Dynamic Nuclear Polarization and the Paradox of Quantum Thermalization

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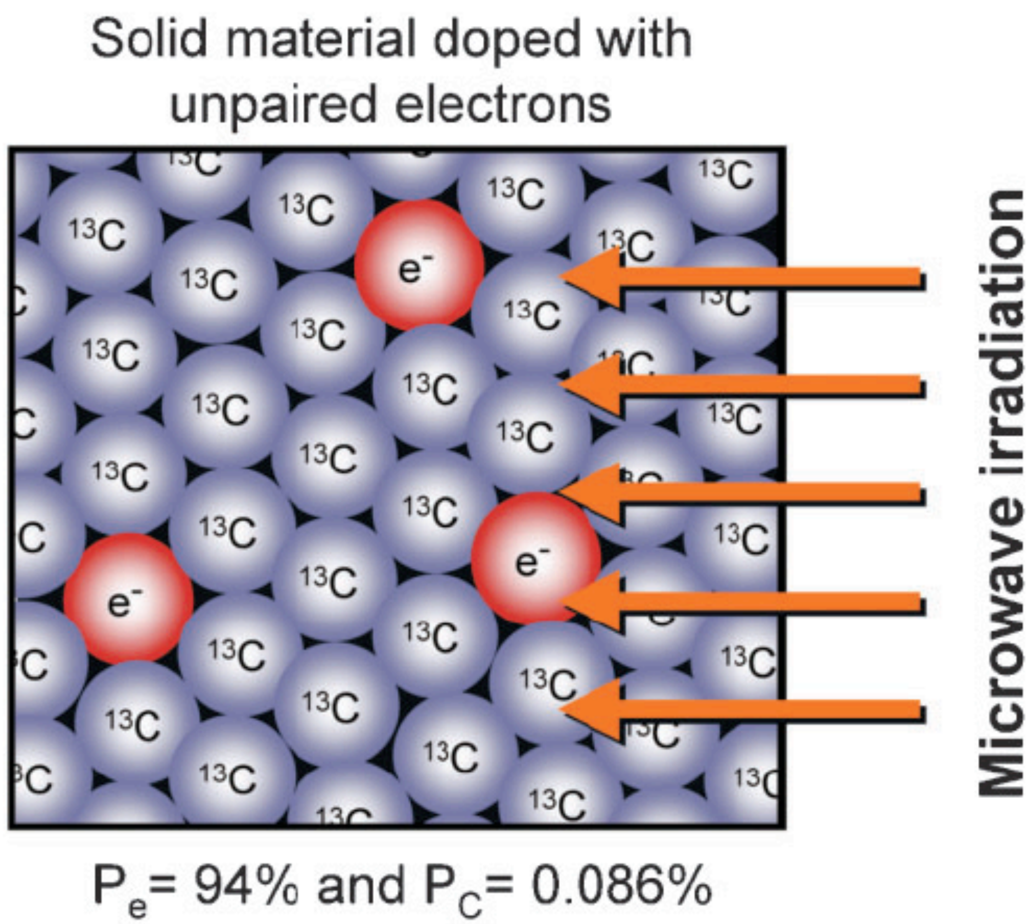
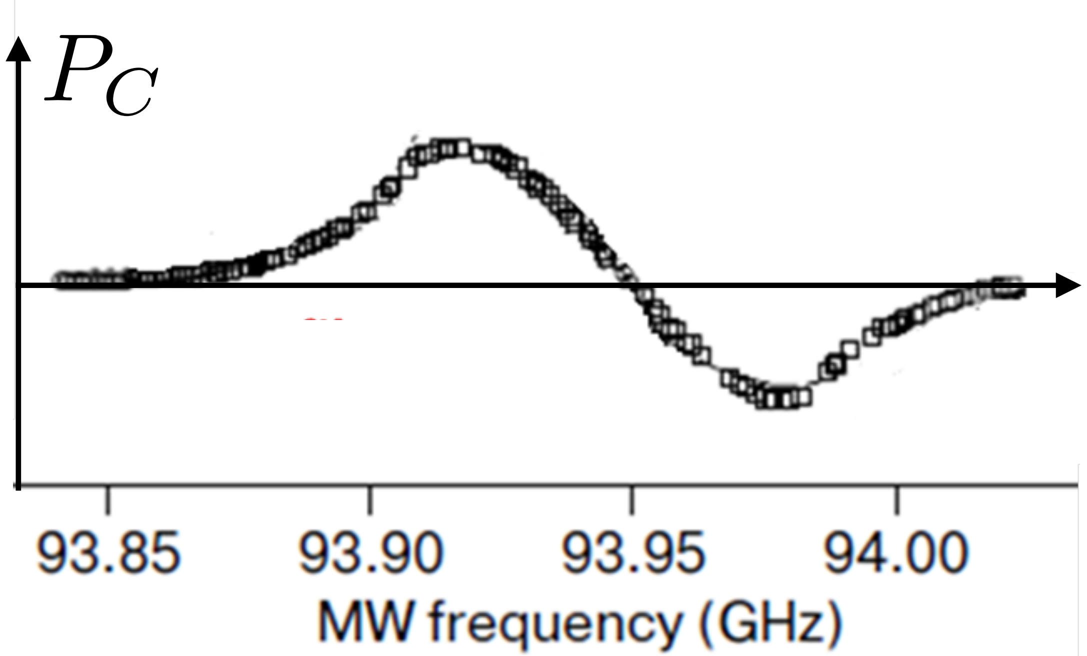
A. De Luca and A. Rosso, Phys. Rev. Lett. 115, 080401, 2015

Dynamic Nuclear Polarisation (DNP)

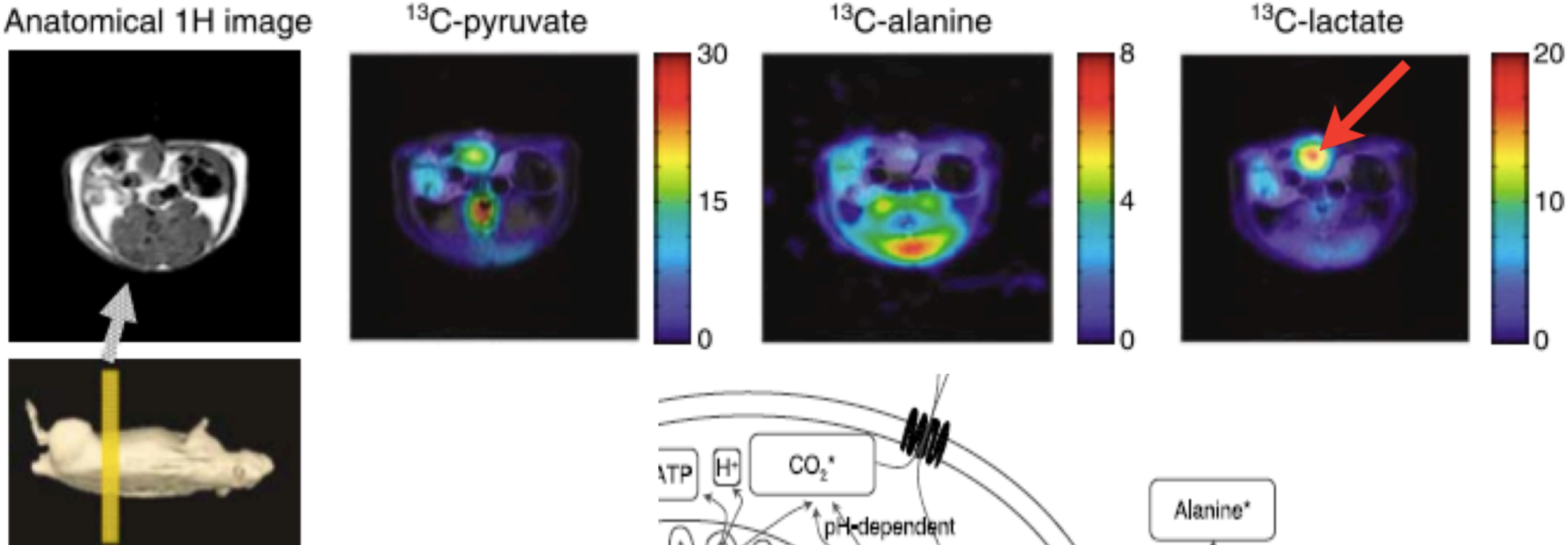


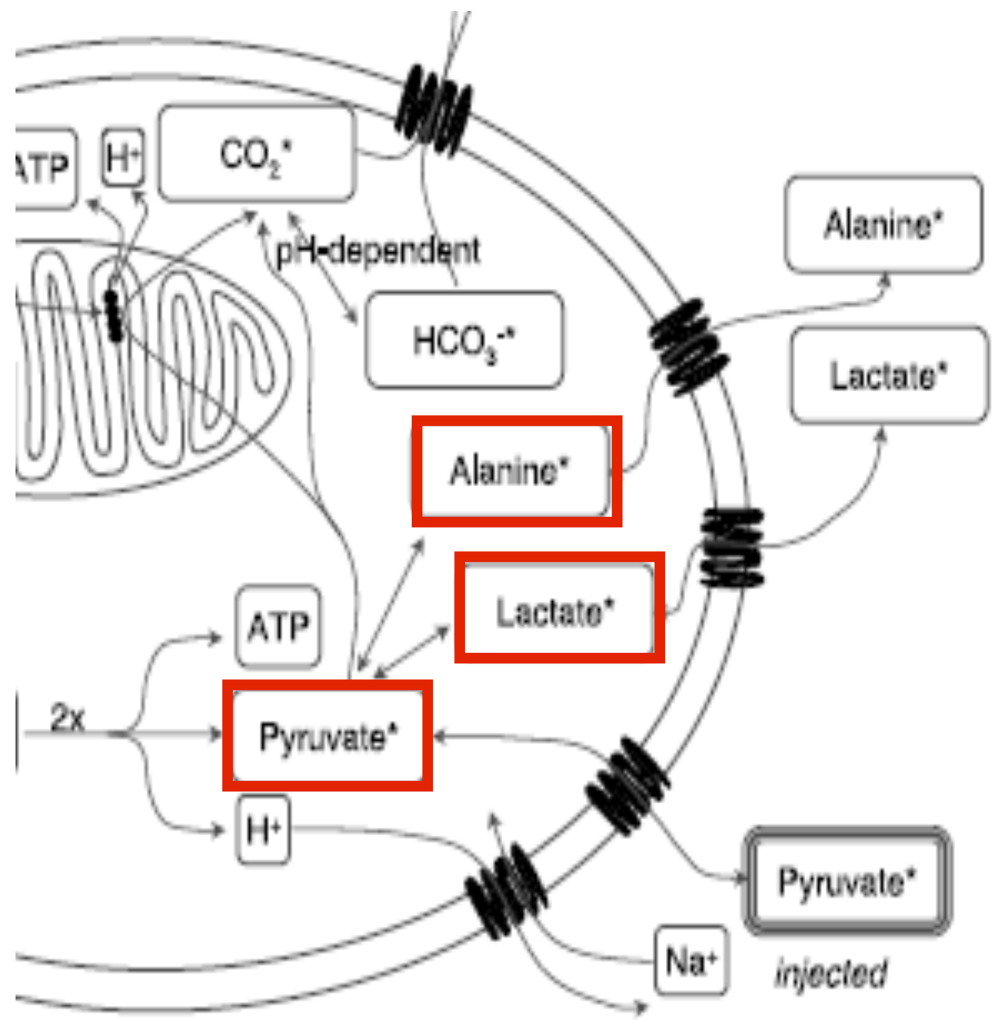
- $T = 1\,\mathrm{K},\ H_0 = 3.3$ Tesla
- $\omega_e \simeq 100$ Ghz
- $\omega_{13C} \simeq 32$ Mhz

DNP profile (after ~ 1 hour):



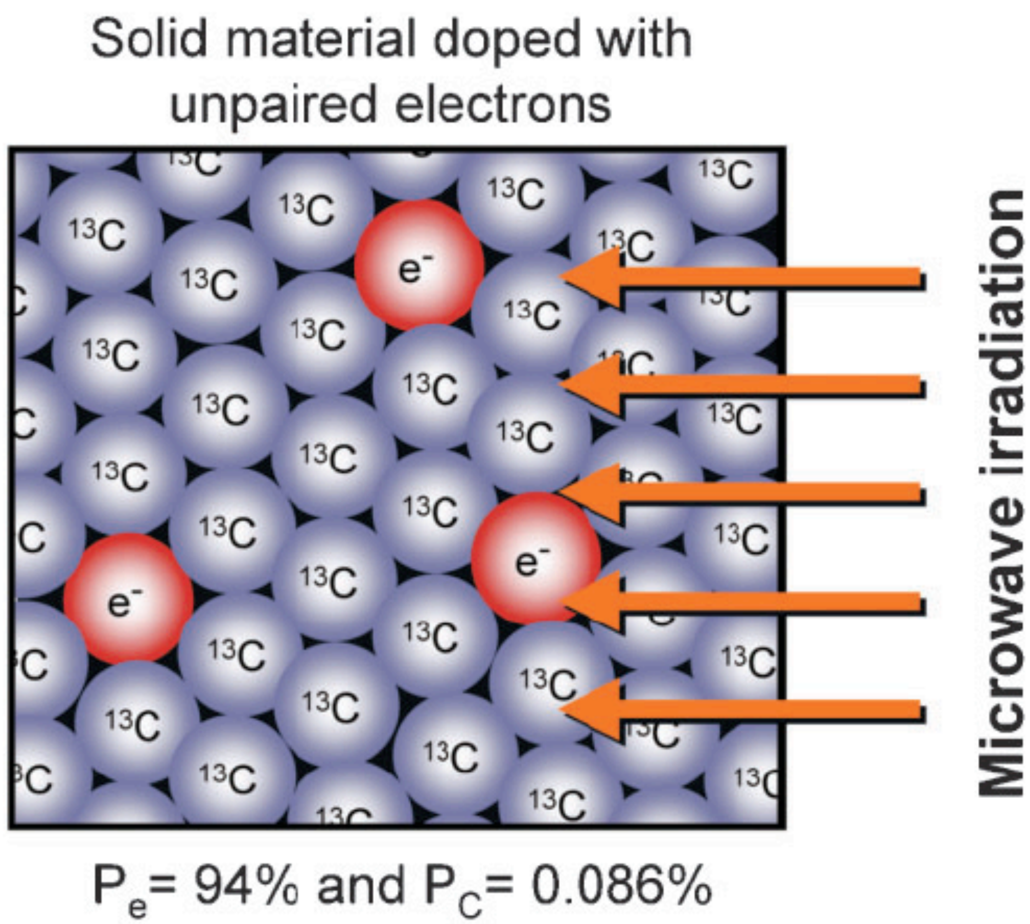
Metabolic Imaging (2006)





Golman et al. Cancer Research 2006.

Dynamic Nuclear Polarisation (DNP)



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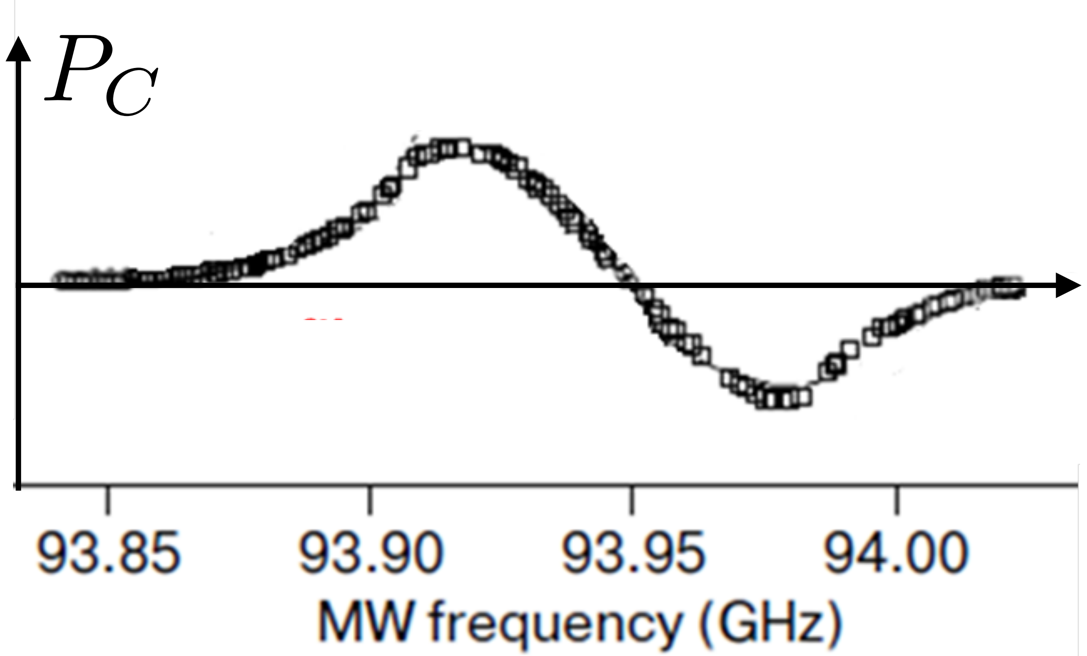


Dilute spins randomly placed in a matrix

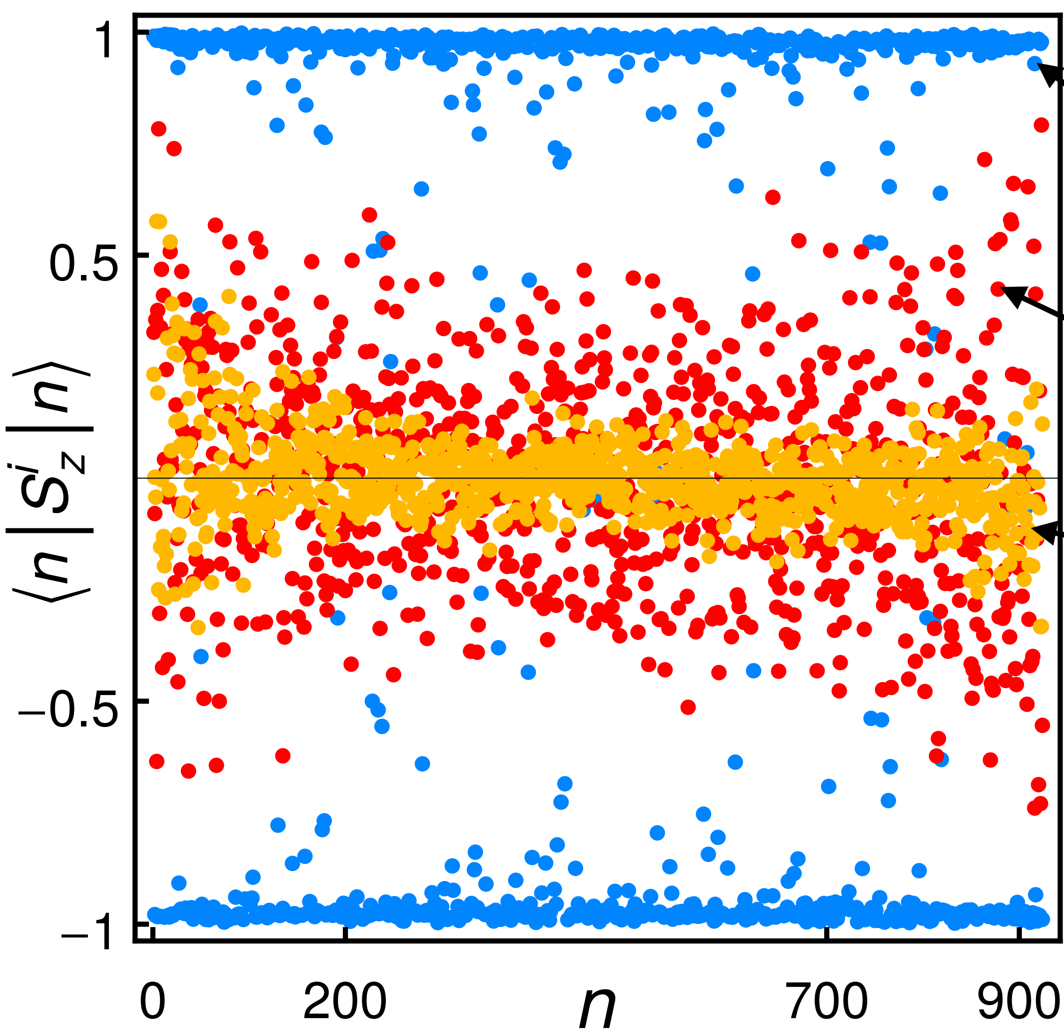
$$\hat{H}_S = \hbar \sum_{i=1}^{N} (\omega_e + \Delta_i)\, \hat{S}_z^i + \sum_{i<j} A_{ij} \left(\hat{S}_+^i \hat{S}_-^j + c.c. \right),$$

- Disorder: $\Delta_i \in (-\frac{\Delta\omega_e}{2}, \frac{\Delta\omega_e}{2})$
- Dipolar interactions: A_{ij} (here we took $A_{ij} \sim U/\sqrt{N}$)

Two conservation laws:

- energy $E = \langle \hat{H}_S \rangle$
- electron polarization $S = \langle \sum_i \hat{S}_z^i \rangle$

Quantum Ergodicity and Eigenstates



$$\Delta\omega_e = 100\text{Mhz}$$

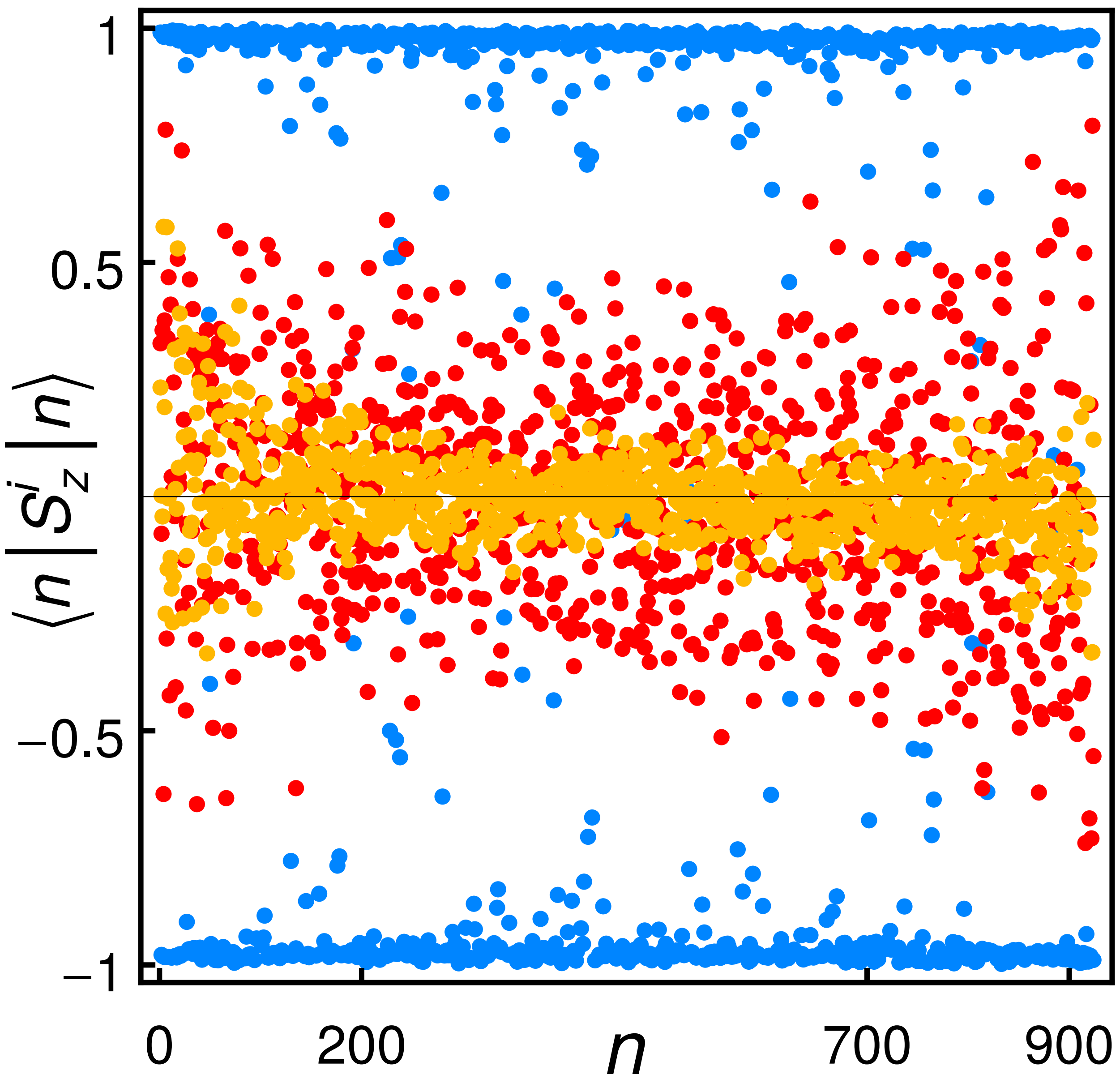
$U = 2\,\text{Mhz}$

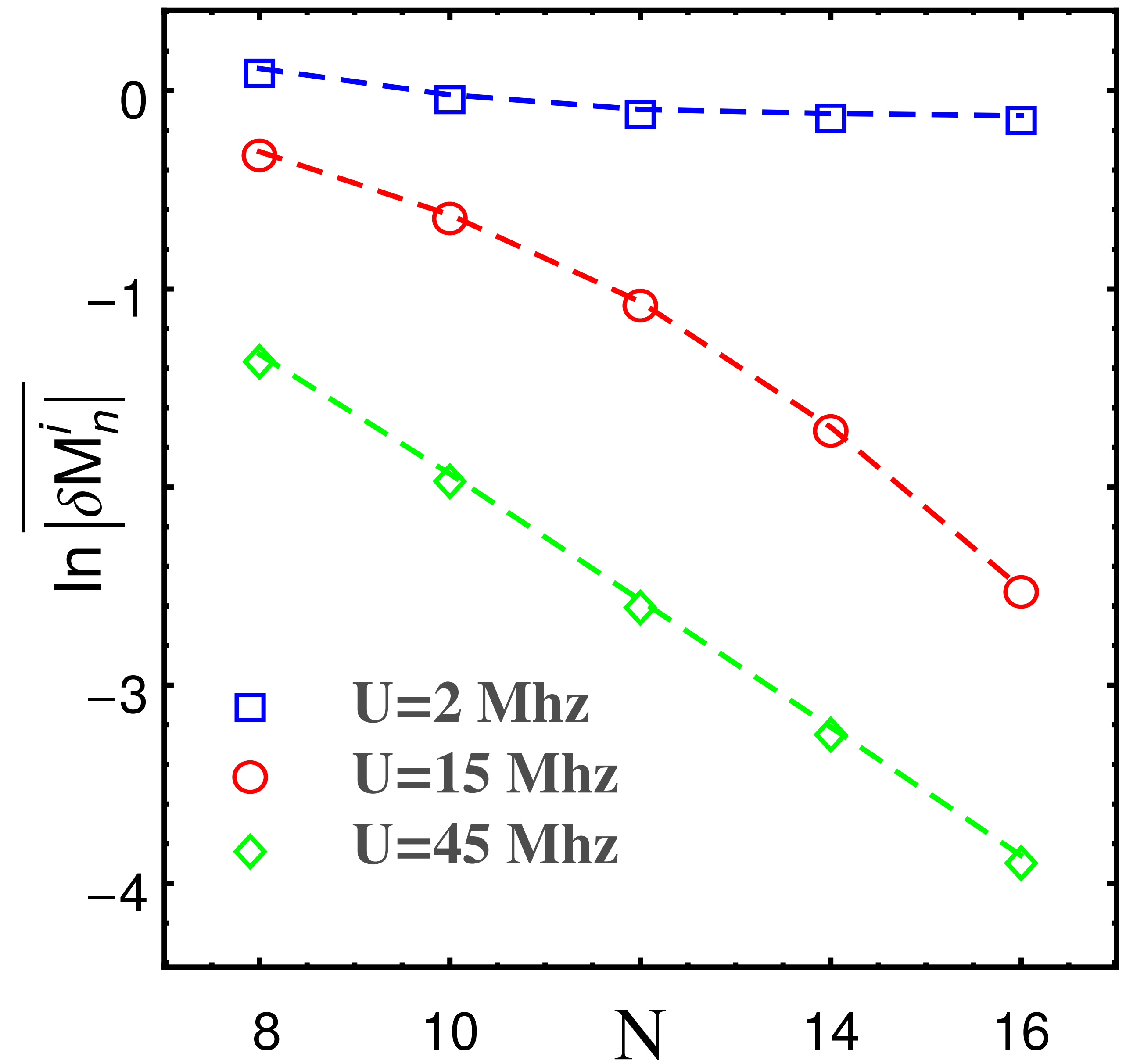
$U = 15\,\text{Mhz}$

$U = 45\,\text{Mhz}$

Eigenstate Thermalization Hypothesis (ETH)

$$\delta M_n^i \equiv \langle n+1|\, S_z^i \,|n+1\rangle - \langle n|\, S_z^i \,|n\rangle$$





$$\hat{\mathcal{H}} = \omega_e(\hat{S}_z^1 + \hat{S}_z^2) + \hat{\mathcal{H}}_{pert}$$

local fields

$$\hat{\mathcal{H}}_{pert} = \Delta_1 \hat{S}_z^1 + \Delta_2 \hat{S}_z^2$$

$$|\uparrow\uparrow\rangle$$

$$|\uparrow\downarrow\rangle \qquad |\downarrow\uparrow\rangle$$

$$|\downarrow\downarrow\rangle$$

$$\langle n|\hat{S}_z^1|n\rangle = \pm\frac{1}{2}$$

interactions

$$\hat{\mathcal{H}}_{pert} = A_{1,2}(\hat{S}_+^1 \hat{S}_-^2 + cc)$$

$$|\uparrow\uparrow\rangle$$

$$\frac{1}{\sqrt{2}}\left(|\downarrow\uparrow\rangle \pm |\uparrow\downarrow\rangle\right)$$

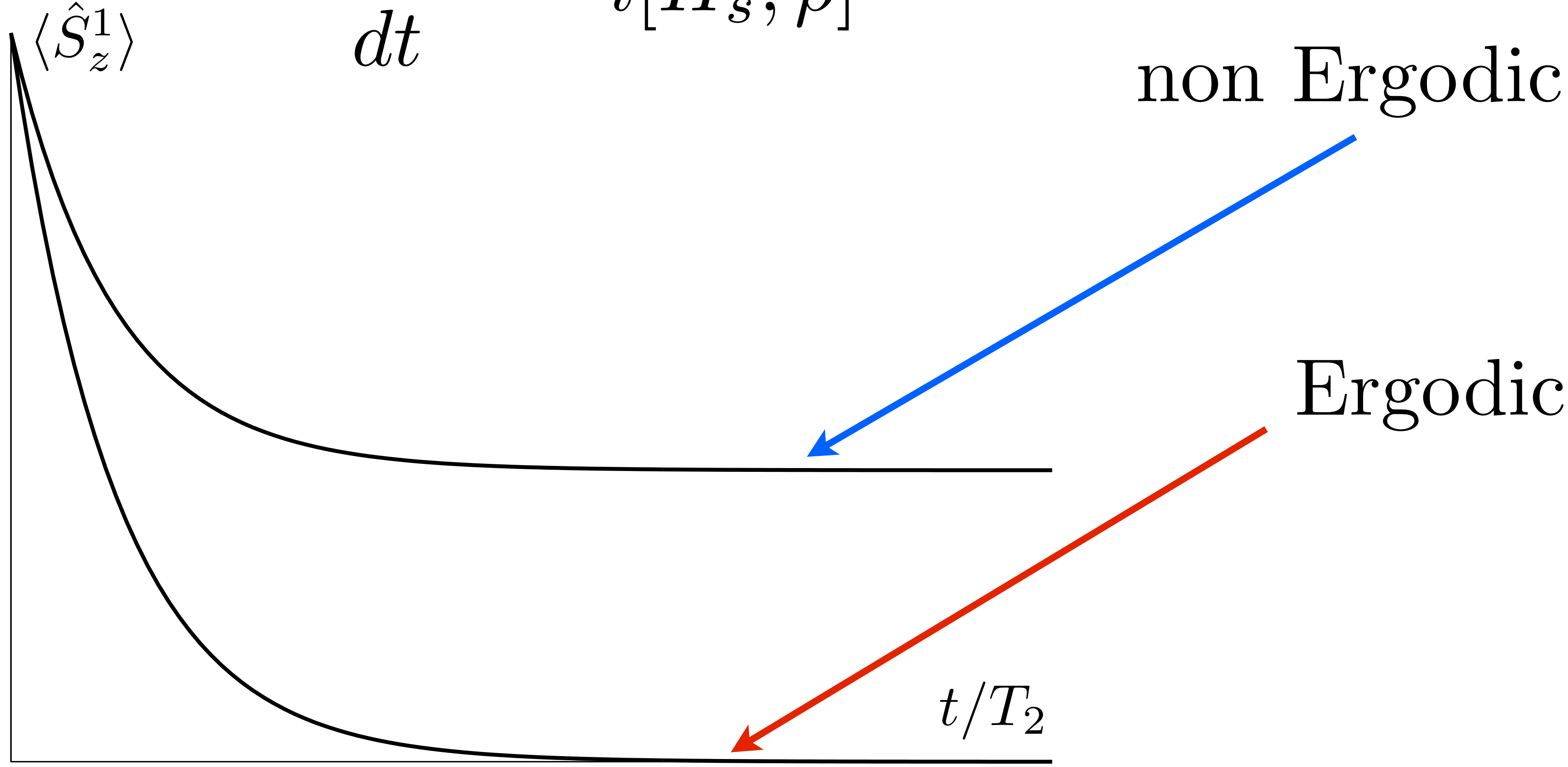
$$|\downarrow\downarrow\rangle$$

$$\langle n|\hat{S}_z^1|n\rangle = 0$$

Quantum Quench

$$\text{At } t = 0 \qquad \Psi(0) = |\uparrow, \downarrow, \downarrow, \ldots\rangle$$

$$\frac{d\rho}{dt} = -i[\hat{H}_s, \rho]$$



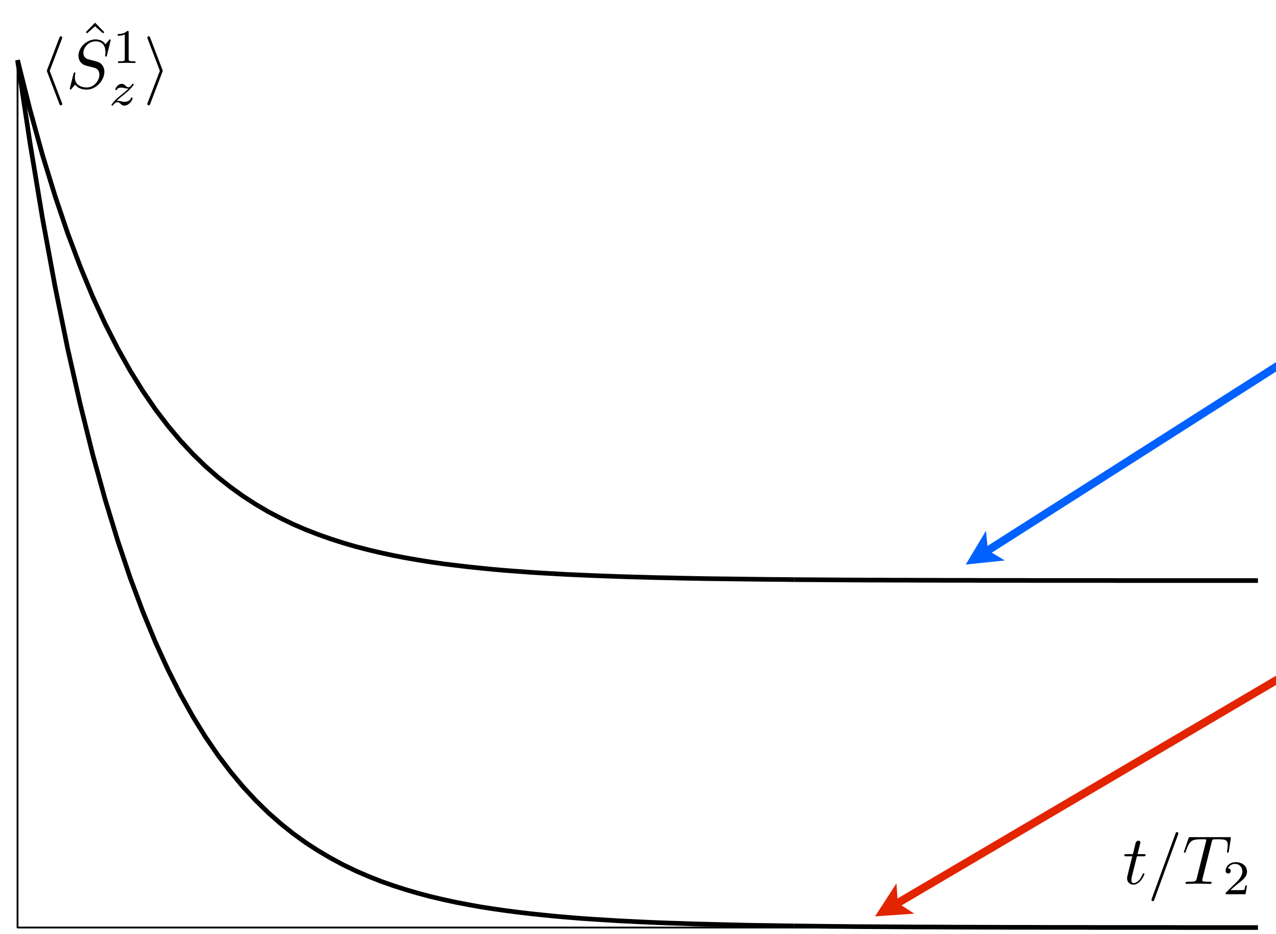
Unitary Evolution

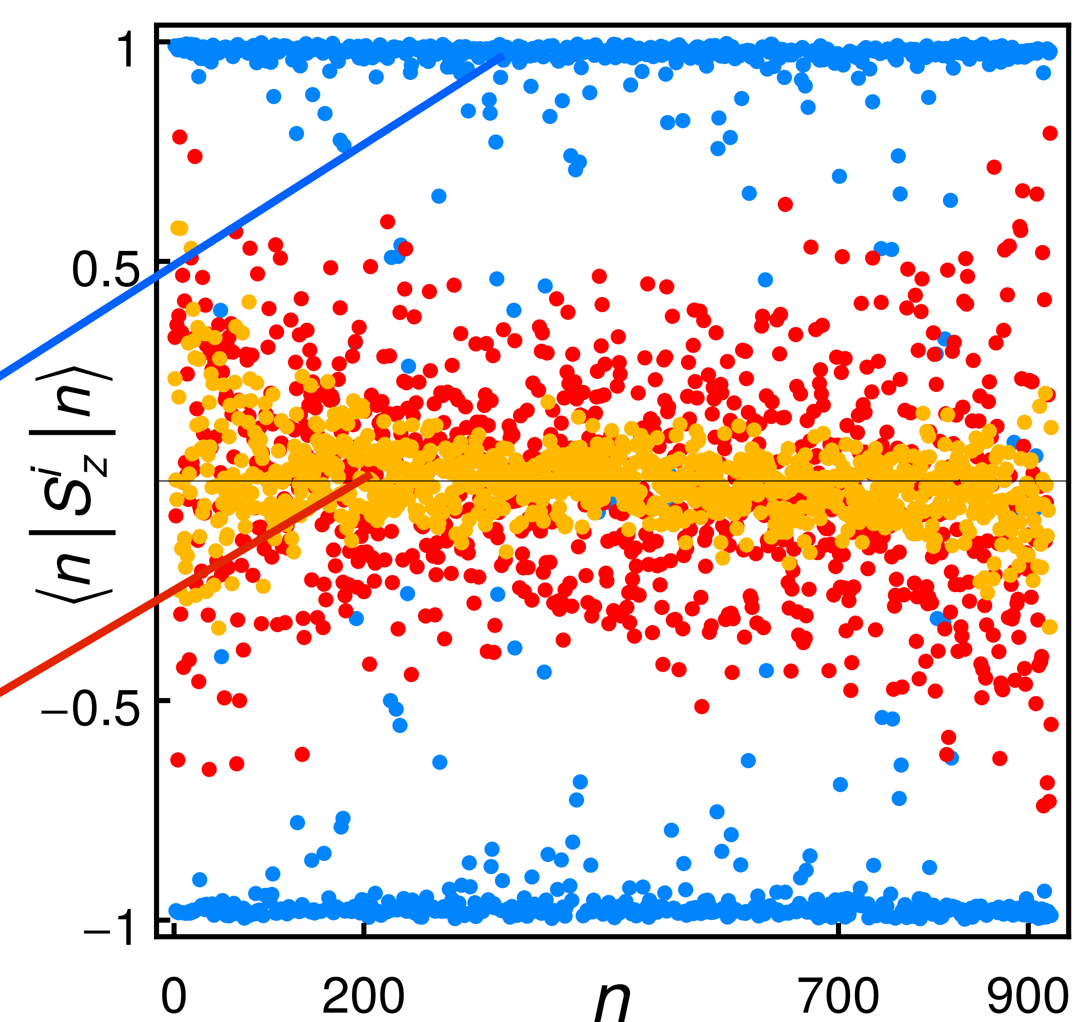
$$\frac{d\rho}{dt} = -i[\hat{H}_s, \rho]$$

$$\rho_{nm}(t) = \rho_{nm}(0)\, e^{-i(E_n - E_m)t}$$

$$\rho_{nn}(t) = \rho_{nn}(0)$$

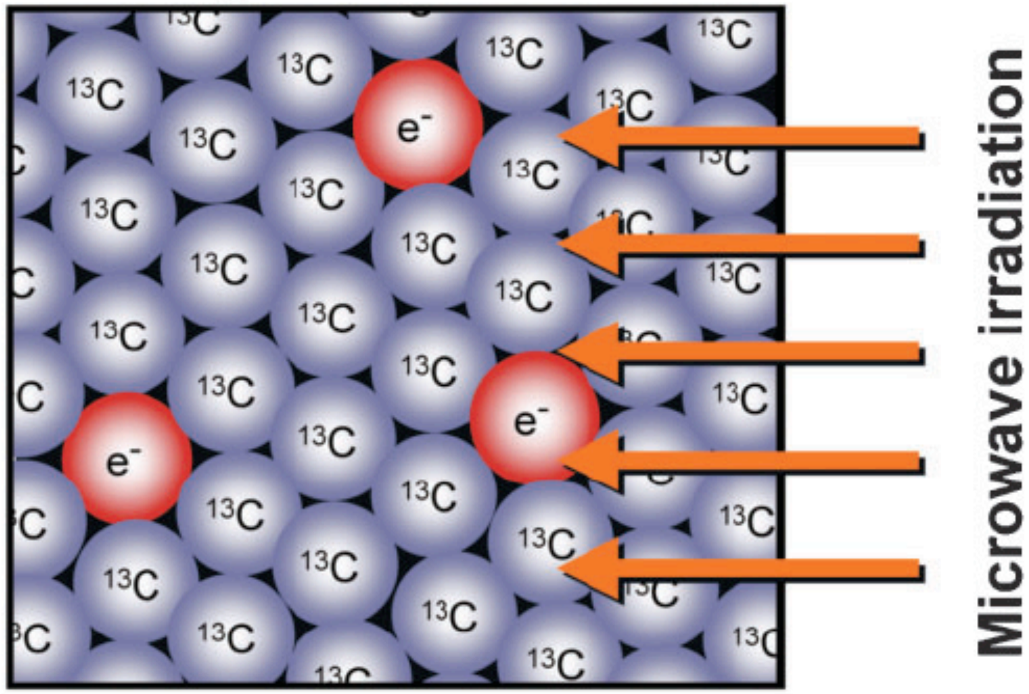
Quantum dynamics preserves eigenstates occupation probability





Dynamic Nuclear Polarisation (DNP)

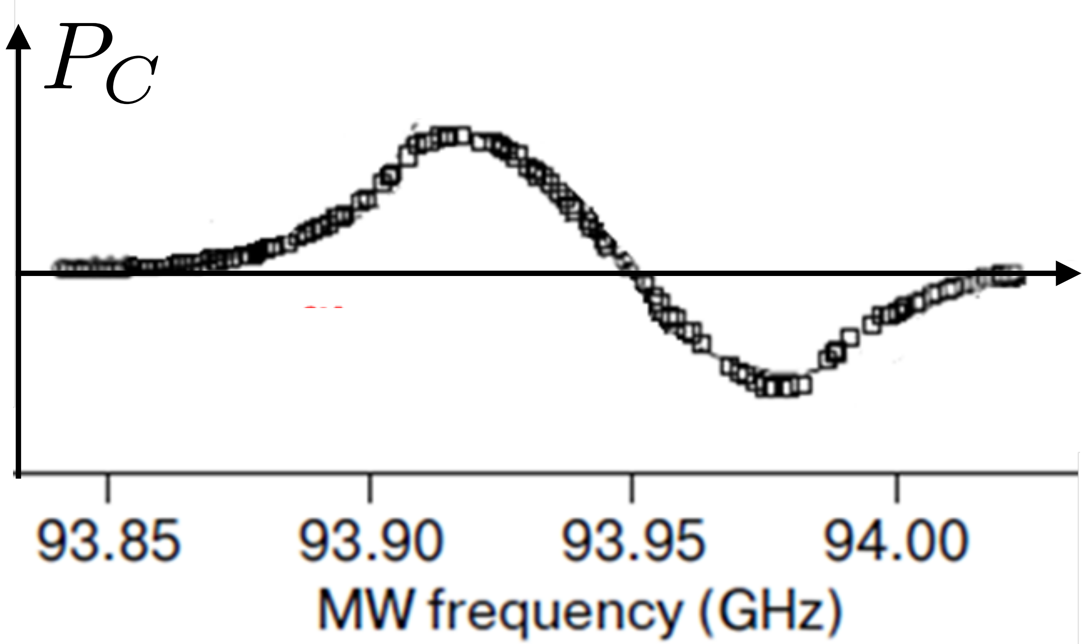
Solid material doped with unpaired electrons



P_e= 94% and P_C= 0.086%

- $T = 1\,\mathrm{K},\ H_0 = 3.3$ Tesla
- $\omega_e \simeq 100$ Ghz
- $\omega_{13C} \simeq 32$ Mhz

DNP profile (after ~ 1 hour):

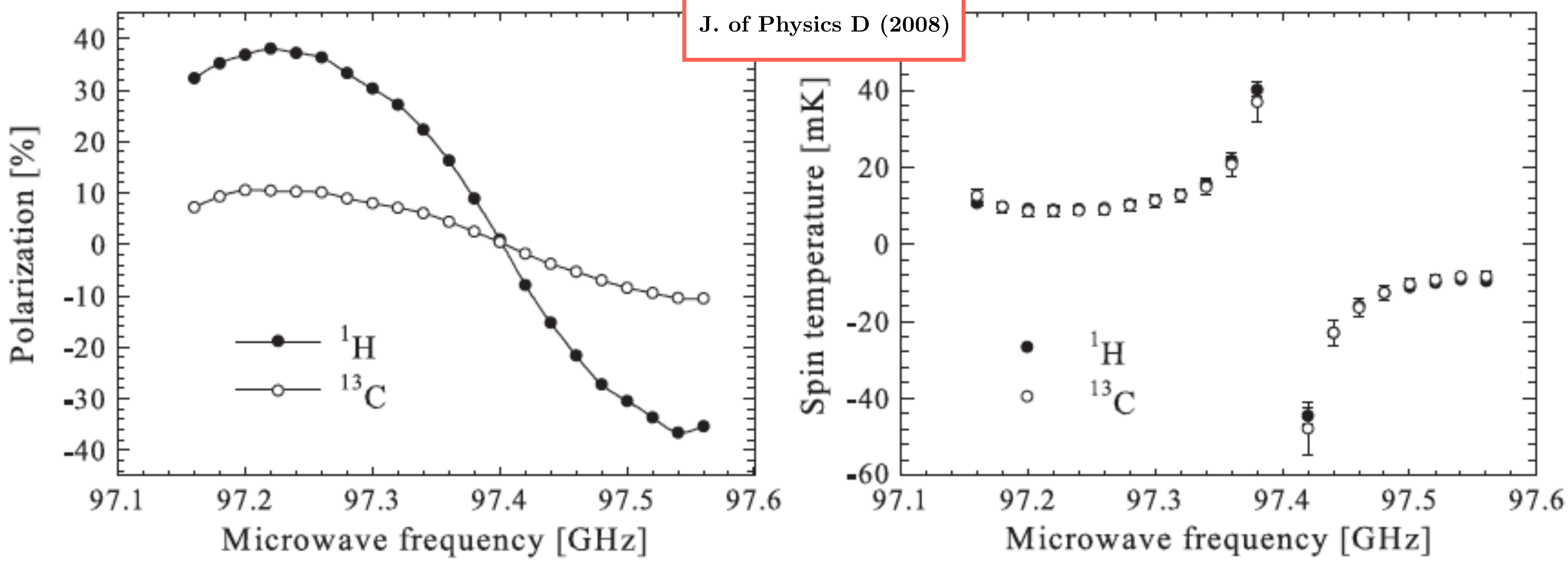


The spin temperature (experiment)

$$P_n = \tanh\left(\beta_s \frac{\hbar \omega_n}{2}\right)$$

$$\omega_{1H} \simeq 127\text{Mhz}$$
$$\omega_{13C} \simeq 32\text{Mhz}$$

J. of Physics D (2008)



MW-irradiated electron spins reach a low *spin temperature*

and cool down nuclear spins

The spin temperature

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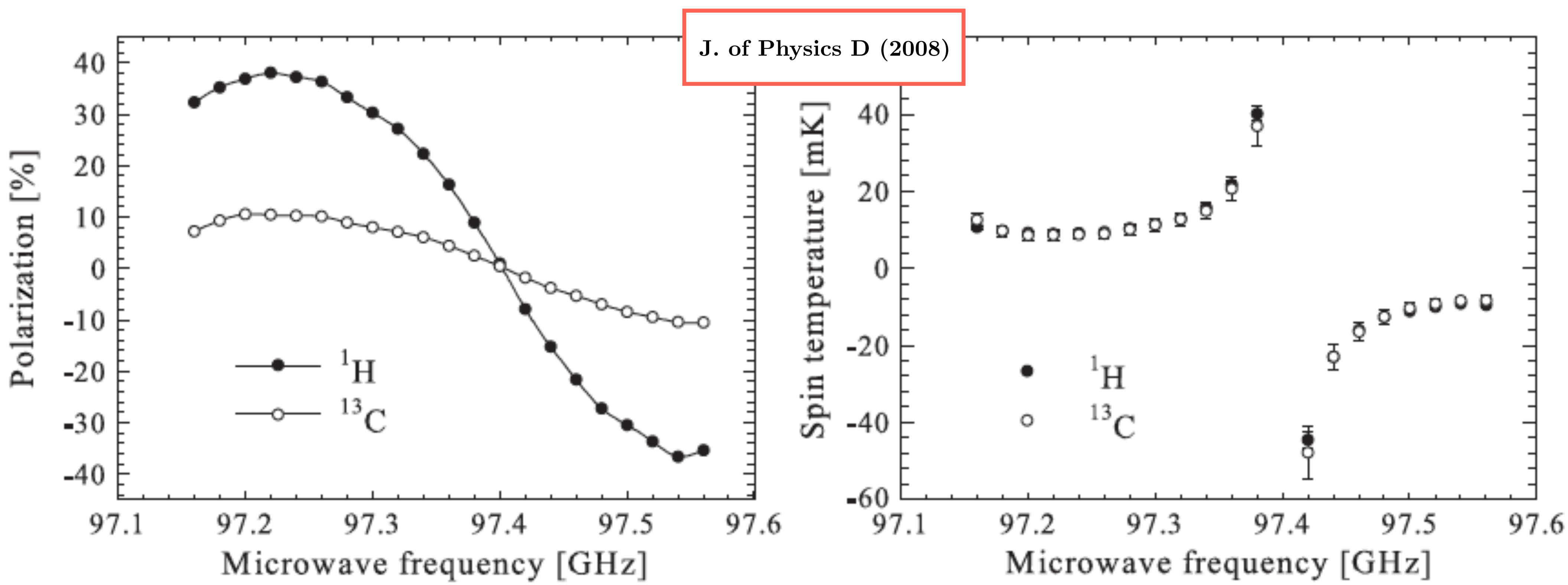


Spin temperature is elusive to microscopic approaches

Theory: Vega group (Weizmann), **Kockenberger group (Nottingham)**

Two challenging ingredients

Coupling with a bath

$$\hat{\mathcal{H}} = \hat{H}_S + \hat{H}_B + \lambda \hat{H}_{SB}$$

MW- irradiation

$$\hat{H}_{MW} = 2\omega_1 \cos(\omega_{MW} t) \hat{S}_x$$

IMPORTANT:

Interactions stronger than coupling with bath and MW

Master equation for occupation probabilities of eigenstates

The master equation

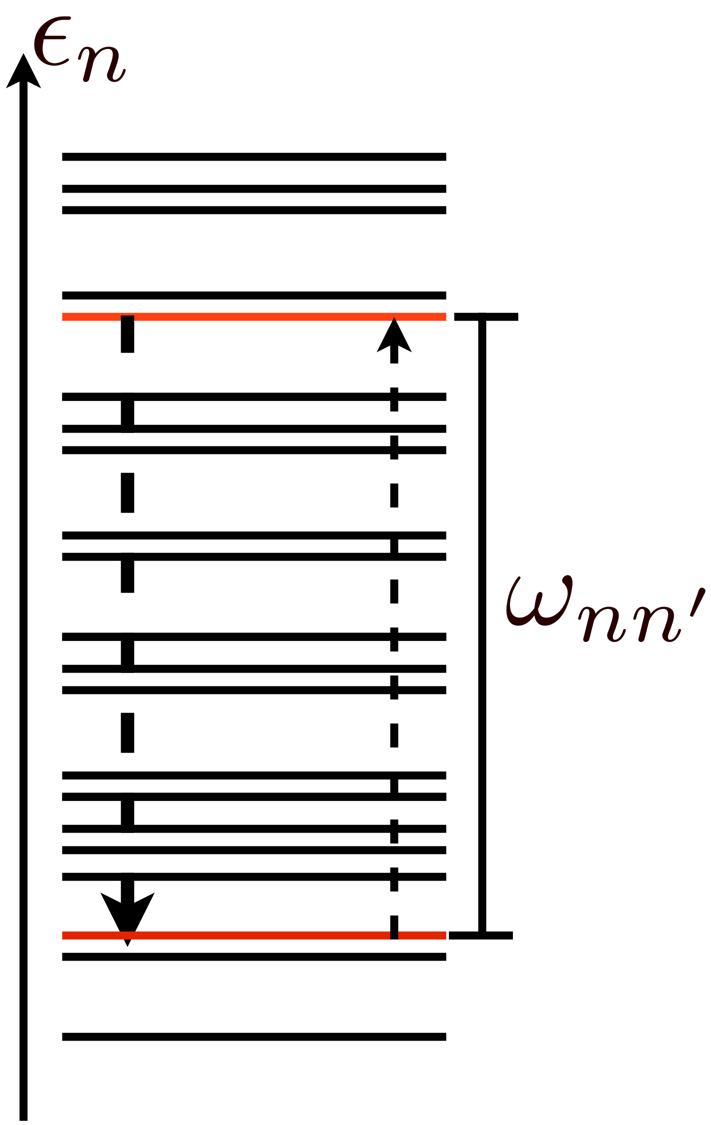
$$\frac{d\rho_{nn}}{dt} = \sum_{n' \neq n} W_{n,n'}\rho_{n'n'} - W_{n',n}\rho_{nn}$$

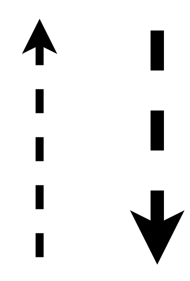
$$W_{n,n'} = W_{n,n'}^{\text{bath}} + W_{n,n'}^{\text{MW}}$$

ρ^{stat} is eigenvector associated to eigenvalue 0

Transitions bath-induced

$$W^{\text{bath}}_{n,n'} = \frac{h_{n,n'}}{T_1} \sum_i |\langle n | \hat{S}^i_\alpha | n' \rangle|^2 \,, \quad \alpha = x, y, z$$



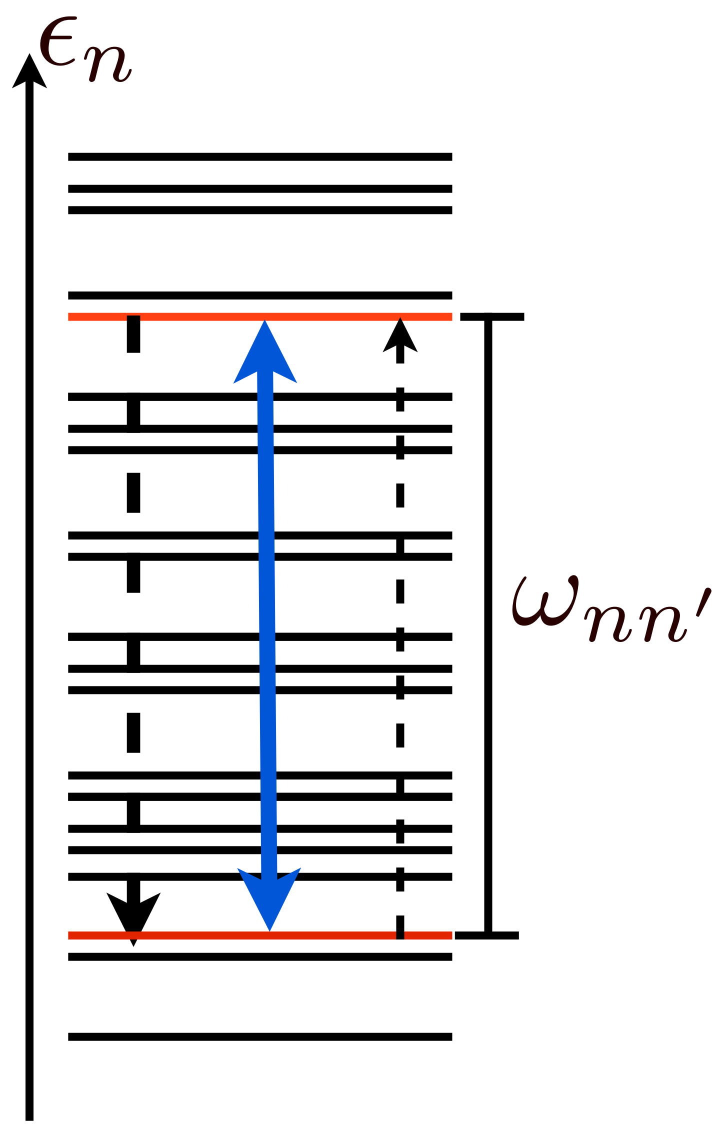


$$\frac{h_{n',n}}{h_{n,n'}} = e^{-\beta \omega_{nn'}}$$

Equilibrium temperature β^{-1}

Transitions MW-induced

$$\hat{H}_{MW} = 2\omega_1 \cos(\omega_{MW} t)\hat{S}_x$$



$$W^{\mathrm{MW}}_{n,n'} = \frac{1}{T_{\mathrm{MW}}} |\langle n|\hat{S}_x|n'\rangle|^2$$

$$\frac{1}{T_{\mathrm{MW}}} = \frac{\omega_1^2 T_2}{1 + (\omega_{nn'} - \omega_{\mathrm{MW}})^2 T_2^2}$$

Resonance condition

$$\omega_{nn'} = \omega_{\mathrm{MW}}$$

Do electron spins hyperpolarize nuclear spins?

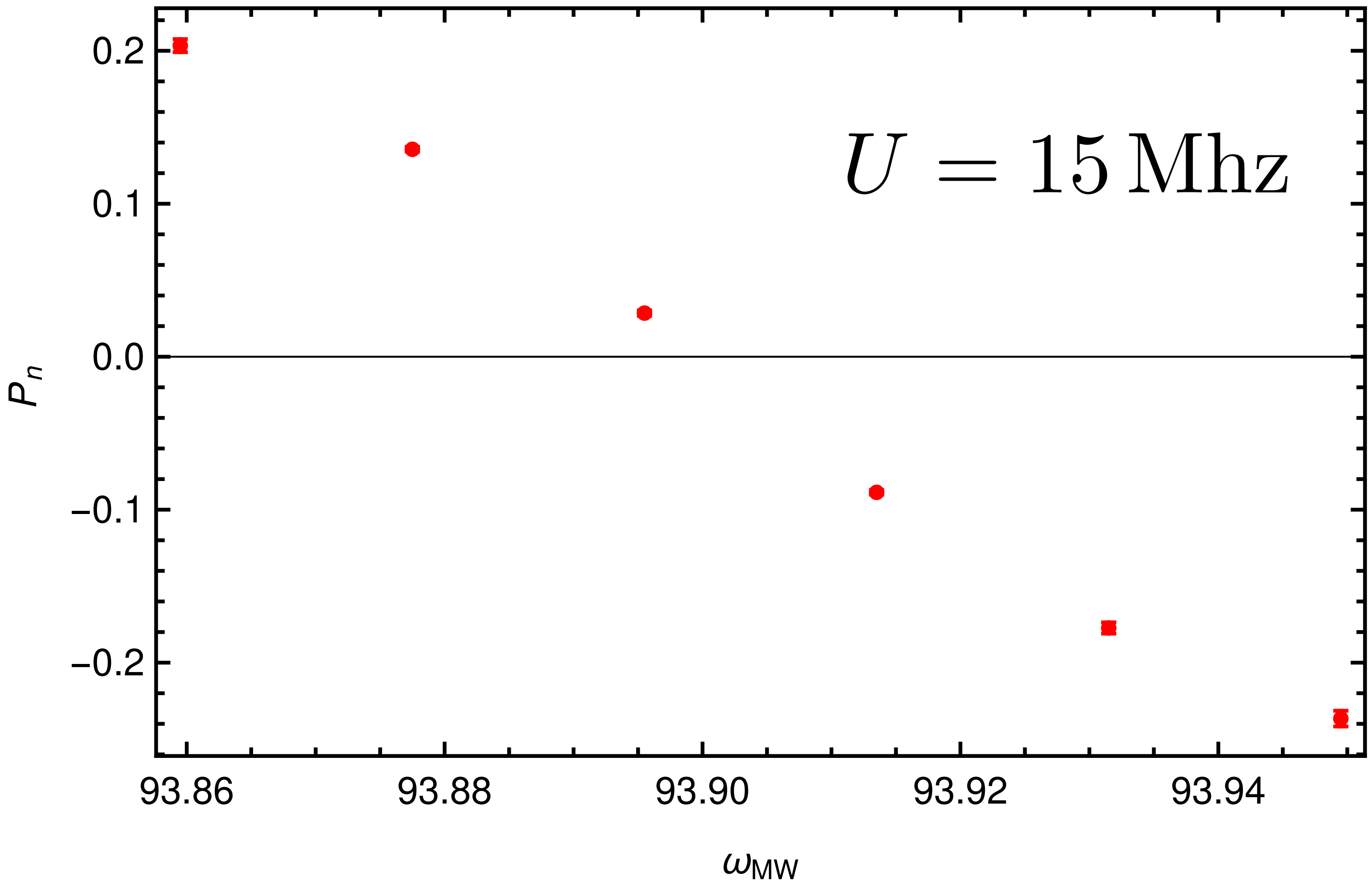
- N electron spins $\hat{S}_z^i, \hat{S}_x^i, \hat{S}_y^i$
- nuclear spin $\hat{I}_z, \hat{I}_x, \hat{I}_y$

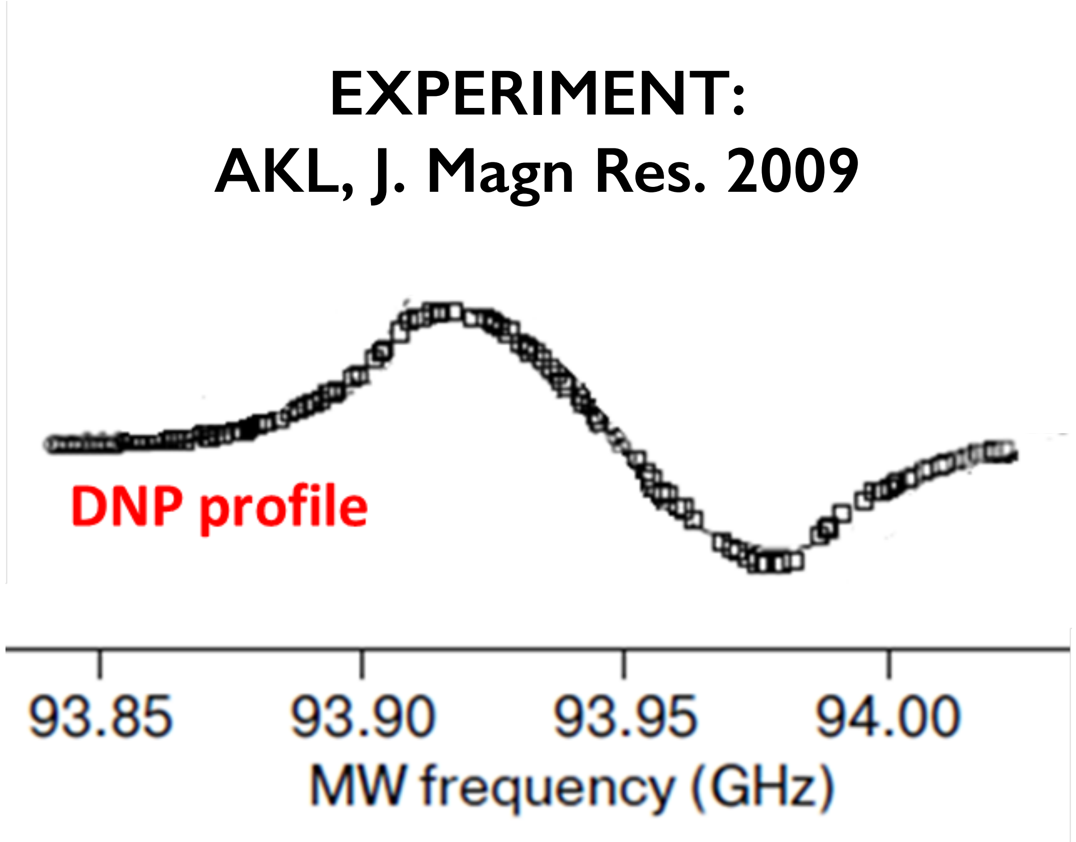
$$\hat{H}_S + \hbar\omega_n \hat{I}_z + \hat{H}_{I+S}$$

$$\hat{H}_{I+S} = \sum_i B_i \left(\hat{S}_z^i \hat{I}_- + \hat{S}_z^i \hat{I}_+ \right)$$

B_i hyperfine interactions, $\overline{B_i^2} = b^2/N$

Yes, they do!





$$N = 12 \text{ electron spins} + 1 \text{ nuclear spin}$$

T_1 (sec.)	T_2 (sec.)	ω_1 (Mhz)	$\Delta\omega_e$ (Mhz)
1	10^{-6}	0.025	108.0

Does the stationary state look thermal?

Two conserved quantities: E, S

Steady state:

$$\rho^{\text{stat}}$$

$$E = \sum_n \epsilon_n \rho_{nn}^{\text{stat}} = \sum_n \epsilon_n \rho_{nn}^{\text{Ans}}$$

$$S = \sum_n s_{z,n} \rho_{nn}^{\text{stat}} = \sum_n s_{z,n} \rho_{nn}^{\text{Ans}}$$

Thermal Ansatz

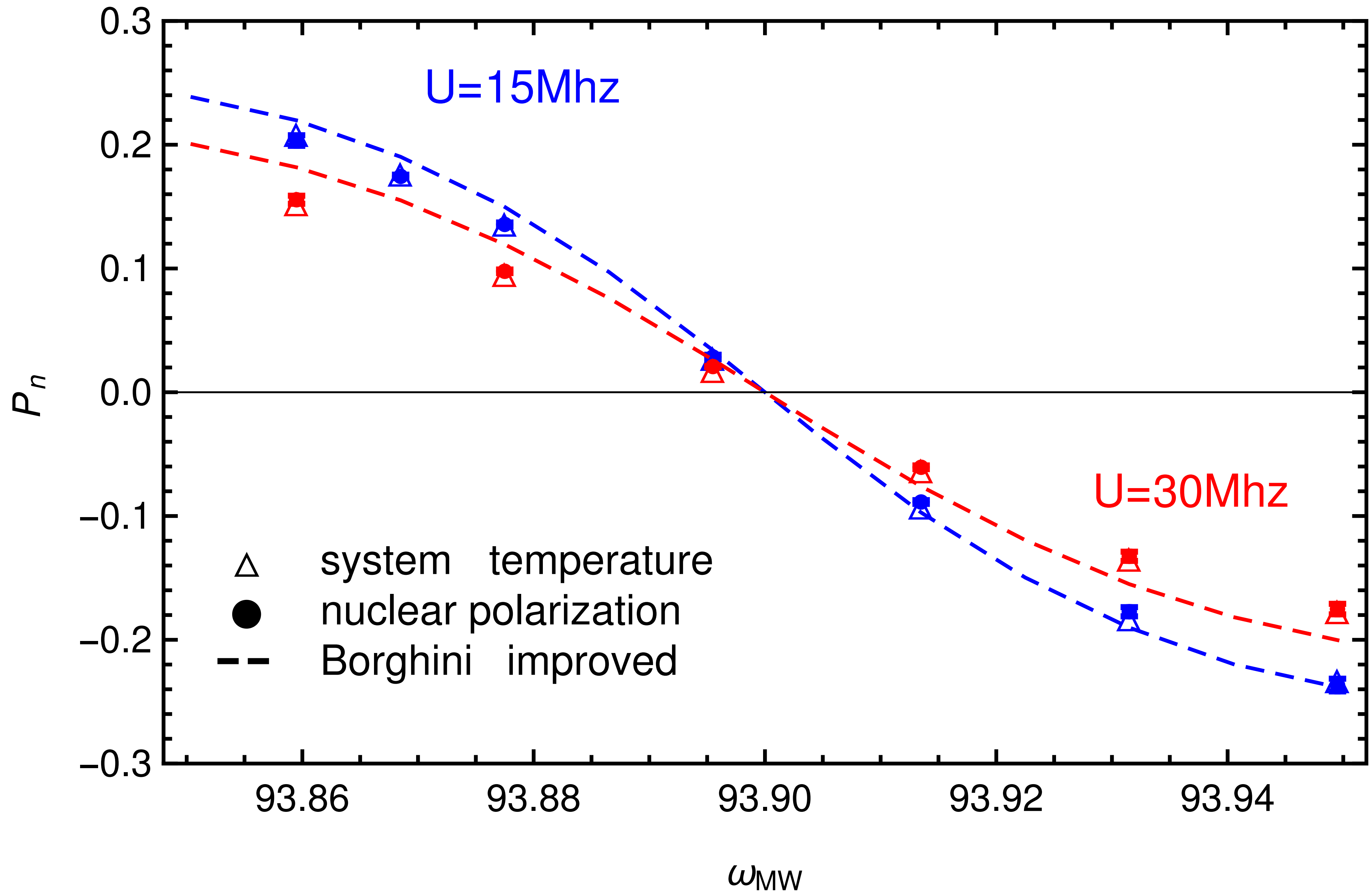
$$\rho_{nn}^{\text{Ans}} \propto e^{-\beta_s(\epsilon_n + h s_{z,n})}$$

From numerical best fit :

β_s and h

$$P_n = \tanh\left(\beta_s \frac{\hbar\omega_n}{2}\right)$$

Yes, it does!



β_S can be predicted analytically for $N \to \infty$

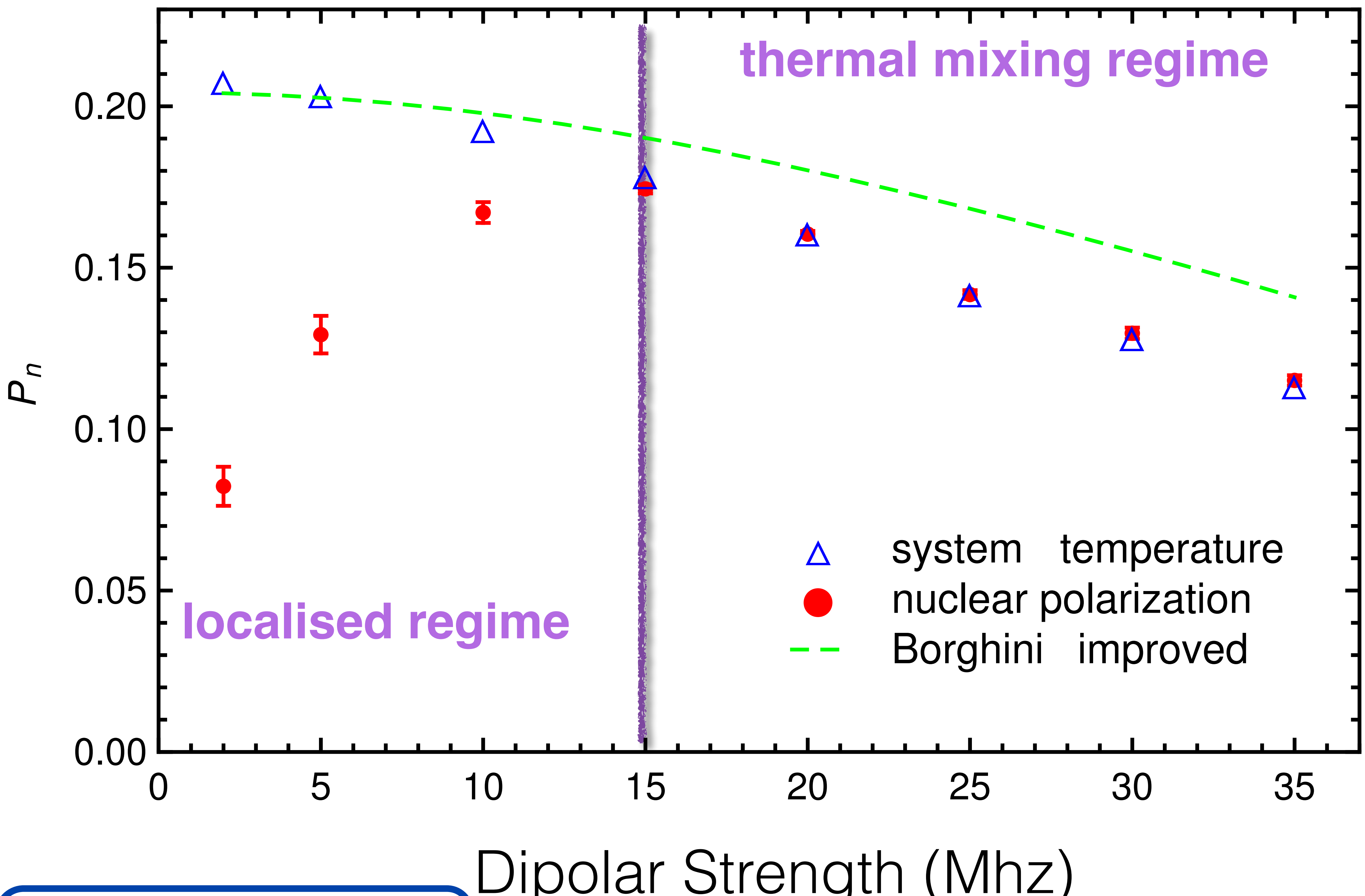
Spin temperature and Quantum Thermalization

- Spin temperature arises in ergodic systems:

  1. memory of local imbalances only in E and S_z
  2. study of eigenstates shows ETH phase

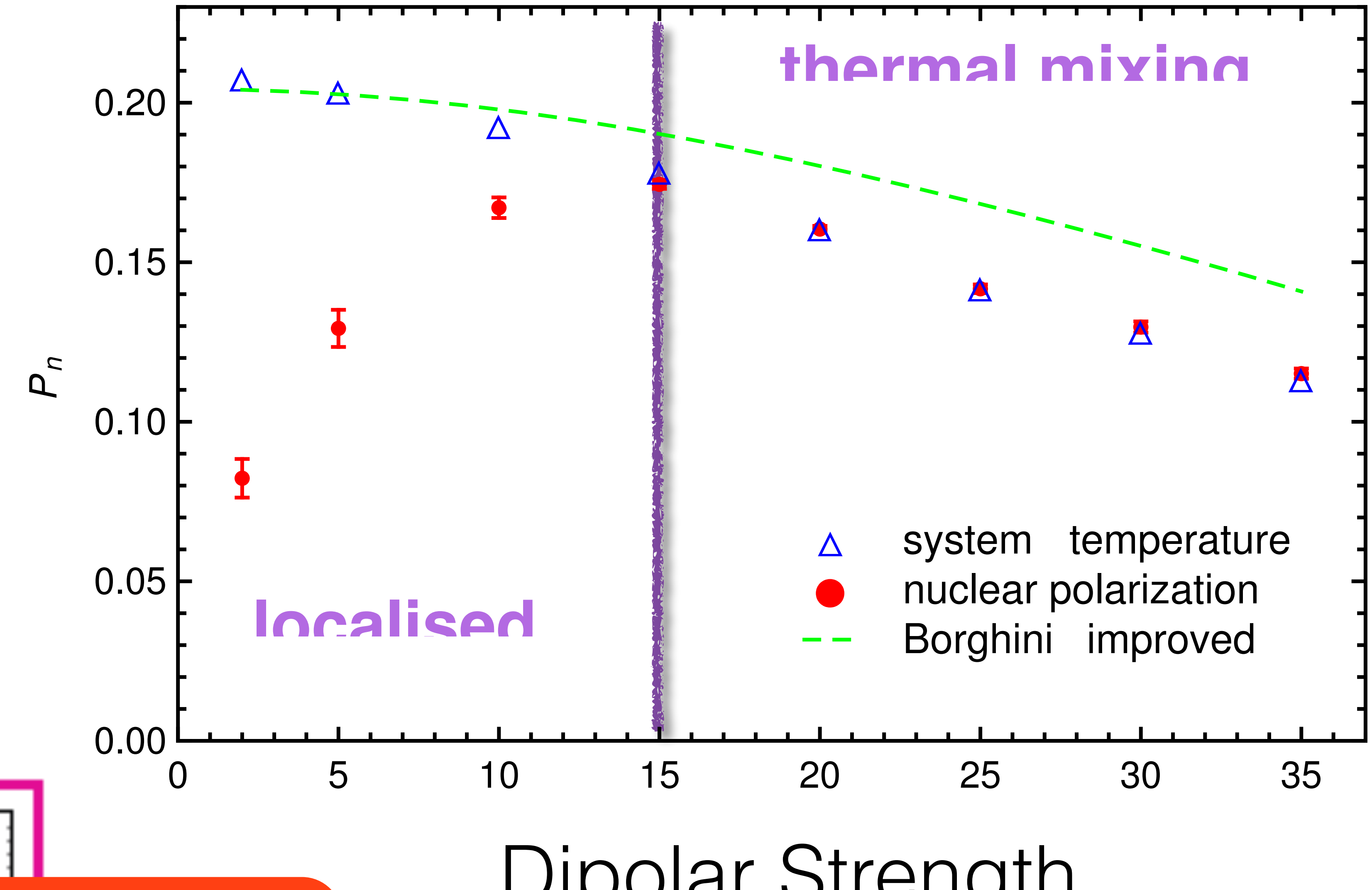
- Spin temperature breakdown: what happens at MBL ?

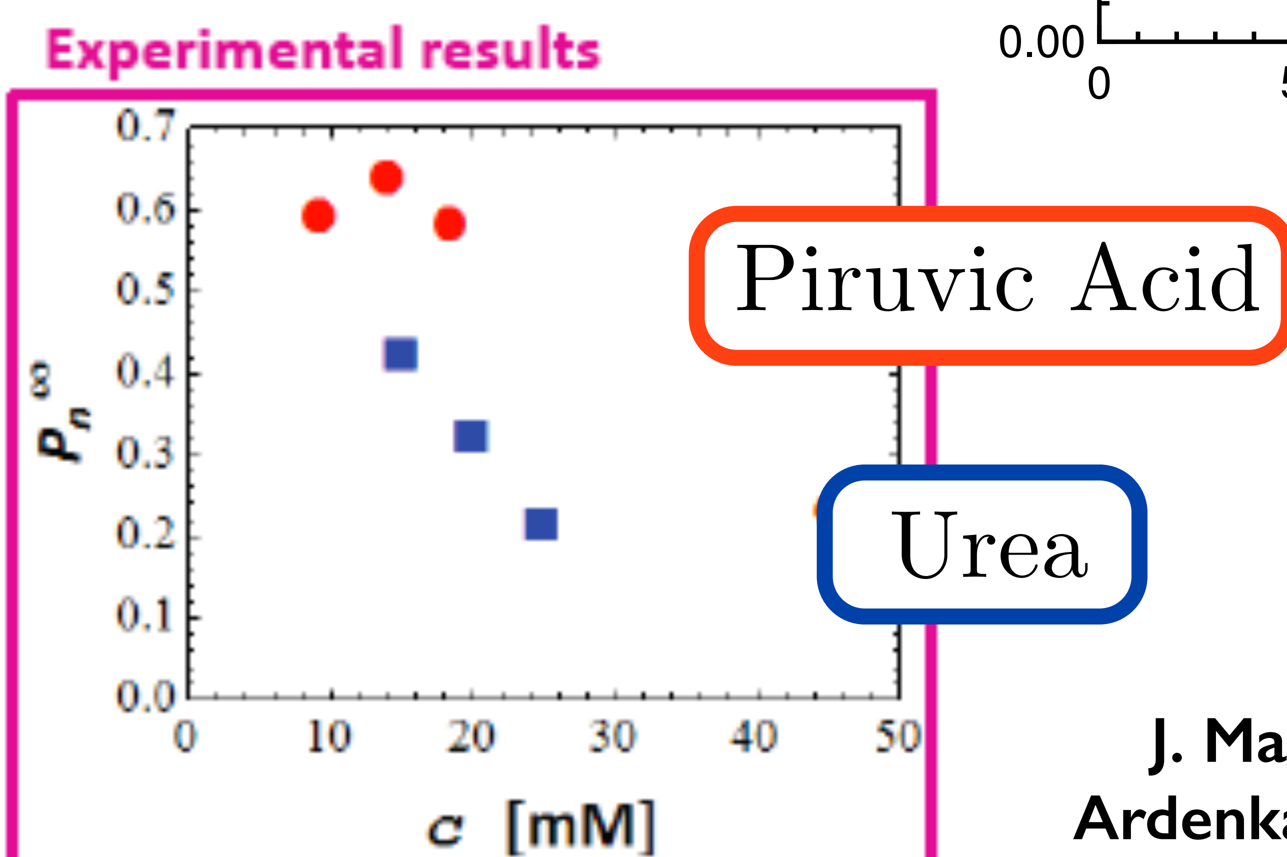
MBL varying radical concentration



$\omega_{MW} = 93.8685 \text{ Ghz}$

Experimental situation





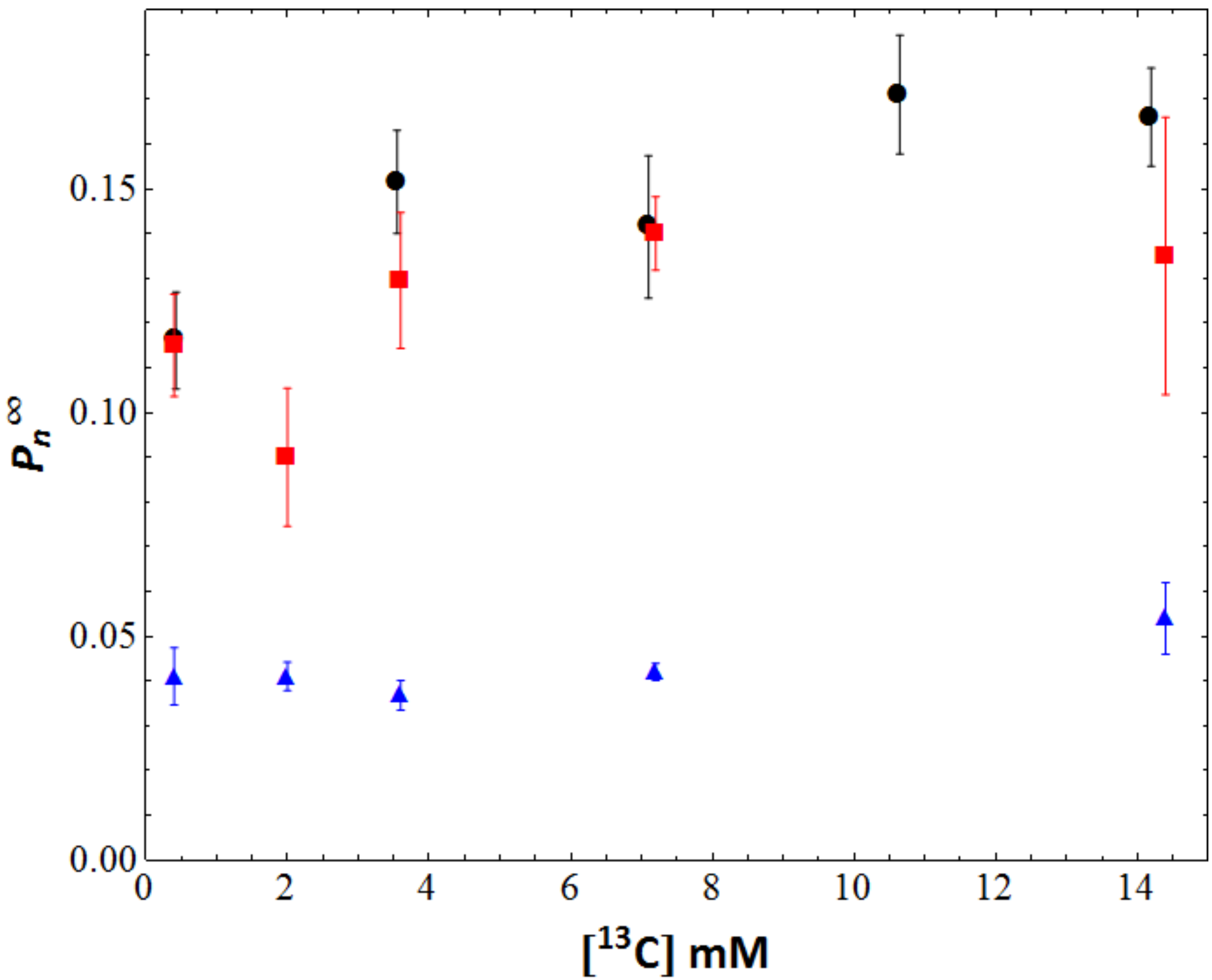
J. Magn Res. 2009;
Ardenkaer-Larsen 2004

Conclusions

- Spin temperature profile in presence of dipolar interactions
- Spin temperature and ETH phase
- Agreement with two experimental facts

Perspectives

- Understand the spin temperature behavior
  (Applications: go beyond trial-and-error strategies)
- DNP samples good candidates to observe
  many body localisation transition



Piruvic acid with 15 mM radical (trytils)

In collaboration with Pavia group, PCCP 2014

The bath: weak coupling and Lindblad

$$\hat{\mathcal{H}} = \hat{H}_S + \hat{H}_B + \lambda \hat{H}_{SB} \qquad \hat{H}_{SB} = 2 \sum_{\substack{j=1 \\ \alpha=x,y,z}}^{N} \hat{S}^j_\alpha \hat{\Phi}^j_\alpha$$

time dependent perturbation theory

$$\frac{d\rho}{dt} = -i[\hat{H}_S, \rho] + \lambda^2 \mathcal{L}\rho$$

Case $N = 1$

$$\rho(t=0) = |\psi_0\rangle\langle\psi_0| \qquad \rho_{eq}(\beta)$$

$$\begin{pmatrix} \rho_{11}(0) & \rho_{12}(0) \\ \rho_{21}(0) & \rho_{22}(0) \end{pmatrix} \xrightarrow{\text{Lindblad time evolution}} \frac{1}{Z} \begin{pmatrix} e^{-\beta\epsilon_1} & 0 \\ 0 & e^{-\beta\epsilon_2} \end{pmatrix}$$

[A] out-off-diagonal terms and dephasing

$$\frac{d\rho_{nm}}{dt} = \underbrace{-i\left(\epsilon_n - \epsilon_m\right)\rho_{nm}}_{\text{oscillations}} \underbrace{- \frac{\rho_{nm}}{T_{2,nm}}}_{\text{decay}}$$

ρ_{nm} averages to 0 on a time scale $T_2 \sim 10^{-6}$ sec.

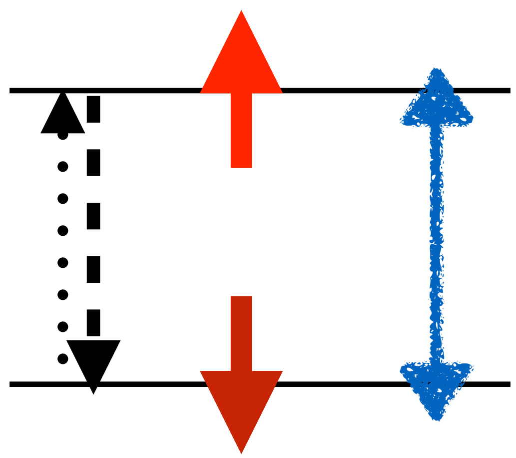
[B] diagonal terms and relaxation

ρ_{nn} relax to $e^{-\beta\epsilon_n}/Z$ on a time scale $T_1 \sim 1$ sec.

$$\begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \xrightarrow[T_2 \approx 10^{-6}\text{sec.}]{\textbf{[A] dephasing}} \begin{pmatrix} \rho_{11} & 0 \\ 0 & \rho_{22} \end{pmatrix} \xrightarrow[T_1 \approx 1\text{sec.}]{\textbf{[B] relaxation}} \begin{pmatrix} \frac{e^{-\beta\epsilon_1}}{Z} & 0 \\ 0 & \frac{e^{-\beta\epsilon_2}}{Z} \end{pmatrix}$$

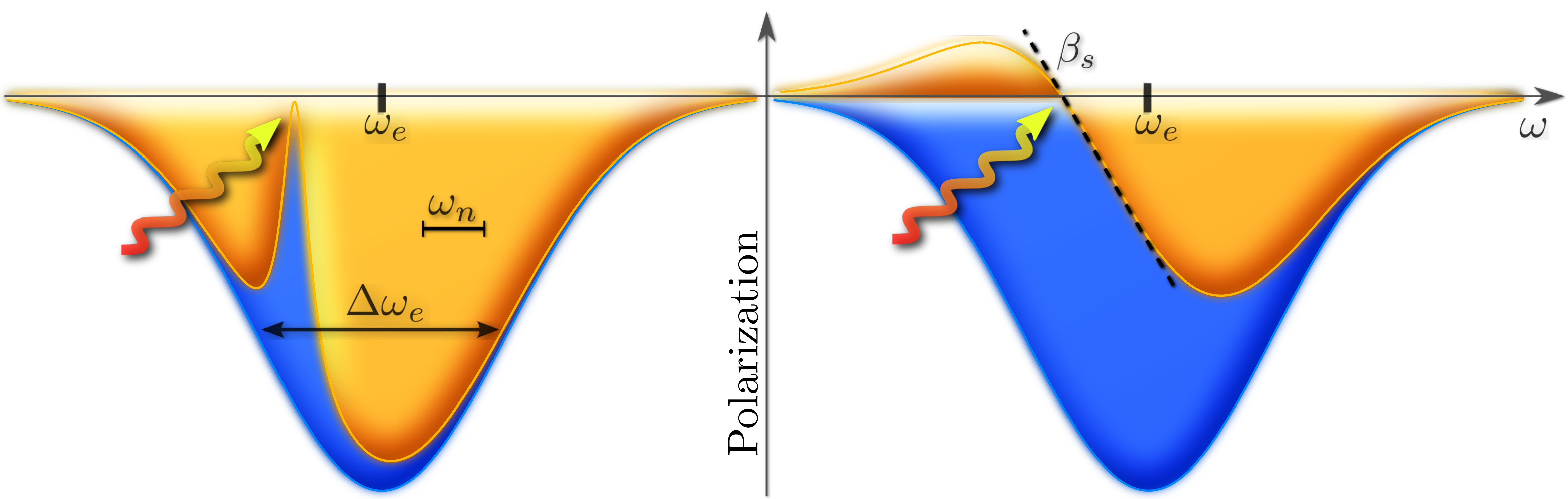
“Trivial” localized case

$$(U = 0), \qquad \hat{\mathcal{H}} = \sum_i (\omega_e + \Delta_i)\hat{S}_z^i, \qquad P_e(\omega) = \langle S_z^i \rangle_{t\to\infty}$$



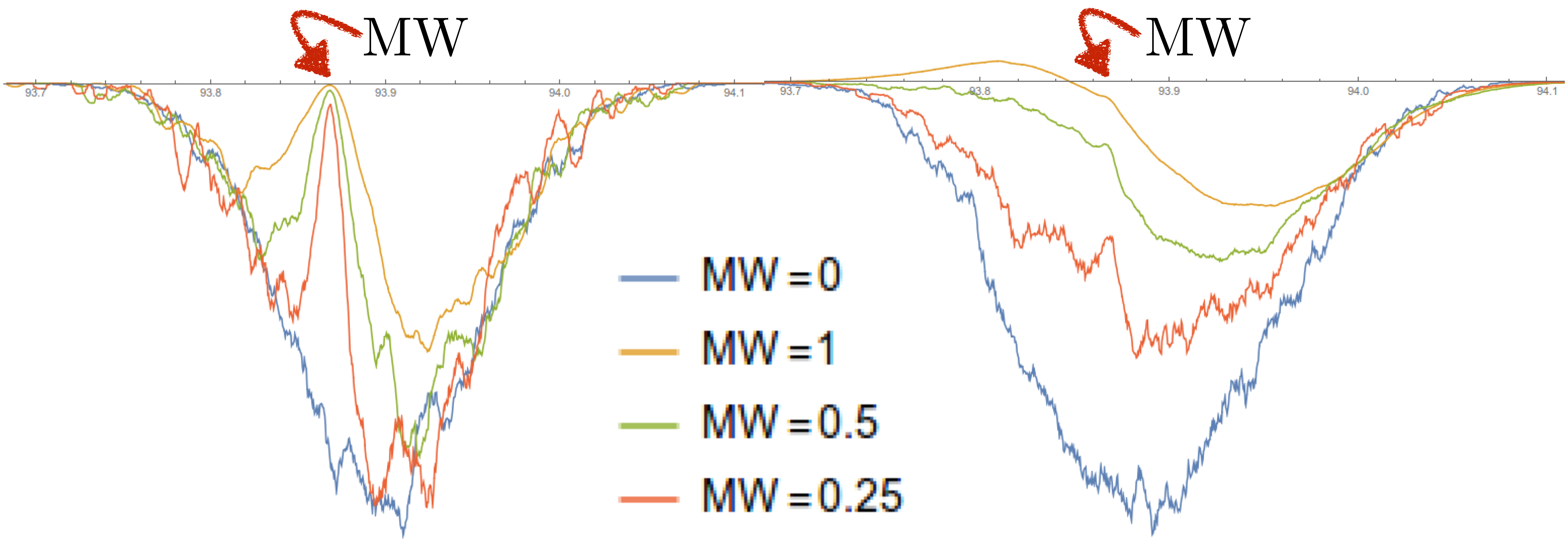
$$\rho_{nn}^{\mathrm{Ans}} \propto e^{-\beta_s(\epsilon_n + h s_{z,n})}$$

Bloch (1946) Borghini (1970)



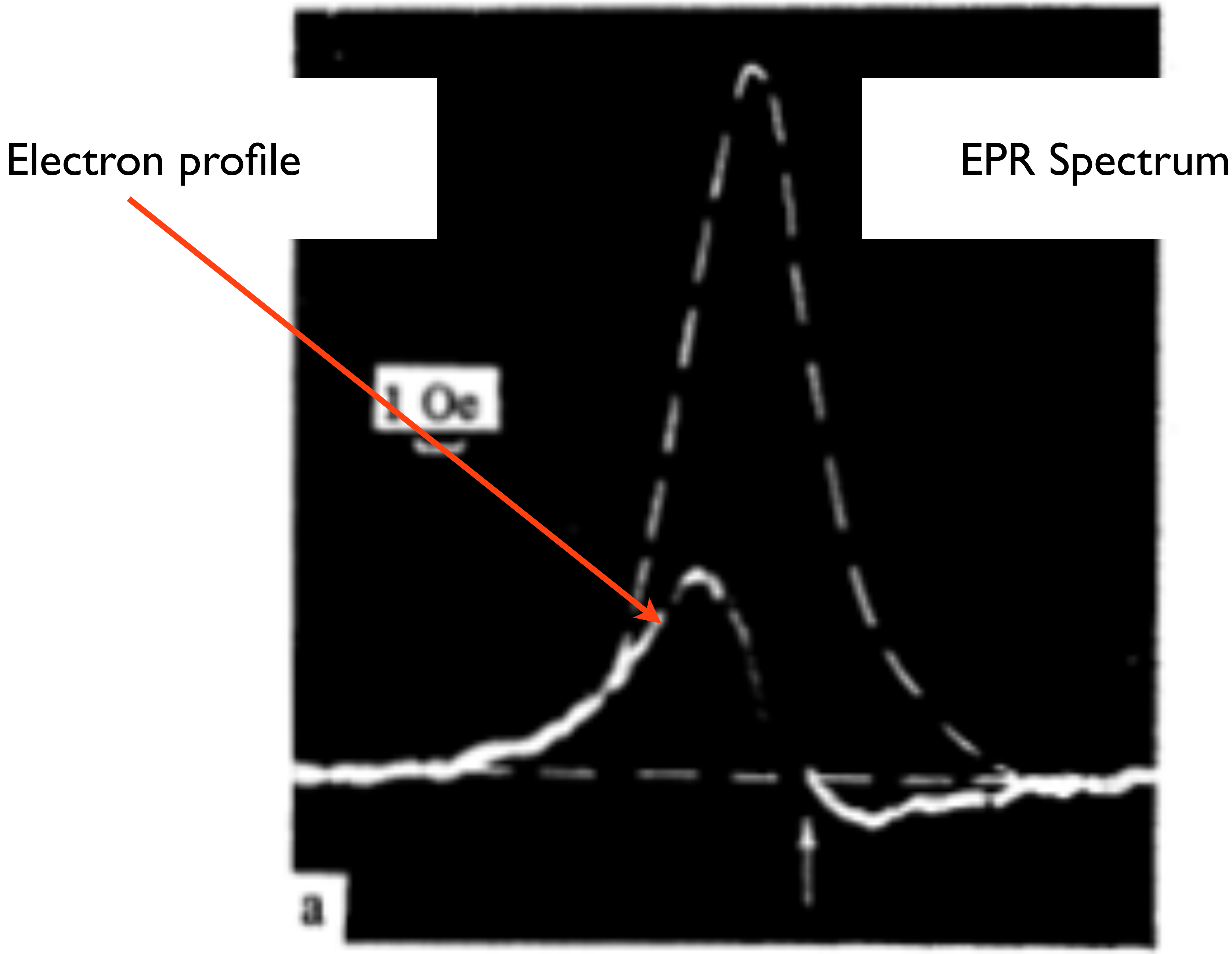
EPR spectrum (numerical simulations)

$U = 1.5\,\mathrm{Mhz}$ $U = 15\,\mathrm{Mhz}$



Localized phase

Thermal phase



Experiments: Atsarkin, Soviet Physics JETP (1970).