Diffusion Fundamentals I

UNIVERSITÄT LEIPZIG

Basic Principles of Theory, Experiment and Application

EIN
STEIN
JAHR
2005
Eine gemeinsame Initiative von Bundesregierung,
Wissenschaft, Wirtschaft und Kultur.

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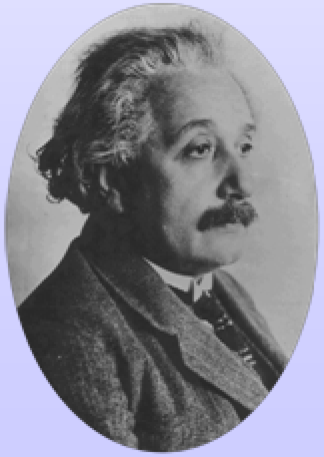
Leipzig, Germany

Molecular Diffusion under Confinement



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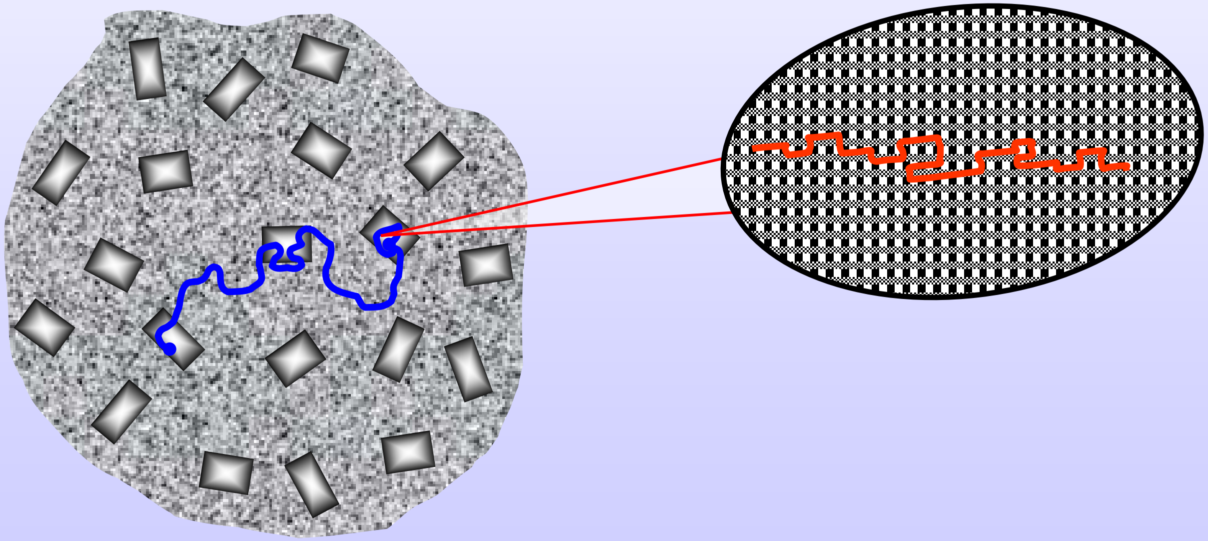
Abteilung Grenzflächenphysik

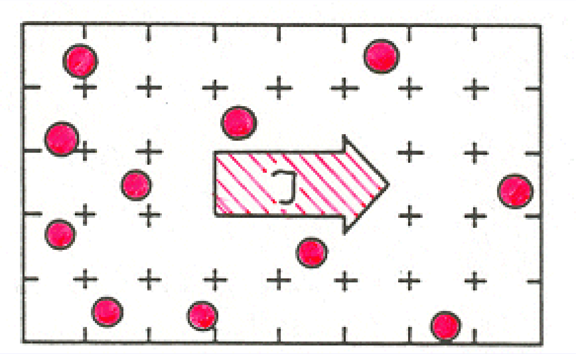
www.diffusion-fundamentals.org

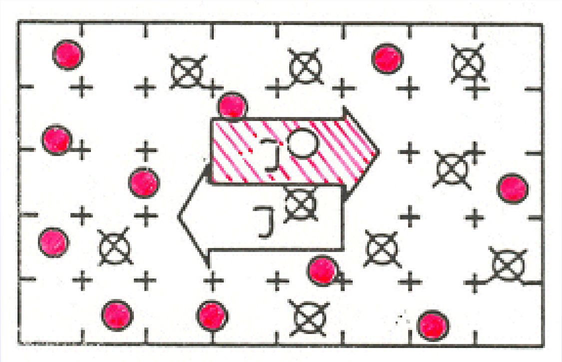
typical host system (zeolite catalyst):

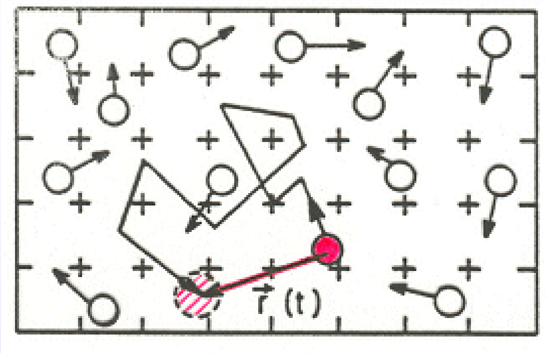


Normal Diffusion:

whenever the diffusion equations apply:



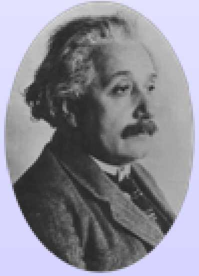




$$j = -D_{\mathrm{T}} \frac{\partial c}{\partial x}$$

$$j^* = -D \frac{\partial c^*}{\partial x}$$

$$\left\langle x^2(t) \right\rangle = 2Dt$$



Einstein equation

(matter conservation)

First

Ficks **Laws**

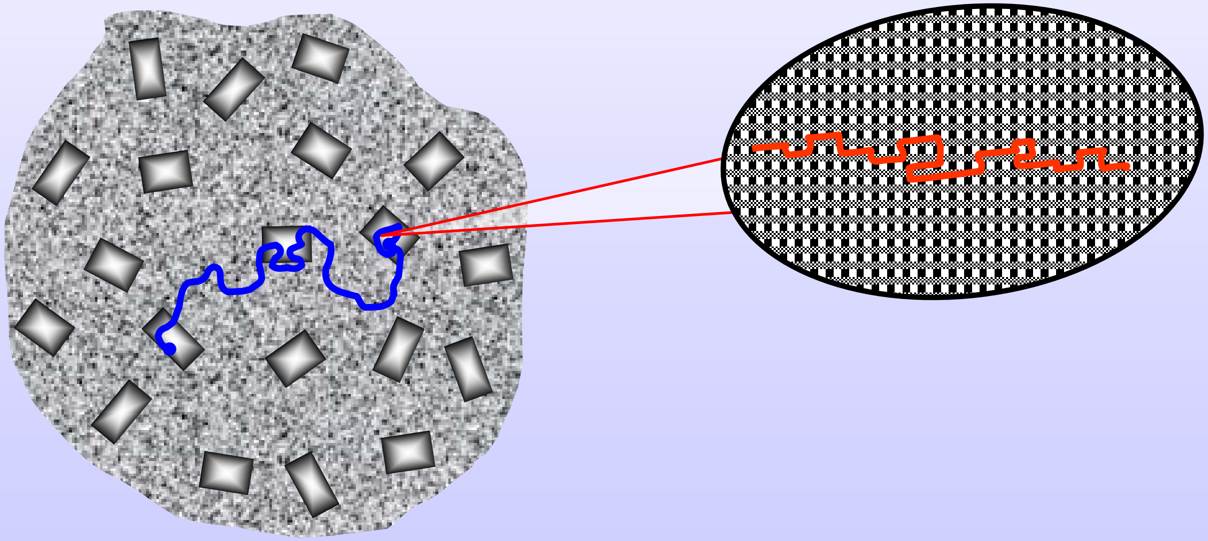
Second

$$\dot{c}^* = D \frac{\partial^2 c^*}{\partial x^2}$$

$$P(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

(PROPAGATOR)

typical host system (zeolite catalyst):



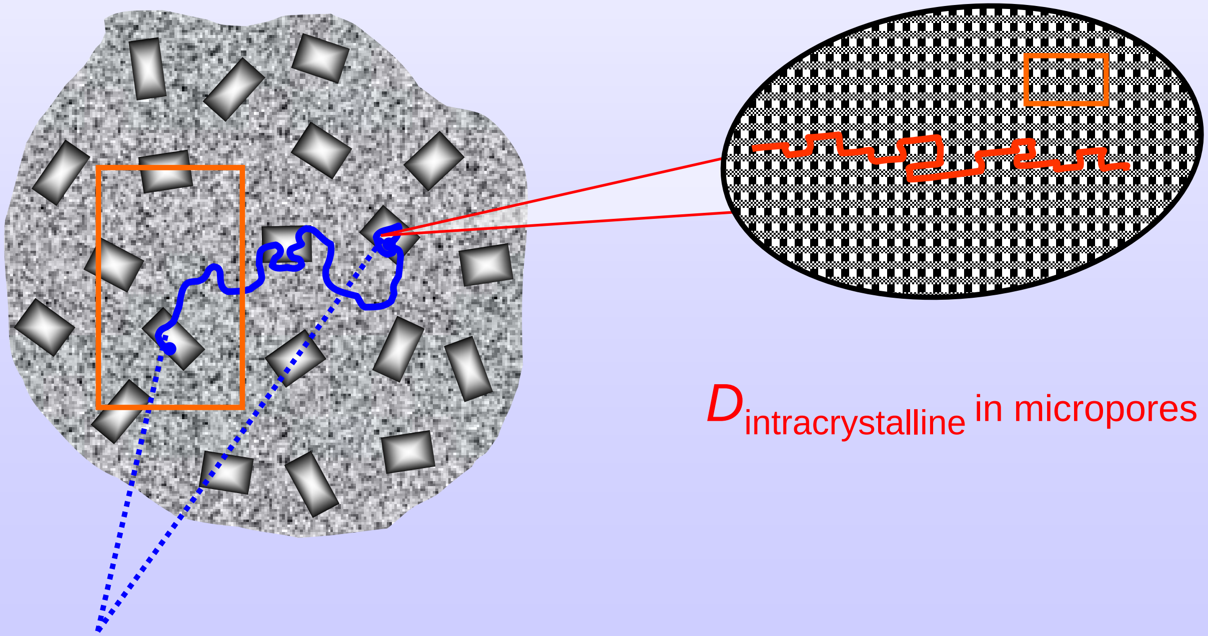
Time and Space Scales in the Diffusion Equation

relevant volume elements on considering

long-range (= intraparticle) diffusion

intracrystalline diffusion

typical host system (zeolite catalyst):



$D_{\text{intraparticle}}$

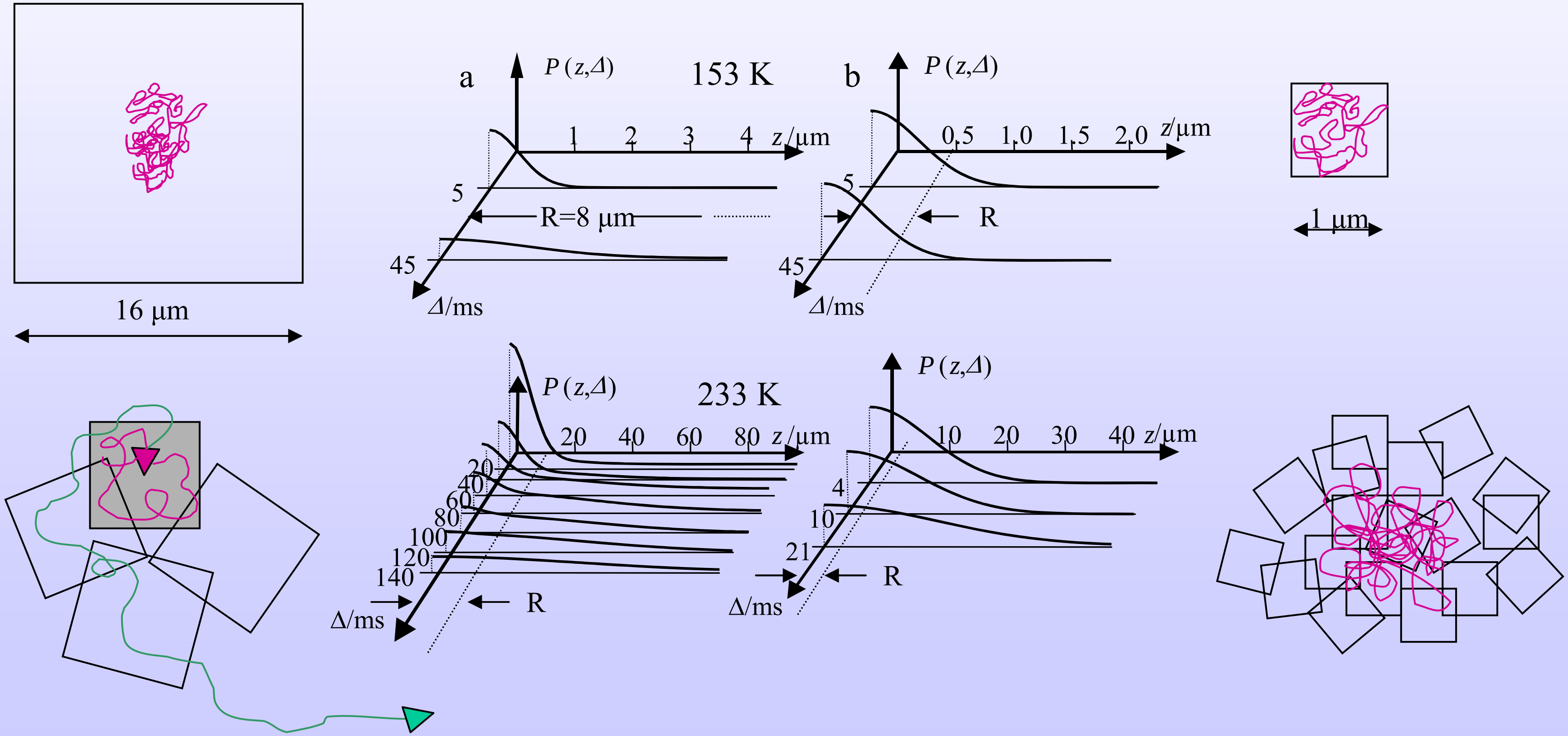
$D_{\text{intracrystalline}}$ in micropores of zeolite crystal

Molecular transport in pores does not necessarily lead to normal diffusion.

cf. Poster Abstracts
Dammers and Coppens, p. 128 (Poster 22),
Zschiegner et al., p. 184 (Poster 35)

Pulsed Field Gradient (PFG) NMR provides **PROPAGATOR** and hence easy means to ascertain normal diffusion

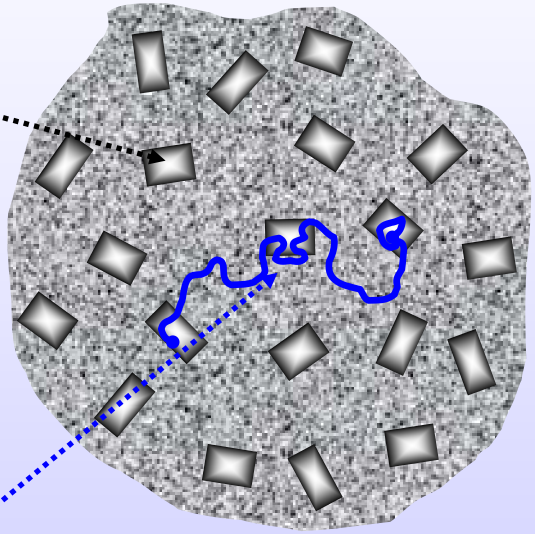
Mean Propagator for Ethane in Beds of NaCaA Crystallites of Different Size



complementary to single-particle tracking

Schob and Cichos 362 (10), Kirstein et al. 452 (116)

Outline:

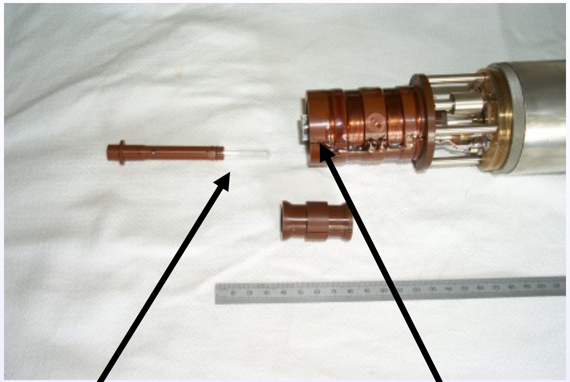


Intracrystalline
Zeolitic Diffusion

Anomalous Diffusion
in Porous Materials

Long-Range Diffusion
with Gas-Phase Intercepts

PFG NMR spectrometer FEGRIS400NT



Sample
d = 7.5 mm
l = 10 mm

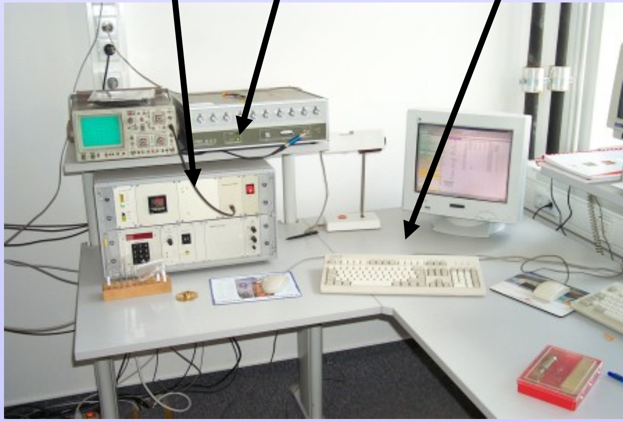
Gradient coil
$g \leq \pm 35$ T/m

Magnet
$B_0 = 9.4$ T

RF Generator

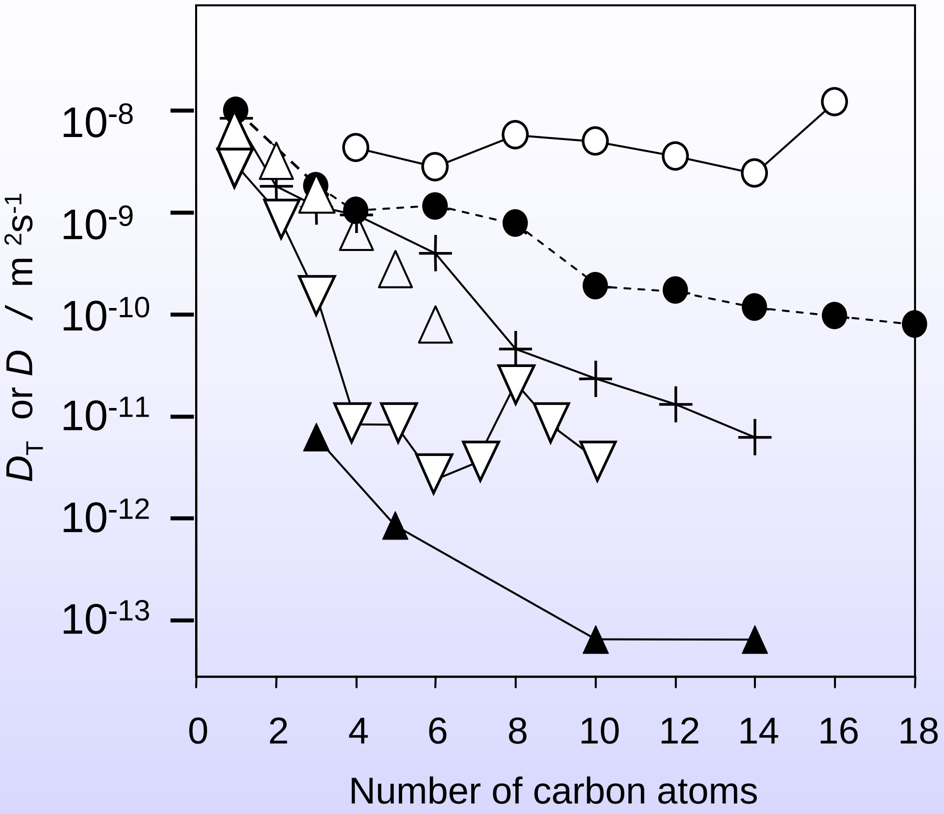
Temperature controller

PC



P. Galvosas, F. Stallmach, G. Seiffert, J. Kärger, U. Kaess, G. Majer, J. Magn. Reson. 151 (2001) 260

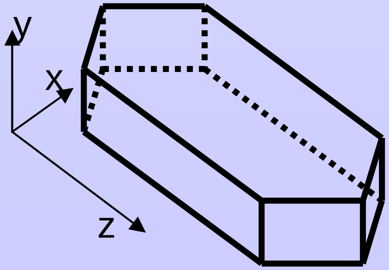
PFG NMR developments: Momot et al. 360 (9), Pampel 582 (97), Södermann and Topgaard 592 (92)

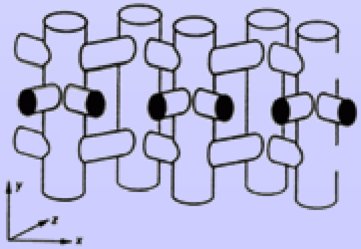


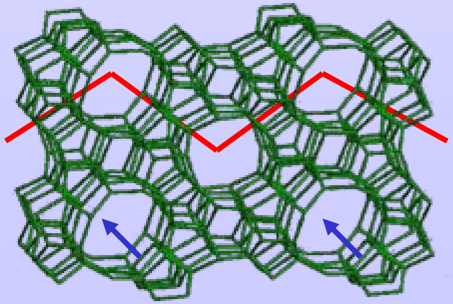
Coefficients of Intracrystalline Diffusion of n-Alkanes in Zeolite MFI at 300K (low concentrations) as a function of the carbon chain length, determined by

MD-simulation (○),
Brownian Dynamics (●),
QENS (+),
Permeation (∇),
ZLC (▲), and
PFG NMR (Δ).

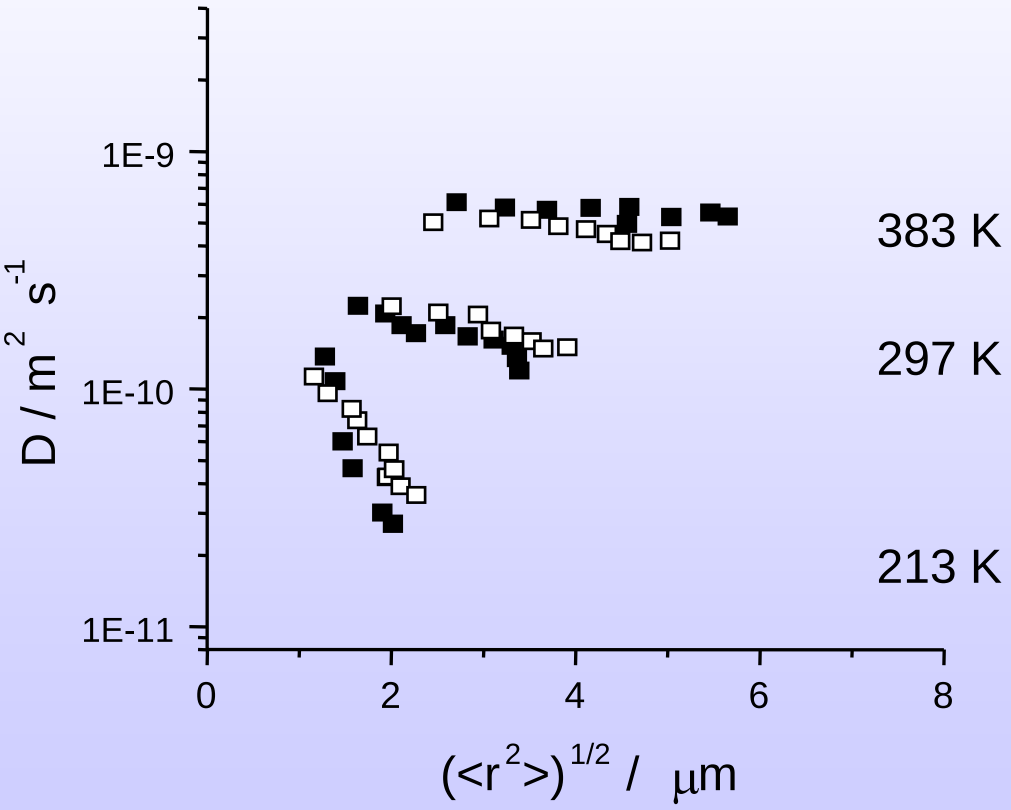
(H. Jobic, in: N.K. Kanellopoulos (Ed.) „Recent Advances in Gas Separation by Microporous Ceramic Membranes“, Elsevier, 2000)







Intracrystalline Diffusion

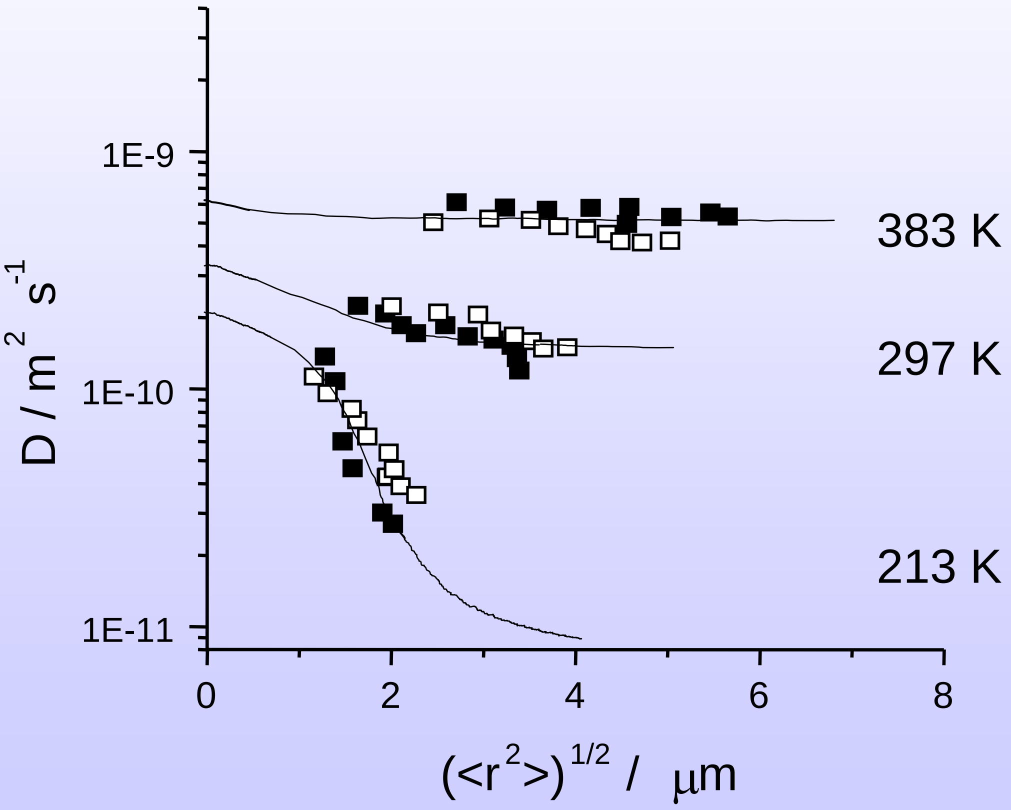


n-Butane/Silicalite-1

two sets of measurement with different samples

Intracrystalline Diffusion

Comparison of the PFG NMR results with the results of MC simulations



n-Butane/Silicalite-1

two sets of measurement with different samples

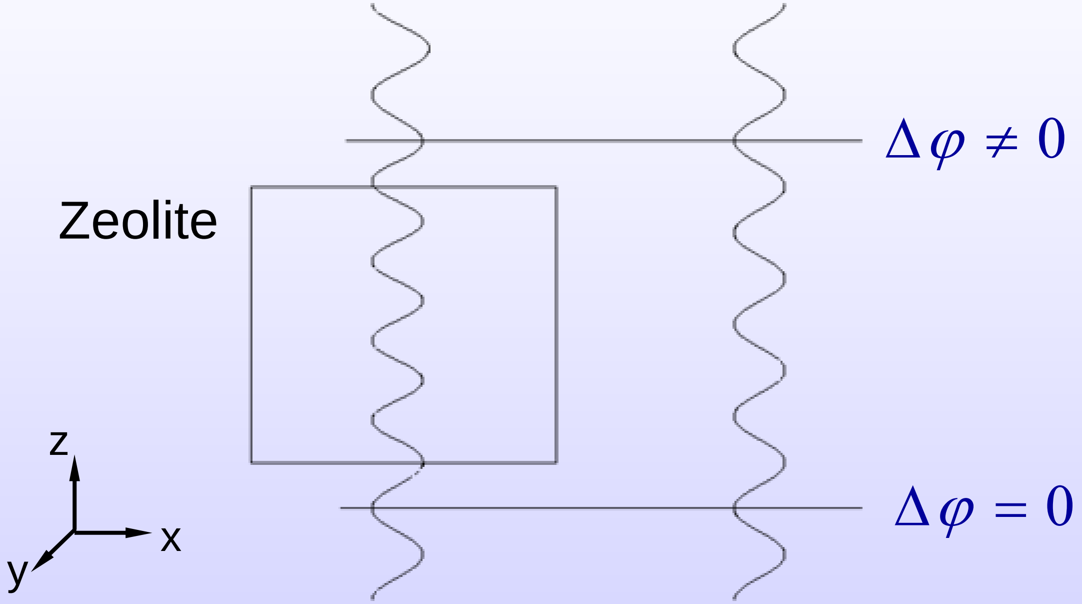
$p_y = 1$ $p_x = 0.32$
$p_z = 0.067$ [1]

$(E_b\text{-}E_d) = 21.5$ kJ/mol
N = 3000 (×1nm)

Aden et al. 424 (103), Takaba et al. 476 (125)

Measuring Principle of Interference Microscopy

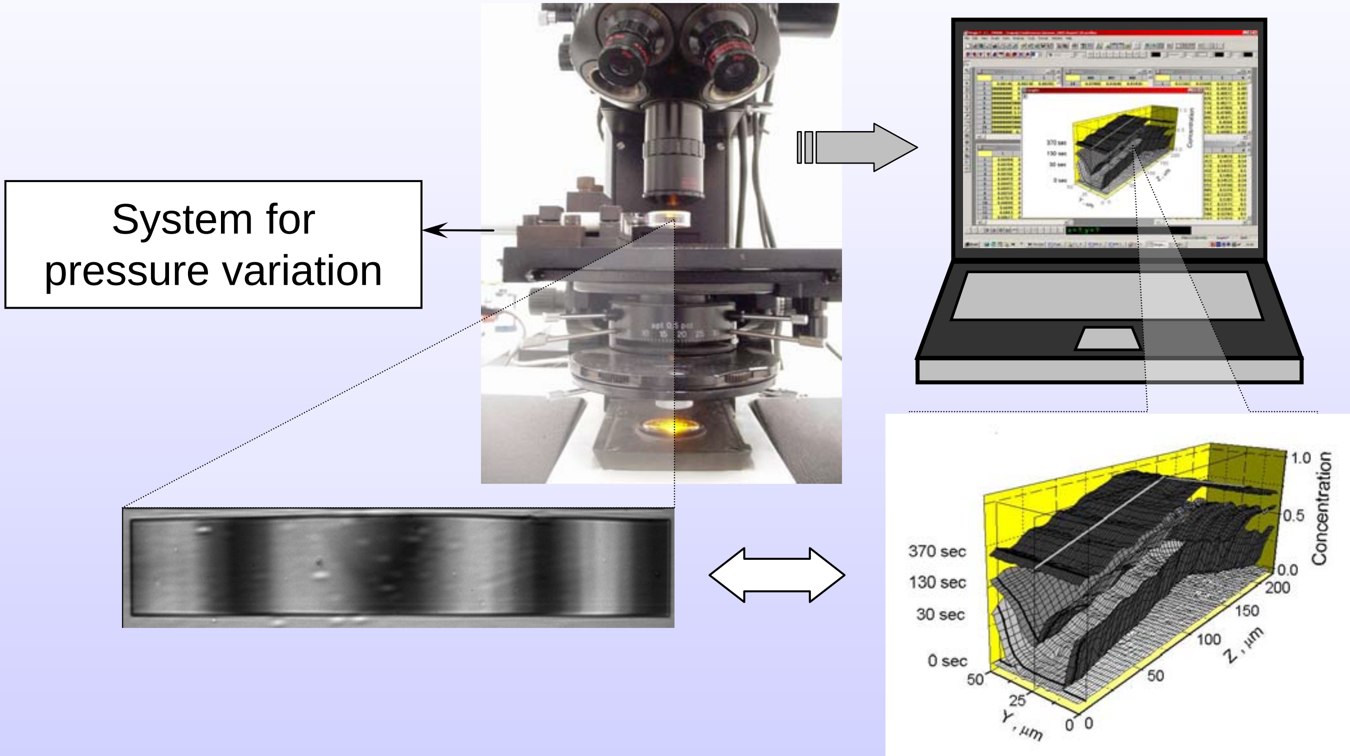
Interference of Beams through Zeolite and Gas Phase



Changing intracrystalline concentration yields change in phase difference $\Delta\varphi\,(x,y;t)$

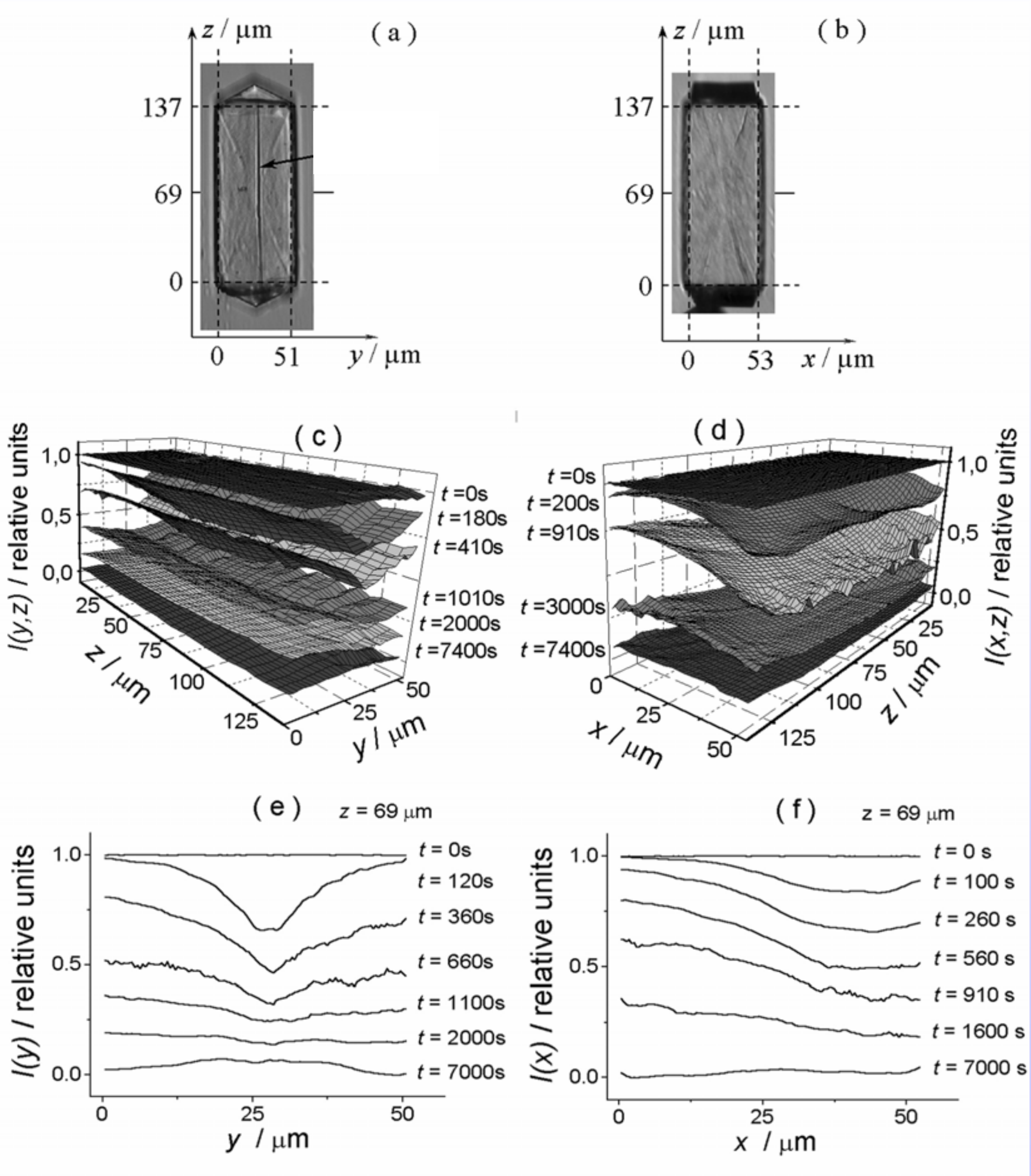
$$\boxed{\Delta\,(\Delta\varphi) \sim \Delta n \sim \Delta c}$$

Measuring Principle of Interference Microscopy

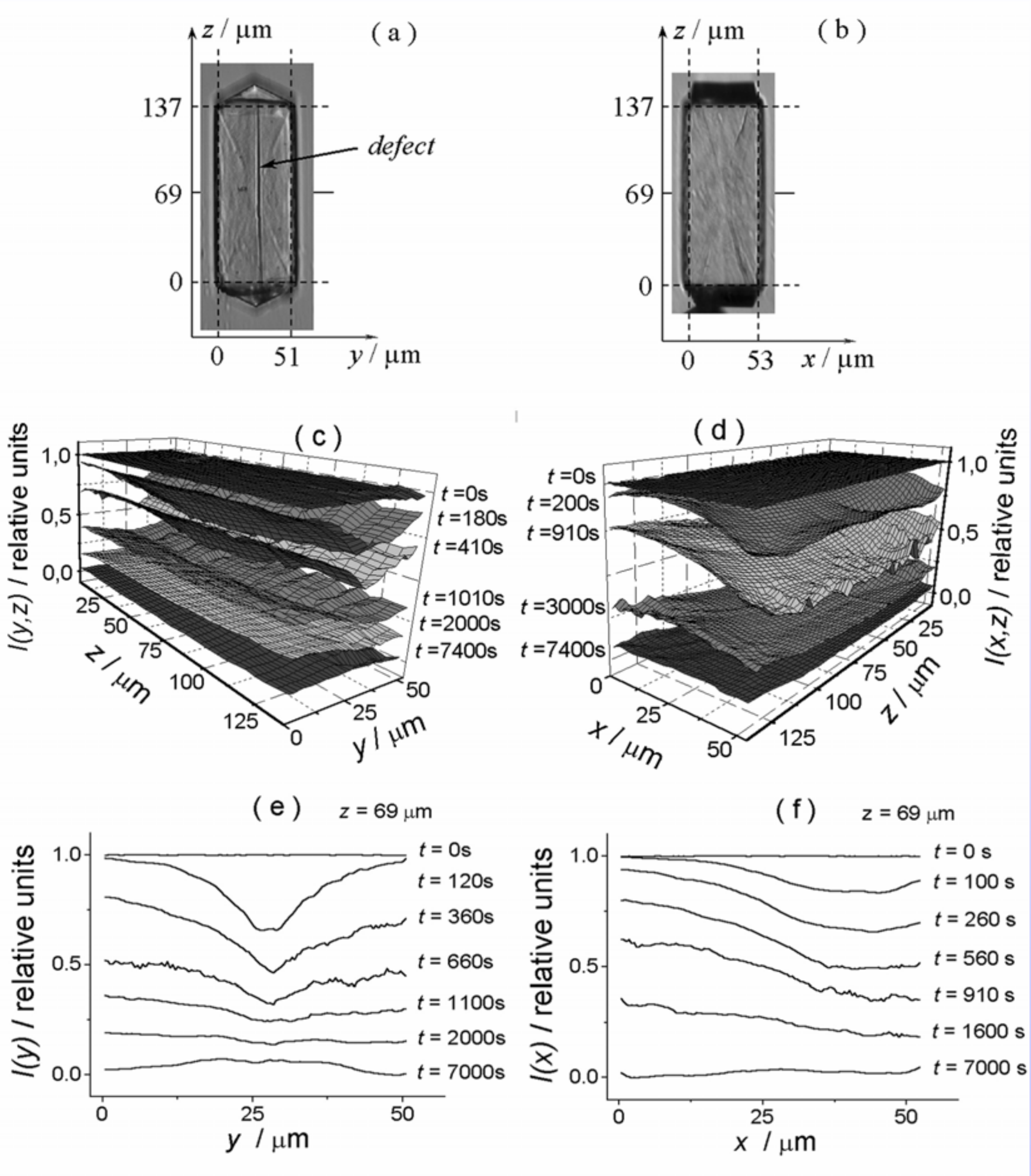


System for pressure variation

Monitoring the Desorption of Isobutane from MFI-type Crystallites



Monitoring the Desorption of Isobutane from MFI-type Crystallites



Medical diagnosis has attained such a high level

that there scarcely exist any really healthy people.

Physical

~~Medical~~ **diagnosis has attained such a high level**

perfect crystal

that there scarcely exist any really ~~healthy~~ ~~people~~**.**

International Research Group „Diffusion in Zeolites“

Bourdin et al. 430 (106); Brandani et al. 432 (133); Laloué et al. 460 (118)

Anomalous Diffusion in Porous Materials

? time dependence of mean square displacement $\left\langle x^2(t) \right\rangle$?

- Subdivide time *t* into n equal time intervals Δt : $\quad t = n\Delta t$

- Consider displacement Δx in each of these time intervals: $\quad x = \sum_{i=1}^{n} \Delta x_i$

$$\longrightarrow \quad \left\langle x^2(t) \right\rangle = \left\langle \left(\sum_{i=1}^{n} \Delta x_i \right)^2 \right\rangle = \sum_{i=1}^{n} \left\langle (\Delta x_i)^2 \right\rangle + \sum_{i \neq j=1}^{n} \left\langle \Delta x_i \Delta x_j \right\rangle$$

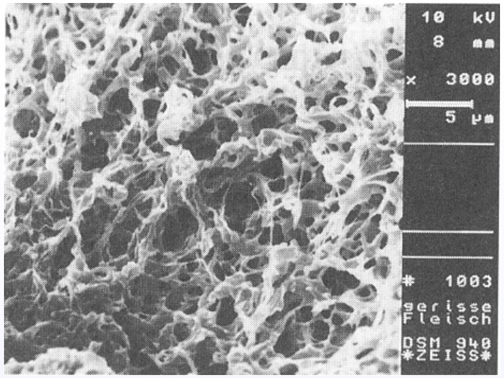
Normal Diffusion $\quad \left\langle x^2(t) \right\rangle = \sum_{i=1}^{n} \left\langle (\Delta x_i)^2 \right\rangle = n \left\langle (\Delta x_i)^2 \right\rangle \sim t$

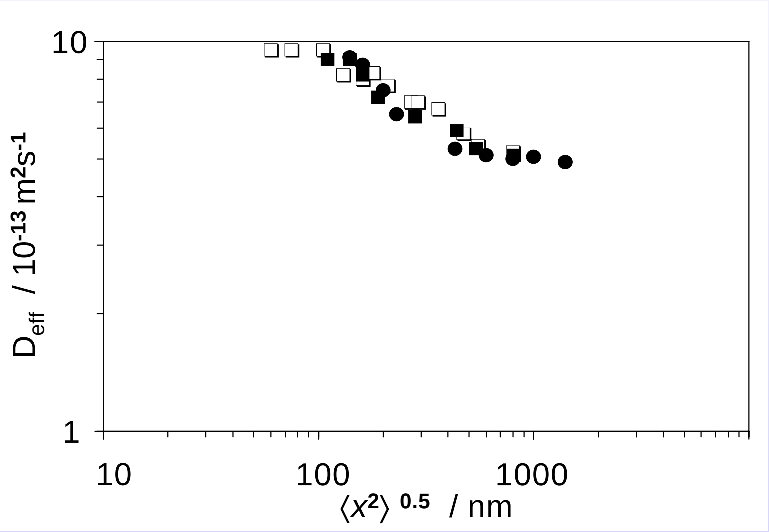
Anomalous Diffusion $\quad \left\langle x^2(t) \right\rangle \sim t^{\chi}$ with $\chi < 1$

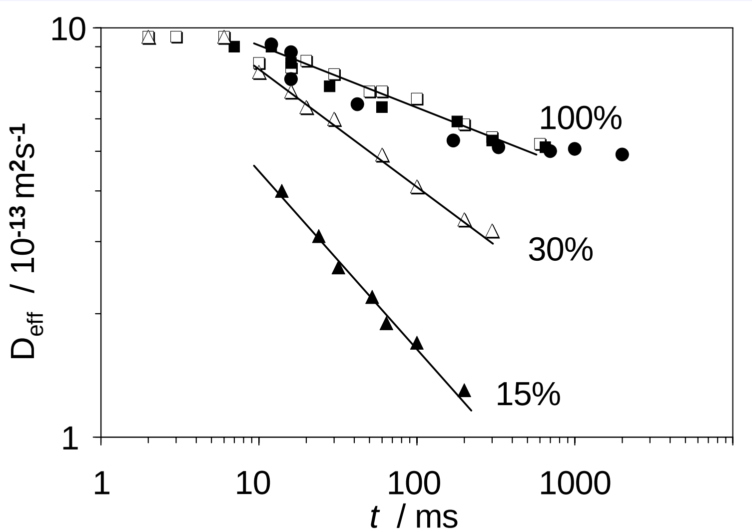
with $\quad D_{\mathrm{app}} = \dfrac{\left\langle x^2(t) \right\rangle}{2t} \longrightarrow D_{\mathrm{app}} \sim t^{\chi - 1} = \dfrac{1}{t^{1-\chi}}$

i.e. apparent diffusivities decreasing with time

Diffusion of PDMS in a polypropylene host matrix:



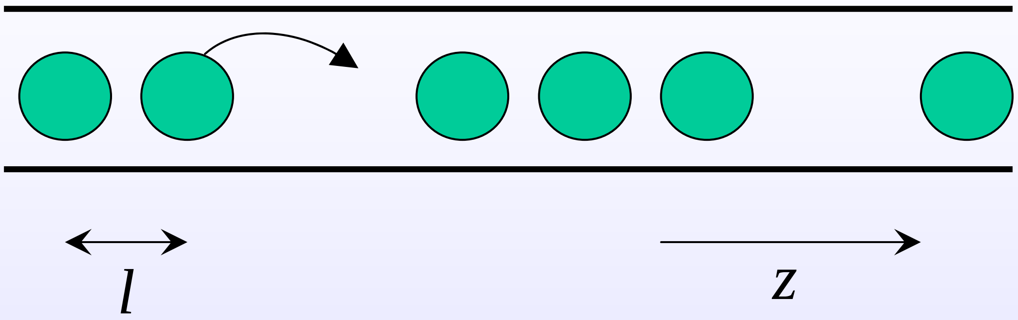




Dependence on the observed displacements at complete pore filling factors

Time dependence for different pore filling factors

Anomalous Diffusion in Porous Materials
Molecular Transport in One-Dimensional Channels: Single-File Diffusion



$$\boxed{P(z,t)=\left(2\pi\left\langle z^2(t)\right\rangle\right)^{-\frac{1}{2}}\exp\left(-\frac{z^2}{2\left\langle z^2(t)\right\rangle}\right)}$$

with $\left\langle z^2(t)\right\rangle = 2F\sqrt{t}$

in contrast to ordinary diffusion, where

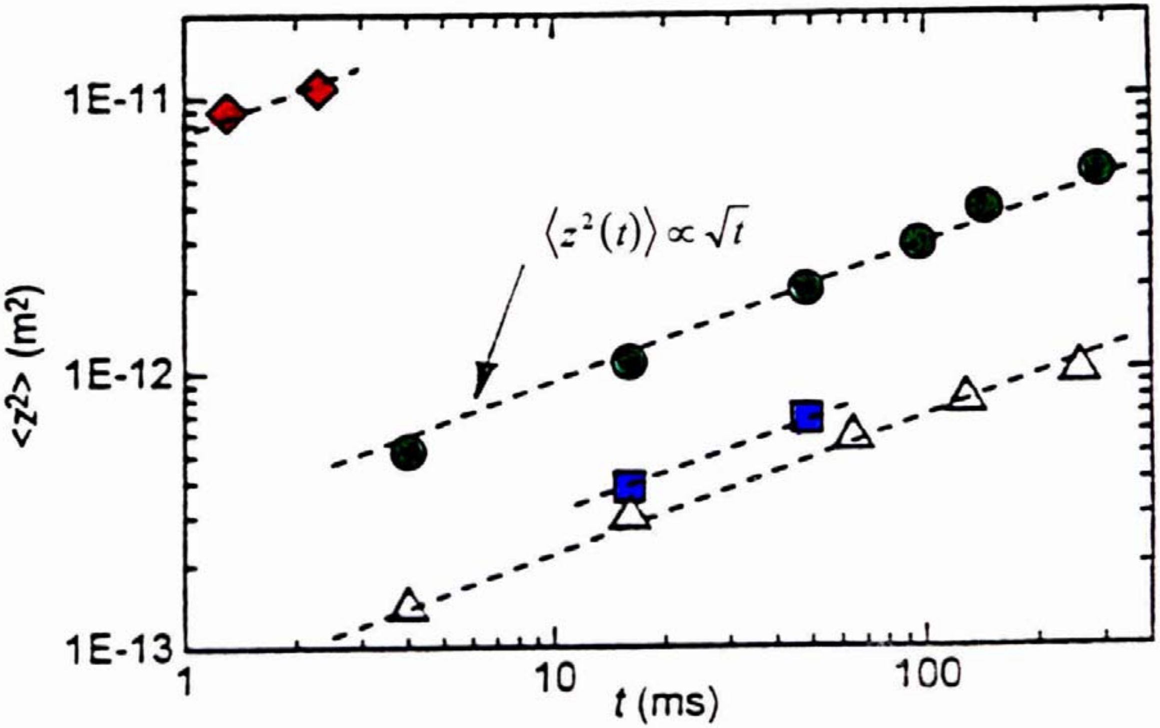
$$\left\langle z^2(t)\right\rangle = 2Dt$$

and $F = (2\pi\tau)^{-1/2}\, l^2\, \dfrac{1-\Theta}{\Theta}$

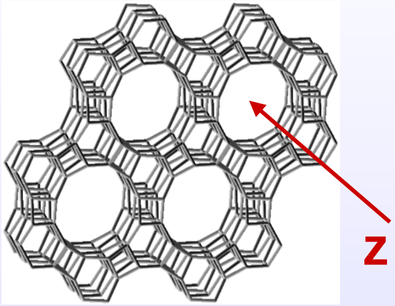
Anomalous Diffusion in Porous Media
Single-File Diffusion

CF_4 in $AlPO_4$-5

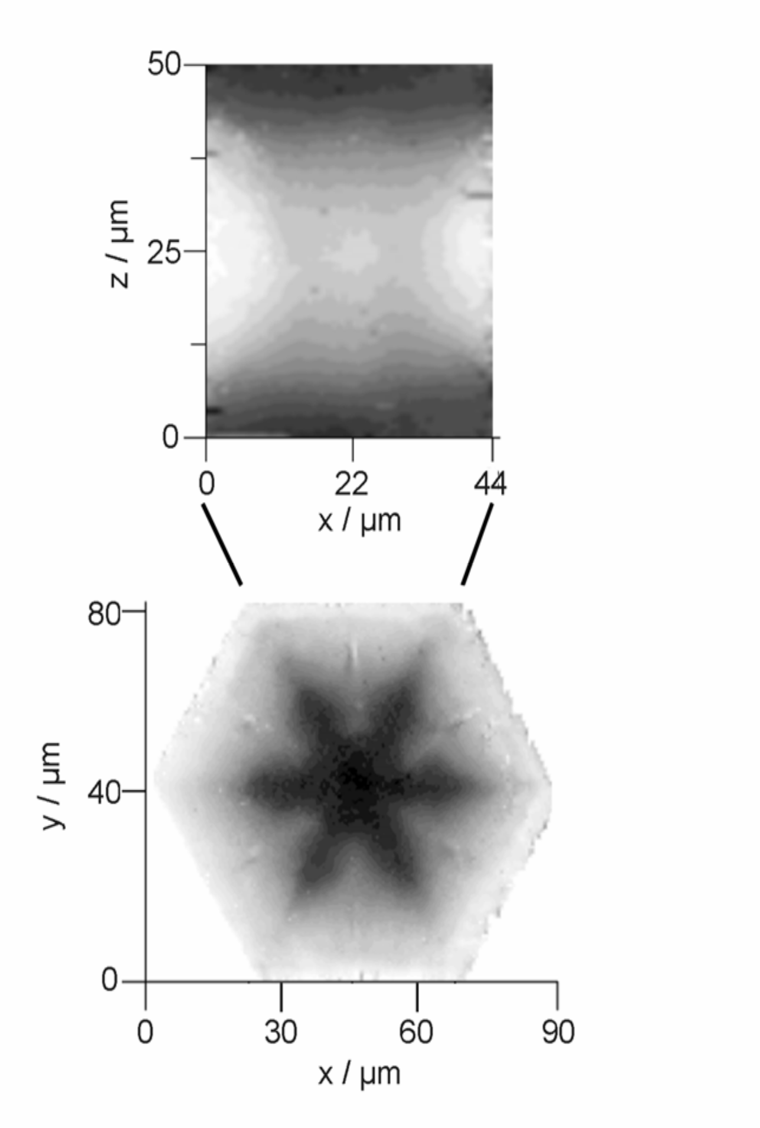
(180 K)

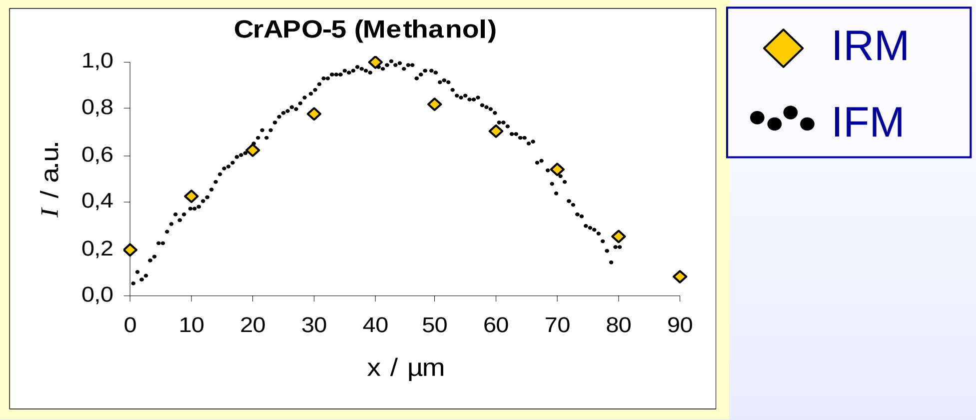


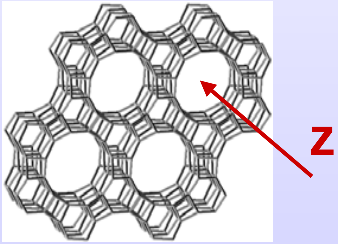
0.005 (◆), 0.05 (●), 0.2 (■), 0.4 (△)
molecules per unit cell



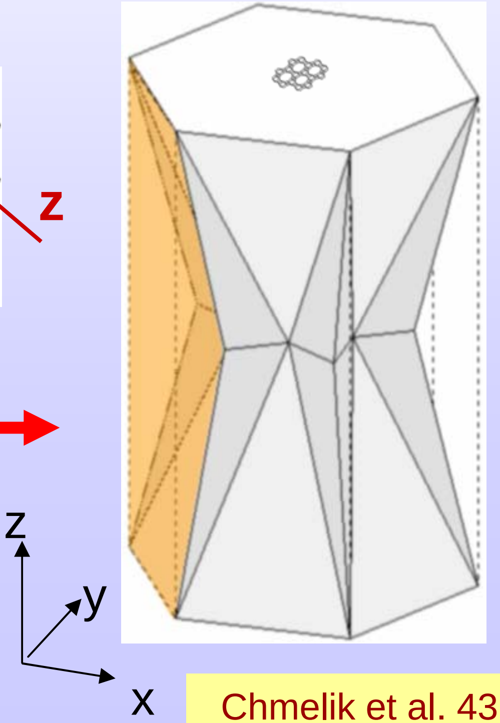
Equilibrium intracrystalline concentration profiles of methanol in a CrAPO-5 crystal





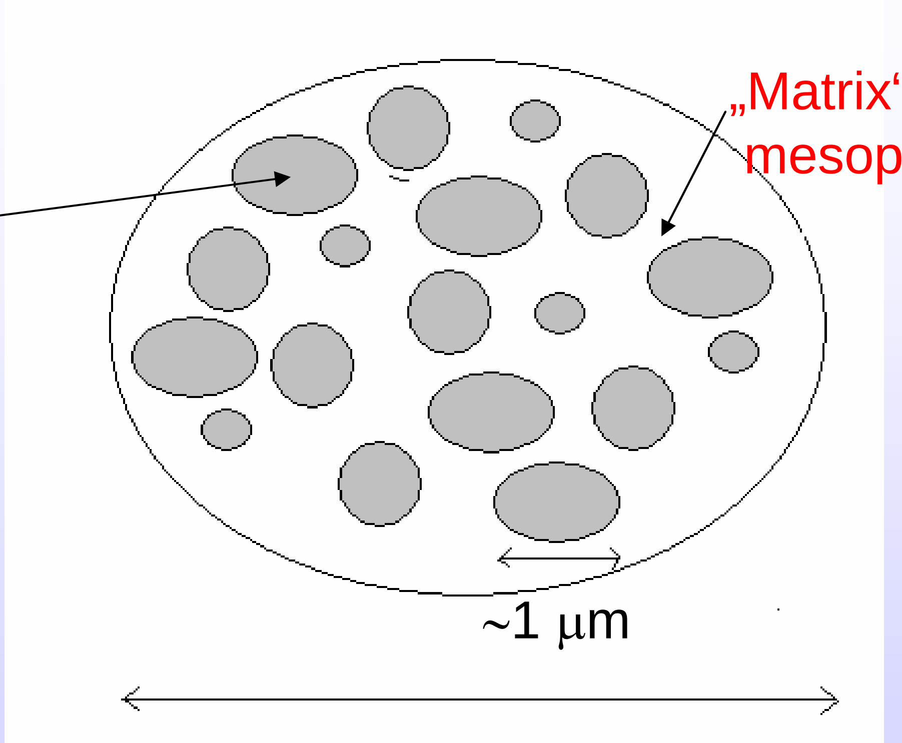


the crystal section inaccessible for methanol



Chmelik et al. 436 (130)

Long-Range Diffusion
Diffusion in FCC$^{+)}$ catalysts



intergrown zeolite crystals

„Matrix“ (SiO_2, Al_2O_3...), mesopores

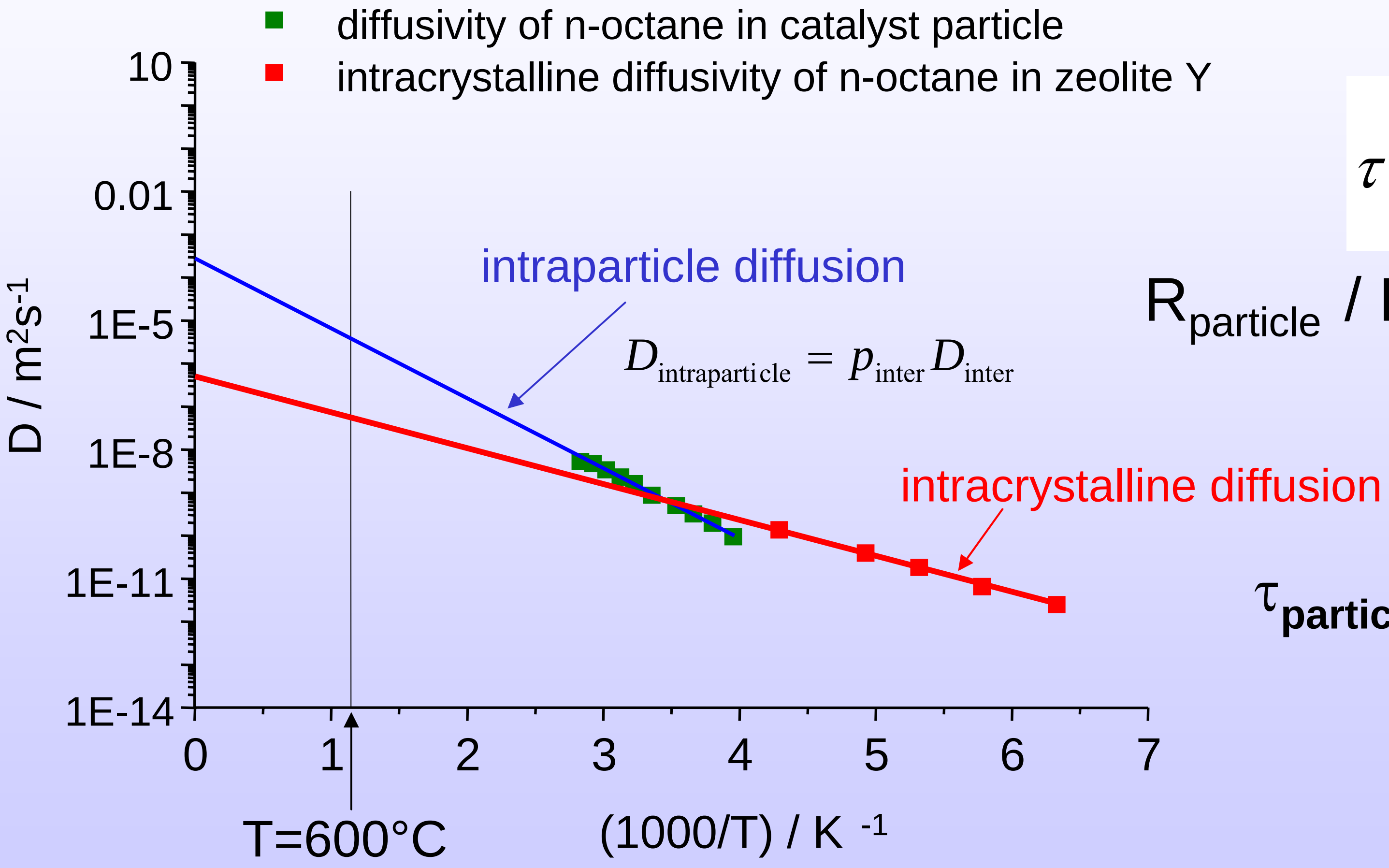
~40 µm

Intraparticle diffusivities

size of intergrown crystals $<<$ $\sqrt{\langle r^2 \rangle}$ $<<$ size of catalyst particle

$^{+)}$ Fluid Catalytic Cracking

n-Octane Diffusion in FCC+) catalysts



$$D_{\text{intraparticle}} = p_{\text{inter}} D_{\text{inter}}$$

$$\tau \sim \frac{R^2}{D}$$

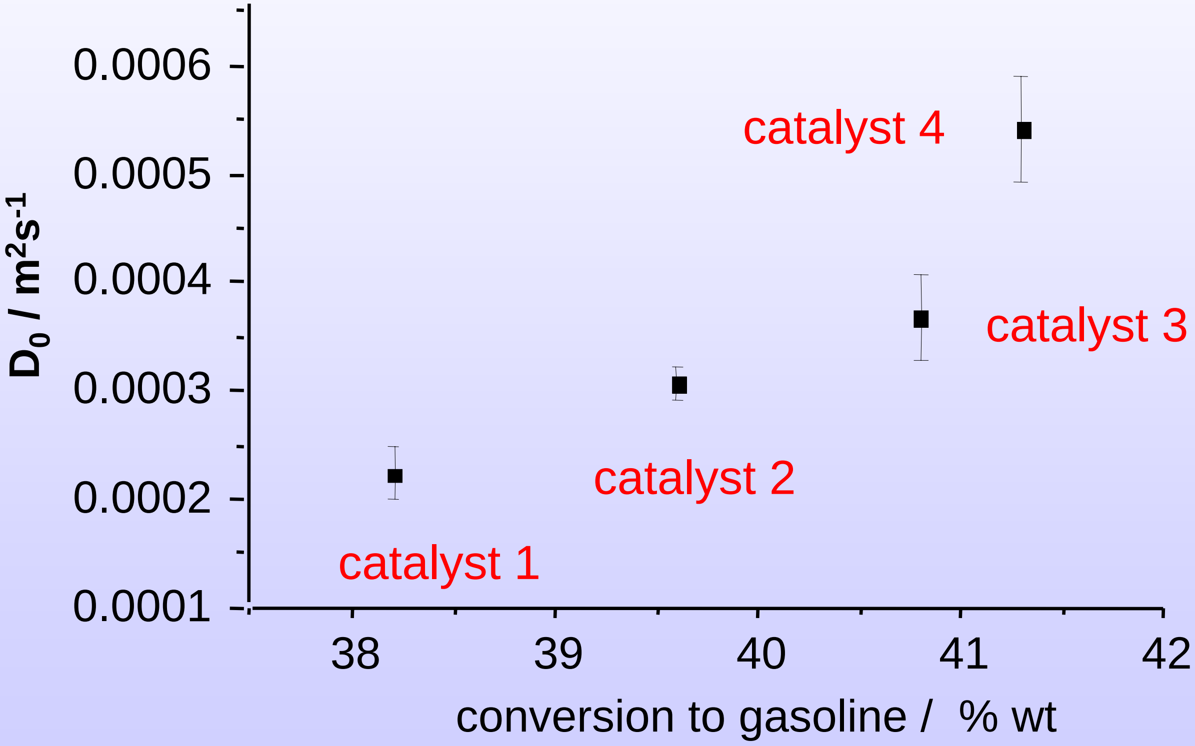
$R_{\text{particle}} / R_{\text{crystal}} \sim 40$

$\tau_{\text{particle}} \geq \tau_{\text{crystal}}$

+) Fluid Catalytic Cracking

Kortunov et al. 458 (140)

Correlations between intraparticle diffusivities and catalytic performance

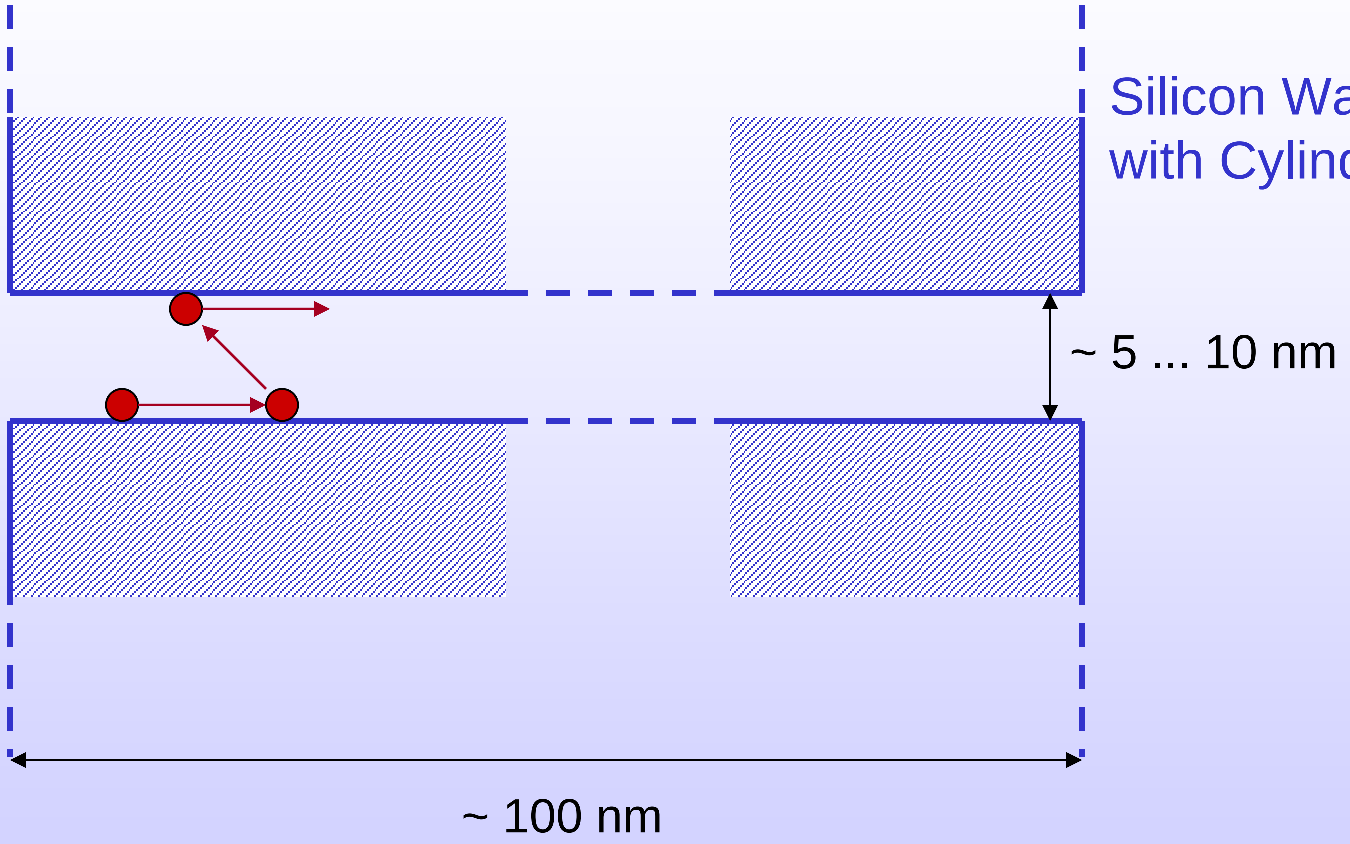


n-octane, 0.62 mmol/g

larger intraparticle diffusivity corresponds in all cases to higher catalytic activity

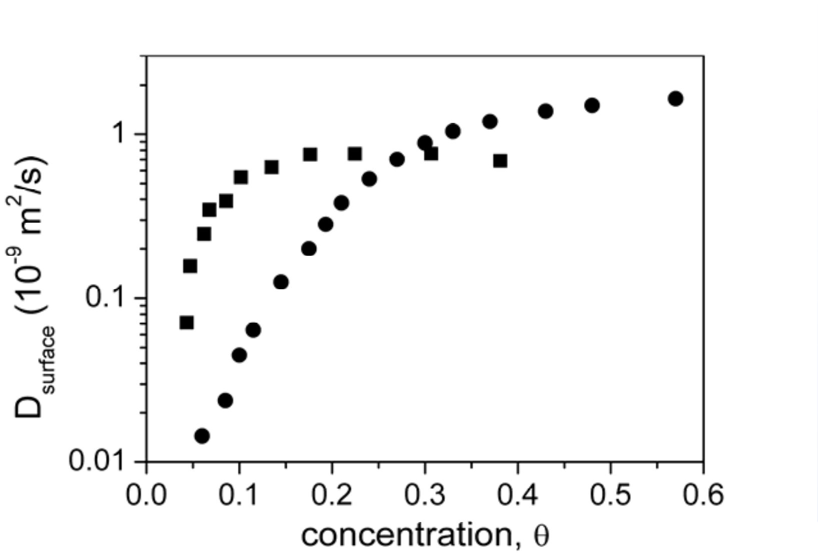
Kortunov et al. 458 (140)

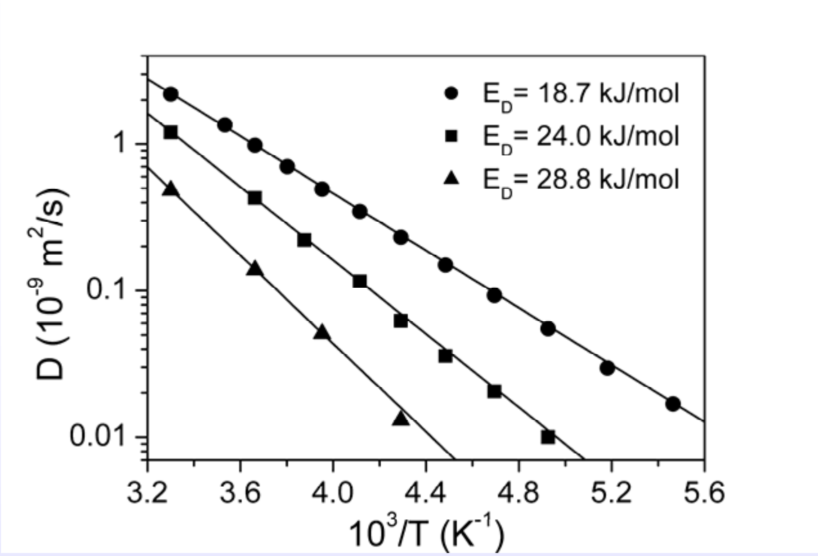
Long-Range Diffusion in Mesopores



$$D_{\text{long-range}} = p_{\text{surface}}\, D_{\text{surface}} + p_{\text{gas}}\, D_{\text{gas}}$$

Diffusion on Silicon Surfaces



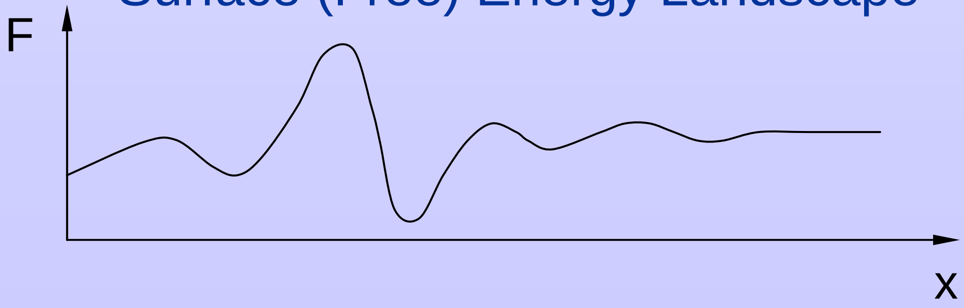


$D_{surface}$ of cyclohexane (squares)
and acetone (circles) in porous
silicon at T = 297K
as a function of loading

Arrhenius plots of $D_{surface}$
for acetone at Θ = 0.6 (circles),
Θ = 0.27 (squares)
and Θ = 0.18 (triangles)

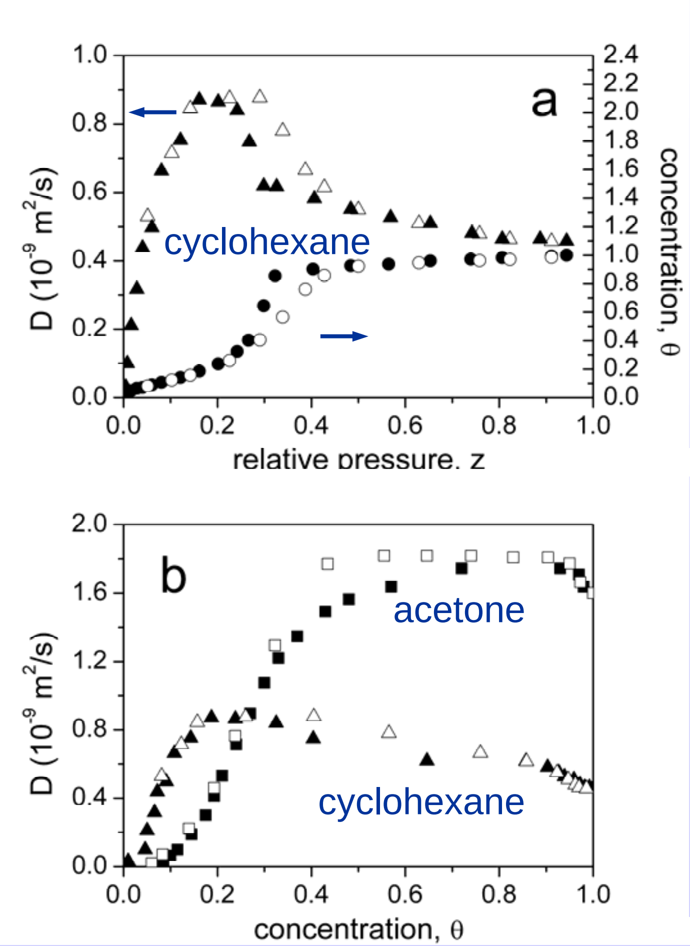
?

Surface (Free) Energy Landscape



Adsorption Hysteresis

How Past rather than Presence Controls Molecular Mobilities

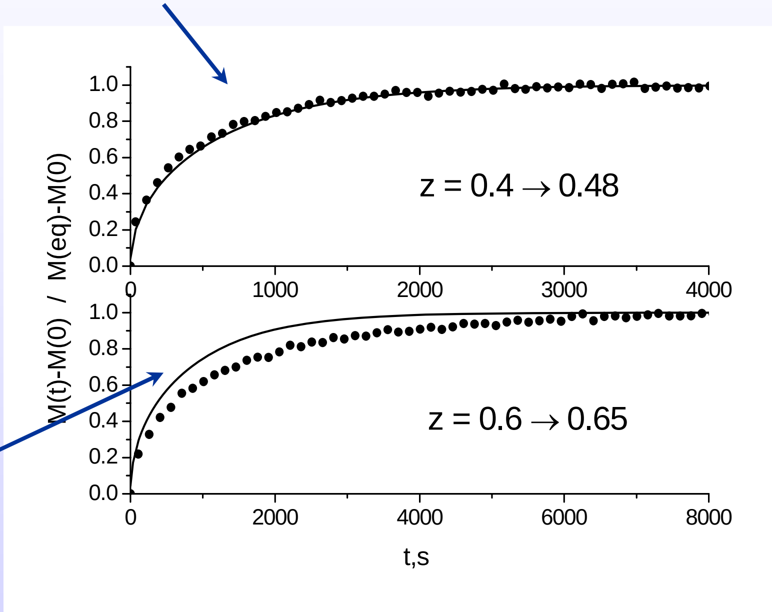


PFG NMR Studies of Hysteresis in Porous Silicon

open symbols: adsorption branch

closed symbols: desorption branch

Excellent agreement between experimental uptake and PFG NMR prediction



Uptake is dramatically slowed down in the range of hysteresis

Combined PFG NMR and Uptake Studies of Hysteresis of Cyclohexane in Vycor Porous Glass

Valiullin et al. 478 (139)

I am deeply obliged to many colleagues and friends in Germany and abroad, particularly to my co-workers and students

Ulf Schemmert Frank Stallmach Karsten Hahn

Frank Rittig

Petrik Galvosas Volker Kukla

as well as to:

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Cordula Krause, Sergey Naumov, Günter Seiffert, Rustem Valiullin, Sergey Vasenkov

for cordial cooperation