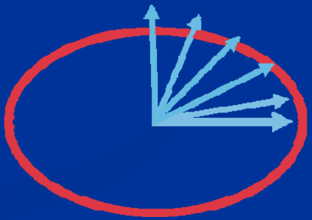
Relaxation Times

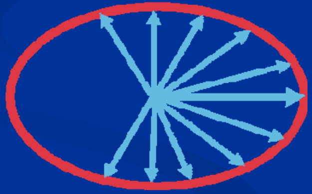
Relaxation = return to equilibrium (Boltzmann) after a pulse, redistribution of energy

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



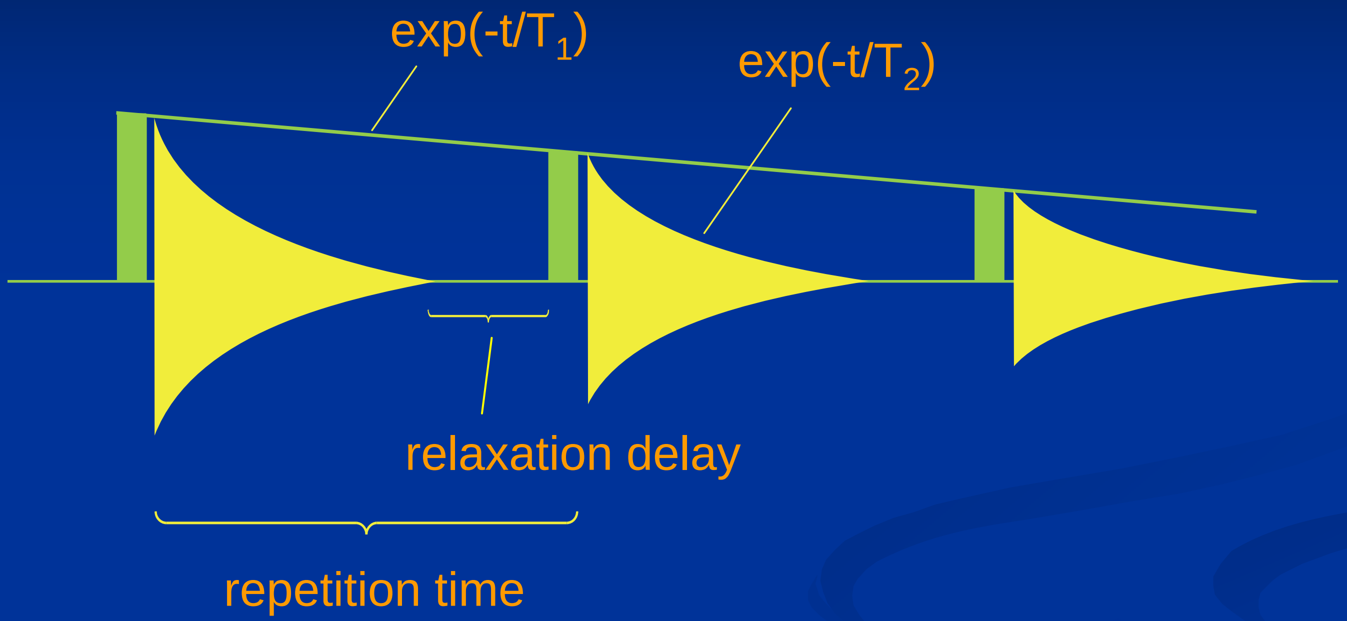
T_2 Transversal, Spin-Spin Relaxation
Dephasing of transversal magnetisation without energy exchange between spins and their environment, entropy



Two important relations between T_1 and T_2 must be remembered

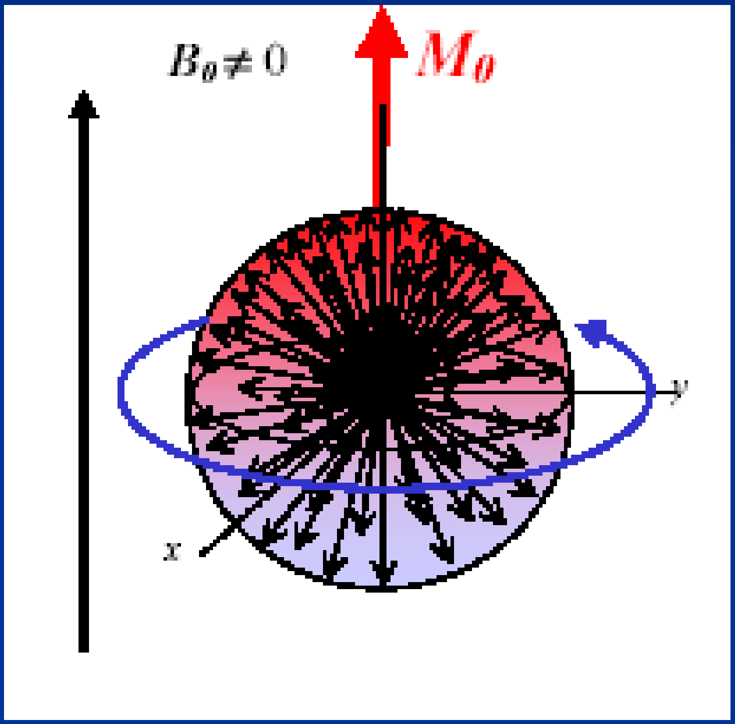
- T_2 cannot be longer than T_1: $T_2 \leq T_1$
- In the „extreme narrowing limit“: $T_2 = T_1$

T_1 and T_2 in Data Acquisition



- T_1 governs the repetition frequency for subsequent transients
- 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 $T_1 = T_2$

Magnetization

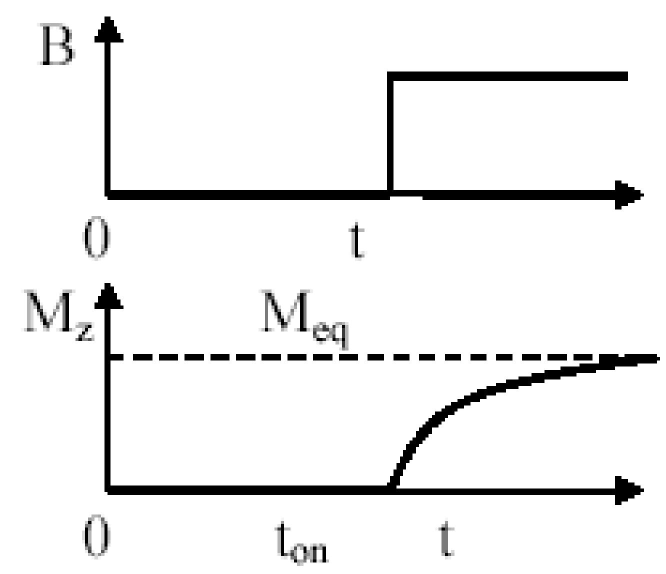


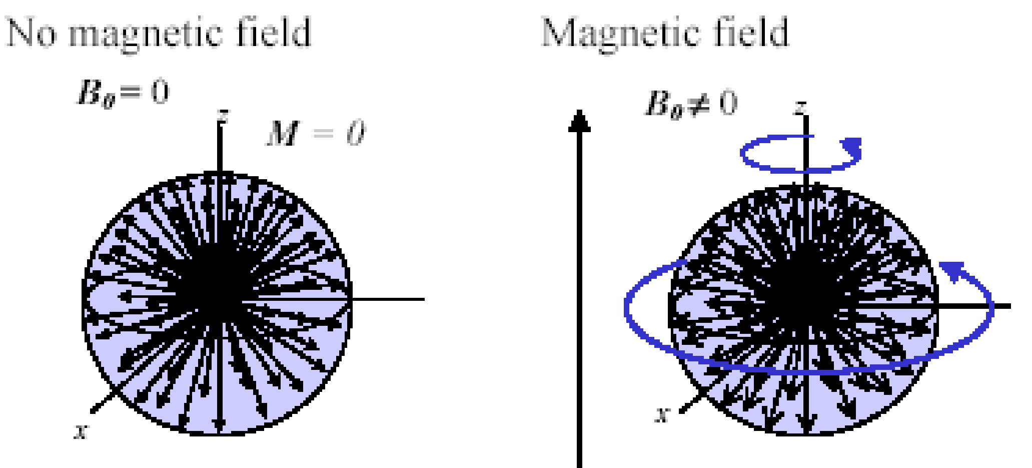
In-Field

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

$$M_0 = \Sigma\, \mu_i$$

Longitudinal Magnetization





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

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

Spin-Lattice Relaxation Time

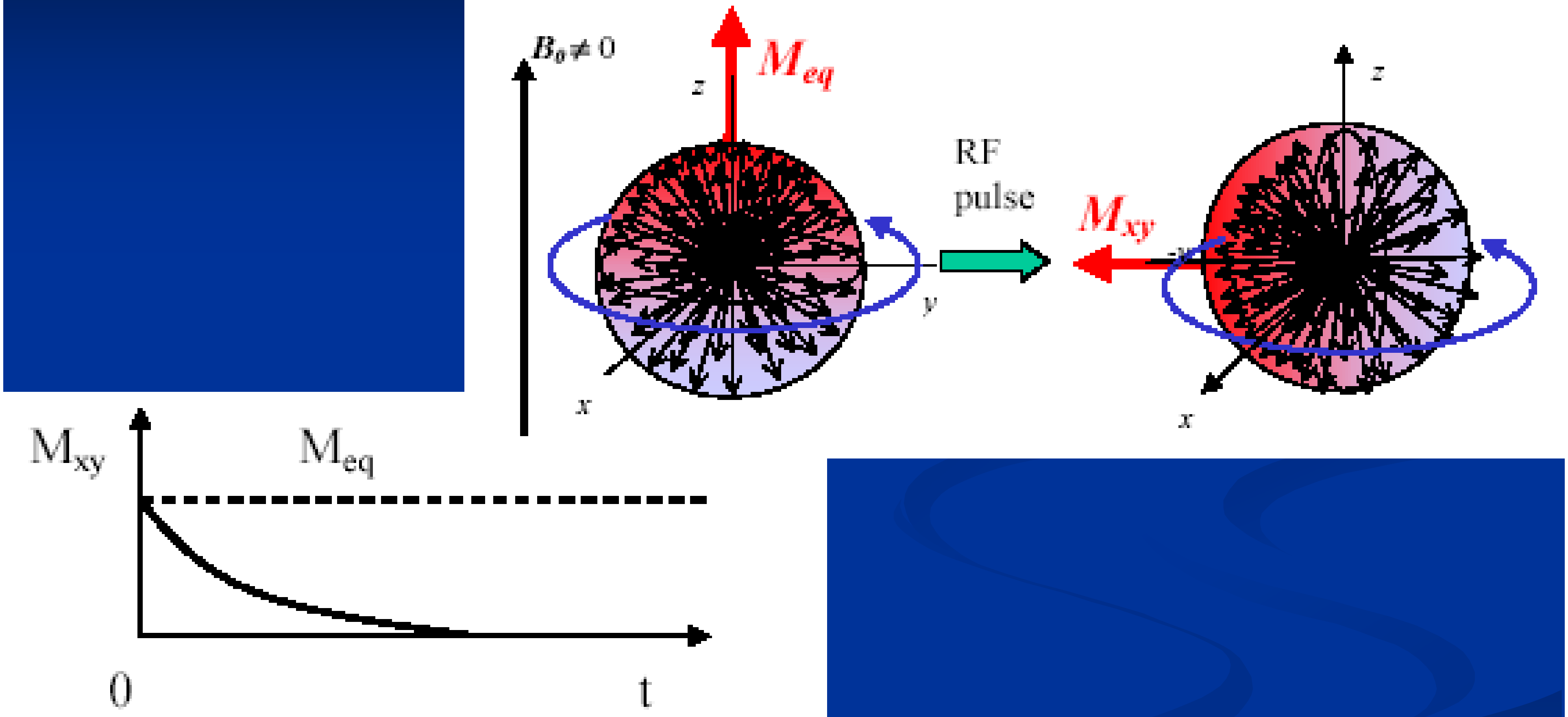
$R_1 = 1/T_1$ [Hz] longitudinal relaxation rate constant

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

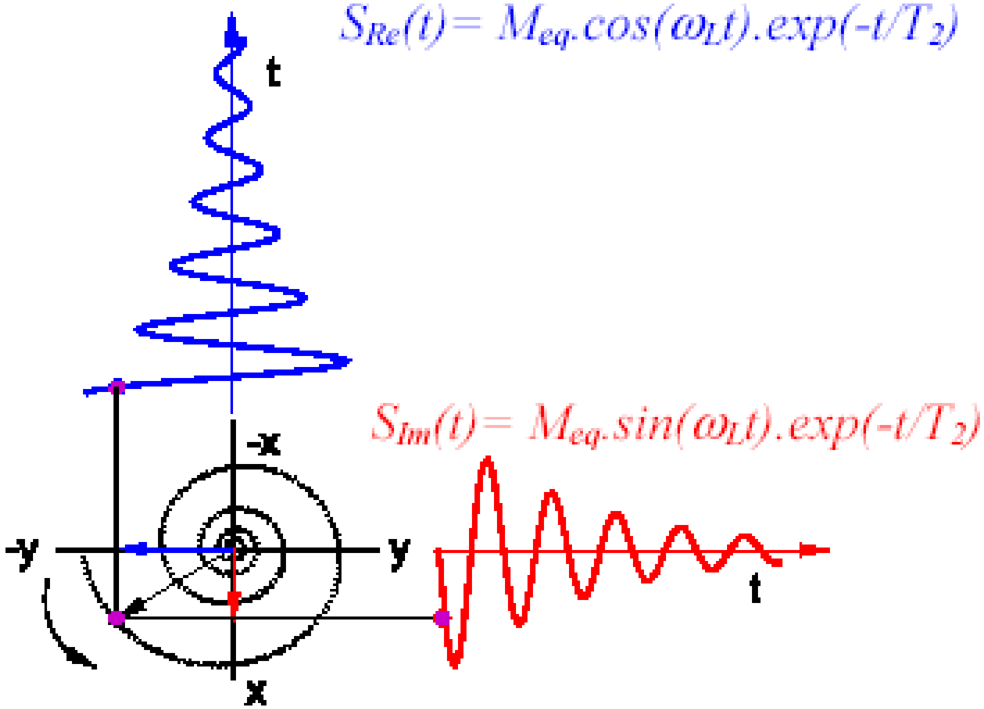
$R_2 = 1/T_2$ [Hz] transverse relaxation rate constant

T_2 [s] transverse relaxation time constant

spin-spin relaxation time

entropy

Free Induction Decay FID



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

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

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

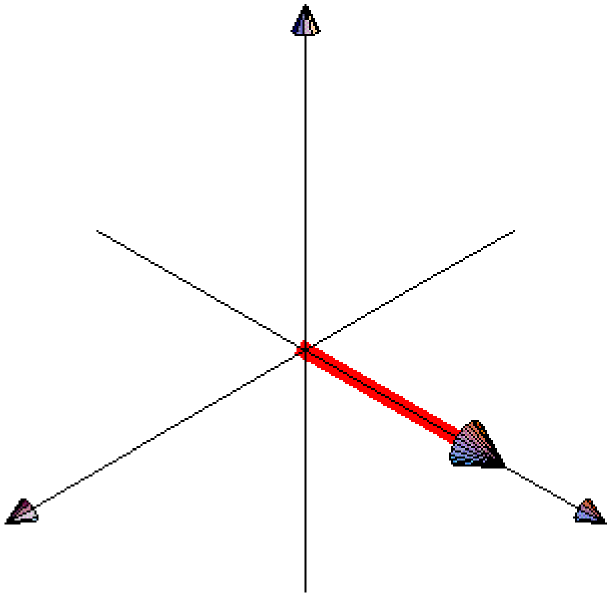
$$= [\cos(\omega_L t) + i\sin(\omega_L t)]\exp(-t/T_2)$$

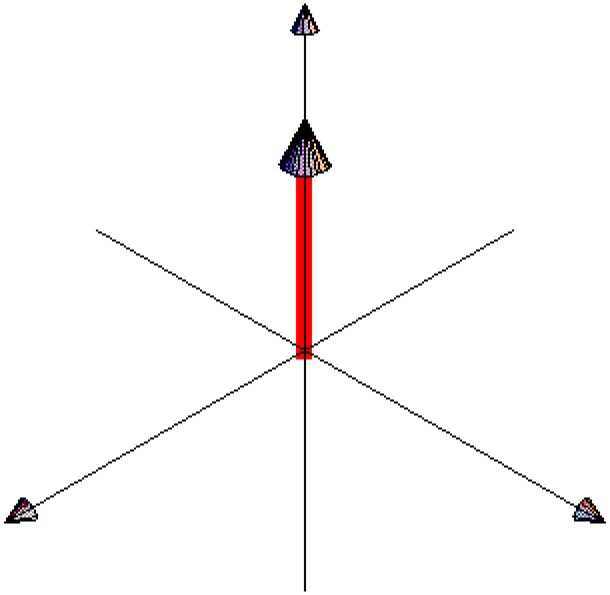
$$= \exp(i\omega_L t)\exp(-t/T_2) = \exp[-(1/T_2 - i\omega_L)t]$$

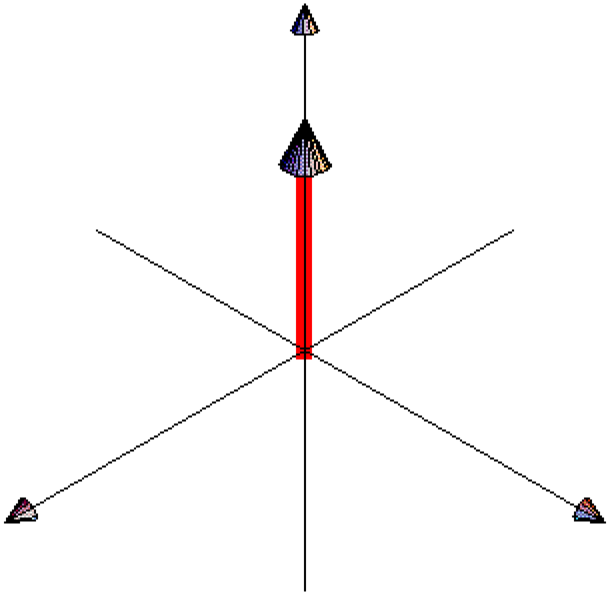
$$\frac{dM_{x'}}{dt} = (\omega_o - \omega) M_{y'} - \frac{M_{x'}}{T_2}$$

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

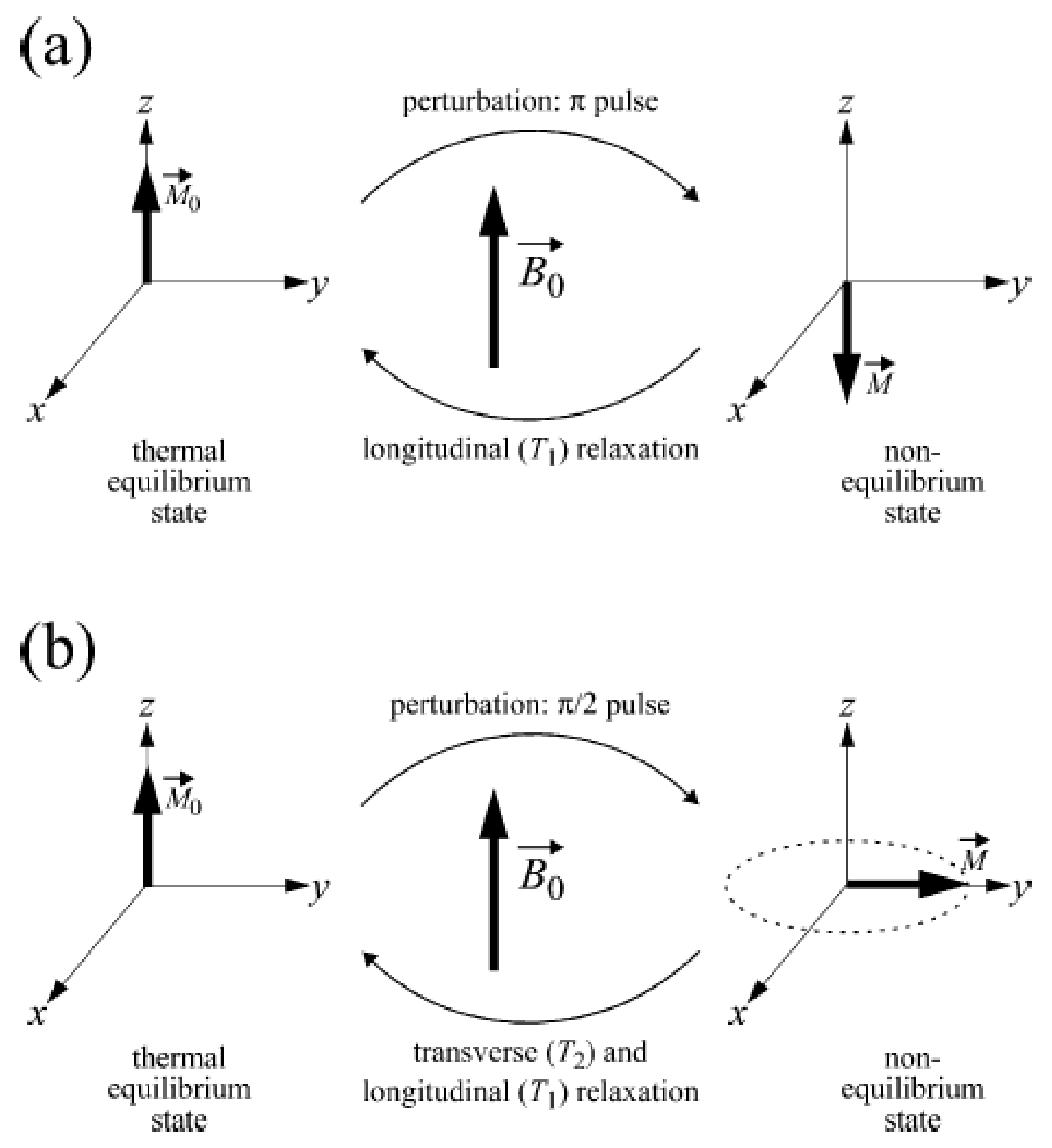
$$\frac{dM_z}{dt} = -2\pi\gamma B_1 M_{y'} - \frac{(M_z - M_{Z_o})}{T_1}$$







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 I with external fluctuating mg. field (dipolar) containing many different frequencies, when it contains $\omega_{L,}$ resonance causes relaxation = emission of excess energy, transition from exited to ground state

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

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	10^{-12} s
polymers, high viscosity	10^{-8} s

Correlation Time τ_C

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

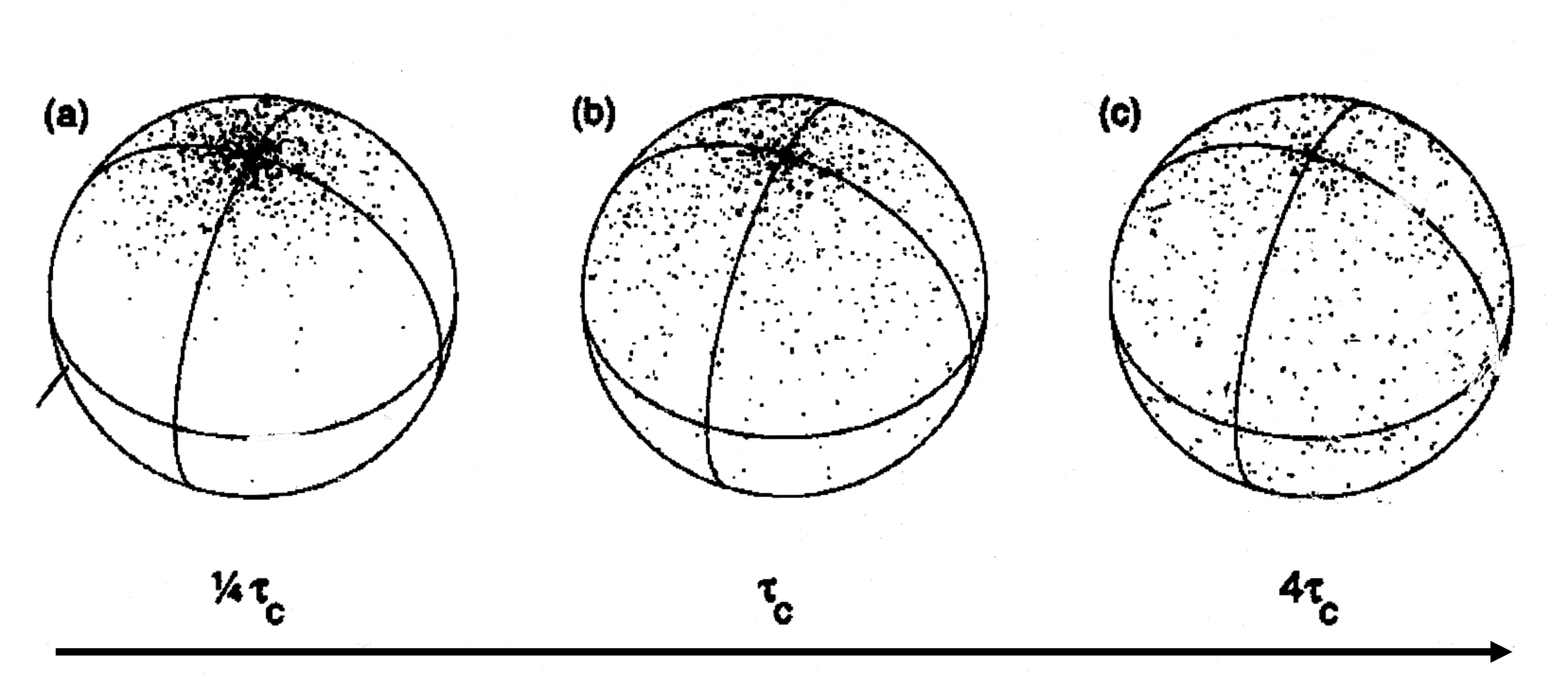
All molecules oriented in the same way,
then τ_C is time in which the orientation is dispersed to 1 rad (~60º)

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

$t >> \tau_C$ random distribution

$1/\tau_C$ = tumbling rate

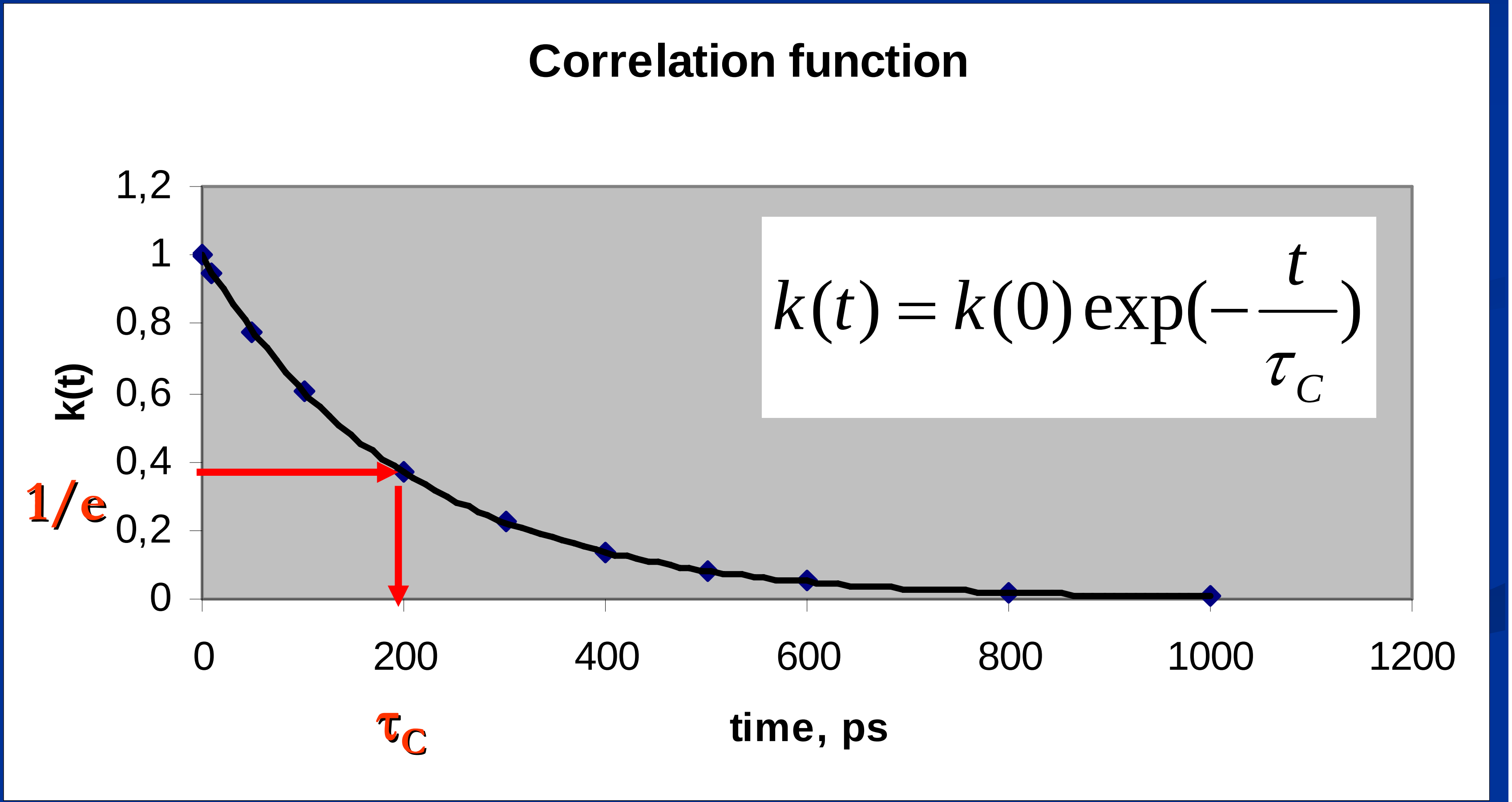
Correlation Time τ_C



Time

Correlation Time τ_C

Correlation function describes molecular tumbling



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

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

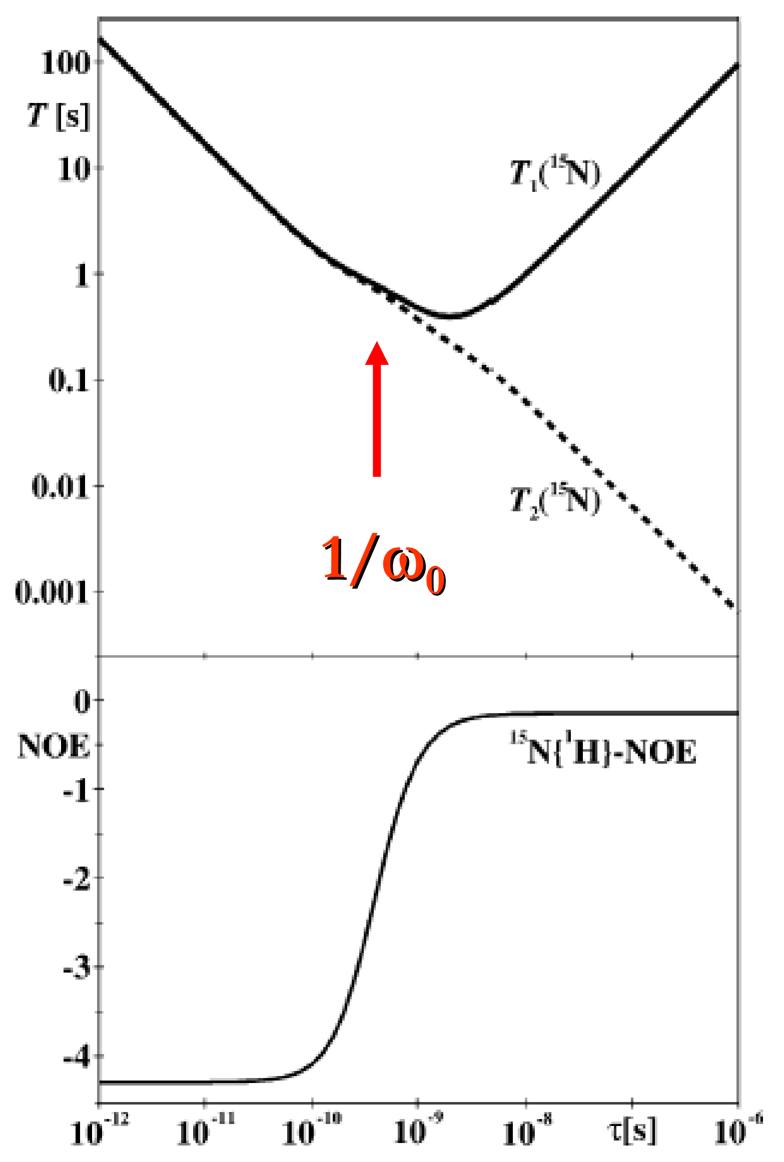
@65 ºC and 65 bar has low viscosity, narrow lines

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

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

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 Time T_1

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:

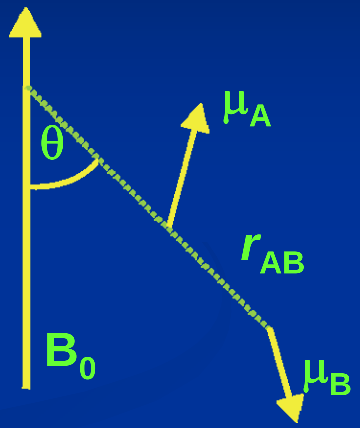
- Direct dipolar interaction of a nuclear spin with other nuclear spins
- Molecular motion in the presence of large chemical shielding anisotropies
- Interaction of a nuclear spin with a nuclear quadrupole

The individual contributions combine to make the total relaxation

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

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
S = spin of nucles B
γ_B = large magnetogyric ratio, faster relaxation, shorter $T_{1,DD}$
substitution H/D
nuclei with large γ (e.g. H) relax nuclei with small γ
$1/r^6_{AB}$ = only directly bound nuclei contribute = intramolecular

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

(in the extreme narrowing limit)

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
$T_{1,DD}$ (τ_c=10^{-11})	**8 s**	**5 s**	**33 s**	**17 s**	**48 min**
$T_{1,DD}$ (τ_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
$T_{1,DD}$ (τ_c=10^{-11})	**17 s**	**42 min**	**34 min**	**160 s**	**400 s**
$T_{1,DD}$ (τ_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)
$T_{1,DD}$ (τ_c=10^{-11})	8 s	24 min	110 min

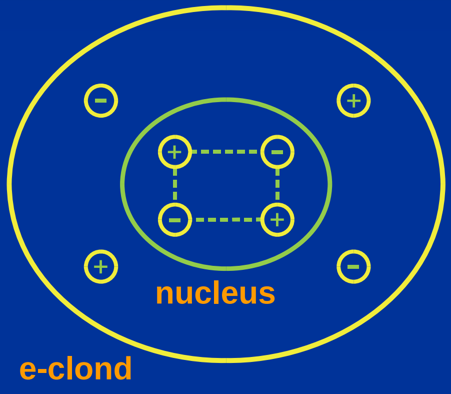
τ_c = 10^{-11}s: medium sized (in)organic molecule

τ_c = 10^{-9} s: small polymer

Quadrupole Induced Relaxation $T_{1,Q}$

The Interaction of a nuclear spin 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.

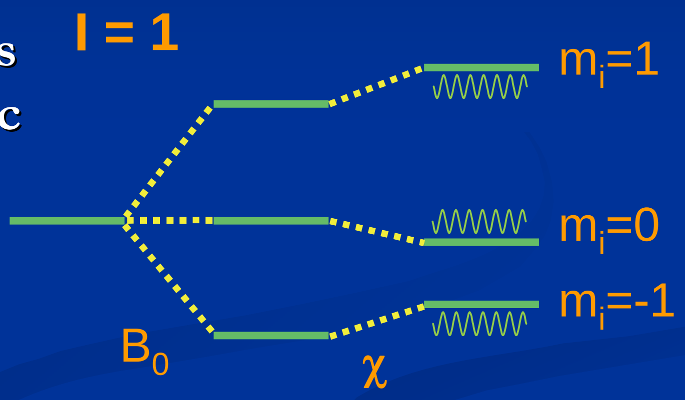
Electric quadrupole moment ***eQ*** = nonspharical distribution of the positive nuclear charge

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)

$$\frac{1}{T_{1,Q}} = \frac{1}{T_{2,Q}} = \frac{3(2I+3)}{40I^2(2I-1)}(1+\frac{\eta^2}{3})(\frac{e^2Qq_{zz}}{h})^2\tau_C$$

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 (η = 0 for axial symmetry)

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

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

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

^{14}N relaxation times:

	Bu_4N^+ (T_d)	$NaNO_3$ (D_{3h})	NNN^-($C_{\infty h}$)	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, $T_{1,CSA}$

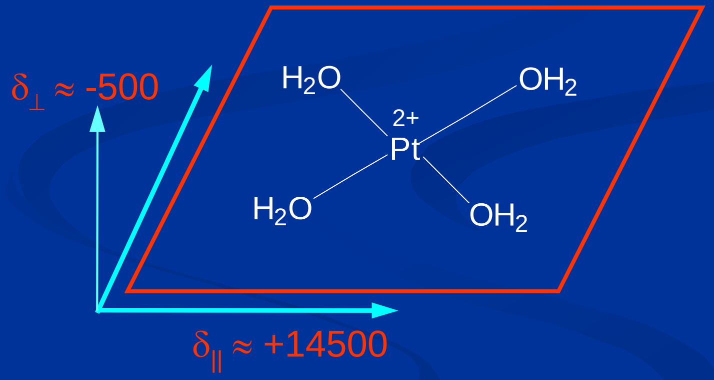
Tumbling of molecules with large chemical shielding anisotropies
Important for nuclei with wide range of chemical shifts: ^{31}P, ^{195}Pt, ^{113}Cd

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
γ(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

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

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

Away from Extreme Narrowing Conditions

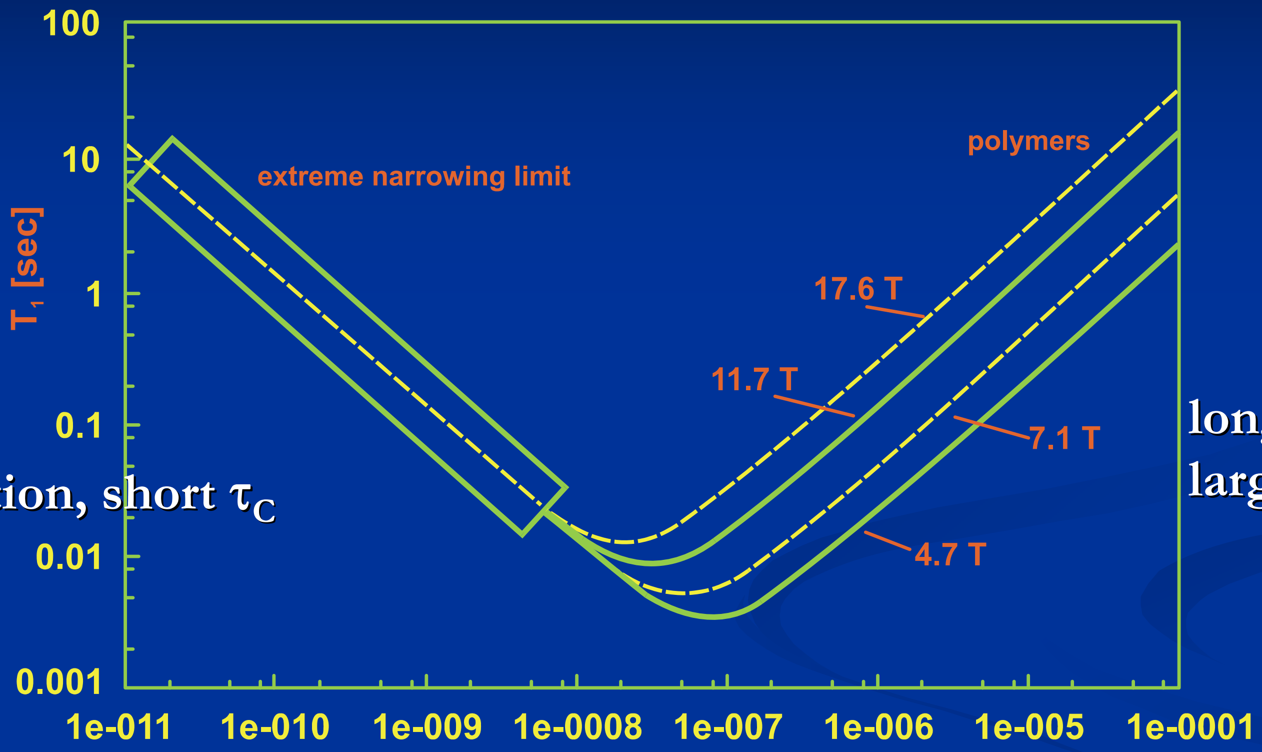
Theoretical analysis of relaxation processes under conditions which fail to fulfil the requirements of extreme narrowing revealed that dependence of T_1 on τ_c follows frequently a relation

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

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

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

The Temerature Dependence of T_1 Relaxation



fast motion, short τ_C

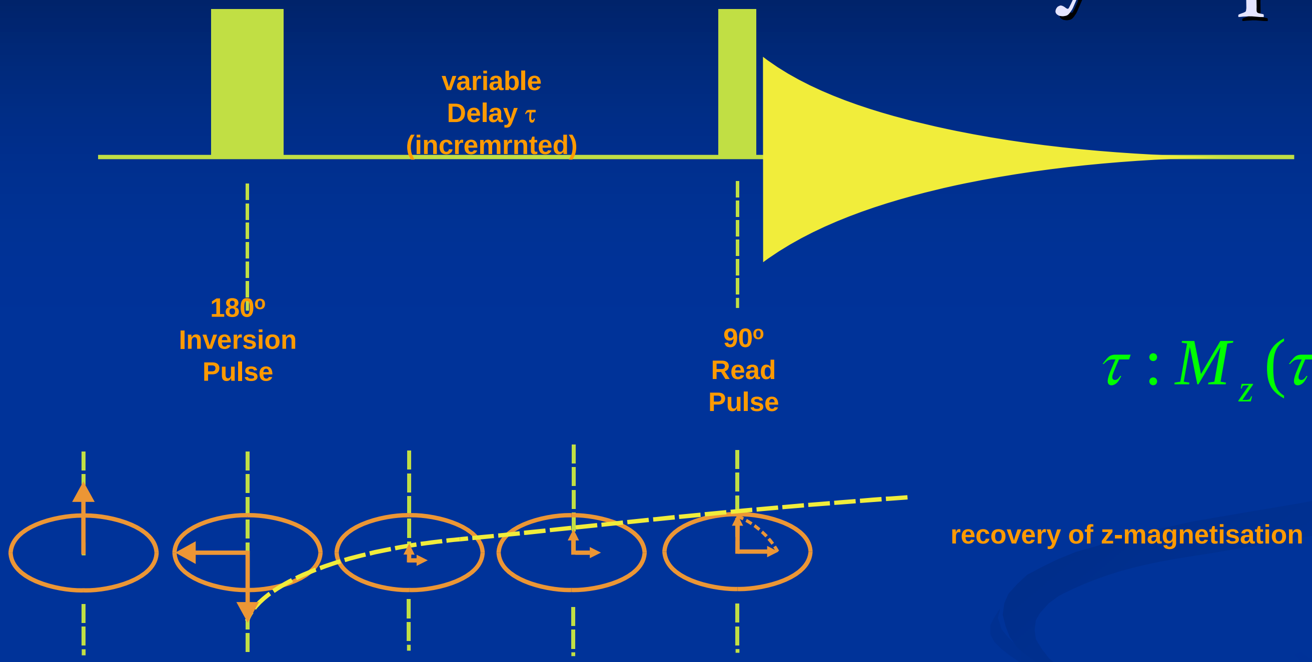
long τ_C
large molecules

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



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

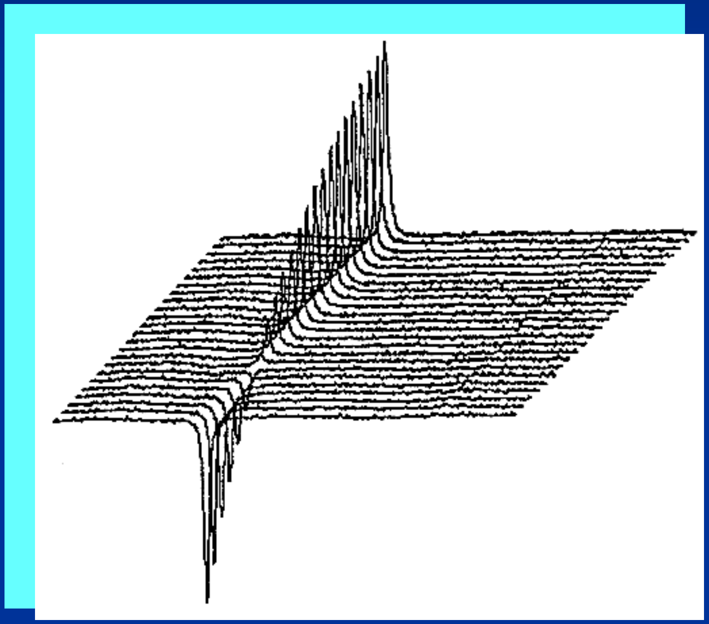
Non-equilibrium z-magnetisation recorvers during delay τ

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

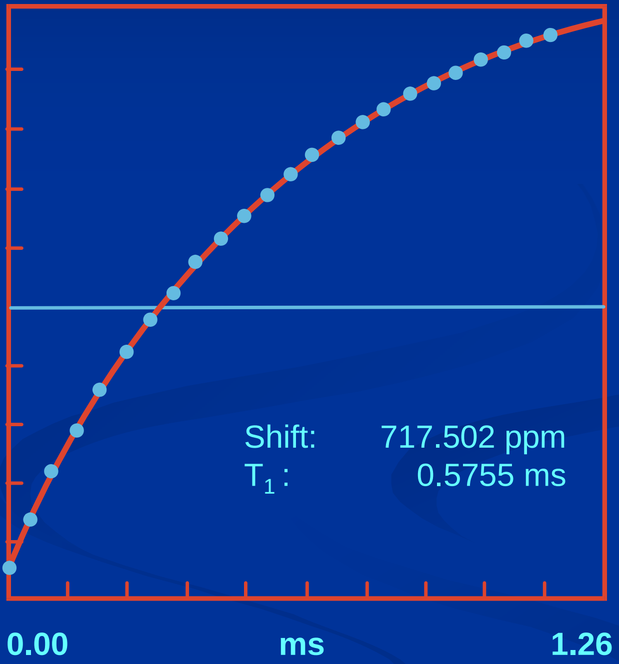
Performing a series of experiments and incrementing τ allows to sample $M_z(\tau)$ at different times

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



⇒



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,

$1/T_{2,\mathrm{true}} >> 1/T_{2,*}$

T_2 may be determined directly from measured linewidth:

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

For I = 1/2-nuclei,

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

T_2 must be measured by a dedicated experiments (CPMG)