MS10
20 may 2025

Fluid transfers in smooth porous material through dynamic NMR relaxometry

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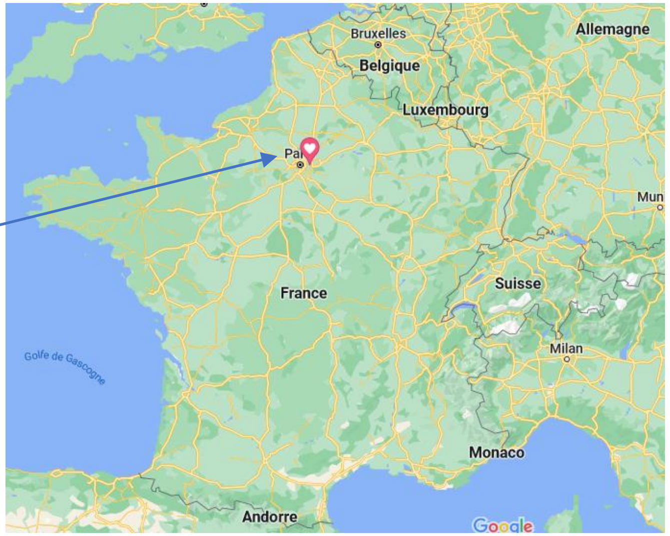


Rheology and Porous Media team building

Ecole des Ponts Paris Tech

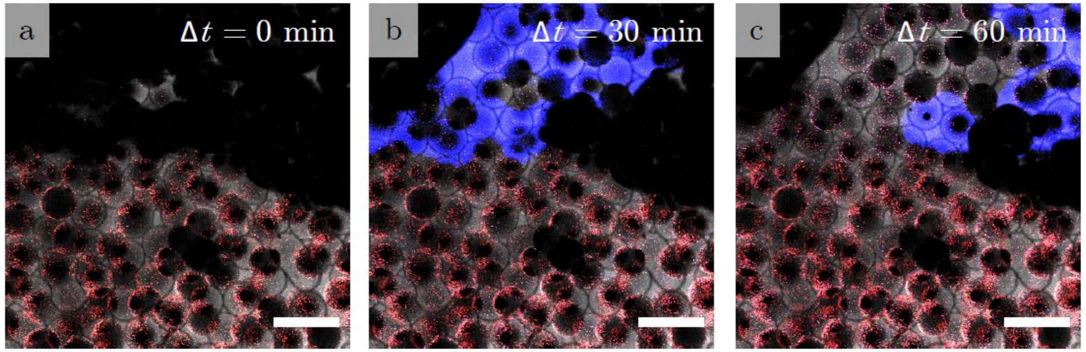
Champs-sur-Marne France

Why develop a new approach ?

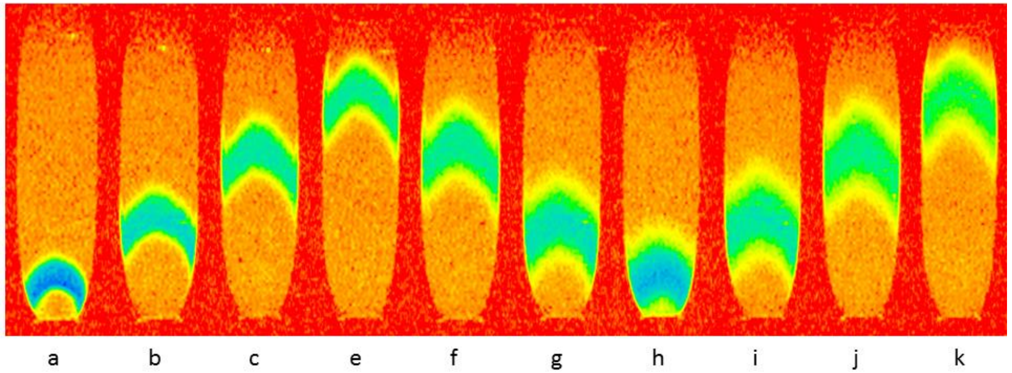
Local interaction **liquid water - porous media**

→ Key concept **to understand hydric transport**

→ **Direct visualisation of** water transfer **through porous network**



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

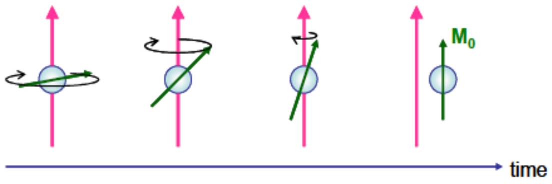
Efficient and general methodology necessary to follow hydric transfer in (heterogenous) porous material out of equilibrium.

→ NMR and MRI : **non invasive**, **multiscale, time and space resolved** approach.

Ex : Drying of…

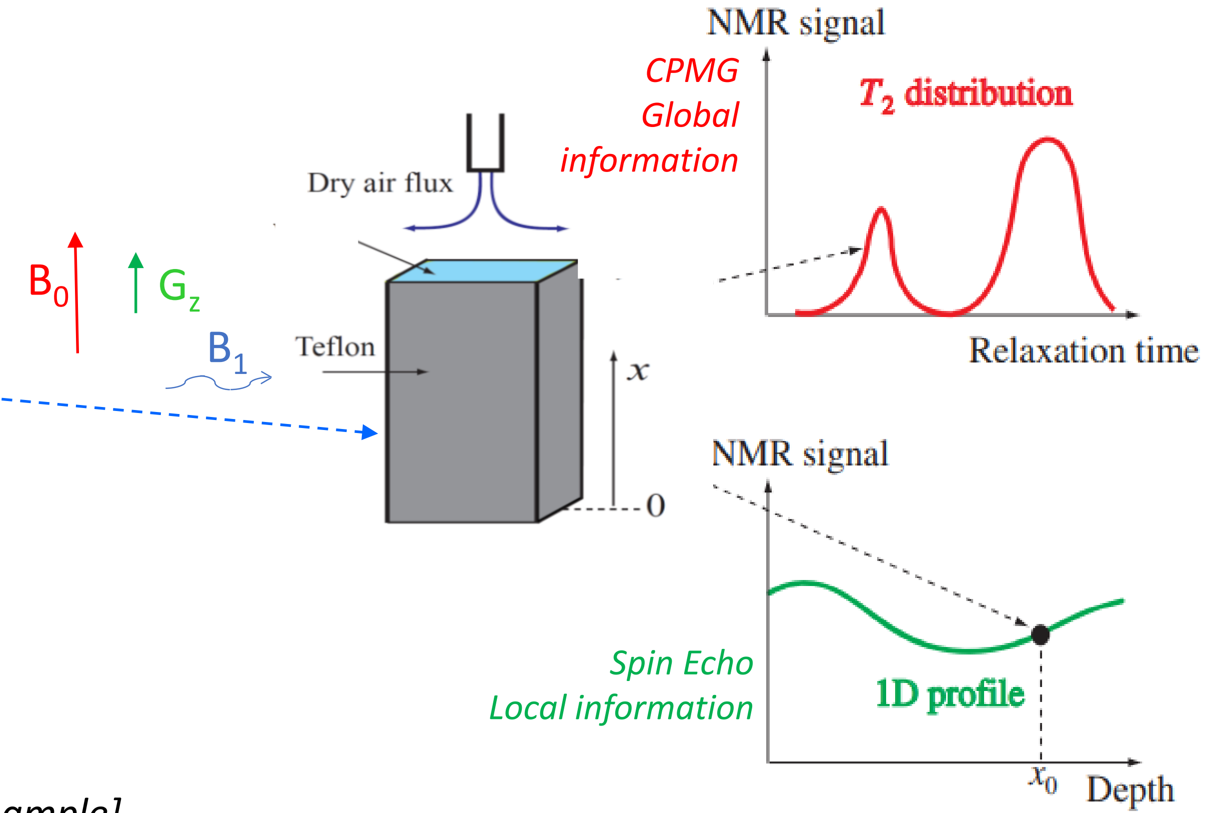
- Saturated nanoporous **silica glass** (undeformable prous medium)
- Colloidal or aluminosilacate **gel** (smooth porous medium).

Standard low field NMR dynamic relaxometry for porous medium, complex fluid,…



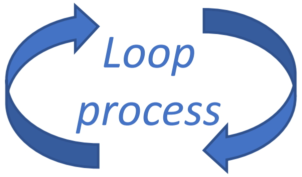
Minispec Brüker 0,5 teslas

+ Vertical gradient field



→ Transverse relaxation time T2 pdf

$\int A.\exp(-t/T2)\, d(\ln(T2))$



$V(sample) \approx 1\ cm^3$

Duration(exp) ≈ 10 min

↗ dry air flux + ↘ distance *[air tube – sample]*

→ « more agressive » drying by the top surface

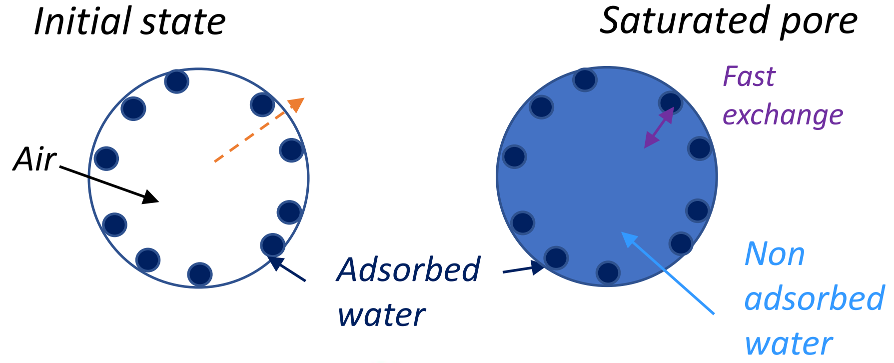
→ NMR of liquid proton (water at 20 °C by default)

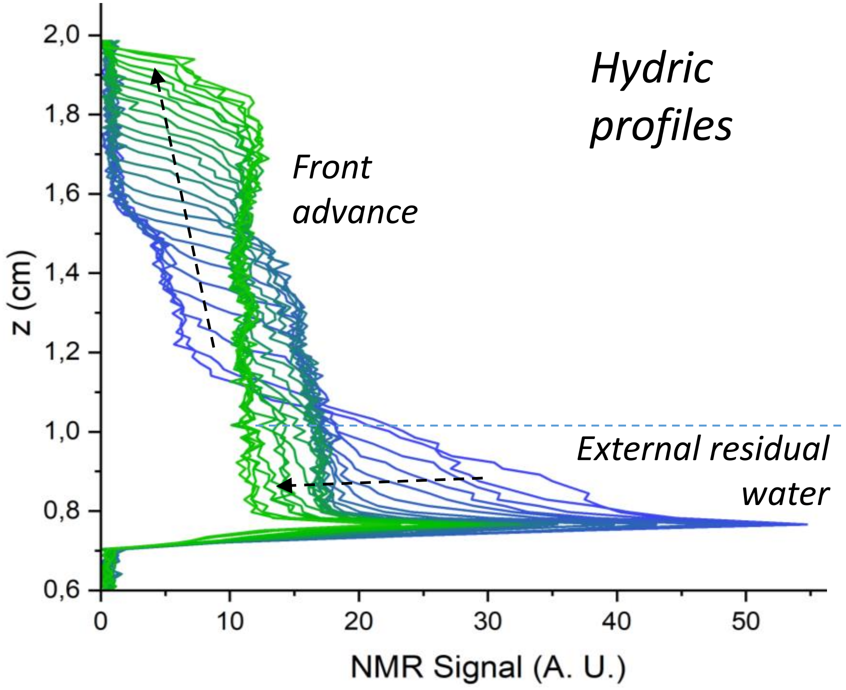
→ Direct access to NMR and MRI observable evolution

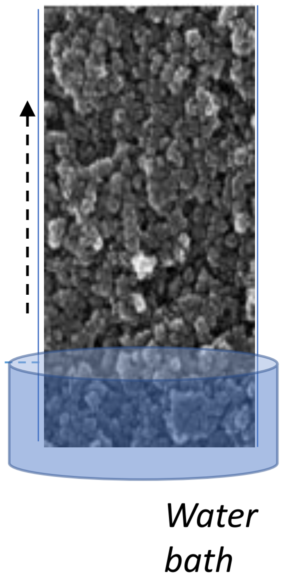
Vycor imbibition

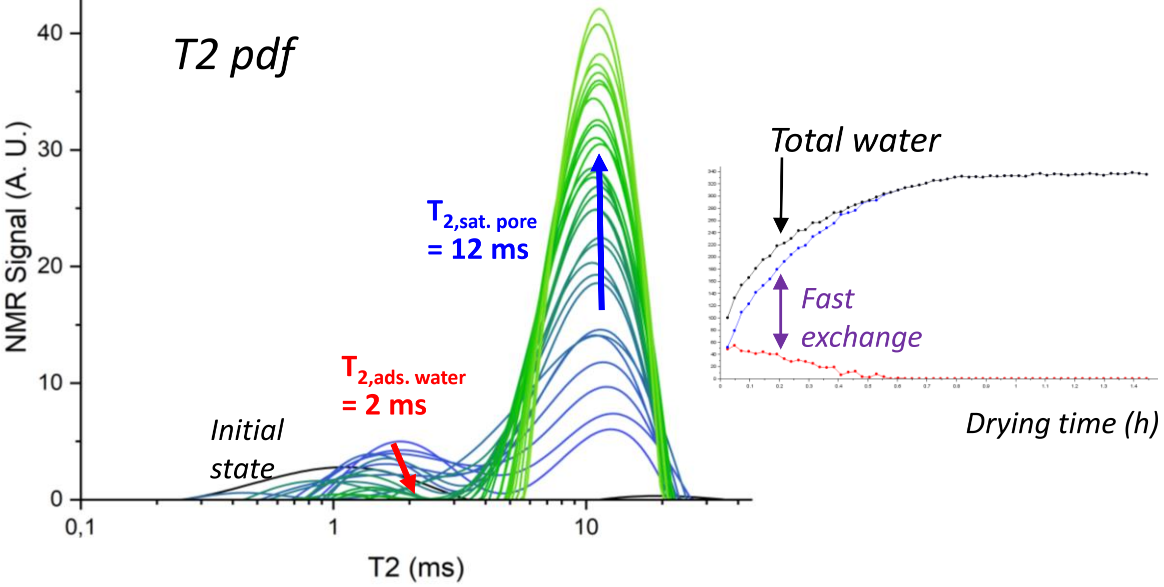
→Pure fused **silica glass** by **3D network of interconnected** tortuous **isotropic monodisperse** pores.

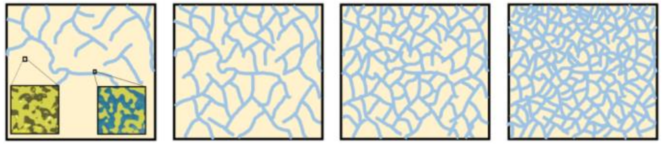
Surface area = 100 m² /g
Pore radius = 4.6 nm
Pore volume = 0.218 cm³ /g
Porosity ≈ 0.3











→ **Fast exchange** surface - bulk water ($T_{2,bulk} >> T_{2,Surface}$)
→ Single peak for saturated pore (Tarr and Browstein, 1979):

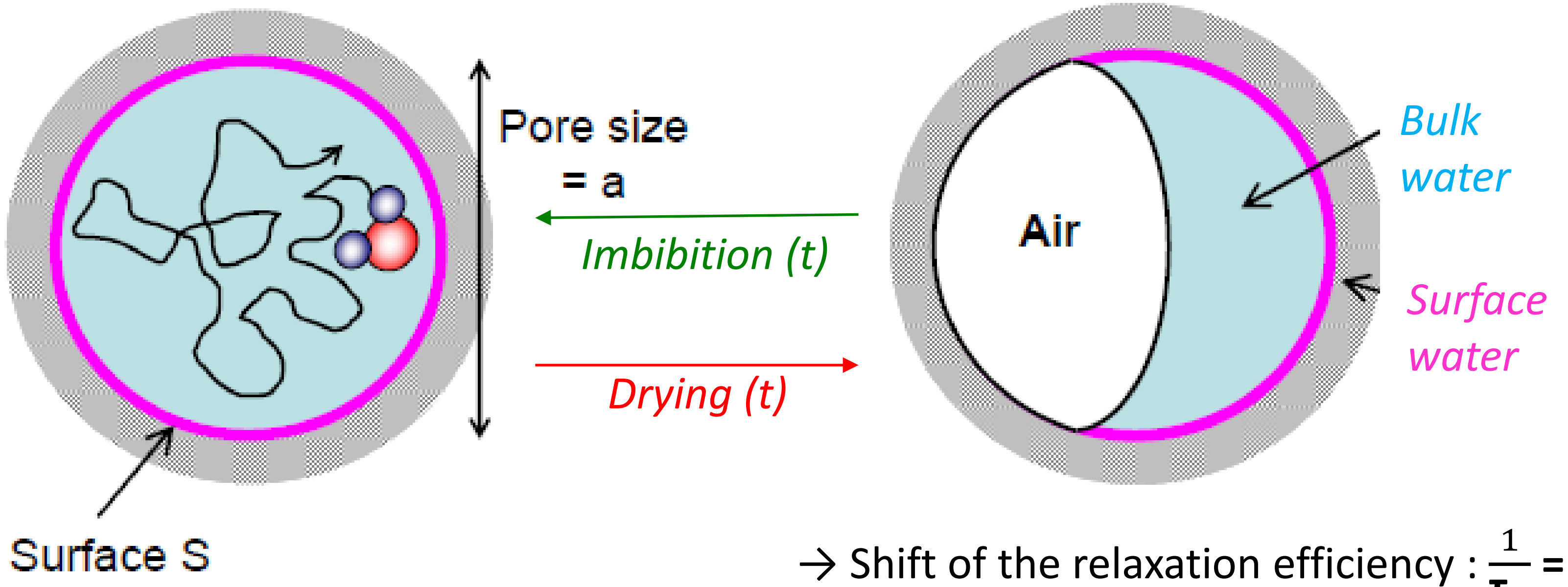
$$\frac{1}{T_{2,\,pore}} = \frac{n_{bulk}}{T_{2,\,bulk}} + \frac{n_{surface}}{T_{2,surface}}$$

$$\frac{1}{T_{2,\,pore}} - \frac{1}{T_{2,\,pure\ liquid}} = r_2 \cdot \frac{S_{pore}}{V_{pore}} = \frac{b}{T_{2,ads}} \cdot \frac{S_{pore}}{V_{pore}}$$

b : molecule thickness (m)
$T_{2,surf}$ (s) and relaxivity r_2 (m/s) → material dependency

Generalisation for partially saturated nanoporous medium

→ **Relaxation = Surface interaction process**



α integral of T2 peak

$$\tau_2 = \frac{T_{2,ads.}}{b} \cdot \frac{V_{water}}{S_{wet}}$$

→ Shift of the relaxation efficiency : $\frac{1}{\tau_2} = \frac{1}{T_{2,\text{ pore}}} - \frac{1}{T_{2,\text{ pure liquid}}}$

→**Vycor : b = 0,38 nm ≈ water molecule size**

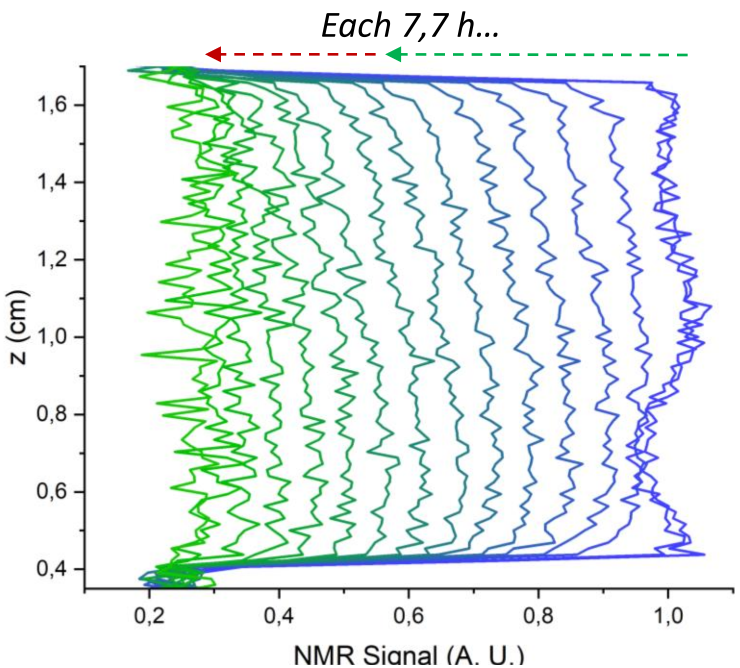
Fast exchange bulk - surface if :

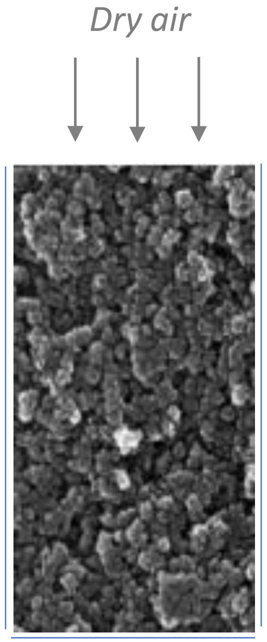
- → **1 molecule** can **explore the surface and the bulk** several times during the time T2 by diffusion
- → **Surface residence time << Diffusion time** inside the pore

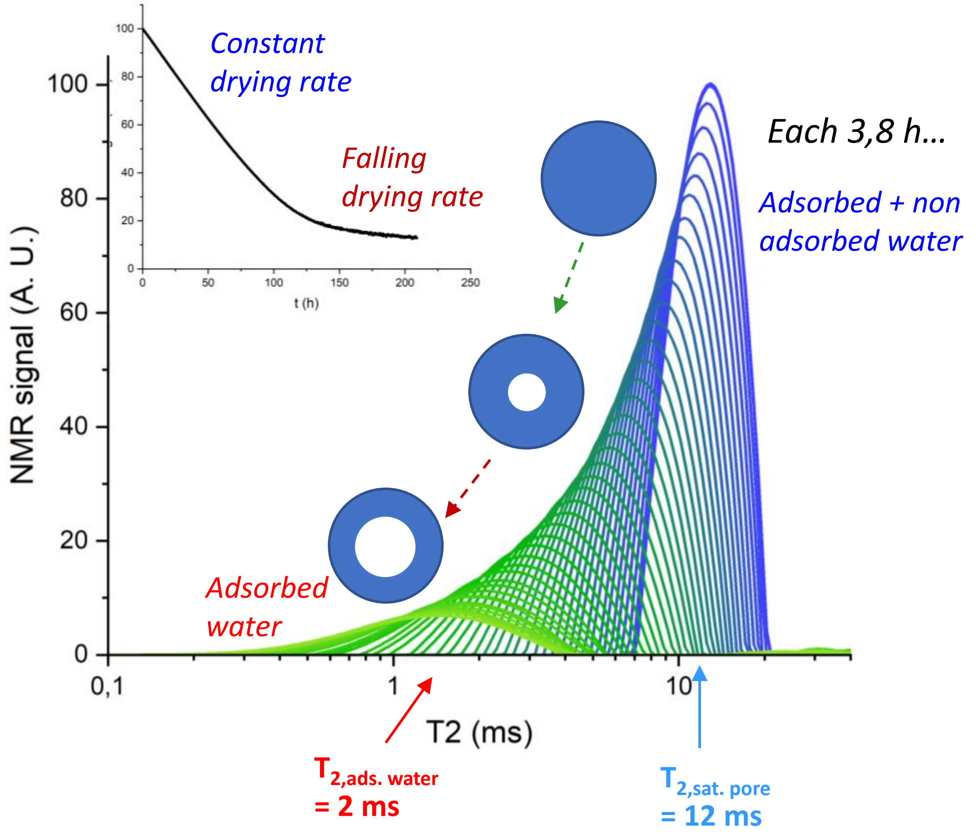
Dynamic relaxometry easier to interpret if :

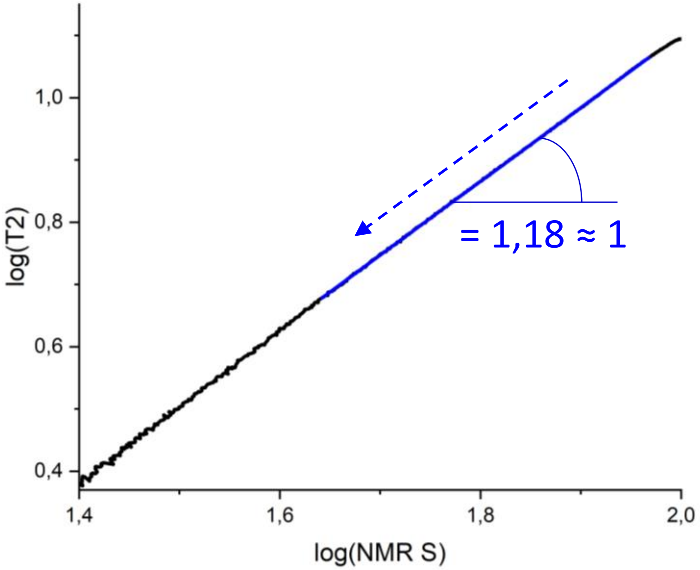
- → **$T_{2,ads.}$ is constant during the** drying i.e. stable roughness, chemistry,…
- → **No gradient** of water content, anistropic **deformation**,…

Vycor slow drying by the top surface









→ Back to **initial state by 2 stages: constant** and **falling drying rate period**.

→ **Homogeneous desaturation**

→ T_2 α V(water)/S(wet)   Peak area α V(water)

S(wet) constant during the constant drying rate period

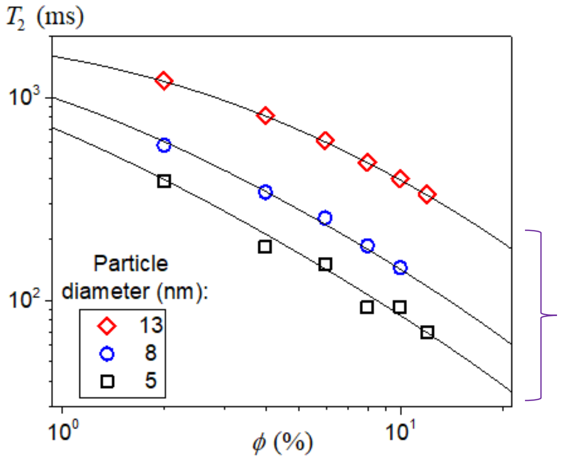
(Power law ≠ 1 : physical inhomogneity effect ?)

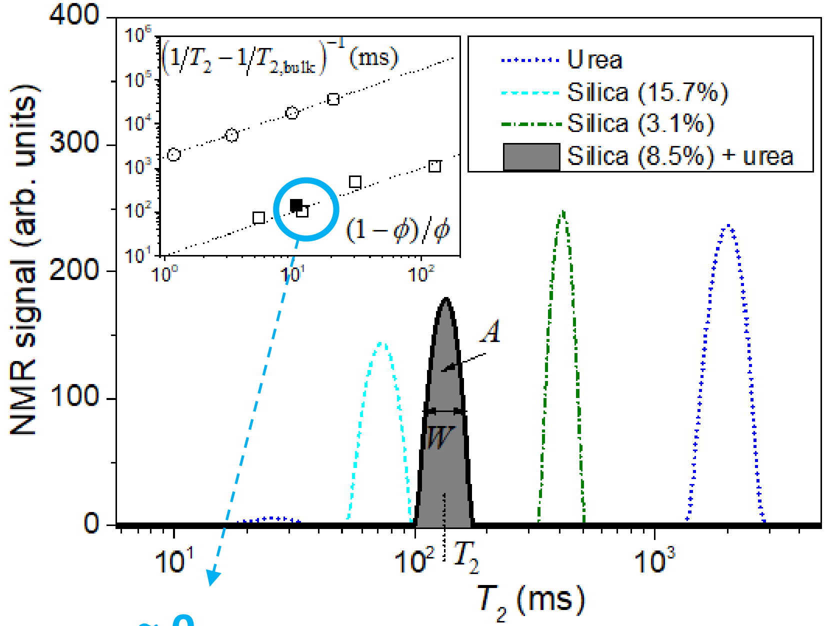
Maillet
Sidi-Boulenouar
Coussot
Langmuir, 2022

Slow drying of colloidal gel (ludox) → Relaxation process investigation

$$\boxed{\frac{S(wet)}{V(water)} \leftrightarrow \frac{\phi}{1-\phi}}$$

T2 for Ludox gel





(○) Urea solution
(□) Suspension

(■) Suspension + Urea
(---) « Basic law »

« Basic » T_2
($T_{2,surf}$ is adjusted)

$$\frac{1}{T_{2,theo}} = \overbrace{\frac{1}{T_{2,bulk}} + \frac{3.b.\Phi}{r.(1-\Phi)}\cdot\frac{1}{T_{2,surf}}} + \overbrace{\left(\frac{\alpha.\Phi_0}{(1-\Phi_0)}\cdot\frac{1}{T_{2,surf,0}}\right)}^{\approx 0} + \left(\frac{3.b.\psi}{r.(1-\psi)}\cdot\frac{1}{T_{2,vap}}\right)$$

Φ : particule volumic fraction
Φ_0 : urea volumic fraction
ψ : Saturation

From fast exchange theory

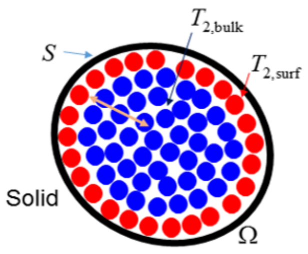
Pure water (2250 ms)

Surface water on Ludox particlue

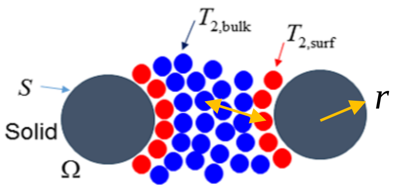
Water close to urea molecule

Vapor water ≠ 0 during desaturation

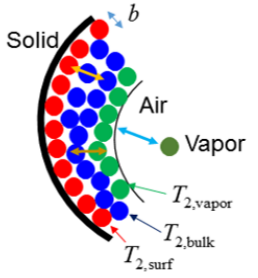
$T_{2,surf}$, $T_{2,surf,0}$ constant
if stable chemical composition of Ludox and urea



Saturated pore



Suspension

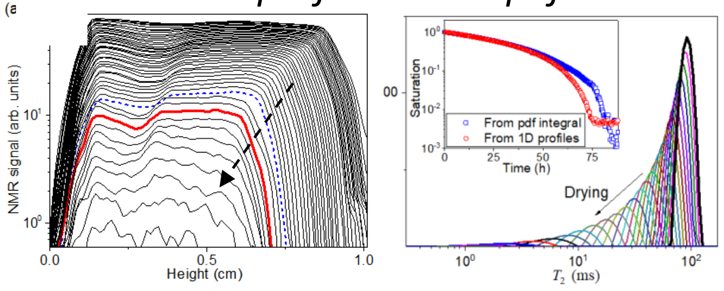


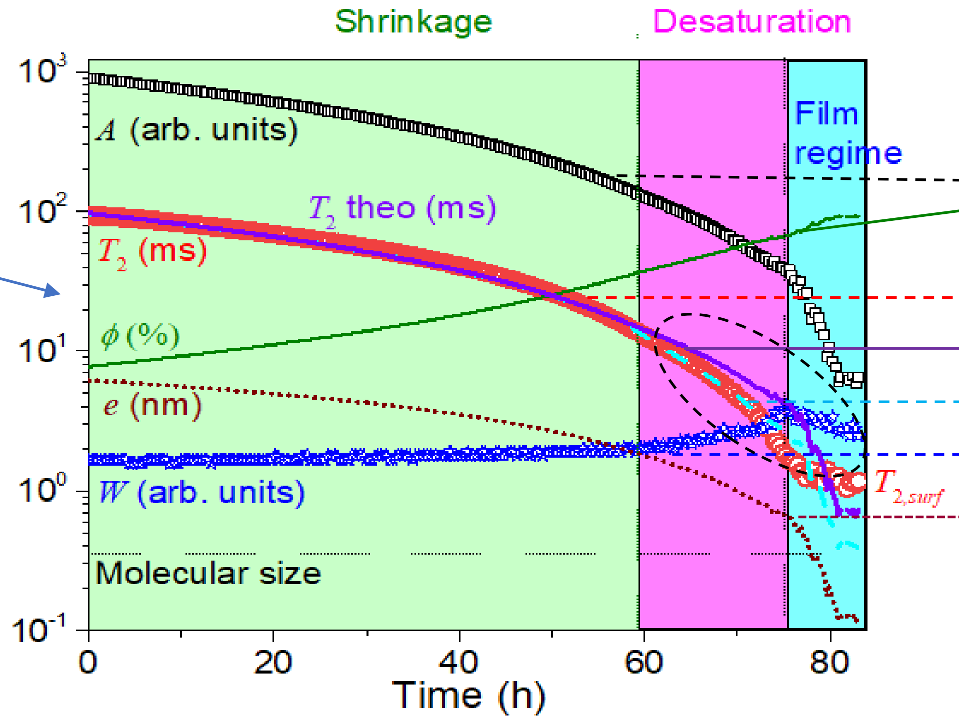
Partially saturated pore

Innovative term of relaxation process in **desaturated nanopore!**
→ Improved model

Slow drying of colloidal gel (ludox) → Model of relaxation vs Experiment

Gel slow drying
(5 nm diameter, φ_i = 8 %)
1D profile and T2 pdf





From Amplitude T2 peak (α water mass)

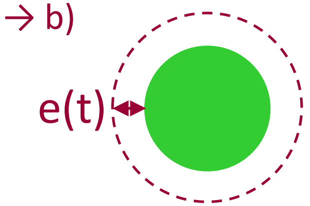
Direct measurment of T2(t)

From T2 basic model

From T2 improved model (vapor) !

From T2 peak shape

From Φ(t) + simple spherical model of water layer (e(t) → b)



Profiles → **Homogenous gel** during the most of the drying → constant W(t)
T2 pdf → **Φ(t)**, **e(t)**,…

3 regimes (shrinkage, desaturation, film) for a **full description** of the drying:

Period 1 → **$T_{2,theo}$(t) predicted** by the **basic model** during the shrinkage
→ Power law [T2 vs NMR Signal] **PL(t) ≈ 1**

Period 2 → **T2(t) predicted by improved model** during desaturation if **$T_{2,vap}$** is adjusted.
$T_{2,basic\ theo}$(t) > **$T_{2,improved\ theo}$(t)** during desaturation.
New relaxation process mandatory! : **$T_{2,vap}$ estimated** inderctly by the « liquid NMR way » !

Period 3 → **$T_{2,surf}$ ≈ constant** during film regime (« molecule by molecule » desorption)

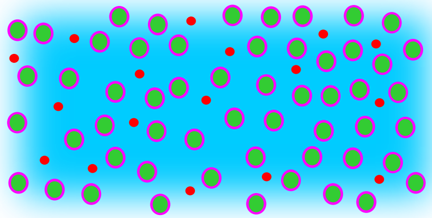
Particles **fully wet**, stable and **ensure the transport** to the top surface

Model scenario of slow drying of colloidal gel (ludox) → Several stages

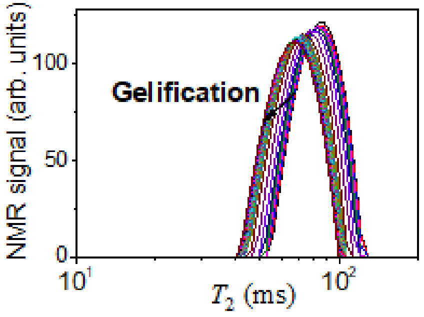
Colloidal gels (solution of Ludox
= silica suspension stabilized by Na_2O)

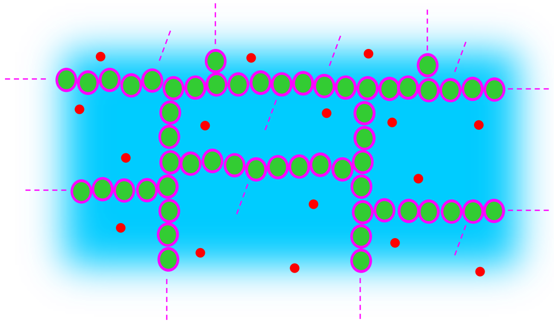
E. Julien
B. Maillet
L. Tocquer
S. Aime
P. Coussot
(Langmuir 2024)

Silica particule
Bulk water
Urea molecule
Surface water
Humid air (in white)

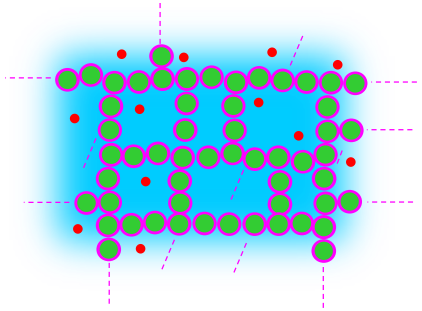


Previous gelification (from brownian motion to lattice)

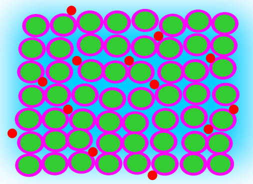




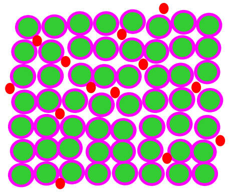
Drying to more ramifications (shrinkage)



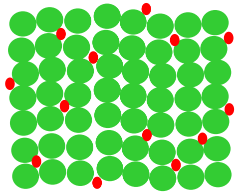
Drying to a compact stack (shrinkage)



Drying to desaturation of bulk water (air invasion)



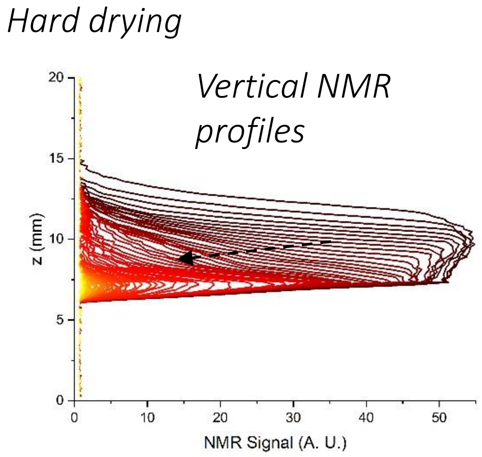
Drying to desaturation of surface water (film)

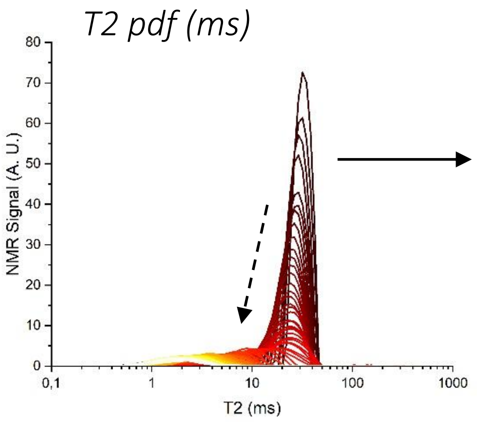


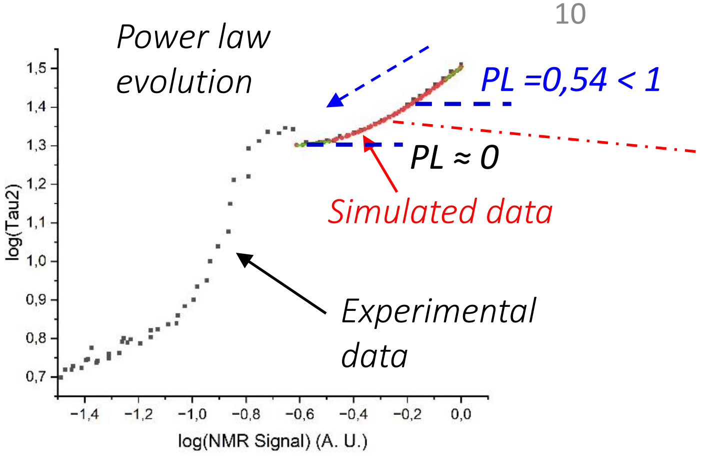
→ Dynamic relaxometry can follow drying step by step

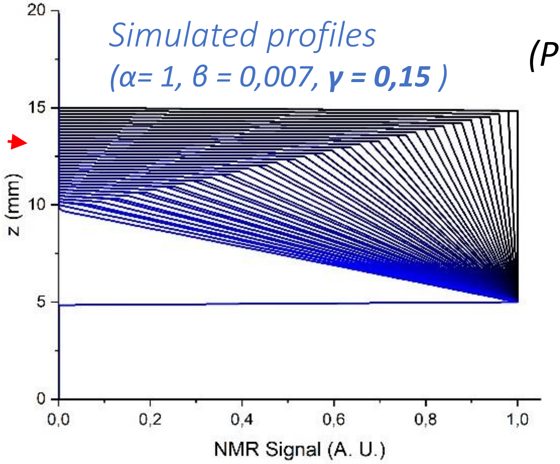
Sidi-Boulenouar R.
Maillet B.
Poulequen P. (CEA)
Carouge M.
Ayturk H.
(Publication in process)

Hard drying of aluminosilicate gel predicted by a simulation (generalized dynamic relaxometry)





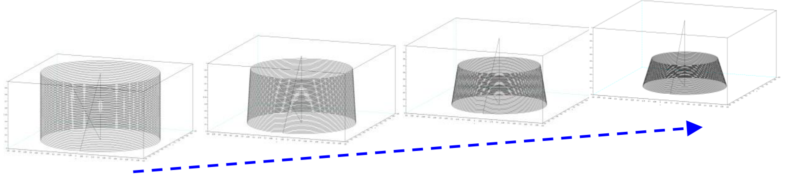


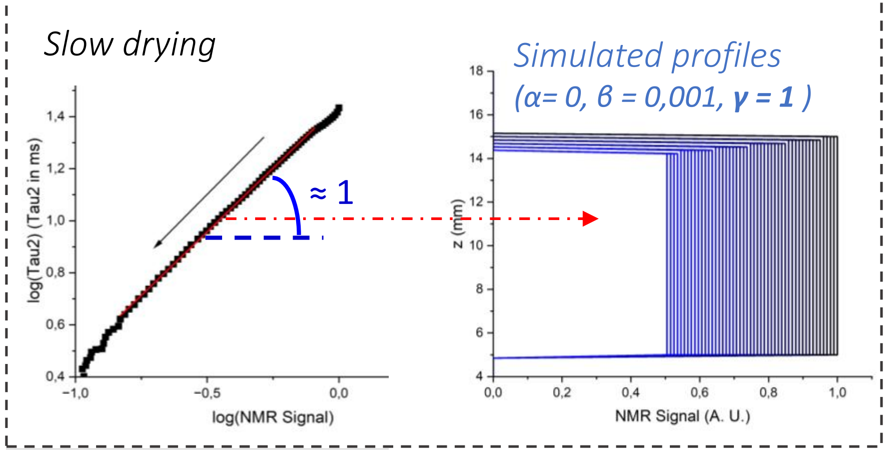


Power law deviation (≠ 1, non linear, inflection point) to the standard law (= 1) despite chemical stabilty of AlSi gel during drying.

→ **Pure physical heterogeneity effect!** (gradient of volume particule, shrinkage, default of particle reconfiguration).

→ **3 parameters to simulate equivalent simplifed linear profiles** in order to predict the realistic power law evolution during the first part of the drying.





→ **Very good** prediction of the gel behaviour **despite strong heterogeneities** thanks to a unique set of paramter of simulation.

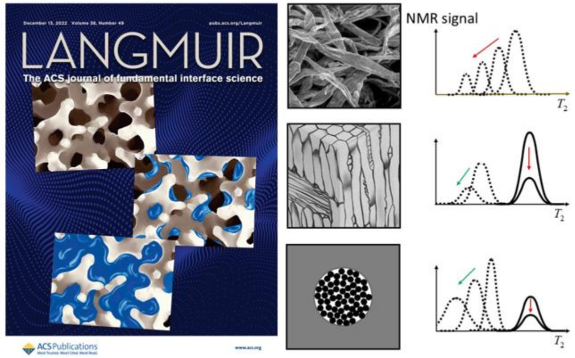
→ **Simplified equivalent profiles well defined.**

→ **Default of reconfiguration** of gel particle can be **quantified** and **folowed**

To conclude and go farther.

NMR dynamic relaxometry:

- Is a **non invasive**, **time** and **spatial resolved** and **multiscale** innovative approach
- Follows all transfer by **hydric profile** and **T2 distribution evolution**
- Catches **power law evolution** of log(T2) vs log(NMR Signal)
- Is available for complex fluid, porous media and **can be generalized** to the **smooth material** as gel, suspension… invaded by other protonic liquid.
- Can be **generalized for all the stages of the drying** → relaxation **« vapor term »**
- … Needs to a **numercial simulation** to be fully interpreted for **smooth material**…
- Can **feed predictive physical** model of hydric transfer…



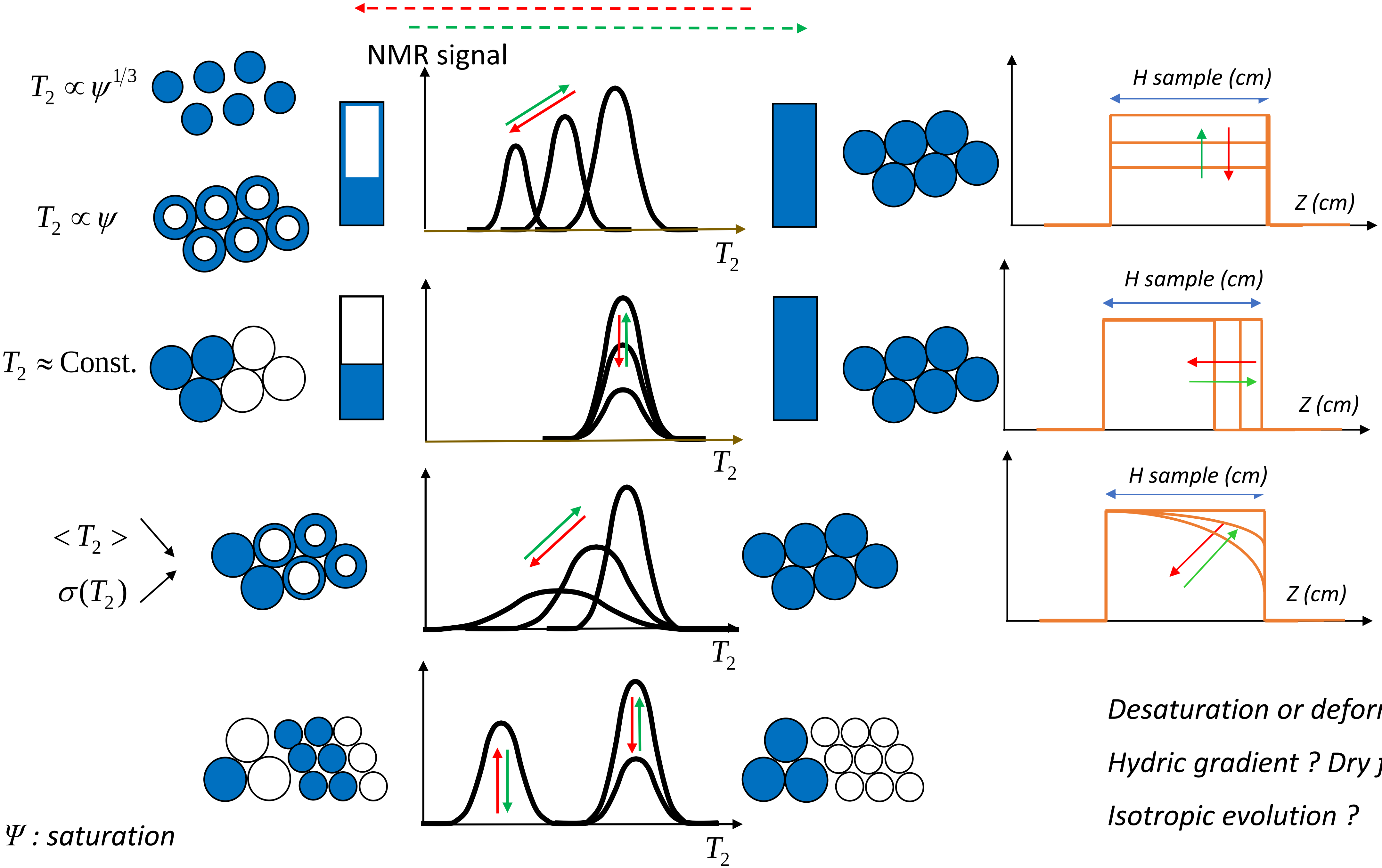
Ph. Coussot
Université Gustave Eiffel

European Research Council
Established by the European Commission

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

Back up…

Main expected results



Ψ : saturation

Desaturation or deformation?

Hydric gradient ? Dry front ? Dewetting ?

Isotropic evolution ?

Bases of NMR relaxometry

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

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

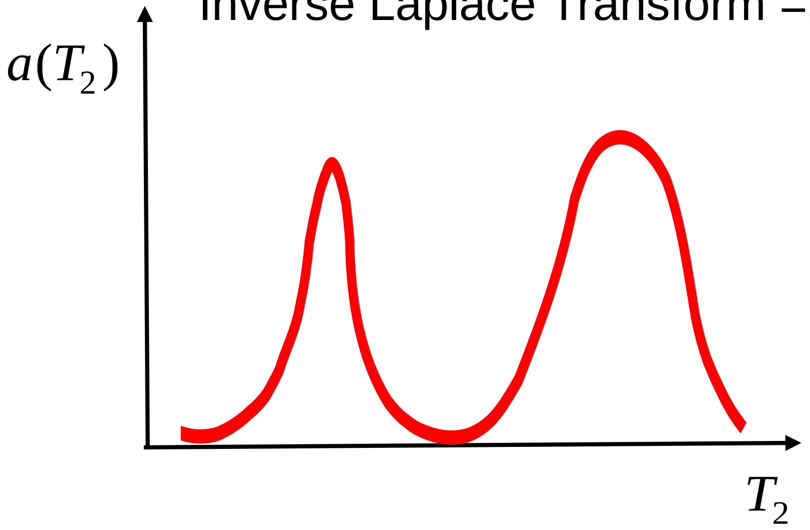
* Relaxation times depend on the molecule environment

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

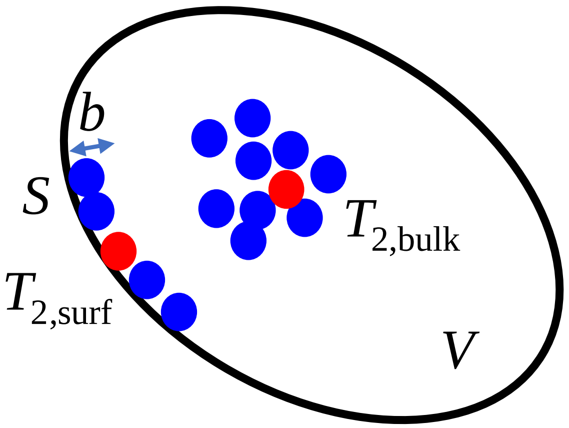
$$s(t) = \int_0^\infty a(\lambda)\left(\exp\left(-\lambda t\right)\right) \mathrm{d}\lambda \qquad T_2 = 1/\lambda$$

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

Inverse Laplace Transform =>



In a pore:
Two main relaxation times:



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

Signal of a given molecule:

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

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

Total time spent over the surface: Δt_{surf}

Brownstein-Tarr (1977)

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

$$\boxed{\varepsilon = \frac{\Delta t_{\mathrm{surf}}}{t}}$$

(Fraction of time spent along the surface)

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

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

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

Si $\varepsilon << 1$

$$\boxed{T_2 \approx \frac{T_{2,\mathrm{surf}}}{b} \frac{V}{S}}$$

Evolution of the pdf depending on material characteristics

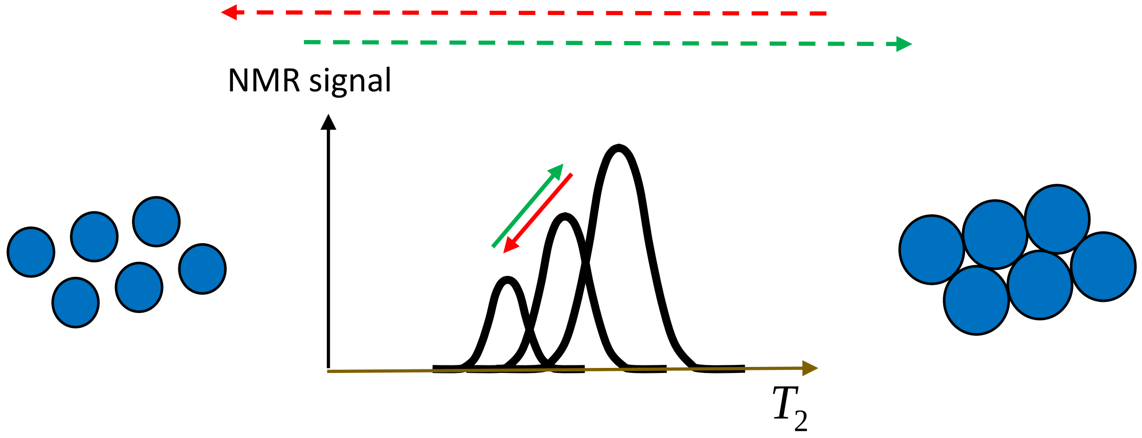
Simple (homogeneous) shrinkage or swelling

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

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

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

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

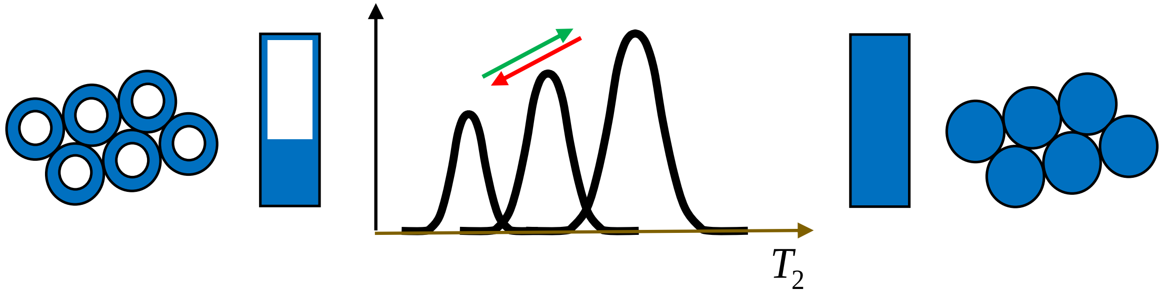


Desaturation without dewetting

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

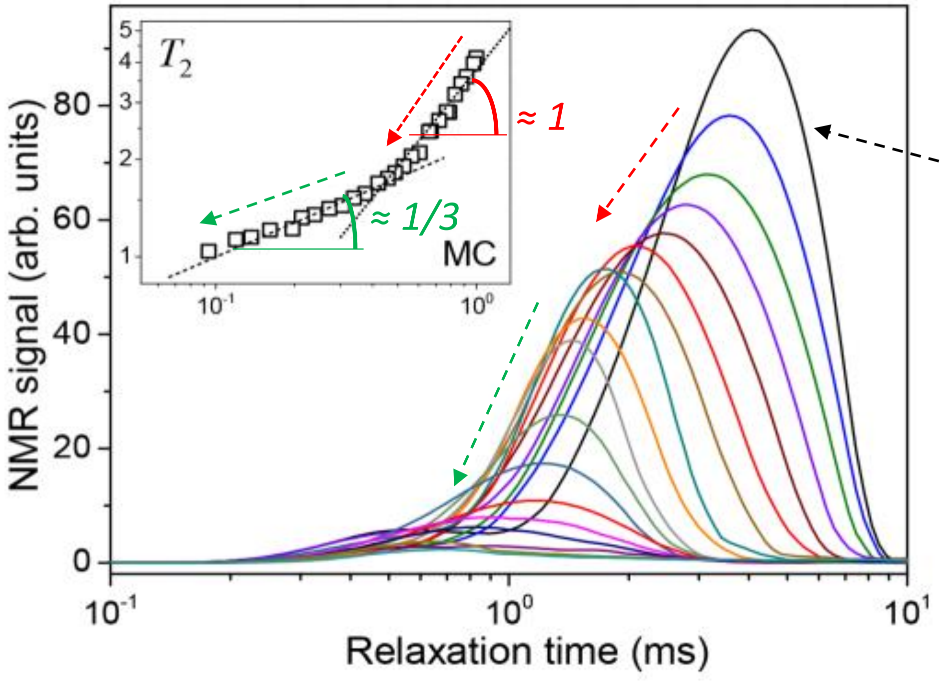
$$\frac{S}{V} \propto \psi^{-1}$$

$$\Rightarrow T_2 \propto \psi$$



Drying of humid cellulose fibers

Maillet, Sidi-Boulenouar, Coussot
Langmuir, 2022

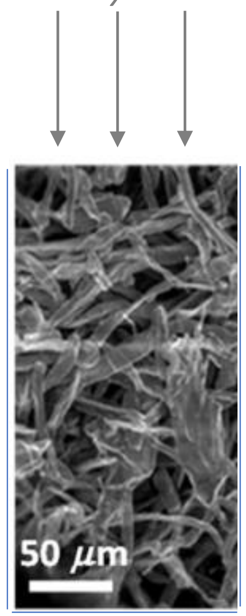


Initial state : Pure humid cellulose

- **Saturated in bound water** (T2 < 5 ms)
  → intrafiber water = nanopore
- **No free water** (T2 > 10 ms)
  → interfiber water = mesopore

l(diff) = √(6.D.T2) ≈ 6 µm >> nanopore…
And r2.a/D < ≈ 10^{-6}
… Surface limited relaxation OK !

Slow
dry air



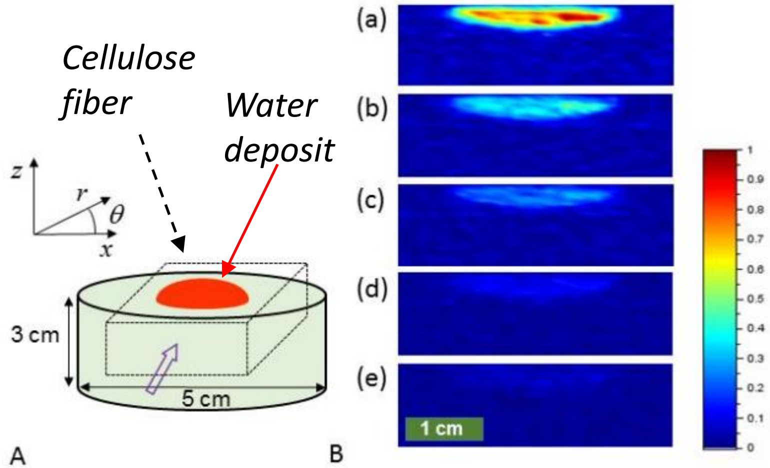
Fibre dimension :
700 x 20 µm

2 clear stages during the desorption:

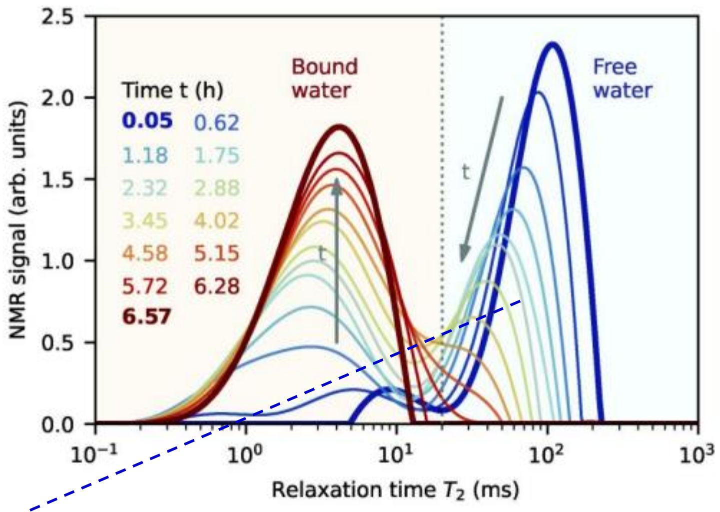
Slope (log(T2) vs log(Peak Area) ≈ **1**
→ Constant wet surface (T_2 α **a^3** and Peak area α **a^3**) ↔ **Non adsorbed** water drying
Slope(log(T2) vs log(Peak area) ≈ **1/3** → Isotropic shrinkage
↔ **Adsorbed bound** water drying (T_2 α V/S α a^1 Peak area α V α a^3)

The fate of a water drop in cellulosic material

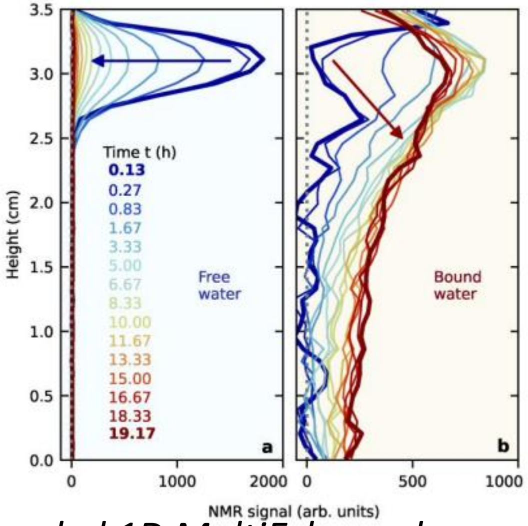
Yan, Zou, Gil-Rocca, Maillet, Saint-Michel, Coussot, 2024



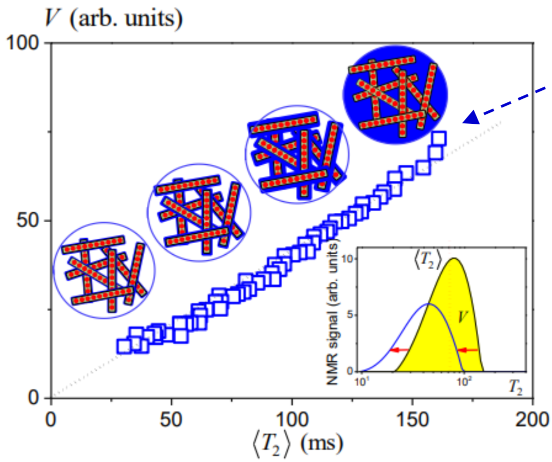
***Free water* dynamic** *in cellulose stack fibers after water drop deposit probed by MRI (MultiEcho) at 6, 12, 18, 36, 66 mn*



T2 pdf evolution *after drop deposit*



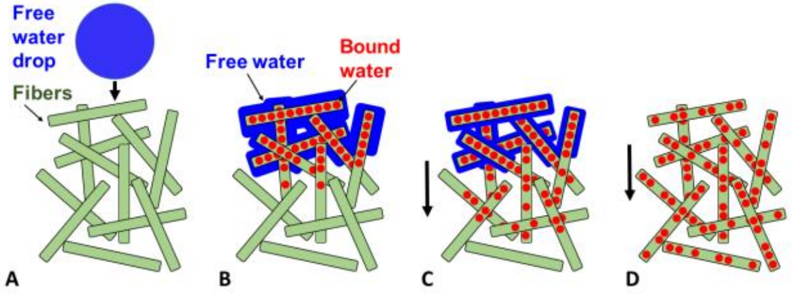
Coupled 1D MultiEcho and Single Point Imaging by MRI
→ ***Free*** **and** ***bound*** ***water vertical profile*** *evolution after drop deposit*



$l(diff) = \sqrt{6.D.T2}$
$\approx 35\ \mu m \gg d(interfibers)$

Dynamic relaxometry for free ! (water)
→ ***$T_{2,\text{free water}}$ is proportionnal to $V_{\text{free ater}}$ i.e. Power law = 1***
→ ***Fiber is fully wet*** *during all the transfer*

Proposed scenario :



A) **Drop** deposit
B) **Interfiber invasion** by **free water**
C) **Free to bound** water slow **transfer with no dewetting of fiber**
D) **Bound water redistribution**

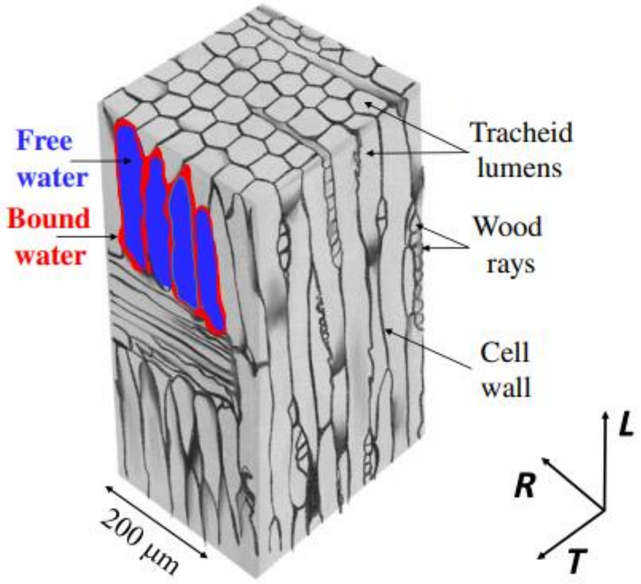
Drying of a green wood

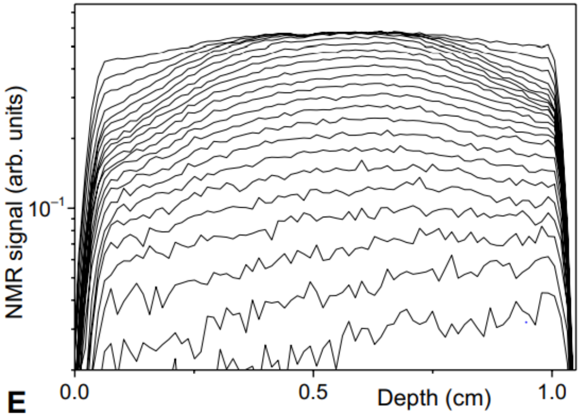
SCIENCE ADVANCES | RESEARCH ARTICLE

APPLIED PHYSICS

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

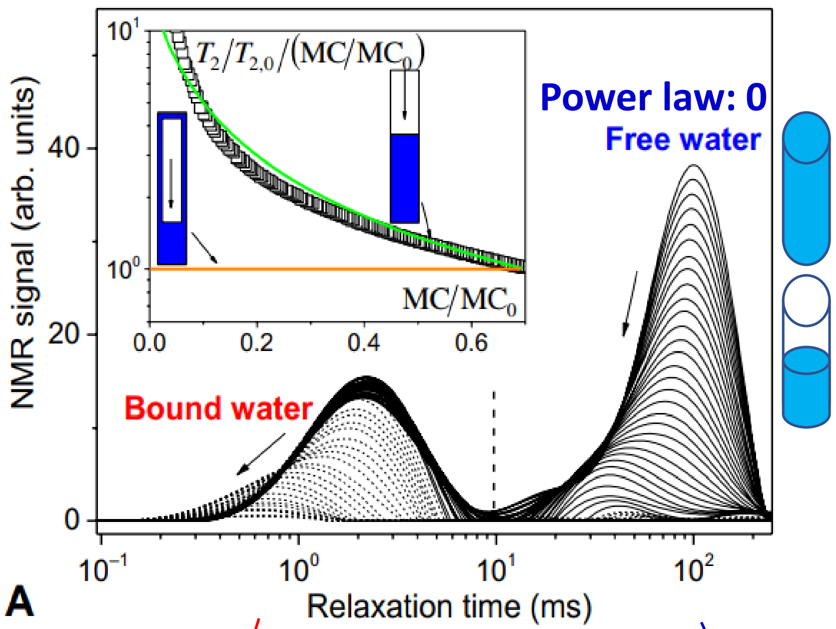
Marion Cocusse[1], Matteo Rosales[1], Benjamin Maillet[1], Rahima Sidi-Boulenouar[1], Elisa Julien[1,2], Sabine Caré[1], Philippe Coussot[1]*

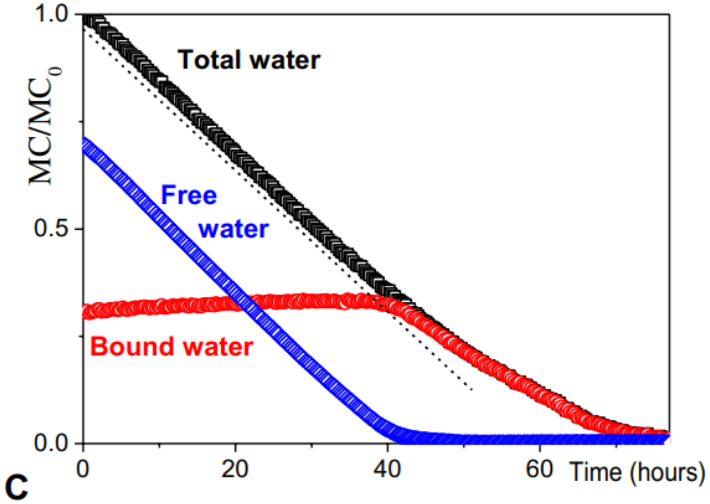




Free water profiles

Weak drying

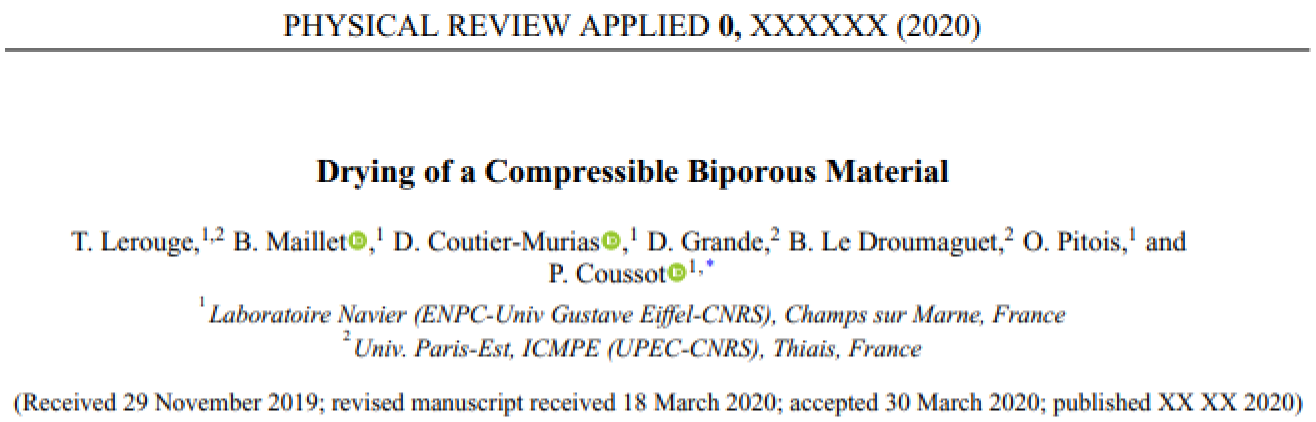




2) T_2(bound water) decreases.
→ **In accordance with contraction**

1) T_2(free water) constant i.e. **Power law = 0**
i.e. dS(wet/S(wet) = dV(water/V(water) .
→ **Total dewetting for tracheids during the constant drying rate period.**

Drying of a smooth biporous material

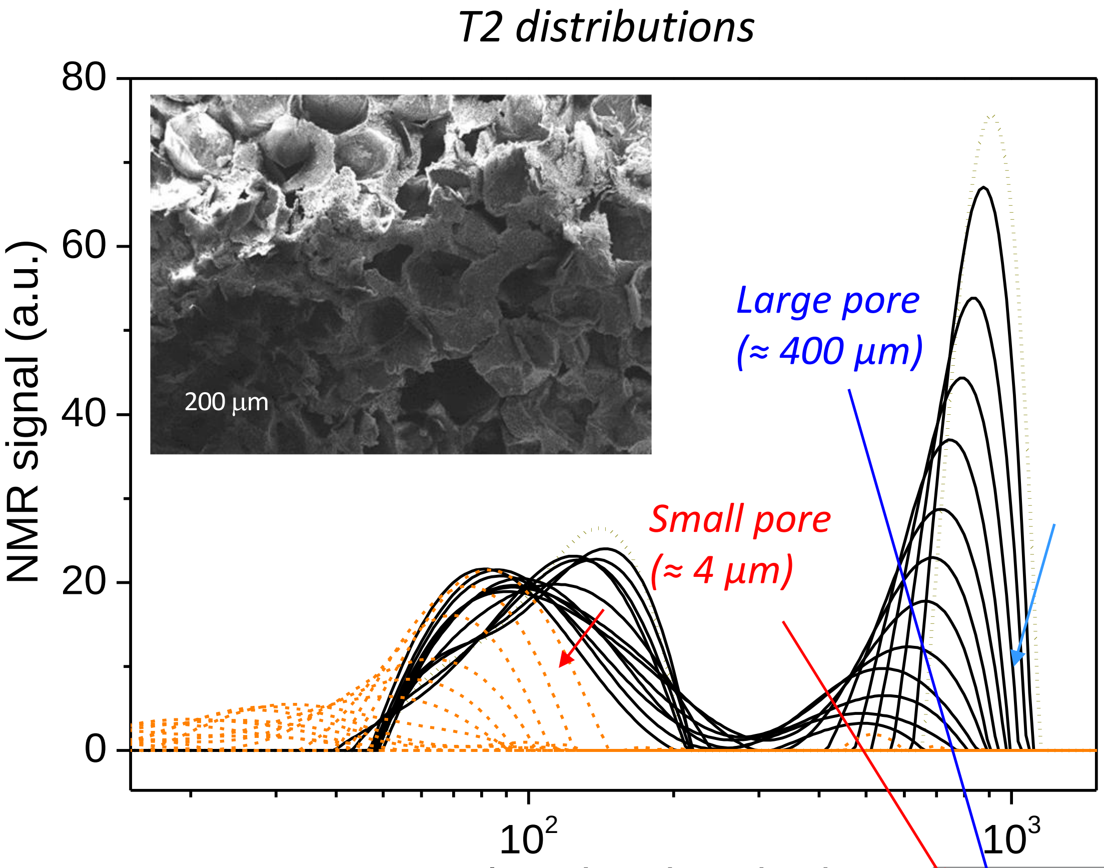

PHYSICAL REVIEW APPLIED **0**, XXXXXX (2020)

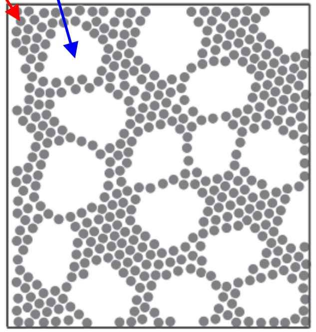
Drying of a Compressible Biporous Material

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*

(Received 29 November 2019; revised manuscript received 18 March 2020; accepted 30 March 2020; published XX XX 2020)





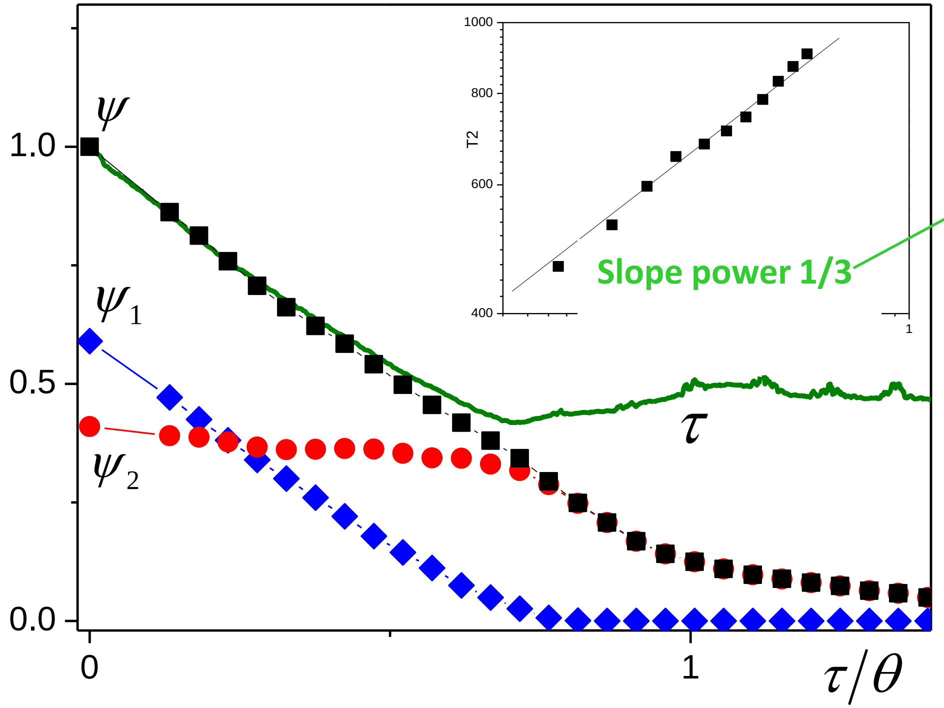
Generalization for all deformations :

Power law : 1/N, N degree of isotropy

1/3 → 3D contraction (spherical shape)

1/2 → 2D contraction(radial fiber contraction)

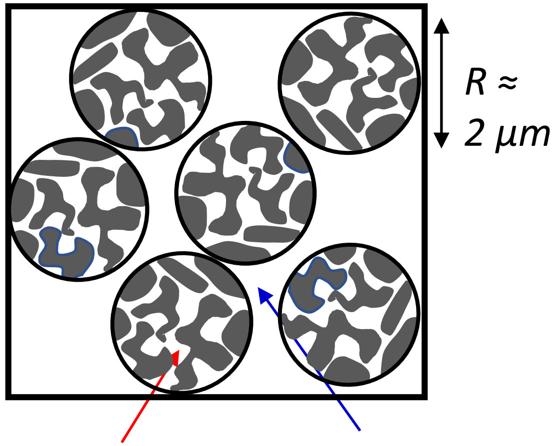
1/1 → 1D contraction (lamellar shape)



T_2 α a and
A α a^3
Isotropic contraction

Drying of porous bead packing

Maillet, Sidi-Boulenouar, Coussot. 2022

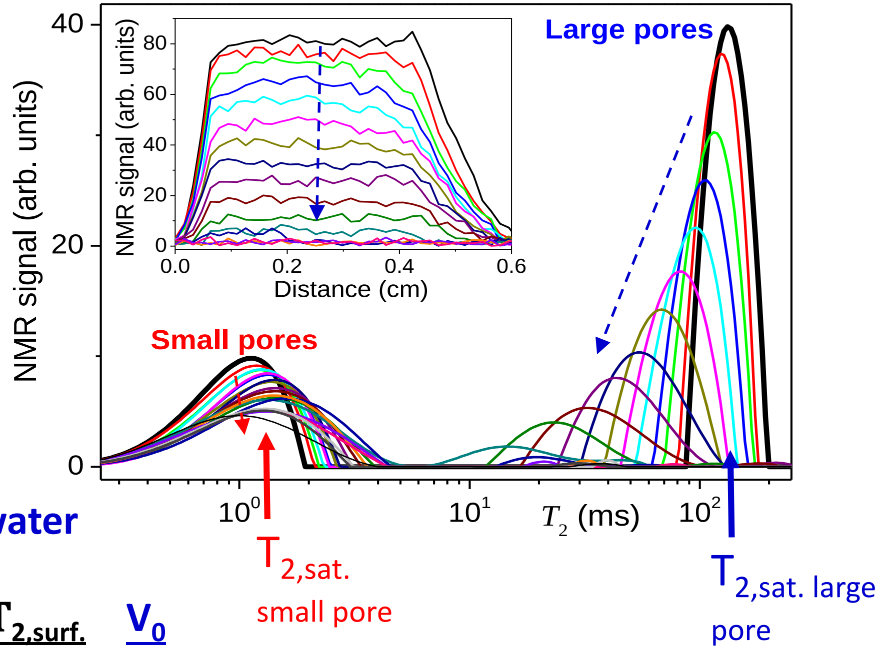


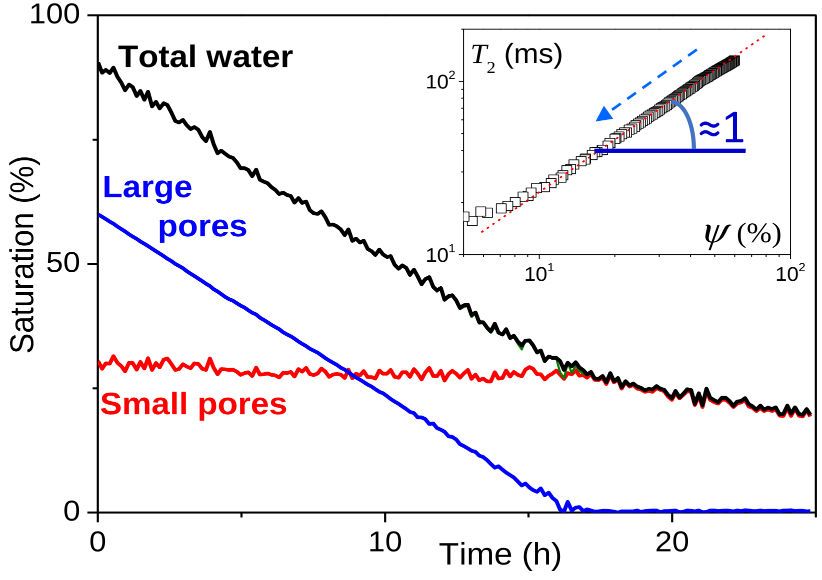
Internal water (small pore)

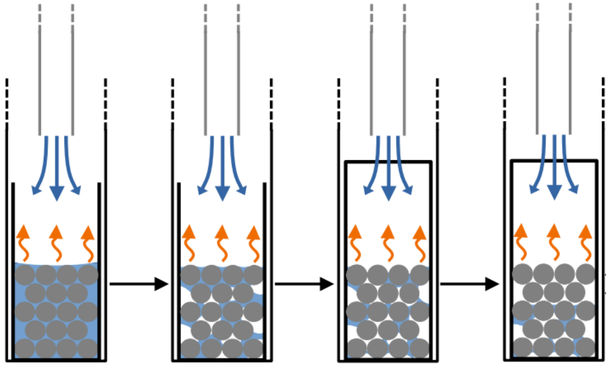
$T_{2,\text{Small Pore}} \approx \frac{T_{2,\text{surf.}}}{b} \cdot \frac{V_1}{S_1}$

Interstitial water (large pore)

$T_{2,\text{Large Pore}} \approx \frac{T_{2,\text{surf.}}}{b} \cdot \frac{V_0}{S_0}$







→ 2 pore sizes **initially filled** and **progressive disappearance** of liquid in **large pores,** very **homogeneous desaturation**

→ **Small pores :**

Saturated untill **full desaturation of large pores (constant wet surface)**

Ensure the transport of liquid toward the free surface **(constant drying rate period)**

It starts to dry slowly **(falling drying rate period)**

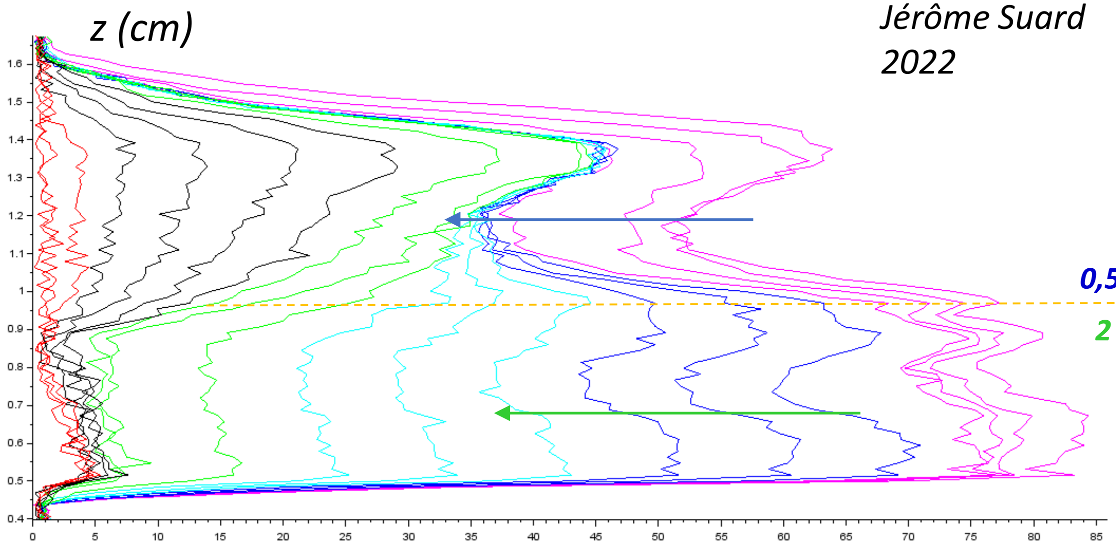
$T_{2,\text{Sat.}}$(Large pore) / $T_{2,\text{Sat.}}$(Small pore) → **Small pore size** ≈ 4,4 nm (Vycor : 4,6 nm)

Sat°$_{\text{Sat.}}$(Large pore) / Sat°$_{\text{Sat.}}$(Small pore) → **Volume fraction of internal water** ≈ 33 % (Vycor : 30 %)

Fast exchange theory → **Specific surface** ≈ 120 m²/ g (Vycor : 100 m²/g)

Drying of 2 layers glass bead packing

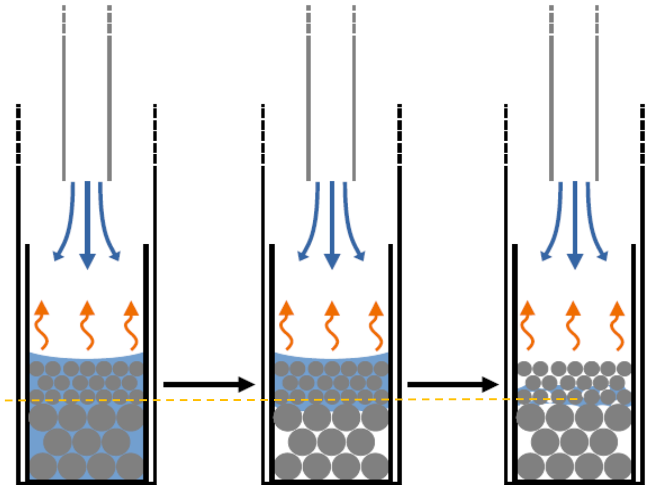
Philippe Coussot
Benjamin Maillet
Rahima Sidi-Boulenouar
Jérôme Suard
2022

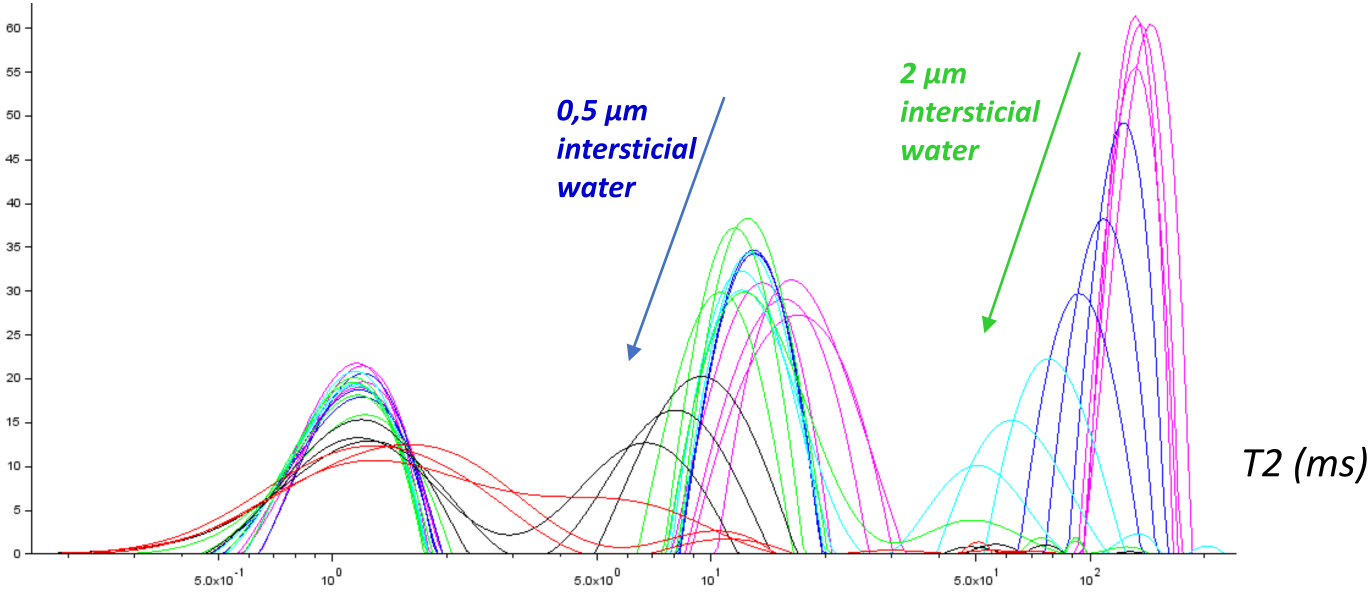


1D Profiles

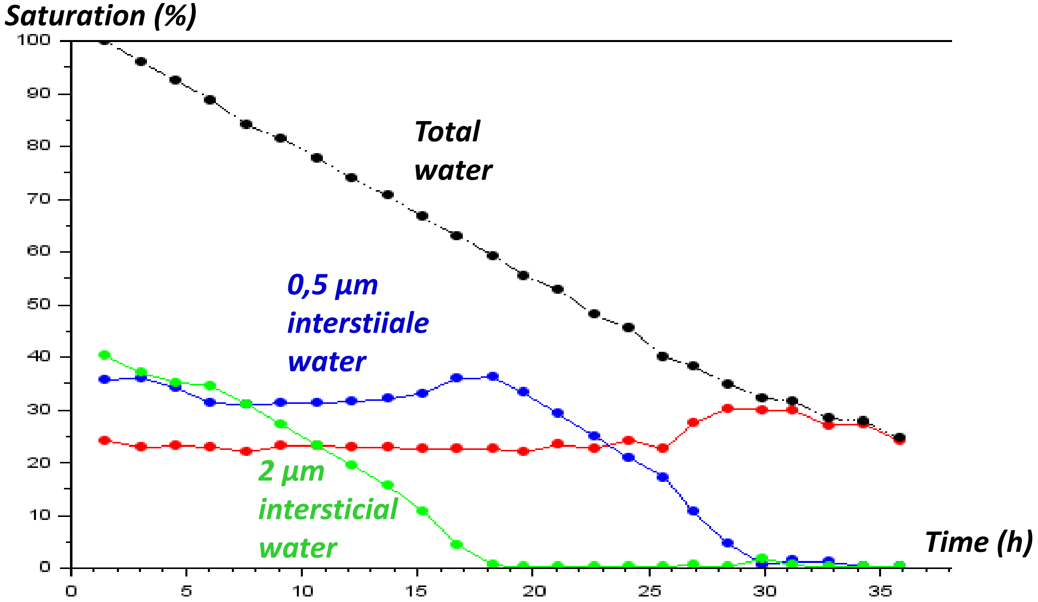
0,5 µm intersticial water

2 µm interstical water

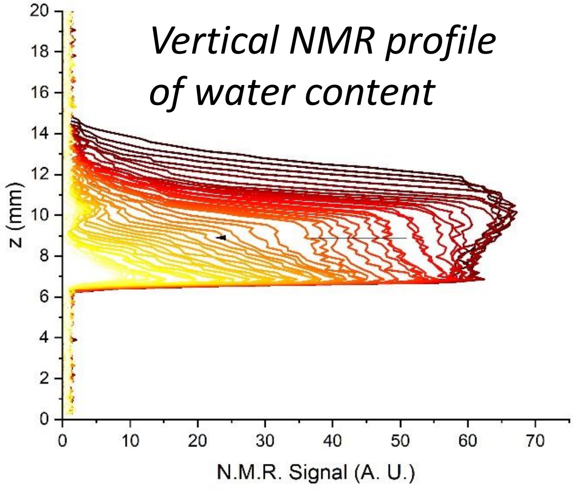


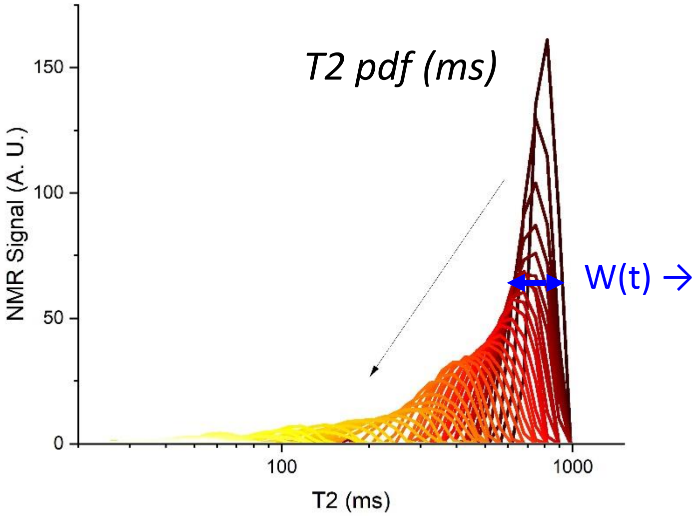


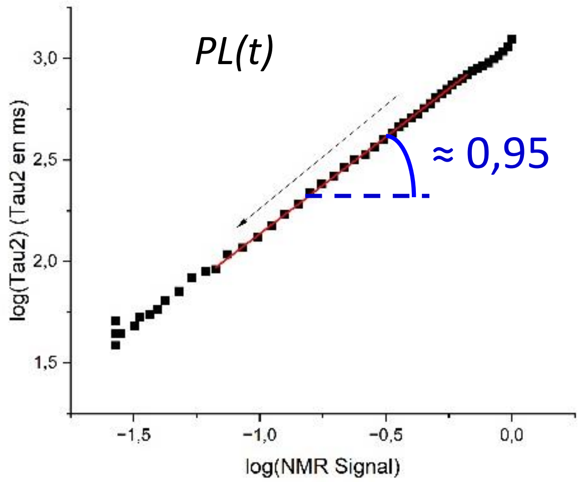
T2 distributions



Slow drying of colloidal gel (ludox) → Focus on the power law evolution







Sidi-Boulenouar
Maillet
Poulequen
Carouge
Ayturk
(Publication in process)

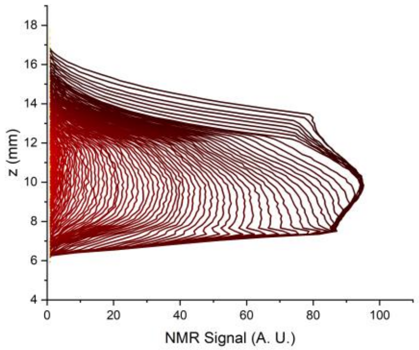
PL(t) = 1 during the hydric transfer if and only if…

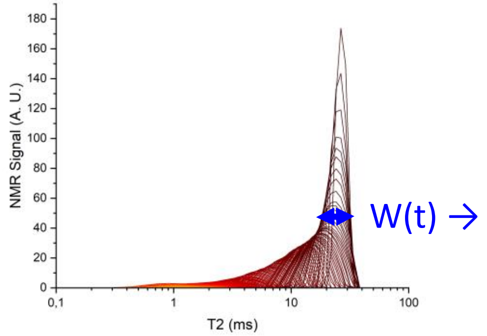
- **Stability** of the particle **chemical composition**
- **Fast exchange (surface and bulk water)** available
- **Full wet** surface
- **No too strong phyical default** (gradient, shrinkage, reconfiguration of the particle network,…)
- **Stable temperature**

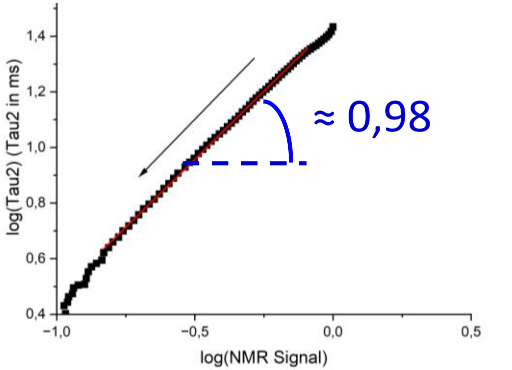
→ **Reference power law** available for simple case only

Soft vs hard drying of aluminosilicate gel

Soft drying



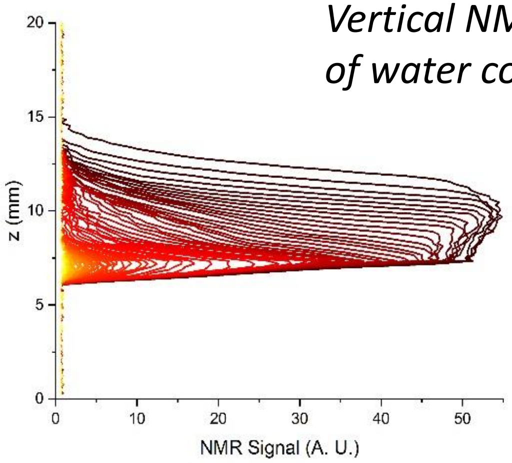


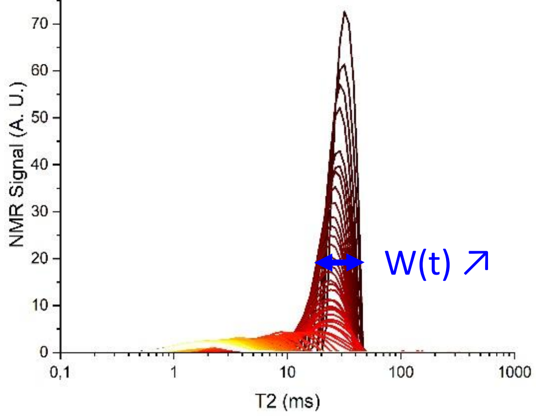


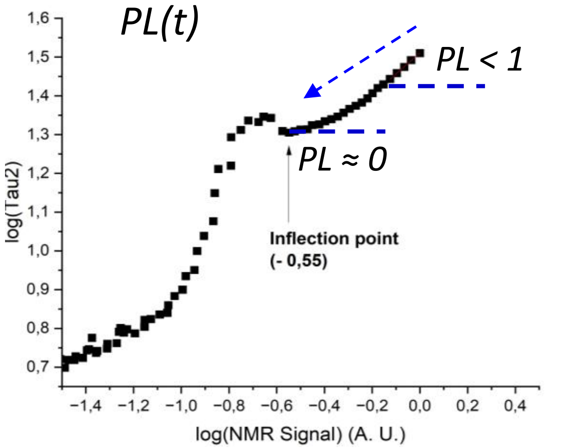
Vertical NMR profile of water content

T2 pdf (ms)

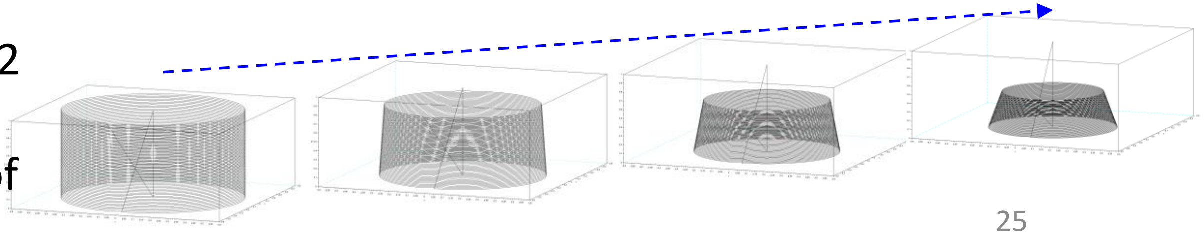
Hard drying







- **PL(t) ≈1** during the most of the **smooth drying** that validates the **chemical stability** of AlSi gel.
- **PL(t) variation** for **hard drying** (< 1, deviation, inflection point, 2 stages…)
  → **Physical default effect ?** (deformation of the gel, gradient of volume fraction, particle reconfiguration)



Presentation of the numerical simulation to predict hydric behavior.

In order to predict a set of **simplified** profiles that matches with PL(t) during the **first part** of the drying (before inflection point).

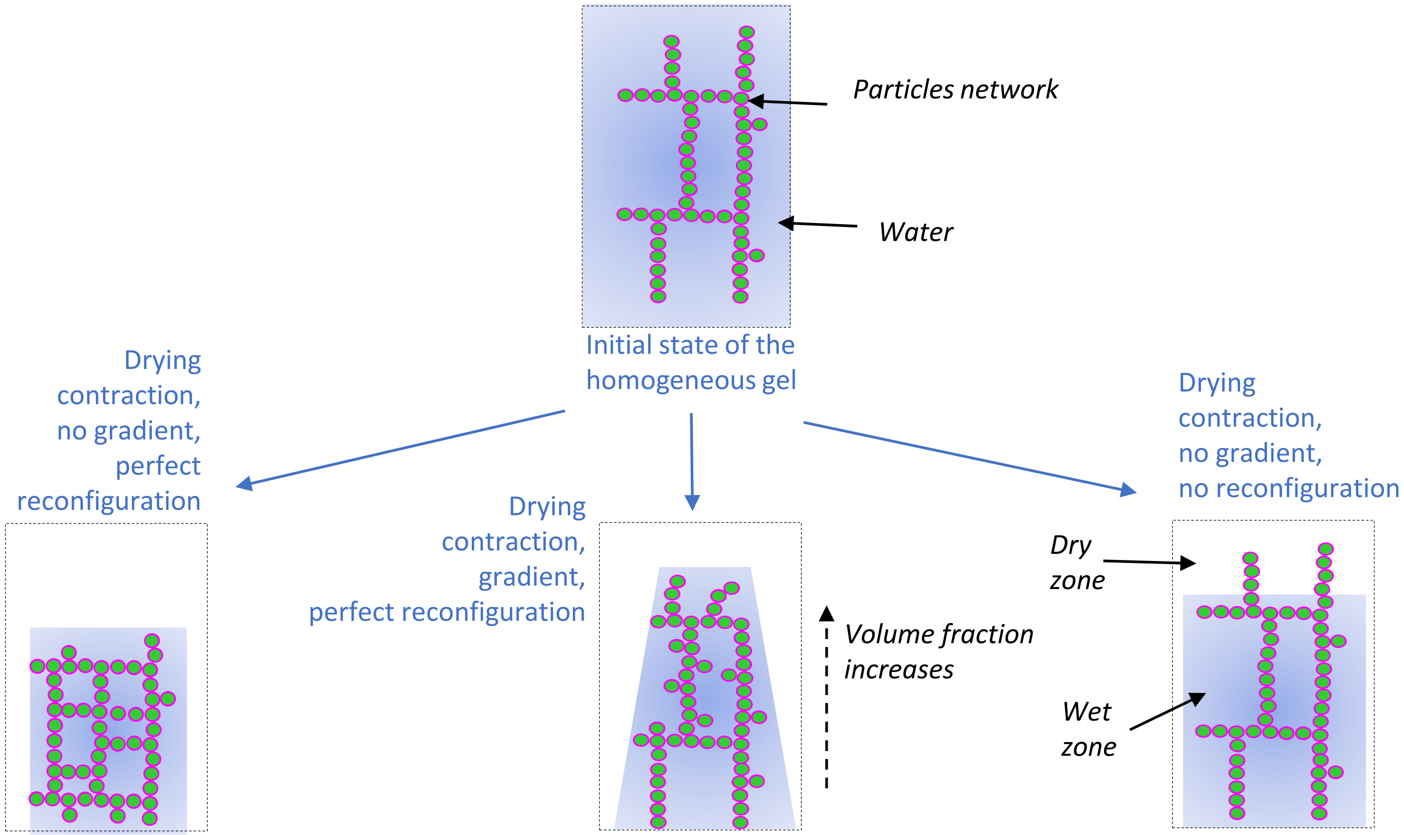
Simplifications:
- **Linear** profiles
- **Chemical stability** of the particle
- **Proportionality local NMR Signal** vs local **ϕ** for each slice.

3 parameters of physical default:

α: gradient parameter
→ deviation to the linearity

β: contraction parameter
→ position of the inflection point

γ: reconfiguration parameter
→ initial PL



Particles network

Water

Initial state of the homogeneous gel

Drying contraction, no gradient, perfect reconfiguration

Drying contraction, gradient, perfect reconfiguration

Drying contraction, no gradient, no reconfiguration

Volume fraction increases

Dry zone

Wet zone

Alpha = 0
Beta > 0
Gamma = 1

Alpha > 0
Beta > 0
Gamma = 1

Alpha = 0
Beta > 0
Gamma =0

Application of the simulation to aluminosilicate gel drying

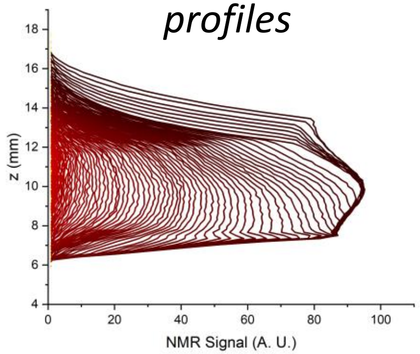
Soft drying of AlSi gel

α = 0

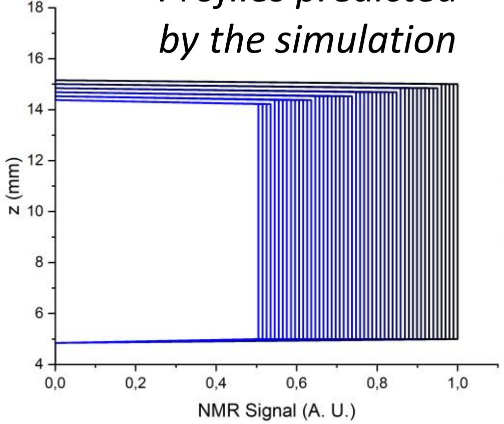
β = 0,001

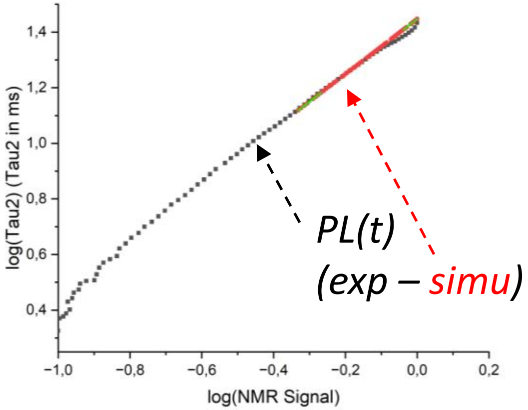
γ = 1

Experimental profiles



Profiles predicted by the simulation





PL(t)

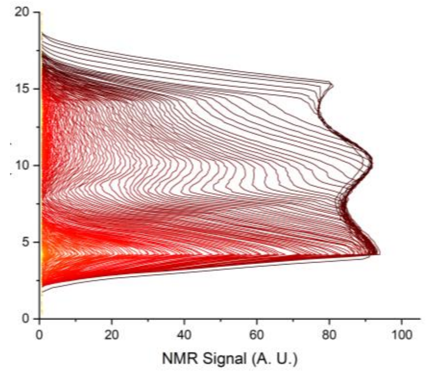
(exp – simu)

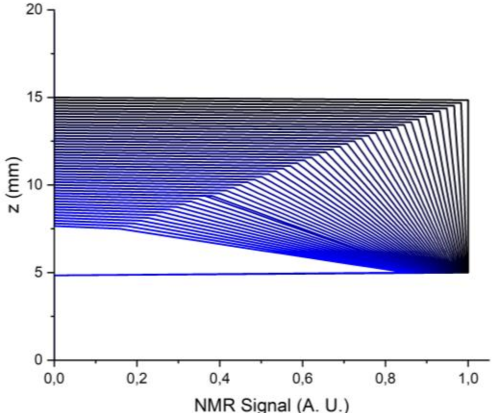
Intermediate drying of AlSi gel

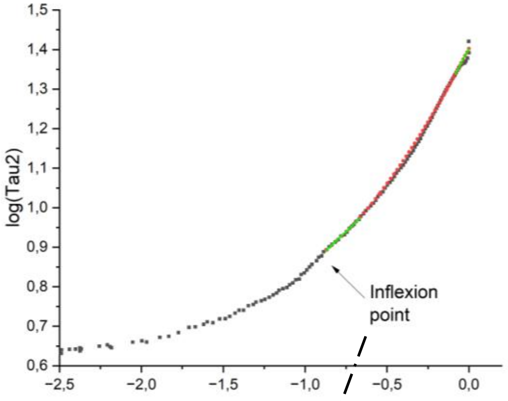
α = 0,7

β = 0,010

γ = 0,75





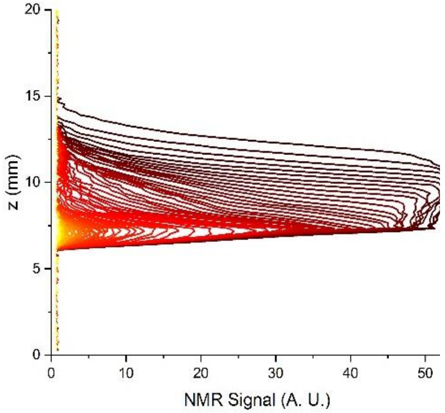


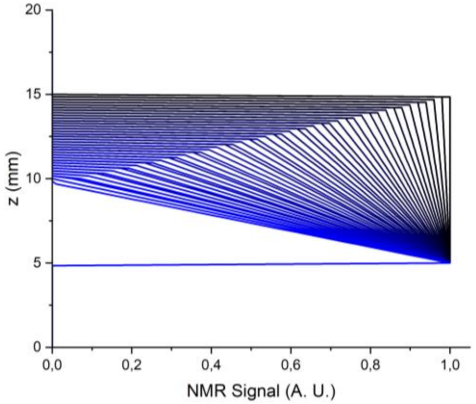
Hard drying of AlSi gel

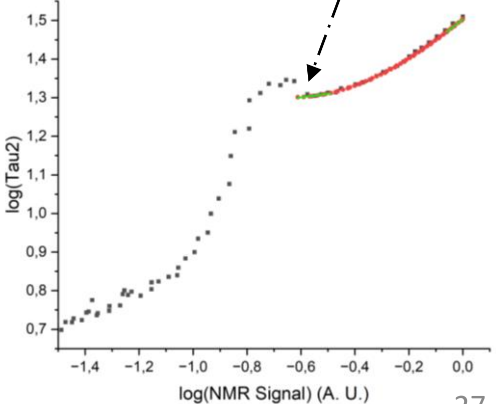
α = 1

β = 0,007

γ = 0,1







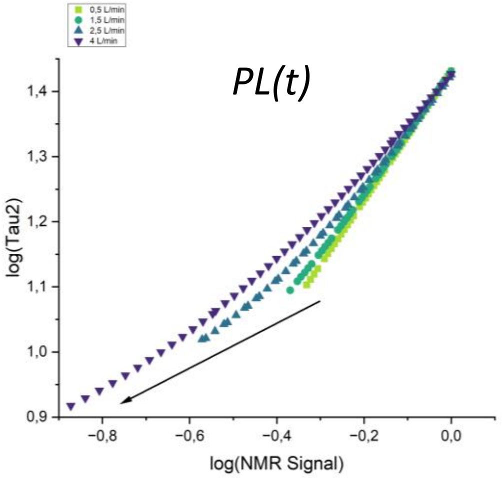
Influence of dry air flux and [NaOH] on the drying gel behaviour.

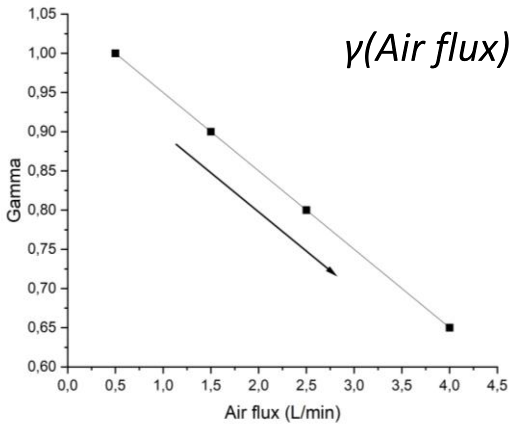
→ **PL(t)** = **robust criterion** to follow the hysdric behavior

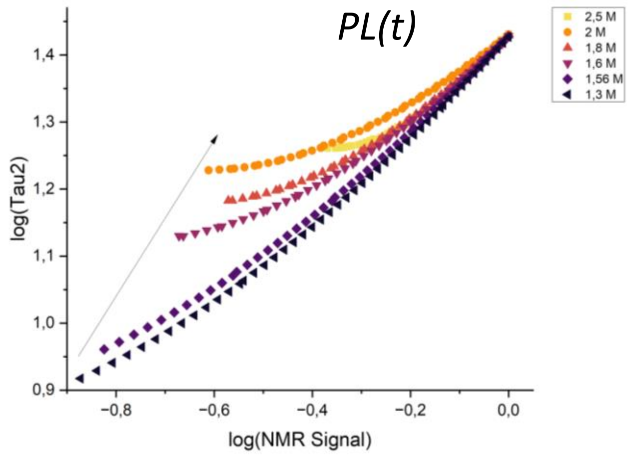
→ Very good **prediction of the hydric behavior** thanks to the simulation

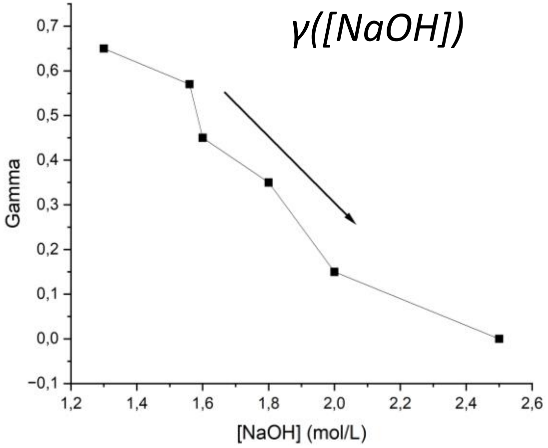
→ **Well defined set of equivalent simpled profiles** that has the same hydric behaviour (despite the complexity of the realistic profiles)

→ The simulation **opens the access to the reconfiguration paramter** (γ) describing the **ability to reconfigure fastly enough the particle network** to keep a well defined volume fraction during the drying









γ is lower (less efficient reconfiguration) for:

- higher air flux
- higher [NaOH] (> standard concentration = 1,3 M)