MS13
22 may 2023

Fluid transfers in nanopores through dynamic NMR relaxometry

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LABORATOIRE NAVIER

École des Ponts ParisTech

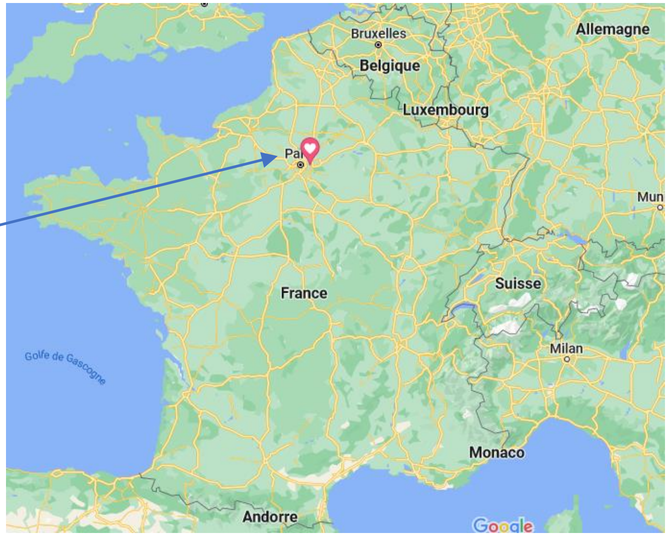
cnrs

Université Gustave Eiffel

Rheology and Porous Media team building

Ecole des Ponts Paris Tech

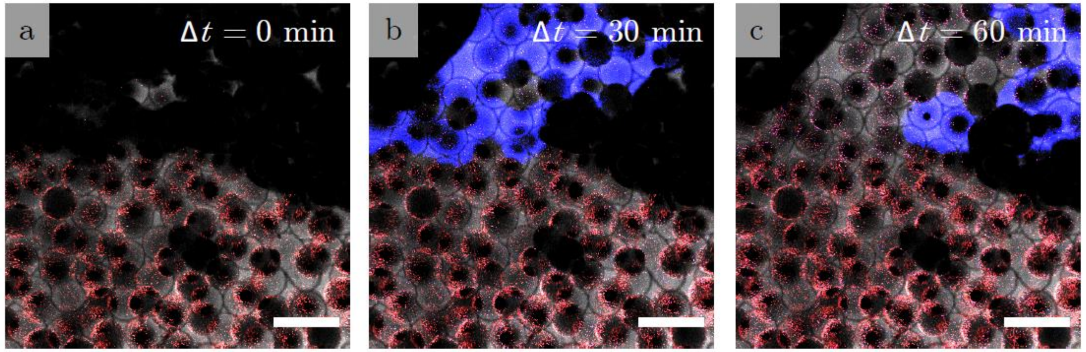
Champs-sur-Marne France



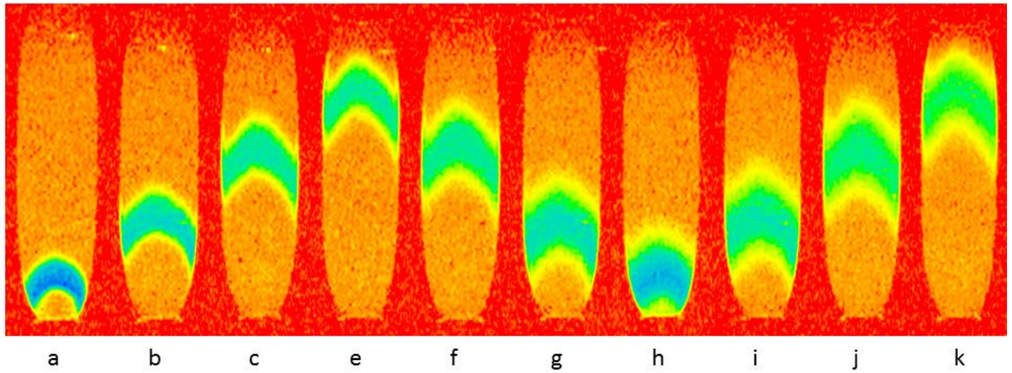
Why can NMR bring obvious analytic information ?

Local interaction **liquid water - porous media**
→ Key concept **to understand transport**

MRI and other imagery techniques
→ **Direct visualisation of** water transfer **in mesopore and macropore**



Using colloidal deposition to mobilize immiscible fluids from porous media
Joanna Schneider, Rodney D. Priestley, and Sujit S. Datta
Phys. Rev. Fluids, 2021



Lehoux et al, Physical Review E, 2016

But, not relevant for the most of nanoporous materials… **Too low spatial and temporal resolution**

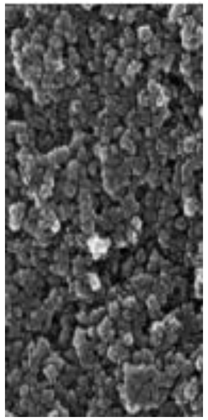
« Dynamic NMR relaxometry »
→ **No invasive, quantitative** and unique **full description of water transfer over time** for the most of **nanoporous** materials !

Exemple : Silica glass

Water trasfer in Vycor

Vycor = pure fused **silica glass** by an isotropic, **3D network of interconnected** tortuous pores.

Surface area = 100 m² /g
Pore radius = 4.6 nm (≈ monodisperse)
Pore volume = 0.218 cm³ /g
Porosity ≈ 0.3



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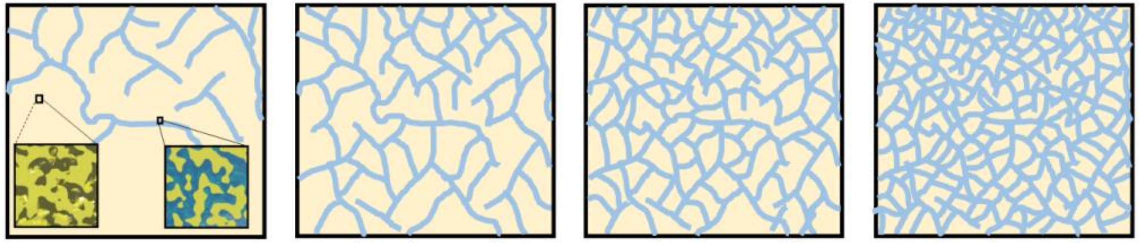
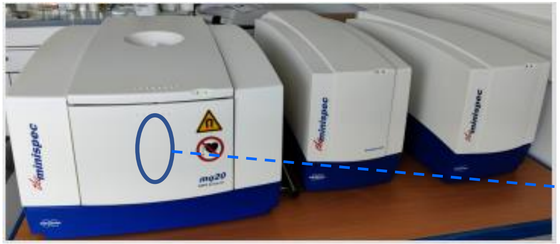
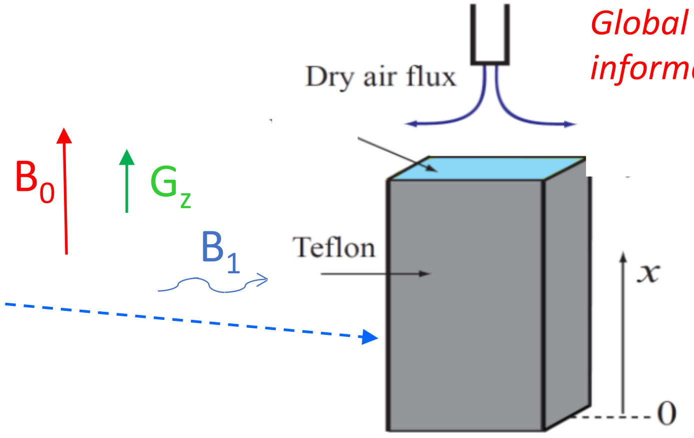
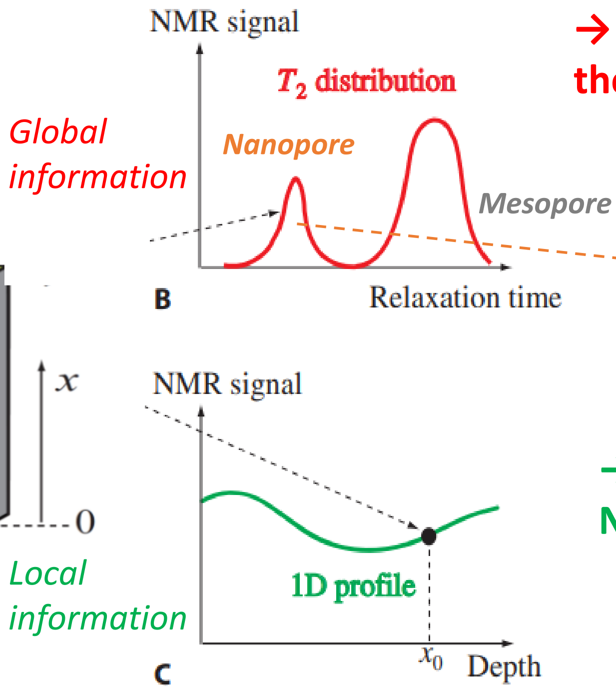


Can we **follow water transfer** as imbibition or drying **directly** by a **non invasive experimental way** ?



Minispec Brüker
0,5 teslas
+ Gradient field





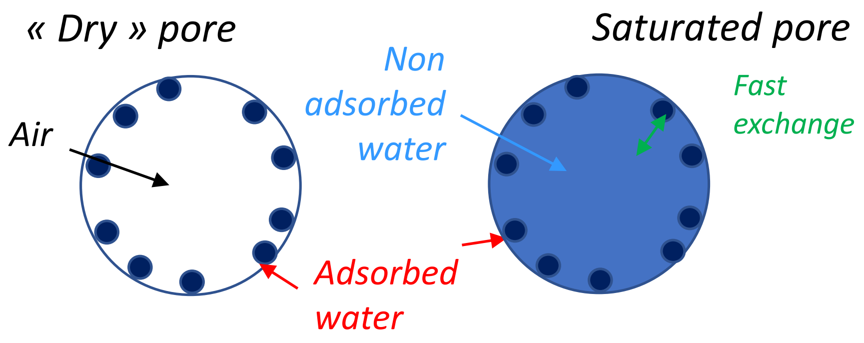
→ **Lower T2…**
the way to the nanopores

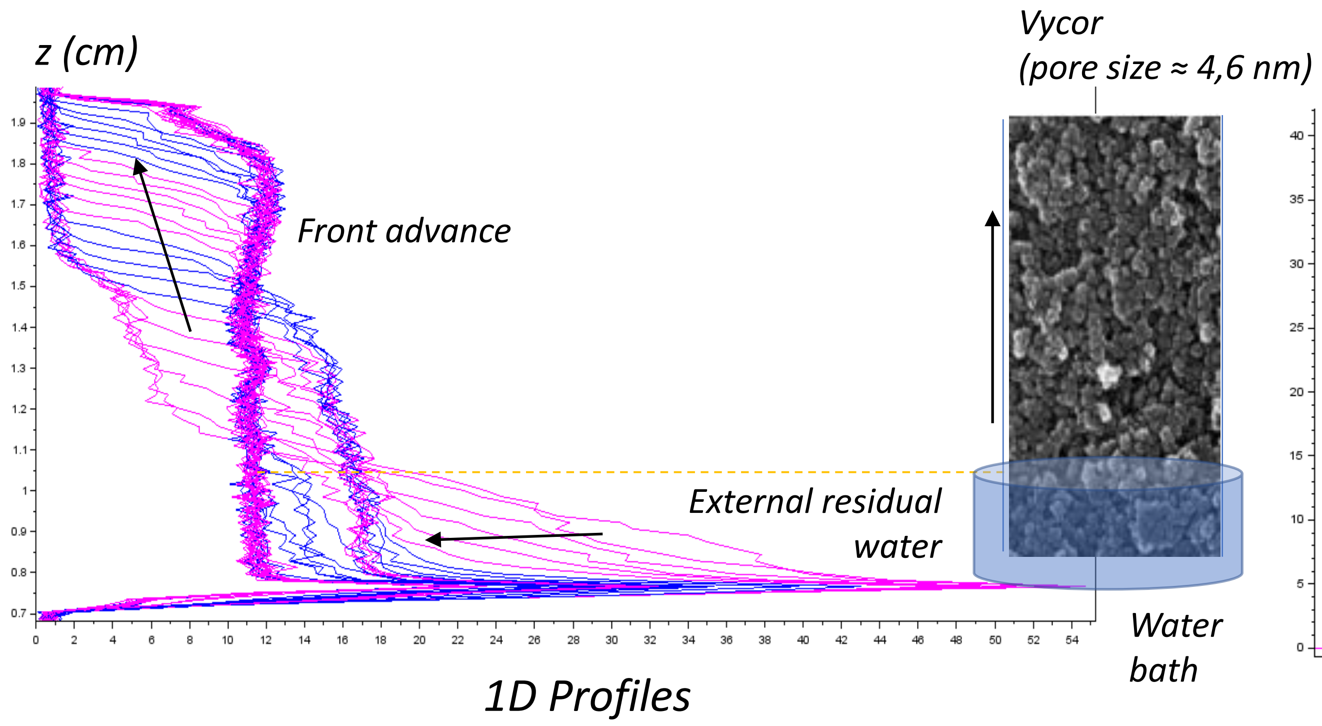
Peak area(t)
T2(t)

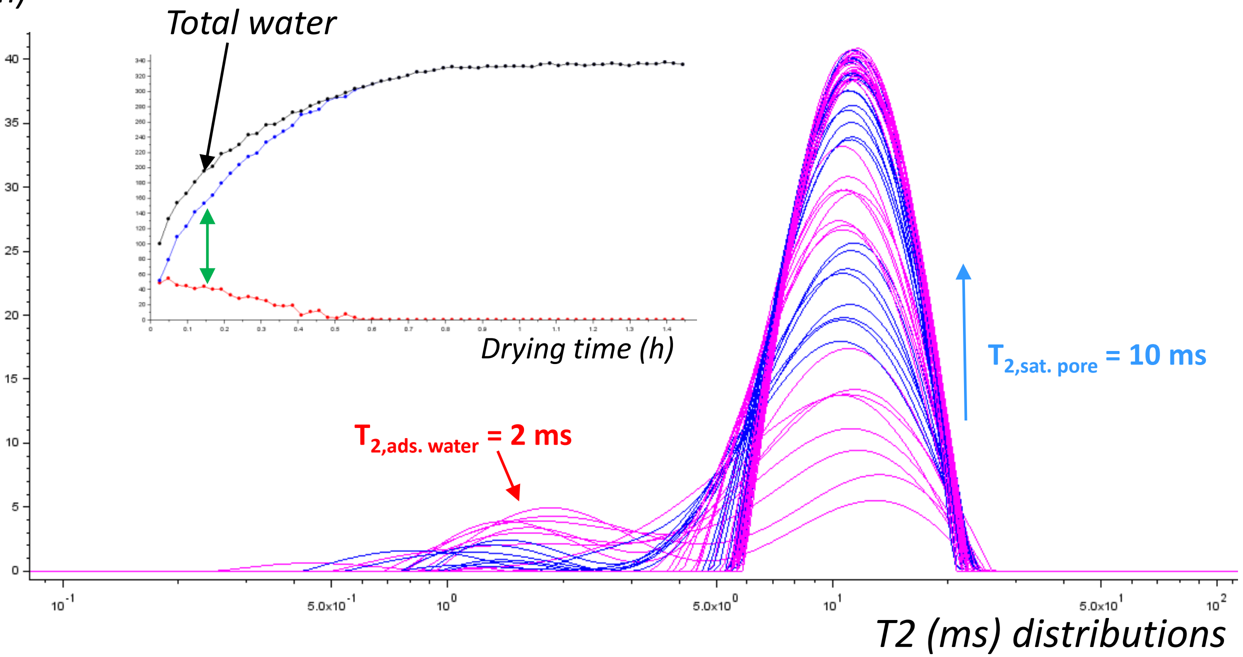
→ **Slice thickness >>**
Nanopore size

Typical size sample : 1 cm³
Typical duration of 1 cycle of experiment : 5 min

Vycor imbibition by the bottom, a way to attribute the relaxation times







→ **Fast exchange** (Nanopore size << √(6.D.T2)) between surface and bulk water is highlighted ($T_{2,bulk} >> T_{2,Surface}$)

→ 1 NMR peak for saturated pore (Tarr and Browstein, 1979):

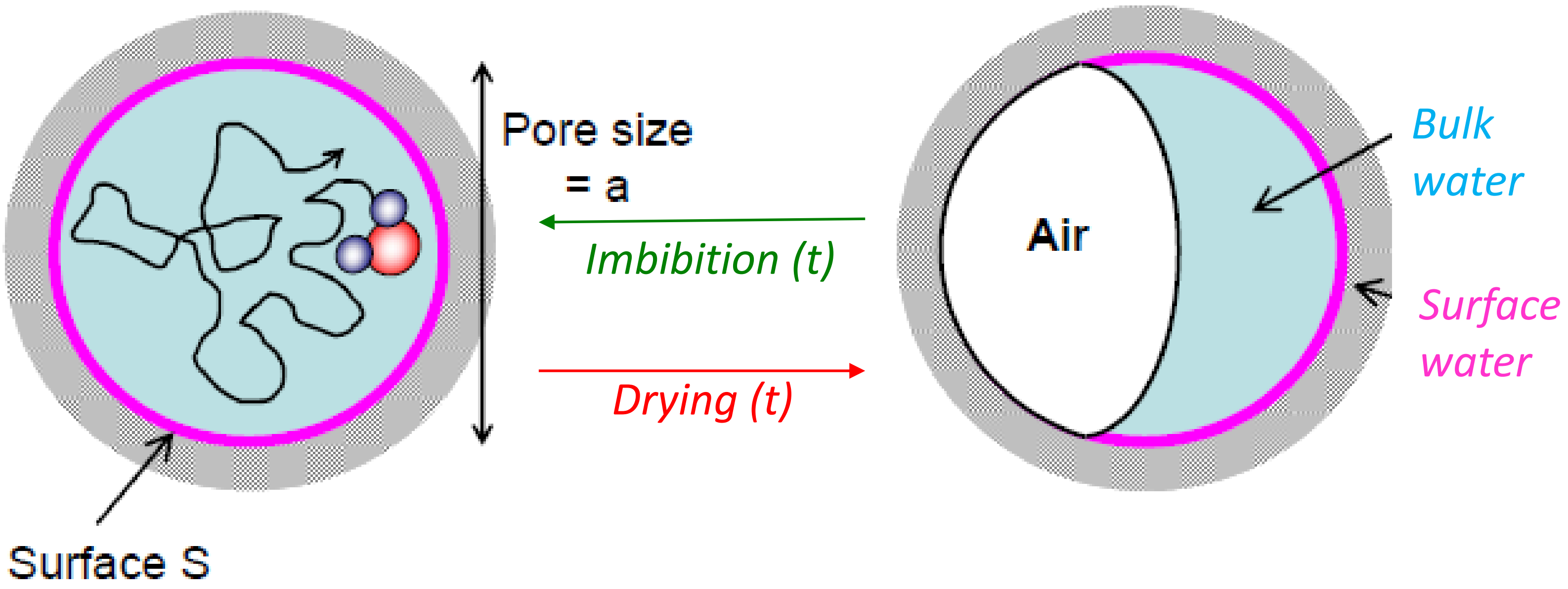
$$\frac{1}{T_{2,\ pore}} = \frac{n_{bulk}}{T_{2,\ bulk}} + \frac{n_{surface}}{T_{2,surface}}$$

$$\frac{1}{T_{2,\ pore}} - \frac{1}{T_{2,\ pure\ liquid}} = \frac{T_{2,ads.}}{b} \cdot \frac{S_{pore}}{V_{pore}}$$

b : molecule thickness

Generalisation for partially saturated nanoporous medium (Relaxation = surface interaction process)

→ Mandatory to fully description of the drying



→ **Fast exchange bulk** and **surface** water

→ **$1/T_{2,\text{Pure liquid}} \ll 1/T_{2,\text{Pore}}$**

$$T_2 \approx \frac{T_{2,ads.}}{b} \cdot \frac{V_{water}}{S_{wet}}$$

→ **Vycor : b = 0,38 nm ≈ water molecule size (full wet surface remaining)**

Vycor slow drying by the top surface

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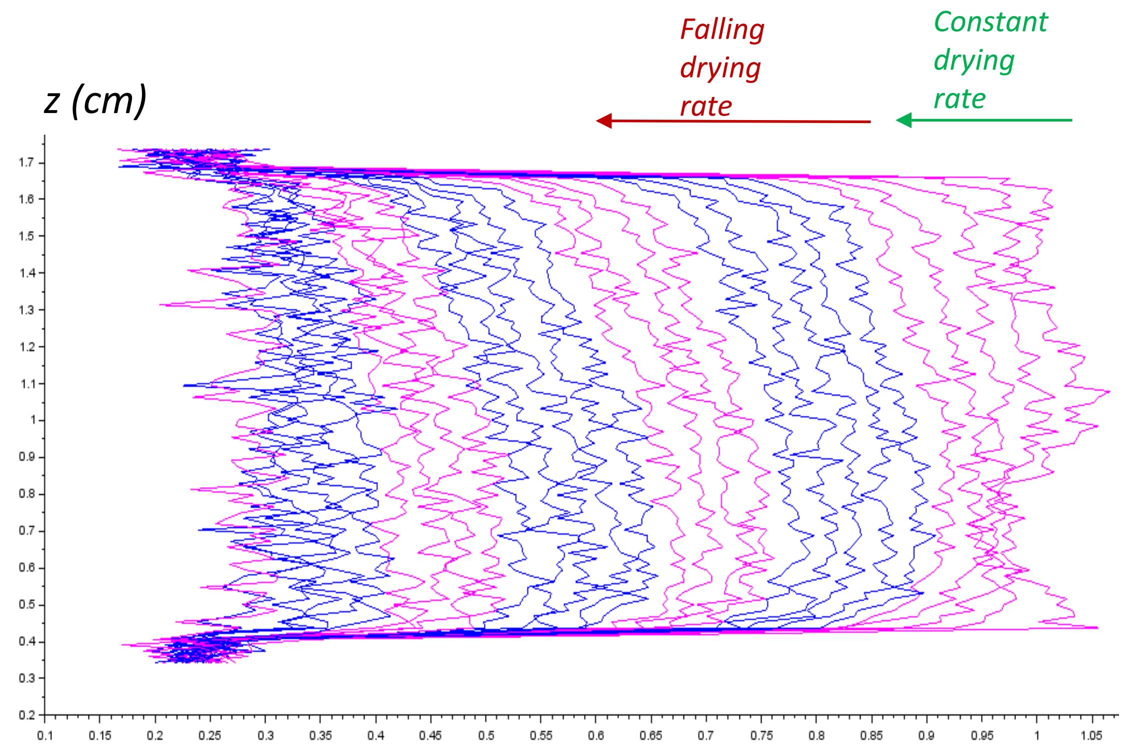
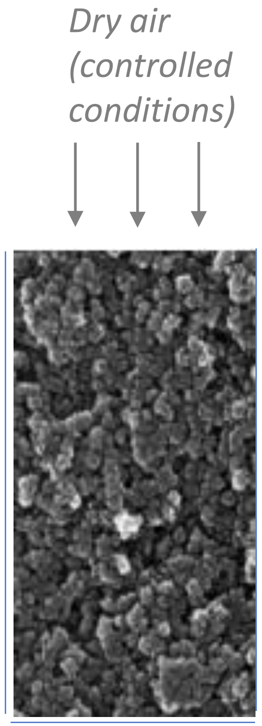
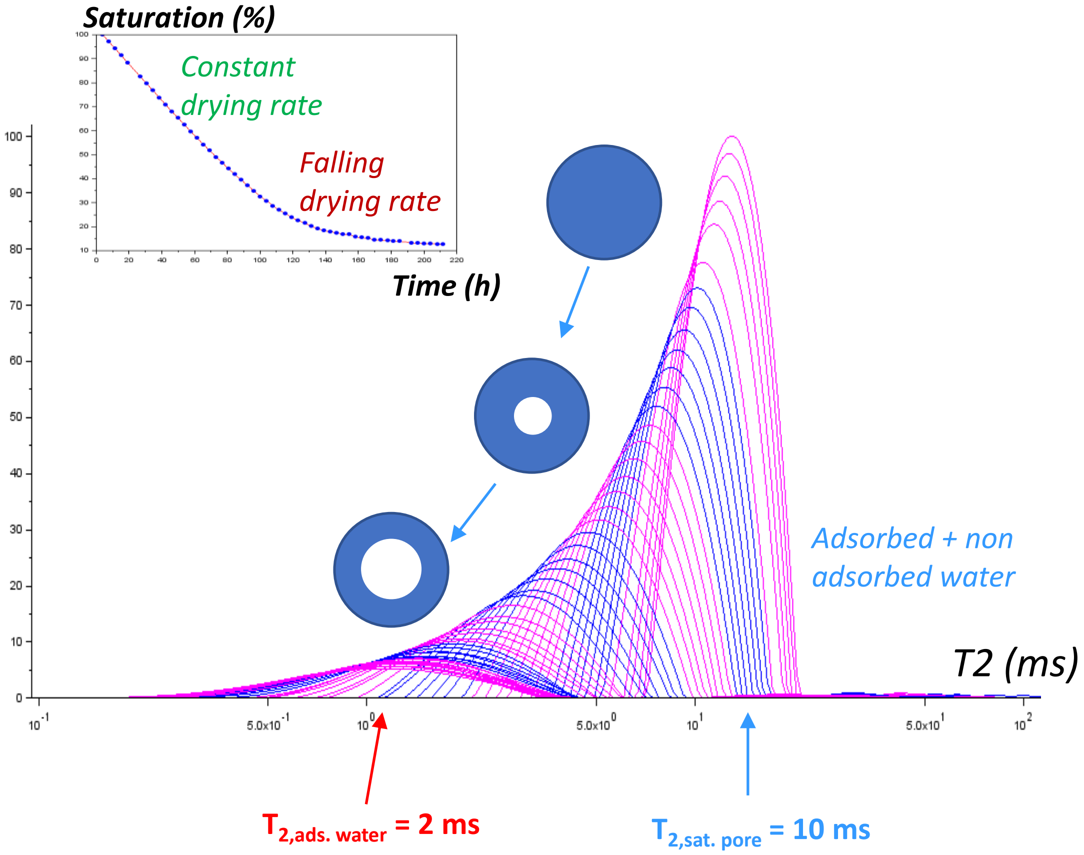
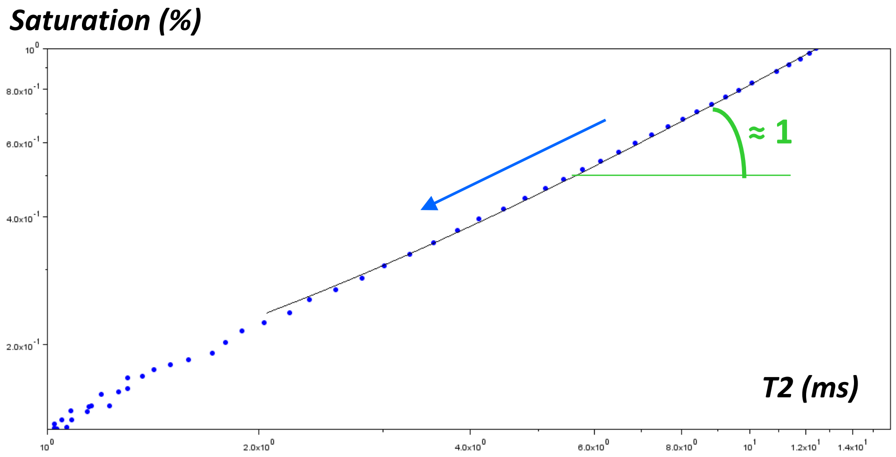


1D Profiles







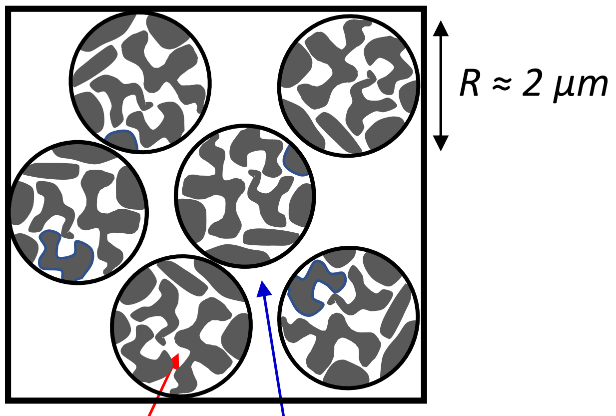
→ Back to **initial state by constant and falling drying rate period.**

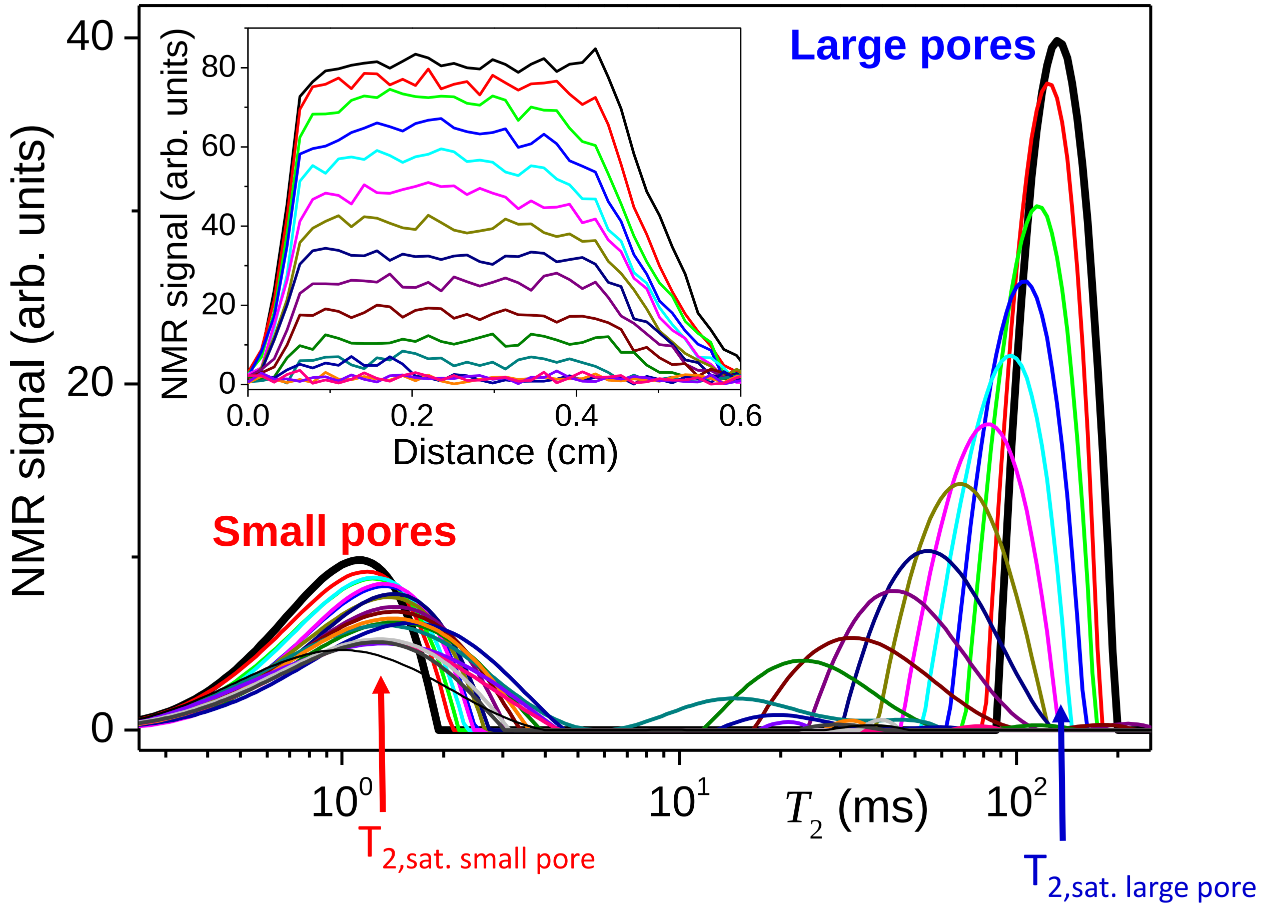
→ **Homogeneous desaturation**

→ T_2 α **a^3**   Peak area α Sat° α **a^3**

S(wet) constant during the constant drying rate period

Drying of porous bead packing





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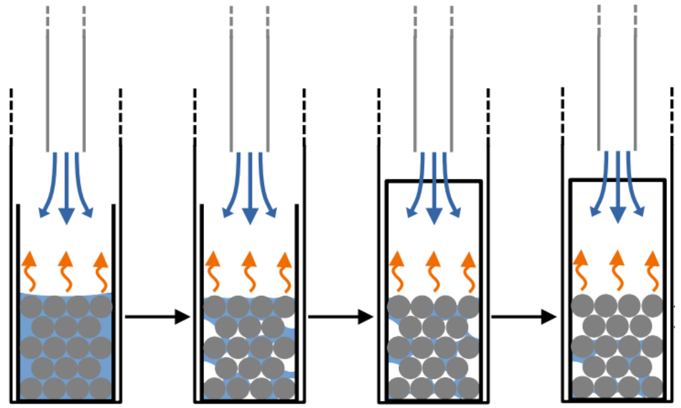
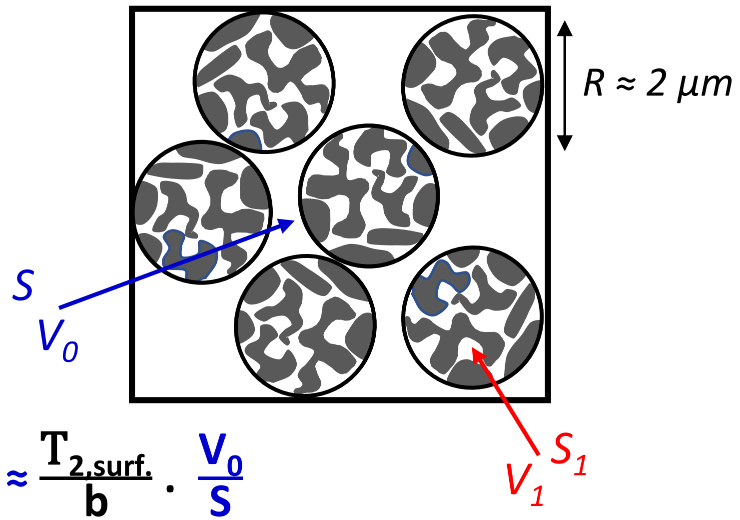
→ 2 pore sizes **initially filled**

→ **Progressive disappearance** of liquid in **large pores, homogeneous desaturation** of large pores (and dry front…)



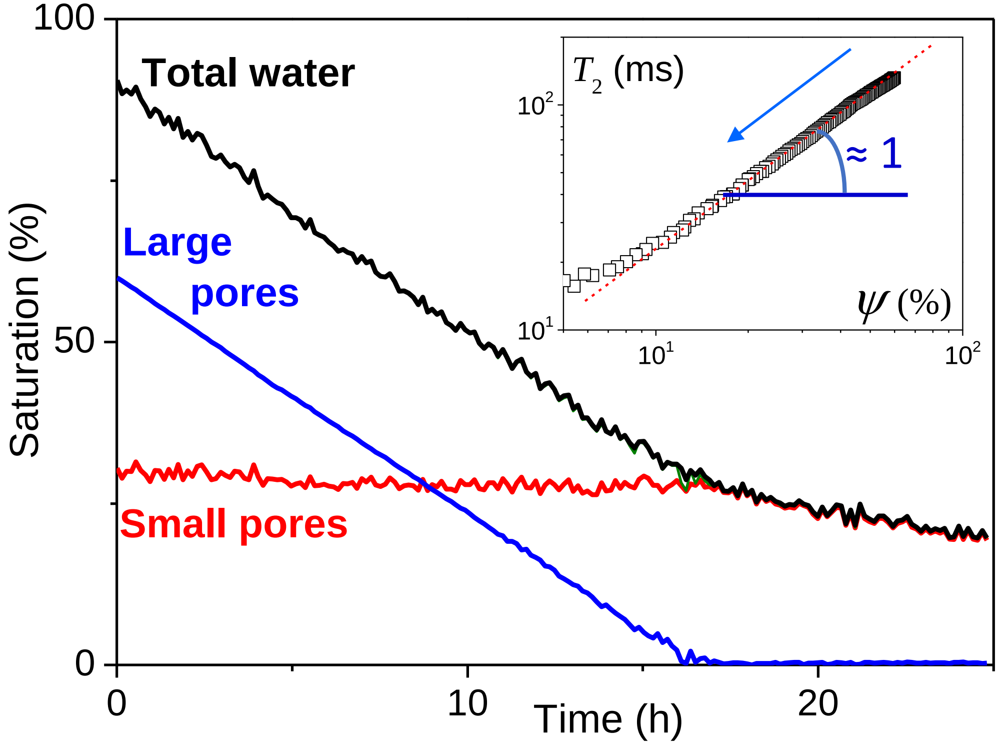
Drying of porous bead packing

From integral of pdf over different ranges of T2…



$$T_{2,\text{Large Pore}} \approx \frac{T_{2,\text{surf.}}}{b} \cdot \frac{V_0}{S}$$

$$T_{2,\text{Small Pore}} \approx \frac{T_{2,\text{surf.}}}{b} \cdot \frac{V_1}{S_1}$$



The **small pores remain saturated** untill **full desaturation of large pores (constant wet surface)** and **ensure the transport** of liquid toward the free surface **(constant drying rate period)**.
Then, small pores start to dry slowly **(falling drying rate period)**.

$T_{2,Sat.}$(Large pore) / $T_{2,Sat.}$(Small pore)	→ **Small pore size** ≈ 4,4 nm	(Vycor : 4,6 nm)
$Sat°_{Sat.}$(Large pore) / $Sat°_{Sat.}$(Small pore)	→ **Volume fraction of internal water** ≈ 33 %	(Vycor : 30 %)
Fast exchange theory (Pore sizes < √(6.D.T2)) :	→ **Specific surface** ≈ 120 m²/ g	(Vycor : 100 m²/g)

To conclude…

Dynamic relaxometry

→ Global and/or local **efficient** and **original time resolved** methodology to **describe fully** liquid transfer, even in **nanoporous materials**
… thanks to **T2 distributions** and **profiles**.

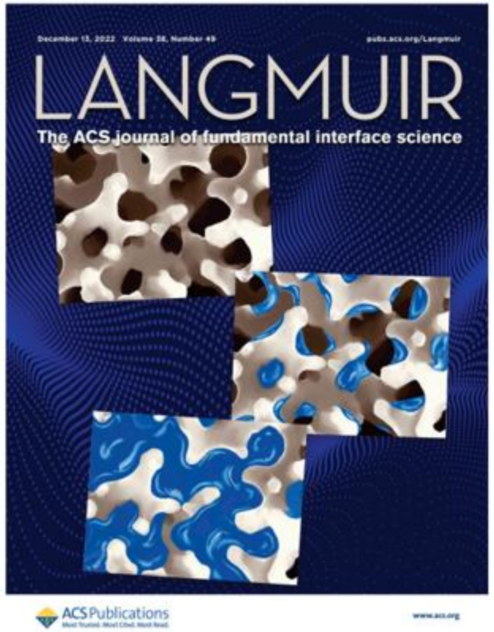
→ Extended to **other (bio-based) material** and **all the water or protonic liquid transfers in nanopores**.

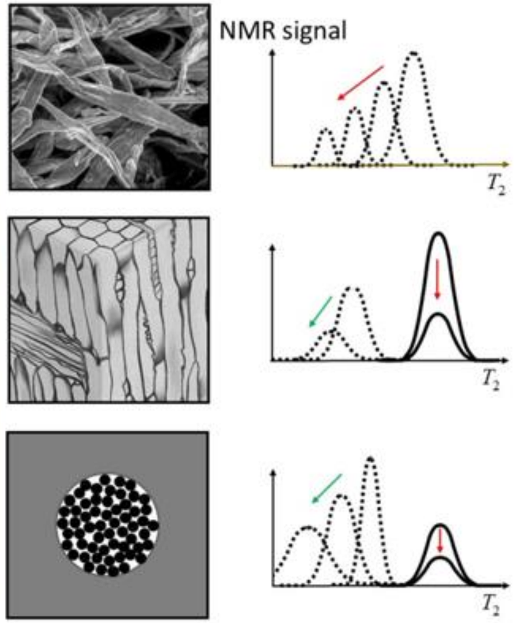
→ Direct validation of **predictive models of water transfer in nanoporous media** !

Ph. Coussot
Université Gustave Eiffel

European Research Council
Established by the European Commission

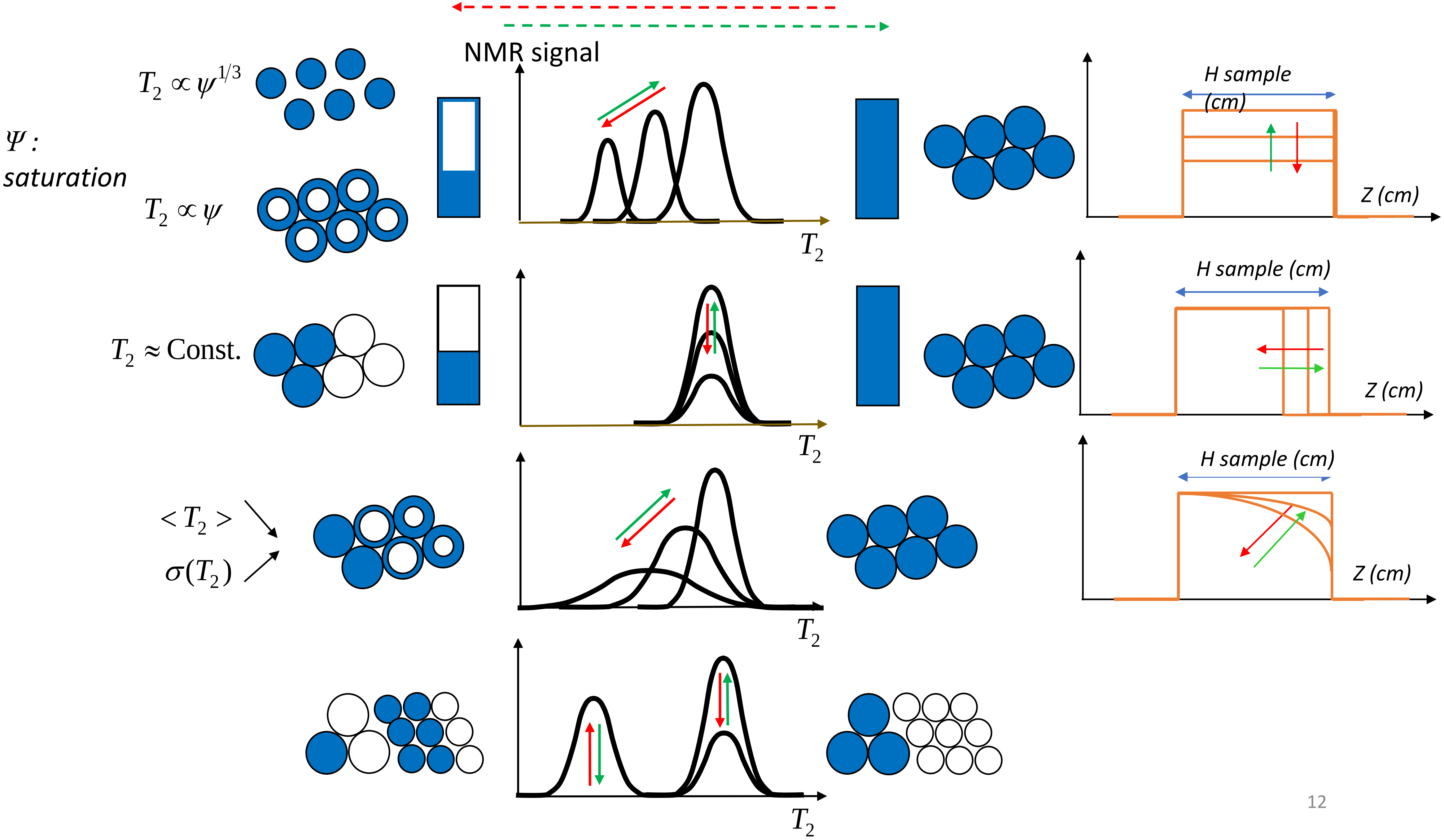
PHYSBIOMAT
From fiber to wall: physical approach to hygrothermal transfers in bio-based construction materials





Thanks for your attention !

Expected results of dynamic relaxometry



Bases of NMR relaxometry

* NMR excitation (Hydrogen proton spin) => Back to equilibrium: *Relaxation* (T_1, T_2)

$$s(t) = s_0 \exp\left(-t/T\right)$$

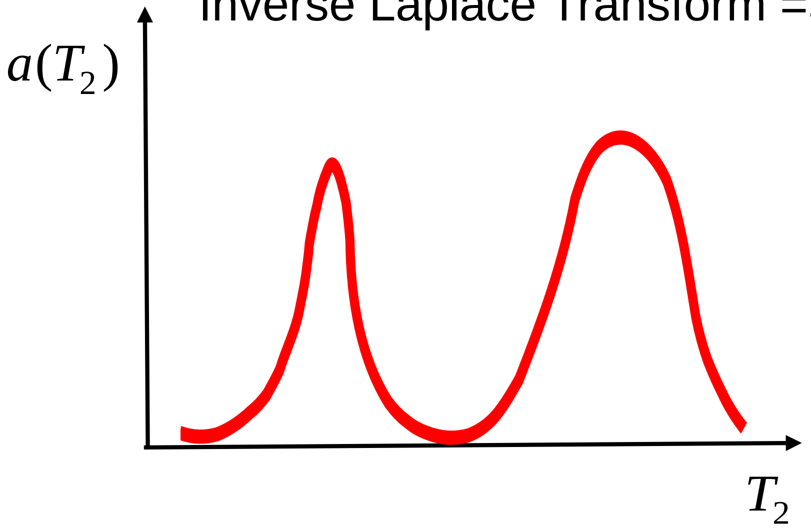
* Relaxation times depend on the molecule environment

* In a porous medium: various possible relaxation times => Total signal:

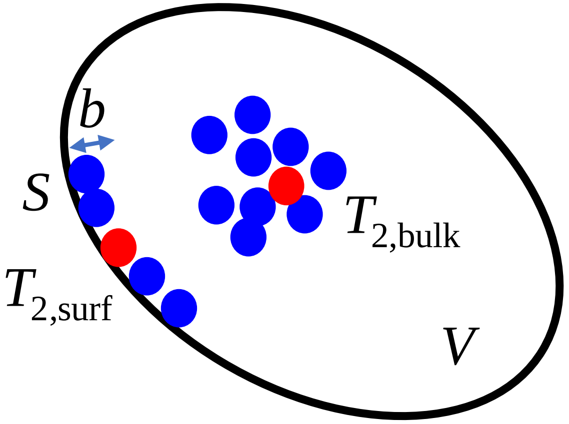
$$s(t) = \int_0^{\infty} a(\lambda)\left(\exp\left(-\lambda t\right)\right) \mathrm{d}\lambda \qquad T_2 = 1/\lambda$$

$a(\lambda)$ *Probability density function*

Inverse Laplace Transform =>



In a pore:
Two main relaxation times:



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

Signal of a given molecule:

$$s(t) \approx s_0 \Pi \exp\left(-\Delta t_i / T_i\right) = s_0 \exp\left(-\sum_{\Sigma \Delta t_i = t} \Delta t_i / T_i\right)$$

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

Total time spent over the surface: Δt_{surf}

Brownstein-Tarr (1977)

« Fast exchange » assumption => at any time: $t = \Delta t_{\text{surf}} + \Delta t_{\text{bulk}}$ $\varepsilon = \dfrac{\Delta t_{\text{surf}}}{t}$

(Fraction of time spent along the surface)

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

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

$$\varepsilon \approx \frac{bS}{V}$$

Si $\varepsilon << 1$ $T_2 \approx \dfrac{T_{2,\text{surf}}}{b} \dfrac{V}{S}$

Evolution of the pdf depending on material characteristics

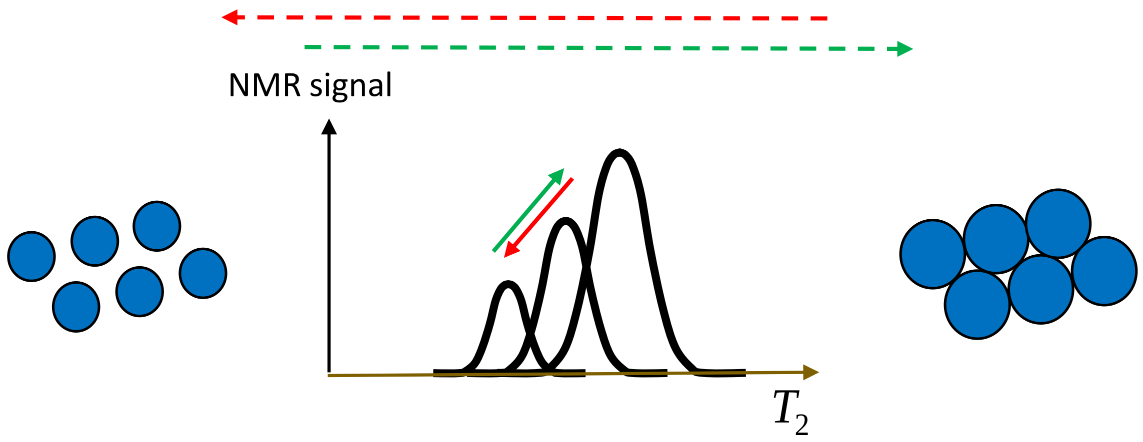
Simple (homogeneous) shrinkage or swelling

$$S \propto r^2;\ V \propto r^3$$

$$\psi = V/V_0 \quad \text{(saturation)}$$

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

$$\Rightarrow T_2 \propto \psi^{1/3}$$

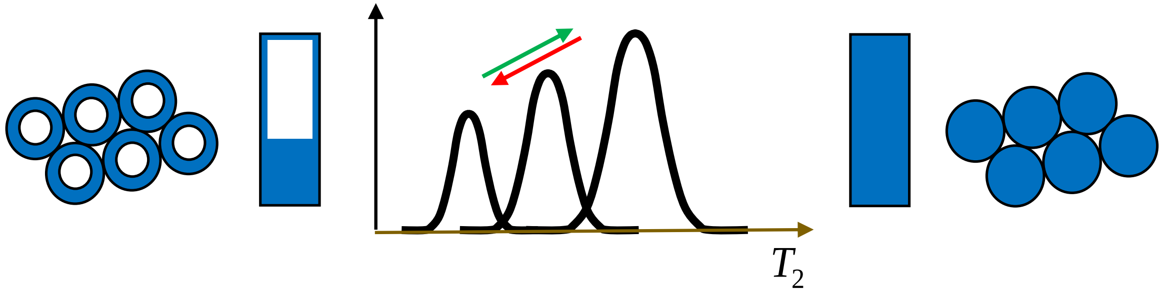


Desaturation without dewetting

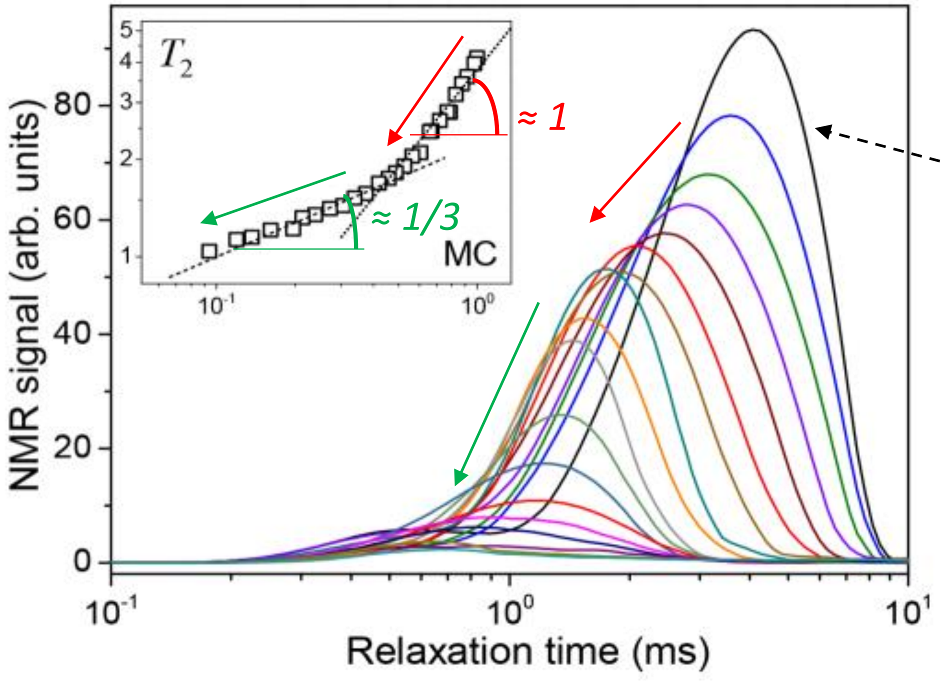
$$S \propto S_0;\ V \propto \psi$$

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

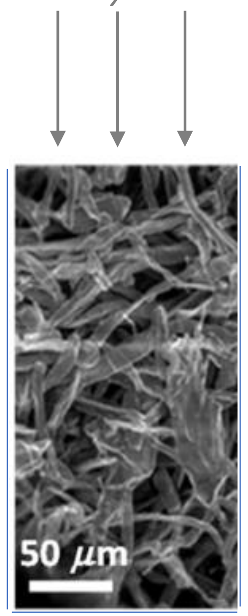
$$\Rightarrow T_2 \propto \psi$$



Drying of humid cellulose fibers by the top surface



Initial state : Pure humid cellulose
- **Saturated in bound water** (T2 < 10 ms)
  → intrafiber water = nanopore
- **No free water** (T2 > 10 ms)
  → interfiber water = mesopore



Fibre dimension :
700 x 20 µm

2 clear stages during the desorption:

Slope (log(T2) vs log(Peak Area) ≈ **1**
→ Constant wet surface (T_2 α $\mathbf{a^3}$ and Peak area α $\mathbf{a^3}$) ↔ **Non adsorbed** water drying

Slope(log(T2) vs log(Peak area) ≈ **1/3** → Isotropic shrinkage
↔ **Adsorbed bound** water drying (T_2 α V/S α a^1 Peak area α V α a^3)

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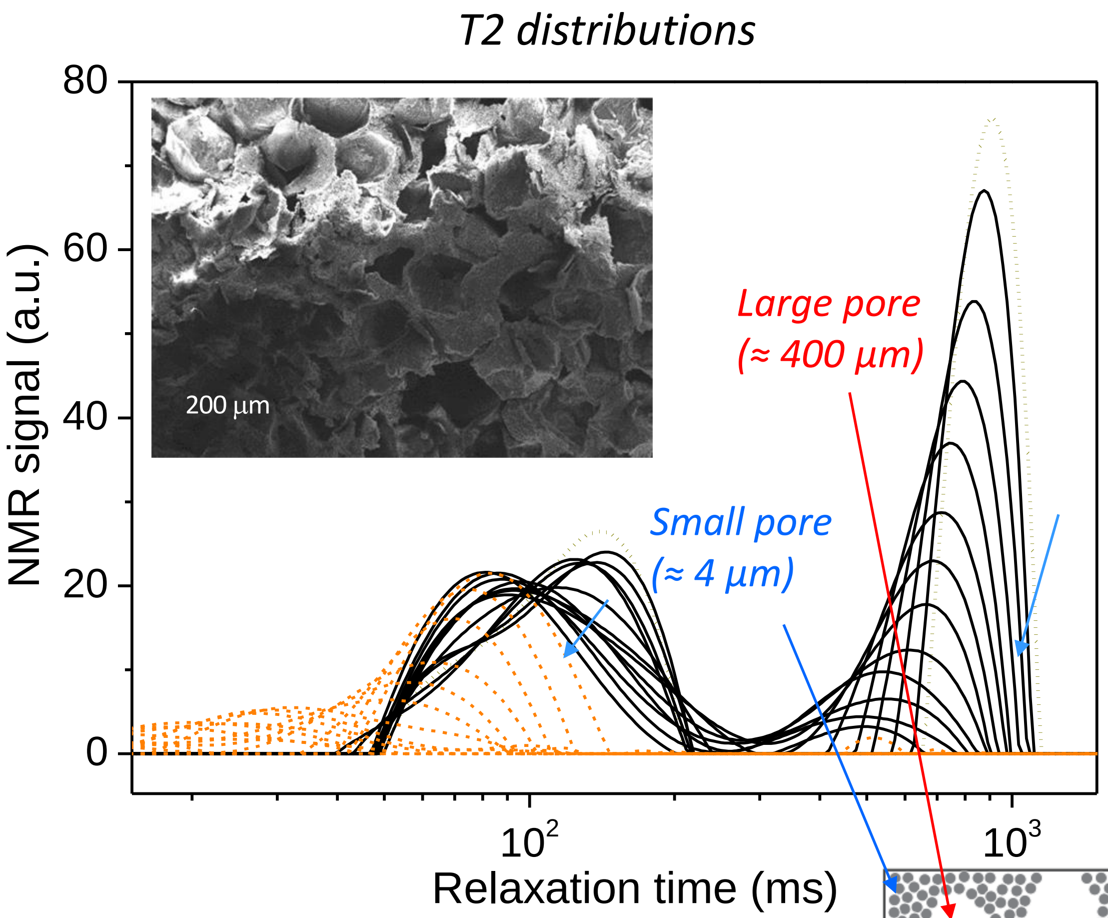
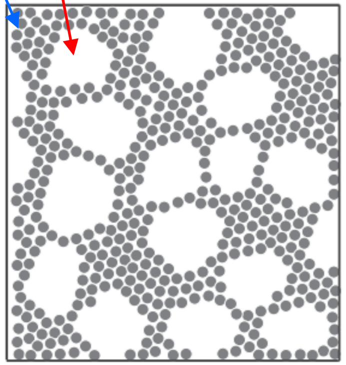
Biporous material drying





PHYSICAL REVIEW APPLIED **0**, XXXXXX (2020)

Drying of a Compressible Biporous Material

T. Lerouge,[1,2] B. Maillet,[1] D. Coutier-Murias,[1] D. Grande,[2] B. Le Droumaguet,[2] O. Pitois,[1] and P. Coussot[1,*]

[1] *Laboratoire Navier (ENPC-Univ Gustave Eiffel-CNRS), Champs sur Marne, France*
[2] *Univ. Paris-Est, ICMPE (UPEC-CNRS), Thiais, France*

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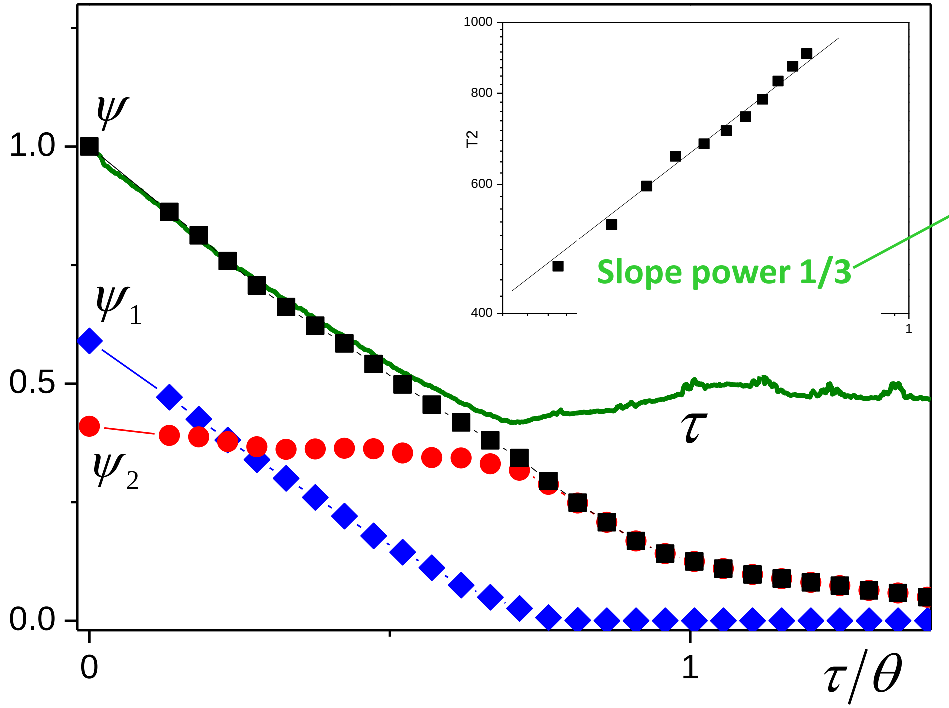


T_2 α a and
A α a^3
Isotropic contraction

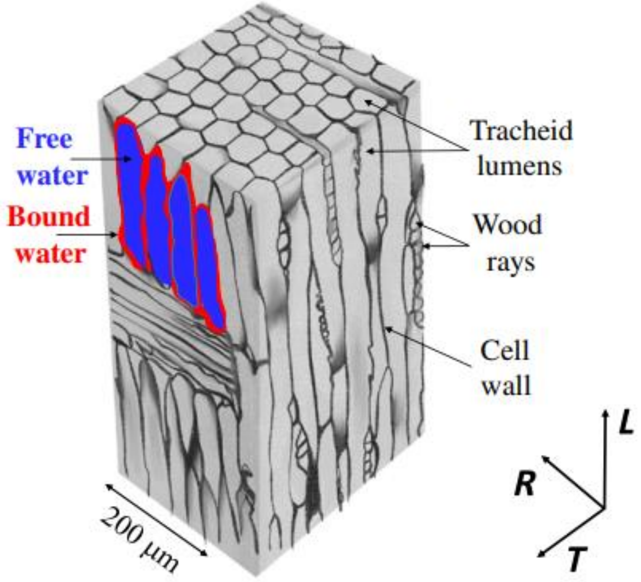
Recent publication (2022).

SCIENCE ADVANCES | RESEARCH ARTICLE

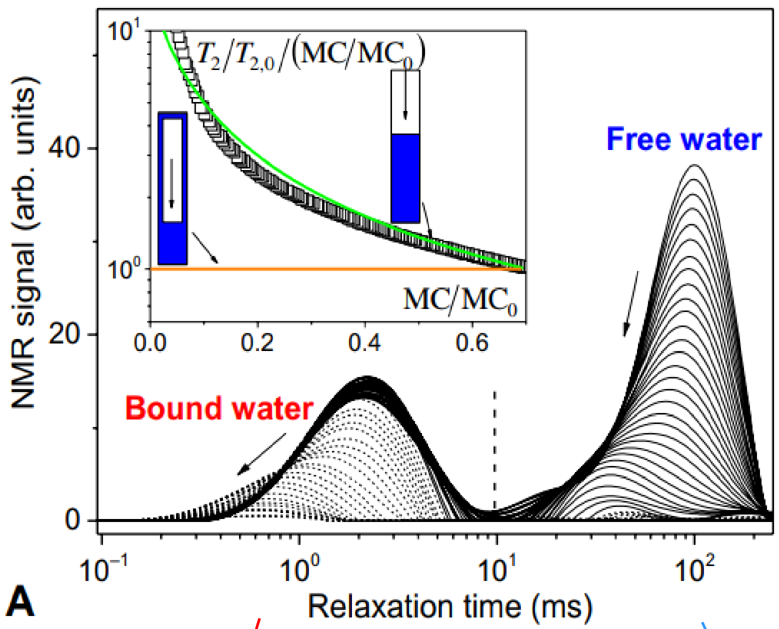
APPLIED PHYSICS

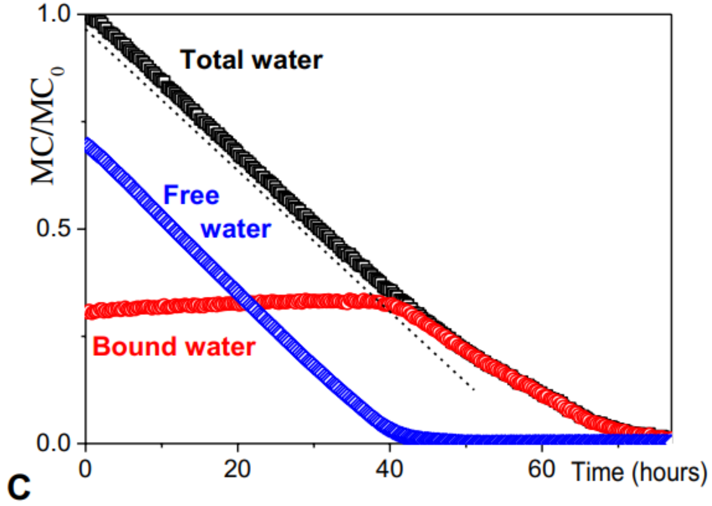
Two-step diffusion in cellular hygroscopic (vascular plant-like) materials

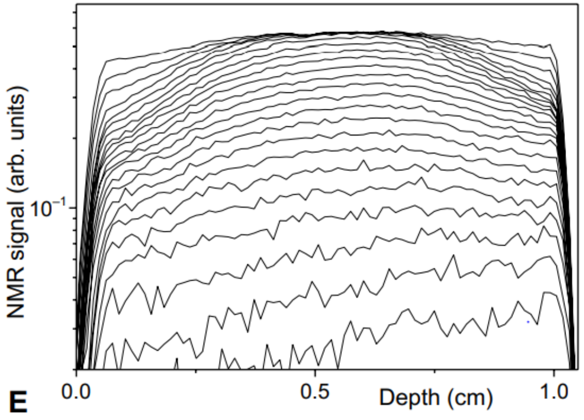
Marion Cocusse[1], Matteo Rosales[1], Benjamin Maillet[1], Rahima Sidi-Boulenouar[1], Elisa Julien[1,2], Sabine Caré[1], Philippe Coussot[1]



Weak drying





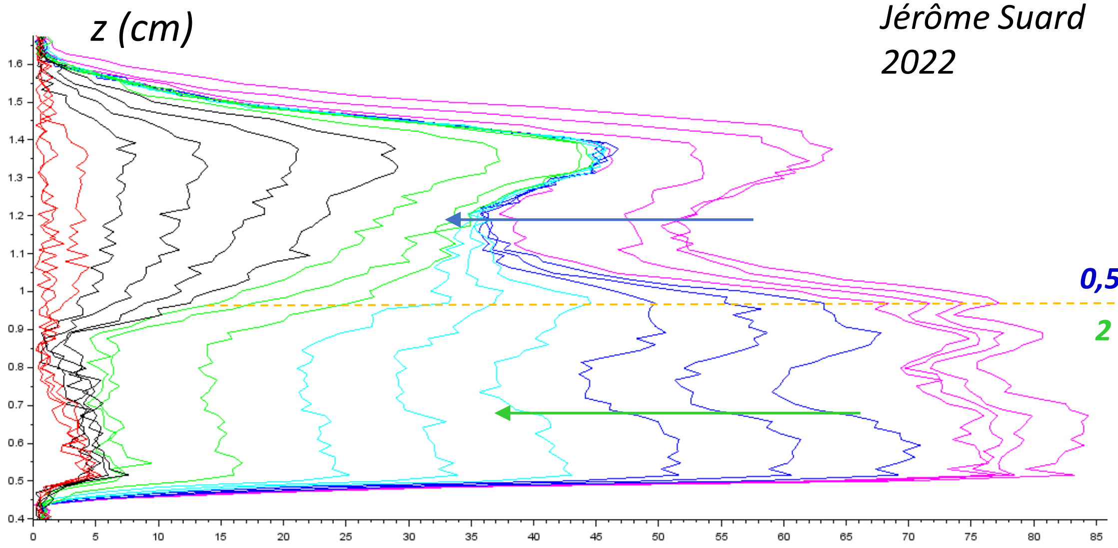


T_2(bound water) decreases.
→ **In accordance with contraction**

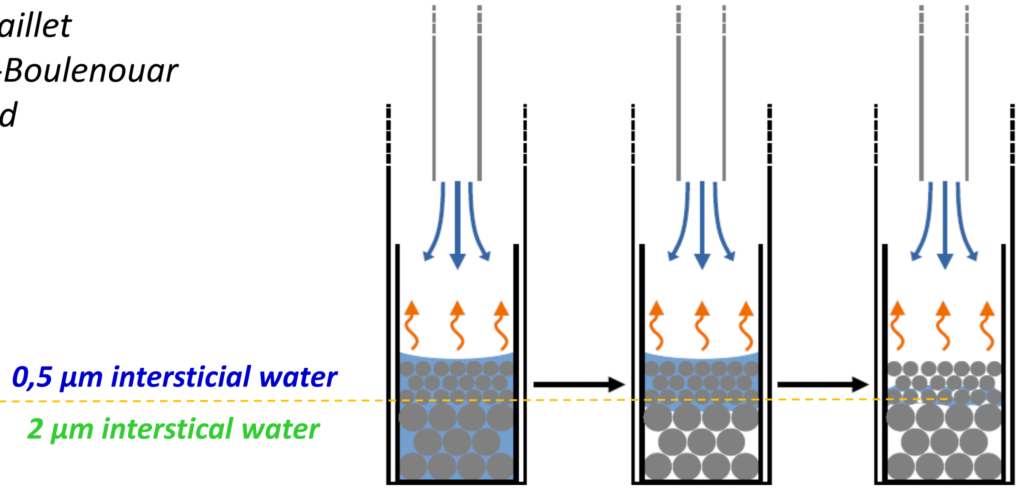
T_2(free water) constant.
→ **Total dewetting for tracheids**

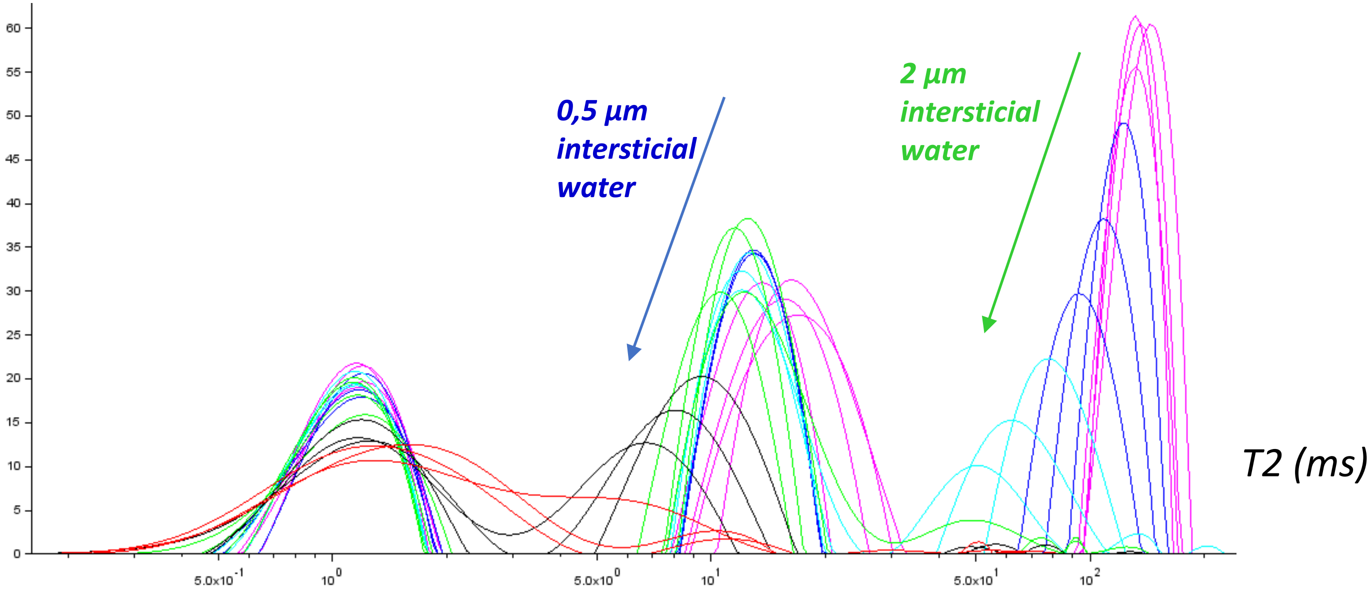
Drying of 2 layers glass bead packing

Philippe Coussot
Benjamin Maillet
Rahima Sidi-Boulenouar
Jérôme Suard
2022



1D Profiles





T2 distributions