

# Using kinetic Monte Carlo simulations for investigating surface barriers in nanoporous materials

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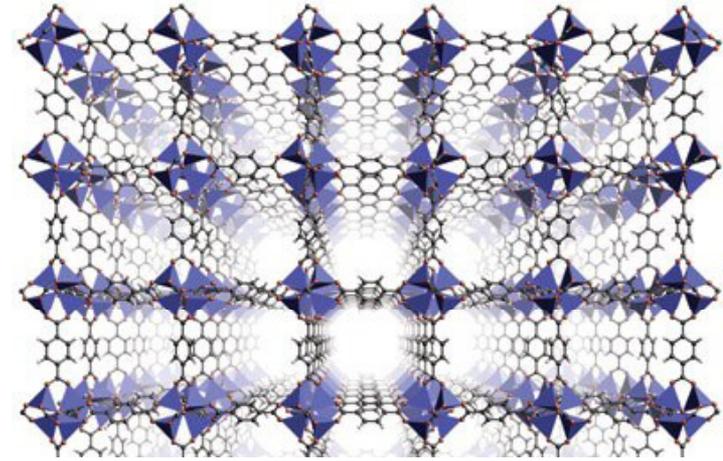
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# Introduction – nanoporous materials

## Nanoporous crystals:

- Periodic, regular structure
- Pore size: few Å - few nm
- Zeolites and metal-organic frameworks (MOF)

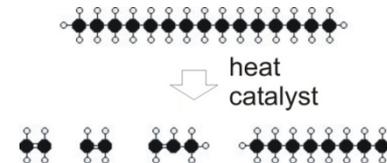


## Applications:

- Adsorption (e.g. of water)
- Ion exchange (e.g. water softener)
- Molecular sieve (mass separation, gas purification)
- Catalysts (e.g. in petrochemistry)



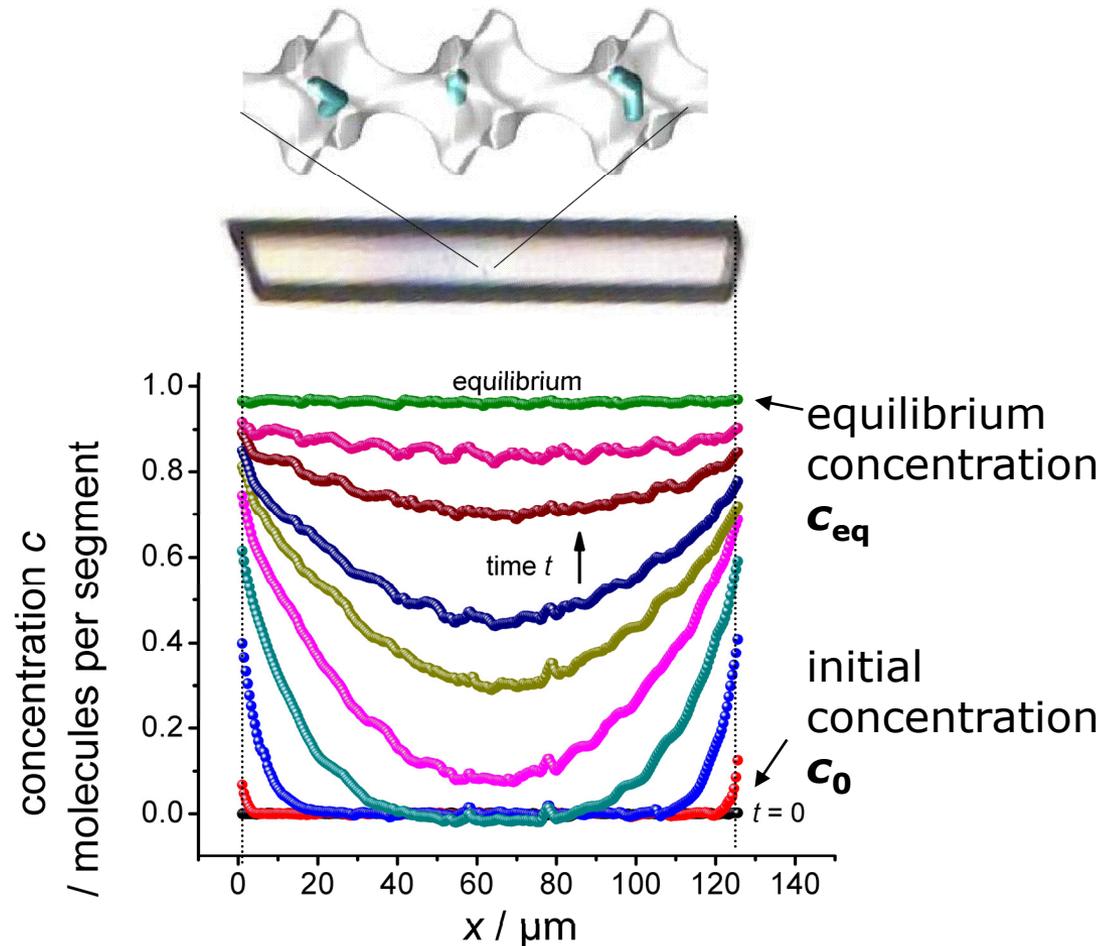
→ Mass transport crucial!



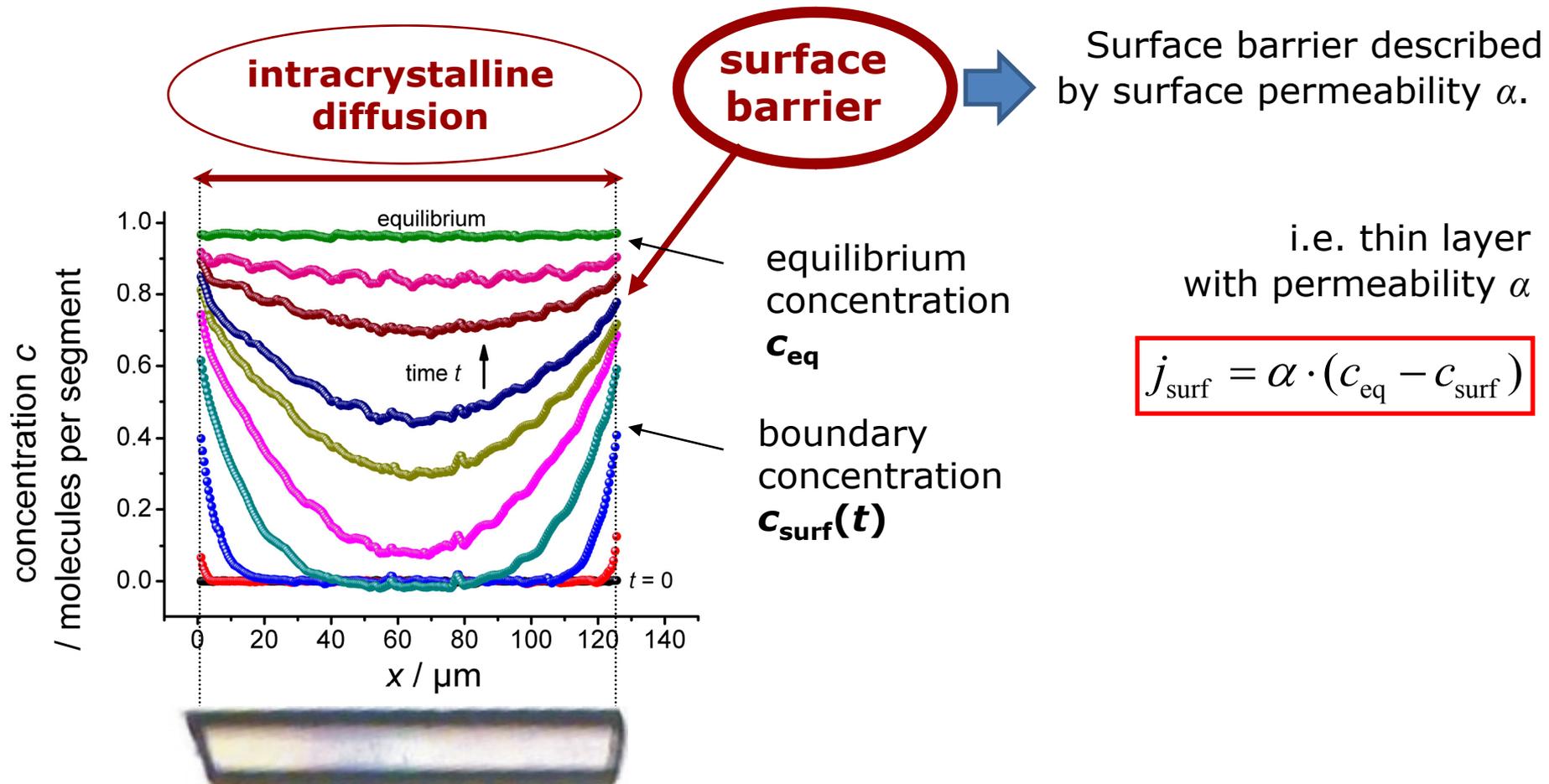
# Experimental data - recorded concentration profiles

Best way for studying mass transfer → concentration profiles!  
(Pressure step → new equilibrium concentration → mass transfer)

Investigated system: **propane in MOF Zn(tbip)** (one-dimensional pore structure)



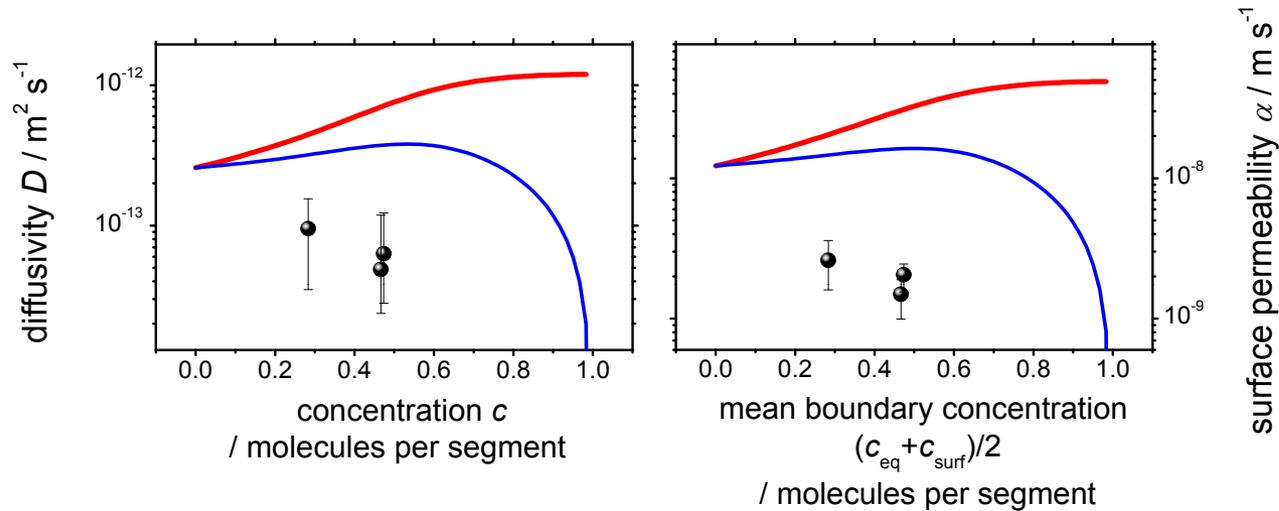
# Experimental data - recorded concentration profiles



→ Mass transfer often limited by surface barriers!  
(not only by diffusion in the bulk crystal)

# Transport parameters of propane in MOF Zn(tbip)

Transport, Maxwell-Stefan and self-diffusivity and surface permeability of propane

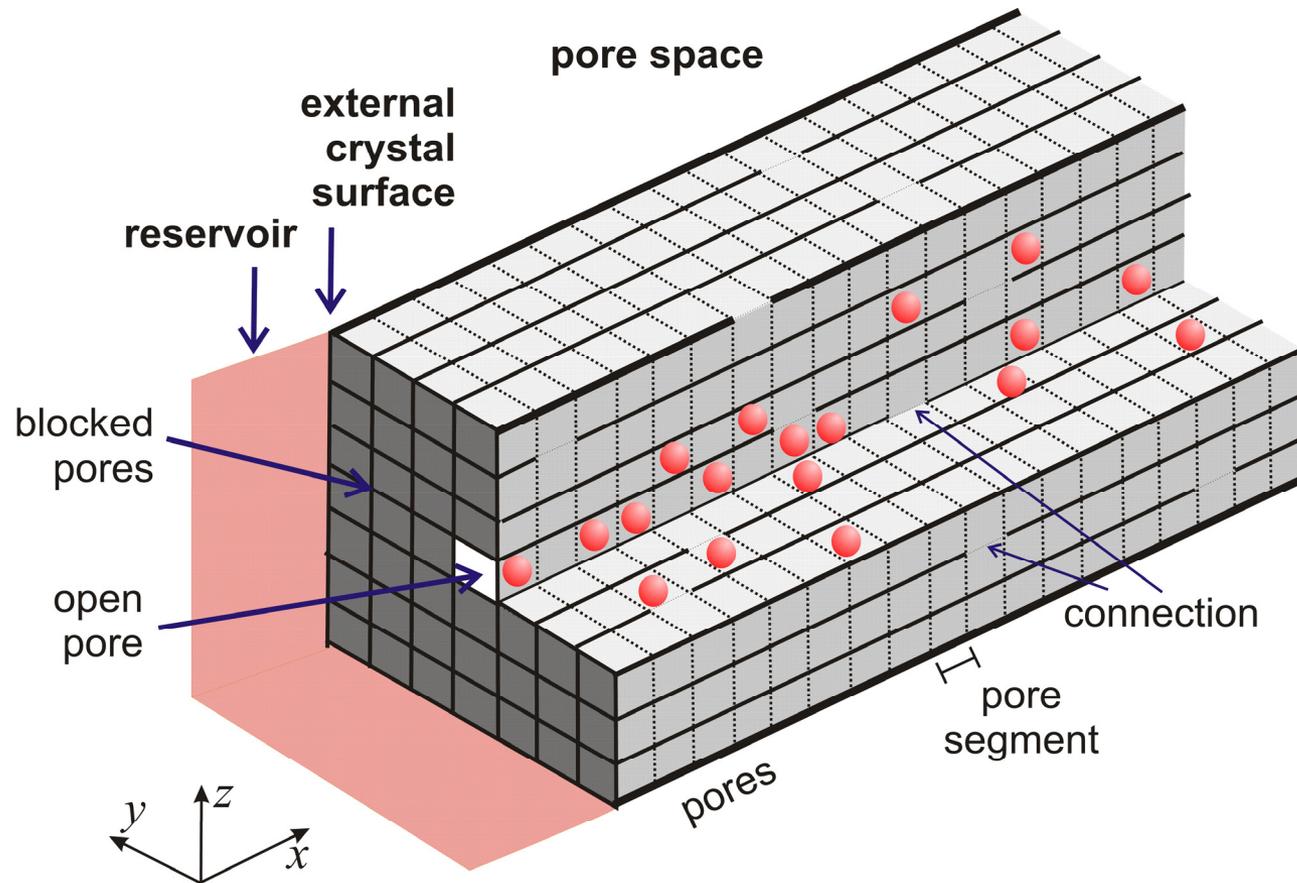


**Diffusivity** and **surface permeability** → **same concentration dependence!**

Furthermore: **Ethane, propane** and **n-butane** → **same  $\alpha / D$**

→ **Both facts can not be explained by a smaller pore diameter at surface or by entropic effects!**

# Model of surface barriers

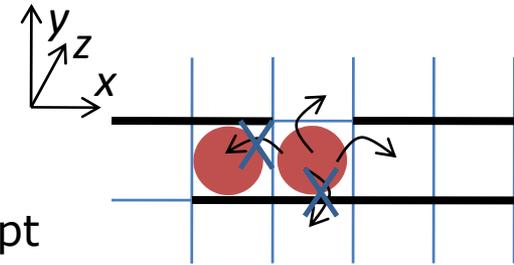


- Crystal structure  $\rightarrow$  lattice (1 pore segment = 1 lattice site)
- Most pore entrances blocked, molecules enter only via open pore entrances (percentage of open pores  $\rho_{\text{open}}$ )
- Parallel pores have cross connections = crystal defects (percentage of cross connections  $\rho_y = \rho_z$ )
- Gas phase = reservoir with fixed concentration ( $c_{\text{eq}}$ )

# Kinetic Monte-Carlo simulations

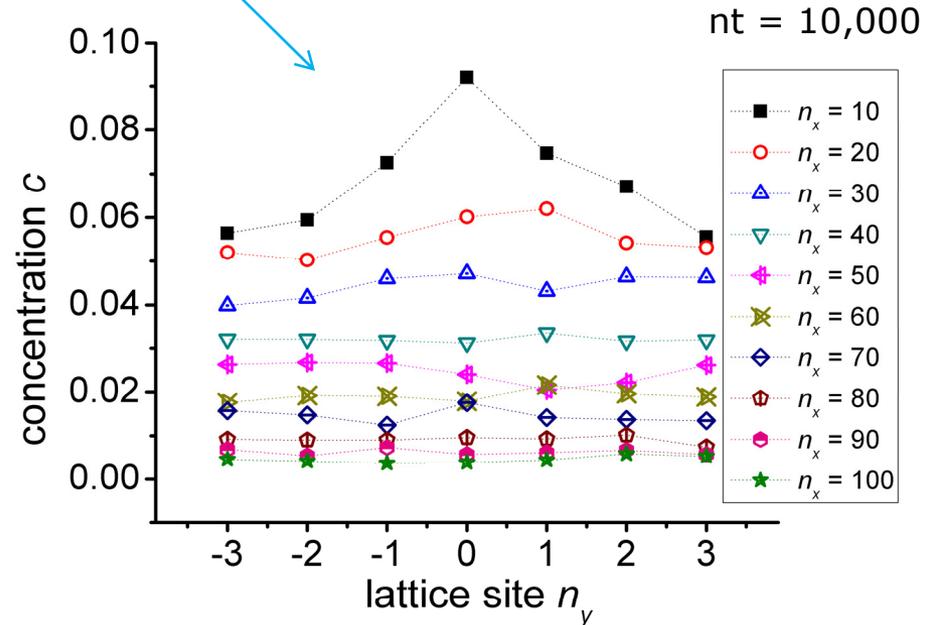
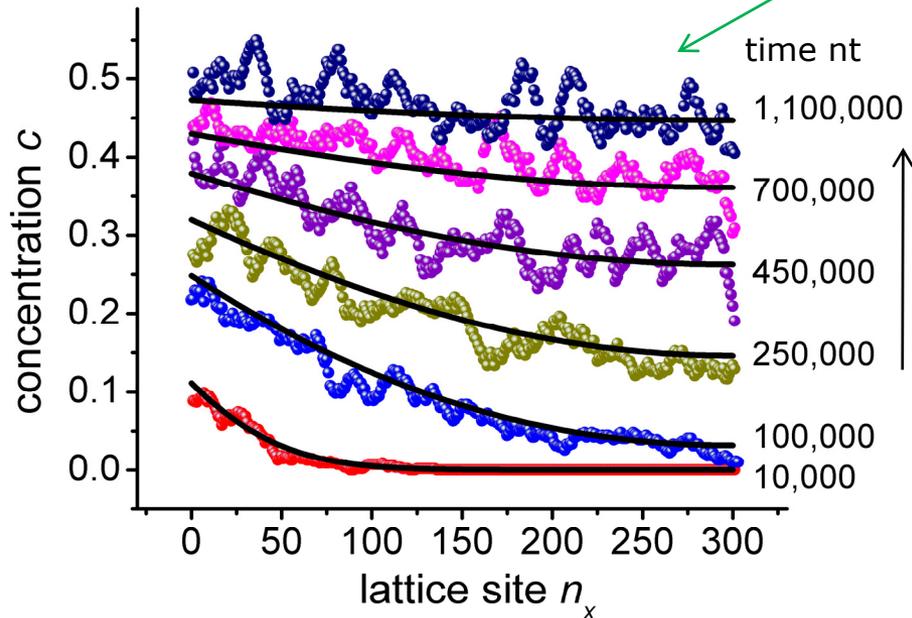
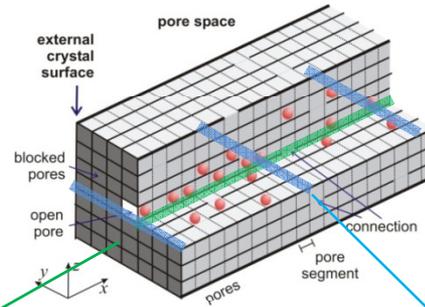
Details for simulations:

- Lattice jump model
- Every time step  $nt \rightarrow$  every molecule makes jump attempt
- Restriction:
  - Each site can be occupied by only one molecule (follows from isotherm)
  - jumps in  $y$ - or  $z$ -direction can only occur when adjacent pores are cross connected
- No interaction between the particles (hard-sphere model) or nearest-neighbour interaction (Reed-Ehrlich model)
- fixed concentration in the reservoir  $c_{eq}$ 
  - $c_{eq} > c_0 \rightarrow$  adsorption experiment
  - $c_{eq} < c_0 \rightarrow$  desorption experiment
  - $c_{eq} = c_0 \rightarrow$  self-diffusion experiment



Assumption: Jump rate in  $x$ ,  $y$  and  $z$  are equal.

# Simulated concentration profiles



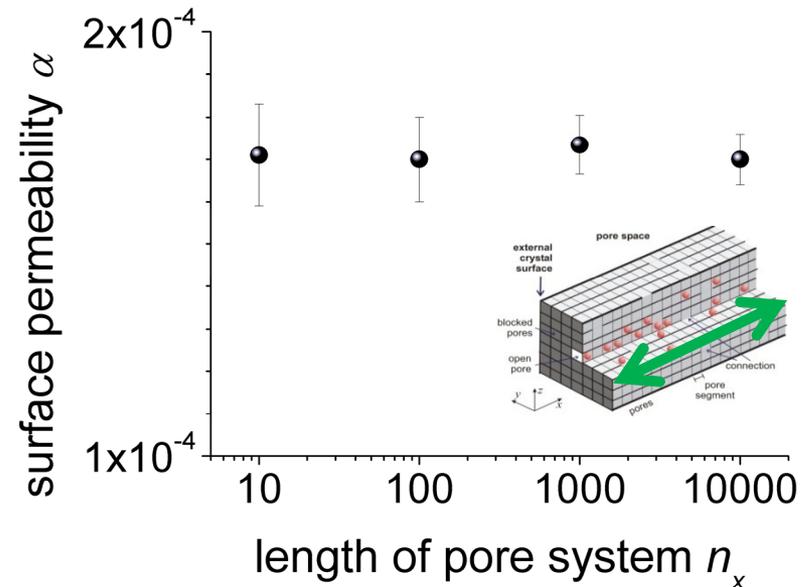
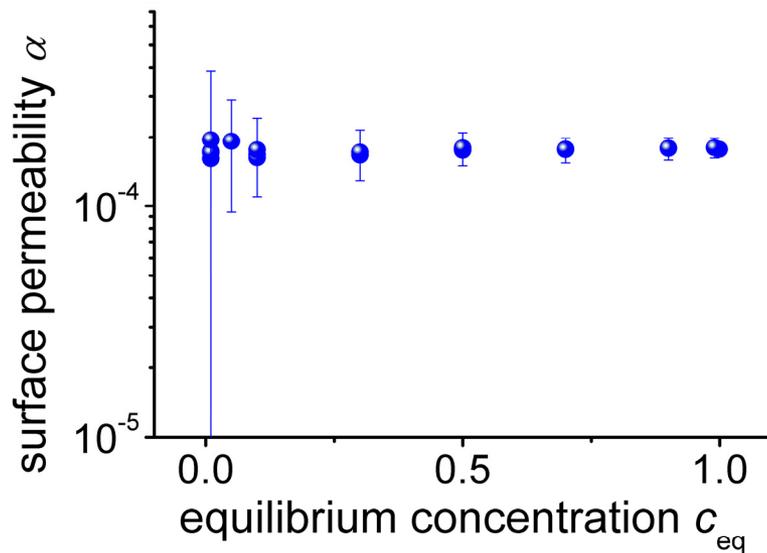
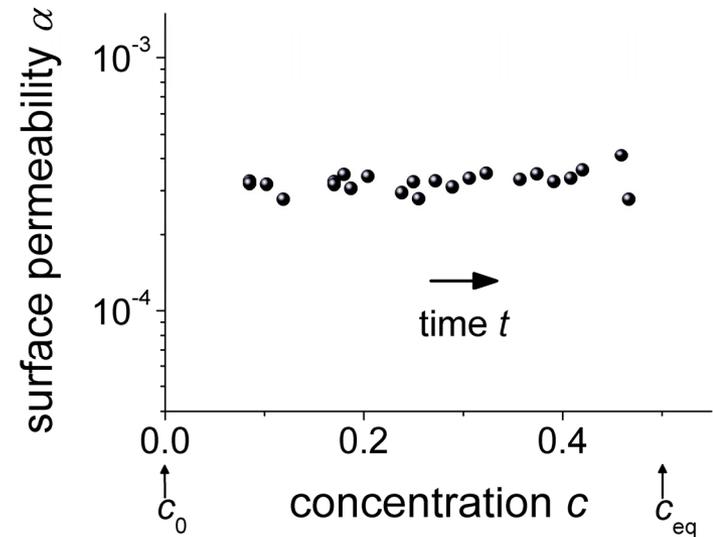
Concentration profiles along  $x$  correspond to solution of diffusion equation with surface barriers. ( $D$  and  $\alpha = \text{const.}$ )

Concentration profiles perpendicular to  $x$  are curved near the surface and flat in the bulk crystal.

# Resulting surface permeability

## Surface permeability

- constant during transfer process (if diffusivity constant;  $\alpha \sim \text{jump rate} \sim D$ )
- independent of equilibrium concentration
- independent of length of pore system

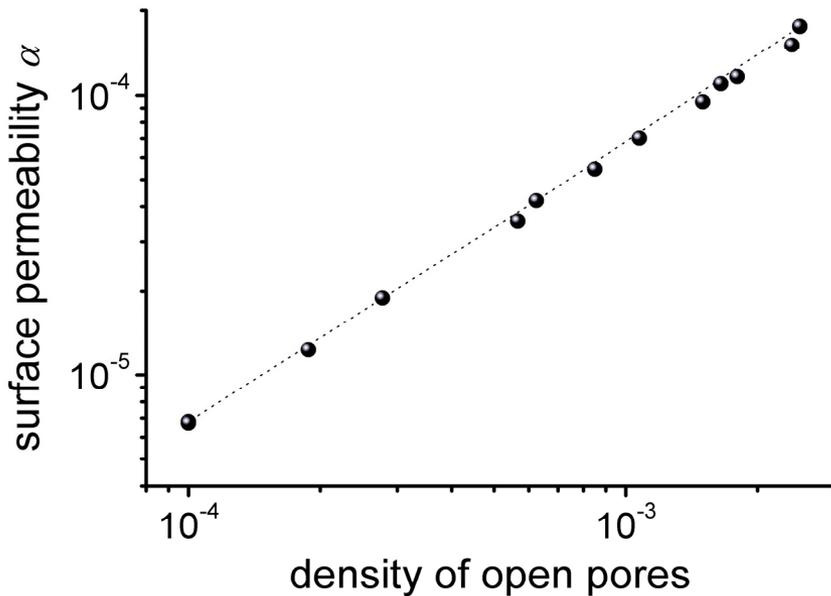


# Resulting surface permeability

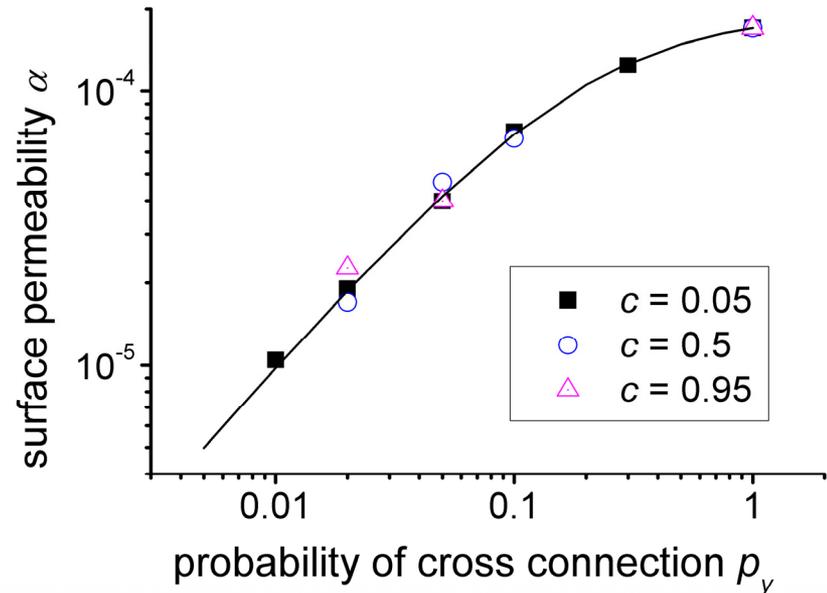
Surface permeability depends on

- fraction of open pores ( $p_{\text{open}}$ )
- probability of cross connections ( $p_y = p_z$ )

→  $\alpha(p_{\text{open}}, p_y)$  and  $\alpha / D = \text{const.}$



$$\alpha \sim p_{\text{open}}$$



$$\alpha \sim \frac{5 \cdot p_y}{1 + 4 \cdot p_y} \cdot \left( 1 - \frac{p_y}{2 + 4 \cdot p_y} \right)$$

# Interaction between particles – Reed-Ehrlich model

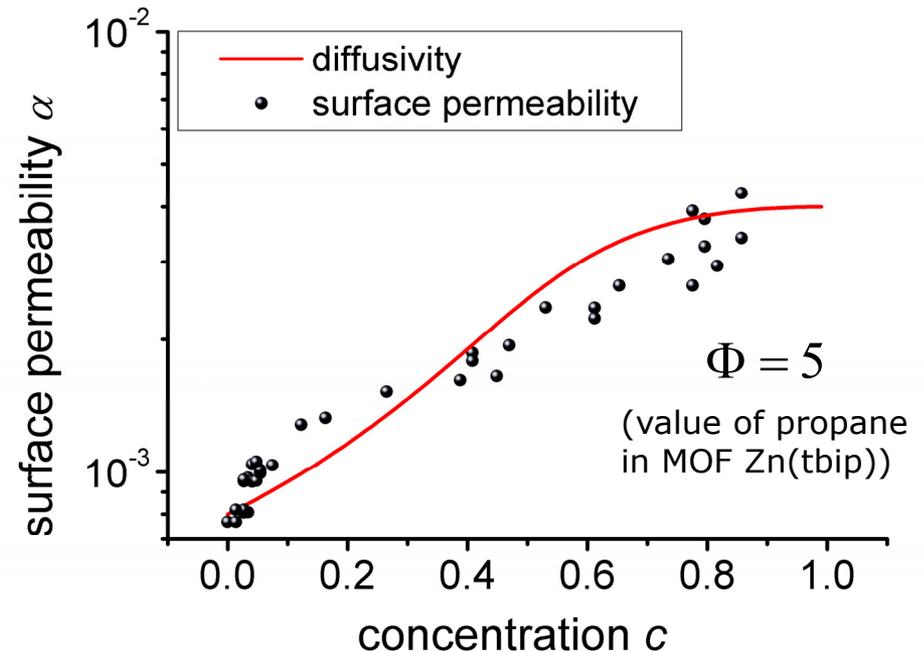
Now: Interaction between particles → Diffusivity concentration dependent

Nearest-neighbour interaction between particles on the lattice

$$\text{Jump rate} \sim \Phi = \exp\left(\frac{\sum U_{\text{Nearest Neighbour}}}{k_b T}\right)$$

(Reed-Ehrlich approach)

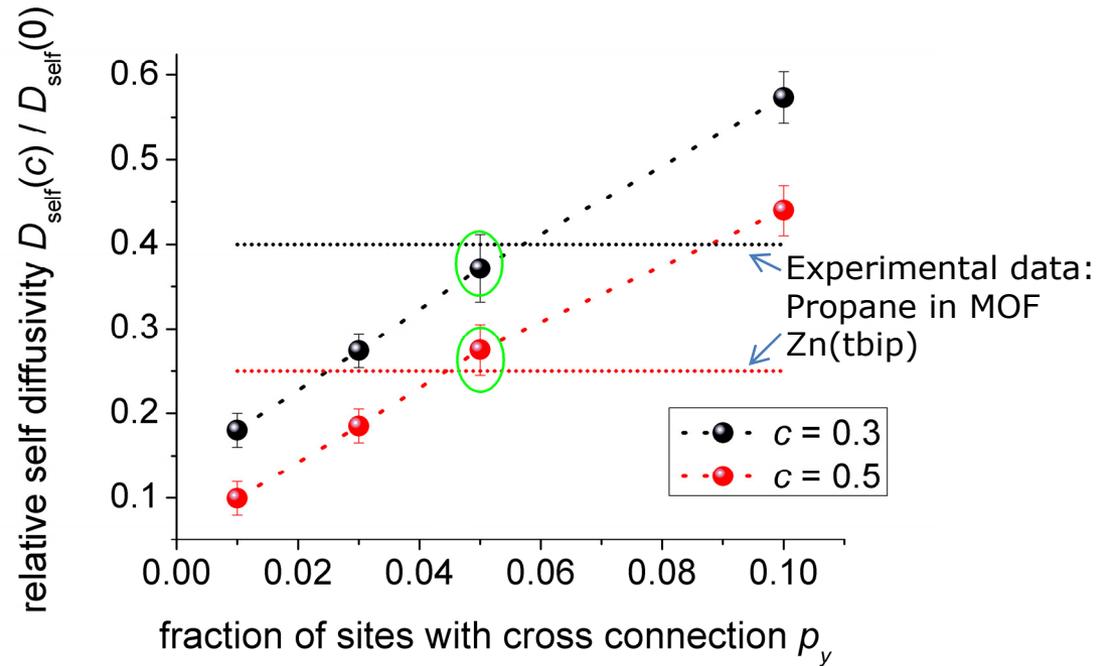
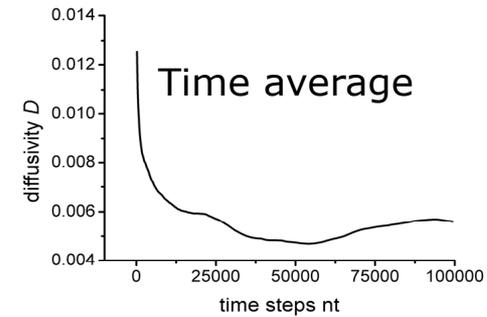
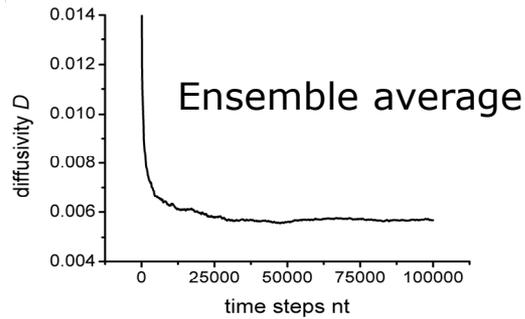
→ concentration dependence  
similar diffusivity



→ **All properties of the surface barriers presented!**

# Determining $p_{\text{open}}$ in MOF Zn(tbip)

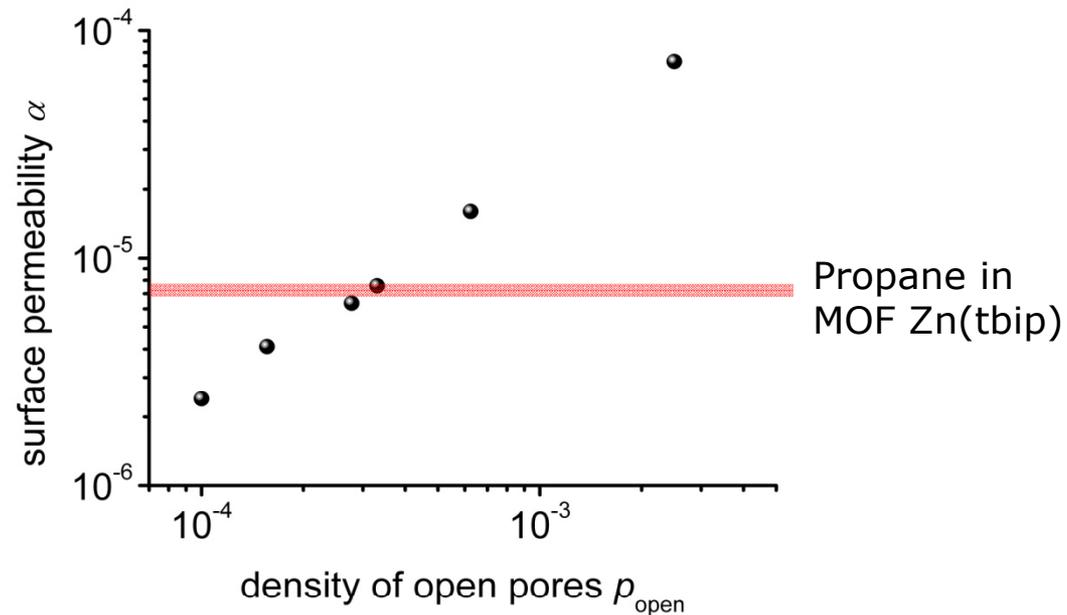
Self-diffusion simulations with concentration  $c = 0.3$  and  $c = 0.5$  ( $\Phi=5$ )



$\rightarrow p_y \approx 0.05$

# Determining $\rho_y$ in MOF Zn(tbip)

$\rho_{\text{open}}$  can be adjusted to fit the experimental data  
( $\rho_y = 0.05$ )



→ Fraction of open surface pores is about 0.033 % , i.e. **one among  $55 \times 55$  pores is open!**

(Under the assumption of equal jump rates in all directions!)

## Conclusion

- Surface barrier represented by a high percentage of totally blocked pores which are cross-connected.
  - Influence of different parameters in the model studied by means of kinetic Monte-Carlo simulations.
  - All properties of the surface barriers of alkanes in MOF Zn(tbip) are very well represented!
- ➔ It can be concluded that the surface barriers are caused by this structure!

# Acknowledgment

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IRTG "Diffusion in Nanoporous Materials"



Studienstiftung des deutschen Volkes



**Studienstiftung**  
des deutschen Volkes

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department at the Fritz-Haber-Institute



MAX-PLANCK-GESELLSCHAFT

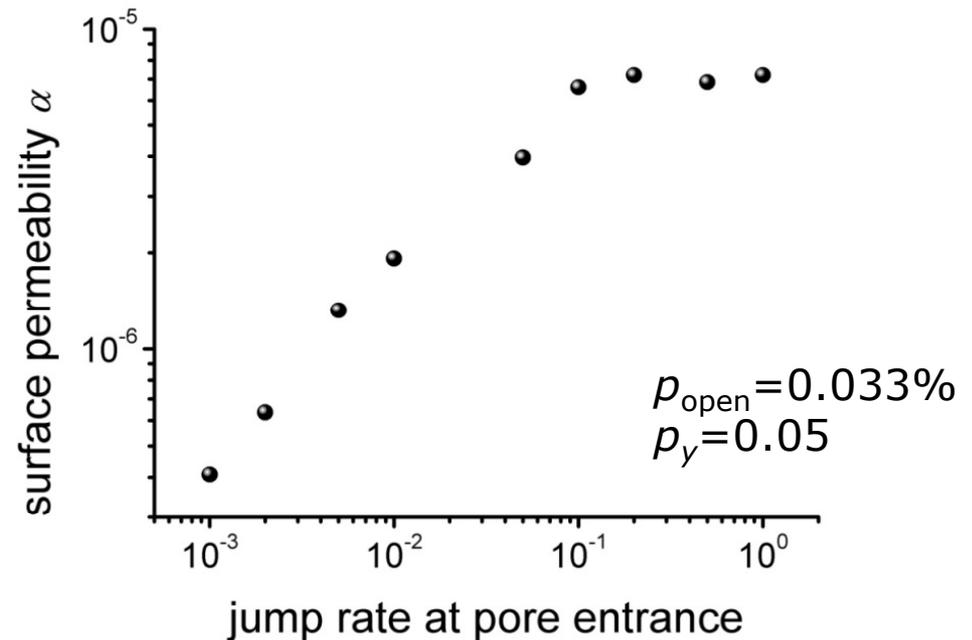
**Many thanks for your attention!**



## Variation of jump rates

Results are only valid under the assumptions of same jump rate everywhere.

What happens if jump rate in surface plane is smaller?



Jump rate in surface up to 1 order of magnitude smaller  $\rightarrow$  no difference!

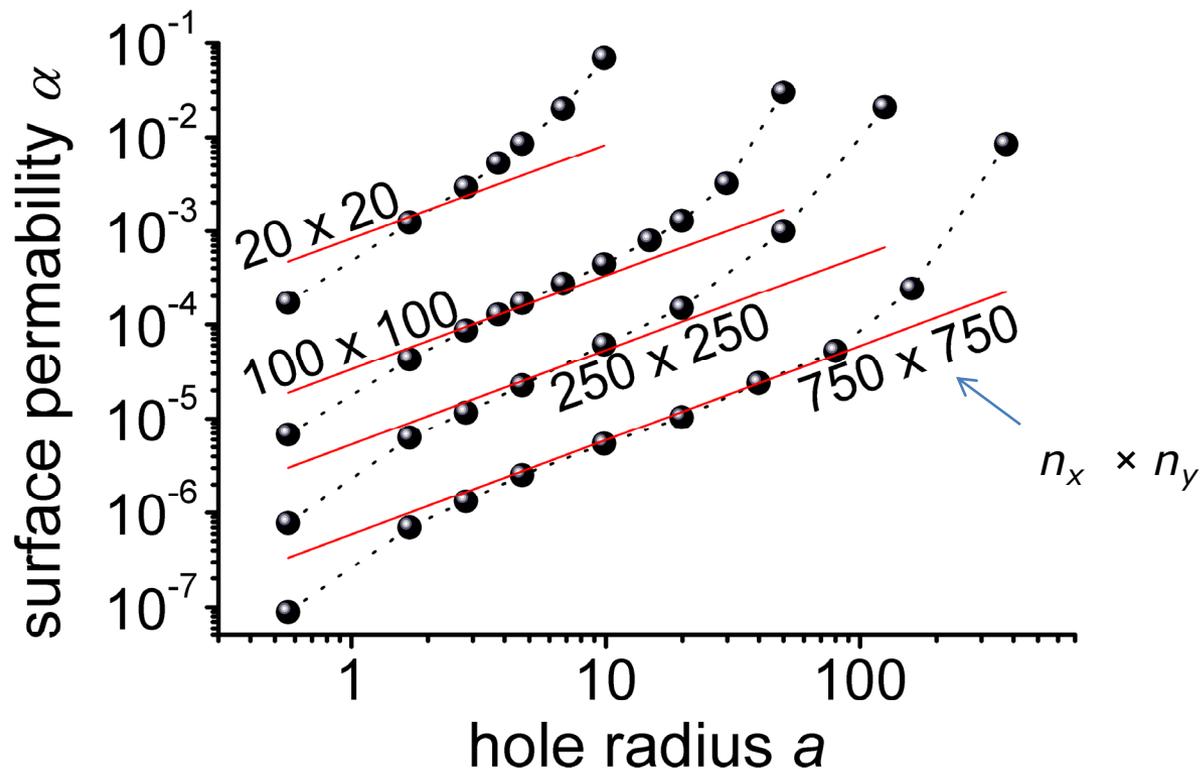
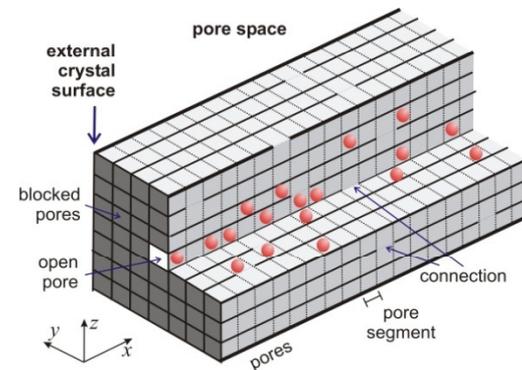
# Simulated results vs. Continuum approach

Comparison with analytical results for continuum system

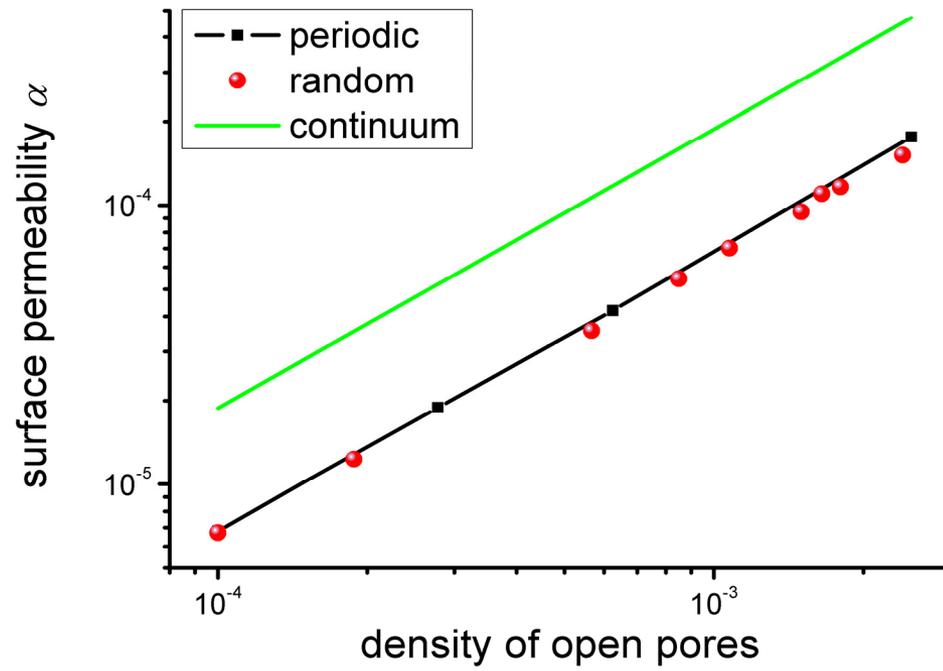
(Dudko, Berezhkovskii, Weiss, J. Phys. Chem, 2005.)

$$\alpha = 2 \frac{D \cdot a}{L^2}$$

→ If lattice can be approximated as continuum, good approximation.



# Periodic or random distribution of open pores



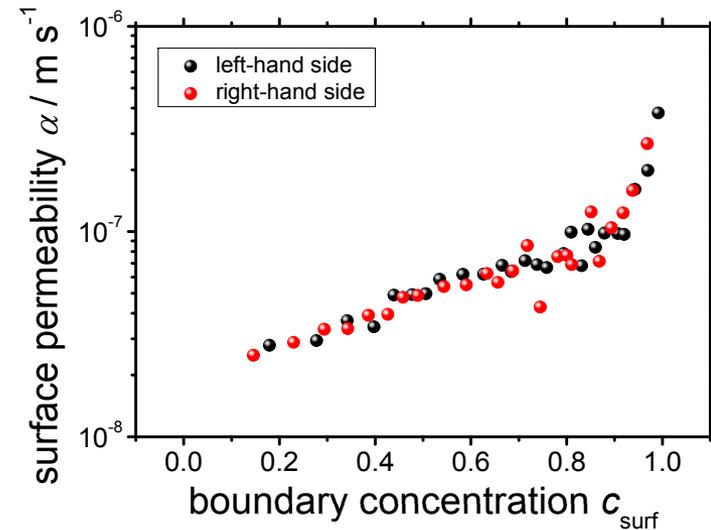
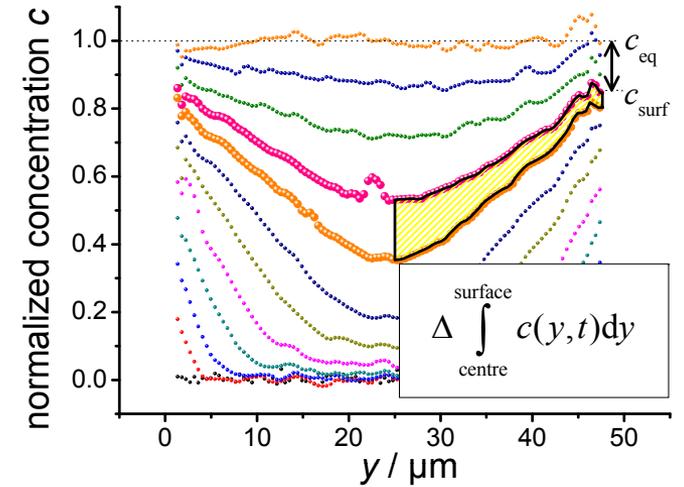
# Mesoscopic description of the surface barriers

Surface barrier described by surface permeability.  
(inversely proportional)

All quantities follow from concentration profiles  
→ Surface permeability experimentally determined!

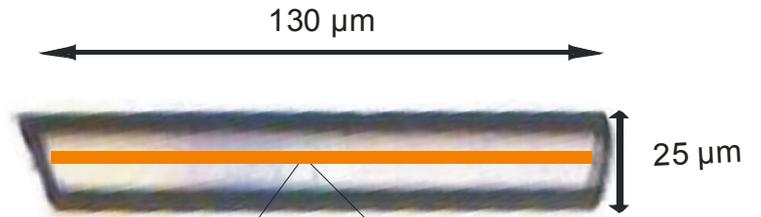
$$j_{\text{surf}} = \alpha \cdot (c_{\text{eq}} - c_{\text{surf}})$$

$$\alpha(c_{\text{surf}}) = \frac{\frac{d}{dt} \int_{\text{centre}}^{\text{surface}} c(t) dy}{c_{\text{eq}} - c_{\text{surf}}}$$

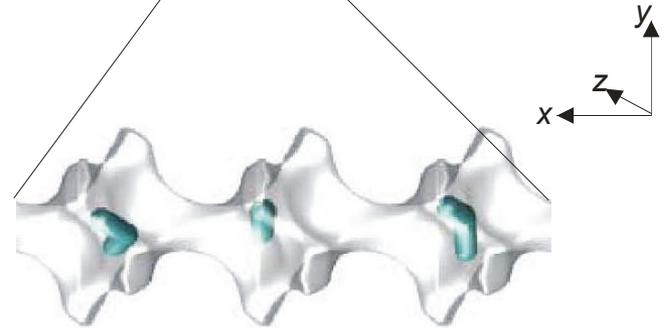


# Crystal structure of MOF Zn(tbip)

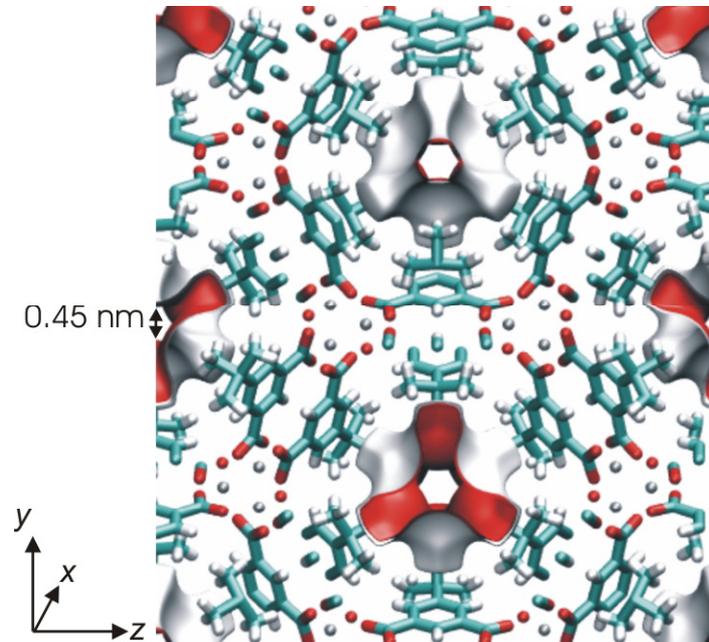
Metal organic framework (MOF) Zn(tbip)



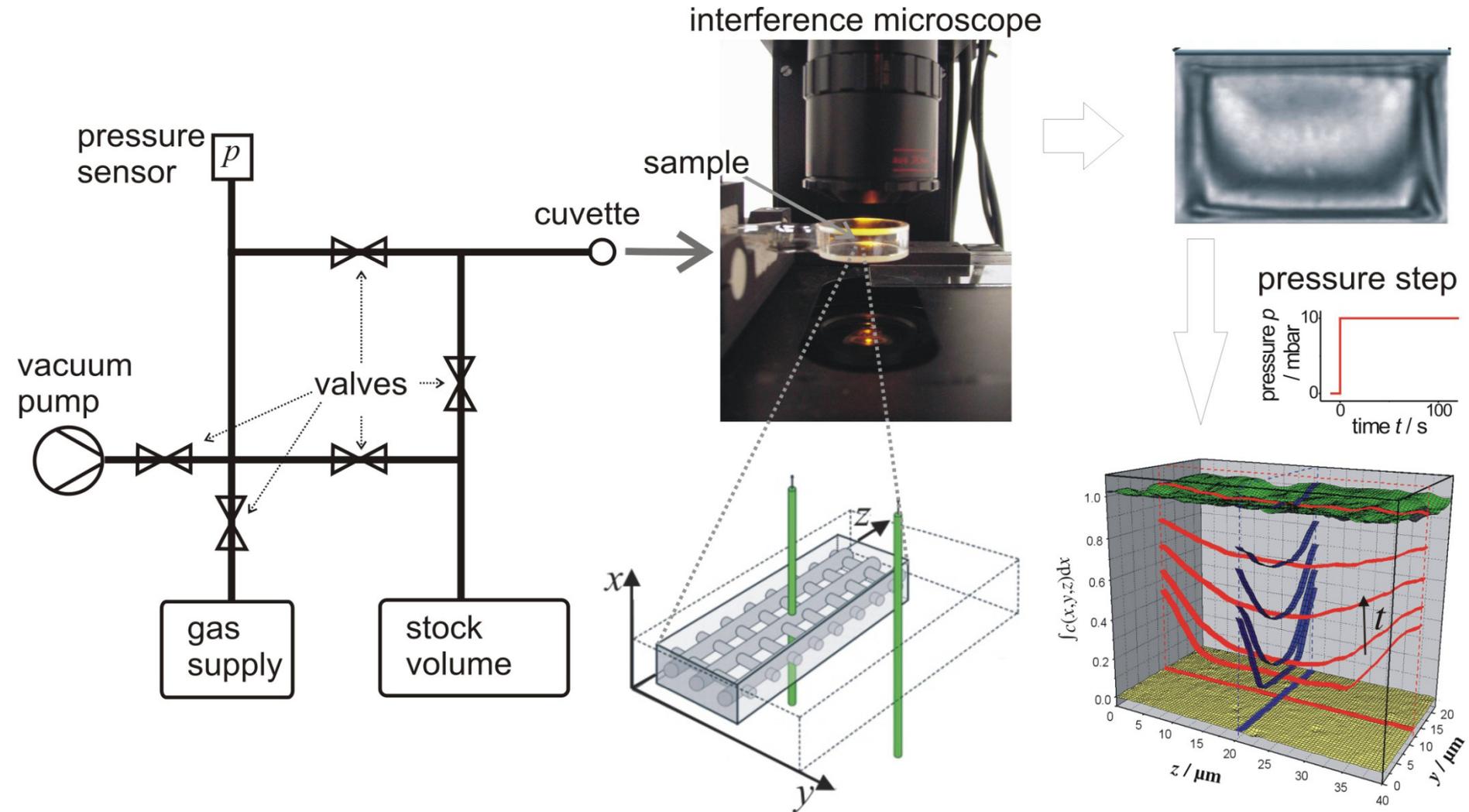
Parallel chains of pore segments



Guest molecule: propane  
(complemented by ethane  
and n-butane)



# Experimental setup of interference microscopy



- Basic principle: optical path length depends on adsorbate concentration.
- Spatial resolution:  $0.5 \mu\text{m} \times 0.5 \mu\text{m}$

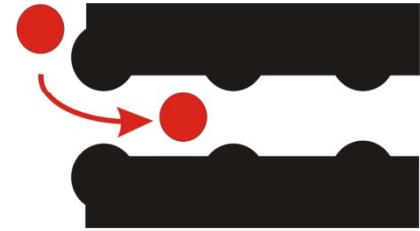
# Sticking probability

Sticking probability  $P_{st}$

= probability that a gas molecule that hits the crystal surface continues its trajectory in the pore space,

i.e.

$$P_{st} = \frac{j_{in}}{j_{\text{gas on surface}}}$$



$$j_{\text{surf}} = \alpha \cdot (c_{\text{eq}} - c_{\text{surf}}) = j_{\text{in}} - j_{\text{out}}$$

→  $j_{\text{in}} = \alpha \cdot c_{\text{eq}}$

- no concentration dependence
- desorption to vacuum:  $c_{\text{eq}}=0, j_{\text{in}}=0$

From kinetic theory of gases

$$j_{\text{gas on surface}} = \frac{N_A \cdot p}{\sqrt{2\pi \cdot R \cdot T \cdot M}}$$

Sticking probability:

- $P_{st} \approx 6 \times 10^{-6}$  for methanol in ferrierite
- $P_{st} \geq 0.01$  for isobutane in silicalite

→ Varies over many order of magnitude!