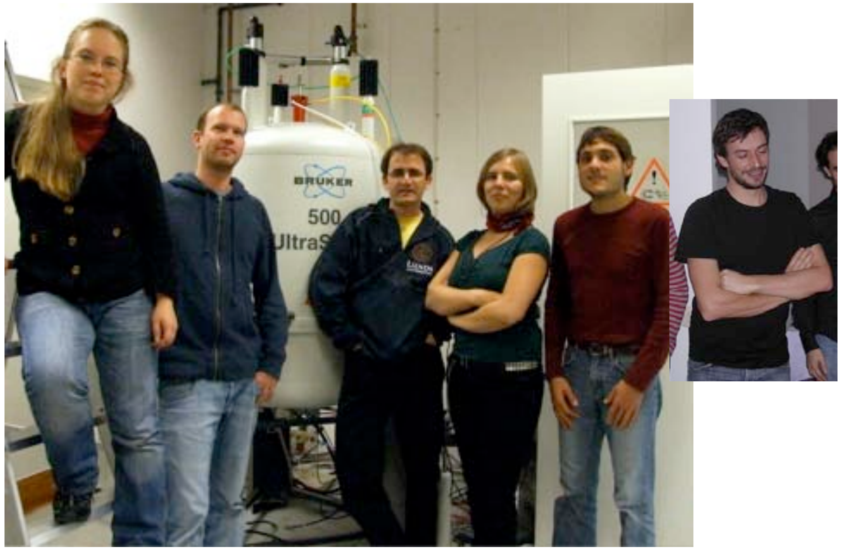
Daniel Topgaard

- Associate Professor
- Physical Chemistry, Lund
- Solid-state NMR of soft matter
- Diffusion NMR of biological tissues

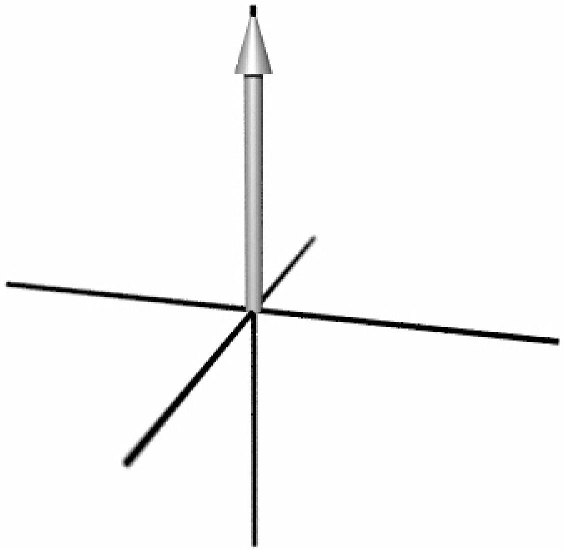


NATURVETENSKAP • TEKNIK • MEDICIN • Stiftelsen för Strategisk Forskning

Vetenskapsrådet

Relaxation - foundations and theoretical concepts

- Nuclear spin and magnetism
- Energy levels and equilibrium
- Rotational motion in liquids
  Fluctuating local magnetic fields
  - autocorrelation function
  - spectral density
- Relaxation times from random field approximation



Nuclear spin and magnetism

$$\boldsymbol{\mu} = \gamma \mathbf{I}$$

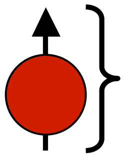
magnetic moment, $\boldsymbol{\mu}$
magnetogyric ratio, γ
angular momentum, $\mathbf{I}$

$\boldsymbol{\mu} \parallel \mathbf{I}$

Properties of elementary particles

- mass: interaction with gravitational field
- charge: interaction with electric field
- spin: interaction with magnetic field

Spin quantum number, *I*

 $|\mathbf{I}| = \hbar\left[I(I+1)\right]^{1/2}$

reduced Planck constant,
$\hbar = h/2\pi = 1.055\times10^{-34}$ Js

- *I*: integer or half-integer
- Examples
  - $I = 1/2$: ^{1}H, ^{31}P, ^{13}C “spin half”
  - $I = 1$: ^{2}H “spin one”
  - $I = 3/2$: ^{23}Na

Space quantization

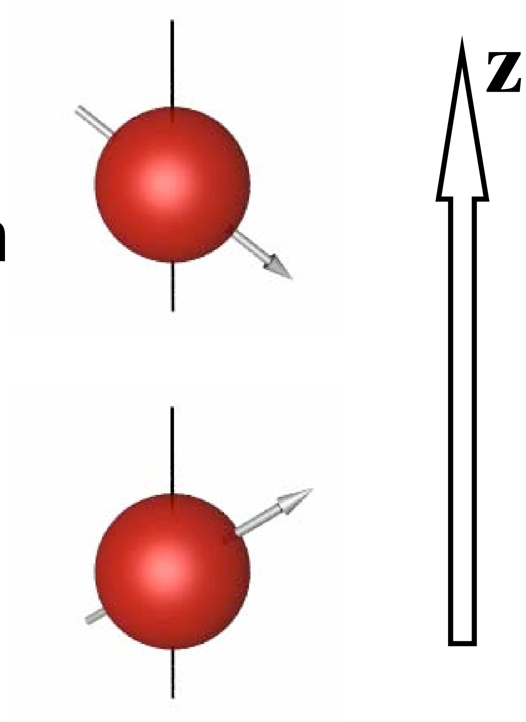
$$I_z = m\hbar$$

z-component of **I**, I_z
magnetic quantum number, *m*
$m = -I, -I+1, \ldots, I-1, I$

I_x, I_y undetermined

$I = 1/2$

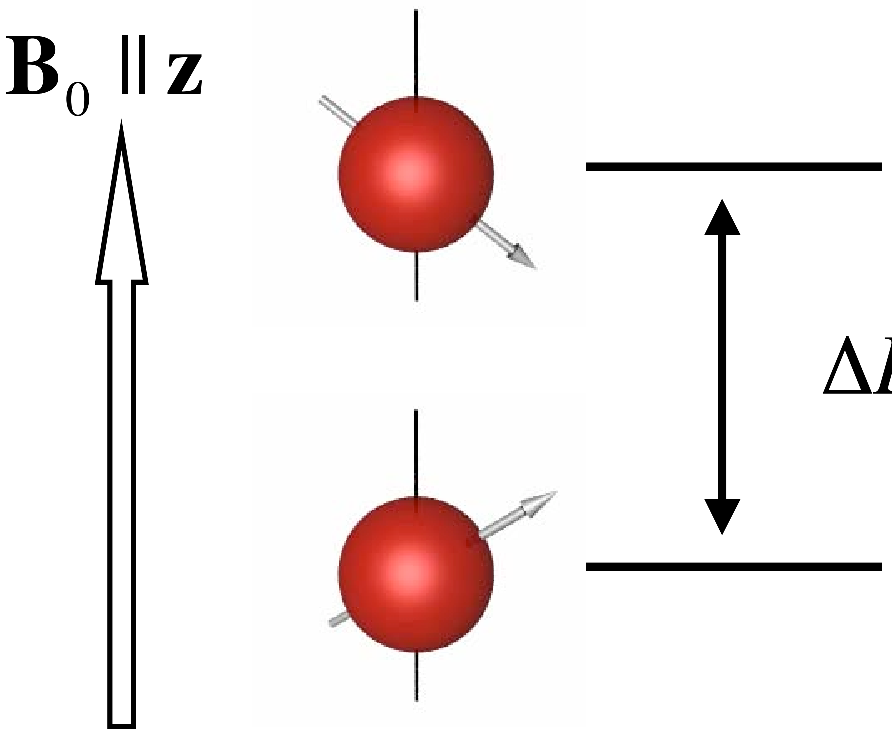
$m = -1/2$
spin down



$m = +1/2$
spin up

Energy levels for *I* = 1/2

$$E = -\mu_z B_0 = -m\hbar\gamma B_0$$



$$m = -1/2$$

$$\Delta E = \hbar\gamma B_0 = \hbar\omega_0$$

Larmor frequency

$$m = +1/2$$

Angular and cyclic frequency

$$\omega = 2\pi\nu$$

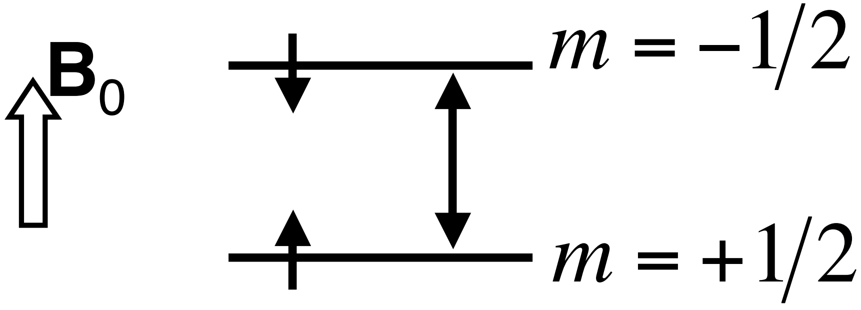
ω: angular frequency [rad·s^{-1}]
ν: cyclic frequency [s^{-1}], [Hz]

ω often used to get rid of factor 2π

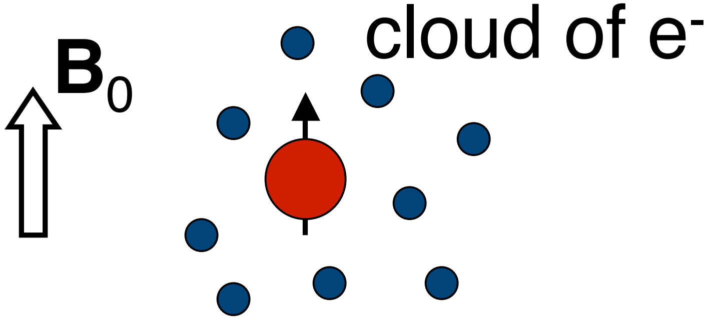
Transitions between levels

- Transitions with $\Delta m = \pm 1$ allowed
- Transitions induced by electromagnetic radiation with frequency

$$\omega_0 = \gamma B_0$$

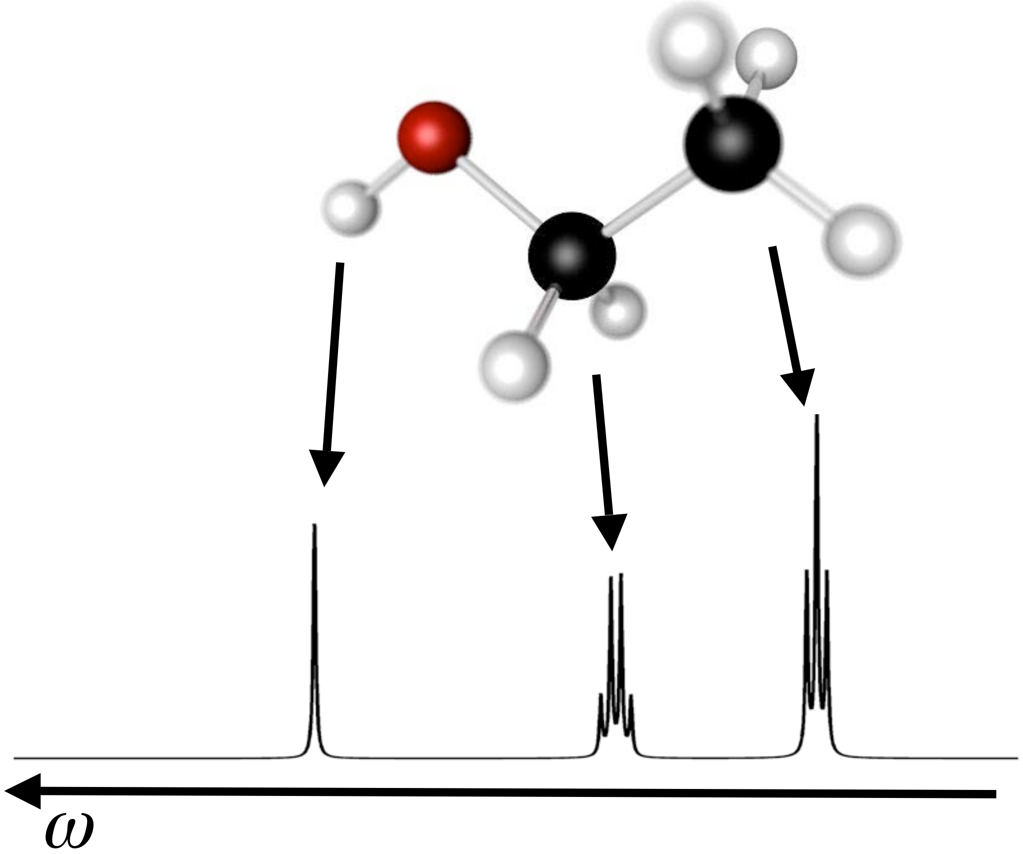


NMR spectroscopy



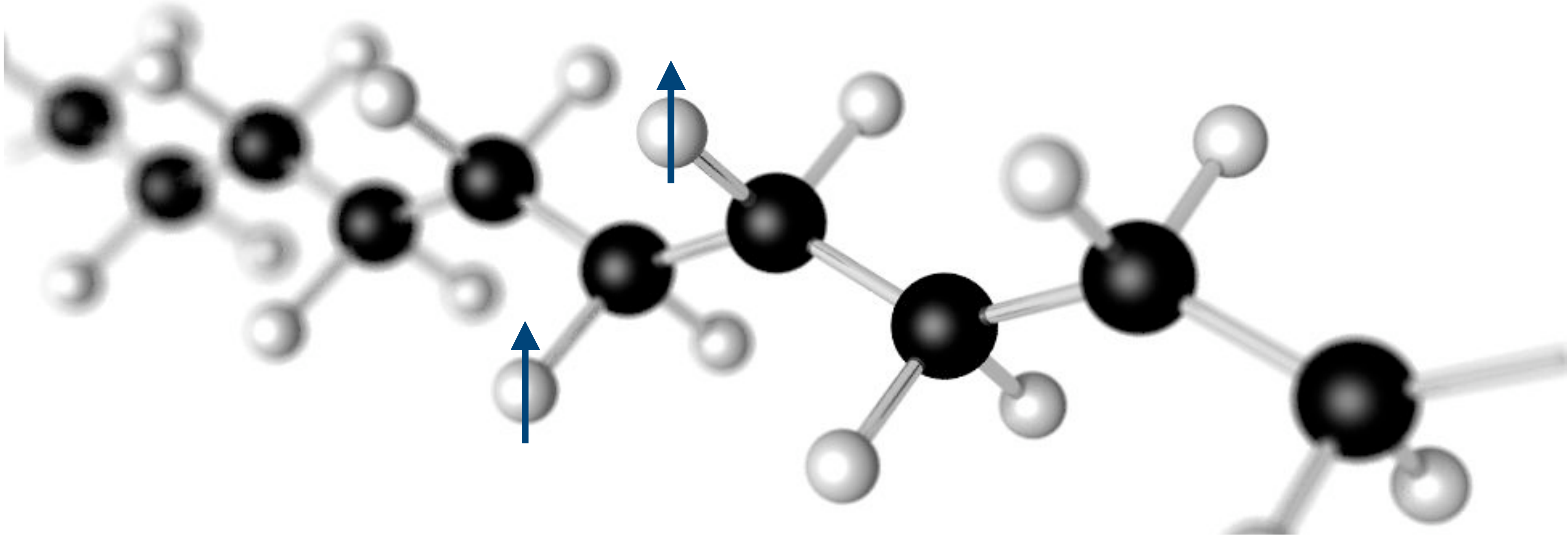
$$\gamma B_0 (1 - \sigma) = \omega_0$$

chemical shielding



Spin-spin couplings

B_0 modified by field from neighboring spins



MR imaging

$$\omega_0(\mathbf{r}) = \gamma B_0(\mathbf{r})$$ ← position

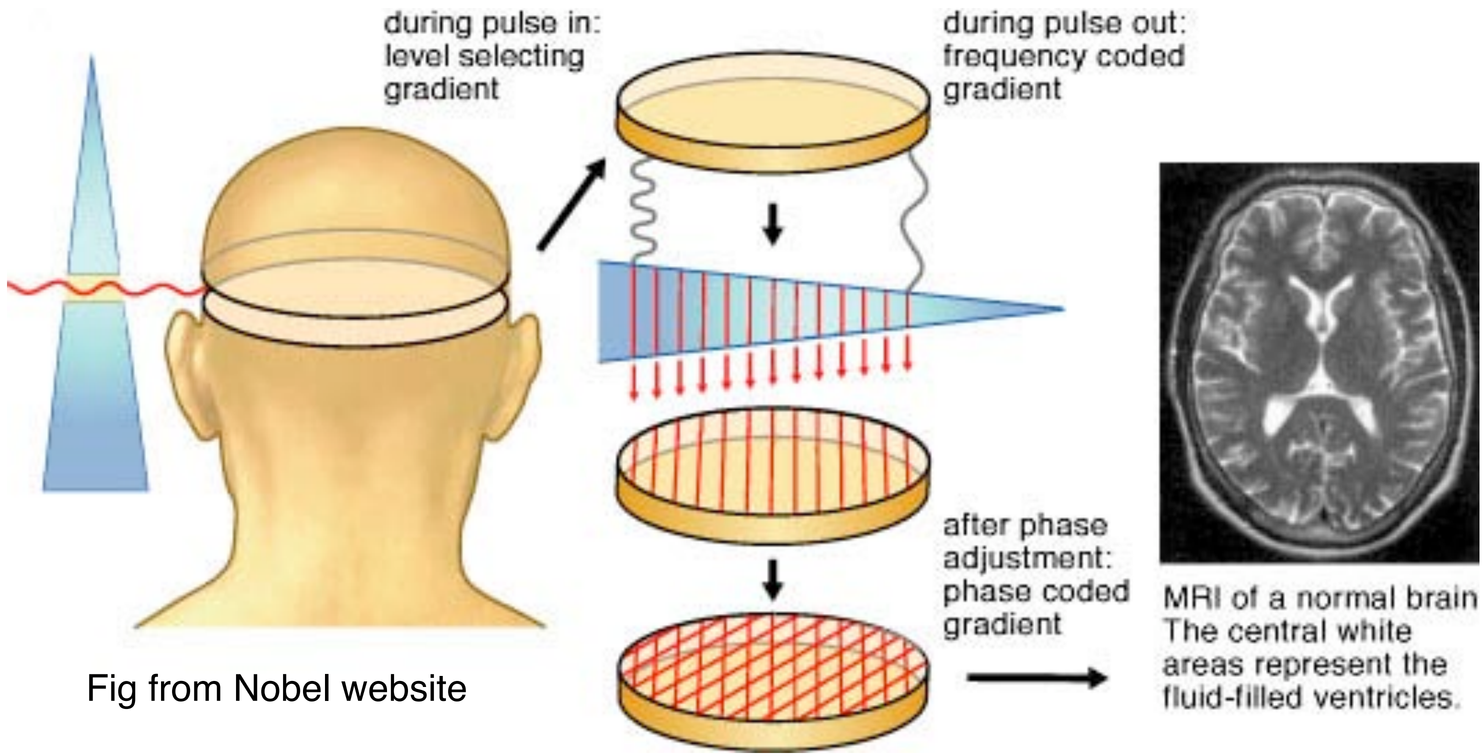


Fig from Nobel website

Resonance condition

$$\omega_0 = \gamma B_0$$

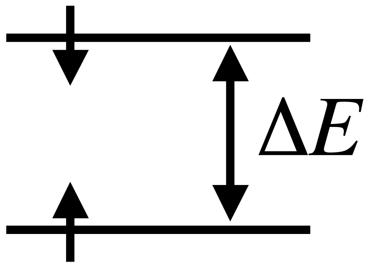
ω_0 depends on:

- external field
- chemical surroundings } spectroscopy
- neighboring spins }
- position — imaging

Populations

Boltzmann distribution at thermal eq.

$$\frac{n_{\downarrow}}{n_{\uparrow}} = e^{-\Delta E/kT}$$

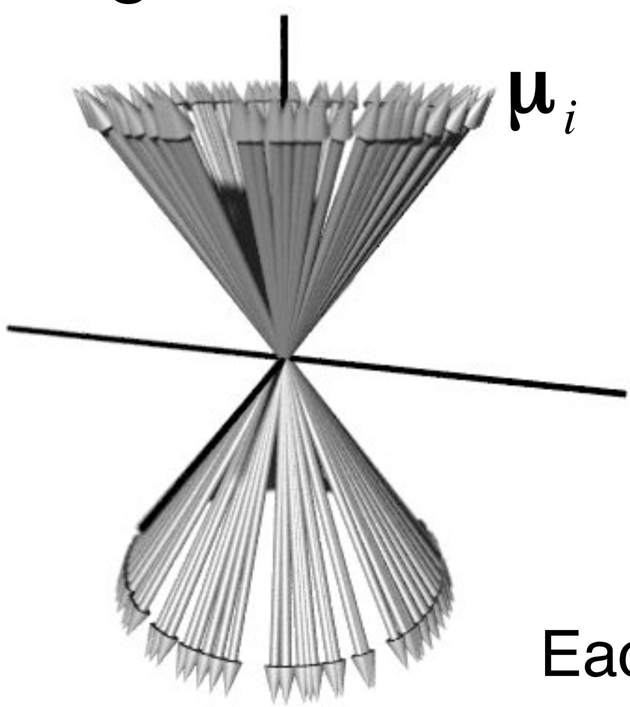


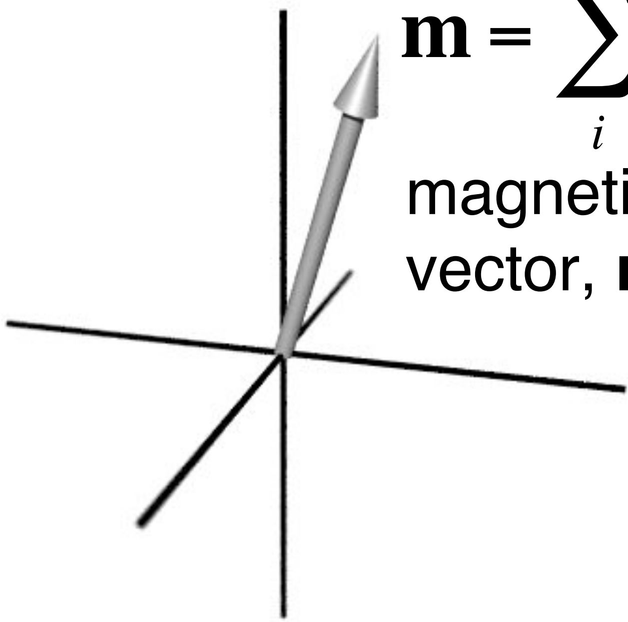
number of spins up, $n_{\uparrow}$
number of spins down, $n_{\downarrow}$
Boltzmann constant, $k = 1.381 \cdot 10^{-23}$ J/K
absolute temperature, T

MR: $\Delta E << kT$

Spin packet

Ensemble of spins experiencing the same magnetic field





$$\mathbf{m} = \sum_i \boldsymbol{\mu}_i$$

magnetization vector, **m**

Each $\boldsymbol{\mu}_i$ obeys quantum laws, but **m** behaves classically!

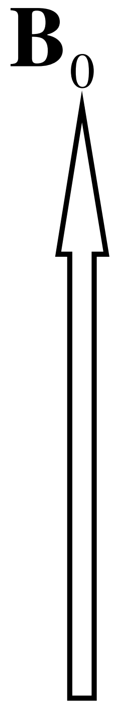
Free precession

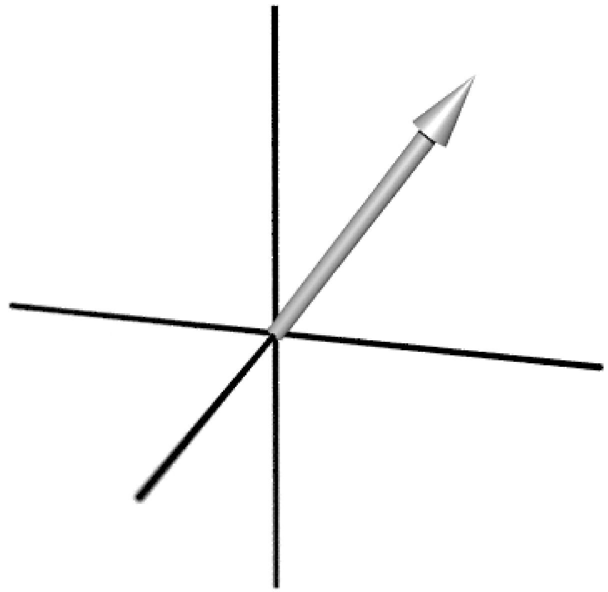
cf. spinning top

$$\frac{\mathrm{d}\mathbf{m}(t)}{\mathrm{d}t} = -\gamma \mathbf{B}_0 \times \mathbf{m}(t)$$

$$\omega_0 = -\gamma B_0$$

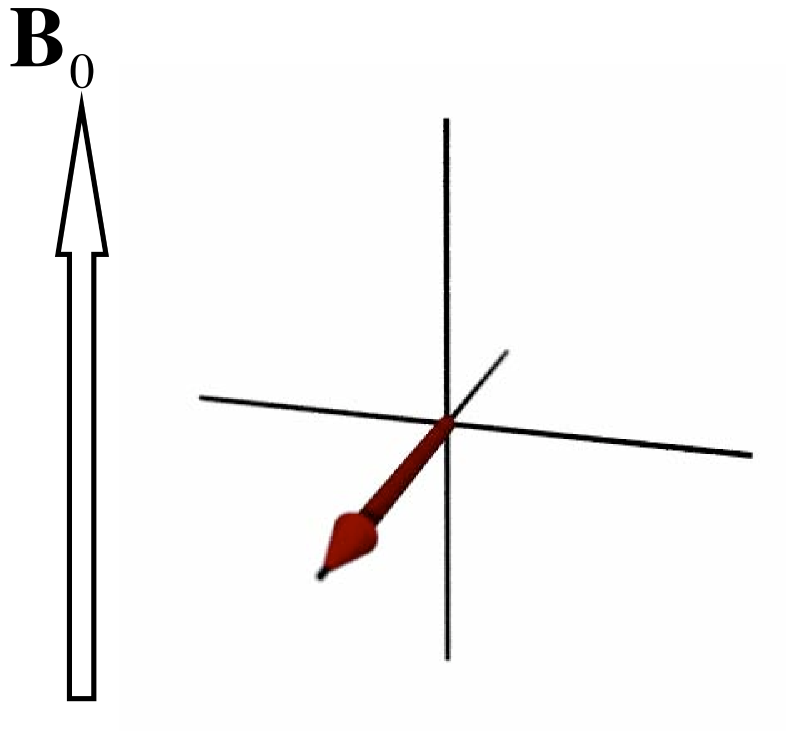
Note sign!
Right-handed
rotation positive





Radiofrequency (RF) field, $\mathbf{B}_1$

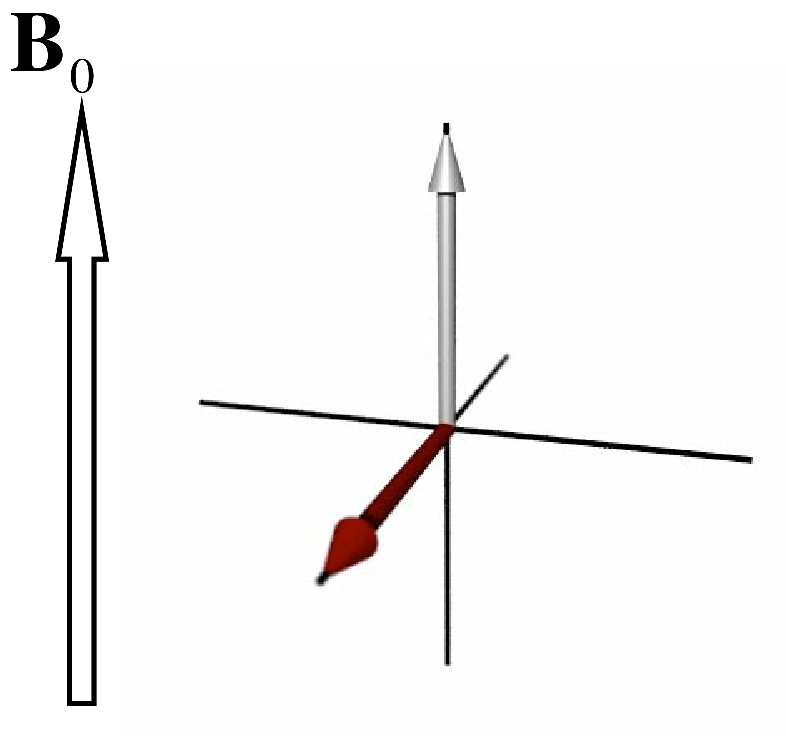
- Magnetic field $\mathbf{B}_1$ ($B_1 << B_0$) rotating in *xy*-plane with frequency ω_{RF}
- Produced by the RF coil



Resonance

- **m** tilted from z-axis if $\omega_{\mathrm{RF}} \approx \omega_0$
- Resonance!

  freq. of perturbation = inherent freq. of the system



$$\frac{\mathrm{d}\mathbf{m}(t)}{\mathrm{d}t} = -\gamma \mathbf{B}(t) \times \mathbf{m}(t)$$

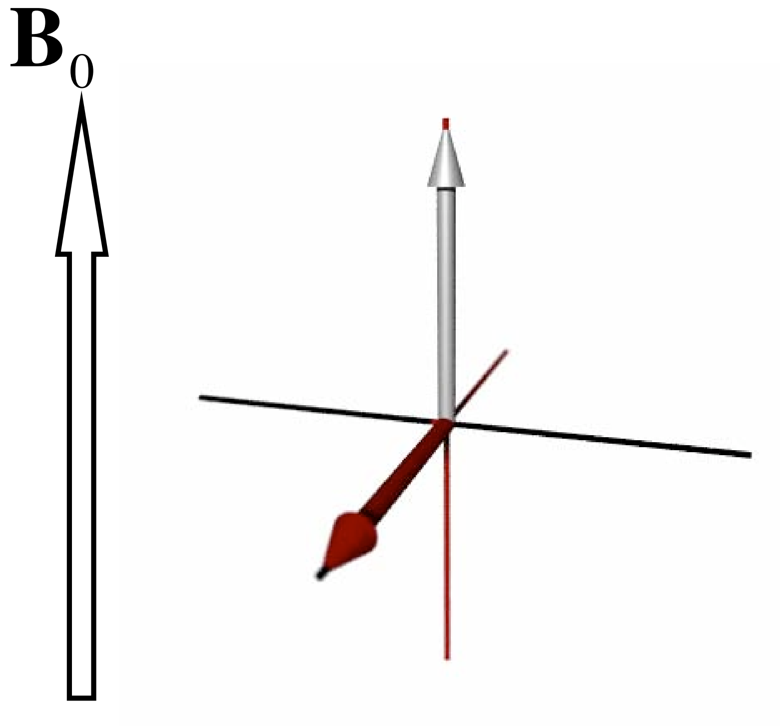
$$\mathbf{B}(t) = \mathbf{B}_0 + \mathbf{B}_1(t)$$

Step into the rotating frame

Motion of **m** appears simpler: rotation of **m** around $\mathbf{B}_1$ with freq. ω_1

$$\omega_1 = -\gamma B_1$$

nutation frequency, ω_1

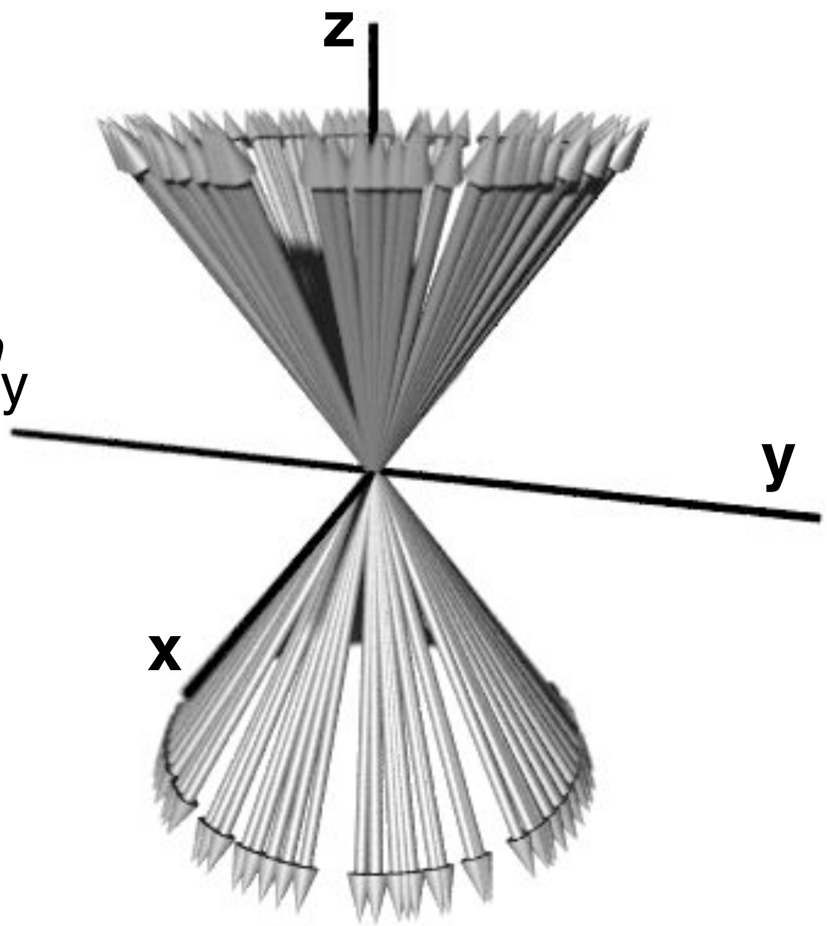


rotating frame often used implicitly

seen from the rotating frame

Polarization and coherence

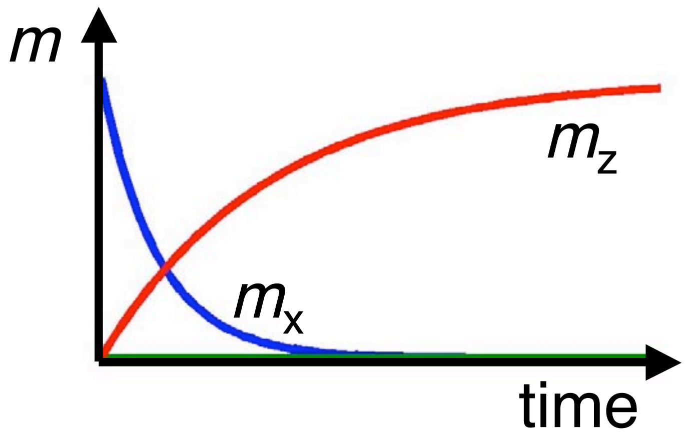
- Longitudinal magnetization m_z
- Transverse magnetization m_x, m_y
- Polarization: $m_z \neq 0$
- Coherence: $m_{x/y} \neq 0$

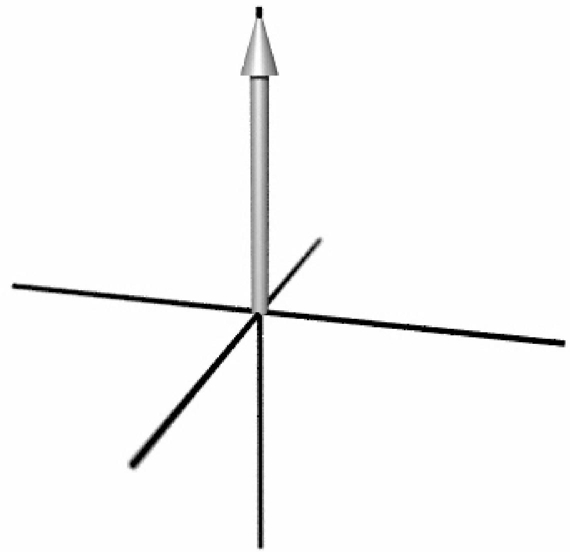


Exponential return to equilibrium

$$m_x = m_0 e^{-t/T_2}$$ transverse

$$m_z = m_0\left(1 - e^{-t/T_1}\right)$$ longitudinal

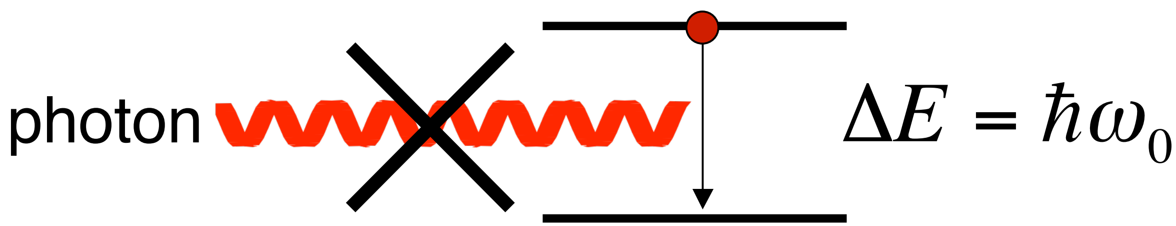




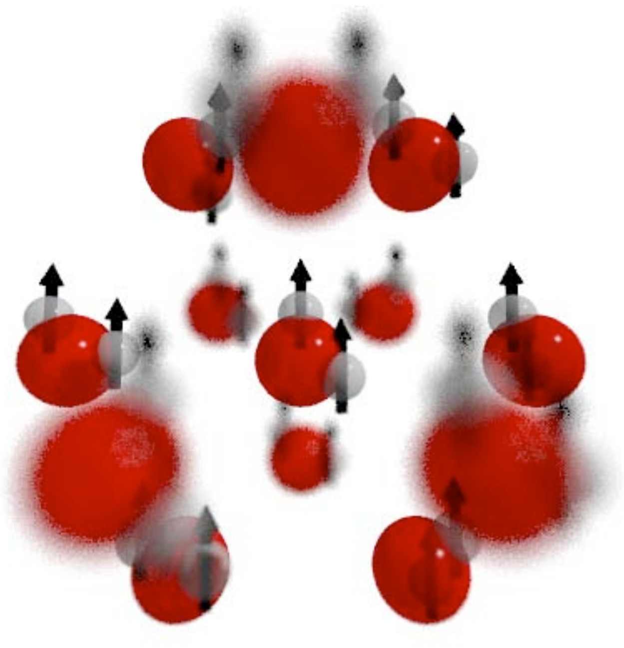
Transitions

No spontaneous emission!

emission rate $\propto \Delta E^3$



Molecular motion in liquids



Origin of fluctuating fields

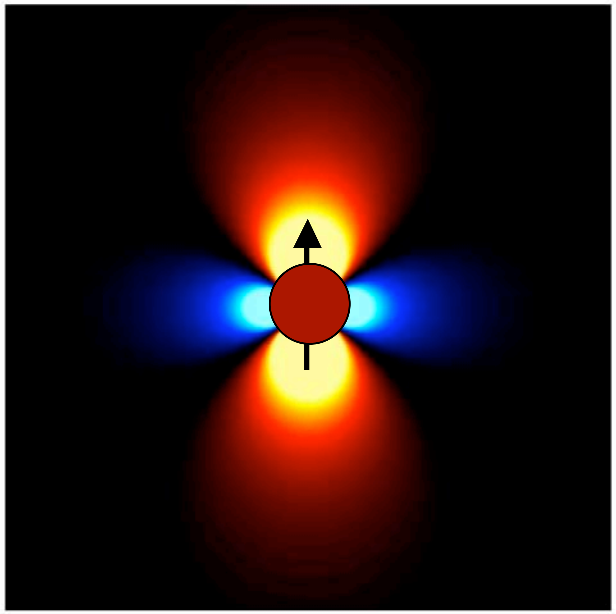
- Neighboring spins
- Unpaired electrons
- Chemical shift anisotropy
- Chemical exchange
- Magnetic susceptibility
- …

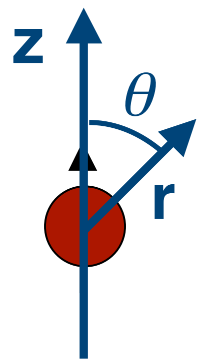
Field from a magnetic dipole

$$B_z \propto \frac{P_2(\cos\theta)}{r^3}$$

$$P_2(\cos\theta) = \frac{1}{2}\left(3\cos^2\theta - 1\right)$$

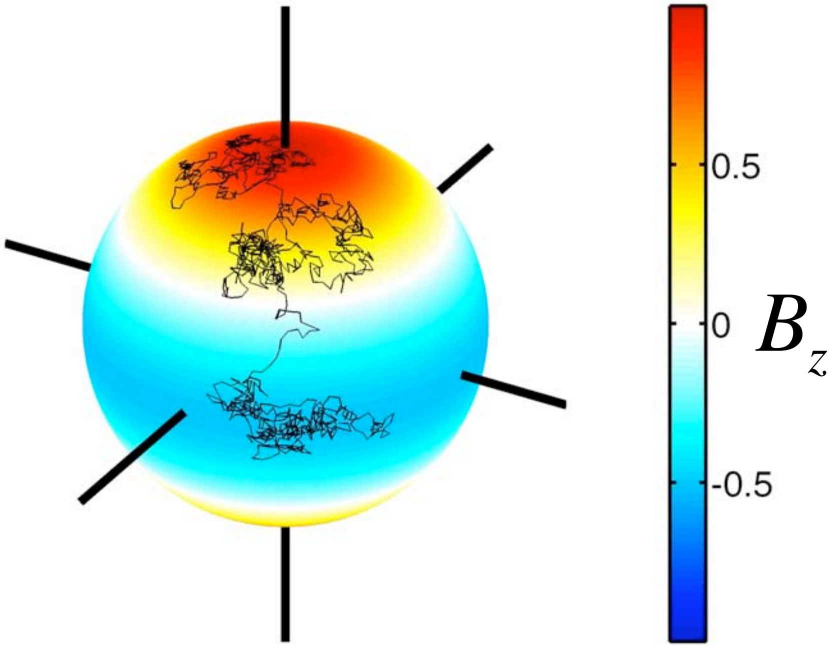
2nd Legendre polynomial, P_2

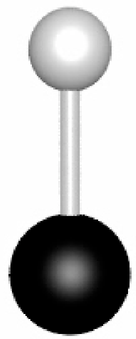




Rotational motion in liquids

- Tumbling
- Random walk on a sphere





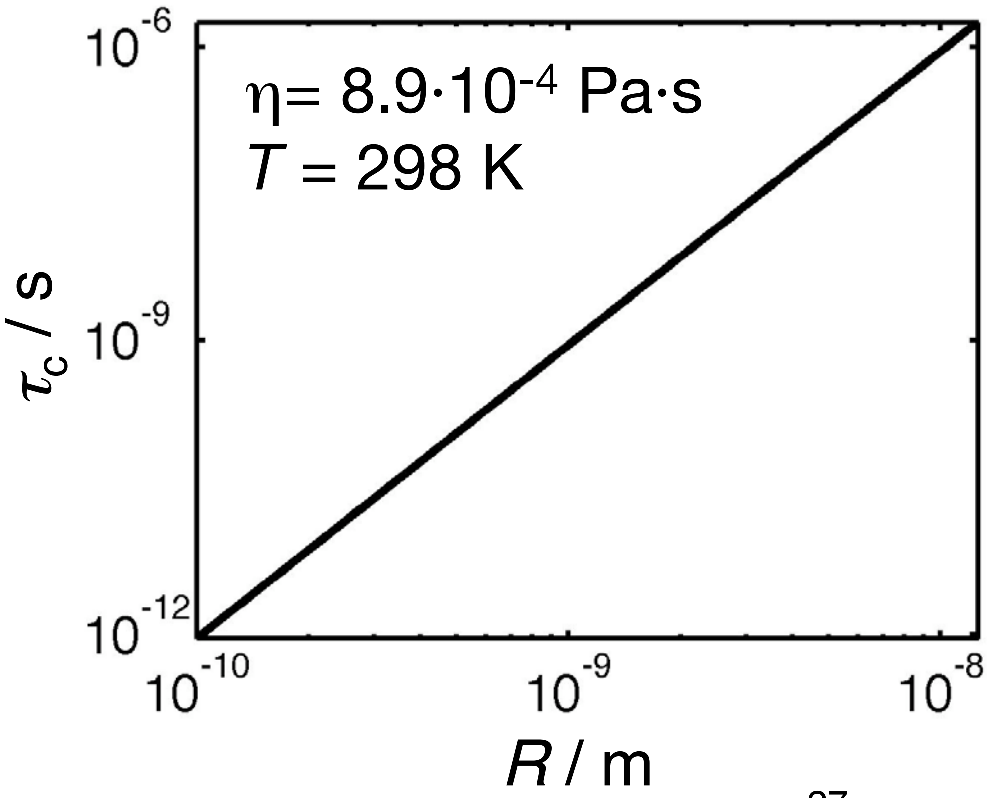
dipole pair

Rotational correlation time, τ_c

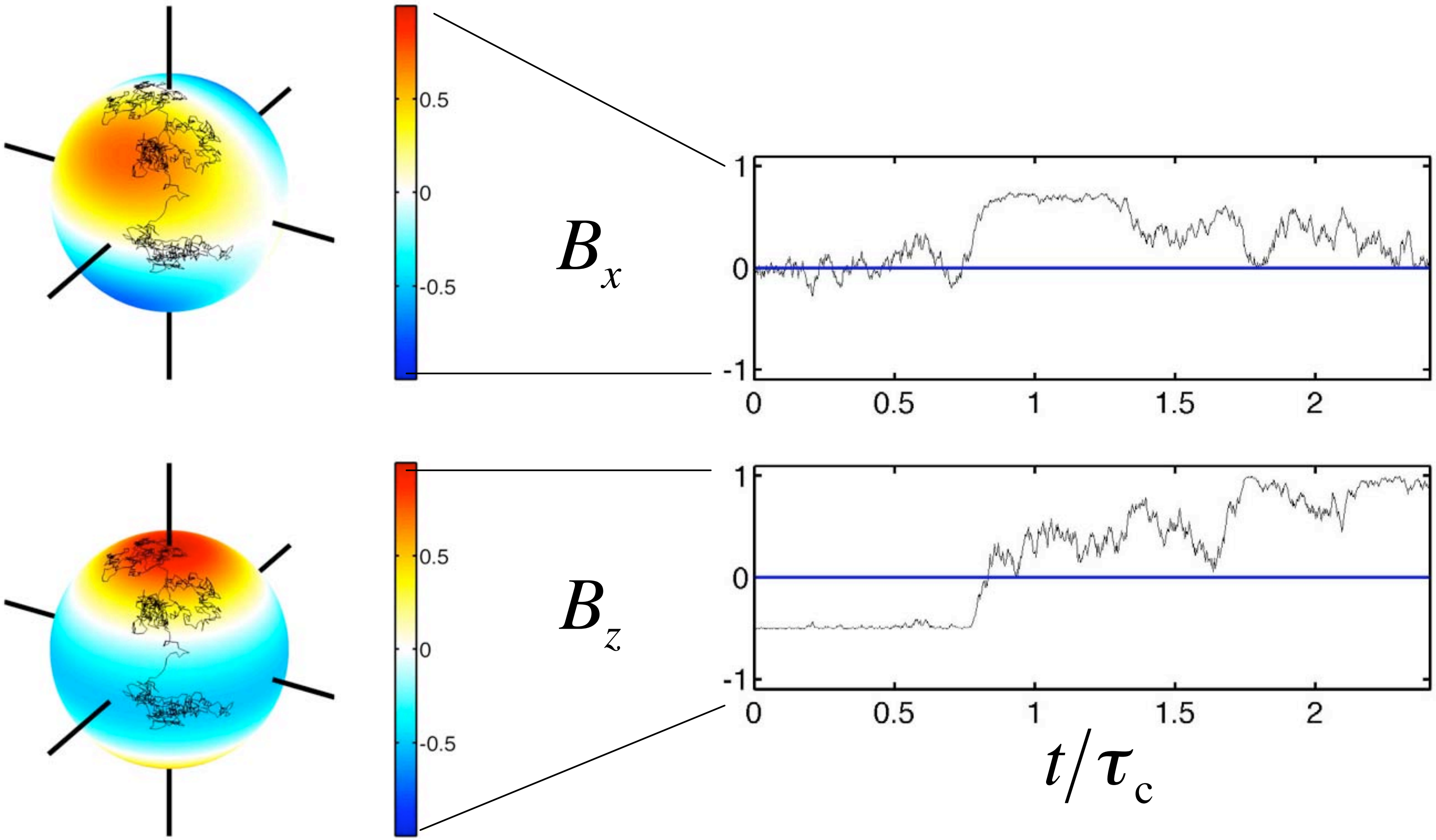
"time to turn 1 rad"

$$\tau_c = \frac{4\pi\eta R^3}{3kT}$$

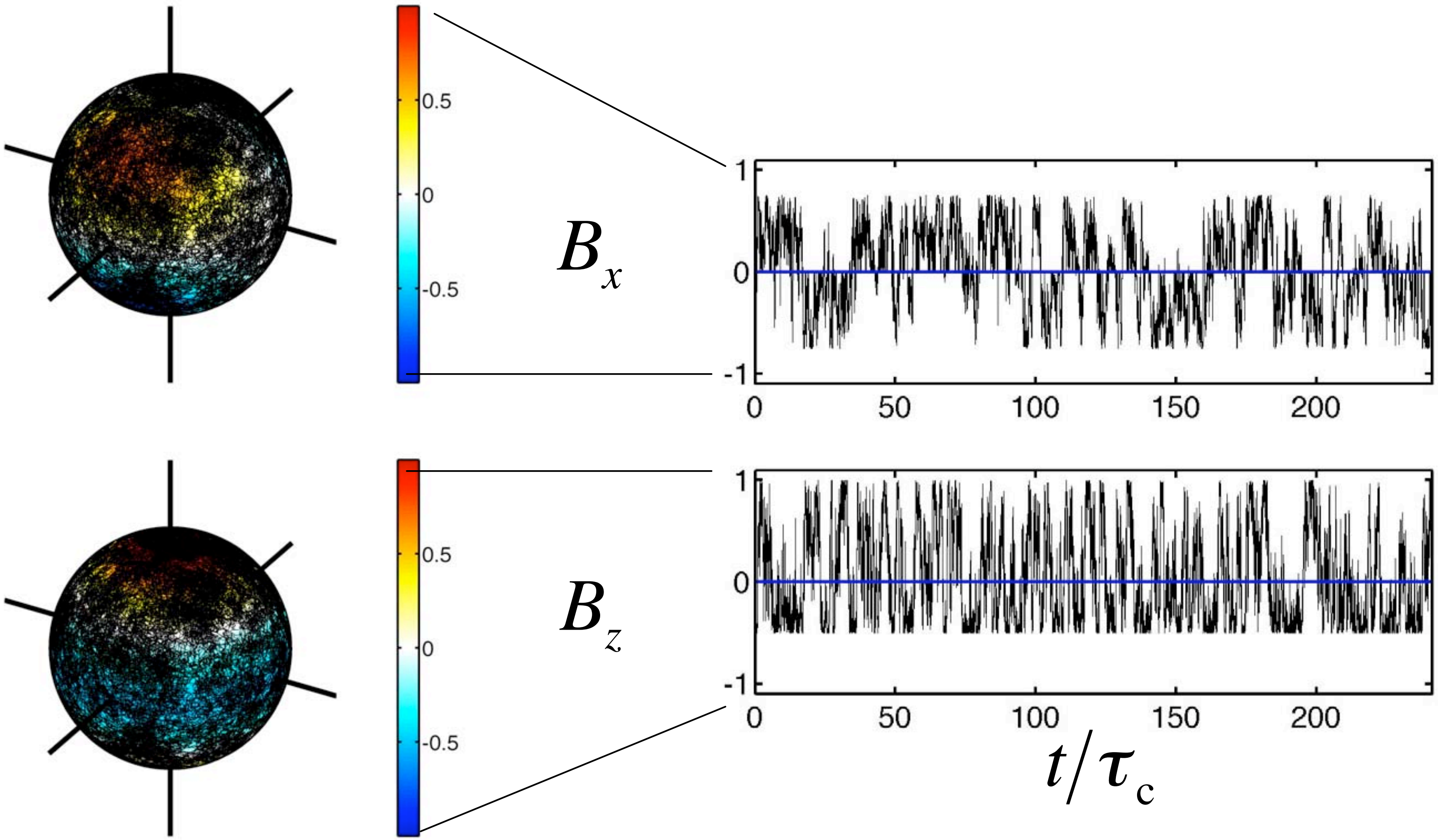
particle radius, *R*
temperature, *T*
Boltzmann const, *k*
viscosity, η



Fluctuating components, B_x B_z



Fluctuating components, B_x B_z

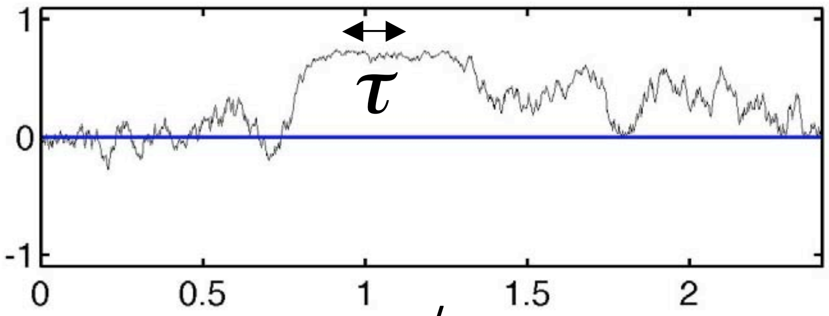


Auto-correlation function, $G(\tau)$

"Memory" function

$$G(\tau) = \int_0^\infty f(t) f(t+\tau) \mathrm{d}t$$

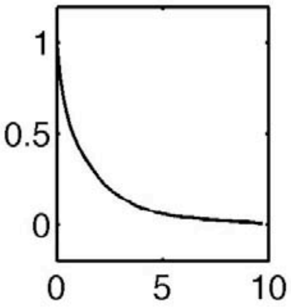
$f(t)$



τ

t/τ_c

$G(\tau)$



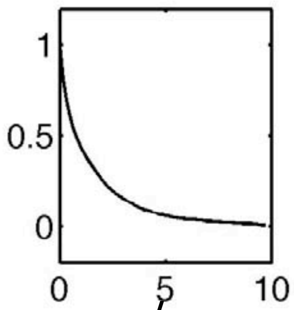
τ/τ_c

Spectral density, $J(\omega)$

Probability of finding a component with frequency ω

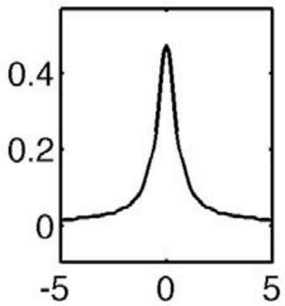
$$J(\omega) = \mathrm{FT}\{G(\tau)\}$$

$G(\tau)$



τ/τ_c

$J(\omega)$

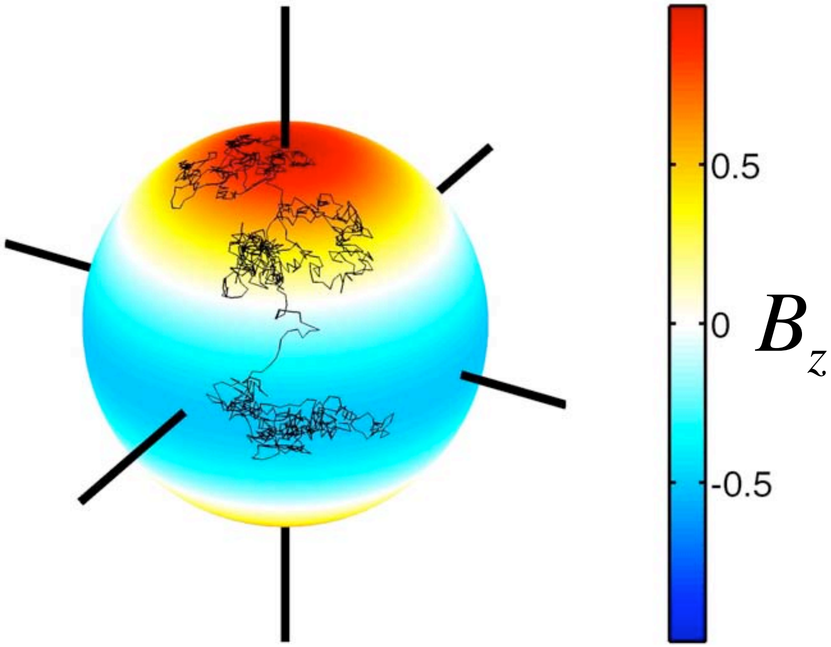


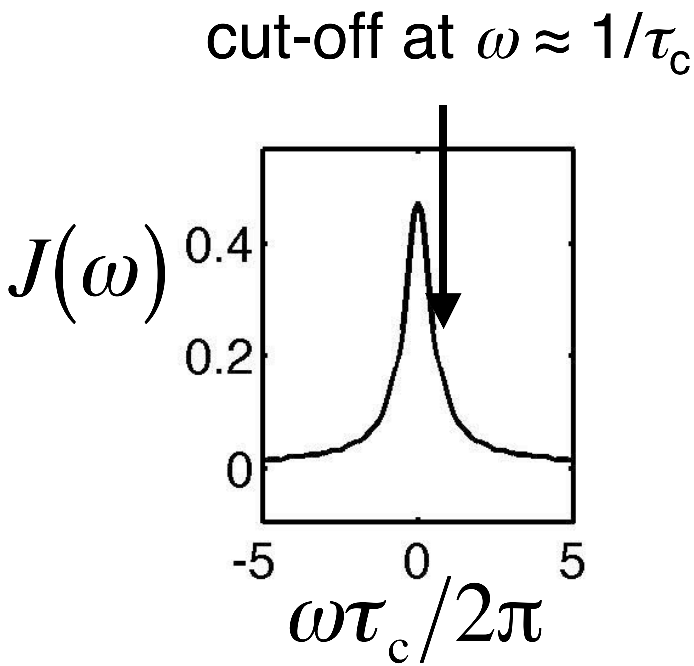
$\omega\tau_c/2\pi$

$$1/T_1 \propto J(\omega_0)$$

Frequency cut-off

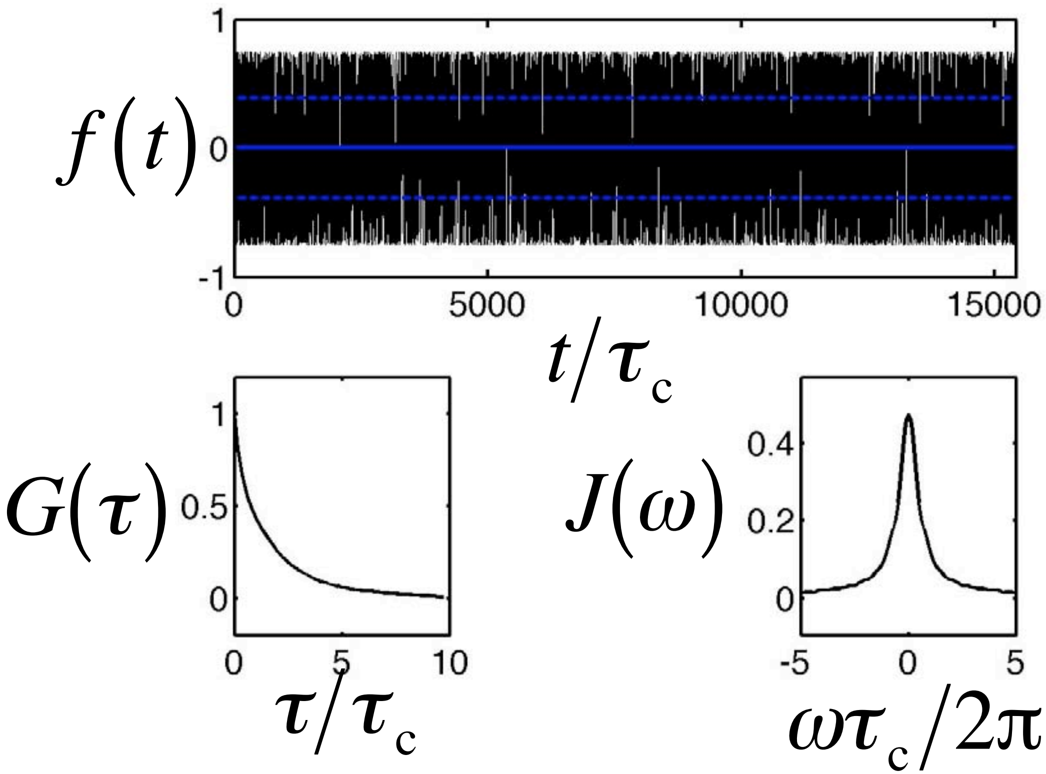
τ_c: "time to turn 1 rad"





Random field approximation

Simulation, dipole pair



Approximation

$$G(\tau) = e^{-\tau/\tau_c}$$

exponential

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

Lorentzian

http://en.wikipedia.org/wiki/Red_noise

Relaxation times/rates

- Longitudinal relaxation rate $R_1 = 1/T_1$
- Transverse relaxation rate $R_2 = 1/T_2$

$$R_1 = \gamma^2 \langle B^2 \rangle J(\omega_0)$$

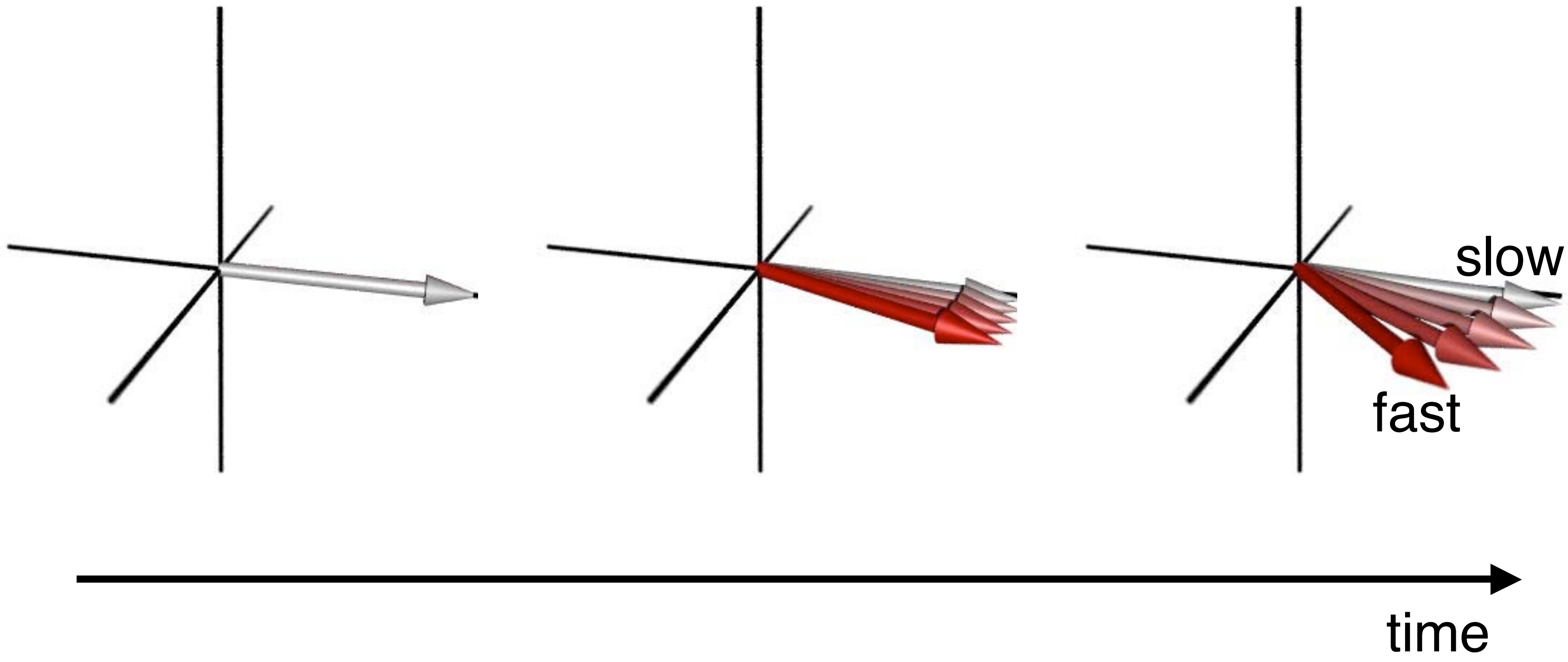
"strength" of fluctuating field

fluctuations at Larmor freq.

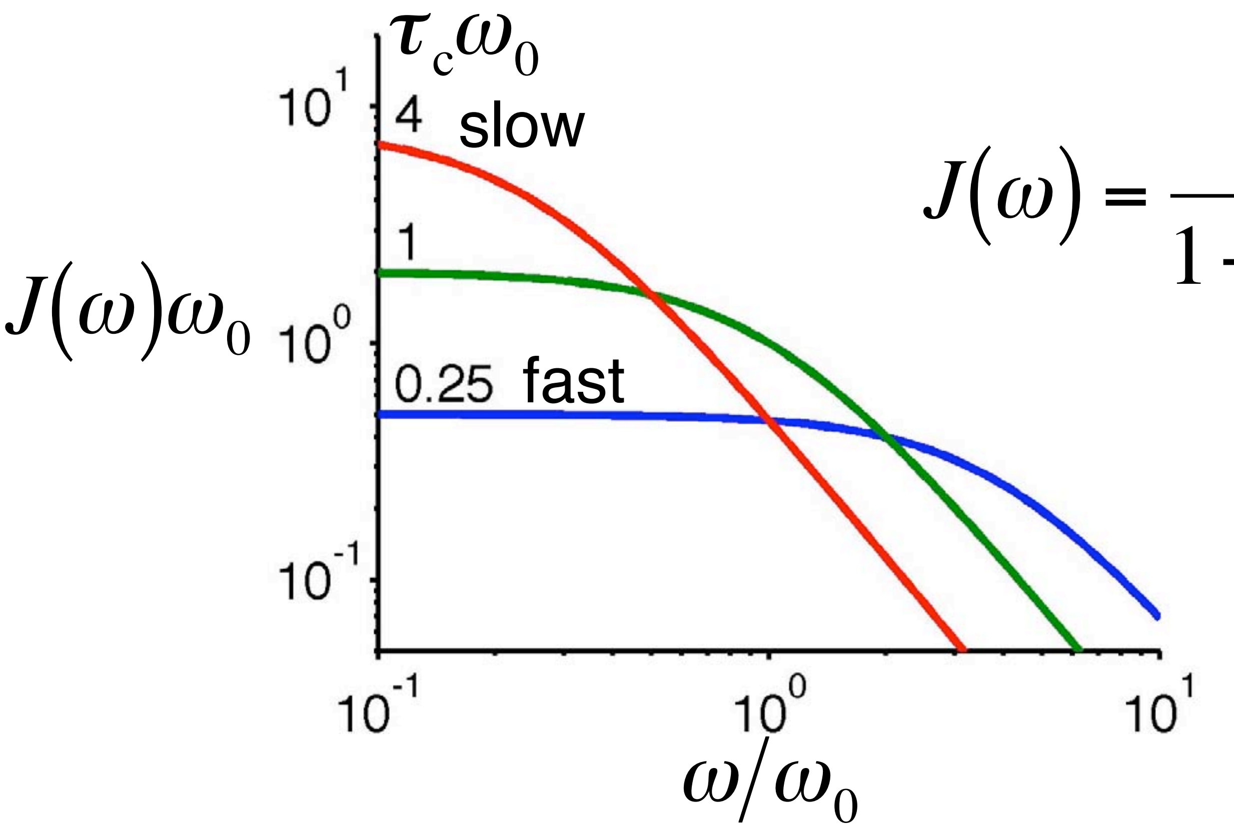
$$R_2 = \frac{1}{2}\gamma^2 \langle B^2 \rangle \left[J(\omega_0) + J(0) \right]$$

static

Transverse relaxation

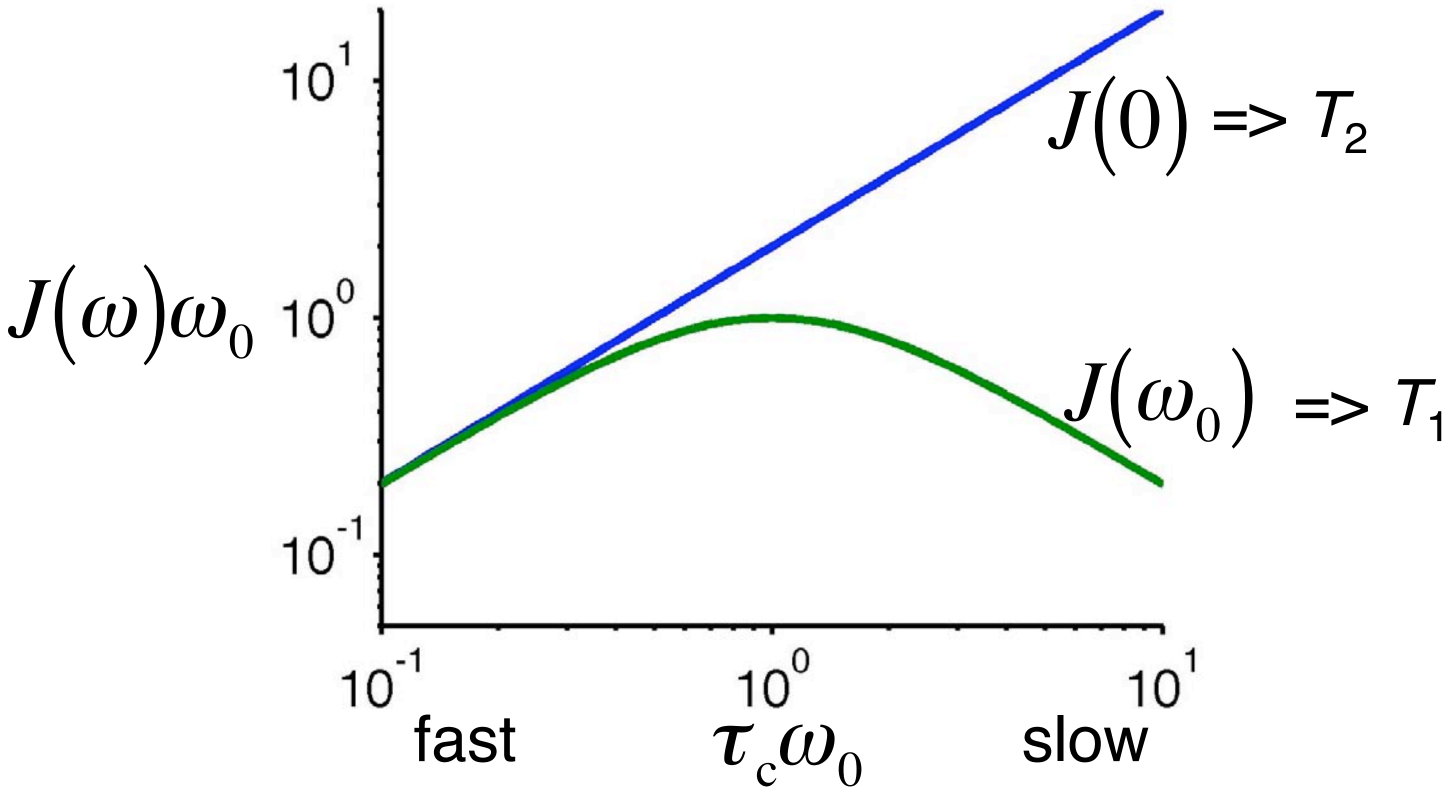


$J(\omega)$ vs. ω



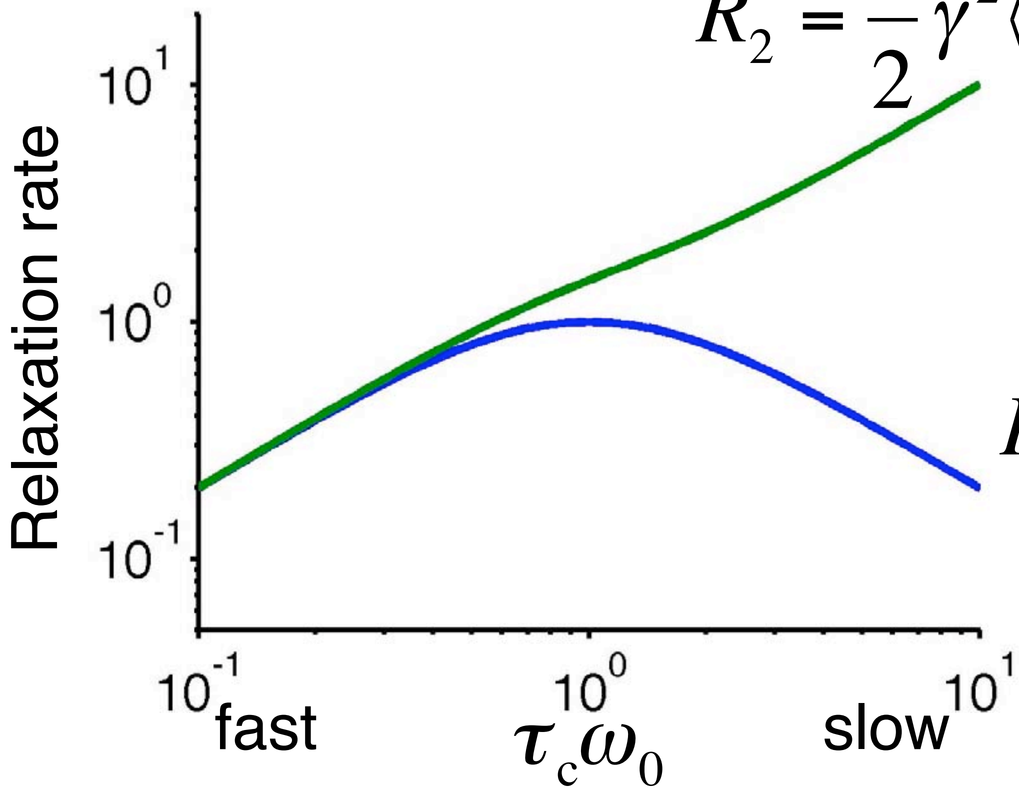
$$J(\omega) = \frac{2\tau_c}{1+\omega^2\tau_c^2}$$

$J(\omega_0)$ and $J(0)$ vs. τ_c



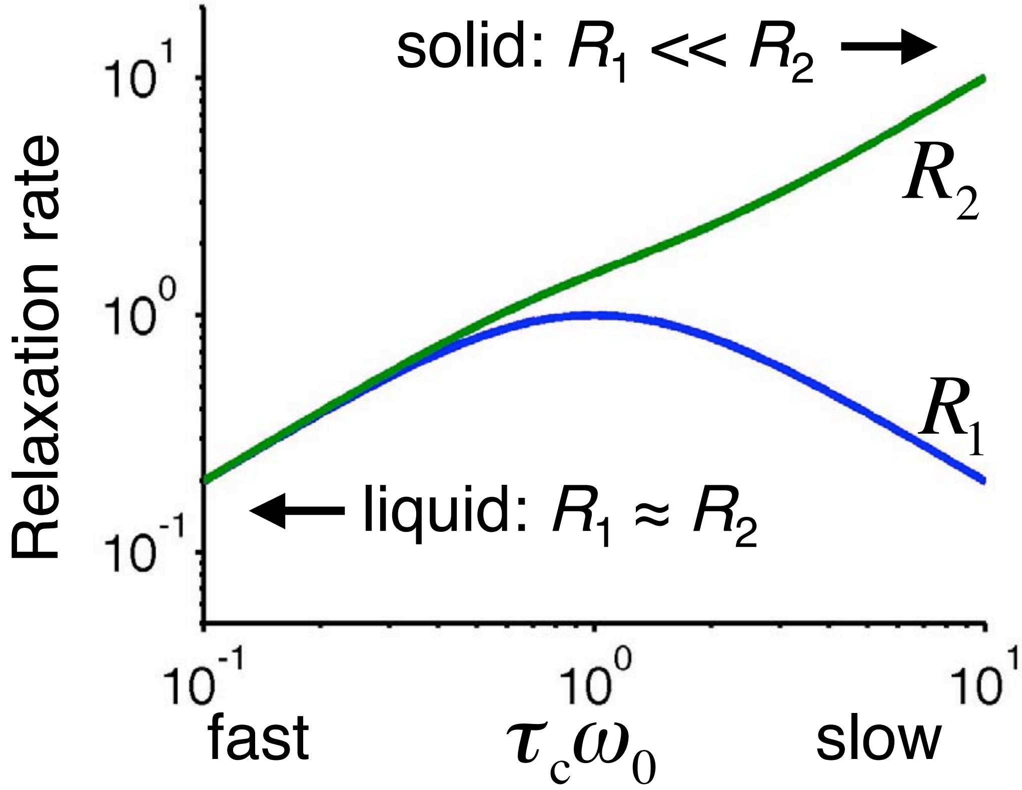
R_1, R_2 vs. τ_c

$$R_2 = \frac{1}{2}\gamma^2\langle B^2\rangle[J(\omega_0) + J(0)]$$



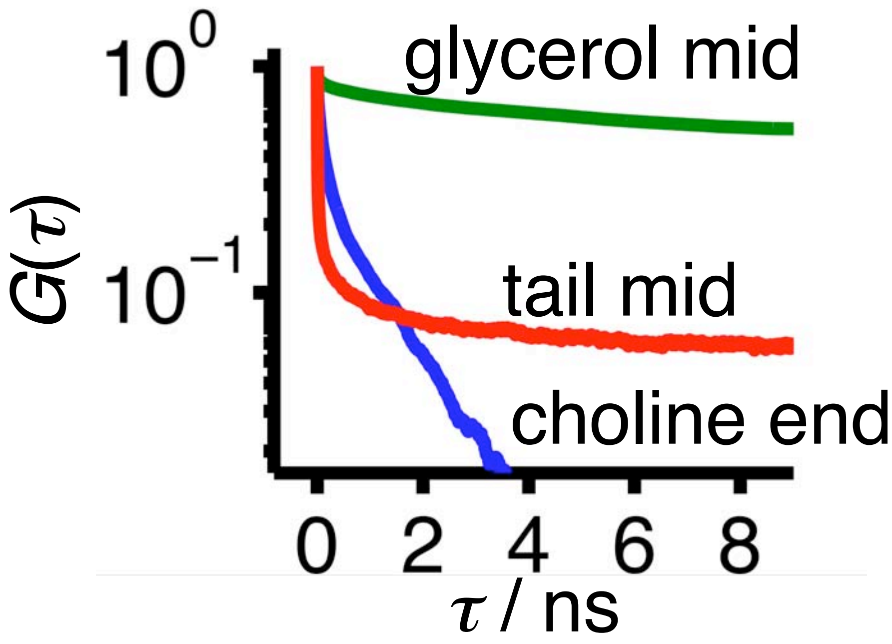
$$R_1 = \gamma^2\langle B^2\rangle J(\omega_0)$$

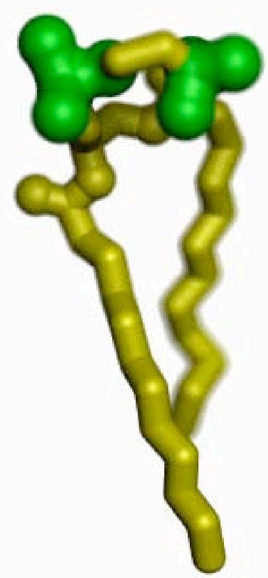
Liquids and solids



Non-exponential correlation

Phospholipid in biomembrane

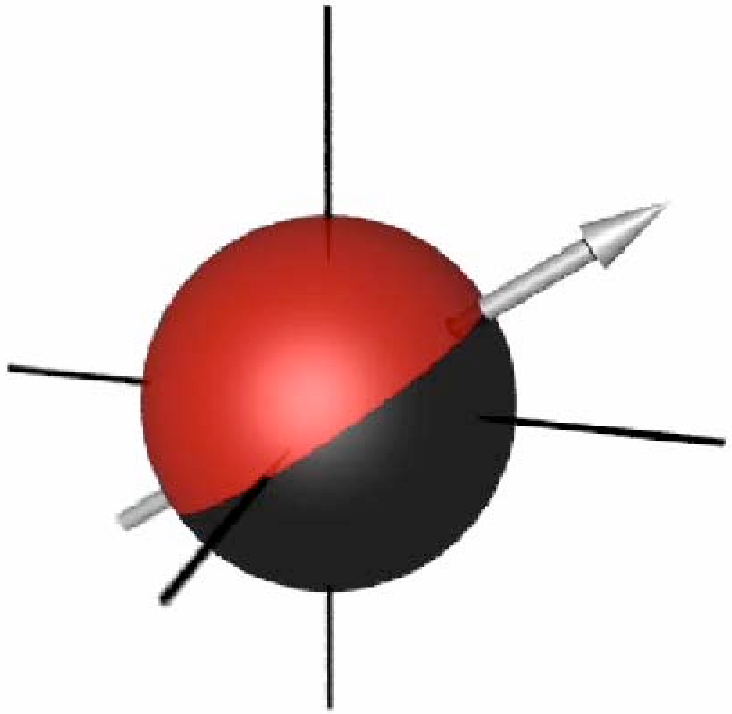




SIMON 10, Topgaard

Repetition

- Nuclear spin: angular momentum and magnetic moment
- Energy levels
  - Populations
  - Transitions
- Precession
- Larmor frequency ω_0



Repetition

- T_1 and T_2
- Fluctuating local fields
- Spectral density