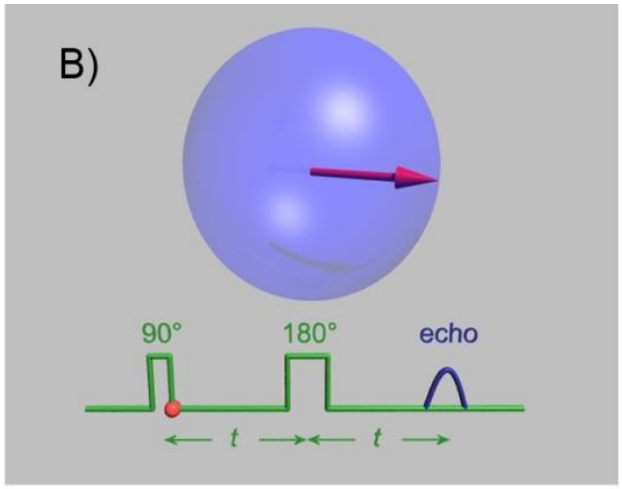
The distribution of the spin in the X'OY' plan after a pulse $\pi/2$ is due to the spin-spin interactions but also to the inhomogeneity of B_0. The spin-echo experiment overcomes the inhomogeneity problem. In addition it is used for several applications of NMR.

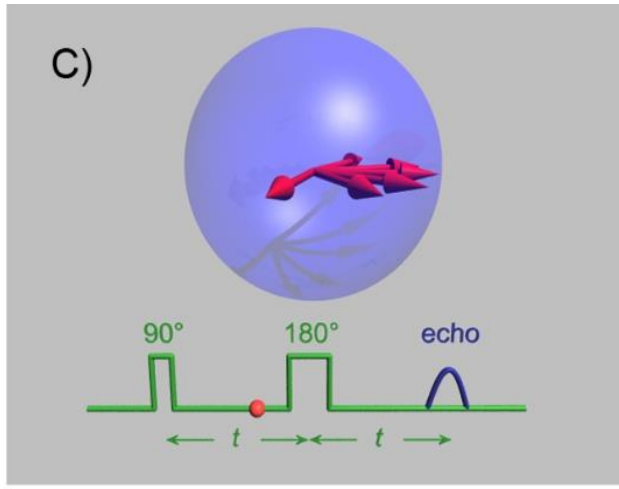
90°, τ, 180° sequence , and observation at time 2τ of a free induction "echo".

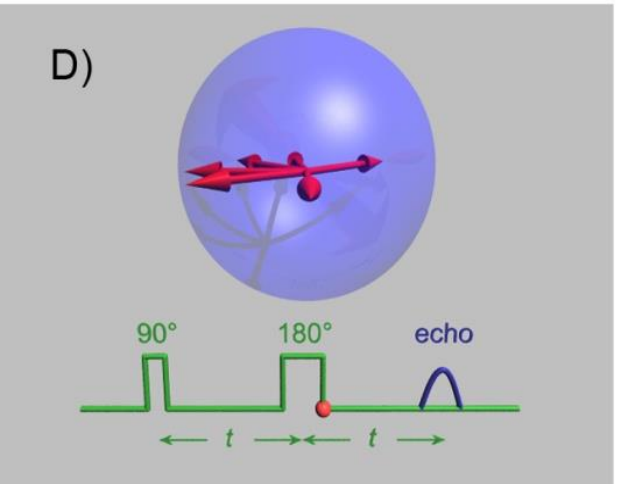


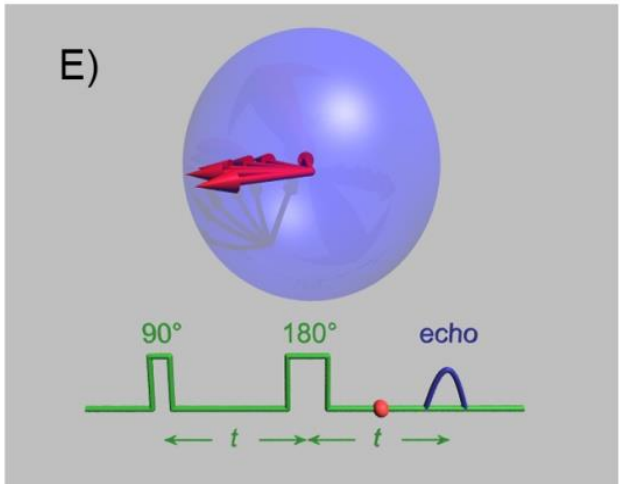
Spin-echo experiment

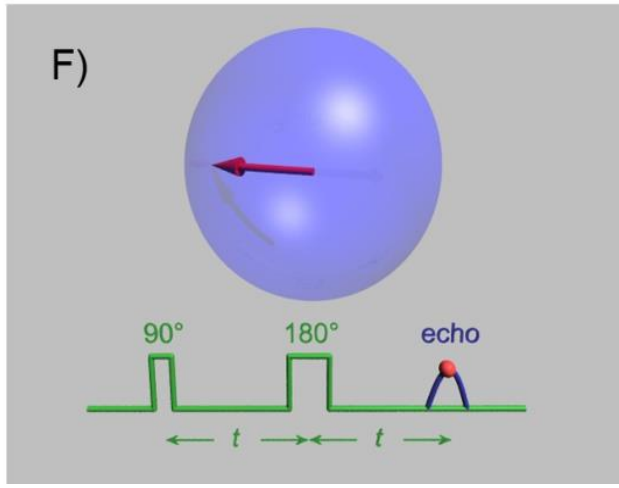




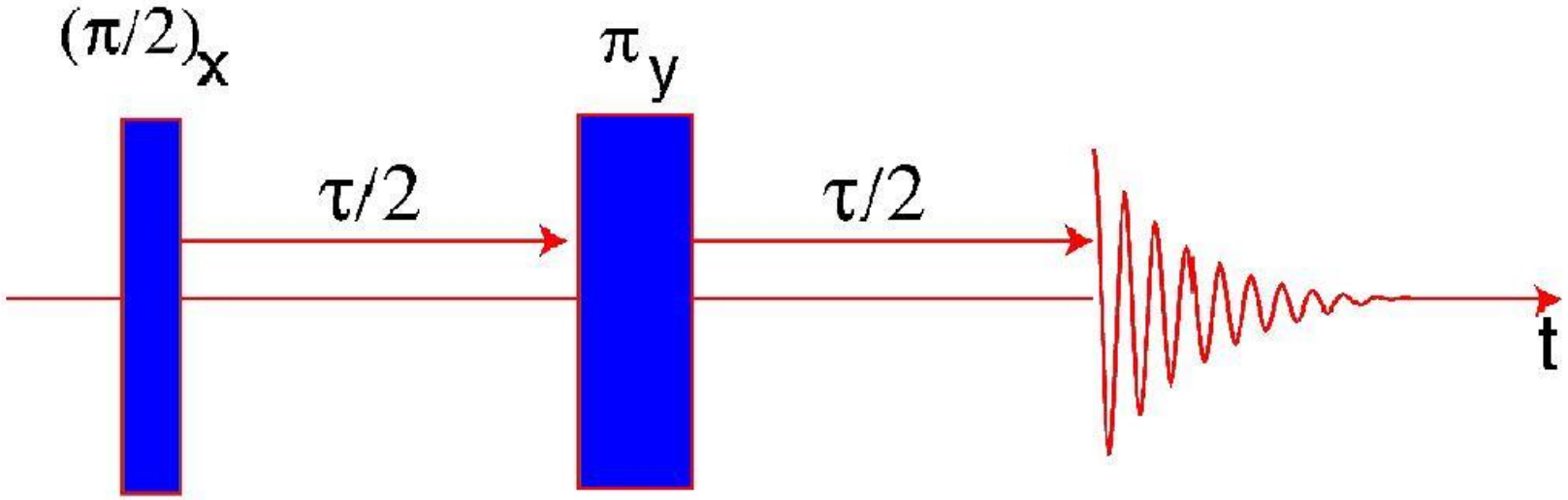








Spin-echo experiment



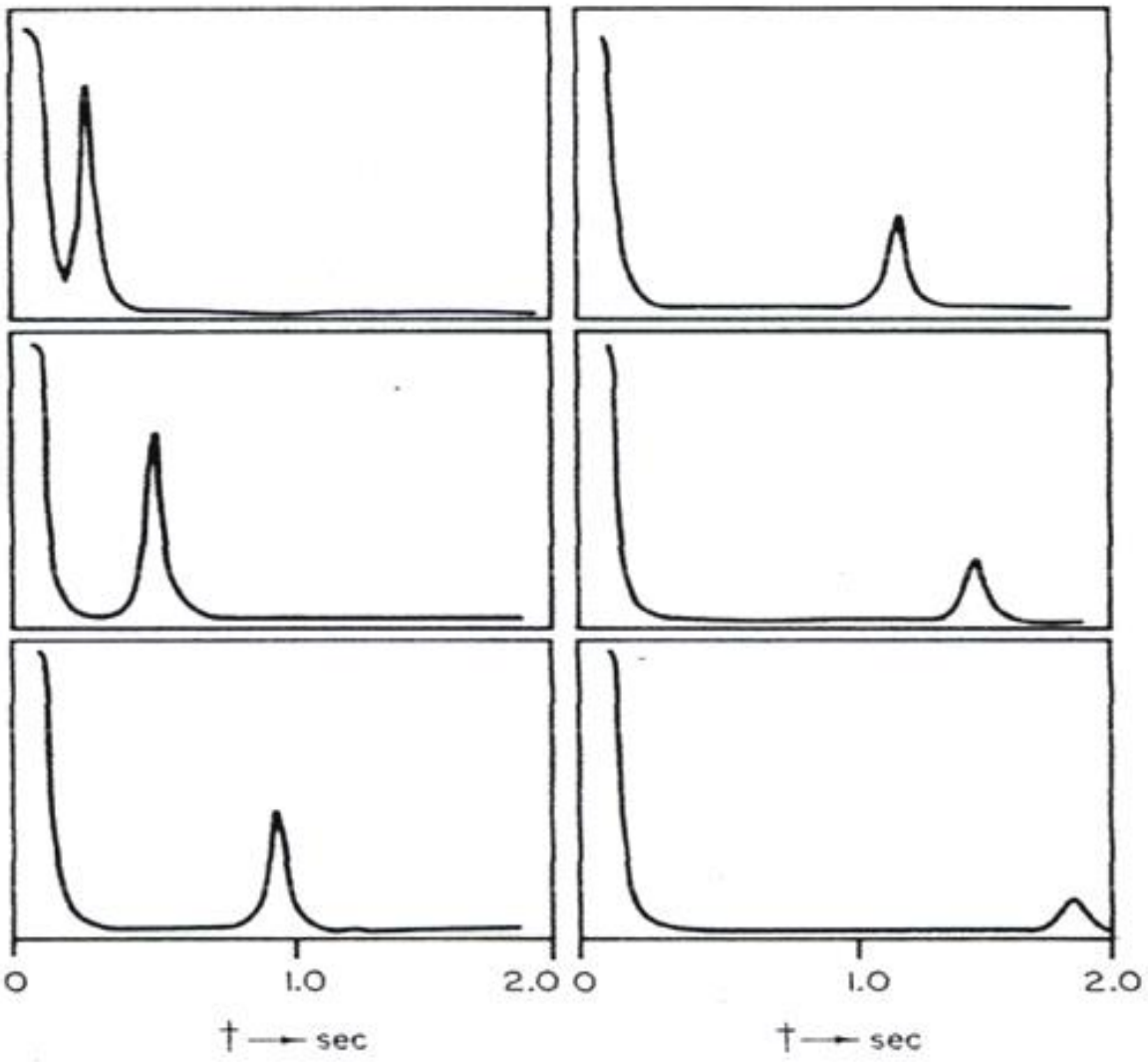
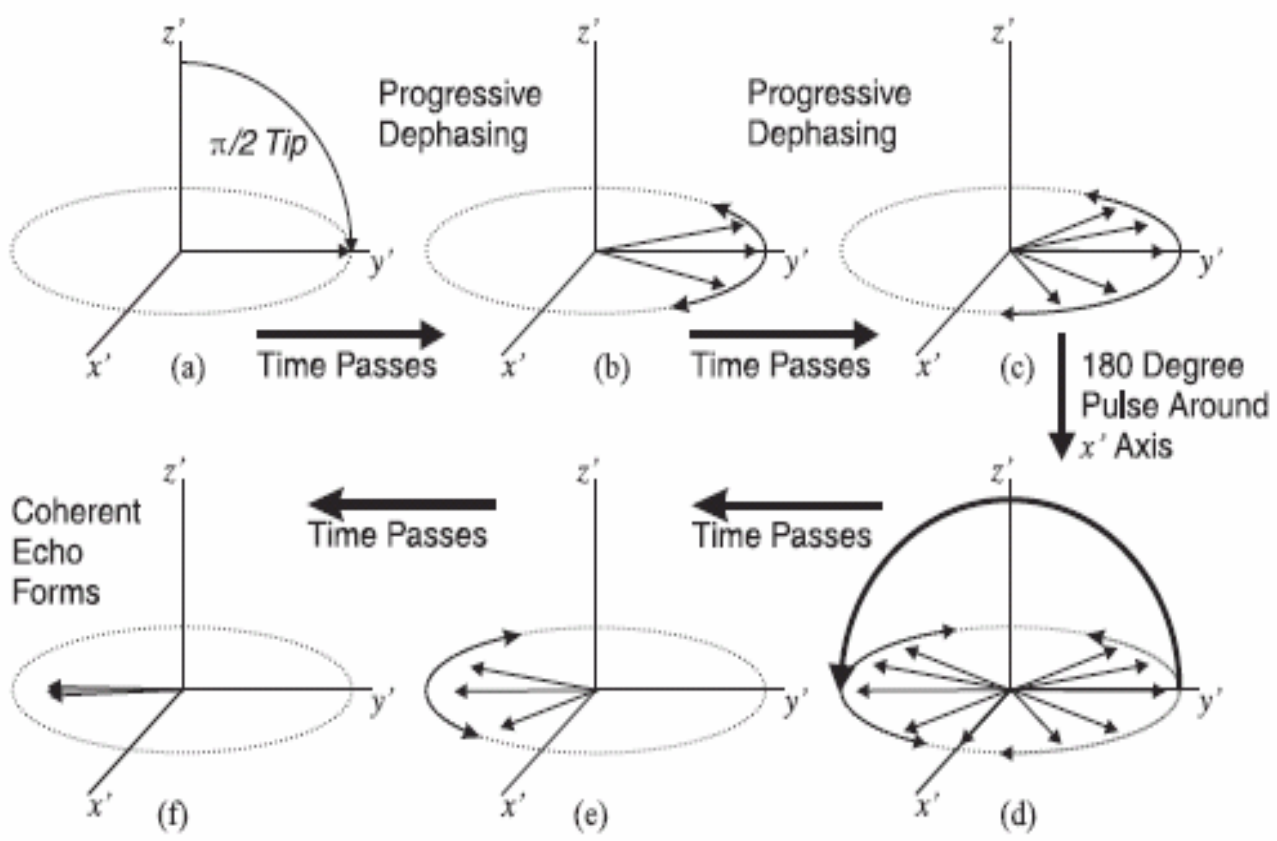
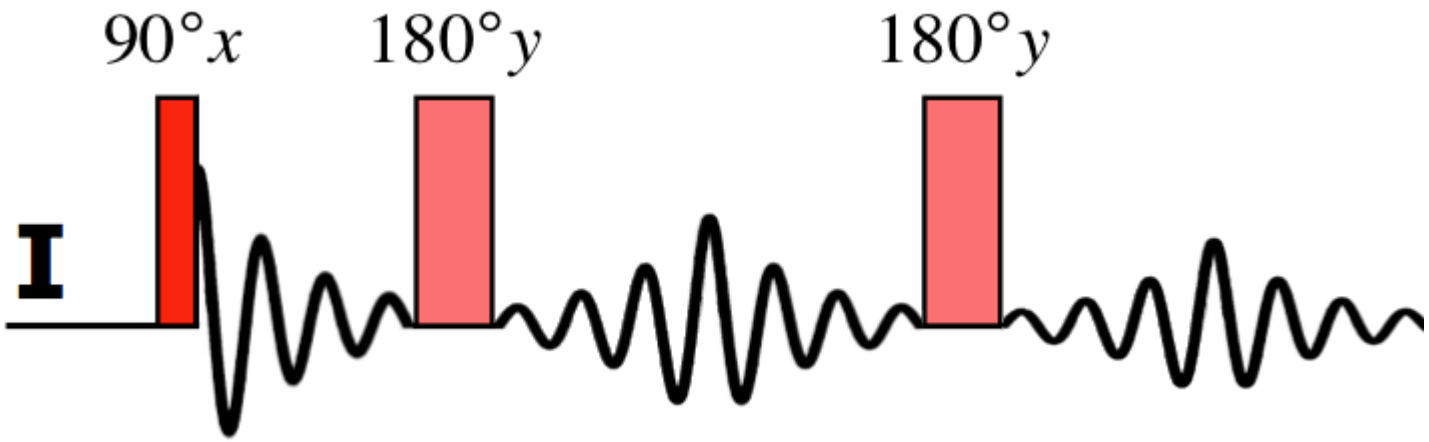


Figure 2.5. A typical Hahn spin-echo experiment, consisting of six 90°, τ, 180° sequences, with τ varying from 0.1–1 sec. Note that the amplitude of the echo decreases as τ increases. In this experiment the echoes are positive, rather than negative as expected, since a diode detector was used, which measures only amplitude, not phase of the signal. (See Chapter 3 for further details on detectors.)

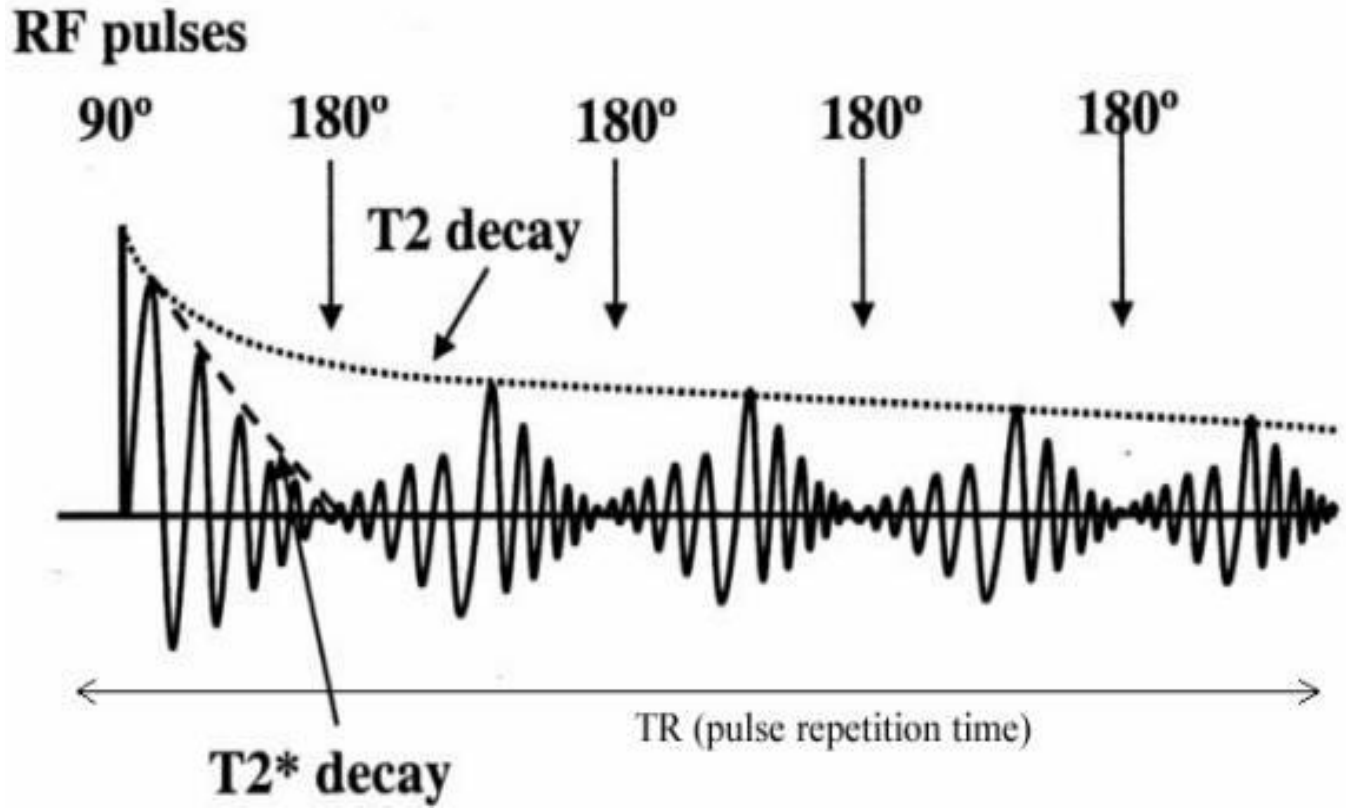
Carr Purcell sequence



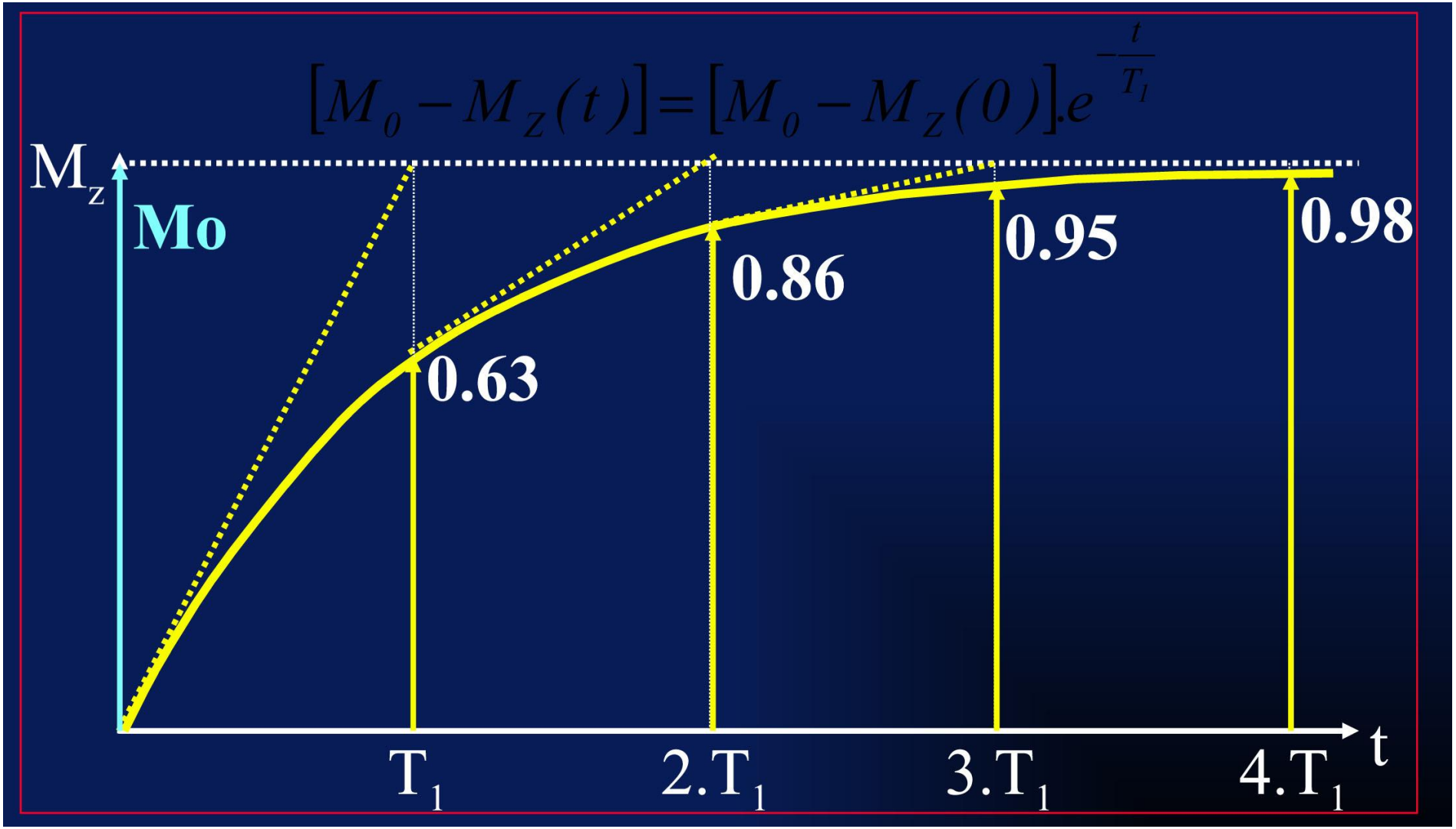
Carr- Purcell sequence

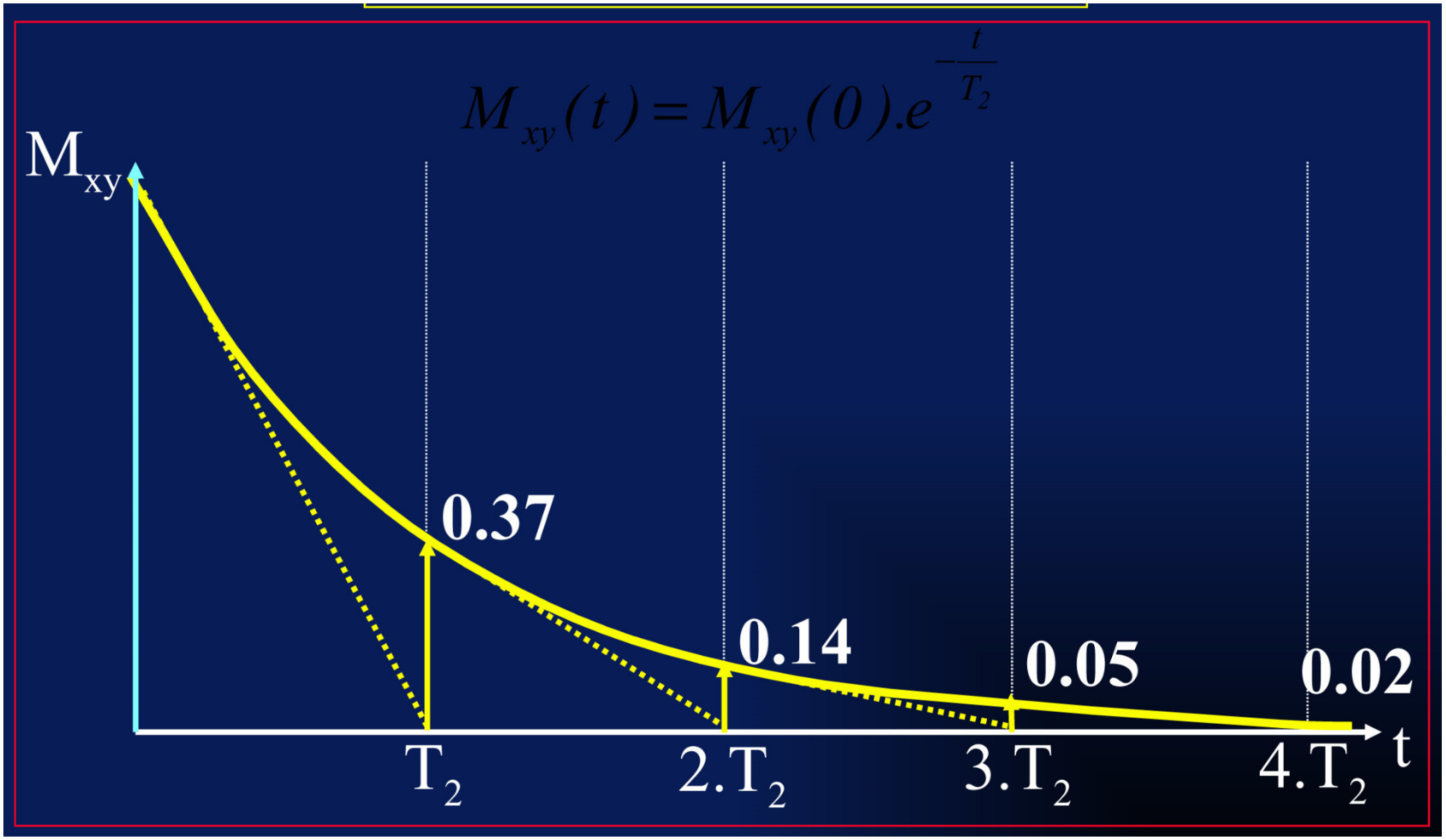


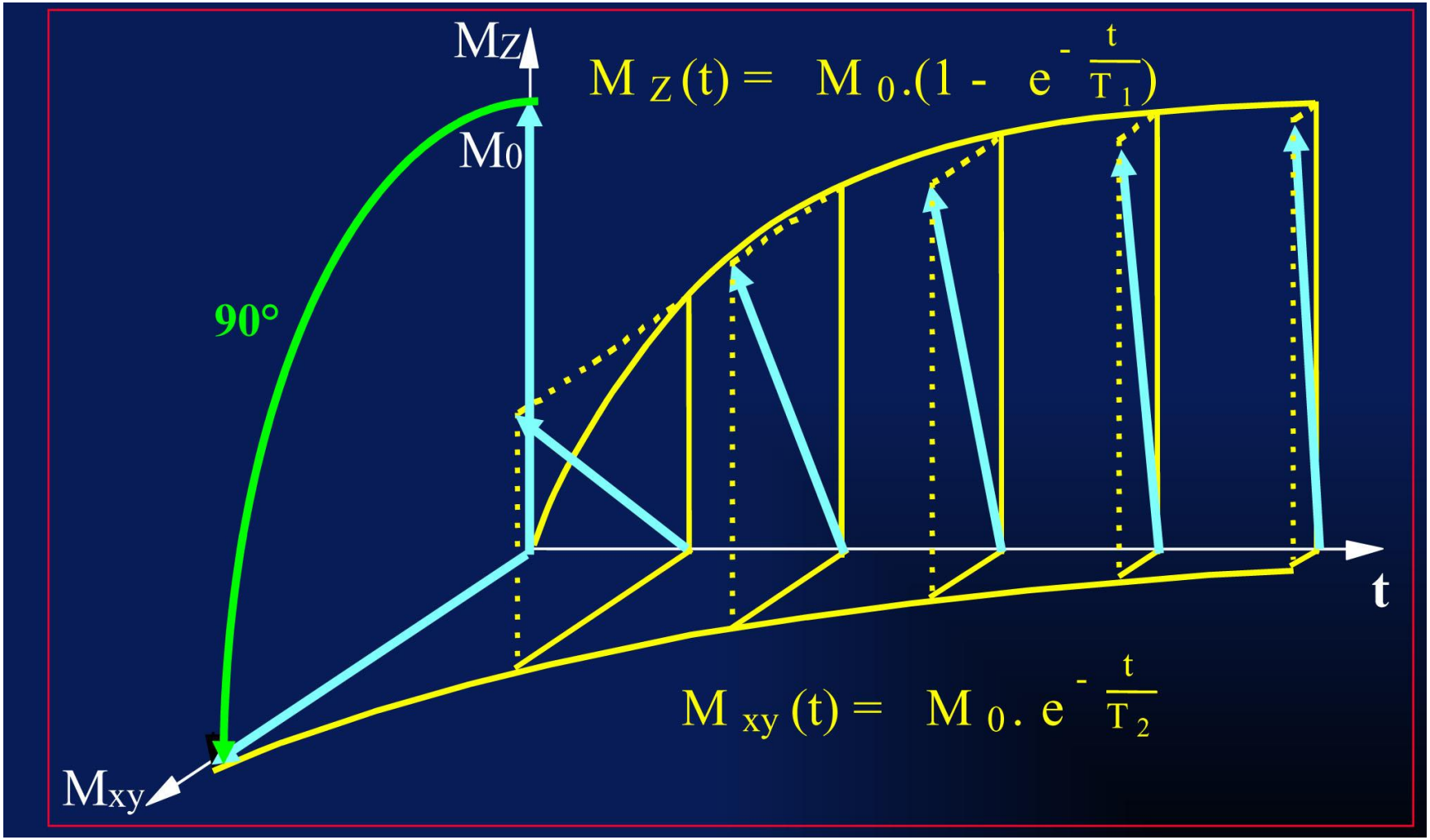
Carr-Purcell sequence



- End of the first part


$[M_0 - M_Z(t)] = [M_0 - M_Z(0)].e^{-\frac{t}{T_1}}$
M_z
Mo
0.63
0.86
0.95
0.98
t
T_1
$2.T_1$
$3.T_1$
$4.T_1$


$M_{xy}(t) = M_{xy}(0).e^{-\frac{t}{T_2}}$
M_{xy}
0.37
0.14
0.05
0.02
T_2
$2.T_2$
$3.T_2$
$4.T_2$
t


Mz
M0
90°
Mxy
t
$M_z(t) = M_0.(1 - e^{-\frac{t}{T_1}})$
$M_{xy}(t) = M_0 . e^{-\frac{t}{T_2}}$