Cross polarization (CP)

‘classical’ description of cross-polarization uses concept of *spin temperature*

this approach is valid as long:
1. system contains a large number of spins
2. strong $^1\text{H}-^1\text{H}$ dipolar couplings are present

**thermodynamic approach:**
- polarization exchange between two reservoirs with different spin temperature coupled to a large reservoir (‘lattice’)
- relaxation to equilibrium
Zeeman interaction

spins rotate with the Larmor frequency $\omega_0$ …

…or, spin up and spin down have an energy difference of $\omega_0$

$(\omega_0 / 2\pi) \sim 500$ MHz

$\omega_0 = \gamma_H B_0$
“Boltzmann’s ingenious concept”

\[ \frac{N_2}{N_1} = \exp \left( -\frac{E_2 - E_1}{kT} \right) \]

low T \quad \rightarrow \quad large population differences \quad \rightarrow \quad high polarization

high T \quad \rightarrow \quad small population differences \quad \rightarrow \quad low polarization
“Boltzmann’s ingenious concept”

- Large splitting \( \rightarrow \) Large population differences \( \rightarrow \) High polarization
- Small splitting \( \rightarrow \) Small population differences \( \rightarrow \) Low polarization

Boltzmann's ingenious concept
“Boltzmann’s ingenious concept”

\[ \text{à high magnetic fields give larger signal} \]

\[ \text{à } ^1\text{H (high } \gamma \text{) more sensitive than } ^{13}\text{C or } ^{15}\text{N (low } \gamma \text{) à CP} \]

\[ \text{à } e^- \text{ (very high } \gamma \text{) used to enhance NMR signal à DNP} \]

\[ \text{à low temperature larger signal than high temperature} \]
Cross polarization (CP)

during CP, both spin-types ($^1$H and $^{13}$C) are ‘spin-locked’

like the Zeeman interaction, the spin-lock pulse gives rise to a splitting (spin up, spin down)
Cross polarization (CP)

since $B_0$, $\gamma_H$ and $\gamma_C$ are all fixed, the Zeeman splitting is different for $^1H$ and $^{13}C$ …

… however, the spin-lock fields $B_1^H$ and $B_1^C$ can be chosen so that the splitting for $^1H$ and $^{13}C$ becomes equal

Hartmann-Hahn Matching
Cross polarization (CP)

**in equilibrium:**
levels separated by $\omega_0$
à occupation of levels according
to real Boltzmann distribution

**during spin lock:**
levels separated by $\omega_1$
with $\omega_1 \ll \omega_0$
à levels are 'compressed'
à occupation of levels looks like
a Boltzmann distribution, but
one for much lower $T$
Cross polarization (CP)

Spin locking $^1\text{H}$ lowers the spin-temperature during spin lock:
relaxation back to the normal temperature with $T_{1\rho}$

'\text{real}' Boltzmann distribution

Low T

High T

Apparent Boltzmann distribution

Lab frame

Rotating frame
Cross polarization (CP)

by matching energy splitting for $^1$H and $^{13}$C (Hartmann-Hahn matching), polarization can be exchanged with conservation of energy

heteronuclear ($^1$H - $^{13}$C) dipolar interaction couples $^1$H and $^{13}$C polarization reservoirs

homonuclear interaction (mostly $^1$H- $^1$H) provides coupling to lattice ($T_1\rho$ relaxation)

equilibration lowers $^{13}$C spin temperature à $^{13}$C polarization first increases (short CP)

coupling to lattice reduces spin temperature à $^{13}$C polarization relaxes (long CP)
Overview

- dipolar interaction
  - Hamiltonian
  - recoupling
  - dipolar truncation

- cross polarization (CP) - part II

- DNP (dynamic nuclear polarization)
Dipolar interaction

the dipolar coupling is the interaction between two magnetic moments \( \mu_1 \) and \( \mu_2 \)

\[
U = \left\{ \frac{\mu_1 \cdot \mu_2}{r^3} - 3 \frac{(\mu_1 \cdot r)(\mu_2 \cdot r)}{r^5} \right\} \frac{\mu_0}{4\pi}
\]

\( \sim \cos \alpha \)

zero for \( \alpha = 90^\circ \)

max for \( \alpha = 0^\circ \)

\( \sim \cos \beta \)

\( \sim \cos \gamma \)

same \( \alpha \)!
**Dipolar interaction**

the dipolar coupling is the interaction between two magnetic moments $\mu_1$ and $\mu_2$

$$U = \left\{ \frac{\mu_1 \cdot \mu_2}{r^3} - 3 \frac{(\mu_1 \cdot r)(\mu_2 \cdot r)}{r^5} \right\} \frac{\mu_0}{4\pi}$$

how does the dipolar coupling look in quantum mechanics?

$$\mu \rightarrow \hat{\mu} = \gamma \hbar \hat{I}$$

(correspondence principle)

$$\hat{H}_{dd} = -\left( \frac{\mu_0}{4\pi} \right) \gamma I \gamma S \hbar \left( \frac{I \cdot S}{r^3} - 3 \frac{(I \cdot r)(S \cdot r)}{r^5} \right)$$
Barth-Jan van Rossum: Solid-state NMR, advanced concepts I

**Dipolar interaction**

\[
\hat{H}_{dd} = -\left(\frac{\mu_0}{4\pi}\right)\gamma_I\gamma_S\hbar\left(\frac{\mathbf{I}\cdot\mathbf{S}}{r^3} - 3\frac{(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})}{r^5}\right)
\]

\[
\hat{H}_{dd} = -\left(\frac{\mu_0}{4\pi}\right)\gamma_I\gamma_S\hbar\left[A + B + C + D + E + F\right]
\]

“dipolar alphabet”

\[
A = \hat{I}_z\hat{S}_z(3\cos^2\theta - 1)
\]

\[
B = -\frac{1}{2}(\hat{I}_x\hat{S}_x + \hat{I}_y\hat{S}_y)(3\cos^2\theta - 1)
\]

\[
C = -\frac{3}{2}[\hat{I}_z\hat{S}_+ + \hat{I}_+\hat{S}_z]\sin\theta\cos\theta e^{-i\phi}
\]

\[
D = -\frac{3}{2}[\hat{I}_z\hat{S}_- + \hat{I}_-\hat{S}_z]\sin\theta\cos\theta e^{+i\phi}
\]

\[
E = -\frac{3}{4}[\hat{I}_+\hat{S}_+]\sin^2\theta e^{-2i\phi}
\]

\[
F = -\frac{3}{4}[\hat{I}_-\hat{S}_-]\sin^2\theta e^{+2i\phi}
\]
**Dipolar interaction**

Zeeman interaction (~500 MHz) $\gg$ dipolar interaction (~50 kHz)

Only terms that commute with Zeeman interaction ($I_z$) remain

- $A, B$ – terms:
  
  commute with $I_z$ ("secular terms") ⇔ no time evolution under $I_z$

- $C, D, E, F$ – terms:
  
  do not commute with $I_z$ ("non-secular terms") ⇔ time evolution under $I_z$
  
  averaged to zero

à ‘truncation’ or ‘quenching’
Dipolar interaction

\[
\hat{H}_{dd} = -\left(\frac{\mu_0}{4\pi}\right) \gamma_i \gamma_s \frac{\hbar}{r^3} \left[ A + B + \boxed{C} + \boxed{D + E + F} \right]
\]

\[
\hat{H}^{\text{homo}}_{dd} = -\left(\frac{\mu_0}{4\pi}\right) \gamma_i \gamma_s \frac{\hbar}{r^3} (3\cos^2\theta - 1) \left[ \hat{I}_z \hat{S}_z - \frac{1}{2} (\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y) \right]
\]

\[
\hat{H}^{\text{hetero}}_{dd} = -\left(\frac{\mu_0}{4\pi}\right) \gamma_i \gamma_s \frac{\hbar}{r^3} (3\cos^2\theta - 1) \hat{I}_z \hat{S}_z
\]

- \(r\) and \(\theta\): spatial parameters
- \(B\)-term only relevant when \(\omega_i \sim \omega_s\)
- Homonuclear case (e.g. \(^1\text{H}-^1\text{H}\))
- Heteronuclear case (e.g. \(^1\text{H}-^{13}\text{C}\))
Dipolar interaction

the dipolar coupling depends on:
- the distance between the spins ($r$)
- the angle $\theta$ between the magnetic field $B$ and the vector connecting the spins

\[
D \propto \frac{1}{r^3} (3 \cos^2 \theta - 1)
\]

\[
\left\langle 3 \cos^2 \theta - 1 \right\rangle \begin{cases} 
= 0 & \text{in isotropic liquids} \\
\neq 0 & \text{in solids or oriented media}
\end{cases}
\]
Recoupling

The time-average of the dipolar coupling is zero but **not** the instantaneous coupling, it is oscillating around zero.
Overview

dipolar interaction
  - Hamiltonian
  - recoupling
  - dipolar truncation

cross polarization (CP) - part II

DNP (dynamic nuclear polarization)
Cross polarization (CP) – part II

Since $B_0$, $\gamma_H$ and $\gamma_C$ are all fixed, the Zeeman splitting is different for $^1H$ and $^{13}C$…

…however, the spin-lock fields $B_1^H$ and $B_1^C$ can be chosen so that the splitting for $^1H$ and $^{13}C$ becomes equal.

$\omega_0^H \neq \omega_0^C$

Hartmann-Hahn Matching
Cross polarization (CP) – part II

the heteronuclear dipolar interaction between $^1$H ($I$-spins) and $^{13}$C ($S$-spins)
drives the polarization transfer:

$$H \sim b \cdot I_z \cdot S_z$$

during CP, the spin lock pulses are along x-axis…

…transform to a frame that rotates around the x-axis
rotating frames

in NMR, everything is rotating…

observation from a frame that rotates itself, makes everything appear static

it is as if the Zeeman interaction has ‘gone’…..

these kind of transformations are quite common in NMR (rotating frame, interaction frame…)
Cross polarization (CP) – part II

the heteronuclear dipolar interaction between $^1\text{H}$ ($I$-spins) and $^{13}\text{C}$ ($S$-spins) drives the polarization transfer:

$$H \sim b \cdot I_z \cdot S_z$$

during CP, the spin lock pulses are along $x$-axis…

…transform to a frame that rotates around the $x$-axis with $\omega_I^H$ (for the $I$ spins) and $\omega_S^C$ (for the $S$ spins)

$$H' \sim b' \cdot (I_z \cdot S_z + I_y \cdot S_y) \cos (\omega_I^H - \omega_S^C)t =$$

$$= b' \cdot (I_z \cdot S_z + I_y \cdot S_y) \quad [\text{for } \omega_I^H = \omega_S^C]$$

Hartmann-Hahn matching!
Cross polarization (CP) – part II

\[ H' \sim b' \cdot (I_z \cdot S_z + I_y \cdot S_y) \]

the magnetization is along x-axis
à transform to a frame with the new \( z' \) axis along the old x-axis

replace \( x, y, z \) as follows:
\[
\begin{align*}
\text{x à z'} & \quad \text{or} \quad I_x \rightarrow I_z \\
\text{y à y'} & \quad \text{or} \quad I_y \rightarrow I_y \\
\text{z à -x'} & \quad \text{or} \quad I_z \rightarrow -I_x \\
\end{align*}
\]

\[ H'' \sim b' \cdot (I_x \cdot S_x + I_y \cdot S_y) \]

rewrite, using raising and lowering operators:
\[
\begin{align*}
I_x &= \frac{1}{2} \left( I^+ + I^- \right) \\
I_y &= -\frac{1}{2} i \left( I^+ - I^- \right)
\end{align*}
\]
Cross polarization (CP) – part II

\[ H'' = b' \cdot (I_x \cdot S_x + I_y \cdot S_y) \]

\[ H'' = b' \left[ \frac{1}{2} (I^+ + I^-) \cdot \frac{1}{2} (S^+ + S^-) + (-\frac{1}{2}i) (I^+ - I^-) \cdot (-\frac{1}{2}i) (S^+ - S^-) \right] \]

\[ H'' = \frac{1}{2} \cdot b' (I^+ \cdot S^- + I^- \cdot S^+) \]

\[
\begin{align*}
I^- & \rightarrow I^- & 0 \\
I^+ & \rightarrow I^+ & 0 \\
I^- & \rightarrow I^+ & \text{all other combinations give zero}
\end{align*}
\]
Cross polarization (CP) – part II

$^1$H net polarization

random

$^1$H

$^{13}$C

$I^- S^+$ $I^+ S^-$

net magnetization is ‘spin-up’ for $^1$H ($I$-spins)
Cross polarization (CP) – part II

net magnetization is ‘spin-up’ for $^1$H ($I$-spins)
Cross polarization (CP) – part II

\[ ^{13}\text{C} \quad ^{1}\text{H} \quad \text{net polarization} \quad \text{random} \quad ^{1}\text{H} \quad ^{13}\text{C} \text{ net-polarization} \]

\[ ^{13}\text{C} \quad ^{1}\text{H} \]

\[ I - S^+ \]