Diffusion Fundamentals VI
Spreading in Nature, Technology and Society
Dresden, August 2015
Pre-School

Diffusion Step by Step: Looking at Molecules in Pore Networks

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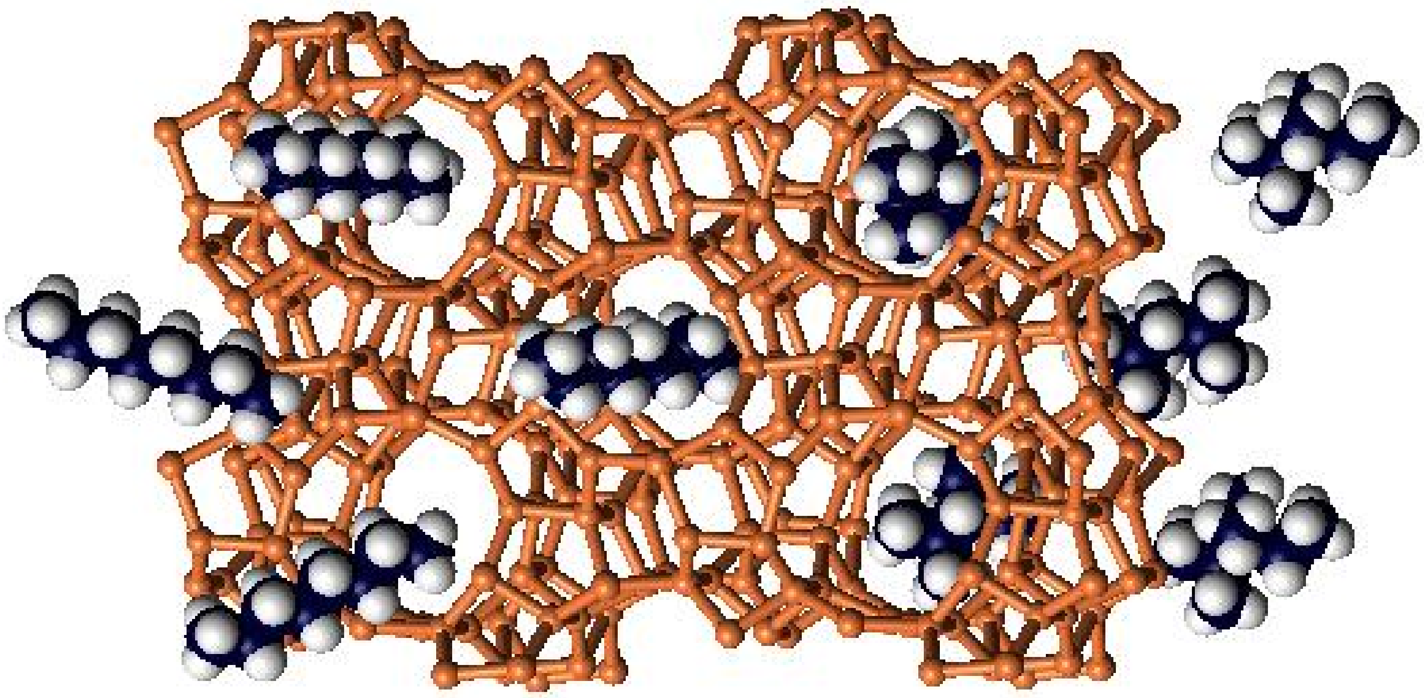
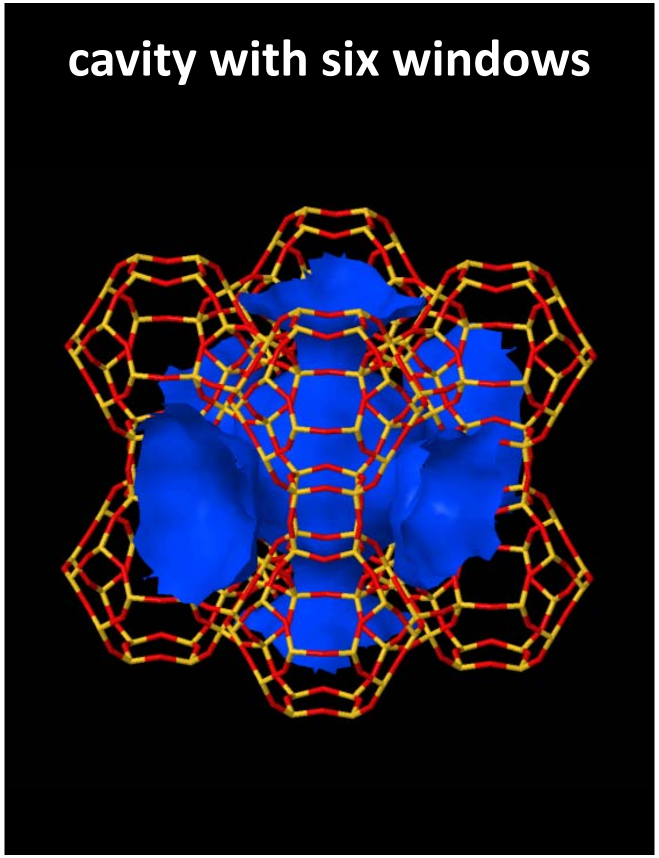
Faculty of Physics and Earth Sciences

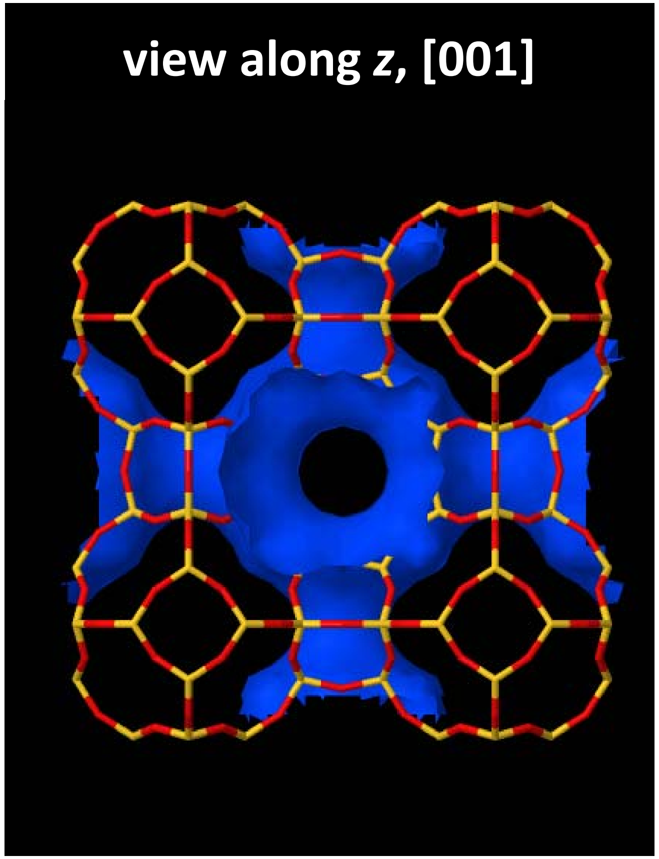
Institute of Experimental Physics

The system under study:
Molecules in nanoporous materials



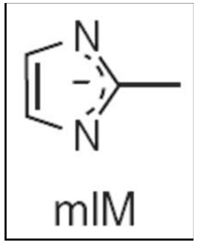
LTA-type structure – cages/narrow windows (3d)





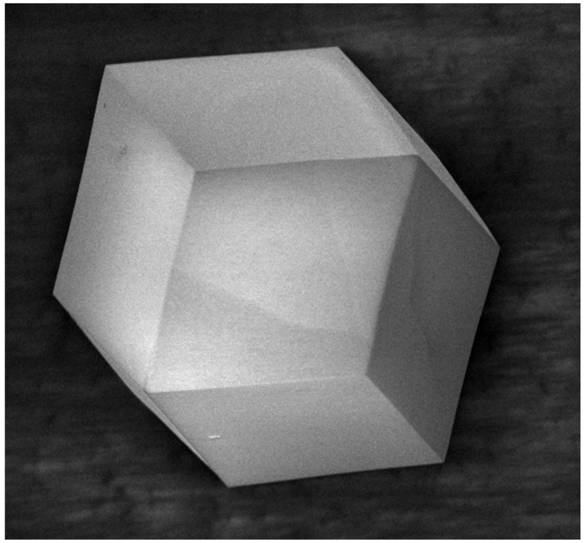
- large cavity (11 Å) framed by six narrow windows (4.1 × 4.1 Å^2)

www.iza-structure.org
STRUCTURE COMMISSION



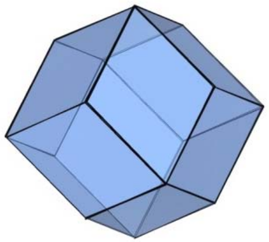
MOFs (Metal-Organic Frameworks) of type ZIF:
Zeolitic Imidazolate Frameworks (ZIF-8 ↔ SOD)

SEM image (J. Caro)

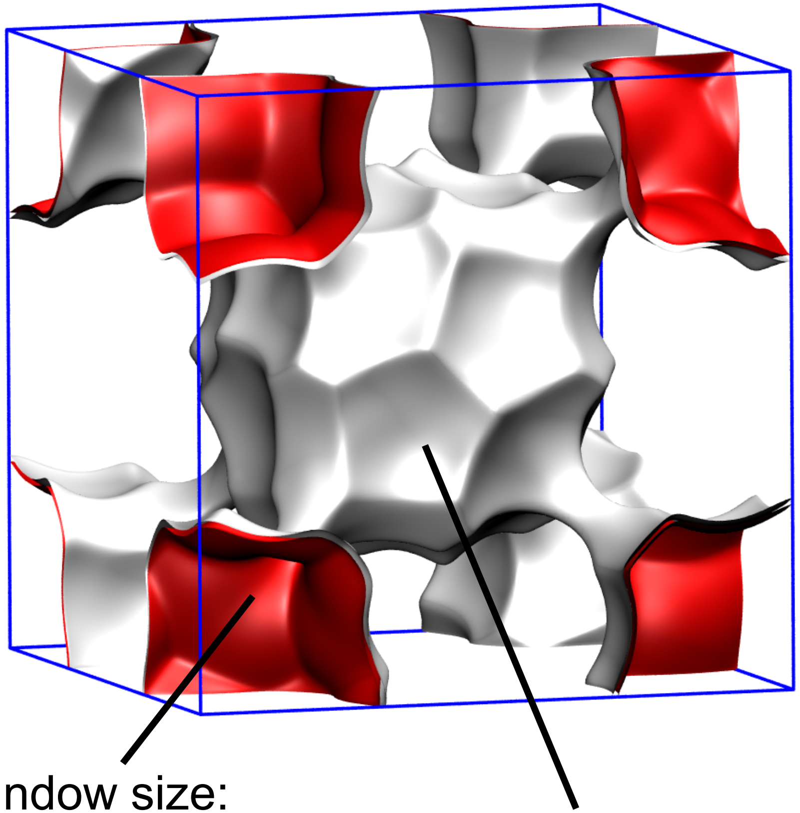


crystal size: up to 300 μm

crystal shape: rhombic dodecahedron



potential landscape (R. Krishna)



window size: ca. 3.4 Å

cavity size: ca. 12 Å

unit cell: a = b = c ≈ 17 Å

in collaboration with J. Caro, Hannover

Introducing into Spreading Fundamental by Looking at Molecules („Guests“) in Nanoporous Materials („Hosts“)

The Benefit of Considering

Molecules as the object of spreading:

- observations with a **large number of diffusants**
- all diffusants („guests“) are **identical**
- diffusants **do not change** their properties with time

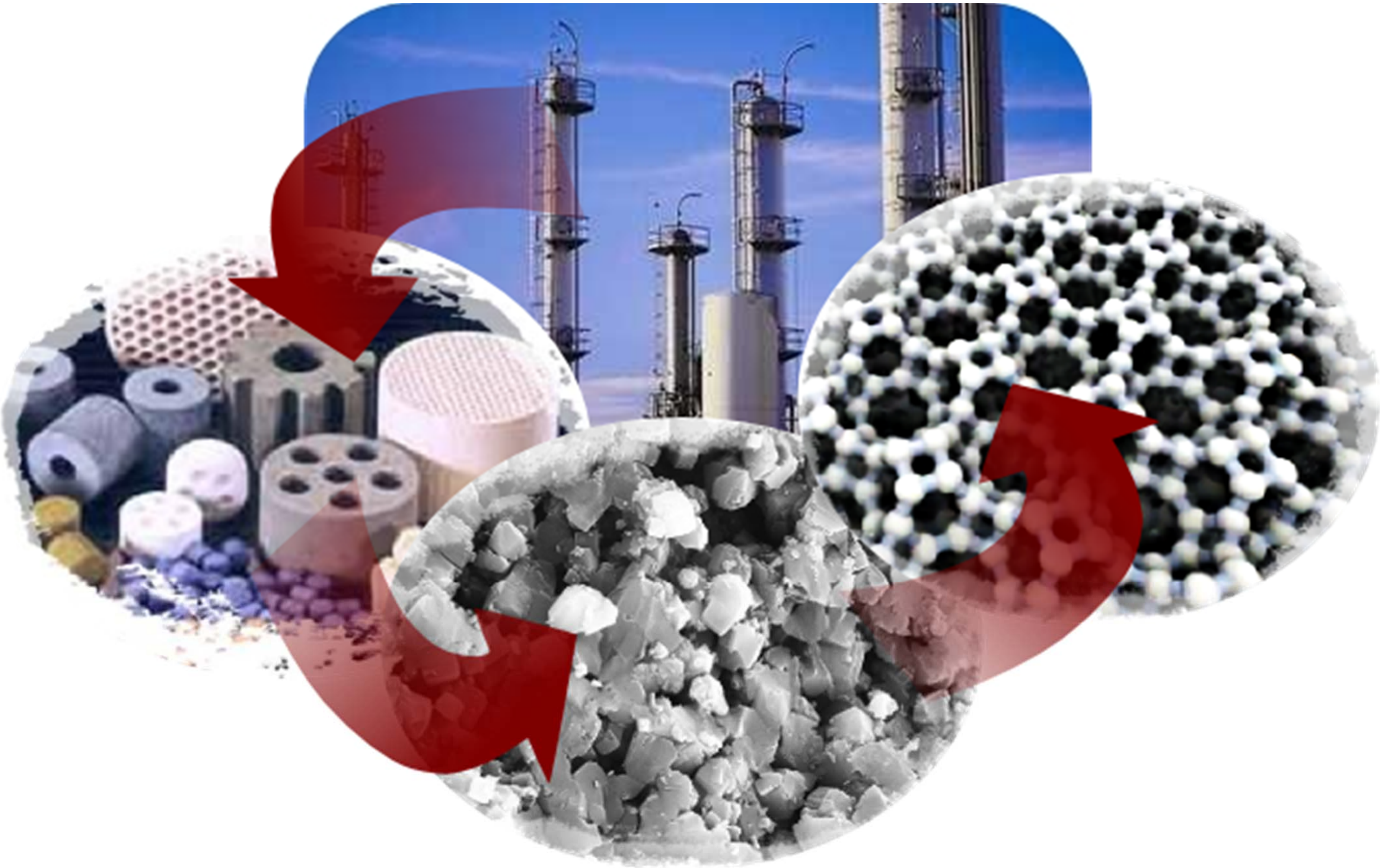
Nanoporous Materials as a host system:

- **well-defined conditions** for guest movement
- option of **deliberate variation** of these conditions

Enabling

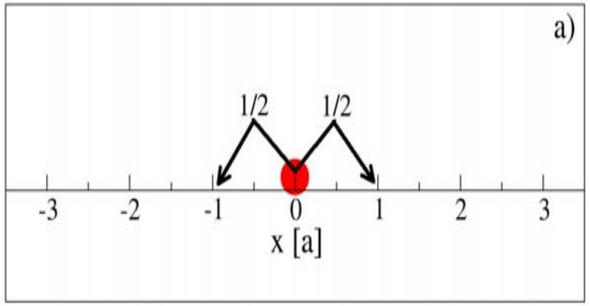
- High **statistical relevance**
- Vast options for **varying initial and boundary conditions**
- High r**eproducibility** of measurement
- Hope for **„simple“ relations** and predictability

Last not Least: Systems of High Technological Relevance



Nanoporous materials are key to many value-adding processes, their performance is controlled by the rate of DIFFUSION

What we have to keep in mind from lesson 1:
Probability distribution



$$P_n(m) = \frac{1}{2} P_{n-1}(m-1) + \frac{1}{2} P_{n-1}(m+1), \qquad t = n\tau, \quad x = ma, \; P_n(m) = aP(x,t)$$

$$P(x,t) = \frac{1}{2} P(x-a, t-\tau) + \frac{1}{2} P(x+a, t-\tau)$$

$$P(x,t) - P(x,t-\tau) = \frac{1}{2} P(x-a, t-\tau) + \frac{1}{2} P(x+a, t-\tau) - P(x, t-\tau)$$

$$\frac{P(x,t) - P(x,t-\tau)}{\tau} = \frac{a^2}{2\tau} \frac{P(x-a, t-\tau) + P(x+a, t-\tau) - 2P(x, t-\tau)}{a^2}$$

$$\frac{\partial P}{\partial t} = \left(\frac{a^2}{2\tau}\right) \frac{\partial^2 P}{\partial x^2}$$

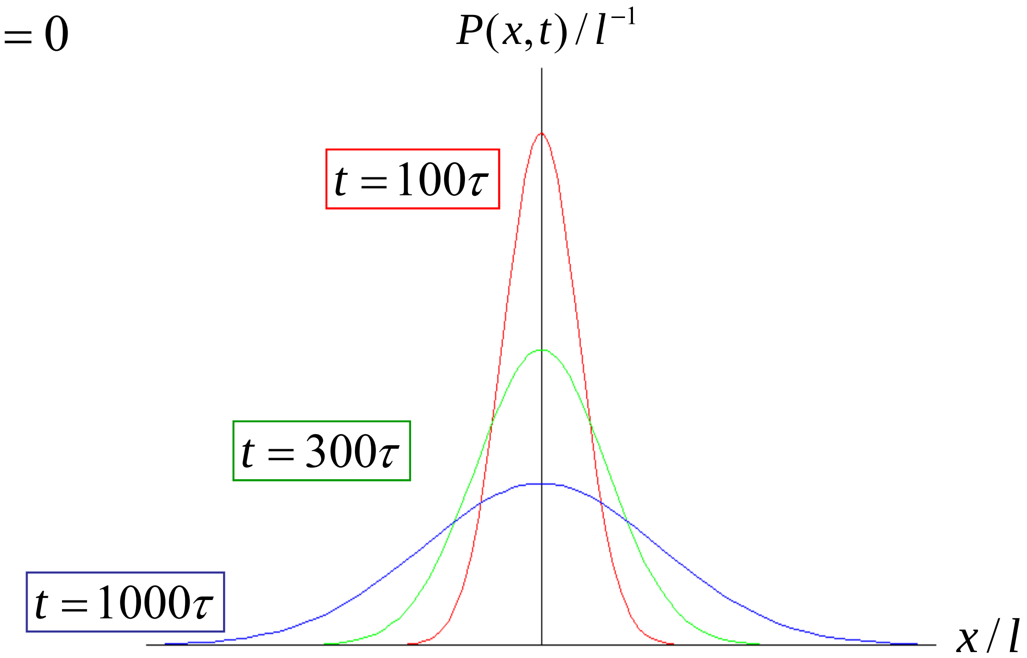
diffusion equation

D ↵

$$c(x,t) \equiv P(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

Probability distribution of the displacements of a random walker (diffusing particle)

starting at $x = 0$

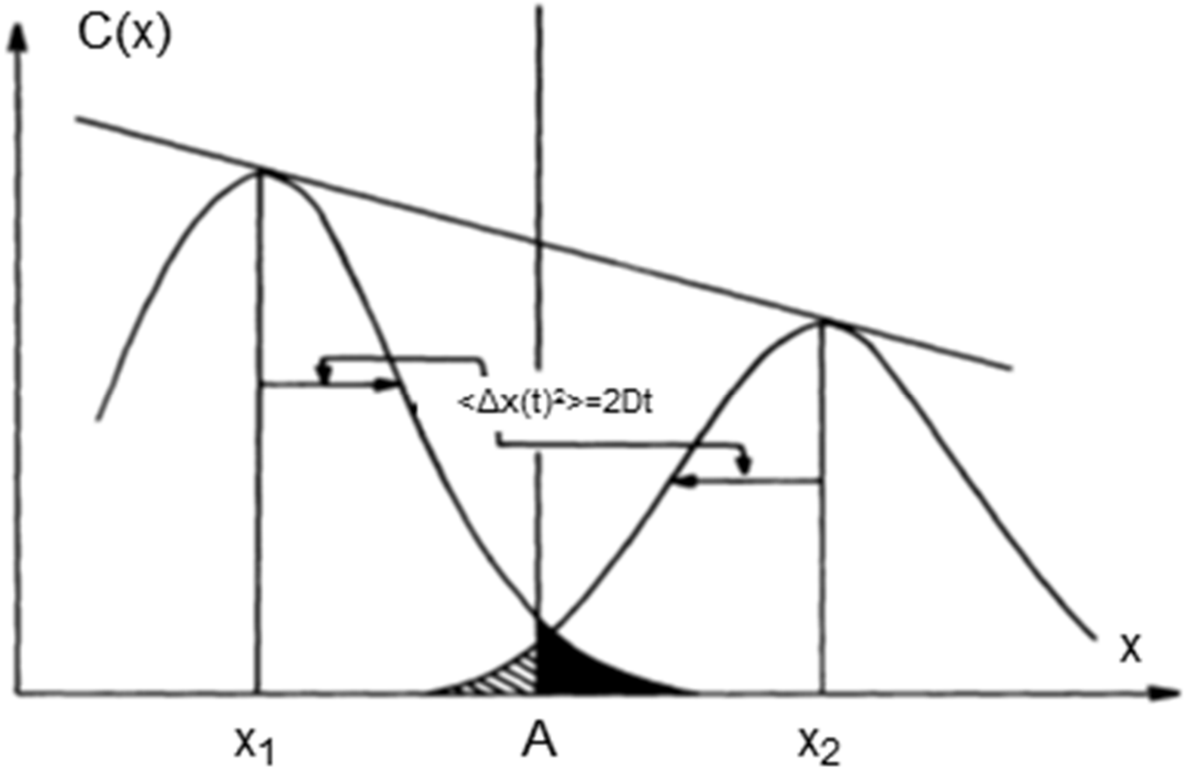


$$c(x,t) \equiv P(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

(PROPAGATOR)

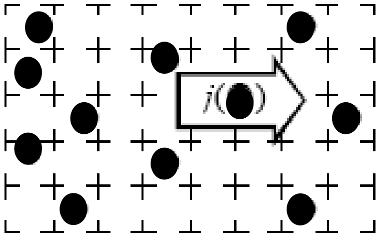
:

Directed Diffusion **Flux**
generated by Undirected **Random walk**
under the influence of a **Concentration Gradient**



Different Situations for Recording Diffusivities

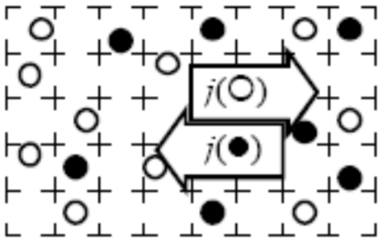
- Transport (or Collective or Chemical) Diffusion



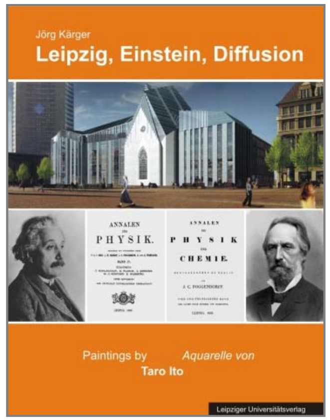
$$j_x = -D_T \frac{\partial c}{\partial x}$$

(Fick's 1st law)

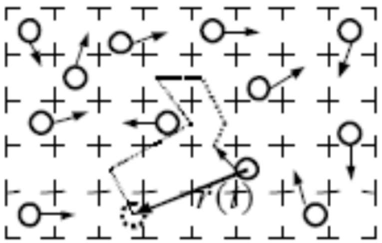
- Self- (or Tracer) Diffusion by Tracer Exchange



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

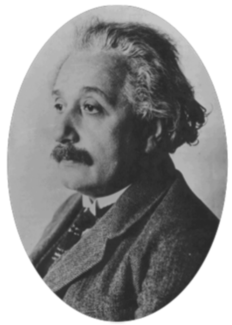


- Self- (or Tracer) Diffusion by Following the Individual Molecules

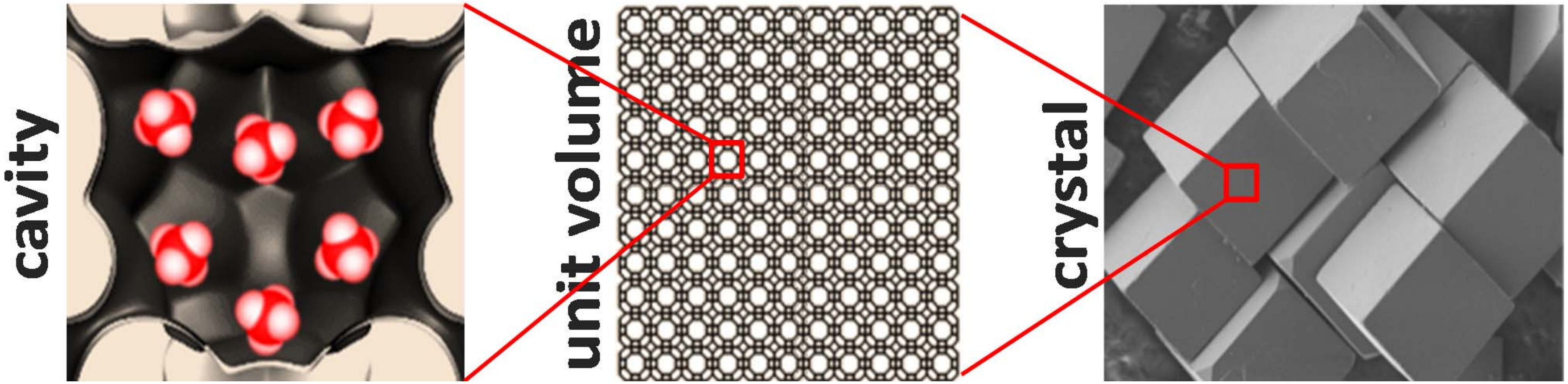


$$< x^2(t) > = 2Dt$$

Einstein Equation
PFG NMR, QENS

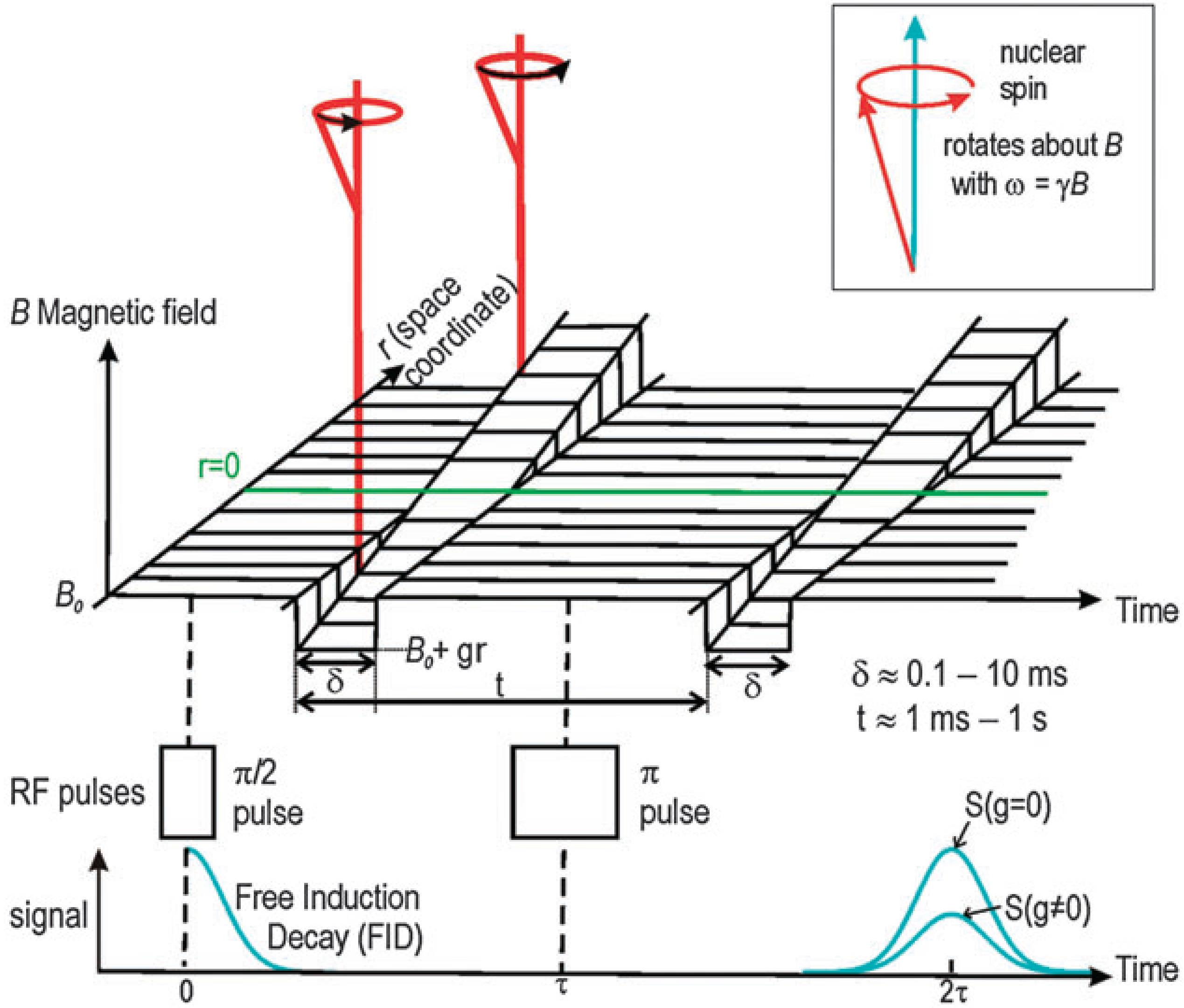


Prerequisite for a meaningful definition of Fluxes and Concentrations as appearing in Fick's laws



Contents:

Diffusion Measurement by Pulsed Field Gradient (PFG) NMR



net phase $\Delta\varphi$ in rotational motion of nuclear spin

After displacement Δz between the two field gradient pulses:

$$\Delta\varphi = \Delta(\omega\delta) = \Delta(\gamma B\delta) = \Delta[\gamma(B_0 + gz)\delta] = \gamma\delta g\Delta z$$

any spin contributes to the signal with the cosine of the phase shift $\gamma\delta g\Delta z$:

$$\Psi(g\delta,t)=\frac{M(g\delta,t)}{M_0(t)}=\int P(z,t)\cos(\gamma\, g\delta\, z)\, dz$$

With $P(z,t)$ denoting the probability density that,
during the observation time t,
a molecule is shifted over a distance z (the „Propagator“)

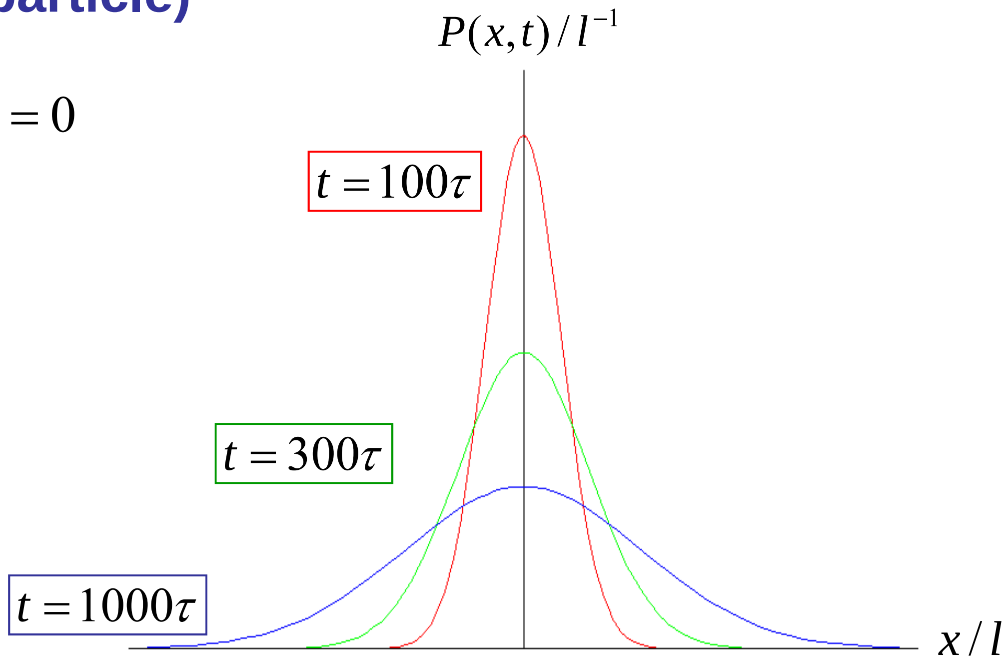
PFG NMR Spin-Echo Attenuation Results as the Fourier Transform of the „Propagator“

Vice versa: Determining the mean „Propagator“ from the Spin-Echo Attenuation:

J. Kärger, W. Heink: The Propagator Representation of Molecular Transport in Microporous Crystallites, J. Magn. Res. 51 (1983) 1-7

Probability distribution of the displacements of a random walker (diffusing particle)

starting at $x=0$



$$c(x,t) \equiv P(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$

(PROPAGATOR)

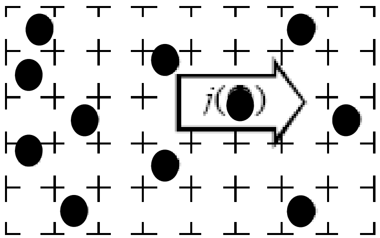
yielding the PFG NMR signal attenuation

$$\Psi(g\delta,t) = \frac{M(g\delta,t)}{M_0(t)} = \int P(z,t)\cos(\gamma g\delta z)\,dz$$

Self- (or Tracer) diffusivity follows directly from the PFG NMR signal attenuation

The different situations in which diffusivities are measured

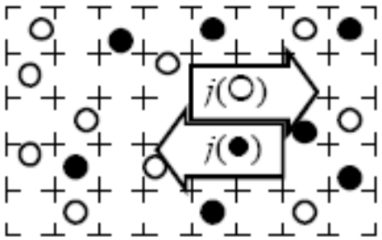
- Transport (or Collective or Chemical) Diffusion



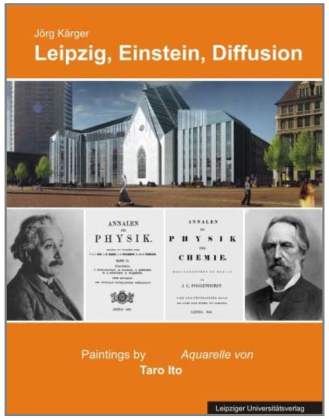
$$j_x = -D_T \frac{\partial c}{\partial x}$$

(Fick's 1st law)

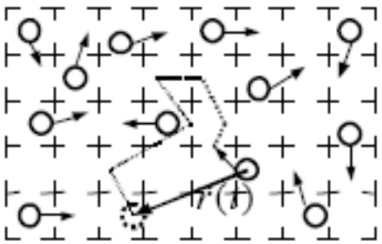
- Self-(or Tracer) Diffusion by Tracer Exchange



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



- Self- (or Tracer) Diffusion by Following the Individual Molecules (QENS, PFG NMR)



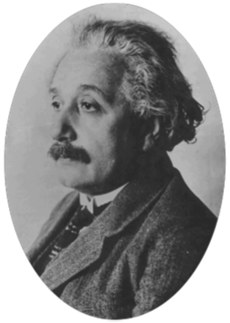
Einstein Equation

$$< x^2(t) > \quad = 2Dt$$

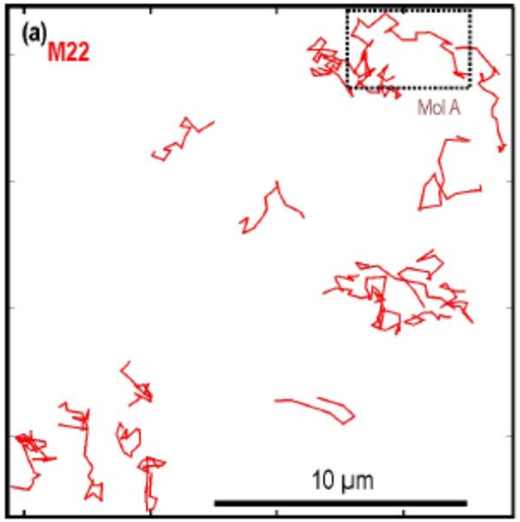
$$Ergodic\ Theorem:$$

$$< x^2(t) >_{time} = \ < x^2(t) >_{ensemble}$$

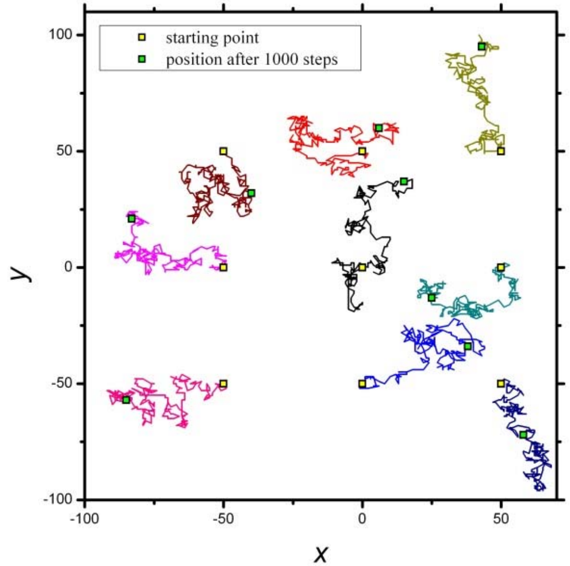
?



Single-Particle Tracking
by Fluorescence Microscopy



Simulated Random Walks
with Constant Step Length

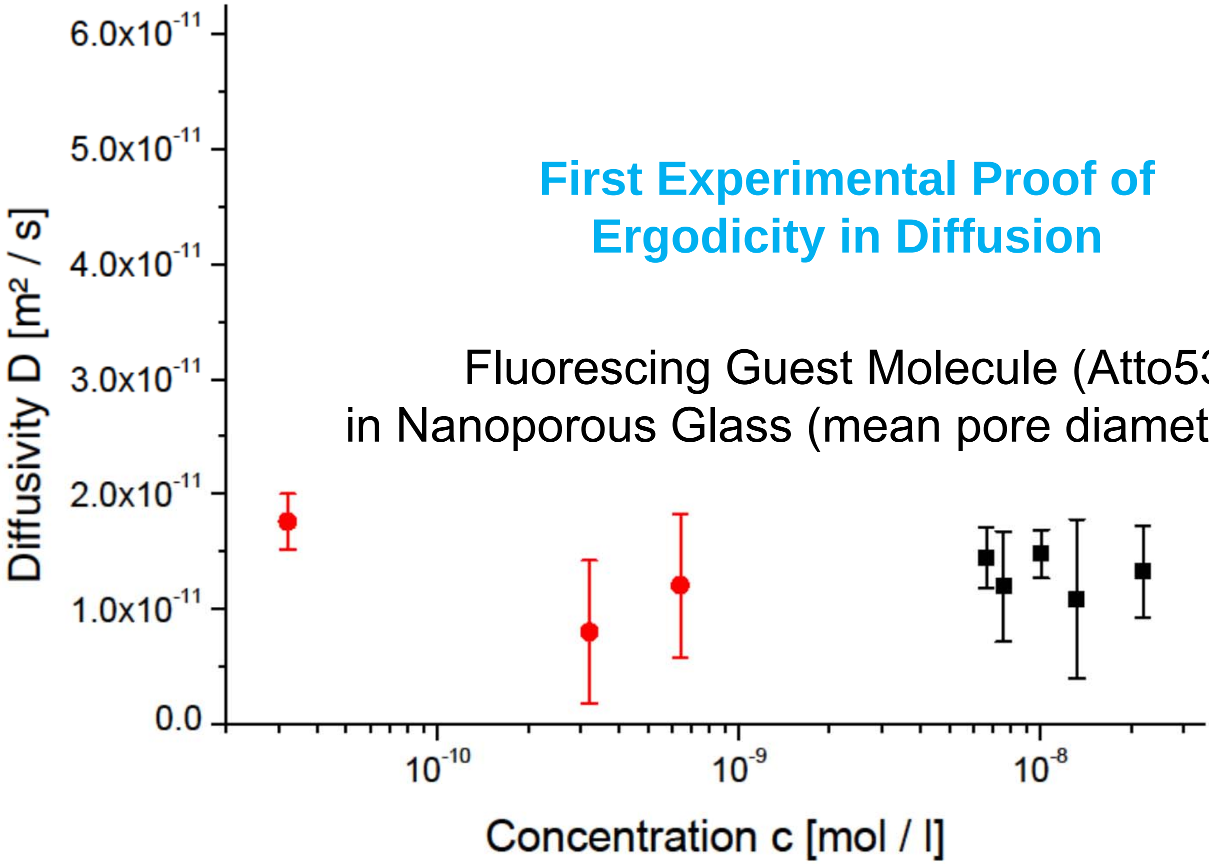


Single-Particle Time-Averaged Mean Squared Displacement

$$\langle r^2(t)\rangle_T = \frac{1}{T-t}\int_0^{T-t}\left[r(t'+t) - r(t')\right]^2 \mathrm{d}t'$$

First Experimental Proof of Ergodicity in Diffusion

Fluorescing Guest Molecule (Atto532)
in Nanoporous Glass (mean pore diameter 3 nm)



Single-Molecule Observation: $D = \langle r^2(t) \rangle / 6t$

$$\langle r^2(t) \rangle_T = \frac{1}{T-t} \int_0^{T-t} \left[r(t'+t) - r(t') \right]^2 dt'$$

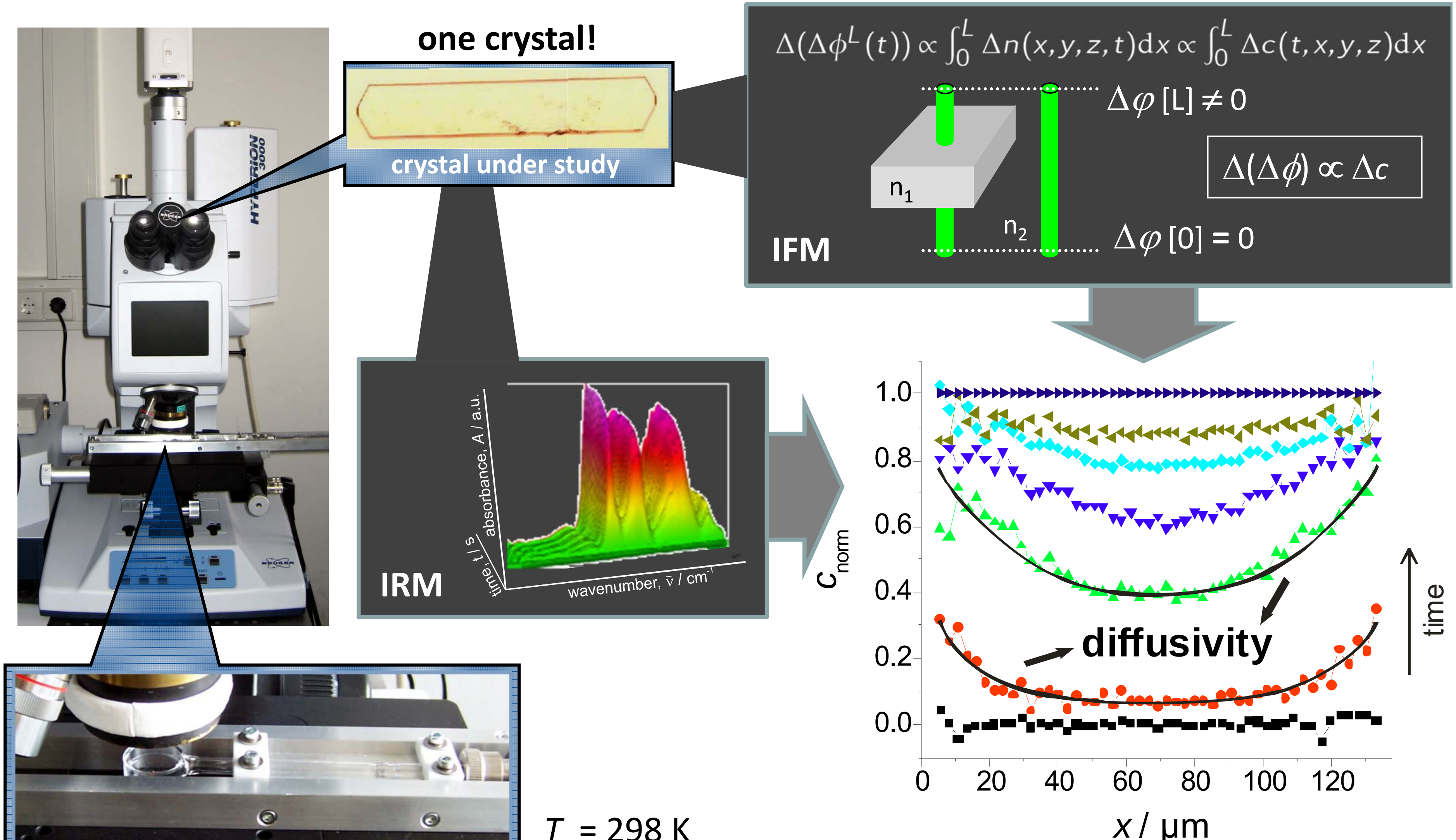
PFG NMR Measurement:

$$< r^2(t) >_{\text{ensemble}} = \int r^2 P(r,t) dr$$

Feil, F. et al: Single-Particle and Ensemble Diffusivities – Test of Ergodicity.
Angew. Chem., Intern. Edit. 51 (2012) 1152

Contents:

IR Microscopy (IRM) and Interference Microscopy (IFM)

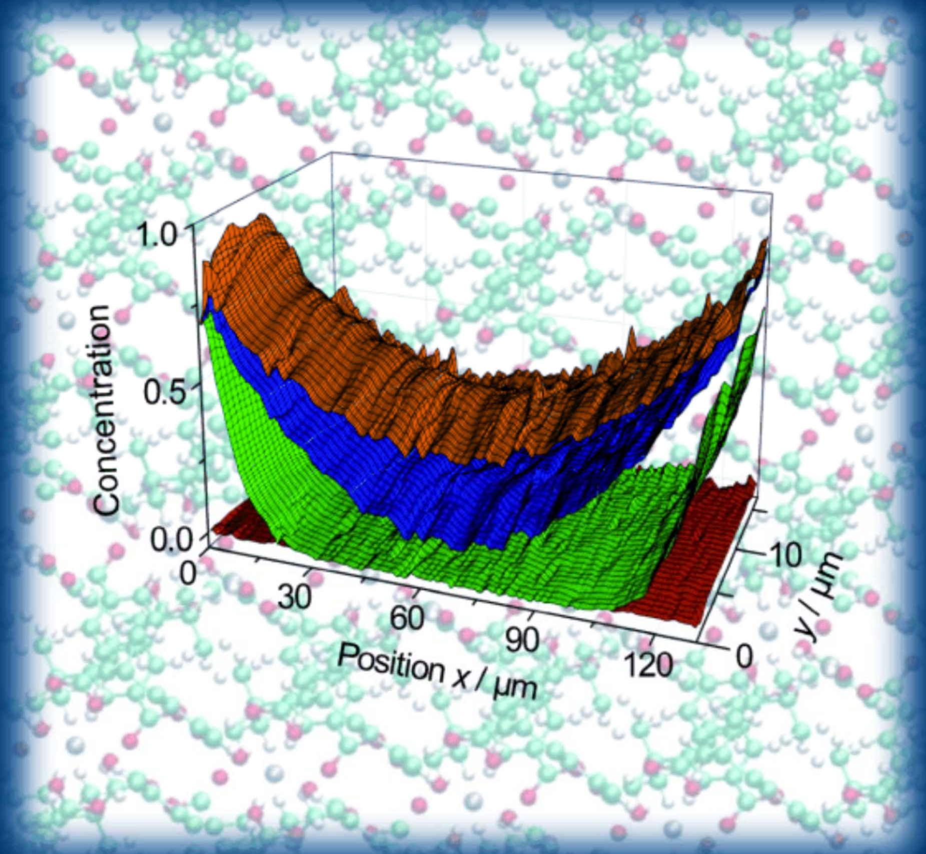


Techniques of

Microimaging

J. Kärger, T. Binder, C. Chmelik, H. Krautscheid, R. Krishna, J. Weitkamp *Nature Materials* 13 (2014) 333–343

A EUROPEAN JOURNAL
CHEMPHYSCHEM
OF CHEMICAL PHYSICS AND PHYSICAL CHEMISTRY



15/2009

A Journal of
ChemPubSoc Europe

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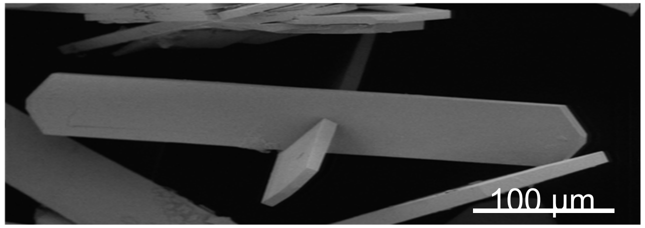
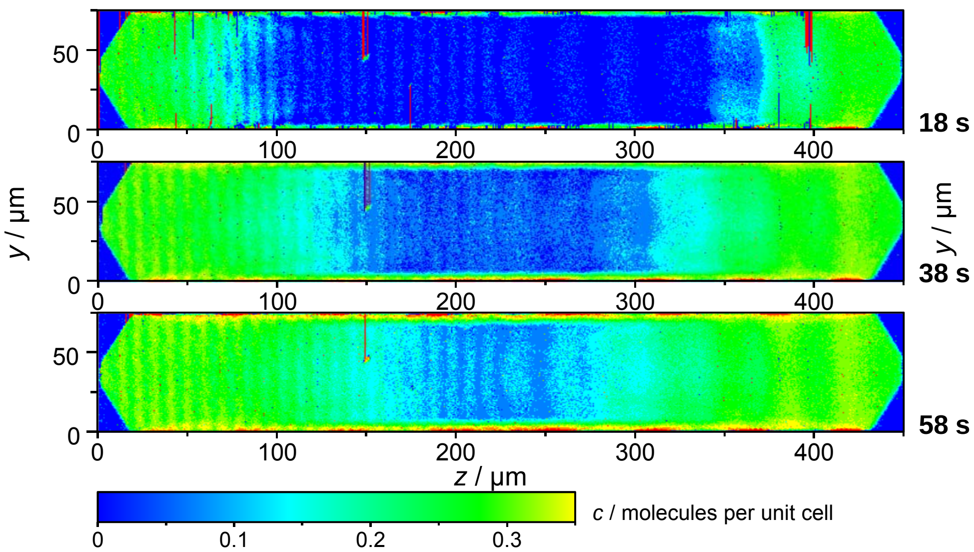
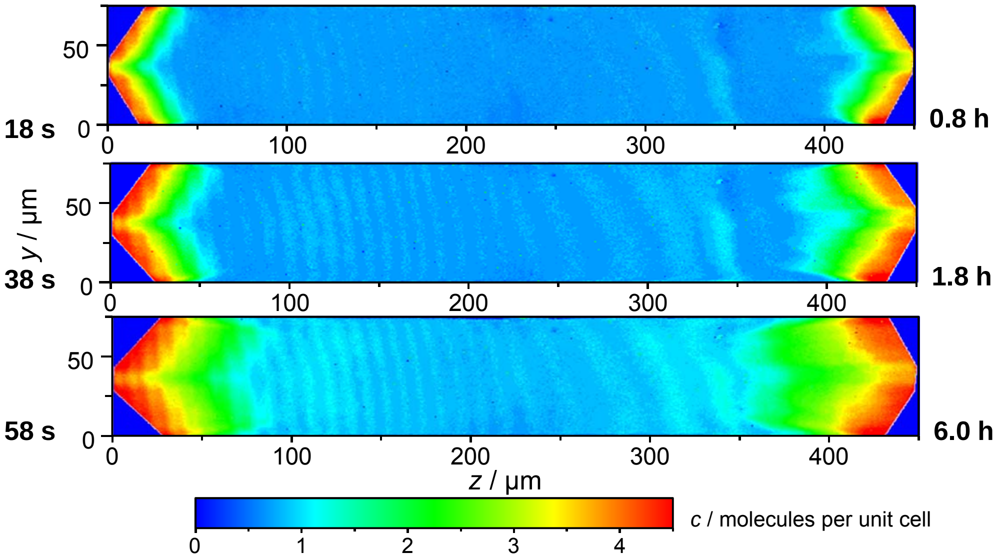
Contents:

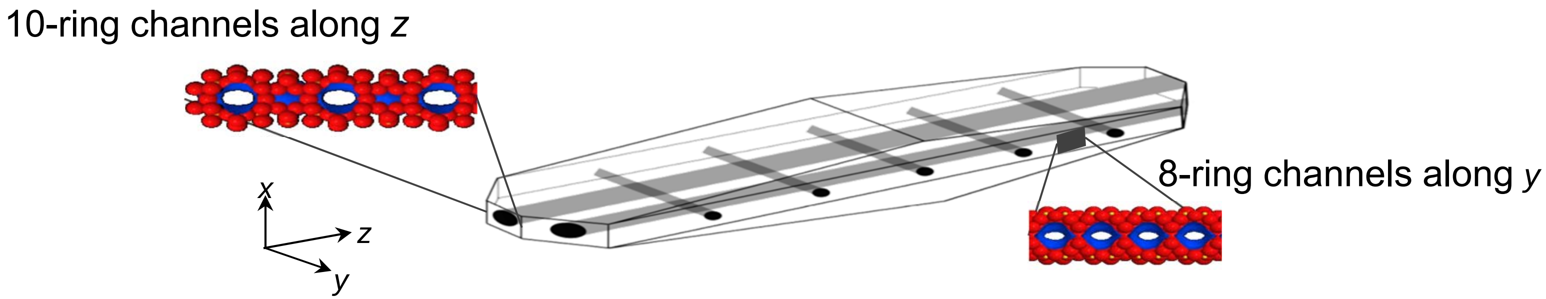
methanol adsorption, pressure step 0 to 0.5 kPa



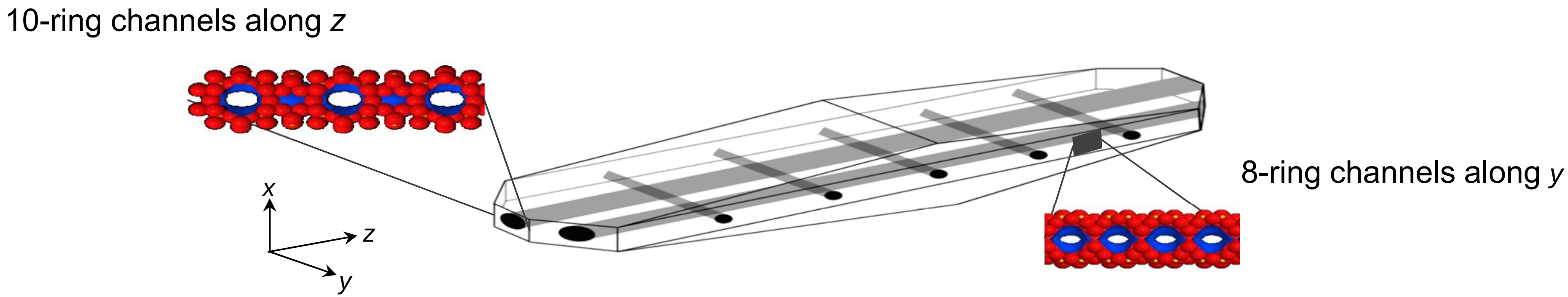
ethanol adsorption, pressure step 0 to 2 kPa

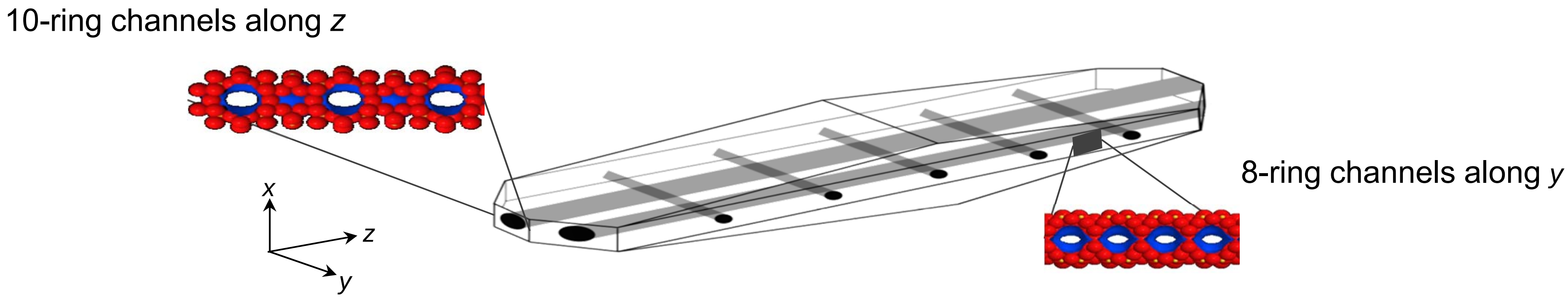






J. Kärger, T. Binder, C. Chmelik, H. Krautscheid, R. Krishna, J. Weitkamp
Nature Materials **13 (2014) 333–343**
F. Hibbe et al: *J. Chem. Phys.* 135, 184201-1-5 (2011).


10-ring channels along z
x
z
y
8-ring channels along y


10-ring channels along z
x
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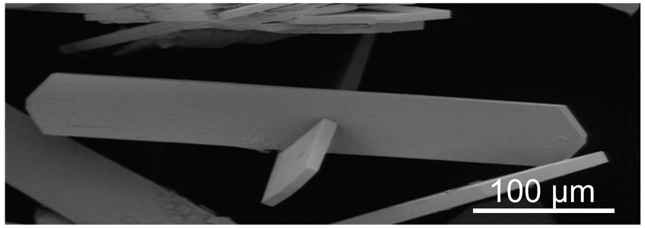
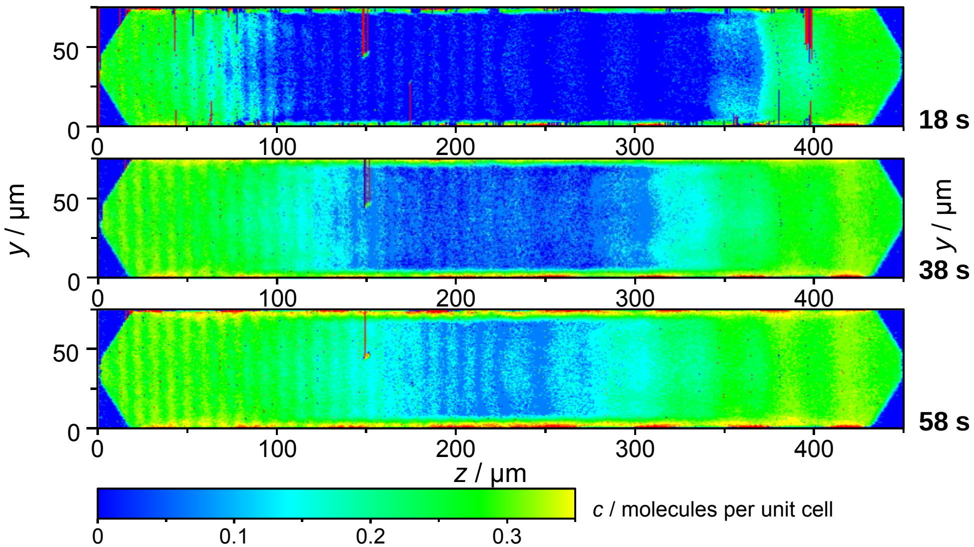
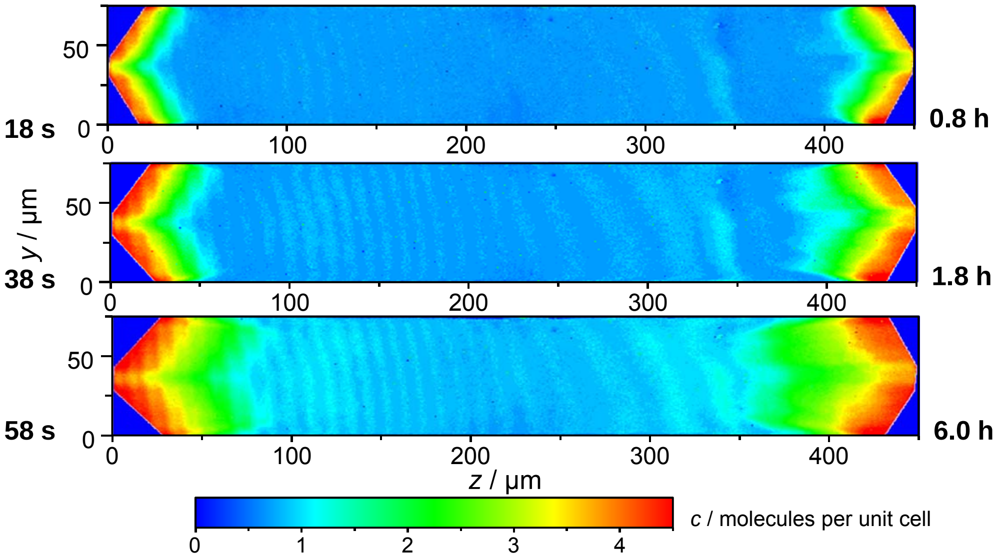
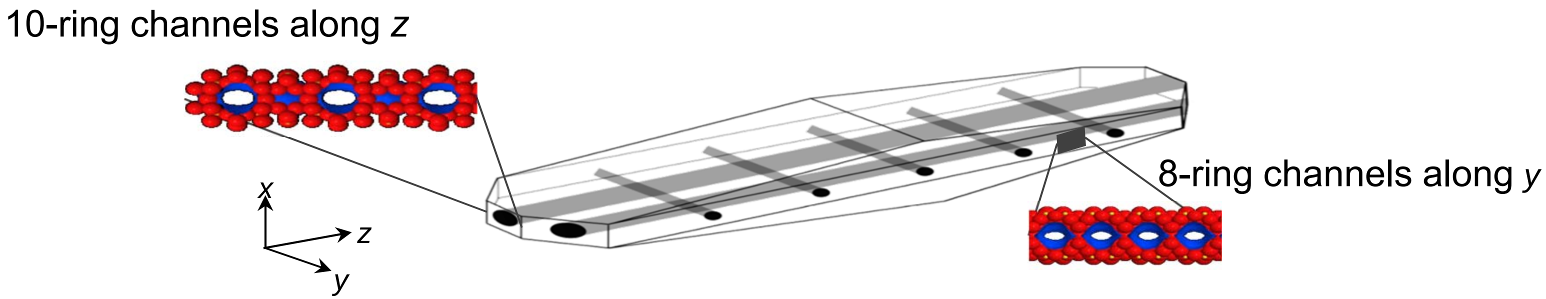
methanol adsorption,
pressure step 0 to 0.5 kPa



ethanol adsorption,
pressure step 0 to 2 kPa







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Contents:

1) Tracing the diffusion path: PFG NMR diffusion measurement

2) Recording transient concentration profiles by microimaging

3) Pore spaces „infested“ by molecules

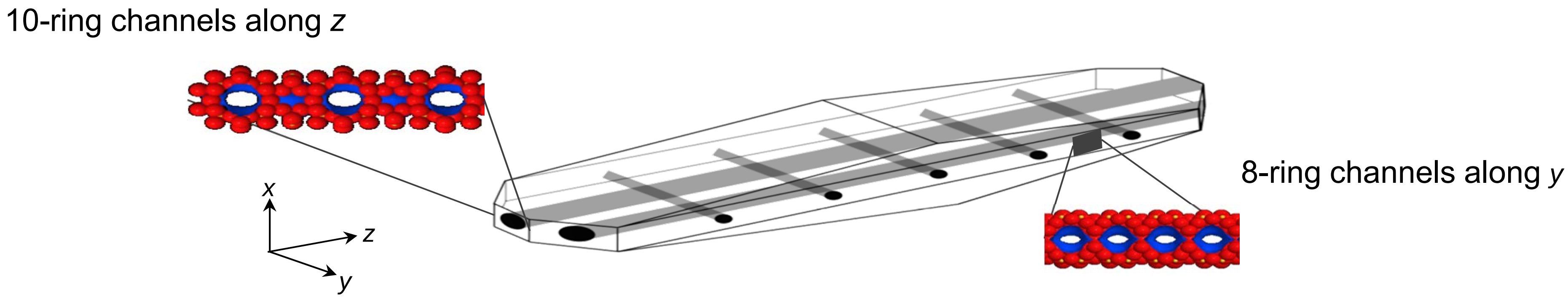
4) Interacting invaders

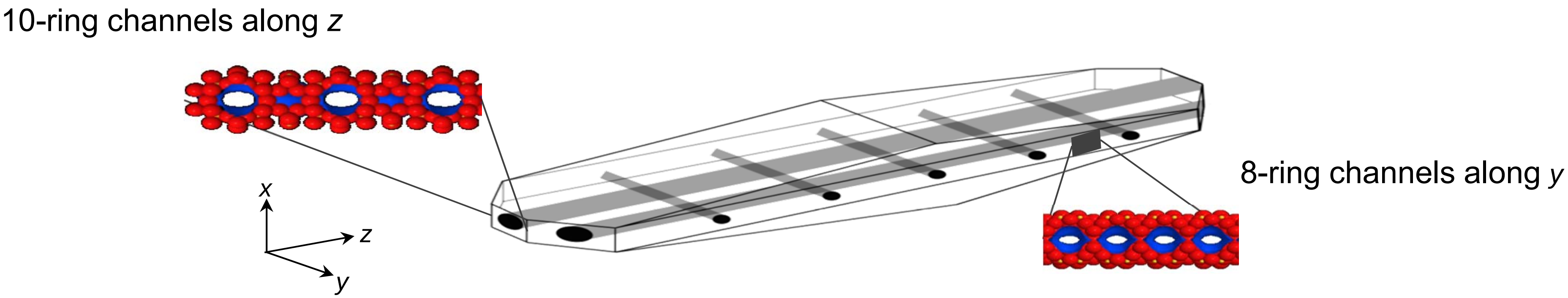
5) The „driving force“ of diffusion

6) Transport barriers and highways

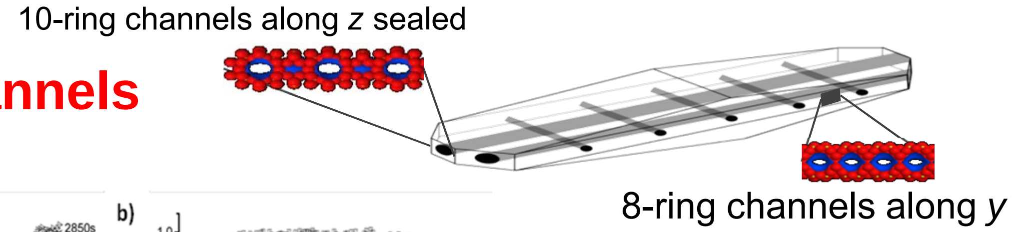
7) Spreading accompanied by guest transformation

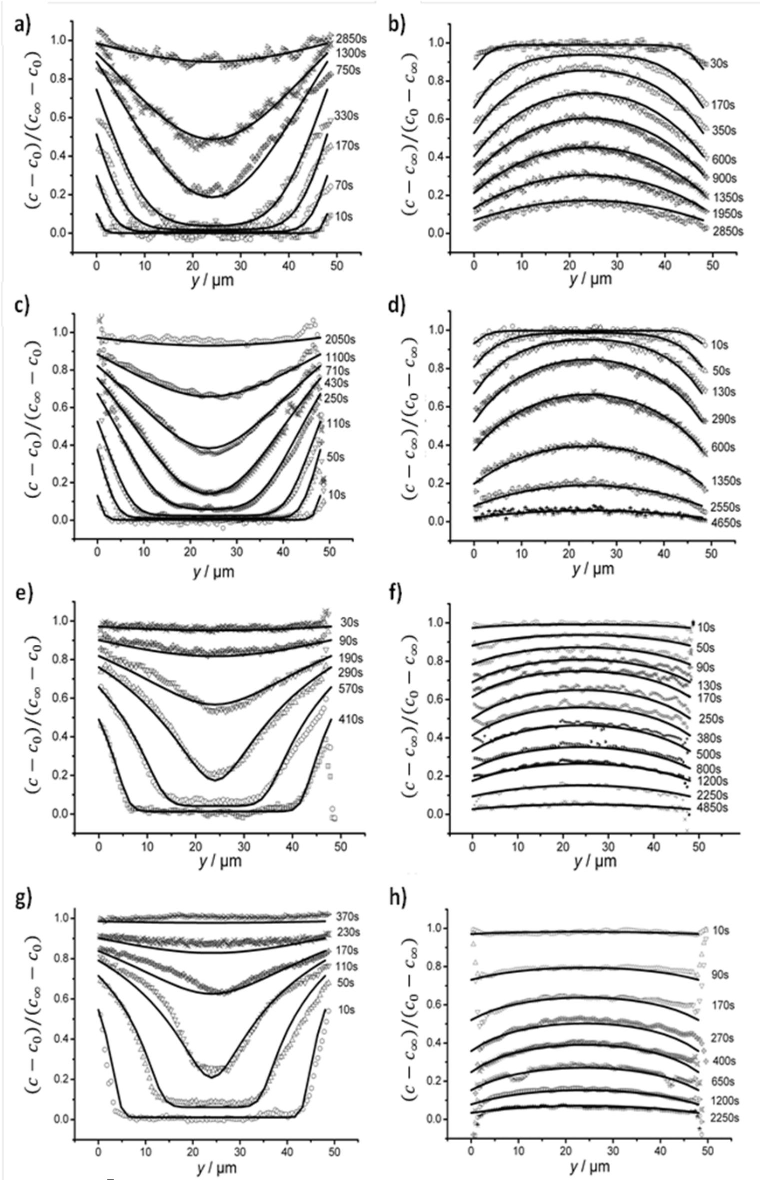
8) Spreading accompanied by host transformation


10-ring channels along z
8-ring channels along y
x
z
y


10-ring channels along z
8-ring channels along y
x
z
y

Uptake and Release of methanol along the 8-ring channels of Zeolite Ferrierite:





0 to 5 mbar | 5 to 0 mbar

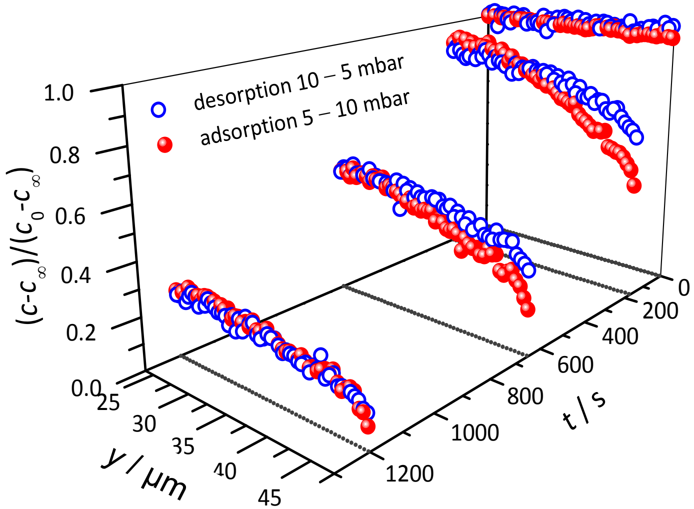
0 to 10 mbar | 10 to 0 mbar

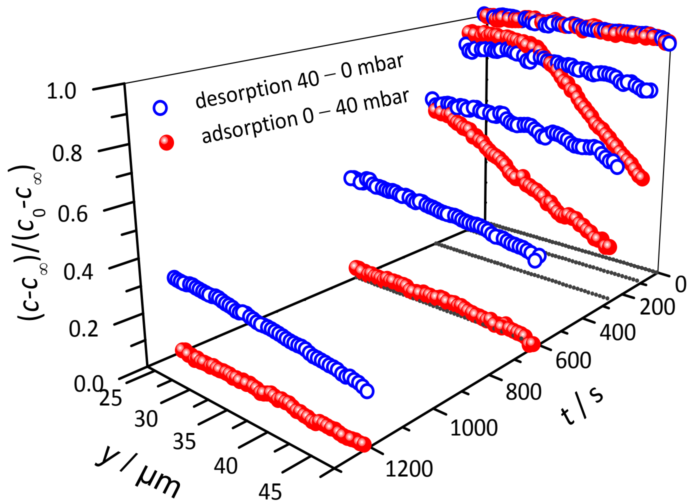
0 to 40 mbar | 40 to 0 mbar

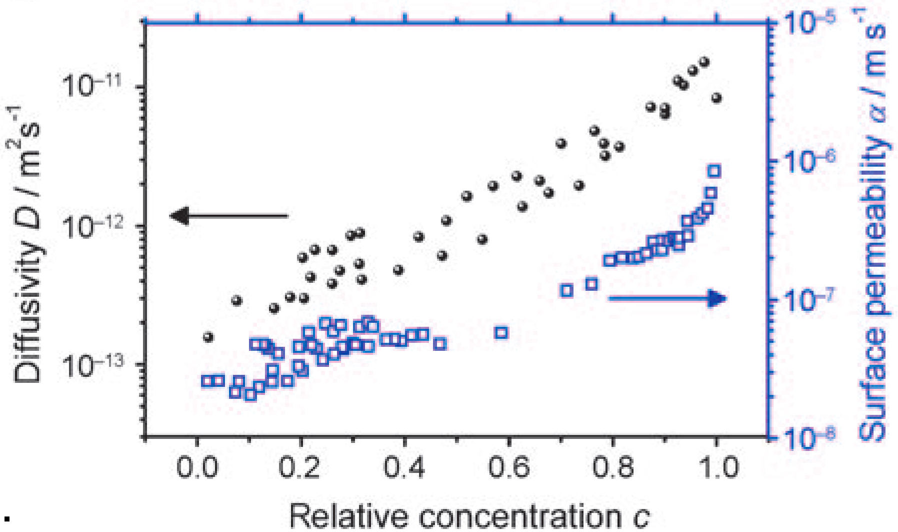
0 to 80 mbar | 80 to 0 mbar

P. Kortunov et al., *J. Phys. Chem. B* 2006, *110*, 23821–23828.

Uptake (Adsorption) and Release (Desorption) of methanol along the 8-ring channels of Zeolite Ferrierite



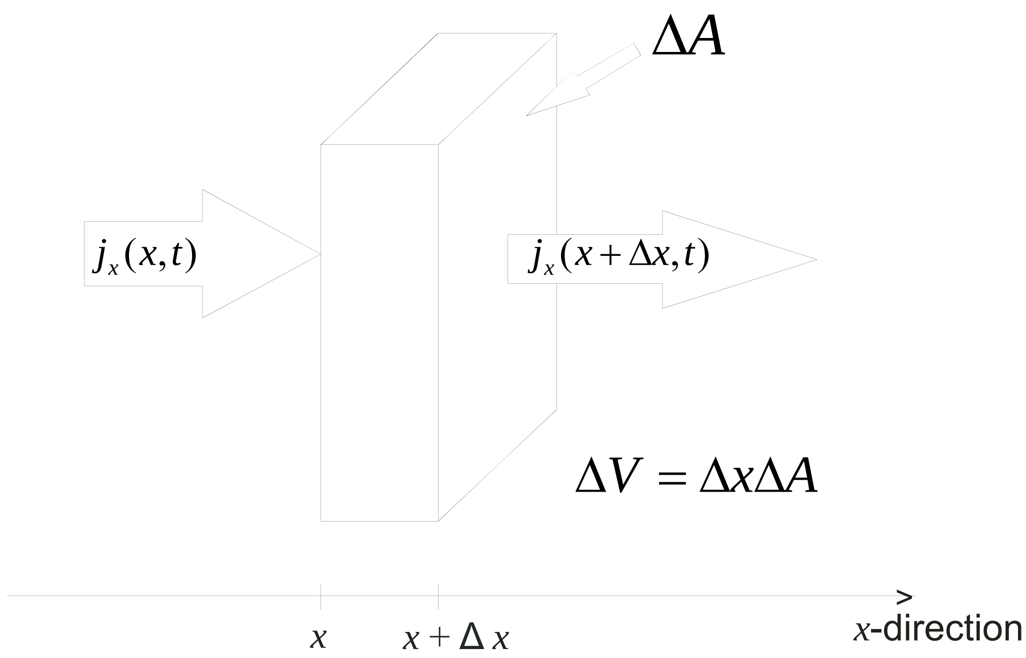




$$j = \alpha(c_{\text{boundary}} - c_{\text{equilibrium}})$$

***C. Chmelik et al. Chem. Phys. Chem.* 2009, *10*, 2623–2627.**

From Fluxes to Concentration Changes



$$\frac{\partial c}{\partial t} \equiv \frac{1}{\Delta V}\frac{\partial N}{\partial t} \approx \frac{1}{\Delta V}\frac{\Delta N}{\Delta t} = \frac{1}{\Delta A \Delta x}\frac{(j_x(x) - j_x(x+\Delta x))\Delta A \Delta t}{\Delta t} = \frac{j_x(x) - j_x(x+\Delta x)}{\Delta x} \approx -\frac{\partial j}{\partial x}$$

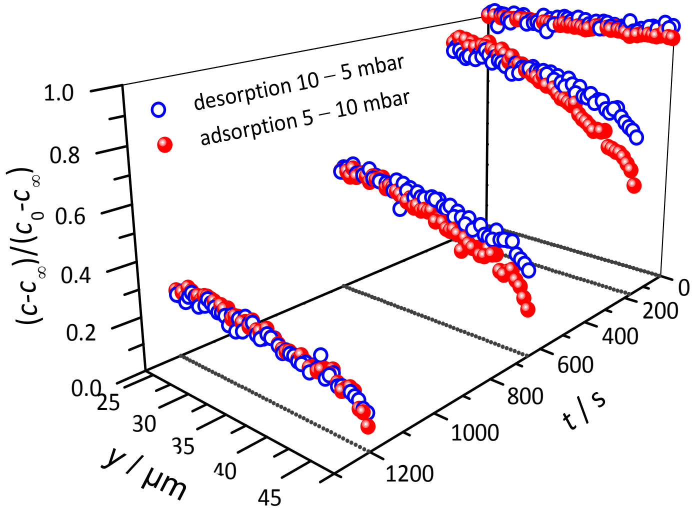
Inserting Fick's 1st law $j = -D\frac{\partial c}{\partial x}$ yields

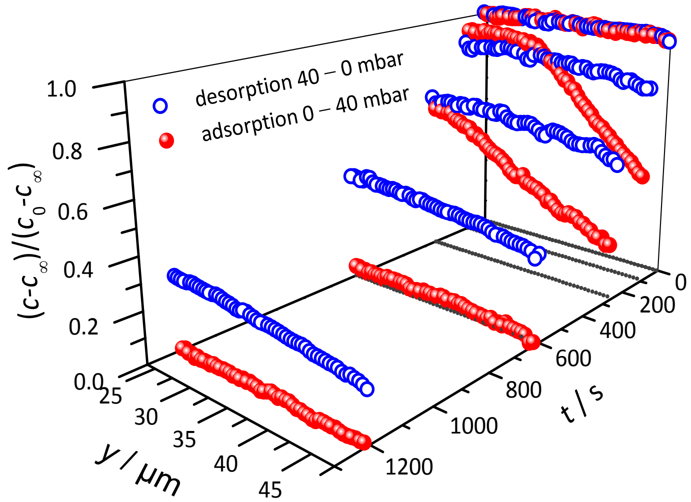
$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) = D\frac{\partial^2 c}{\partial x^2} + \frac{\partial D}{\partial x}\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} + \frac{\partial D}{\partial c}\left(\frac{\partial c}{\partial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

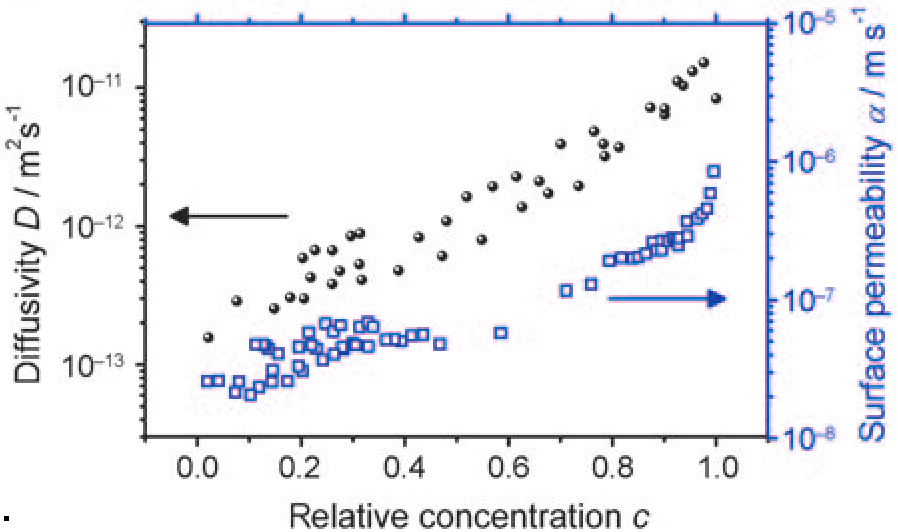
(Fick's 2nd law)

$$= D\frac{\partial^2 c}{\partial x^2}$$ (for constant diffusivities)

Uptake (Adsorption) and Release (Desorption) of methanol along the 8-ring channels of Zeolite Ferrierite



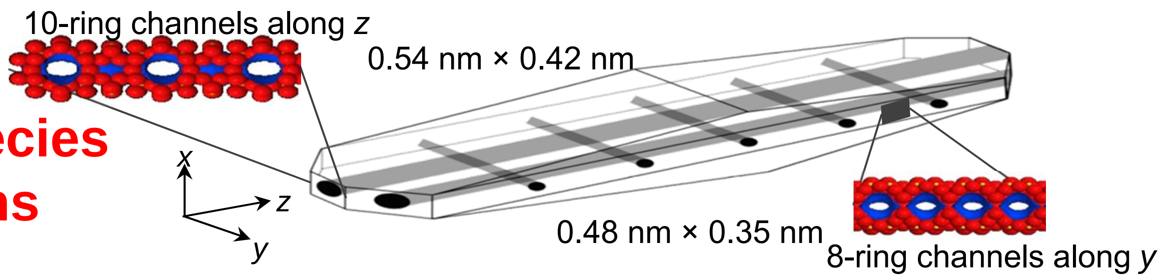


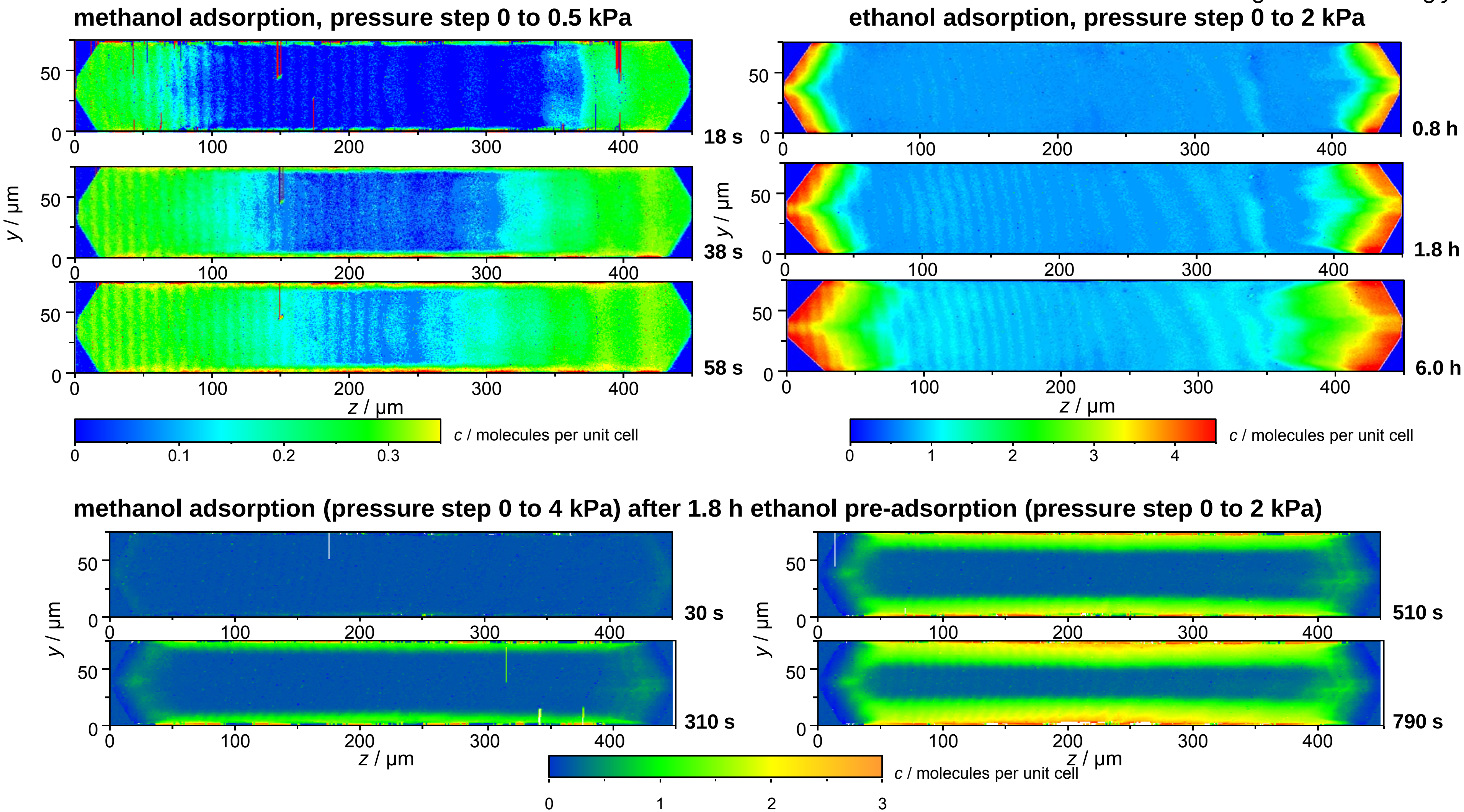


$$j = \alpha(c_{\text{boundary}} - c_{\text{equilibrium}})$$

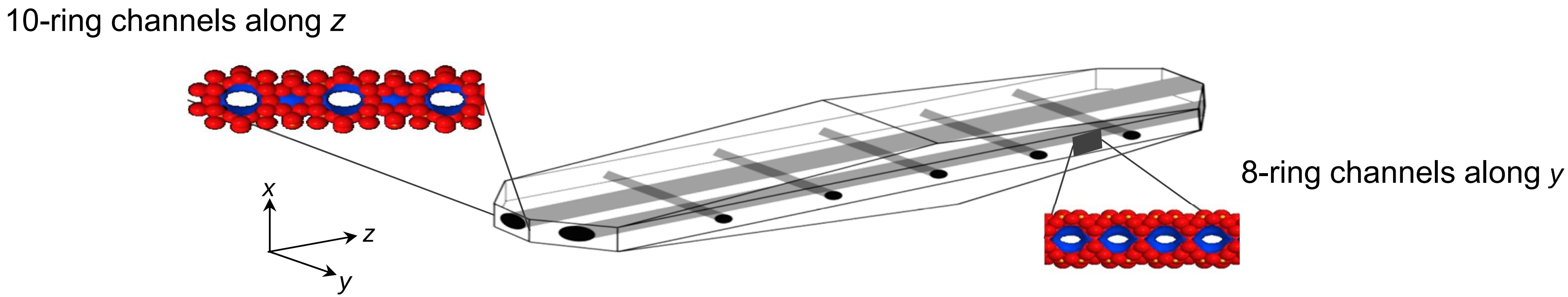
***C. Chmelik et al. Chem. Phys. Chem.* 2009, *10*, 2623–2627.**

Infestation by Second Species Changes Diffusion Paths

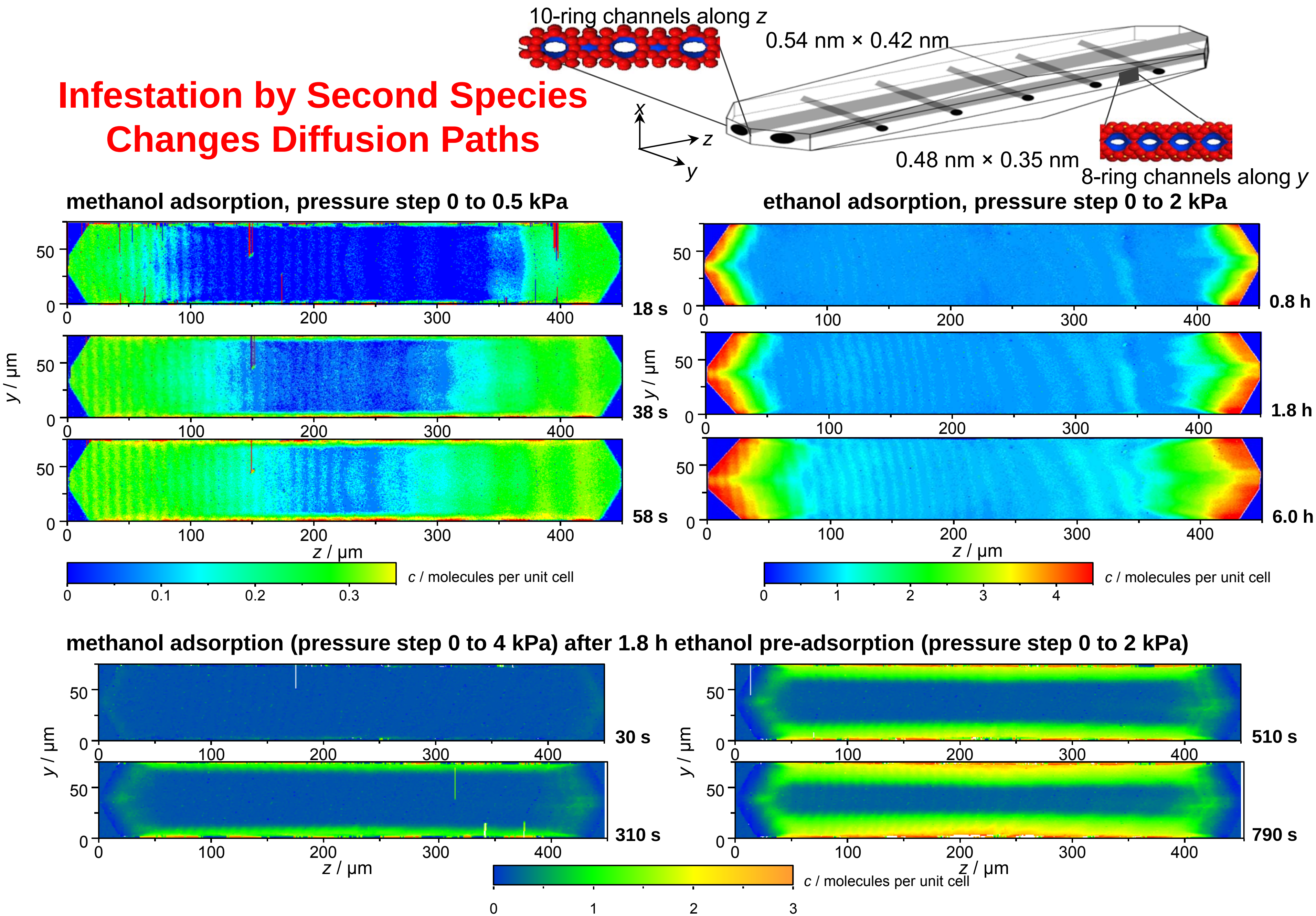




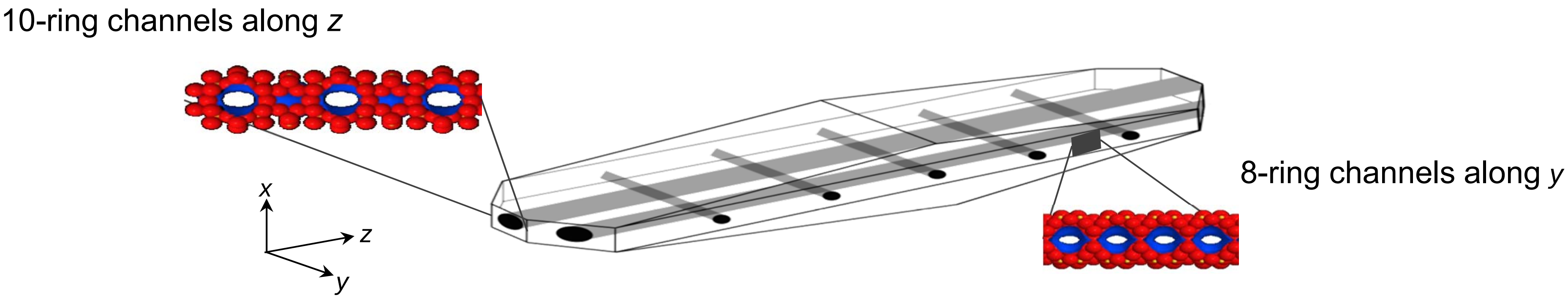
J. Kärger, T. Binder, C. Chmelik, H. Krautscheid, R. Krishna, J. Weitkamp
Nature Materials **13 (2014) 333–343**


10-ring channels along z
8-ring channels along y
x
z
y

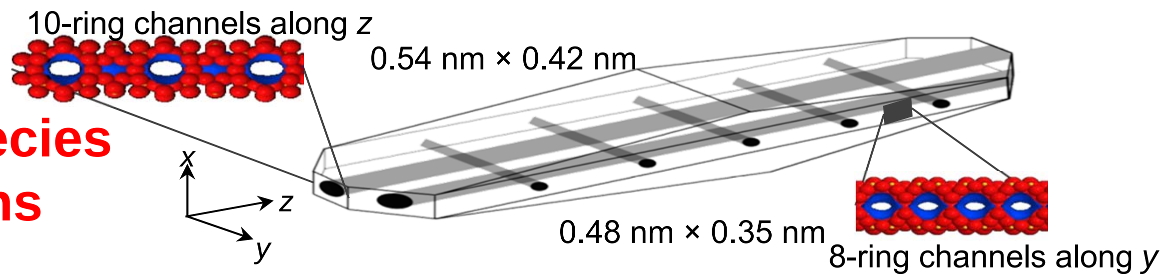
Infestation by Second Species Changes Diffusion Paths



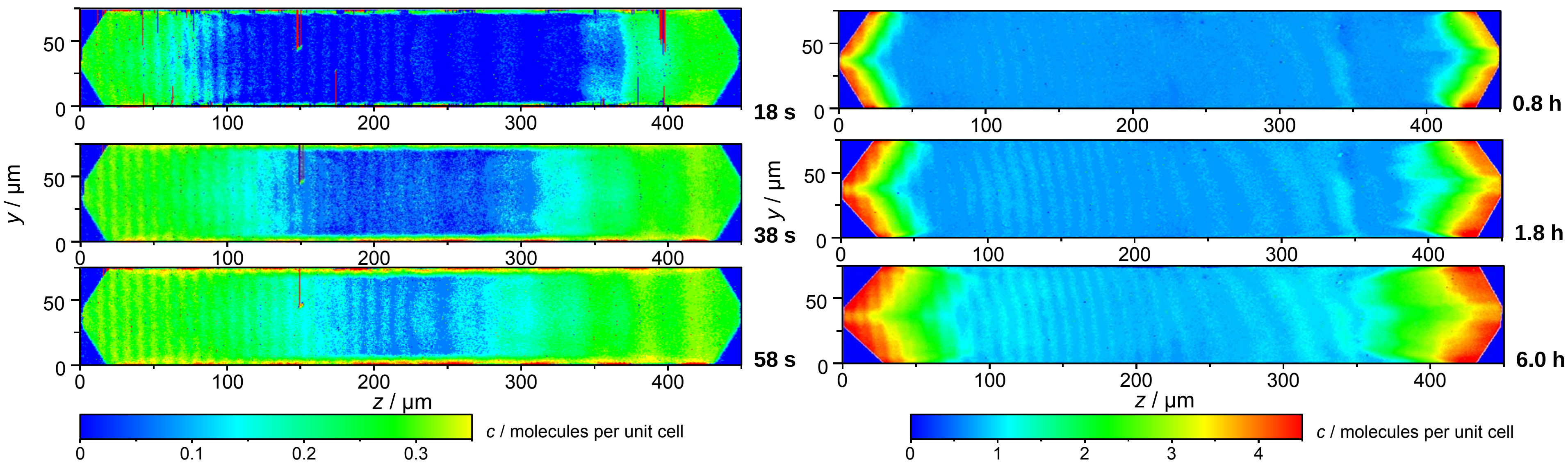
J. Kärger, T. Binder, C. Chmelik, H. Krautscheid, R. Krishna, J. Weitkamp
Nature Materials **13 (2014) 333–343**


10-ring channels along z
8-ring channels along y
x
z
y

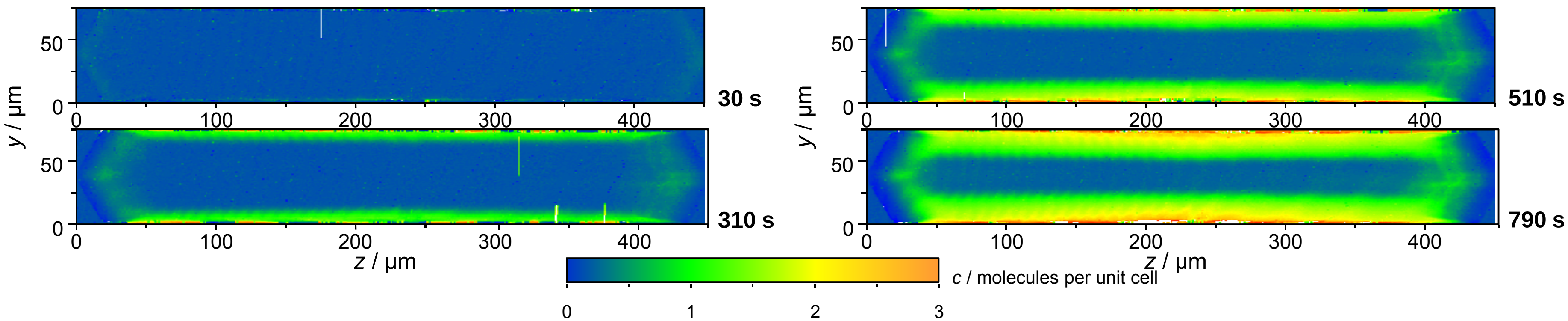
Infestation by Second Species Changes Diffusion Paths



methanol adsorption, pressure step 0 to 0.5 kPa | **ethanol adsorption, pressure step 0 to 2 kPa**



methanol adsorption (pressure step 0 to 4 kPa) after 1.8 h ethanol pre-adsorption (pressure step 0 to 2 kPa)



J. Kärger, T. Binder, C. Chmelik, H. Krautscheid, R. Krishna, J. Weitkamp
Nature Materials **13 (2014) 333–343**

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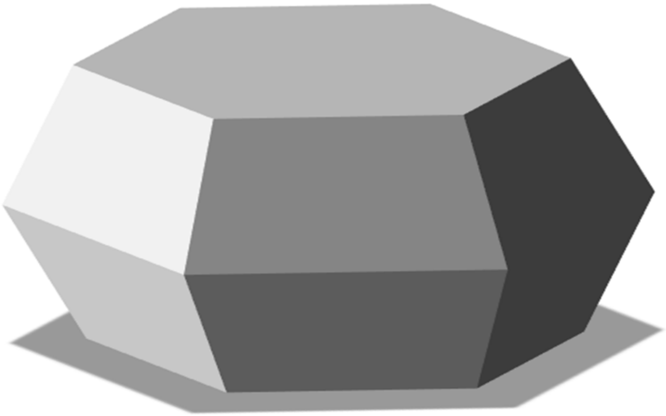
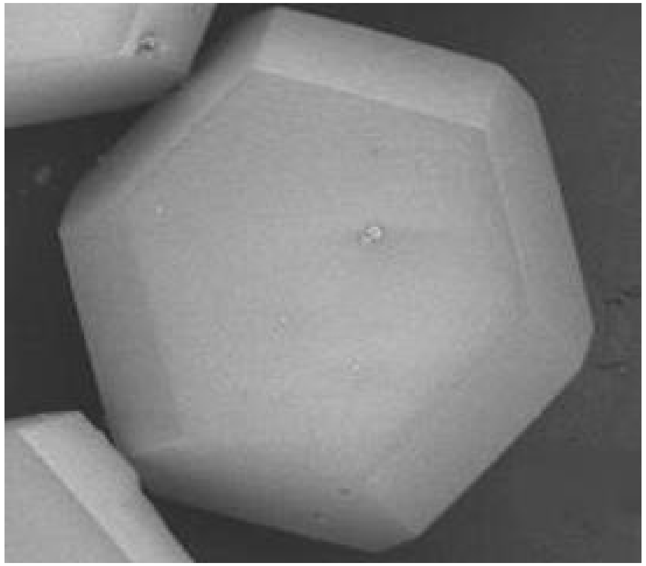
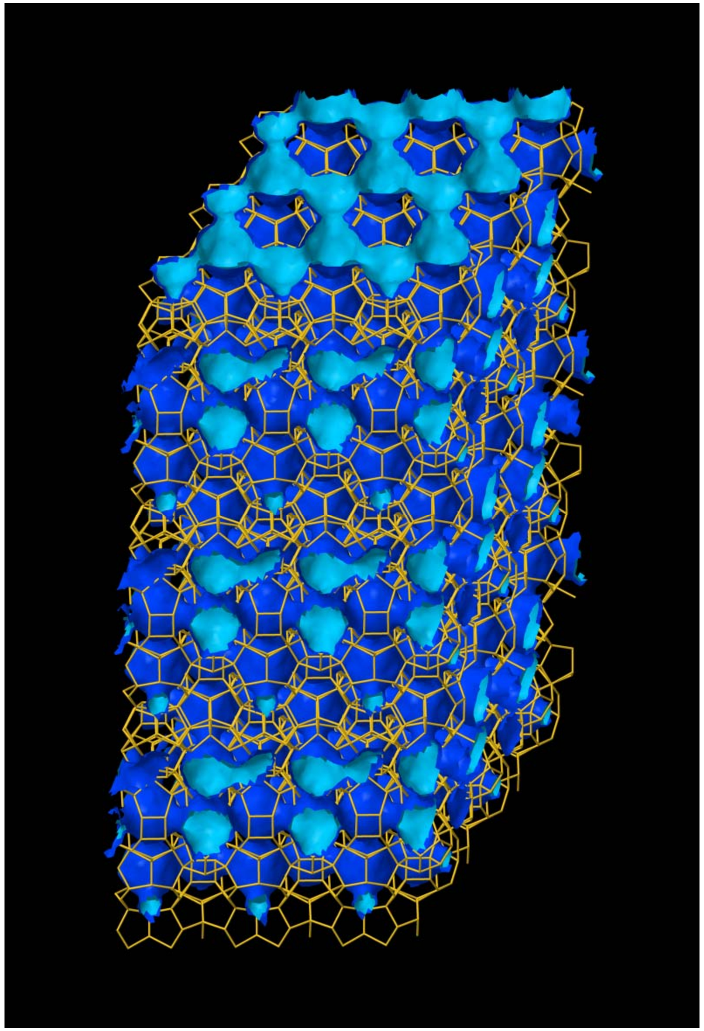
Diffusion uphill?

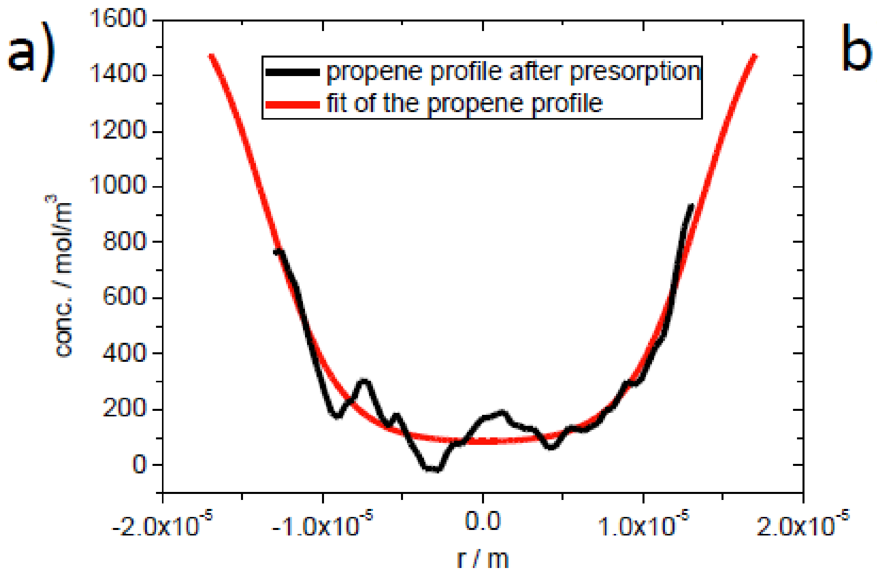
Our Working Horse: **Zeolite ZSM-58 (Structure Type DDR)**



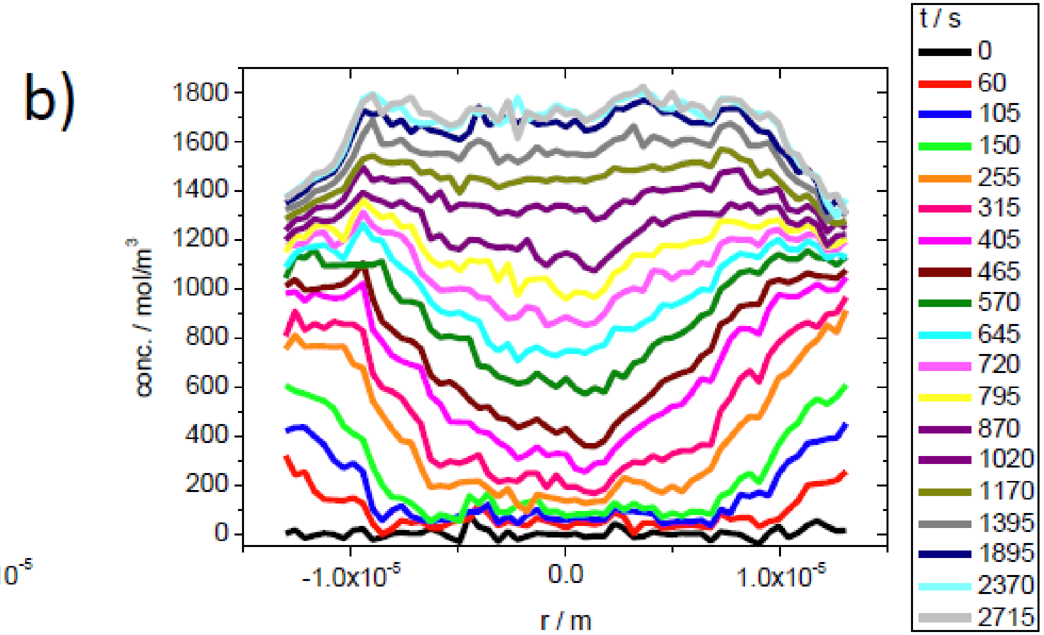




Evolution of Ethane Concentration in DDR after Propene Pre-Adsorption



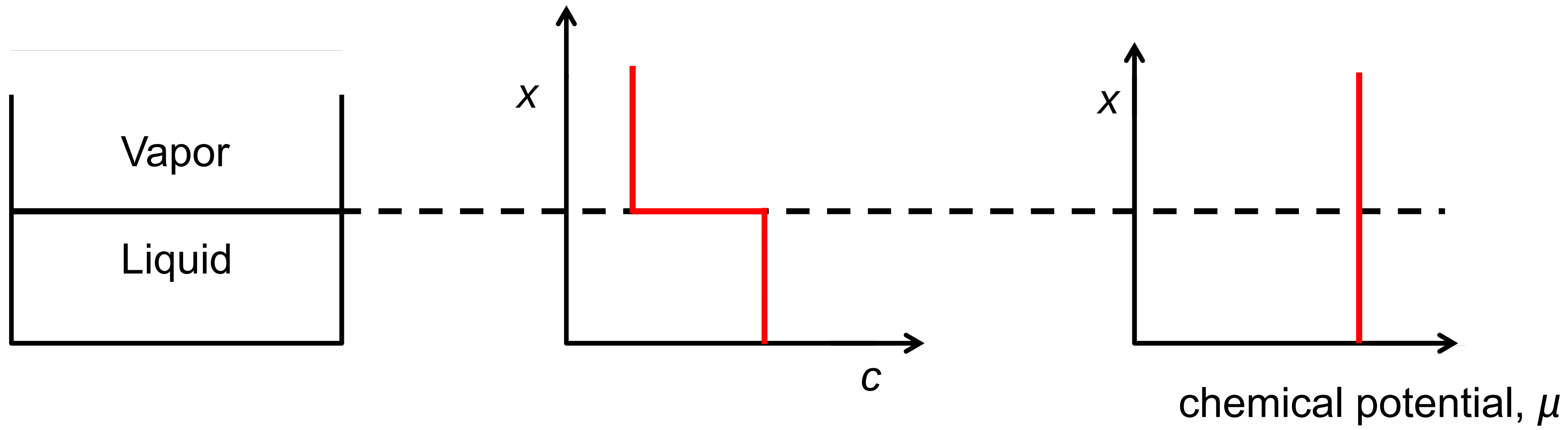
Propene Concentration in DDR
after 7 hours in propene atmosphere



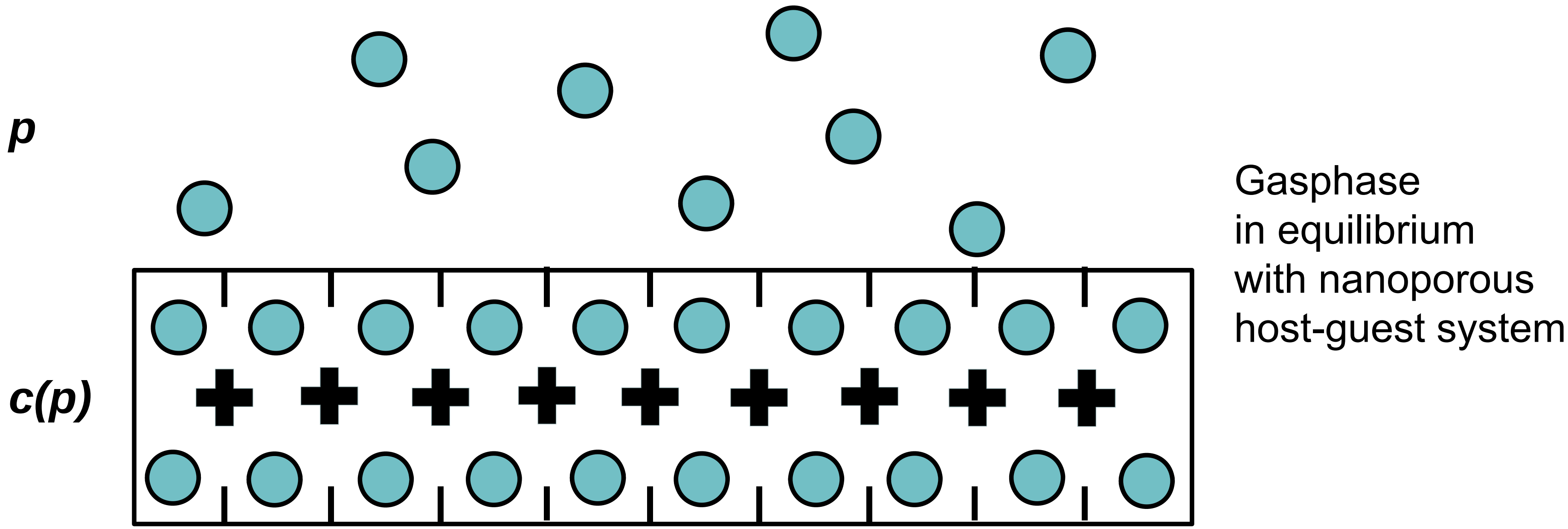
Evolution of Ethane Profile in DDR
under the influence of pre-adsorbed propene

A. Lauerer, T. Binder, C. Chmelik, E. Miersemann, J. Haase, D. M. Ruthven, J. Kärger, Nature Communications 6, 7697 (2015).

Driving Force of Diffusion



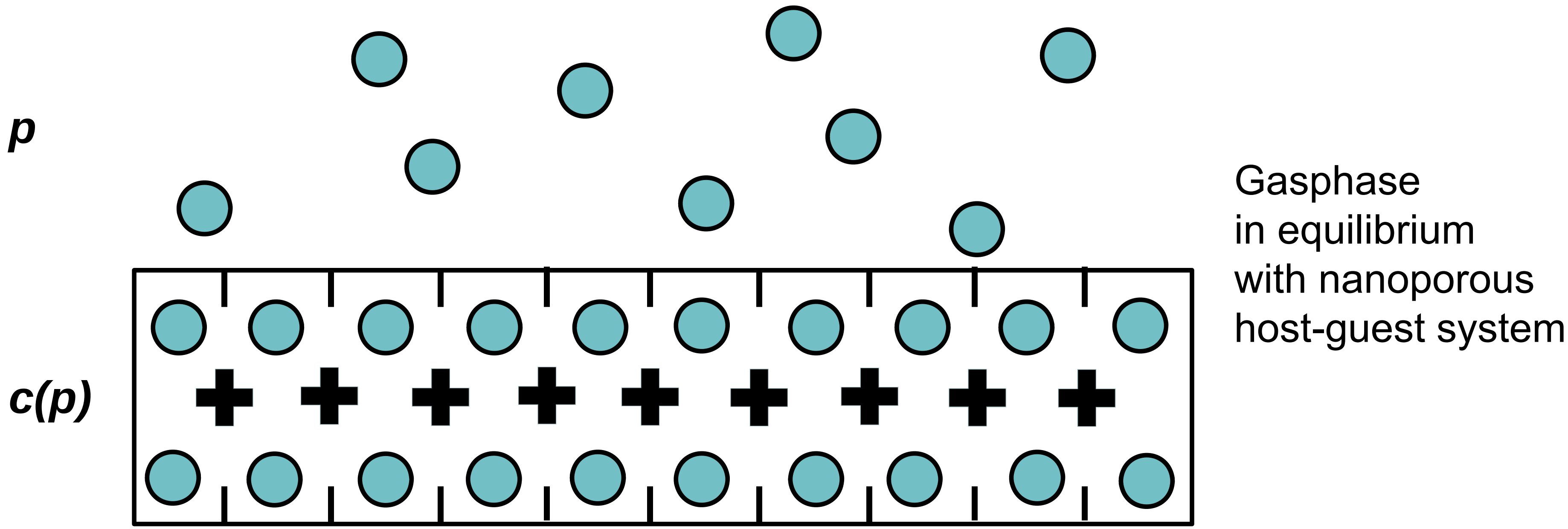
$$\mu = RT \ln p_{equilibrium}$$



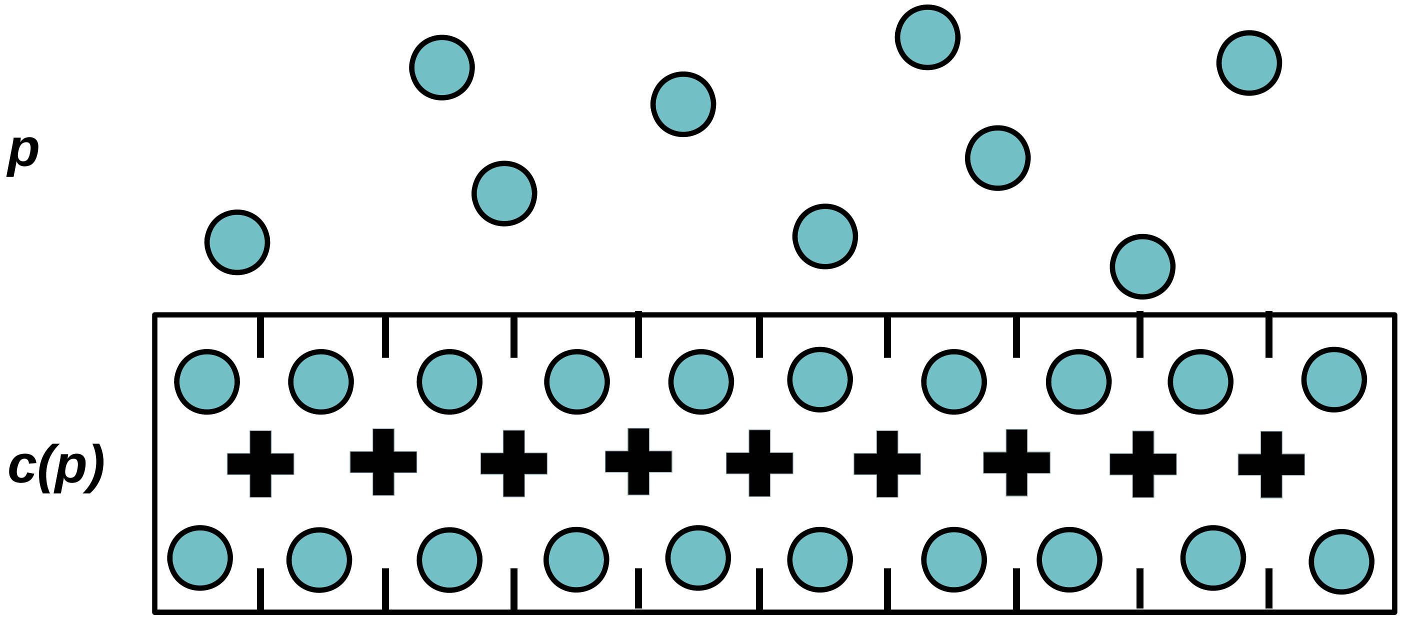
Driving Force of Diffusion

$$\mu = RT \ln p_{equilibrium}$$

Correlations between chemical potential and guest pressure are here and in the following explicitly mentioned only for completeness:
All relevant features of mass transfer are accesible
by simply considering the respective equilibrium gas pressure



Driving Force of Diffusion



Gasphase
in equilibrium
with nanoporous
host-guest system

Single-component host-guest system

$$j \propto c\frac{\partial \mu}{\partial x} \propto c\frac{\partial lnp}{\partial x} \propto c\frac{\partial lnp(c)}{\partial c}\frac{\partial c}{\partial x} = \frac{\partial lnp(c)}{\partial lnc}\frac{\partial c}{\partial x}$$

yields Fick's 1st law

$$j = \text{concentration dependent factor} \times \frac{\partial c}{\partial x}$$

Different Situation with two Components:
Equilibrium pressure and hence the chemical potential is now a function of both components:

$$p_{ethane} = p(c_{ethane}, c_{propene})$$

Instead of the procedure just considered for one-component guests

$$j \propto c\frac{\partial\mu}{\partial x} \propto c\frac{\partial lnp}{\partial x} \propto c\frac{\partial lnp(c)}{\partial c}\frac{\partial c}{\partial x} = \frac{\partial lnp(c)}{\partial lnc}\frac{\partial c}{\partial x}$$

The presence of two guest components (1,2) must be considered:

$$j_{ethane(1)} \propto c_1\frac{\partial\mu_1}{\partial x} \propto c_1\left[\frac{\partial lnp(c_1,c_2)}{\partial c_1}\frac{\partial c_1}{\partial x} + \frac{\partial lnp(c_1,c_2)}{\partial c_2}\frac{\partial c_2}{\partial x}\right]$$

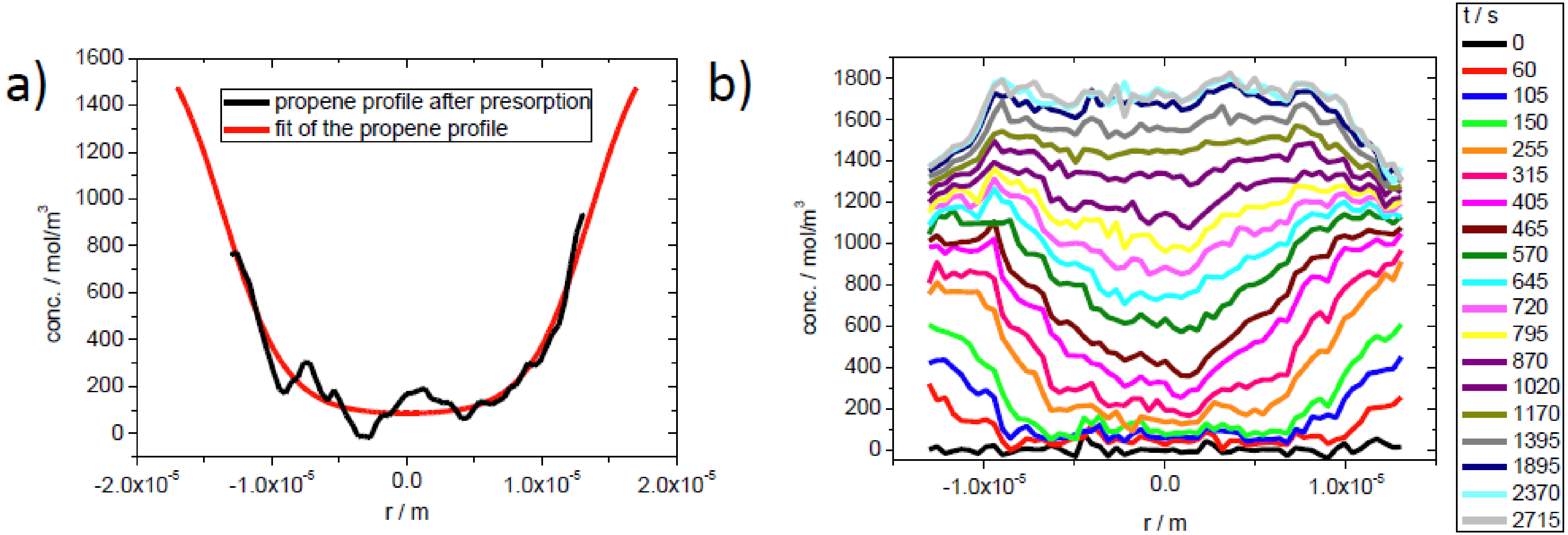
Flux is seen to depend on both concentration gradients:

$$\boldsymbol{j_1 = -D_{11}\frac{\partial c_1}{\partial x} - D_{12}\frac{\partial c_2}{\partial x}}$$

Generalized Fick‘s 1st Law

Flux of component 1 is pushed by concentration gradients of components 1 AND 2!

Evolution of Ethane Concentration in DDR after Propene Pre-Adsorption

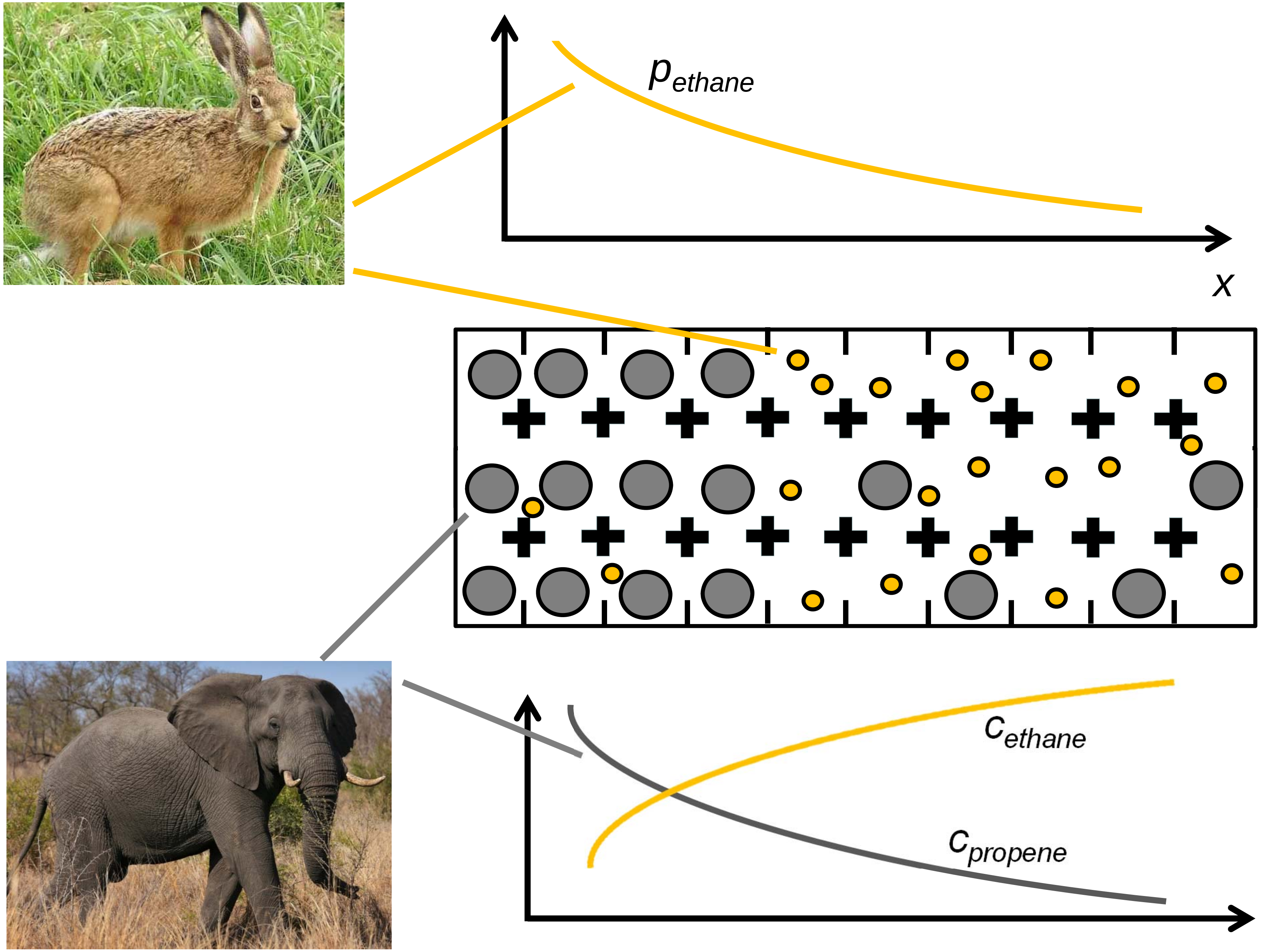


$$j_{ethane} = -D_{11}\frac{\partial c_{ethane}}{\partial x} - D_{12}\frac{\partial c_{propene}}{\partial x}$$

Back to the roots: Mass transfer is driven by gradient in chemical potential (and thus in pressure) of considered species rather than by (only) the concentration of this species

$$j_{ethane} \propto \frac{\partial \mu_{ethane}}{\partial x} \propto \frac{\partial \ln p_{ethane}}{\partial x}$$

Uphill Diffusion and Overshooting

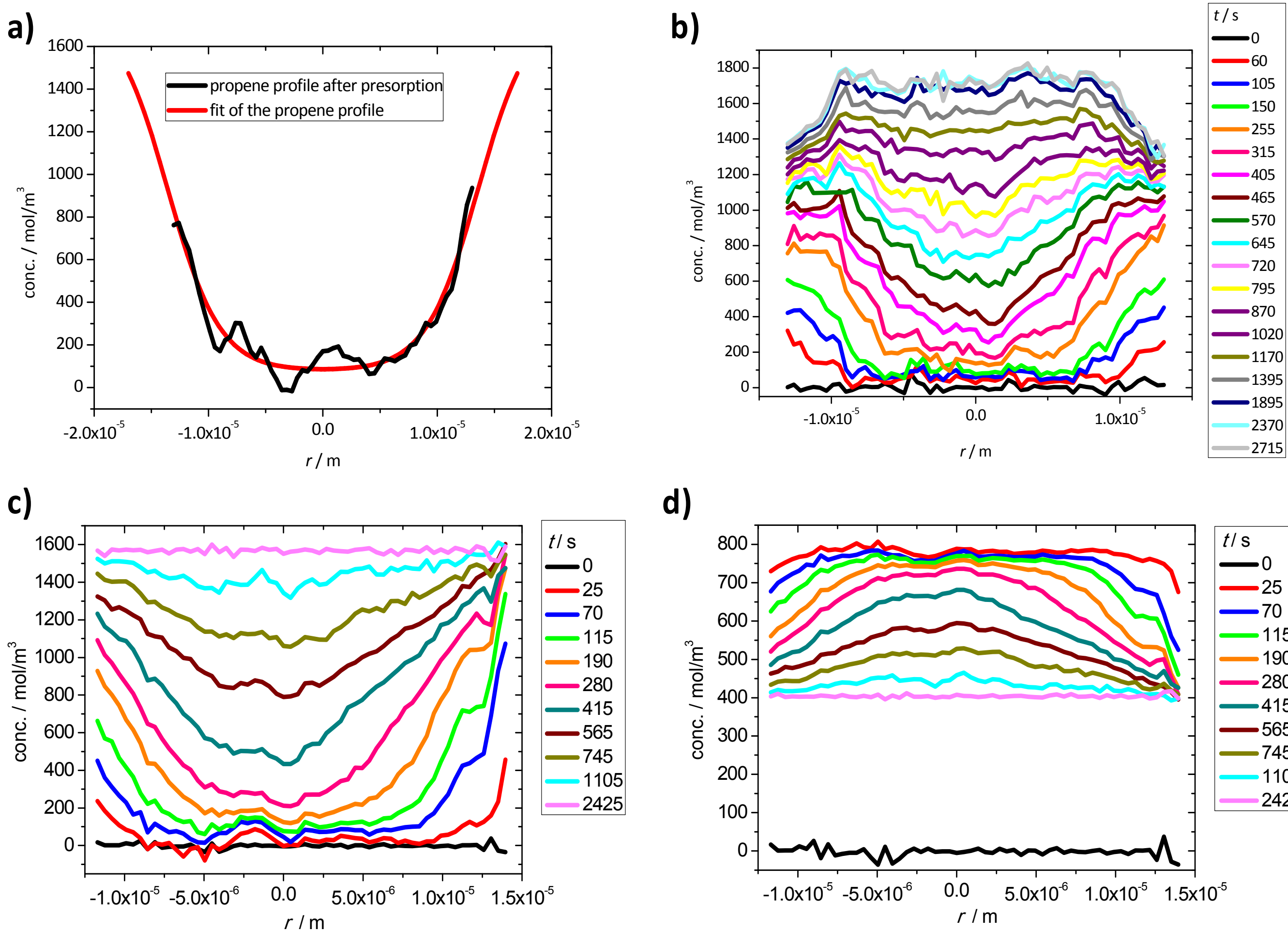


Uphill Diffusion and Overshooting

Decreasing propene concentration pushes ethane „uphill“

Propene with Ethane as the „fast“ component

Ethane as the „slow“ component with CO_2



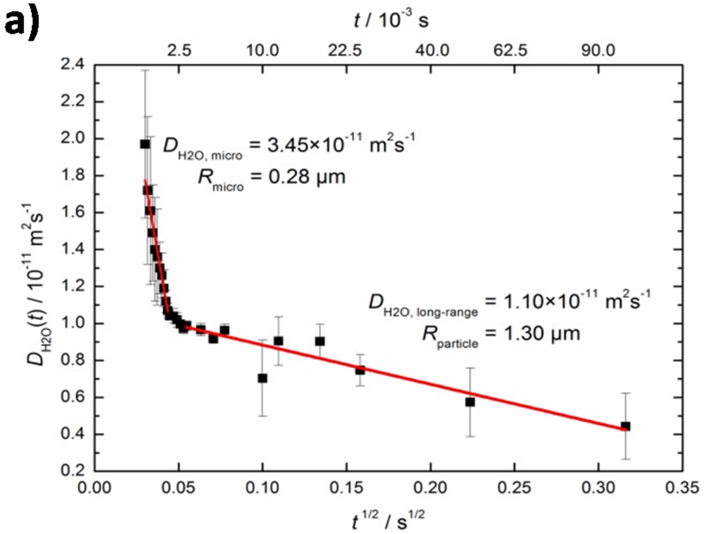
In parallel with ethane uptake and equilibration, CO_2 „overshoot“ is vanishing

A. Lauerer, T. Binder, C. Chmelik, E. Miersemann, J. Haase, D. M. Ruthven, J. Kärger, Nature Communications 6, 7697 (2015).

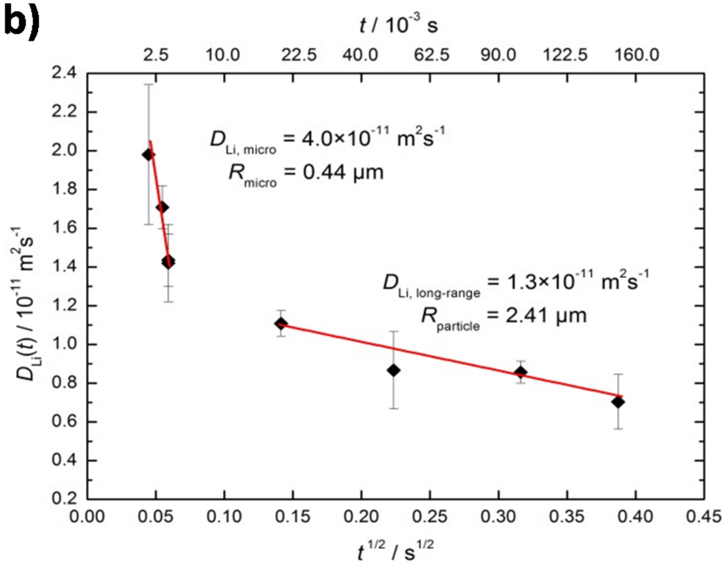
Contents:

Evidence of **Internal Barriers** by Time-Dependent PFG NMR Diffusivities of
Water (a) at 25° C and of lithium cations (b) at 100 °C
in hydrated zeolite Li-LSX

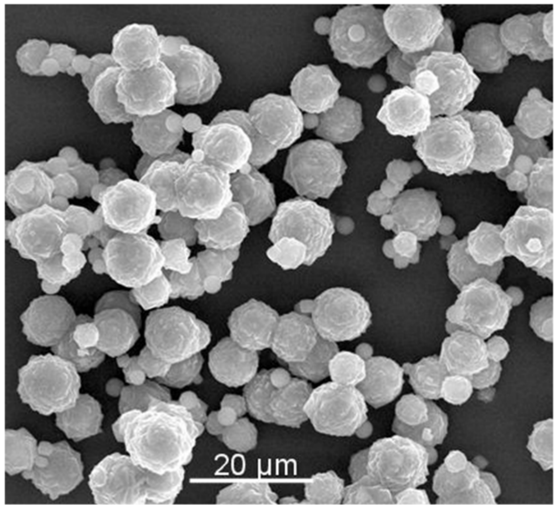
a)



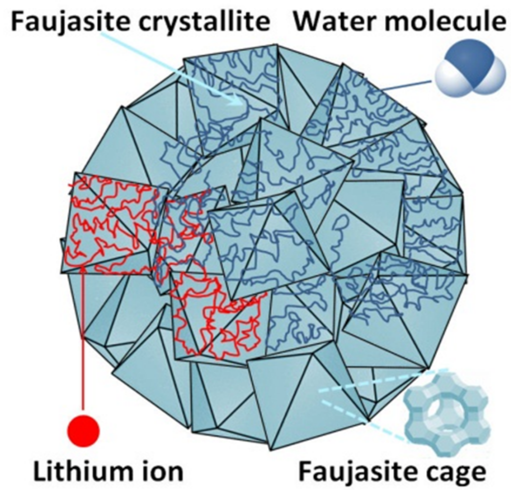
b)



c)

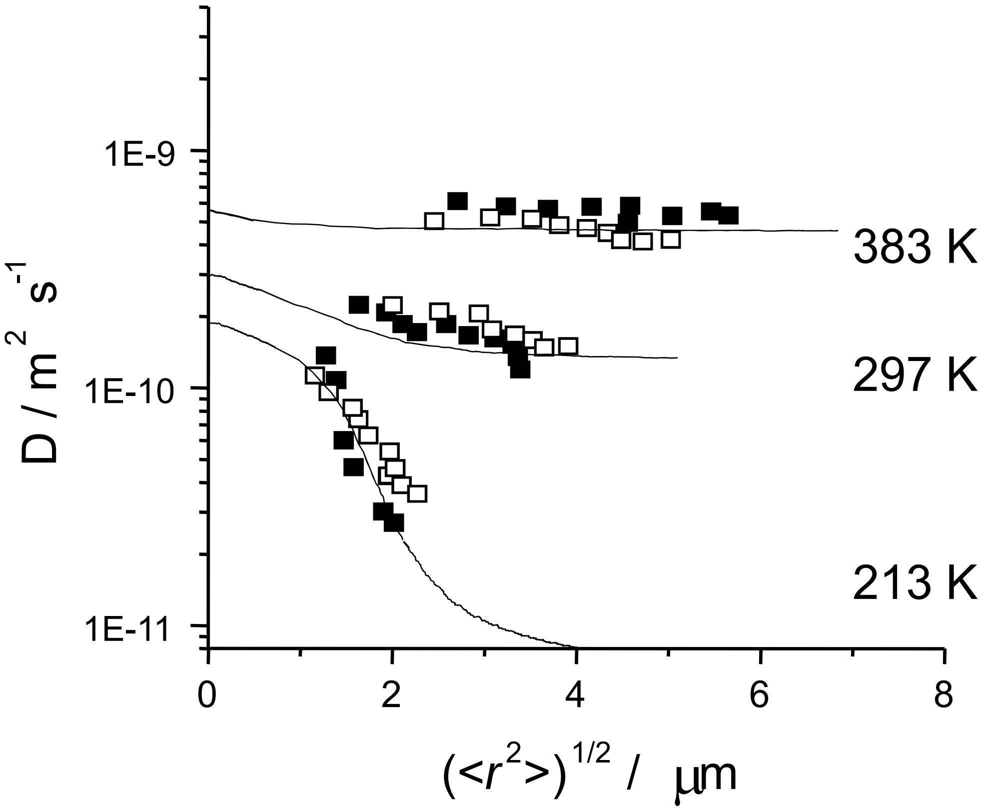


d)

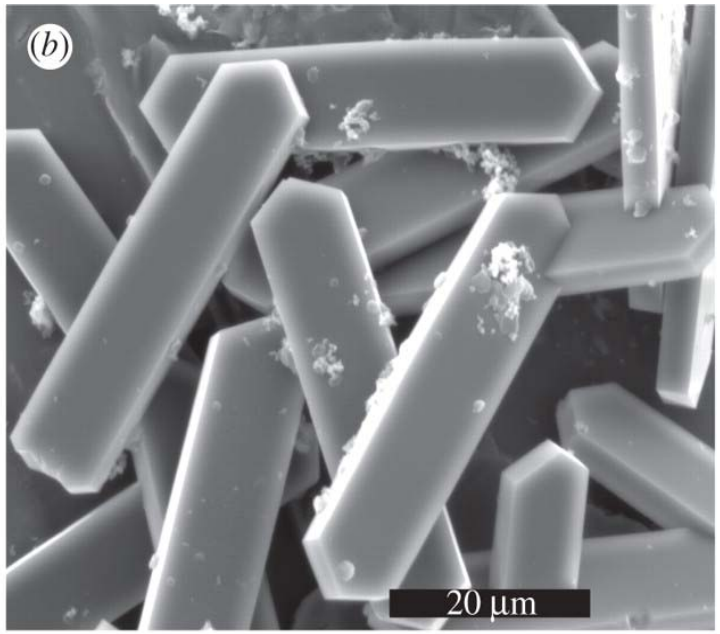


S. Beckert et al.
J. Phys.Chem.C
2013, *117*,
24866–24872

Evidence of Intracrystalline Barriers by PFG NMR Diffusivities in seemingly perfect crystals



n-Butane / Silicalite-1



yielding an effective intracrystalline diffusivity

$$\frac{1}{D_{eff}} \approx \frac{1}{D} + \frac{1}{\alpha l}$$

with α and l denoting the permeability and spacing of the intracrystalline barriers

S. Vasenkov and J. Kärger, Microporous Mesoporous Mat. 55, 139 (2002).

Medical diagnosis has attained such a high level

that there scarcely exist any really healthy people.

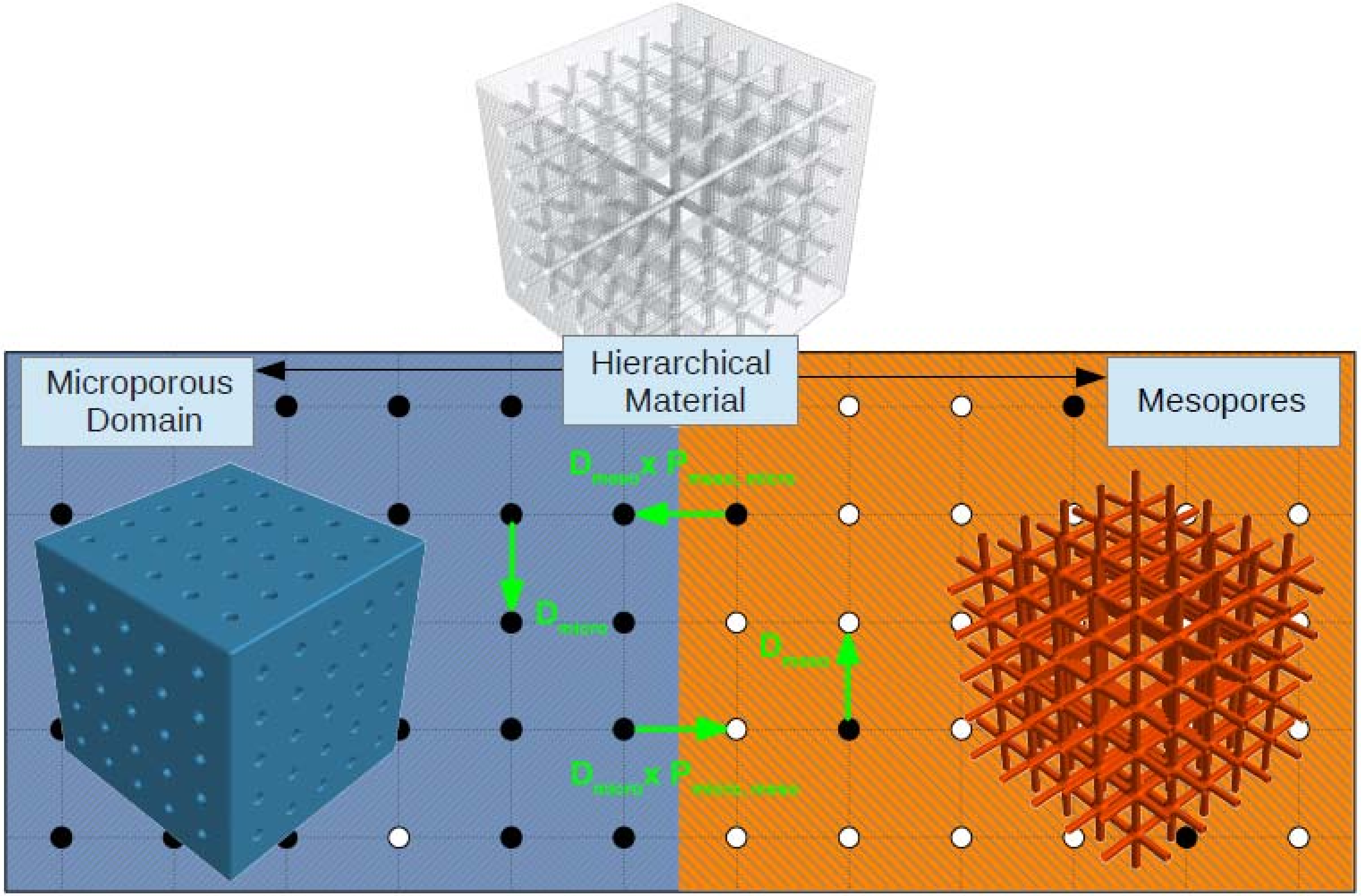
Physical

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

perfect crystals

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

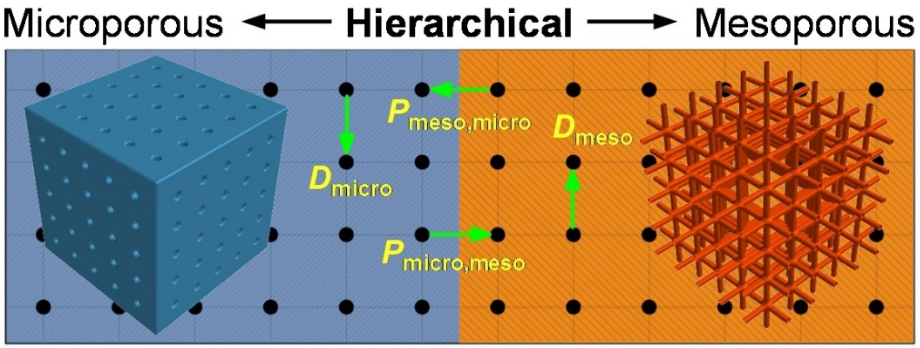
„Highway"-Enhanced Mass Transfer in Microporous Materials

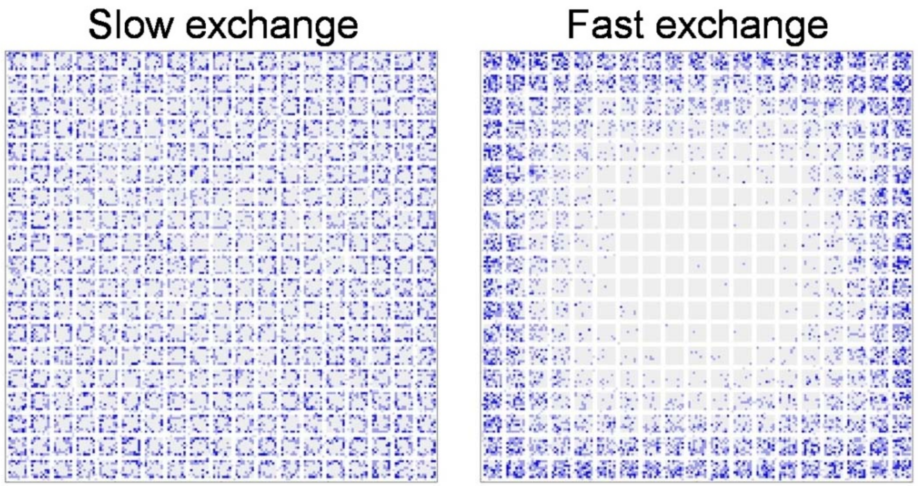


Schneider, D.; Kondrashova, D.; Valiullin, R.; Bunde, A.; Kärger, J. Chem. Ingen. Techn. submitted

Time constant of uptake and release by diffusion limitation: $\tau_{\mathrm{Diff}} = \frac{R^2}{15D}$:

Transport Enhancement in Pore Hierarcies:

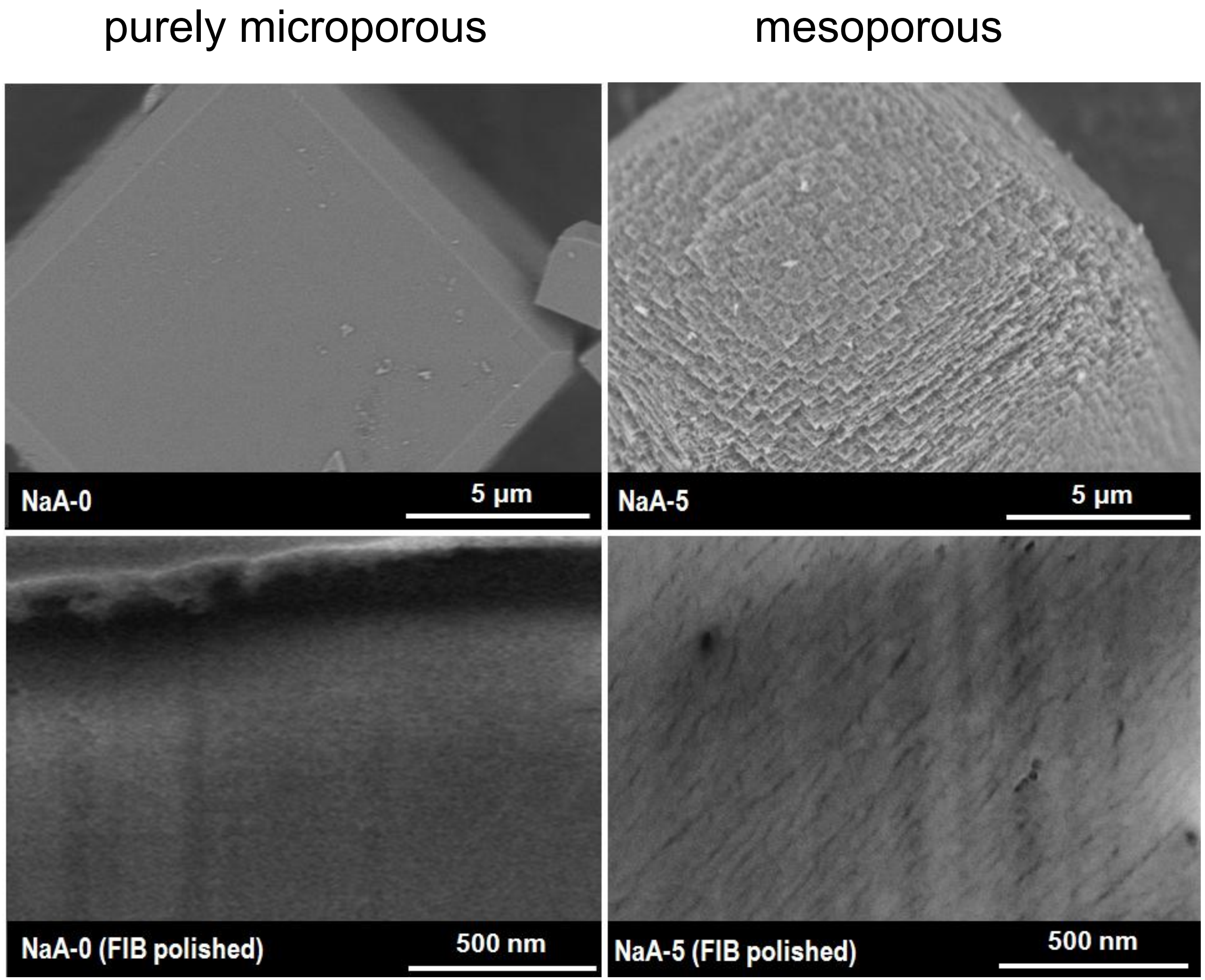




$$\tau_{\mathrm{Diff}}^{\mathrm{slow\ exchange}} = \frac{R_{\mathrm{micro}}^2}{15D_{\mathrm{micro}}} \qquad \tau_{\mathrm{Diff}}^{\mathrm{fast\ exchange}} = \frac{R_{\mathrm{cryst}}^2}{15(p_{\mathrm{meso}}D_{\mathrm{meso}} + D_{\mathrm{micro}})}$$

Schneider, D.; Kondrashova, D.; Valiullin, R.; Bunde, A.; Kärger, J. Chem. Ingen. Techn. submitted

Zeolite LTA

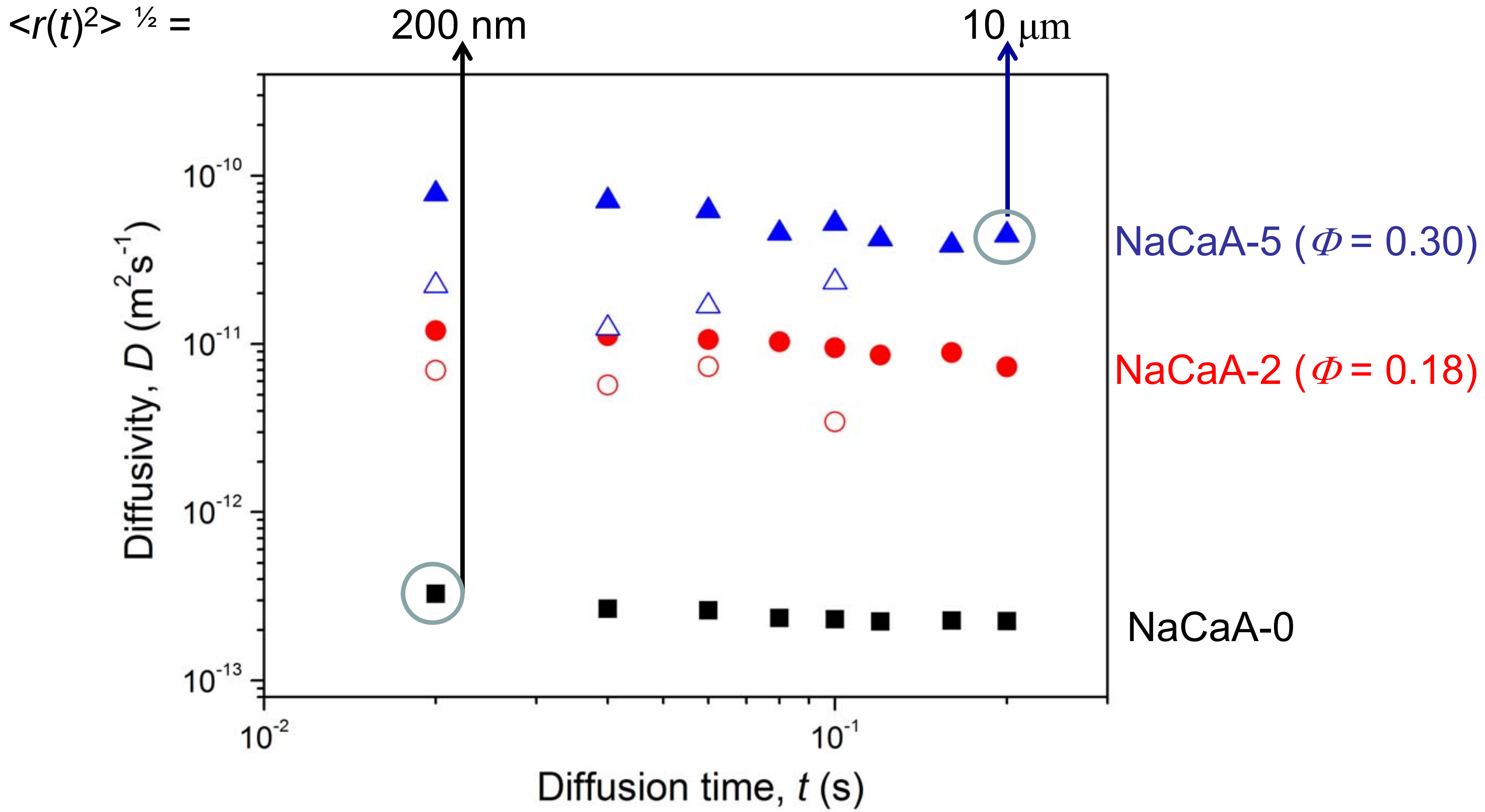


Mehlhorn, D.; Valiullin, R.; Kärger, J.; Cho, K.; Ryoo, R.: ChemPhysChem 13 (2012)1495-1499

Propane Diffusivity in (mesoporous) Zeolite LTA at 25°C

$<r(t)^2> = 6Dt$ →

mean diffusion path lenghts covered by PFG NMR



D. Mehlhorn; R. Valiullin, J. Kärger, K. Cho, R. Ryoo, ChemPhysChem 13 1495 (2012)

J. Kärger, R. Valiullin, Chem. Soc. Rev. 42, 4172 (2013).

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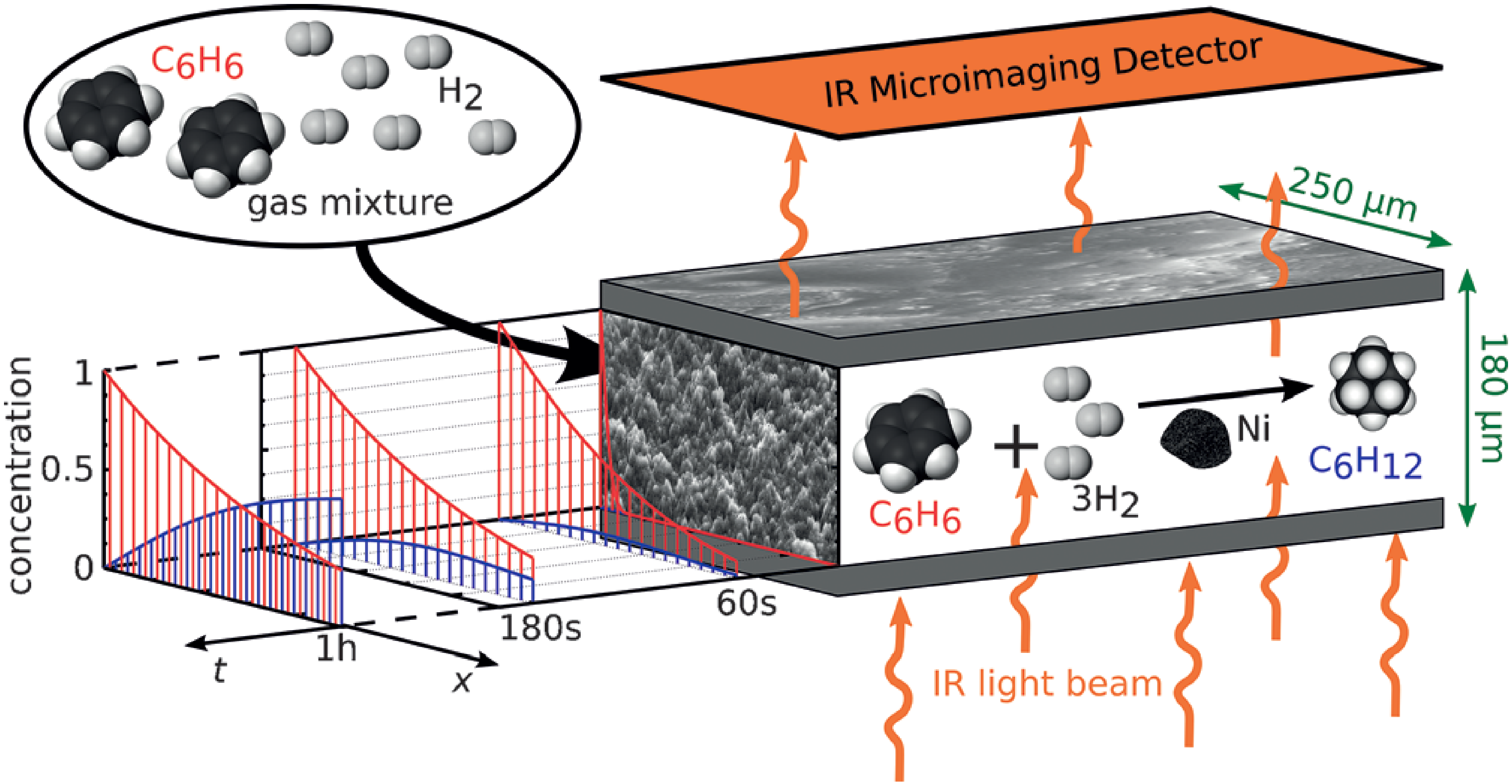
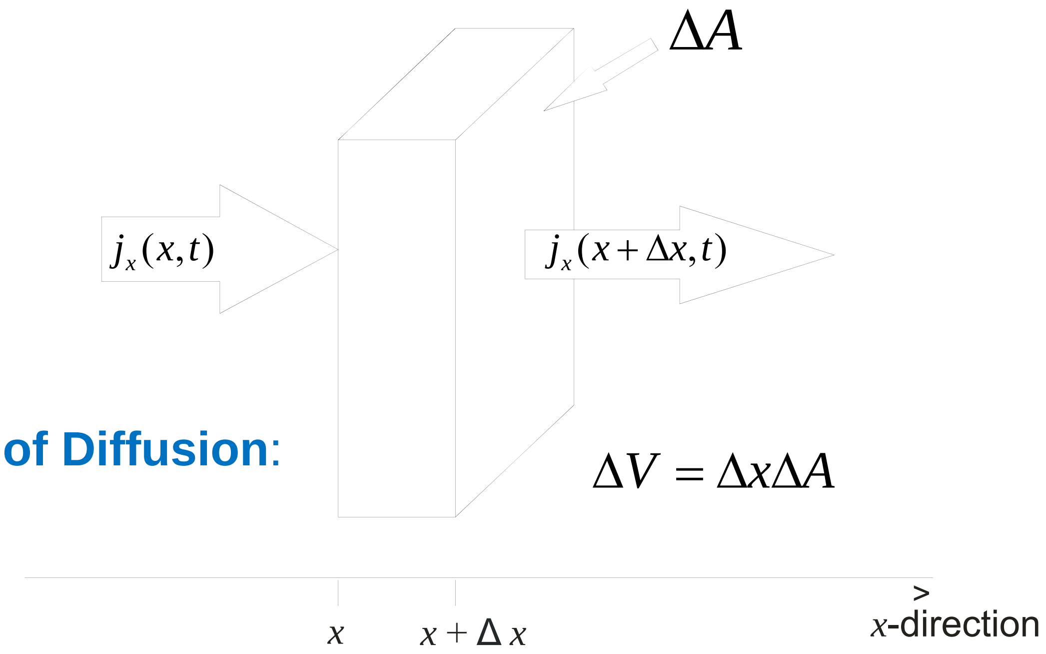
In-situ Recording of Chemical Reactions
Hydrogenation of Benzene to Cyclohexane



T. Titze *et al.*, Angew. Chem. Int. Ed. 54, 5060 (2015)

Extending Fick's 2nd Law:
Change of Concentration by Diffusion AND Conversion



Add to effect of Diffusion:

$$\frac{\partial c_1}{\partial t} = \left(\frac{\partial c_1}{\partial t}\right)_{\text{Diffusion}} + \left(\frac{\partial c_1}{\partial t}\right)_{\text{Conversion}}$$

$$= -\frac{\partial j_1}{\partial x} - kc_1$$

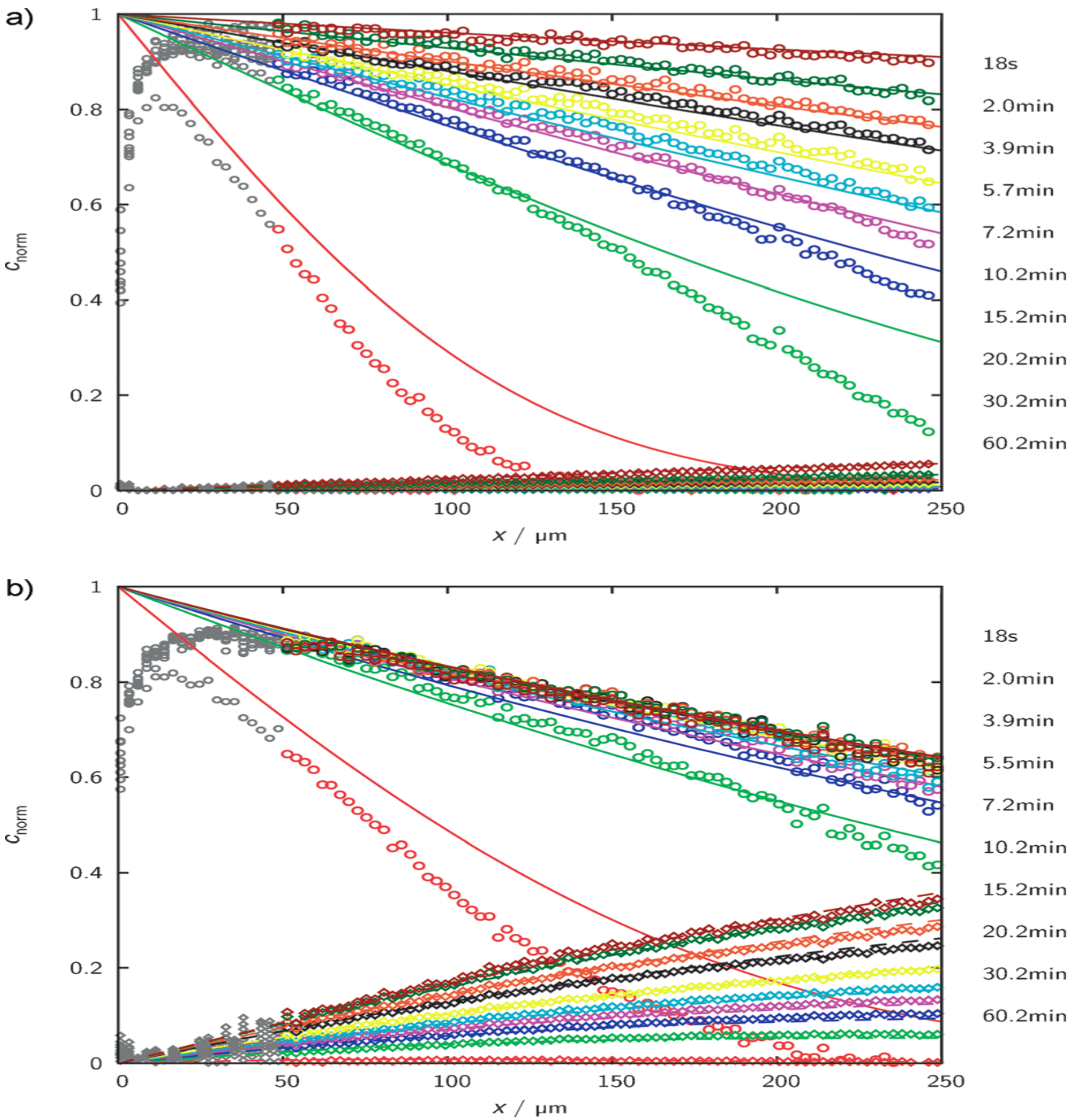
$$= D\frac{\partial^2 c_1}{\partial x^2} - kc_1$$

effect of Conversion (reaction)
In our case:
irreversible reaction
from species 1 to 2

$$\frac{\partial c_2}{\partial t} = D\frac{\partial^2 c_2}{\partial x^2} + kc_1$$

25°C

75°C



Conversion from **Benzene** (top) **to Cyclohexane** (bottom) upon **uptake by a nanoporous glass** with dispersed Ni particles as a catalyst

T. Titze *et al.*, Angew. Chem. Int. Ed. **54,** 5060 (2015).

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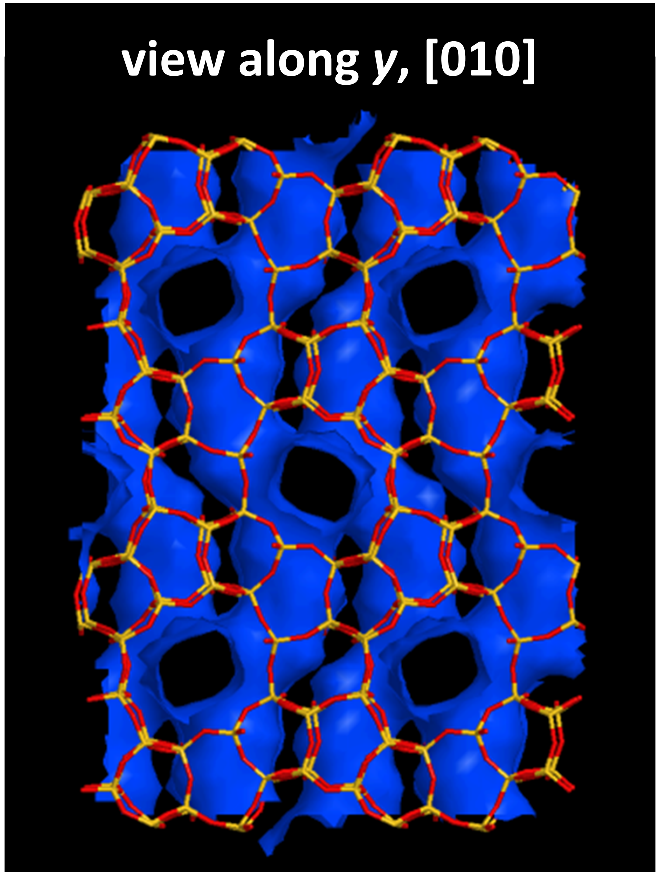
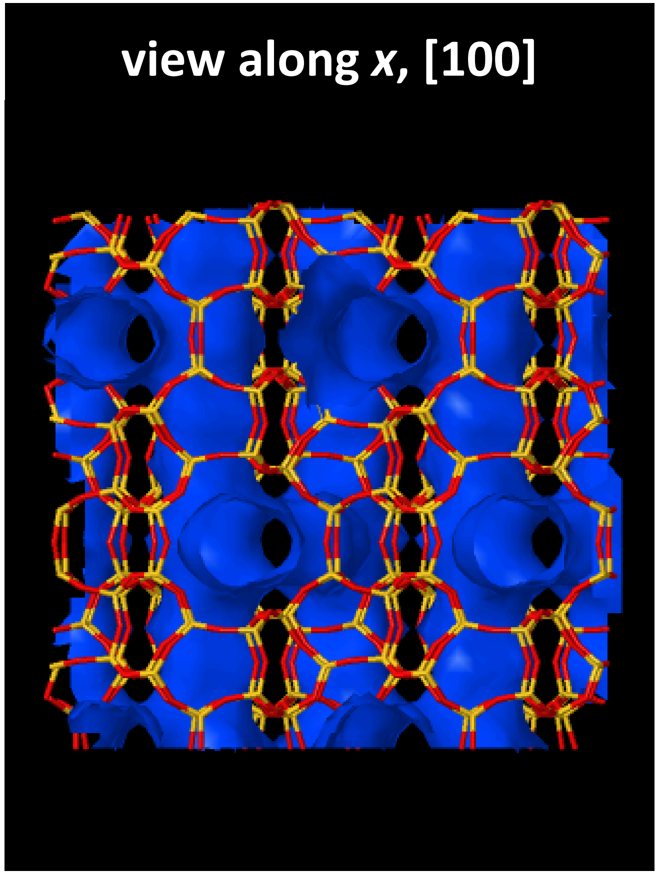
MFI-type structure – intersecting channels (3d)

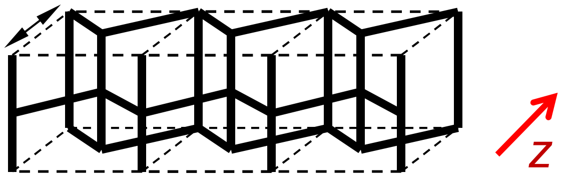




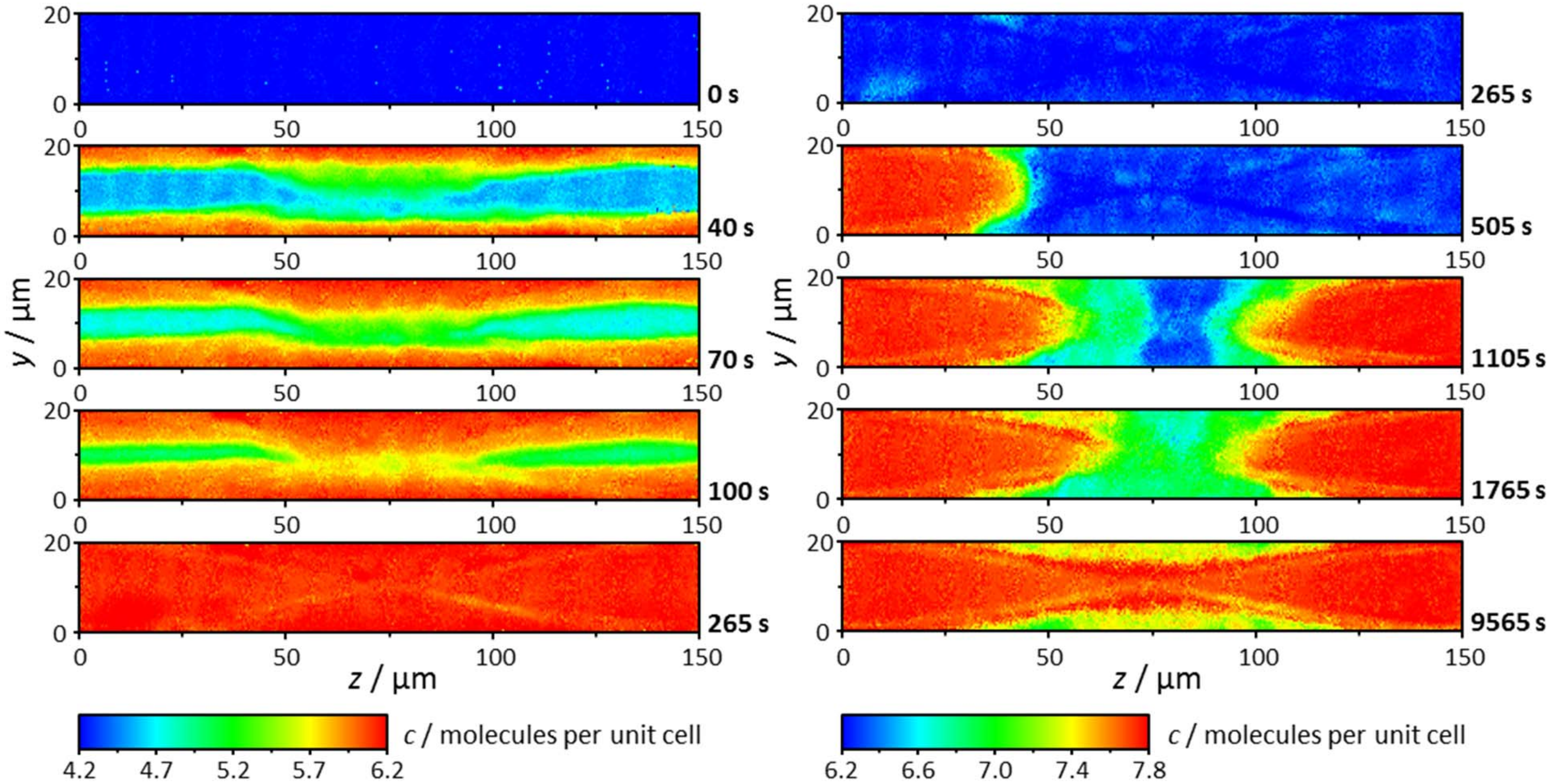
- 10-membered ring zigzag-channels (5.5 × 5.1 Å^2) along *x* [100]
- 10-membered ring straight channels (5.6 × 5.3 Å^2) along *y* [010]

www.iza-structure.org
STRUCTURE COMMISSION

Benzene adsorption in zeolite MFI, pressure step 0.5 to 1 kPa

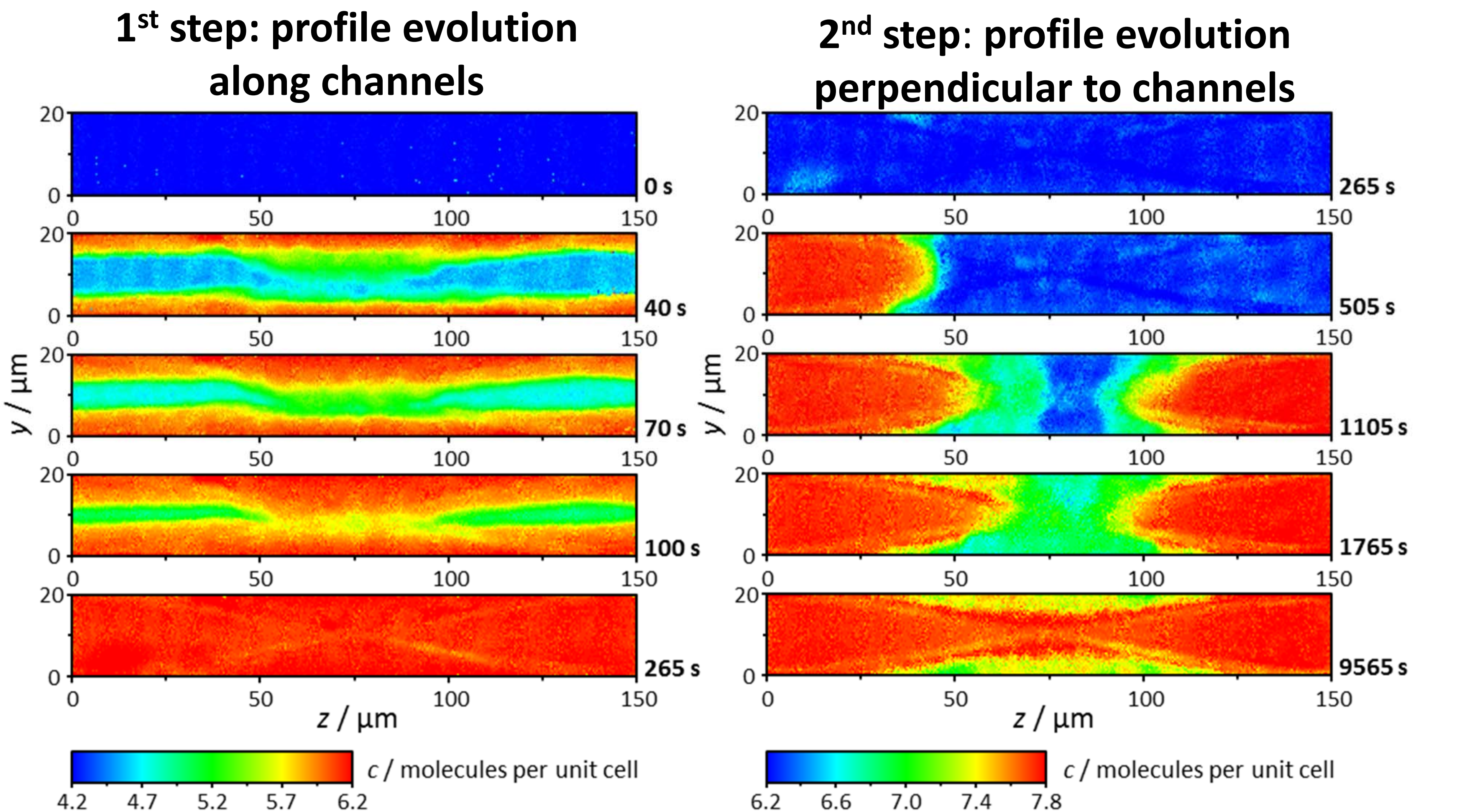


1st step: profile evolution along channels | **2nd step: profile evolution perpendicular to channels**



J. Kärger, T. Binder, C. Chmelik, F. Hibbe, H. Krautscheid, R. Krishna, and J. Weitkamp, *Nature Materials* 13 (2014) 333–343

Benzene adsorption in zeolite MFI, pressure step 0.5 to 1 kPa



After a Couple of Minutes the Presence of the Guest starts to Change the Host, which takes a Couple of Hours

J. Kärger, T. Binder, C. Chmelik, F. Hibbe, H. Krautscheid, R. Krishna, and J. Weitkamp, *Nature Materials* 13 (2014) 333–343

Molecules Spreading in Pore Spaces

- Observation of Molecular Spreading
- Infestation of New Territories
- Interaction between Invaders of One and Various Species
- The Driving Force of Infestation
- Barriers and Highways
- Conversion of Invadors during Invasion
- Invadors-Induced Changes of the Territory

Molecules Spreading in Pore Spaces

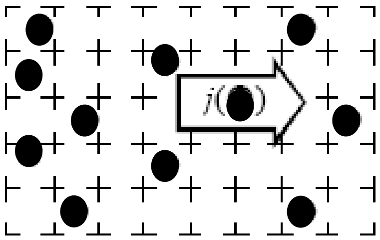
- Observation of Molecular Spreading
- Infestation of New Territories
- Interaction between Invaders of One and Various Species
- The Driving Force of Infestation
- Barriers and Highways
- Conversion of Invaders during Invasion
- Invaders-Induced Changes of the Territory

Surprises may be Hidden Anywhere

- Optional, if needed for discussion:

Correlating Diffusion under Equilibrium and Non-Equilibrium

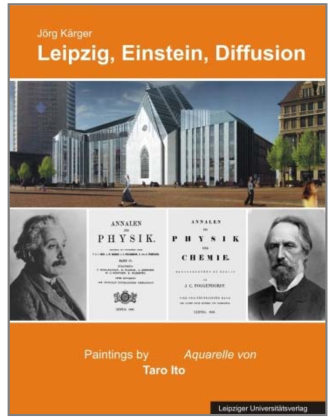
- Transport (Collective, Chemical) Diffusion

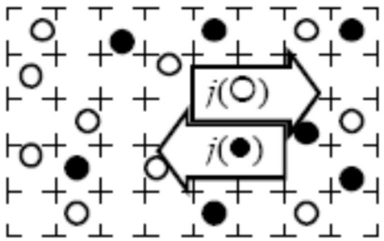


$$j_x = -D_T \frac{\partial c}{\partial x}$$

(Fick's 1st law)

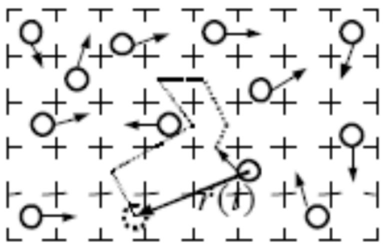
- Self- (Tracer) Diffusion by Tracer Exchange





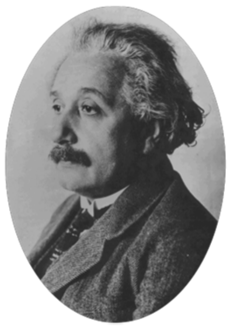
$$j_x^* = -D \frac{\partial c^*}{\partial x}$$

- Self- (Tracer) Diffusion by Following the Individual Molecules (QENS, PFG NMR)

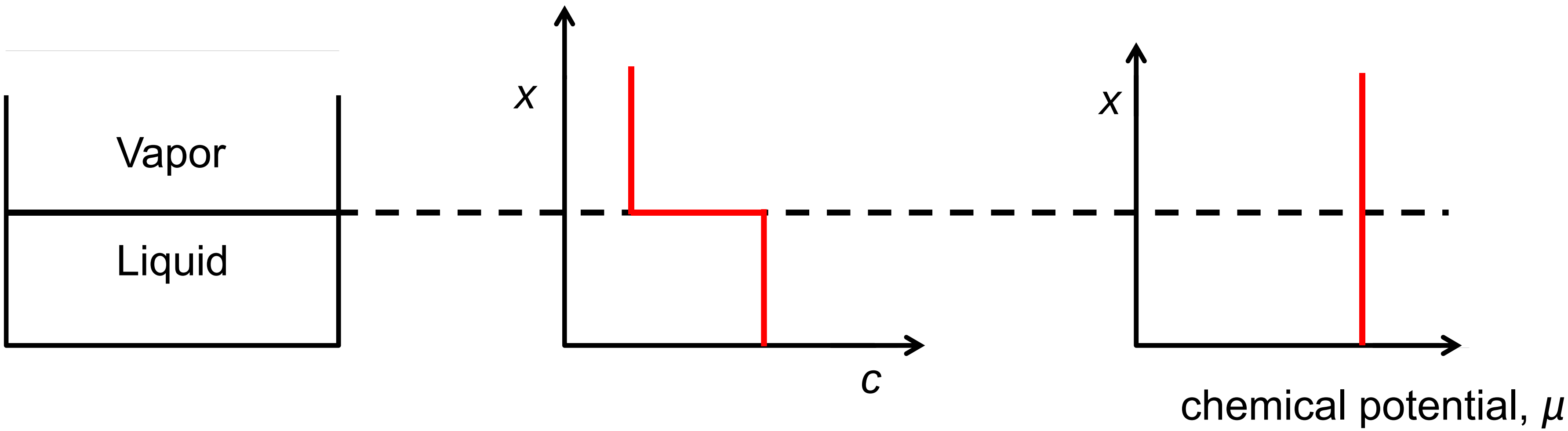


$$< x^2(t) > = 2Dt$$

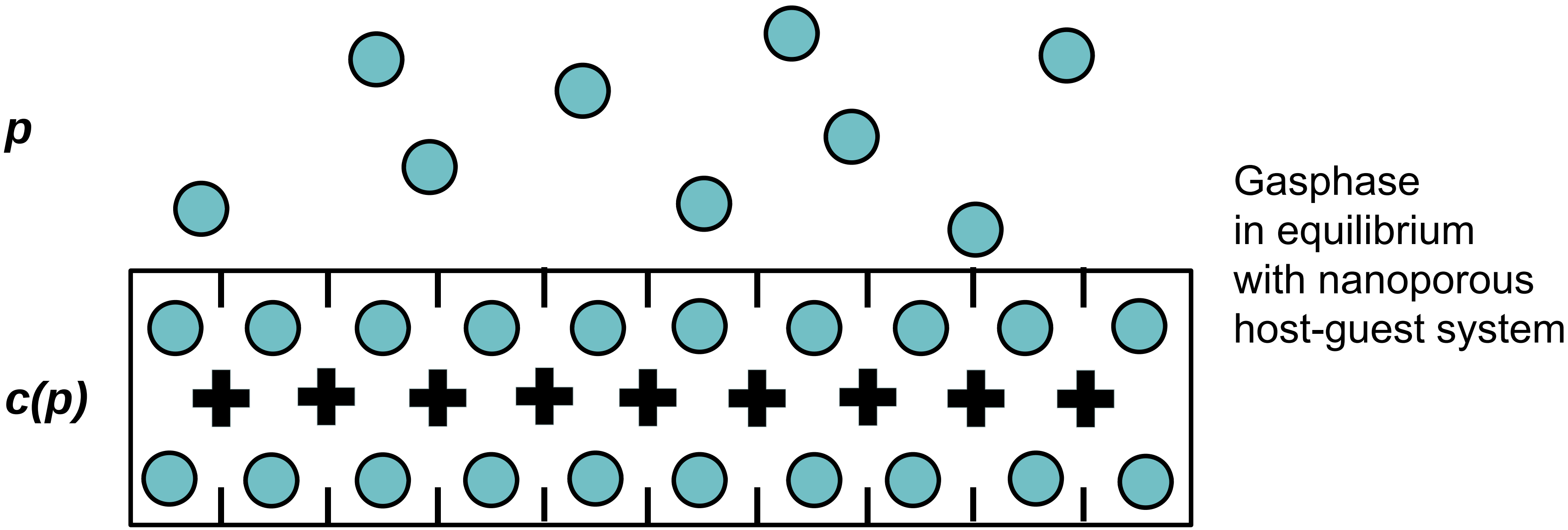
Einstein Equation



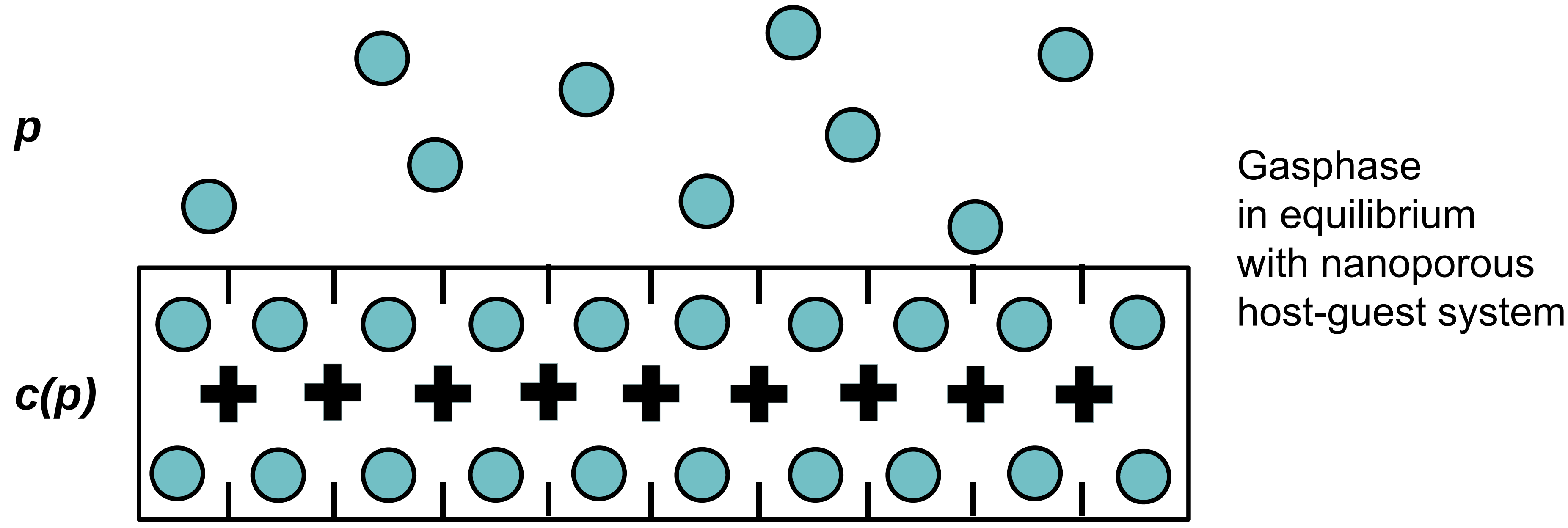
Driving Force of Diffusion



$$\mu = RT \ln p_{equilibrium}$$



Driving Force of Diffusion



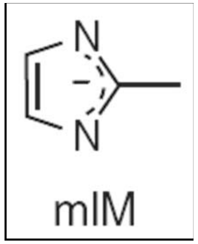
Single-component host-guest system

$$j \propto c\,\frac{\partial \mu}{\partial x} \propto c\,\frac{\partial \ln p}{\partial x} \propto c\,\frac{\partial \ln p(c)}{\partial c}\,\frac{\partial c}{\partial x} = \frac{\partial \ln p(c)}{\partial \ln c}\,\frac{\partial c}{\partial x}$$

yields Fick's 1st law

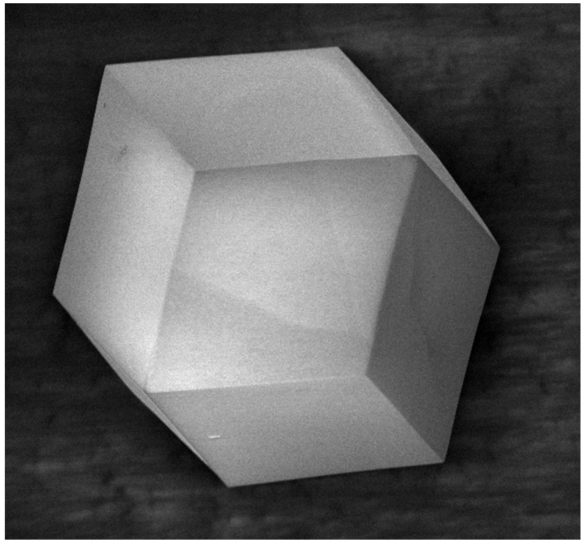
$$j = \text{concentration dependent factor} \times \frac{\partial c}{\partial x}$$

Our Probe System



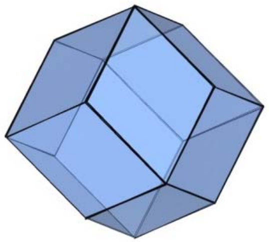
MOFs (Metal-Organic Frameworks) of type ZIF: Zeolitic Imidazolate Frameworks (ZIF-8 ↔ SOD)

SEM image (J. Caro)

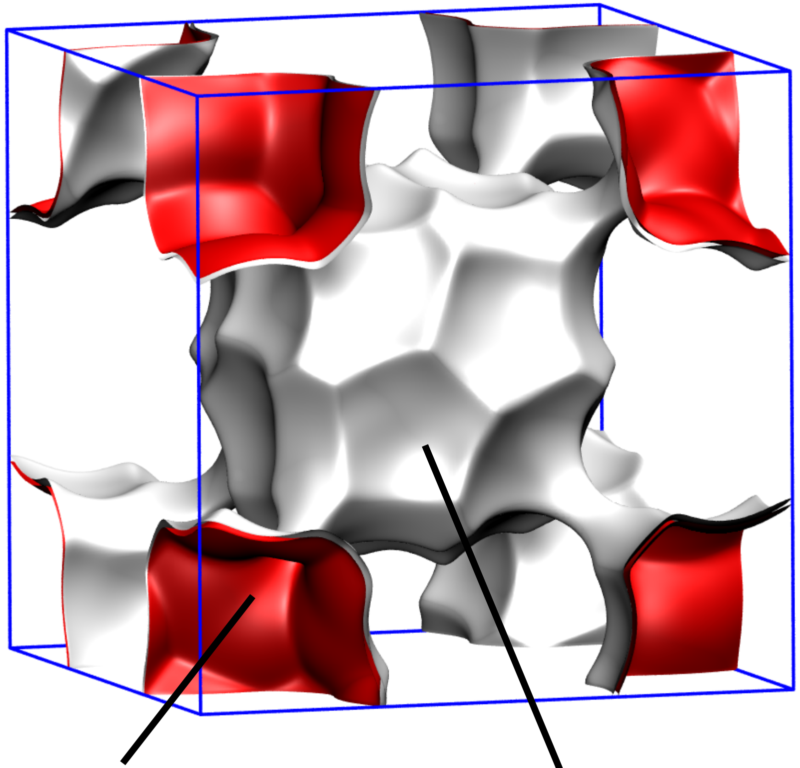


crystal size: up to 300 µm

crystal shape: rhombic dodecahedron



potential landscape (R. Krishna)



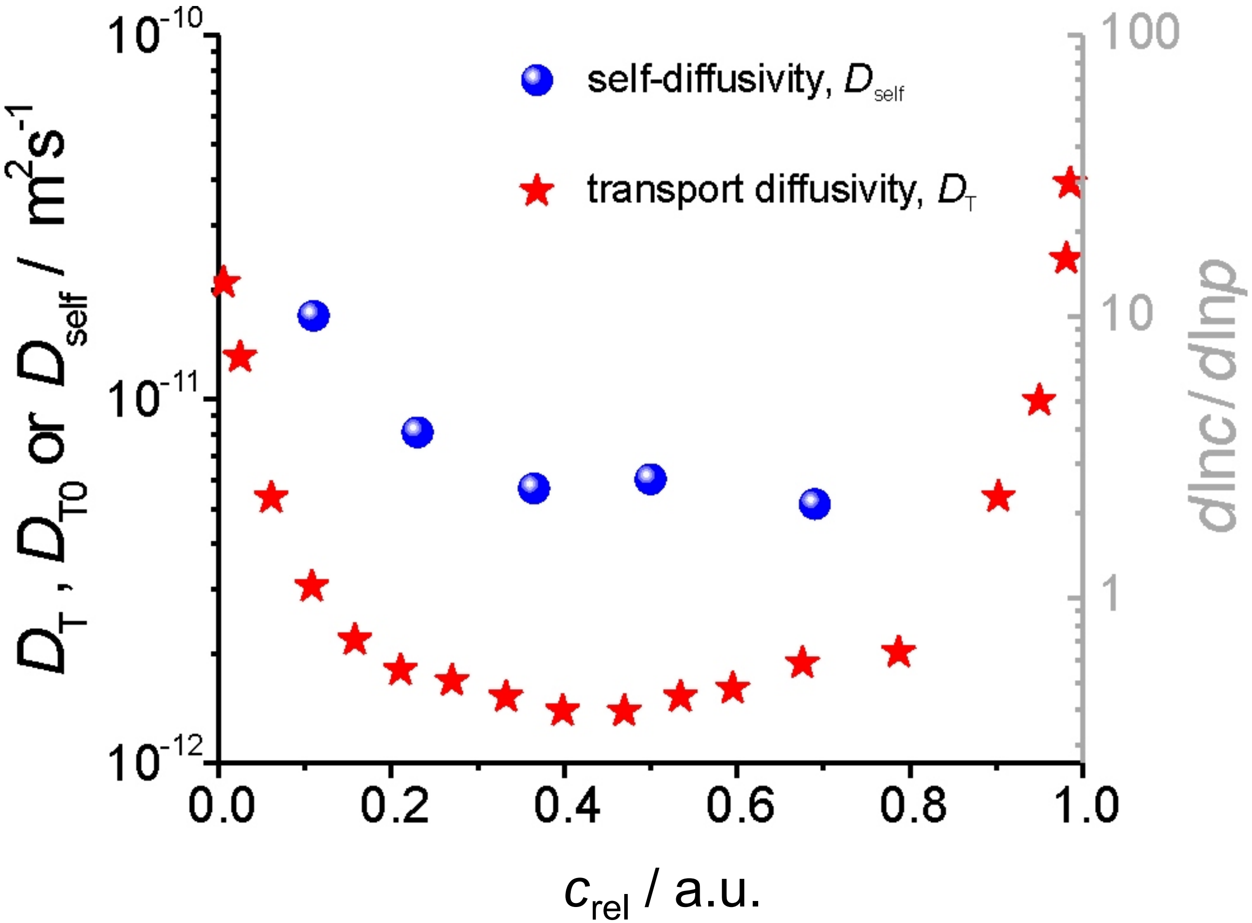
window size: ca. 3.4 Å

cavity size: ca. 12 Å

unit cell: a = b = c ≈ 17 Å

in collaboration with J. Caro, Hannover

Methanol in ZIF-8

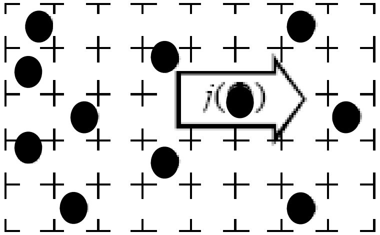


- $D_{self} > D_T$: Faster by opposing the stream?

C. Chmelik, H. Bux, J. Caro, L. Heinke, F. Hibbe, T. Titze, and J. Kärger; "Mass Transfer in a Nanoscale Material Enhanced by an Opposing Flux", ***Phys. Rev. Lett.*** **104 (2010) 085902.**

Equilibrium versus Non-Equilibrium

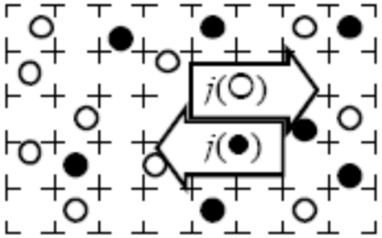
- Transport (Collective, Chemical) Diffusion



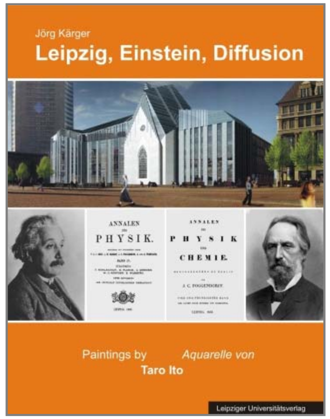
$$j_x = -D_T \frac{\partial c}{\partial x}$$

(Fick's 1st law)

- Self- (Tracer) Diffusion by Tracer Exchange



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

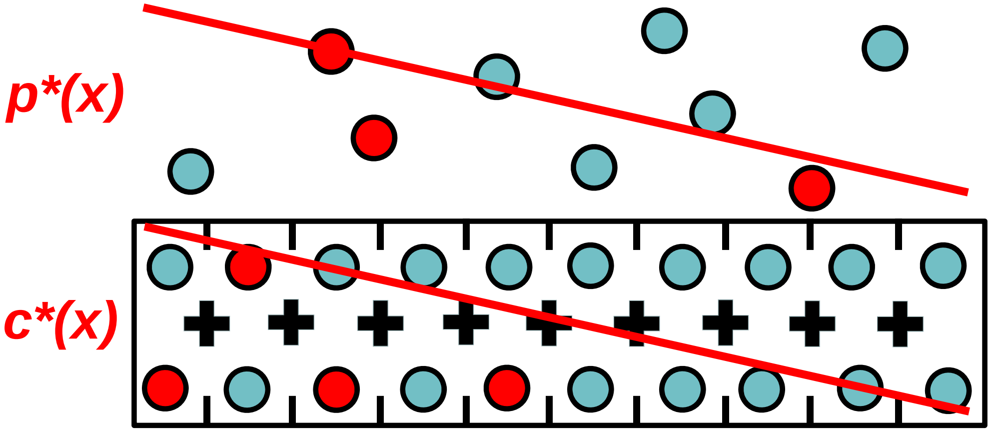


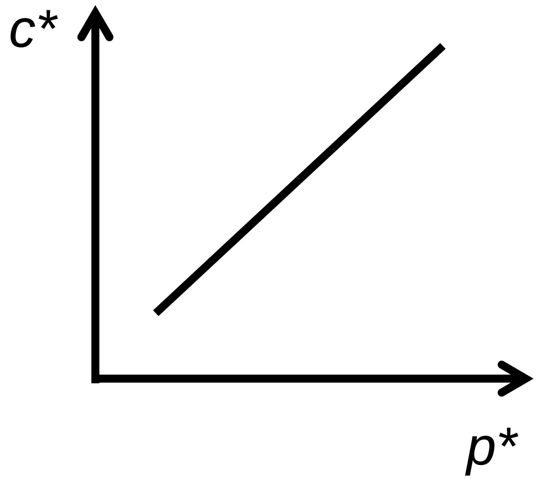
$$j \propto c \frac{\partial \mu}{\partial x} \propto c \frac{\partial \ln p}{\partial x} \propto c \frac{\partial \ln p(c)}{\partial c} \frac{\partial c}{\partial x} = \frac{\partial \ln p(c)}{\partial \ln c} \frac{\partial c}{\partial x} = \frac{\partial p / \partial c}{p/c} \frac{\partial c}{\partial x}$$

Implying identical concentration gradients we may thus note:

$$\frac{D^*}{D_T} = \frac{j^*}{j} = \frac{\partial \ln p^*}{\partial \ln c^*} \Big/ \frac{\partial \ln p}{\partial \ln c}$$

Tracer Diffusion





Equilibrium

$$j \propto c\frac{\partial \mu}{\partial x} \propto c\frac{\partial \ln p}{\partial x} \propto c\frac{\partial \ln p(c)}{\partial c}\frac{\partial c}{\partial x} = \frac{\partial \ln p(c)}{\partial \ln c}\frac{\partial c}{\partial x} = \frac{\partial p/\partial c}{p/c}\frac{\partial c}{\partial x}$$

Tracer (or Self-) Diffusion: $\frac{\partial p^*}{\partial c^*} = \frac{p^*}{c^*}$

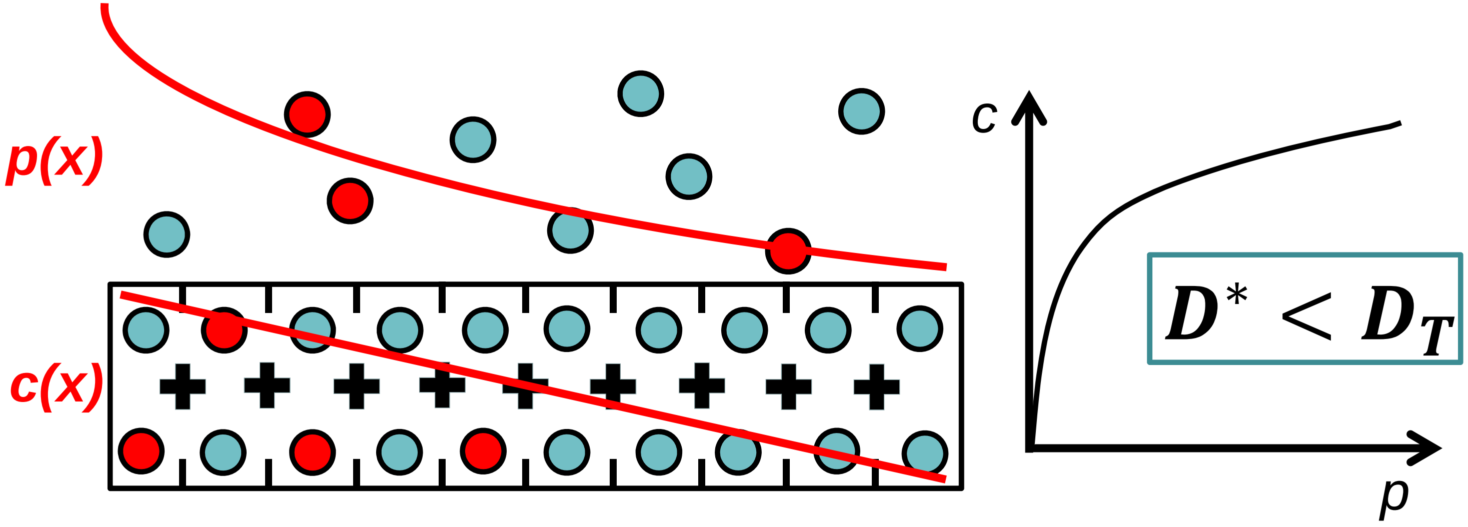
$$\frac{D_T}{D^*} = \frac{j}{j^*} = \frac{\frac{\partial \ln p(c)}{\partial \ln c}}{1}$$

$$D^* = D_T\frac{\partial \ln c}{\partial \ln p} = D_T\frac{\partial c/\partial p}{c/p}$$

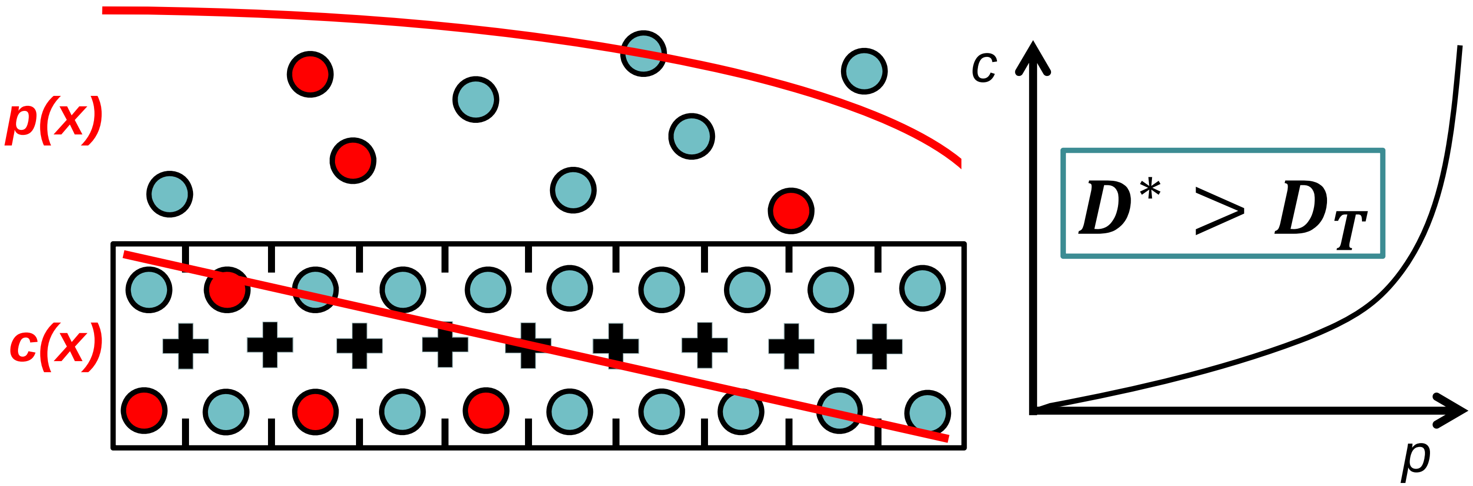
Non-Equilibrium

$$D^* = D_T \frac{\partial \ln c}{\partial \ln p} = D_T \frac{\partial c/\partial p}{c/p}$$

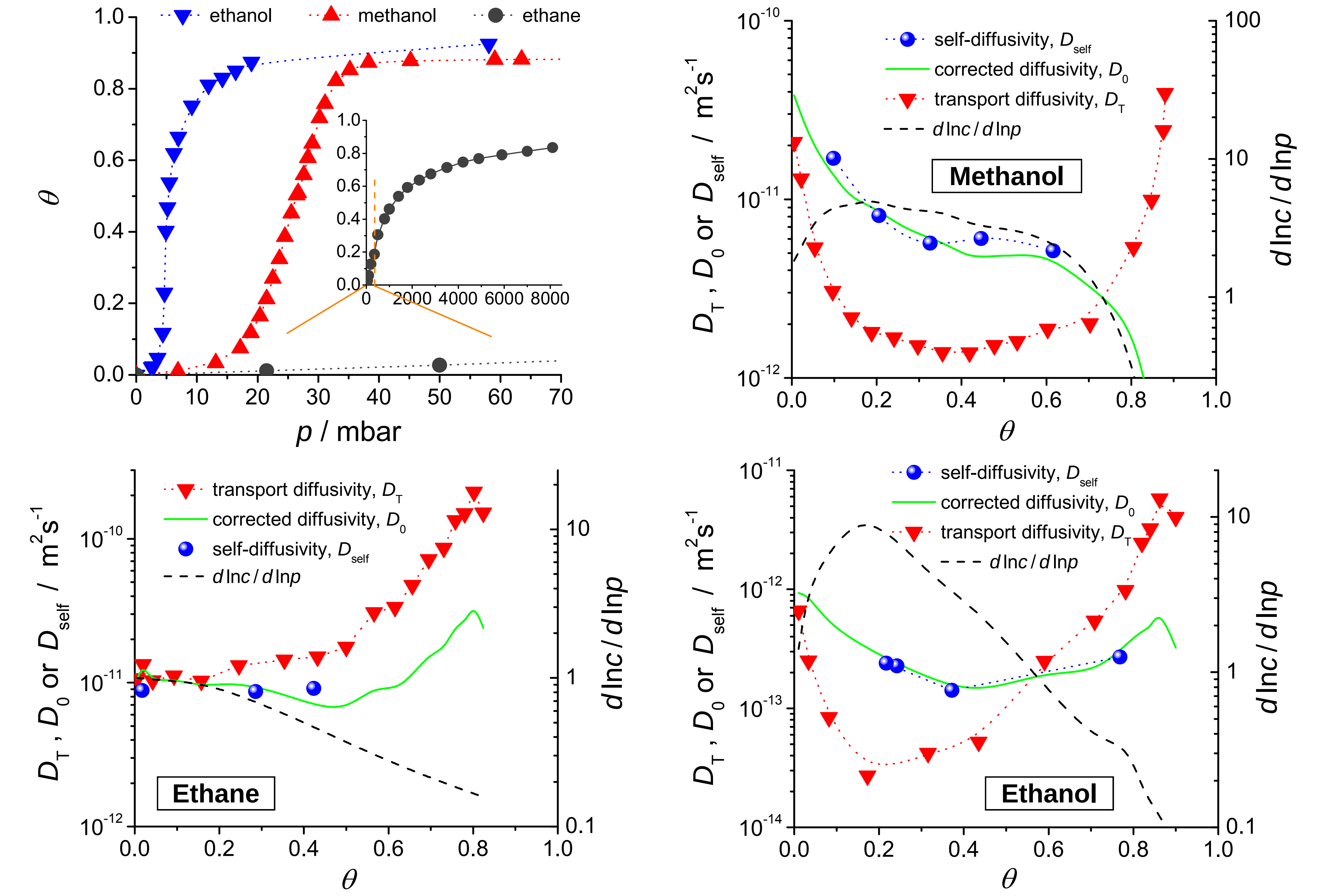
Competitive Adsorption



Mutual Attraction



Methanol, Ethanol and Ethane in ZIF-8



Methanol, Ethanol and Ethane in ZIF-8

Unique experimental proofs:

- $D_{self} = D_0 = D_T$ for $c \rightarrow 0$
- Correlating equlibrium and non-equilibrium quantities
- $D_{self} > D_T$ possible