Package of Research Projects **"Diffusion in Zeolites"**

by CNRS (France), DFG (Germany), EPSRC (United Kingdom), NSF (USA)

Extension for the Period from 2006-2009

Project 5

Studying Zeolitic Diffusion by Interference and IR Microscopy

Jörg Kärger

Sergey Vasenkov (Gainesville, University of Florida)

Pavel Kortunov (Exxon-Mobil)

Christian Chmelik

DB Shah (Cleveland University)

Lars Heinke

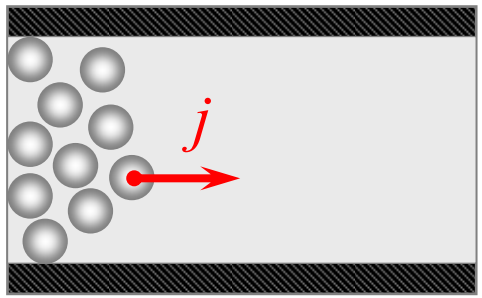
Despina Tzoulaki

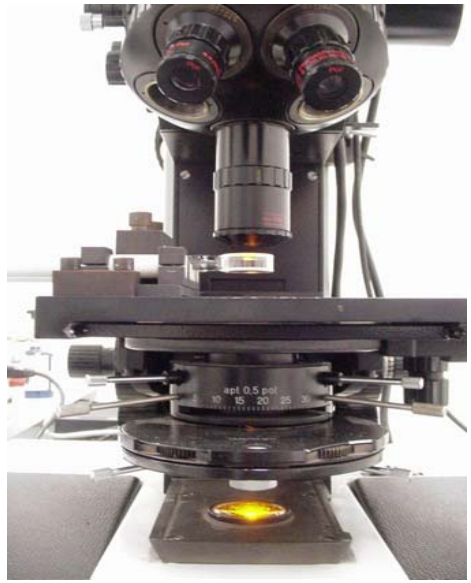
What do we measure?

Interference Microscopy (IFM)

$$j = - D_{(T)} \, \mathrm{grad} \, c$$

transport diffusion

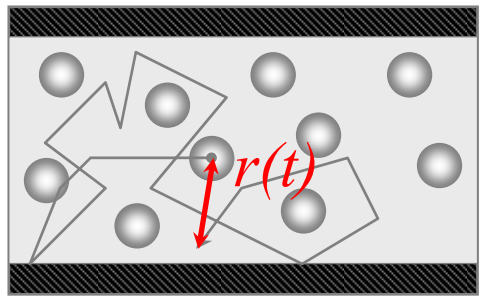




Pulsed Field Gradient (PFG) NMR

$$\langle r^2(t) \rangle = 2D\,t$$

self-diffusion



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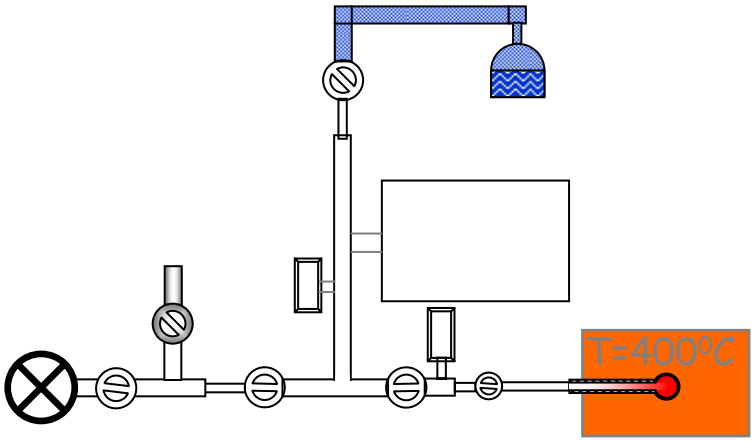
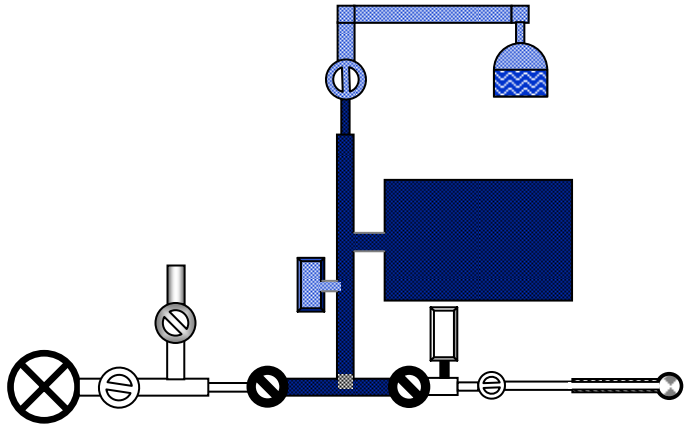
Adsorption system and cycles

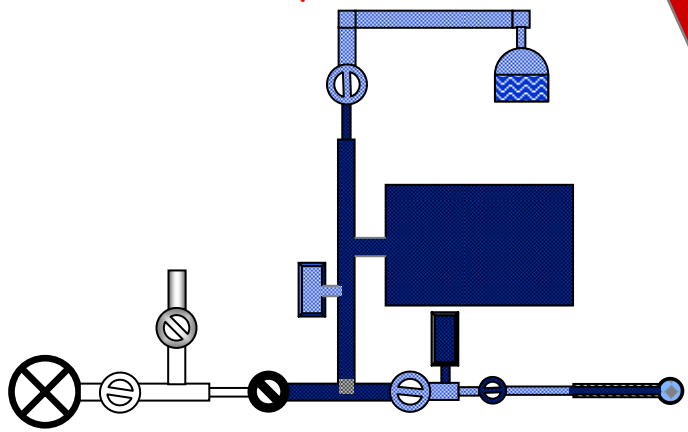
1. Pumping / Activation



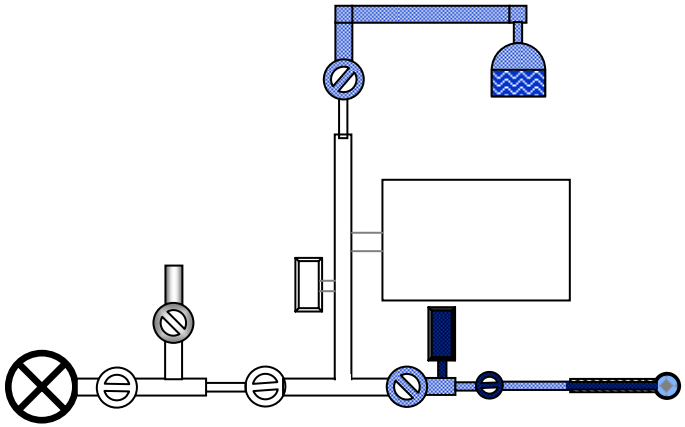
2. Preparation for adsorption



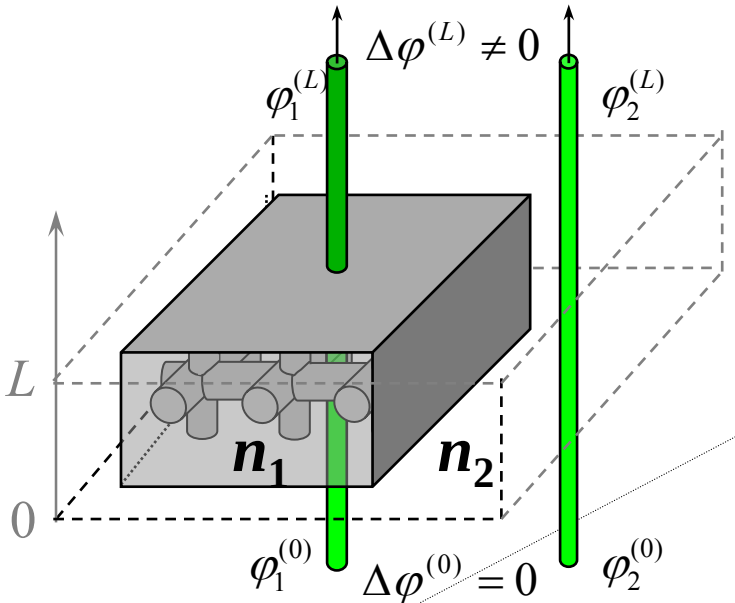
3. Adsorption

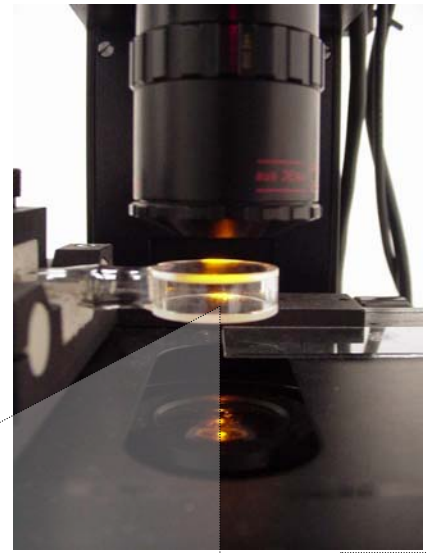


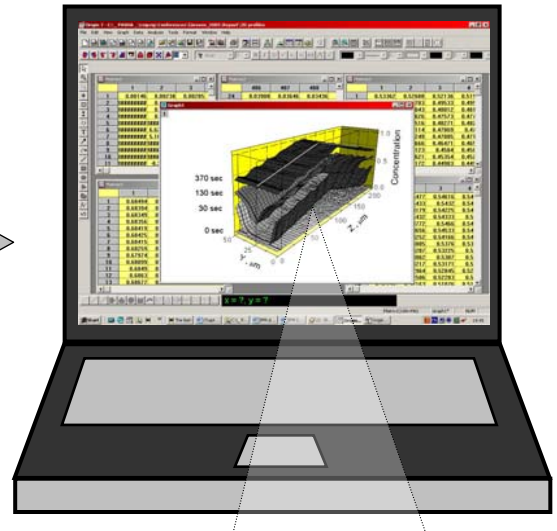
4. Preparation for desorption



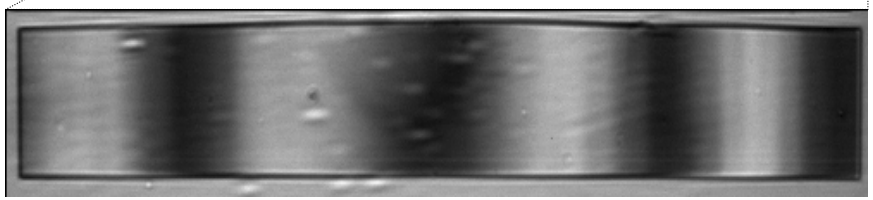
IFM Technique

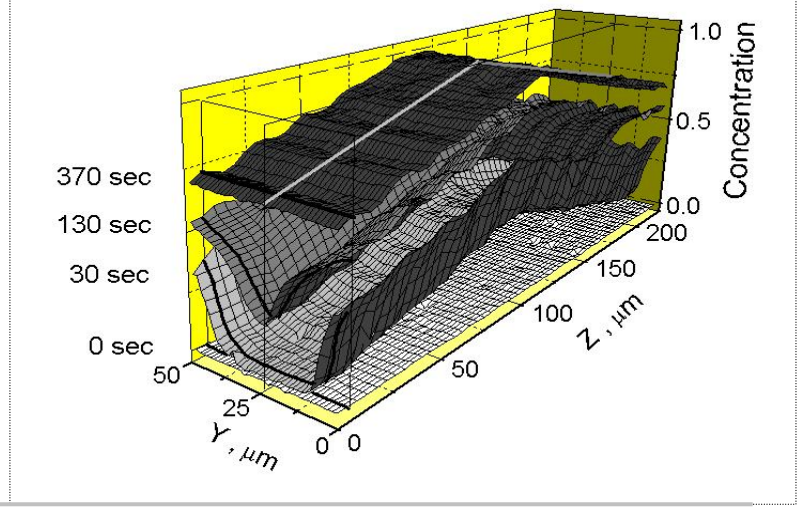






$$\Delta\varphi \sim \Delta n \sim \Delta c$$





Spatial resolution: 0.5 μm × 0.5 μm

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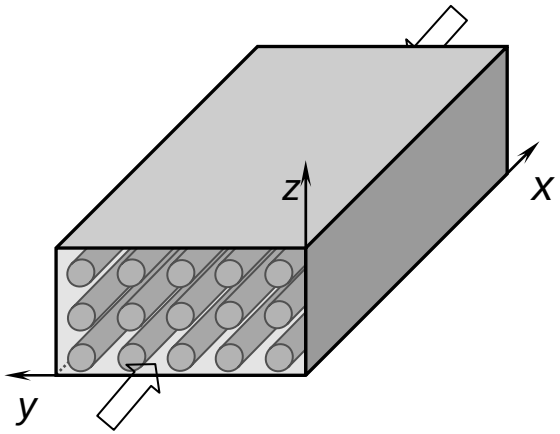
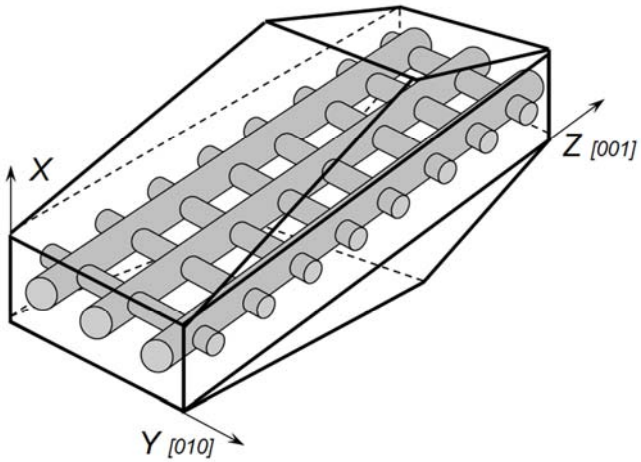
Outline

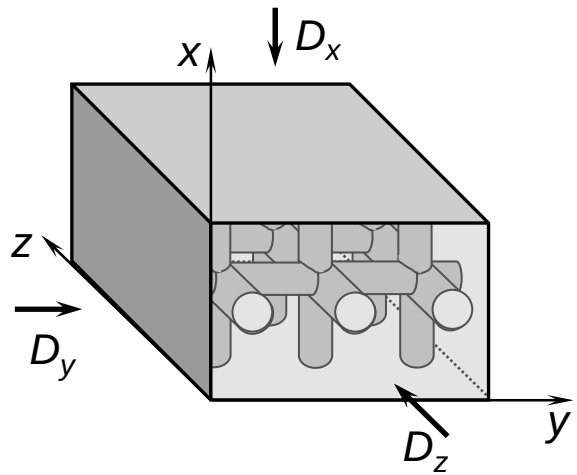
(a) 1-D pore structure of the MOF crystals



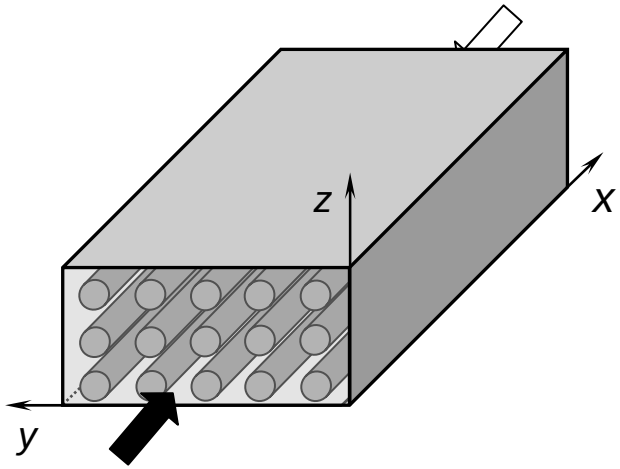
(b) 2-D pore structure of the Ferrierite zeolite



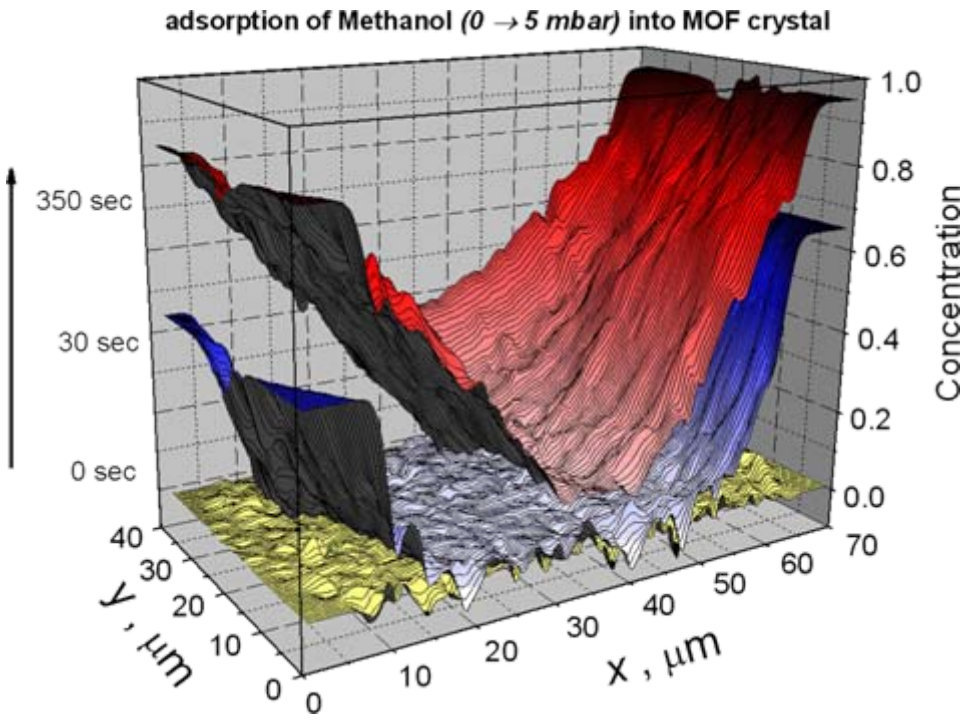
(c) 3-D pore structure of the SAPO STA-7



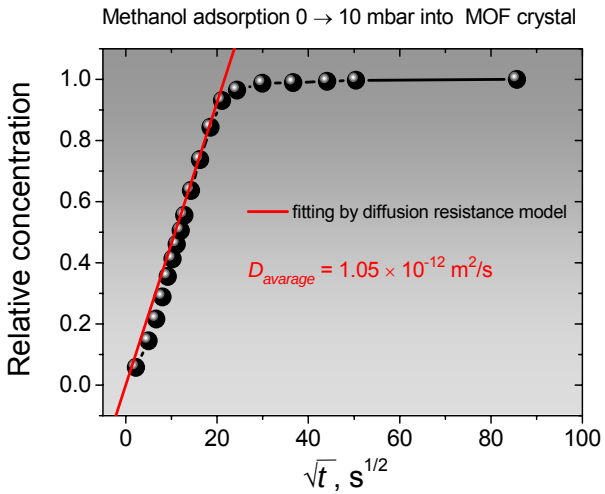
1-D pore structure of MOF crystal (*)



Interference microscopy technique:



Macroscopic adsorption techniques:



(*) D.N. Dybtsev, H. Chun, S.H. Yoon, D. Kim and K. Kim; *J. Am. Chem. Soc.*, 2004, 126, 32-33

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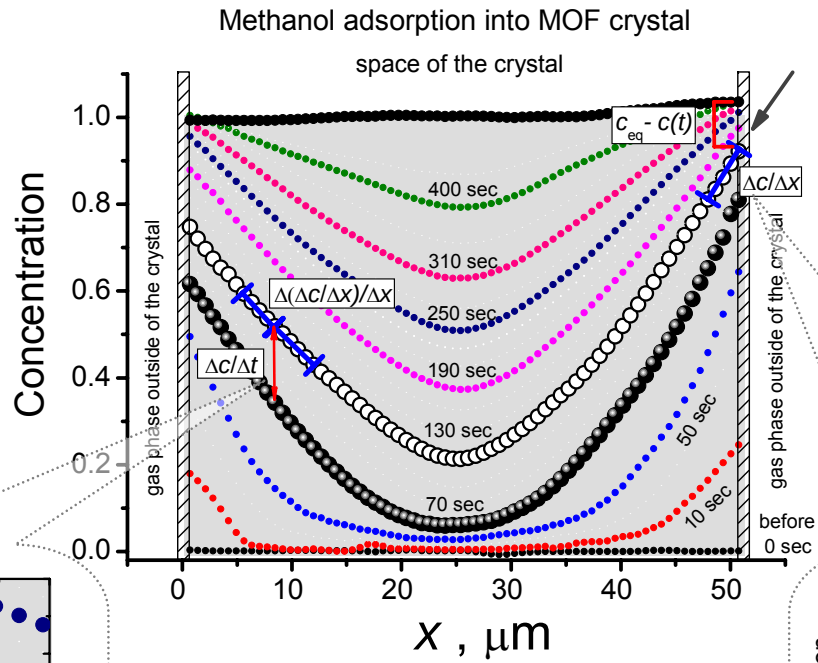
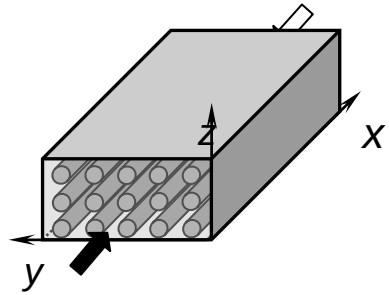
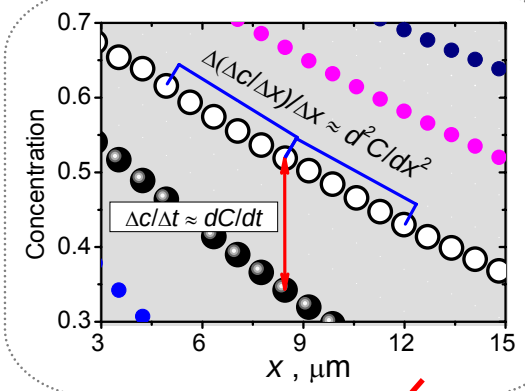
First and second Fick's laws

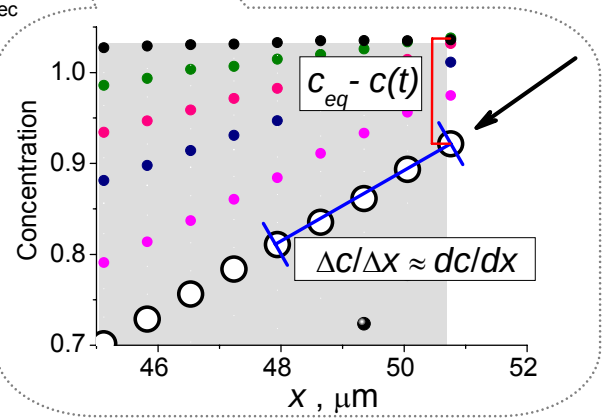




Local DIFFUSION



Surface PERMEABILITY



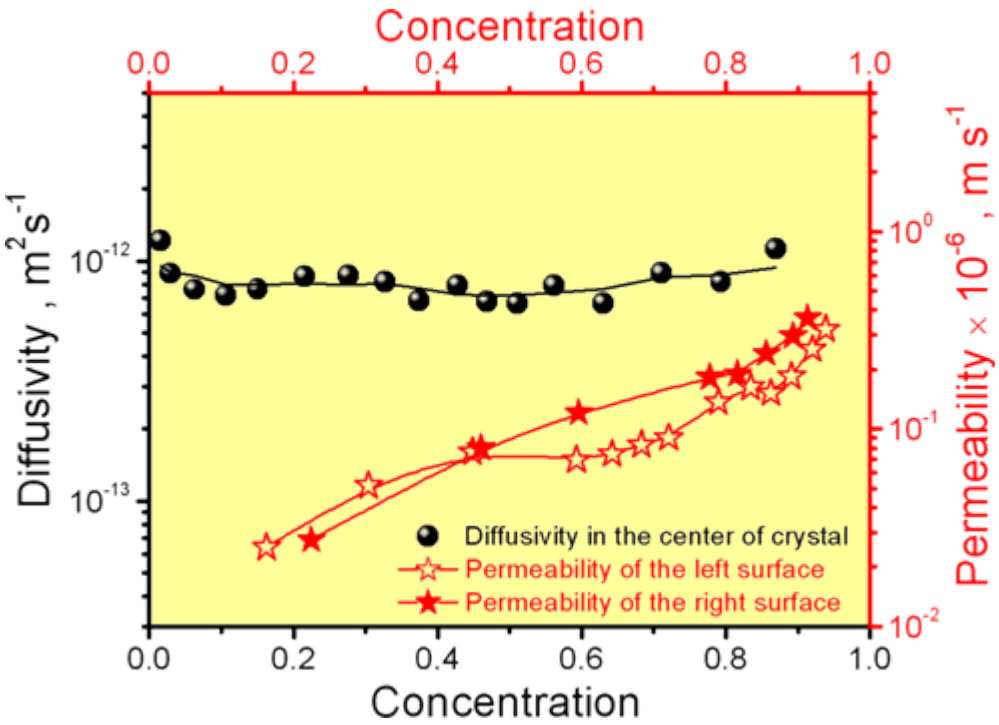
$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D(c,x)\frac{\partial c}{\partial x}\right] = D(c,x)\frac{\partial^2 c}{\partial x^2} + \frac{\partial D(c,x)}{\partial c}\cdot\left(\frac{\partial c}{\partial x}\right)^2$$

$$j = \alpha\left(c_{eq} - c(t)\right) = D\left(c(t)\right)\cdot\frac{dc}{dx}$$

1-D diffusion in the MOF crystal

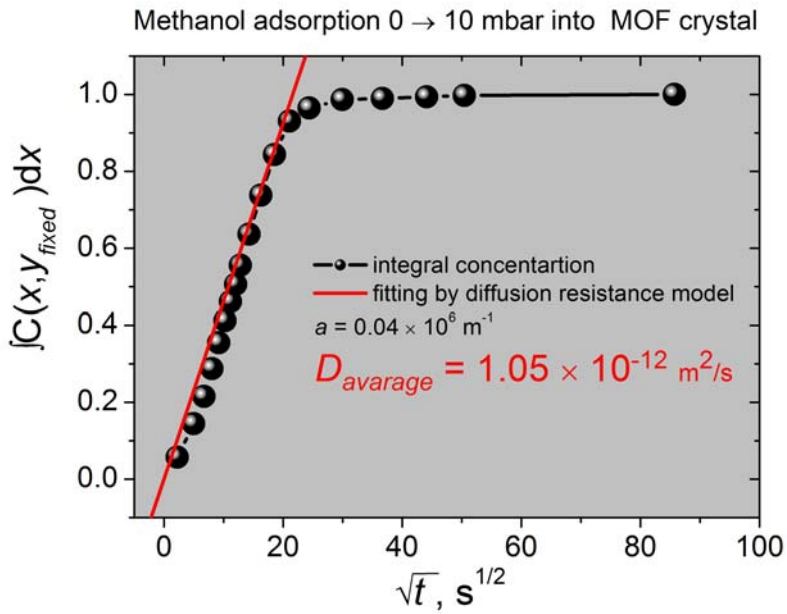
Local DIFFUSION
(microscopic analysis)

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D(c,x)\frac{\partial c}{\partial x}\right] = D(c,x)\frac{\partial^2 c}{\partial x^2} + \frac{\partial D(c,x)}{\partial c}\cdot\left(\frac{\partial c}{\partial x}\right)^2$$



Average DIFFUSION
(macroscopic analysis)

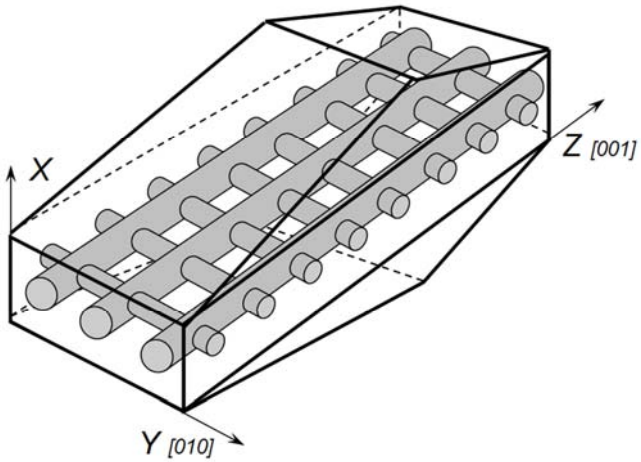
$$\frac{c_t - c_0}{c_\infty - c_0} \approx 2a\sqrt{\frac{Dt}{\pi}}$$



Outline

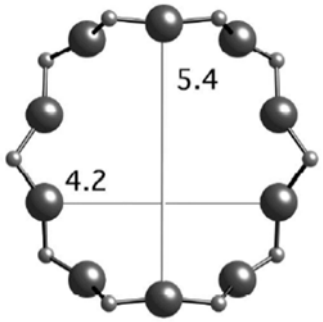
(a) 1-D pore structure of the MOF crystals

(b) 2-D pore structure of the Ferrierite zeolite

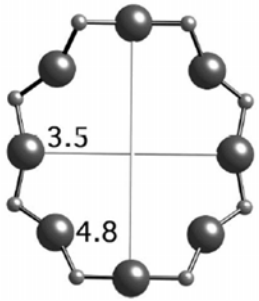


(c) 3-D pore structure of the SAPO STA-7

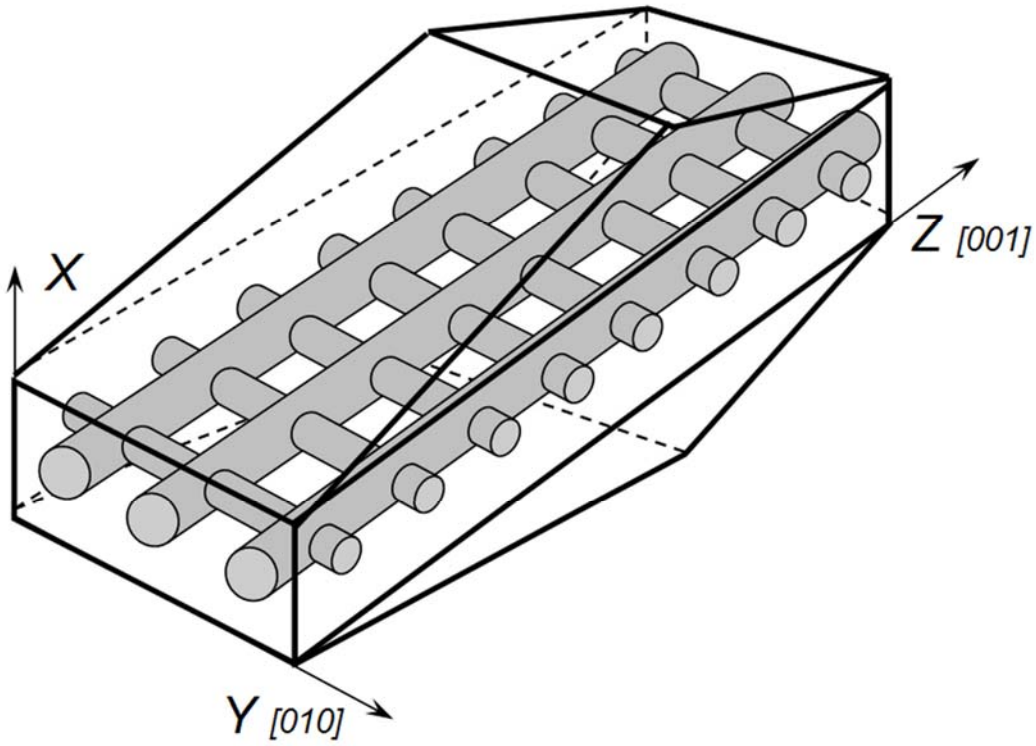
2-D pore structure of Ferrierite crystals



10-ring viewed along [001]



8-ring viewed along [010]



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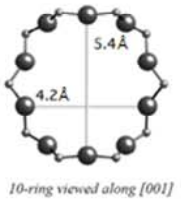
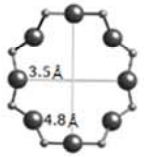
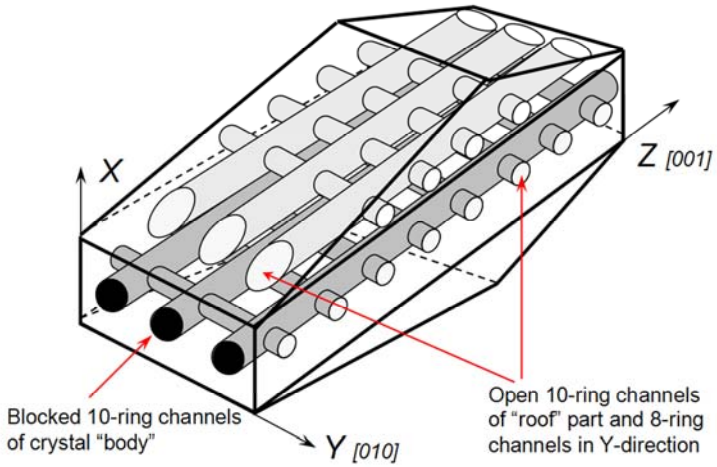
Directions of methanol adsorption in Ferrierite crystal

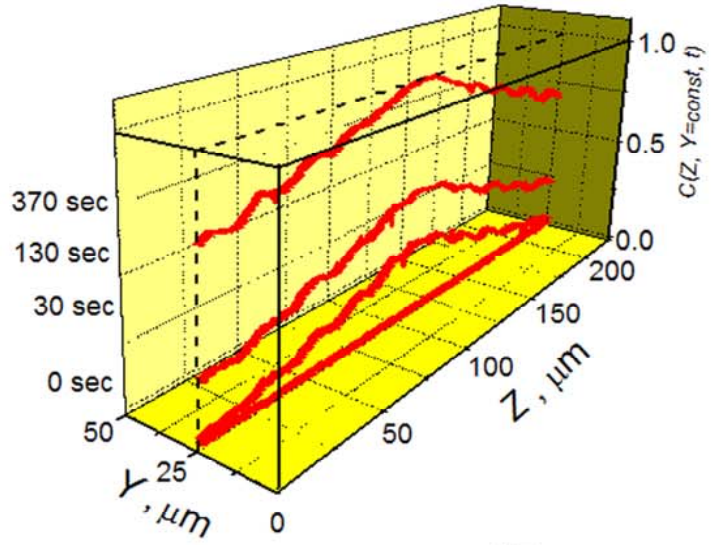


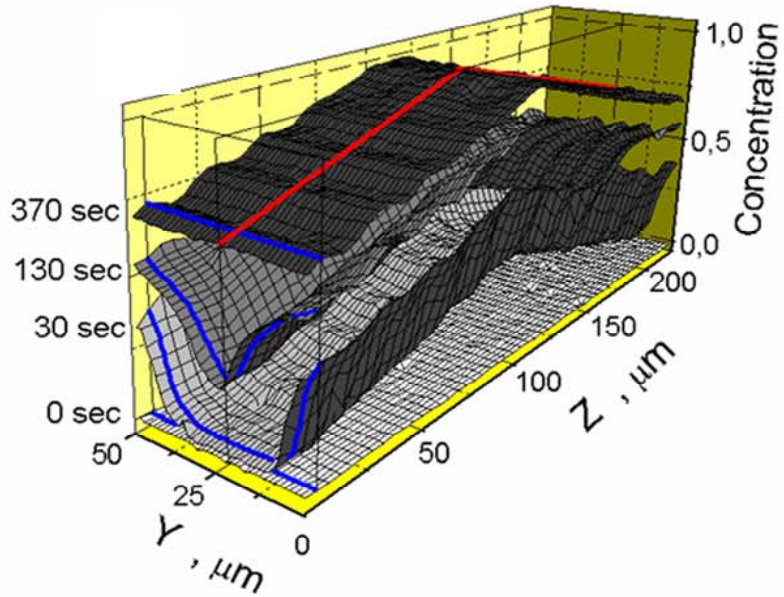
10-ring viewed along [001]

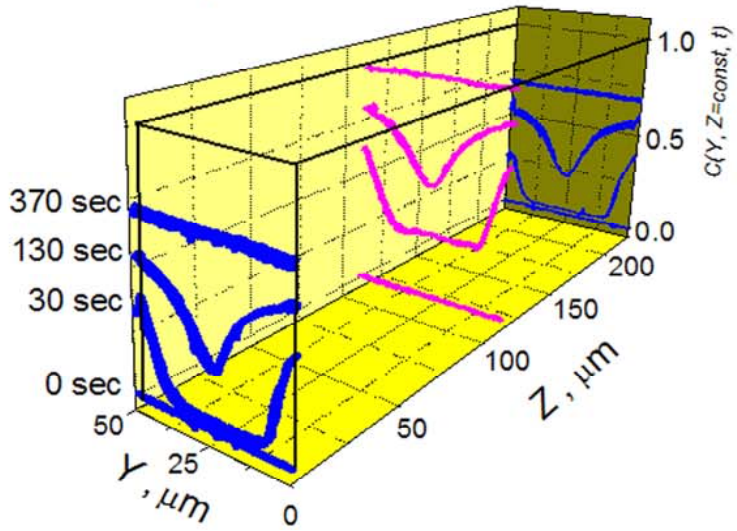


8-ring viewed along [010]

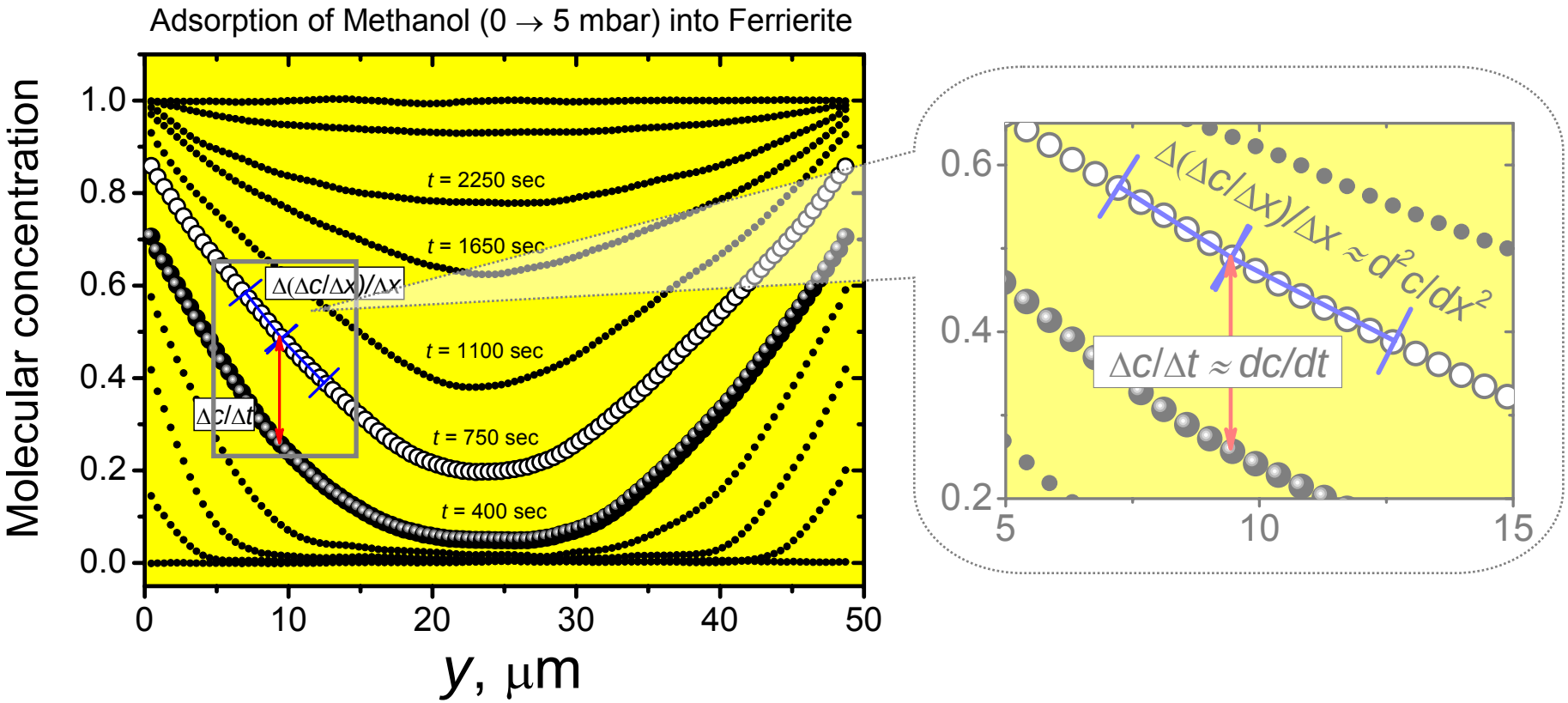








Local diffusion and surface resistance



Fick's Second Law:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left[D(c,x)\frac{\partial c}{\partial x}\right] = D(c,x)\frac{\partial^2 c}{\partial x^2} + \frac{\partial D(c,x)}{\partial c}\cdot\left(\frac{\partial c}{\partial x}\right)^2$$

$x = 24$ μm

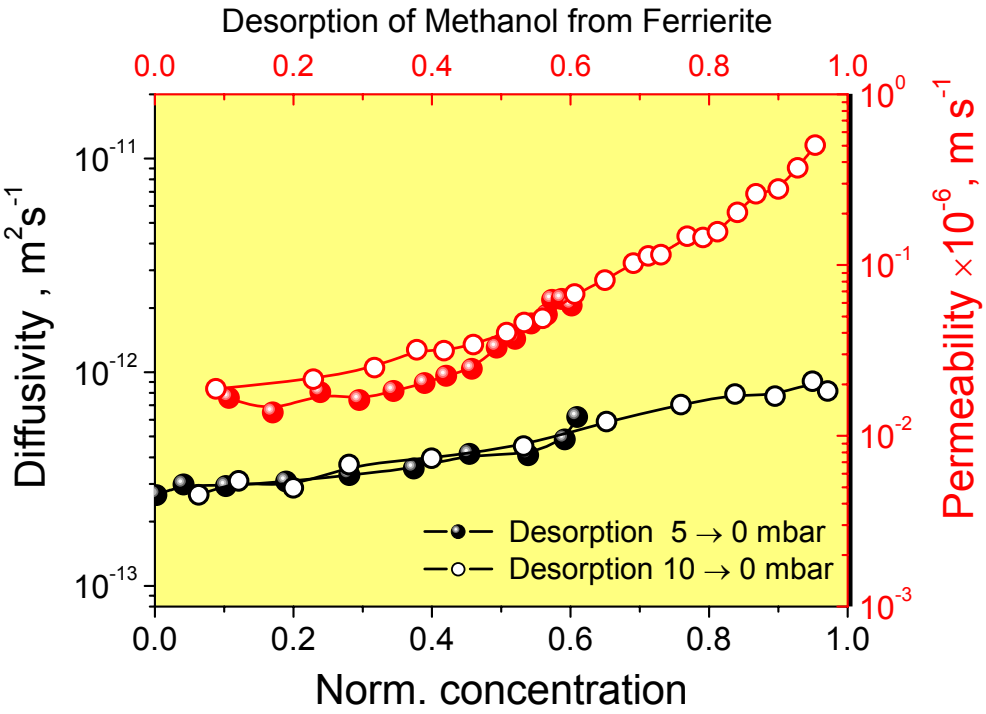
Fick's First Law:

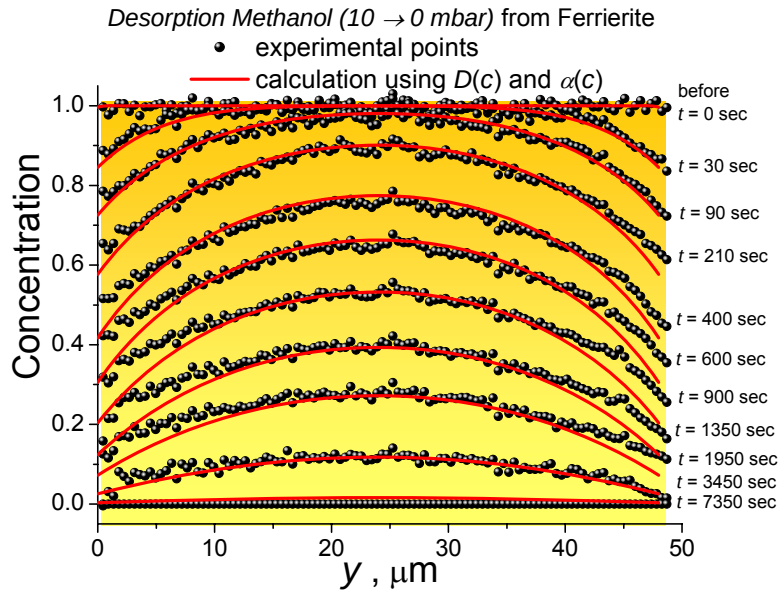
$$j = \alpha\left(c_{eq} - c(t)\right) = D\left(c(t)\right)\cdot\frac{dc}{dx}$$

Concentration dependence of the molecular diffusivity

Local DIFFUSION

TEST





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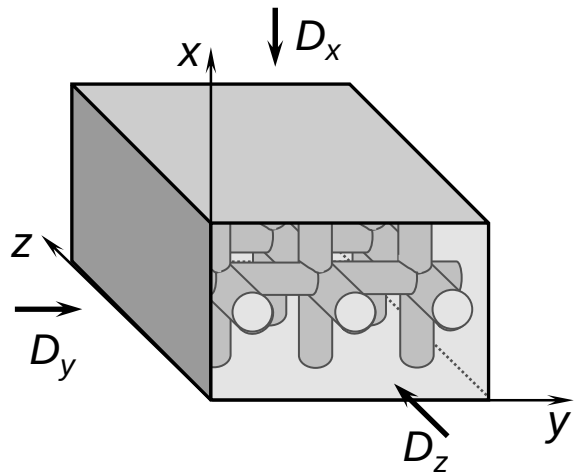
Outline

(a) 1-D pore structure of the MOF crystals

(b) 2-D pore structure of the Ferrierite zeolite

(c) 3-D pore structure of the SAPO STA-7



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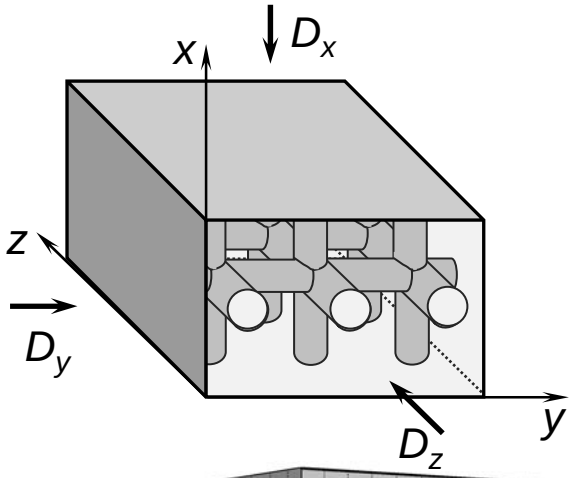
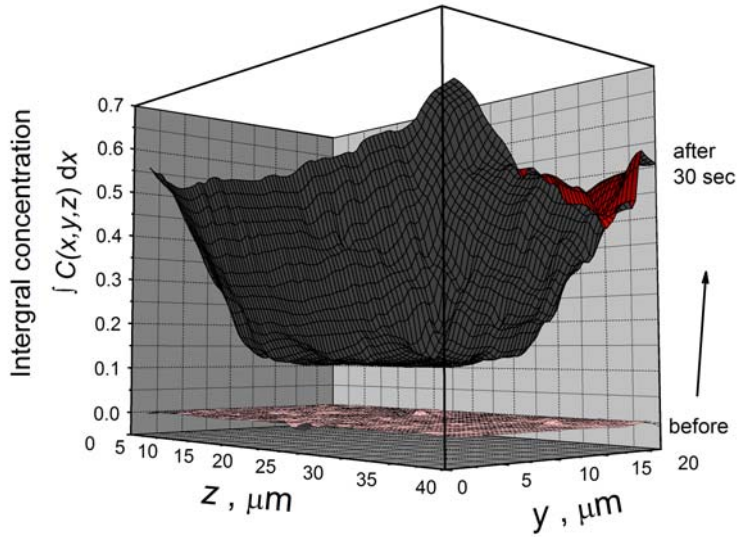
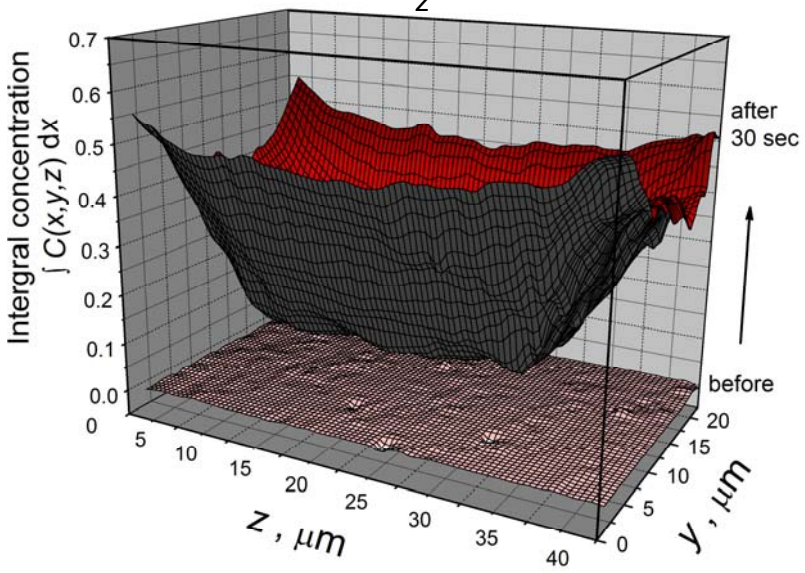
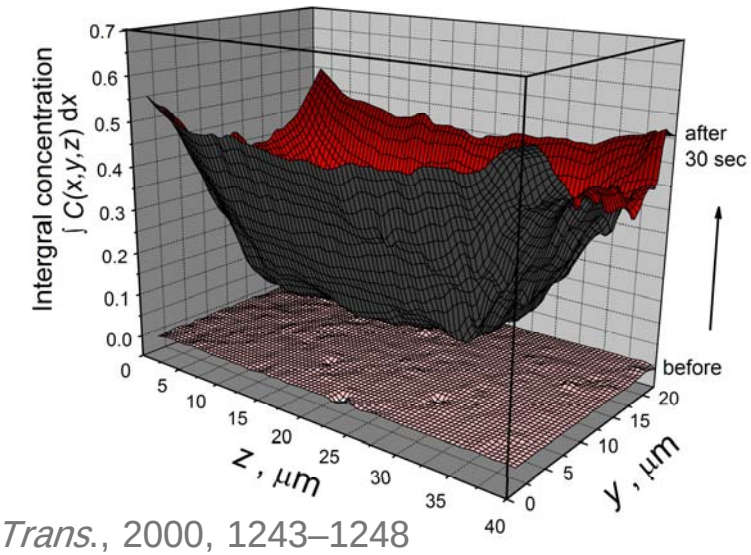
3-D pore structure of STA-7 materials (*)



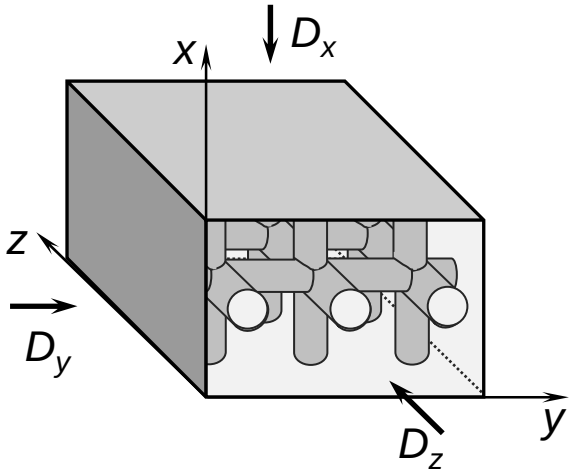


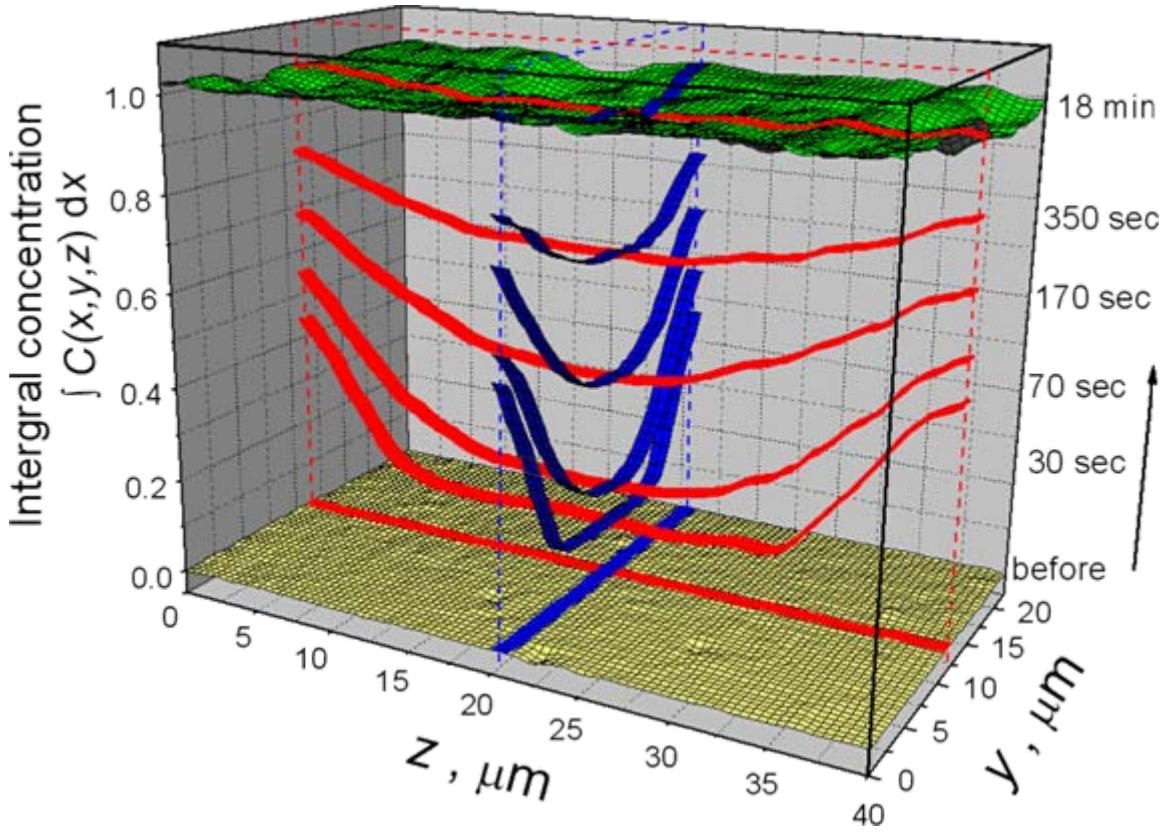




(*) Paul A. Wright, Martin J. Maple et al., *J. Chem. Soc.*, *Dalton Trans.*, 2000, 1243–1248

3-D pore structure of STA-7 materials





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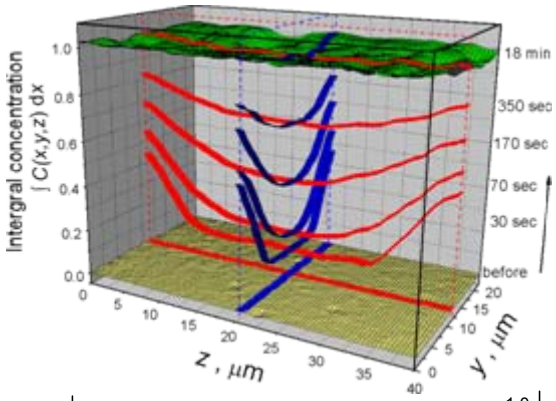
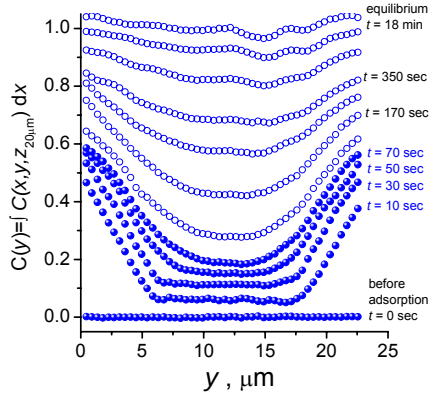
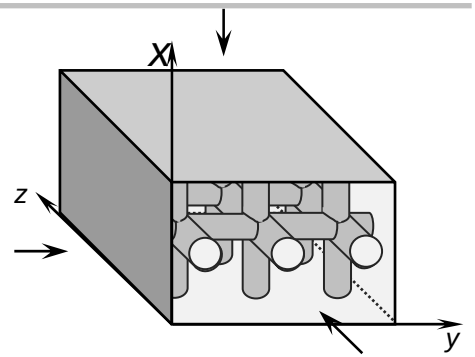
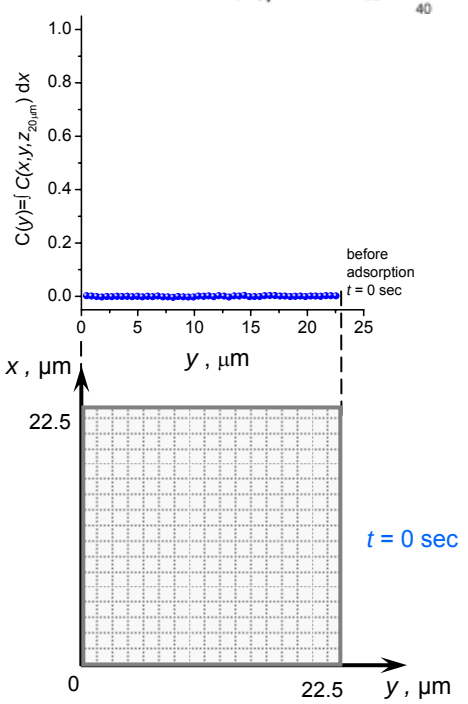
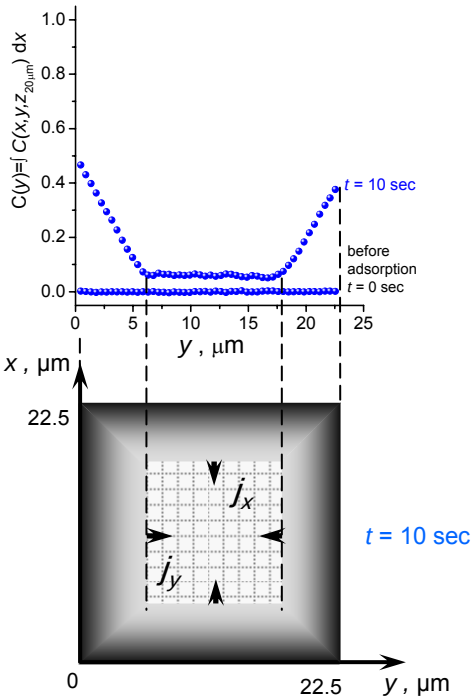
Uptake in *y*- and *x*-directions

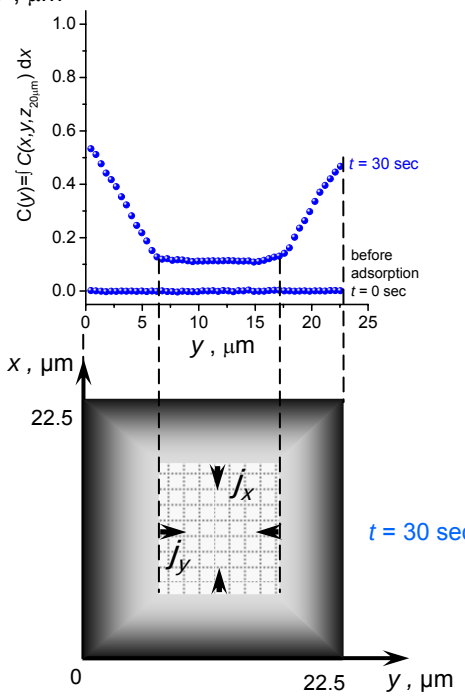


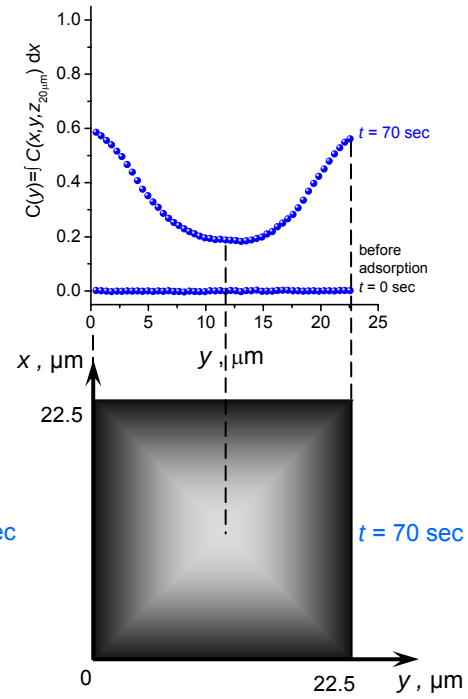












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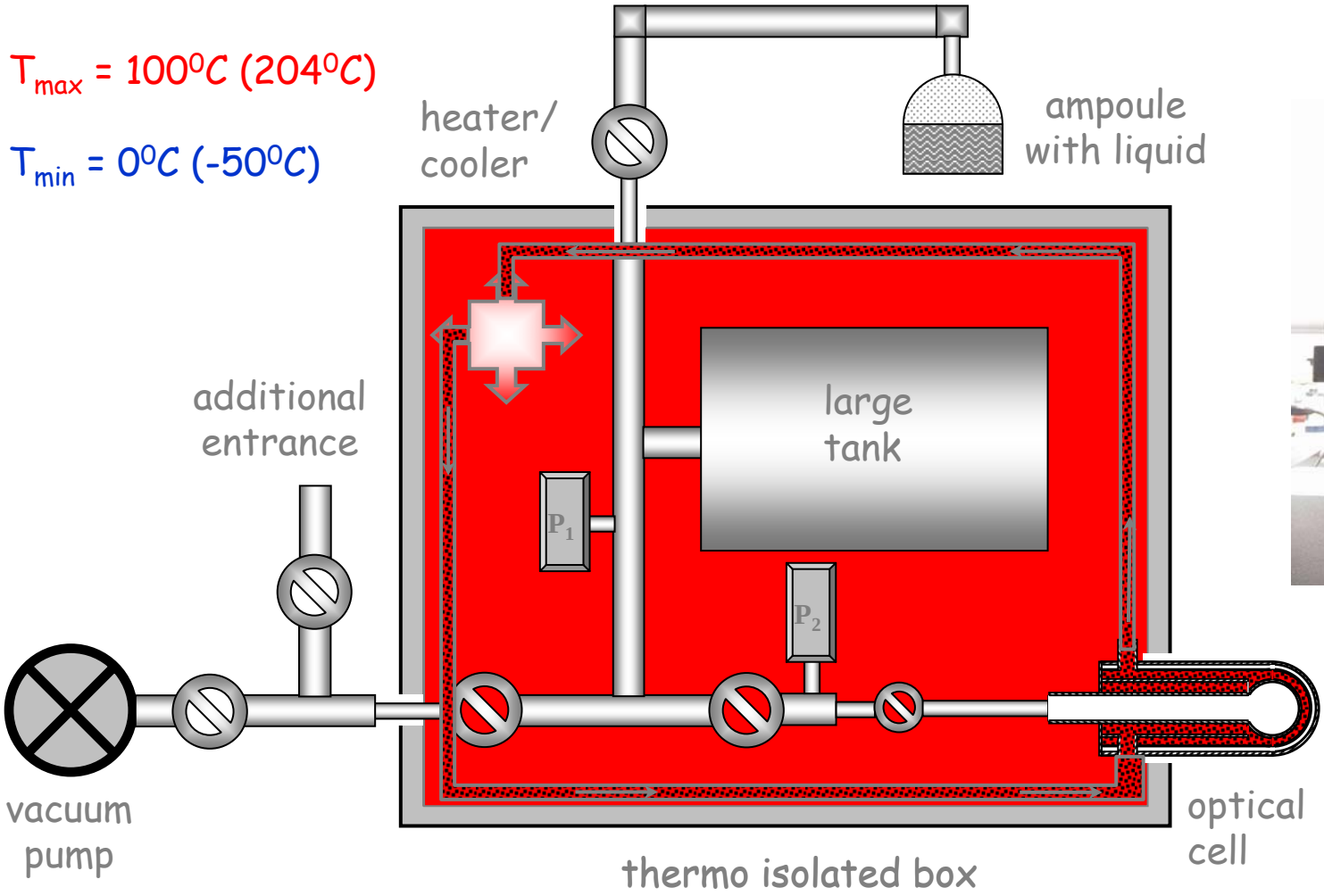
IFM perspectives...

T_{max} = 100°C (204°C)

T_{min} = 0°C (-50°C)



interference
microscope