Applicaton of liquid state NMR for characterization of porous materials

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GINOP-2.3.2-15-2016-00008

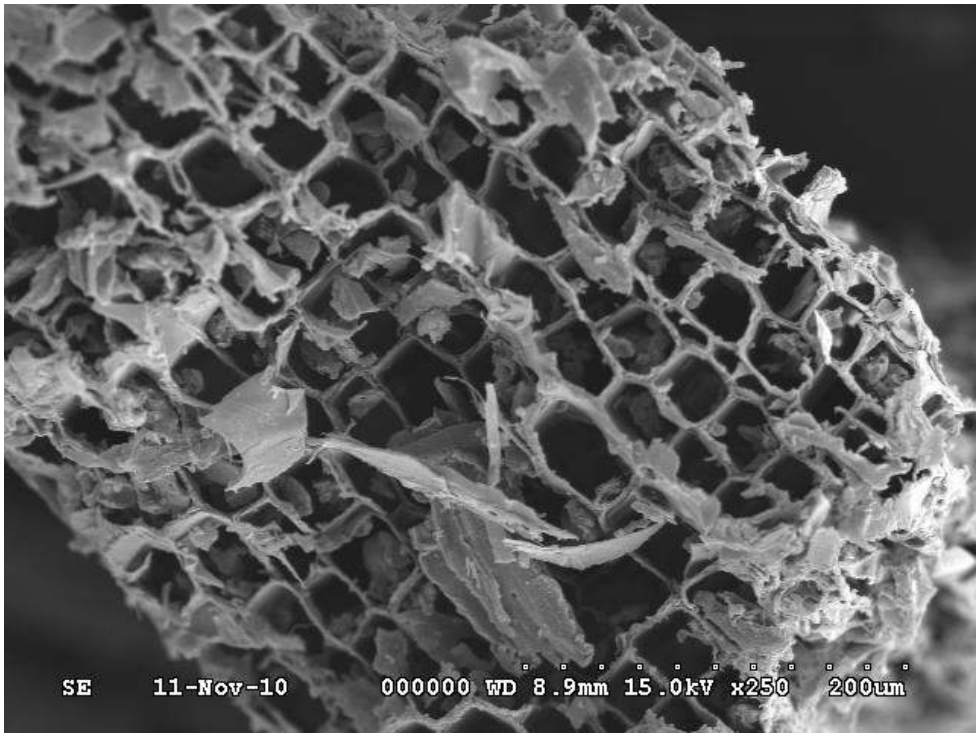
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… and Krisztina László

I hate solid state chemistry

Why? Because it is difficult?

Macropores > 50 nm
Mesopores 2–50 nm
Micropores < 2 nm



gas/vapor adsorption (0,3 - 300 nm)
(distribution)

Hg-porosimetry (3 nm – 360 μm)
(distribution, invasiv)

Krio-porosimetry (5 - 200 nm)
(distribution, detection
calorimetry)

Hindered diffusion (1 - 200 μm)

(theory is not ready yet)

Pore size distribution: still a challenge

Gas and vapor adsorption is the dominant method

S. **B**runauer, P.H. **E**mmett, E. **T**eller: *Adsorption of gases in multi-molecular layers*, J. Am. Chem. Soc. 60 (**1938**) 309–319.

E.P. **B**arrett, L.G. **J**oyner, P.P. **H**alenda, The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms, J. Am. Chem. Soc. 73 (**1951**) 373–380.

failed to distinguish between different pore structure morphologies, to account for the effects of microporosity, and to predict the pore sizes, which could be independently determined from X-ray diffraction (XRD) and transmission electron microscopy (TEM) with the precision unavailable earlier.

DFT

N.A. Seaton, J. Walton, N. Quirke, *A new analysis method for the determination of the pore-size distribution of porous carbons from nitrogen adsorption measurements*, Carbon 27 (1989) 853–861.

After two decades of DFT methods development for porous materials characterization, there still remain a number of issues, which are not currently resolved.

Challenge: adsorption-induced deformation of porous framework. This effect is negligible for silicas and carbons *etc.* but it is substantial for aerogels…

Is there a superior method ? Of course, not. But NMR…

model



reality



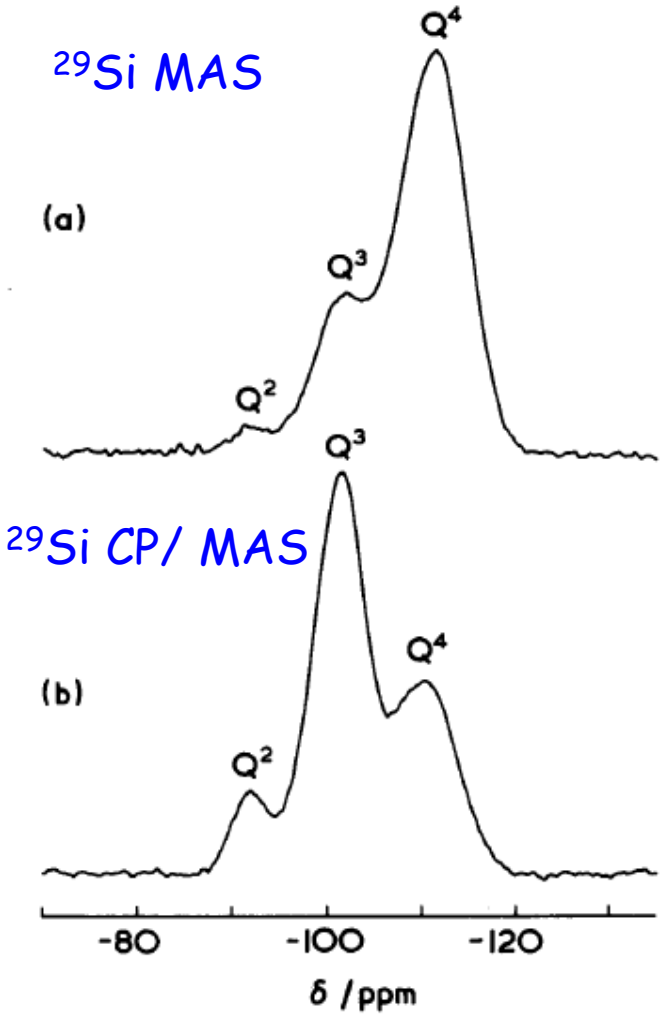
Solid state NMR for solids. Does it go without saying?

1. It is „dry" indirect method (chemical shift shows the state of Si-atoms)

2. Q^n means the number of bridging O of 4 O atoms.

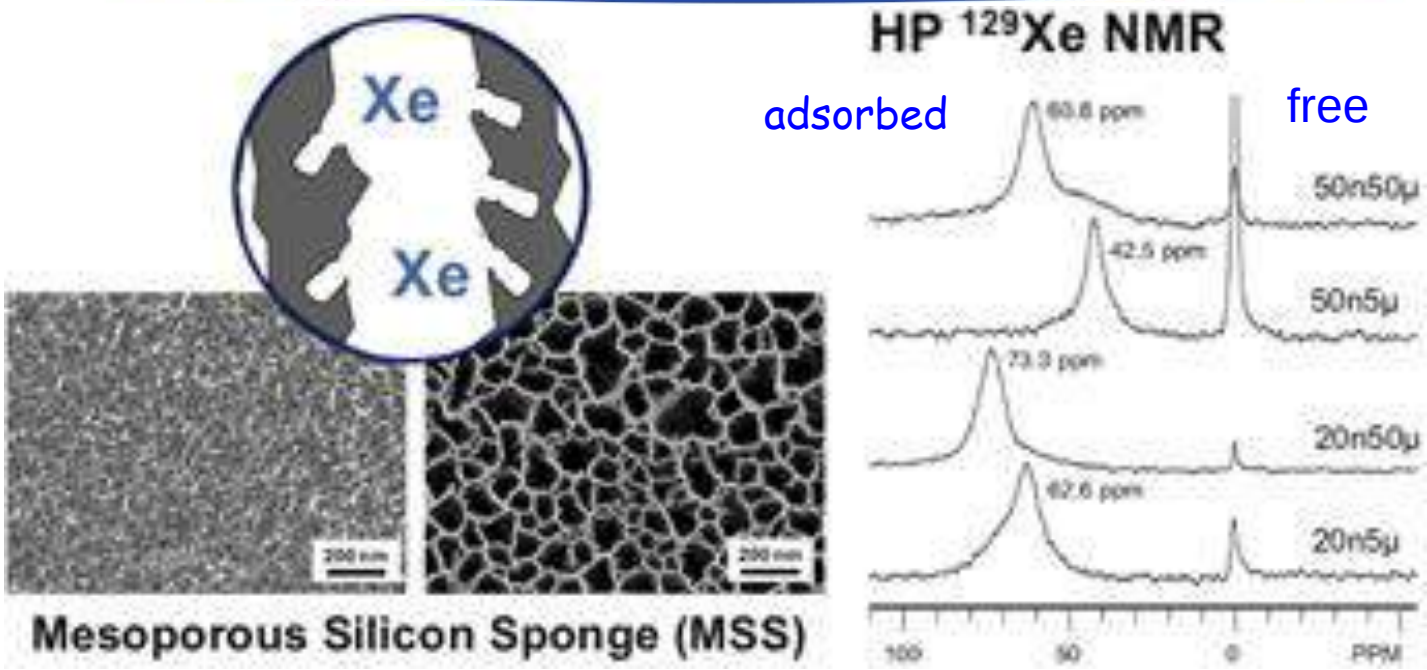
3. It may be in connection to number of inner surface silicon atoms

4. It requires still high technical skills



Exotic NMR

^{129}Xe-NMR

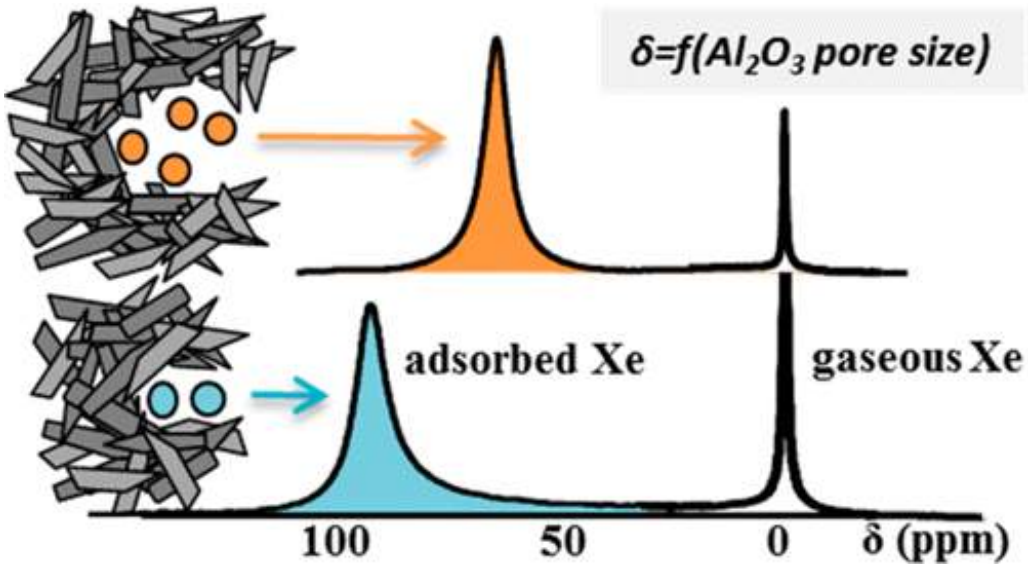


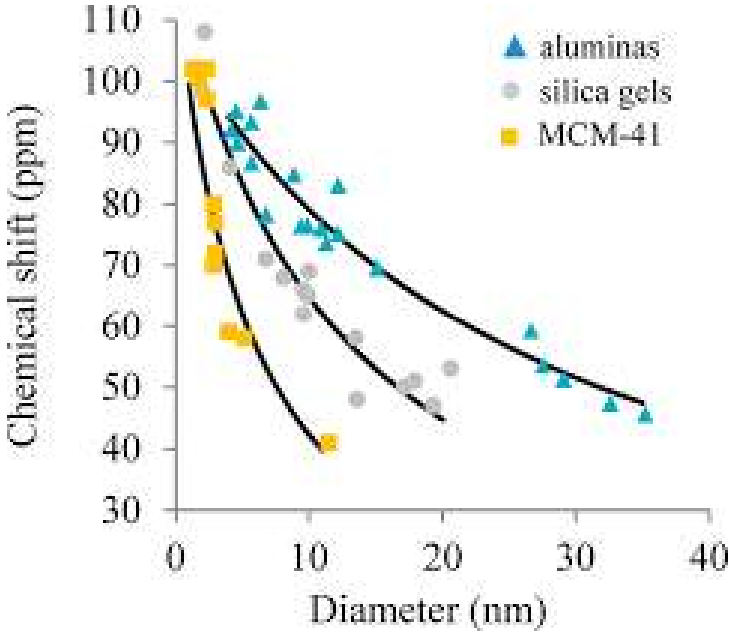
20n(pore)50µ (partcle), 20n5µ, 50n50µ, and 50n5µ silicas

Chemical shift decreases with increasing pore size in a given particle size.
Empirical, difficult and expensive.

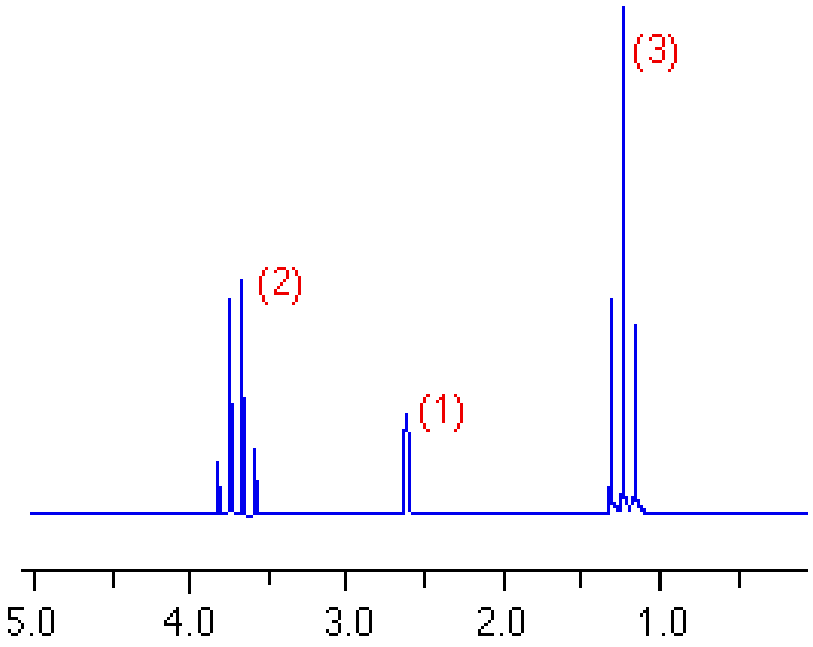
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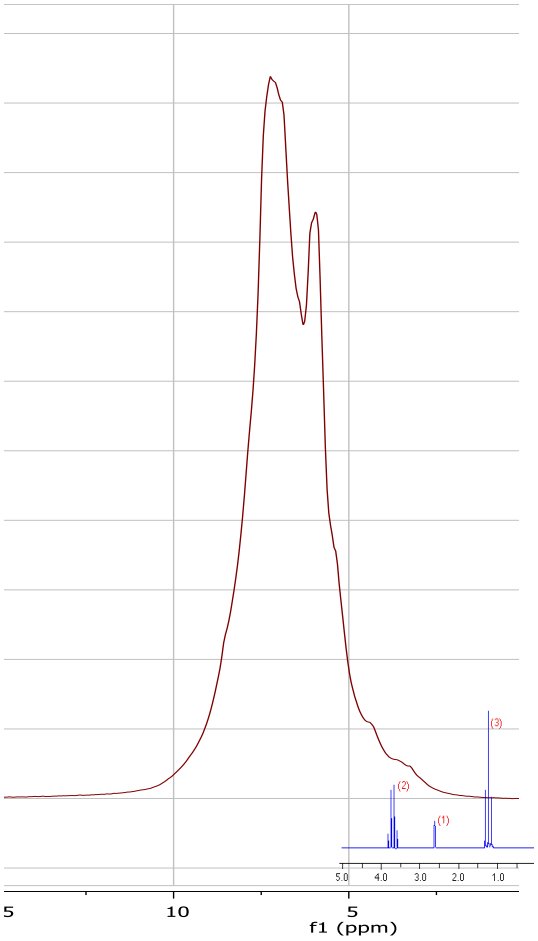
^{129}Xe-NMR


δ=f(Al2O3 pore size)
adsorbed Xe
gaseous Xe
100
50
0
δ (ppm)


Chemical shift (ppm)
110
100
90
80
70
60
50
40
30
0
10
20
30
40
Diameter (nm)
aluminas
silica gels
MCM-41

Liquid state NMR

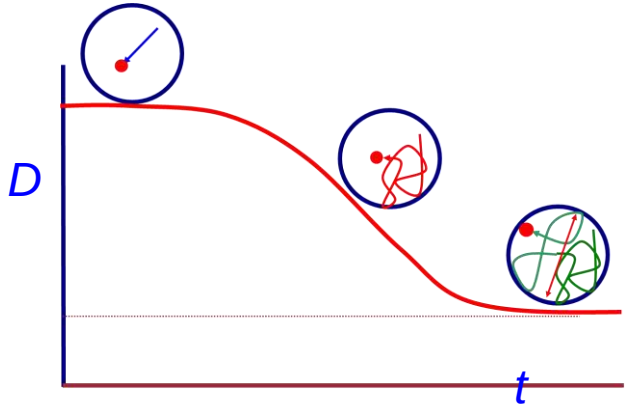




Why liquid state NMR spectroscopy? Experiments „in action"!

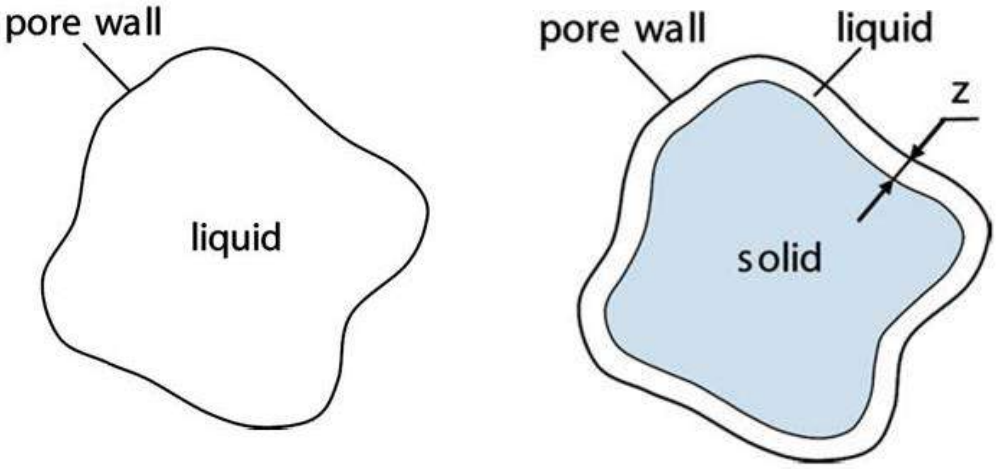
- NMR-cryoporometry
  - The melting/freezing point depression depends on the S/V ratio…
    size, size distribution, shape?
- Low Field NMR relaxation
  - Interaction between the given molecules and their environment
  - Transverse NMR (T_2) relaxation time depends on the S/V ratio in pores
- Self-diffusion
  - Restricted and hindered diffusion in porous systems: $D(t) \propto S/V$ ratio
- NMR MOUSE





Cryoporometry: an old method

Gibbs-Thomson equation:



$$\boxed{T_{eq} - T_0} = -\frac{V_M \gamma_{sl} T_0}{\Delta H} \frac{S_s}{V_s} = \boxed{-K_c \frac{S_s}{V_s}}$$

T_{eq}: measured melting point

T_0: melting point in bulk

γ_{sl} surface tension
V_m: molar volume
S_s: surface
V_s: volume
ΔH: melting enthalpy

O. V. Petrov, I. Furó, *Prog Nucl Magn Reson Spectr* 54 (2009) 97-122

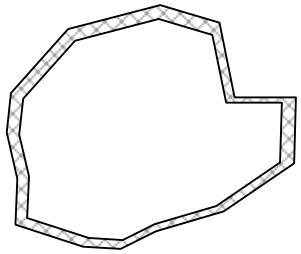
Cryoporometry: free energy analysis

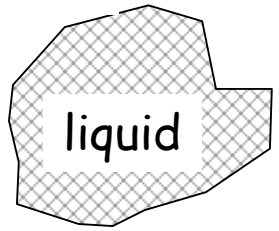
$$F_m = \frac{\mu_l V}{V_{M,l}} + \gamma_{lw} S$$

$$F_f = \frac{\mu_l (V - V_s)}{V_{M,l}} + \gamma_{lw} S + \frac{\mu_s V_s}{V_{M,s}} + \gamma_{sl} S_s$$

$$\Delta F = F_f - F_m = \frac{(\mu_s - \mu_l) V_s}{V_{M(l,s)}} + \gamma_{sl} S_s$$

$$\mu_s - \mu_l = \frac{\Delta H (T - T_0)}{T_0}$$





Ehrenfest

$$\left(\frac{\partial \mu_s}{\partial T}\right)_p - \left(\frac{\partial \mu_l}{\partial T}\right)_p = -S_{M,s} + S_{M,l} = \Delta_{tr} S = \frac{\Delta H_{tr}}{T_{(tr)0}}$$

$$\mu_s - \mu_l = \frac{\Delta H_{tr}}{T_{(tr)0}} (T - T_0)$$

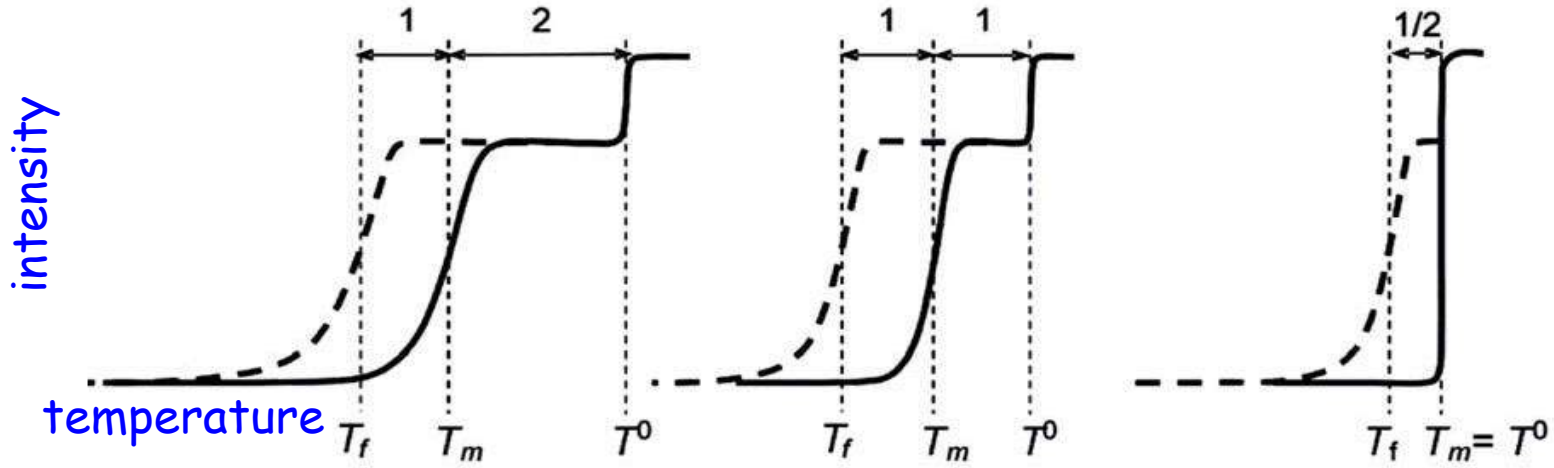
$\Delta F = 0$ ha $T = T_{eq}$ legyen $\Delta T_{eq} = T_{eq} - T_0$

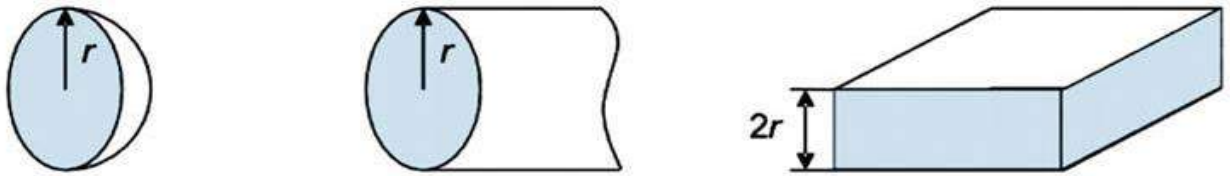
$$\Delta T_{eq} = -\frac{V_M \gamma_{sl} T_0}{\Delta H} \frac{S_s}{V_s} = -\frac{K_c}{r_{spheric}}$$

$$\Delta T_{eq} = -K_c \frac{S}{V}$$

NMR cryopormetry
liquid state NMR solid is not visible!

Experiment melting/freezing curves

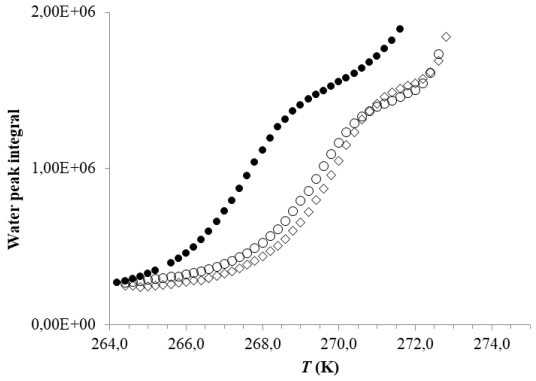


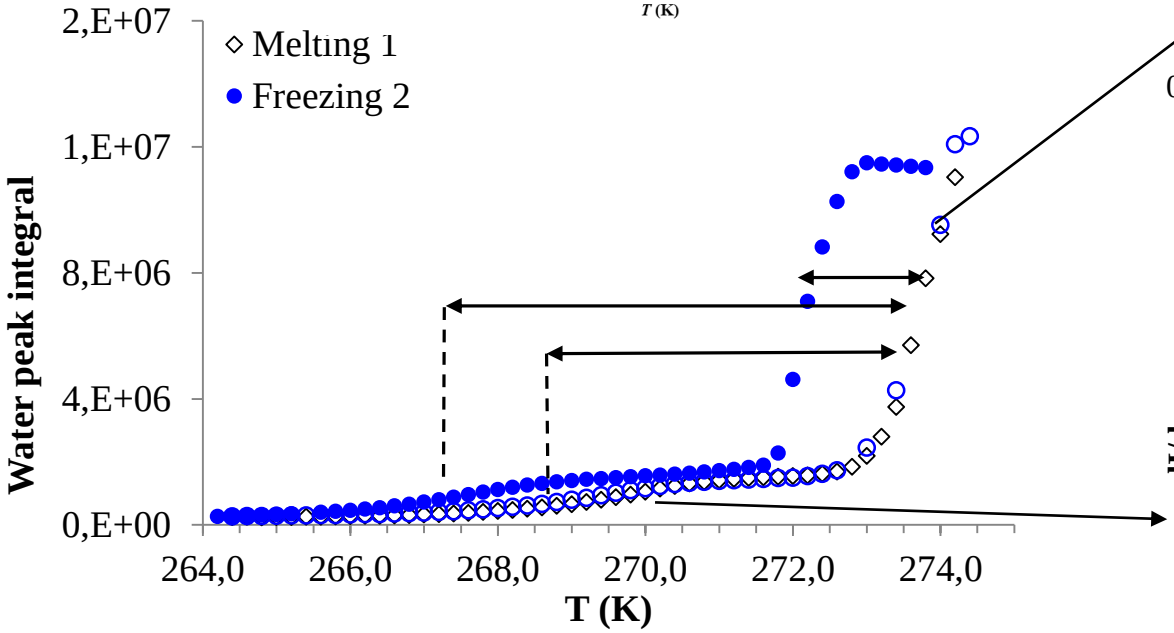


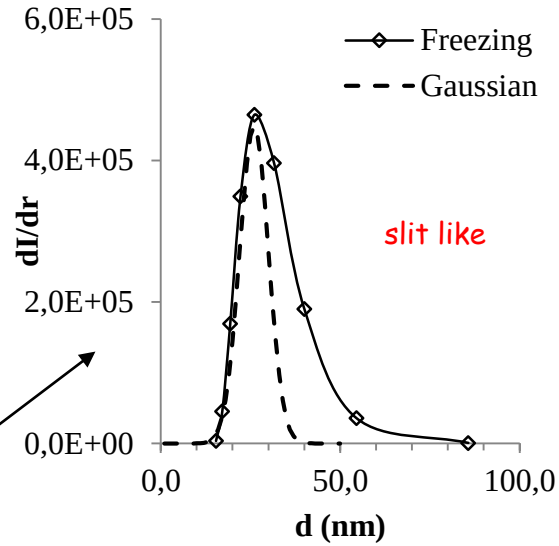
shape	$\lvert\Delta T_f\rvert$	$\lvert\Delta T_m\rvert$
sphere	$3K_c/r$	$2K_c/r$
cylinder	$2K_c/r$	K_c/r
slit	$K_c/2r$	0

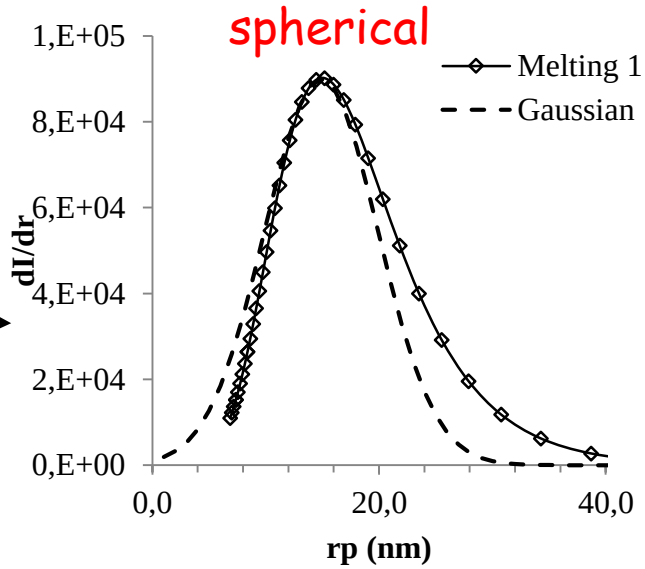
O. V. Petrov, I. Furó, *Prog Nucl Magn Reson Spectr* 54 (2009) 97-122

RF hydrogel to aerogel: motivation (?)

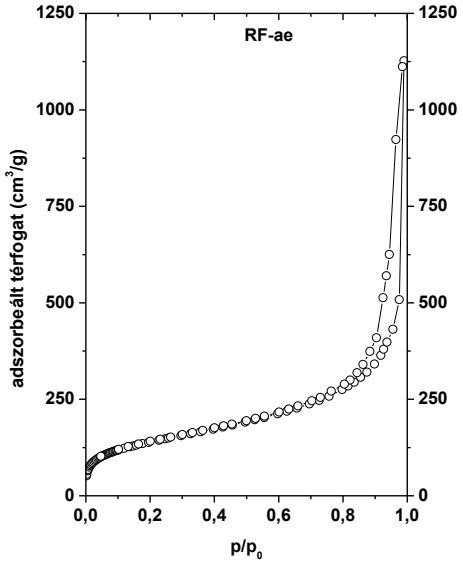


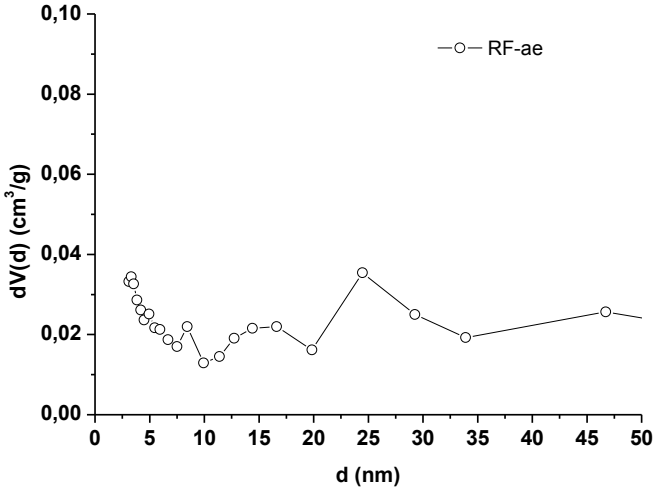


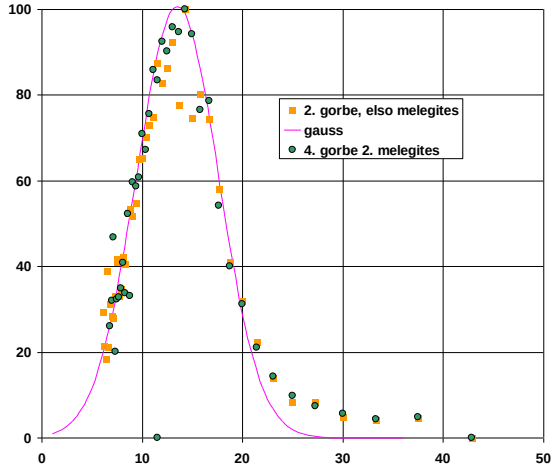




Resorcinol-formaldehyd polymer aerogel







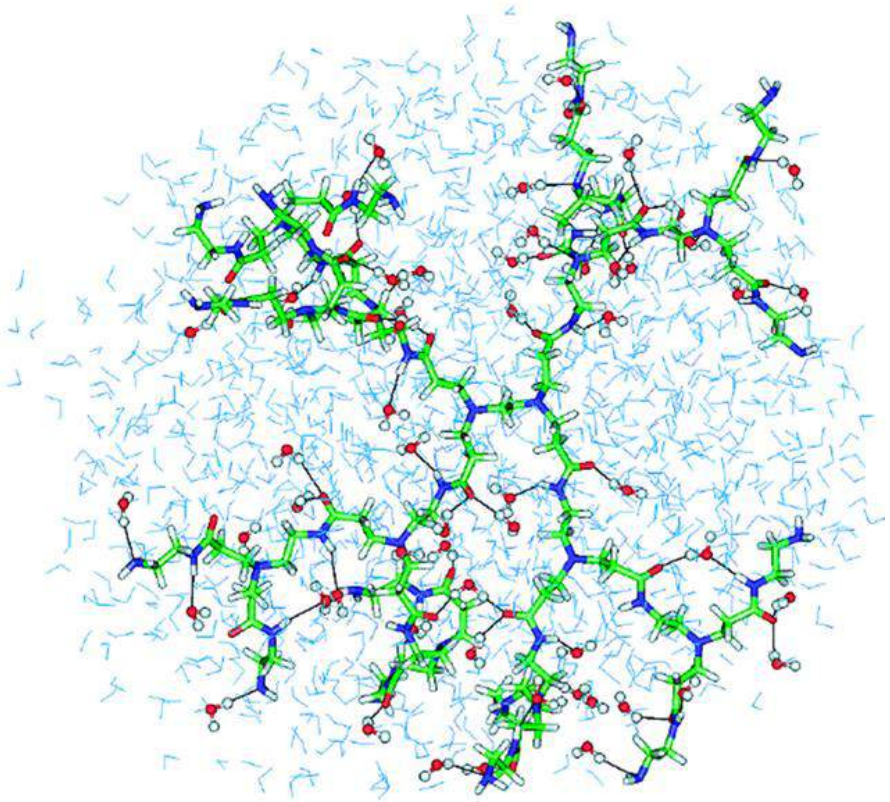
Cryoporometry on dendrimers: porous soft materials

Experiment:

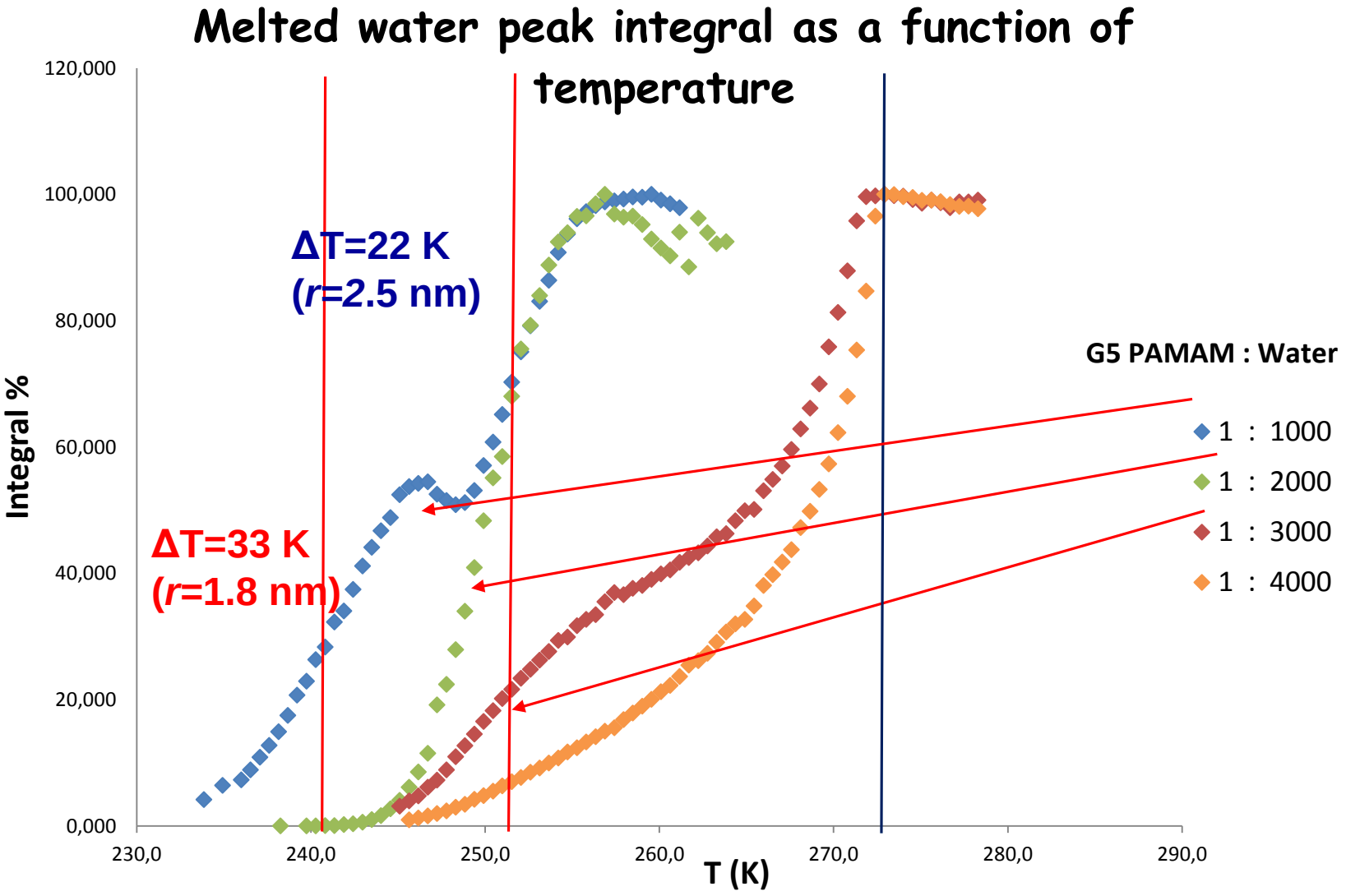
Liophilized G5_PAMAM.NH_2
(in plastic NMR tube ☺)

Water addition in four steps
(at least one week between
the experiments):

1000 moles water/mole dendrimer
(repeated 2 weeks later)
2000 moles water/mole dendrimer
3000 moles water/mole dendrimer
4000 moles water/mole dendrimer

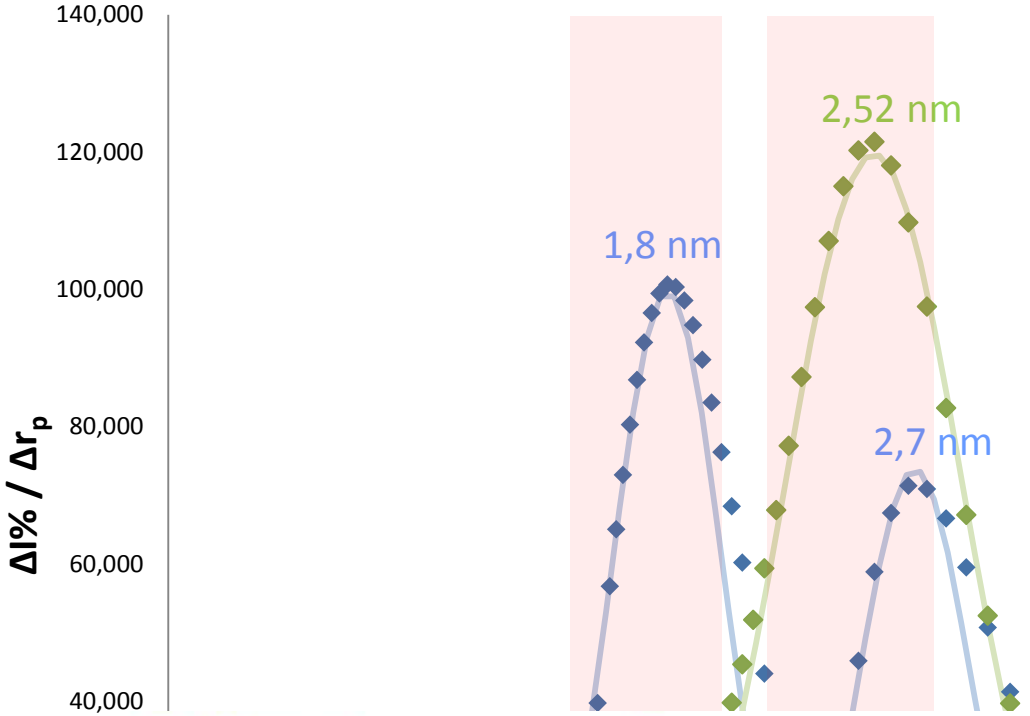


Melting curves of gelated G5 PAMAM

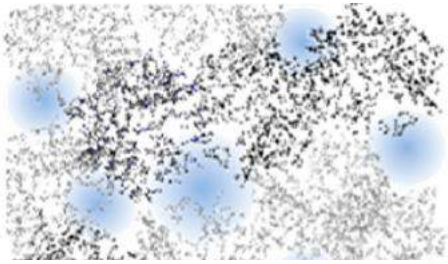


Pores in gelated G5 PAMAM

Pore size distribution



The diameter of hydrated dendrimer is 6.2 nm



G5 PAMAM : Water

- 1 : 1000
- Gauss
- 1 : 2000
- Gauss
- 1 : 3000
- auss
- : 4000
- auss

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Article

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NMR Characterization of PAMAM_G5.NH_2 Entrapped Atomic and Molecular Assemblies

Mónika Kéri,[†] Chen Peng,[‡] Xiangyang Shi,[‡,§] and István Bányai*[,†]

Az NMR relaxometry

NMR relaxation times

Longitudinal relaxation: T_1

Transvers relaxation: T_2

Dipolar relaxation mechanism (LF-^{1}H-NMR)

Coupling to the environment protons:

Orientation of magnetic dipoles

Time periode of proximity

$$\left(\frac{1}{T_i}\right) = \frac{4\gamma_I \gamma_S h^2 S(S+1)}{3r_{IS}^6}\tau_c$$

Experiments: Bruker Minispec

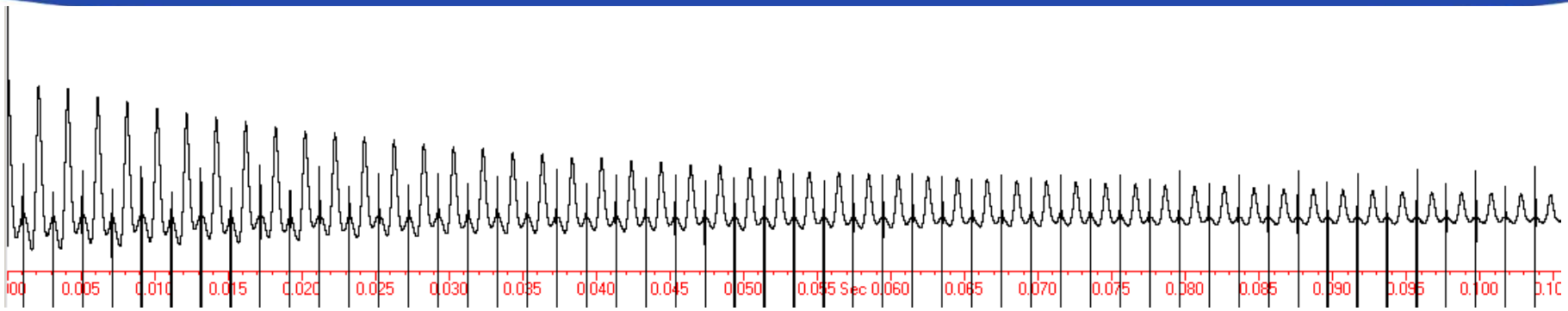


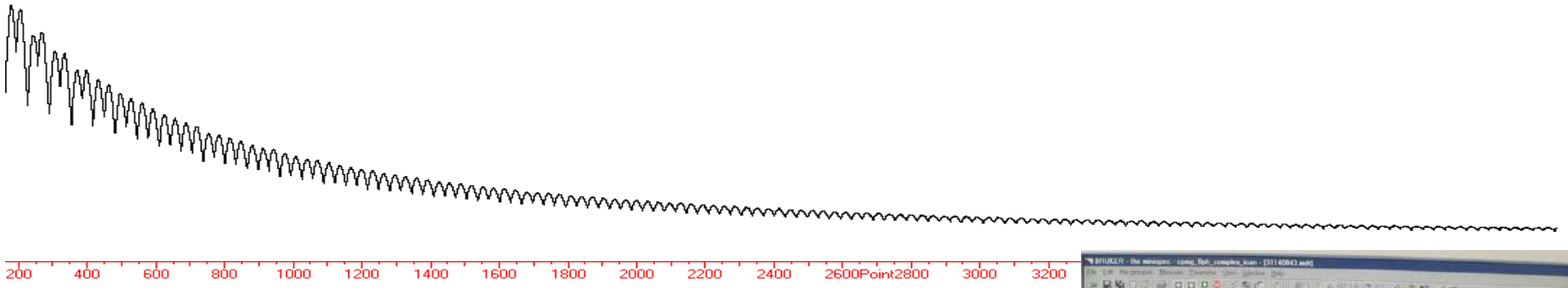
Low resolution

CPMG echos

Hahn echos

Mesurement of transverse relaxation time

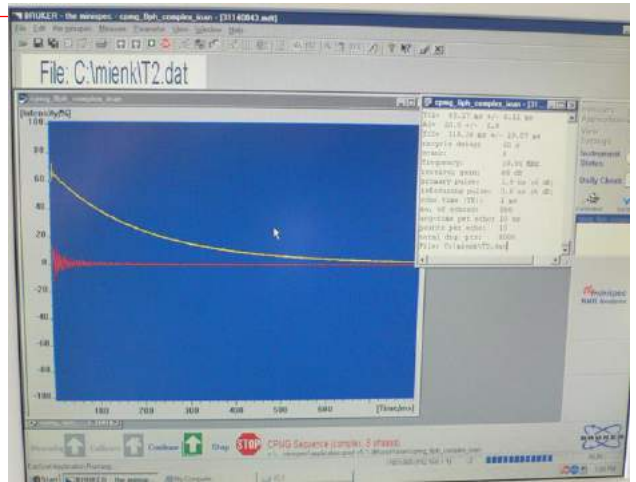




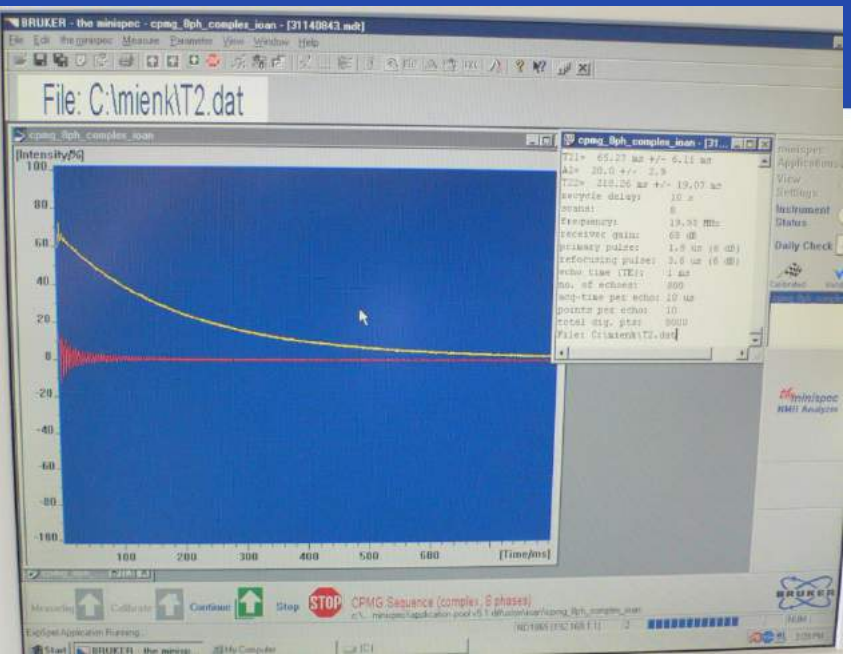
Tipically:

- 80-600 μs echo time
- 400-1000 echos

$$I = \sum_{1} I_0 \exp\left(-\frac{2}{T_2} \times \tau\right)$$



Application of relaxometry

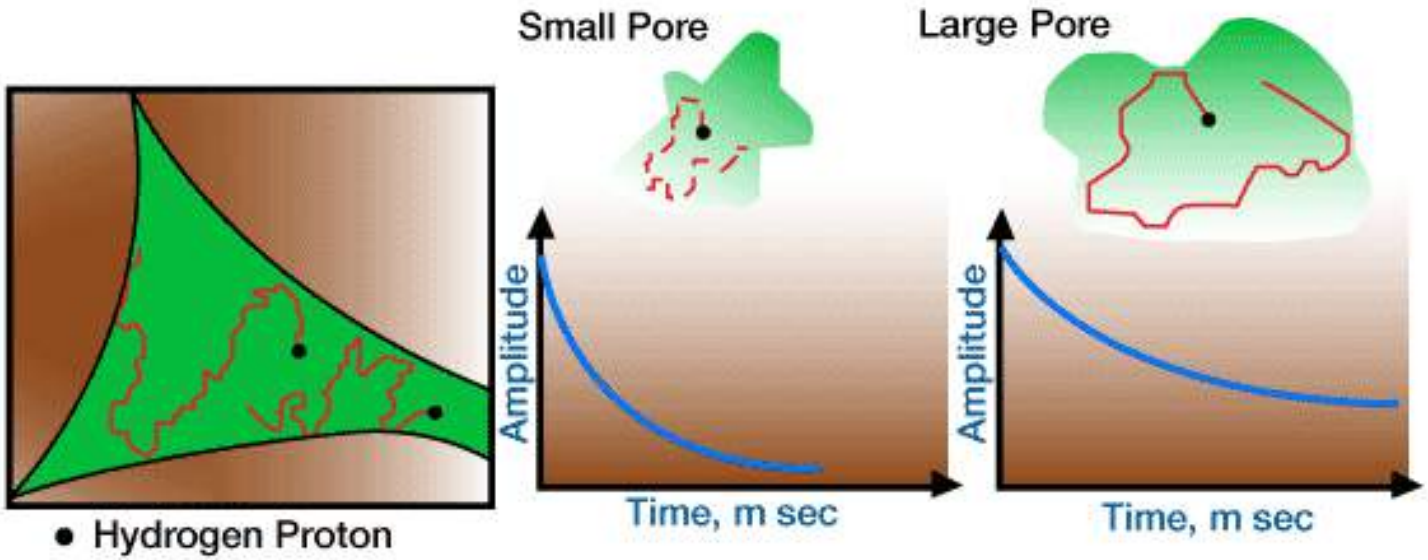








Transvers relaxation in porous systems



model

- The relaxation is fast on surfaces
- Diffusion is fast therefore we measure the average relaxtion rate

$$\frac{1}{T_2} = \frac{V_s}{V}\frac{1}{T_{2s}} + \frac{V_b}{V}\frac{1}{T_{2b}}$$

Model - Conditions

$$\frac{1}{T_2} = \frac{V_s}{V}\frac{1}{T_{2s}} + \frac{V_b}{V}\frac{1}{T_{2b}}$$

If

V_0 is the volume is loaded with water

T_{2s} surface while T_{2b} bulk water protons relaxation time

Titration: $V_{add} < V_0$ „pudes" form : T_2 increases if the size of puddles increase but its is constant when the number puddles increases

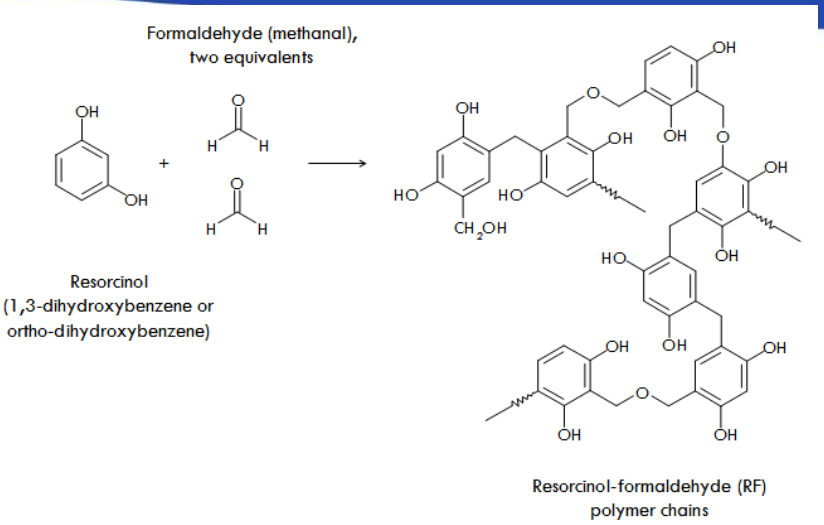
The volume of puddles proporptional to linear size $V \sim r^3$

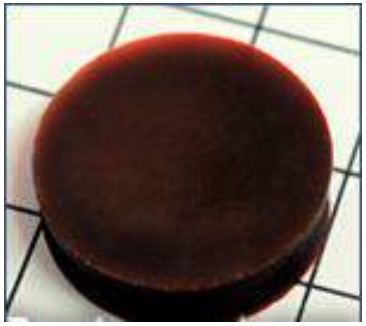
Volume of bulk $V_b \sim (r-l)^3$ l is the thickness of surface layer

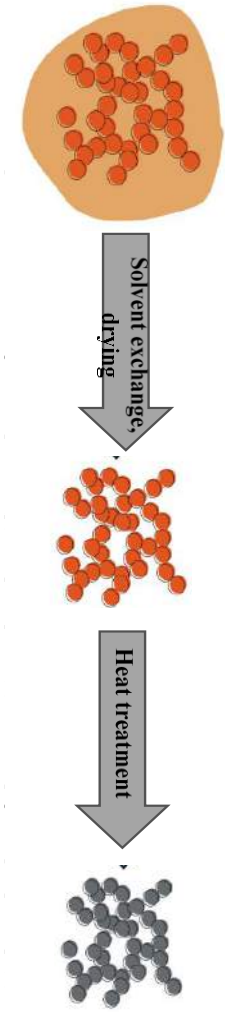
Dimensionless pore size $\rho = r/l$

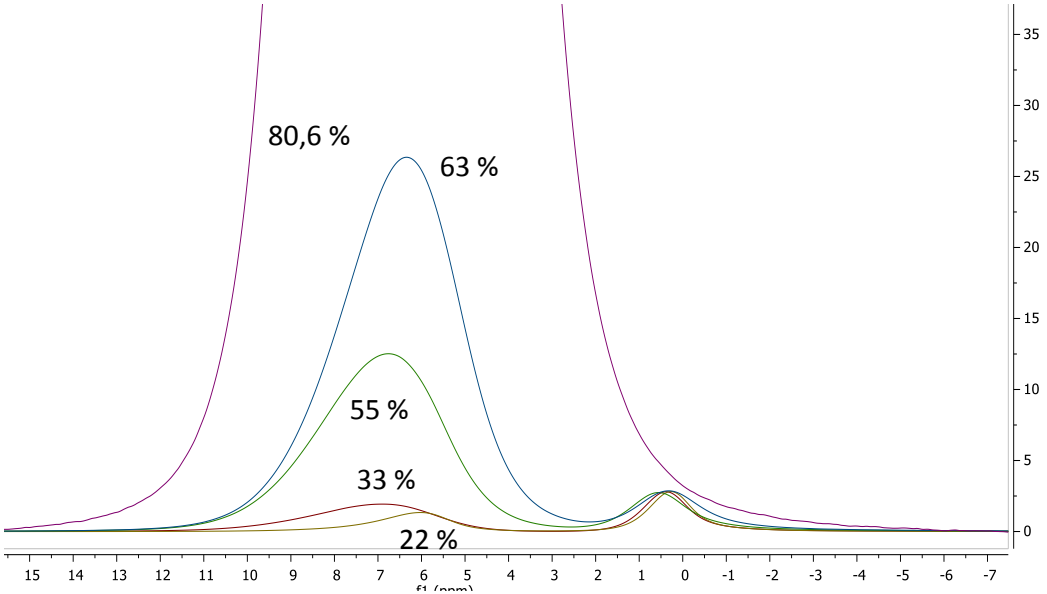
$$\rho = \left\{1 - \left[\left(\frac{T_{2s}}{T_2} - 1\right) \Big/ \left(\frac{T_{2s}}{T_{2b}} - 1\right)\right]^{1/3}\right\}^{-1}$$

Resorcinol-formaldehyde (RF) carbon aerogels

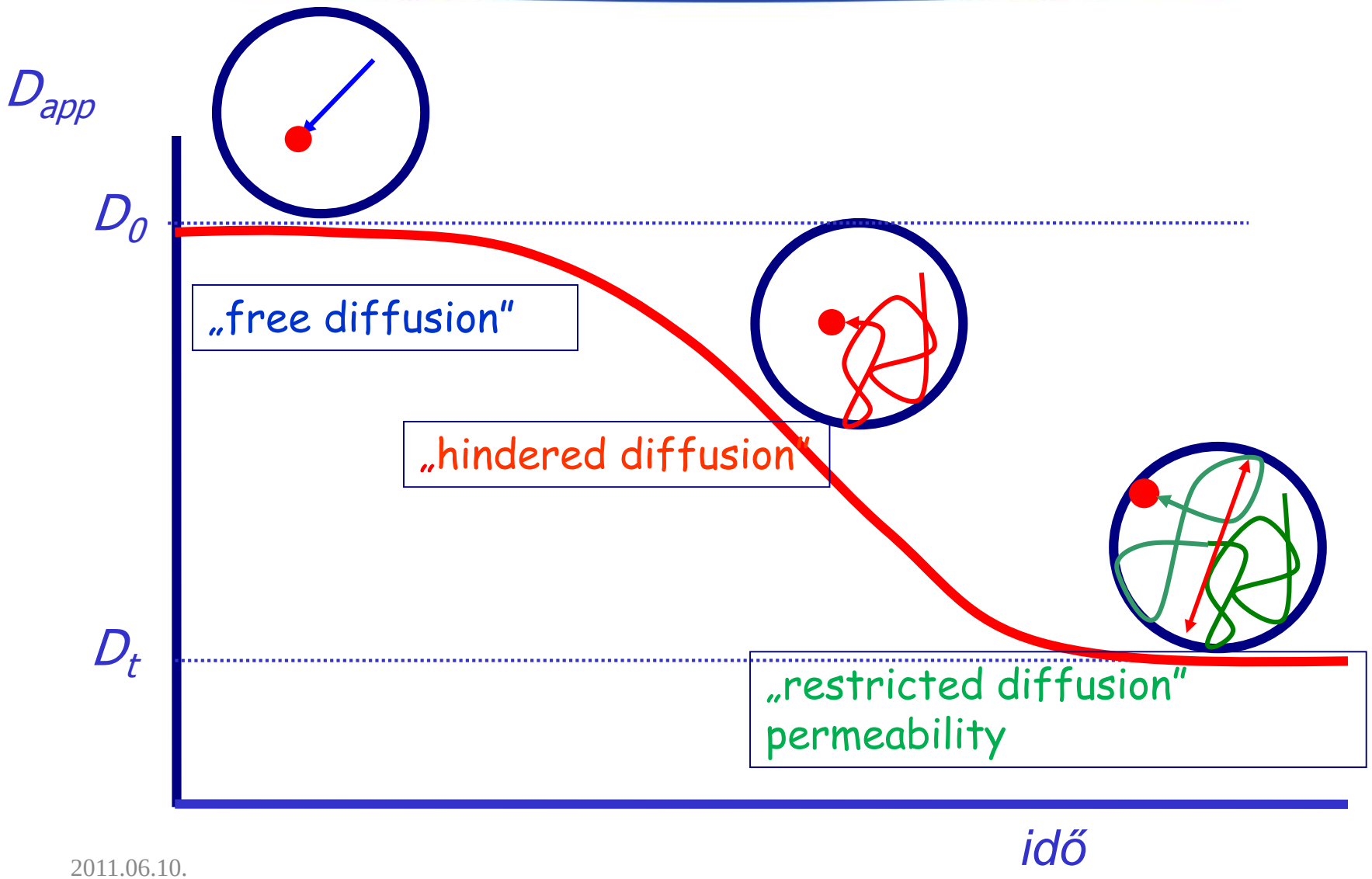






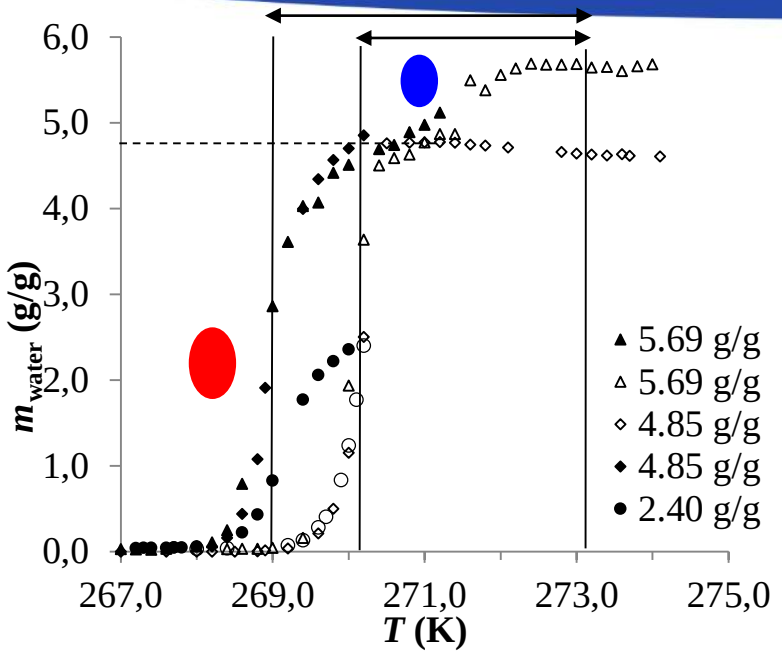


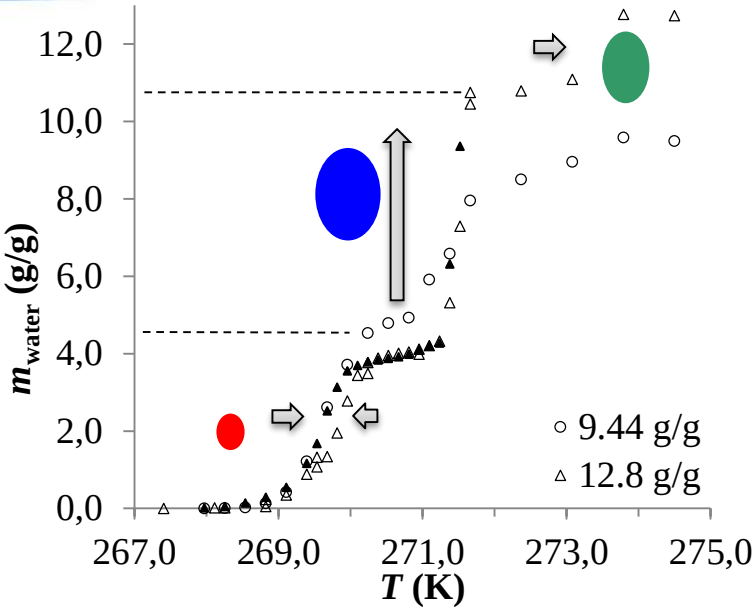
Diffusiometry: time dependence of D



Combination of the three methods for carbon aerogels

The RF carbon aerogel: cryoporometry titration

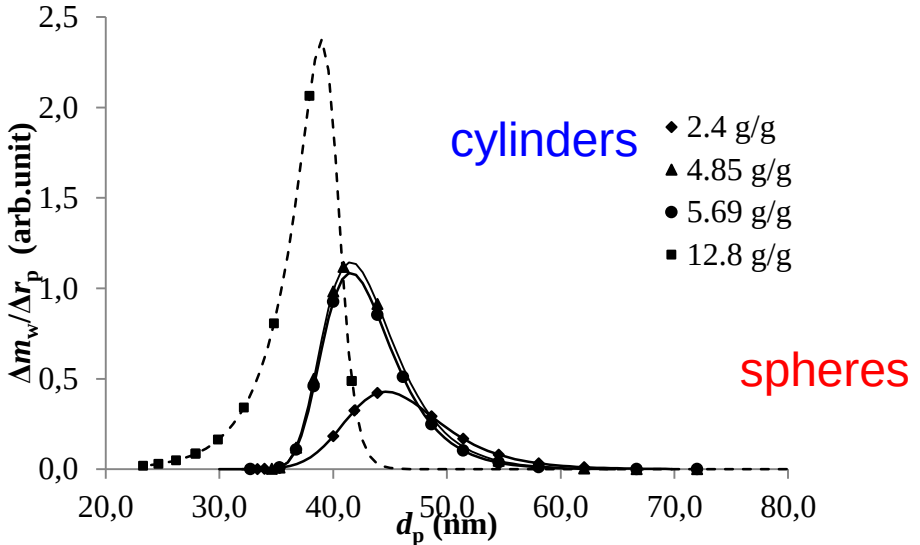




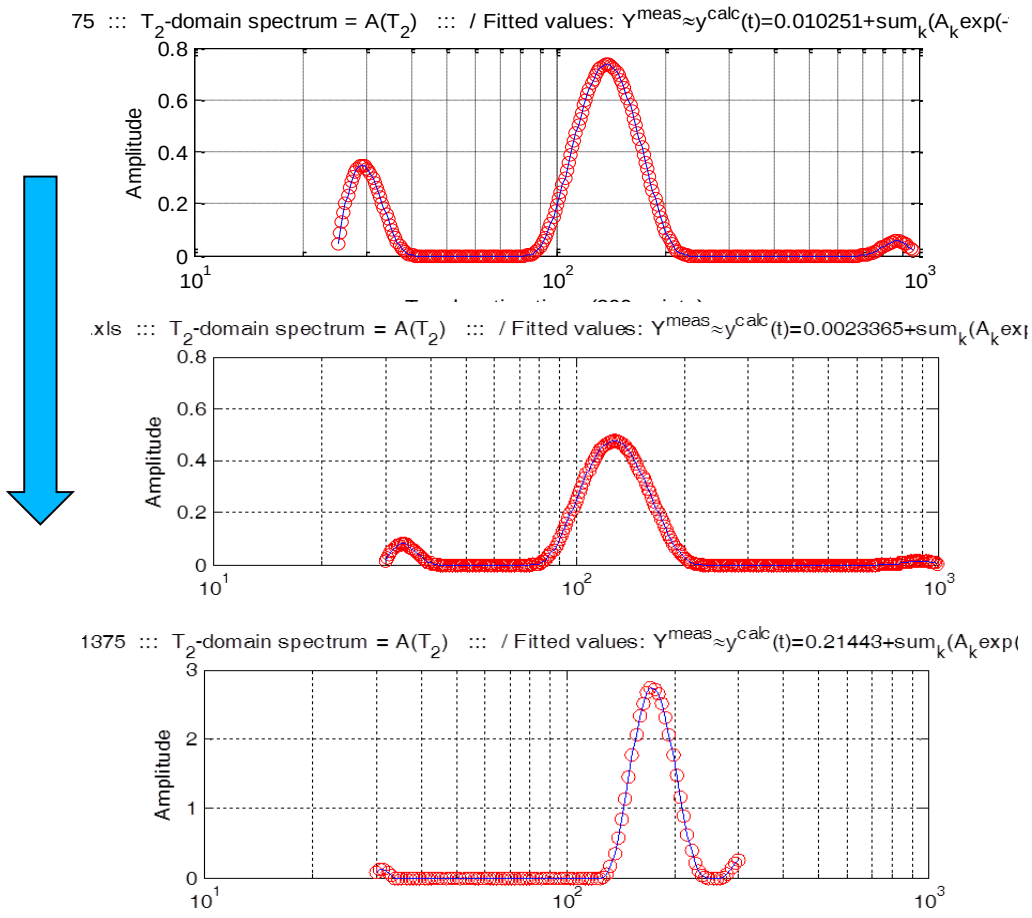
1. Until *cca.* 5 g/g one spherical pore appears

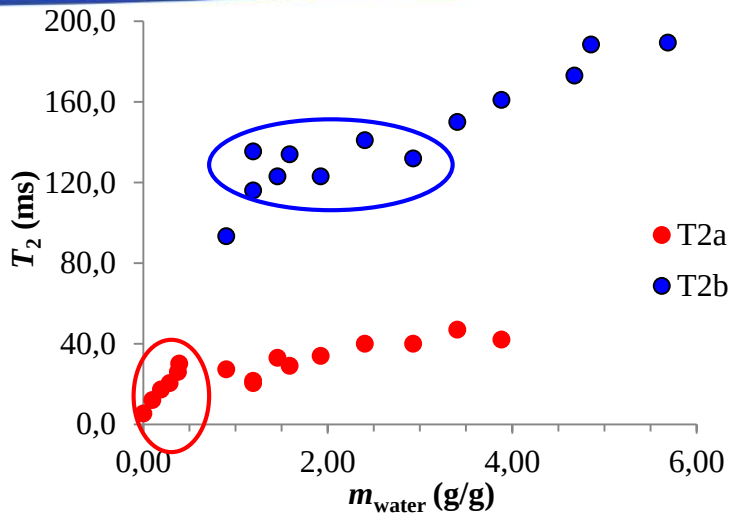
2. Above 5 g/g another pore with no hysteresis

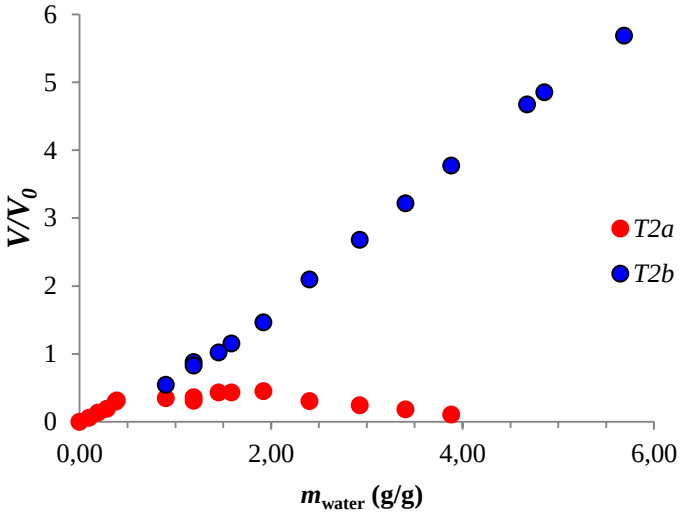
3. Above 9 g/g the bulk water is present



The RF carbon aerogel: low-field NMR relaxometric titration







Quantitative evaluation:until 6g w/1g

$$\frac{1}{T_2} = \frac{V_s}{V} \times \frac{1}{T_{2s}} + \frac{V_b}{V} \times \frac{1}{T_{2b}}$$

Two sites model of one pore completely filled and diffusion controlled

$$\frac{1}{T_2} = \xi \frac{S}{V_0} \frac{1}{f^k} + \frac{1}{T_{2b}}$$

ξ surface relaxivity

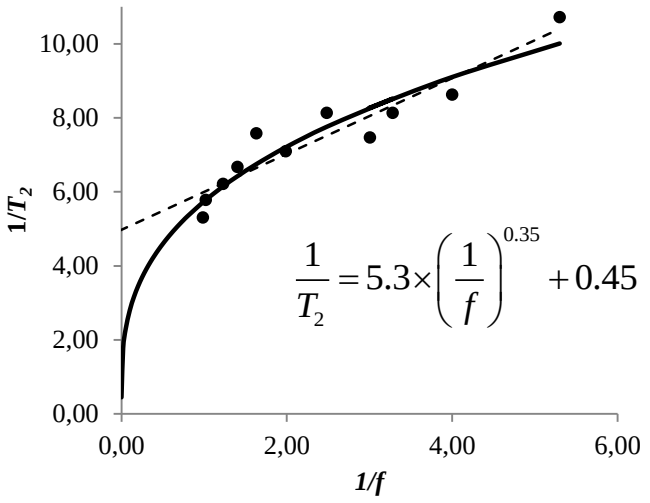
f filling factor

k exchange constant $(k = 1)$

Two sites model of one pore partially filled and kinetically controlled

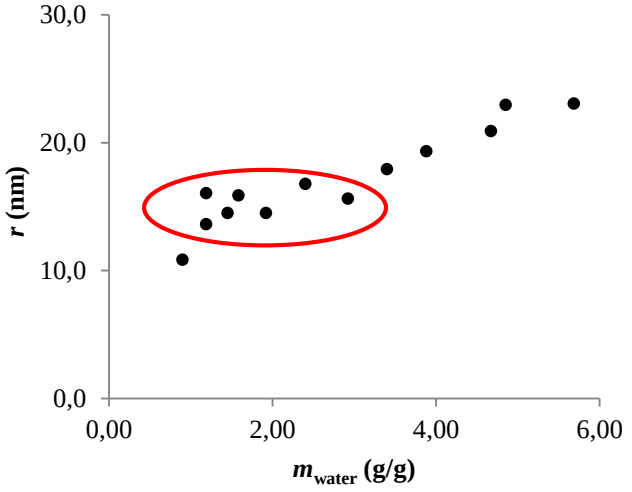
$$\xi = l\left(\frac{1}{T_{2s}} - \frac{1}{T_{2b}}\right)$$

l thickness of surface layer

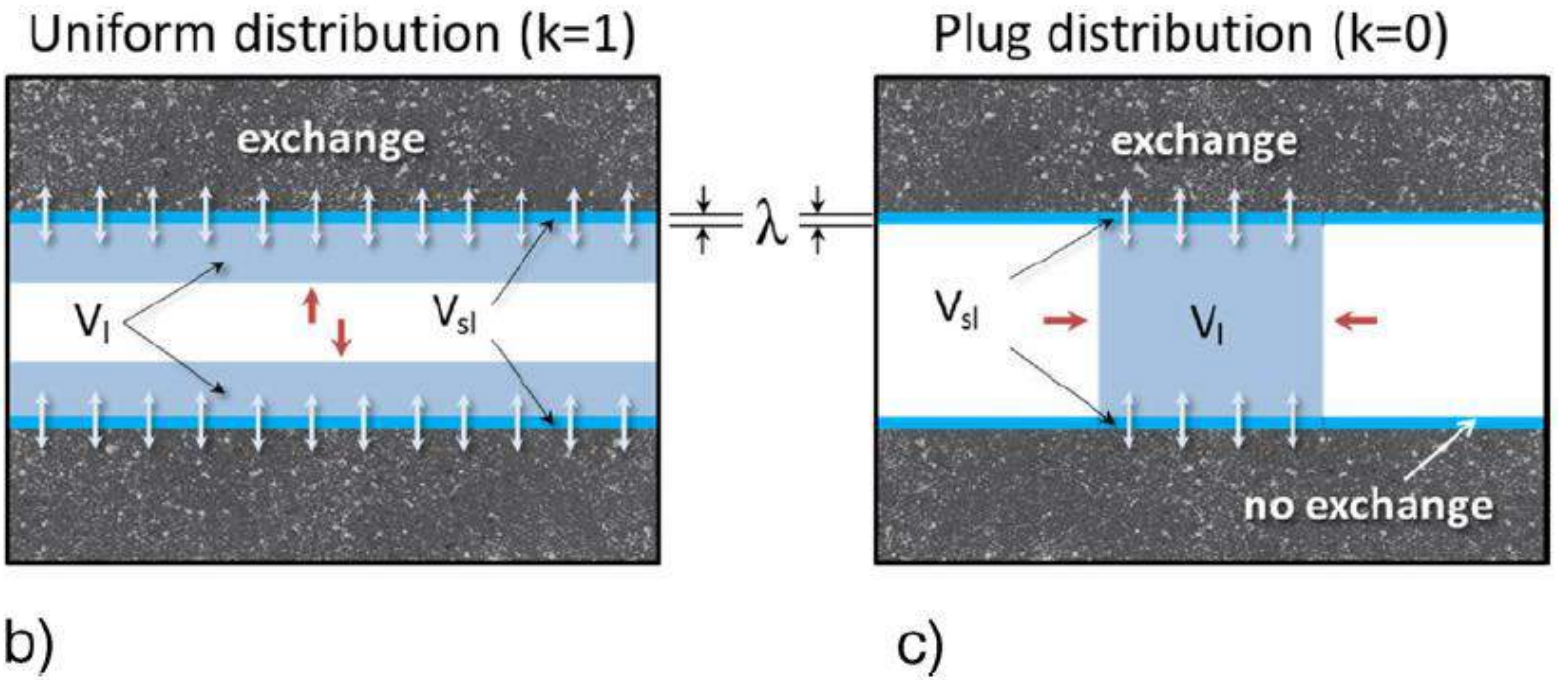


After parameter fitting we found

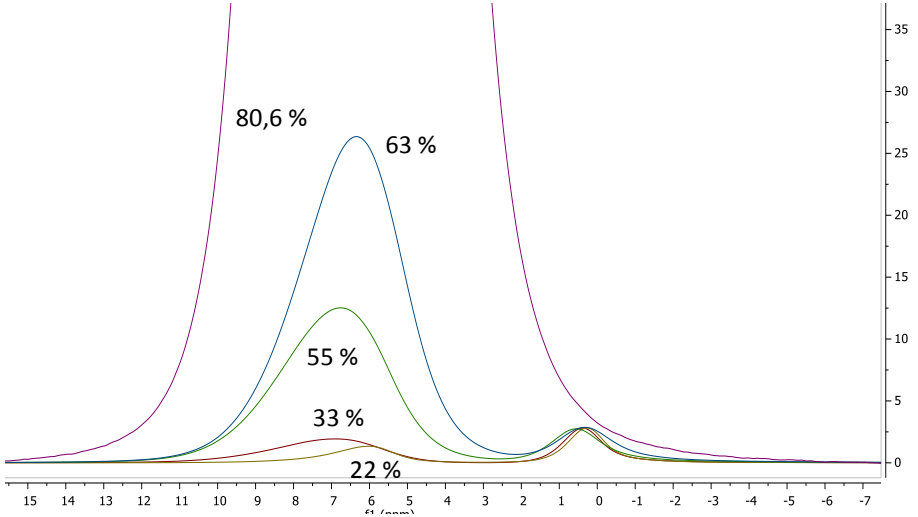
T_{2b} (s)	k	S/V_0 (m^{-1})	ξ (m/s)	T_{2s} (s)	l (nm)
2.2	0.35	1.43×10^{8}	3.71×10^{-8}	0.0053	0.197

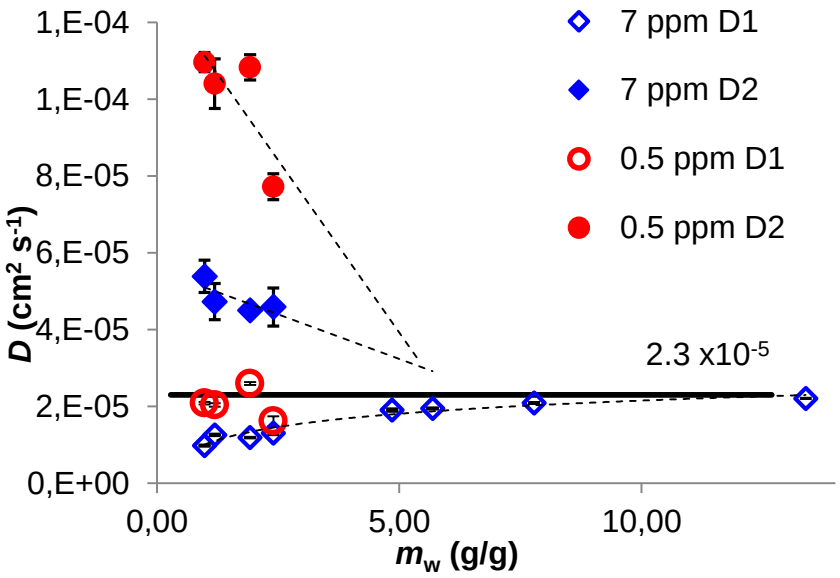


Meaning of kinetic factor

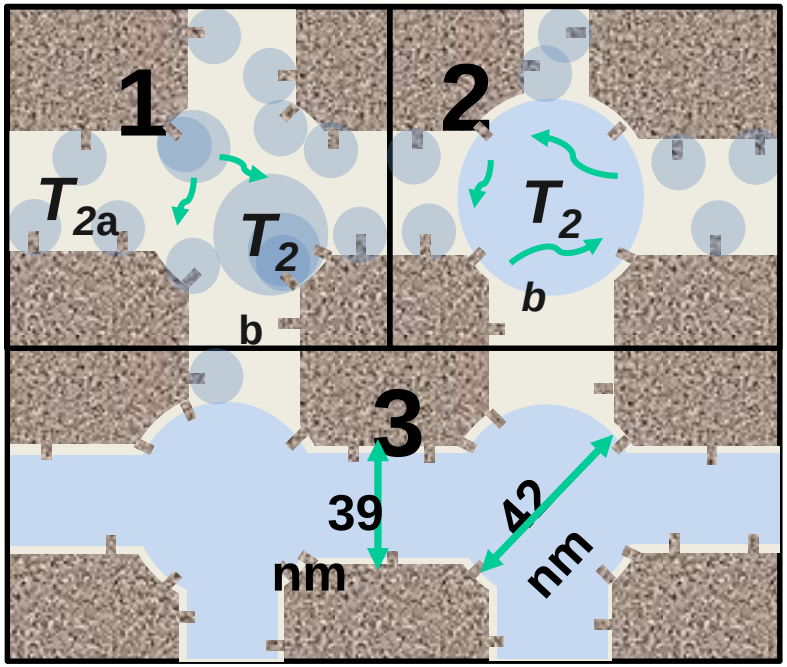


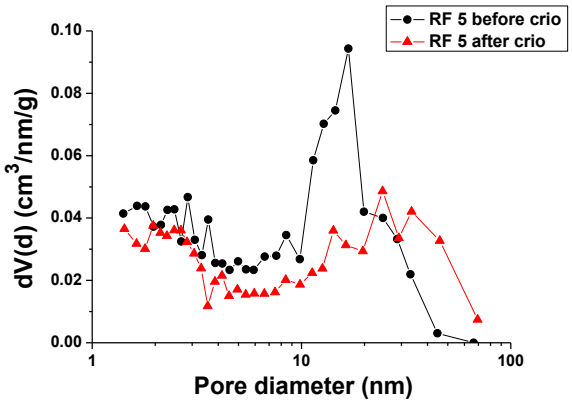
Difuusion of water in RF carbon aerogels

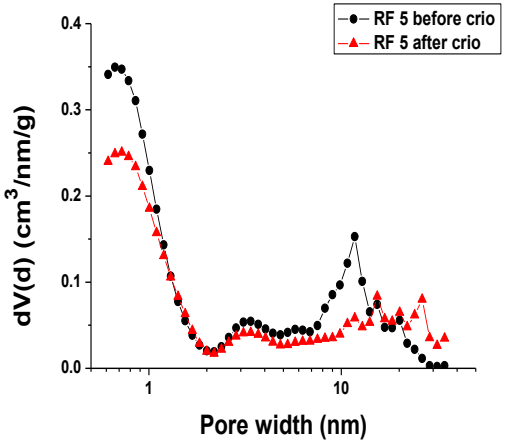




Model from NMR and conclusions







THANK YOU FOR YOUR ATTENTION!

Debreceni Kémiai K+F Műhely

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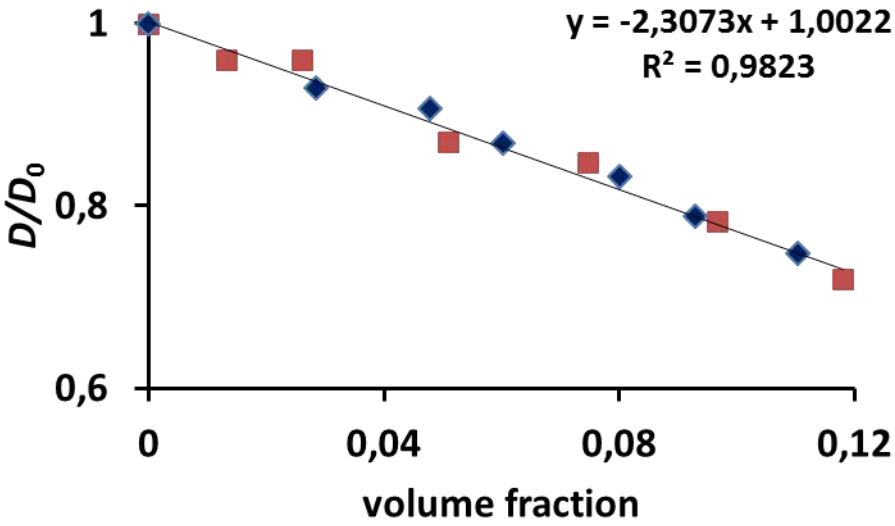
SZÉCHENYI 2020

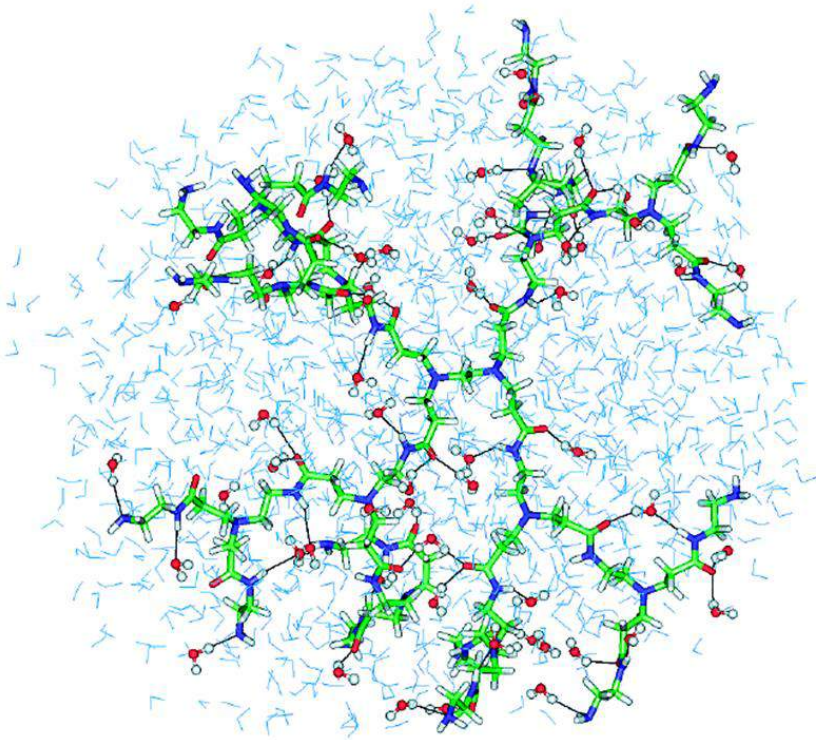
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G5_PAMAM dendrimers as „'hard sphere" colloids





No observable association
in this concentration range

Soft Matter

RSC Publishing

PAPER

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View Journal

Cite this: DOI: 10.1039/c2sm26726h

Self-diffusion of water and poly(amidoamine) dendrimers in dilute aqueous solutions†

István Bányai,*[a] Mónika Kéri,[a] Zoltán Nagy,[a] Márta Berka[a] and Lajos P. Balogh[b]

A modell további tulajdonságai

A teljes feltöltéskor: $V_{add} > V_0$ a „tócsák” pórusok lesznek.

Ha több „tócsa” (pórus) van és nincs köztük „keveredés” akkor, mindegyikre

$$\frac{1}{T_{2i}} = \frac{V_{si}}{V_i}\frac{1}{T_{2s}} + \frac{V_{bi}}{V_i}\frac{1}{T_{2b}}$$

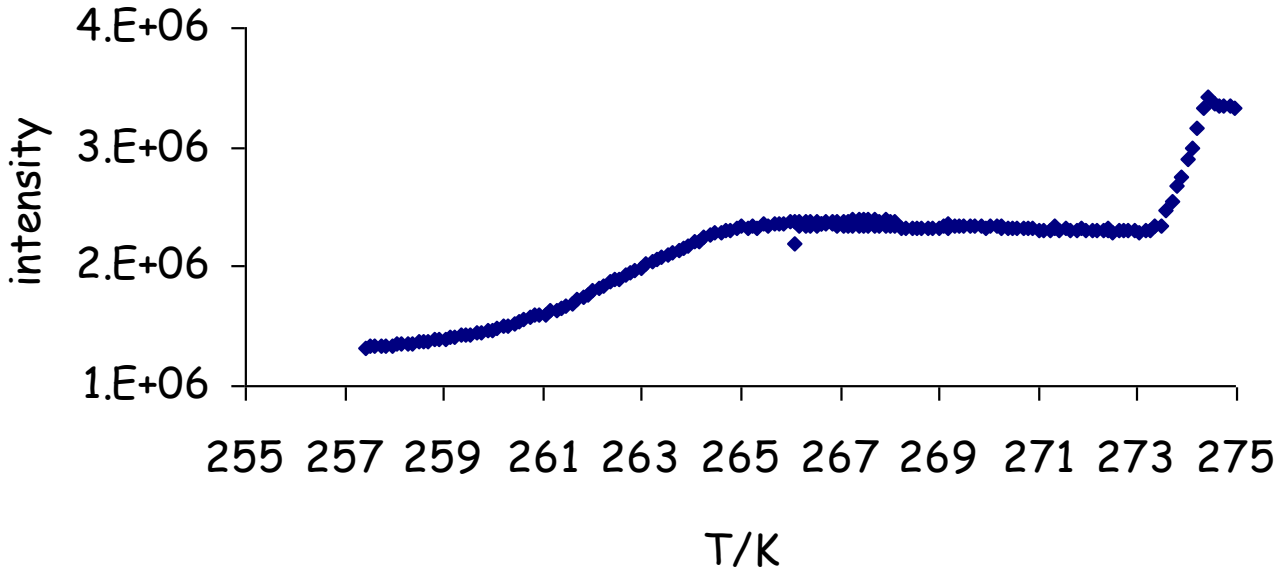
Ha teljes a keveredés akkor „átlagérték”-et kapunk

Ha van is meg nem is… azaz a keveredés és a relaxáció azonos időskálán következik be

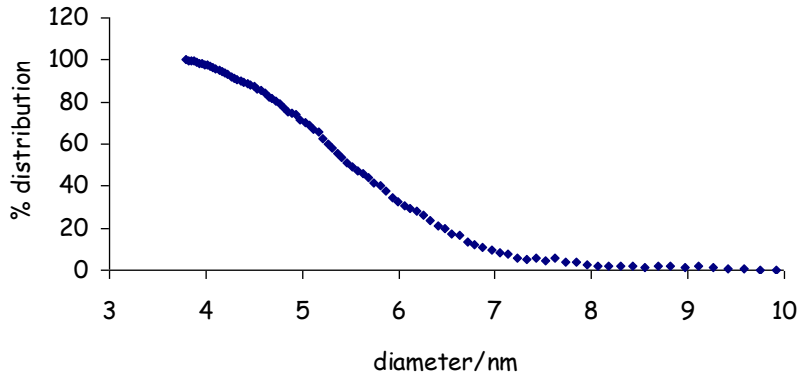




Kieselgel 60



Size and size distributions

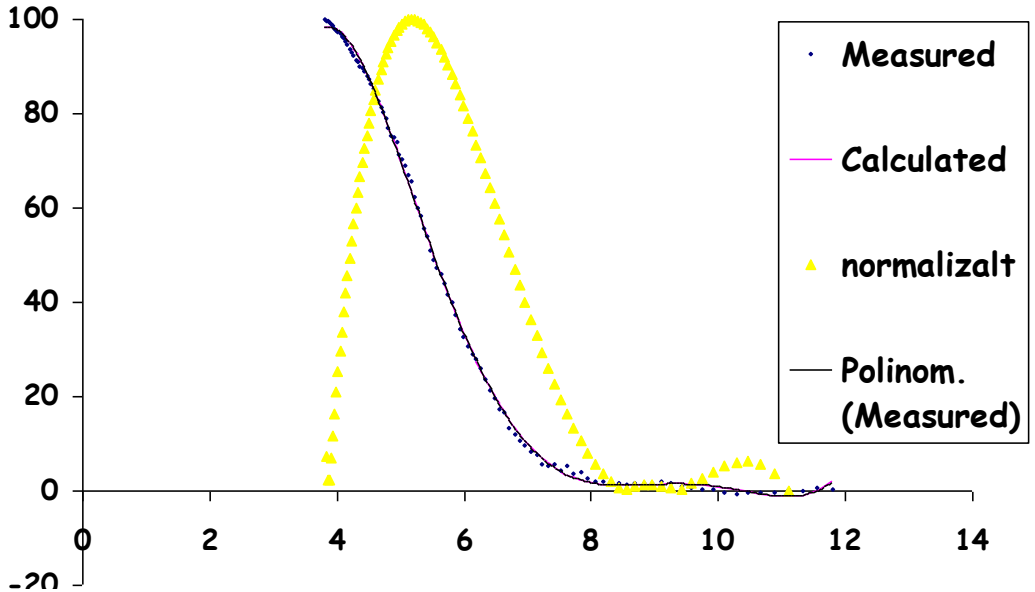


Commercial silica gel is available in

Table 1 Characteristics of the silicates used for modification of the carbon paste, and the square wave voltammetric response of the corresponding SMCPEs

Materials	Specific surface area[a] ($m^2\ g^{-1}$)	Average pore size (nm)	Silanol con-centration[b] (mmol g^{-1})	Voltammetric signal[c] (μA)
Kieselgel 60	425	6	3.8	21
Aerosil-200	200	10	1.4[e]	8
MCM-41	1050	2.9	8.0[f]	10
Stöber silica	4[d]	0.3	5.2	0.6

[a] From BET N_2 adsorption experiments
[b] By thermogravimetry, with respect to the dry silica mass
[c] Currents sampled in stripping square wave voltammetry using the SMCPE, after 5 min accumulation at pH 4.5 in 10^{-5} M Hg(II) and 60 s electrolysis in 0.1 M HNO_3
[d] This value is underestimated because N_2 is too large to probe the internal microstructure of Stöber beads [43]
[e] This value is underestimated because the surface of Aerosil-200 is covered by bonded siloxane groups which can be hydrolyzed in aqueous medium [44]
[f] As determined from ^{29}Si NMR spectroscopy, after integration of the deconvoluted peaks assigned to $(SiO)_3SiOH$ and $(SiO)_4Si$ sites



A krioporozimetria gondjai

A víz tágulása és esetleges romboló hatása, túlhűtés

Más oldószer alkalmazása: ciklohexán *K* nagyobb, *T* nagyobb (nedvesítés kérdése)

Az egyenlet szigorúan csak a szilárd darabkára igaz, de a pórusméretnek megfelel, ha a vízréteg igen vékony. „large porelimit".
K_c = 30 nm/K (25 elméletileg, de a felületi feszültség bizonytalan)

A geometria fontos és a hiszterézist is magába foglalja:

Gömb:	$\Delta T_m = -3K_c/r$	$\Delta T_m = -2K_c/r$
Henger:	$= -2K_c/r$	$-K_c/r$
Rés:	$= -K_c/2r$	

„Pore" (?) size distrubution in dendrimer gels (soft matter)

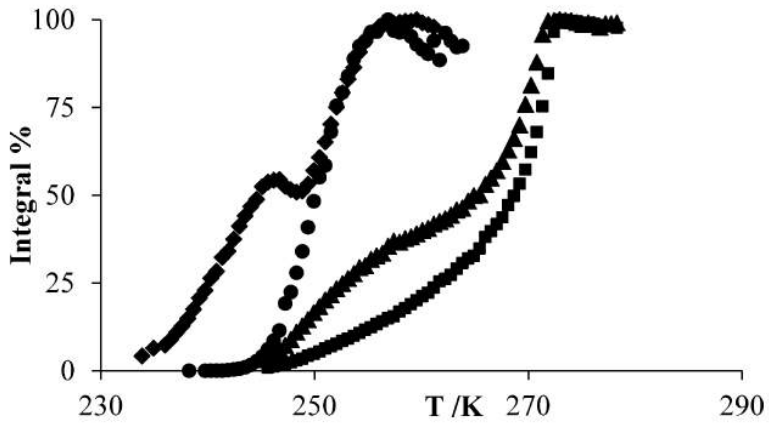


Figure 3. Changes of the integrated intensity of the liquid water peak as a function of temperature. The water dendrimer ratio is (◆) 1000, (●) 2000, (▲) 3000, and (■) 4000.

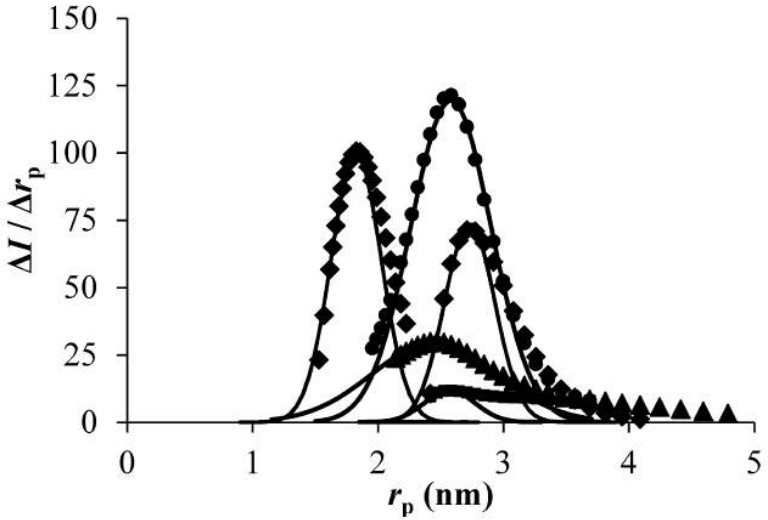


Figure 4. Pore size distribution curves of the swelling G5.NH_2 polymer defined by the radius. The water dendrimer ratio is (◆) 1000, (●) 2000, (▲) 3000, and (■) 4000. Lines represent the Gaussian distribution with the best parameters.

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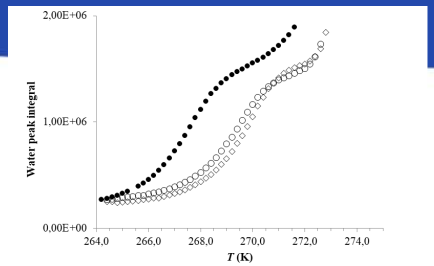
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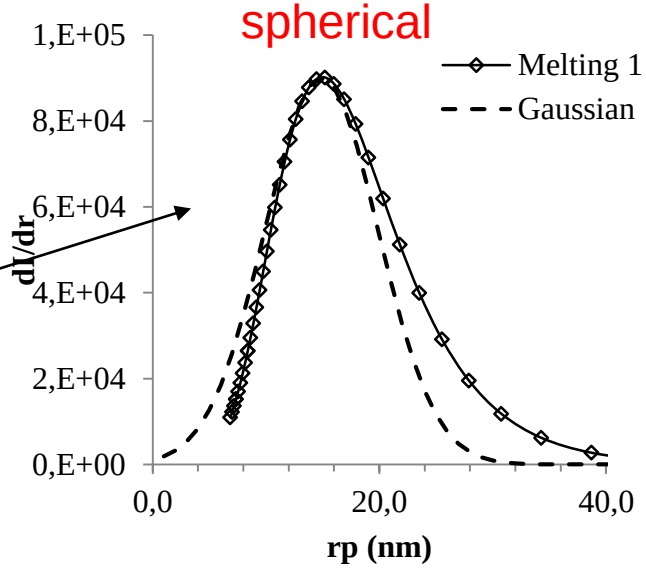
NMR Characterization of PAMAM_G5.NH_2 Entrapped Atomic and Molecular Assemblies

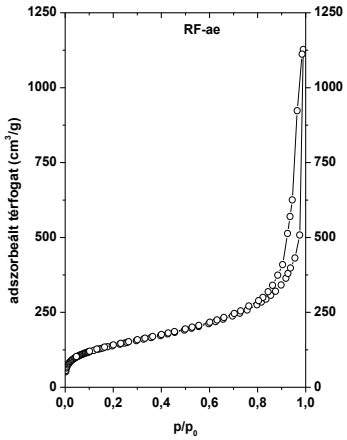
Mónika Kéri,[†] Chen Peng,[‡] Xiangyang Shi,[‡,§] and István Bányai*[,†]

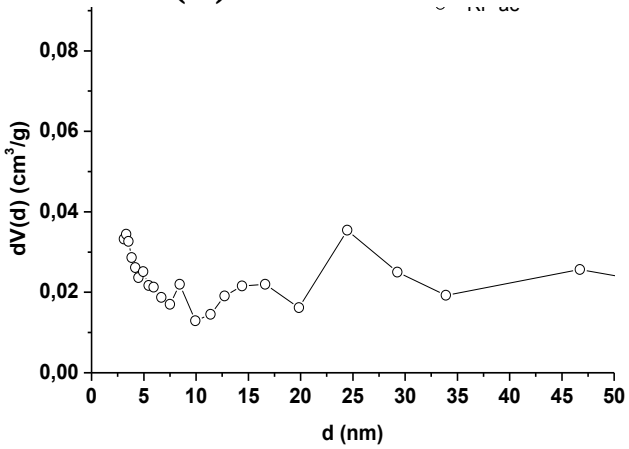
RF hydrogel to aerogel: motivation (?)

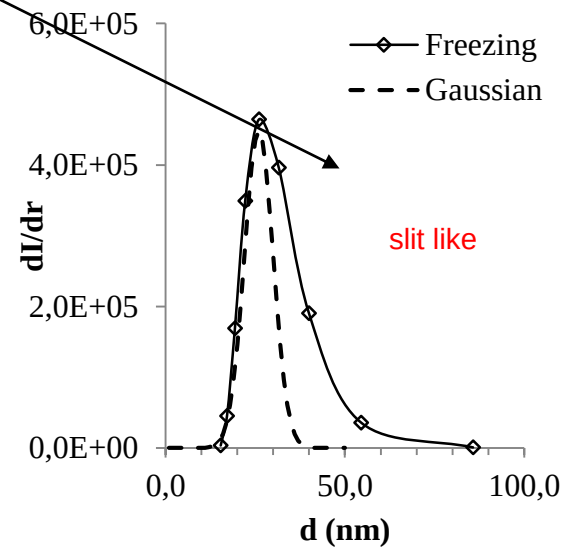


spherical









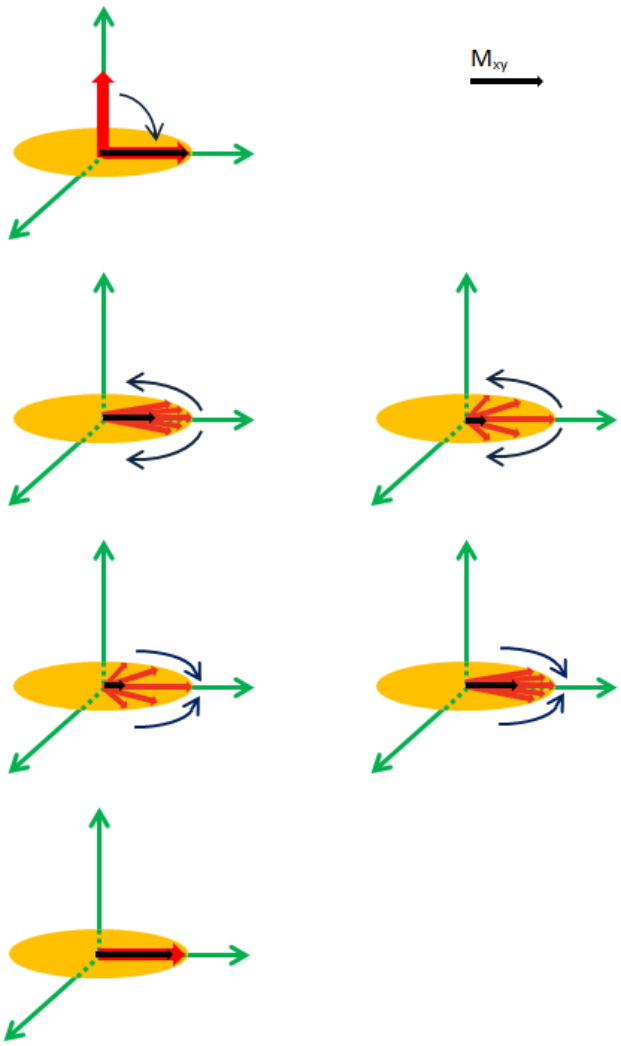
Spin-ekhó generálása

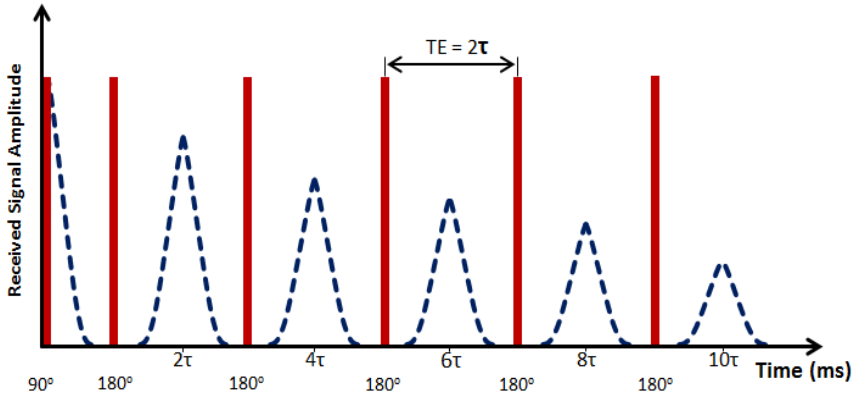
Applying 90° B1 pulse at time 0.

De-phasing after turning off the B1

At time **τ** ms, a 180° B1 pulse is applied to reverse the phase angles and thus initiates re-phasing.

Re-phasing is complete, and a measurable signal (a spin echo) is generated at time **2τ** ms.





Ahányszor ismételjük, annyiszor kisebb ekhót kapunk.

Diffúzió porózus rendszerekben:
...ált diffúzió

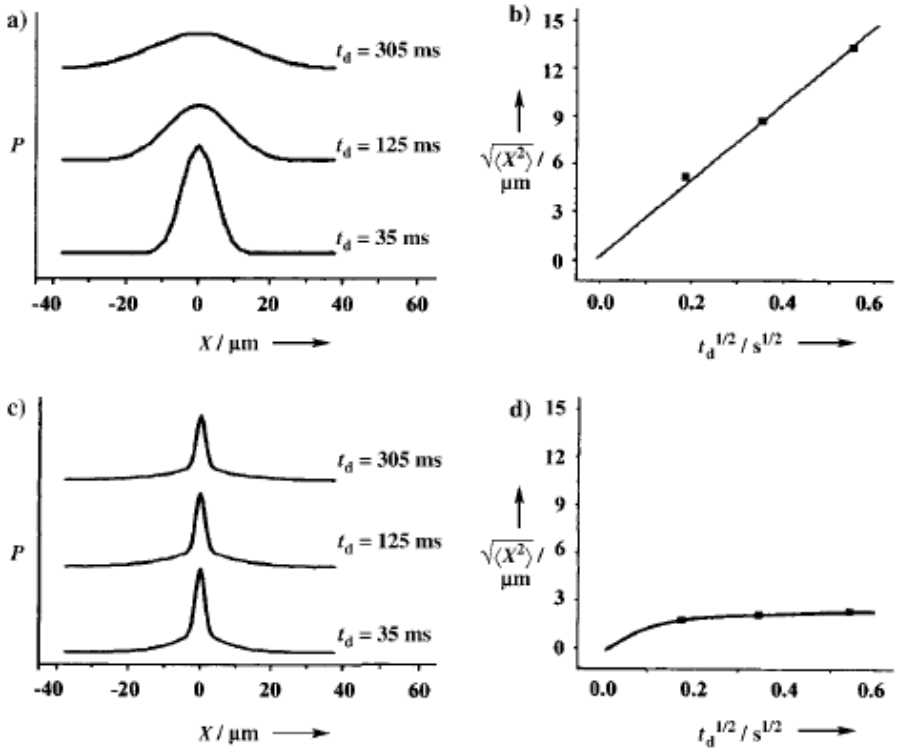


Figure 1. a), b) Free diffusion in a solution of *tert*-butanol; c), d) restricted diffusion (water in optic nerve). a), c) displacement distribution profiles; b), d) root-mean-square of the displacement *X* calculated from the full width at half height of the displacement distribution profiles shown in (a) and (c), respectively, against the square root of the diffusion time The slope of the straight line in (b) provides the self-diffusion coefficient of *tert*-butanol (2.7×10^{-6} $cm^2 s^{-1}$).[26c].

Diffúzió porózus rendszerekben:
...ált diffúzió

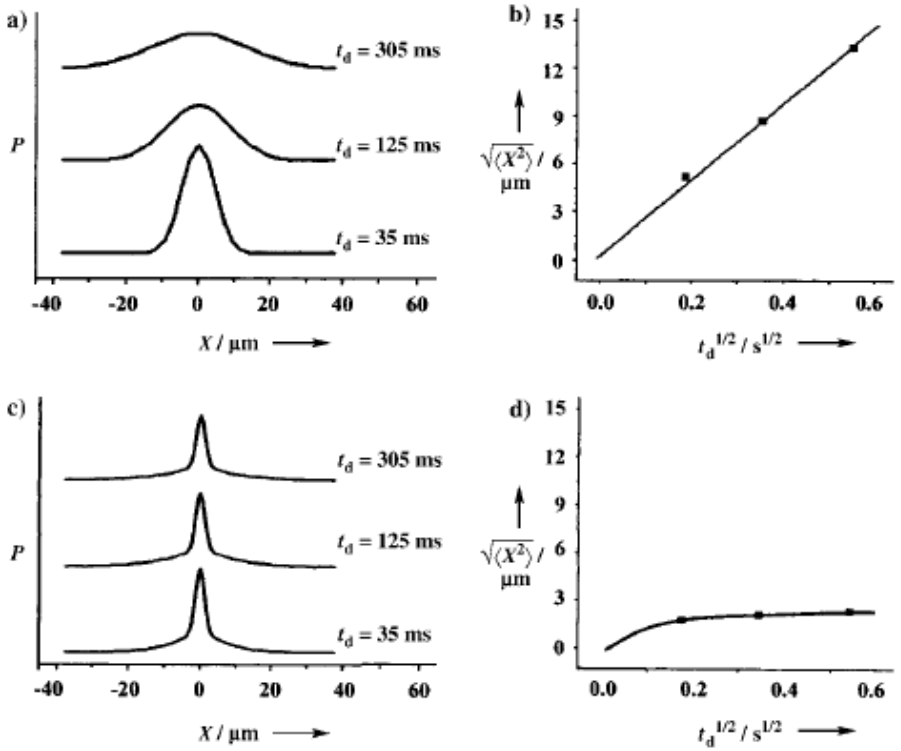
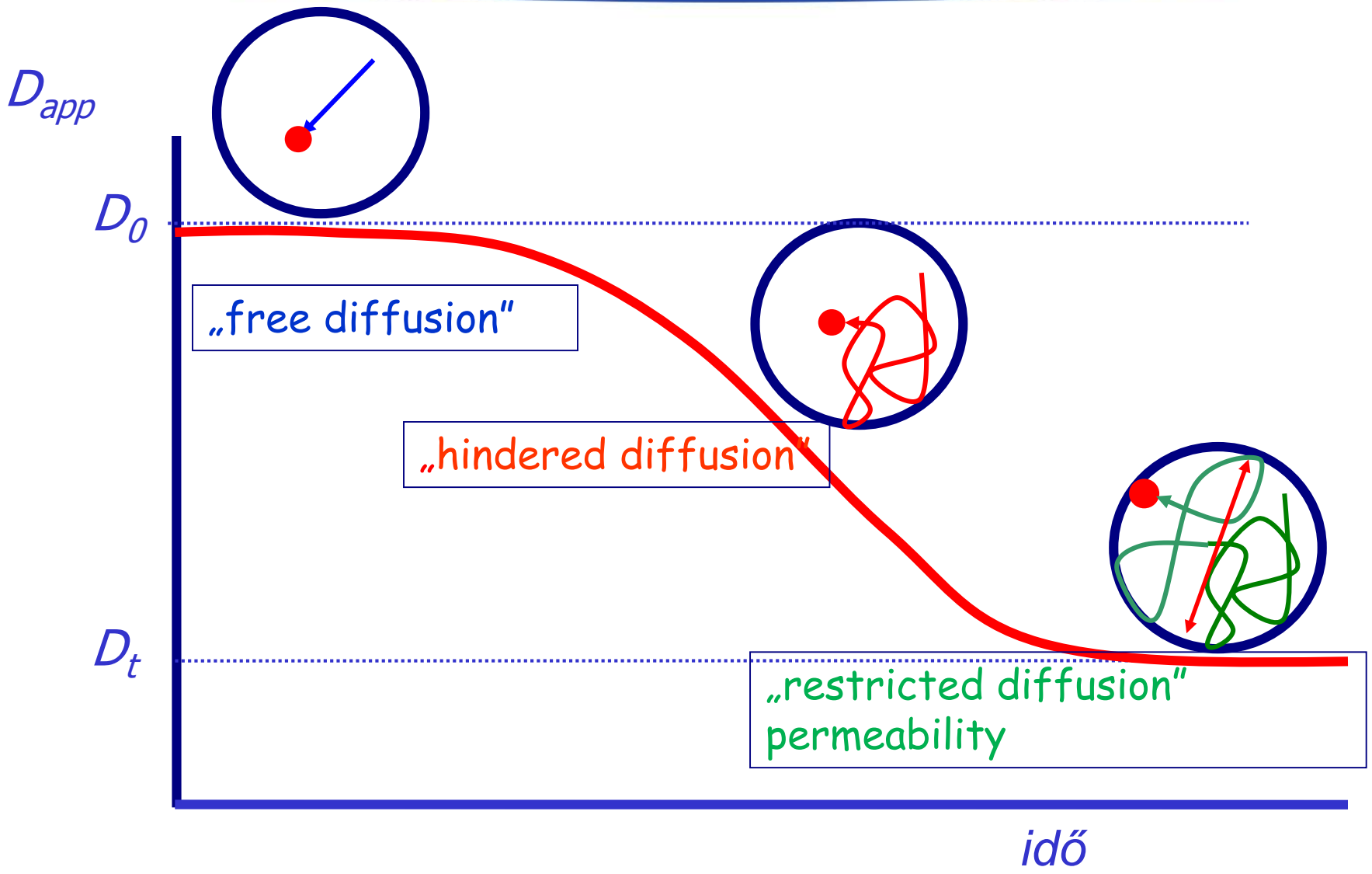
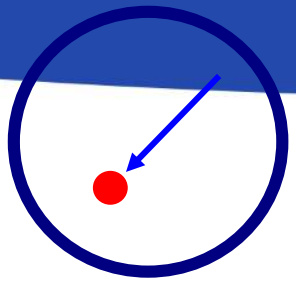


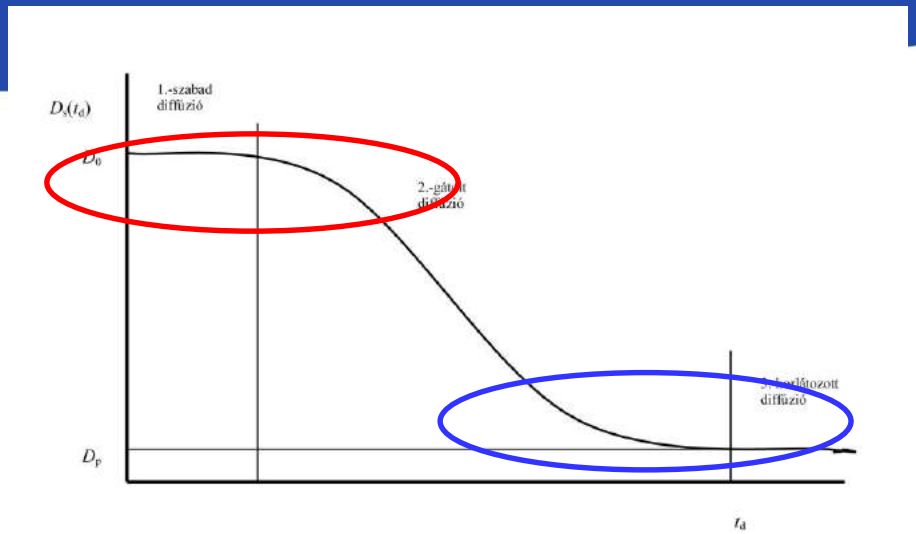
Figure 1. a), b) Free diffusion in a solution of *tert*-butanol; c), d) restricted diffusion (water in optic nerve). a), c) displacement distribution profiles; b), d) root-mean-square of the displacement *X* calculated from the full width at half height of the displacement distribution profiles shown in (a) and (c), respectively, against the square root of the diffusion time The slope of the straight line in (b) provides the self-diffusion coefficient of *tert*-butanol (2.7×10^{-6} $cm^2 s^{-1}$).[26c].

Time dependence of D



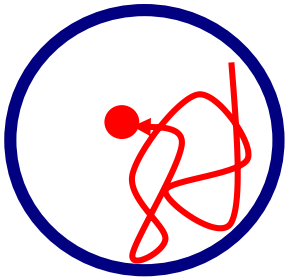
Közelítések





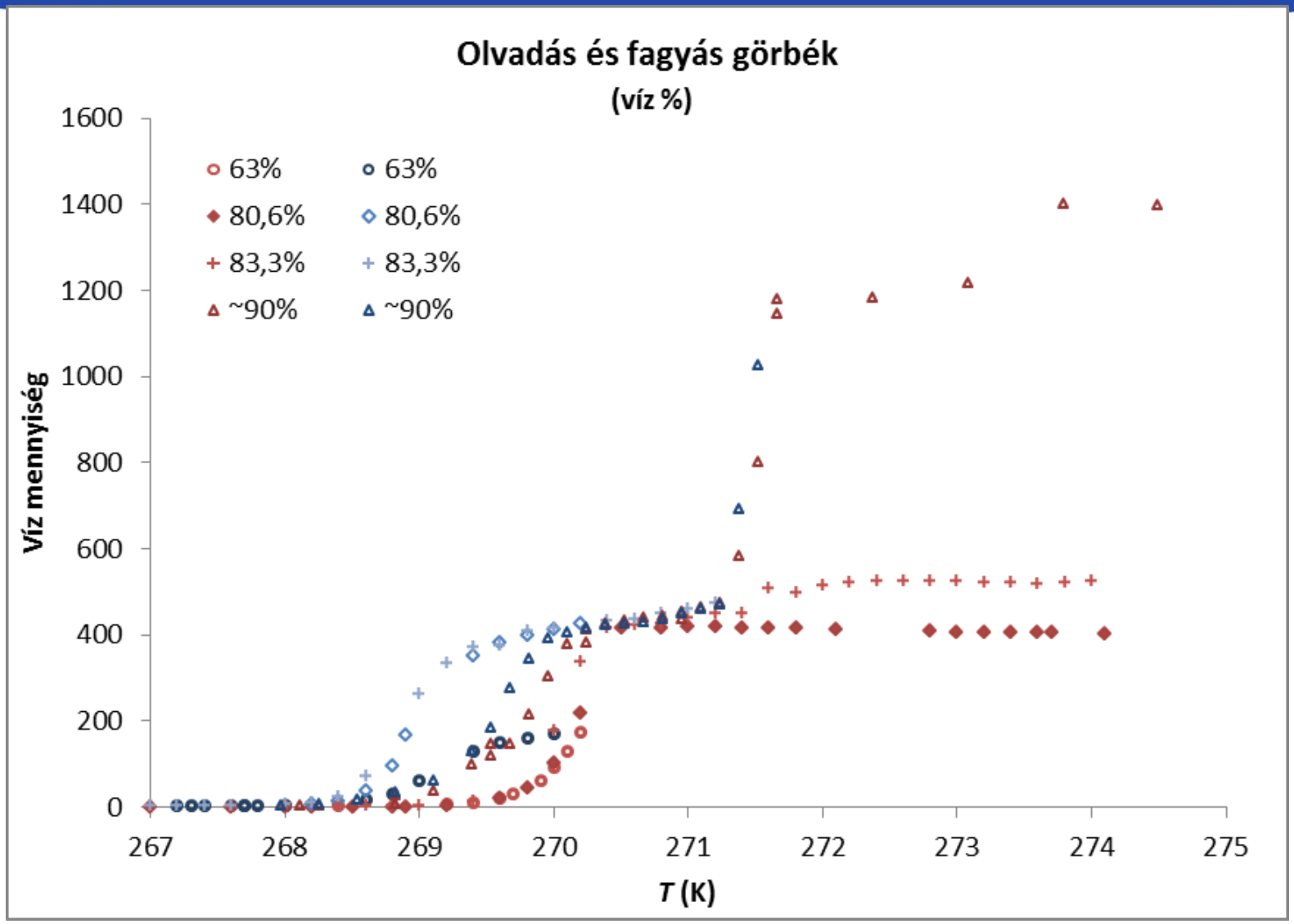
$$D(t) = D_0\left[1-\alpha^2 K\frac{4}{3d}\frac{S}{V}\sqrt{\frac{D_0}{\pi}}\sqrt{t}\right]$$

$$D^{eff}(t_d) = \frac{\left[D(t_d)-D_\infty\right]D_0}{D_0-D_\infty}$$



$$D_s = \frac{\langle a^2\rangle}{6t_D}$$

Teljes felvizezés



Elektronmikroszkópia

