

NMR alkalmazása porózus anyagok, kolloidok vizsgálatára

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Debreceni Egyetem
Fizikai Kémiai Tanszék
2018

Mottó

- „Ha csak kalapácsod van
mindent szegnek nézel.”

graffiti

Történeti elemek

- 1938 Isador Rabi (1944 Nobel díj, fizika)
 - ^7Li és ^{35}Cl NMR molekulásugárban
- 1946 F. Bloch és E.M.Purcell (1952 Nobel díj, fizika)
 - víz (F.B., Stanford), paraffin (E.M.P, MIT)
- 1960-70 szupravezető mágnesek
- 1966 impulzus technika (R. Ernst, 1991, kémia)
- 1971 a normális és daganatos szövetek eltérő relaxivitása (Damadian et al.)
- 1973 " a paprika" (Lauterbur et al.)
- 1976 "az agy " (Moore és Hinsaw)

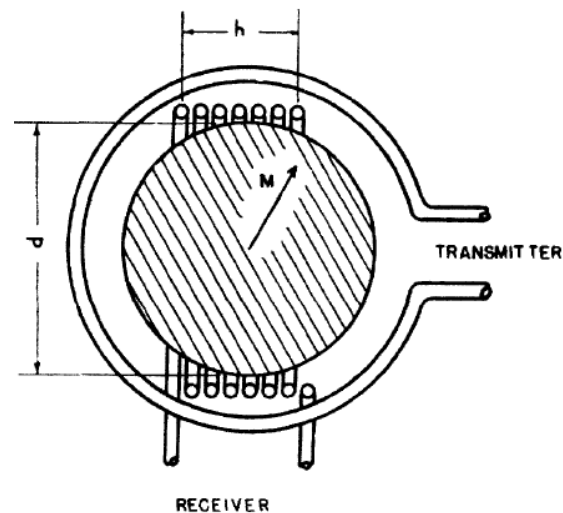
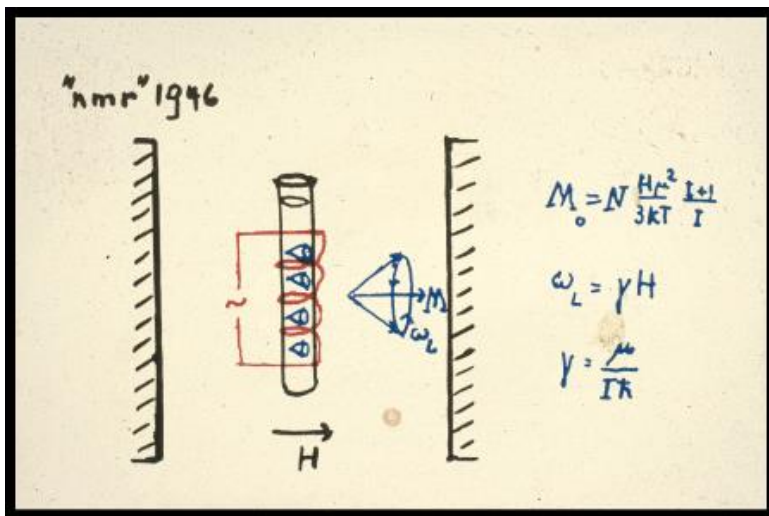
Az „igazi” alapítók



Felix Bloch
Stanford University, CA



Edward Mills Purcell
MIT, MA



A mágnesség

A mágneses erő: $\mathbf{F} = C \frac{p_1 p_2}{r^2} \frac{\mathbf{r}}{r}$ ($F = C \frac{p_1 p_2}{r^2}$) $C = \text{áll}$

A mágneses dipólus momentum: $\mathbf{m} = p\mathbf{l}$ ($m = pl$)

ahol p a póluserősség [Wb] vagy [Vs]

A mágneses térerősség:

a p elemi mágneses töltésre ható erő mágneses térben arányos annak nagyságával:

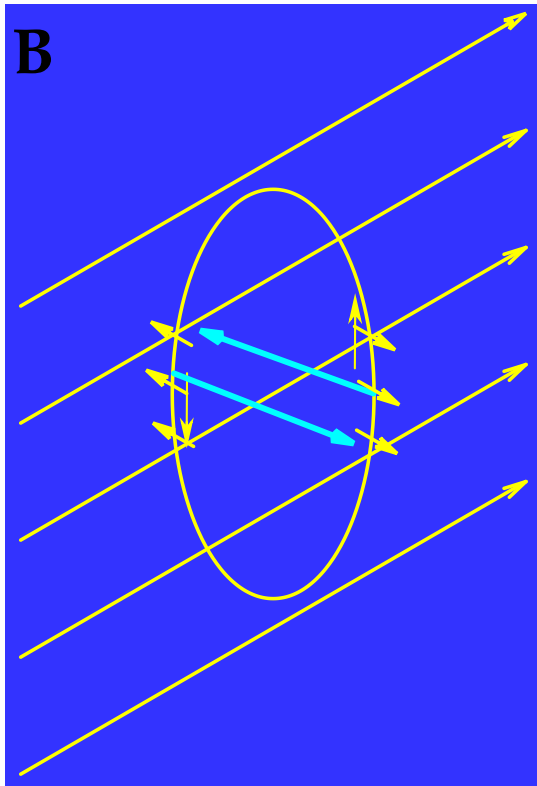
$$\mathbf{F} = \mathbf{H}p$$

ahol H a mágneses tér erőssége

$$\mathbf{M}_f = \mathbf{mH}$$

A mágneses dipólust az \mathbf{M} forgatónyomaték \mathbf{H} irányába forgatja $\phi=0$

Mágnesség 2



$$\mathbf{M} = \frac{\mathbf{m}}{V}$$

A térfogategységre eső
mágneses momentum:
mágnesezettség vektor
v. mágneses polarizáció

$$\mathbf{M} = \kappa \mathbf{H}$$

A H mágneses tér képes
polarizálni az anyagokat
 κ = szuszceptibilitás

$$\mathbf{B} = \mu \mathbf{H}$$

B a mágneses indukció
vektor

μ = mágneses permeabilitás

Az köráram mágneses térben

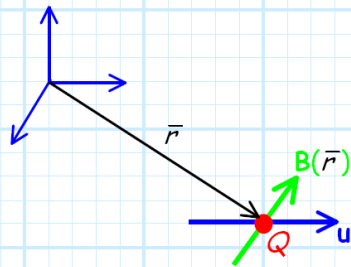
Our note book in physics

The Magnetic Force

Say a **charge** Q is located at some **point** in space (denoted by position vector \vec{r}), and is moving with velocity \mathbf{u} .

Likewise, there exists **everywhere** in space a magnetic flux density (we neither know nor care **how** this field was **created**).

The value (both magnitude and direction) of the magnetic flux density vector **at point** \vec{r} is $\mathbf{B}(\vec{r})$:

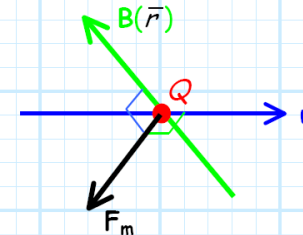


Q: Our "field theory" of electromagnetics says that the magnetic flux density will apply a **force** on the moving charge (i.e., **current**). Precisely what is this force (i.e., its magnitude and direction)?

A: The answer is not quite as simple the electric force equation. The **force** \mathbf{F}_m on charge Q moving at velocity \mathbf{u} is :

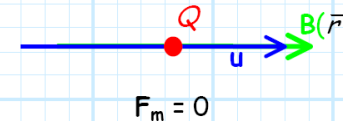
$$\mathbf{F}_m = Q \mathbf{u} \times \mathbf{B}(\vec{r})$$

Note therefore, that the resulting force \mathbf{F}_m will be **orthogonal** to both the **velocity** vector \mathbf{u} and the **magnetic flux density** vector $\mathbf{B}(\vec{r})$. E.G.,:



Note the **maximum** force is applied when the magnetic flux density vector is **orthogonal** to the velocity vector (i.e., $\theta = 90^\circ$).

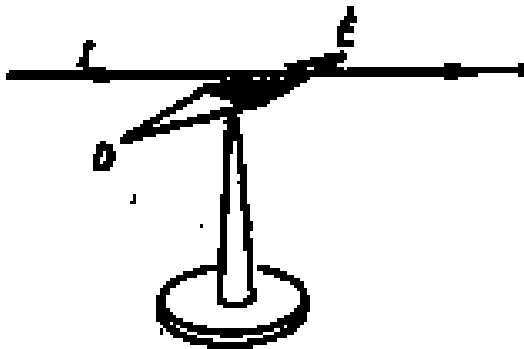
Alternatively, the force on the charge will actually be **zero** if the magnetic flux density is **parallel** to the velocity vector (i.e., $\theta = 0^\circ$):



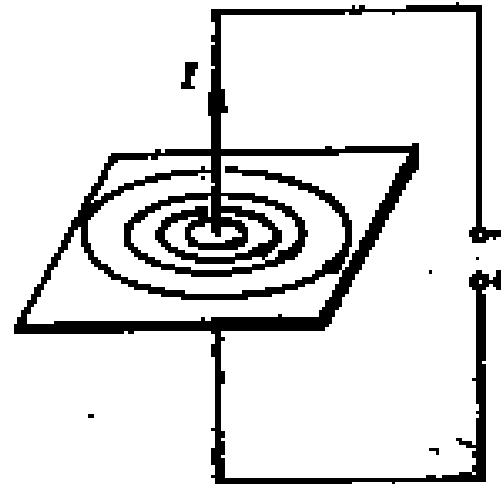
Note there is **no** equivalent situation for the **electric** force—the only way \mathbf{F}_e can be zero is if the electric field $\mathbf{E}(\vec{r})$ is **zero**!

Mágneses kölcsönhatások I.

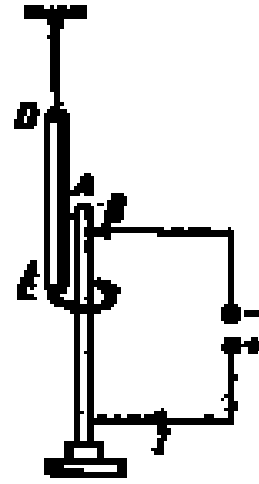
- Budó: Kísérleti fizika II



181,1. ábra

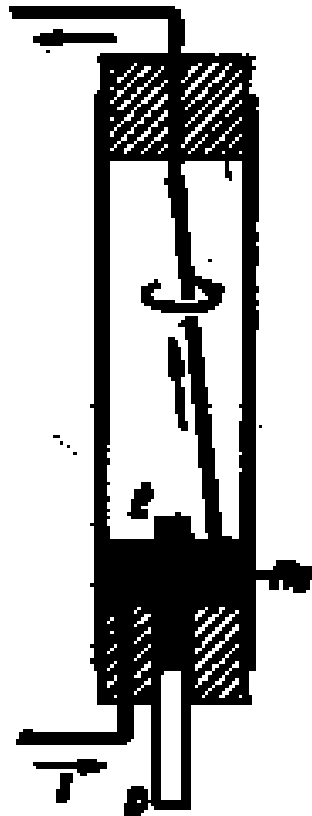


181,2. ábra



181,3. ábra

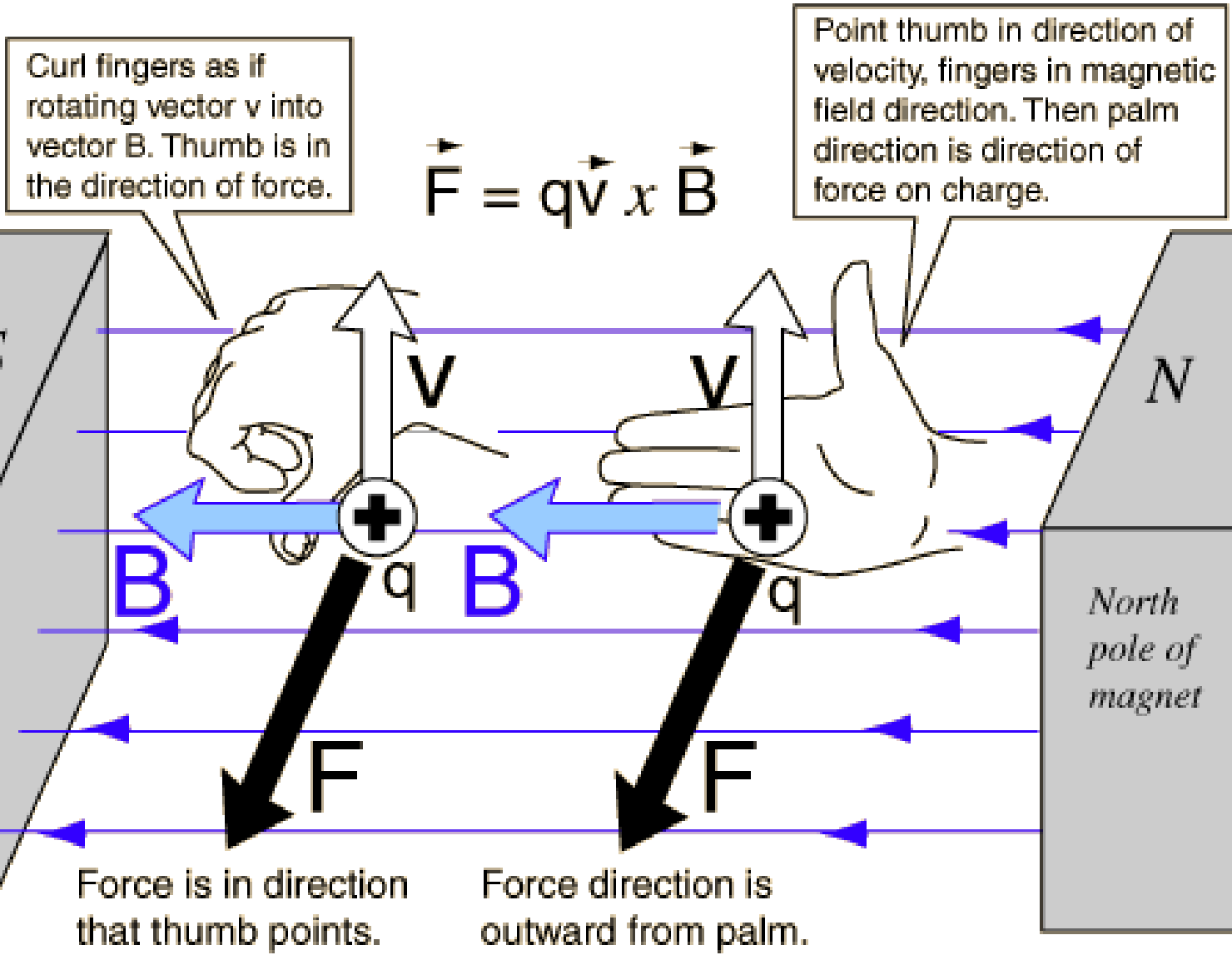
Larmor-precesszió



103.3. ábra

$$\nu \sim \mathbf{B}_0$$

Nature of magnetic force



Mozgások

$$\Omega f = \omega f$$

Példák:

$$\mathbf{H}\Psi = E\Psi \quad \mathbf{H} = -\frac{\hbar}{2m} \frac{d^2}{dx^2} + V \quad \text{Hamilton-operátor}$$

$$\hat{\mathbf{P}}\Psi = p\Psi \quad \hat{\mathbf{P}} = \frac{\hbar}{i} \frac{d}{dx} \quad \text{Impulzus operátor}$$

A kvantummechanika nem más mint valamely operátor sajátfüggvényeinek meghatározását célzó erőfeszítés.
Az eredmény a sajátérték(ek) meghatározása

Periódikus mozgás

Egy gömb alakú test forgó mozgása: $-\frac{\hbar^2}{2m}\nabla^2\Psi = E\Psi$

$$\nabla^2\Psi = \frac{\partial^2(\Psi)}{\partial r^2} + \frac{2}{r}\frac{\partial(\Psi)}{\partial r} + \frac{1}{r^2}\Lambda^2\Psi + V \quad \Lambda^2\Psi = \frac{1}{\sin^2\Theta}\frac{\partial^2\Psi}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\phi}{\partial\theta}\right)$$

$r = \text{állandó} = R$

$$\Lambda^2\Psi = -\frac{2IE\Psi}{\hbar^2} \quad I = mr^2$$

$$Y_{1,\pm 1} = \mp m_l \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{im_l\phi}$$

$$E = l(l+1)\frac{\hbar^2}{2I} \quad l = 0, 1, 2, \dots$$

$$E = \frac{J^2}{2I}$$

l és m_l ahol $m_l = l, \dots, -l$

$$J = \sqrt{l(l+1)}\hbar \quad l = 0, 1, 2, \dots$$

Degenerált, de nem mágneses térben

Az atommag

Az atommagnak is van pályája és spinje, sőt töltése is. Ha egy töltött testnek van eredő impulzus momentuma, Akkor ahhoz mágneses momentum is csatlakozik:

$$\mu = -g \frac{e}{2m} J = \gamma J$$

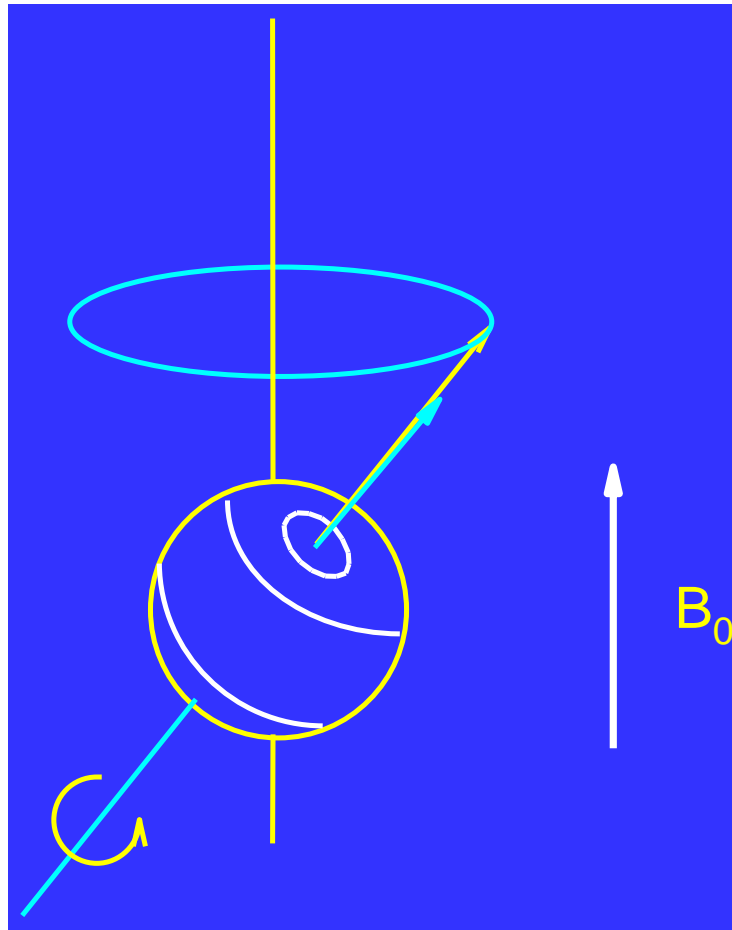
Mivel a J kvantált így a mágneses momentum is

$$\mu = -g \frac{e}{2m_p} \sqrt{I(I+1)} \hbar = g \mu_N \sqrt{I(I+1)} \hbar \quad I = 0, 1/2, 1, 3/2, \dots$$

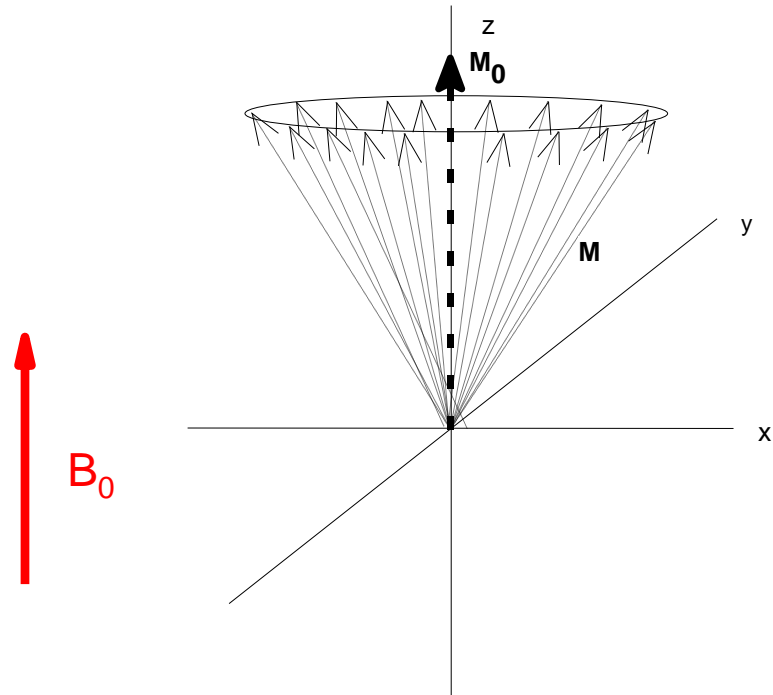
$$\mu_z = M_l \hbar \quad M_l = -I, -I+1, 0, \dots, I-1, I$$

A mágneses momentum soha nem lehet egyenlő saját z komponensével ! (Heisenberg-reláció)
Ez szabja meg a vektor irányát a B_0 -hoz képest

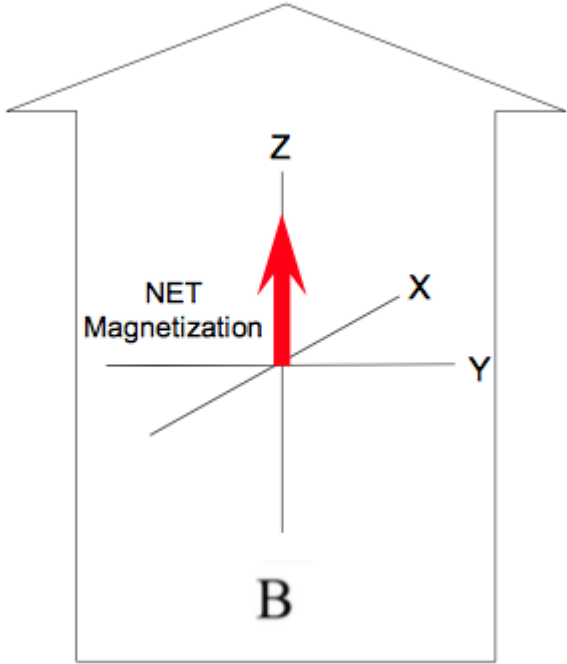
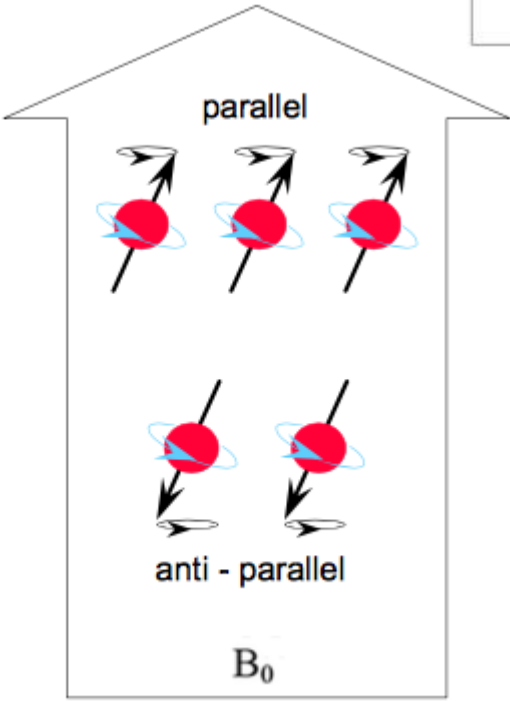
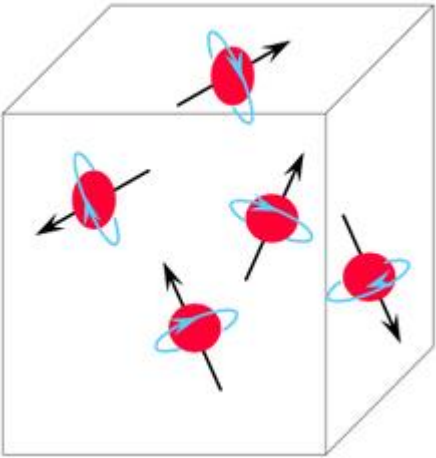
Atommag viselkedése



$$\omega = -\gamma B_0$$



Az atommag viselkedése



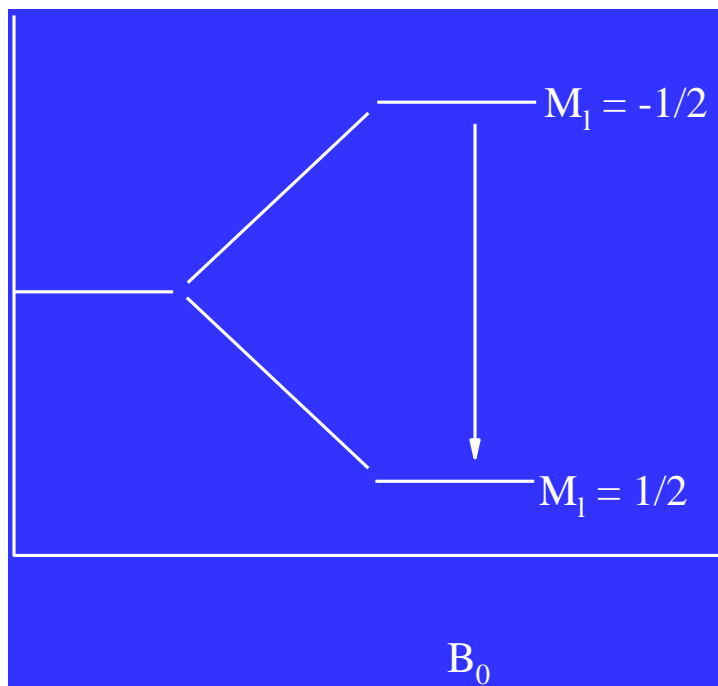
Atommag viselkedése

Mágneses térben a „magspin” szerint egy közel parallel es egy közel anti-parallel beállítás alakulhat ki, ha $I=1/2$.

Az utóbbi energiája nagyobb.

$$E = -\mu_z |\mathbf{B}_0| = -\gamma J_z |\mathbf{B}_0| = -\gamma M_I \hbar |\mathbf{B}_0|$$

$$M_I = -I, -I+1, \dots, I-1, I$$



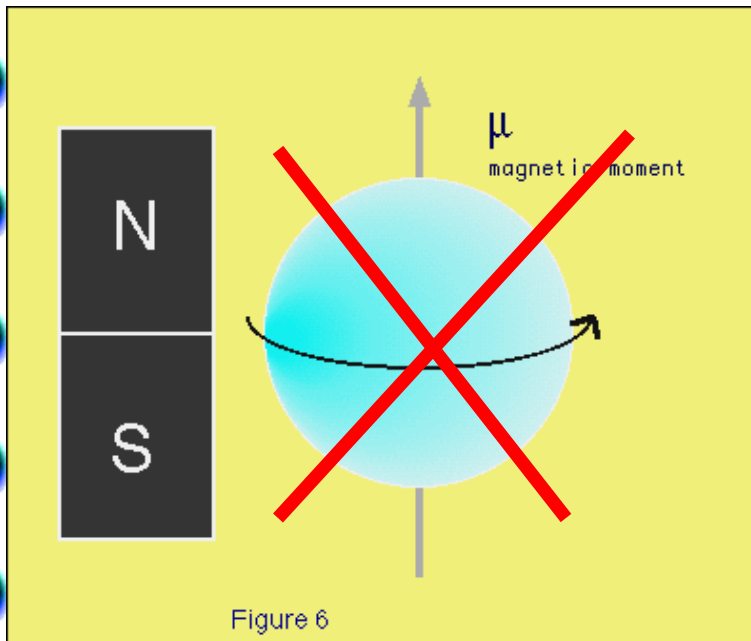
$$\Delta E = \gamma \hbar \Delta M_I B_0$$

$$\Delta M_I = 1$$

$$\nu = \gamma / 2\pi B_0$$

ami ^1H magra 100 MHz 2.3 T téren ,
Larmor precesszió

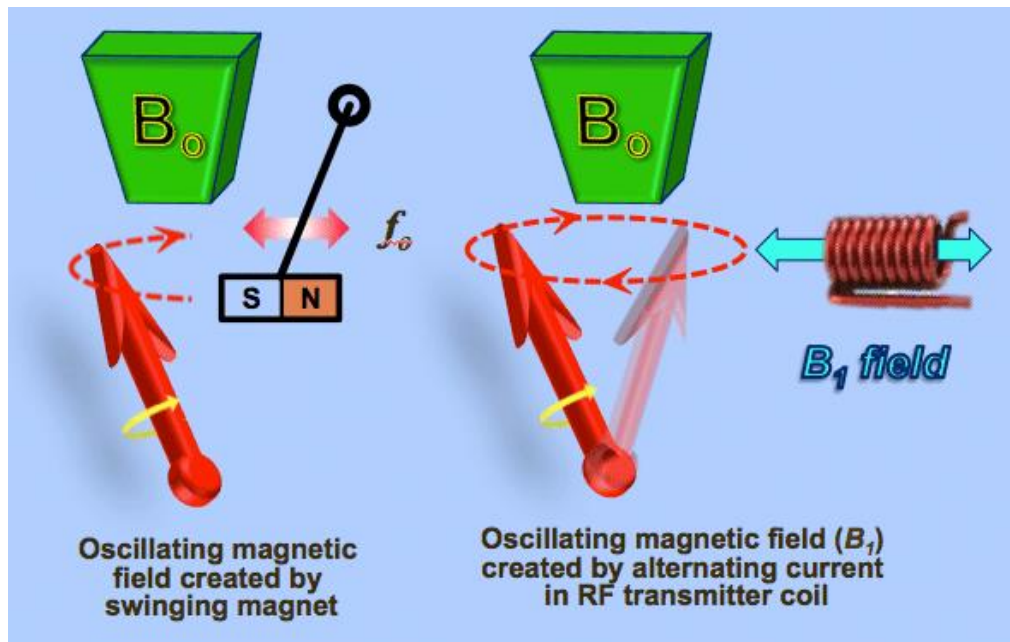
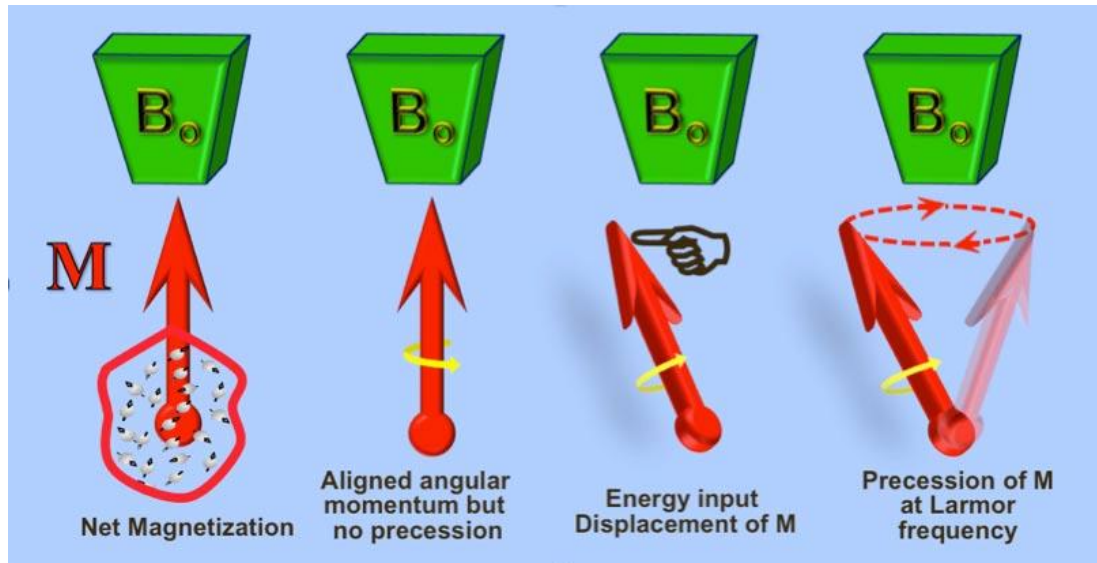
AZ NMR JELENSÉG: szörnyűség



- A nukleonok mágneses saját- és pályamomentuma, valamint töltése illetve töltéssel-oszlása miatt:

$$\mu = -\gamma\mu_N\sqrt{I(I+1)}\hbar$$
$$I = 0, 1/2, 1, 3/2, \dots$$

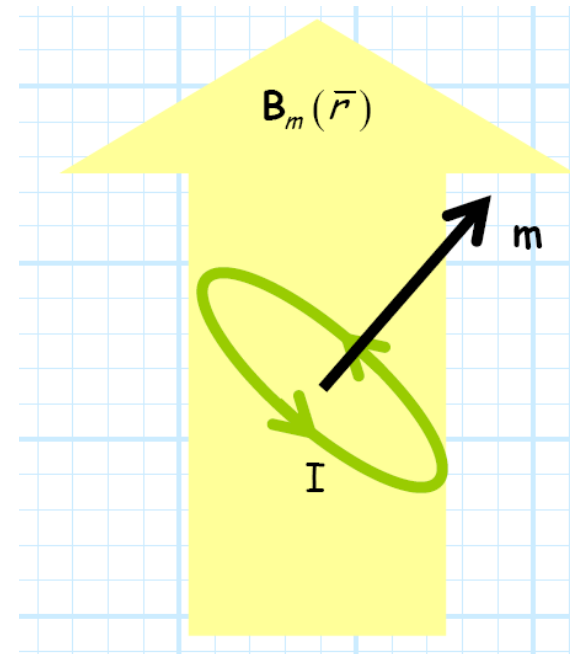
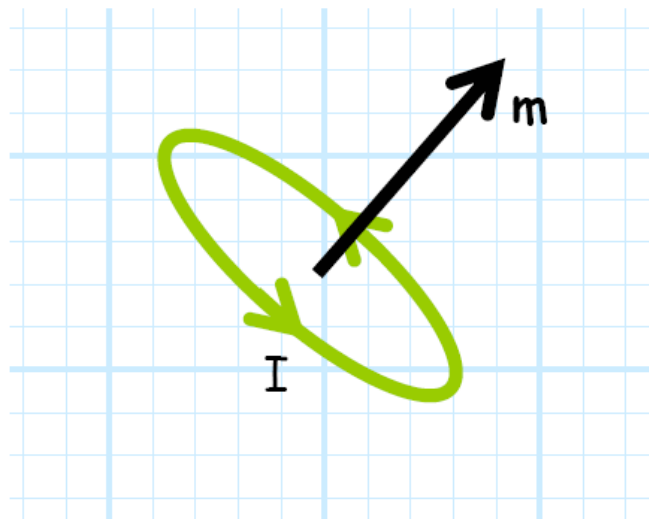
Egy jó ábra!



A decorative vertical wavy line on the left side of the slide, composed of overlapping, rounded, wave-like shapes in black and blue.

A makroszkópos mágnesezettség

Makroszkópikus mágneses dipólus mágneses térben

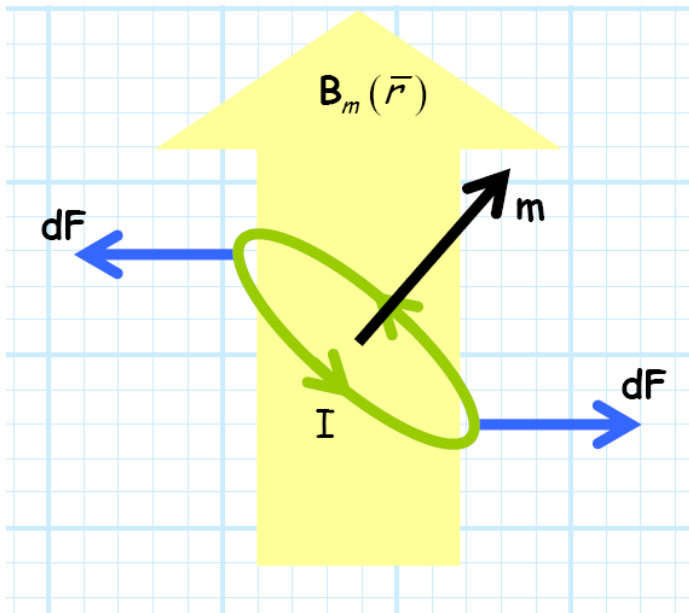


Take one magnetic dipole moment represented by current loop which creates it.

„Immerse” it into magnetic field

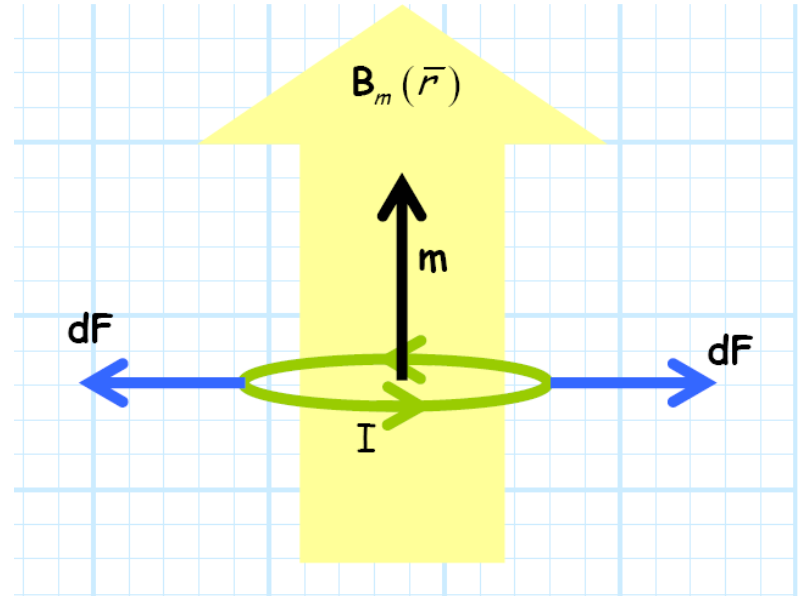
Ampère 1820 magnetic double layer (molecular loops)

A dipólus mozgása



Lorentz force acts, no move because the total resultant force is zero

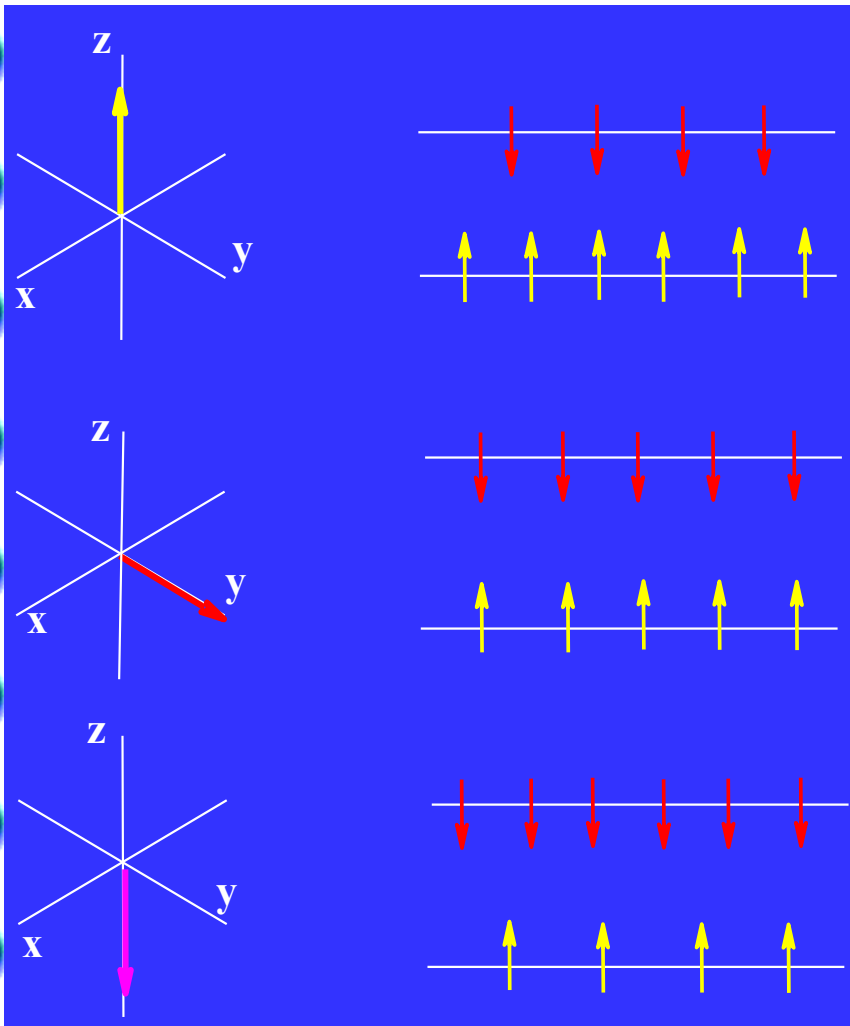
$$\oint_c \overline{Idl} \times \mathbf{B}_m(\vec{r}) = 0$$



There is torque rotates \mathbf{m} until it aligns \mathbf{B}

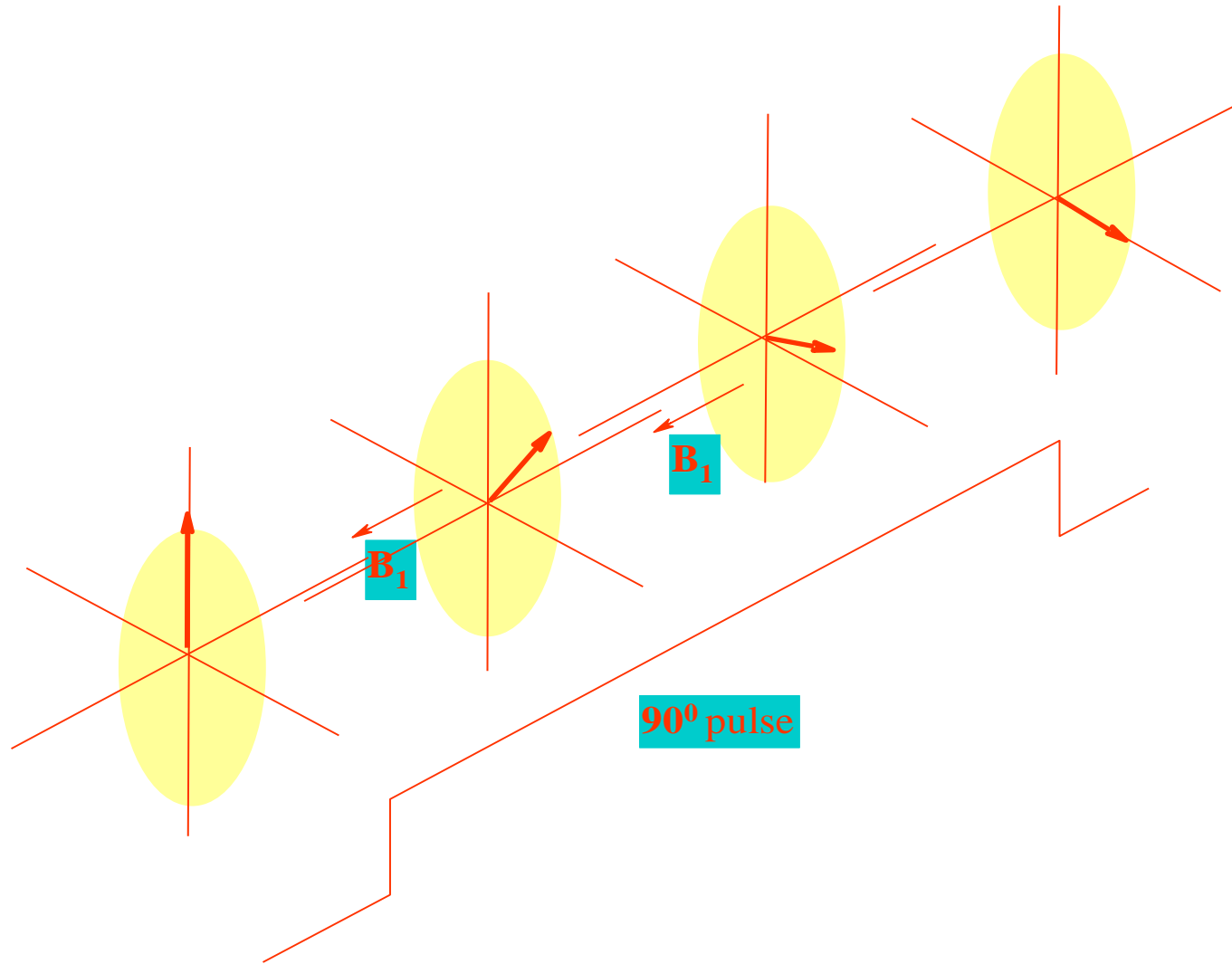
$$\mathbf{T}_m = \mathbf{m} \times \mathbf{B}(\vec{r})$$

Molekuláris és klasszikus kép

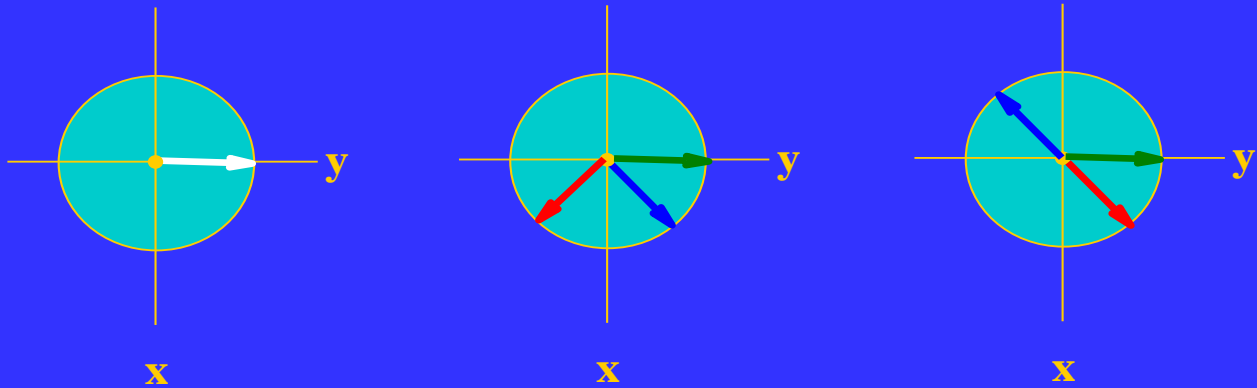


- egyensúlyi állapot
 $M_0 = M_z$
- gerjesztett állapot
 $M_0 = M_y$
- populáció inverzió
- $M_0 = M_{-z}$
- spin physics

A gerjesztés



A kémiai eltolódás

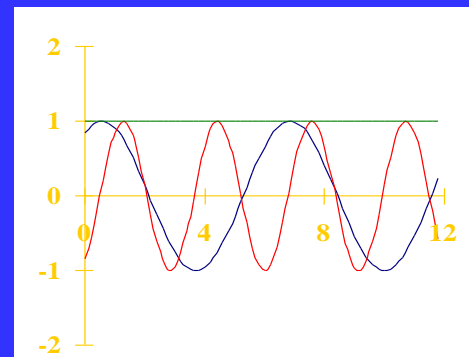


off

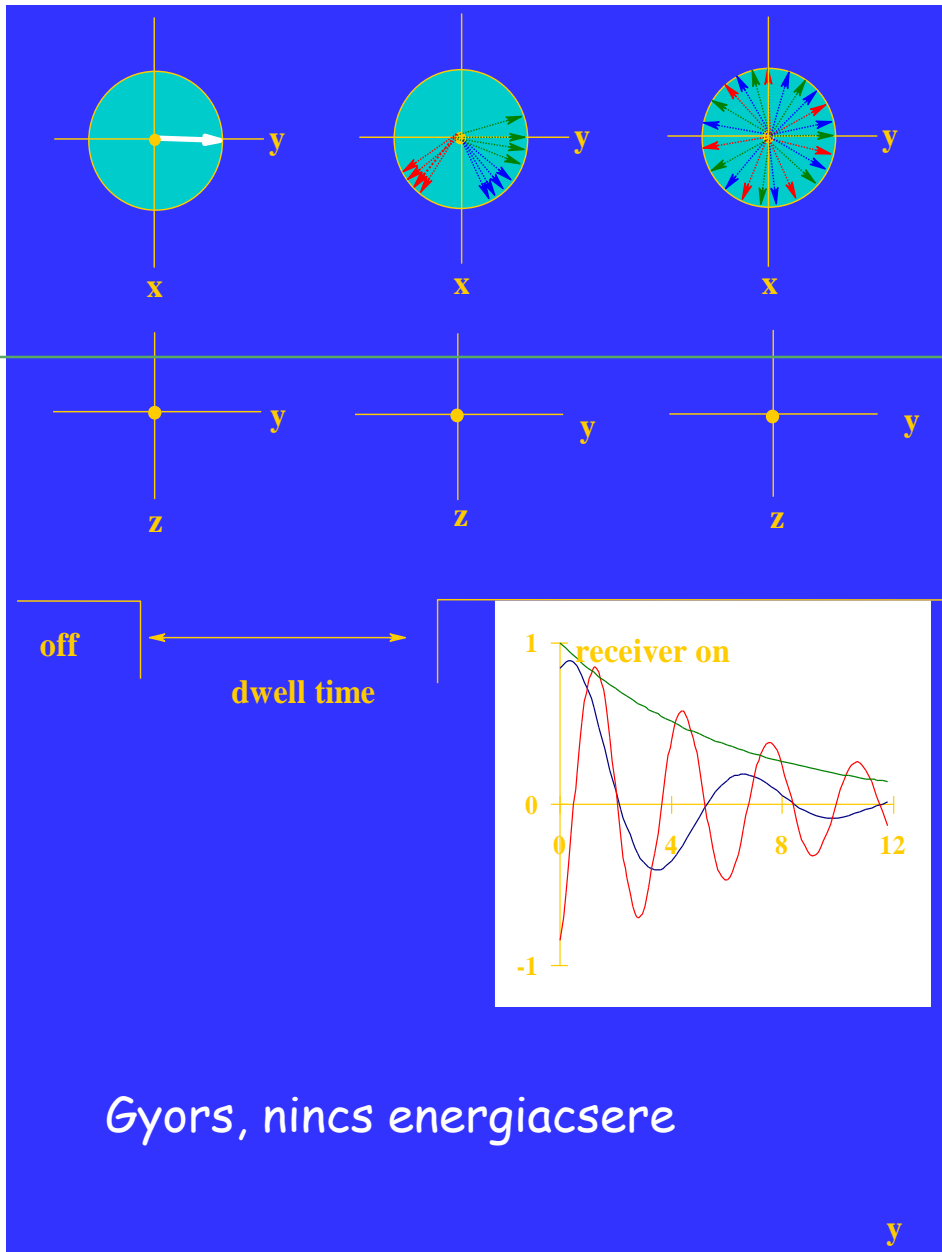
dwelt time

receiver on

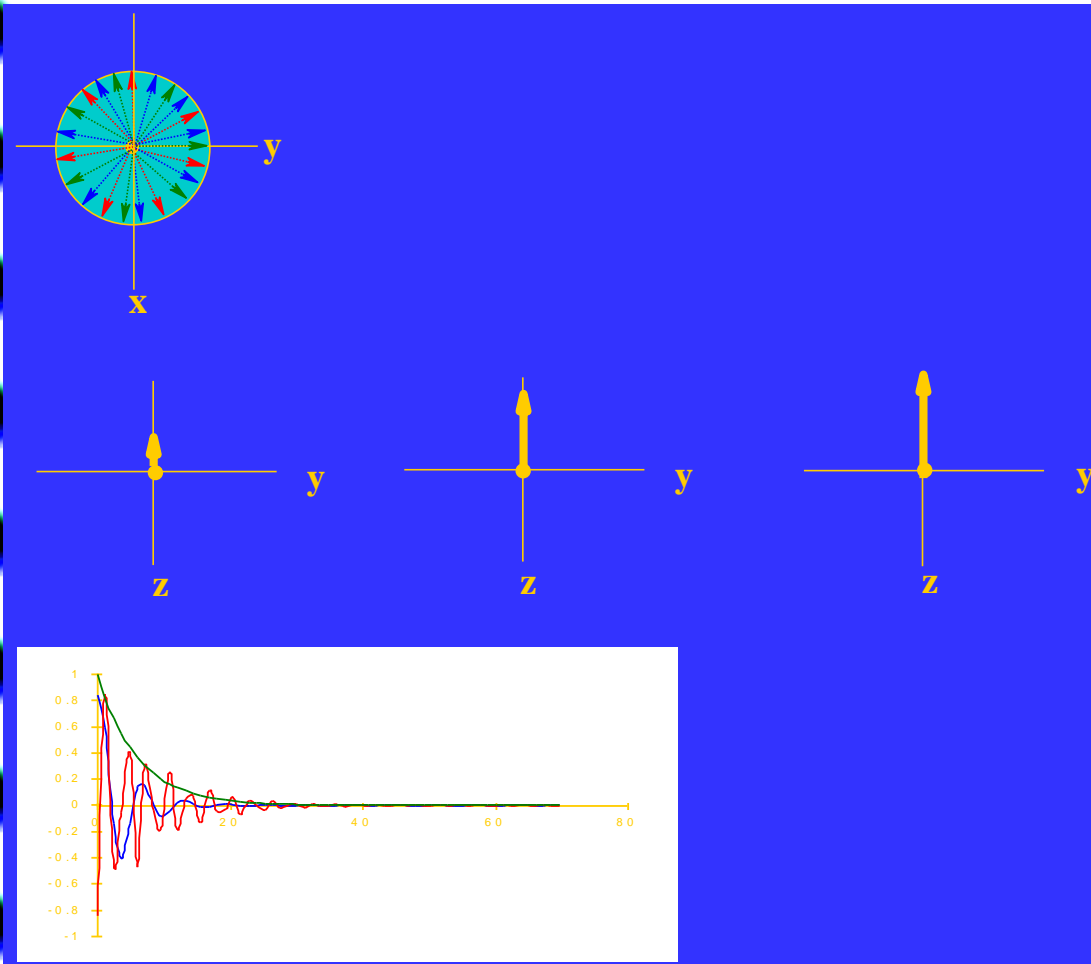
Szerves kémia!???



Transzverzális relaxáció (T_2)



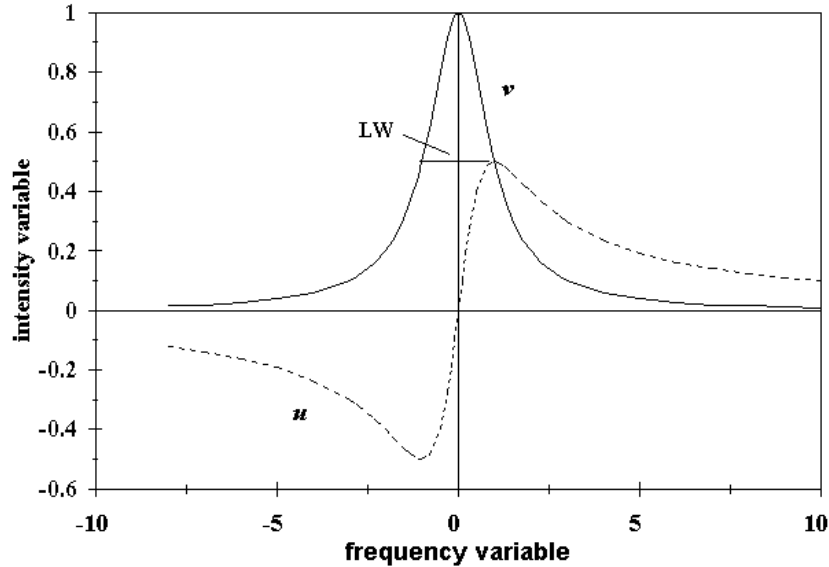
Longitudinális relaxáció (T_1)



- A kvantitatív NMR lényeges eleme
- Lassúbb mint a transzverzális relaxáció

Impulzus szekvenciák!!!!

FID és spektrum

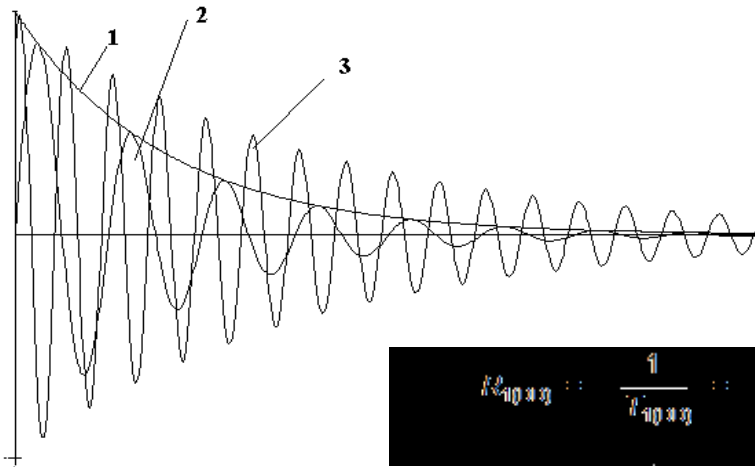


- Lineáris egyenletrendszerként

$$LW = \frac{1}{\pi T_2}$$

- Fourier-transzformáció

$$f(\omega) = \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt$$



- - fázis korrekció

$$T_{1\rho} \approx \frac{1}{T_{1\rho}} \approx \gamma_x \gamma_H \left(\frac{h}{2\pi} \right)^2 \gamma_N \gg \frac{1}{T_{1\rho}}$$

Relaxáció és rotációs korrelációs idő

$$T_1^{-1} = \frac{2}{5} \frac{\gamma^4 \hbar^2}{r^6} I(I+1) \tau_c \left[\frac{1}{1 + \omega^2 \tau_c^2} + \frac{4}{1 + 4\omega^2 \tau_c^2} \right]$$

$$T_2^{-1} = \frac{1}{5} \frac{\gamma^4 \hbar^2}{r^6} I(I+1) \tau_c \left[3 + \frac{5}{1 + \omega^2 \tau_c^2} + \frac{2}{1 + 4\omega^2 \tau_c^2} \right]$$

Az NMR spektrum egyenlete

Bloch-egyenletek

$$\frac{dM_z}{dt} = -\gamma B_1 v + \frac{(M_0 - M_z)}{T_1}$$

Forgó koordinátarendszer
 B_1 x irányú

$$M_x = u ; M_y = v$$

$$\frac{du}{dt} = -(\omega_o - \omega_i)v - \frac{u}{T_2}$$

Megoldása stacionárius állapotokra.

$$\frac{dv}{dt} = (\omega_o - \omega_i)u - \frac{v}{T_2} + \gamma B_1 M_z$$

Egy jelre „on resonance”

$B_1 = 0$ esetén a FID !!!!!

Az NMR aktív magok

Az NMR-spektroszkópia szükséges feltétele a nullától különböző magspin ($I \neq 0$)

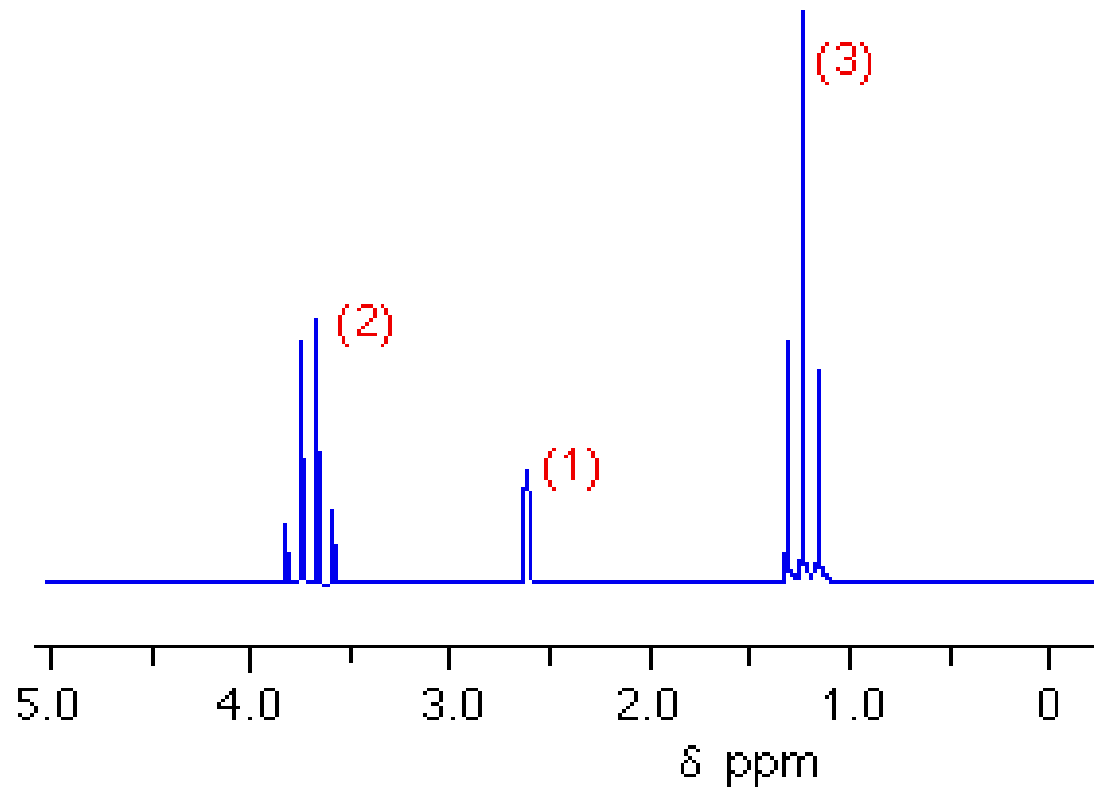
– $I=0$ mind a protonok mind a neutronok száma páros (^{12}C , ^{16}O)

– $I=1/2$ ha tömegszáma páratlan (^1H , ^3H , ^{13}C , ^{15}N , ^{19}F , ^{57}Fe , ^{113}Cd)
vagy a protonok, vagy a neutronok száma páratlan.

– $I=k$ ($k=1,2,..$) mind a protonok mind a neutronok száma páratlan
(^2H , ^{14}N)

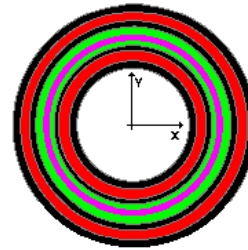
Etanol NMR spektruma

nmr spectrum for ethanol, $\text{CH}_3\text{CH}_2\text{OH}$ - source SDBS

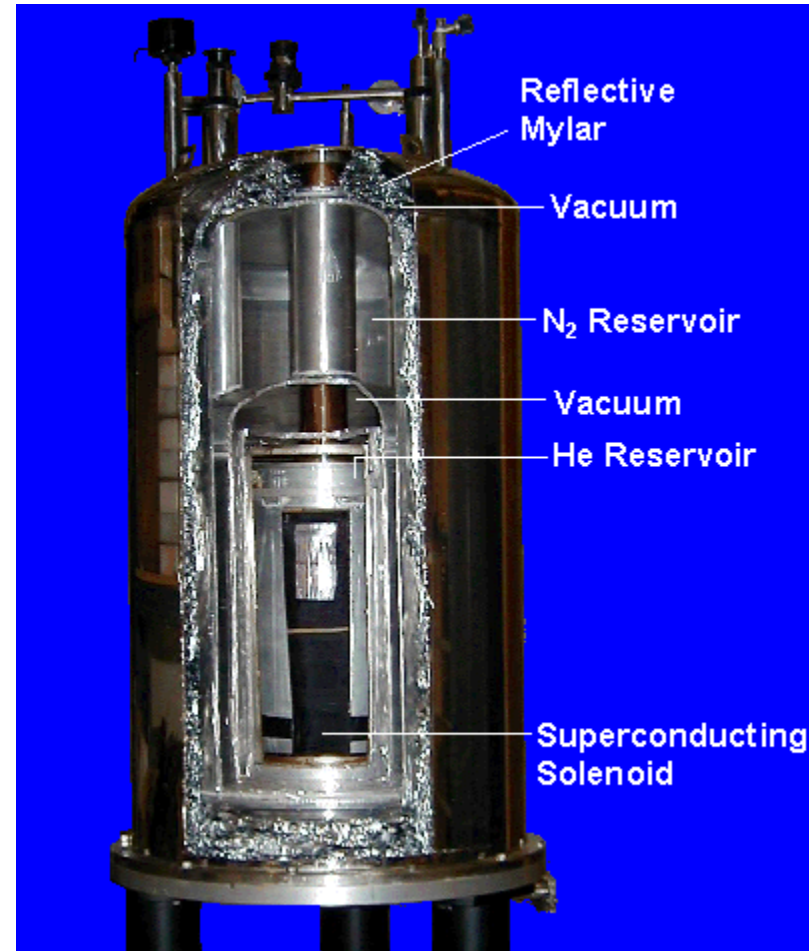
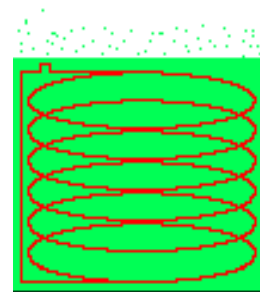


A paraméterek: kémiai eltolódás, intenzitás, vonalszélesség (T_2)

Mágnés



- Vacuum
- Liquid Helium
- Liquid Nitrogen
- Container & Support
- Superconducting Coil

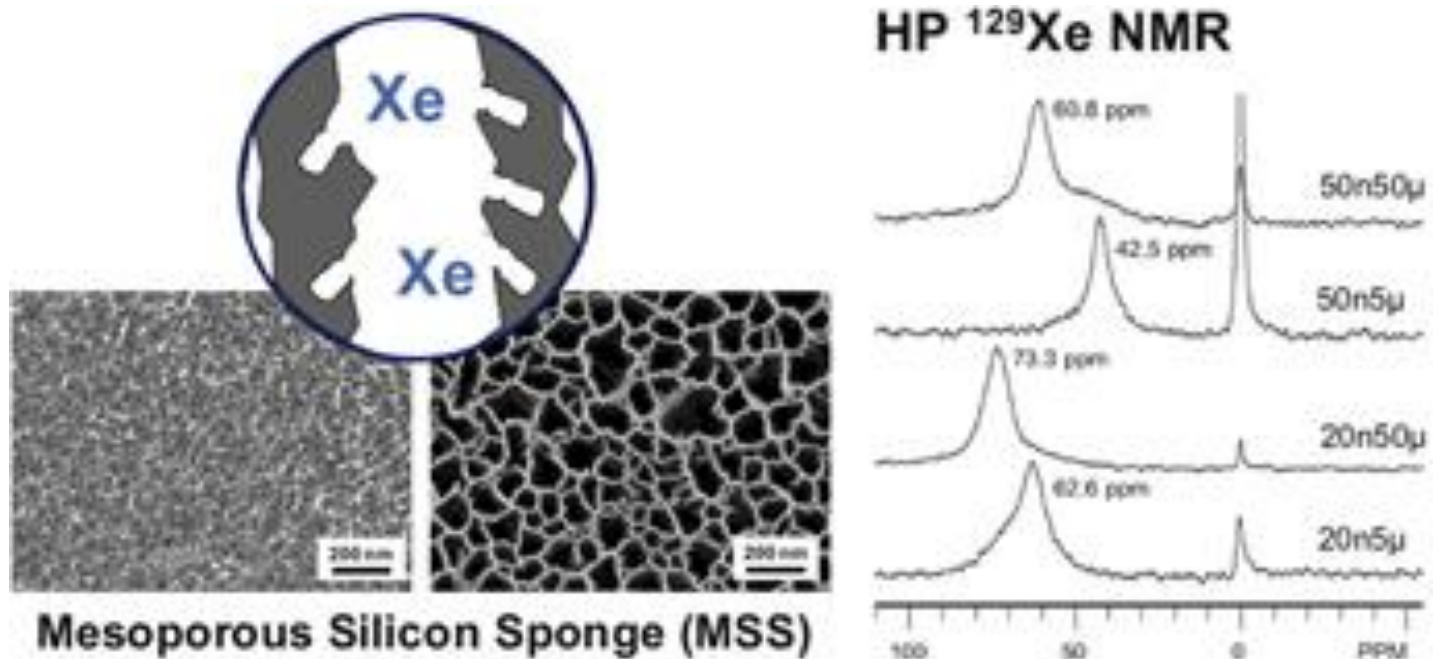




Pórusos rendszerek

Miért ne alkalmazzuk az NMR-t

^{129}Xe -NMR



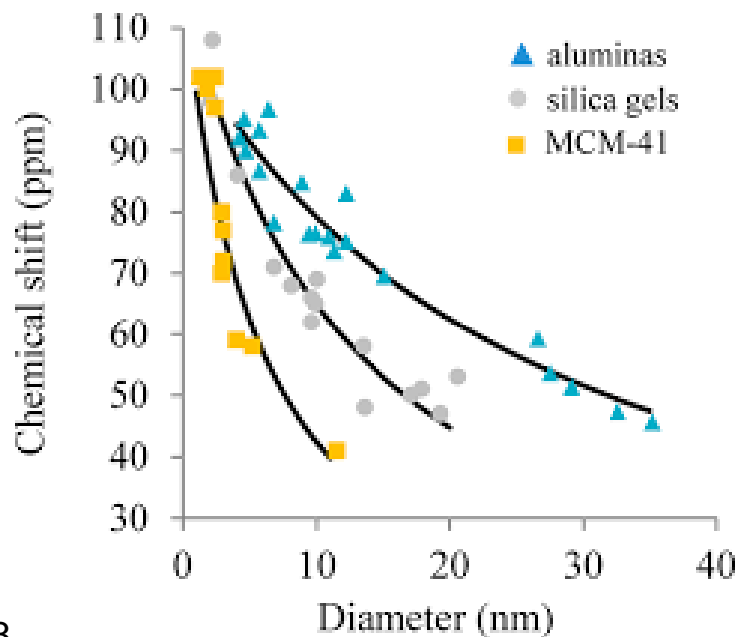
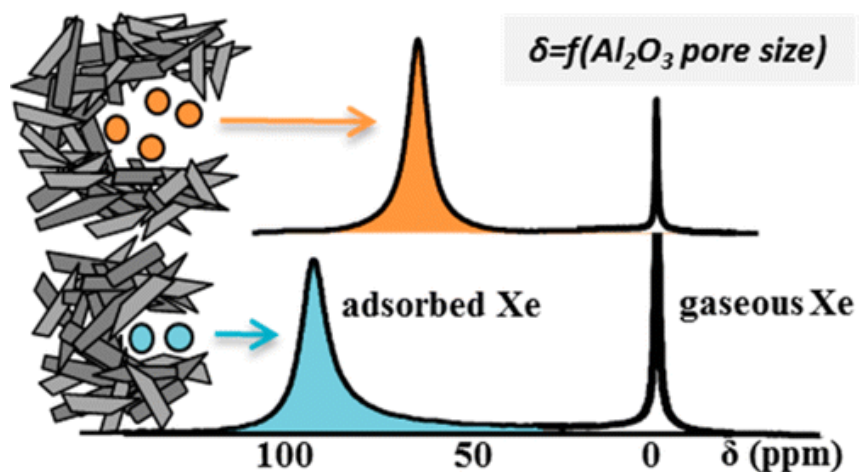
The HP ^{129}Xe NMR spectra taken at 300 K for 20n50 μ , 20n5 μ , 50n50 μ , and 50n5 μ silicas

A keskeny jel a szabad Xe, míg a széles az adszorbeált Xe jele.

A kémiai eltolódás csökken, ha nő a **pórusméret**.

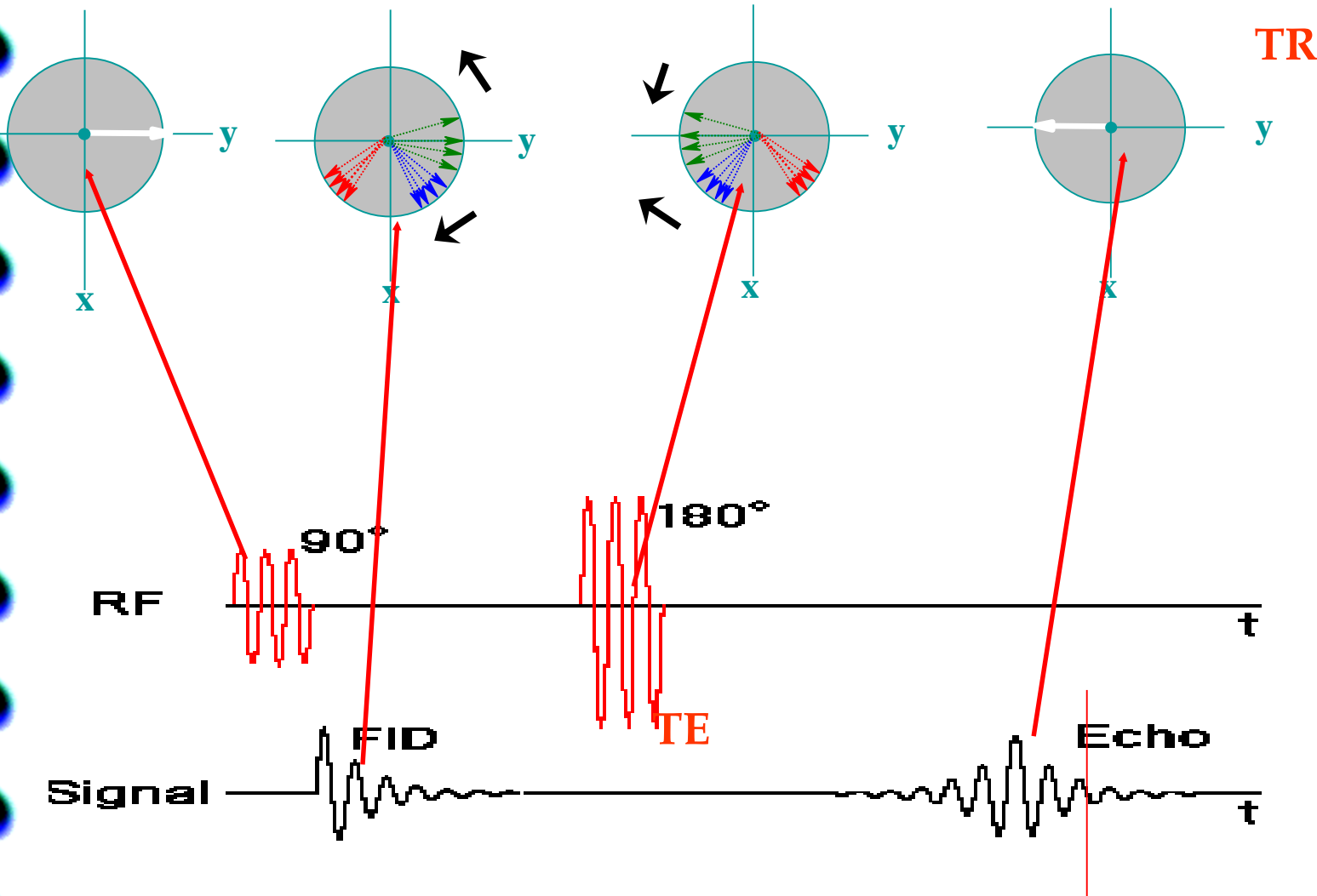
Adott pórusméret esetén a kémiai eltolódás csökken, a növekvő **részecskemérettel**

^{129}Xe -NMR



A spin-ekhó: a relaxáció és inhomogenitás

A kémiai eltolódás!!!



TR



NMR diffuziómetria

A diffúzió (irreverzibilis)

- Anyagfluxus *koncentráció-különbség* hatására:

$$J = -D \frac{dc}{dz}$$

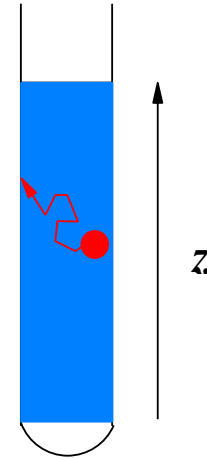
- Az *ok* a kémiai potenciál különbsége:

$$J = \frac{Dc}{RT} F \quad F = -\frac{RT}{c} \left(\frac{dc}{dz} \right)_{p,T}$$

- Mérési módszerek: *mindenféle konc. mérés, fénytörés stb*

Reverzibilis diffúzió (Brown-mozgás)

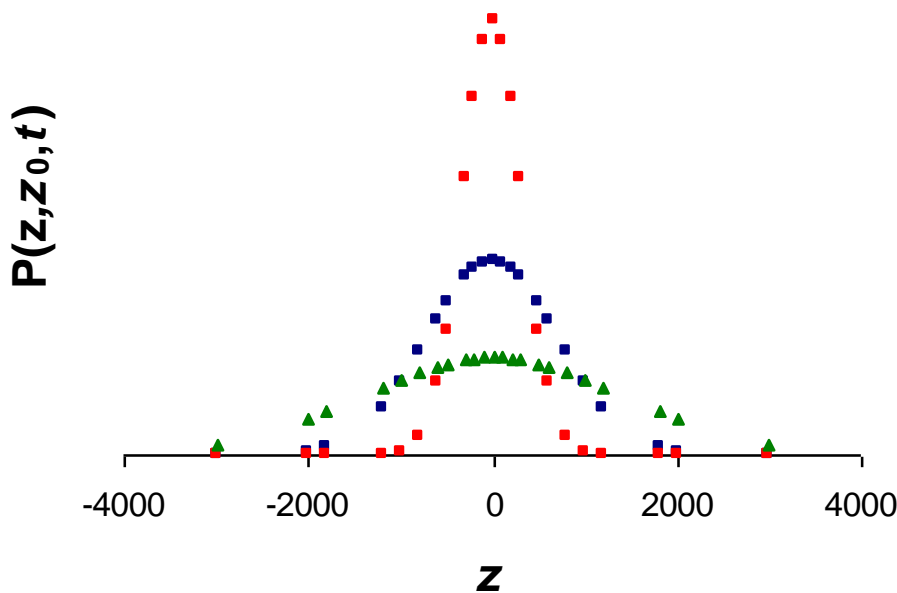
- Saját diffúzió:
 - nincs koncentráció-gradiens
 - Saját „méretének” megfelelő távolságot ugrik (λ) τ idő alatt
 - t idő alatt $N = t/\tau$
 - Csak z koordináta mentén mozog:
„egy dimenziós bolyongás”



Annak a valószínűsége, hogy t idő múlva z helyen lesz:

$$P(t) = \left(\frac{2\tau}{\pi t} \right)^{1/2} e^{-\frac{z^2\tau}{2t\lambda^2}} \quad D = \frac{\lambda^2}{2\tau}$$

Véletlen bolyongás



Einstein-Smoluchowski:

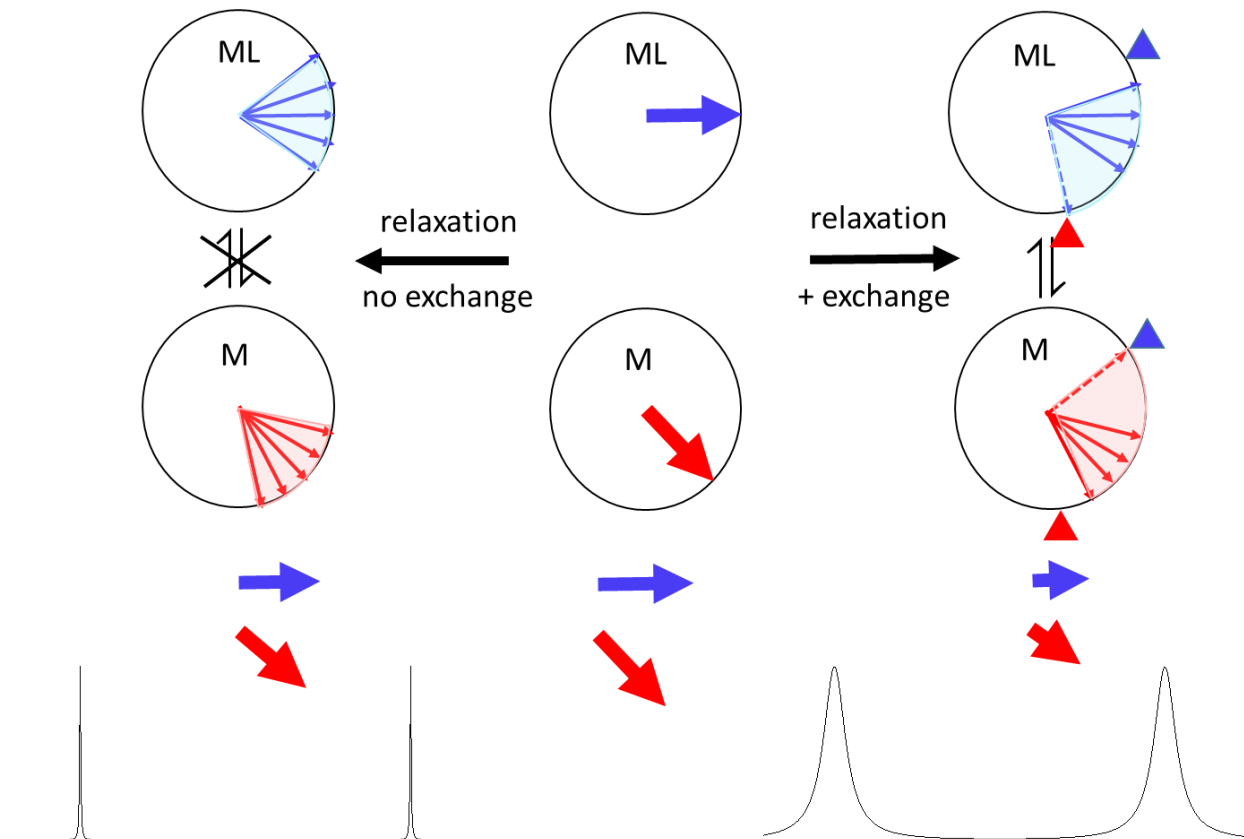
$$D = \frac{k_B T}{f}$$

Einstein-Stokes:

$$D = \frac{k_B T}{6\pi\eta r_h}$$

Mérése: *radioaktív nyomjelzés amely nehéz, sok minta kell, hosszú és nem igaz. Megoldás NMR*

A spin ekhó



$$LW = 1/T_2^* / \pi = (1/T_2 + k_{obs}) / \pi$$

Valódi relaxáció, amely véletlenszerű

diffúzió

A Hahn-ekhó

C.S. Johnson / Progress in Nuclear Magnetic Resonance Spectroscopy 34 (1999) 203–256

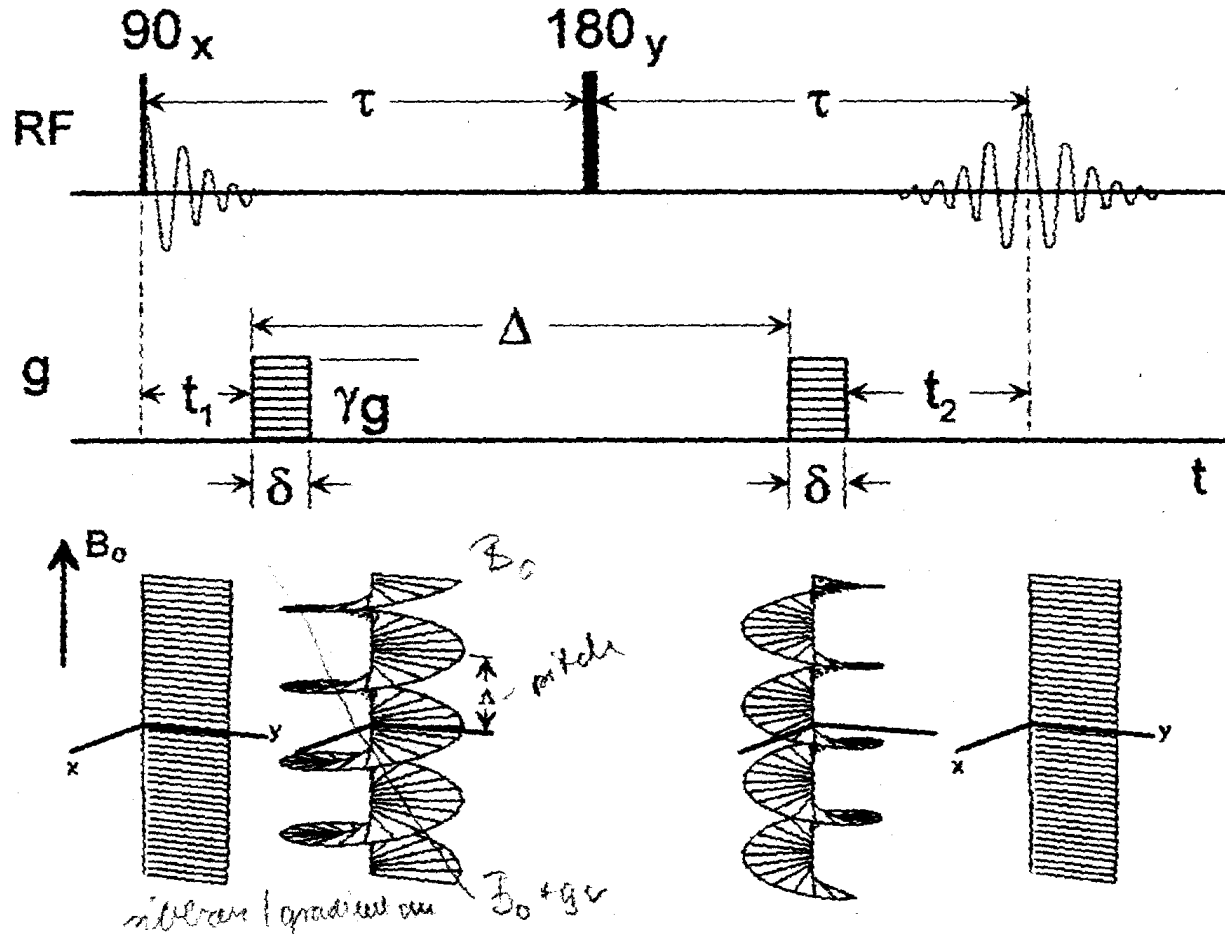
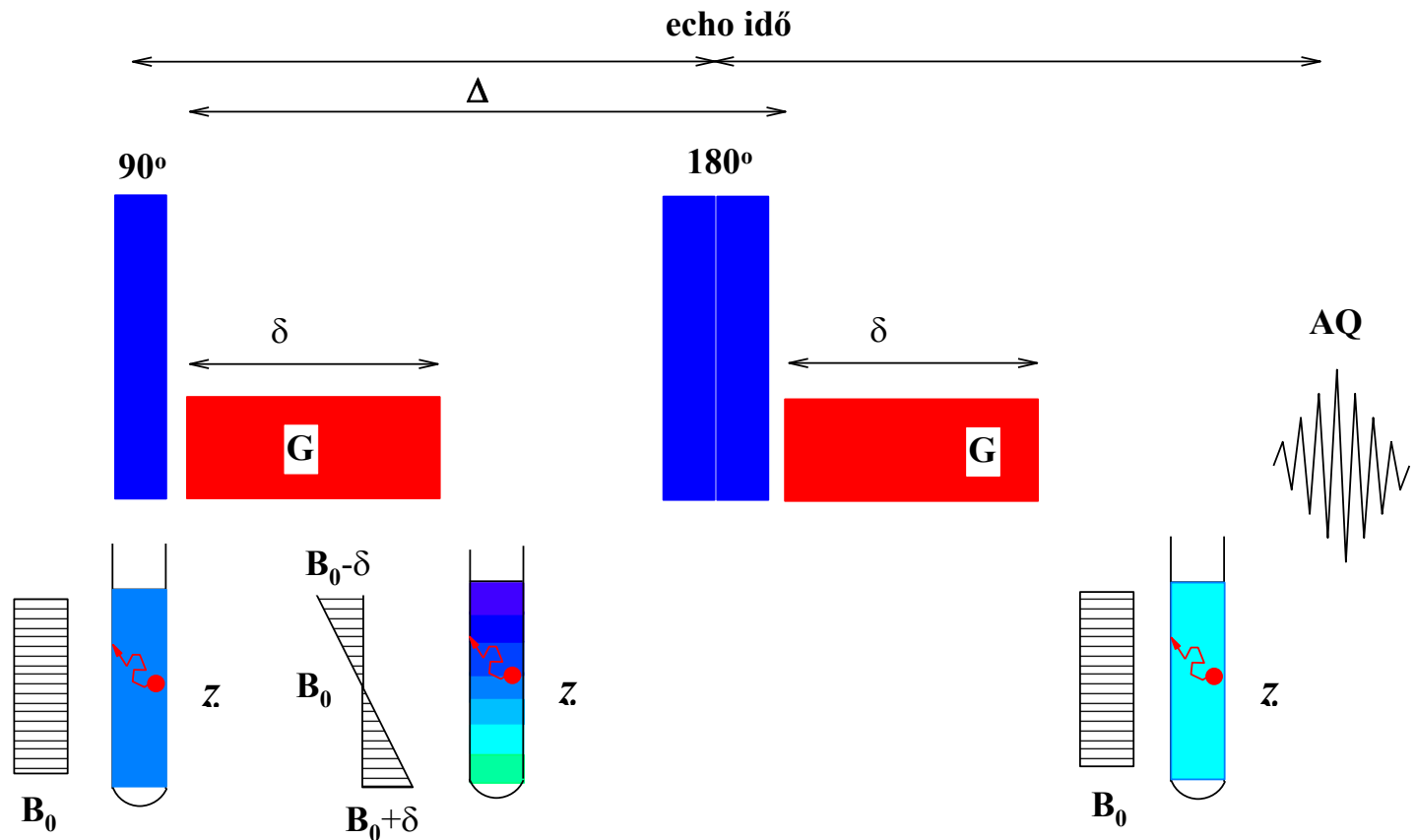


Fig. 1. The simple Carr–Purcell spin echo (SE) often called the Hahn echo.

$$S(2\tau) = M_0 \exp(-2\tau/T_2) \exp[-Dq^2(\Delta - \delta/3)]$$

diffúzió

„Óda a spin echo-hoz” (1950)



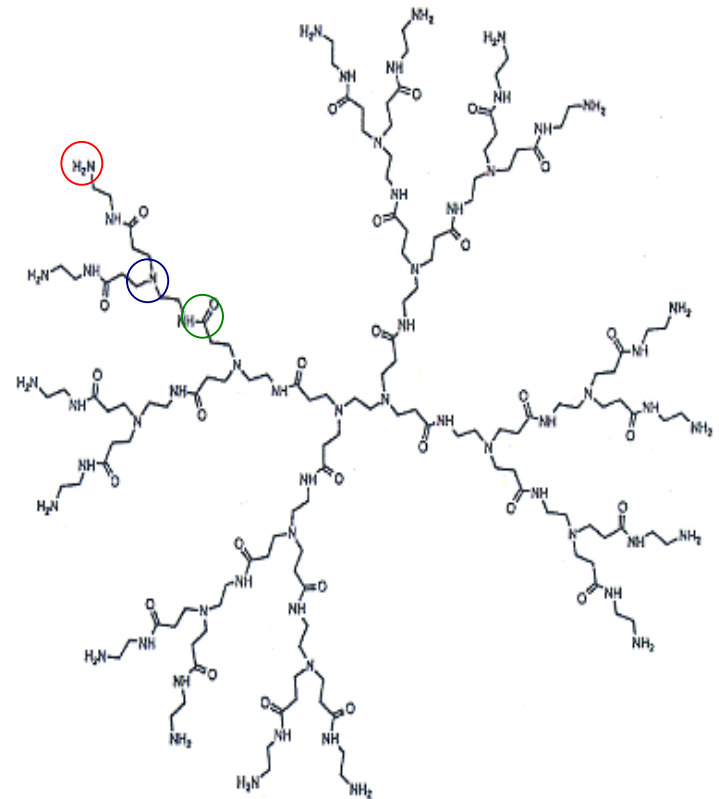
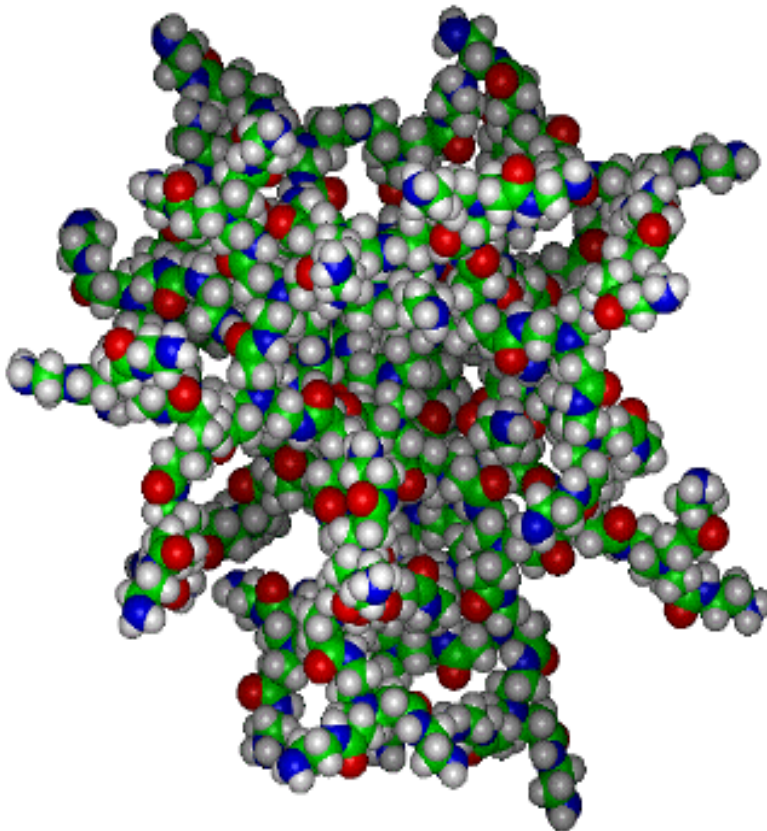
$$I = I_0 e^{-1/T_2^* 2\tau} \times e^{-\gamma^2 \delta^2 (\Delta - \delta/3) D g^2}$$

Az NMR előnyei és hátrányai

- Nem kell koncentráció gradiens
- Nincs izotóp effektus
- Rövid kísérleti idő (néha...)
 - Milyen magot mérünk
 - Mekkora a relaxáció sebesség
- Pontos és könnyű kiértékelés (ha egyszerű)
- Drága (DE 3-4 MFt három készülék fenntartása 84 MFt/5 év fejlesztés, 3-500 MFt egy új készülék)
- A gradiens mérőfej esetleges hiánya (6 MFt)
- Sok emberi gátlás és félreértés (0 Ft)

PAMAM_Gx.NH₂ (a prototípus)

- Gyakorlatilag gömb alakú polielektrolitok



Diffúzió porózus rendszerekben: gátol

Diffusion NMR Spectroscopy

Szabad diffúzió

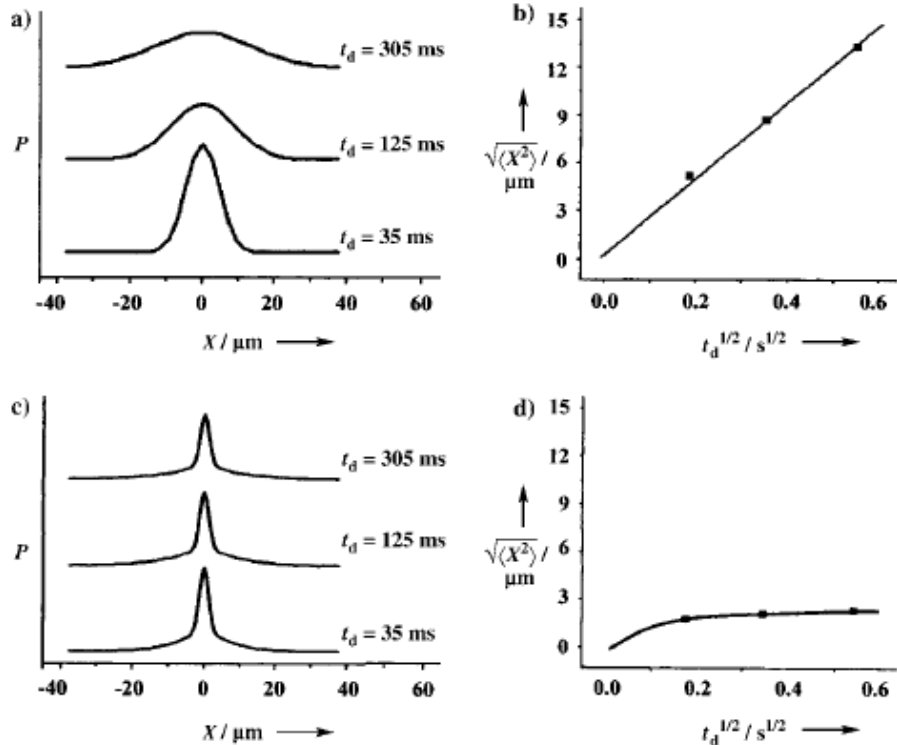
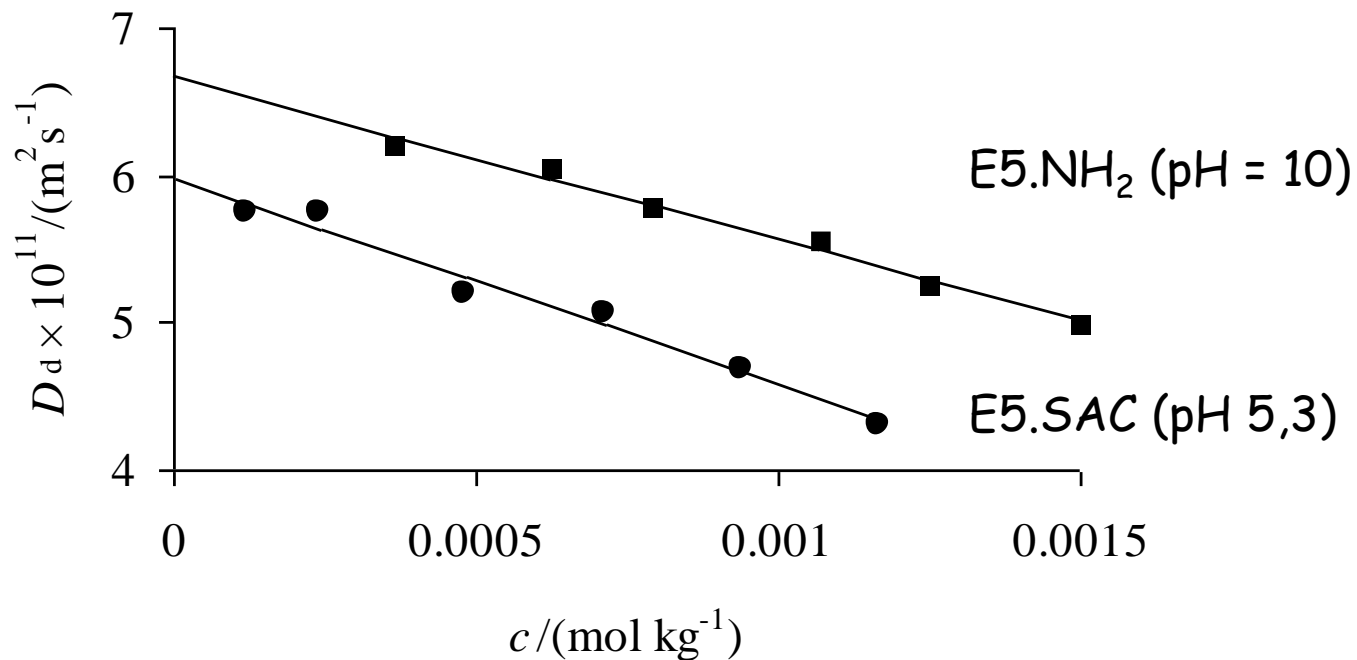


Figure 1. a), b) Free diffusion in a solution of *tert*-butanol; c), d) restricted diffusion (water in optic nerve). a), c) displacement distribution profiles; b), d) root-mean-square of the displacement X calculated from the full width at half height of the displacement distribution profiles shown in (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 ($2.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).^[264]

Gátolt diffúzió

Dendrimerek diffúziója: méret helyben



Saját pH amely 9,8 és 5,3
(izoelektromos pont)

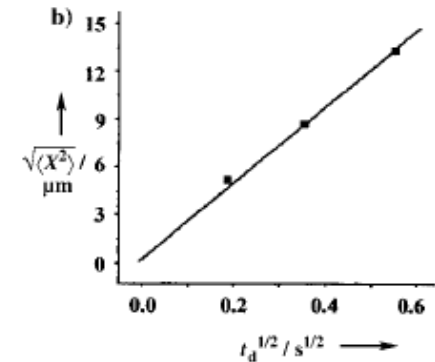
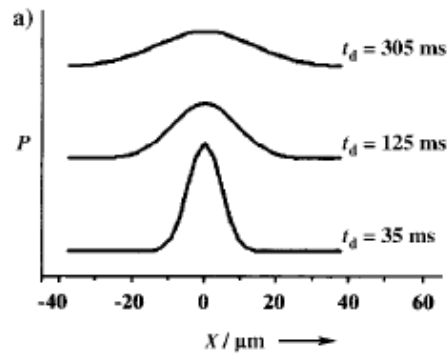
$R_H(\text{E5.NH}_2) = 3.05 \text{ nm}$
(2.15 nm TEM)

$R_H(\text{E5.NH}_2) = 3.37 \text{ nm}$

Diffúzió porózus rendszerekben: gátolt diffúzió

Diffusion NMR Spectroscopy

Szabad diffúzió



Gátolt diffúzió

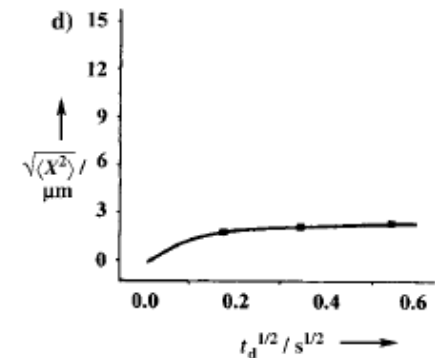
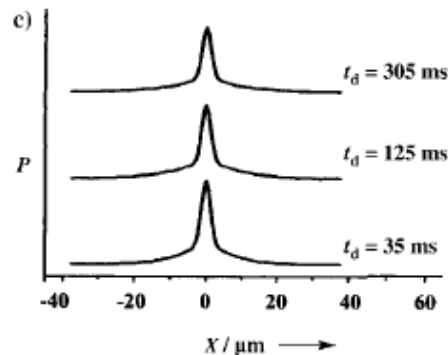
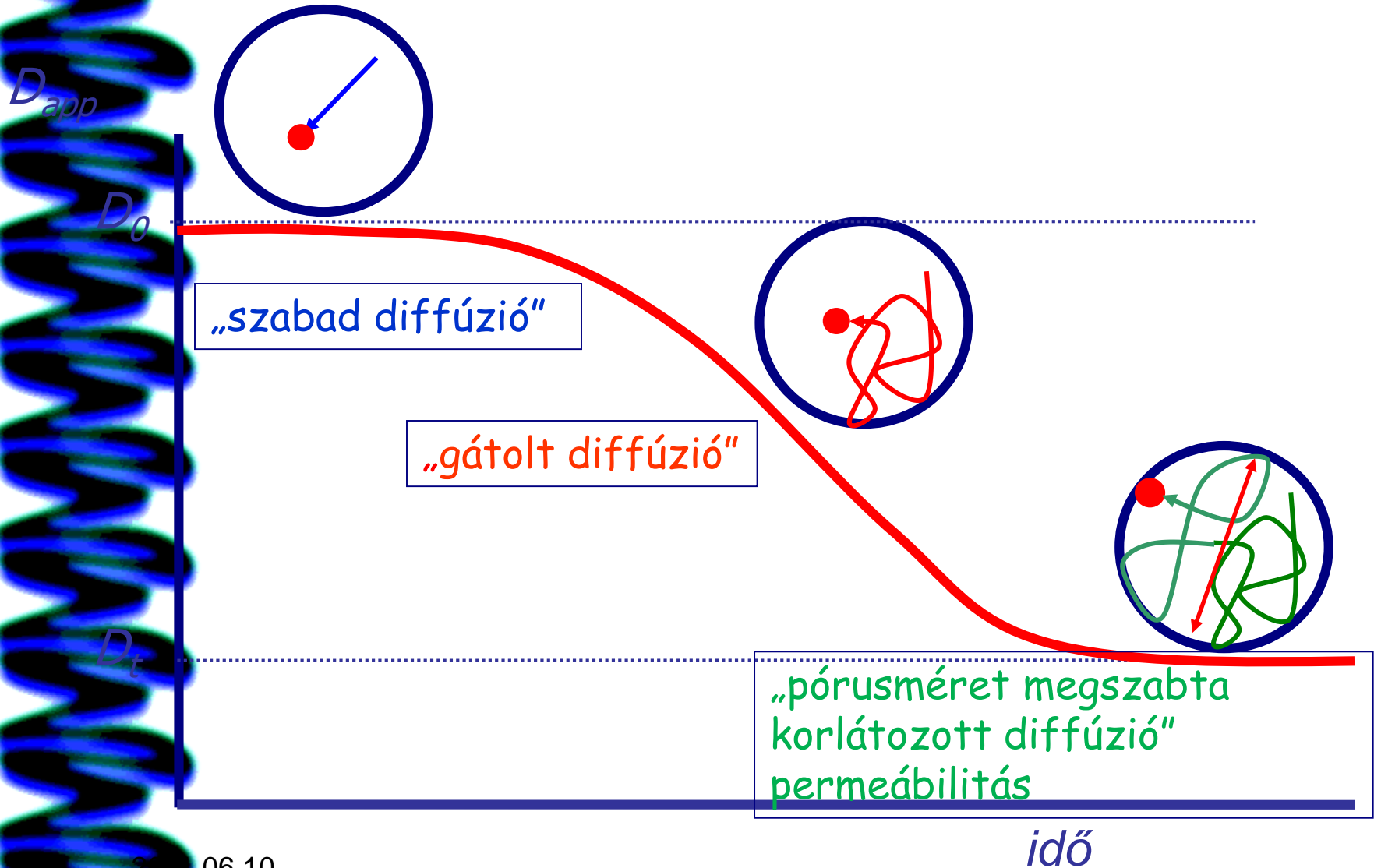
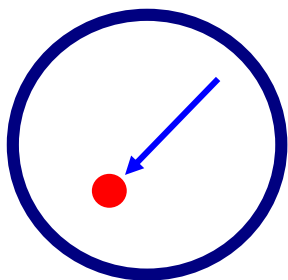


Figure 1. a), b) Free diffusion in a solution of *tert*-butanol; c), d) restricted diffusion (water in optic nerve). a), c) displacement distribution profiles; b), d) root-mean-square of the displacement X calculated from the full width at half height of the displacement distribution profiles shown in (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 ($2.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).^[26c]

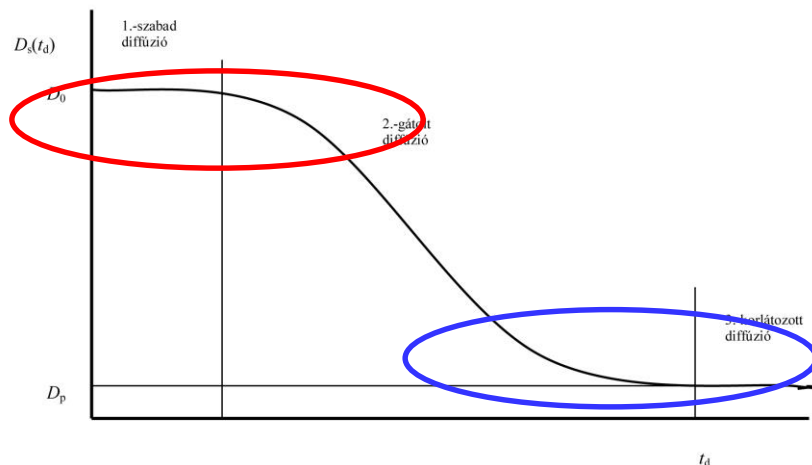
Mért diffúziós együttható függése a diffúzió időtől pórusos rendszerekben



Közelítések

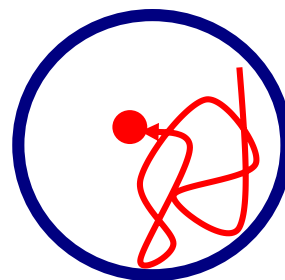


Különböző szakaszban
érvényes egyenletek?



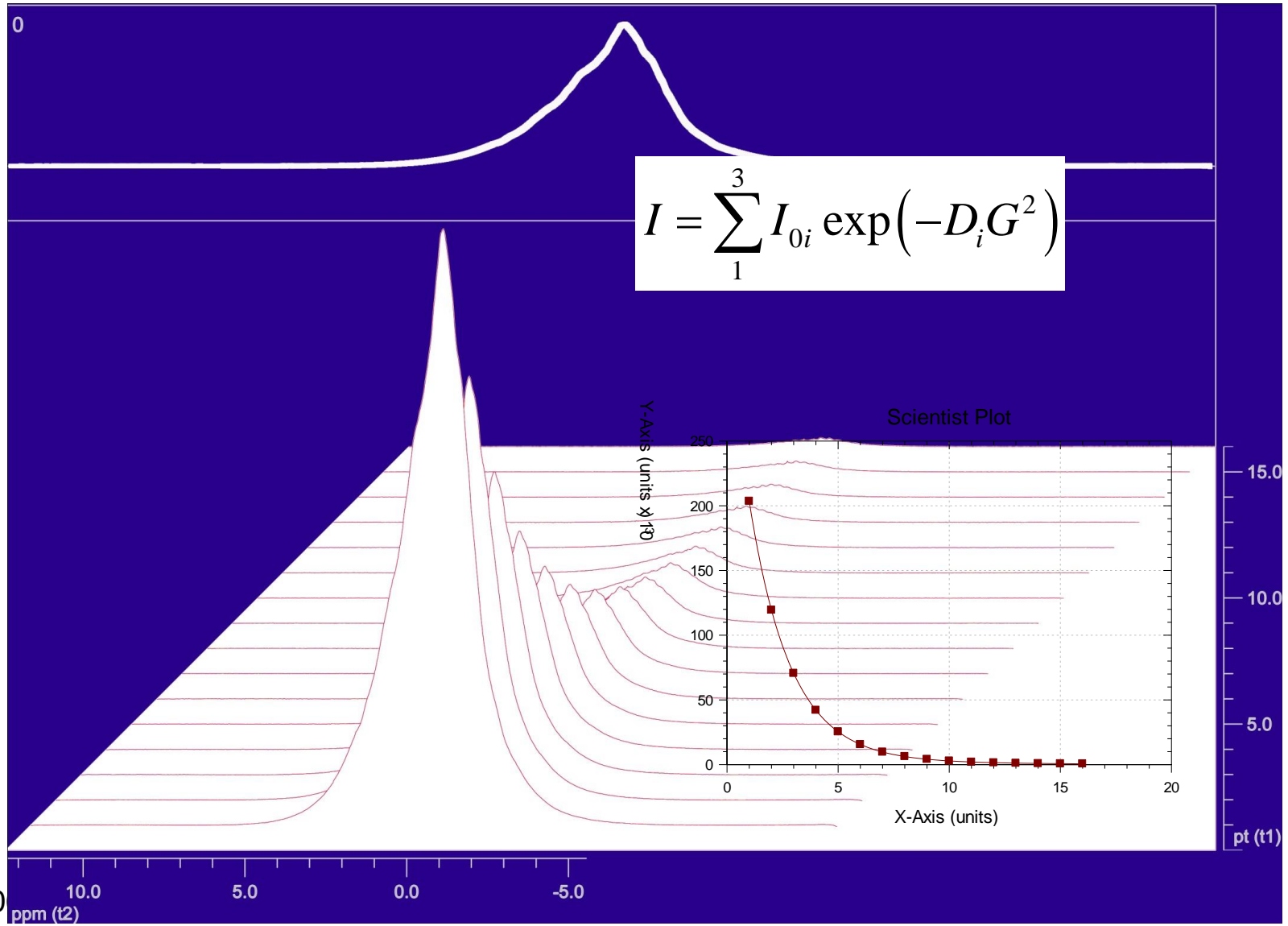
$$D(t) = D_0 \left[1 - \alpha^2 K \frac{4}{3d} \frac{S}{V} \sqrt{\frac{D_0}{\pi}} \sqrt{t} \right]$$

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

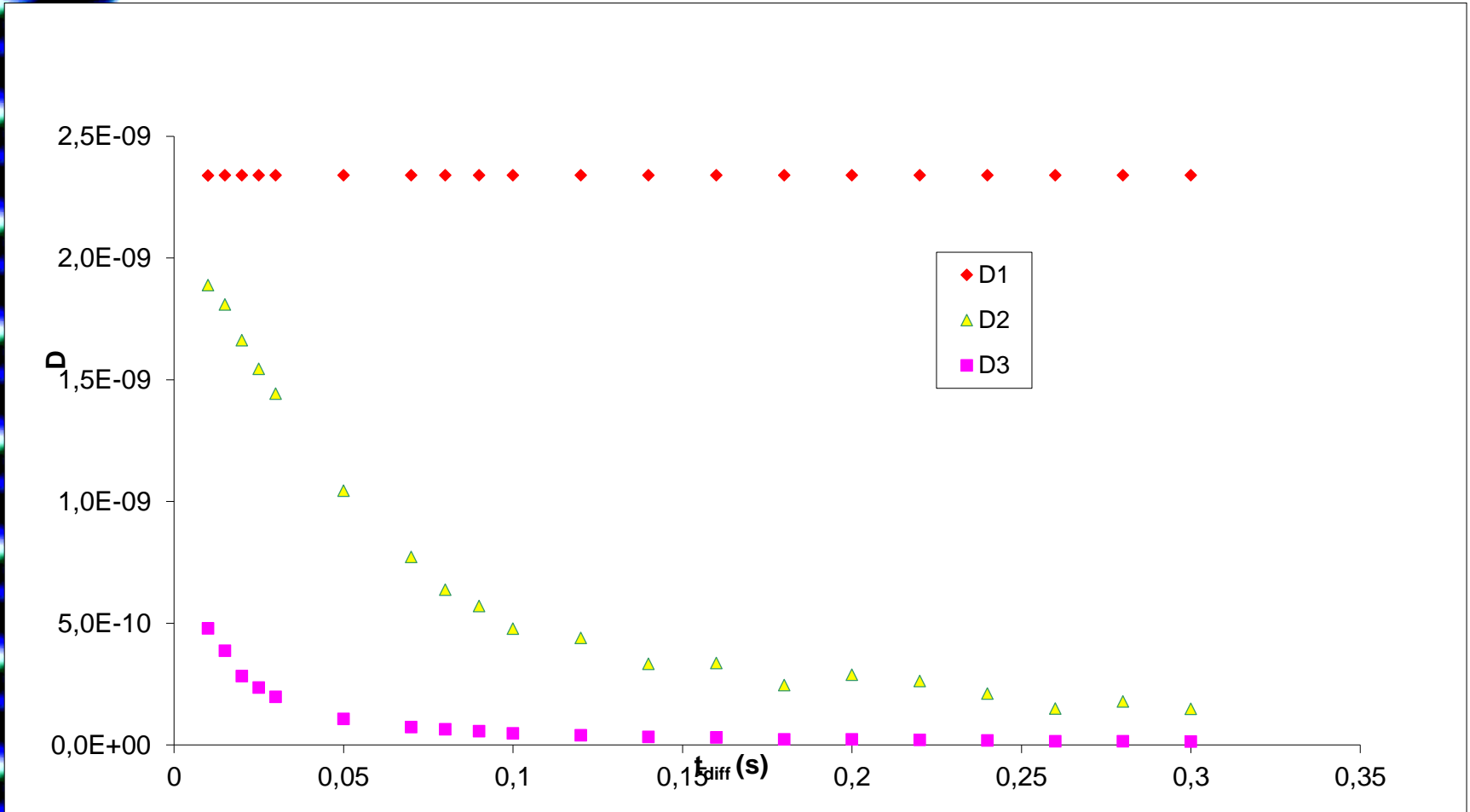


$$D_s = \frac{\langle a^2 \rangle}{6t_D}$$

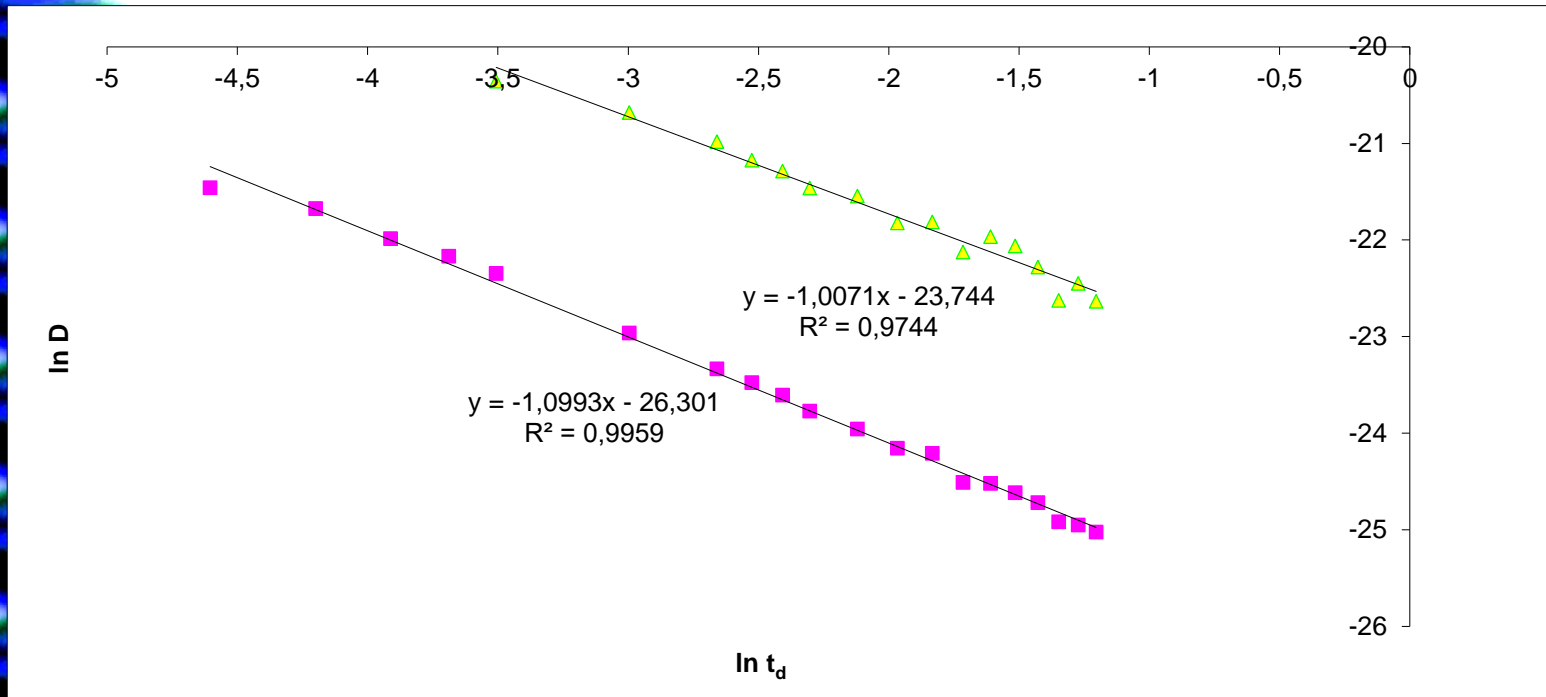
Tipikus mérési eredmények



Gátolt diffúzió nedves fűrészporban



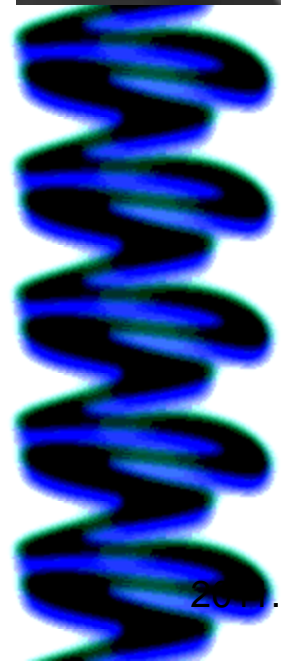
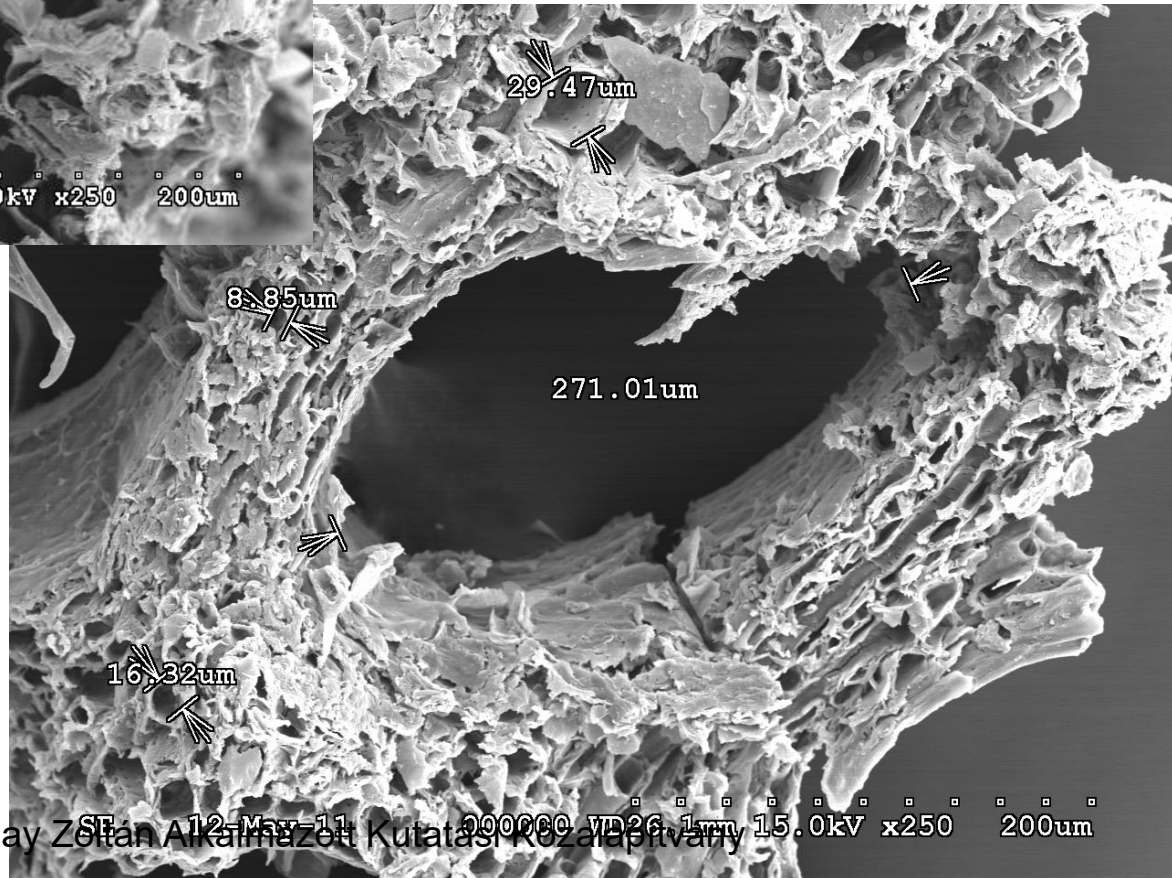
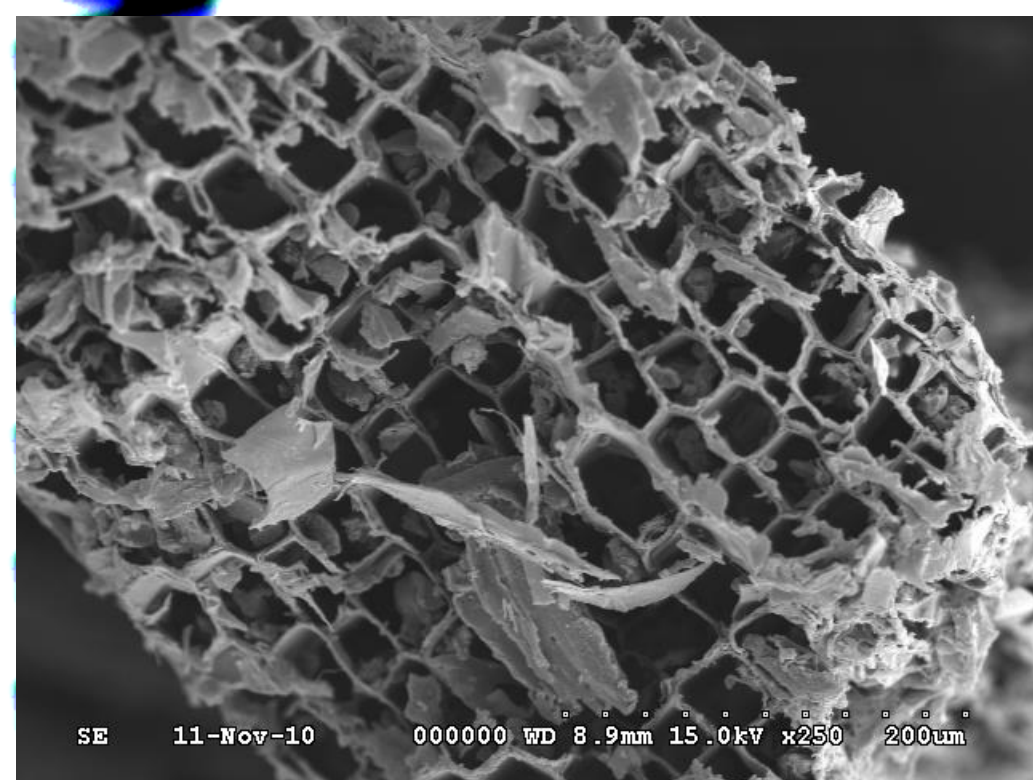
Értékelés



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

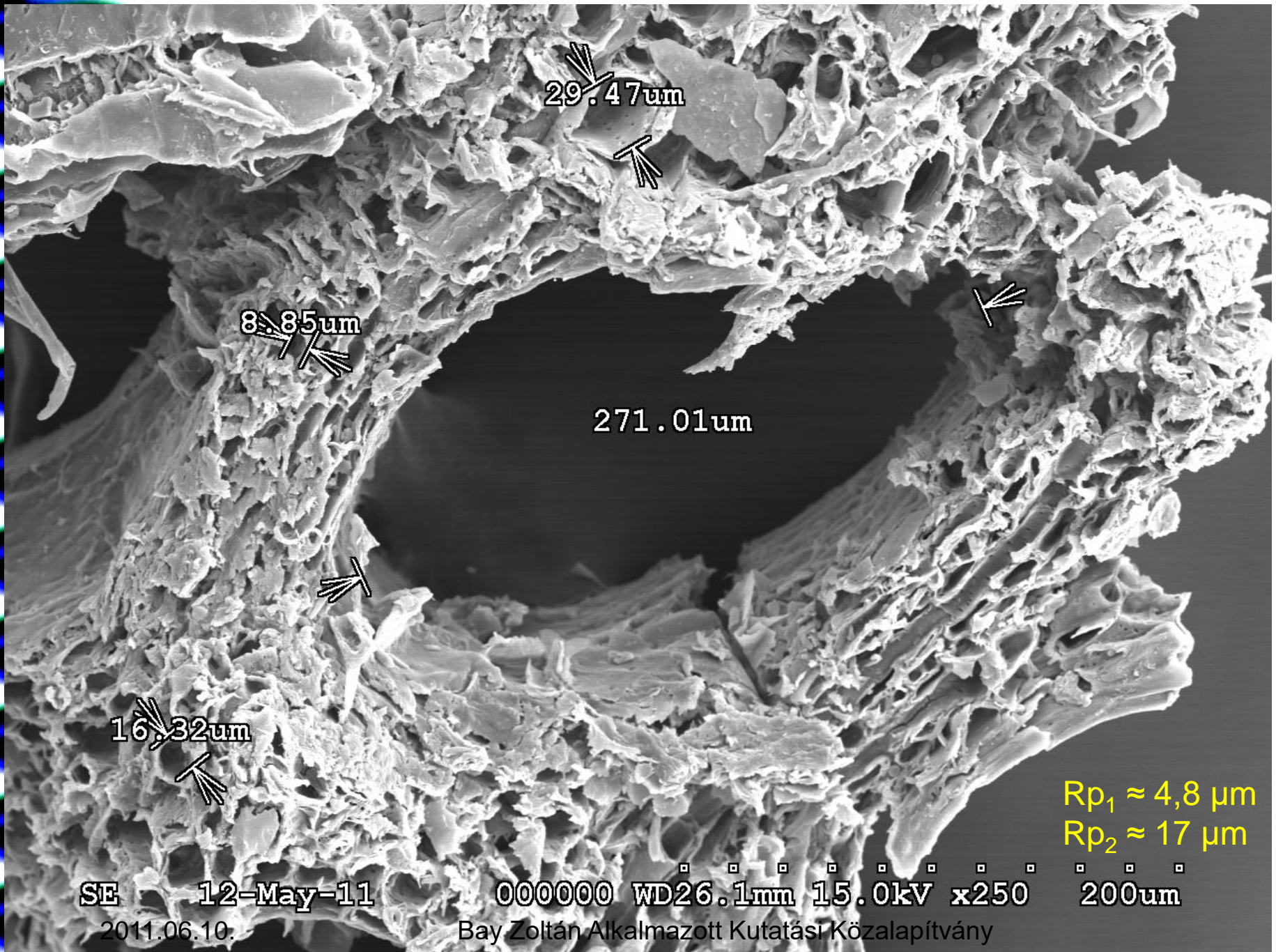
$$D_s = \frac{\langle a^2 \rangle}{6t_D}$$

SEM felvételek



2011.06.10.

Bay Zoltán Alkalmazott Kutatási Közalapítvány



29.47 μm

8.85 μm

271.01 μm

16.32 μm

$Rp_1 \approx 4,8 \mu m$
 $Rp_2 \approx 17 \mu m$

SE 12-May-11

000000 WD26.1mm 15.0kV x250

200um

2011.06.10.

Bay Zoltán Alkalmazott Kutatási Közalapítvány

A módszer korlátai

Brüker 400 MHz max. gradiens: 50 Gauss/cm

	δ	Δ
Min.	1 ms	6 ms
Max.	16 ms	T_1 relaxációtól függ

D	Rp	
$7,7 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$	650 μm	Max .
$2,3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ (T= 300K)	100 μm	Max .
	$\approx 0.2 \mu\text{m}$	Min.



NMR krioporozimetria (1993)

Krioporozimetria: egy kis termodinamika

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

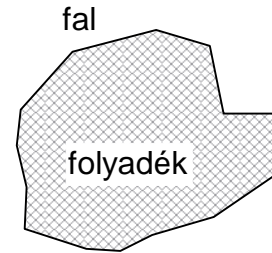
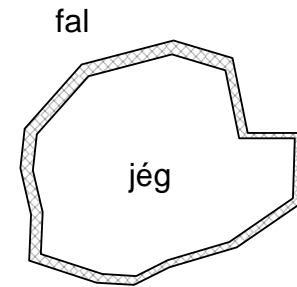
$$F_f = \frac{\mu_l (V - V_s)}{V_{M,l}} + \gamma_{lw} S + \frac{\mu_s V_s}{V_{M,s}} + \gamma_{sl} S_s$$

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

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

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

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



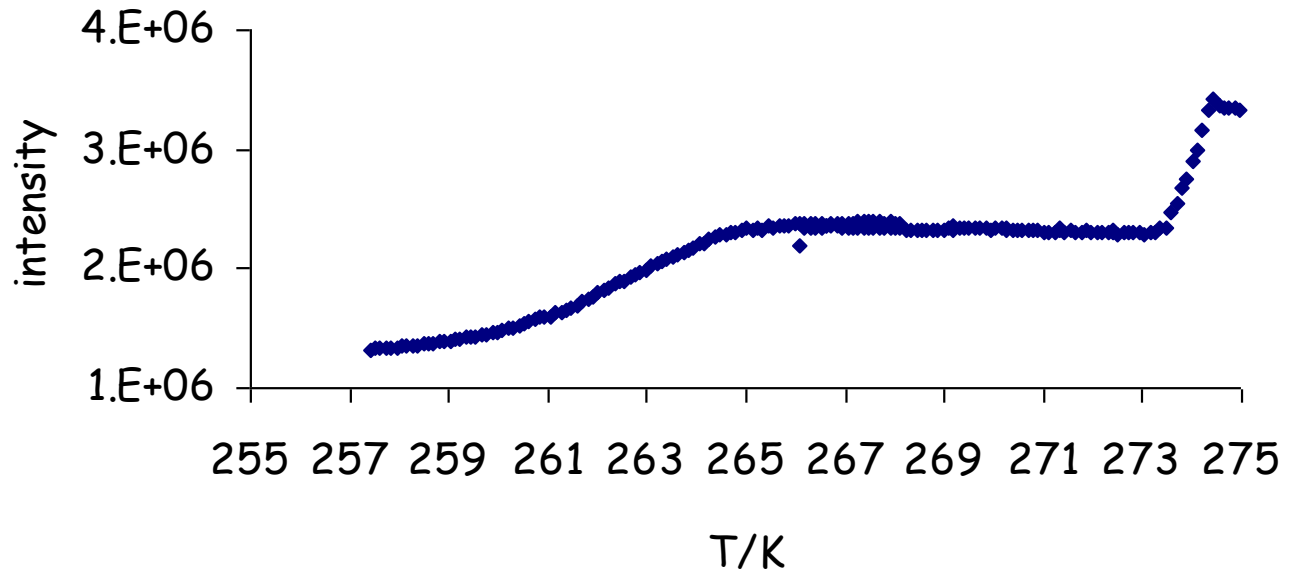
Ehrenfest

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

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

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

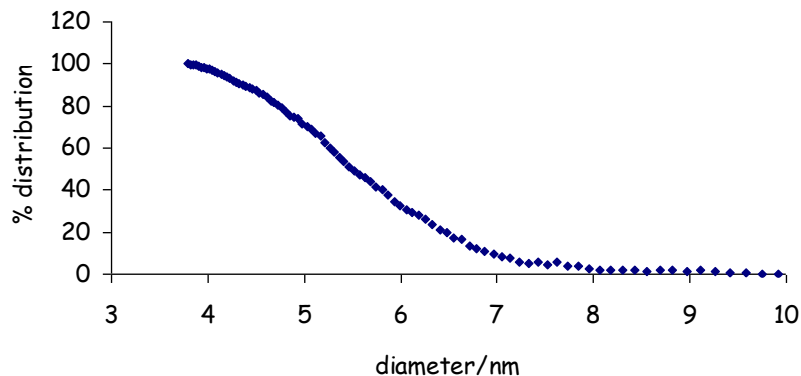
Kieselgel 60



1D spin echo, 8 impulzus, echo idő 1.8-2.6 ms

T várakozási idő: 300 s, lépték 0,1 K
eurotherm szabályzás

Size and size distributions



Commercial silica gel is available in grains or globular granules 5-7 to 10^{-2} mm in size. Various brands of silica gel have a mean effective pore diameter of 20–150 angstroms and a specific surface of 10^2 - 10^3 m²/g.

Warning! The following article is from The Great Soviet Encyclopedia (1979). It might be outdated or ideologically biased.

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 concentration ^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 N₂ adsorption experiments

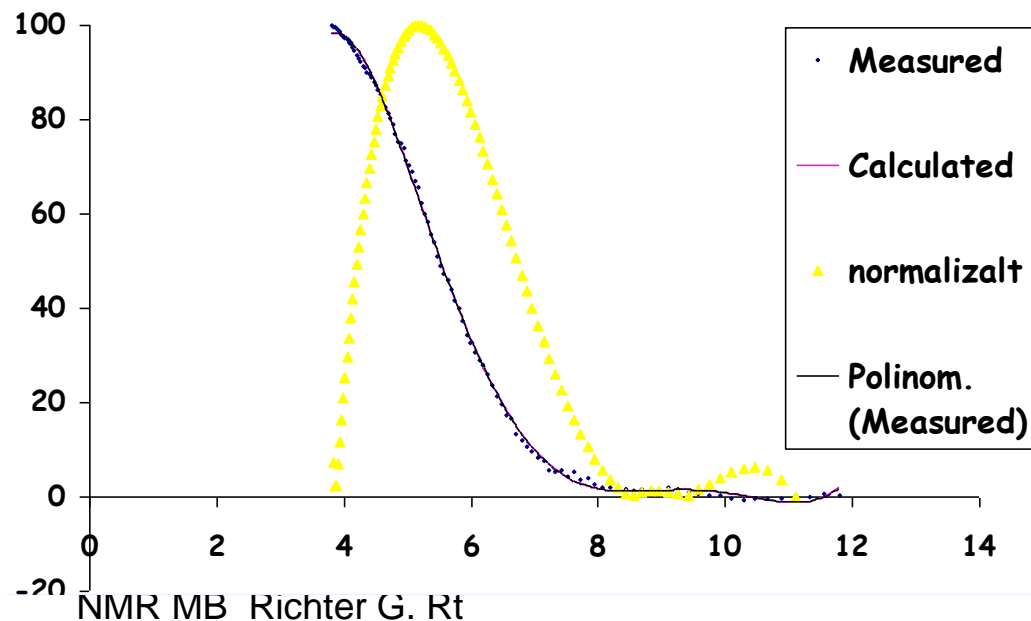
^b By thermogravimetry, with respect to the dry silica mass

^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 HNO₃

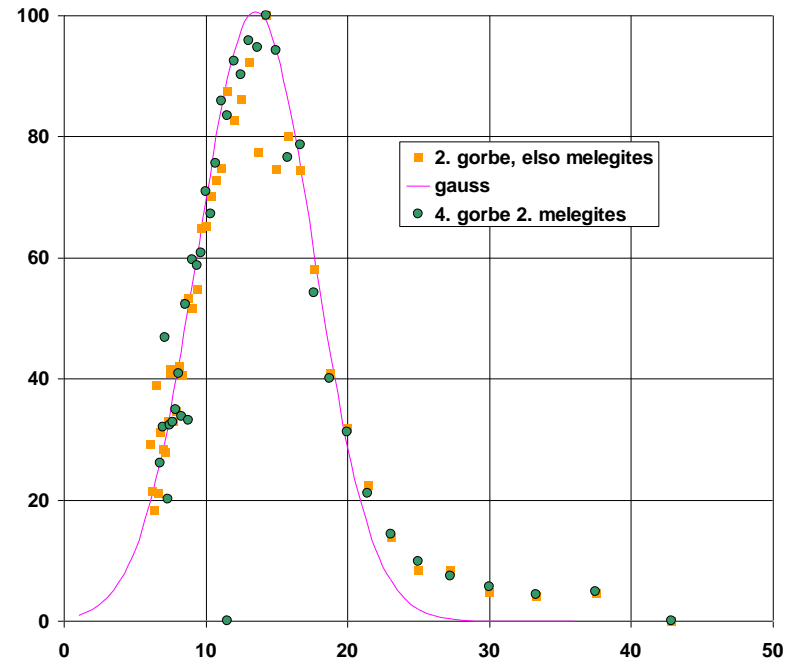
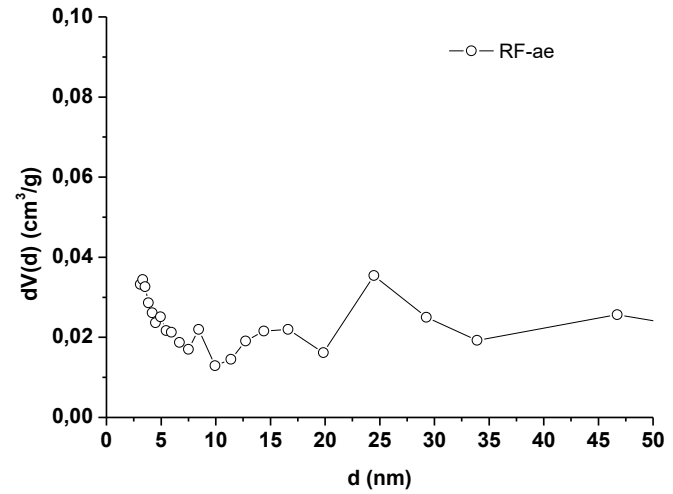
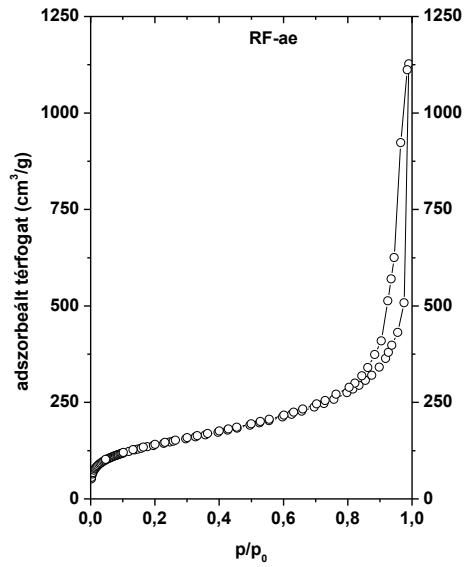
^d This value is underestimated because N₂ is too large to probe the internal microstructure of Stöber beads [43]

^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 ²⁹Si NMR spectroscopy, after integration of the deconvoluted peaks assigned to (SiO)₃SiOH and (SiO)₄Si sites



Rezorcín-formaldehid polimer gél



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”.

$K_c = 30 \text{ nm/K}$ (25 elméletileg, de a felületi feszültség bizonytalan)

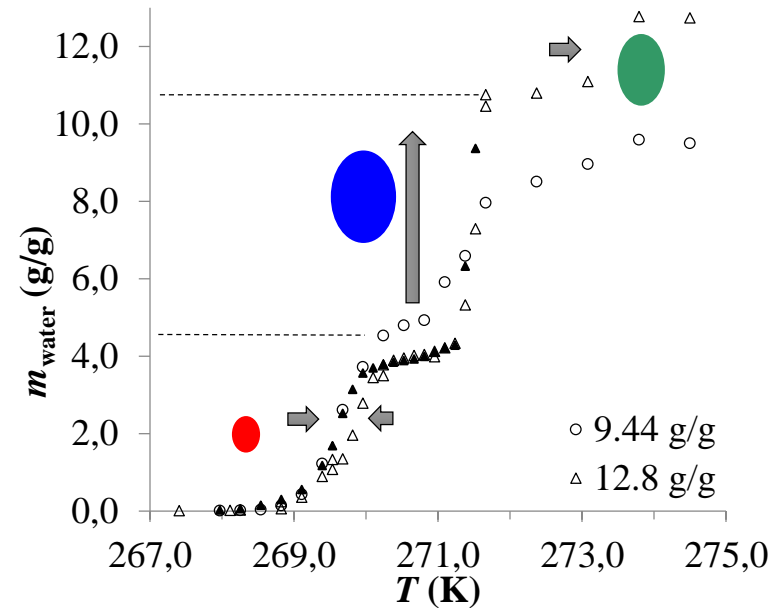
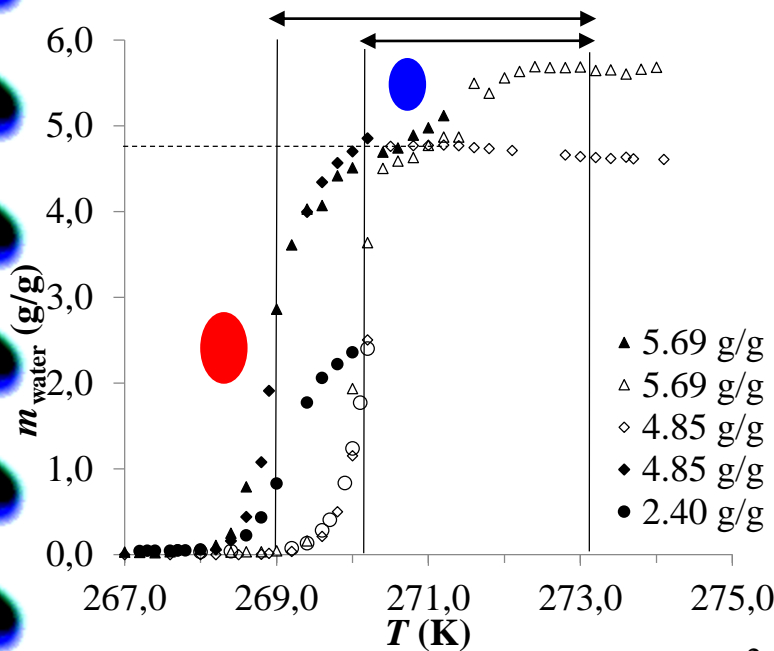
A geometria fontos és a hiszterézist is magába foglalja:

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



NMR relaxometria

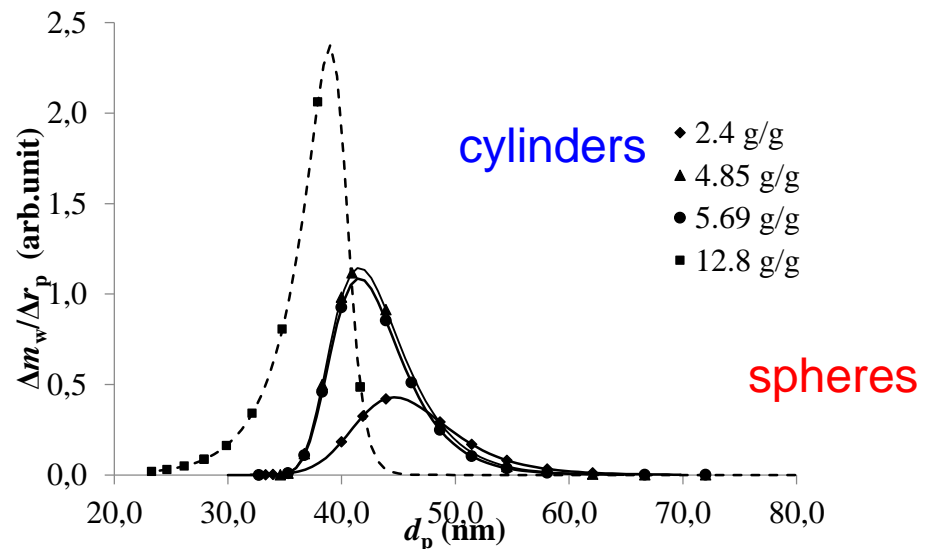
The RF carbon aerogel: cryoporometry titration



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

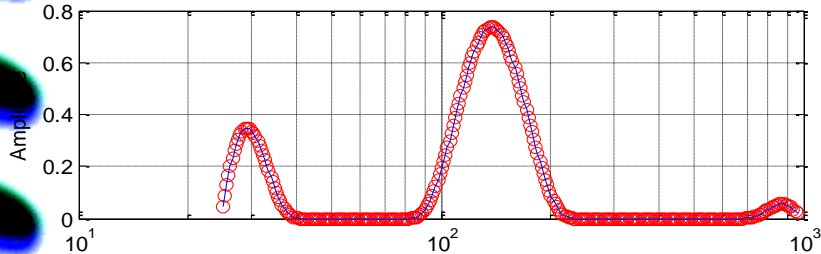
2. Above 5 g/g another pore with no hysteresis

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

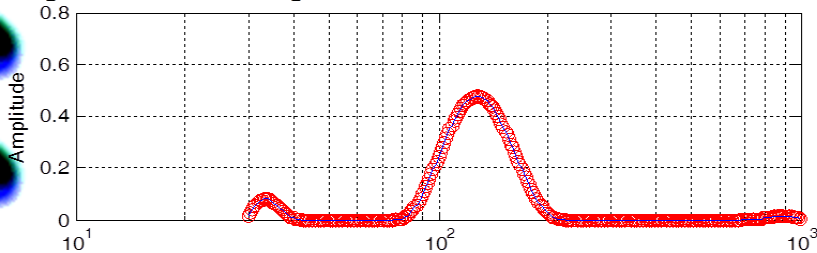


The RF carbon aerogel: low-field NMR relaxometric titration

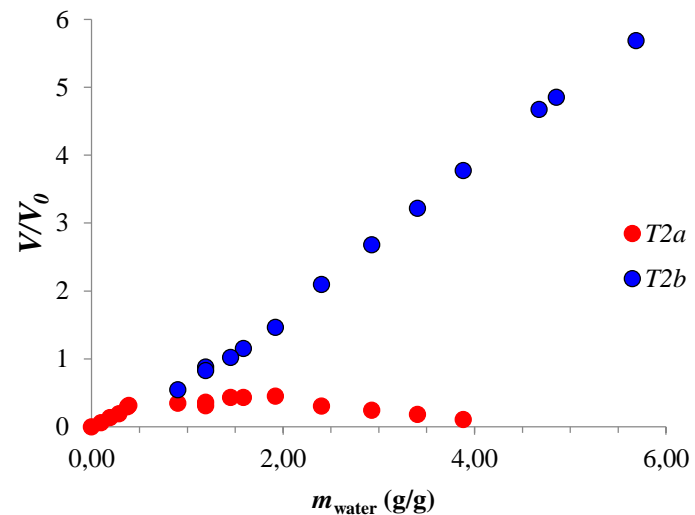
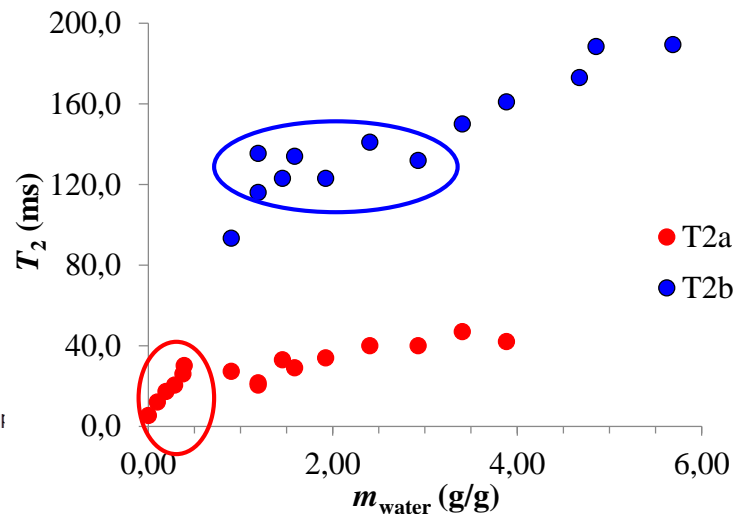
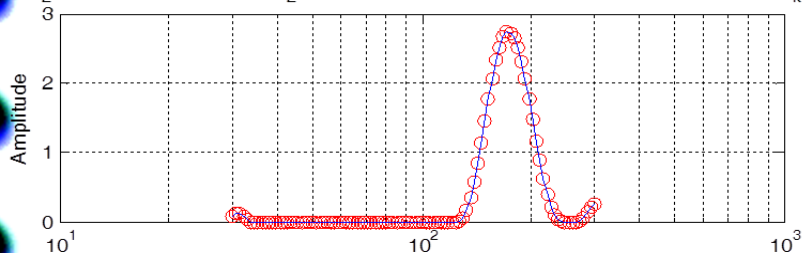
75 :: T₂-domain spectrum = A(T₂) :: / Fitted values: $\gamma^{\text{meas}} \approx \gamma^{\text{calc}}(t) = 0.010251 + \sum_k (A_k \exp(-$



xls :: T₂-domain spectrum = A(T₂) :: / Fitted values: $\gamma^{\text{meas}} \approx \gamma^{\text{calc}}(t) = 0.0023365 + \sum_k (A_k \exp(-$



100% :: T₂-domain spectrum = A(T₂) :: / Fitted values: $\gamma^{\text{meas}} \approx \gamma^{\text{calc}}(t) = 0.21443 + \sum_k (A_k \exp(-$



Quantitative evaluation

Two sites model of one pore completely filled and diffusion controlled

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

Two sites model of one pore partially filled and kinetically controlled

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

ξ surface relaxivity

f filling factor

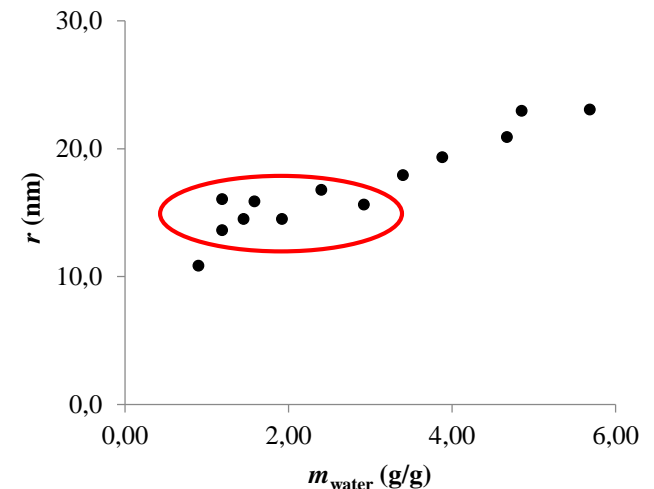
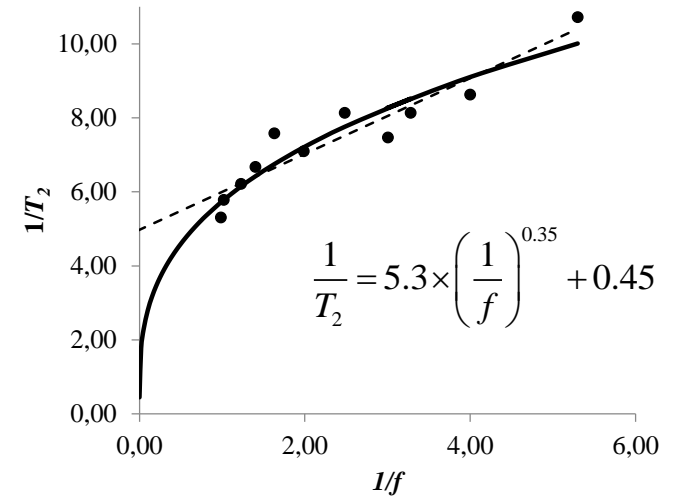
k exchange constant ($k = 1$)

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

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



NMR diffusiometry and conclusions

