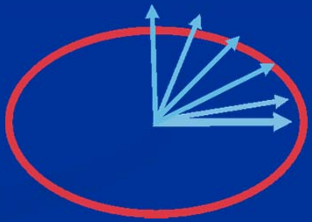
Relaxation Times

Relaxation = return to equilibrium (Boltzmann) after a pulse, redistribution of energy

Relaxation can be described for isolated spins by the Bloch Equations, the total relaxation is determined by two characteristic time constants:

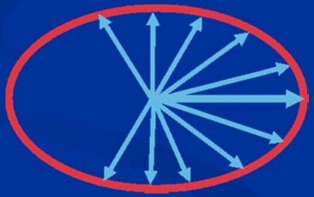
T_1

Longitudinal, Spin-Lattice Relaxation
Build up of longitudinal magnetisation via energy exchange between spins and their environment („lattice“)
enthalpy



T_2

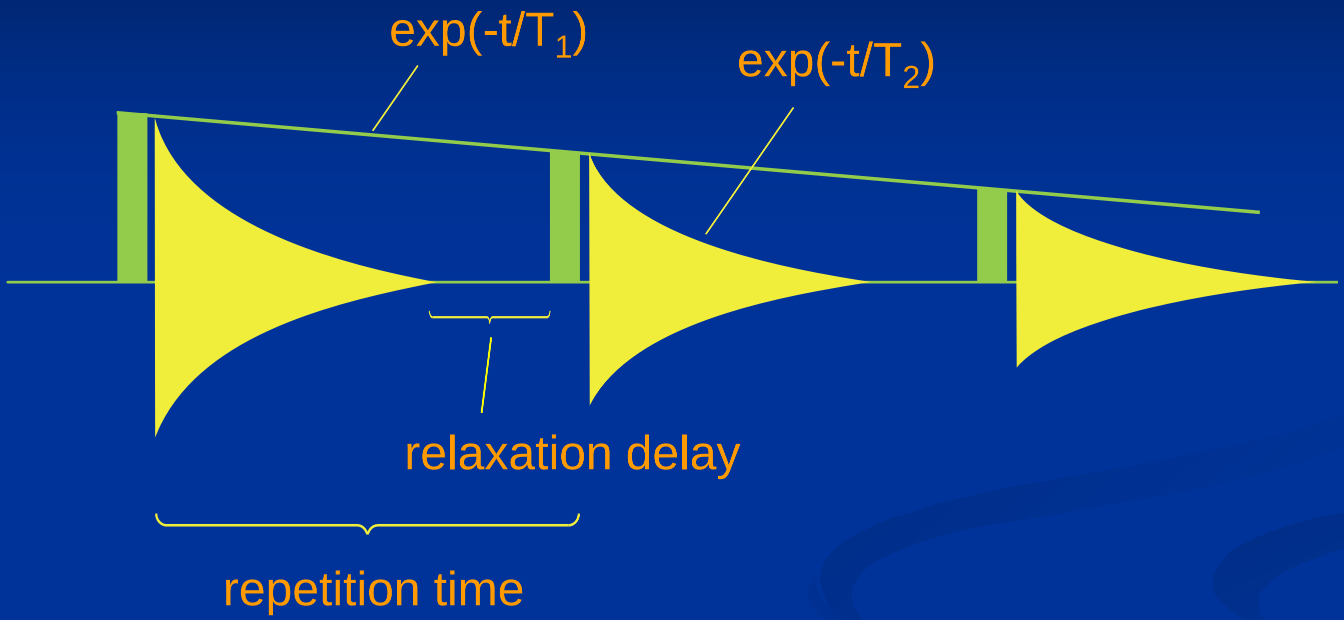
Transversal, Spin-Spin Relaxation
Dephasing of transversal magnetisation without energy exchange between spins and their environment, entropy



Two important relations between T_1 and T_2 :

- T_2 cannot be longer than T_1 : $T_2 \leq T_1$
- In the „extreme narrowing limit“: $T_2 = T_1$

T_1 and T_2 in Data Acquisition

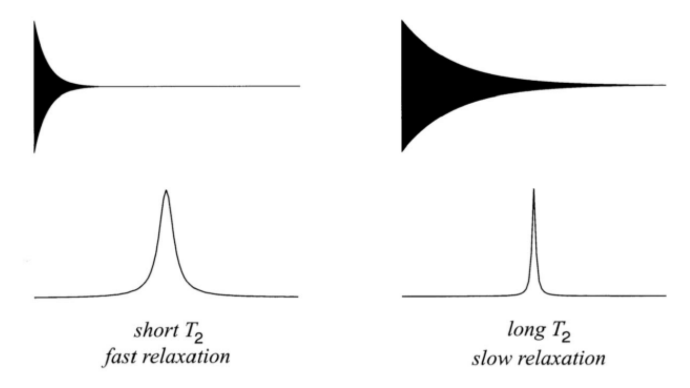


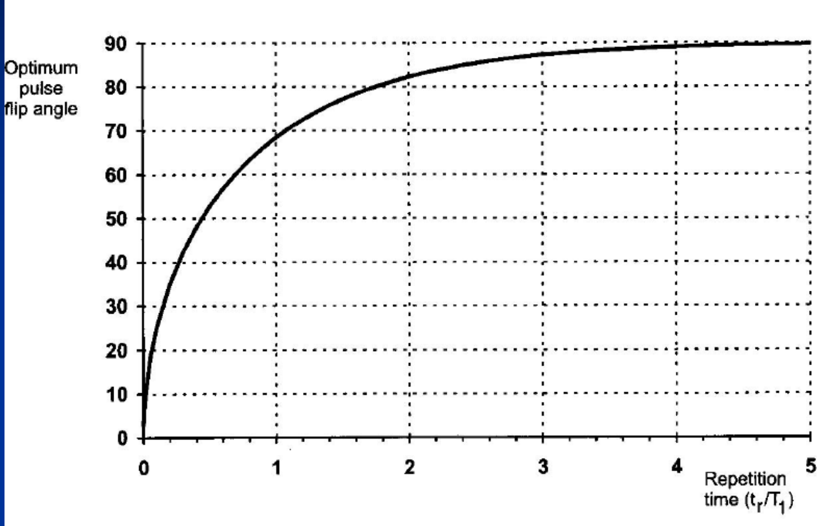
T_1 governs the repetition frequency for subsequent transients (scans)
Relaxation delay = 5 T_1

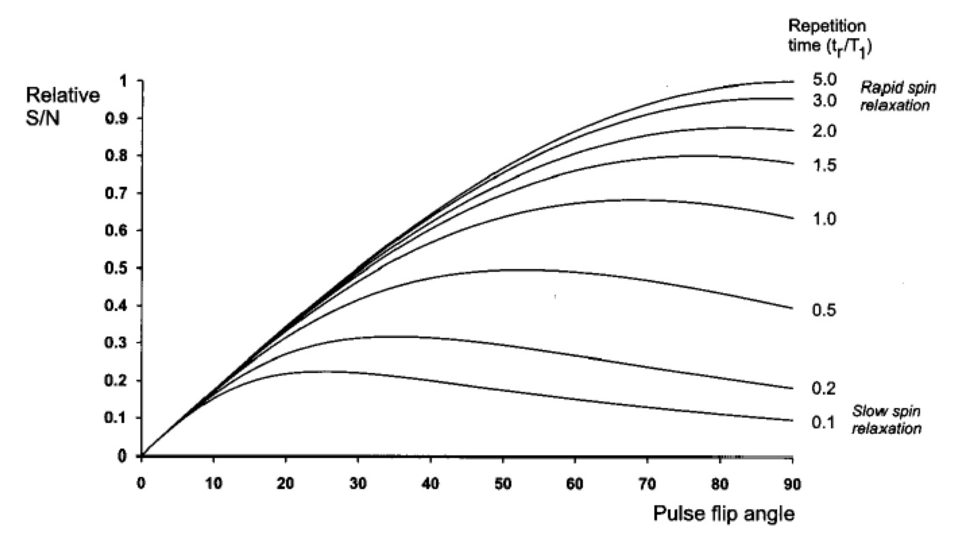
T_2 governs the decay time constant of individual FID's

Optimum sensitivity of the NMR experiment is obtained if $T_1 = T_2$

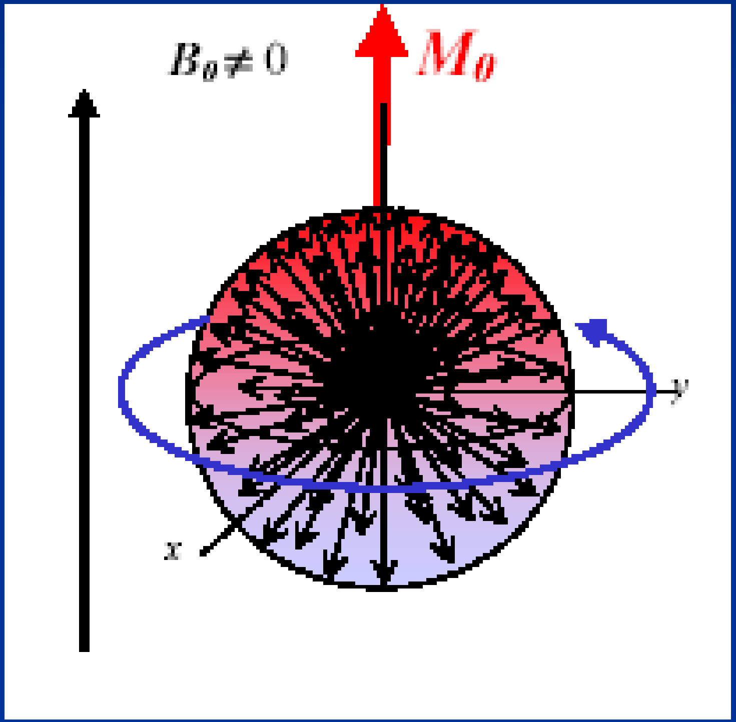
T_1 and T_2 in Data Acquisition







Magnetization

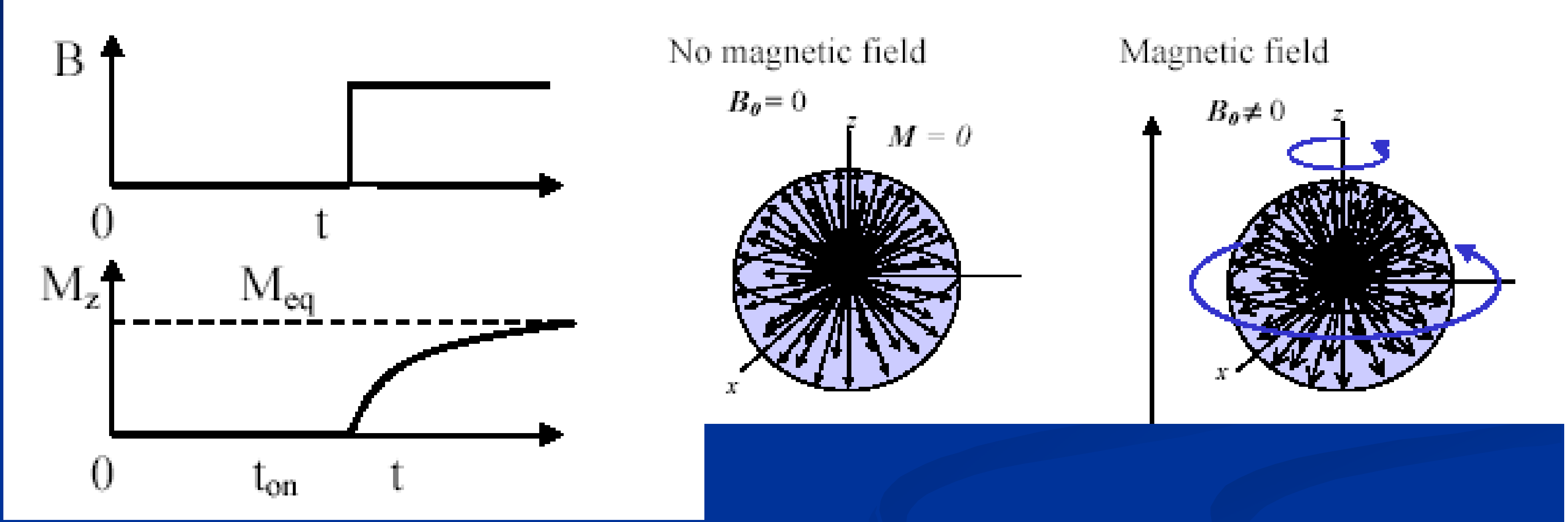


In-Field

More nuclei point in parallel to the static magnetic field.
The macroscopic magnetic moment, M_0

$$M_0 = \Sigma\ \mu_i$$

Longitudinal Magnetization



$$\frac{d}{dt}M_Z = R_1(M_{eq} - M_z) = \frac{1}{T_1}(M_{eq} - M_z)$$

$$M_z(t) = M_{eq}(1 - e^{\frac{-(t-t_{on})}{T_1}})$$

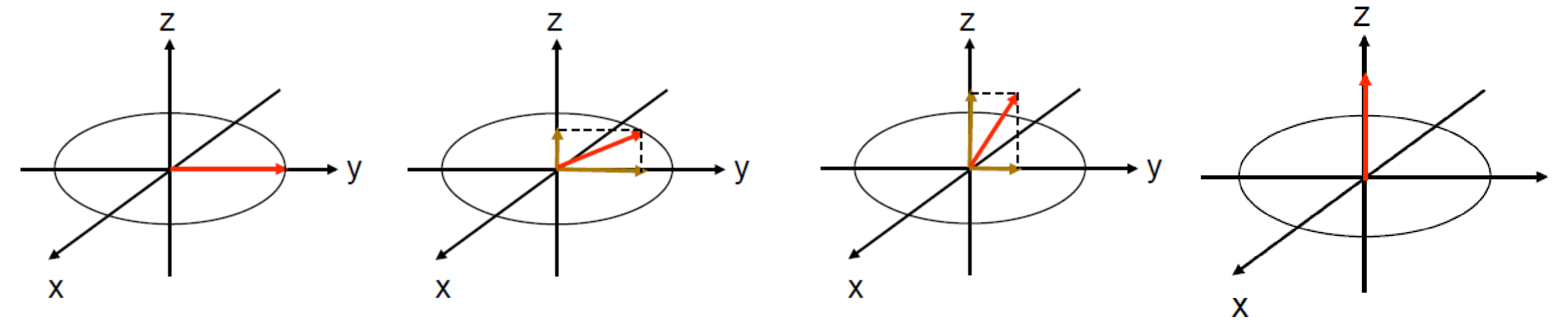
Spin-Lattice Relaxation Time

$R_1 = 1/T_1$ [Hz] longitudinal relaxation rate constant

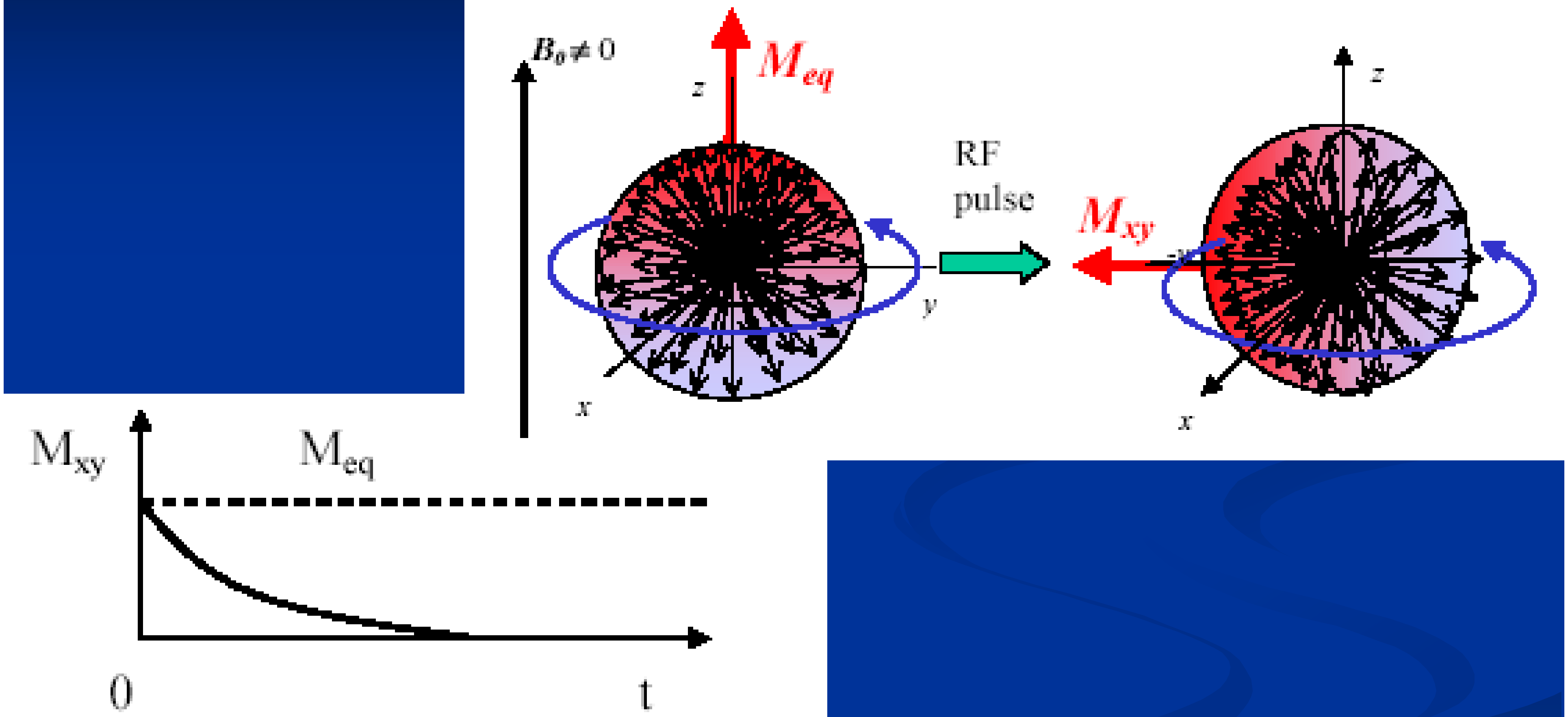
T_1 [s] longitudinal relaxation time

spin-lattice relaxation time

enthalpy



Transverse Magnetisation



$$\frac{d}{dt}M_{xy} = -R_2 M_{xy} = \frac{-1}{T_2}M_{xy} \quad M_{xy}(t) = M_{eq}e^{\frac{-t}{T_2}}$$

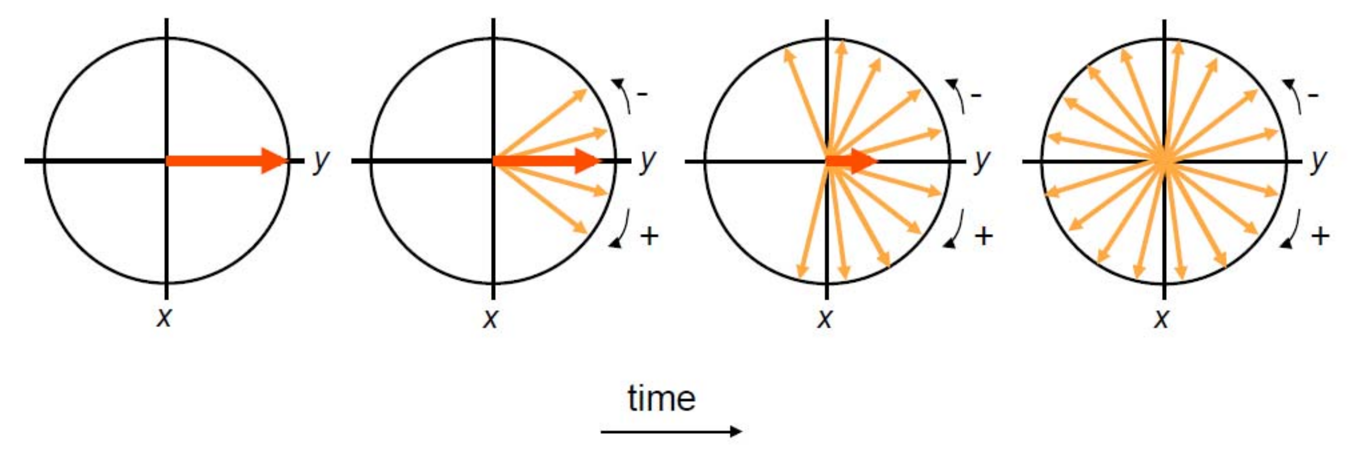
Spin-Spin Relaxation Time

$R_2 = 1/T_2$ [Hz] transverse relaxation rate constant

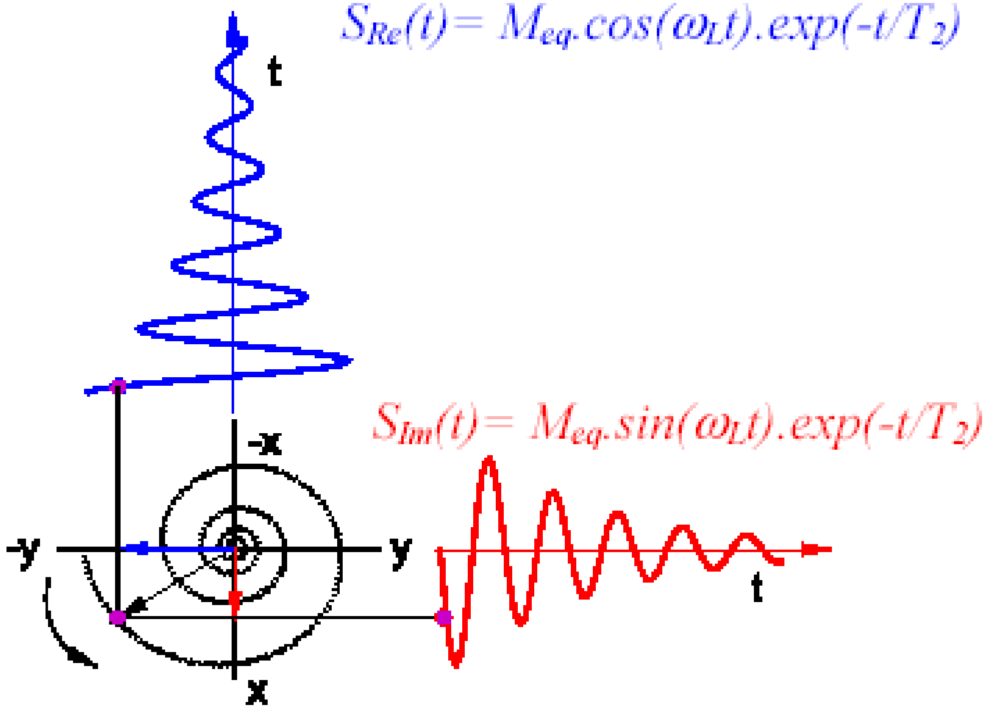
T_2 [s] transverse relaxation time constant

spin-spin relaxation time

entropy



Free Induction Decay FID



$S_{Re}(t) = M_{eq}.\cos(\omega_L t).\exp(-t/T_2)$

$S_{Im}(t) = M_{eq}.\sin(\omega_L t).\exp(-t/T_2)$

$S(t) = S_{Re}(t) + iS_{Im}(t)$

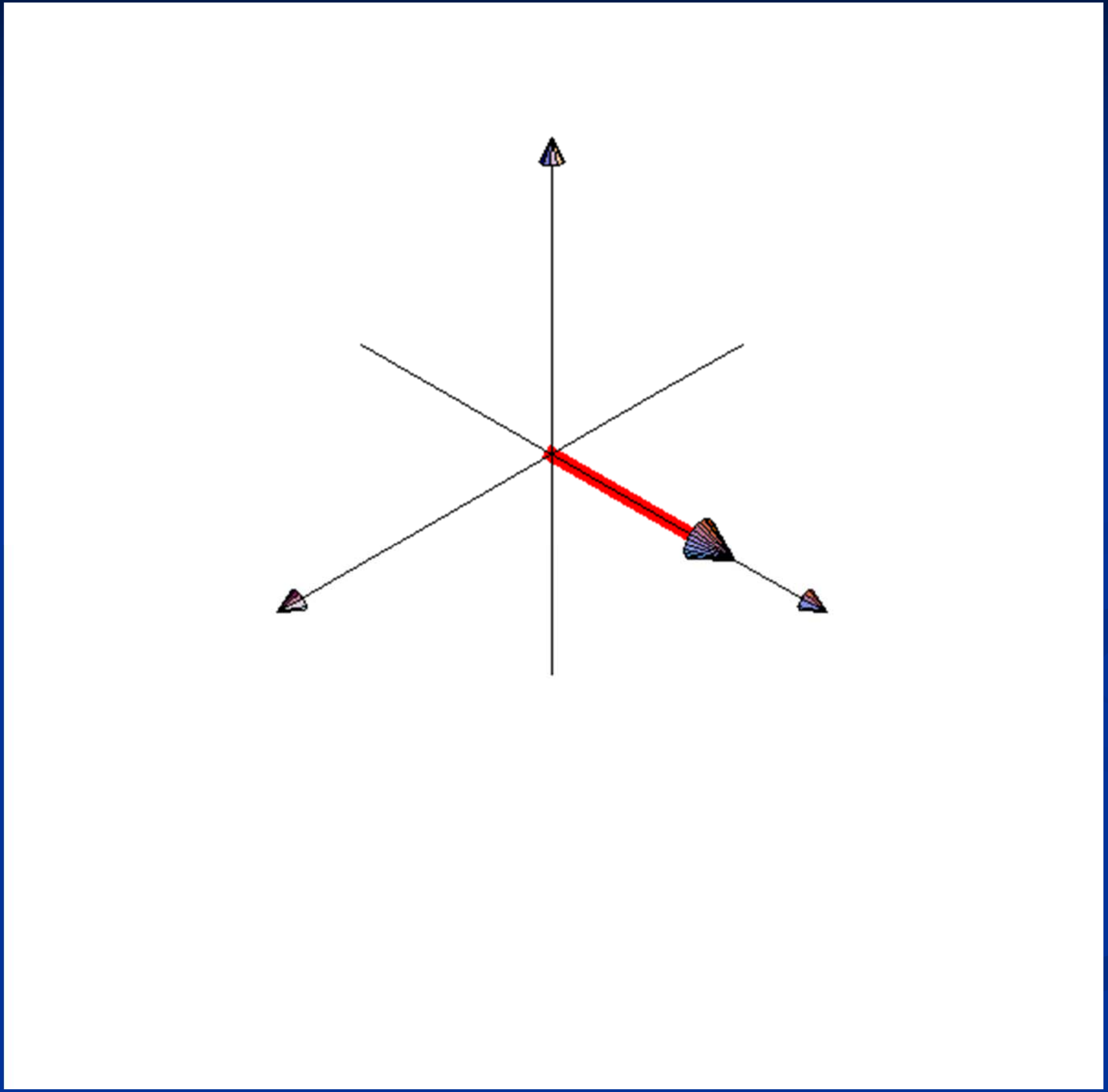
$= [\cos(\omega_L t) + i\sin(\omega_L t)]\exp(-t/T_2)$

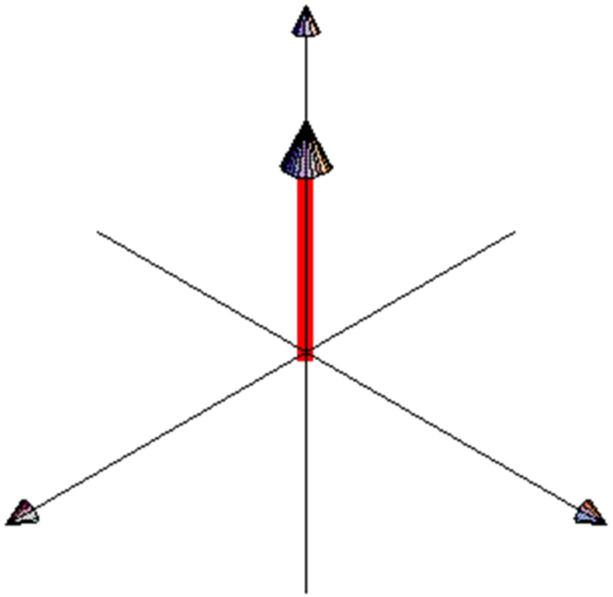
$= \exp(i\omega_L t)\exp(-t/T_2) = \exp[-(1/T_2 - i\omega_L)t]$

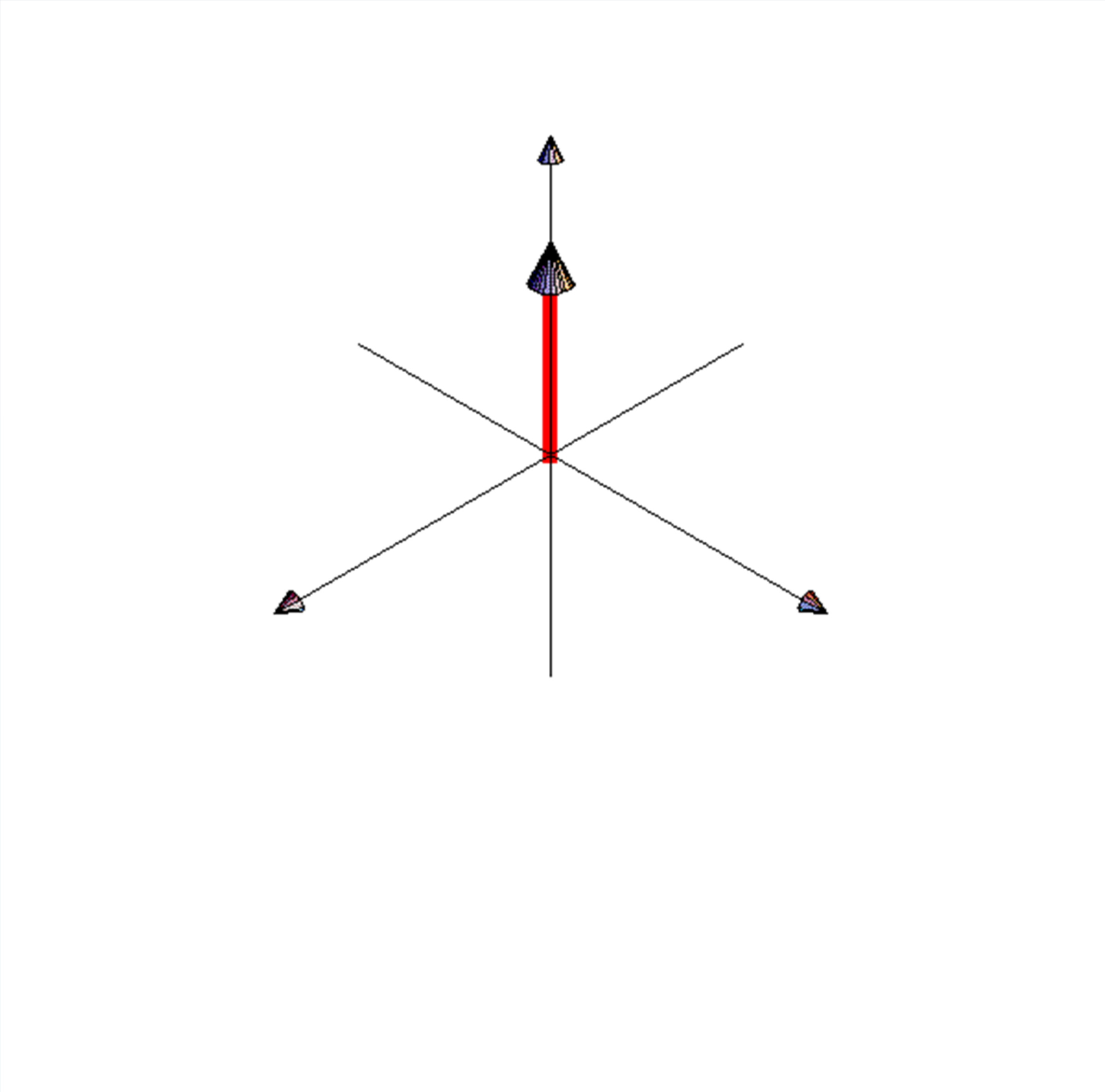
$$\frac{dM_{x'}}{dt} = (\omega_o - \omega) M_{y'} - \frac{M_{x'}}{T_2}$$

$$\frac{dM_{y'}}{dt} = -(\omega_o - \omega) M_{x'} + 2\pi\gamma B_1 M_z - \frac{M_{y'}}{T_2}$$

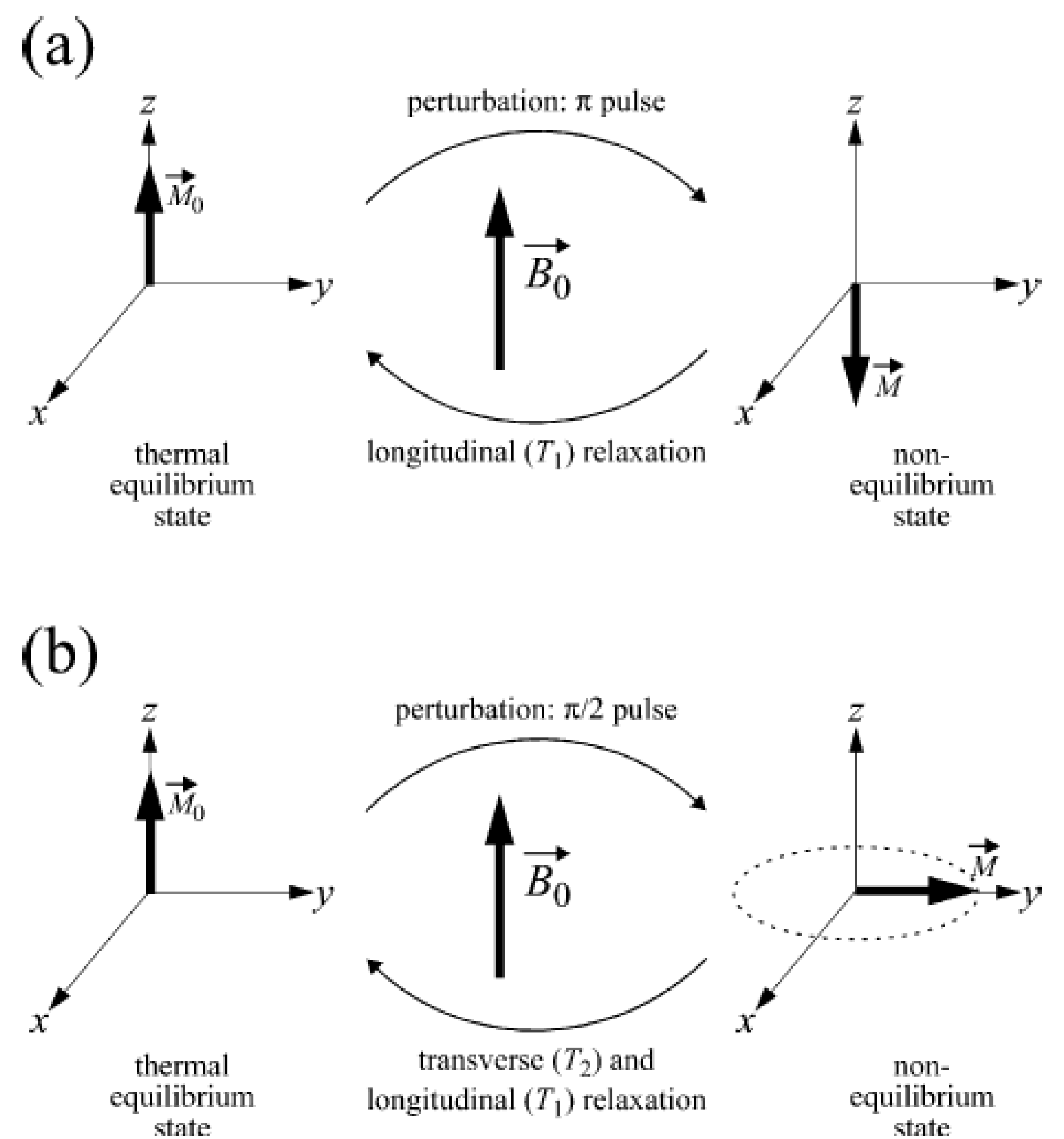
$$\frac{dM_z}{dt} = -2\pi\gamma B_1 M_{y'} - \frac{(M_z - M_{z\circ})}{T_1}$$







Relaxation = Return to Equilibrium



Relaxation

Relaxation in other types of spectroscopy:

- spontaneous emission (not in NMR) fluorescence, phosphorescence

- collisional deactivation

(not in NMR, molecular tumbling does not change orientation of I, always along B_0)

- **stimulated emission**

lasers

magnetic interactions of nuclear spin with external fluctuating mg. field (dipolar) containing many different frequencies, when it contains ω_L, resonance causes relaxation = emission of excess energy, transition from exited to ground state

Spectral Density Function

Nuclear spin relaxation

- not a spontaneous process
- requires stimulation by suitable fluctuating fields to induce the spin transitions

Longitudinal relaxation requires a time-dependent magnetic field fluctuating at the Larmor frequency

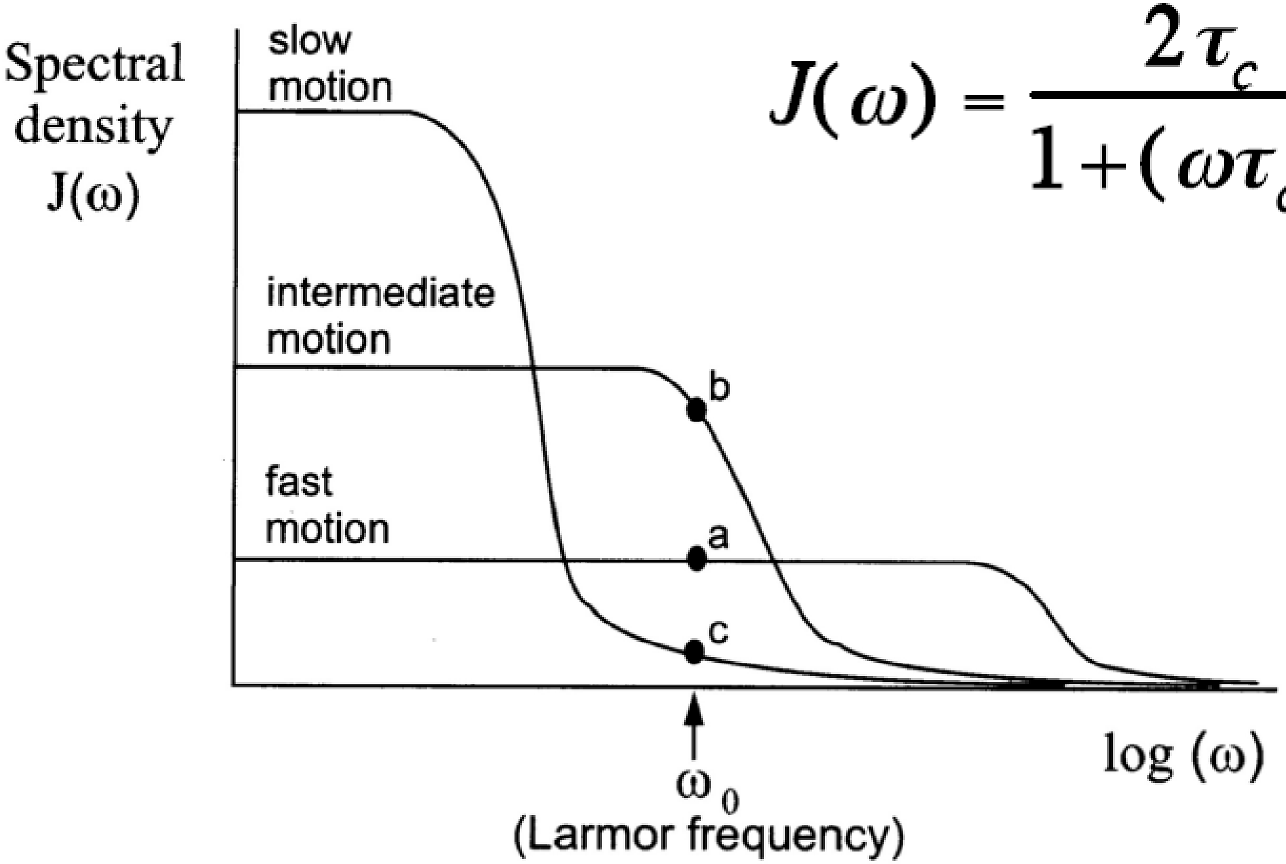
Time-dependence = motions of the molecule (vibration, rotation, diffusion...)
Molecules "tumble" in solution - characterized by a rotational correlation time - τ_C
The probability function of finding motions at a given angular frequency ω can be described by the spectral density function - $J(\omega)$

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

Spectral Density Function

Frequency distribution of the fluctuating magnetic fields

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



Correlation Time τ_C

Correlation Time τ_C describes molecular tumbling

1. Look at one molecule

τ_C = average time during which a molecule stays in one orientation, until a collision changes its orientation

small molecules, low viscosity	short	10^{-12} s
polymers, high viscosity	long	10^{-8} s

Correlation Time τ_C

2. Look at a group of molecules (1 mole)

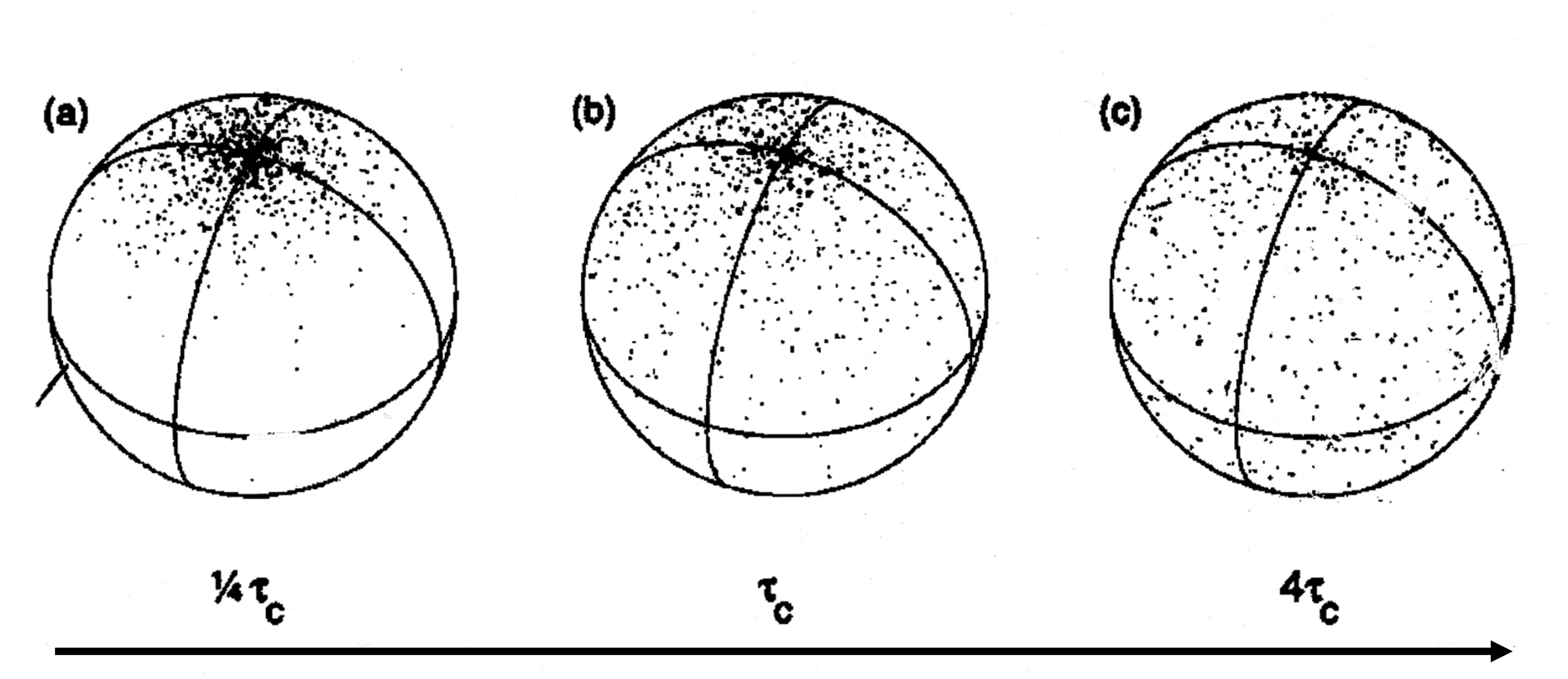
All molecules oriented in the same way,
then τ_C is time in which the orientation is dispersed to 1 rad (~60º)

$t < \tau_C$ molecules are close to the original orientation

$t >> \tau_C$ random distribution

$1/\tau_C$ = tumbling rate

Correlation Time τ_c

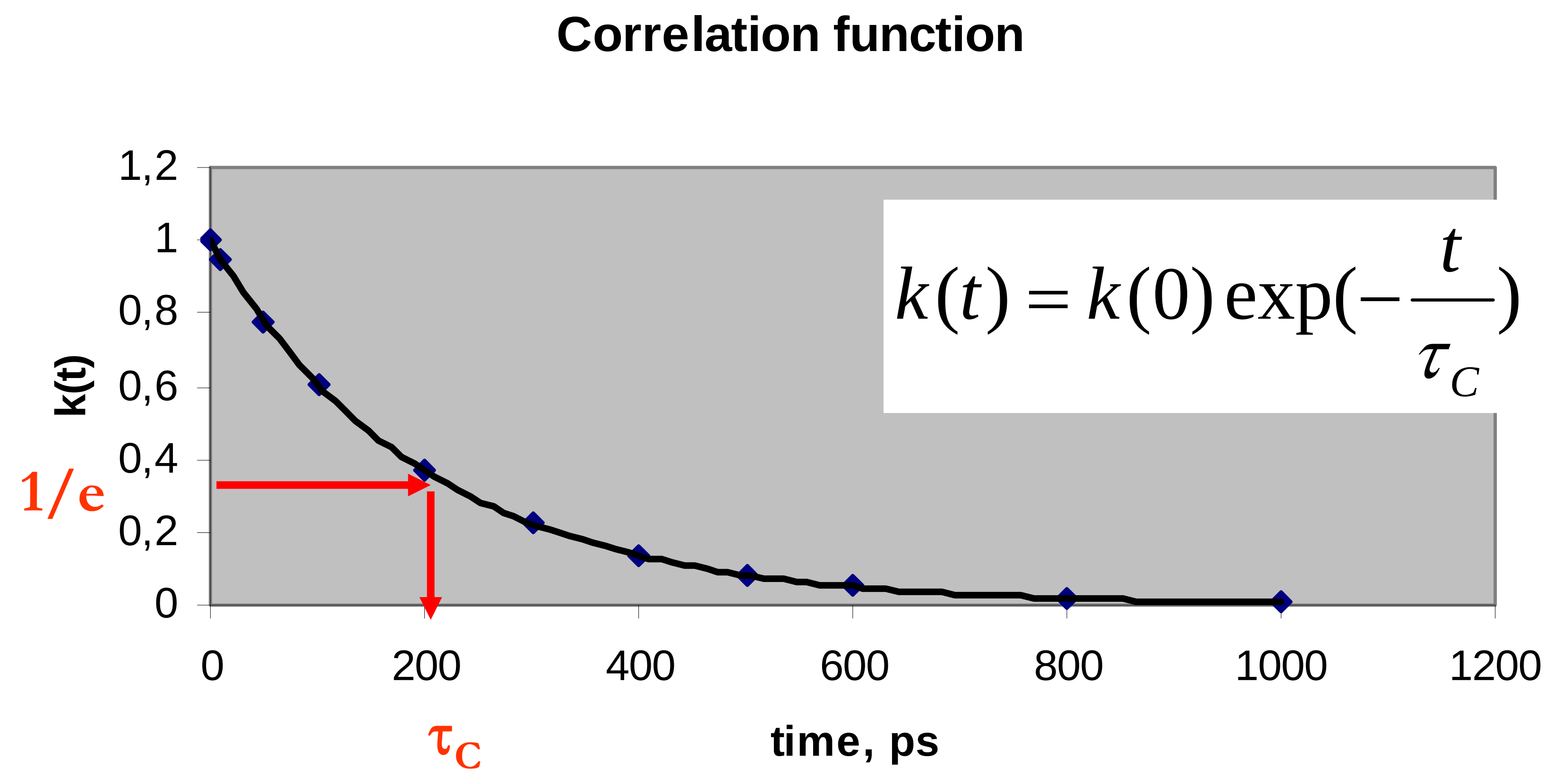


Time

Correlation Time τ_C

Correlation function describes molecular tumbling

How the actual orienation correlates with the original one



$$k(t) = k(0)\exp(-\frac{t}{\tau_C})$$

Correlation Time τ_C

$\tau_C <> 1/\omega_0$ poor energy transfer, T_1 long, narrow lines

$\tau_C = 1/\omega_0$ effective energy transfer, T_1 short, fast relaxation, wide lines

$$\tau_C = \frac{1}{6D} = \frac{\eta V}{k_B T} = \frac{4\eta\pi a^3}{3k_B T}$$

η = viscosity, high η = slow tumbling, long τ_C, wide lines

a = molecular diameter, large particles = long τ_C, wide lines

T = temperature, high T = fast tumbling = short τ_C, narrow lines

Correlation Time τ_C

Approximate rule

τ_C [ps] ~ M_r in H_2O at room temp.

Supercritical CO_2 is a good NMR solvent

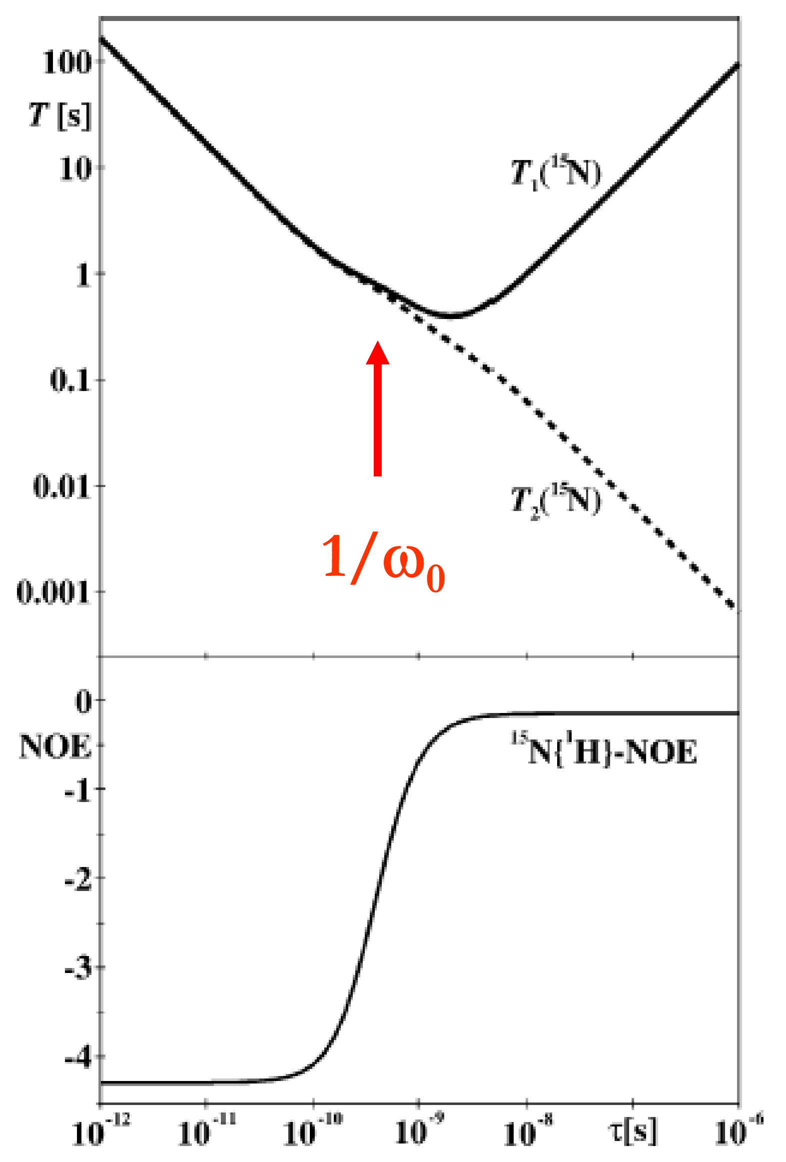
@65 °C and 65 bar has low viscosity, narrow lines

Correlation Time τ_C

extreme narrowing

$T_1 = T_2$ = long
sharp lines

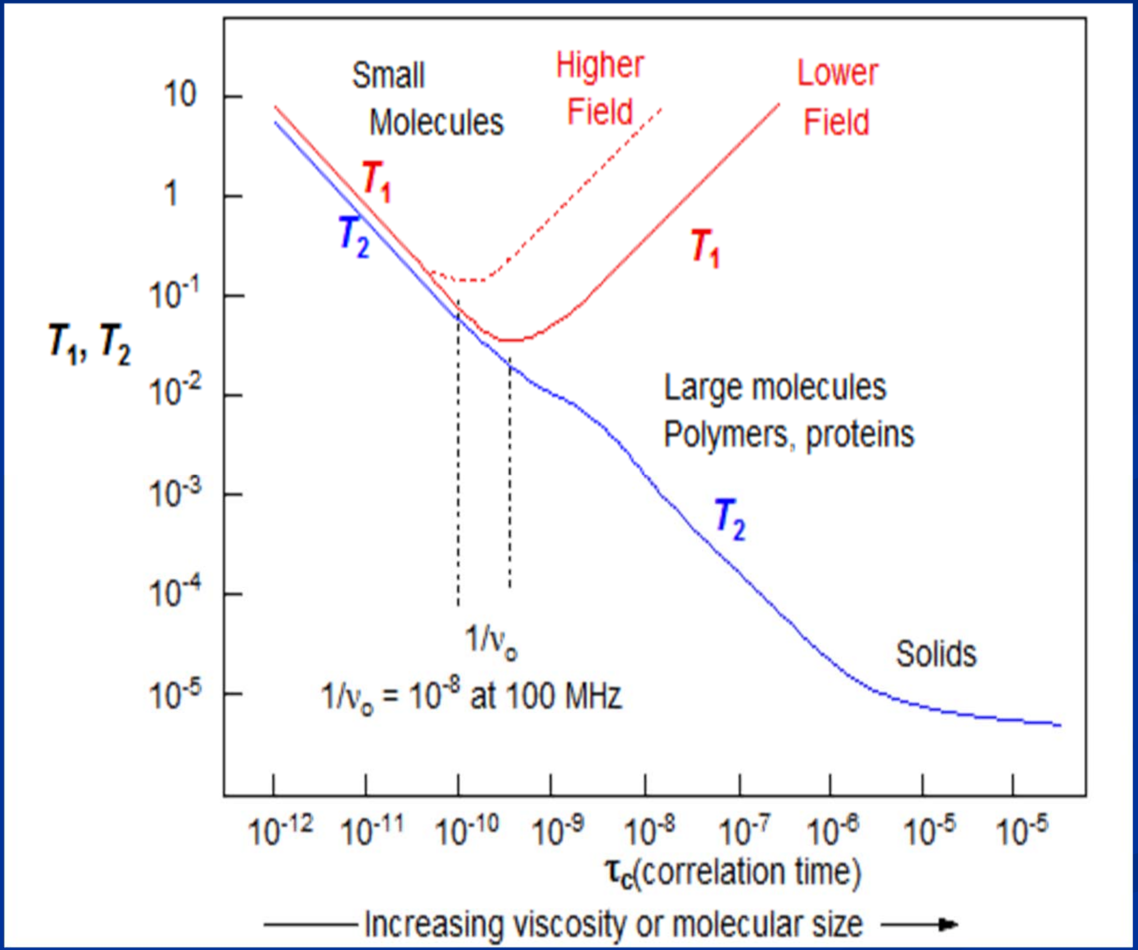
short τ_C = fast tumbling,
small molecules,
low viscosity



long τ_C = slow tumbling
rigid molecules,
high viscosity

Relaxation Times vs Correlation Time

extreme narrowing
$T_1 = T_2$ = long
sharp lines



short τ_C =
fast tumbling

small molecules

low viscosity

long τ_C =
slow tumbling

rigid molecules

high viscosity

The Influence of Correlation Times on Relaxation

- Correlation times are not molecular constants, but depend on a number of factors, e.g. temperature, effective molecular size, solvent viscosity…
- Variation of these factors may induce changes in τ_c of several ordes of magnitude.
- These changes may lead to violation of the „extreme narrowing“ conditions, and introduce the necessity for a more concise treatment of the correlation time dependence of relaxation times.

Linewidth

T_1 = lifetime of a nucleus in a certain energy state

Heissenberg uncertainity principle

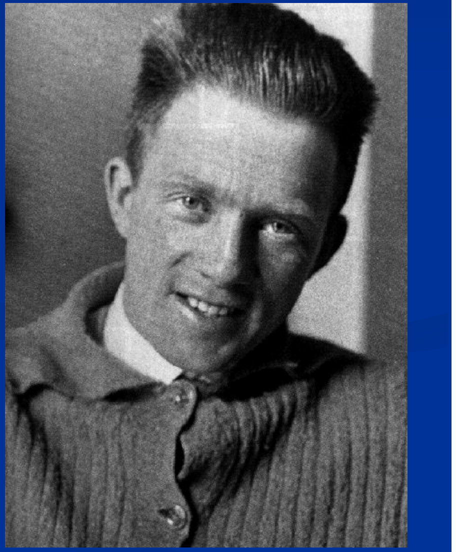
$\Delta E \ \Delta t \geq h/2\pi$ $\qquad h = 6.626\ 10^{-34}$ J s

$h\ \Delta\nu_{1/2}\ T_1 \geq h/2\pi$

$\Delta\nu_{1/2} \geq 1/T_1$ $\qquad \Delta\nu_{1/2} \geq 1/\pi T_2$

High relaxation rate = short relation times

= wide lines in spectra



Werner Heisenberg
(1901-1976)
NP in physics 1932

Linewidth

Relaxation rate
$$R = \sum_i \frac{1}{T_i}$$

Linewidth
$$\Delta \nu_{1/2} \approx \frac{1}{T_1} + \frac{1}{T_2}$$

short τ_C = fast tumbling = long $T_1 \geq T_2$

$$\Delta \nu_{1/2} \approx \frac{1}{T_1} + \left(\frac{1}{T_2}\right)$$

long τ_C = slow tumbling = long T_1, short T_2
Linewidth is given by T_2

$$\Delta \nu_{1/2} \approx \frac{1}{\pi T_2}$$

Relaxation

Solution NMR

usually $T_2 = T_1$ (small/medium molecules, fast tumbling rate, non-viscous liquids)

Some process like scalar coupling with quadrupolar nuclei, chemical exchange, interaction with a paramagnetic center, can accelerate the T_2 relaxation such that T_2 becomes shorter than T_1.

Solid state NMR

T_1 is usually much larger than T_2. The very fast spin-spin relaxation time provide very broad signals

Measuring the experimental line width to determine the T_2 relaxation time,
the experimental line width depends also on the inhomogeneity from the magnetic field:

$$1/T_2^* = 1/T_2 + 1/T_2(\text{inhomogeneity})$$

Inhomogeneity is more critical for nuclei with higher frequency $\Delta\nu = \gamma B_0$

Relaxation Mechanisms

Fluctuating magnetic fields (of the right amplitude and frequency) make spins exchange energy with their environment

Important mechanisms to generate these fluctuating magnetic fields are:

- Direct dipolar interaction of a nuclear spin with other nuclear spins
- Molecular motion in the presence of large chemical shielding anisotropies
- Interaction of a nuclear spin with a nuclear quadrupole
- Scalar coupling of nuclear spins
- Paramagnetic relaxation by unpaired electrons
- Spin rotation

The individual contributions combine to make the total relaxation

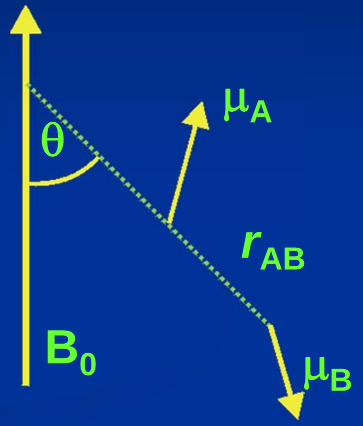
$$\frac{1}{T_1} = \frac{1}{T_{1,DD}} + \frac{1}{T_{1,CSA}} + \frac{1}{T_{1,Q}} + \ldots..$$

Relaxation Mechanisms

Interaction	Range of interaction (Hz)	Relevant parameters
Dipolar coupling	10^4 - 10^5	abundance of magnetically active nuclei size of their magnetogyric ratio
Quadrupolar coupling	10^6 - 10^9	size of quadrupolar coupling constant electric field gradient at the nucleus
Paramagnetic	10^7 -10^8	concentration of paramagnetic impurities
Scalar coupling	10 - 10^3	size of the scalar coupling constants J
Chemical Shift Anisotropy (CSA)	10 - 10^4	size of the chemical shift anisotropy CSA symmetry at the nuclear site
Spin rotation		

Dipolar Relaxation $T_{1,DD}$

The Direct Interaction of a Nuclear Spin with other Spins



INTRAMOLECULAR

The magnetic moment of a nuclear spin B influences the local field at the position of a neighbouring nucleus A:

$$B_{loc}(A) = B_{loc,0}(A) + D$$

D denotes the dipolar coupling constant which is defined as

$$D = \frac{\hbar \mu_0}{8\pi^2} \frac{\gamma_A \gamma_B}{r_{AB}^6} (1 - 3\cos^2\theta)$$

Brownian motion of the sample containing nuclei **A** and **B** induces a fluctuation of **θ** which leads in turn to a time dependent modulation of the local magnetic field **$B_{loc}(A)$**.

Dipolar Relaxation $T_{1,DD}$

The contribution of this modulation to the T_1 relaxation of nucleus A can be expressed in terms of a characteristic time constant $T_{1,DD}$:

τ_c = molecular correlation time
μ_0 = vacuum permeability
S = spin of nucles B
γ_B = magnetogyric ratio, large value = faster relaxation of A, shorter $T_{1,DD}$
nuclei with large γ (e.g. H) relax neighbouring nuclei
$1/r^6_{AB}$ = only directly bound nuclei contribute = intramolecular

(in the extreme narrowing limit)

$$\frac{1}{T_{1,DD}(A)} = \frac{\mu_0^2 \hbar^2 \gamma_A^2 \gamma_B^2}{12\pi^2 r_{AB}^6}\left[S(S+1)\right]\tau_C$$

Substitution H/D: If H is replaced by D, in the X-D bond, the X-nuclei relax much slower than in the corresponding X-H due to the lack of dipole-dipole relaxation, γ_H is 6.5 time larger than γ_D.

^{13}C - ^{1}H Dipolar Relaxation $T_{1,DD}$

T_1 relaxation of ^{13}C by directly attached protons :

τ_c = molecular correlation time
n_H = number of attached protons
γ_H = magnetogyric ratio of H
$1/r^6_{CH}$ = 109 pm

$$\boxed{\frac{1}{T_{1,DD}\left({}^{13}C\right)} = \frac{n_H \mu_0^2 \hbar^2 \gamma_C^2 \gamma_H^2}{16\pi^2 r_{CH}^6}\tau_C}$$

(in the extreme narrowing limit)

Protonated carbons relax faster in ^{13}C NMR than quarternary carbons

Dipolar Relaxation $T_{1,DD}$

INTERMOLECULAR

$$\frac{1}{T_{1,DD(\mathrm{inter})}} = \frac{N_0 \pi h^2 \gamma^4}{2Da} = \frac{3\pi^2 \gamma^4 \hbar^2 \eta N_0}{k_B T}$$

N_0 = number of molecules in m^3
D = difussion coefficient
T = temp, high T narrows lines

$$D = \frac{k_B T}{6\pi\eta a}$$

Protons relax both inter and intramolecularly

C_6H_6 neat	$T_1(H) = 19$ s
C_6H_6 diluted in CS_2	$T_1(H) = 90$ s

I: The Influence of the observed nucleus A in a A-H fragment:

A	^{31}P	^{13}C	^{29}Si	^{15}N	^{103}Rh
$\gamma(X)$	10.84	6.73	-5.32	-2.71	-0.85
r_{AH} [Å]	1.4	1.1	1.4	1.0	1.6
$T_{1,DD}$ ($\tau_c=10^{-11}$)	**8 s**	**5 s**	**33 s**	**17 s**	**48 min**
$T_{1,DD}$ ($\tau_c=10^{-9}$)	**80 ms**	**50 ms**	**330 ms**	**170 ms**	**29 s**

II: The Influence of the neighboring nucleus X in an A-X fragment (A=^{15}N):

X	^{1}H	^{31}P	^{13}C	^{11}B	^{51}V
$\gamma(X)$	26.75	10.84	6.73	8.59	7.05
r_{AX} [Å]	1.0	1.7	1.4	1.3	1.8
S(S+1)	0.75	0.75	0.75	3.75	3.75
$T_{1,DD}$ ($\tau_c=10^{-11}$)	**17 s**	**42 min**	**34 min**	**160 s**	**400 s**
$T_{1,DD}$ ($\tau_c=10^{-9}$)	**170 ms**	**25 s**	**20 s**	**1.6 s**	**4 s**

III: The Influence of the internuclear distance in a N···H fragment:

r_{AX} [Å]	1.0	2.1	2.7
	(N-H)	(N-C-H)	(N-C-C-H)
$T_{1,DD}$ ($\tau_c=10^{-11}$)	8 s	24 min	110 min

$\tau_c = 10^{-11}$s: medium sized (in)organic molecule

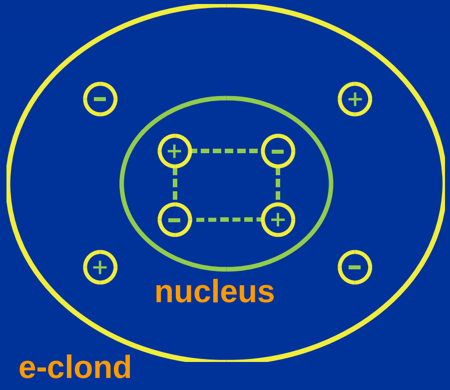
$\tau_c = 10^{-9}$ s: small polymer

Quadrupole Induced Relaxation $T_{1,Q}$

The Interaction of a nuclear spin I with a quadrupole moment

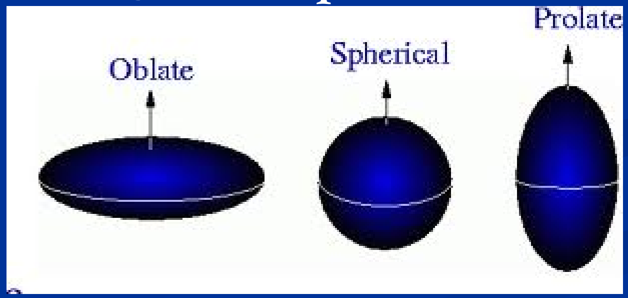
Nuclei I > ½

Nuclei with *I* > ½ possess an electric quadrupole moment *eQ* which is quantized according to its oriention in the electric field gradient *(efg)* of the electrons if the local symmetry is less than spherical.



Due to strong coupling between eQ and I, the nuclear magnetic spin levels depend on both B_0 and the efg.

Electric quadrupole moment *eQ* = nonspherical distribution of the positive nuclear charge



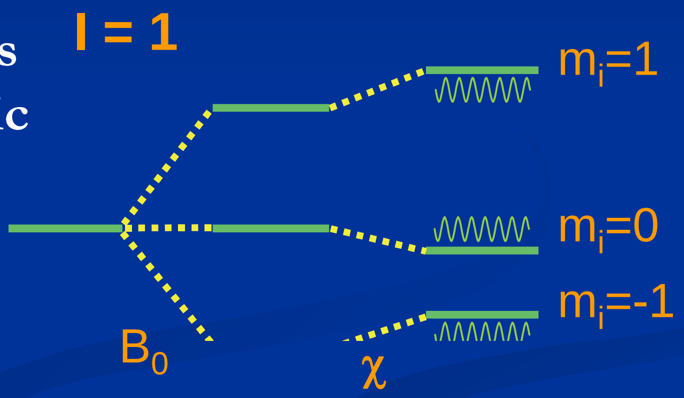
$Q < 0$ $Q = 0$ $Q > 0$

Quadrupole Induced Relaxation $T_{1,Q}$

BROWNIAN MOTION of sample molecules modulates the different m_I energies which leads to a stochastic modulation of the local magnetic field $B_{loc}(A)$.

Tumbling = spread of energy levels

in solution the average transition energy does not change but the spread contributes to relaxation



Quadrupole Induced Relaxation $T_{1,Q}$

The contribution to $T_1(A)$ can be expressed in terms of a characteristic time constant $T_{1,Q}$ (extreme narrowing limit)

$$\frac{1}{T_{1,Q}} = \frac{1}{T_{2,Q}} = \frac{\pi^2 3(2I+3)}{10I^2(2I-1)}(1+\frac{\eta^2}{3})(\frac{e^2Qq_{zz}}{h})^2\tau_C$$

τ_c = correlation time

I = nuclear spin

Q = nuclear quadrupole moment (Q ≠ 0 for I > ½)

q_{ZZ} = electric field gradient

$q_{ZZ} = 0$ for high symmetry (spherical, Cl^-, cubic T_d, O_h, ClO_4^-, SO_4^{2-}, AsF_6^-

η = asymmetry parameter ($\eta = 0$ for axial symmetry)

$$\eta = \frac{q_{yy} - q_{xx}}{q_{zz}}$$

Quadrupole Induced Relaxation $T_{1,Q}$

Q - the electric quadrupole moment of the nucleus

A large moment results in efficient relaxation of the nucleus by molecular motion, very broad lines.
$^{125}I^-$ in water ($I = 5/2$, $Q = -0.79$) has $\nu_{1/2} = 1800$ Hz
All other iodo compounds are much less symmetric and have lines so broad their NMR signals cannot be detected.

Deuterium ($I = 1$, $Q = 0.00273$) and ^6Li ($I = 1$, $Q = 0.0008$) have among the smallest electric quadrupole moments of all isotopes and are easy to observe and usually give lines sharp enough to resolve J coupling.

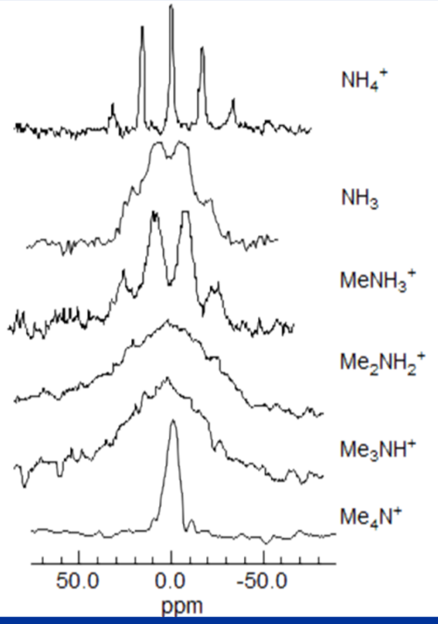
^{55}Mn ($I = 5/2$, $Q = 0.55$)

Quadrupole Induced Relaxation $T_{1,Q}$

q_{ZZ} - the electric field gradient (EFG)

The Quadrupole coupling vanishes in a symmetrical environment

symmetrical $[NH_4]^+$: $q_{zz} = 0$ and therefore has very long $T_1 = 50$ s
CH_3CN : $q_{zz} = 4$ MHz and $T_1 = 22$ ms



^{14}N I = 1

3 MHz ^{14}N NMR spectra

$^1J_{NH}$ = 40 Hz

(I = 1, Q = 0.016)

Quadrupole Induced Relaxation $T_{1,Q}$

Nuclear Quadrupole Coupling Constant, NQCC $\chi = e^2 q_{zz} Q / \hbar$

Linewidth factor

$$l = \frac{Q^2(2I+3)}{I^2(2I-1)}$$

I	1	3/2	5/2	3	7/2	4
1 [Q^2]	5	1.33	0.32	0.20	0.16	0.10

The larger the I nuclear spin, the faster relaxation, the shorter $T_{1,Q}$, the broader lines

I. The Influence of the electric field gradient q_{zz}:

^{14}N relaxation times:

	Bu_4N^+ (T_d)	$NaNO_3$ (D_{3h})	$\mathrm{N}N\mathrm{N}^-$($C_{\infty h}$)	MeSCN($C_{\infty v}$)	DABCO($C_{\infty v}$)
c[MHz]	0.04	0.745	1.03	3.75	4.93
$T_{1,Q}$	**1.8 s**	**85 ms**	**29 ms**	**2 ms**	**0.6 ms**

^{55}Mn relaxation times:

	Mn_2CO_{10}	$BrMn(CO)_5$	$HMn(CO)_5$	$CpMn(CO)_3$
c[MHz]	3.05	17.46	45.7	64.3
$T_{1,Q}$	**3.8 ms**	**0.46 ms**	**74 µs**	**32 µs**

II. The Influence of *Q* and *I*: $T_{1,Q}$ in $[M(CO)_6]$

M =	^{95}Mo	^{97}Mo	^{187}Re$^{(+)}$	^{185}Re$^{(+)}$	^{181}Ta$^{(-)}$
$Q[10^{-28}\ m^2]$	0.12	1.1	2.6	2.8	3
I	5/2	5/2	5/2	5/2	7/2
Q(2I+3)/(2I-1)	0.30	2.75	6.50	7.00	10.5
$T_{1,Q}$	**>450 ms**	**53 ms**	**141 µs**	**122 µs**	**48 µs**
$W_{1/2}$ [Hz]	<0.7	6	2250	2600	6700

CSA Induced Relaxation, $T_{1,CSA}$

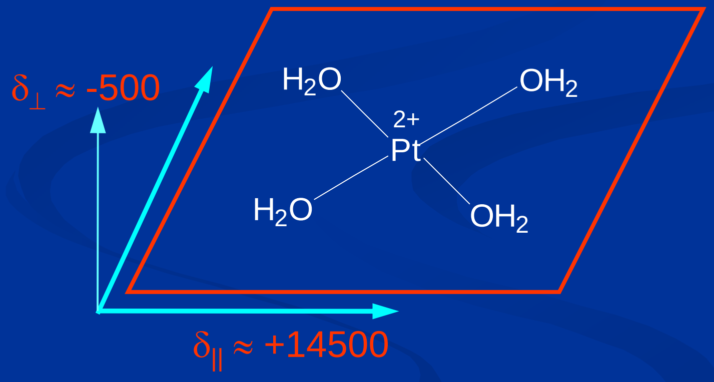
Tumbling of molecules with large chemical shielding anisotropies
Important for nuclei with wide range of chemical shifts: ^{31}P, ^{195}Pt, ^{113}Cd

Magnetic shielding is anisotropic and may vary for different orientations of the magnetic field B_0 with respect to the molecular frame.

Chemical Shielding Anisotropy CSA

$$\Delta\sigma = \sigma_{zz} - \tfrac{1}{2}(\sigma_{xx} - \sigma_{yy})$$

$$\Delta\sigma = \sigma_{//} - \sigma_{\perp}$$



BROWNIAN MOTION of sample molecules induces time dependent modulation of σ and thus a stochastic fluctuation of the effective local magnetic field $B_{0,loc}(A)$.

CSA Induced Relaxation, $T_{1,CSA}$

The contribution to $T_1(A)$ can be expressed in terms of a characteristic time constant:

$$\frac{1}{T_{1,CSA}(A)} \approx B_0^2 \gamma_A^2 (\Delta\sigma)^2 \tau_C$$

(in the extreme narrowing limit)

τ_c = molecular correlation time
$\Delta\sigma$ = shielding anisotropy
B_0 = magnetic field strength = wide lines in strong magnets !!!!

I: The Influence of the observed nucleus A in ($\Delta\sigma$ = 100 ppm; B_0 = 7 T):

A	^{31}P	^{13}C	^{15}N
$\gamma(X)$	10.84	6.73	-2.71
$T_{1,CSA}$ ($t_c=10^{-11}$)	130 s	340 s	35 min
$T_{1,CSA}$ ($t_c=10^{-9}$)	1.3 s	3.4 s	21 s

II: The Influence of the magnetic field B_0 (nucleus ^{195}Pt; $\Delta\sigma$ = 1000 ppm):

B_0 [T]	4.7	7.1	11.7	17.6
$\nu(^1H)$ [MHz]	200	300	500	750
$T_{1,CSA}$ ($t_c=10^{-11}$)	10 s	4 s	1.6 s	0.7 s
$T_{1,CSA}$ ($t_c=10^{-9}$)	100 ms	40 ms	16 ms	7 ms

III: The Influence of the shielding anisotropy (nucleus ^{195}Pt; B_0 = 7 T):

$\Delta\sigma$ [ppm]	15	150	1500	15000
$T_{1,CSA}$ ($t_c=10^{-11}$)	5.5 h	3.3 min	2 s	20 ms
$T_{1,CSA}$ ($t_c=10^{-9}$)	3.3 min	2 s	20 ms	0.2 ms

$\tau_c = 10^{-11}$s: medium sized (in)organic molecule; $\tau_c = 10^{-9}$ s: small polymer;

Spin Rotation Induced Relaxation, $T_{1,SR}$

Tumbling molecule = bonding electrons move and induce magnetic field around the molecule. Important for small fast rotating molecules with high symmetry: SF_6, PCl_3, PtL_4

$$\frac{1}{T_{1,SR}} = \frac{2Vk_BTC^2}{3\hbar^2}\tau_j$$

V = moment of inertia
C = SR constant
τ_j = time in which a molecule changes its angular momentum, e.g. time between collisions

Hubbard (if $\tau_j << \tau_C$, valid for small molecules below b. p.) $\tau_j \tau_C = \frac{V}{6k_BT}$

Contributions of CSA versus SR

	$[Pt(P^tBu_3)_2]$	$[Pt(PEt_3)_3]$	$[Pt\{(P(OEt)_3\}_4]$
symm	linear	trigonal	tetrahedral
T_1 [s] @ 9.4 T	0.03	2.4	5.6
CSA %	100	50	10
SR %	0	50	90

SR important at high T, high symmetry
CSA important at high B_0, low symmetry

Scalar Coupling Induced Relaxation, $T_{1,SC}$

Two nuclei coupled through J_{AB} and one of them relaxes fast = the fast spin orientation change of B is transferred to A

•exchange of B nucleus (e.g. H exchange)
τ = lifetime of the exchange process

•quadrupolar nucleus B
$\tau = T_{2q}$ quadrupolar relaxation time

Spin A

$$\frac{1}{T_{1,SC}} = \frac{8\pi^2 J^2}{3}(S+1)S\frac{\tau}{1+(\varpi_I - \varpi_S)^2\tau^2}$$

S = spin of B

Paramagnetic Relaxation, $T_{1,e}$

Dipolar relaxation by electron magnetic moment
Transfer of unpaired electron density onto a nucleus

O_2 in the solvent
TM ions

$$\frac{1}{T_{1,e}} = \frac{4\pi^2\gamma^2\eta N_p\mu_{eff}^2}{k_B T}$$

N_p = concentration of paramagnetic species in m^3
μ_{eff} = magnetic moment of e, thousand times larger than magnetic moment of nuclei, even small conc. of paramagnetic species shortens considerably relaxation time, wide lines
η = viscosity

Relaxation agent $Cr(acac)_3$ can be added to the solution of a slow relaxing compound (^{13}C, ^{29}Si,..) to shorten the acq. delay

Paramagnetic Relaxation, $T_{1,e}$

$$\frac{1}{T_{1,e}} = \frac{(\mu_0 \gamma_I \gamma_S \hbar)^2}{12\pi^2 r^6} S(S+1)\tau_C + \frac{(\mu_0 \gamma_S a_N)^2}{24\pi^2} S(S+1)\tau_e$$

dipole-dipole term **contact term**

τ_c = molecular correlation time
τ_e = electron correlation time
a_N = electron-nucleus spin coupling constant

Relaxation Mechanisms

Approaches to distinguish the various relaxation mechanisms:

1. by the strength of the interaction :
   Paramg > Q > DD > CSA > J

2. by the use of isotopic substitution to identify the DD

3. by the field dependence:
   CSA is proportional to B_0 (applied field).
   Quadrupole interaction is inversely proportional to B_0

4. by their temperature dependence

Away from Extreme Narrowing Conditions

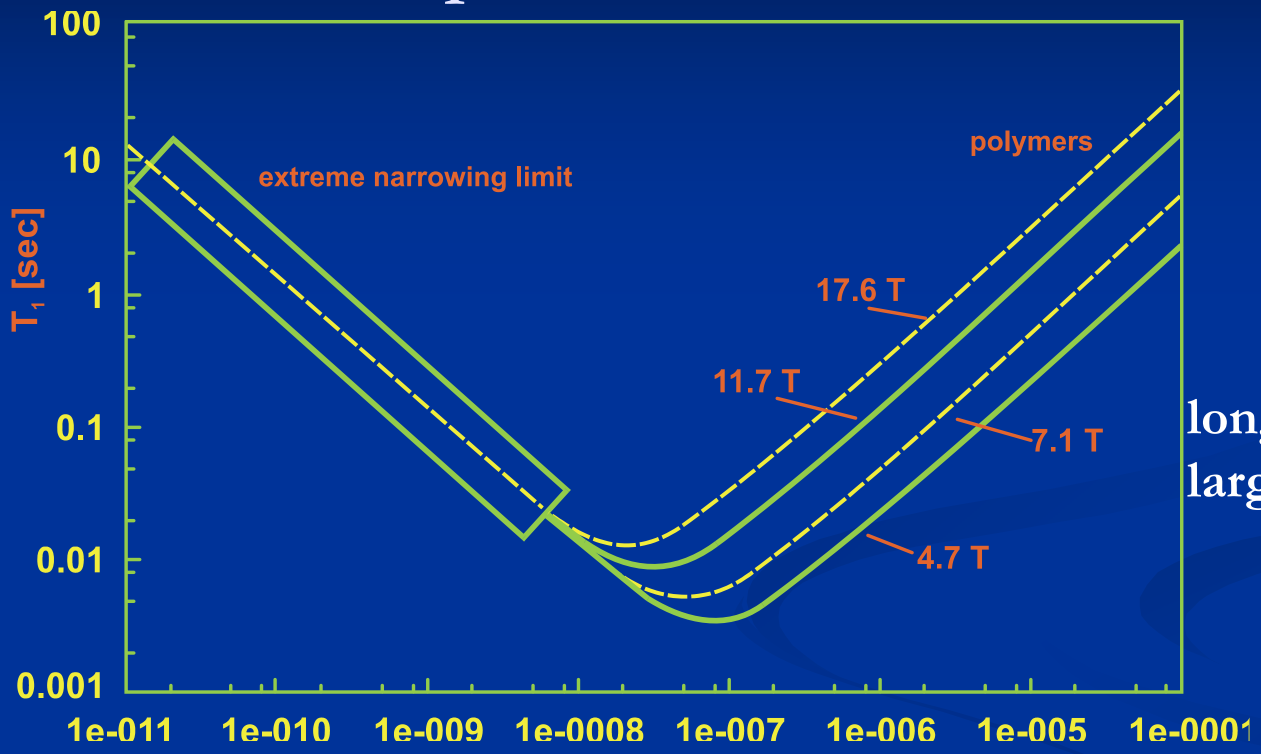
Theoretical analysis of relaxation processes under conditions which fail to fulfil the requirements of extreme narrowing revealed that dependence of T_1 on τ_c follows frequently a relation

$$\frac{1}{T_1} \propto \frac{\tau_c}{1+\omega^2\tau_c^2}$$

$\omega = \nu_{Zeeman}/2\pi$

This relation allows a more detailed analysis of temperature effects on relaxation.

The Temerature Dependence of T_1 Relaxation



long τ_C
large molecules

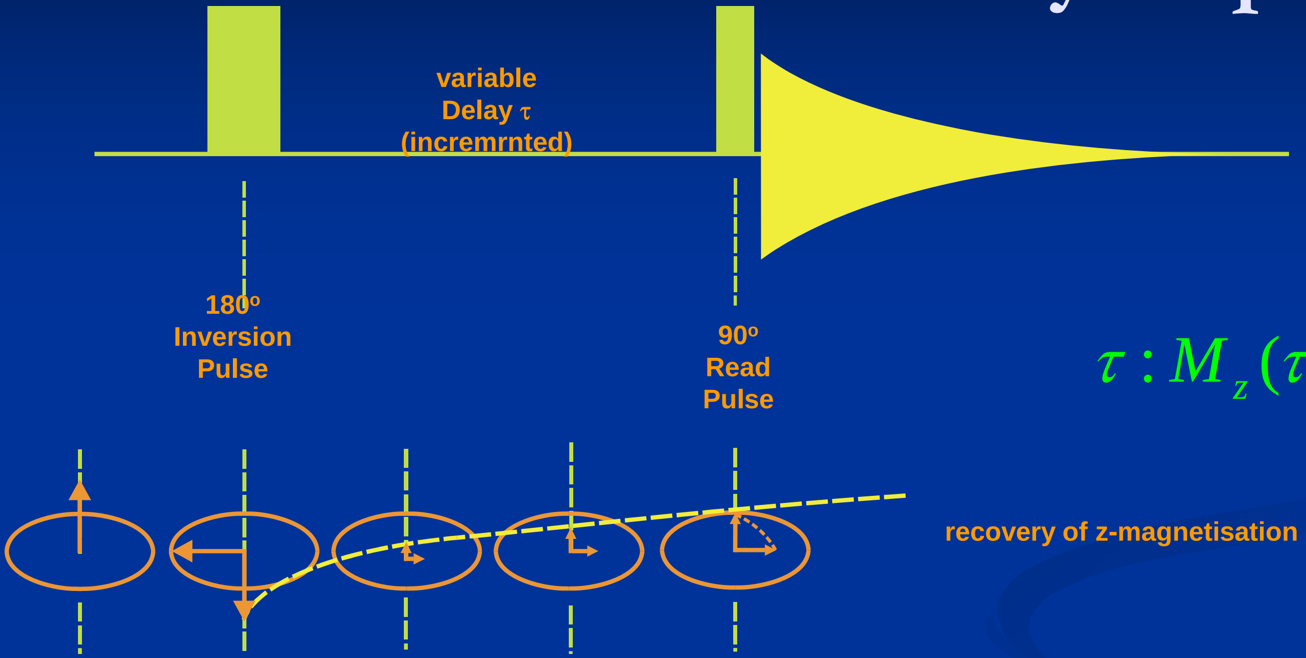
fast motion
short τ_C

T_1 is independent of B_0 in the extreme narrowing regime ($\omega^2\tau^2 << 1$)

T_1 goes through a minimum (optimum relaxation conditions, $\omega^2\tau^2 \approx 1$, very efficient relaxation)

T_1 depends on B_0 if $\omega^2\tau^2 >> 1$

Measurement of T_1
The Inversion Recovery Experiment



variable Delay τ (incremrnted)

180º Inversion Pulse

90º Read Pulse

recovery of z-magnetisation

$$\tau : M_z(\tau) = M_z^0(1-2e^{-\tau/T_1})$$

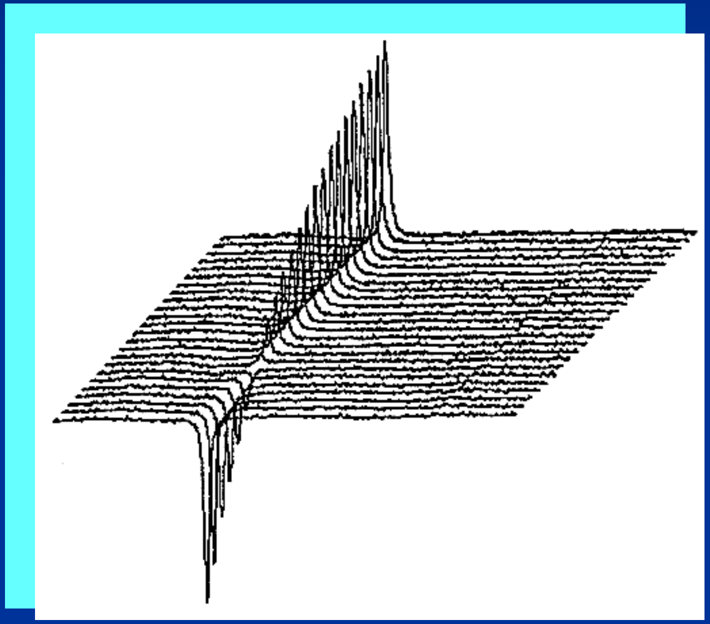
Non-equilibrium z-magnetisation recorvers during delay τ

$M_z(\tau)$ is converted into observable magnetisation by the read pulse

Performing a series of experiments and incrementing τ allows to sample $M_z(\tau)$ at different times

T_1 is obtained from a fit of observed signal intensities as a function of τ

Measurement of $T_1(^{51}V)$ for a Vanadium Complex



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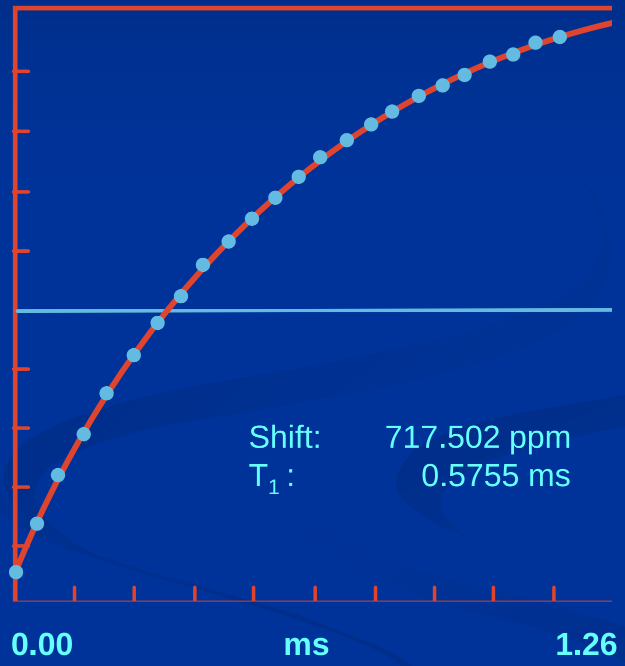


Relaxation Time T_2

T_2 relaxation occurs without energy transfer ⇒ „entropic process“.

The characteristic time constant T_2 is connected with the linewidth:

$$\frac{1}{T_2} = \frac{1}{T_{2,true}} + \frac{1}{T_2^*} = \pi \Delta w_{1/2}$$

T_2^* describes the effect of magnetic field inhomogeneities, i.e. mostly bad shimming

Relaxation Time T_2

For most I = n/2-nuclei,

$1/T_{2,true} >> 1/T_2^*$

T_2 may be determined directly from measured linewidth:

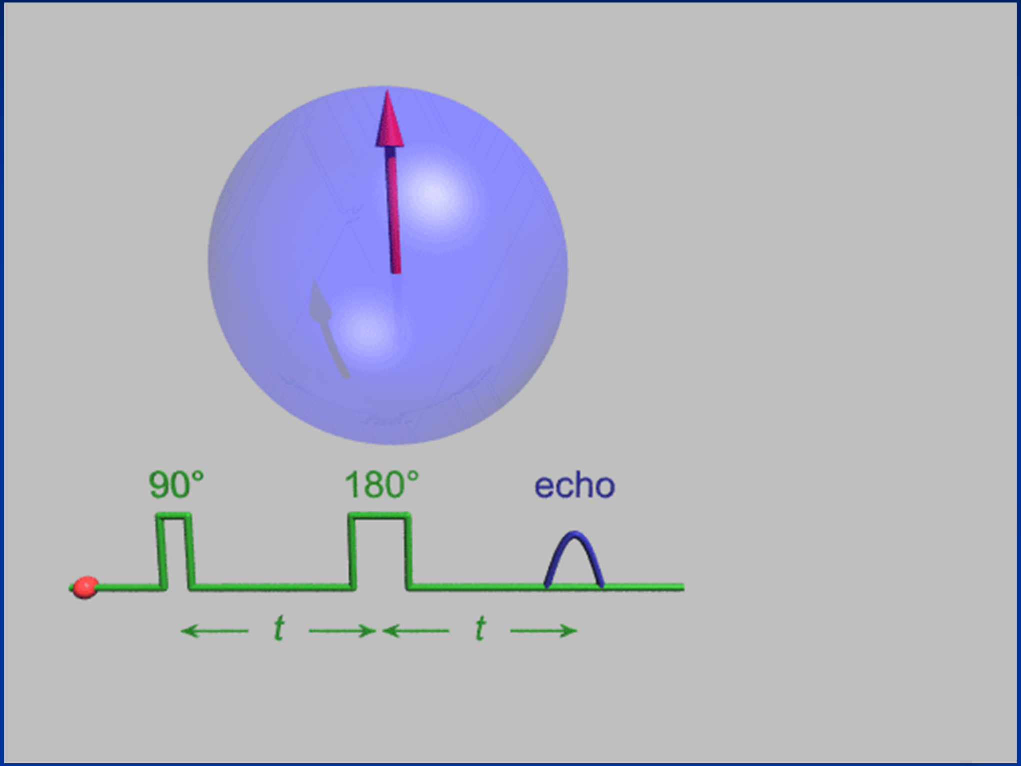
$\pi \Delta w_{1/2} = 1/T_2 \approx 1/T_{2,true}$

For I = 1/2-nuclei,

$1/T_{2,true} \leq 1/T_2^*$

T_2 must be measured by dedicated experiments (spin echo or CPMG)

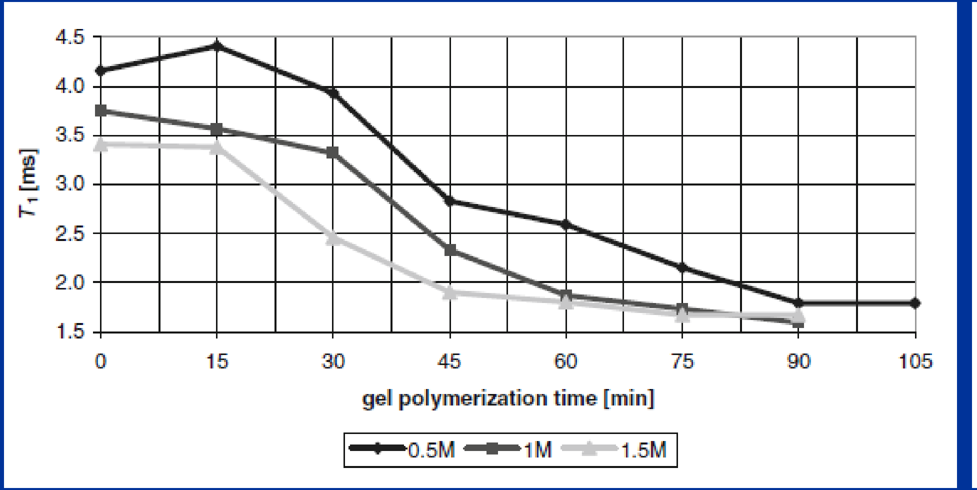
Relaxation Time T_2

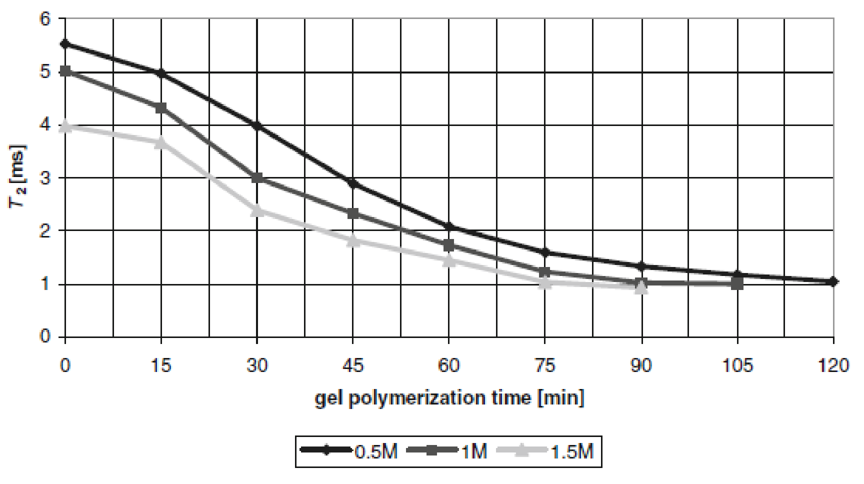


Mg. field inhomogeneity refocused at the end of the 2nd delay.
Echo after the $2t$ delays - the size of this echo will only be affected by the spin-spin relaxation processes

^{23}Na Relaxation Time

- Methyl methacrylate (MMA) with $NaClO_4$ in propylene carbonate (PC)
- Polymerization initialized with UV radiation and the BBE initiator
- ^{23}Na nucleus (I = 3/2) has a large electric quadrupole moment, which causes its extreme sensitivity to the nearest neighbor coordination
- T_1 - the inversion recovery
- T_2 - the spin-echo technique





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