Recent Developments in the Measurement of Diffusion in Zeolites

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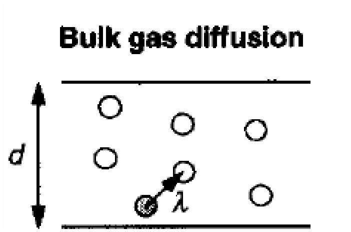
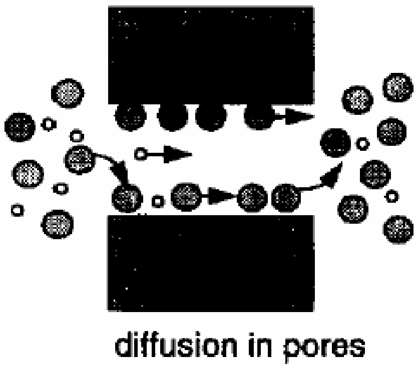
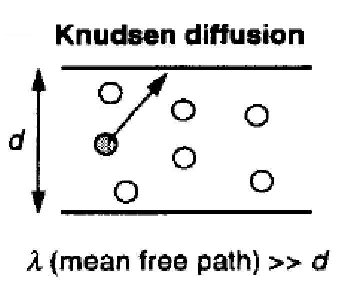
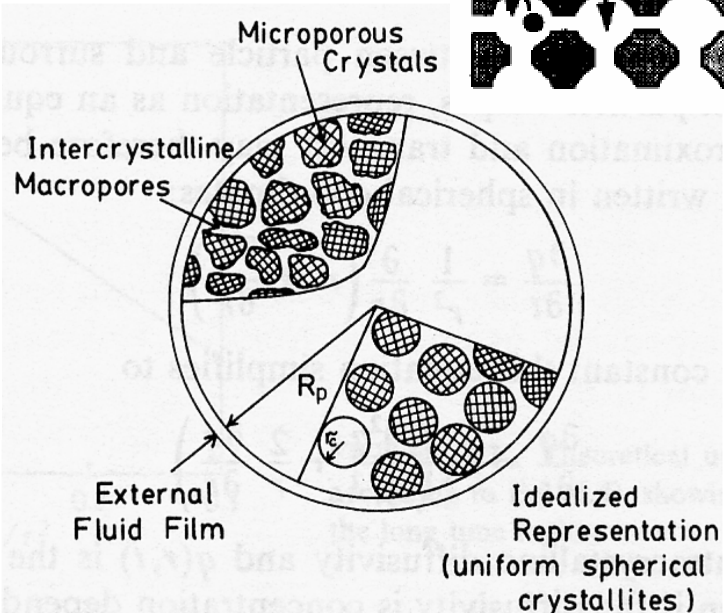
Johannes Lercher, Andreas Jentys (Munich – Germany)
Reiner Staudt, Andreas Möller (Leipzig, INC – Germany)
Douglas Ruthven (Maine – USA)
D.B. Shah (Cleveland – USA)
Wolfgang Schmidt (Mülheim – Germany)

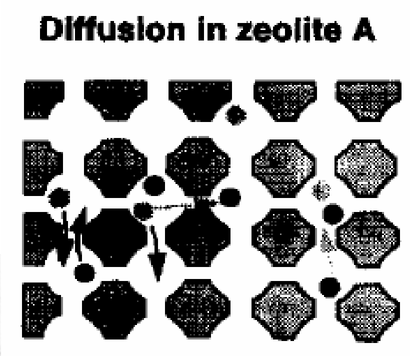
Mass Transport Mechanisms

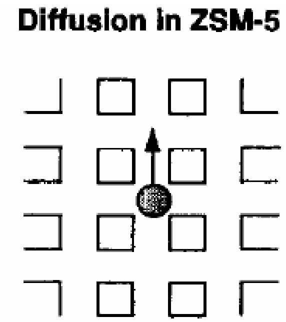


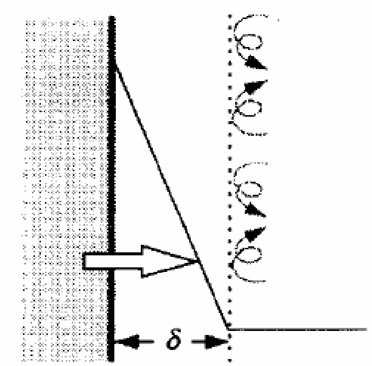








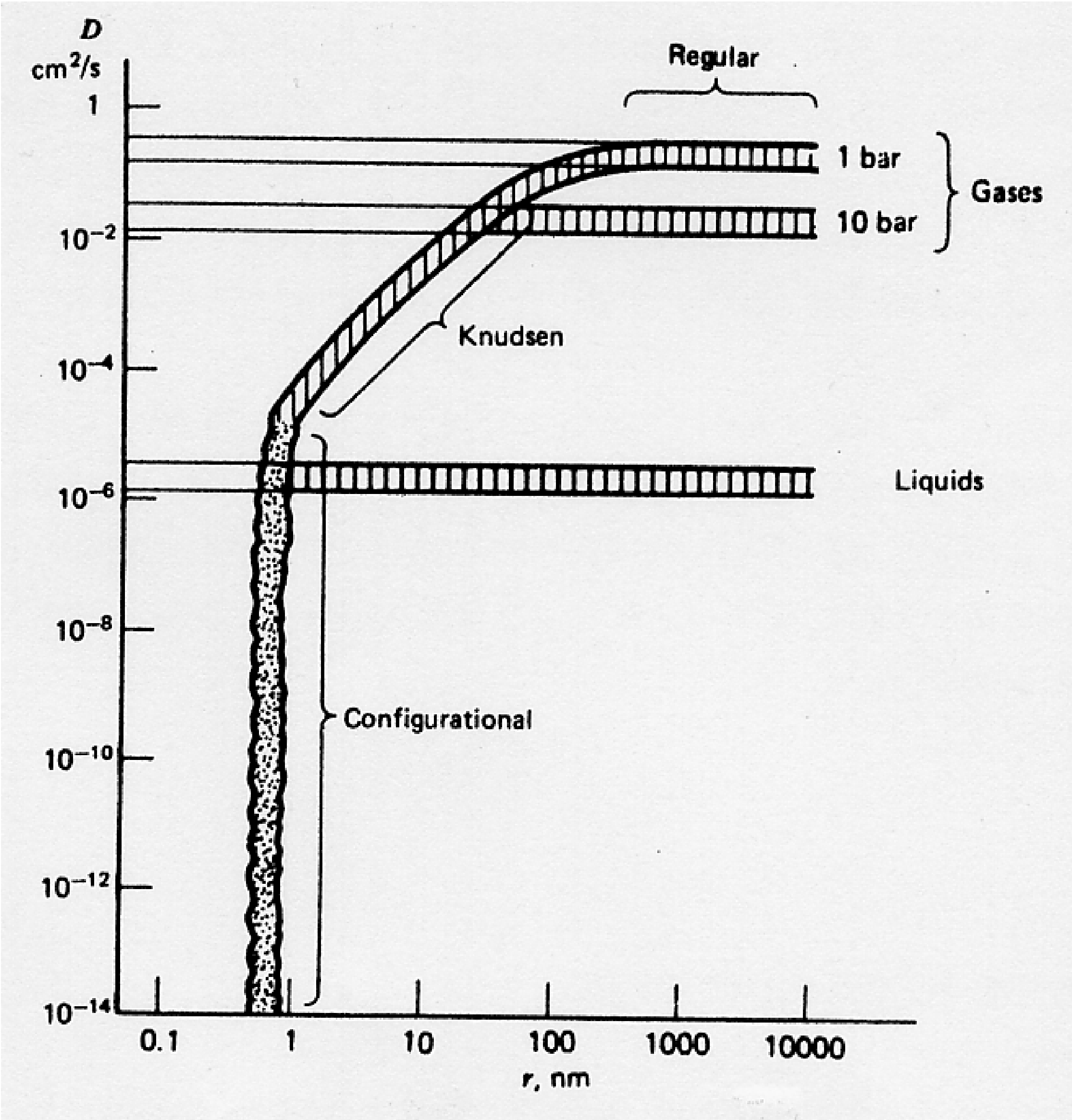




External
fluid film

From Ruthven (1984) and Krishna and Wesselingh (1997)

Range of diffusivities



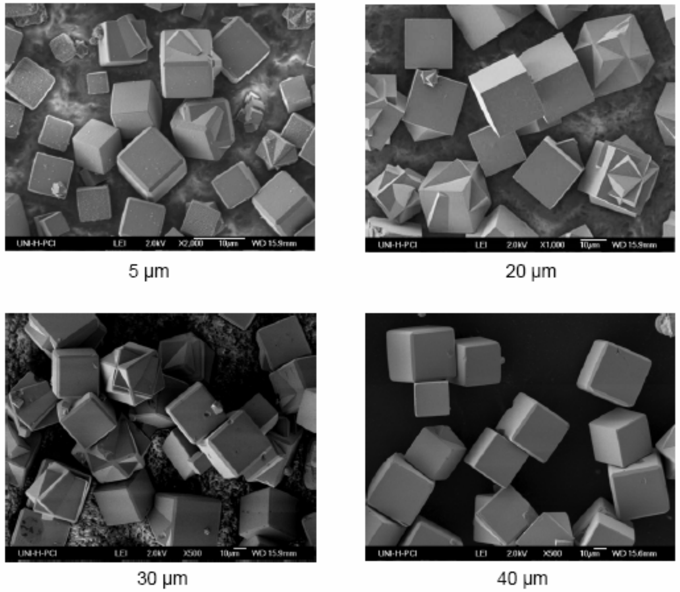
International Research Consortium

Kick-off meeting
DECHEMA – House,
Frankfurt, January 2004

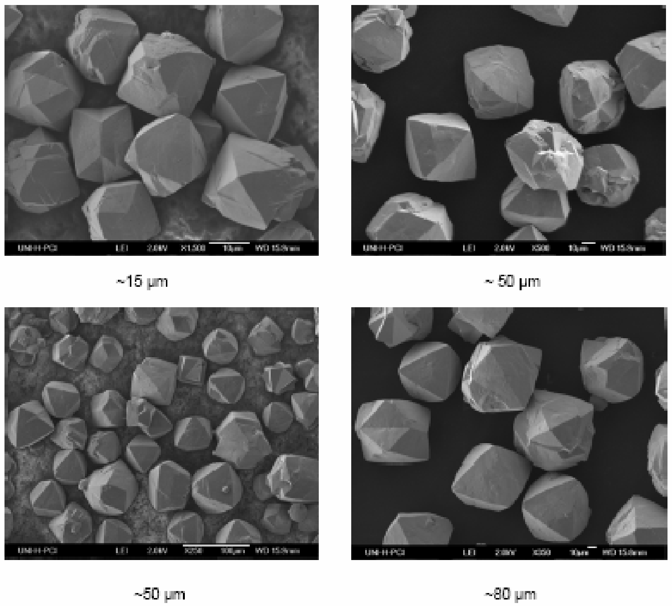
On a hike before the
progress meeting,
Leipzig, September 2004

http://www.diffusion-fundamentals.org

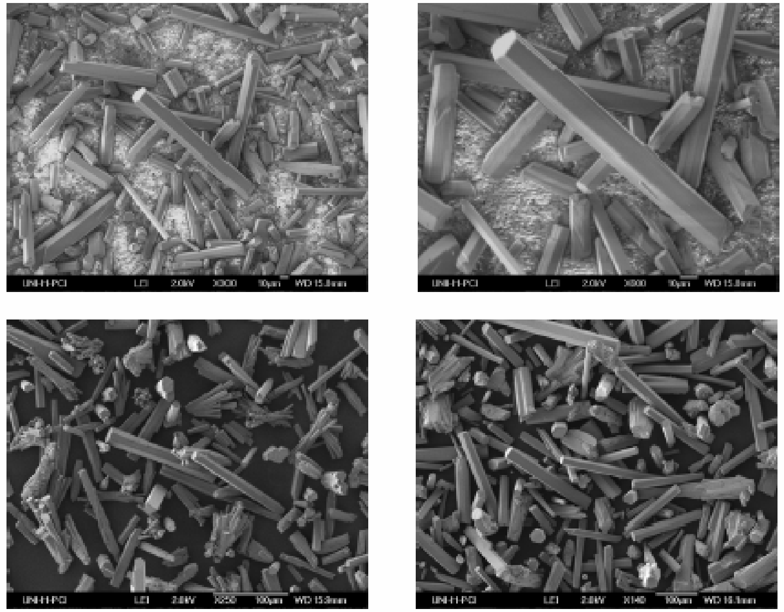
Zeolite synthesis – Jürgen Caro, Wolfgang Schmidt



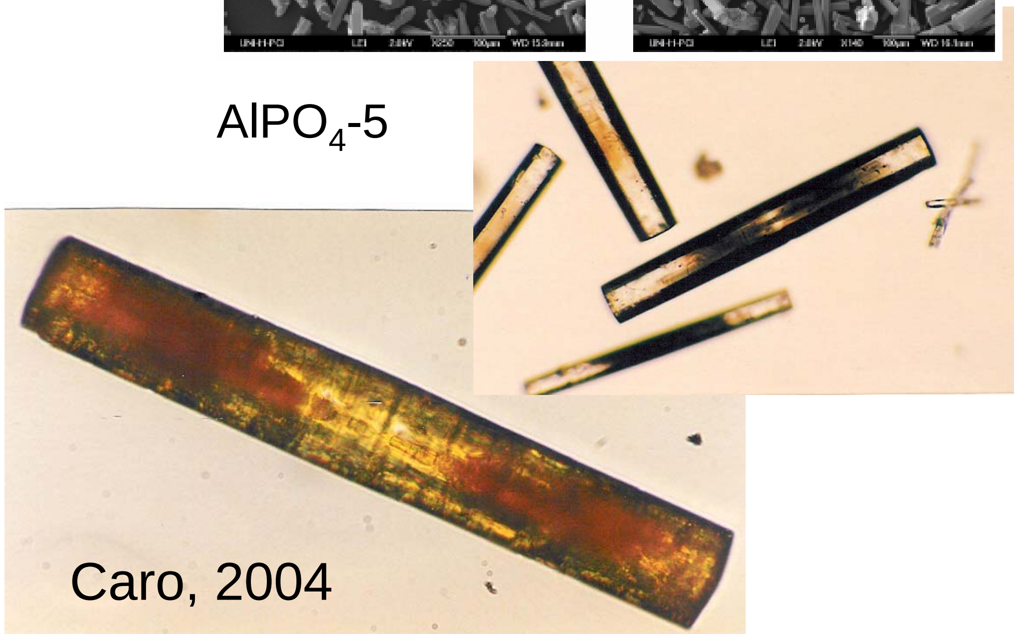
LTA



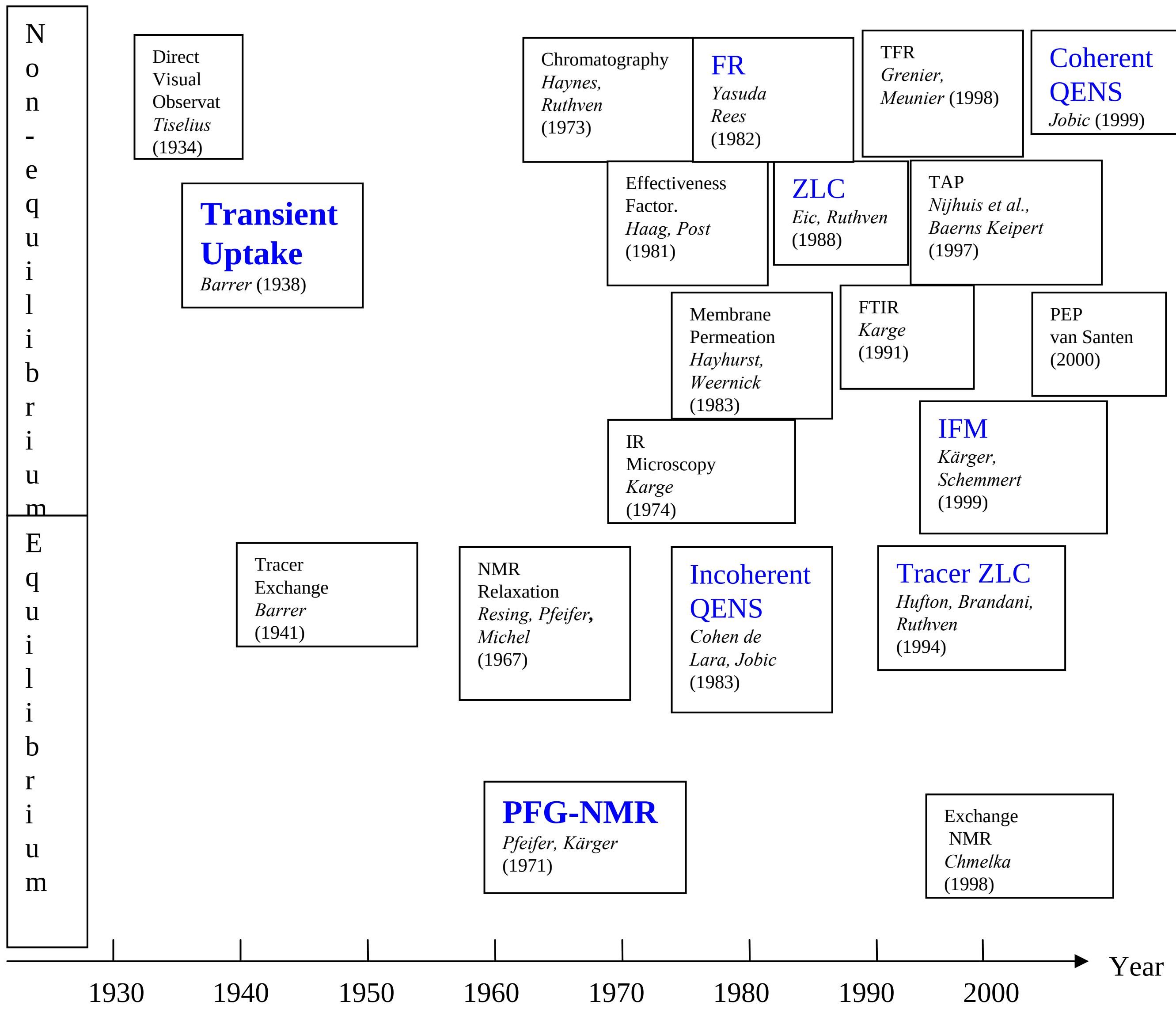
X



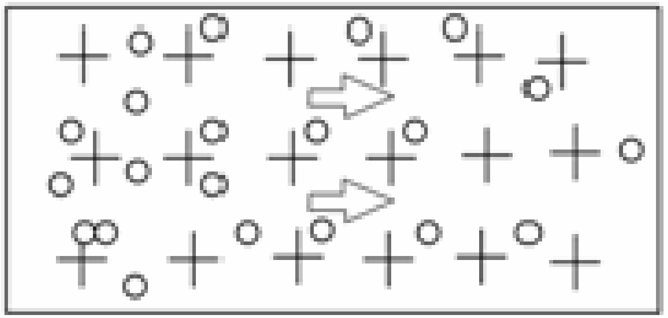
$AlPO_4$-5



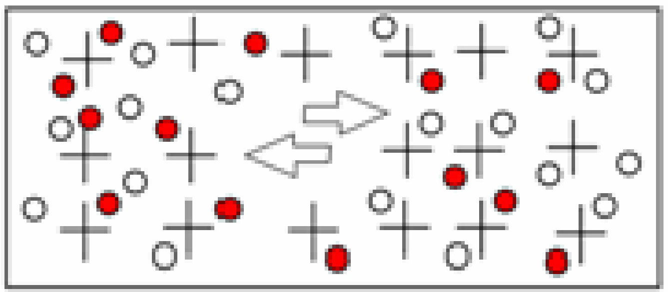
Historical Development of Diffusion in Zeolites Measurements



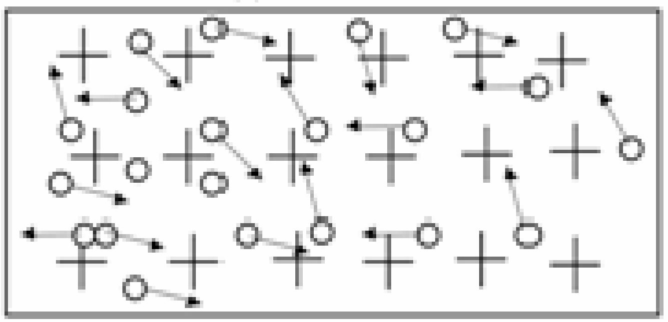
Transport, Tracer and Self Diffusion



(a)Transport Diffusion



(b)Tracer Diffusion



(c)Self Diffusion

Most macroscopic methods measure mass transfer in the presence of a concentration gradient

Most microscopic methods measure self diffusion

Microscopic vs Macroscopic measurements

- Microscopic

Measurement over very short time and length scales.

The RMSD is related to the diffusion coefficient through the Einstein equation.

Limit on slower diffusing species.

- Macroscopic

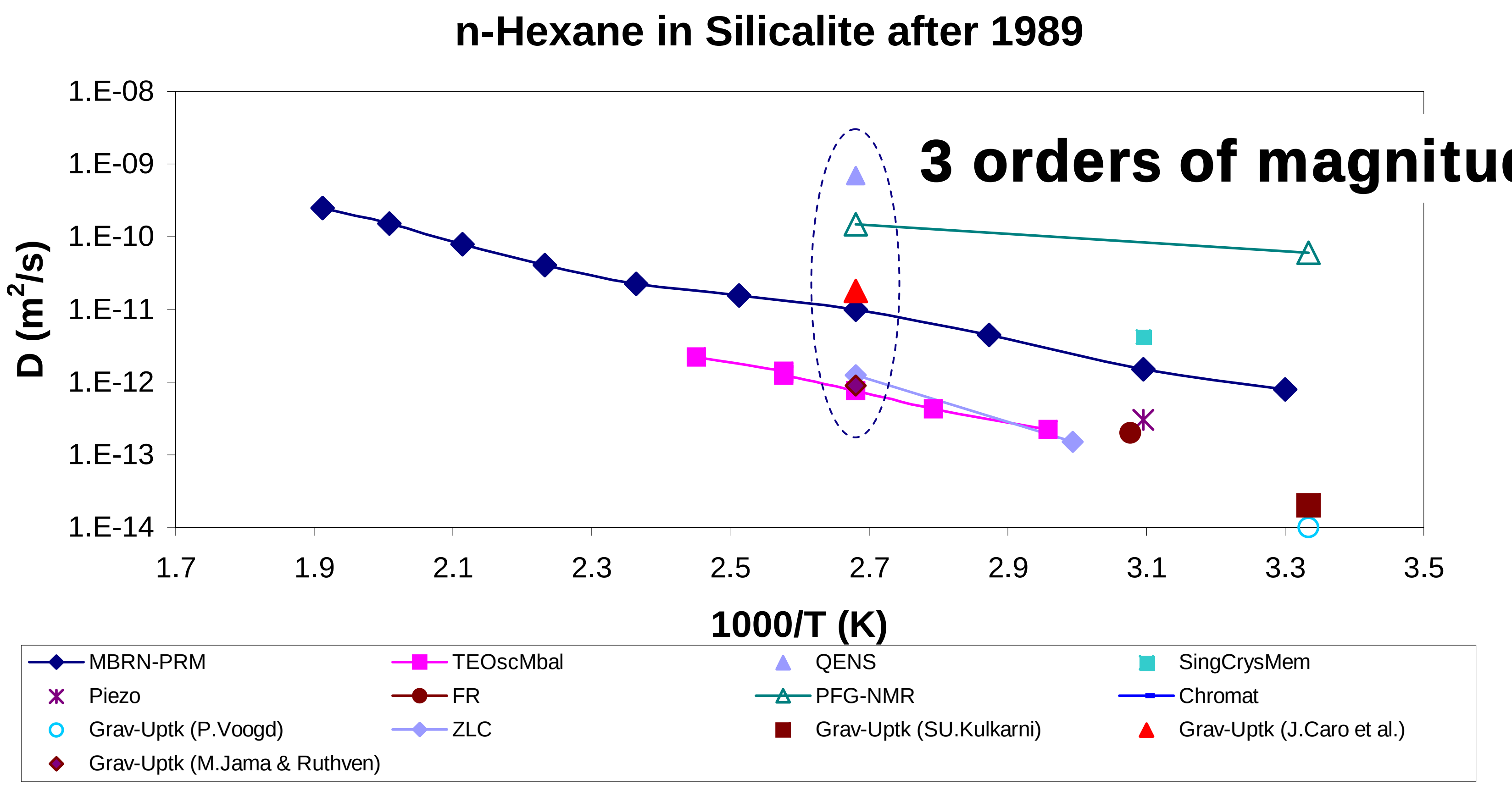
Measurement over the entire crystal length scale and process time scale.

Typically the gas phase concentration or pressure is monitored and through a mass balance the adsorbed phase composition is obtained.

The mass flux under unsteady state conditions is typically measured.

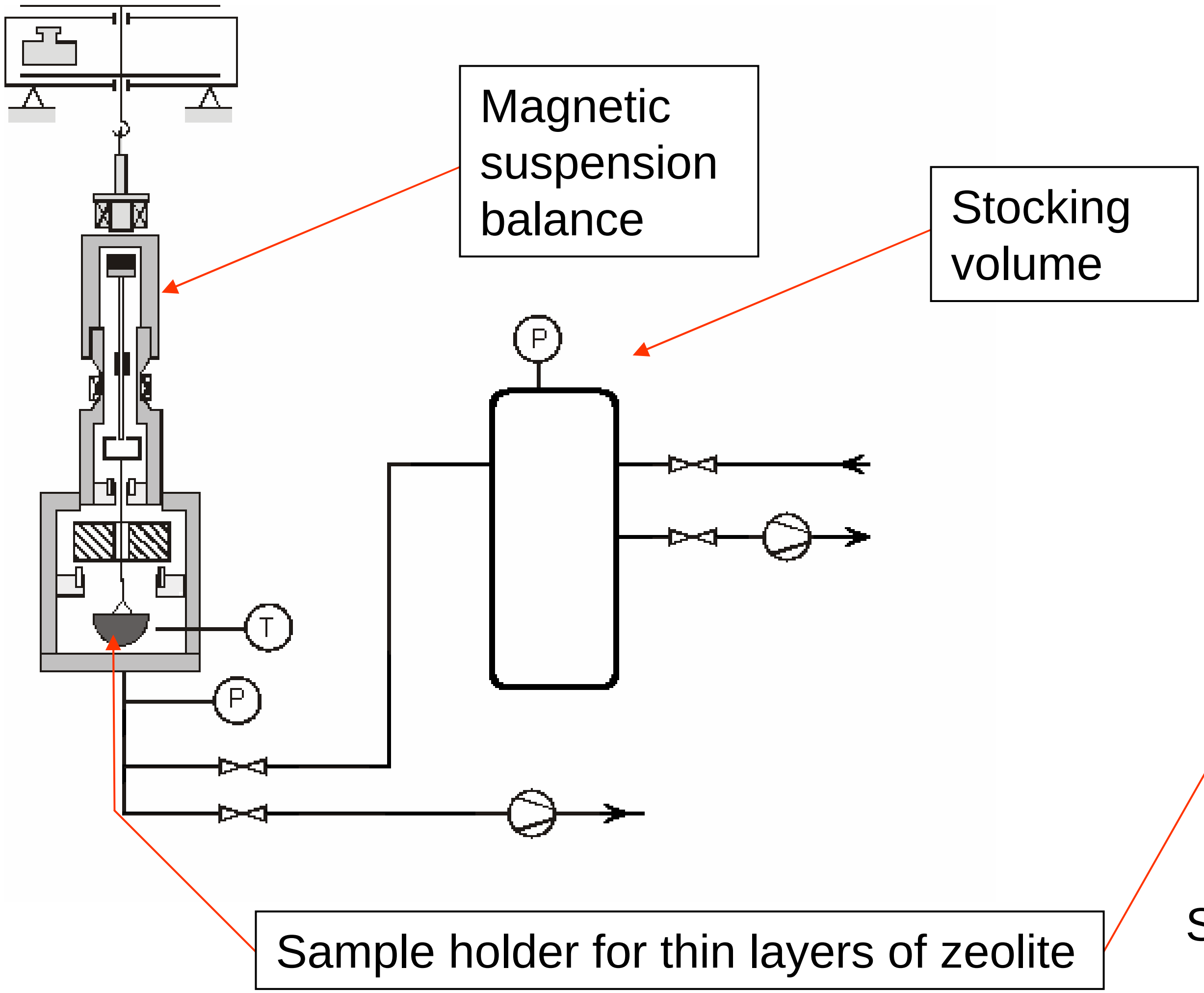
Limit on faster diffusing species.

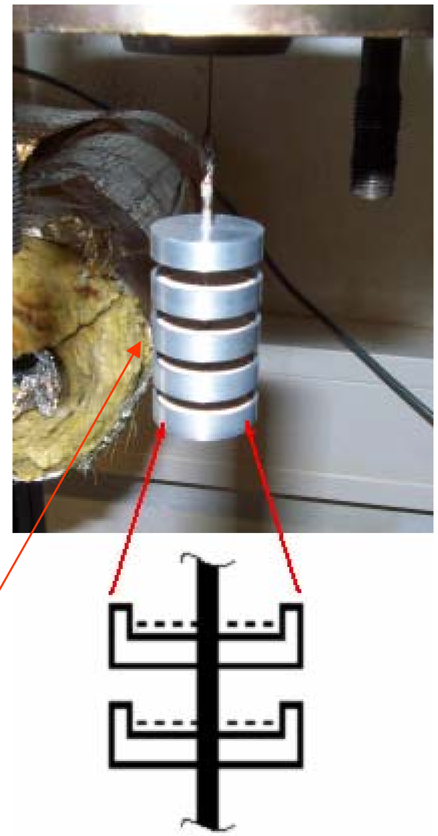
Some recent measurements…



Gravimetric uptake – Reiner Staudt

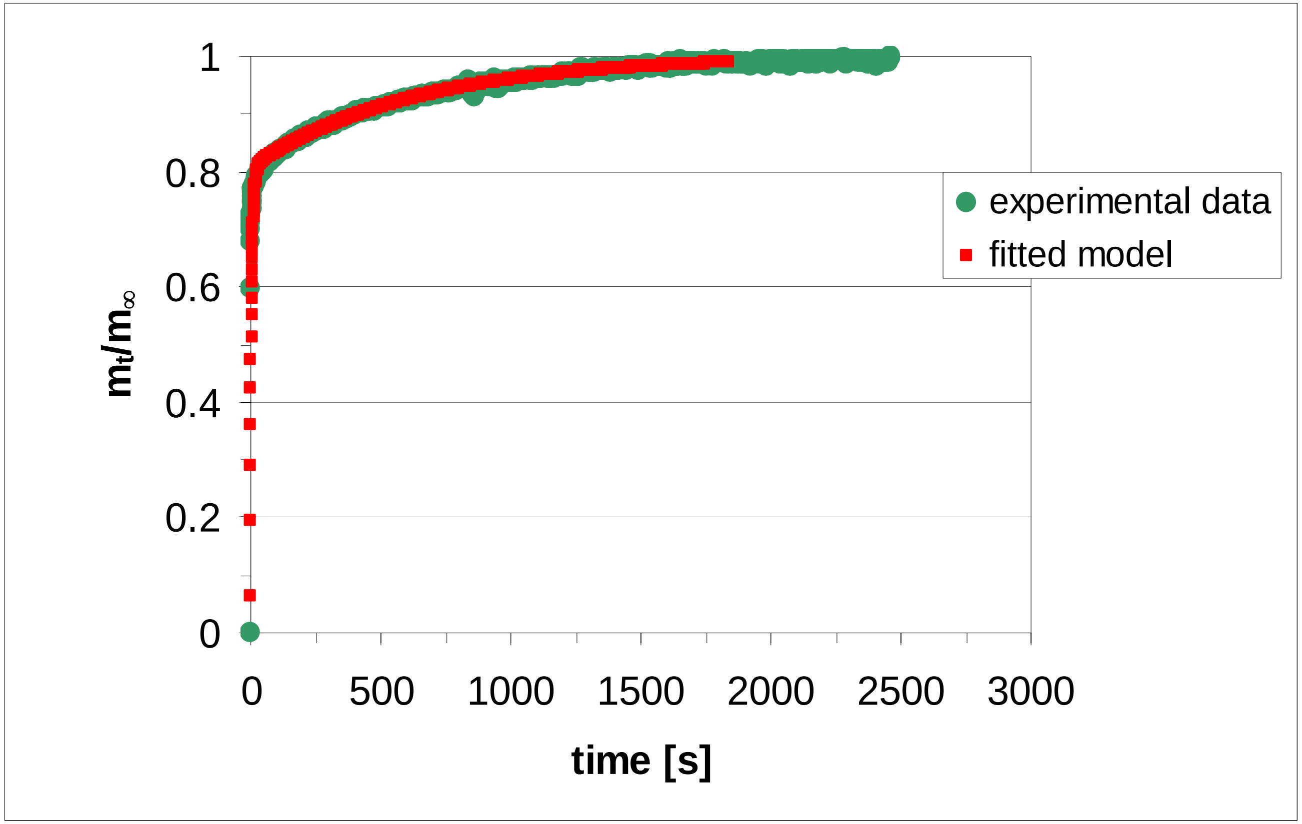
Measurement: transport D at medium to high concentrations



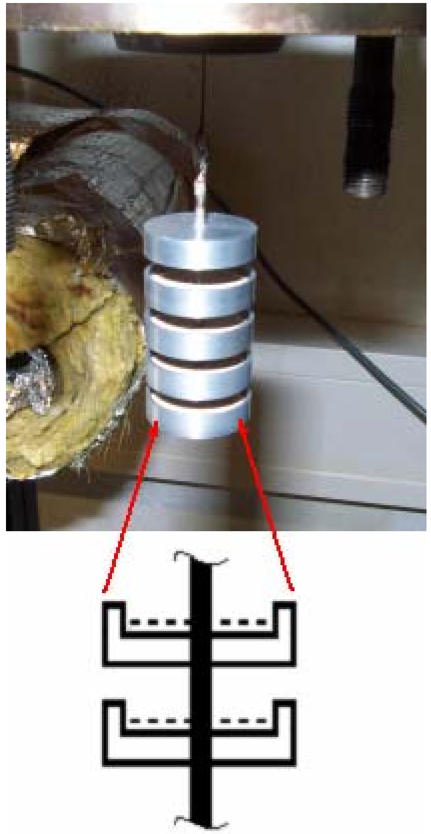


Sample mass = 150-300 mg

Gravimetric uptake – System at INC Leipzig

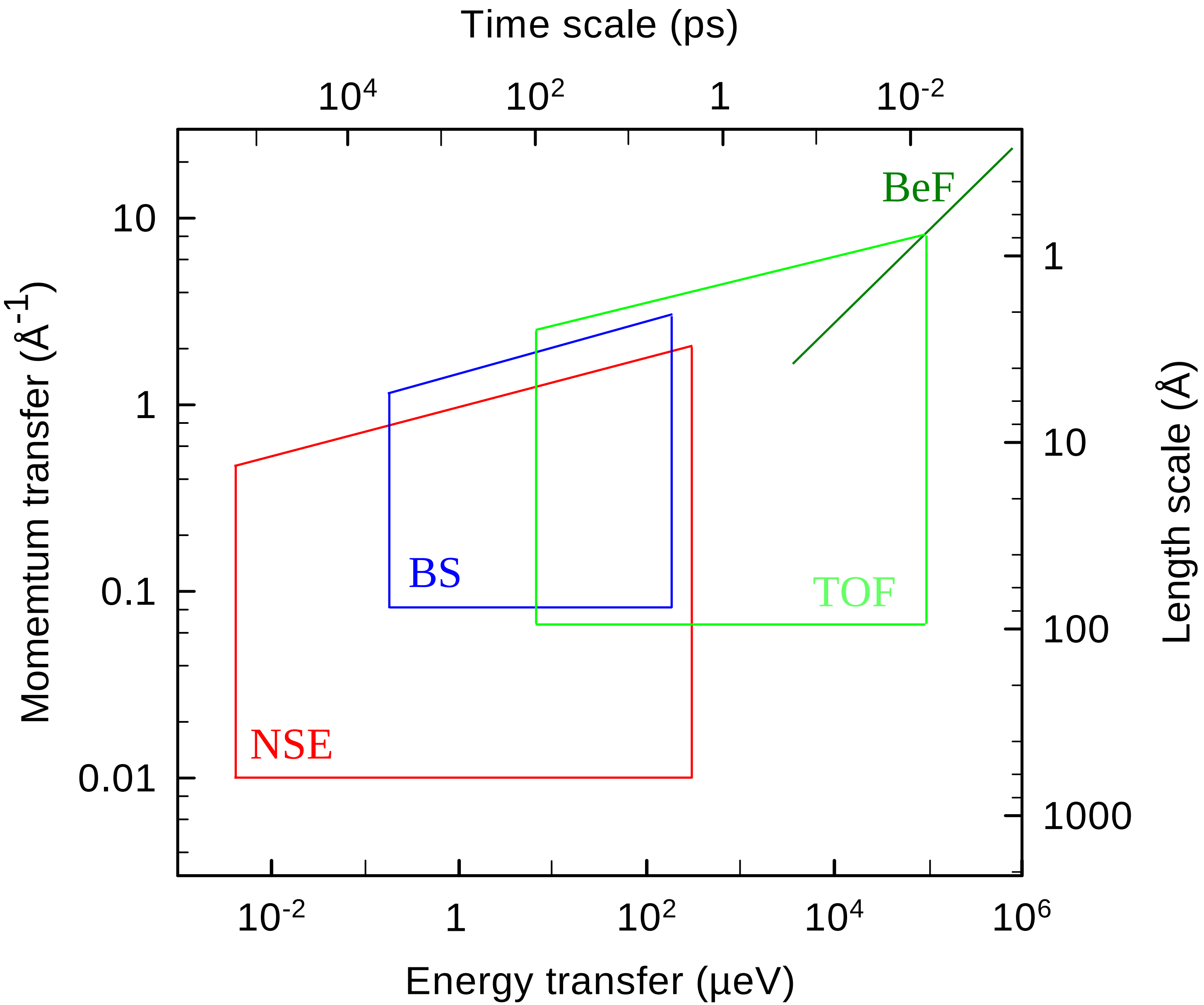


n-Butane in Silicalite – strong heat effects. Staudt 2005



Almost a monolayer on each tray.

QENS/NSE – Length and Time Scales – Hervé Jobic



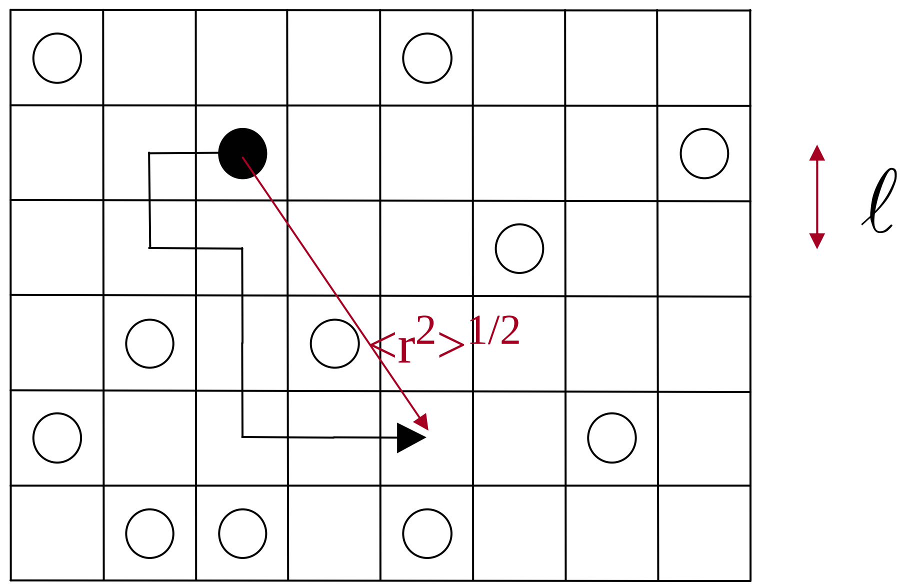
QENS/NSE what is measured

QENS, NSE (coherent scattering: D, C, N, O…)

Transport diffusivity

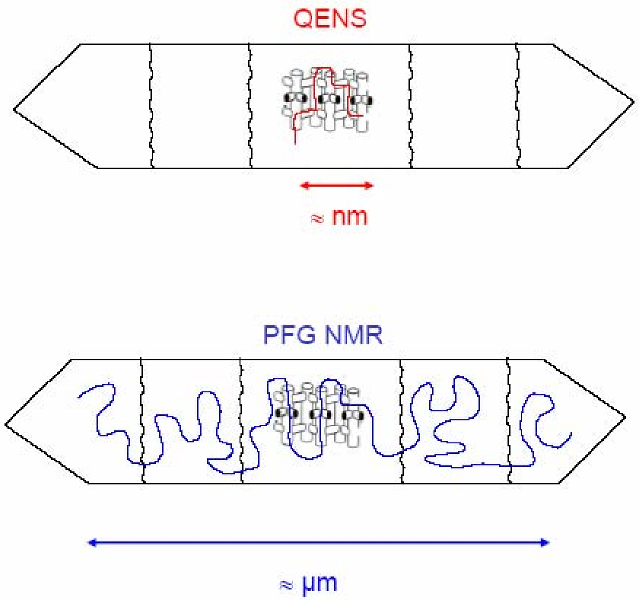
QENS (incoherent scattering: H)

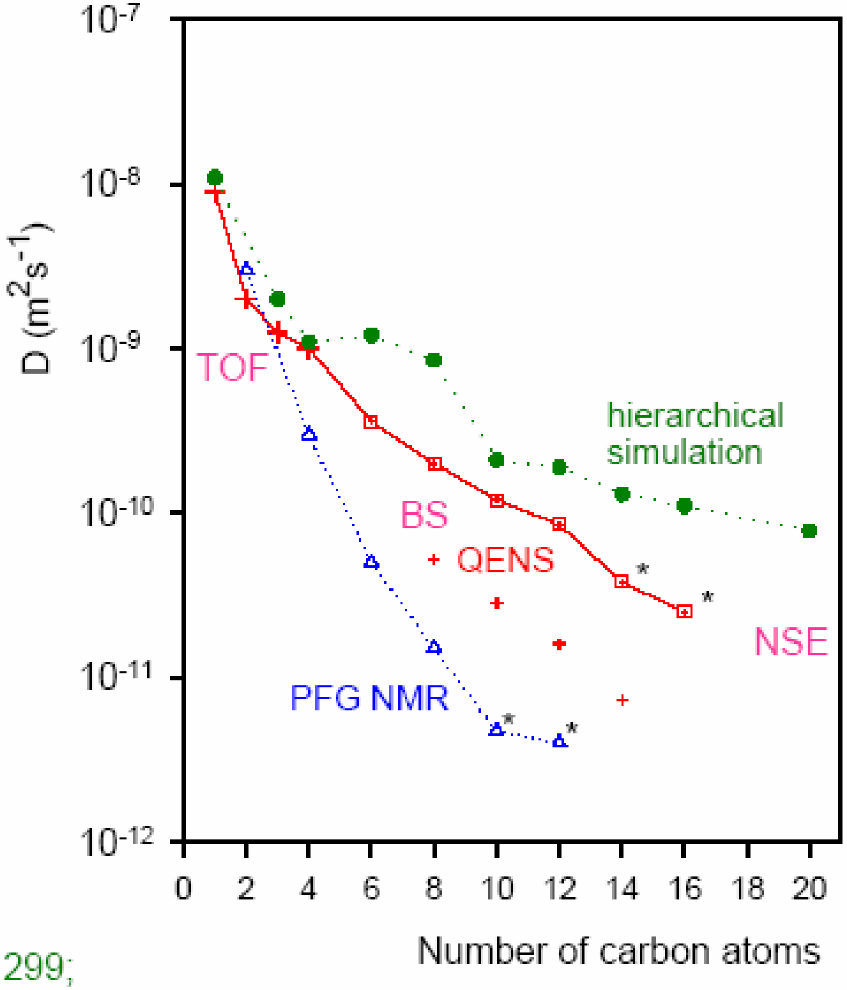
$$D_{Self} = \frac{1}{6}\frac{\langle r^2(t)\rangle}{t} = \frac{\ell^2}{6\tau}$$



For some system both D_{Self} and D_{Trans} can be measured, but only over short lenght/time scales.

Ds *n*-alkanes / silicalite
(T = 300 K)



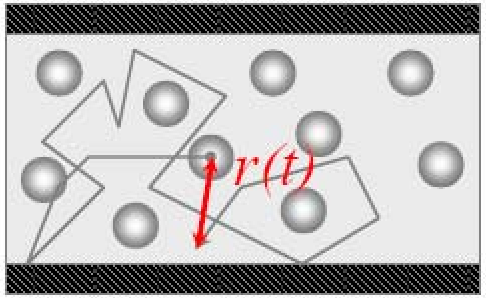


Microp .Mesop. Mater. <u>90</u> (2006) 299;
J.Phys. Chem. B <u>110</u> (2006) 1964

PFG-NMR – Jörg Kärger

$$<r^2(t)> = 2D\,t$$

self-diffusion



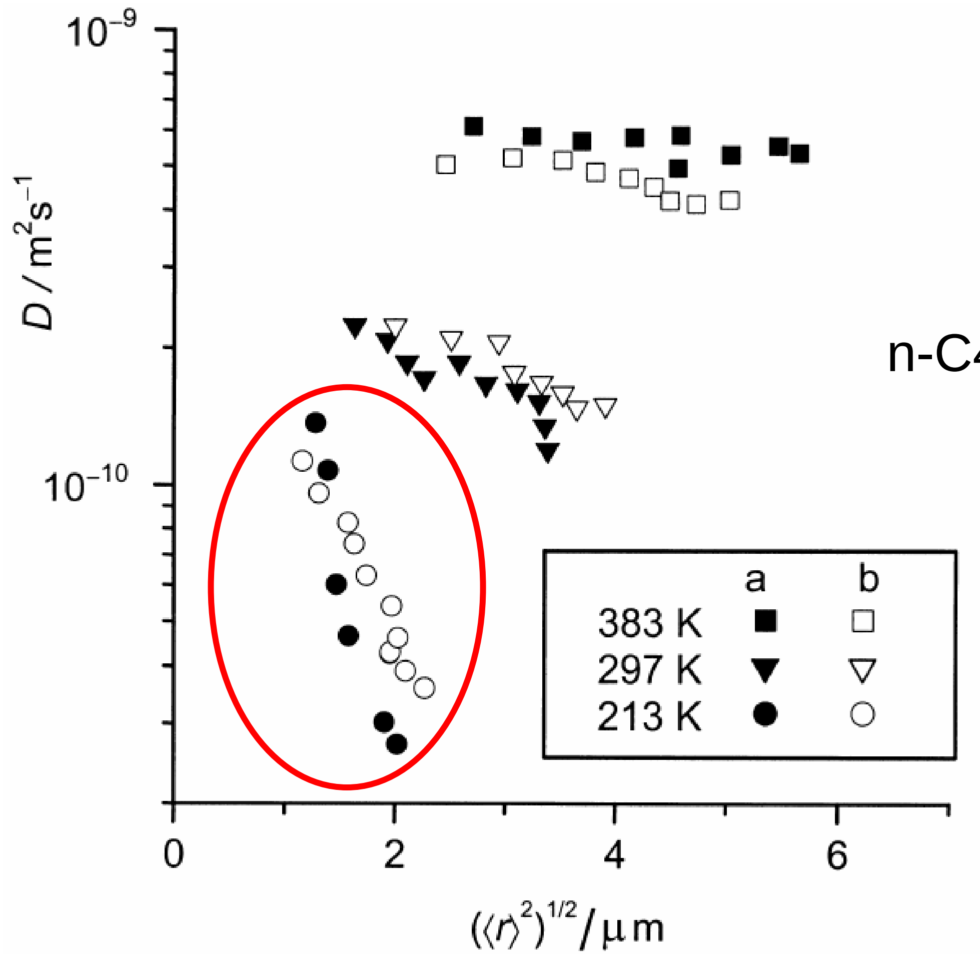
The attenuation of the NMR signal ψ is given by

$$\psi(t,\gamma\delta g) = \exp\left[-\frac{1}{2}\gamma^2\delta^2 g^2\left\langle r^2(t)\right\rangle\right]$$

The lower limit of detection is 100 nm for the displacement and an observation time of the order of 100 ms.

i.e. a minimum $D_{Self} \approx 10^{-14} m^2 s^{-1}$

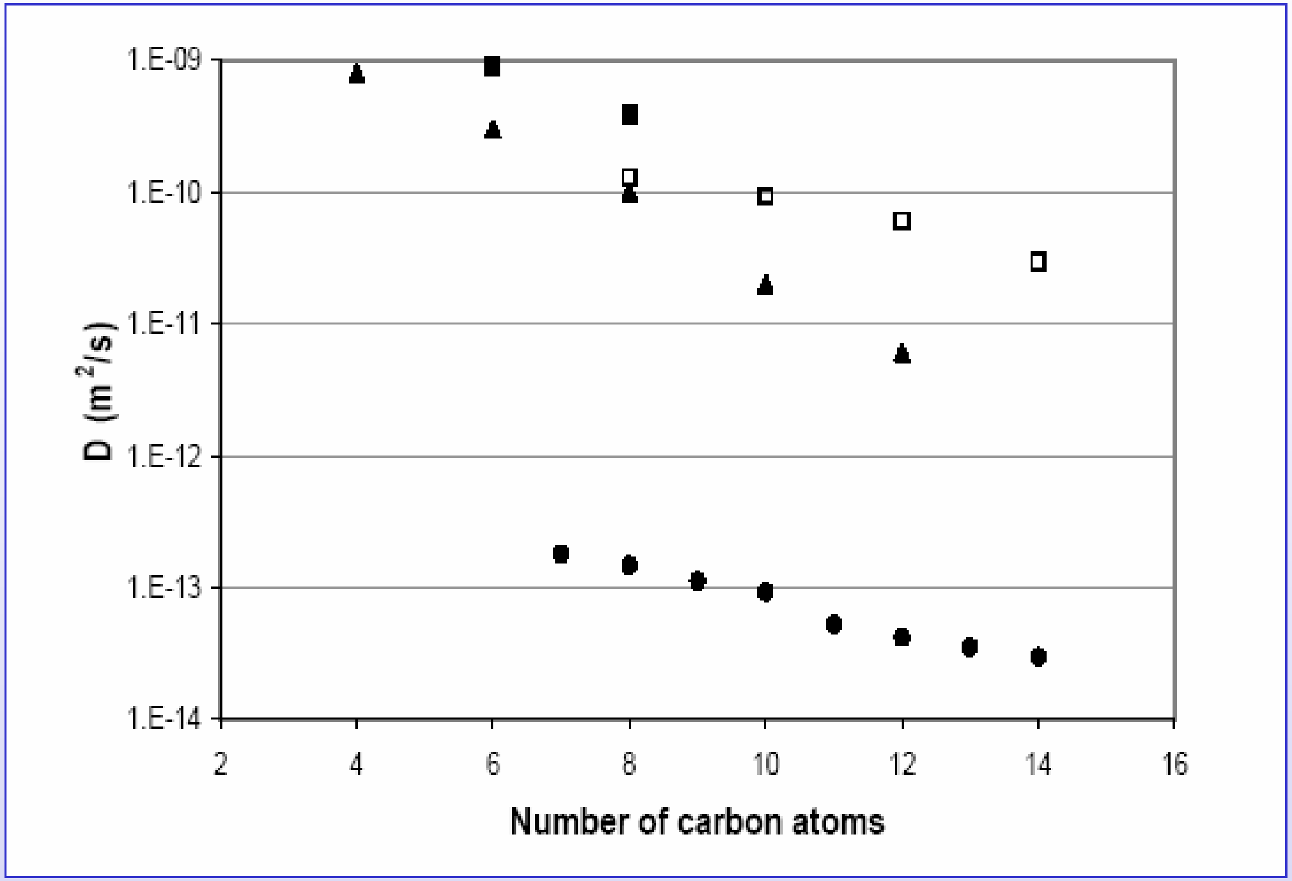
PFG-NMR – evidence of internal barriers



n-C4 in Silicalite-1

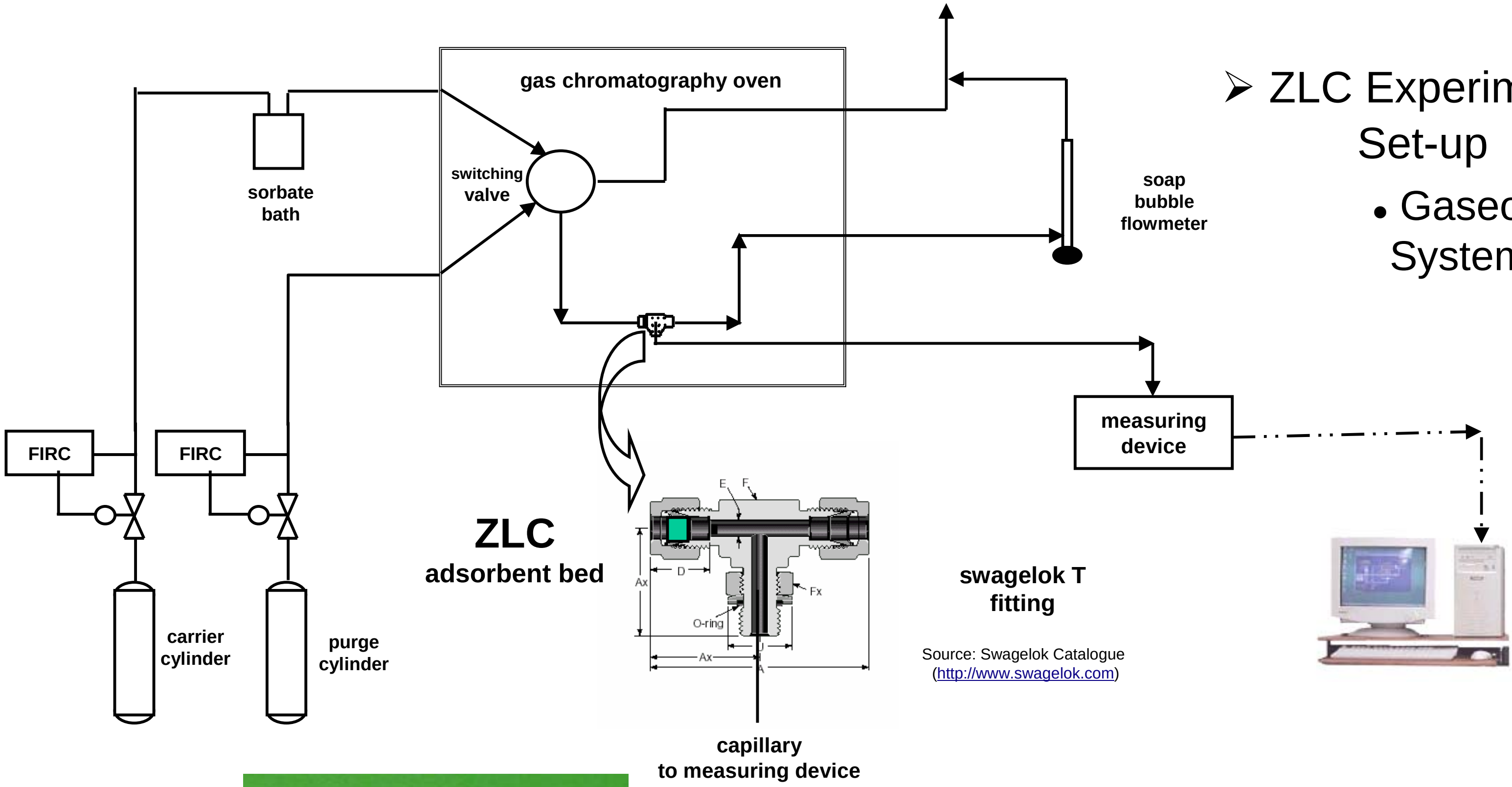
gure 8. Dependence of PFG NMR diffusivities on the mean diffusion path for butane in two different samples of silicalite-1 (open and filled symbols) at 3 K (○,●), 297 K (▽,▼), and 383 K (□,■) [34].

Only kinetic experiments carried out with different techniques on the same crystals can detect the existence of internal barriers!



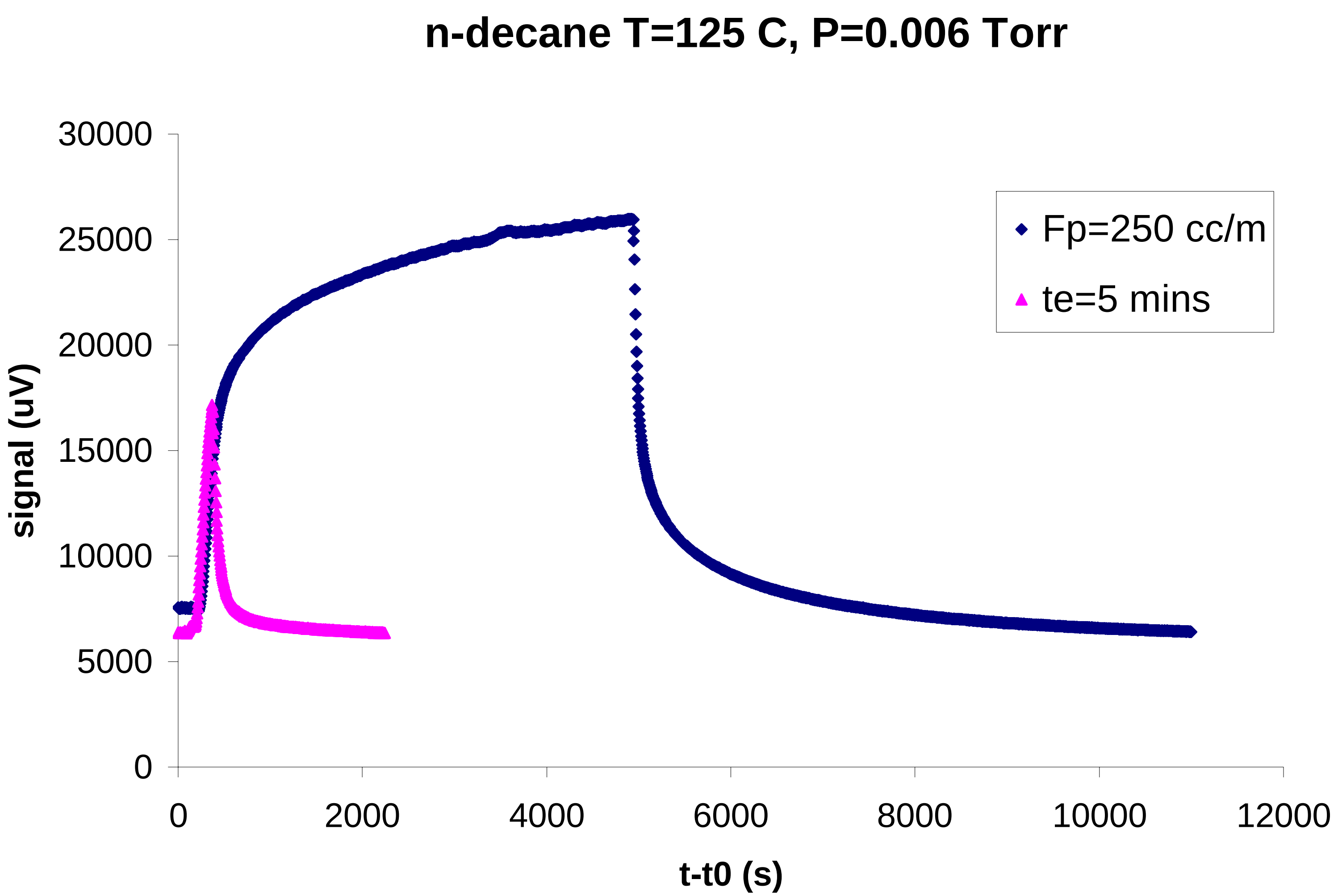
n-alkanes in MFI at a loading corresponding to 6 carbons per channel crossing.
Comparison of experimental results at 423K.
■ QENS new data; □ QENS; ▲ PFG-NMR ; ● ZLC.

The ZLC apparatus



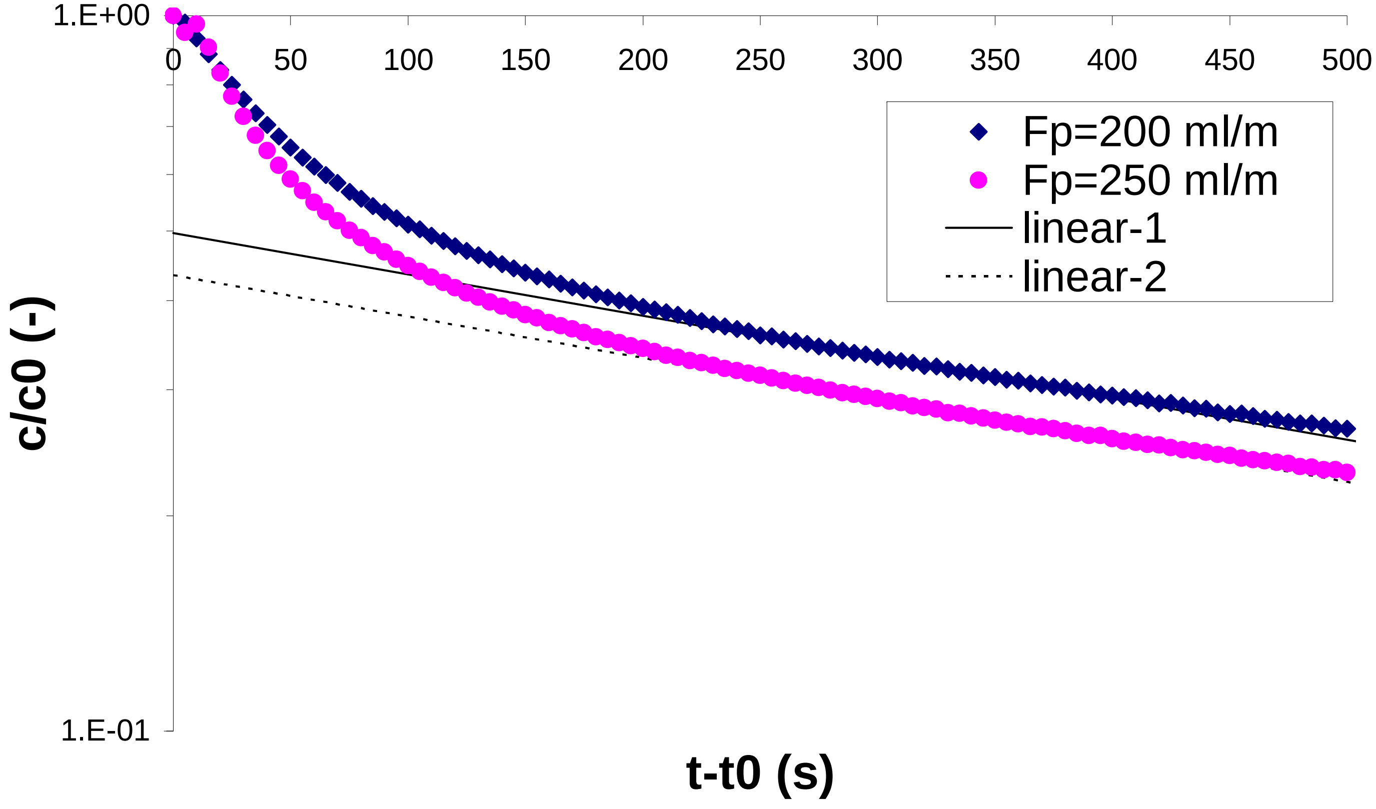
- ZLC Experimental Set-up
  - Gaseous Systems

Experimental Signals - Silicalite

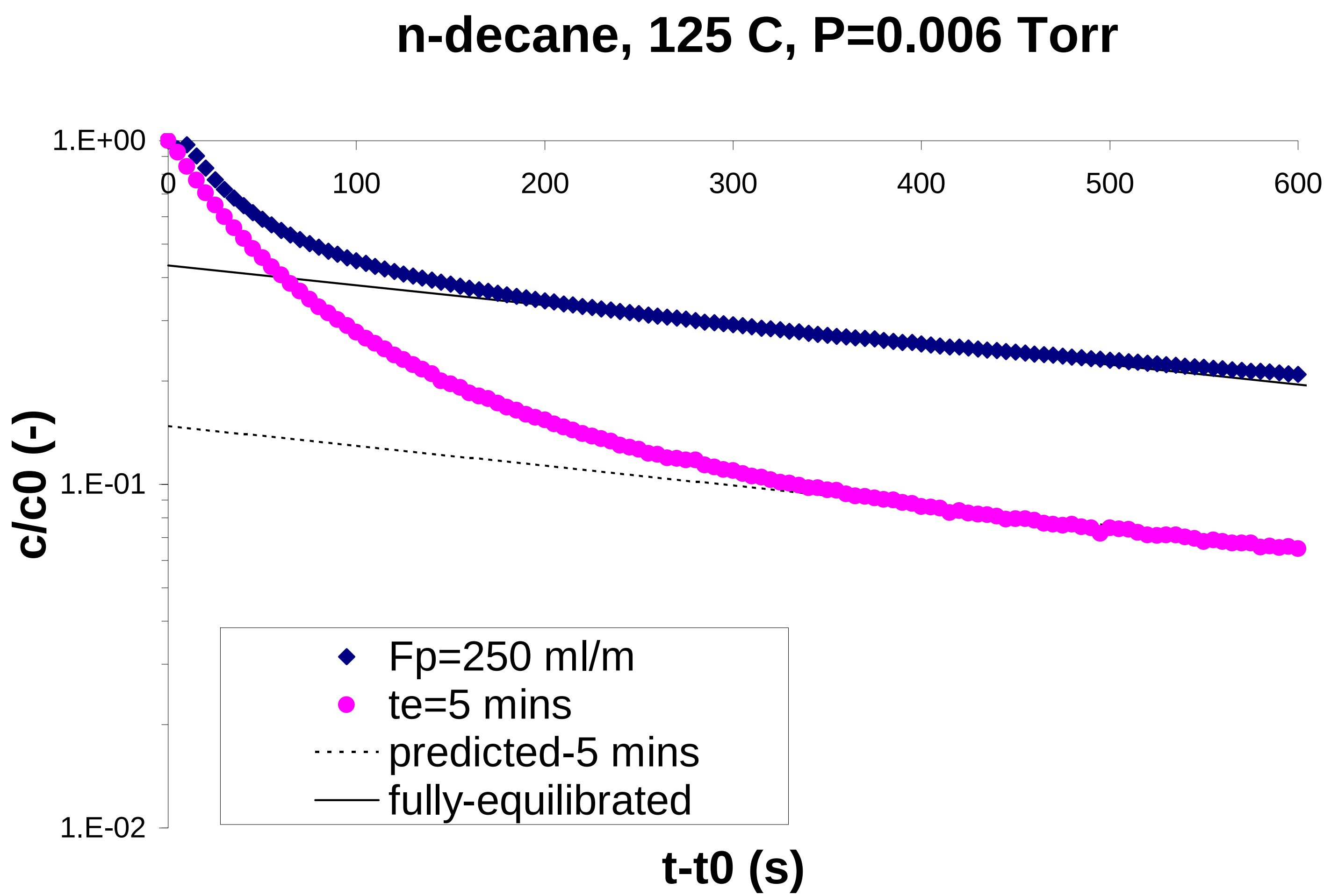


Determination of D_0

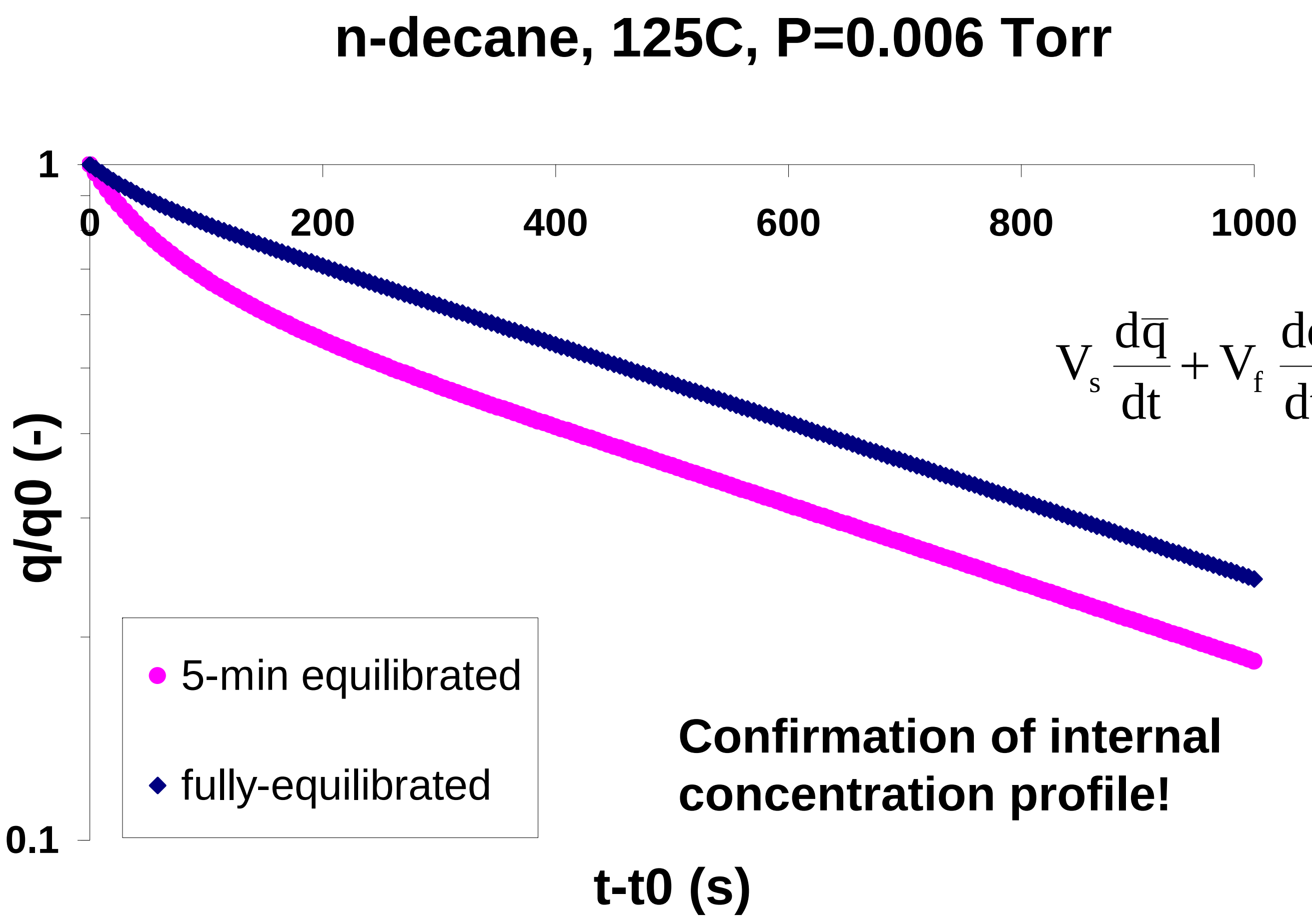
n-decane, 125C, P=0.006 Torr



Check D_0 with Partial-Loading Experiment



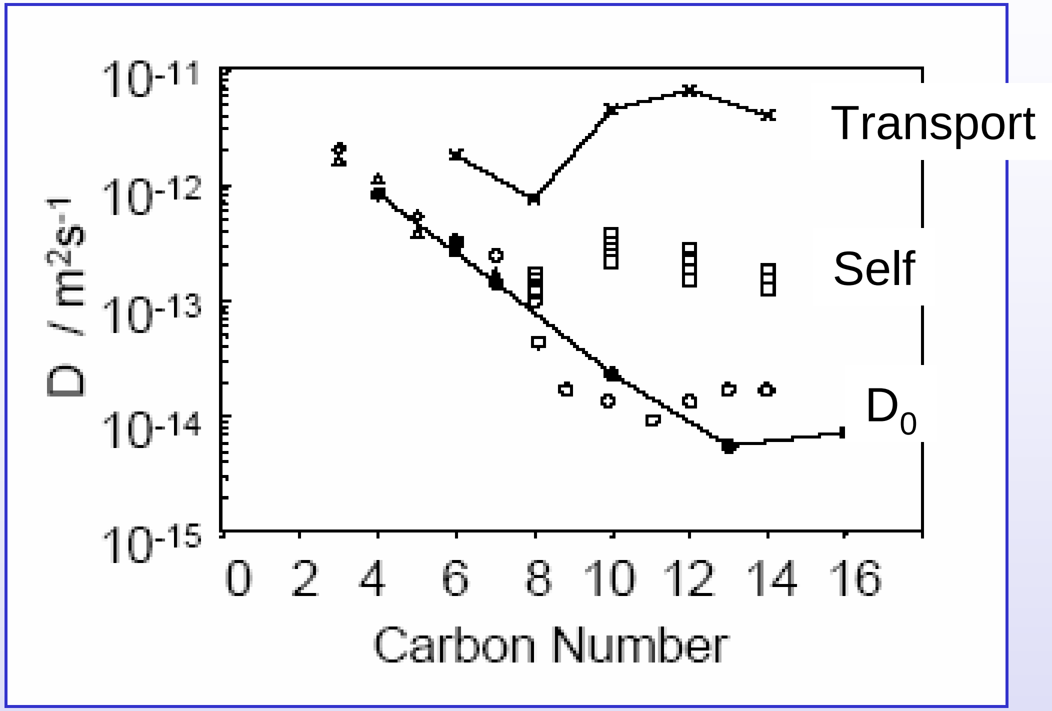
Adsorbed Phase Concentration



$$V_s \frac{d\bar{q}}{dt} + V_f \frac{dc}{dt} + Fc = 0$$

Confirmation of internal concentration profile!

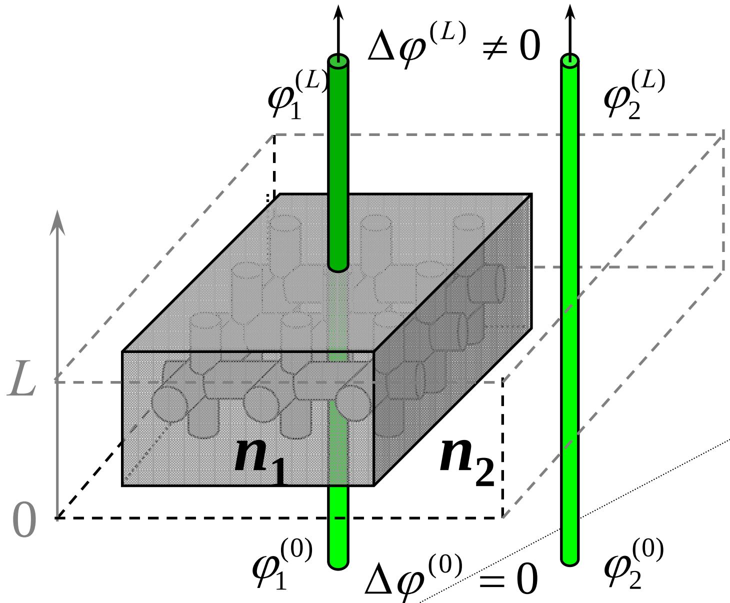
Diffusion of n-alkanes in 5A

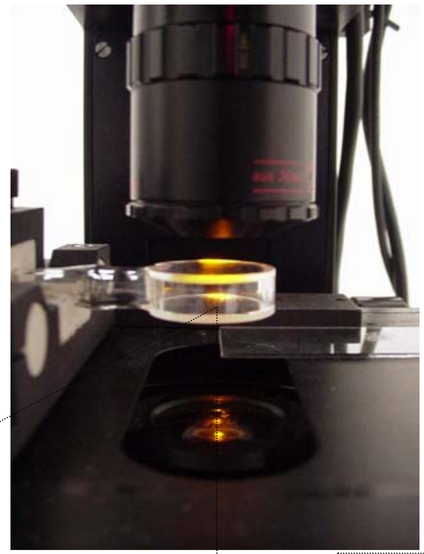


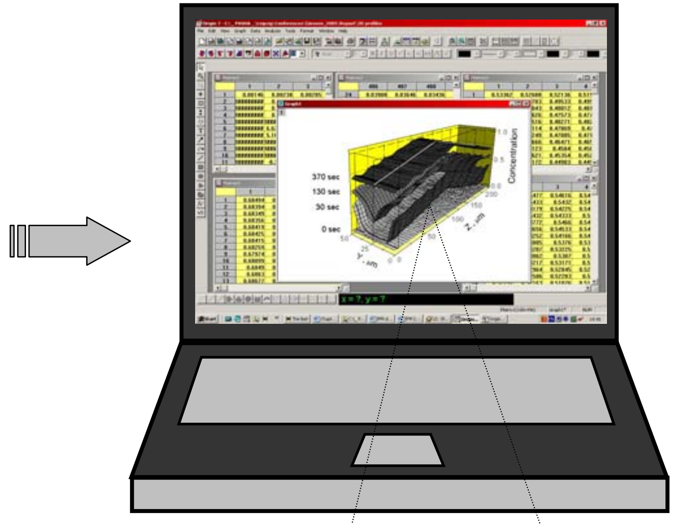
n-alkanes in NaCaA:
Variation of diffusivity with carbon number (at 473K).
NSE **x**
ZLC ● and o
PFG NMR data at 1 molecule/cage Δ and □, and 2 molecules/cage ◊ .

IFM Technique

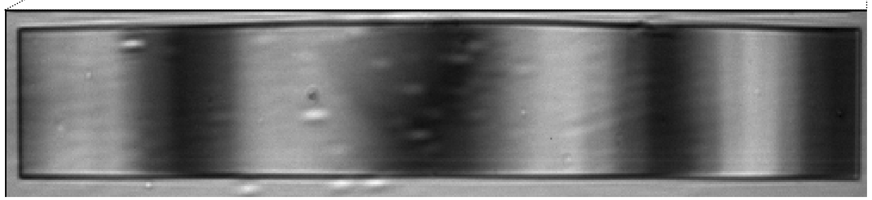
Department of Interface Physic
UNIVERSITY OF LEIPZIG

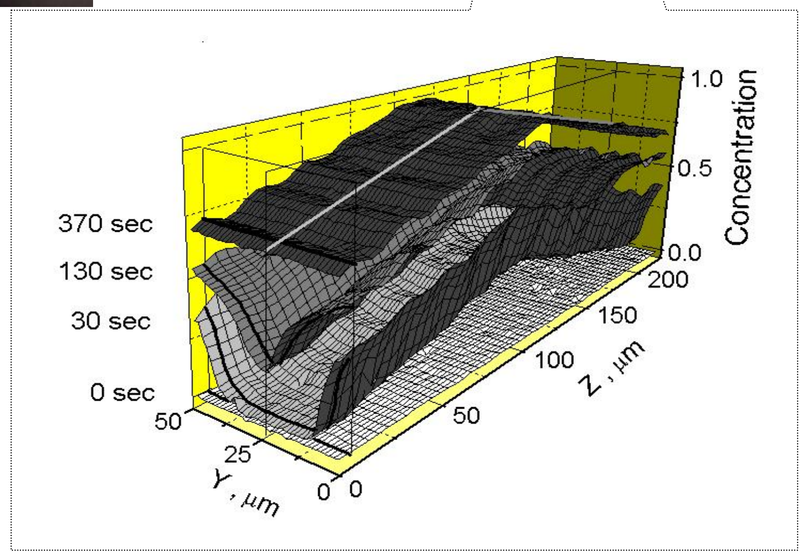






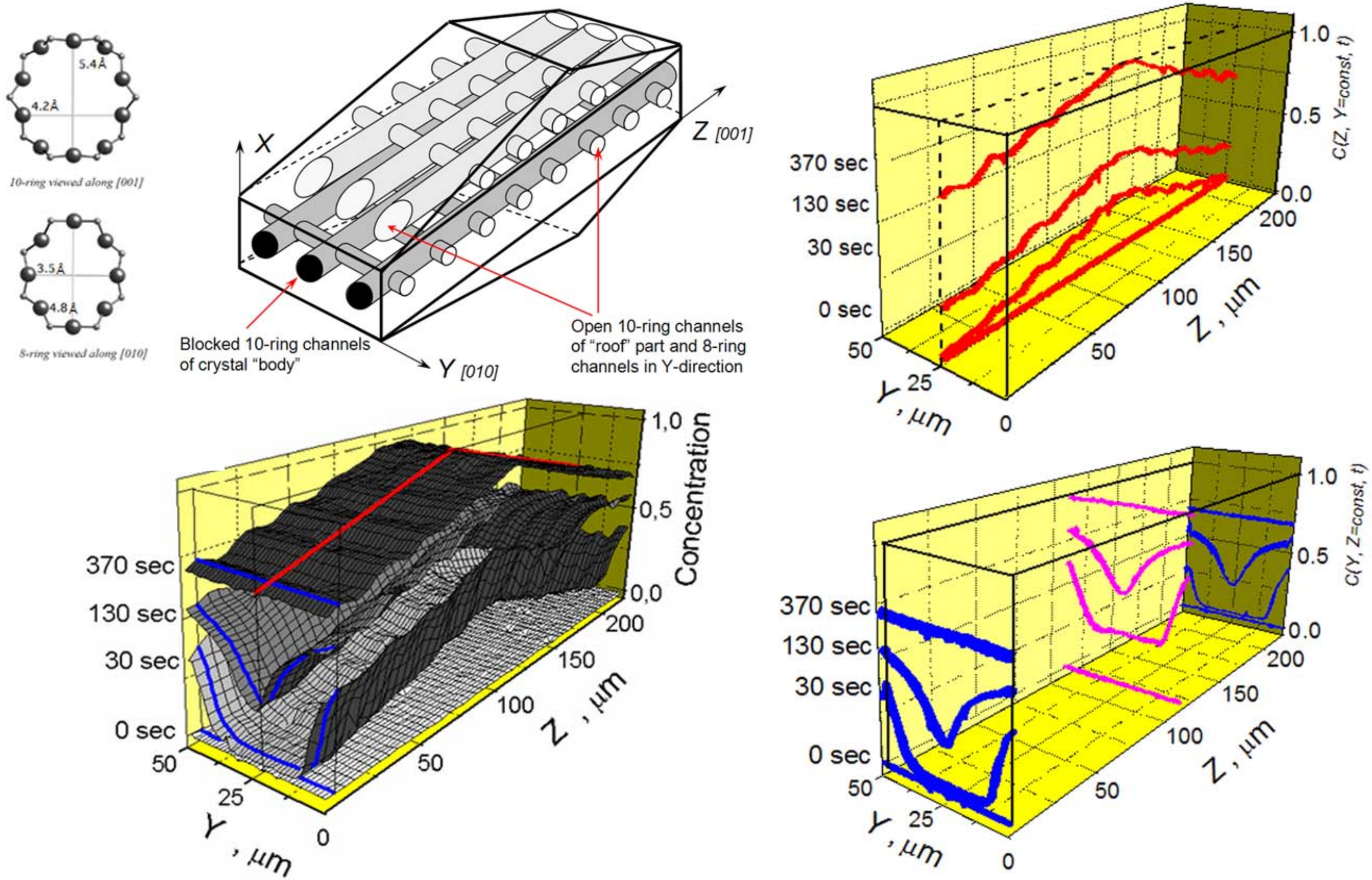
$$\boxed{\Delta\varphi \sim \Delta n \sim \Delta c}$$





Spatial resolution: 0.5 µm × 0.5 µm

Directions of methanol adsorption in Ferrierite crystal

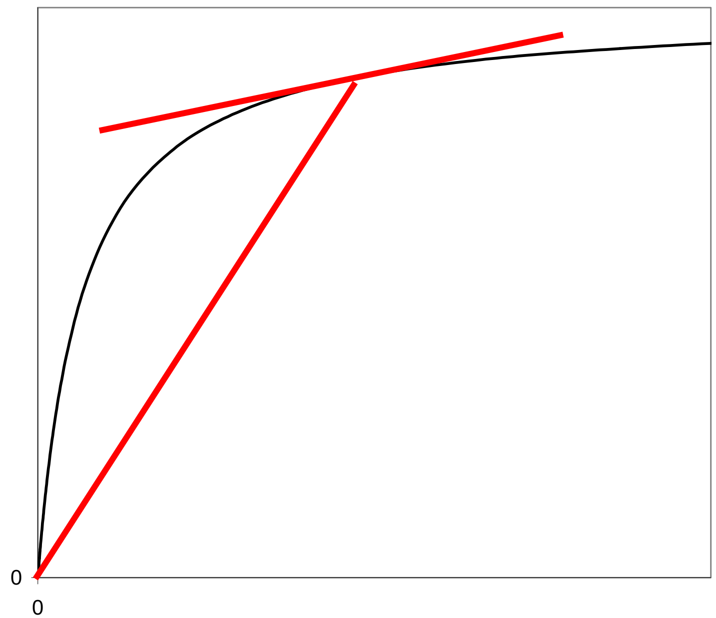


Darken Correction

$$\frac{d\ln P_A}{d\ln q} = \frac{q}{P_A} \Big/ \frac{dq}{dP_A}$$

Secant Tangent

Need VERY ACCURATE equilibrium data to evaluate the derivative.



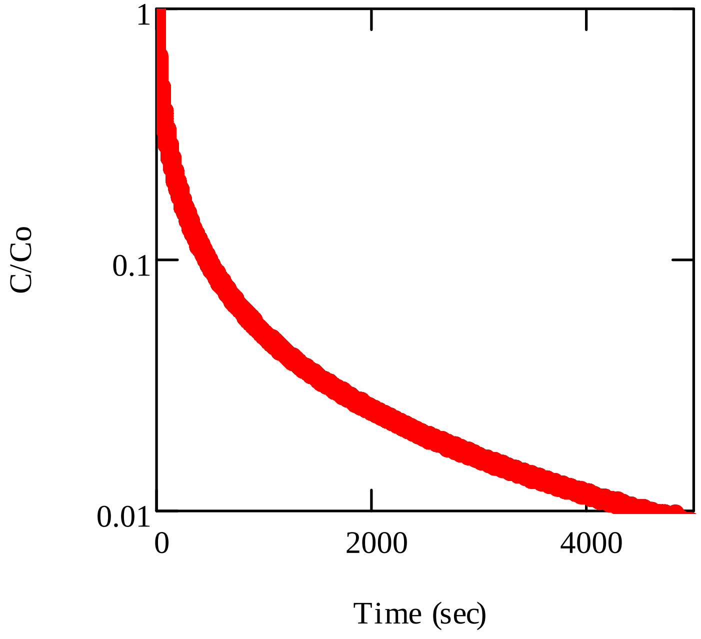
Langmuir

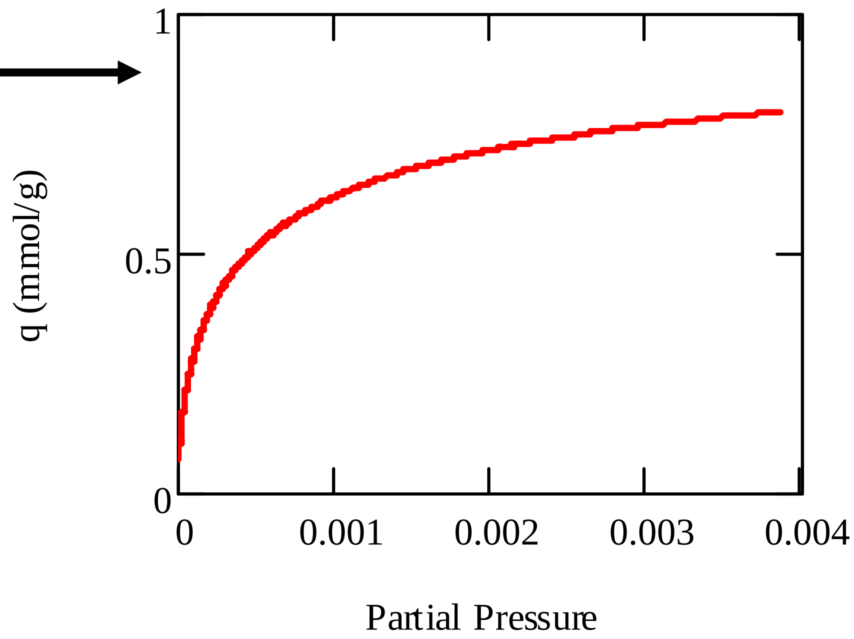
$$\frac{d\ln P}{d\ln q} = \frac{1}{1-q/q_S} = \begin{cases} 1 \text{ if } P = 0 \\ \infty \text{ if } P = \infty \end{cases}$$

ZLC Measurement of Darken Correction

$$q^{*}V_S = \left(\int_0^{\infty} \frac{y}{1-y} dFt - \int_0^{t} \frac{y}{1-y} dFt - V_F \cdot y \right) \frac{P}{RT}$$

Federico Brandani, Douglas Ruthven, and Charles G. Coe
Ind. Eng. Chem. Res. 2003, 42, 1451-1461

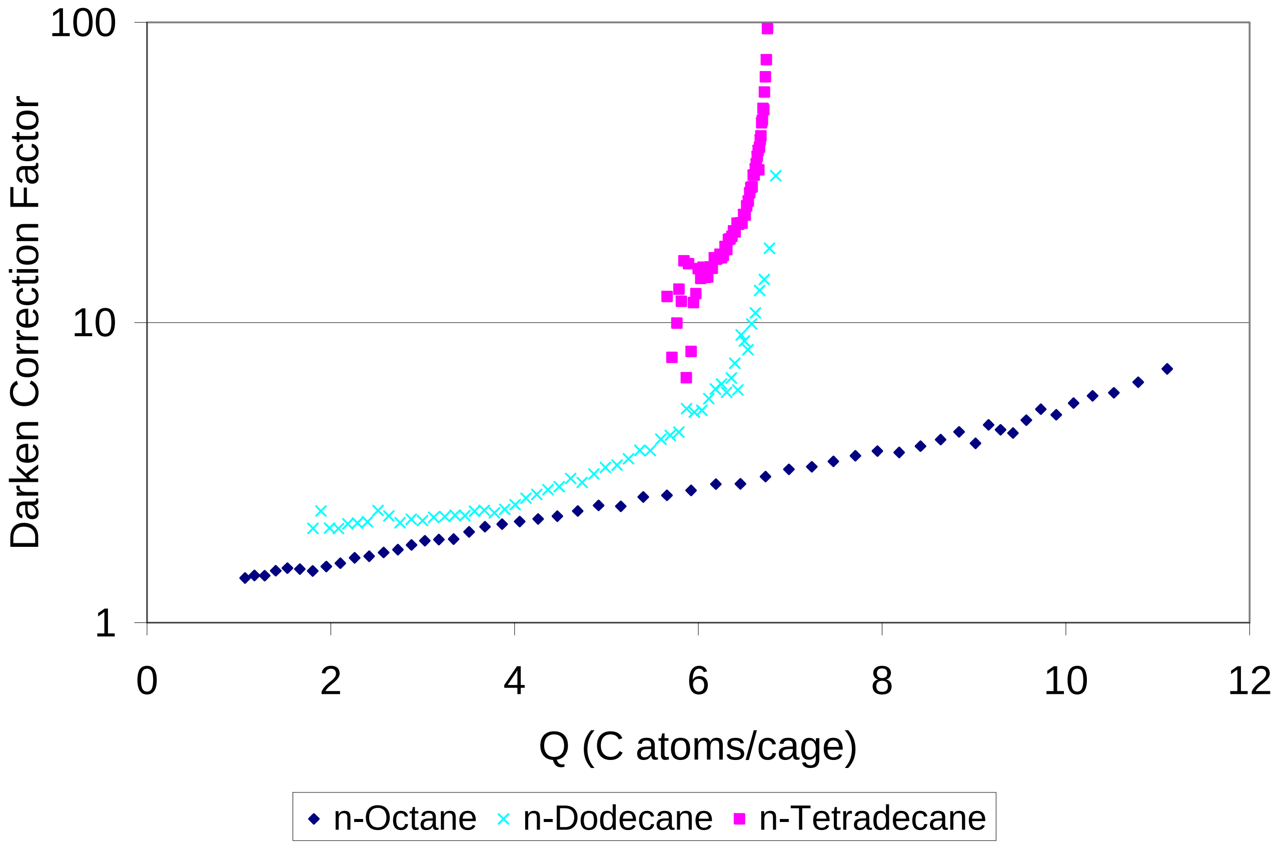




Thousands of equilibrium data points in less than 2 hours!

ZLC Measurement of Darken Correction

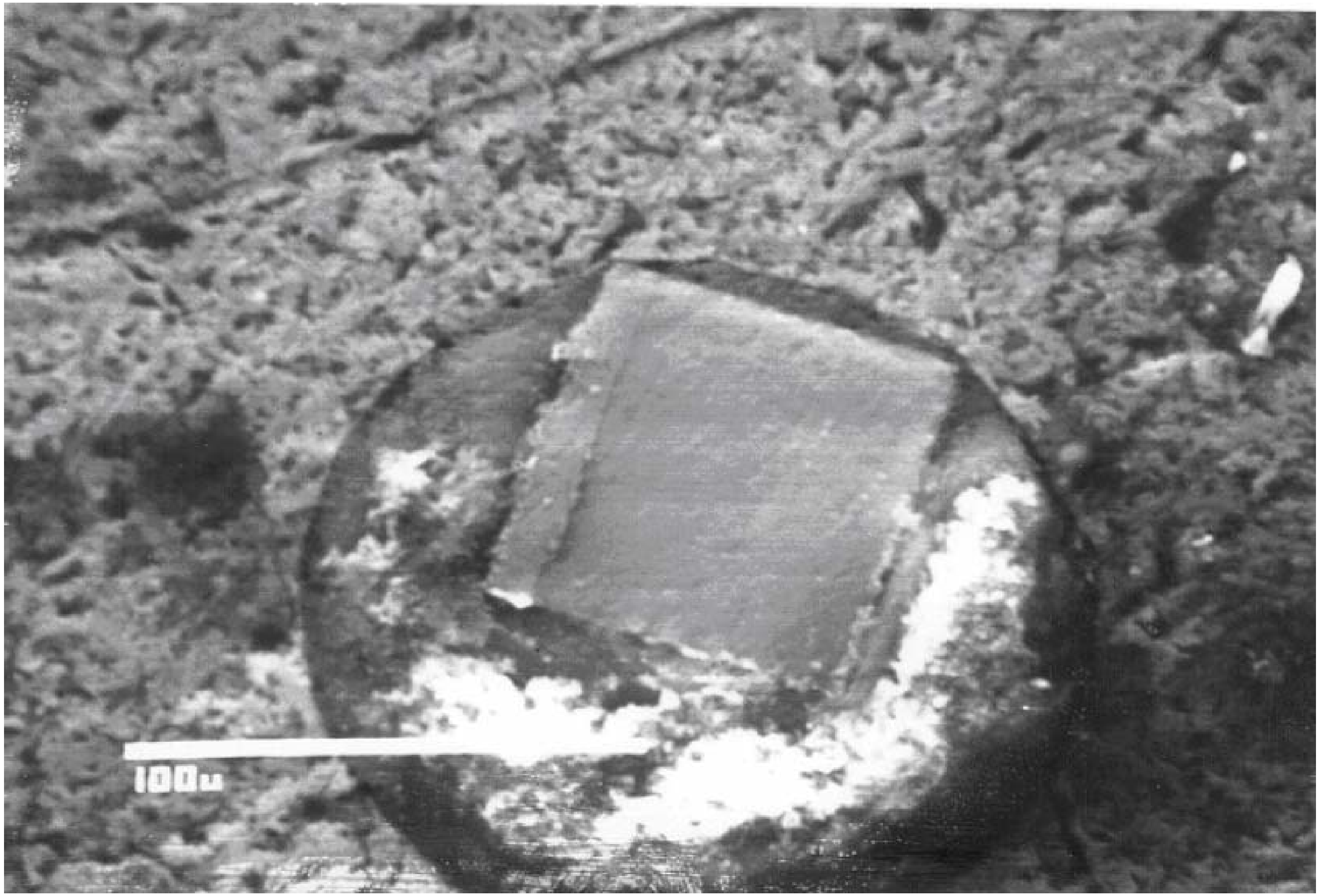
Experimental measurements carried out on 5A crystals at UOP (Douglas Galloway)



GOOD NEWS!!!

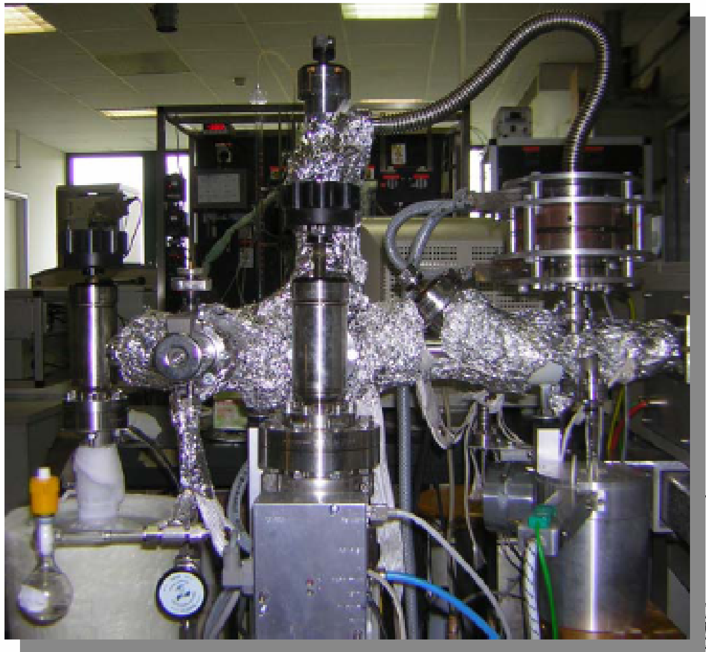
- New funding from DFG for continuation programme 2007-2009.
- Additional experimental techniques
- New materials
- Extend work to mixtures

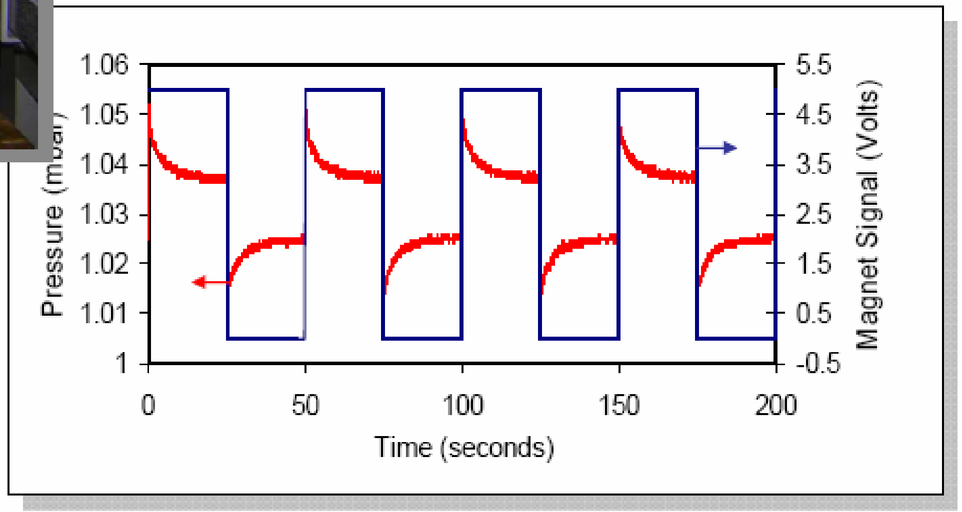
Single crystal membrane – D.B. Shah



Frequency Response – Andreas Jentys

Square-wave volume modulation





TECHNISCHE UNIVERSITÄT MÜNCHEN

Diffusion Fundamentals II

August 26-29, 2007

L'Aquila, Italy

www.diffusion-fundamentals.org

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