6ème école d'automne du GdR

Mesurer, Comprendre et Modéliser le Comportement Multiphysique des Matériaux Bio et Géosourcés



RMN/IRM pour la caractérisation des transferts en milieu poreux

Philippe Coussot

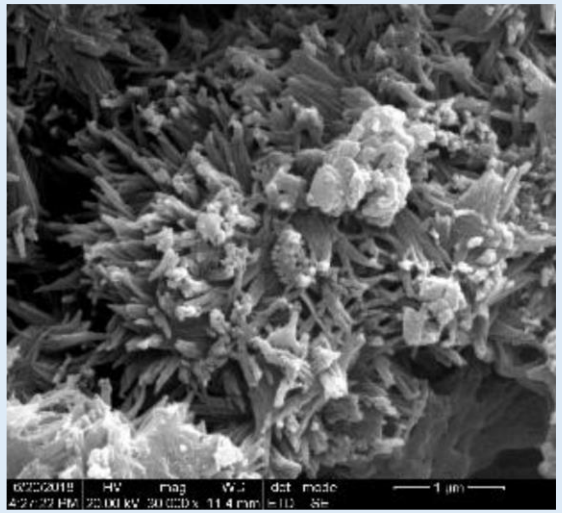
Laboratoire Navier

erc Funded by the European Union

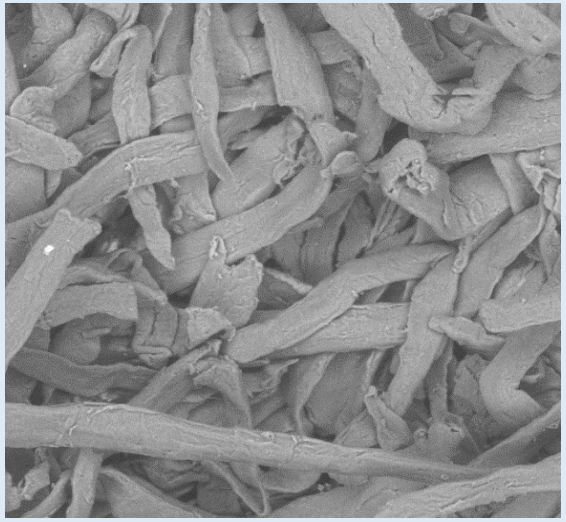
12 au 15 octobre 2026 à Pornichet

GeM Institut de Recherche en Génie Civil et Mécanique — Nantes Université — CENTRALE NANTES — cnrs

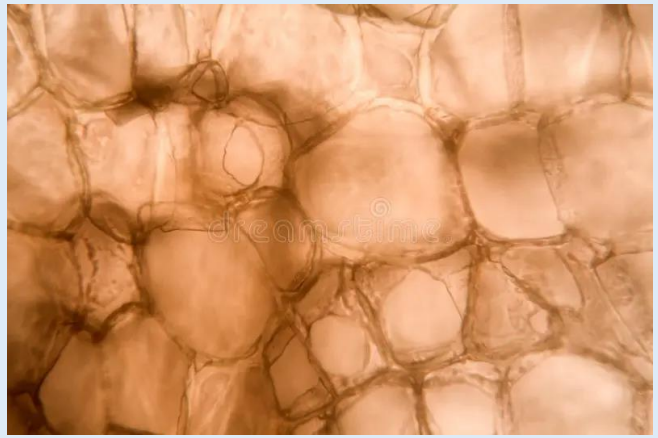
Various techniques for imaging porous media structure at different scales



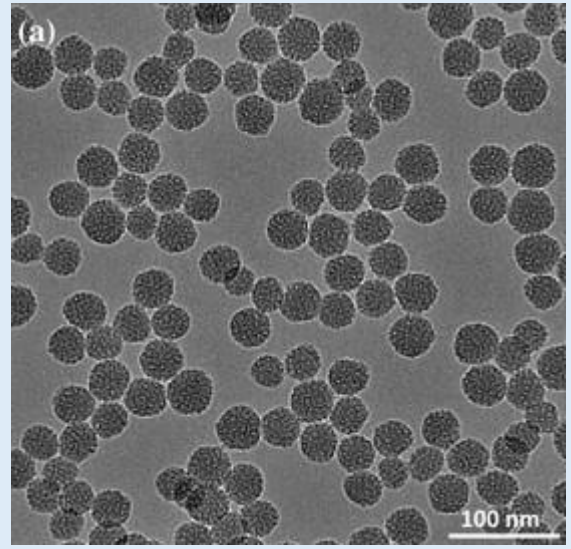
Cement



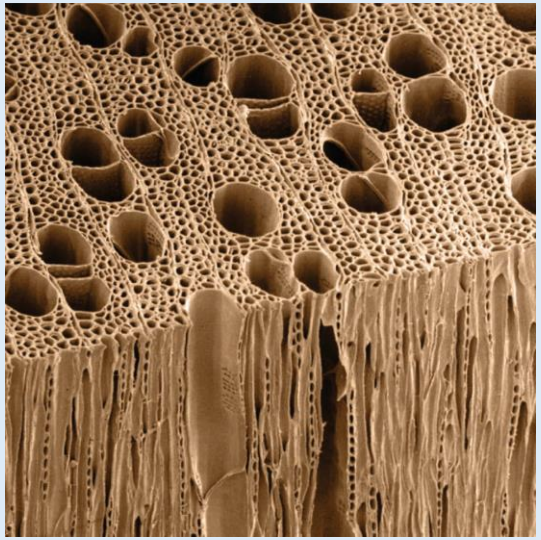
Cellulose



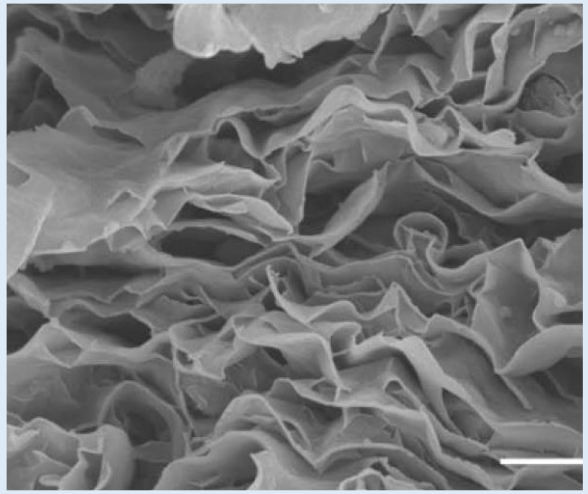
Carrot



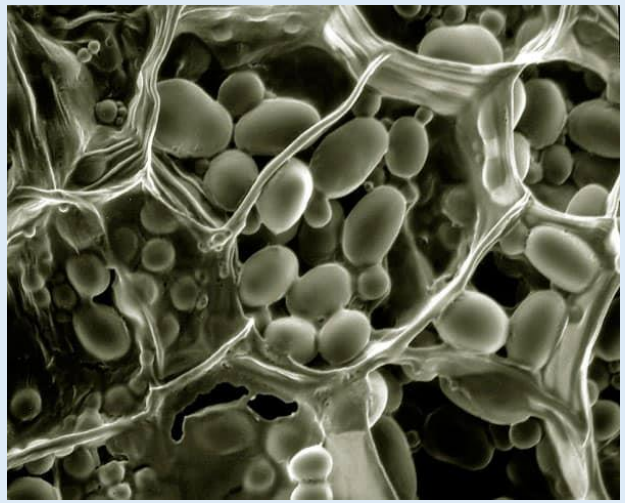
Colloidal suspension



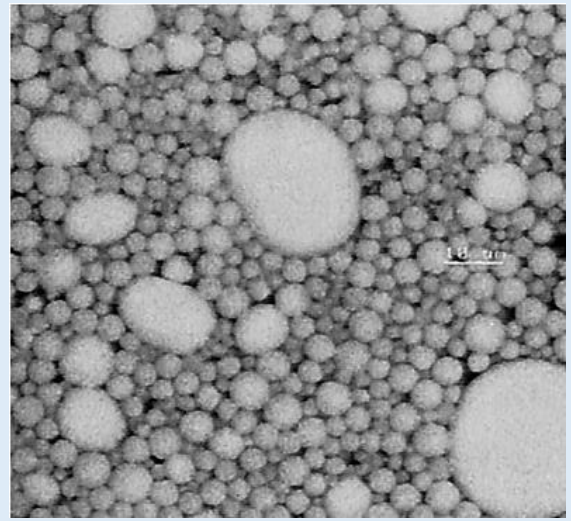
Wood



Clay



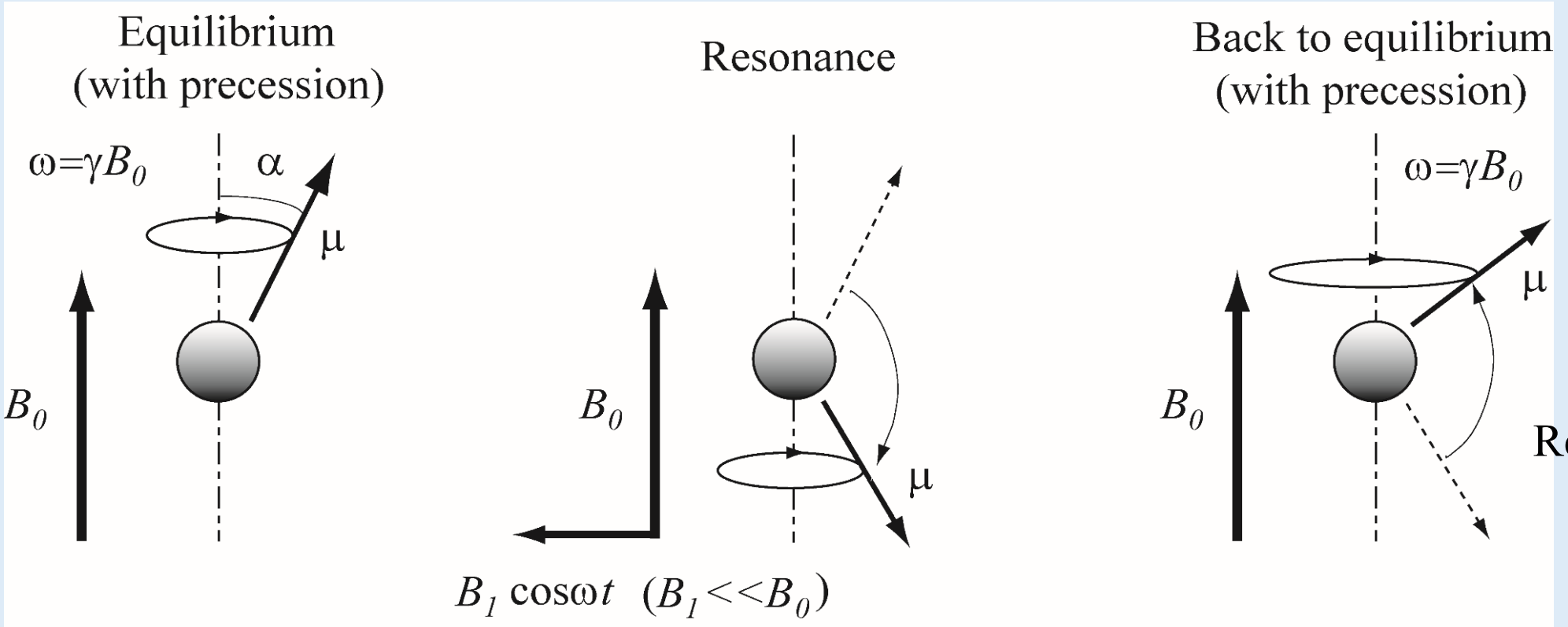
Potato



Mayonnaise

BUT what technique for quantification of : Liquid flow – Particle motion - Adsorption - Phase changes – Transfers between pores - Particle or pore size changes ?

NMR principle (mechanical analogy)



γ Gyromagnetic ratio

Relaxation: Longitudinal component T_1
(« spin-lattice » relaxation)

Transversal component T_2
(« spin-spin » relaxation)

From a few ms to a few seconds

NMR signal of an elementary material volume during precession + relaxation :

$$dS \propto \rho(\mathbf{r})\,\mathrm{d}\mathbf{r}\exp\left[i\omega t - t/T_2\right]$$

NMR signal of an elementary material volume during precession + relaxation :

$$dS \propto \rho(\mathbf{r})\,\mathrm{d}\mathbf{r}\exp\left[i\omega t - t/T_2\right]$$

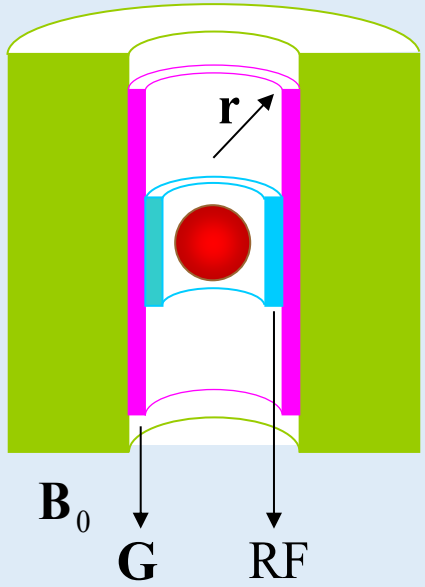
Liquid mass

$$S \propto \int \rho(\mathbf{r})\,\mathrm{d}\mathbf{r} = m_{\text{protons}}$$

Atom spin type

$$\omega \propto \gamma$$

Liquid/solid configuration and interactions T_2



+ Gradient of main magnetic field: $\mathbf{B} = \mathbf{B}_0 + \mathbf{G}\cdot\mathbf{r}$

G Tensor

$$\mathbf{G}_z = \mathbf{z}\cdot\mathbf{G}$$

$$\omega = \gamma B_0 + \gamma \mathbf{G}_z \cdot \mathbf{r}$$

Magnetic resonance imaging

Velocity imaging

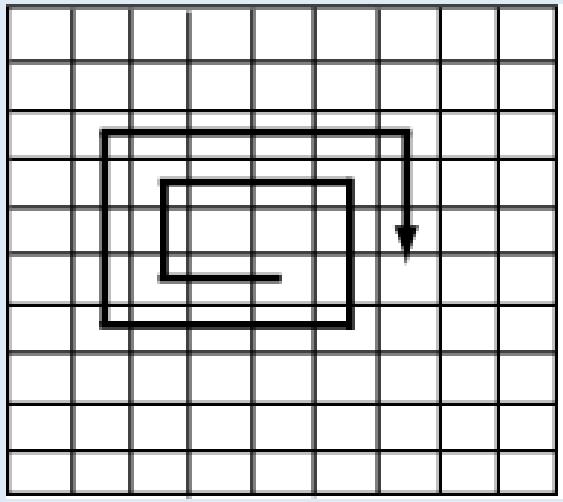
Diffusion

Magnetic resonance imaging

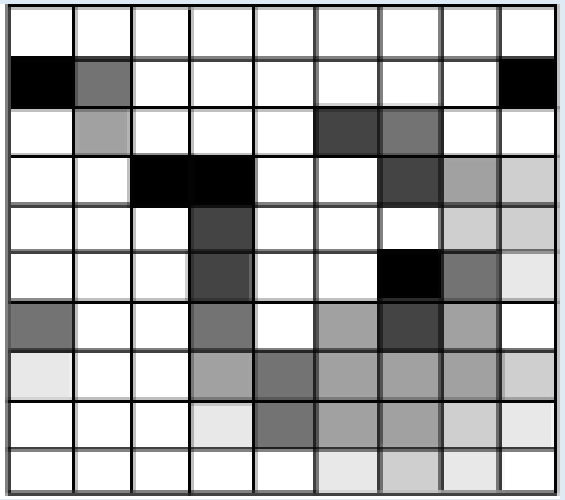
Phase shift: $\Delta\varphi = \gamma \mathbf{G}_z \cdot \mathbf{r}t$ (neglecting relaxation effect)

Total signal $S(t) \propto \iiint \rho(\mathbf{r}) \exp[i\gamma \mathbf{G}_z \cdot \mathbf{r}t] d\mathbf{r} = S(\mathbf{k})$ = *Fourier transform*

$\Rightarrow$ Local spin density (inverse Fourier transform) $\rho(\mathbf{r}) = \iiint S(\mathbf{k}) \exp[-i\gamma \mathbf{G}_z \cdot \mathbf{r}t] d\mathbf{k}$ with $\mathbf{k} = \gamma \mathbf{G}_z t / 2\pi$



k-space



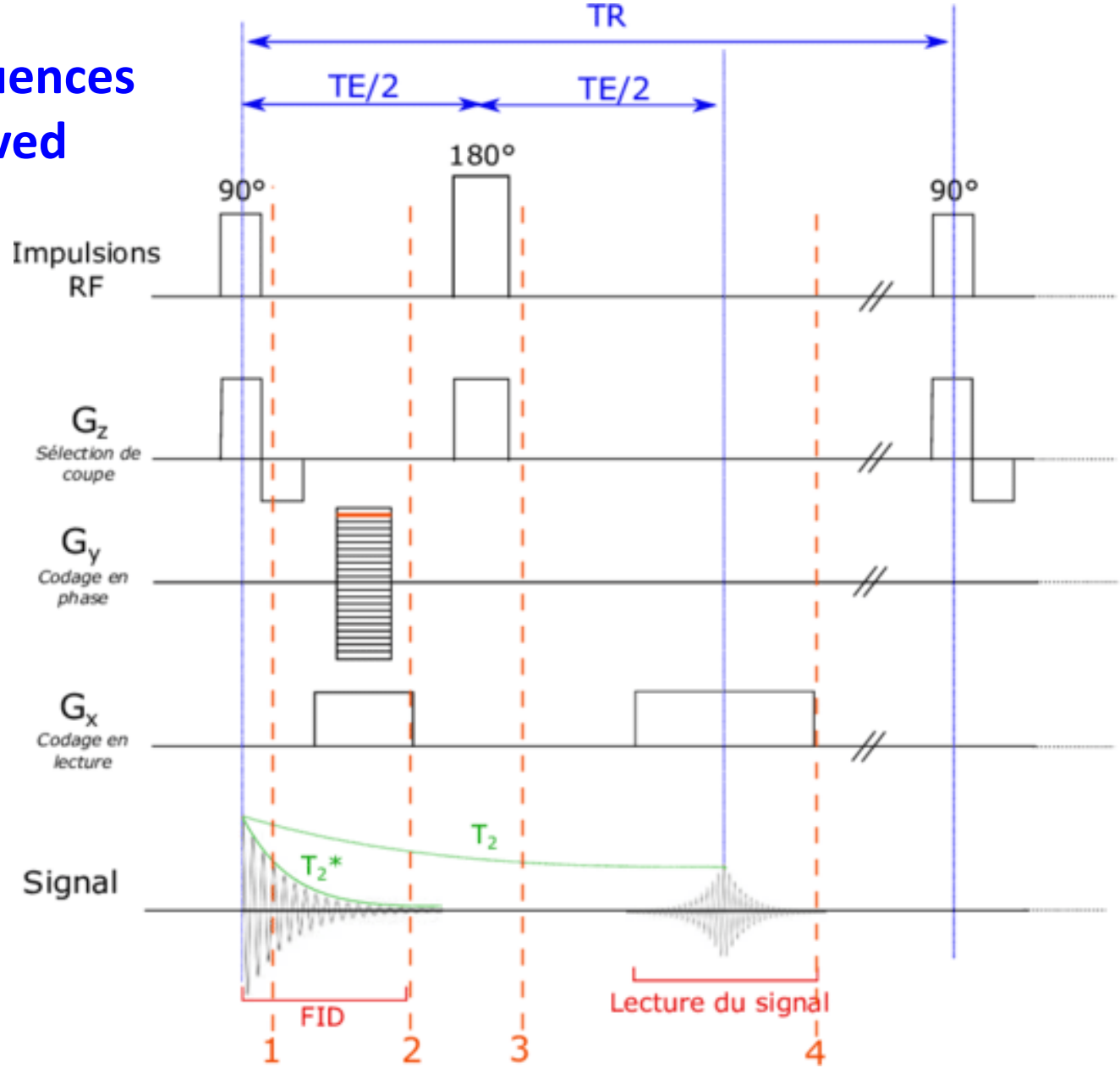
Real space

Zucchini



F. Bertrand

Developing NMR or MRI sequences fitted to materials and observed processes:
A research work in itself

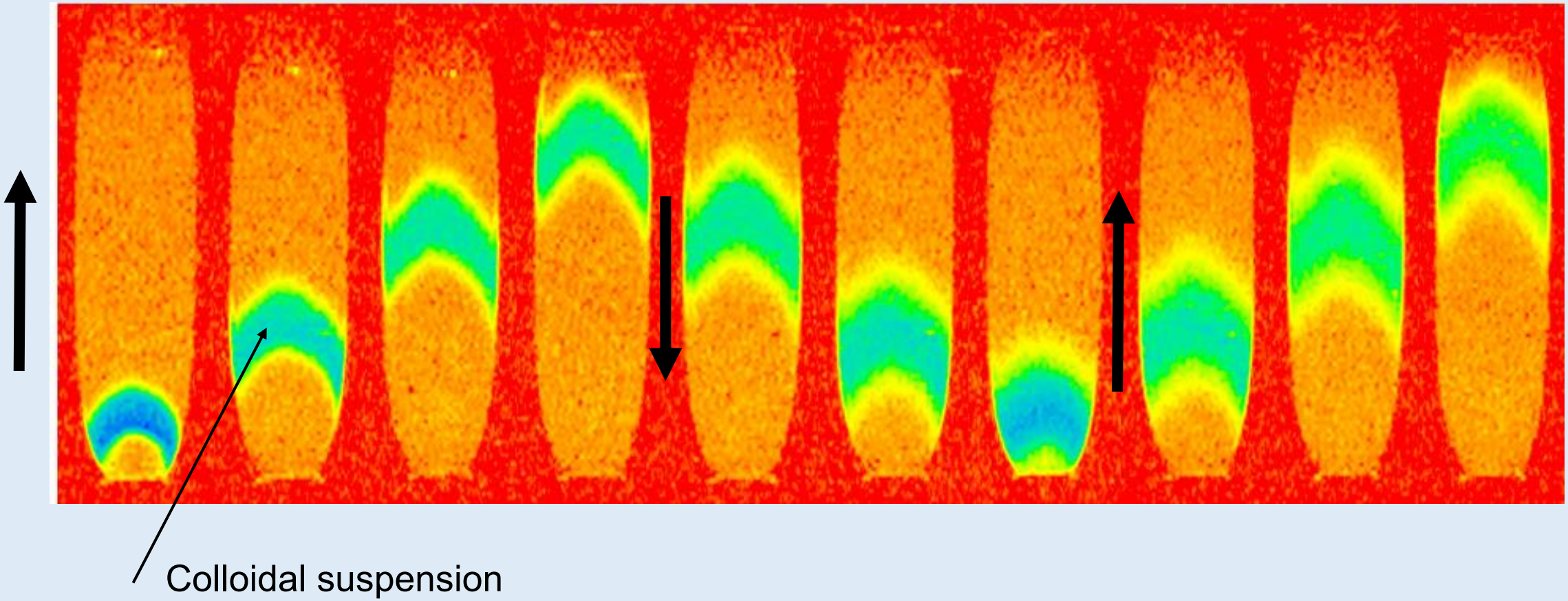


Séquence d'imagerie en echo de spin

P. Lefevre, Thèse Univ. Lorraine, 2017

Imaging weighted by relaxation time

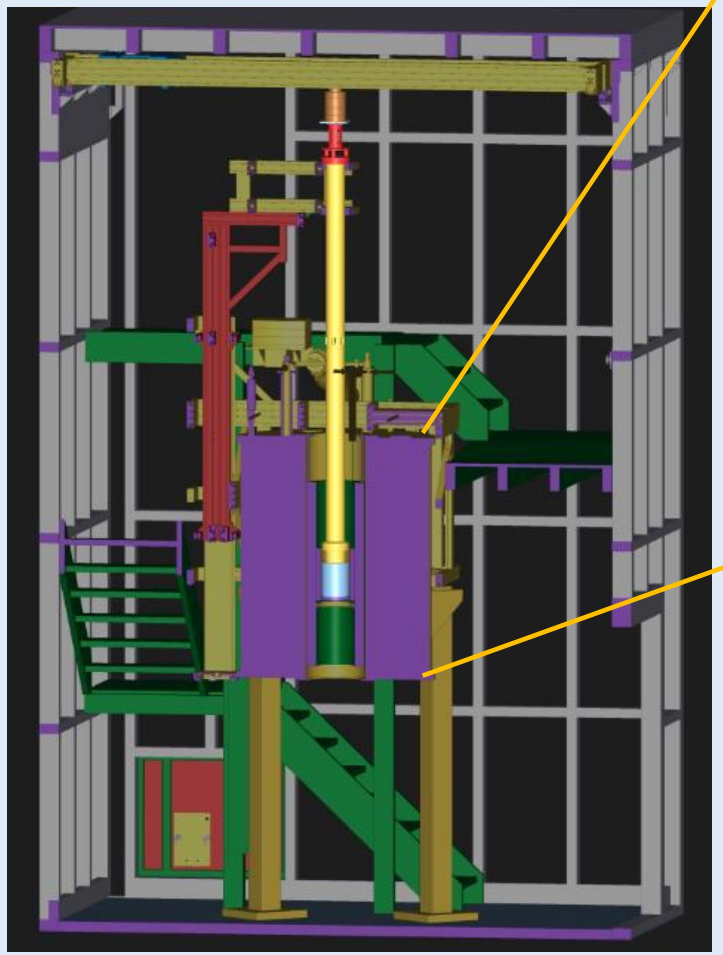
Mechanical dispersion in model porous medium:
Injection of a step of paramagnetic colloidal particle suspension (faster relaxation) in a water flow through a glass bead column, then flows alternating upwards and downwards



Lehoux et al, *Physical Review E* (201

Magnetic Resonance Imager

Laboratoire Navier



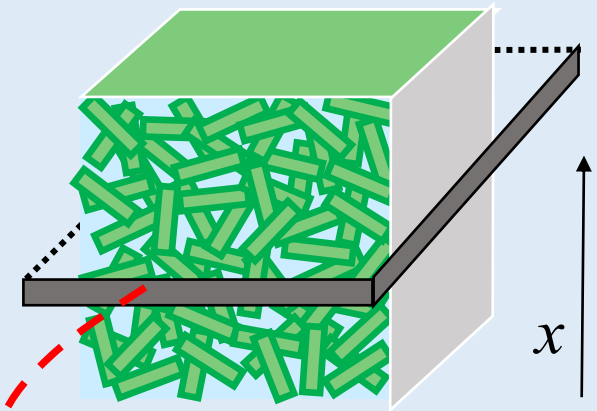
6 m

Bruker, 0.5 T

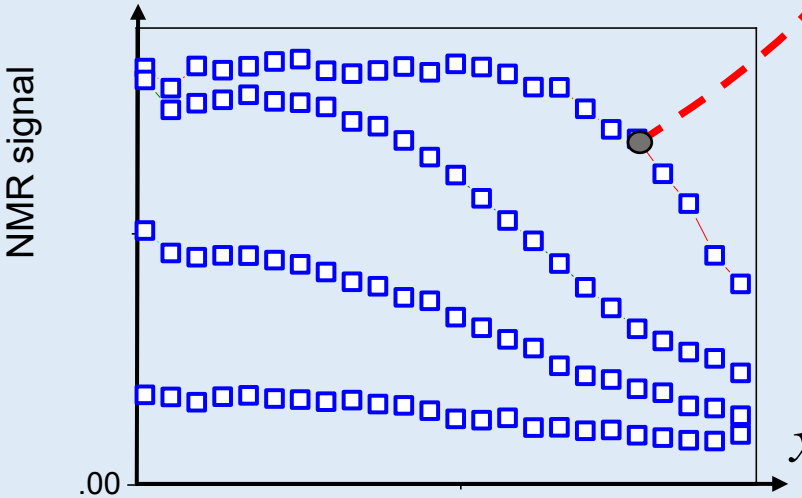
40 cm



Magnet + coils



Sample

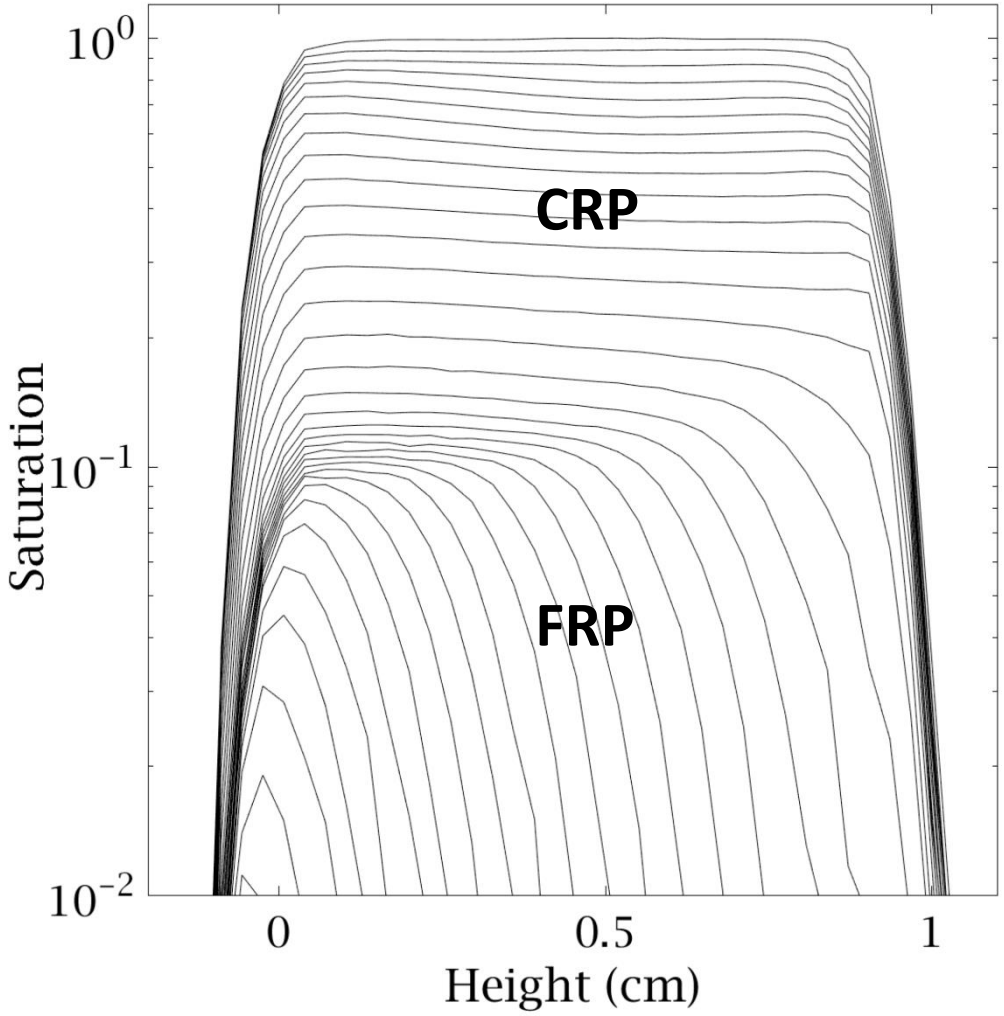


« 1D profiles » over time

+ Distinction of different liquid phases

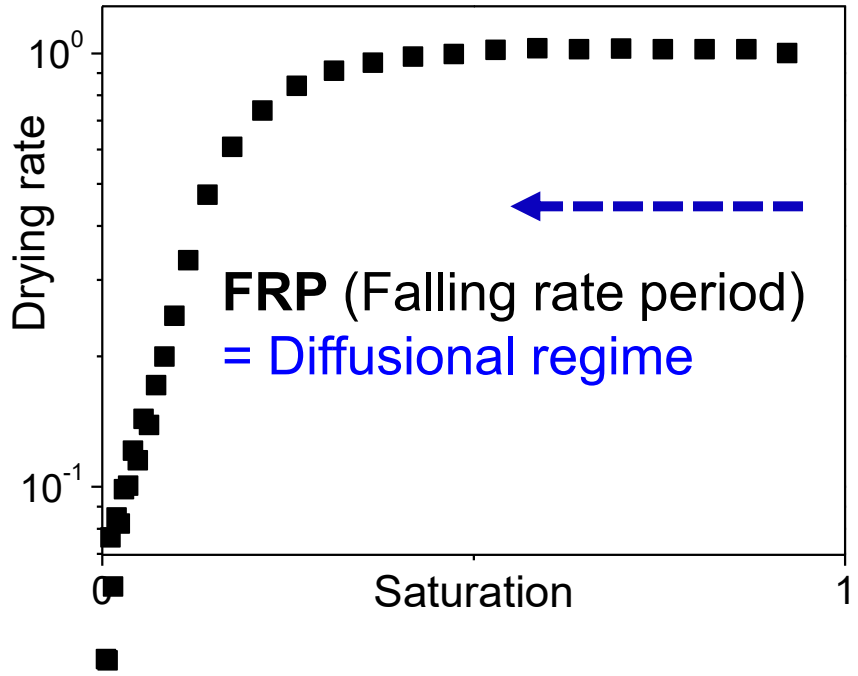
Example: Drying of hydrophilic bead packing filled with pure liquid

Bead packing (1.5 micron)



MRI saturation distribution

CRP (Constant Rate Period)
= Equilibrium regime



J. Thiery et al., *Phys. Rev. E* (2017)

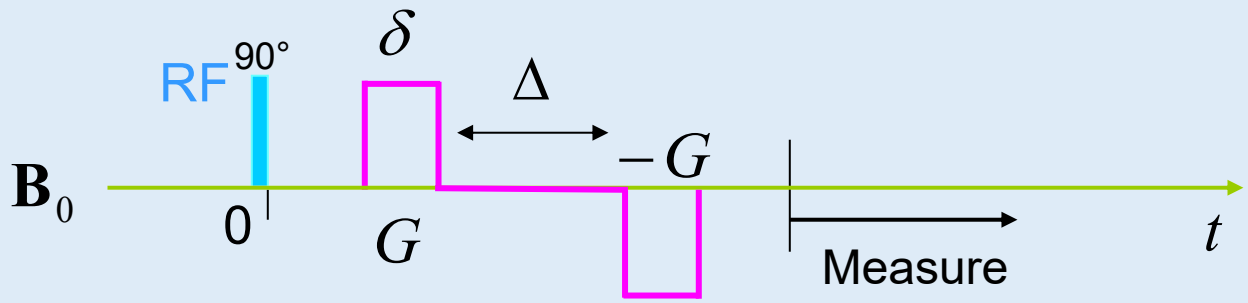
Velocity imaging

Motion ⟹ $\mathbf{r}(t) = \mathbf{r}_{t=0} + t\mathbf{v}_{t=0} + O(t^2)$

$$\Delta\varphi = \gamma \int_{\tau<t} \mathbf{G}_z(\tau)\cdot\mathbf{r}(\tau)\,\mathrm{d}\tau = \gamma \int_{\tau<t} \mathbf{G}_z(\tau)\cdot\mathbf{r}_{t=0}\,\mathrm{d}\tau + \gamma \int_{\tau<t} \mathbf{G}_z(\tau)\cdot\tau\mathbf{v}_{t=0}\,\mathrm{d}\tau$$

If $\int_{\tau<t} \mathbf{G}_z(\tau)d\tau = 0$ and $\mathbf{p} = \gamma \int_{\tau<t} \mathbf{G}_z(\tau)\tau\,\mathrm{d}\tau$ ⟹ **Phase shift** $\boxed{\Delta\varphi = \mathbf{p}\cdot\mathbf{v}_{t=0}}$

NMR sequence:
(Gradient history)



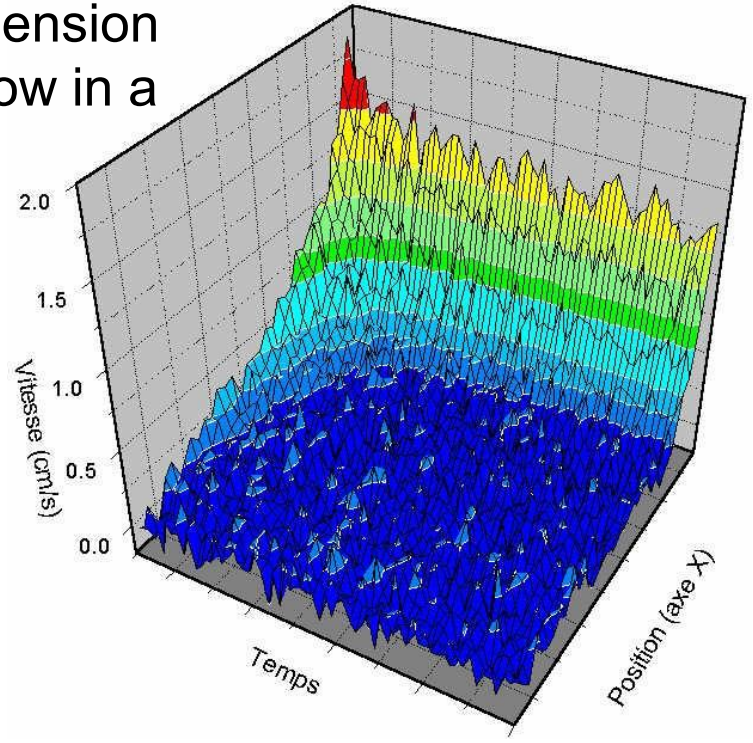
⟹ **Phase shift** $\boxed{\Delta\varphi = \gamma \int_t \mathbf{G}_z(t)\cdot\mathbf{r}(t)\,\mathrm{d}t = \gamma v_{t=0} G\delta\Delta}$ $(\delta << \Delta)$

Rem.: Not affected by noise on signal

Velocity imaging: examples

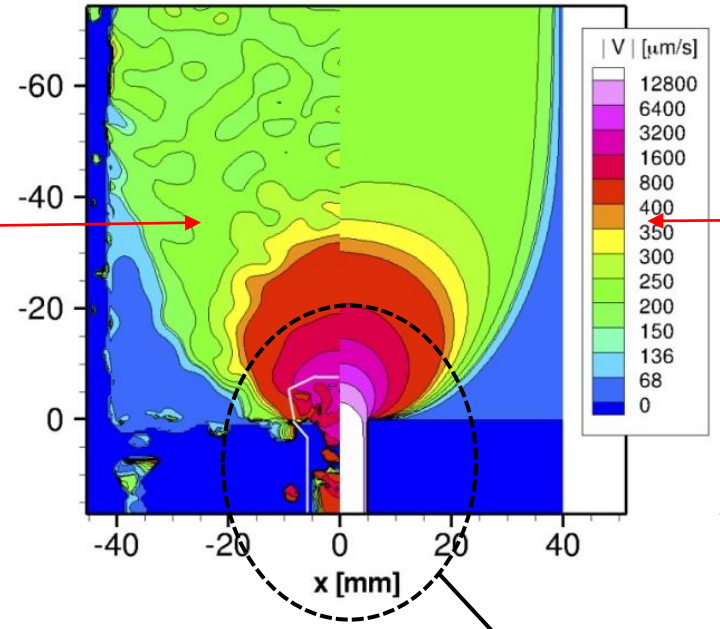
Coussot, *Experiments in Fluids* (2020)

Laponite suspension (thixotropic) flow in a Couette cell

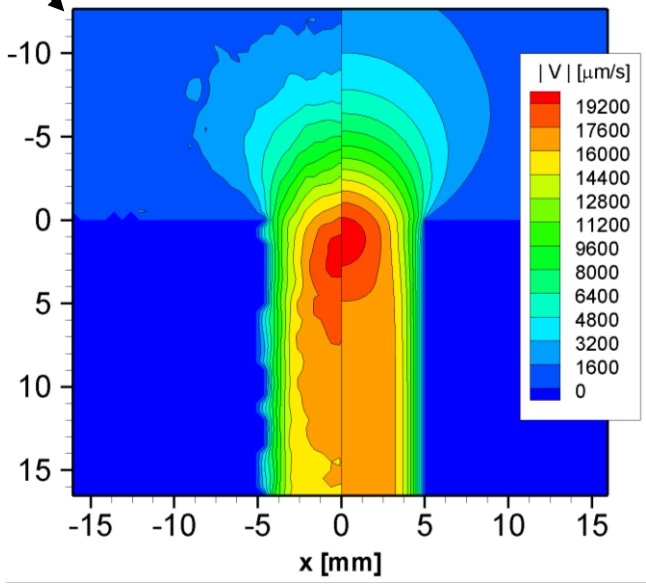


MRI data

Numerical simulation



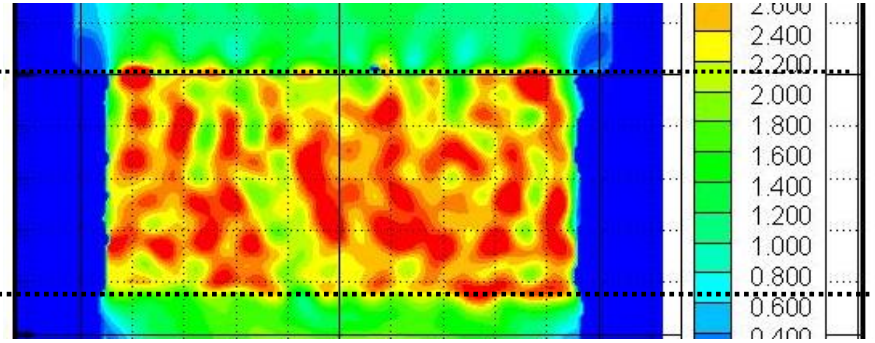
Yield stress fluid flow through a contraction



Rabideau et al, *JNNFM* (2010)

MR velocimetry of a fluid through a bead packing: no hope

Bead packing
D=3 mm



Probability density function of velocity

Total NMR signal in sample

$$S = \iiint \rho(\mathbf{r}) \exp[ikv] d\mathbf{r}$$

$$k = \gamma G \delta \Delta$$

$$S(k) = m_0 \int_v f(v) \exp(ikv) dv$$

f **Probability density function**

$$\Rightarrow f(v) \propto \int_k S(k) \exp(-ikv) dk$$

$\Rightarrow$ Travel across *k* space

See e.g., Chevalier et al, *PRE*, 2014

Diffusion

Different paths of each molecule over time *t:* $\mathbf{r}(t)$

$$\left\langle \mathbf{r}(t)^2 \right\rangle = 6 D_0 t$$

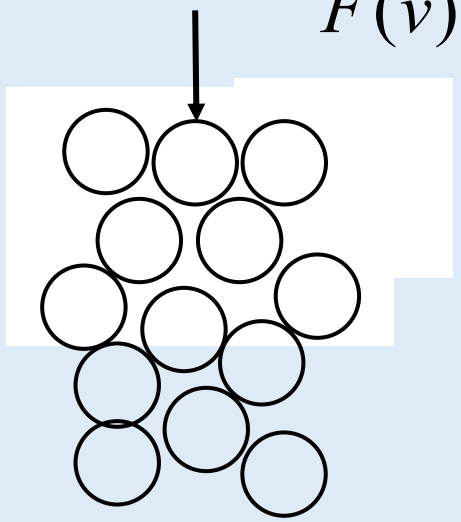
D_0 Self-diffusion coefficient

$$\Rightarrow \varphi(t) = \gamma B_0 t + \sum_{0<\tau<t} \gamma \mathbf{G}_z \cdot \mathbf{r}(\tau) \, \mathrm{d}\tau$$

$$\Rightarrow \left\langle \exp(i \Delta \varphi(t)) \right\rangle = \exp\left(-\frac{1}{3} \gamma^2 G^2 D_0 t^3 \right)$$

Distribution function for complex fluids through a bead packing

$$F(v) = \int_v f(u)du$$



Emulsion:

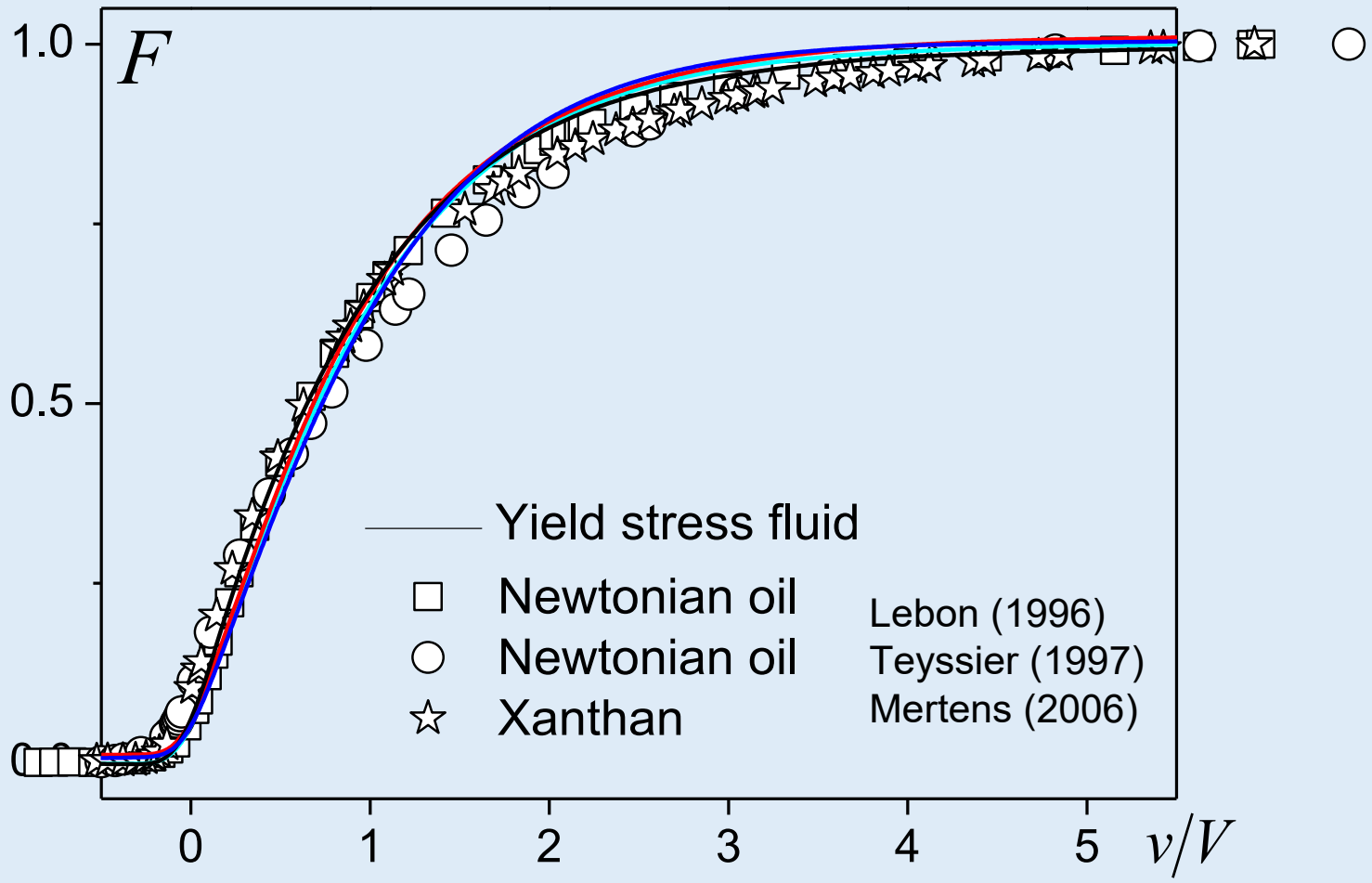
$\tau_c = 74Pa$

$k = 13.5\text{Pa.s}^n$

$n = 0.4$

$V \in [0.04 - 1.3\ \text{mm.s}^{-1}]$

$D = 0.5 \text{ ou } 2\ \text{mm}$



⇒ **Identical Probability Densities**

⇒ **Identical local velocity fields?**

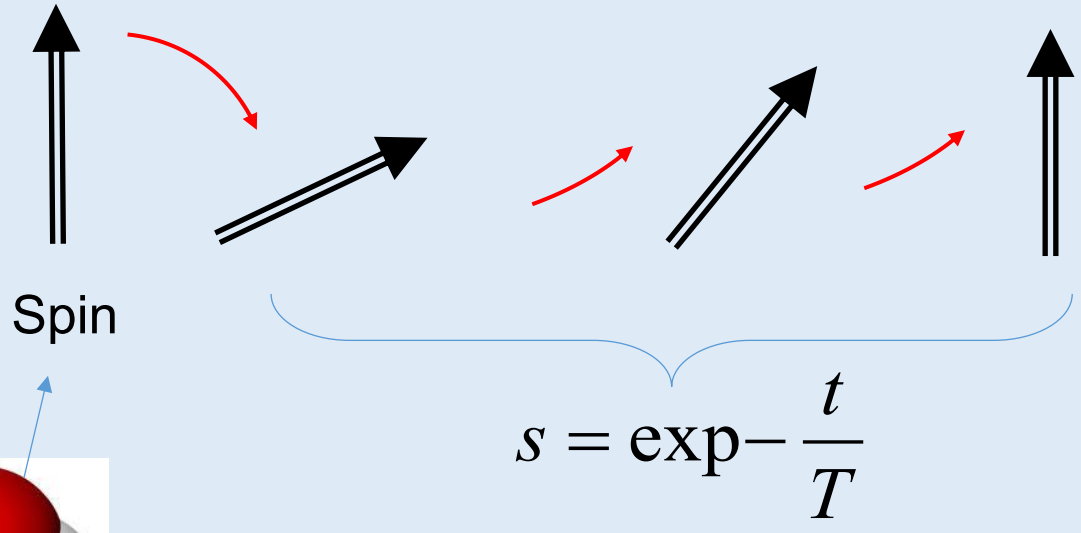
Chevalier et al, *Physical Review E* (2014)

Nuclear Magnetic Resonance Relaxometry

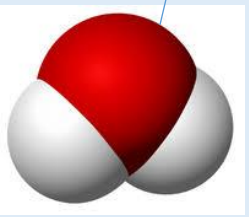




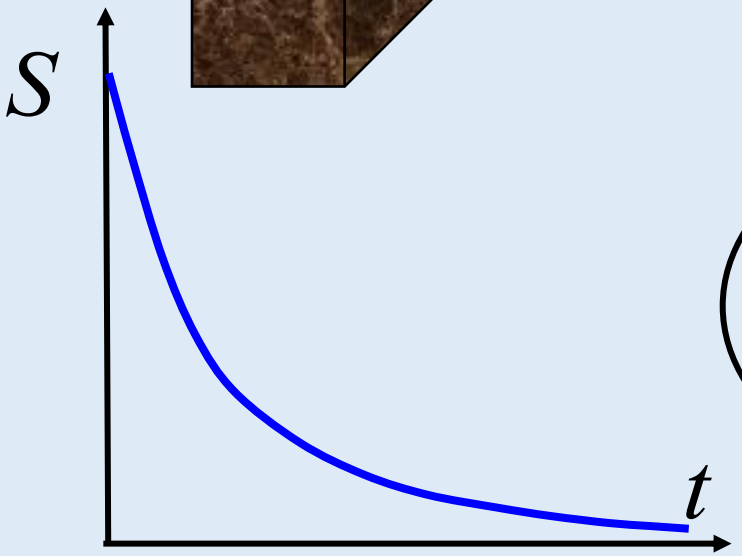
At distance, inside matter

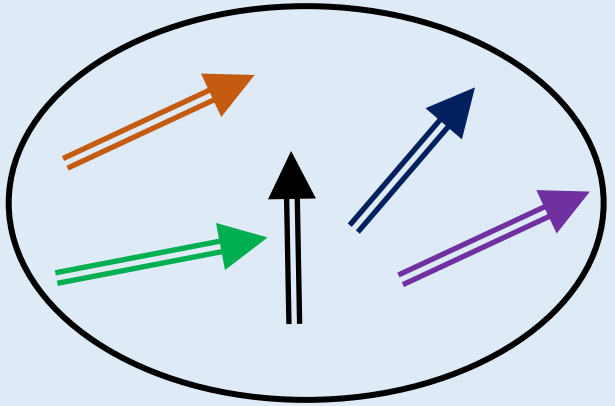


$$s = \exp -\frac{t}{T}$$



Each molecule





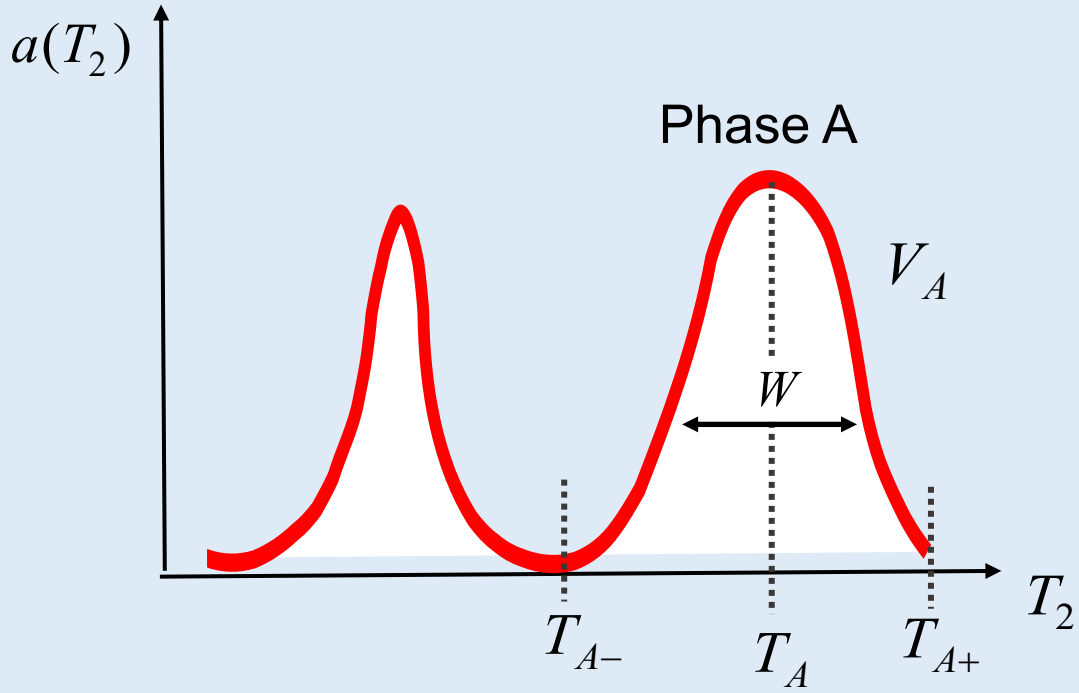
Molecule state and environment

$$S = \sum_i \exp -\frac{t}{T_i}$$

Relaxometry: Probability density function (pdf)

Total signal: $s(t) = \int_0^\infty a(\lambda)\left(\exp\left(-\lambda t\right)\right)\mathrm{d}\lambda$ $\quad T_2 = 1/\lambda$

$a(T_2)$ **Probability density function (pdf)**



$\Rightarrow$ **« Dynamic NMR Relaxometry »:**

Physical appreciation of the pdf evolutions / time

Quantitatively robust trends (despite Laplace transform artefacts**):**

1. Volume fraction of each liquid phase: $\psi_A = \dfrac{V_A}{V_{total}} = \int_{T_{A-}}^{T_{1A+}} a(\lambda)\,\mathrm{d}\lambda$ $\quad \psi_A(t)$

2. Relative evolution of relaxation time: $T_A(t)/T_A(0)$

3. Relative evolution of peak width: $W(t)/W(0)$

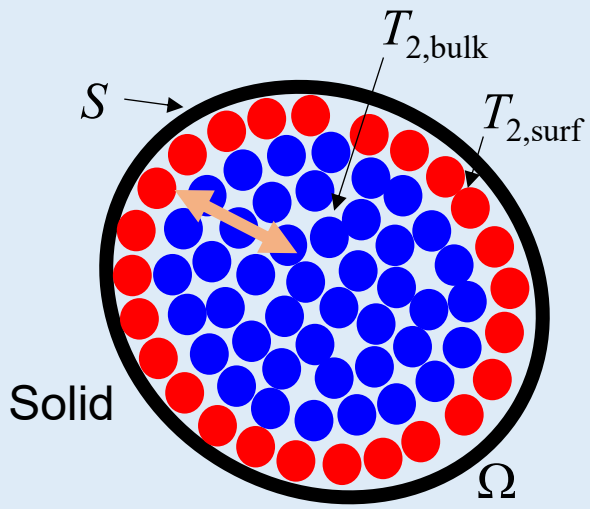
Relaxation vs material characteristics (simplistic approach)

Hyp.: A molecule successively spends some times in different environnements associated with different relaxation times

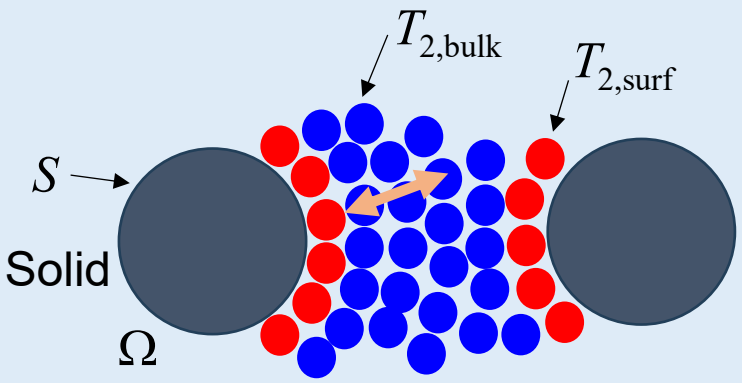
ΔT_i Time spent in state with relaxation time T_i

$$\Rightarrow s(t) = s_0 \prod_i \exp\left(-\frac{\Delta t_i}{T_i}\right) = s_0 \exp\left(-\sum_{\Sigma \Delta t_i = t} \frac{\Delta t_i}{T_i}\right)$$

In a liquid-solid mixture (suspension or porous medium), two main relaxation times:



Saturated pore



Suspension

S = Wetted area

V = Liquid volume

b = Thickness of adsorbed layer

$$T_{2,surf} << T_{2,bulk}$$

$$\Rightarrow \sum_i \frac{\Delta t_i}{T_i} = \frac{\Delta t_{\text{surf}}}{T_{2,\text{surf}}} + \frac{\Delta t_{\text{bulk}}}{T_{2,\text{bulk}}}$$

Δt_{surf} Total time spent over the surface

« Fast exchange » assumption: thanks to a sufficient number of transports throughout the pore during the relaxation, each molecule finally reaches each region in proportion to its volume

(Brownstein-Tarr 1977)

Characteristic distance between solid surfaces: r

Characteristic time for reaching a distance *r by* self-diffusion: $r^2/6D_0 << T_{2,\text{bulk}}$

For water, approximately: $r < 100$ microns

$$\Rightarrow \frac{1}{T_2} = \frac{1-\varepsilon}{T_{2,\text{bulk}}} + \frac{\varepsilon}{T_{2,\text{surf}}}$$

Fraction of time spent along the surface: $\varepsilon = \frac{\Delta t_{\text{surf}}}{\Delta t_{total}} \approx \frac{bS}{V}$

$$\Rightarrow s(t) = s_0 \exp - t/T_2$$

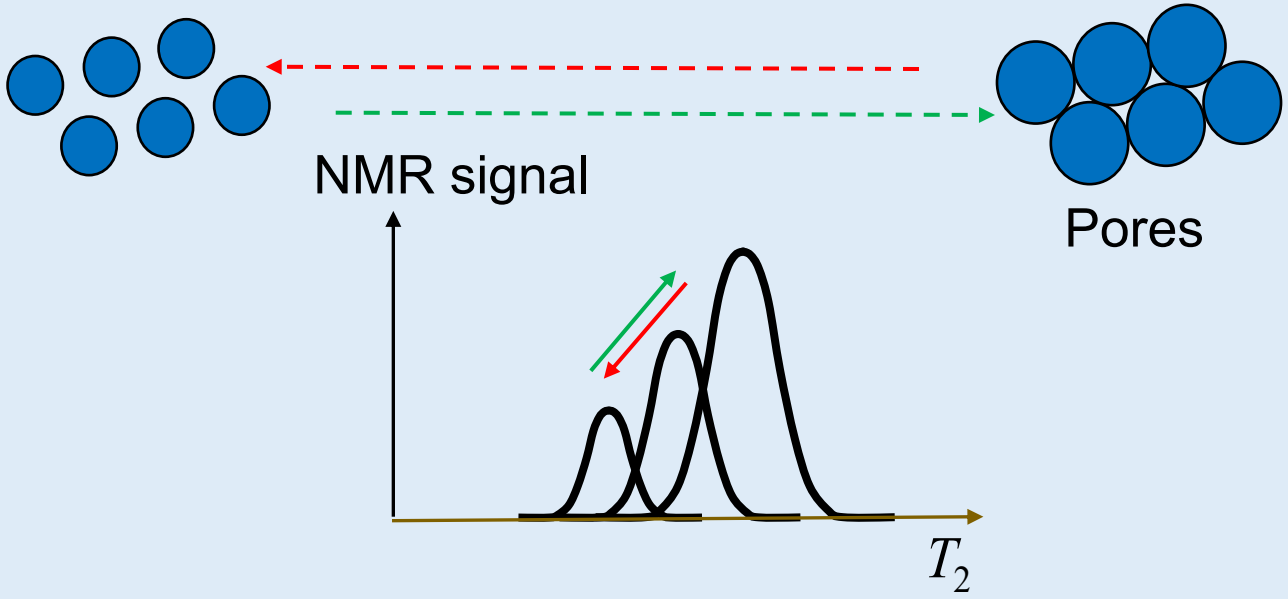
$$\boxed{\frac{1}{T_2} = \frac{1}{T_{2,\text{bulk}}} + \frac{1}{T_{2,\text{surf}}}\frac{bS}{V}}$$

$$T_2 << T_{2,\text{bulk}} \Rightarrow \boxed{T_2 \approx \frac{T_{2,\text{surf}}}{b}\frac{V}{S}}$$

$\Rightarrow$ **The relaxation time is in general not simply proportional to the pore size**

Evolution of the pdf depending on the characteristics of a porous medium

Homogeneous shrinkage or swelling



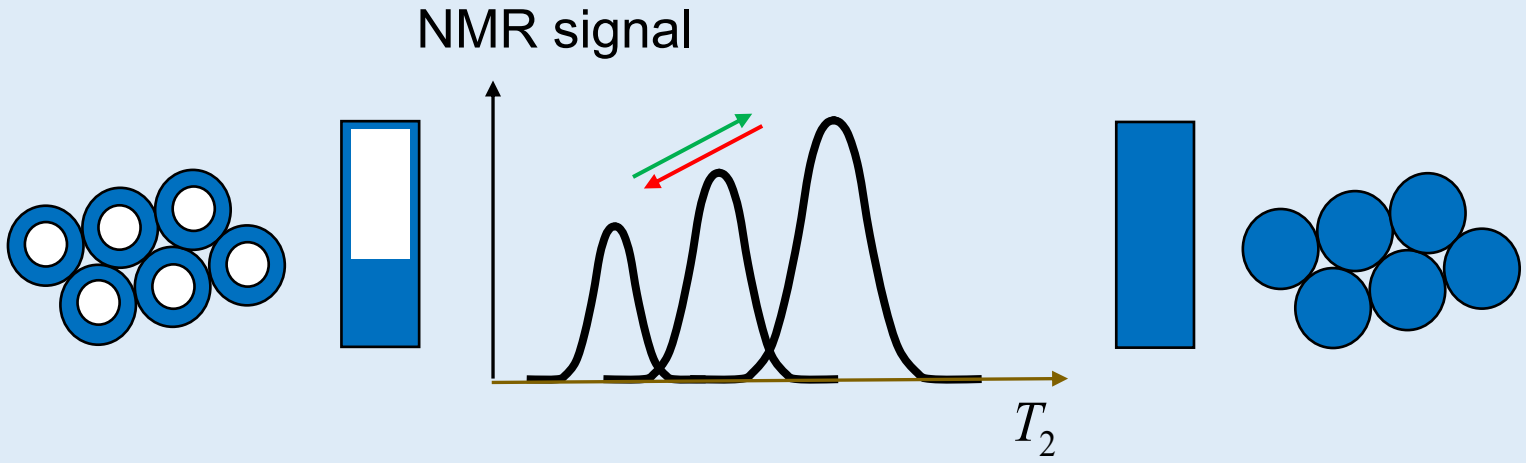
r Characteristic pore scale

Ex.: Spherical pores

$S \propto r^2 \quad V \propto r^3 \quad \psi = V/V_0$ (« **saturation** »)

$$\frac{S}{V} \propto \frac{1}{r} \propto \psi^{-1/3} \Rightarrow \boxed{T_2 \propto \psi^{1/3}}$$

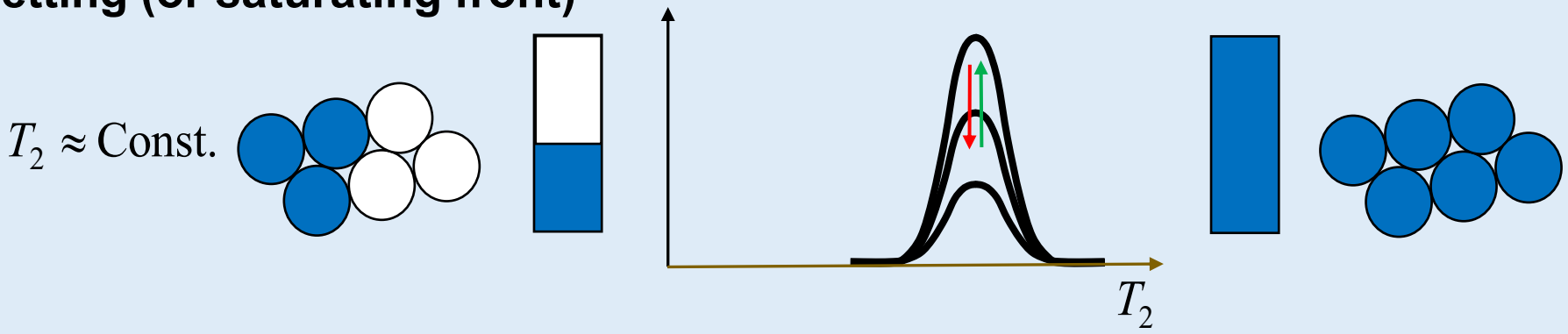
Homogeneous desaturation without dewetting



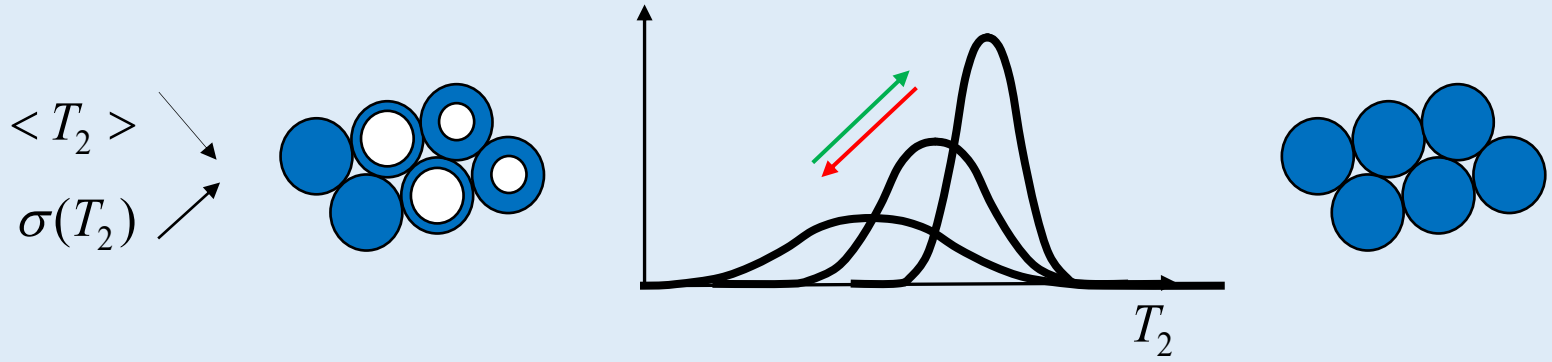
$S \propto S_0; \; V \propto \psi$

$$\frac{S}{V} \propto \psi^{-1} \Rightarrow \boxed{T_2 \propto \psi}$$

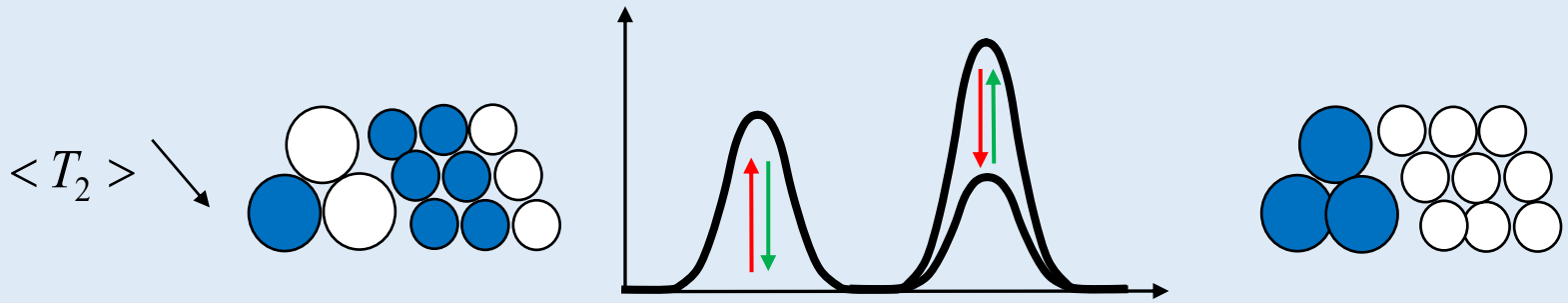
Desaturation with dewetting (or saturating front)



Heterogeneous desaturation without dewetting

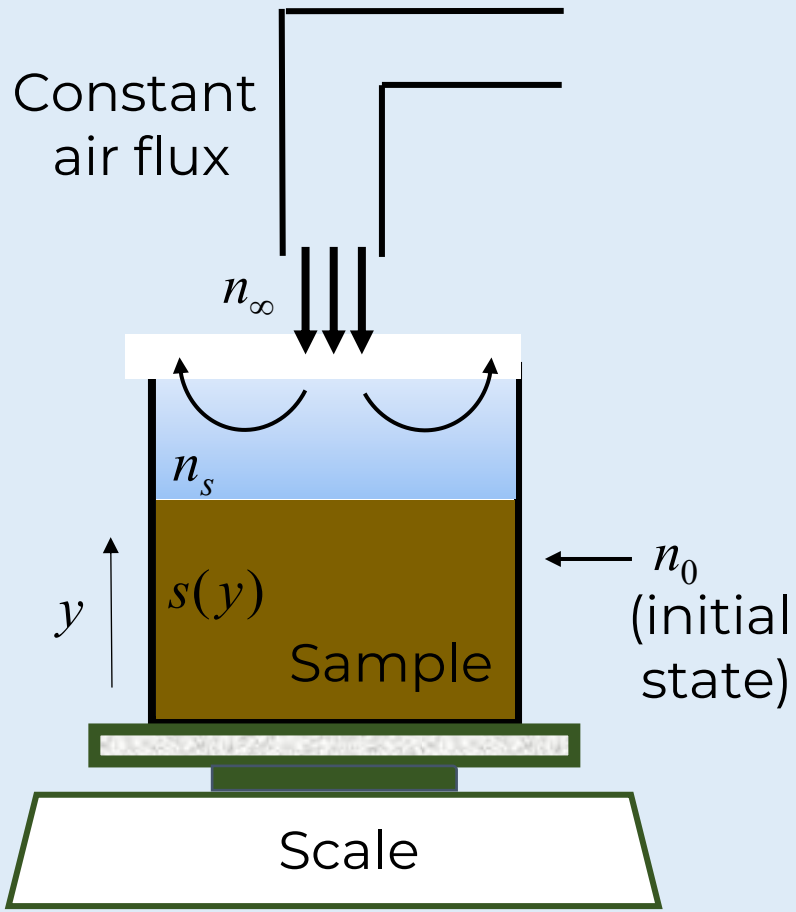


Transfer between pore types

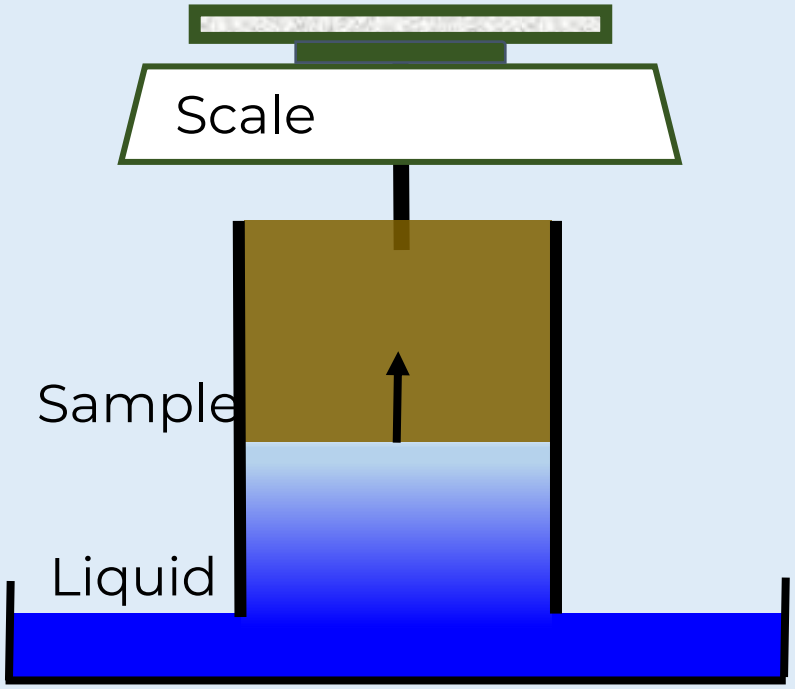


Maillet et al, *Langmuir*, 2022

Drying



Imbibition

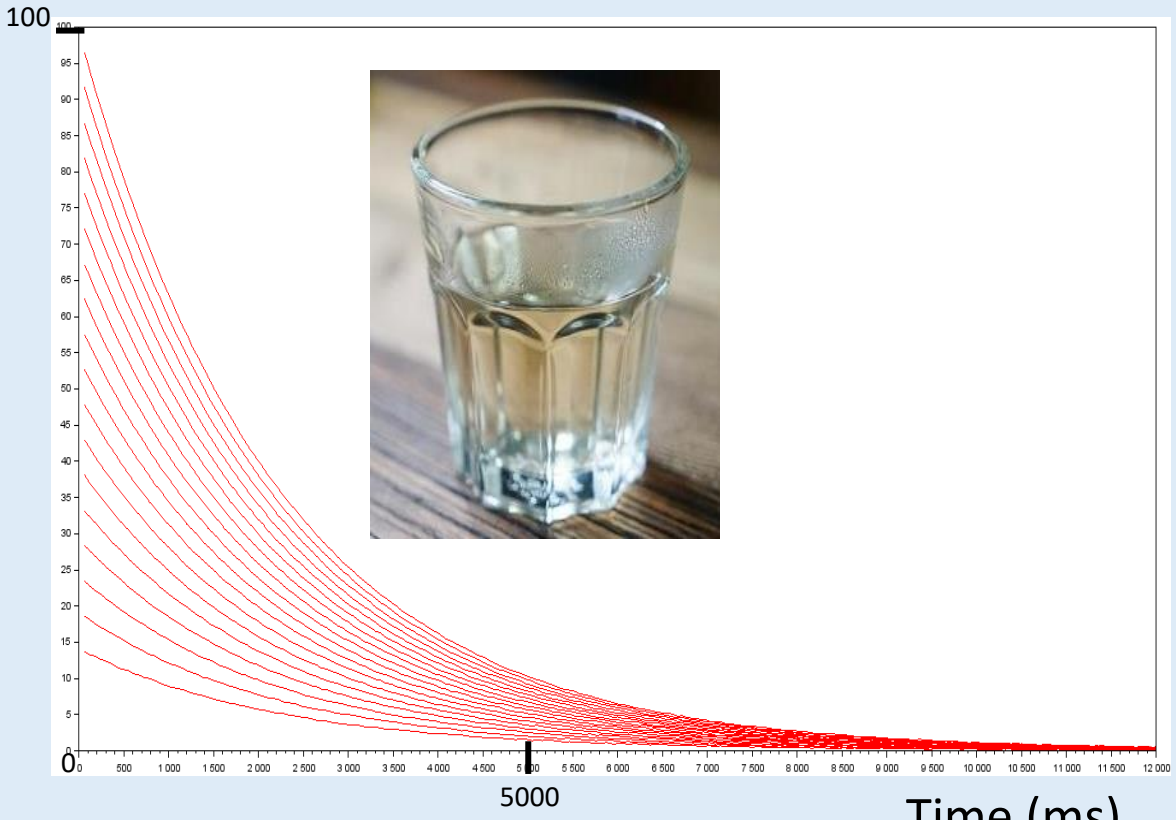


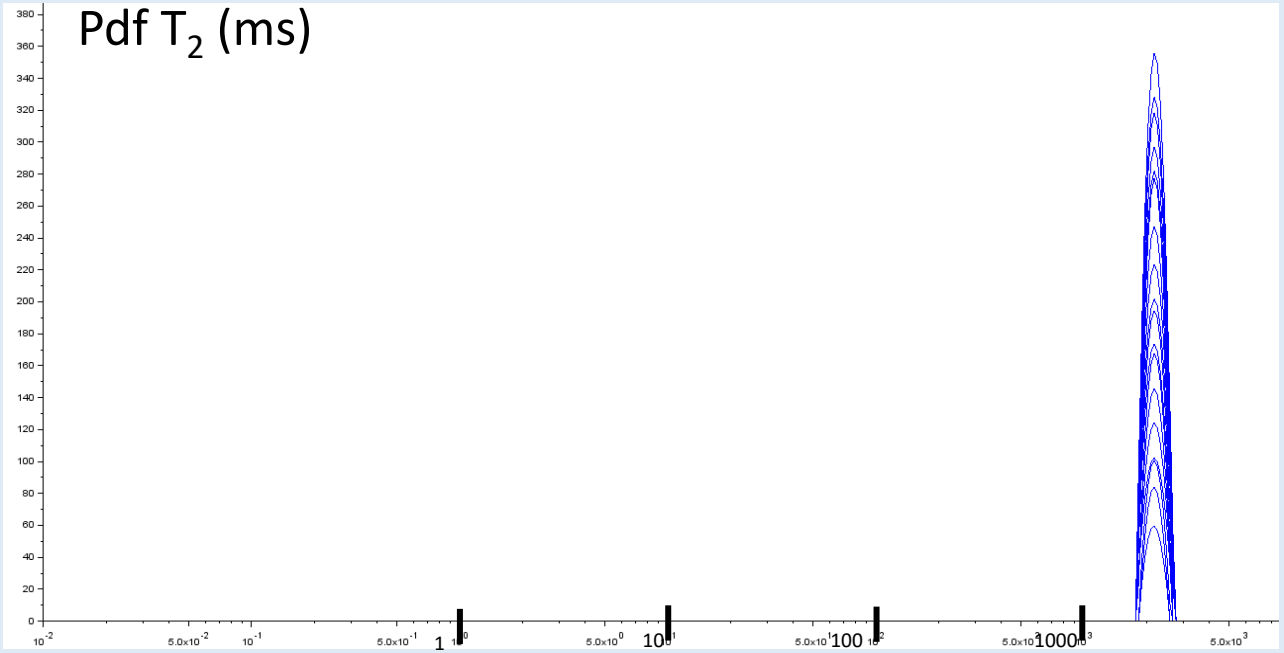


Dynamic relaxometry: Drying a « glass of water »

$$T_{2,\mathrm{bulk}} \approx 2300 \text{ ms}$$

NMR signal (Arb. Unit)

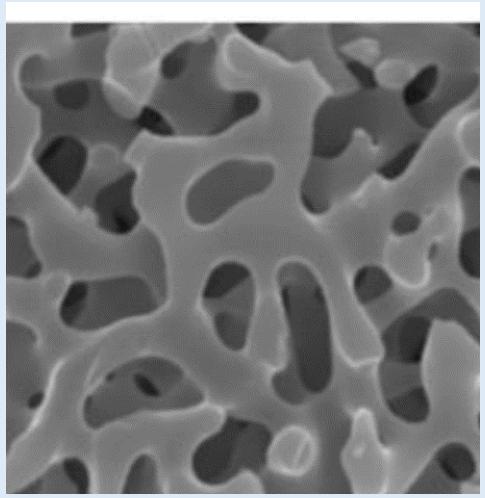




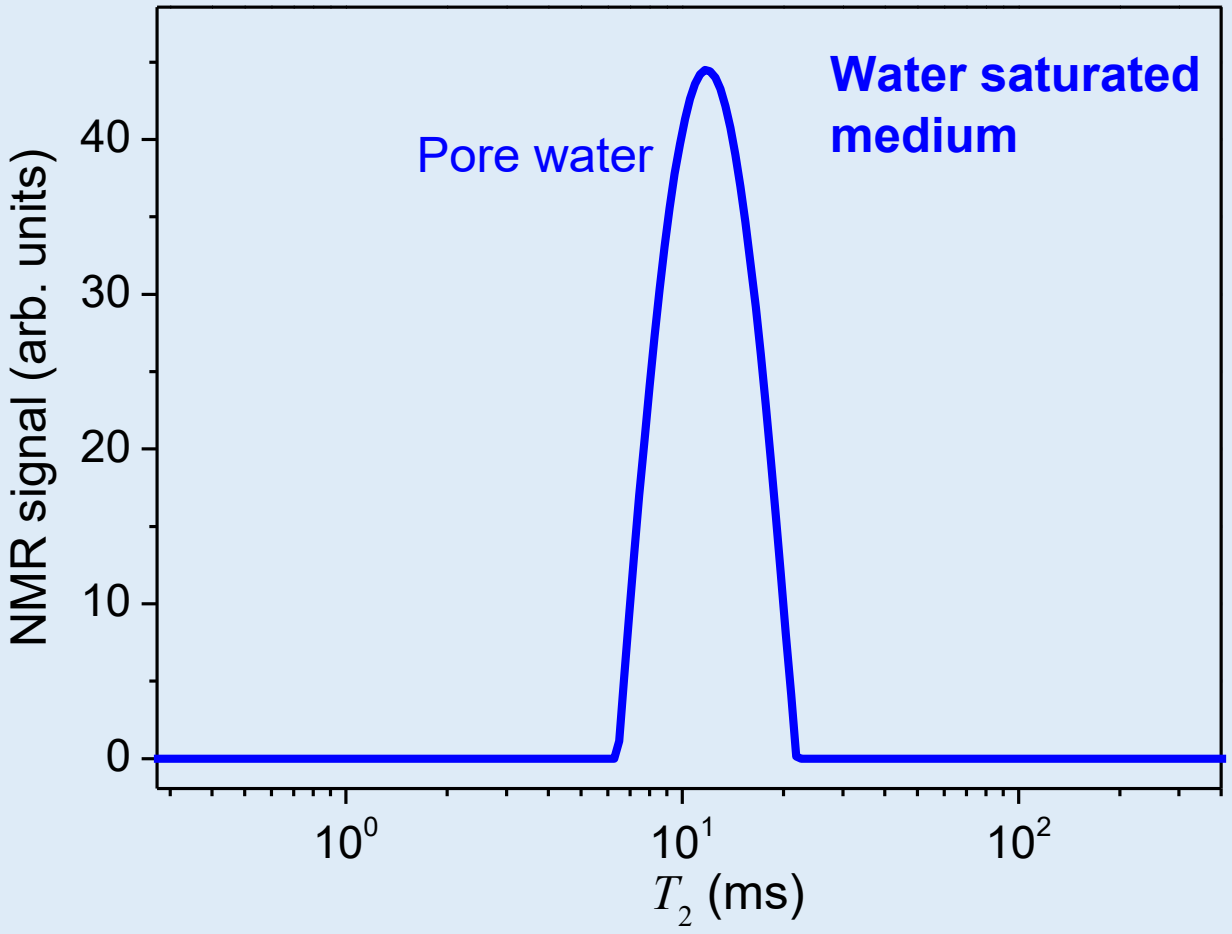
Assuming (here unrealistic) fast-exchange $\dfrac{1}{T_2} = \dfrac{1}{T_{2,\mathrm{bulk}}} + \dfrac{1}{T_{2,\mathrm{surf}}}\dfrac{bS}{V}$ $\Rightarrow \dfrac{1}{T_2} \approx \dfrac{1}{T_{2,\mathrm{bulk}}}$

Nanoporous medium

Porous silica glass (Vycor)



Specific surface: S=100 m^2/g
Average pore radius R=4.6 nm
Pore volume V=0.218 cm^3/g

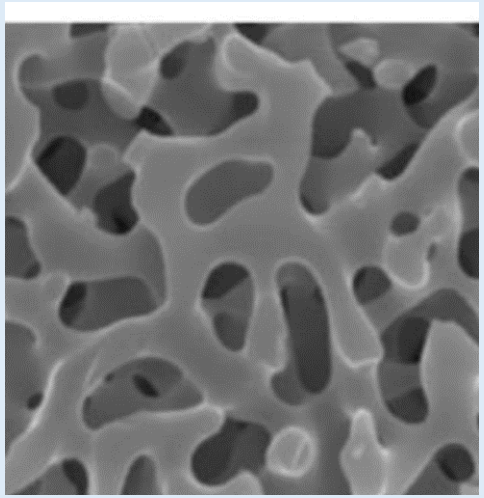


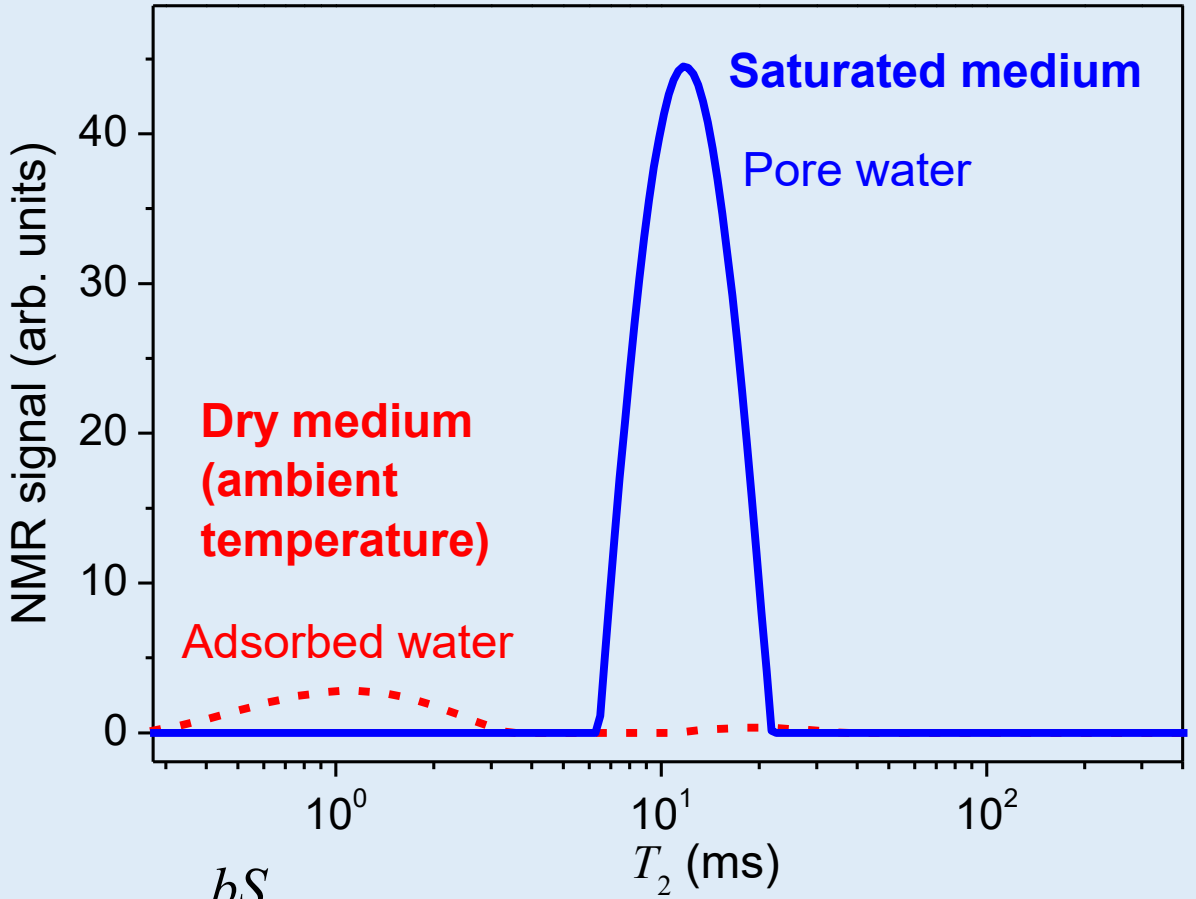
$$\frac{1}{T_{2,\text{pore water}}} = \frac{1}{T_{2,\text{bulk}}} + \frac{1}{T_{2,\text{surf}}}\frac{bS}{V} \quad \Rightarrow \quad \frac{1}{T_{2,\text{pore water}}} \approx \frac{1}{T_{2,\text{surf}}}\frac{bS}{V}$$

Maillet et al, *Phys. Rev. Appl.*, 2022

Nanoporous medium

Porous silica glass (Vycor)





Total NMR signal of adsorbed water *I*

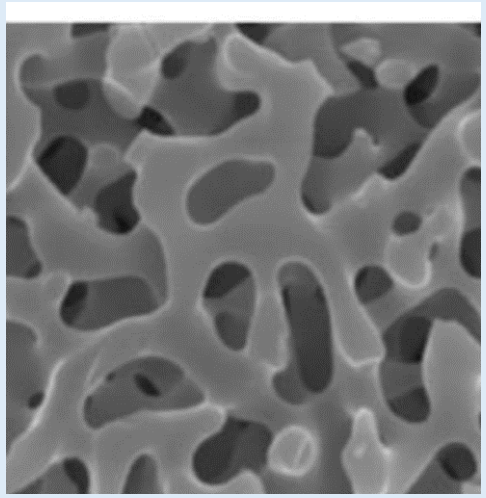
Total NMR signal of pore water at saturation $= \frac{bS}{V} \Rightarrow b \approx 0.38 \text{ nm}$ (about water molecule size)

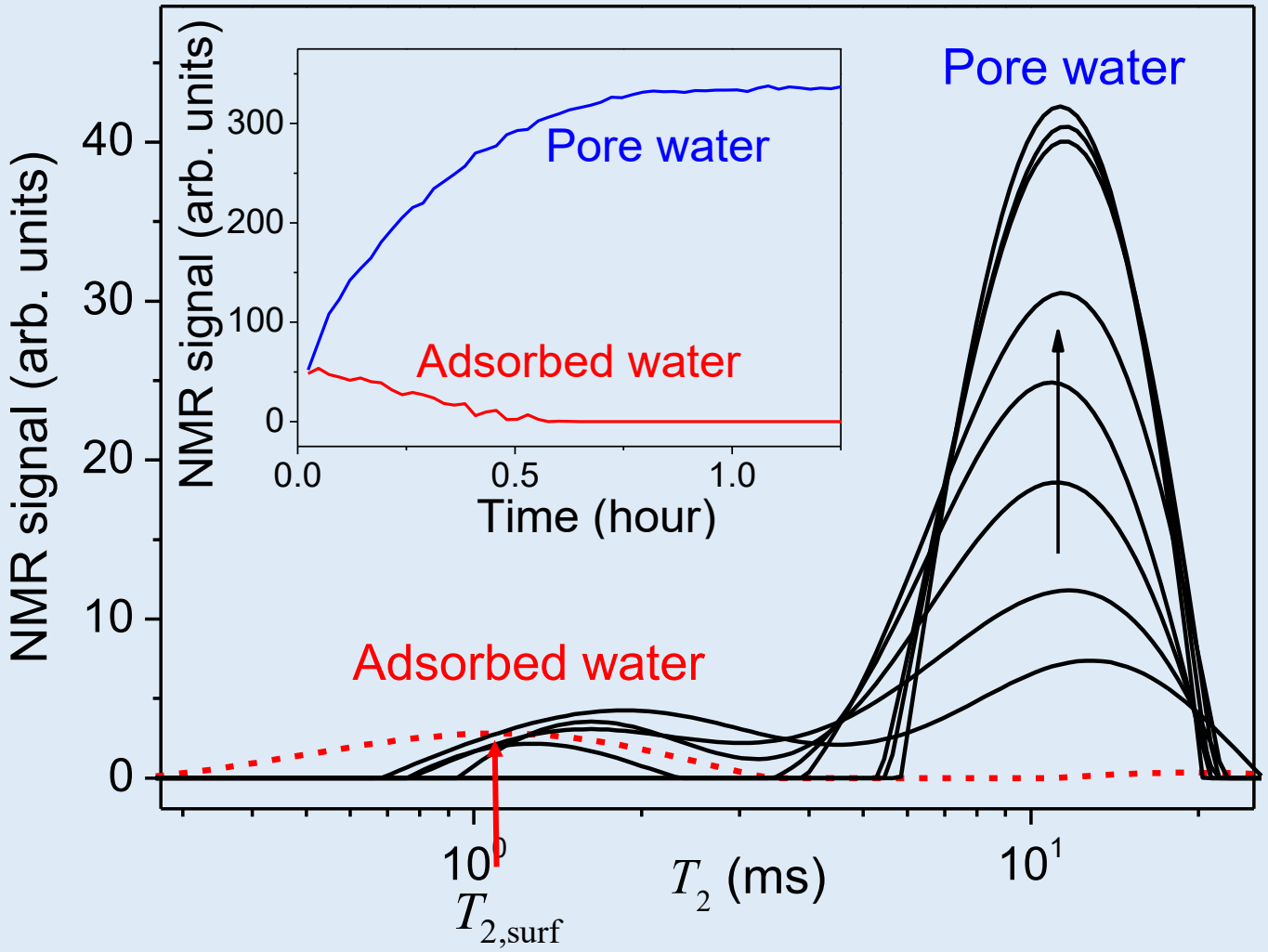
$$T_{2,\text{adsorbed water}} \approx T_{2,\text{surf}} \approx 1 \text{ ms} \quad \Rightarrow T_{2,\text{pore water}} \approx T_{2,\text{surf}} \frac{V}{bS} \approx 10 \text{ ms}$$

Rem.: The left peak does not appear with saturated medium because adsorbed water exchanges with pore water leading to the right peak

Imbibition in a nanoporous medium

Porous silica glass (Vycor)





Pore water signal growth with constant T_2

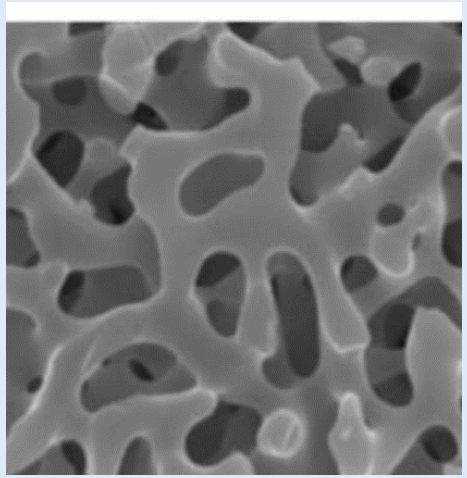
+ Similar rate of disappearance of adsorbed water

$\Rightarrow$ Progressive invasion of pores by saturating front

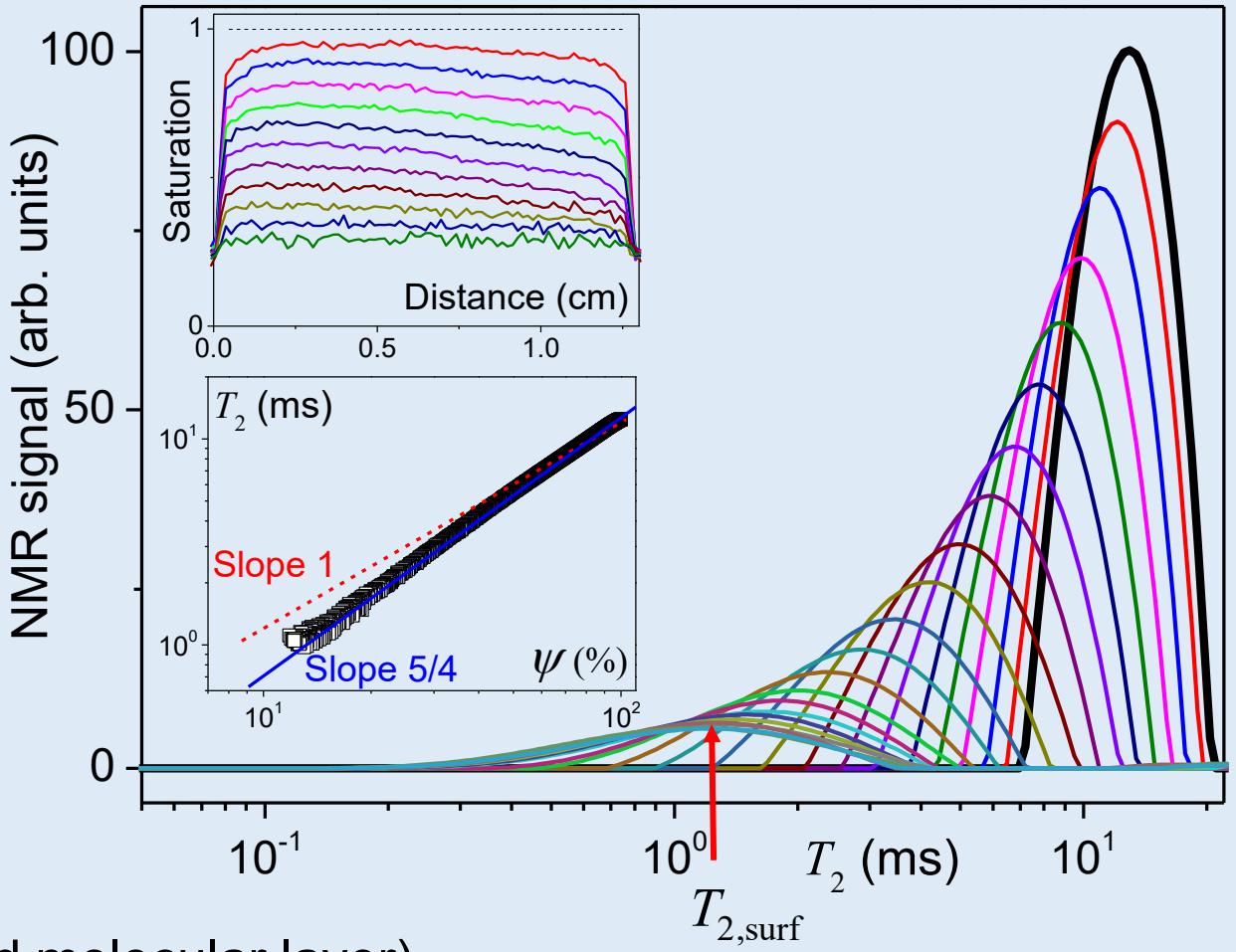
Maillet et al, *Phys. Rev. Appl.*, 2022

Drying of a nanoporous medium

Porous silica glass (Vycor)



10 nm



1) Back to initial state (adsorbed molecular layer)

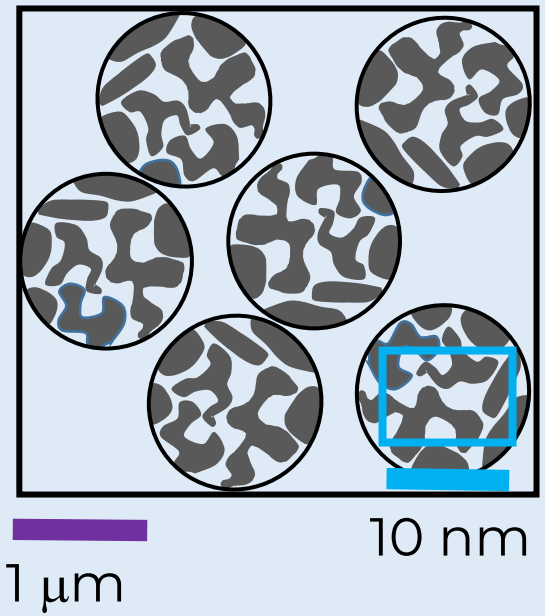
2) Homogeneous desaturation: T_2 decrease, no significant pdf spreading
Confirmed by uniform 1D MRI profiles

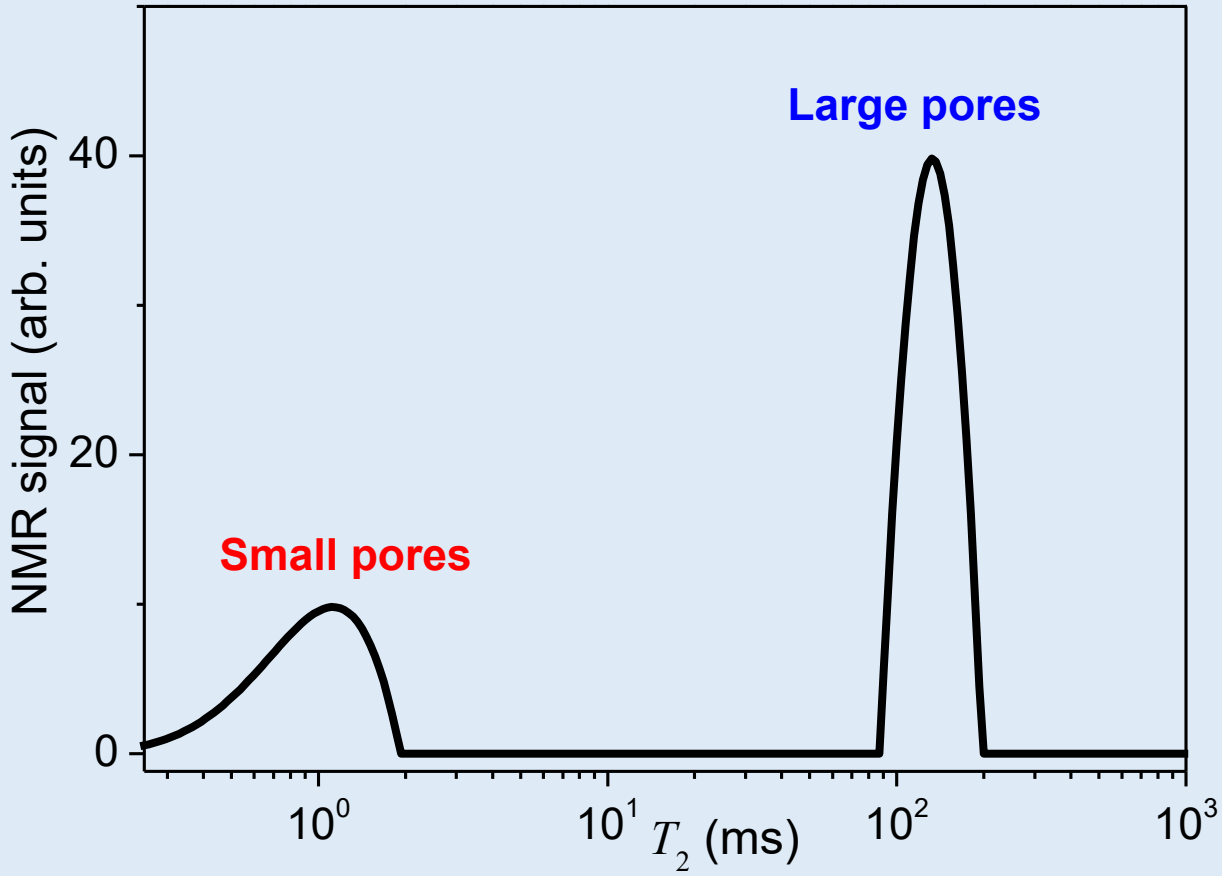
3) Desaturation without dewetting: $T_2 \propto \psi$

Maillet et al, *Phys. Rev. Appl.*, 2022

Two pore size medium

Porous silica bead packing



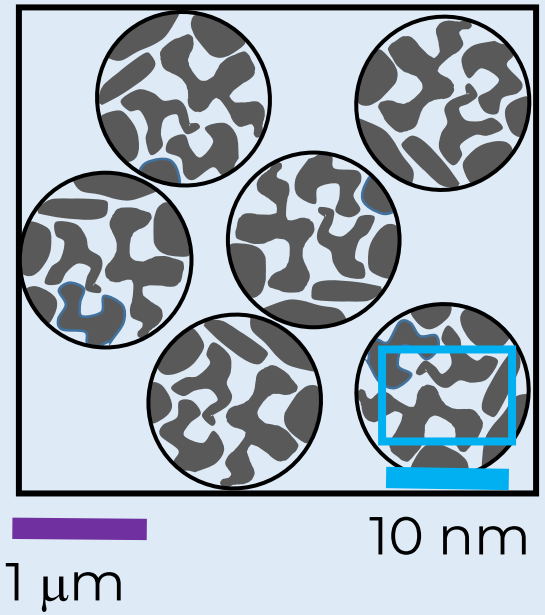


- No significant exchange between the two water populations
- Ratio of total NMR signal of each peak => Fractions of porosities
- Ratio of T_2 => Estimation of V/S for bead porosity (V/S is known for a simple bead packing)

Maillet et al, *Langmuir*, 2022

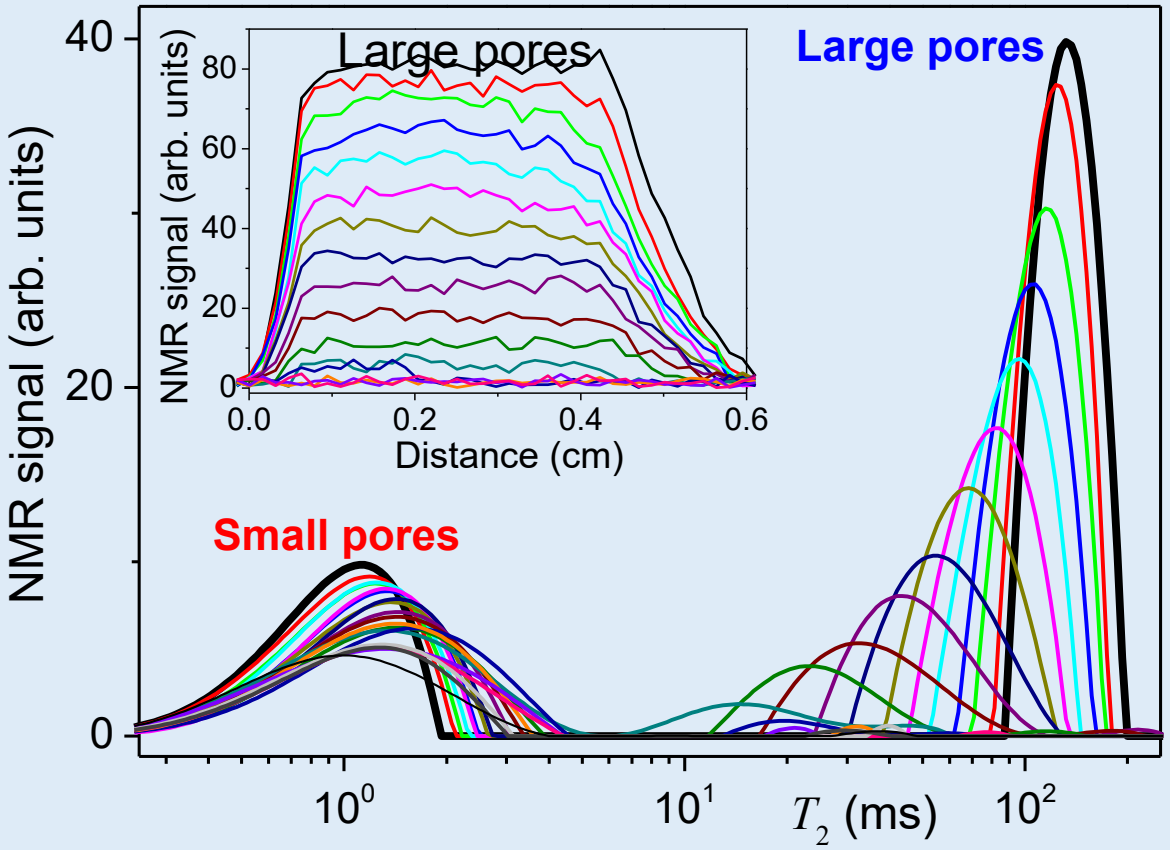
Drying of a two pore size medium

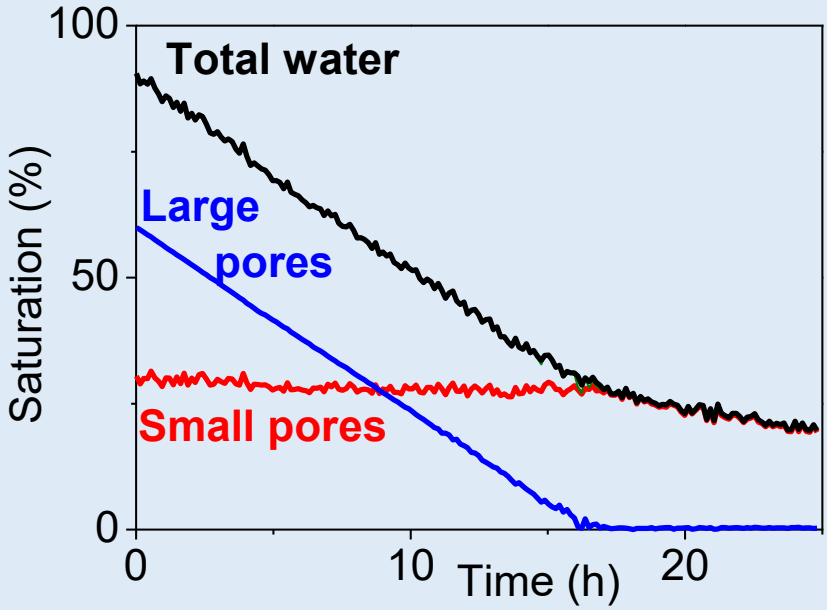
Porous bead packing



Silica beads

Initially saturated





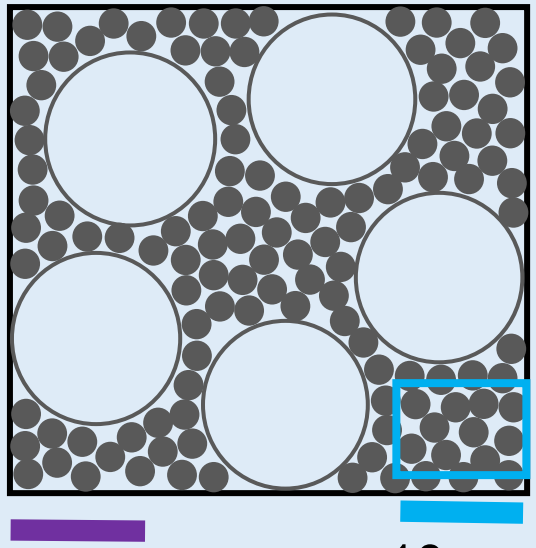
1) First, disappearance of liquid in large pores

2) Homogeneous desaturation: T_2 decrease, no significant pdf spreading
Confirmed by uniform 1D MRI profiles (only water in large pores imaged)

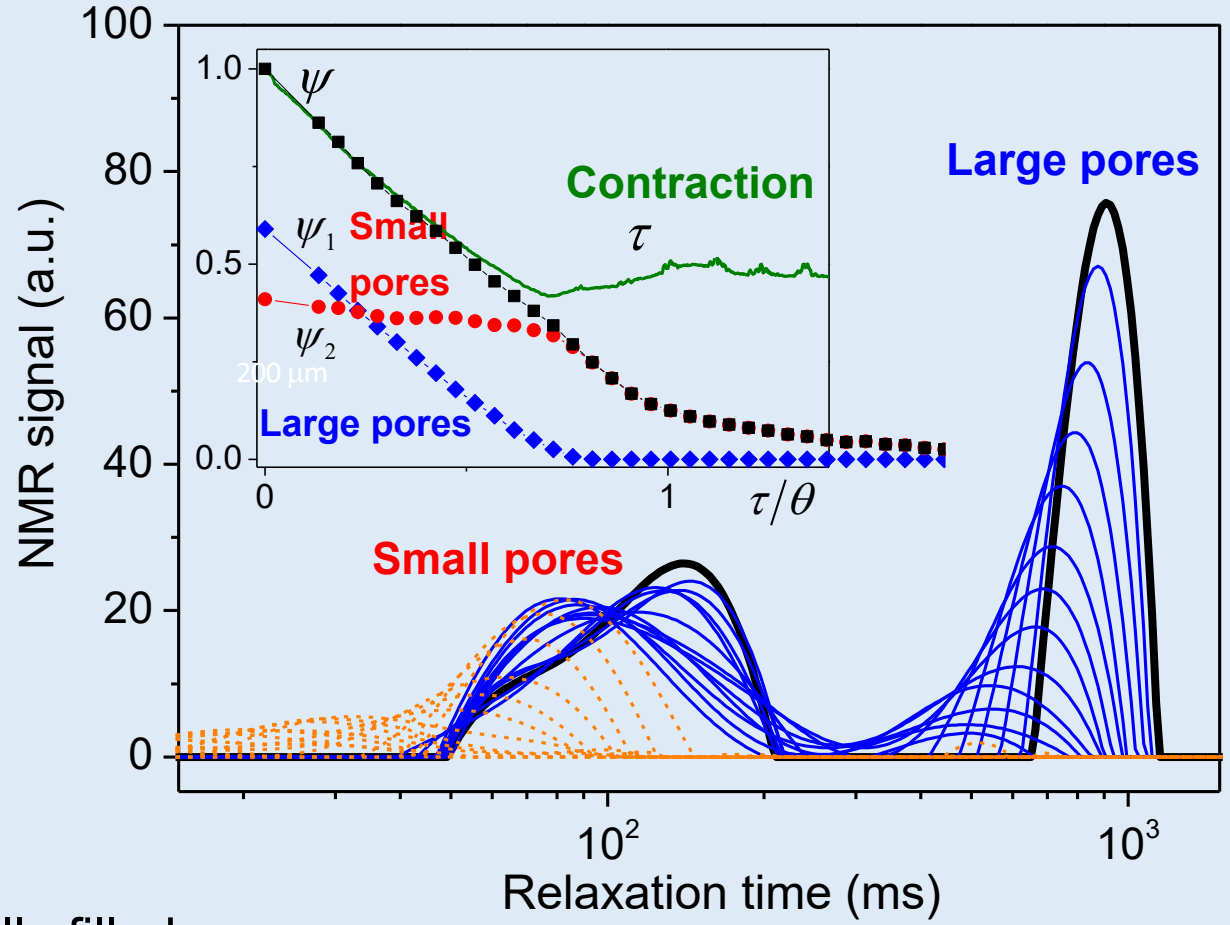
Maillet et al, *Langmuir*, 2022

Drying of a compressible biporous medium

Large pores/fine porous matrix



Salt inclusions in a matrix of polymers, reticulation followed by salt removal



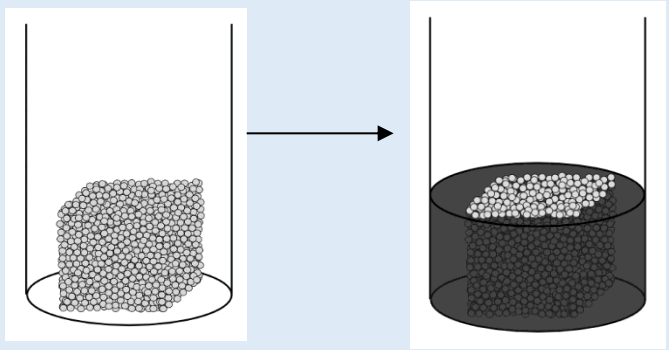
1) Two distinct T_2 : two pore sizes initially filled

2) Large pores desaturate first, homogeneously (limited pdf spreading), but by contraction

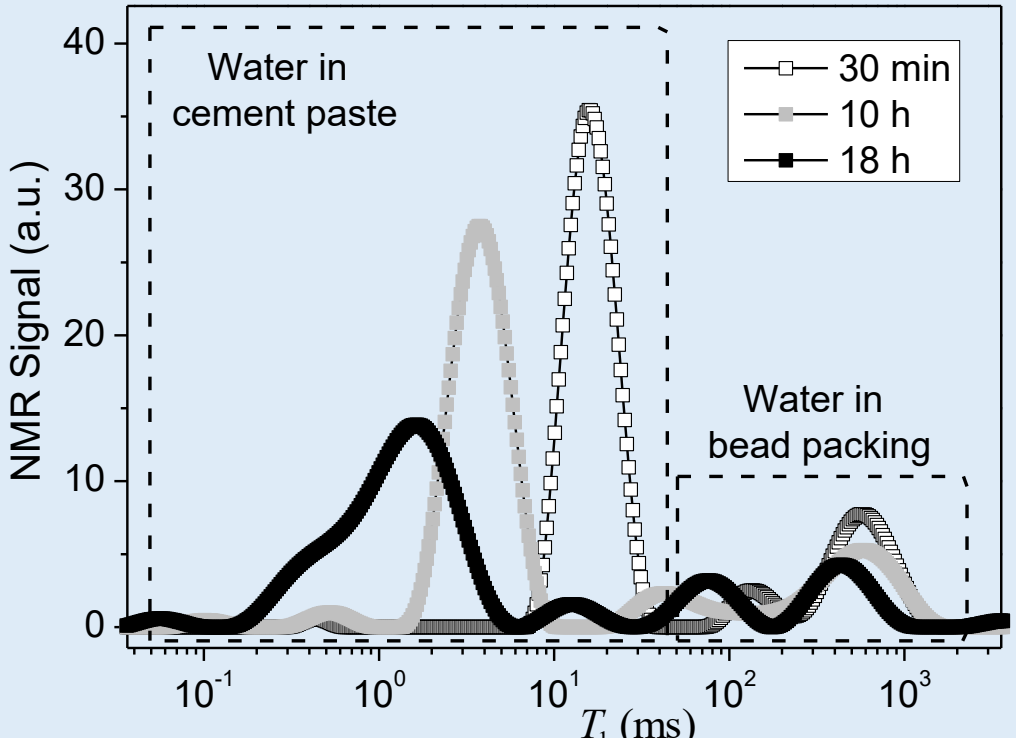
3) Small pores then desaturate homogeneously,
And maintain a constant drying rate for some time

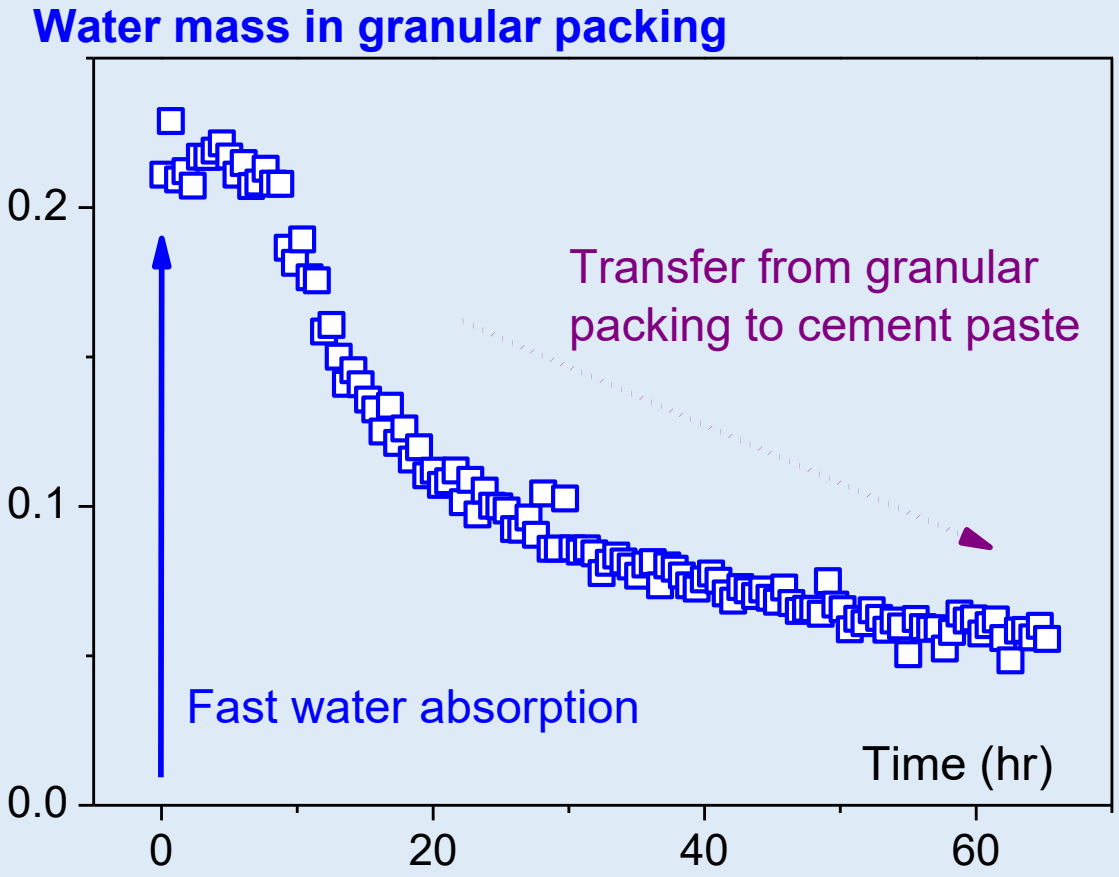
Lerouge et al, *Phys. Rev. Applied*, 2020

Transfers between a cement paste and a porous medium



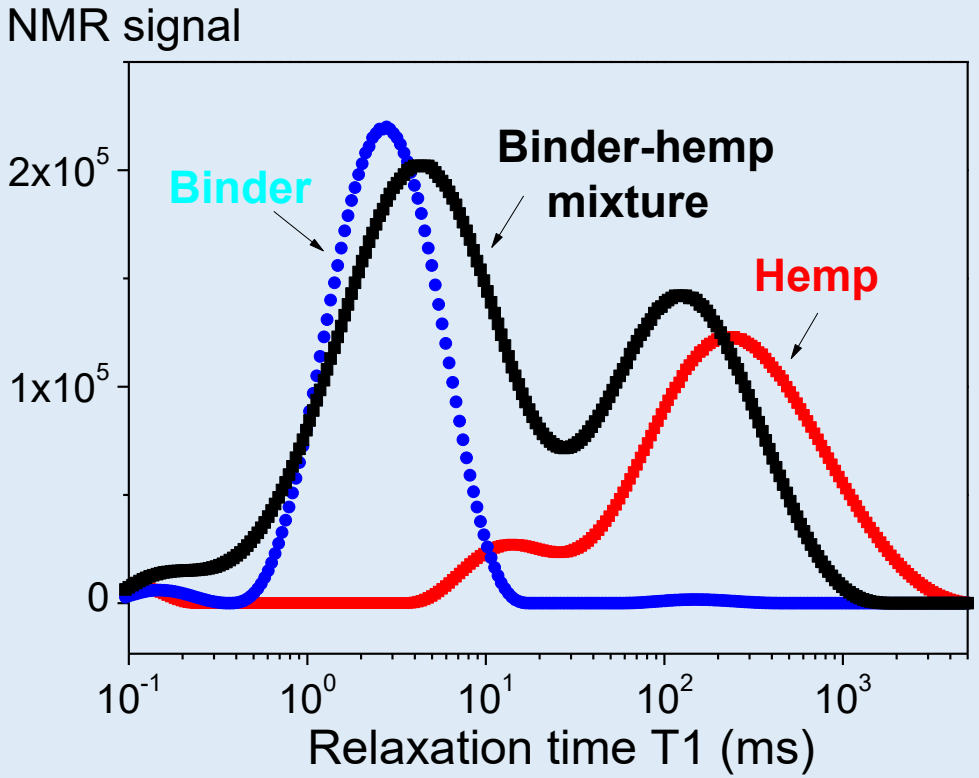
Sintered bead packing (180 μm)
+ pâte de ciment





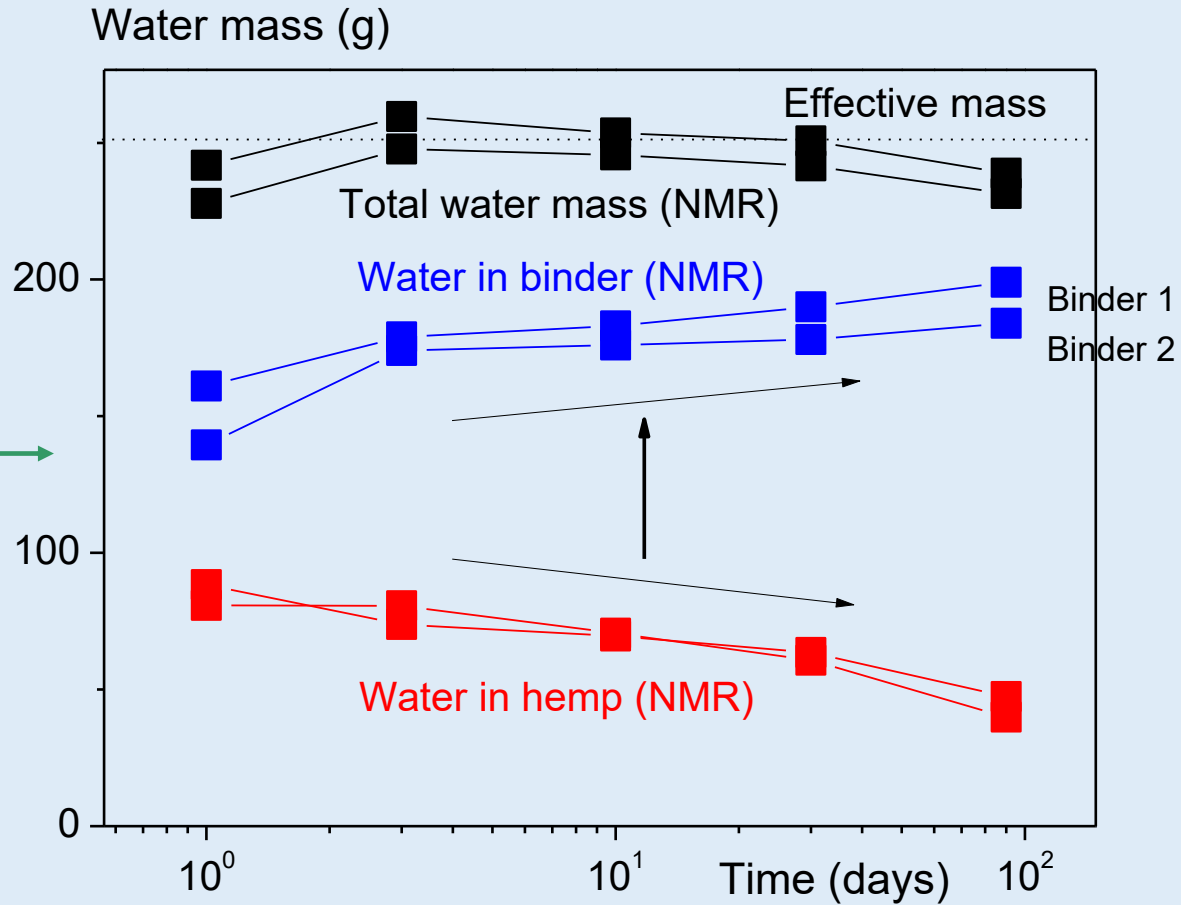
Fourmentin et al, *Cement and Concrete Research* (2016)

Transfer of water in hemp concrete





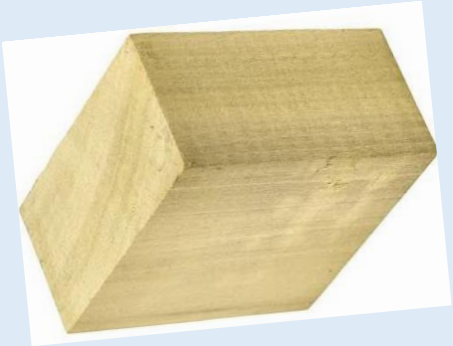
Evolution In time



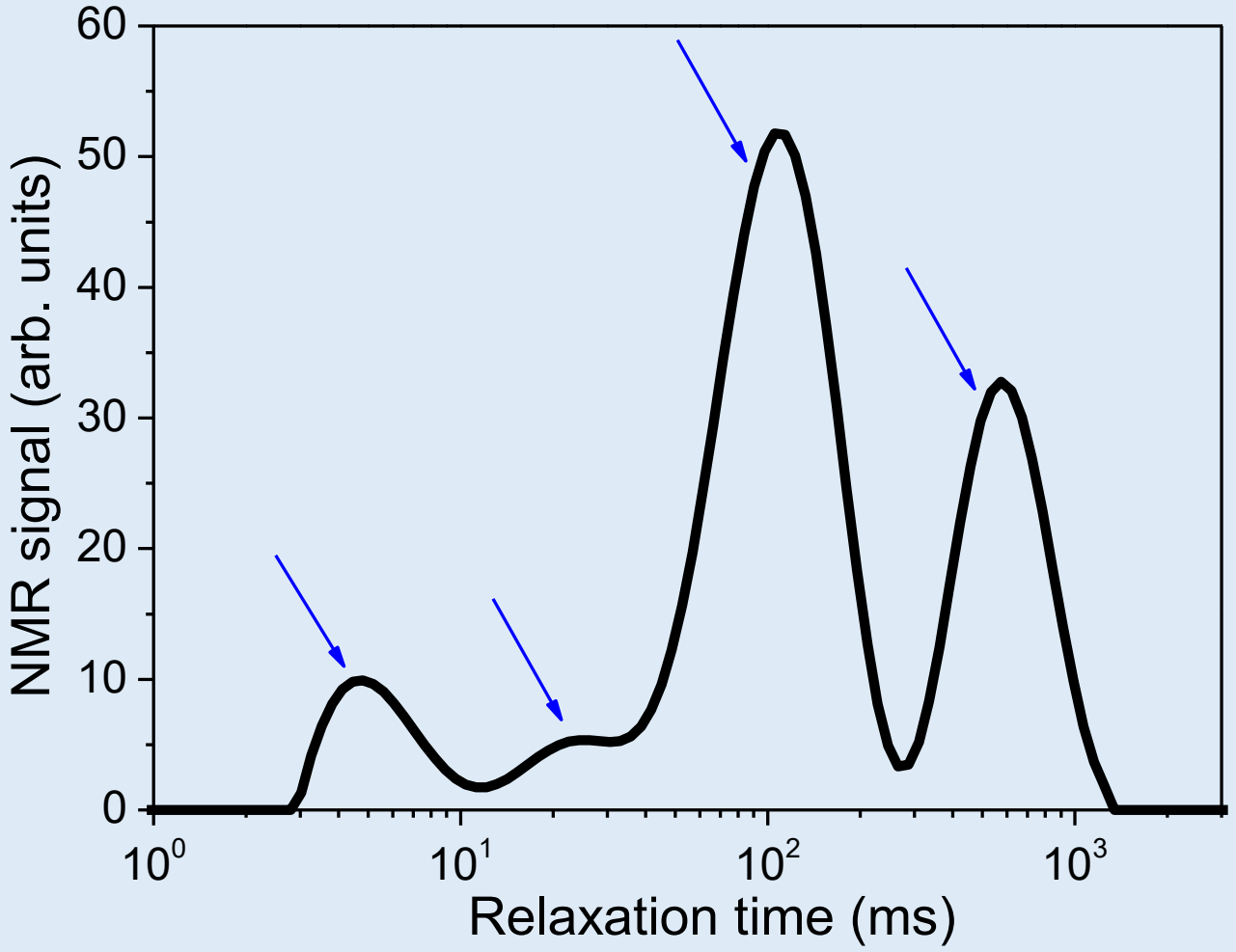
Faure et al., *CCR*, 2012

NMR relaxometry of water saturated poplar sample





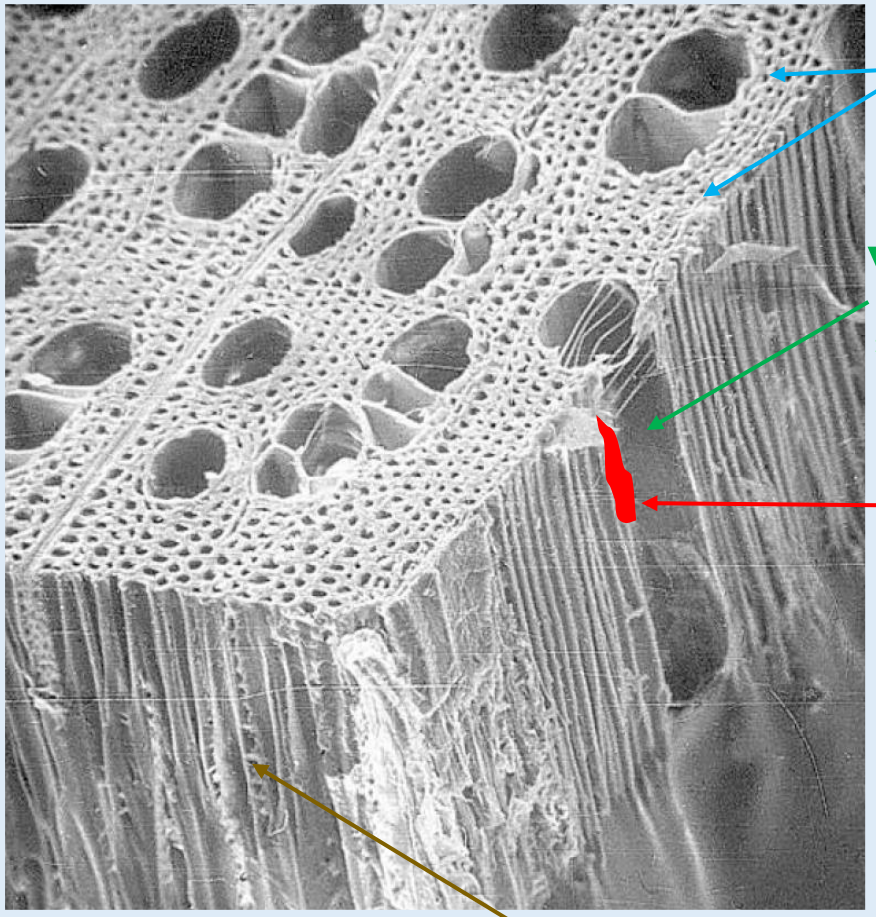
Immersed in water
for several days

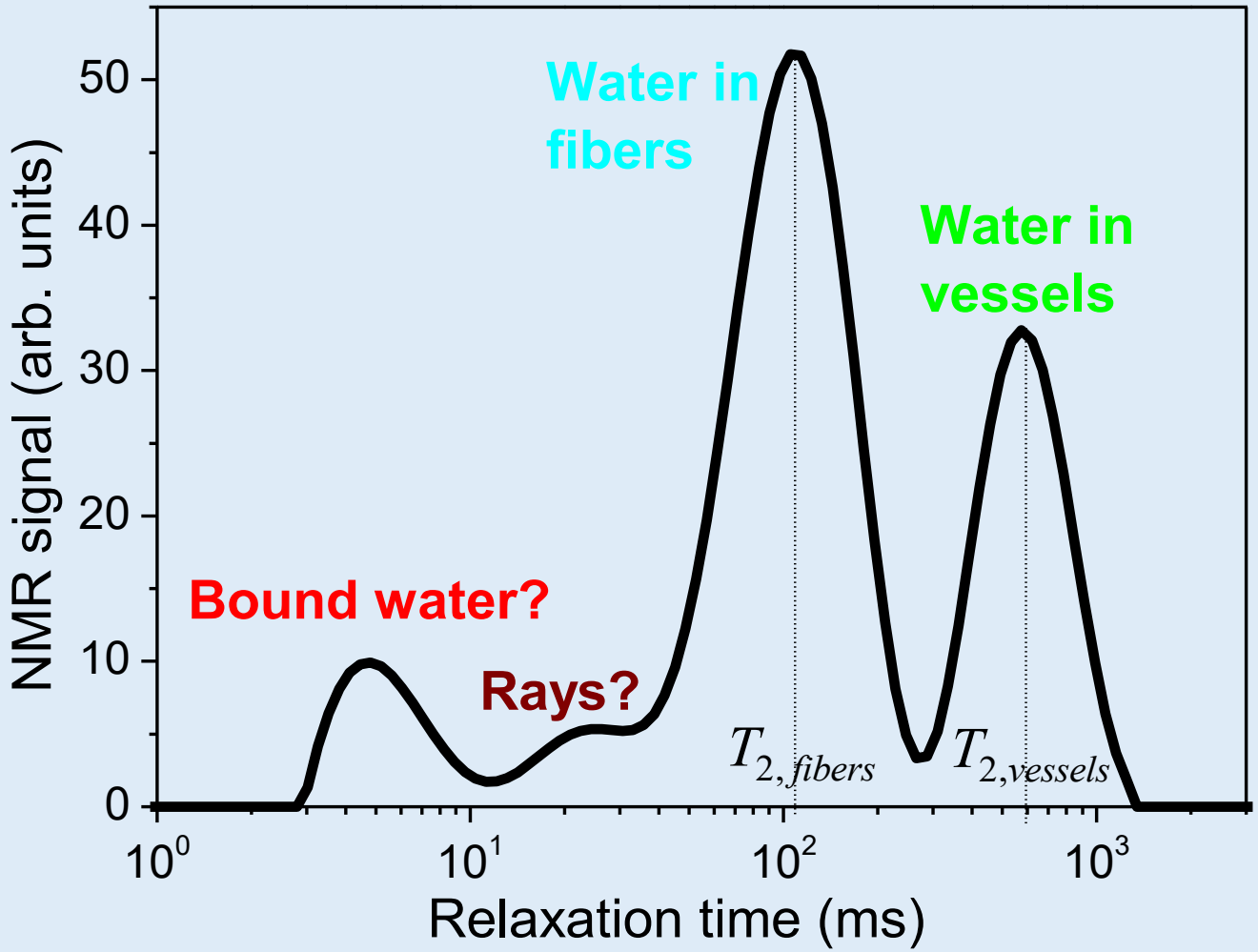


- At least four water populations
- With poor exchanges (tiny or no connections)
- In a wide range of states (pore size?)

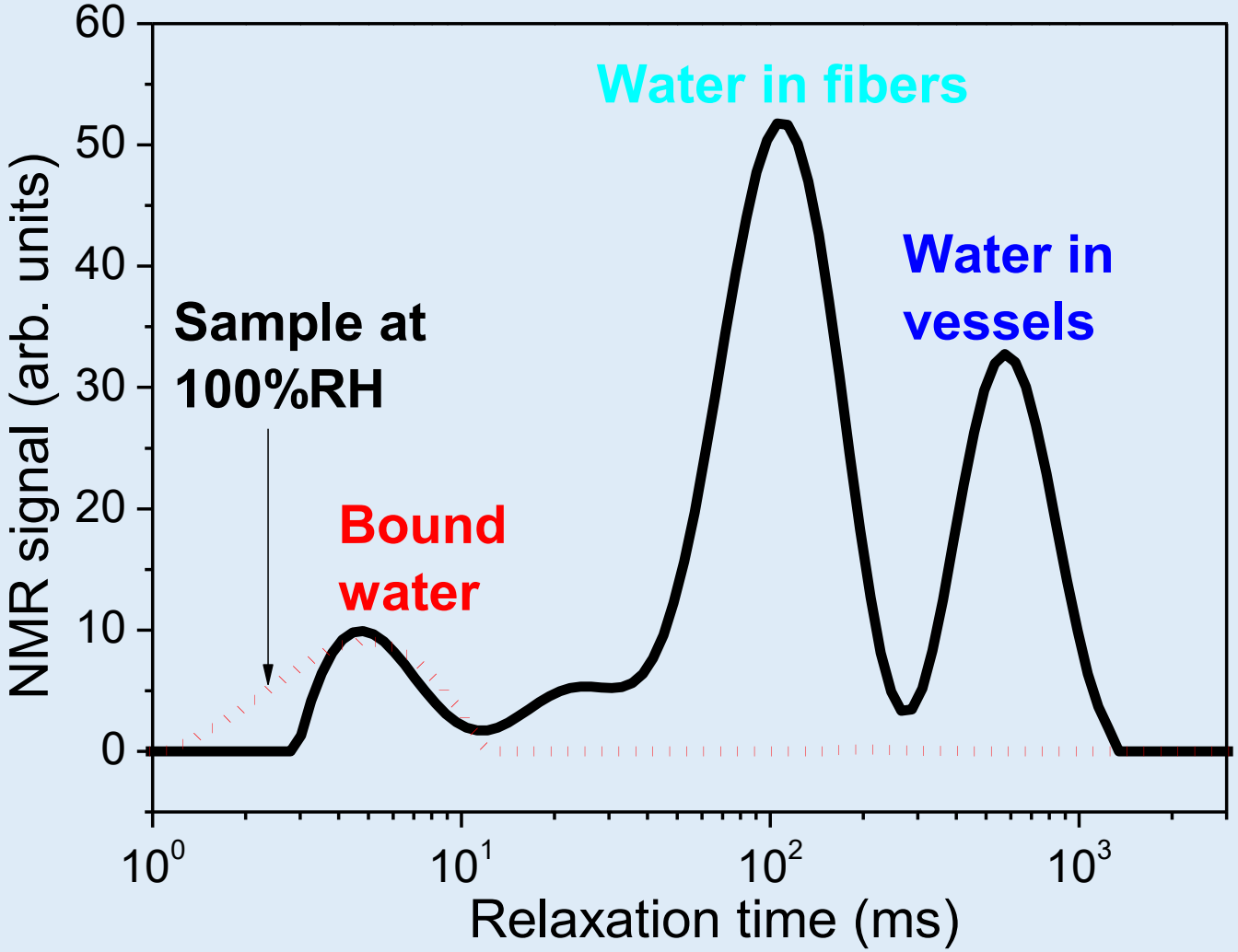
NMR relaxometry of water saturated poplar sample

Poplar structure





(For cylinders) $T_{2,fibers}(\approx 100\ \text{ms}) \approx \frac{T_{2,\text{surf}}}{b}\frac{V}{S} \approx \frac{T_{2,\text{surf}}}{b}\frac{r}{2} \Rightarrow \frac{1}{T_{2,vessels}} = \frac{1}{T_{2,\text{bulk}}} + \frac{1}{T_{2,\text{fibers}}}\frac{r}{R} \approx 700\ \text{ms}$



- Left peak = water molecules without exchange with liquid water in pores

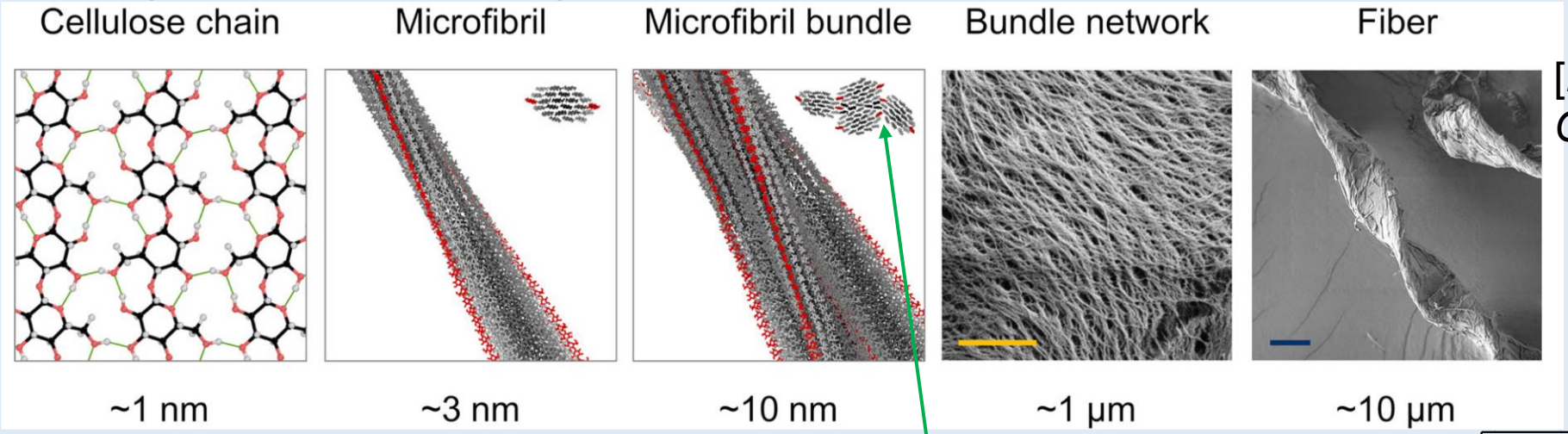
⇒ Not along solid surfaces of fibers, rays or vessels

⇒ Absorbed in the solid phase

Bound water in cellulose fiber structure

Cristalline organization

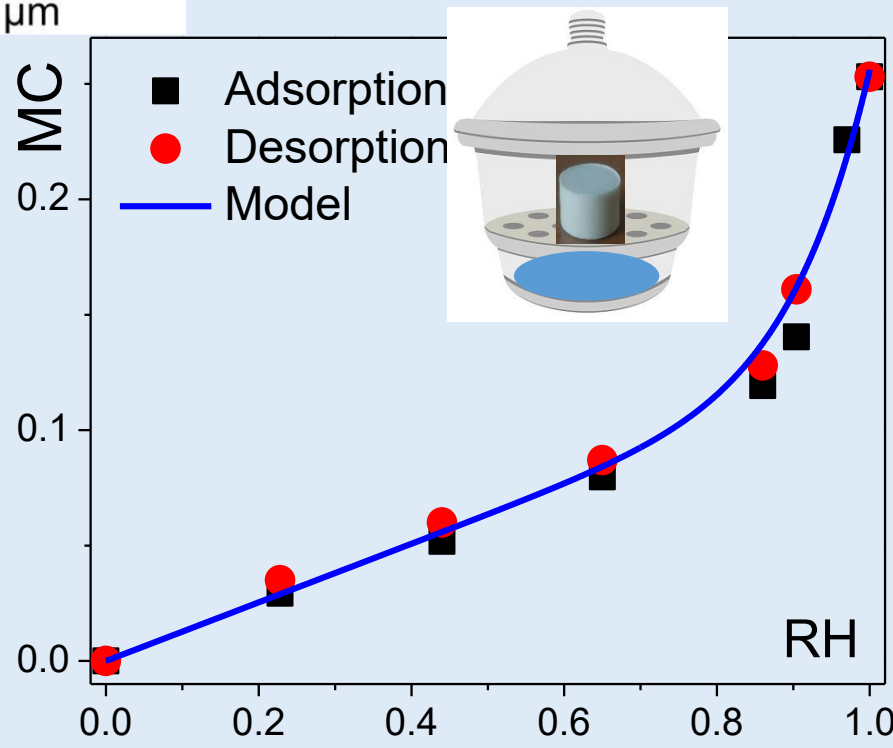
« Amorphous regions » between microfibrils



[*Paajanen et al, Cellulose, 2019*]

Relative Humidity >0 => **Bound water**

up to MC=30% !



At the origin of swelling

Sorption curve

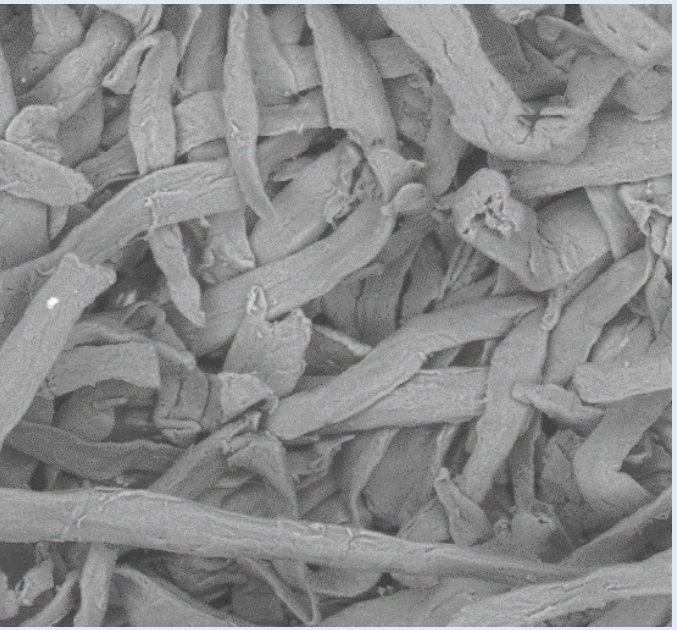
$$\mathrm{MC} = f(\mathrm{RH})$$

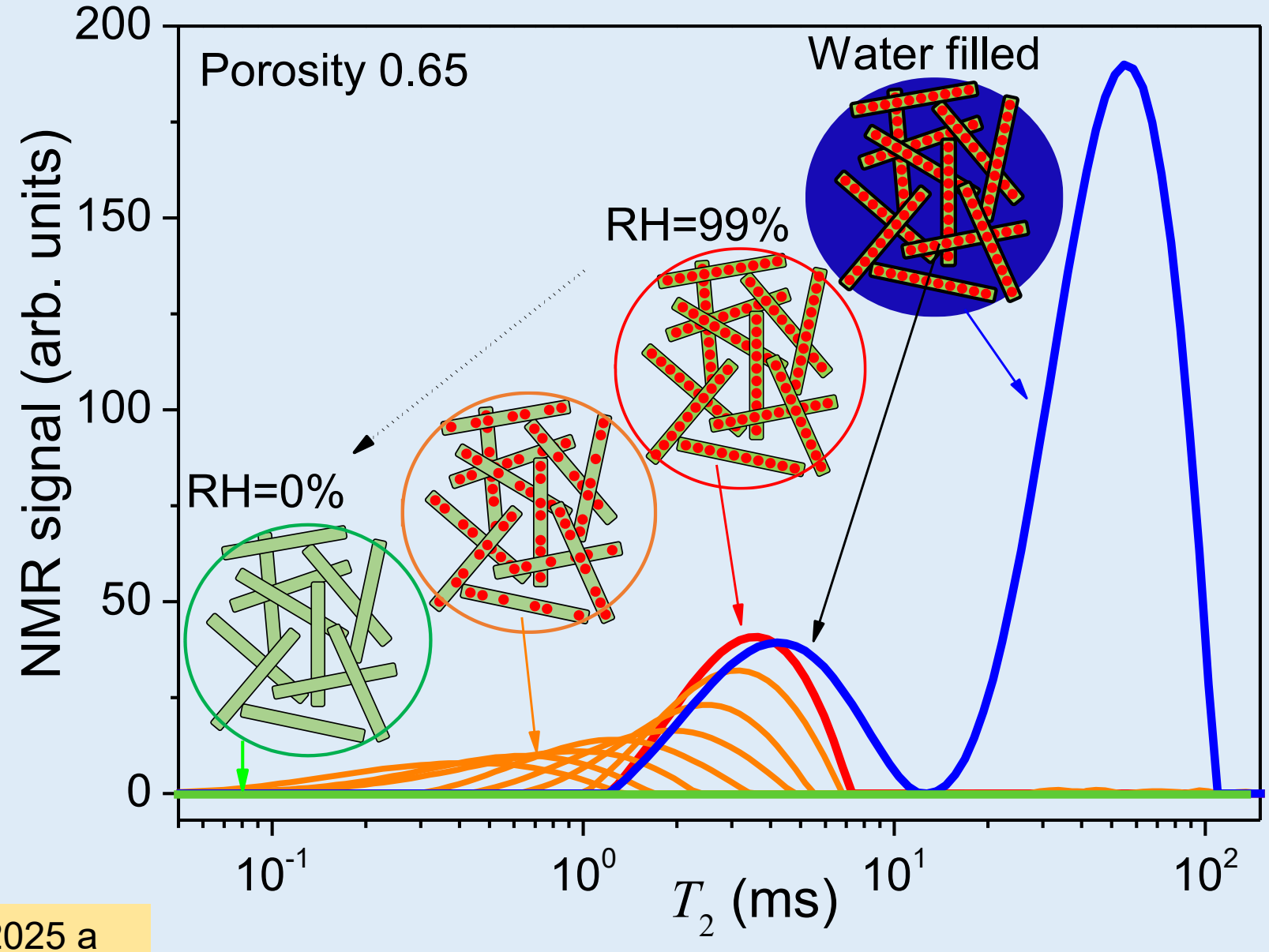
at equilibrium

Moisture Content:

MC=water mass inside sample/ dry sample mass

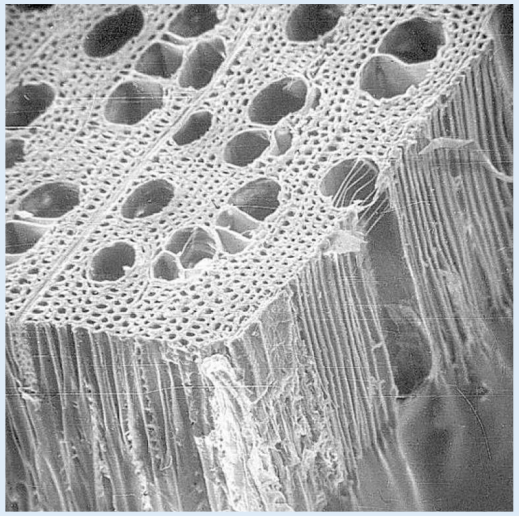
NMR relaxometry of cellulose fiber stack under different hygric conditions

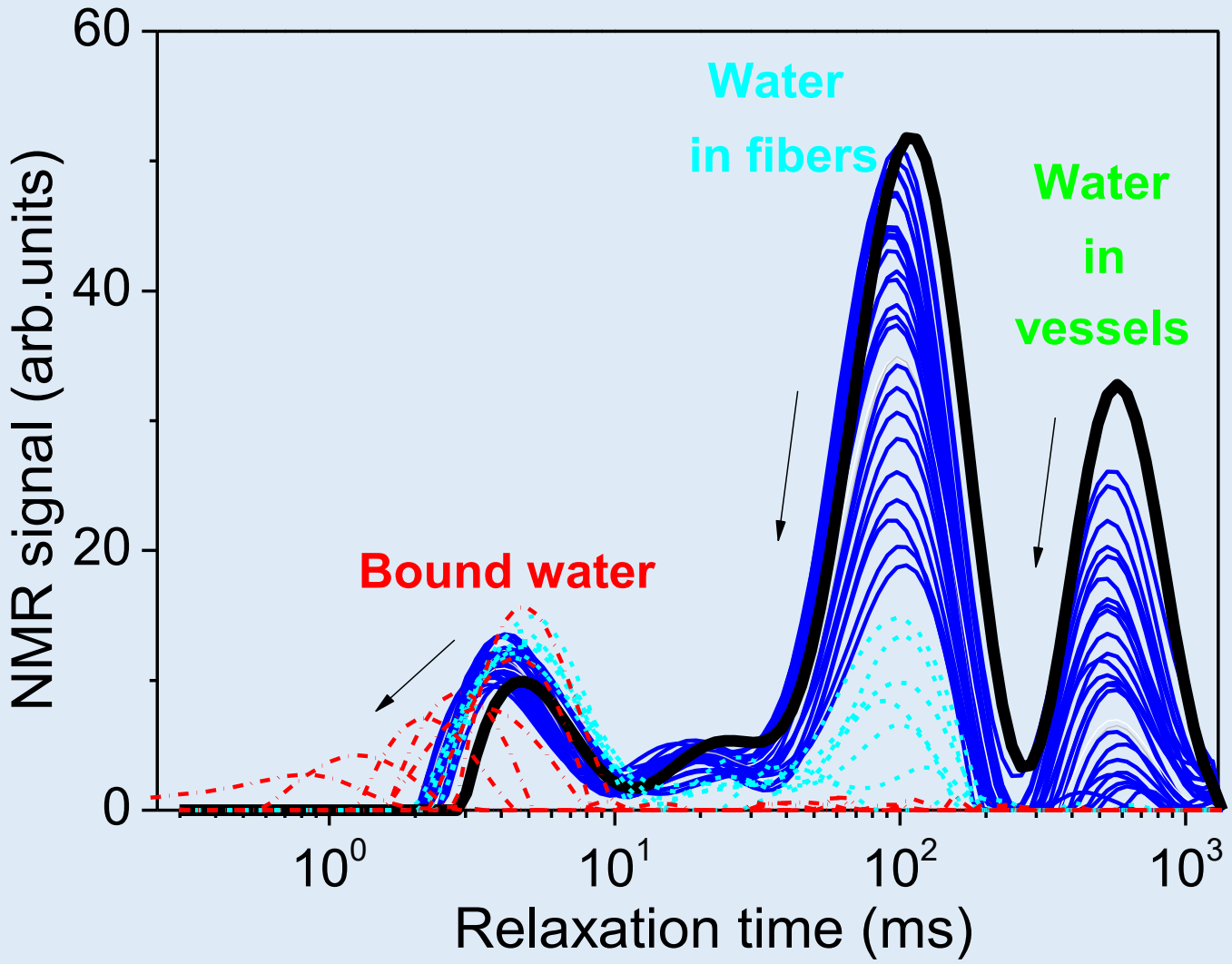




Yan et al, *Physical Review Applied*, 2025 a

NMR relaxometry of a drying poplar sample (initially saturated)



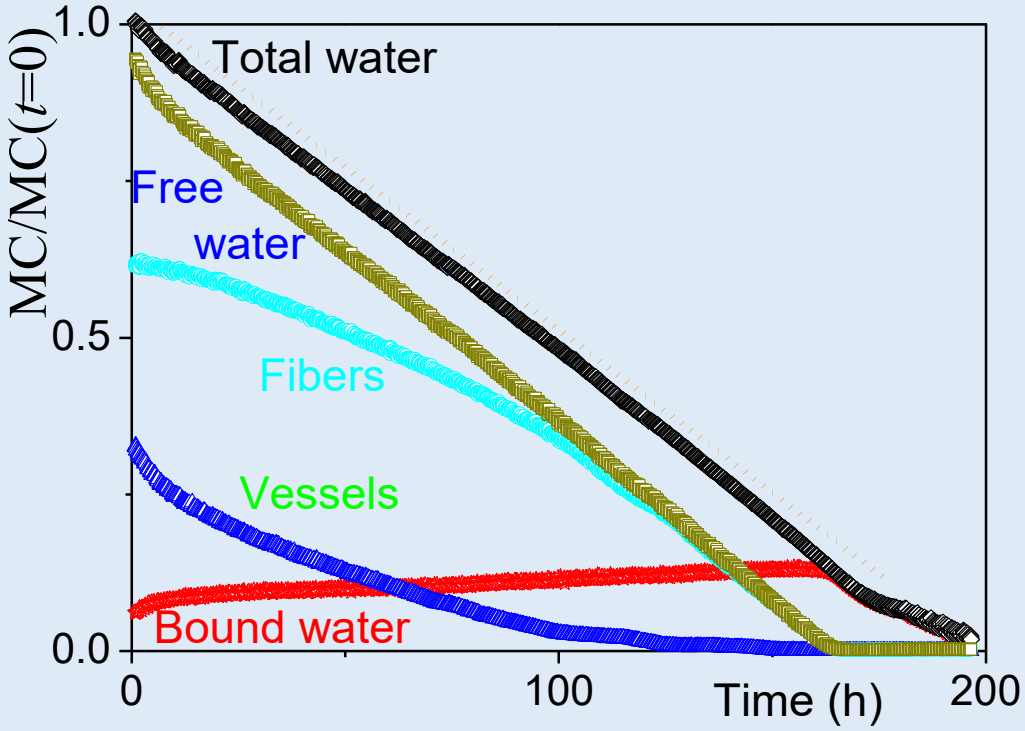


Progressive disappearance of peaks: water extraction

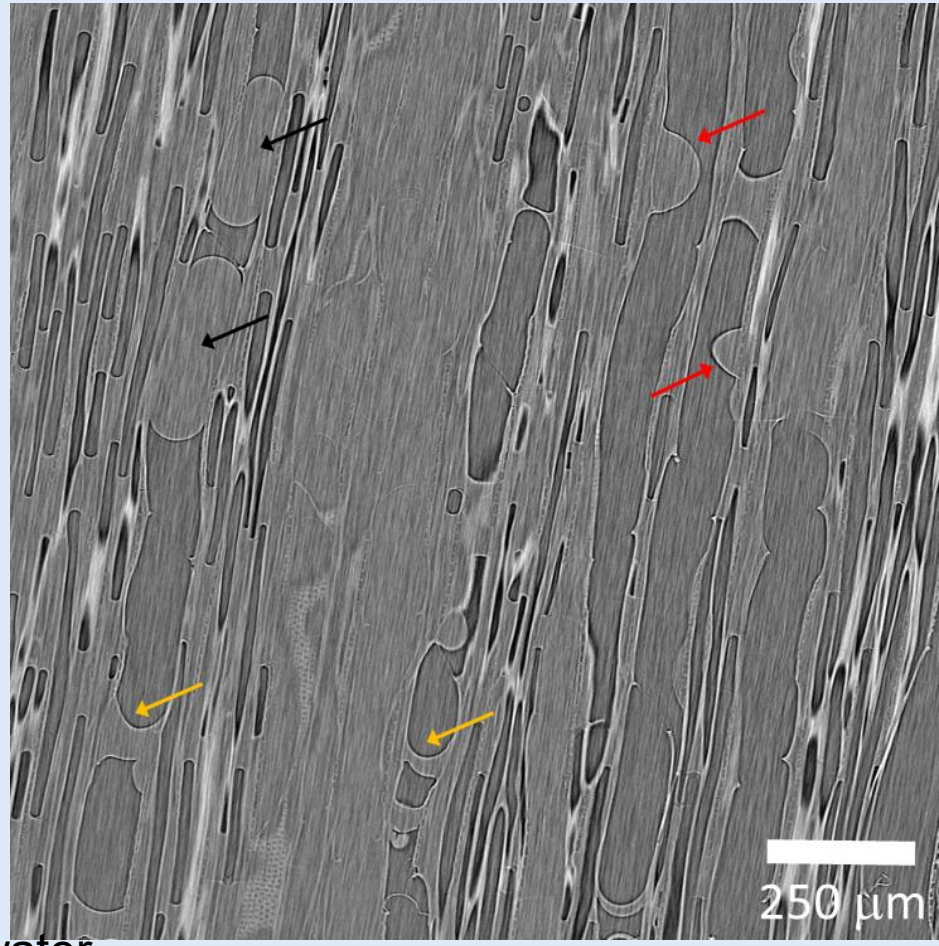
Penvern et al, *Phys. Rev. Applied*, 2020

NMR relaxometry of a drying poplar sample (initially saturated)

Integral of pdf over the ranges of T2 associated with each water state (in water fraction):



Synchrotron images

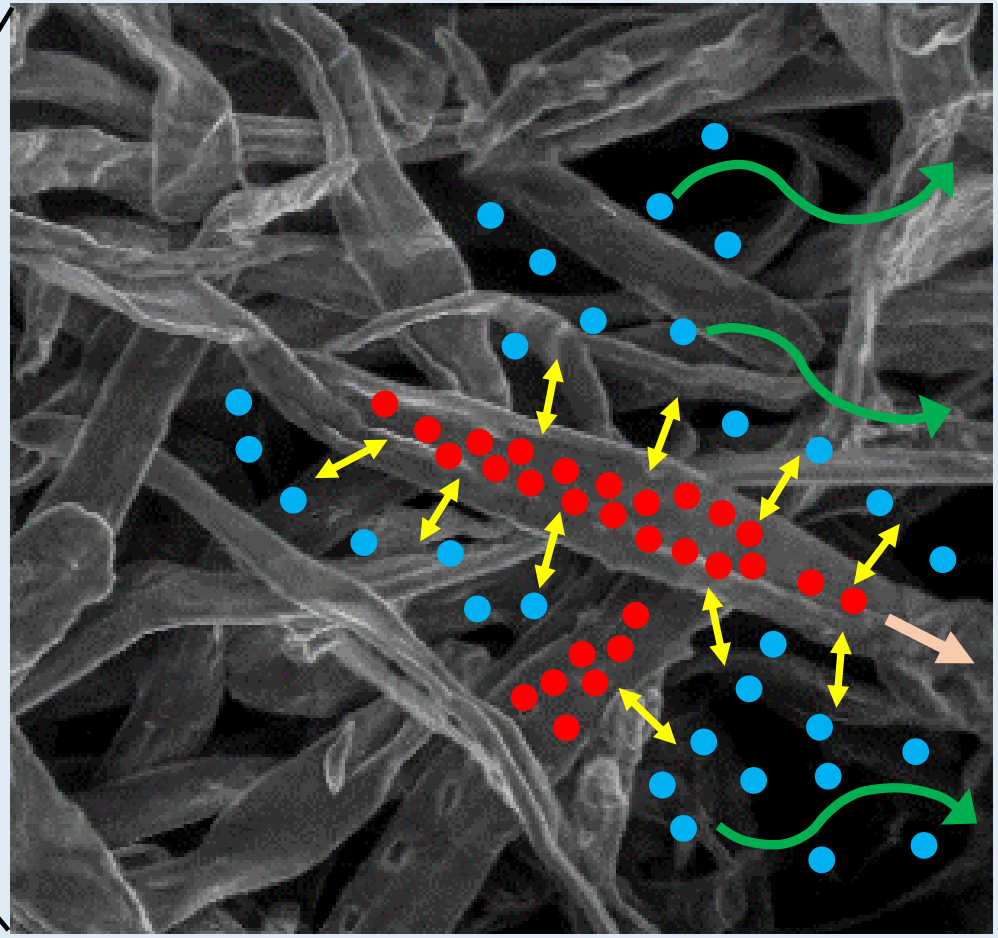


- Bound water fraction remains constant until no more free water (Bound water increase: artefact, resulting from the (neighbouring) fiber peak decrease)
- Fiber and vessel peak remain constant => dewetting (V/S constant) (confirmed by Synchrotron pictures) => no liquid flow towards free surface
- Almost constant drying rate over complete drying => bound water controls the drying, by absorbing then transporting, as bound water, the initially free water

Penvern et al, *Phys. Rev. Applied*, 2020

Water transport in a cellulose fiber stack (hygroscopic conditions)





Water vapor molecule

Bound water molecule

Sorption or desorption

Vapor or

Bound water diffusion

Bound water diffusion through solid network:

D_b

Vapor diffusion through the porous network:

D_v

Exchange:

$F_{exchange}$?

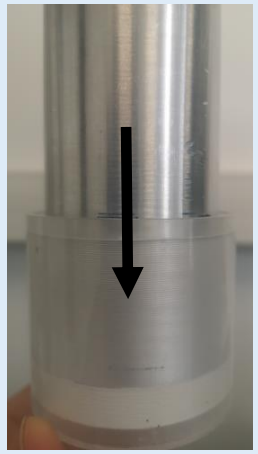
Ma et al, *Phys. Rev. Applied*, 202

Bound water diffusion in a cellulose fiber stack

Cellulose fibers (strips)

300 μm x 10 μm x 1 μm

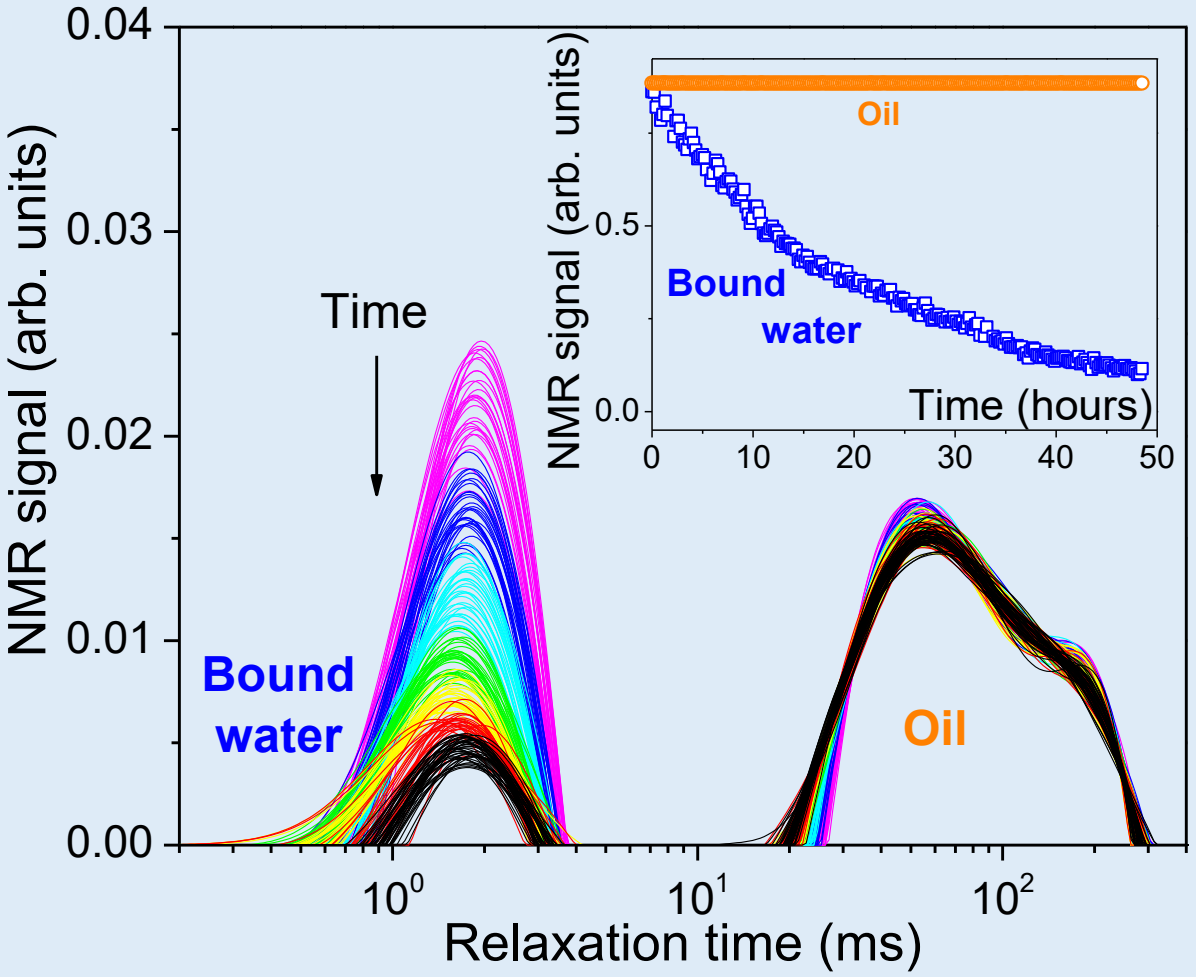




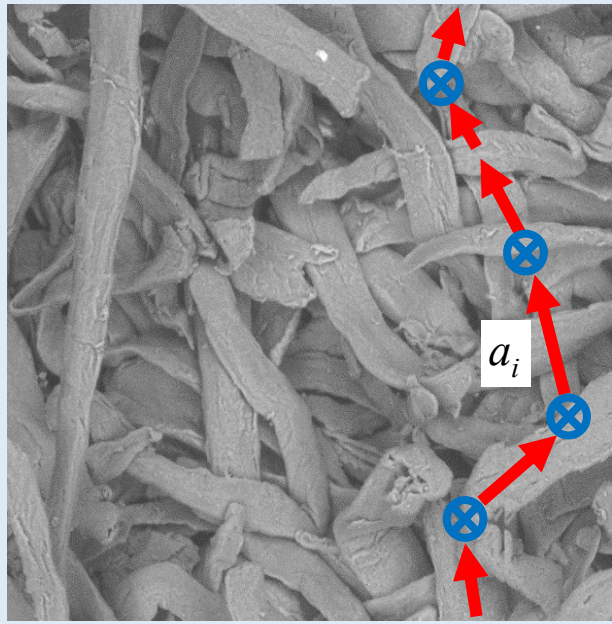
$0.2 < \varepsilon < 0.8$



Filled with oil



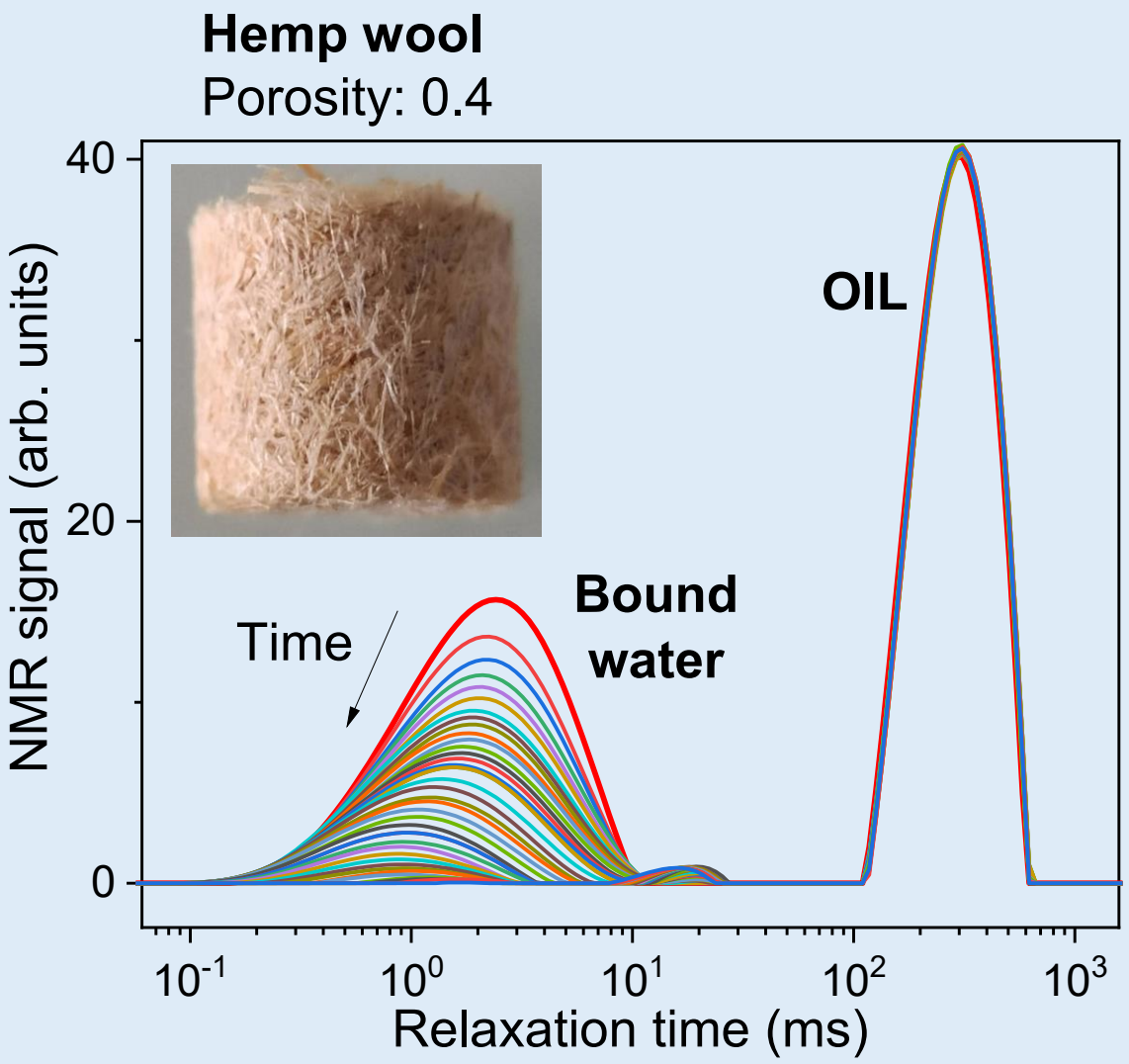
⇒ **Diffusion along fiber axis**

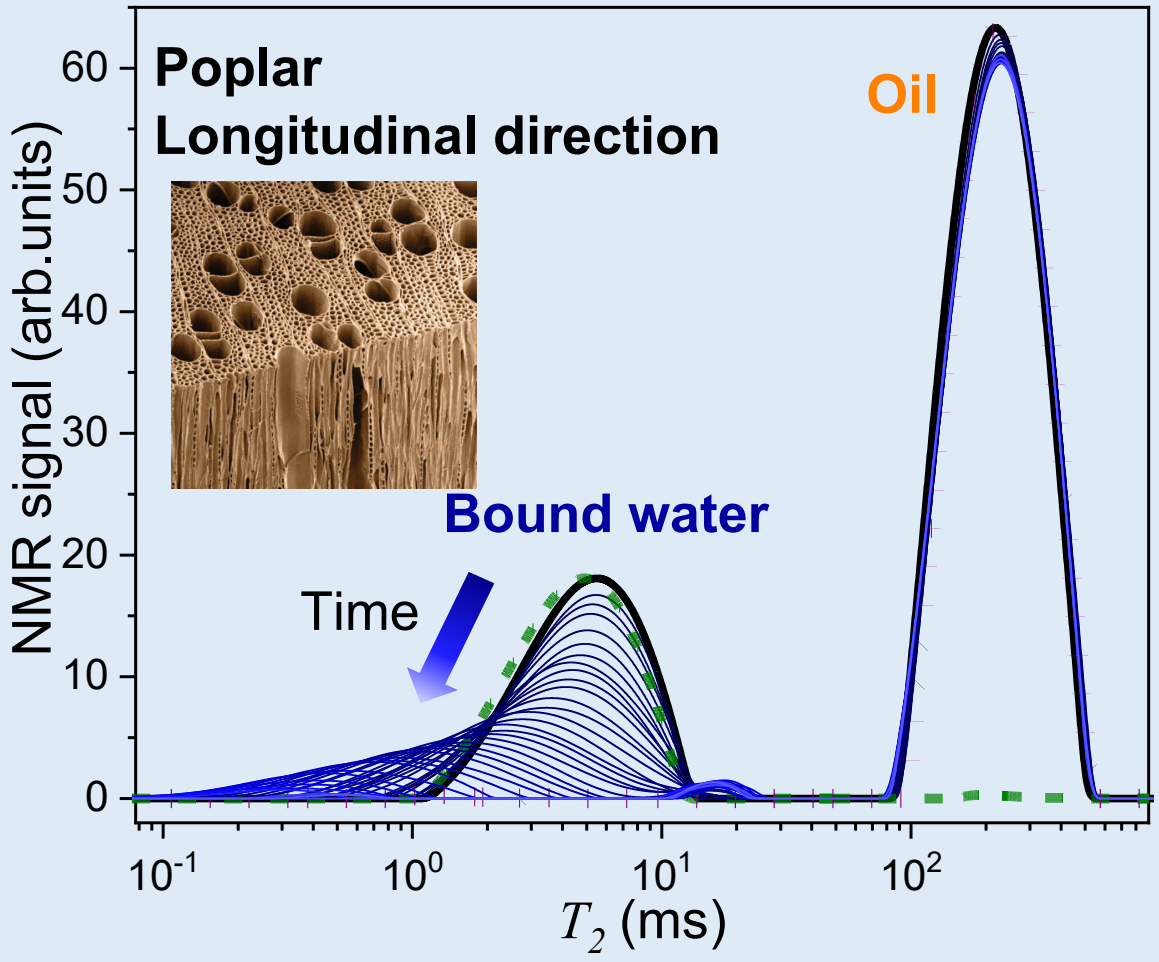


50 mm

Zou et al, *Cellulose*, 2023

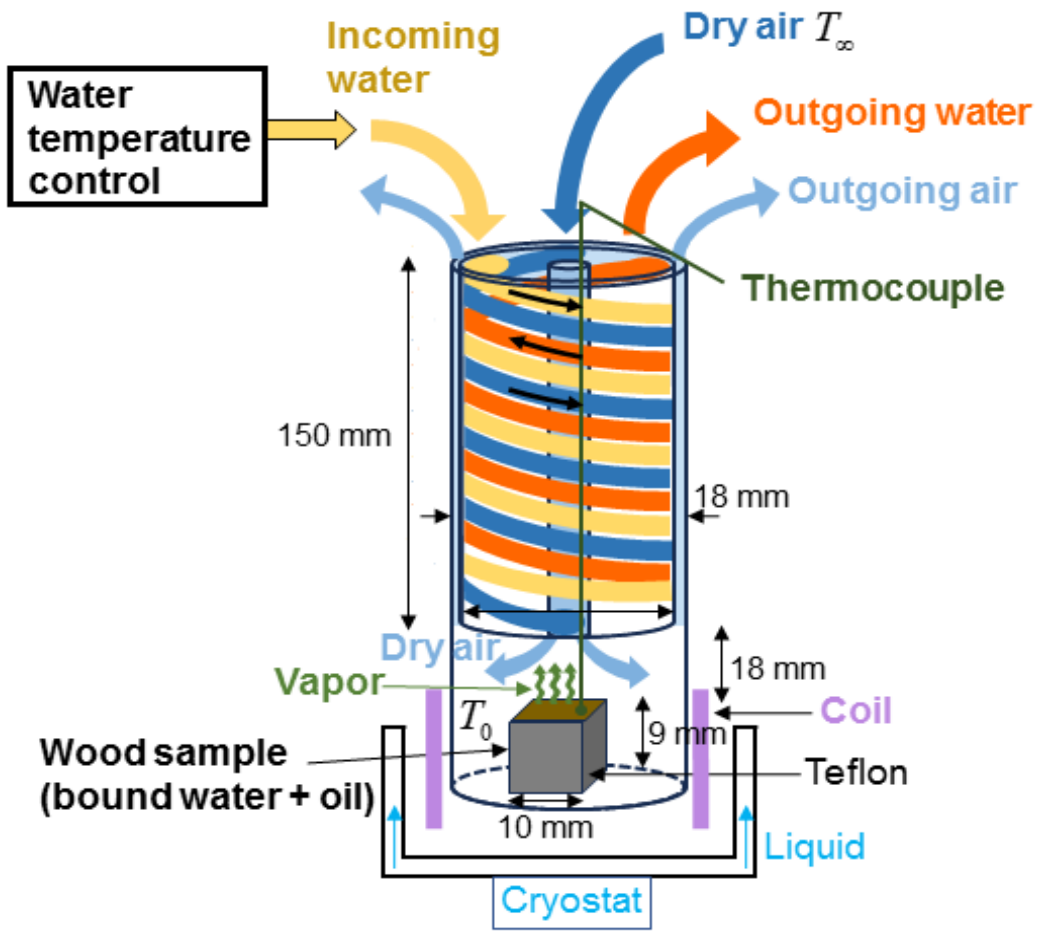
Bound water diffusion in other fiber stacks or wood filled with oil

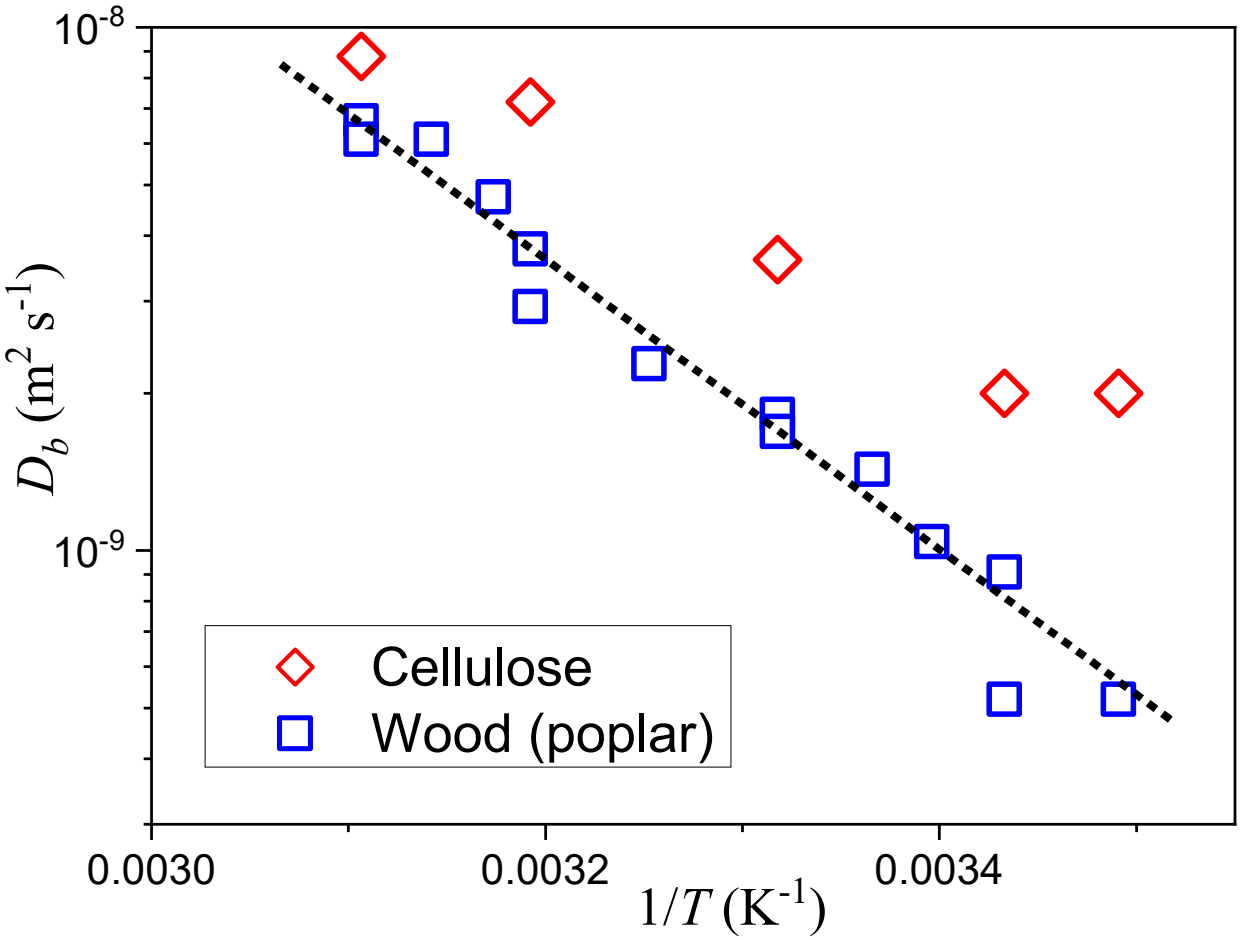




Yan et al, *Physical Review Applied*,

Bound water diffusion in wood or cellulose: impact of temperature





$$D_b = D_\infty \exp -\left(w/(k_B T)\right)$$

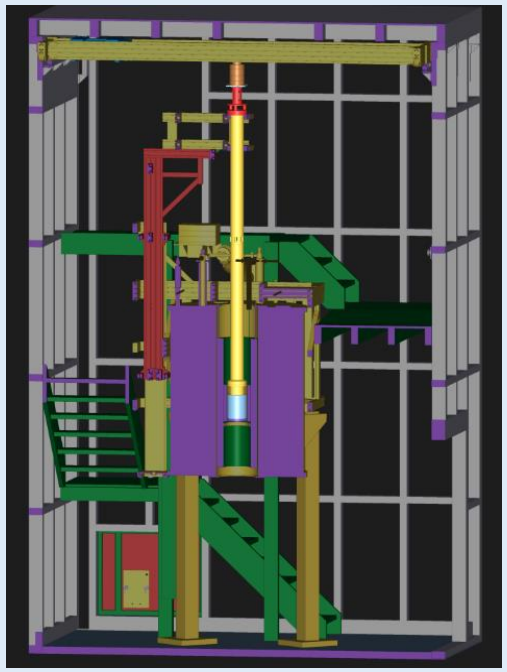
w=53 kJ mol^{-1}

→ Latent heat$_{water}$ = 45 kJ mol^{-1}

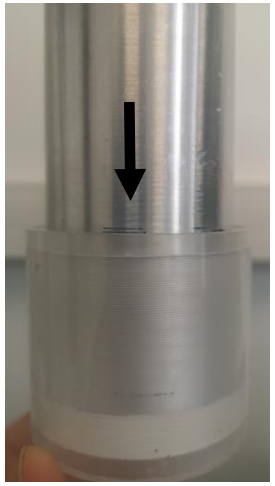
Yan et al, *Physical Review Applied*, 2025 b

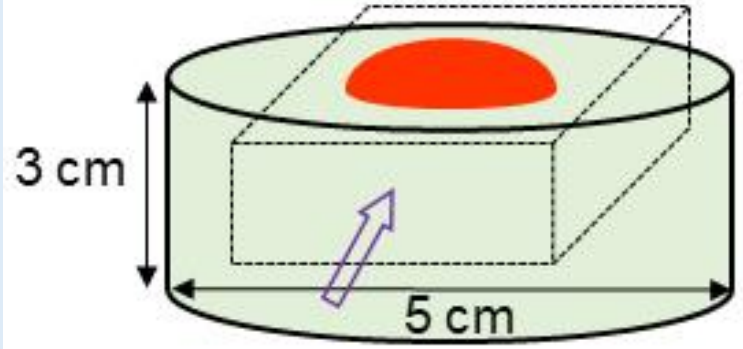
Magnetic resonance imaging of a water droplet in cellulose fiber stack

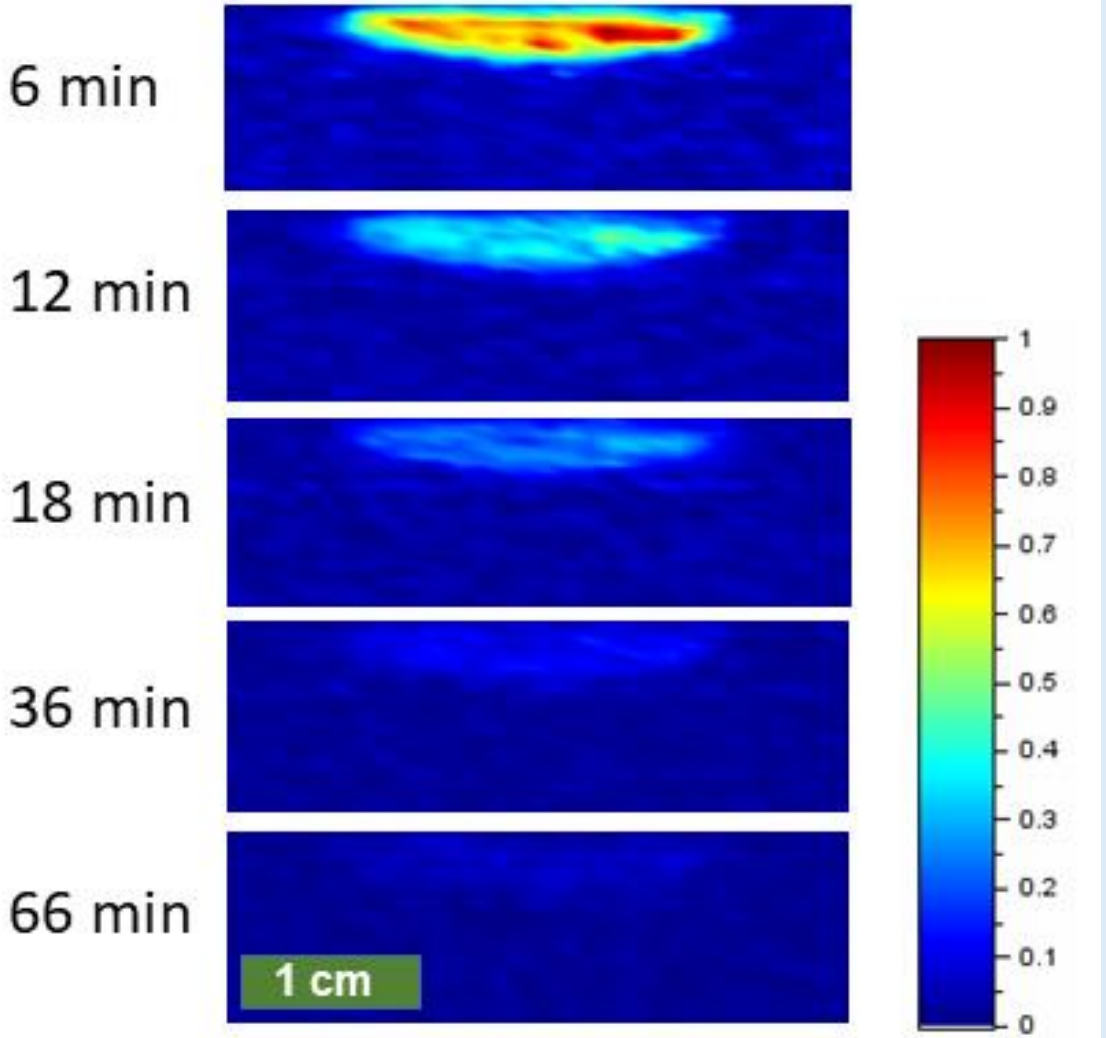
(Only free water imaged)







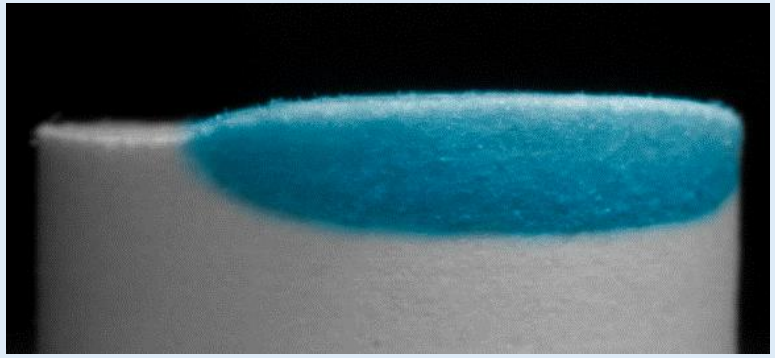




In a closed container
=> No drying

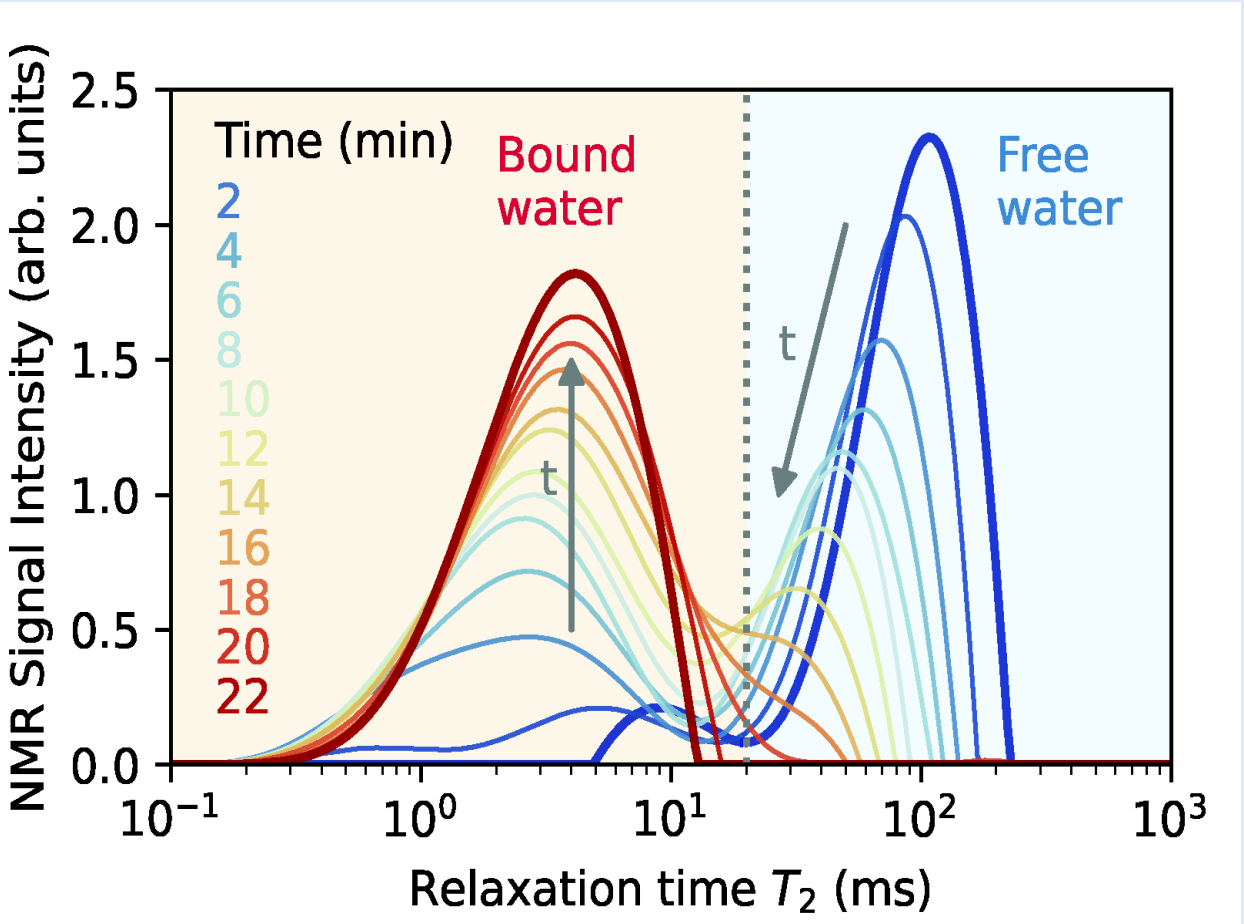
Yan et al, *Phys. Rev. Appl.*, 2025

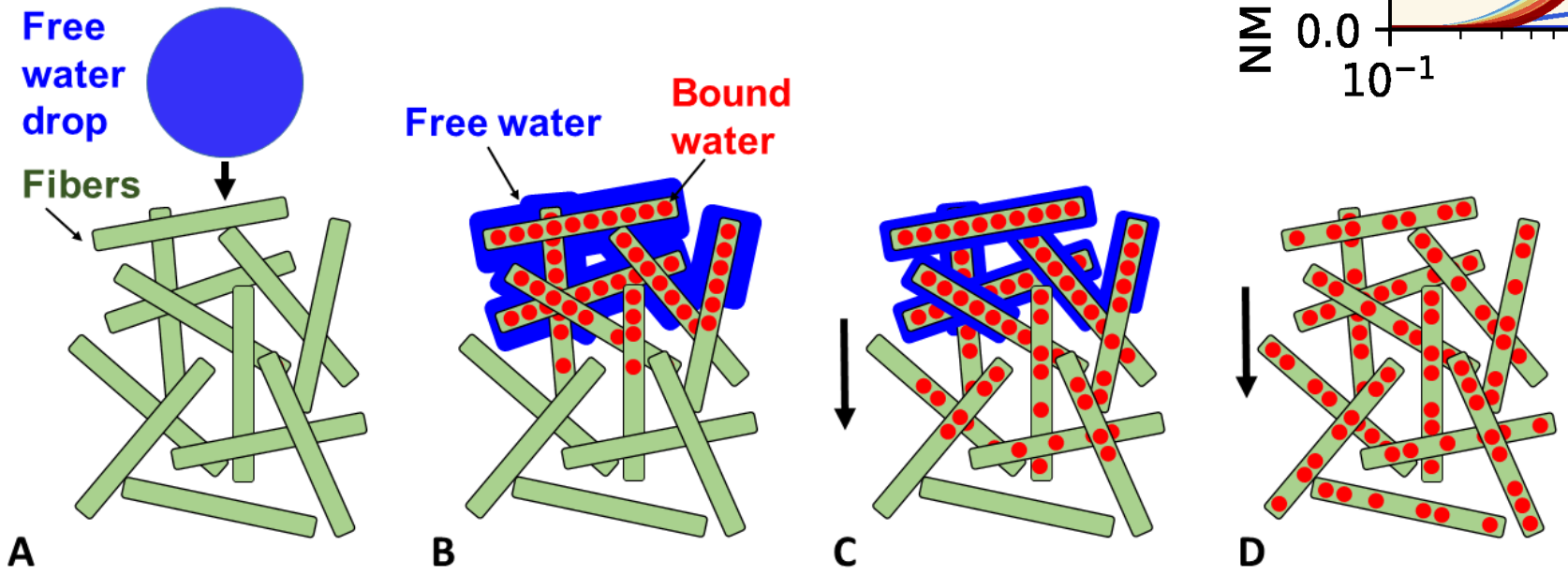
The fate of a water droplet on a cellulose fiber stack



First seconds

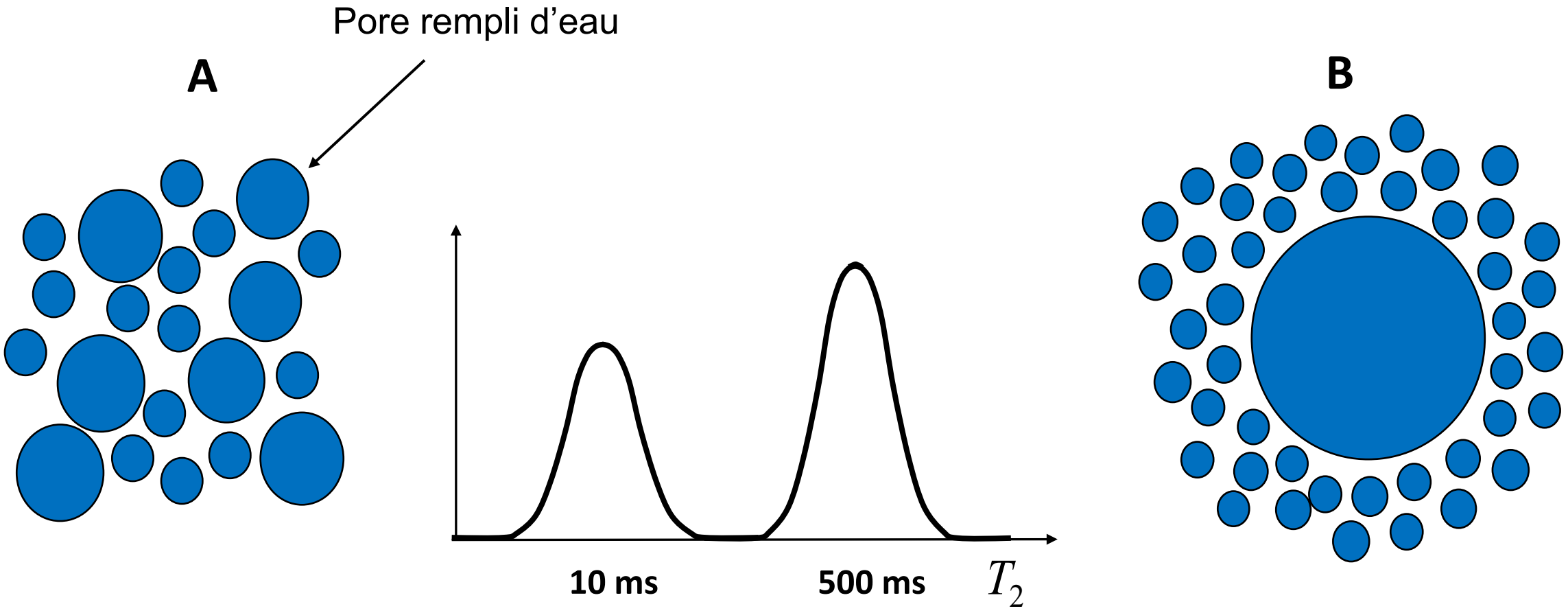
In a closed container → 2 hours:





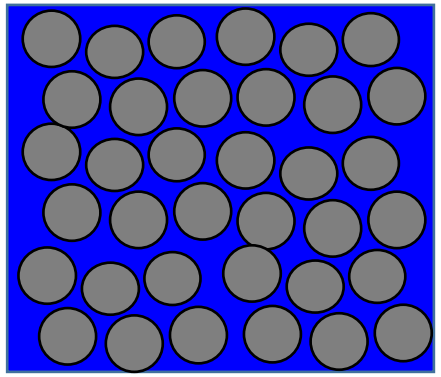
Yan et al, *Phys. Rev. Appl.*, 2025

QUESTION 1



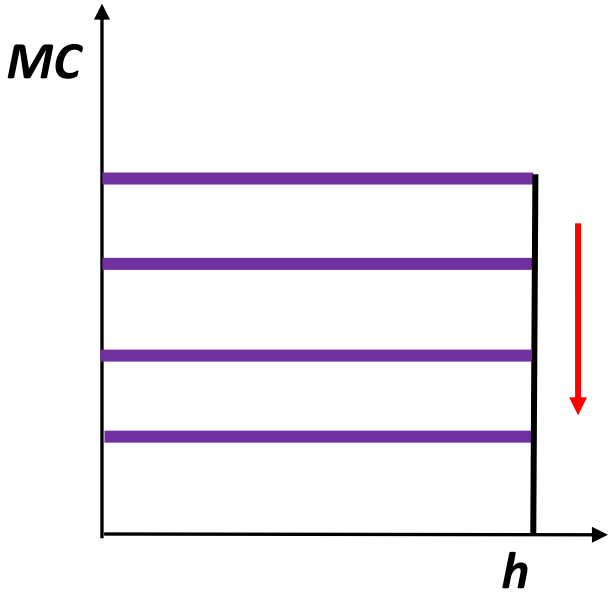
A ou B ?

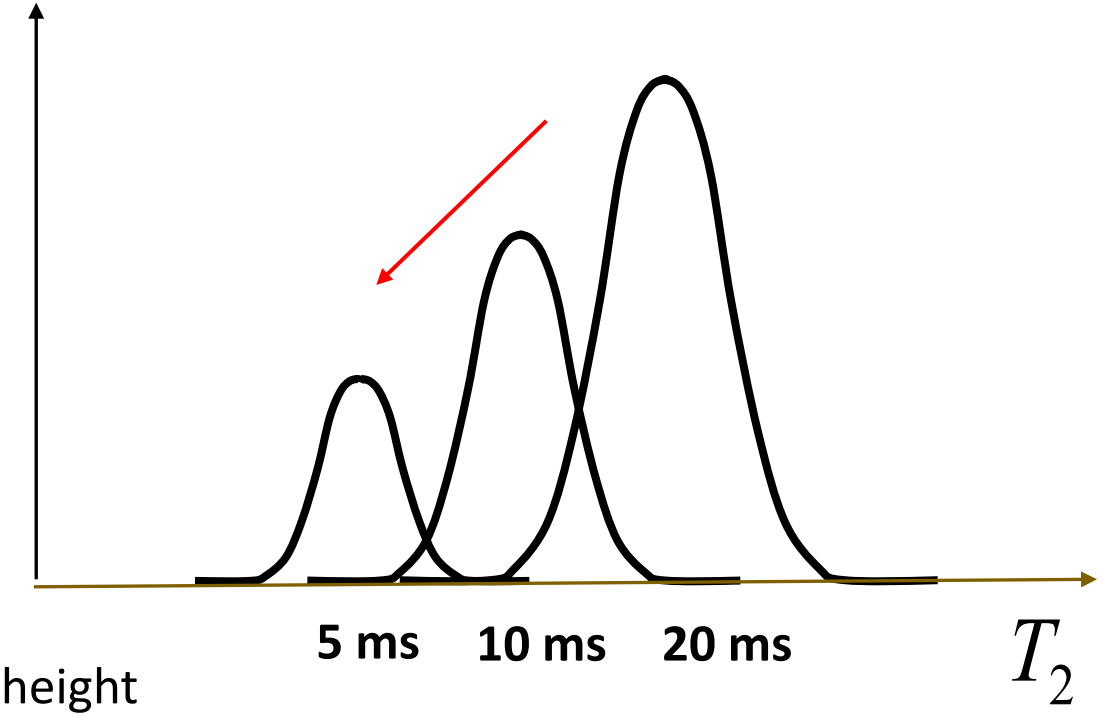
QUESTION 2



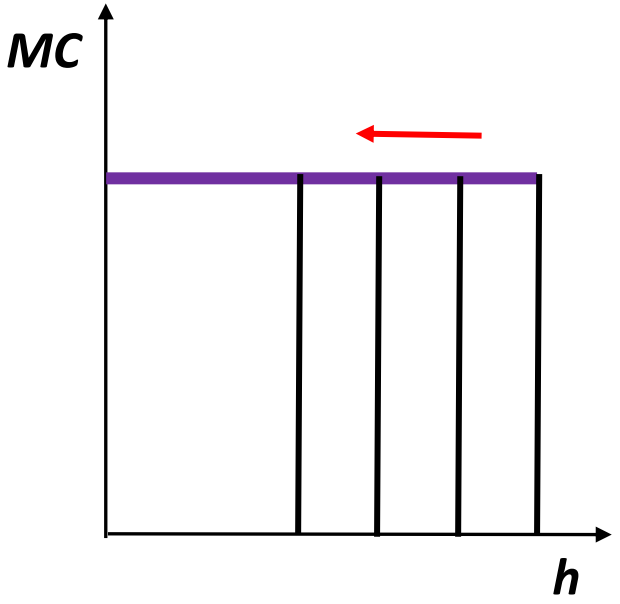
Drying

A





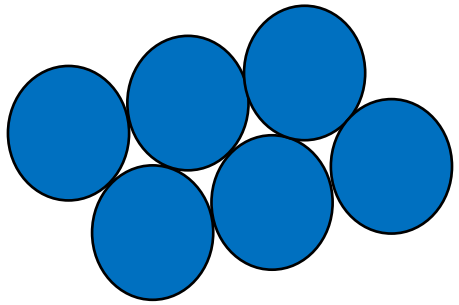
B



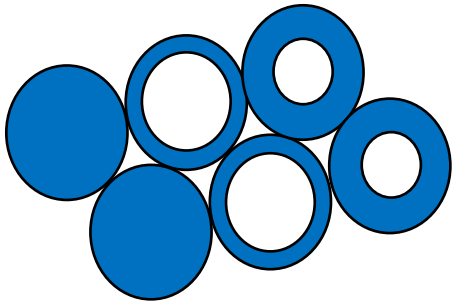
Liquid distribution along sample height

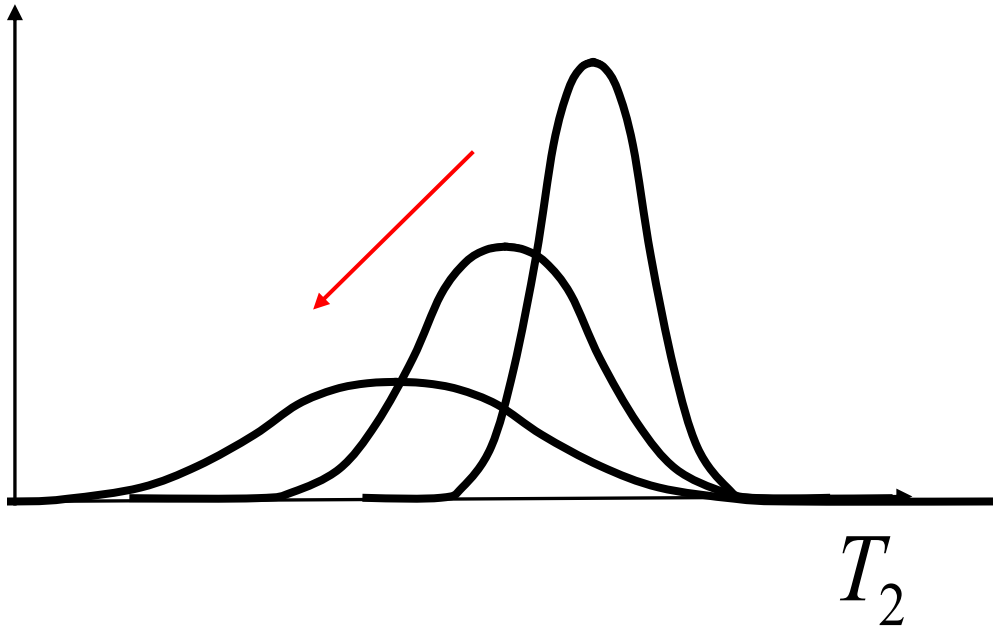
A ou B ?

QUESTION 3

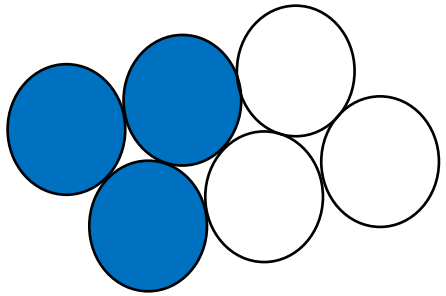


A





B



A ou B ?