



Combining theory and neutron scattering to understand molecular diffusion in porous materials

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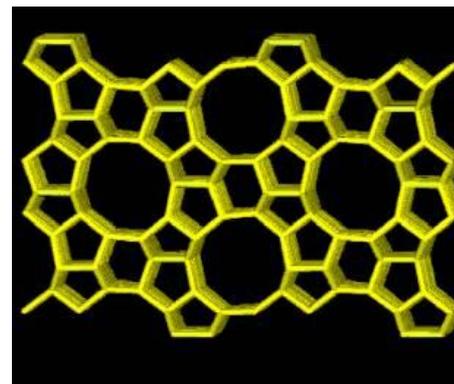
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Zeolites: crystalline microporous solids

(micropores have diameter < 1 nm)

Very widely used in industrial catalysis

Simplest form is SiO_2 , but Al substitution + cations introduce catalytically active sites

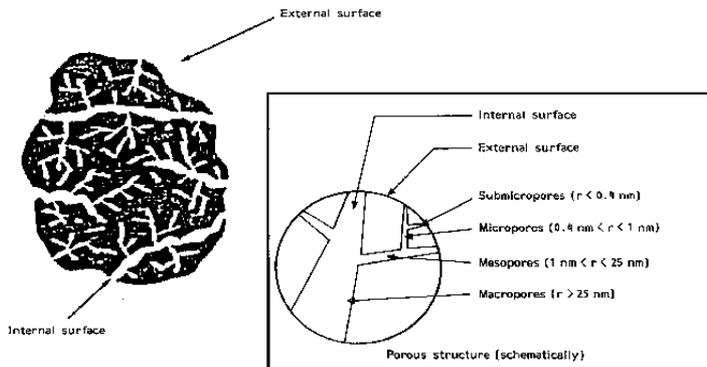
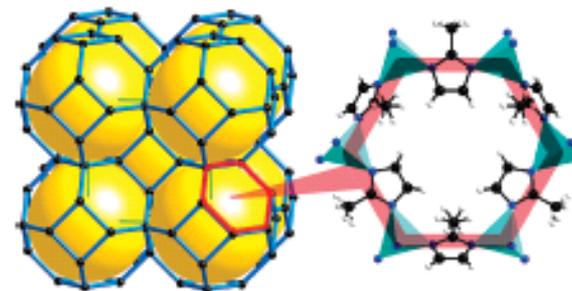


MOFs (metal-organic frameworks)

Crystalline materials with micropores and mesopores

Wide range of chemical functionality

Not yet used commercially, but intense research interest



www.activated-carbon.com

Porous carbon (activated carbon)

Disordered materials with micropores, mesopores, and macropores
Nominally C, but many functional groups
Very widely used commercially as adsorbents



High internal surface area → pores concentrate chemical species

e.g. Density of CO₂ in zeolite 13X at 1 atm, 298 K is 74x larger than CO₂ gas phase density

Well defined & spatially separated catalytic sites

e.g. MOFs to “heterogenize” homogeneous catalysts, Lee, Hupp et al., Chem. Soc. Rev. 38 (2009) 1450

Shape and size selectivity in adsorption and catalysis

e.g. Selective dehydration of n-butanol relative to iso-butanol on zeolite CaA

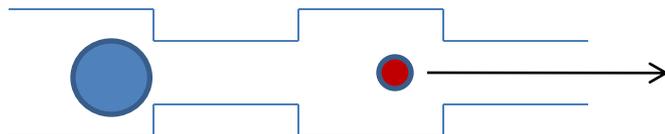
Selective cracking of linear alkanes relative to branched alkanes in H-SZM-5

P. B. Weisz, Pure & Appl. Chem. 52 (1980) 2091

Selective transport due to difference in molecular diffusion rates

e.g. CO₂ diffuses ~100x faster than CH₄ in zeolite DDR, making this a good membrane material

Jee and Sholl, J. Am. Chem. Soc., **131** (2009) 7896





Quantum chemistry (DFT): suitable for short range chemistry

But typical unit cells for porous crystals have 10^2 - 10^3 atoms
and dispersion interactions are critical

Molecular simulations: suitable for 10^3 - 10^5 atoms and sampling of configurations

But reliability of interatomic forcefields is critical

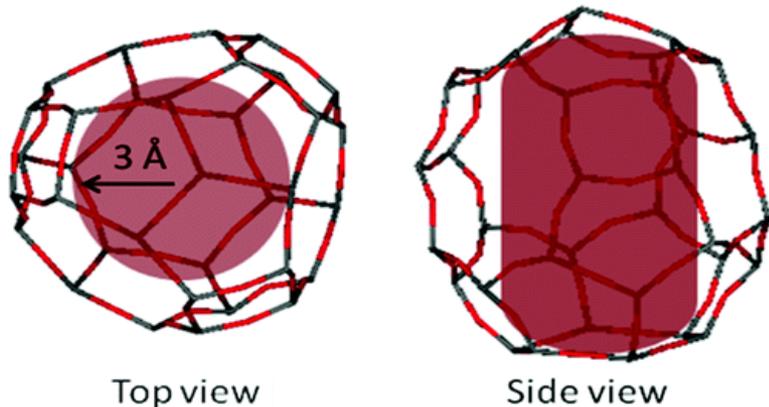
Forcefields for simulations of zeolites/MOFs

- Dispersion interactions (pairwise LJ potentials, mixing rules)
- Electrostatic interactions (atom centered point charges, non-polarizable charges often assigned by chemical intuition)
- Forcefield parameters may be adjusted to match experimental data (e.g. adsorption isotherms predicted using GCMC)



Example: CO₂ and CH₄ in DDR

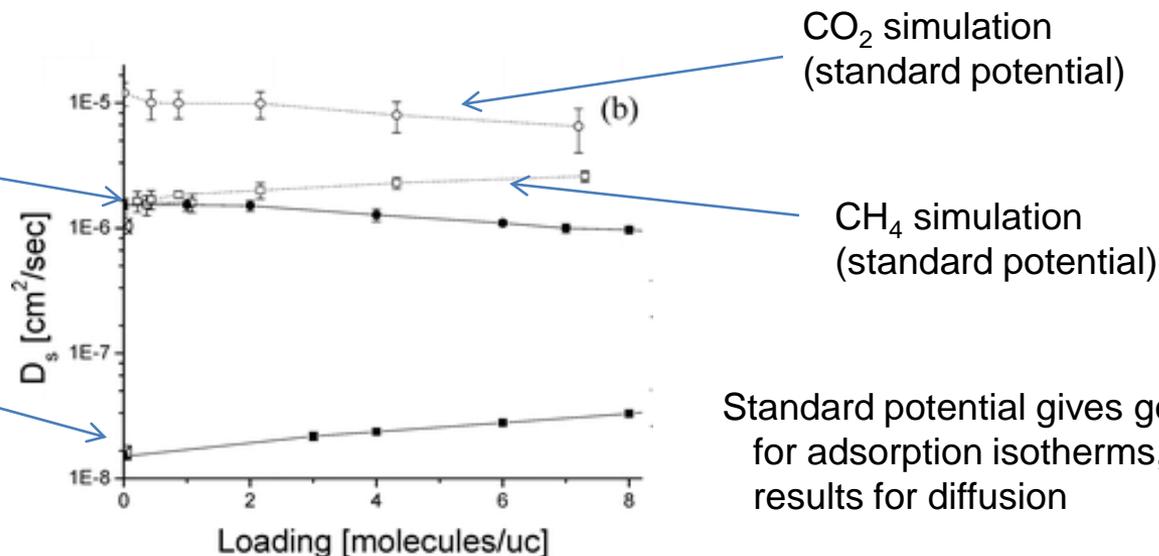
Jee and Sholl, J. Am. Chem. Soc., **131** (2009) 7896



DDR is a silica zeolite with 8 member rings connecting cages

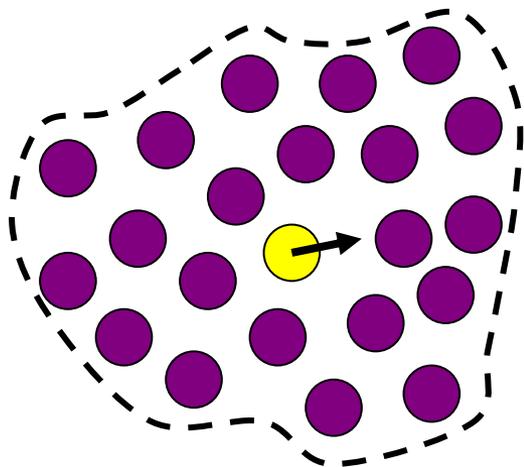
CO₂ experiment (PFG-NMR)

CH₄ experiment (PFG-NMR)





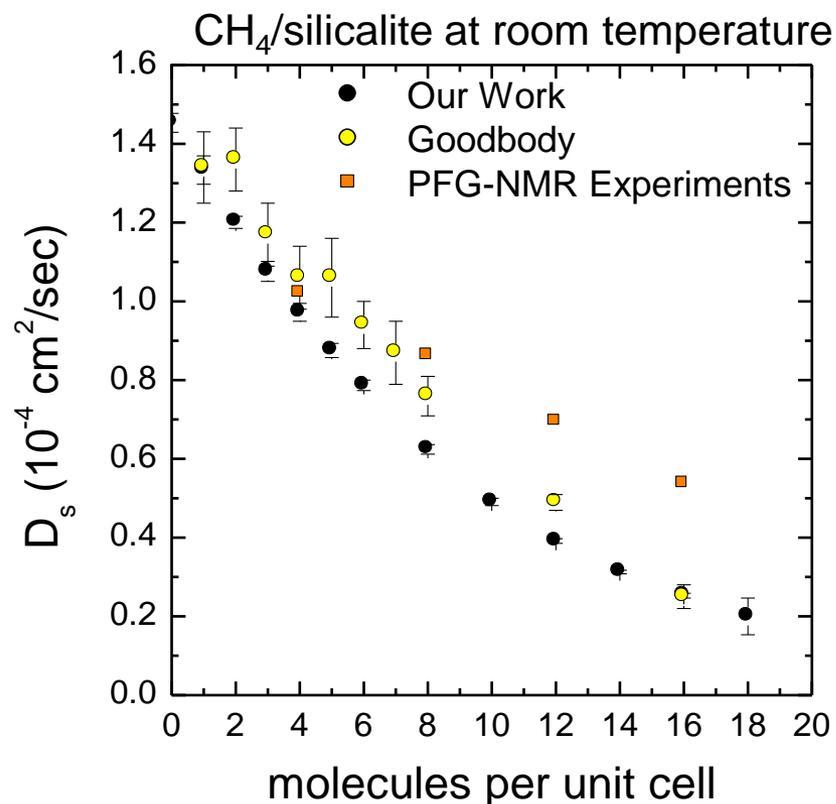
Self-diffusivity, D_s , measures mobility of a tagged particle.
Experimentally accessible via PFG-NMR and QENS.

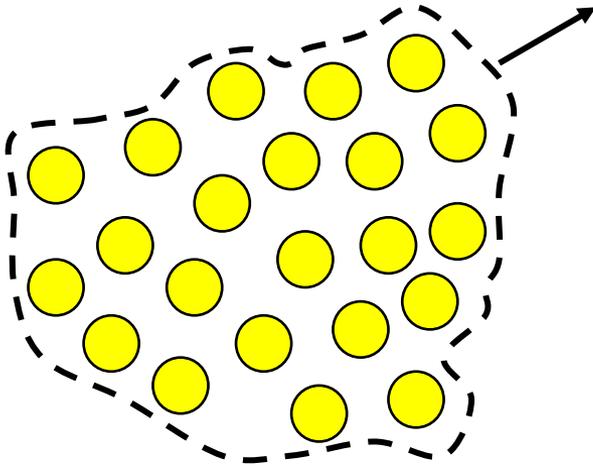


$$D_s = \lim_{t \rightarrow \infty} \frac{1}{6t} \left\langle \frac{1}{N} \sum_{l=1}^N \|\mathbf{r}_l(t) - \mathbf{r}_l(0)\|^2 \right\rangle$$

This is straightforward to compute from
MD trajectories.

Same definition in mixtures.





The Fickian diffusivity, D , is the proportionality constant in Fick's law of diffusion :

$$\vec{J} = -D\nabla c_i$$

(a.k.a transport diffusivity)

The Fickian diffusivity can be written without approximation as

$$D(c) = D_0(c) \left(\frac{\partial \ln f}{\partial \ln c} \right)$$

Corrected diffusivity
(a.k.a. MS diffusivity
for single-component case)

Thermodynamic correction
factor (from isotherm)

D_0 can be computed from MD, and isotherm $(c(f))$ can be computed from GCMC



MD for diffusion (order of magnitude estimates):

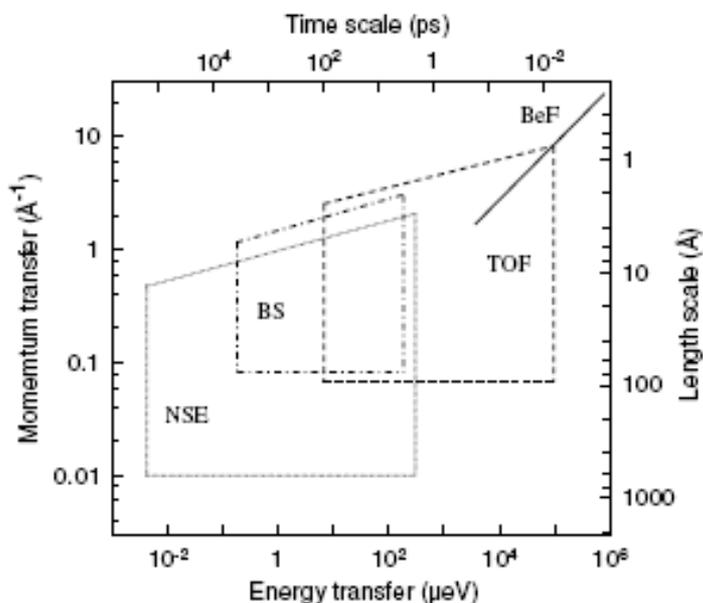
$$T \sim 100 \text{ ns} = 10^{-7} \text{ s}$$

$$L > 1 \text{ nm} = 10^{-9} \text{ m}$$

$$D \sim L^2/T > 10^{-10} \text{ m}^2\text{s}^{-1} = 10^{-6} \text{ cm}^2\text{s}^{-1}$$

Typical diffusivity in liquid state: $10^{-5} \text{ cm}^2\text{s}^{-1}$ (Toor's law)

Simulation of slower diffusion requires TST or other coarse-graining



Neutron scattering for diffusion

Jobic and Theodorou, *Micro. Meso. Mater.* 102 (2007) 21.

Length and time scales well matched with MD

Incoherent scattering → self diffusivity

Coherent scattering → transport diffusivity

Both diffusivities can be measured simultaneously from a single equilibrium experiment (if both coherent and incoherent scattering occurs)



Subtleties in Obtaining D From Neutron Scattering

Jobic and Theodorou, Micro. Meso. Mater. 102 (2007) 21

$$I_s(Q, t) = \exp(-D_s Q^2 t)$$

Intermediate self-scattering function

$$S_{inc}(Q, \omega) = \frac{1}{\pi} \frac{D_s Q^2}{(\omega^2 + (D_s Q^2)^2)}$$

Time Fourier transform

$$\Delta\omega_{inc}(Q) = D_s Q^2$$

Half-width at half maximum

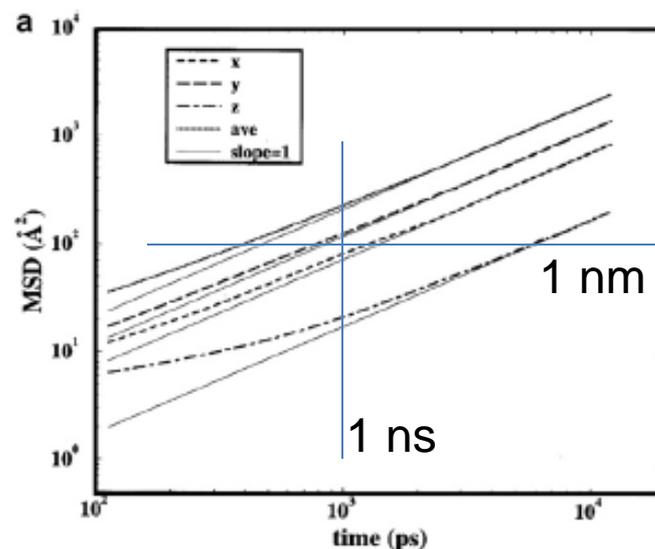
This is only valid for small Q (i.e. large distances). For large Q, details depend on atomic-scale mechanism

e.g. Chudley/Elliott (assume constant jump distance and residence time)

Hall/Ross (assume distribution of jump distances)

Computed mean square displacements
for CH₄ in silicalite at 300 K from MD

Straight lines show large distance scaling





Examples

- (a) “Simple” crystalline materials – silicalite
- (b) Chemically complex crystalline materials – MOFs
- (c) Disordered porous materials – porous carbons
- (d) Mixtures of adsorbed species

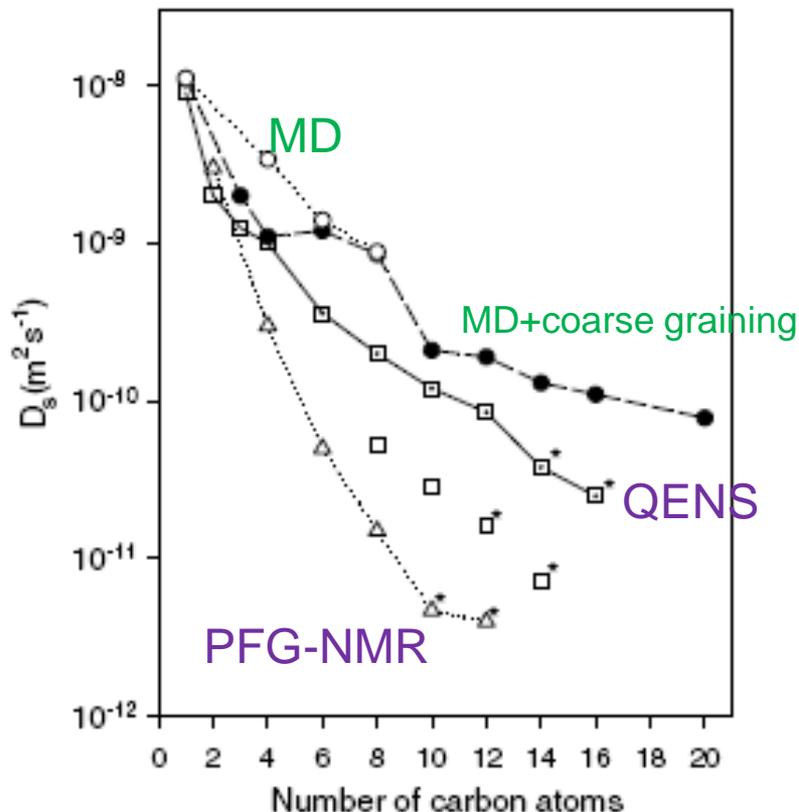


Example 1: n-alkanes in silicalite

Jobic and Theodorou, Micro. Meso. Mater. 102 (2007) 21

Silicalite is SiO_2 form of ZSM-5 – one of easiest zeolites to synthesize

Self diffusion of n-alkanes measured as a function of chain length



All data from low concentration of adsorbed n-alkanes

Agreement between MD and QENS is reasonable

PFG-NMR gives systematically lower D_s than QENS

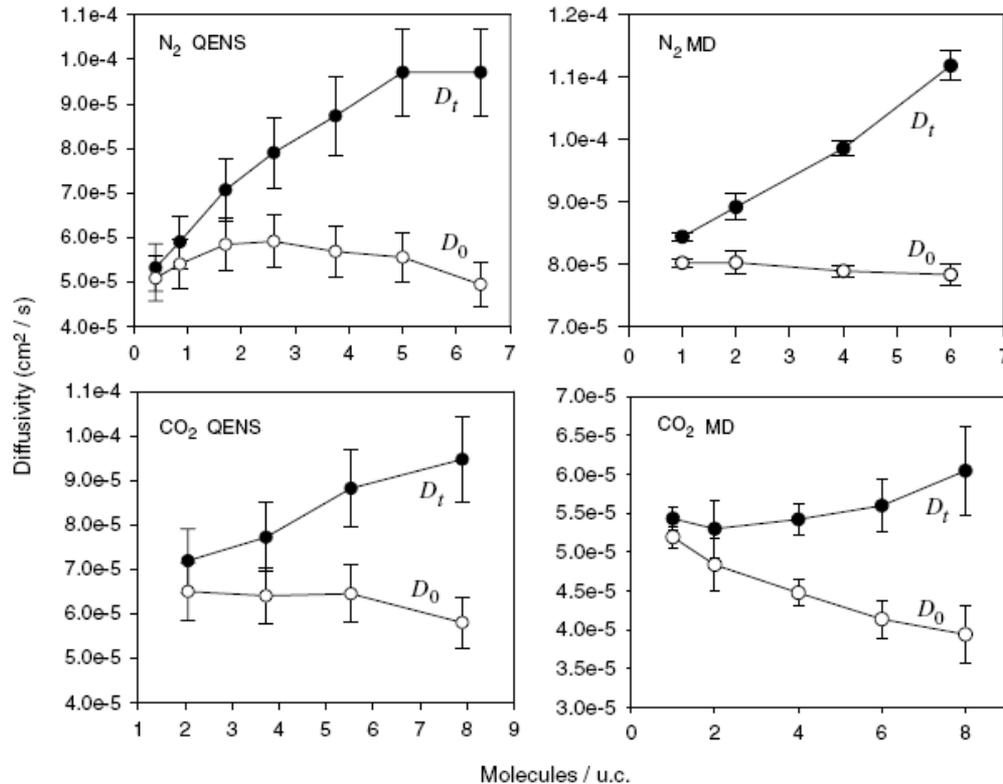
For QENS, $L \sim \text{nm}$

For PFG-NMR, $L \sim \text{microns}$



Example 2: N₂ and CO₂ in silicalite

Jobic and Theodorou, Micro. Meso. Mater. 102 (2007) 21



N₂ at 200 K; CO₂ at 300 K

Transport diffusion measured with QENS
Corrected diffusivity then obtained using adsorption isotherms

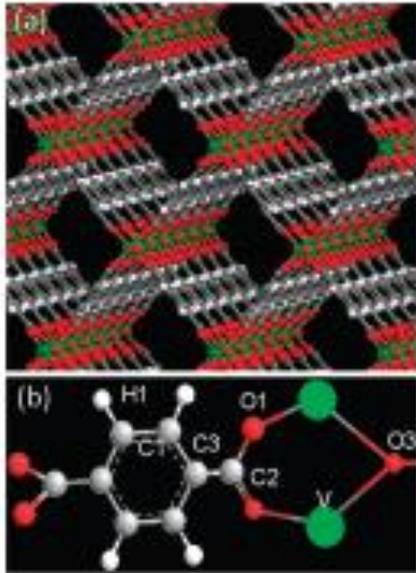
Recall that D_s typically decreases as concentration increases

Agreement between MD simulations and experiment is good



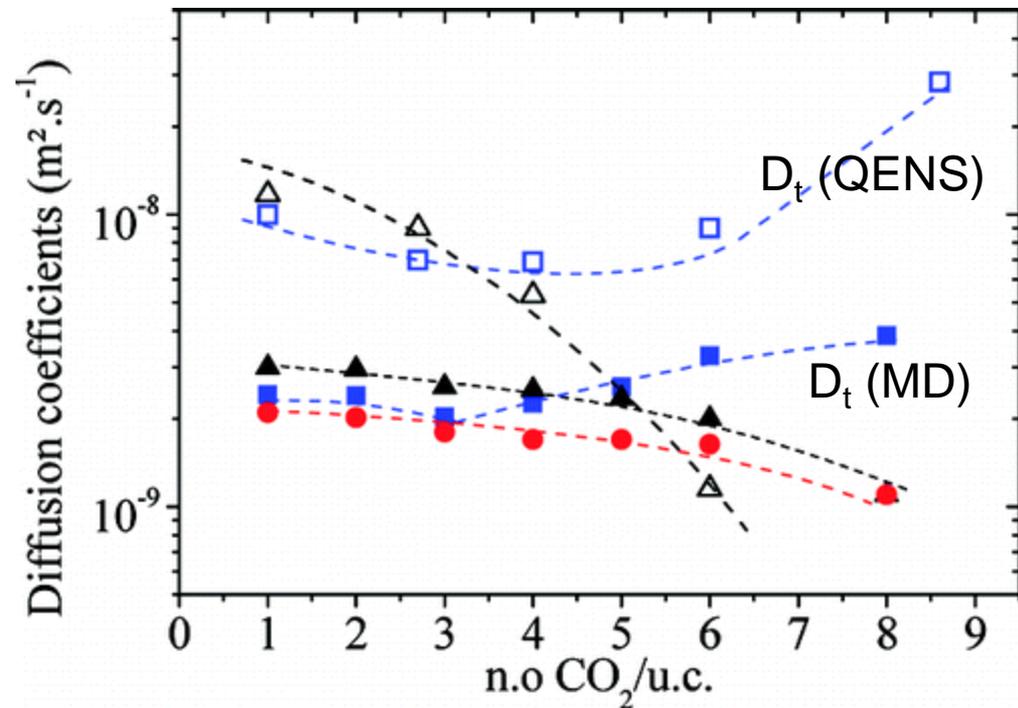
Example 3: CO₂ Diffusion in MOFs

Salles et al., ACS Nano 4 (2010) 143



MIL-47(V): Corner sharing V⁴⁺O₄ tetrahedra
1,4-benzenedicarboxylate linkers

CO₂ scatters coherently → only D_t accessible in expts.



MD results are 5-10x smaller
than experimental observations

Diffusivities are similar to liquid-like
bulk samples



Example 4: H₂ and D₂ diffusion in porous carbons

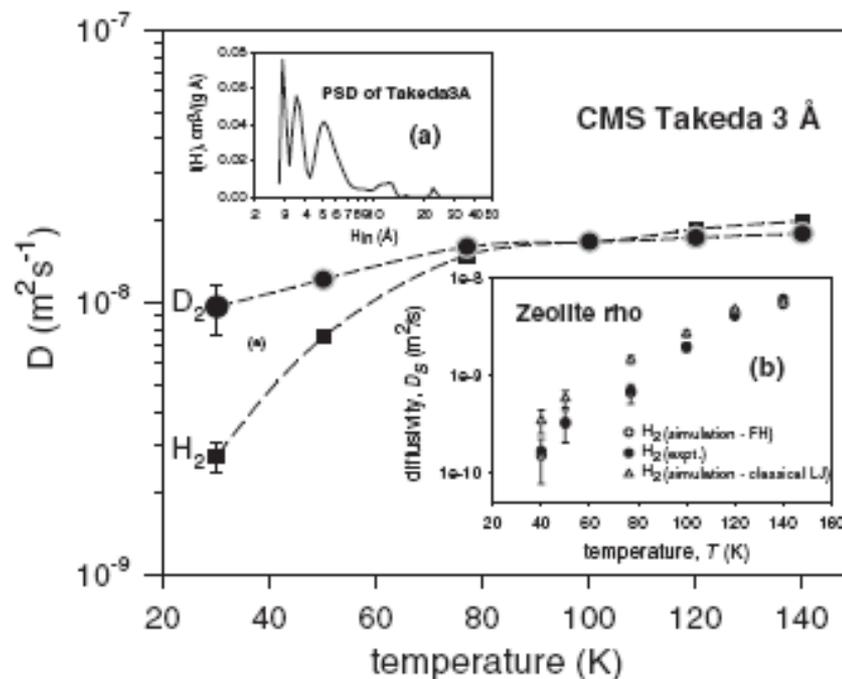
Nguyen, Jobic, and Bhatia, Phys. Rev. Lett. 105 (2010) 085901

Quantum effects are well known in low temperature adsorption
(D₂ has stronger binding energy than H₂ due to zero point energy)
What are isotopic effects on diffusion?

Experiments with Takeda 3 Å
carbon molecular sieve
(disordered material)

Also experiments and MD for
zeolite rho for H₂
(ordered material)

MD shows importance of quantum
effects (ZPE) at low temperature
(using Feynman-Hibbs formalism)

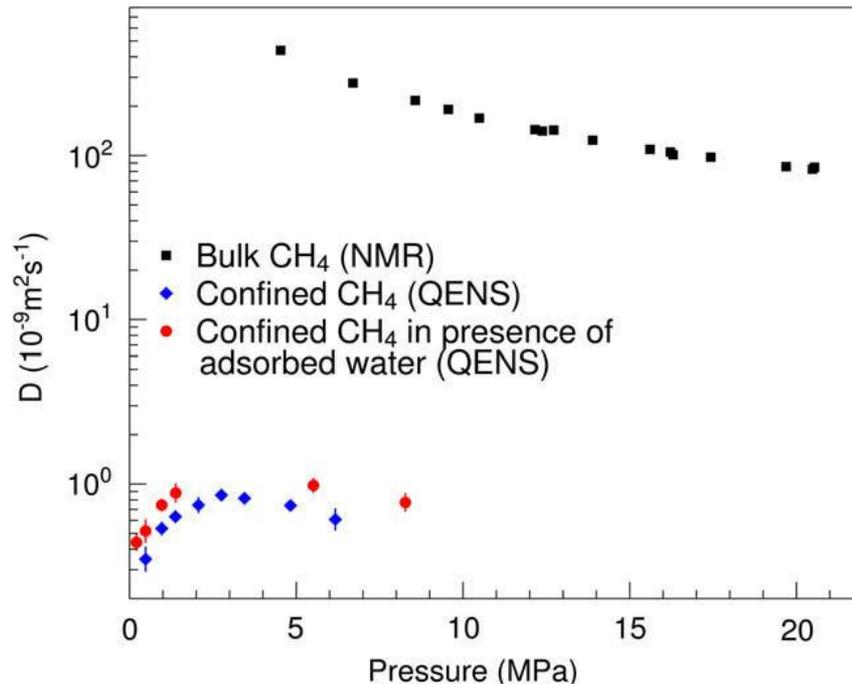




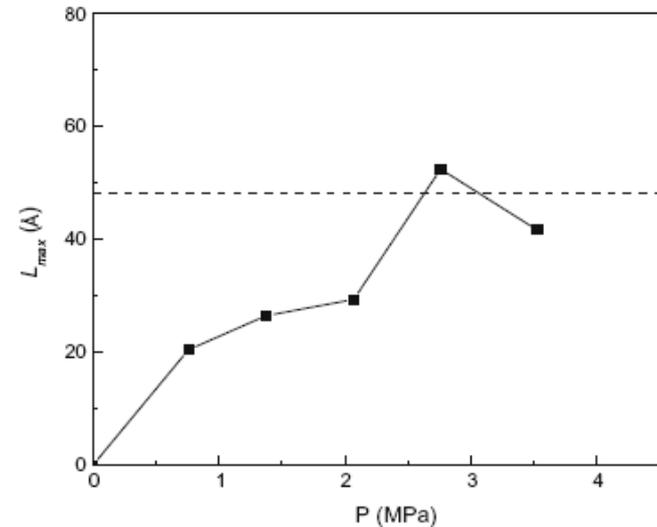
Example 5: CH₄ diffusion in carbon aerogel

Chathoth, Mamontov et al, Micro. Meso. Mater. 132 (2010) 148

Carbon aerogel: disordered materials with surface area 480 m²/g, avg. pore diameter ~5 nm
QENS used to probe CH₄ diffusion; SANS used to probe pore filling



Diffusion of confined CH₄ is liquid-like

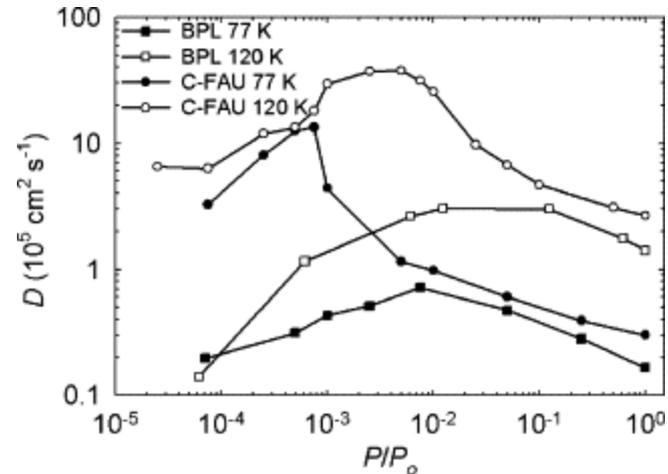
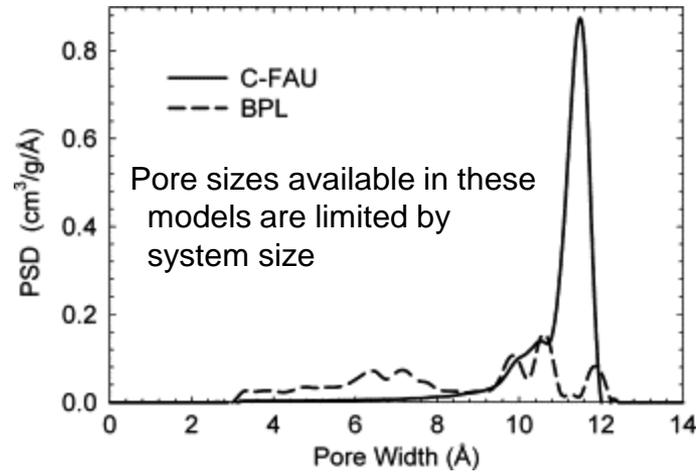
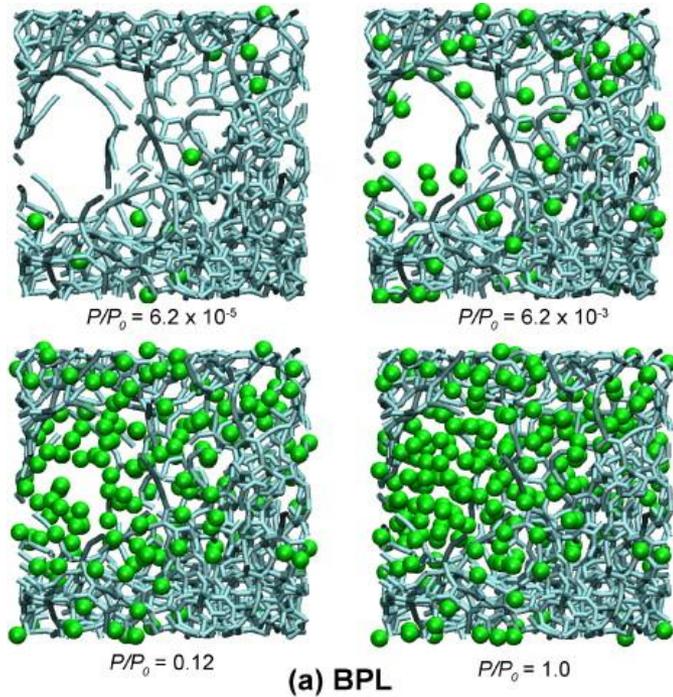


Maximum pore size filled as a function of CH₄ pressure

Example 6: Ar diffusion in a porous carbon

Moore et al., Appl. Surf. Sci. 256 (2010) 5131

Structure for disordered carbon developed via Reverse Monte Carlo from experimental XRD data





Mixture diffusion

Sholl, Acc. Chem. Res. 39 (2006) 403

Almost all practical examples (e.g. porous catalysts) involve chemical mixtures

Mixture diffusion can include phenomena not possible in single component diffusion (e.g. net transport against gradient in concentration)

Initial condition

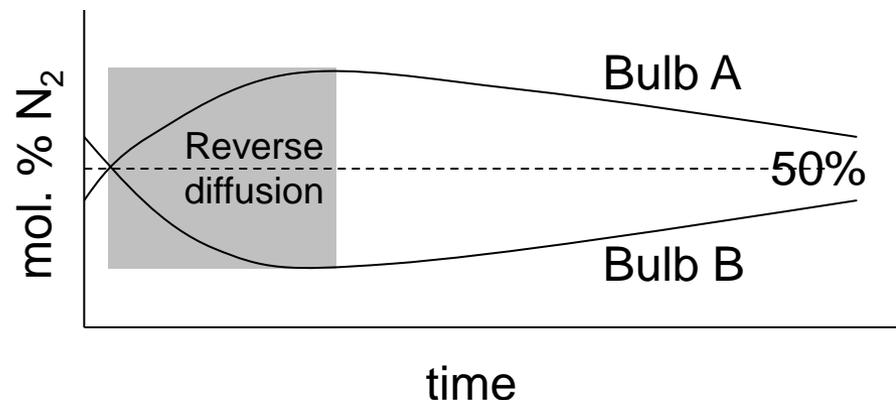
$P = 100 \text{ kPa}$
 $T = 298 \text{ K}$
46 mol% N_2
54 mol% H_2

Bulb A

$P = 100 \text{ kPa}$
 $T = 298 \text{ K}$
52 mol% N_2
48 mol% CO_2

Bulb B

Duncan and Toor, 1962



Simulation of mixtures is straightforward (if individual components are accessible)

Available of experimental data lags behind simulation

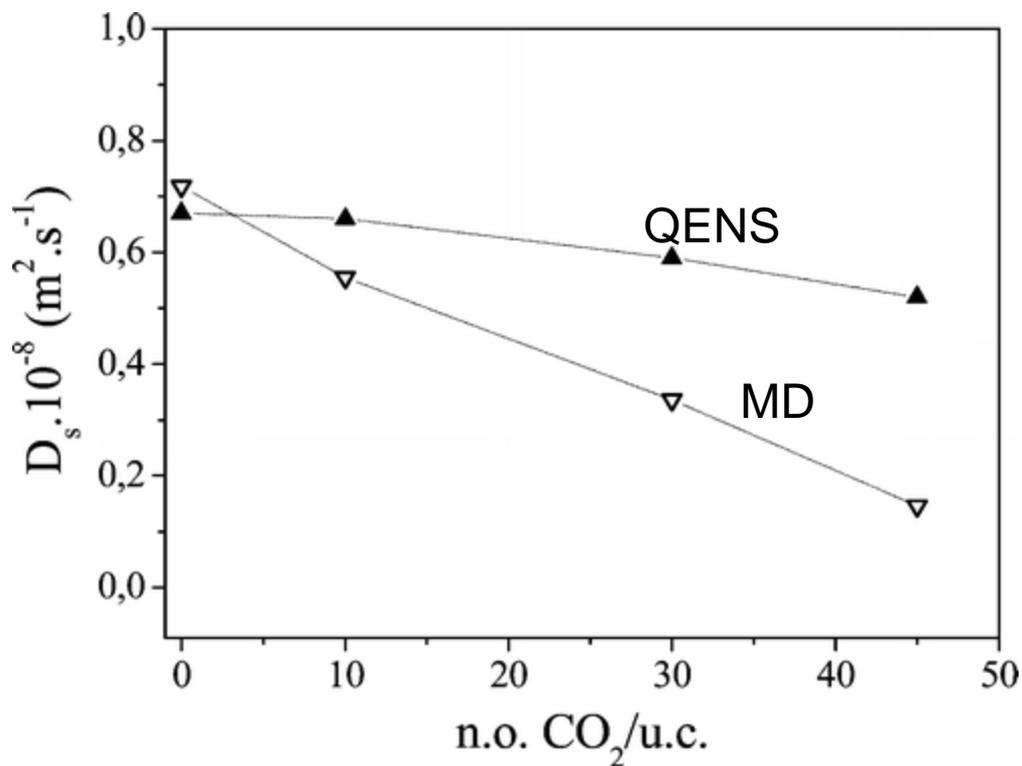


Example 7: CH₄ and CO₂ diffusion in zeolite NaY

Deroche et al., J. Phys. Chem. C 114 (2010) 5027

NaY: zeolite with large pores, Si/Al = 2.4, Na counterions

CH₄/CO₂ mixture: QENS dominated by incoherent scattering from H (CO₂ “invisible”)



CH₄ self diffusivity at constant
CH₄ loading as CO₂ loading
is varied

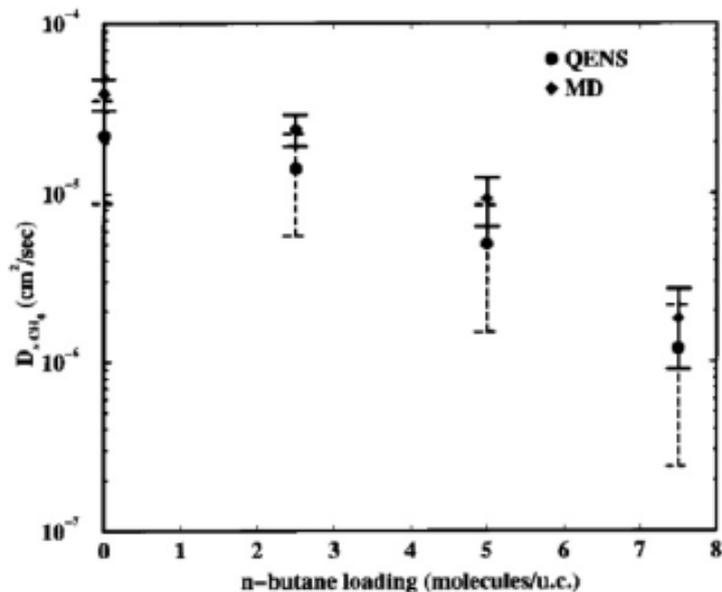


Example 8: CH₄ and n-butane diffusion in silicalite

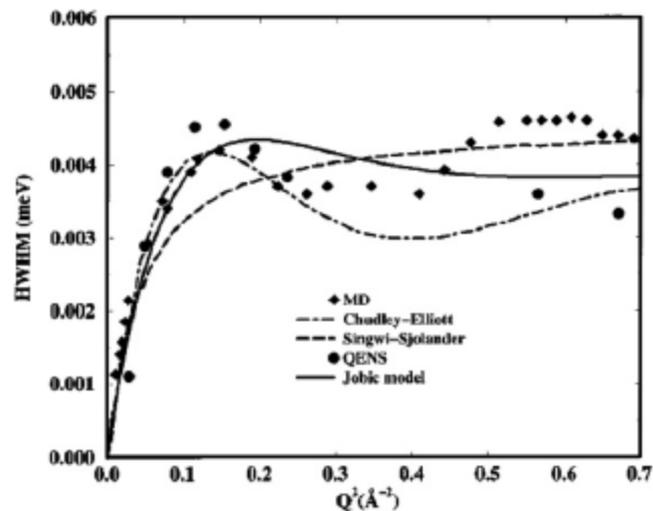
Jobic and Theodorou, Micro. Meso. Mater. 102 (2007) 21

QENS using CH₄/C₄D₁₀ mixtures → examine CH₄ self diffusion via incoherent scattering from H

Constant CH₄ loading of 4 molecules/unit cell

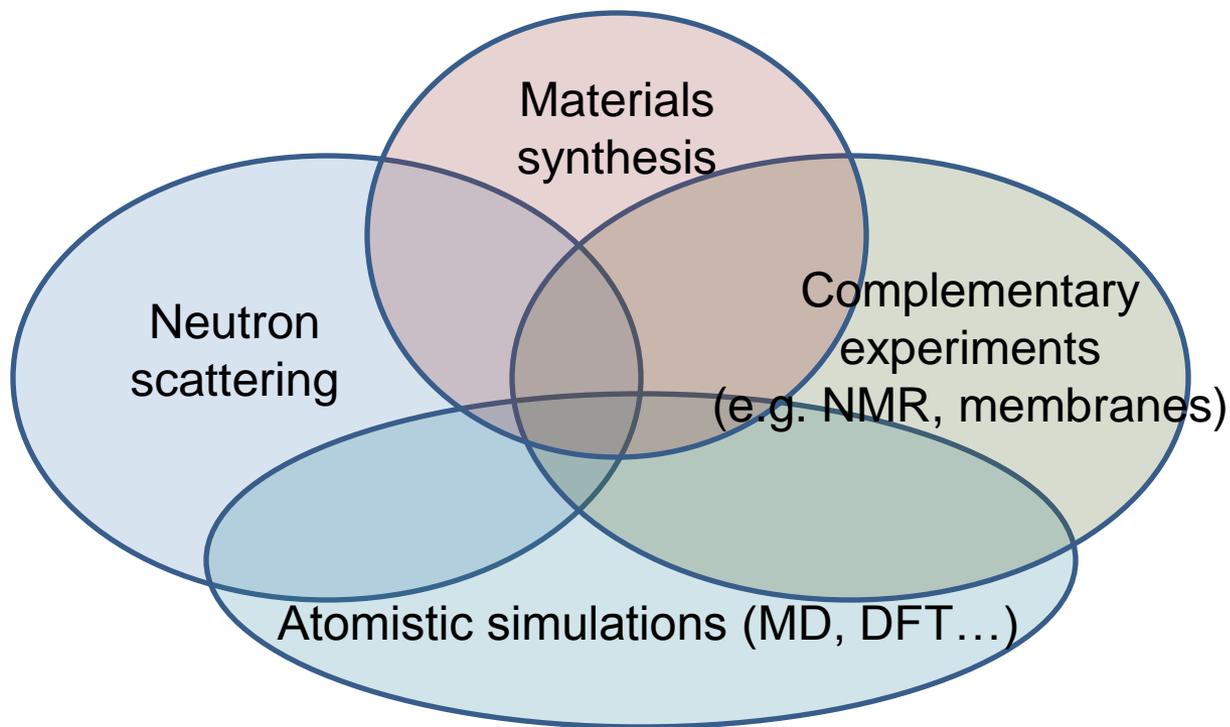


Half width at half maximum vs. Q²





Opportunities/Challenges



Diffusion in materials with “unusual” properties (e.g. zeolite DDR)

Diffusion in H-rich solids and flexible solids (e.g. MOFs)

Diffusion of chemical mixtures (e.g. “molecular traffic control” in zeolites”)

Diffusion in hierarchical materials (e.g. polycrystalline zeolite films)