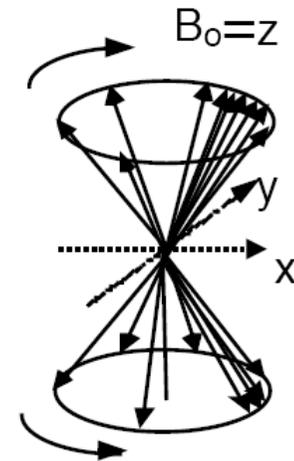
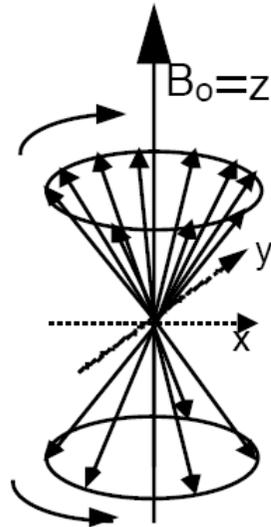


# Relaxation



Excitation

- Different populations
- No phase coherence

$T_1$

$T_2$

- Equal populations
- Partial phase coherence

Relaxation



## Perché dobbiamo preoccuparci del rilassamento?

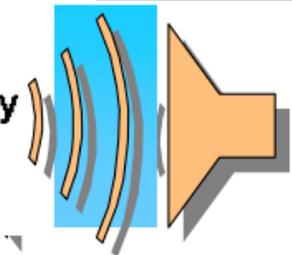
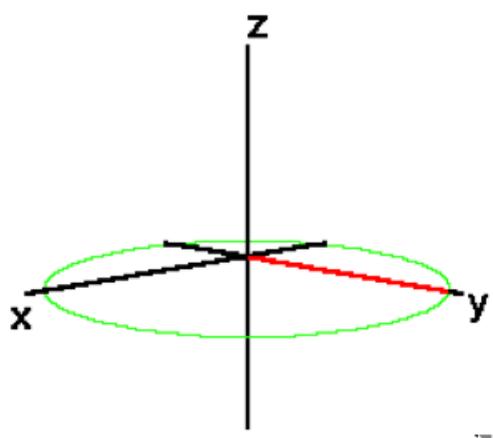
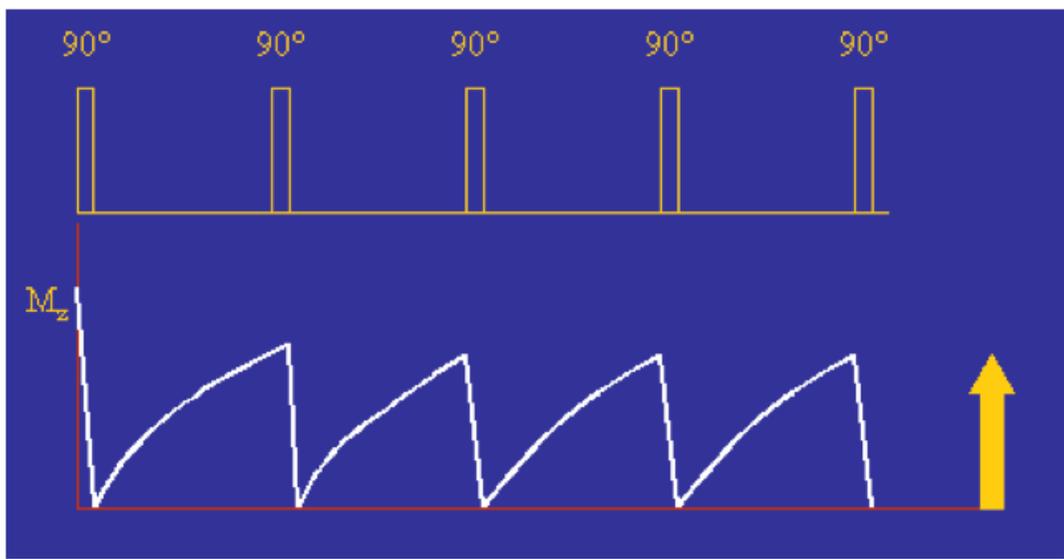
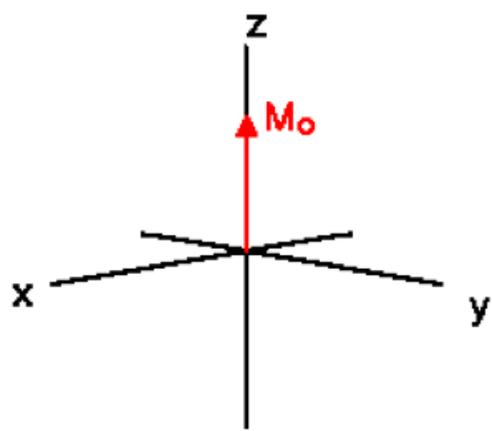
	UV vis	IR	ESR	NMR
$\lambda$	500 nm	10000 nm	3 cm	0.5m
$\nu$	6.00E+14	3.00E+13	9.99E+09 (10 GHz)	<b>6.00E+08</b> <b>(600 MHz)</b>
$\Delta E$ (J)	3.97E-19	1.99E-20	6.62E-24	3.97E-25
kJ/mol	2.39E+02	1.19E+01	3.99E-03	2.39E-04
N/N°	2.268E-42	8.275E-03	0.998403	<b>0.999904</b>

☹️ NMR tecnica a bassa sensibilità

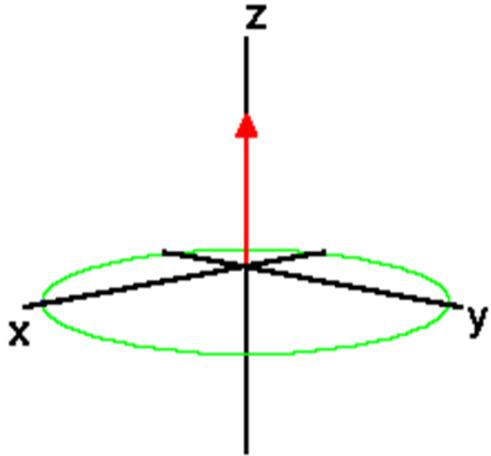
☹️ una scansione non basta

😊 dobbiamo ripristinare la magnetizzazione  $M_z$

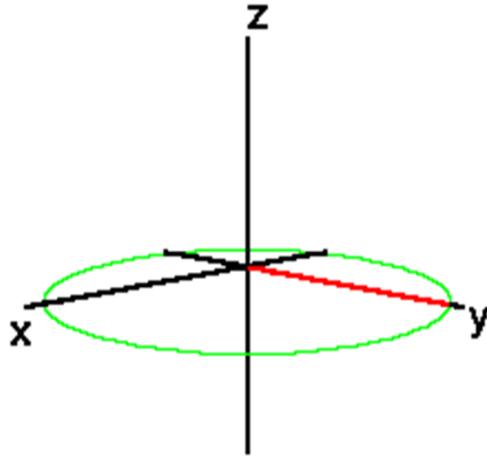
$B_0$



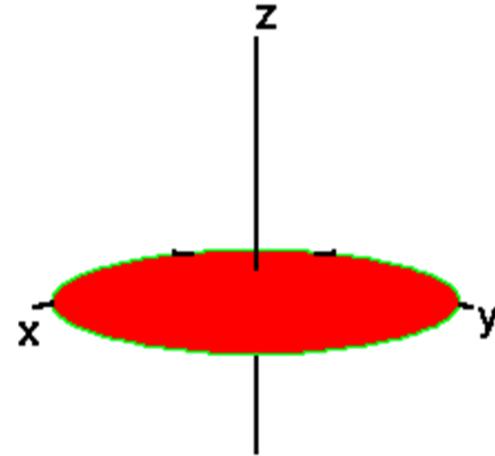
# Relaxation



Excitation

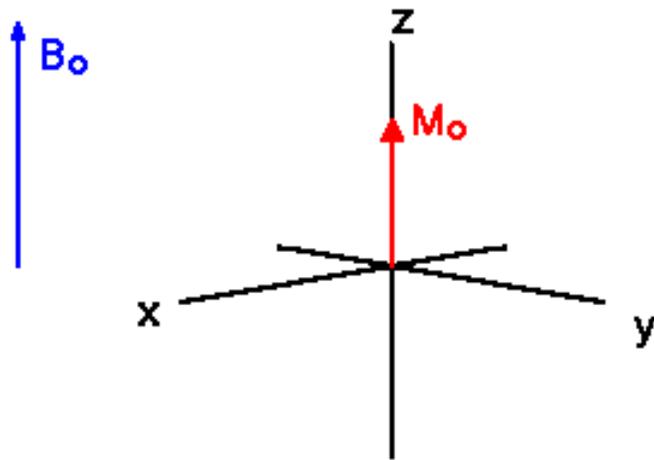


Signal



Relaxation

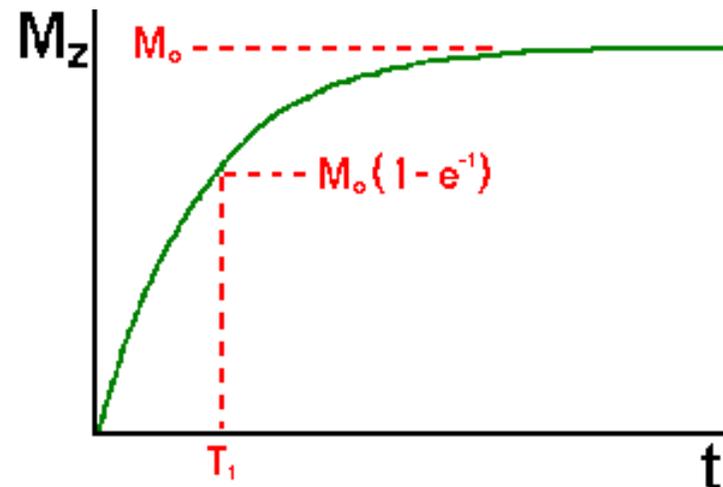
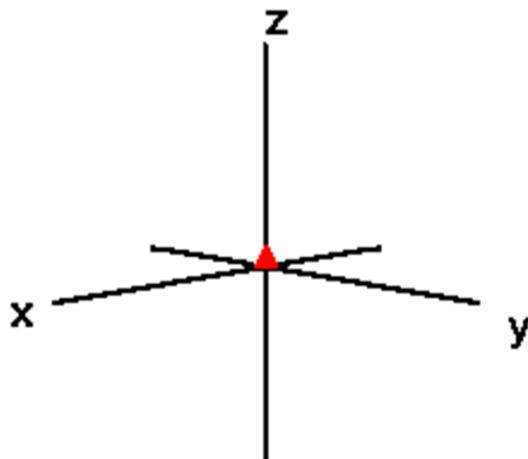
# Spin-lattice Relaxation: $T_1$ processes

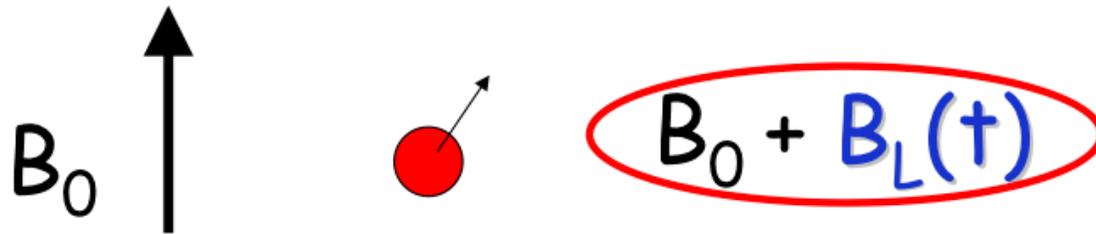


$$M_z = M_0$$

$M_z$  is the longitudinal magnetization

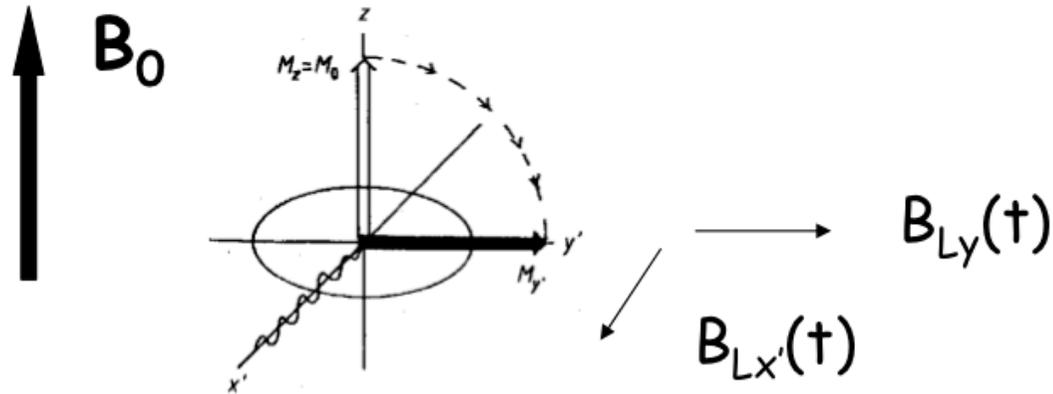
$$M_z = M_0 (1 - e^{-t/T_1})$$





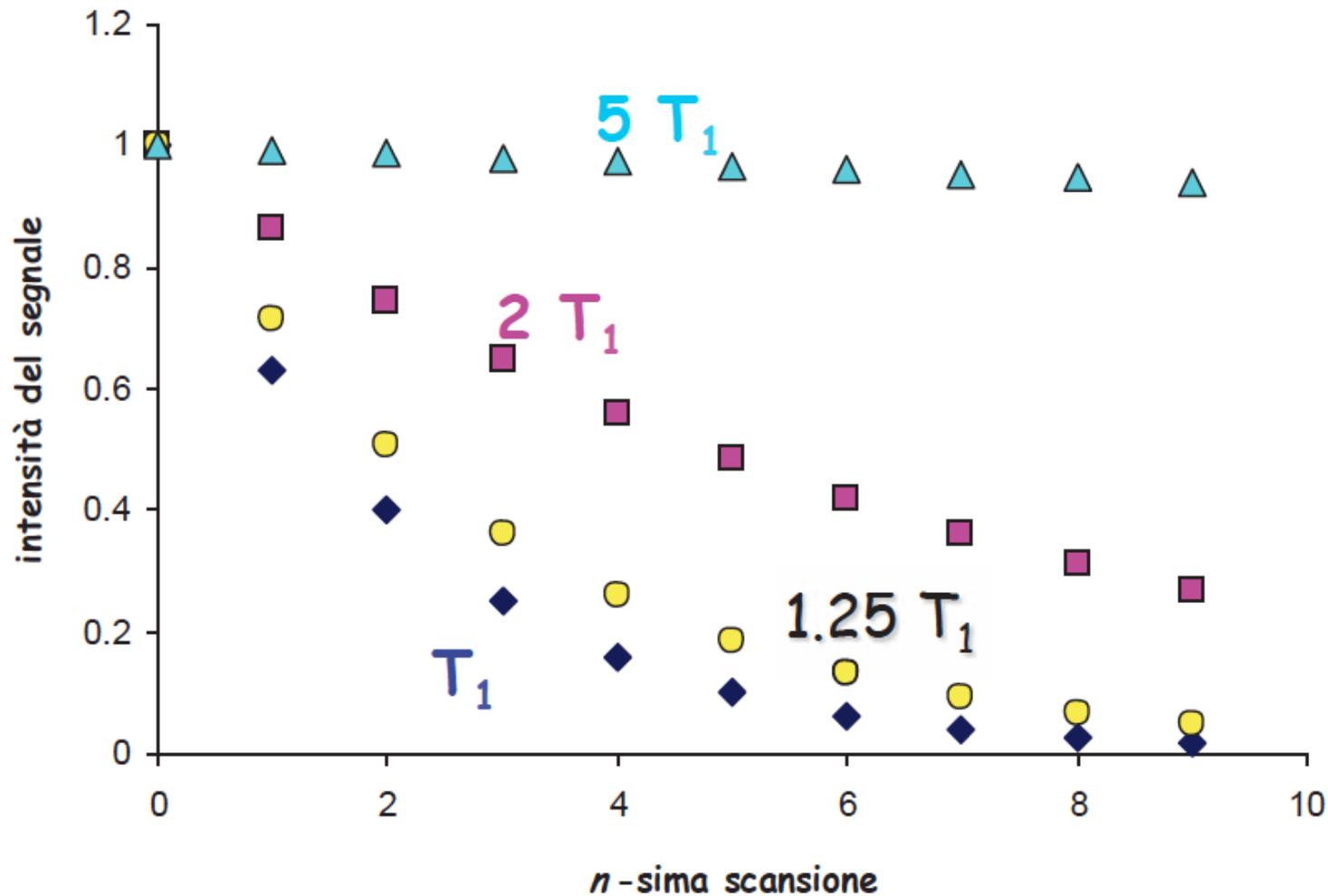
☞ Le componenti del campo locale che fluttuano nel piano  $xy$  permettono il rilassamento della magnetizzazione longitudinale.

$\perp B_0$



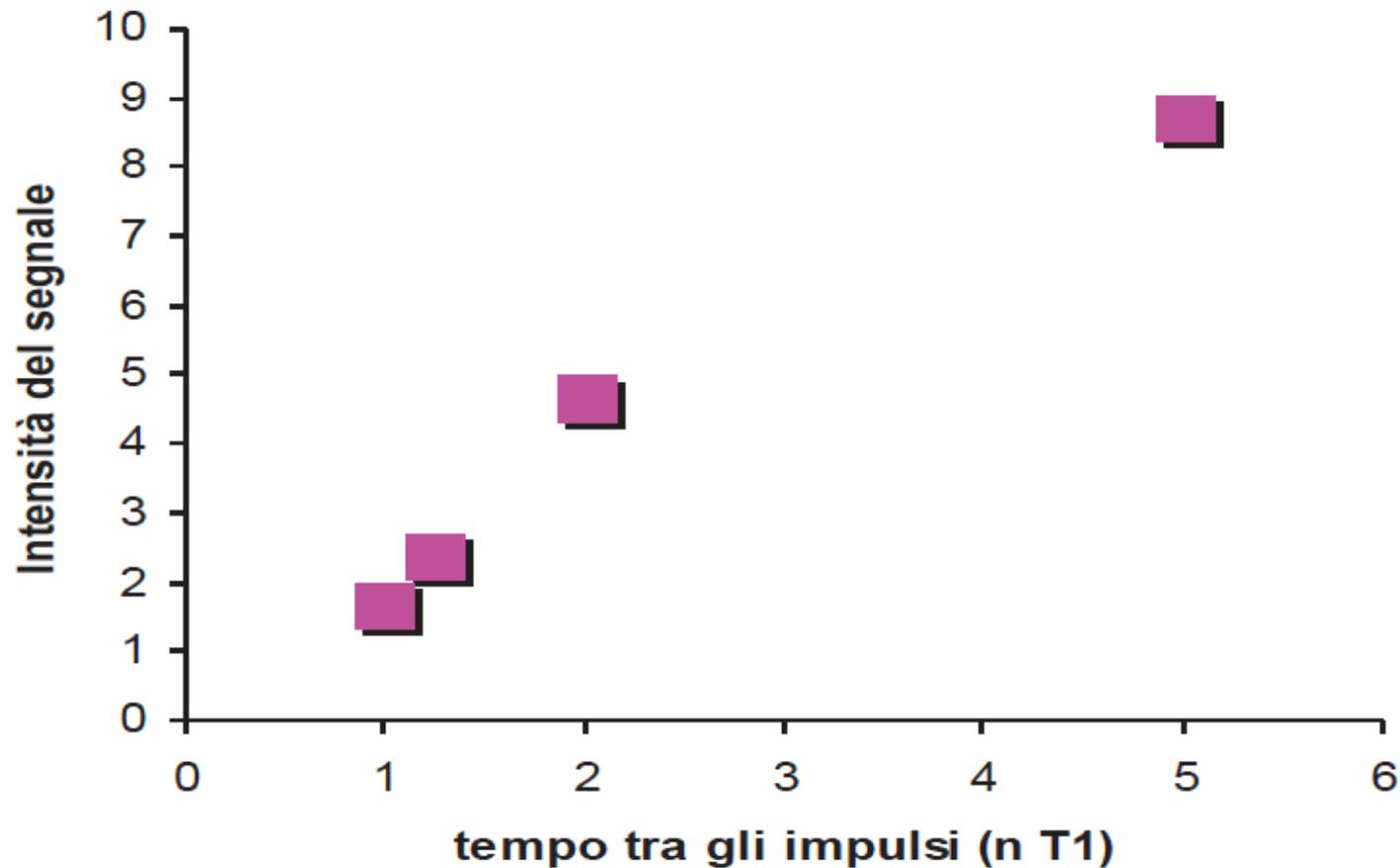
$$M_z = M_0 (1 - \exp(-t / T_1))$$

Valore di  $M_z$  dopo  $n$  scansioni se il tempo tra un impulso e il successivo è....



Dopo 10 scansioni l'intensità totale registrata dovrebbe essere  $10 M_0$  ma invece è

repetition time	$T1$	$1.25*T1$	$2*T1$	$5* T1$
Intensità	1.69	2.37	4.66	8.7



...dopo un tempo  $t = 5T_1$

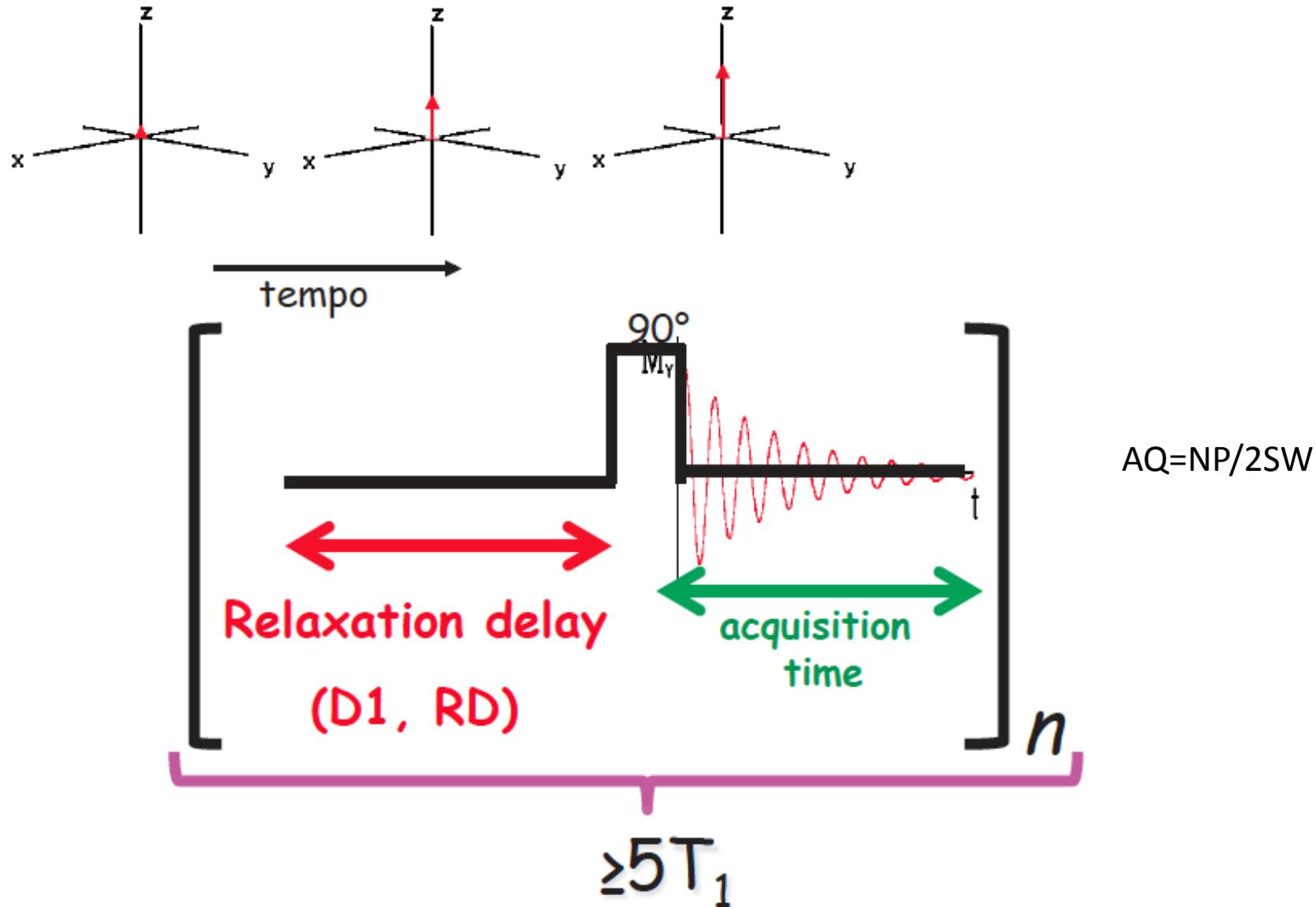
☞ che percentuale della magnetizzazione è tornata lungo  $z$ ?

$$M_z = M_\infty(1 - \exp(-t / T_1)) = M_\infty(1 - e^{-5}) = M_\infty(1 - 0.00674) \\ = 0.99326 M_\infty$$

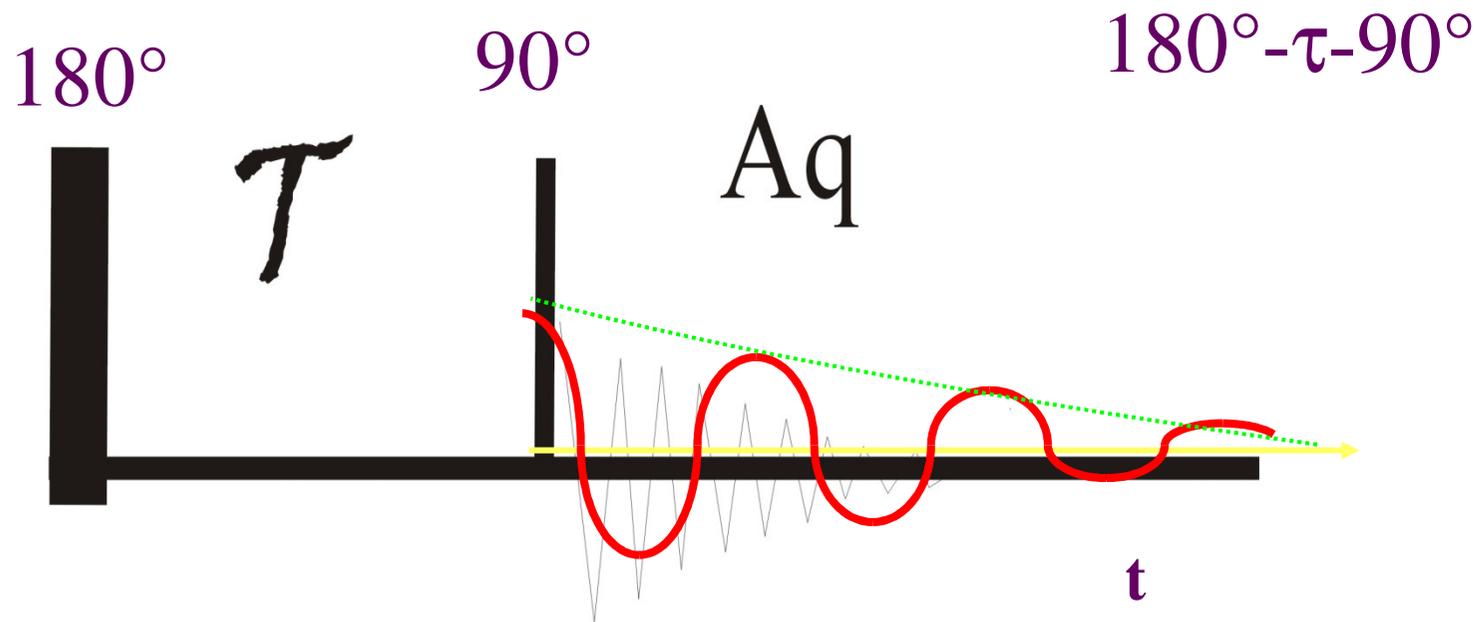
☞ che percentuale è ancora nel piano  $xy$ ?

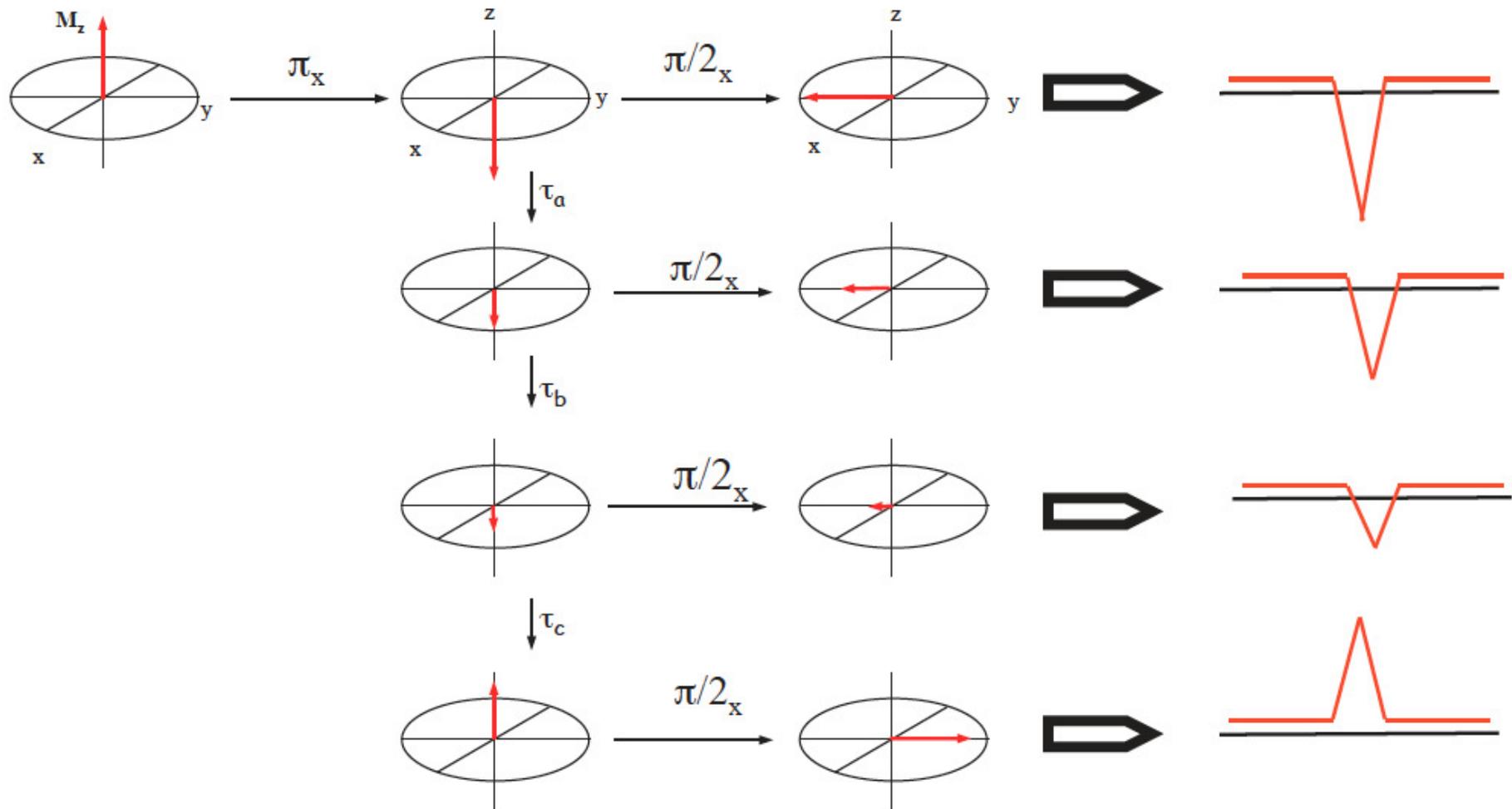
$$M_y = M_\infty \exp(-t / T_2) = M_\infty (e^{-5}) = 0.00674 M_\infty$$

☞ ..per un effettivo ritorno all'equilibrio di  $M_z$



# $T_1$ measurement: Inversion Recovery



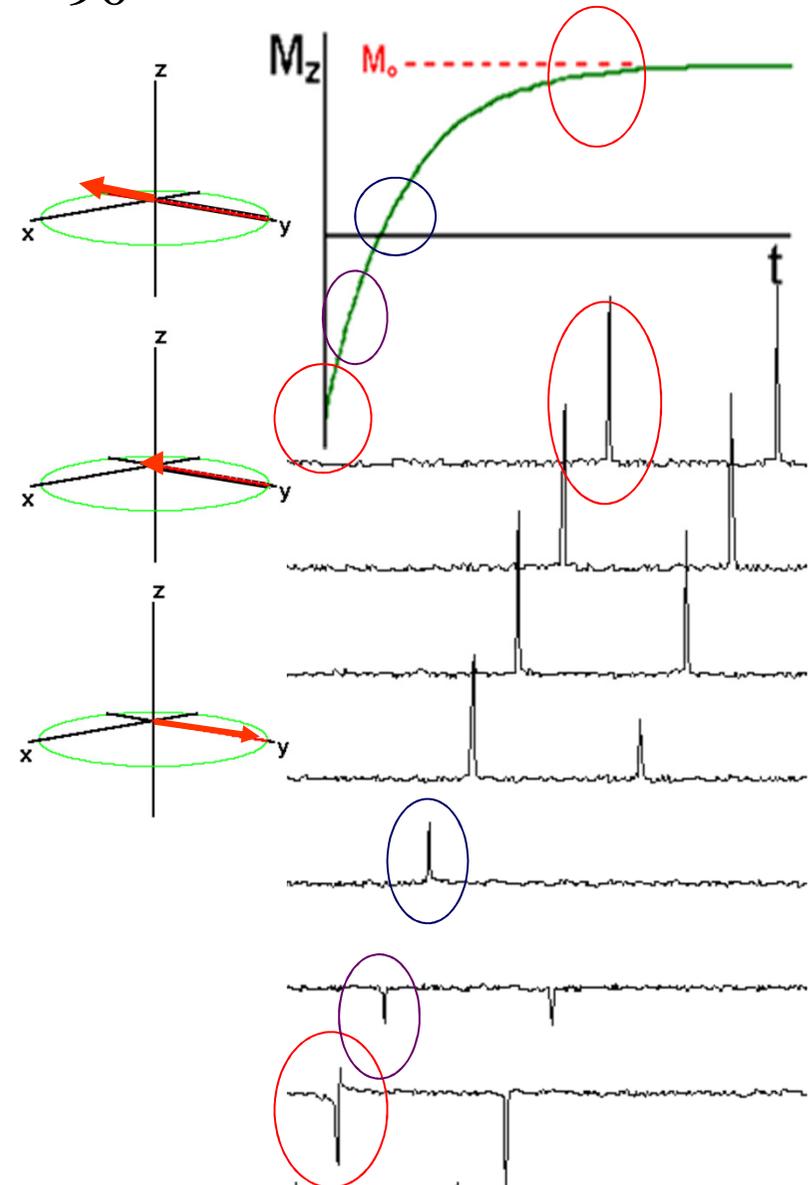
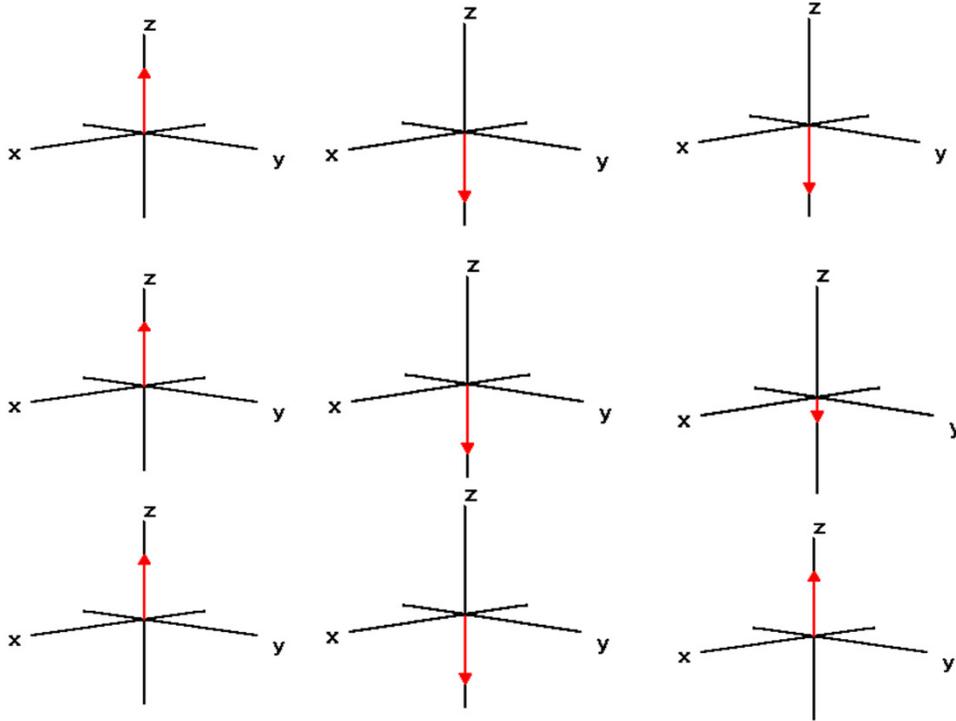


# Inversion recovery

180°

-τ-

90°



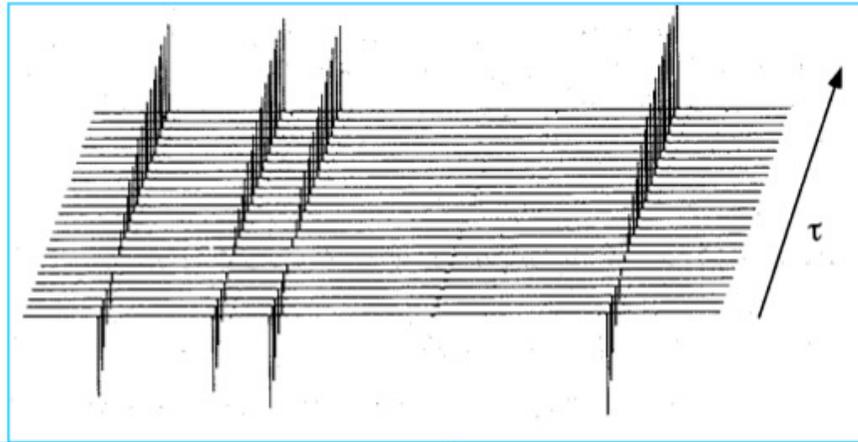
$$M_z(t) - M_0 = [M_z(0) - M_0] \exp(-t/T_1) \quad M_z(0) = -M_0$$

$$M_z(t) = -2M_0 \exp(-t/T_1) + M_0$$

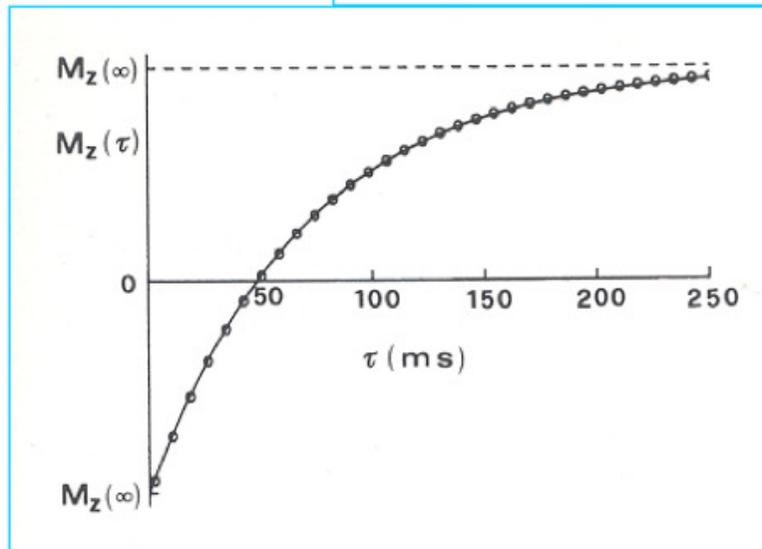
$$M_z = M_0 (1 - 2e^{-t/T_1})$$



## Analisi dei dati



$$M_z = M_0 (1 - 2e^{-t/T_1})$$



$$M_z(t) = M_0 (1 - 2 \exp(-R_1 t))$$

$$M_z(t) = A(1 - B \exp(-Ct))$$

fitting non lineare di 3 parametri

oppure linearizzazione

$$M_0 - M_z(t) = 2 M_0 \exp(-R_1 t)$$

$$\ln(M_0 - M_z(t)) = \ln(2 M_0) - R_1 t$$

Quando  $M_z(t)$  si annulla [ $\tau_{nul}$ ]

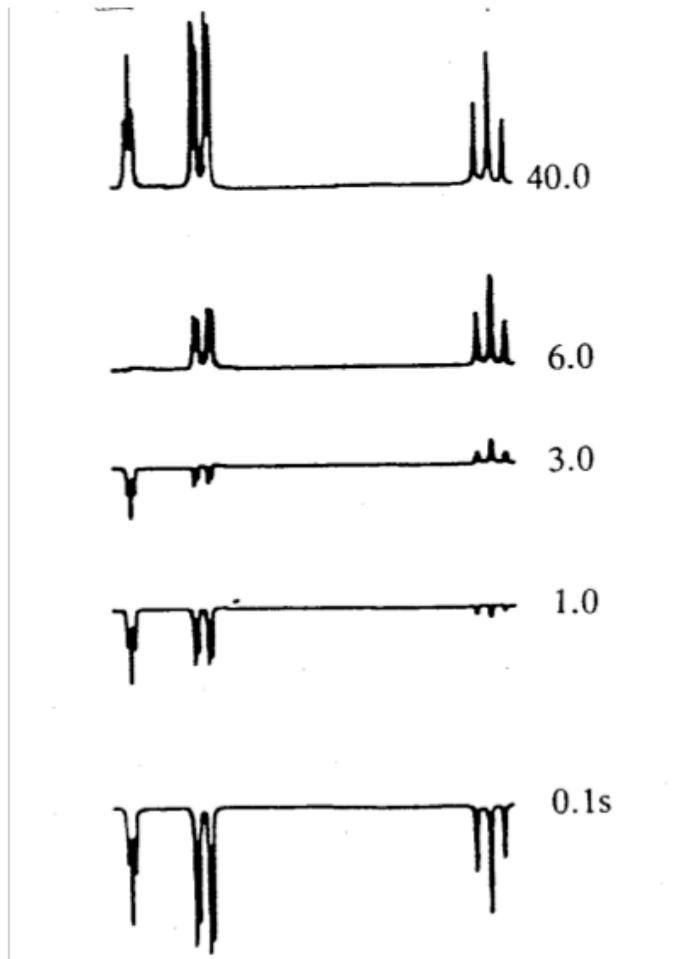
$$\ln(M_0 - M_z(t)) = \ln(2 M_0) - R_1 t$$

$$\ln(M_0) = \ln(2 M_0) - R_1 \tau_{nul}$$

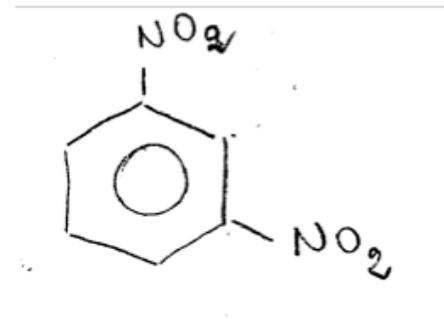
$$R_1 \tau_{nul} = \ln 2$$

$$R_1 = \ln 2 / \tau_{nul}$$

ovvero  $T_1 \approx \frac{\tau_{nul}}{\ln 2}$

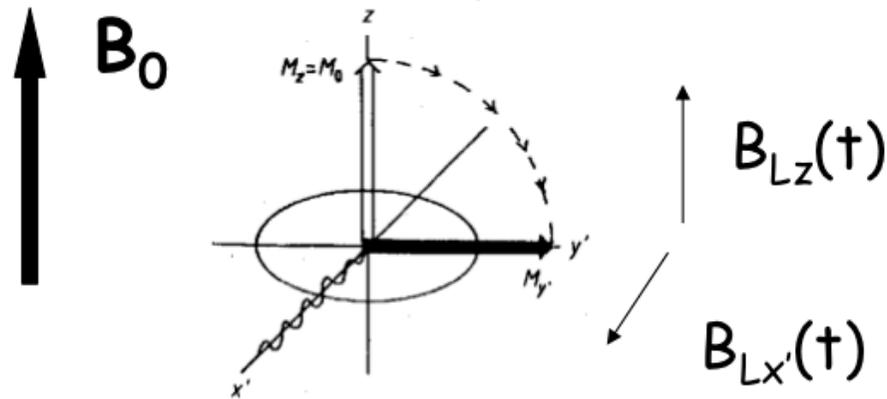


*m*-dinitrobenzene

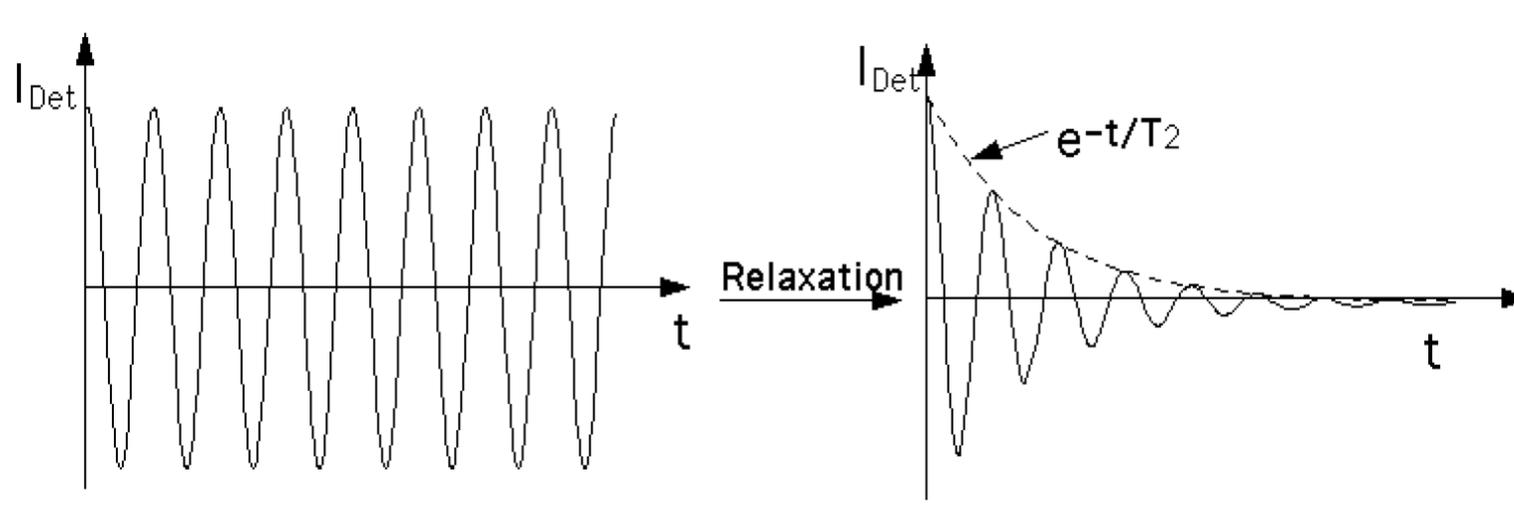


$$T_1 \approx \frac{\tau_{nvl}}{\ln 2}$$

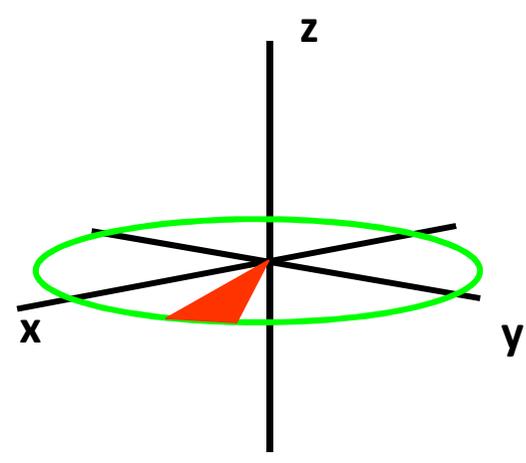
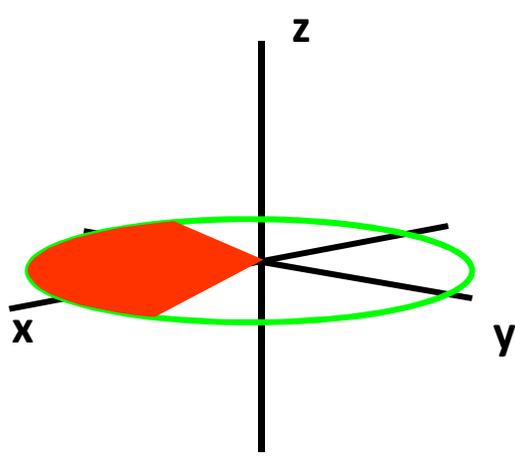
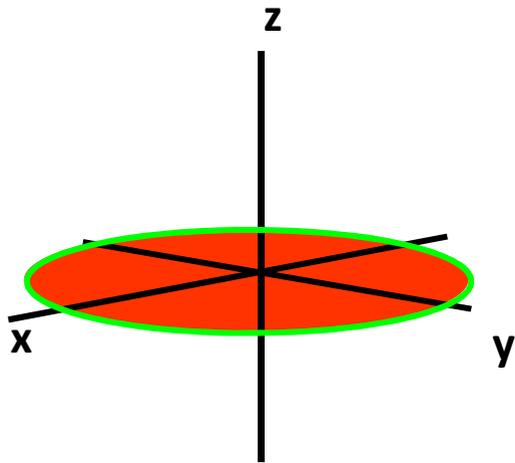
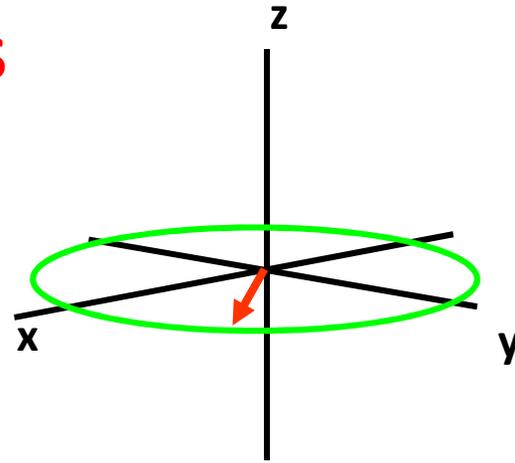
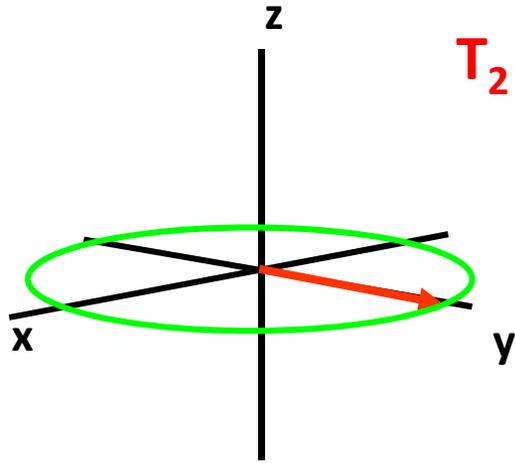
  $B_0$   Le componenti del campo locale che fluttuano nei piani  $x'z$  o  $y'z$  permettono il rilassamento della magnetizzazione trasversale ( $M_{x'}$  o  $M_{y'}$ ).



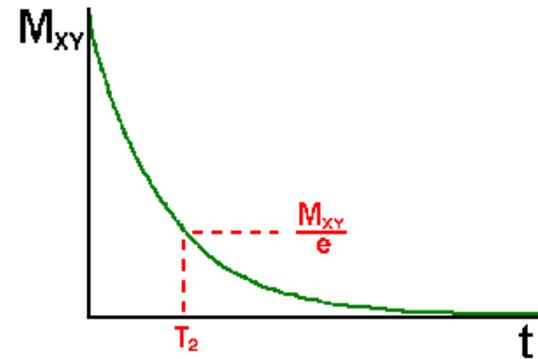
# Spin-spin Relaxation



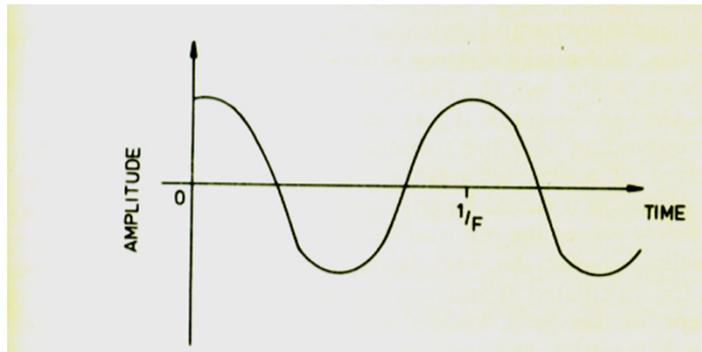
# T<sub>2</sub> PROCESSES



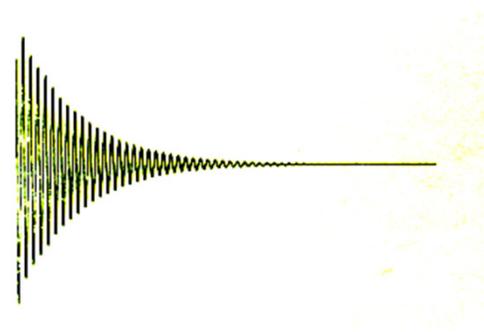
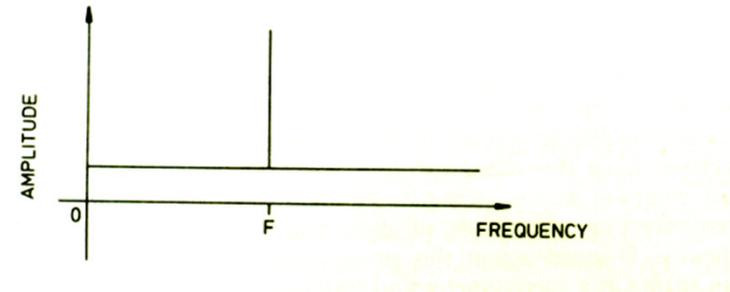
$$M_{xy} = M_{xy0} e^{-t/T_2}$$



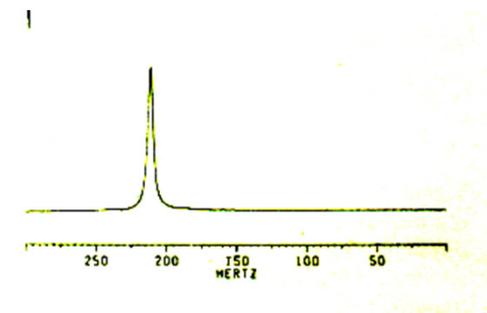
# The effects of Relaxation



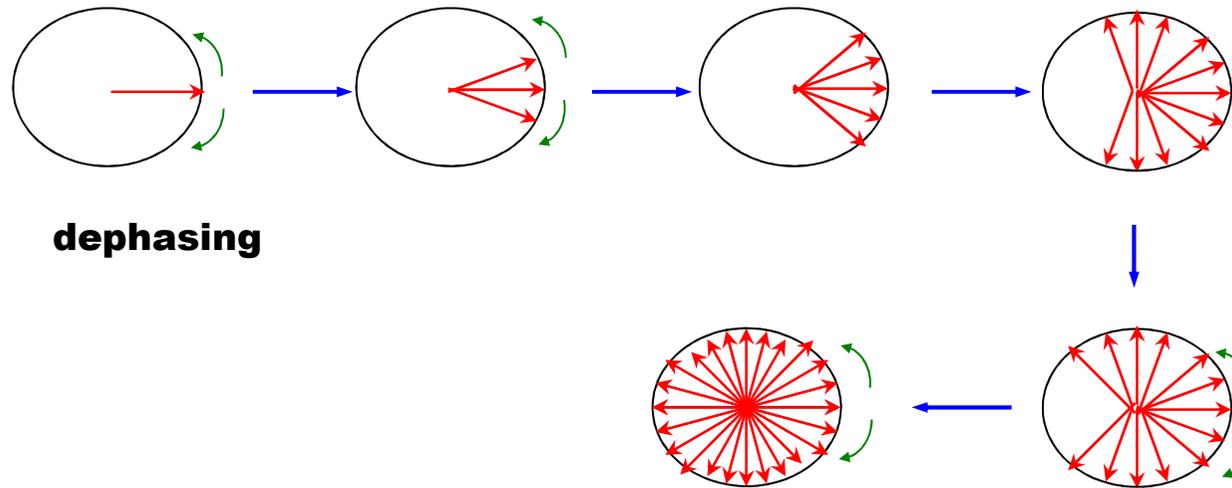
FT  
→



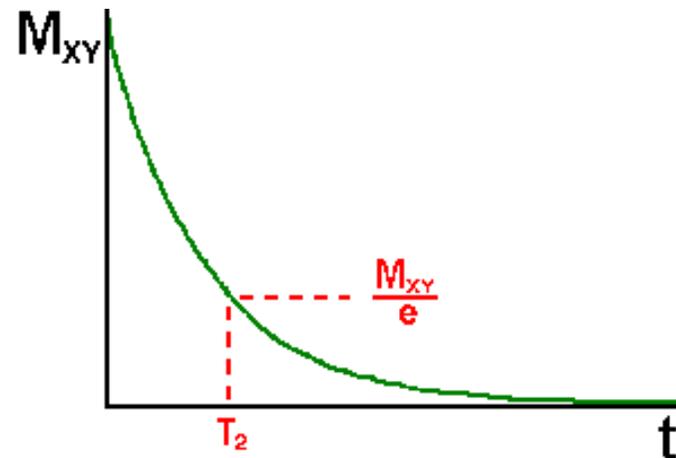
FT  
→

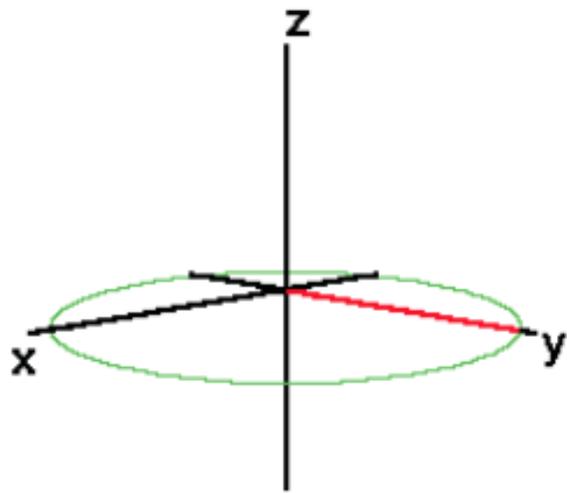


# Spin-spin Relaxation: $T_2$ processes

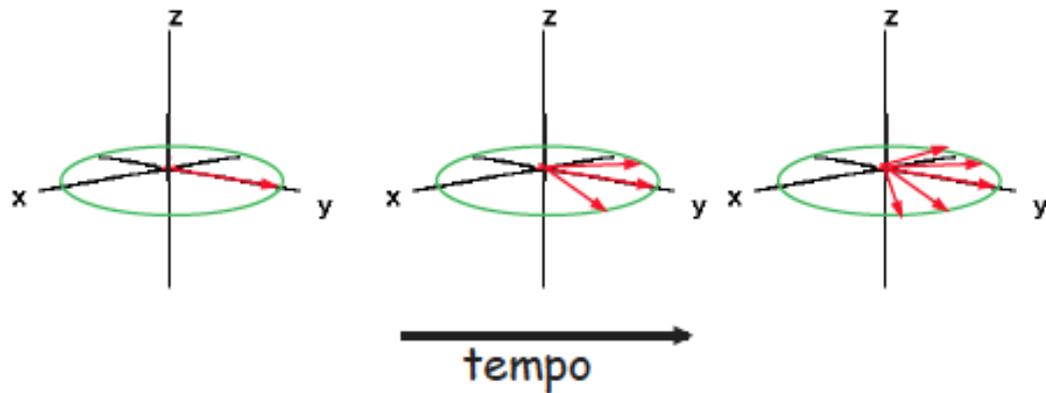


$$M_{XY} = M_{XY0} e^{-t/T_2}$$





## Ritorno all'equilibrio di $M_{xy}$



$$\frac{dM_y}{dt} = -k_2(M_y)$$

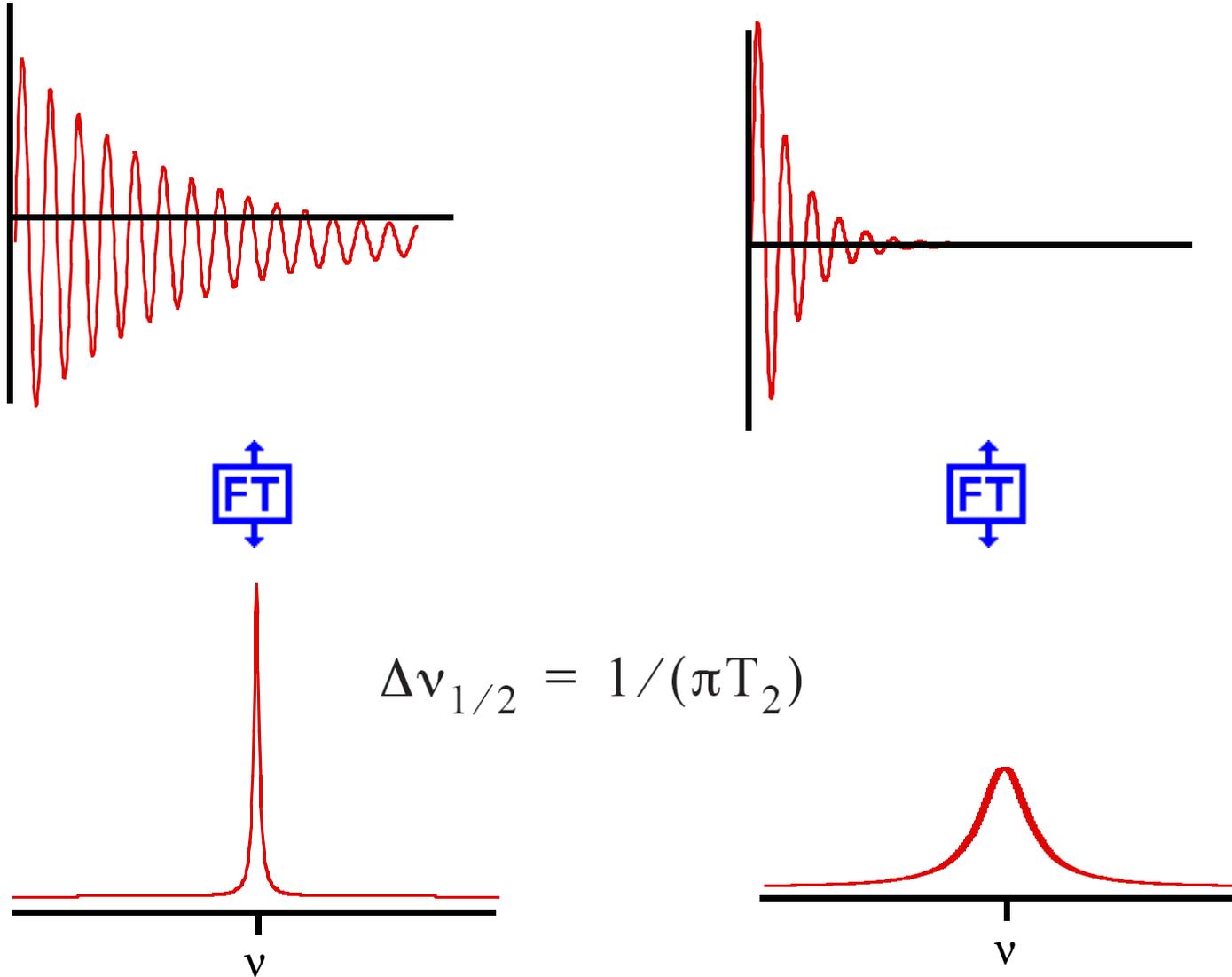
$$\frac{dM_y}{dt} = -R_2(M_y)$$

$k_2$  costante di velocità ( $s^{-1}$ )  $\rightarrow R_2$

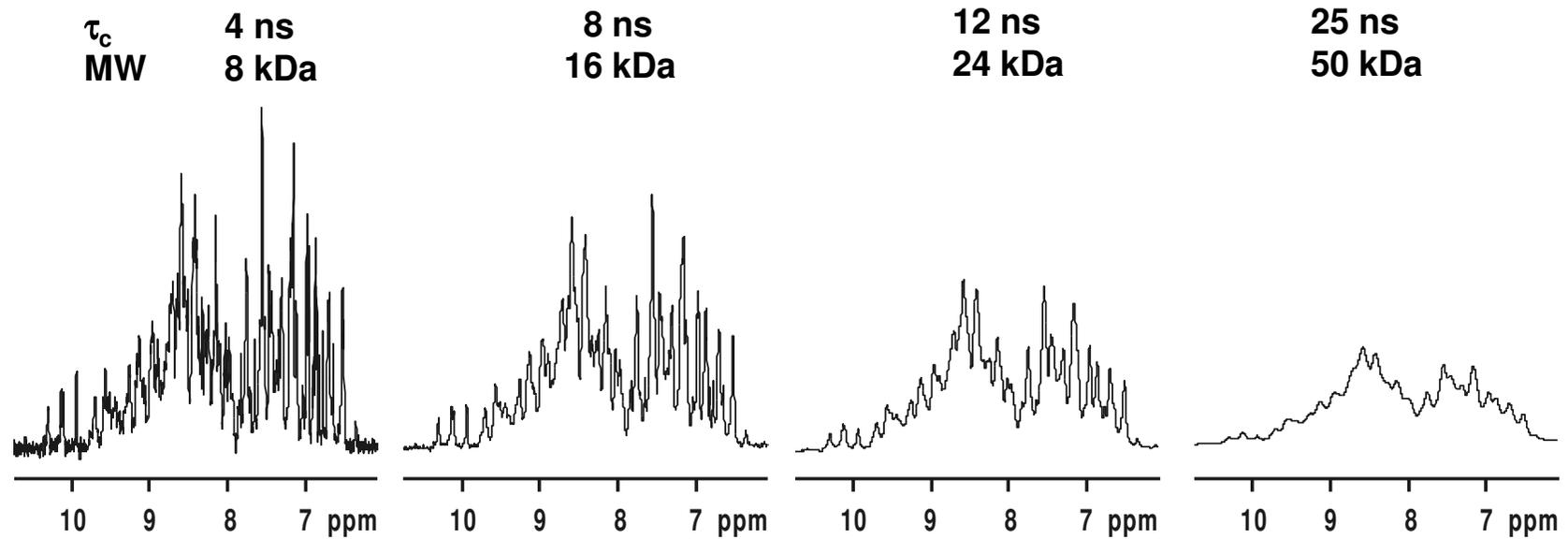
$$M_y = M_\infty \exp(-R_2 t)$$

$R_2$  velocità di rilassamento trasversale  
 $T_2 = (R_2)^{-1}$  tempo di rilassamento trasversale

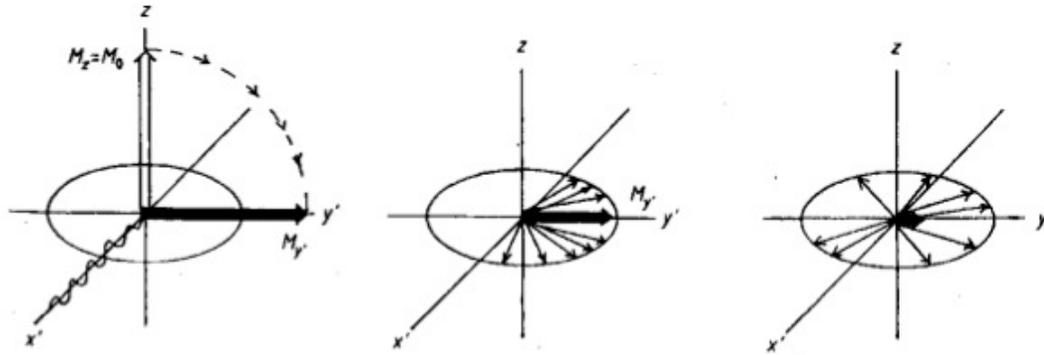
# The effects of Relaxation



# Relaxation and molecular size



## Misure di $T_2$



Perdita di coerenza nel piano xy dovuta

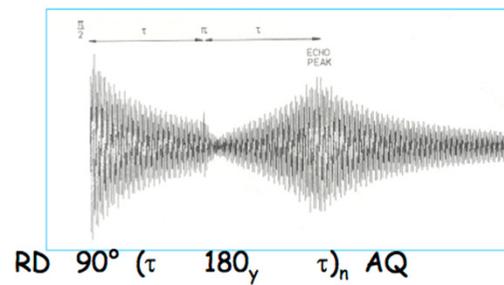
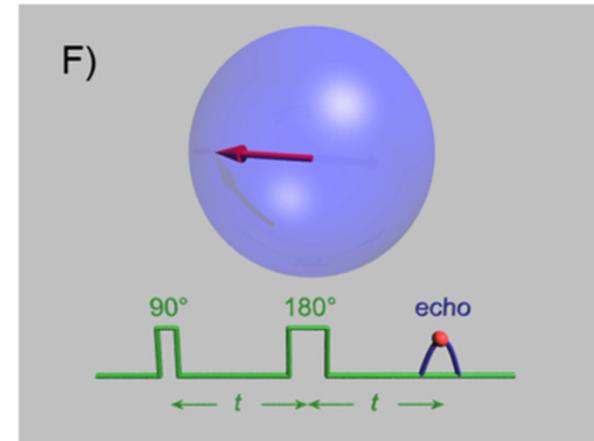
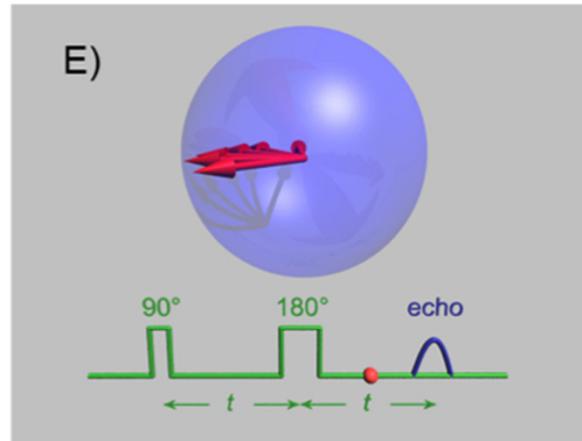
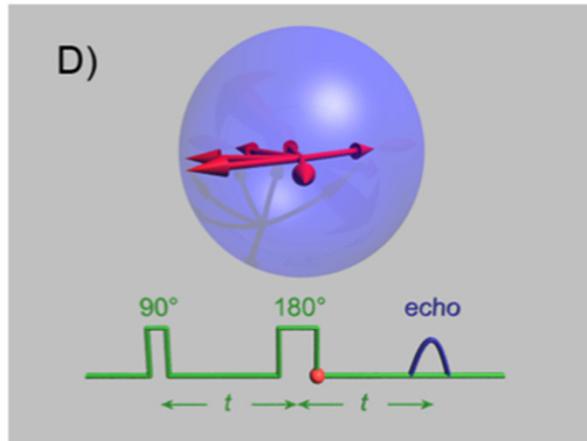
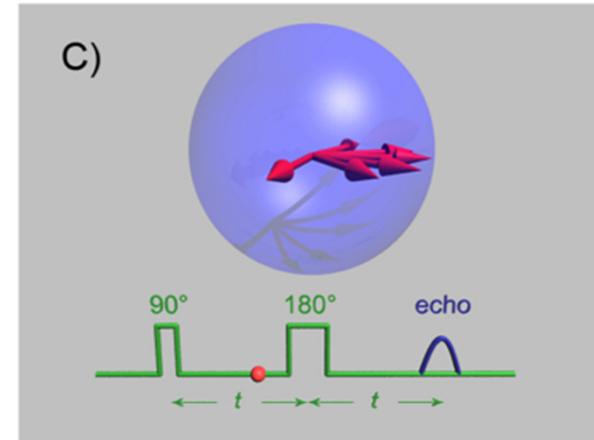
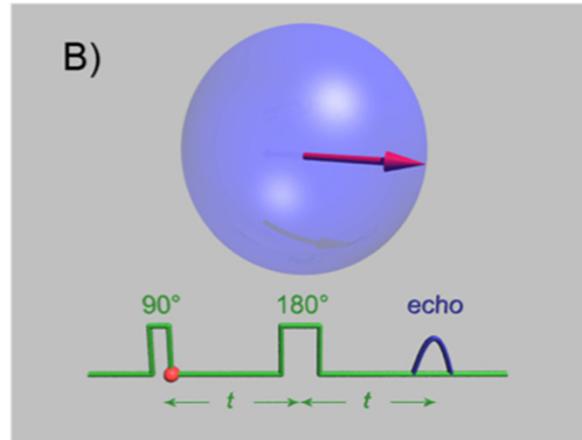
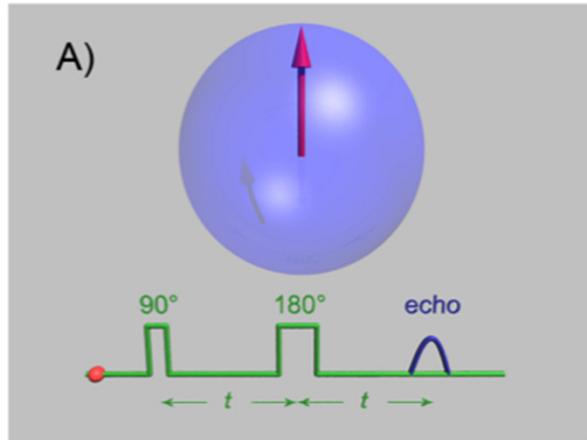
- sia all'interazione con  $B_{Lz}$
- sia alle disomogeneità del campo  $B_0$  nel campione

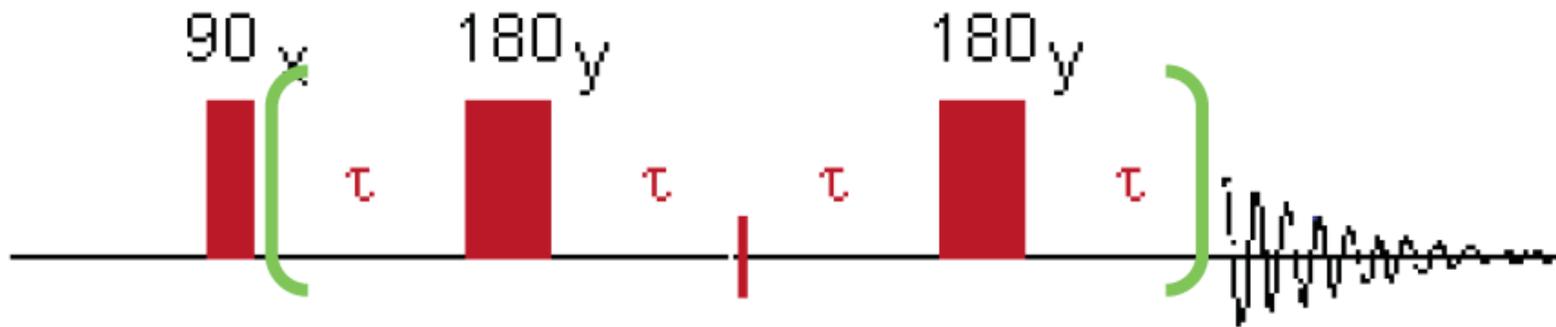
$$R_2^* = R_2 + R_{dis} \quad \text{--->} \quad (T_2^*)^{-1} = (T_2)^{-1} + (T_{dis})^{-1}$$



La larghezza di riga non ci da immediatamente il  $T_2$

## T<sub>2</sub> measurement: spin-echo



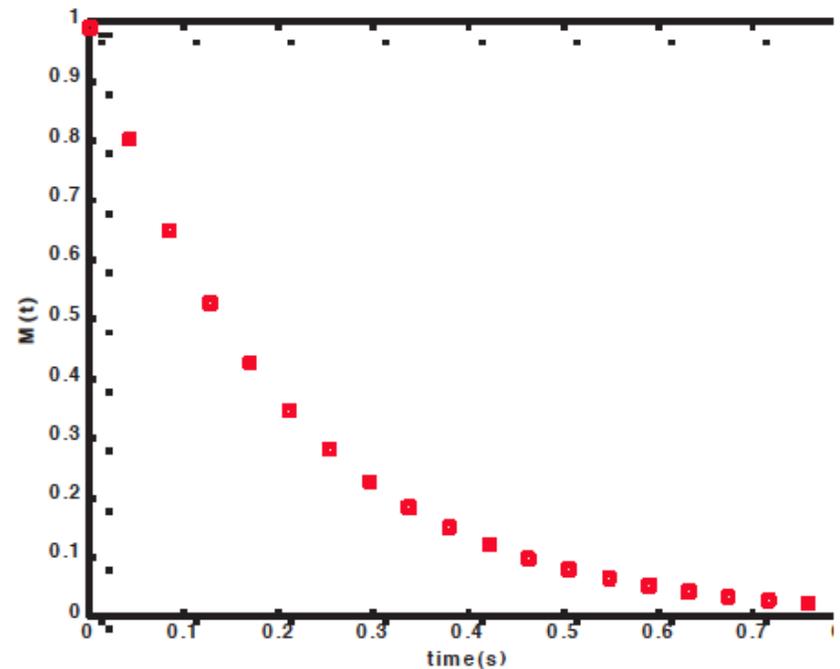


- compensa le imperfezioni dell' impulso  $\pi$
- non ha effetti di off-res

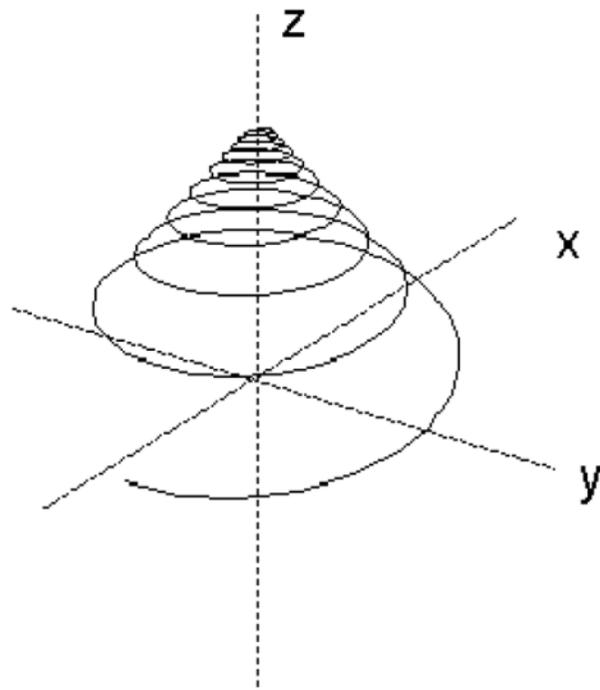
RD  $90^\circ$  ( $\tau$   $180_y$   $\tau$ )  $2n$  AQ

$$M(t) = M(\infty) \exp(-2t / T_2)$$

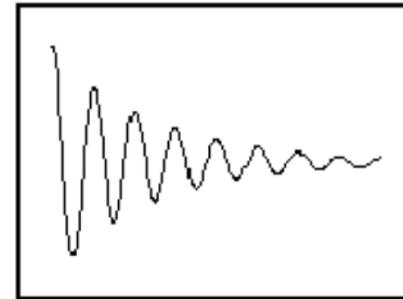
$T_2$  200 ms



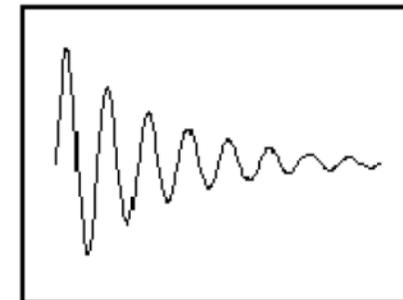
# The effects of Relaxation



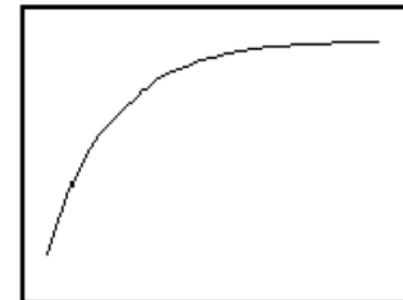
$M_x$



$M_y$



$M_z$



$$M_z = M_\infty (1 - \exp(-t / T_1))$$

$$M_y = M_\infty \exp(-t / T_2)$$

...dopo un tempo  $t$

 che percentuale della magnetizzazione è tornata lungo  $z$ ?

 che percentuale è ancora nel piano  $xy$ ?



## Perché dobbiamo preoccuparci del rilassamento?

➤ per la calibrazione degli impulsi

➤ per avere integrazioni affidabili

➤ per impostare correttamente esperimenti più complessi