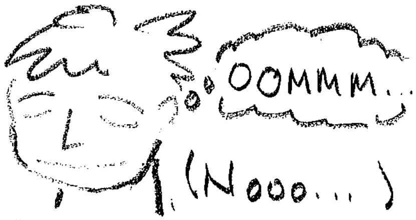
Relaxation in NMR



"Relaxation" means the processes that involve the return of a spin system to an equilibrium configuration.

Important time constants:

T_1 → Characteristic time to return to equilibrium longitudinal magnetization
often called "spin-lattice" relaxation time

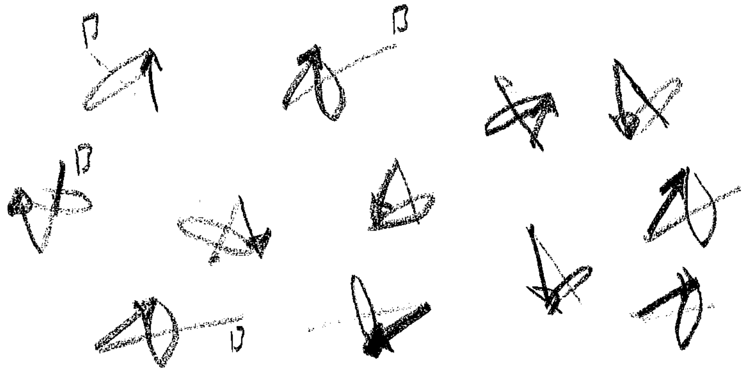
T_2 → Characteristic time for spin coherence to disappear
often called "spin-spin" relaxation time

- What determines these times?
- What is relationship to measured signals?

NMR Physics - A cartoon review

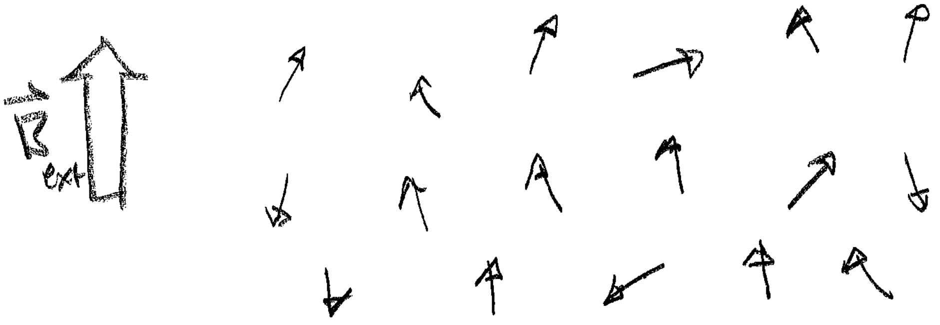
System = Bunch of "spins" (magnetic moments and angular momentums)

These are your spins



Each spin precesses about local $\vec{B}$ with ang freq $\boxed{\omega = \gamma B}$

These are your spins in an External Field $\vec{B}_{ext}$



Now, spins have a net alignment towards $\vec{B}_{ext}$

Extra energy due to $\vec{B}_{ext}$ is

$$E_B = \sum_{\substack{\text{all}\\ \text{spins}}} -\vec{\mu}_i \cdot \vec{B}_{ext} = -\left(\sum \vec{\mu}_i\right)\cdot \vec{B}_{ext}$$

$$= -\underset{\substack{\uparrow \\ \text{Net magnetization}}}{\vec{M}} \cdot \vec{B}$$

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Remember, for one spin, $E_B = -\vec{\mu}\cdot\vec{B}$

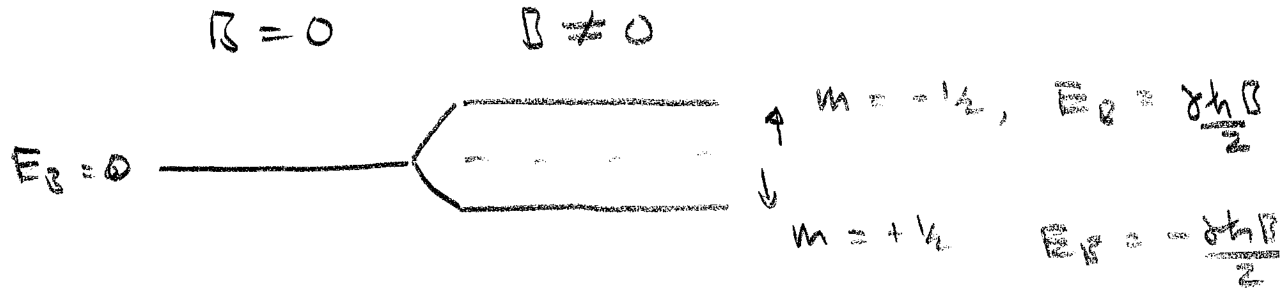
or $E_B = -\mu_z B$ (since $\vec{B}$ defines "z")

$$= -S_z \gamma B = -\gamma \hbar m\, B$$

(angular momentum

Where $m = \pm \frac{1}{2}$ for a spin-$\frac{1}{2}$ particle (proton)

This gives the famous ENERGY LEVEL DIAGRAM



$\Delta E_B = \gamma\hbar B = \hbar\omega$ ← Energy of a photon

$$\boxed{\omega = \gamma B}$$

So... Frequency of photon needed to flip spin is same as precession frequency!

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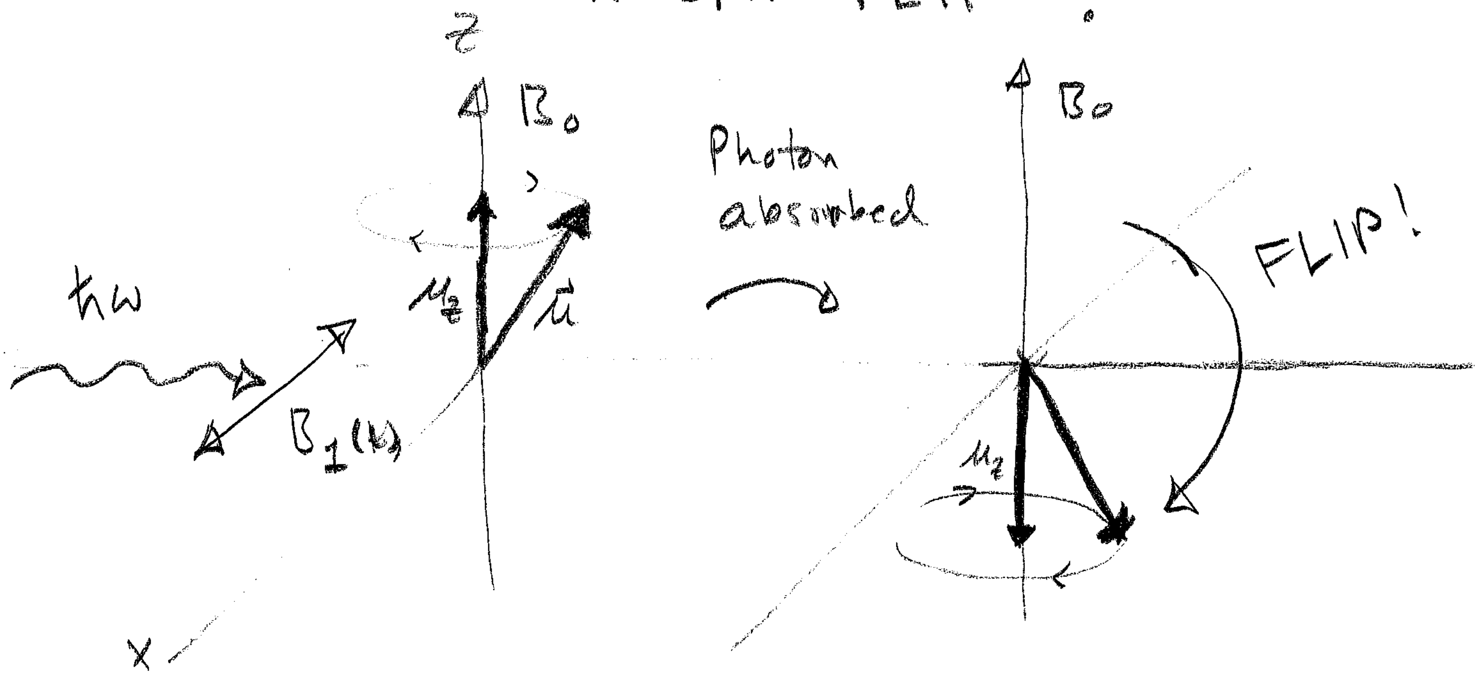
WHITHER A SPIN FLIP ?



When perpendicular field is applied At just the right frequency (γB) Precession about *net* field $\vec{B}_0 + \vec{B}_1(t)$ can *invert* spin component μ_z. Now energy of spin is *increased*

What if $B_1(t)$ is left on?

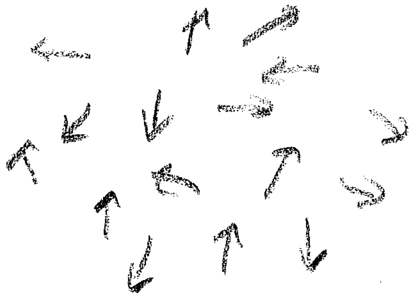
→ Spin flips back again, *giving* up energy gained in *first flip*. Eventually, *no net energy* is transferred between spins & $\vec{B}_1$ field

What if $B_1(t)$ is turned off and left off?

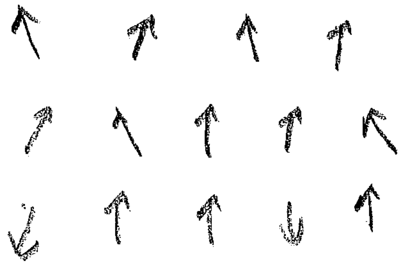
Spin will feel local field variations and RELAX back toward $\vec{B}_0$.

To recap, in pictures, with a bunch of spins

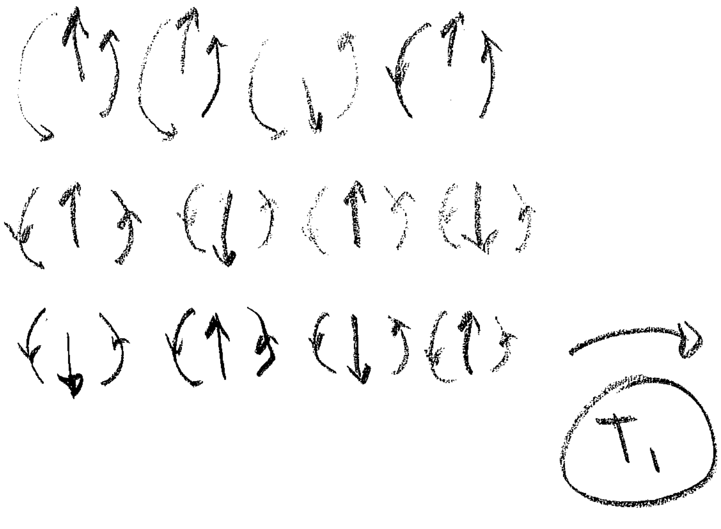
Everybody random $\vec{B}=0$



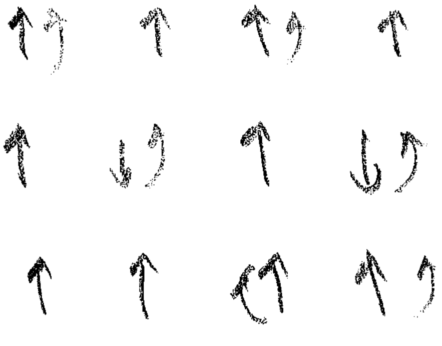
ATTENTION! $\vec{B}_0 \neq 0$



PARTAAY! $\vec{B}_0+\vec{B}_1(t)$



BACK TO WORK $\vec{B}_1$ off

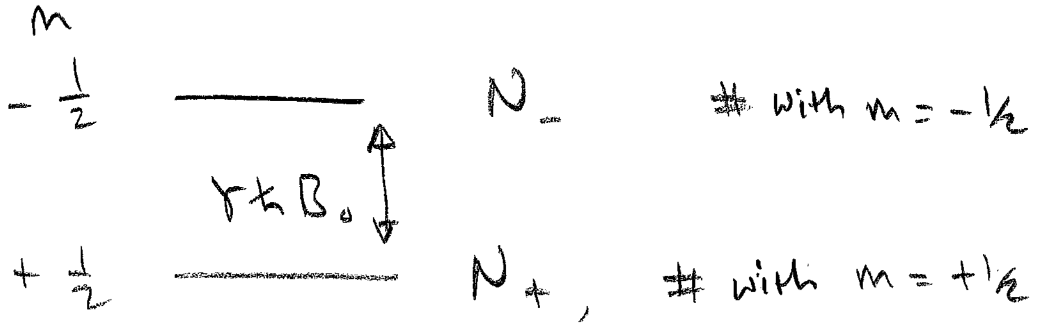


T_1 is characteristic time to "relax" back to equilibrium in $\vec{B}_0$

#6

Now, for some math. A simple model of relaxation (T_1)

"Two-state system" (A statistical mechanic's favorite)



A "rate equation"

$$\frac{dN_+}{dt} = N_- W_{-+} - N_+ W_{+-}$$

The 'W's' are rates that depend on interactions between spins & field.

Consider first a $B_1(t)$ field that is tuned to resonance. From QM

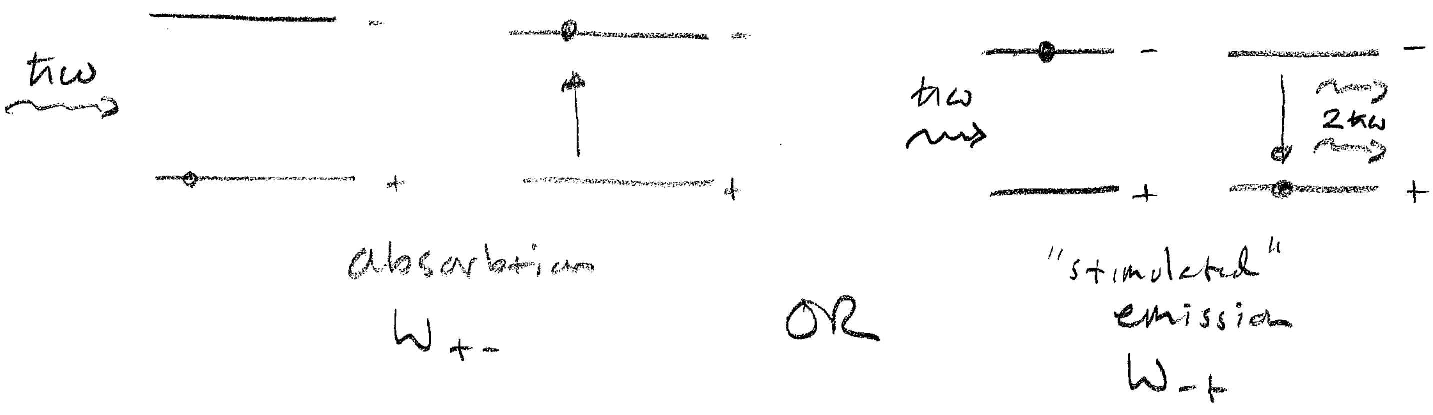
$$W_{+-} = W_{-+} = \frac{2\pi}{\hbar} \left| \langle i | \mathcal{H} | f \rangle \right|^2 \rho(E)$$

Matrix element connecting initial & final state

"Density of states"

Notice symmetry of QM rule (Fermi's "Golden Rule")

Implies that $W_{+-} = W_{-+}$



$\Rightarrow$ Same idea in QM as continued precession about oscillating field $\Leftarrow$

So, in terms of this interaction

$$\frac{dN_+}{dt} = W(N_- - N_+)$$

Define $N = N_+ + N_-$ (total spins)

$n = N_+ - N_-$ (difference)

$N_+ = \frac{N+n}{2}$, $\frac{dN_+}{dt} = \frac{1}{2}\frac{dn}{dt}$

$$\Rightarrow \quad \frac{dn}{dt} = -2Wn$$

So $$\boxed{n = n_0 e^{-2Wt}}$$

Difference in up spins vs down spins disappears <u>exponentially</u> on application of $B_1(t)$

If no $\vec{B}_1(t)$?

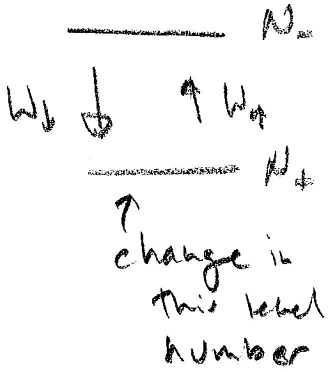
We know That $N_-^0 \neq N_+^0$ ← Equilibrium Values

$$\frac{N_-^0}{N_+^0} = \frac{e^{-\gamma\frac{\hbar B}{2}/kT}}{e^{\gamma\frac{\hbar B}{2}/kT}} = e^{-\gamma\hbar B/kT} < 1$$

Recall from stat. mech, That probability of finding a system in energy state E_n when it is in contact w/ temperature bath at temperature T is proportional to $e^{-E_n/kT}$. ← "Boltzmann Factor"

Define $W_\uparrow$, $W_\downarrow$ to be rates of transition when $B_1(t)$ is off. These cannot be the same as $W_{+-} = W_{-+} = W$

$$\frac{dN_+}{dt} = N_- W_\downarrow - N_+ W_\uparrow$$



At steady state $\frac{dN_+}{dt} = 0$

$$\Rightarrow N_-^0 W_\downarrow = N_+^0 W_\uparrow \Rightarrow \frac{N_-^0}{N_+^0} = \frac{W_\uparrow}{W_\downarrow} \neq 1$$

Using same substitutions as before

$N_+ = \frac{N+n}{2}$, $N_- = \frac{N-n}{2}$

get

$$\frac{1}{2}\frac{dn}{dt} = \frac{N-n}{2}(W_\downarrow) - \left(\frac{N+n}{2}\right)(W_\uparrow)$$

↓

some algebra

↓

$$\frac{dn}{dt} = \left[N\left(\frac{W_\downarrow - W_\uparrow}{W_\downarrow + W_\uparrow}\right) - n\right](W_\uparrow + W_\downarrow)$$

And yet more algebra ...

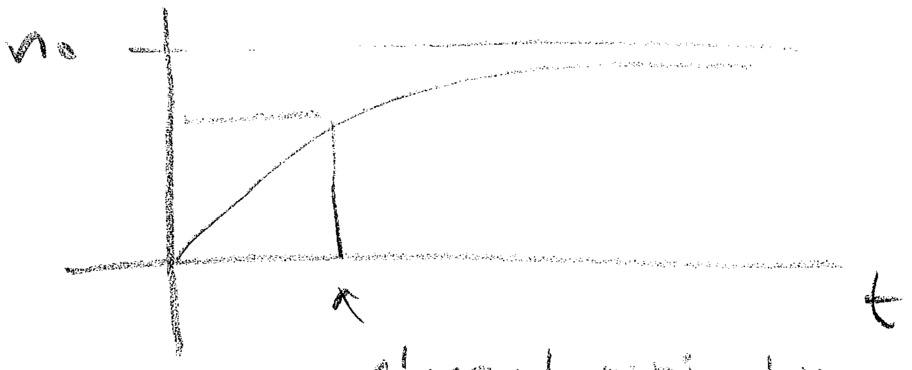
$$\frac{N_-^0}{N_+^0} = \frac{N-n_0}{N+n_0} = \frac{W_\uparrow}{W_\downarrow}$$

Leads to $$n_0 = N\left(\frac{W_\downarrow - W_\uparrow}{W_\uparrow + W_\downarrow}\right)$$

or $$\frac{dn}{dt} = [n_0 - n]\left(W_\uparrow + W_\downarrow\right)$$

Which has solution

$$n = n_0\left(1 - e^{-t(W_\uparrow + W_\downarrow)}\right)$$



characteristic time $T_1 = \frac{1}{W_\uparrow + W_\downarrow}$

When B_1 is applied, we have <u>2</u> rates

$$\frac{dn}{dt} = \underbrace{-2Wn}_{\text{RF field hw transitions}} + \underbrace{\frac{n_0 - n}{T_1}}_{\text{static field relaxation}}$$

<u>At</u> <u>steady</u> <u>state</u> $\frac{dn}{dt} = 0$

$$2Wn = \frac{n_0 - n}{T} \xrightarrow{\text{some math}} \boxed{n = \frac{n_0}{1 + 2T_1W}}$$

Notice that if T_1 is <u>short</u> and/or W is <u>weak</u>, $\underline{n \to n_0}$

But if T_1 is <u>long</u> or W is <u>strong</u>

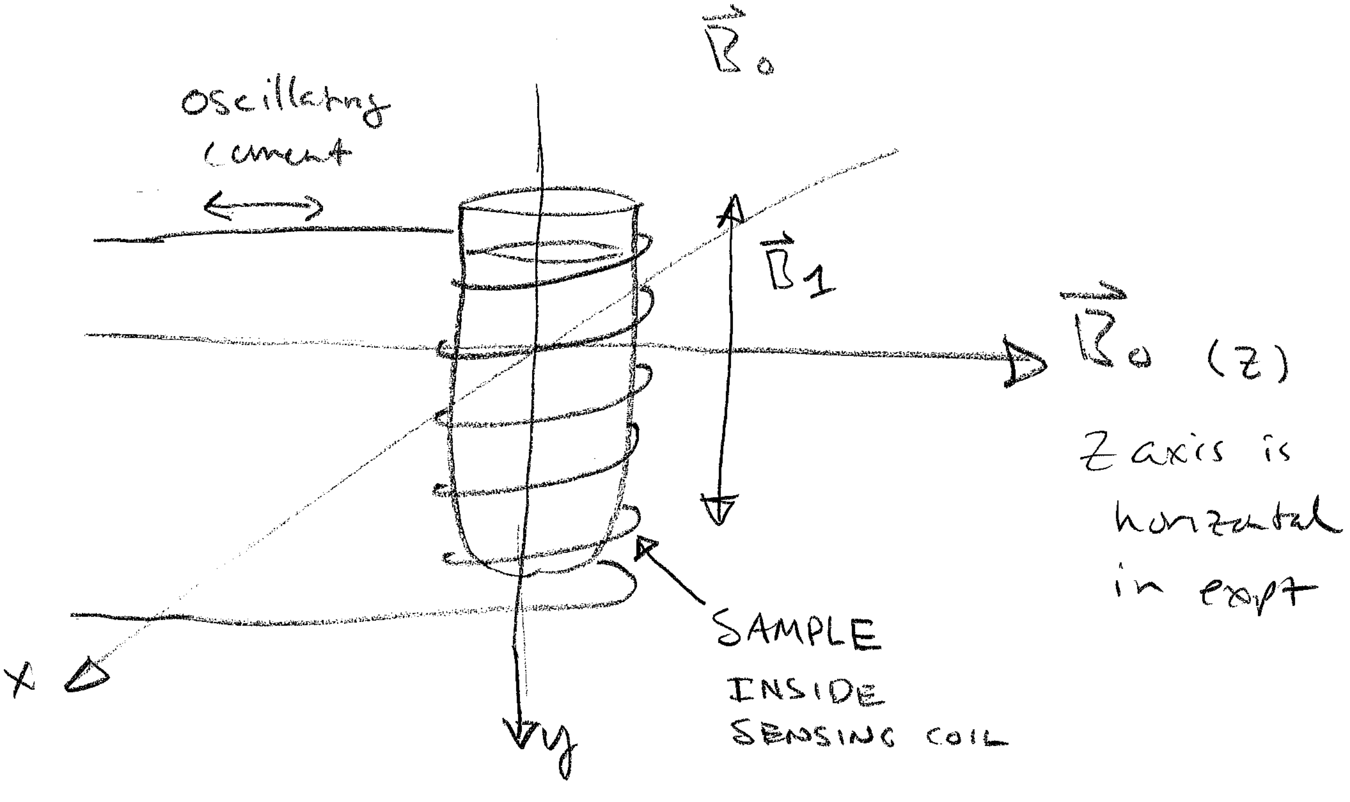
$\underline{n \to 0}$

$$\boxed{\text{SATURATION}}$$

#12

Once saturation occurs, no net energy transfer from field occurs, and thus no signal can be measured.

HOW DOES SIGNAL APPEAR?



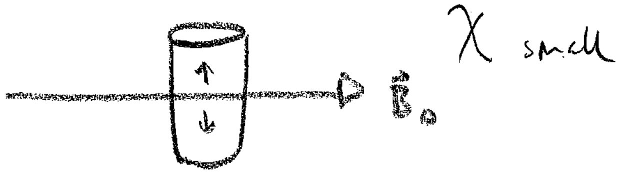
$\vec{B}_1$ field oscillates perpendicularly to $\vec{B}_o$. When $\vec{B}_1$ has frequency $\omega = \gamma B_o$, effect on spins is greatest (see next lecture...)

2 Methods:

$\boxed{\text{OLD SCHOOL}}$

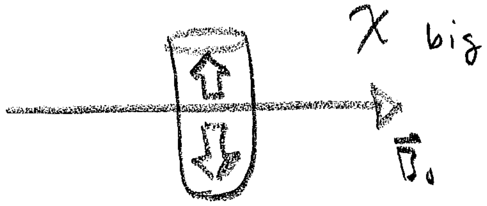
"Continuous" NMR – $B_1(t)$ always on

"OFF" resonance, $\omega \neq \gamma B_0$



Weak response in plane perp. to $\vec{B}_0$

"On" resonance, $\omega = \gamma B_0$



Strong response in plane perp. to $\vec{B}_0$

- The magnetic susceptibility of the spins is frequency dependent
- Inductance of sensing coil also depends on frequency
- so, electronic circuit that uses coil has frequency sensitivity.

$$\underbrace{L_0}_{\text{Inductance of coil w/ no core}} \to \underbrace{L_0(1+4\pi\chi(\omega))}_{\text{Inductance of coil with frequency dependent } \chi}$$

Continuous Method can work as long as B_1 field is weak and/or T_1 is short.

Need to avoid saturation in order to Maximize $\chi(\omega)$.

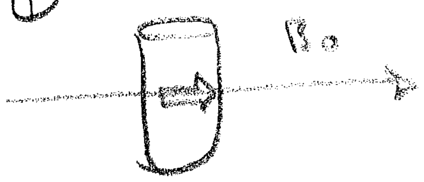
"Pulsed" NMR

NEW SCHOOL

$B_1(t)$ very strong, but on for very short time

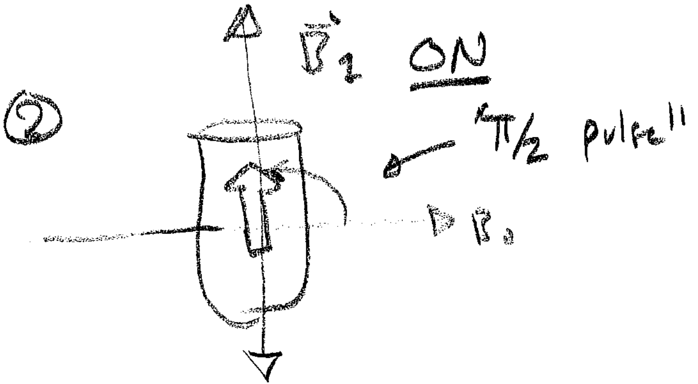
$\vec{B}_1 = 0$

①



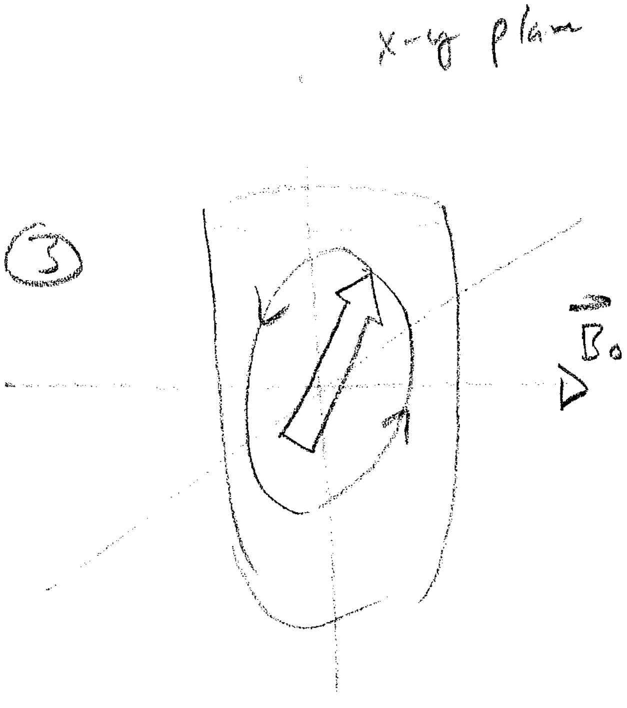
Equilibrium

②



Short $\vec{B}_1$, on resonance tips Net magnetization into plane perpendicular to $\vec{B}_0$

③



Net $\vec{M}$ precesses about $\vec{B}_0$, induces signal in coil

"FREE INDUCTION DECAY"

#15

As the Net moment is made up of individual spins, The precession of the net moment is a consequence of the precession of the individual spins.

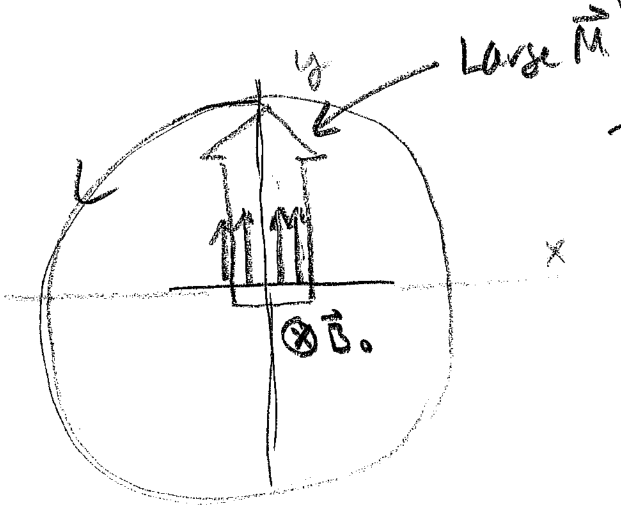
- Different spins precess at different rates — They see different fields
  - ↳ External field inhomogeneity.
  - ↳ Motion of spins through body of sample.
  - ↳ Interaction of spin with its neighbor
  - ↳ Interaction of spin with "lattice".

Net moment in x-y plane disappears over time, characterized by "T_2" parameter.

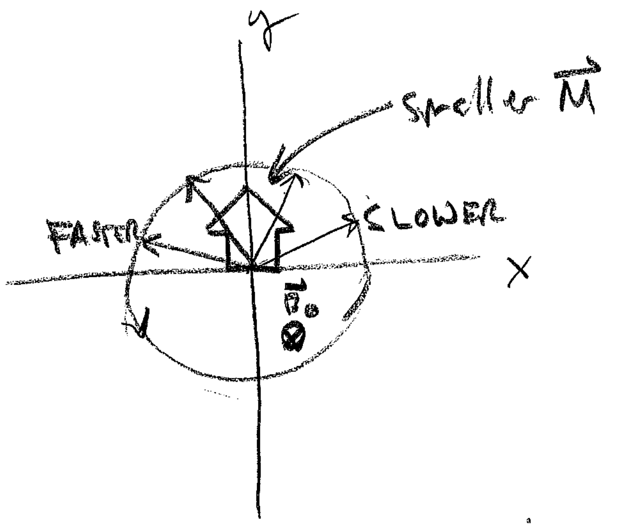
$T_2 \Longleftrightarrow$ spin-spin dephasing or spin-spin "relaxation"

- Over sufficient time, Net Magnetization Relaxes back to equilibrium – "T_1" parameter.

Here are some pictures:

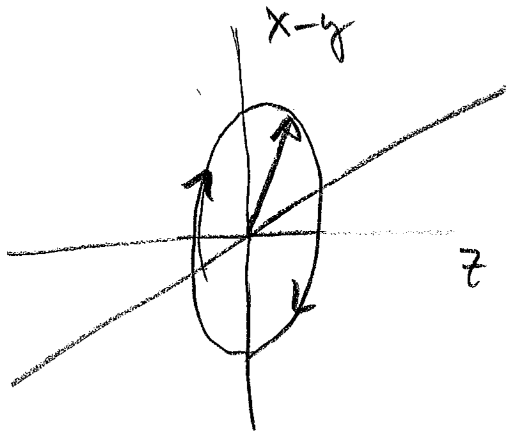


all in phase

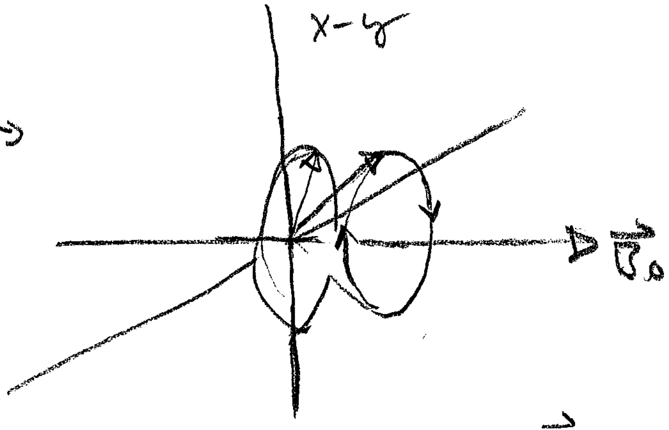


Losing phase coherence

As spins precess, They also get tipped back toward $\vec{B}_0$



Spin lying in X-y Plane



Spin tilted toward $\vec{B}_0$ smaller projection in X-y-plane

Since both types of processes can occur, it is not surprising that T_1 & T_2 are related.

An Intuitive model for T_2

If there is only a fixed variation in magnetic field in the z direction, then the spins in different parts of the sample would dephase at a fixed rate.

Each spin precesses with $\omega_i = \gamma B_{zi}$

where $B_{zi} = B_0 + \boxed{b_{zi}} \leftarrow$ variation in field at location of spin i

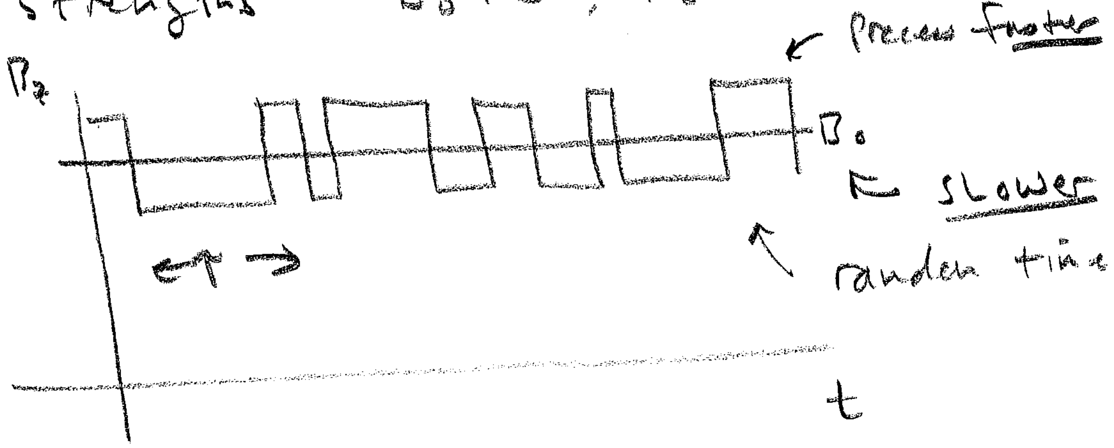
so $\omega_i = \gamma B_0 + \gamma b_i = \omega_0 + \Delta\omega_i$

Expect characteristic dephase due to fixed field variation: $\Delta\omega T_2 \approx 1$ radian or $\frac{1}{T_2^0} = \gamma \Delta b$ where Δb gives typical spread in fixed field

This would be OK if spins were *fixed* in space. But in liquid, spins *move*.

Field fluctuations are *not fixed in time*

Extend model: Assume spin sees 2 field strengths $B_0 + b$, $B_0 - b$ as it moves



Overall phase variation from nominal stays close to zero, but different spins get out of sync.

τ = *mean time* in one of fields

#19

During a time τ in the field

Phase of precession increases by

$$\gamma(B_0+b)\tau = \gamma B_0\tau + \gamma b\tau$$

Over time t, the Net Mean square

dephasing is $\overline{(\Delta\phi)^2} = n(\gamma b\tau)^2$

↑ number of intervals of time τ in t

So $\overline{(\Delta\phi)^2} = \frac{t}{\tau}(\gamma b\tau)^2 = t\gamma^2 b^2\tau$

In this case, for a mean square dephasing of 1 radian, $T_2 \simeq t$

or $T_2\gamma^2 b^2\tau = 1$

$$\boxed{\frac{1}{T_2^{\textcircled{2}}} = \gamma^2 b^2 \tau}$$

#20

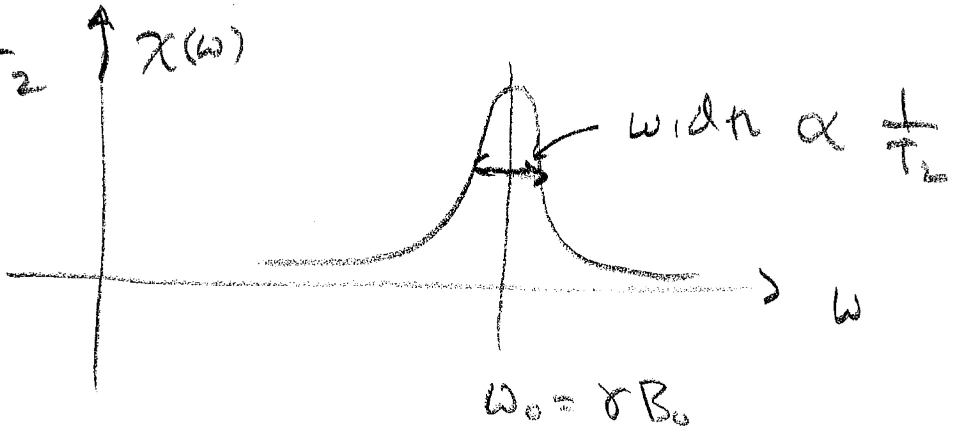
This is a VERY INTERESTING FORMULA $\Rightarrow$ IF τ is short (lots of variations between + b & -b in time)

THEN T_2 is LONG!

This is phenomenon of "motional narrowing"

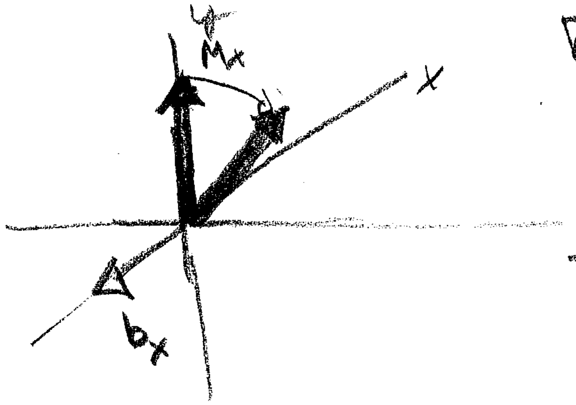
Overall, spins remember their phase as they move around. Motion causes phase variation to average out over time.

Term "Narrowing" comes from continuous method study - resonance width is proportional to $1/T_2$



Extend model further

Also see decay in transverse (x-y plane) magnetization due to tipping of spin back to z axis.



$\vec{b}_x \times \vec{M} \rightarrow$ torque on $\vec{M}$ towards z

So, any fluctuations in b_x or b_y will lead to a decrease in $\vec{M}$ projected on x-y plane.

HOWEVER...

① ONLY FLUCTUATIONS AT $\omega \approx \omega_0$ are important

② b_x, b_y ONLY ACT ON COMPONENTS PERPENDICULAR TO THEM

(After much handwaving...)

$$\frac{1}{T_2^{(3)}} \simeq \gamma^2 \cdot \frac{1}{2}\left[\overline{\tilde{b}_x^2}(\omega_0) + \overline{\tilde{b}_y^2}(\omega_0)\right]$$

where $\overline{\tilde{b}_x^2}(\omega)$, $\overline{\tilde{b}_y^2}(\omega)$ represent the "spectral densities" of the magnetic field at a frequency ω. (Note, $\overline{\tilde{b}^2}(\omega)$ has units of (field)^2 × (time))

The "½" indicates that the x, y components only affect part of $\vec{M}$

OK DAVE, WHAT'S A SPECTRAL DENSITY?

#23

"SPECTRAL DENSITY" gives the strength of field within a range of frequency.

Like "density" – $\frac{\text{Mass}}{\text{unit volume}}$

"spectral density" $\frac{\text{Magnetic energy}}{\text{unit frequency}}$ ← Prop to B^2

← Prop. to 1/Time

Spectral density is the Fourier transform of the "auto-correlation" function of the B feild

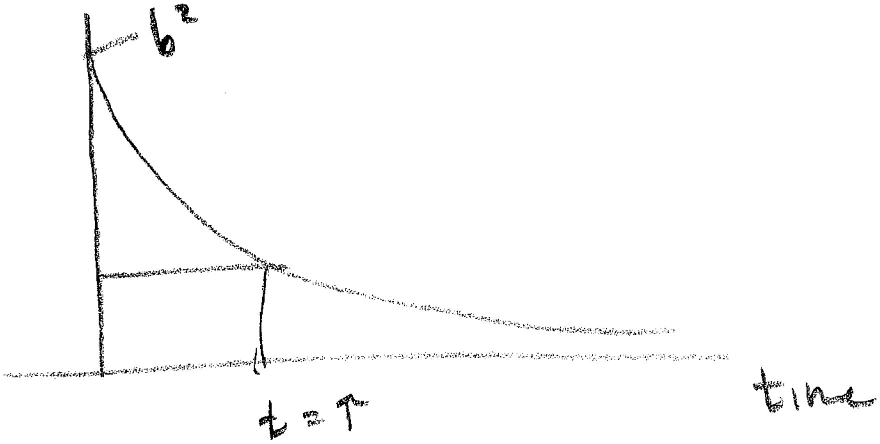
Auto correlation

1. Take measure of b(t)
2. Take measure of b(t + τ)
3. Multiply together.
4. Average all such products for all time t.

Thus, $\langle b(t) b(t+\tau) \rangle_t$ is auto correlation fctn

$\Rightarrow$ A way to say how much variation there is in a randomly varying field over time

A useful model, when $b(t)$ is random is to assume $\langle b(t) b(t+\tau) \rangle = \overline{b}^2 e^{-|\tau|/\tau_0}$



If τ_0 is short, fluctuations are very rapid

If τ_0 is Long, fluctuations are slow

#25

Fourier transform gives spectral density

$$\overline{b^2}(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} \langle b(t)\, b(t+\tau)\rangle_t \, e^{i\omega\tau}\, d\tau$$

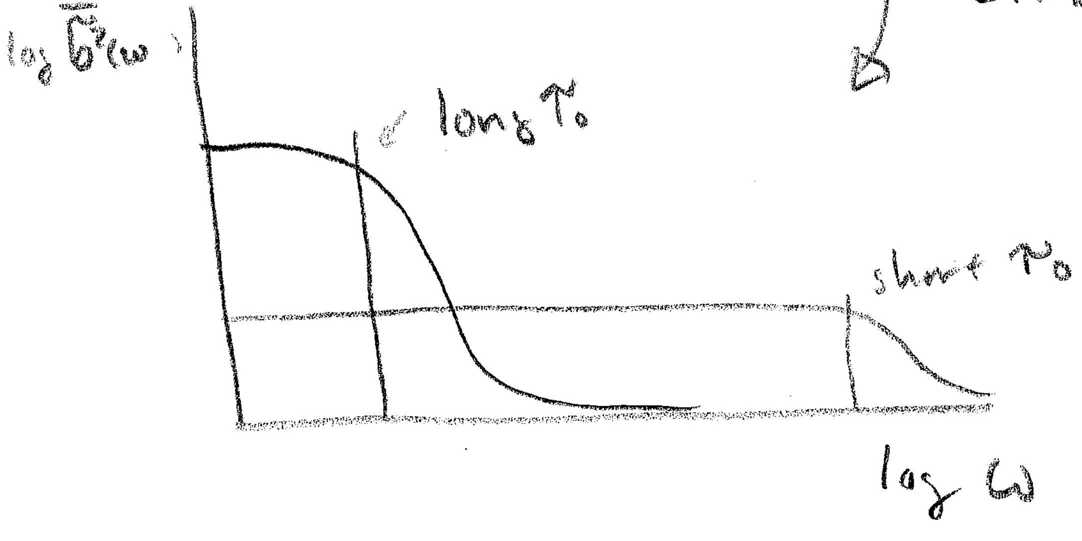
$$= \frac{1}{2}\int_{-\infty}^{\infty} \overline{b^2}\, e^{-|\tau|/\tau_0} e^{i\omega\tau}\, dt$$

$$= \frac{1}{2}\overline{b^2}\int e^{-|\tau|/\tau_0 + i\omega t}\, dt$$

↓ some math

$$= \overline{b^2}\, \frac{\tau_0}{1+\omega^2\tau_0^2}$$

LOOKS LIKE



UNDER ASSUMPTION THAT $b_x^2 = b_y^2 = b_z^2$

(Isotropic fluctuations)

$$\frac{1}{T_2^{(3)}} = \gamma^2 \overline{b^2} \frac{\tau_0}{1 + \omega_0^2 \tau_0^2}$$

Important: ω_0 is resonant frequency

γB_0 ← depends on proton & B_0

τ_0 is characteristic correlation time ← Depends on material properties

So, Different materials & conditions may have different T_2 s!

#27

Ignore external field variations,

Then <u>intrinsic</u> T_2 time looks like

This
$$\frac{1}{T_2} = \gamma^2 \overline{b^2} \tau_0 + \gamma^2 \overline{b^2} \frac{\tau_0}{1+\omega_0^2\tau_0^2}$$

Same basic model can apply to T_1, except here, there is no "zero frequency" term. $\underline{T_1}$ depends on b_x, b_y components tipping spin toward or away from z axis

$$\frac{1}{T_1} = \gamma\left[b_x^2(\omega_0) + b_y^2(\omega_0)\right]$$

(No term if z)

$$= 2\gamma^2\overline{b^2}\frac{\tau_0}{1+\omega_0^2\tau_0^2}$$

Plot these

- Minimum in T_2 when $\tau_0 \omega_0 \approx 1$
- when τ_0 is short, $T_1 \approx T_2$, both long MOTIONAL-NARROWED LINES
- when τ_0 is long, T_1 is long
  T_2 is short

THIS IS WHY WE USE LIQUIDS IN THESE EXPTS