Adsorption and Diffusion of Guest Molecules in Zeolites and MOFs Studied by Molecular Simulation

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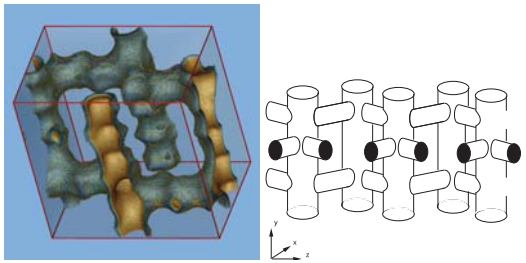
Zeolites: Properties

- microporous channel structure
- crystalline, SiO_2 building blocks
- substitution of Si^{4+} by Al^{3+} and a cation (e.g. Na^+ or H^+)
- typical poresize: $4 - 12\mathring{A}$
- synthetic and natural; >190 framework types

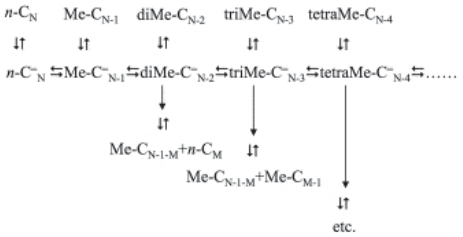
MFI-type Zeolite



Silicalite: MFI-type zeolite without non-framework cations

Zeolites: Applications

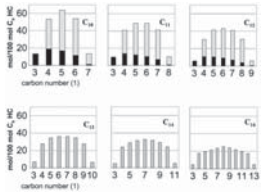
- ion exchanger (laundry powder)
- size-selective separation
- catalytic cracking/isomerization of hydrocarbons



Maesen et al, J. Catal. (2004), 221, 241.

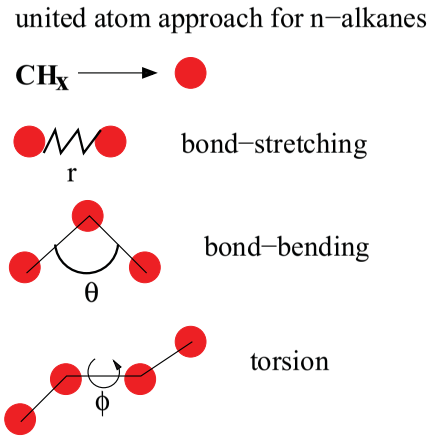
Zeolites: Why Simulations ?

- experiments can be time consuming (even weeks/months)
- multicomponent systems are just as easy/difficult to simulate as single-component systems
- structure of guest molecules inside zeolites; simulations provide fundamental understanding
- screening of framework structures (>190)

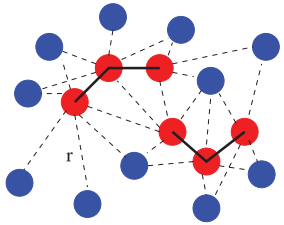


Hydrocracking on FAU; Maesen et al, J. Catal. (2004), 221, 241.

Force field: Bonded Interactions



Non-Bonded Interactions: Lennard-Jones (+ Electrostatics)



oxygen atom (=zeolite)

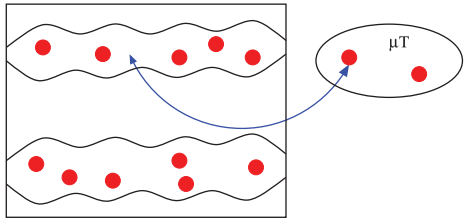
CH_X atom (=hydrocarbon)

Grand-Canonical (μVT) Ensemble (GCMC)

- system coupled to particle reservoir at chemical potential μ and temperature T statistical weight (positions $\mathbf{r}^N$, $\beta = 1/(k_B T)$)

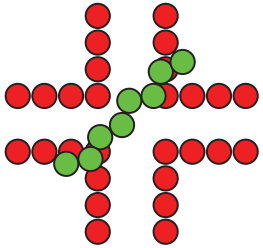
$$\mathcal{W}(N, \mathbf{r}^N) \sim \frac{V^N}{N! \Lambda^{3N}} \exp[\beta \mu N - \beta U(\mathbf{r}^N)]$$

- trial moves to *(1)* exchange particles with reservoir *(2)* displace adsorbed guest molecules inside zeolite
- equilibrium: $\mu_{\text{gas}} = \mu_{\text{zeolite}}$; measure average $\langle N \rangle$ for given μ and T



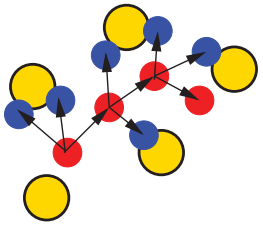
Random Insertion of Chains

Chain Length	Fraction without overlaps
1	10^{-2}
2	10^{-4}
3	10^{-6}
...	...
8	10^{-16}



Rosenbluth Scheme (1)

- Grow chain step by step
- Generate k trial directions for each segment
- Selecting the best direction is most likely
- Resulting bias is removed in the MC acceptance rules



Rosenbluth Scheme (2)

1. Place first monomer at a random position
2. For the next monomer (i), generate k trial directions ($j = 1 \cdots k$) each with energy u_{ij}
3. Select trial direction $j^\star$ with a probability

$$P_{j^\star} = \frac{\exp[-\beta u_{ij^\star}]}{\sum_{j=1}^{k} \exp[-\beta u_{ij}]}$$

4. Continue with step 2 until the complete chain is grown (N monomers)

Rosenbluth Scheme (3)

Probability to select certain monomer (k trial directions)

$$P_{j^\star} = \frac{\exp[-\beta u_{ij^\star}]}{\sum_{j=1}^{k} \exp[-\beta u_{ij}]}$$

Probability to generate the chain (N monomers)

$$P_{\text{chain}} = \frac{\prod_{i=1}^{N} \exp[-\beta u_{ij^\star}]}{\prod_{i=1}^{N} \sum_{j=1}^{k} \exp[-\beta u_{ij}]} = \frac{\exp[-\beta U_{\text{chain}}]}{W}$$

Rosenbluth weight W:

$$W = \prod_{i=1}^{N} \sum_{j=1}^{k} \exp[-\beta u_{ij}]$$

Note: u_{ij} is the energy of trial direction j for monomer i

Configurational-Bias Monte Carlo (1)

- Generate chains using the Rosenbluth scheme
- Accept/Reject a new configuration of a chain in such a way that detailed balance is obeyed
- Split potential energy into "**bonded**" (bond-stretching, bending, torsion) and "**non-bonded**" (i.e. Lennard-Jones or Coulombic) interactions
- Generate (k) trial positions according to **bonded** interactions (unbranched chain: l, θ, ϕ are independent)

$$\begin{aligned} U_{\rm bonded} &= U_{\rm stretch}(l) + U_{\rm bend}(\theta) + U_{\rm tors}(\phi) \\ P(l) &\sim dl\, l^2 \exp[-\beta u(l)] \\ P(\theta) &\sim d\theta\, \sin(\theta) \exp[-\beta u(\theta)] \\ P(\phi) &\sim d\phi\, \exp[-\beta u(\phi)] \end{aligned}$$

Configurational-Bias Monte Carlo (2)

- Generate a trial configuration using the Rosenbluth scheme. k trial segments $\{\mathbf{b}\}_k = \{\mathbf{b}_1 \cdots \mathbf{b}_k\}$, each trial segment is generated according to

$$P(\mathbf{b}) \sim \exp[-\beta u_{\rm bonded}(\mathbf{b})]$$

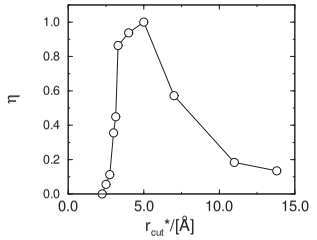
- Compute non-bonded energy, select configuration i with a probability

$$P(\mathbf{b}_i) = \frac{\exp[-\beta u_{\rm non-b}(\mathbf{b}_i)]}{\sum_{j=1}^{k} \exp[-\beta u_{\rm non-b}(\mathbf{b}_j)]} = \frac{\exp[-\beta u_{\rm non-b}(\mathbf{b}_i)]}{w_l}$$

- Continue until chain is grown, $W(n) = \prod_{l=1}^{n} w_l$
- Similar procedure for old configuration, generate $k-1$ trial positions (trial position 1 is the old configuration itself), leading to $W(o)$
- Accept/reject with a probability

$$\text{acc}(o \rightarrow n) = \min(1, W(n)/W(o))$$

Significant Speedup: Dual-Cutoff CBMC



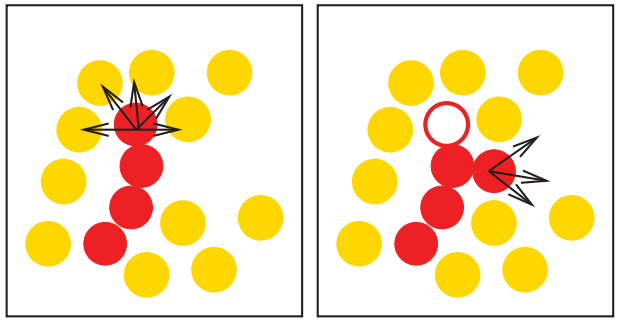
- Grow chain with approximate potential; $W^\star$
- Correct for difference later
  (δu, difference real and approximate potential for *selected* configuration)

$$\text{acc}(o \rightarrow n) = \min\left(1, \frac{W^\star(n)}{W^\star(o)} \times \exp[-\beta[\delta u(n) - \delta u(o)]]\right)$$

Dead-End Alley

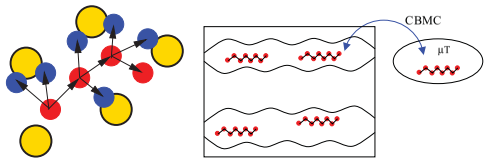
Recoil Growth: Avoid Dead Alleys

Consta, Vlugt, Wichers Hoeth, Smit, Frenkel, Mol. Phys. (1999), 97, 1243-1254.



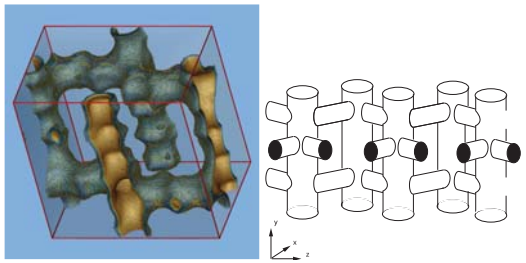
Adsorption Simulations of Alkanes in a Zeolite: GCMC

- displacement of a randomly selected chain
- rotation of a randomly selected chain
- (partial) regrow of a randomly selected chain using CBMC
- exchange (insertion or deletion) of a chain with the reservoir using CBMC
- identity change of a chain using CBMC (only for mixtures)



Simulation Results on MFI (Silicalite)

no cations (yet)



Henry Coefficient of n-alkanes

CN	K_H 573K [mol/kg/Pa]		K_∞ [mol/kg/Pa]		Q [kJ/mol]	
	Sim.	Exp.	Sim.	Exp.	Sim.	Exp.
5	3.04×10^{-6}	2.99×10^{-6}	2.33×10^{-11}	2.64×10^{-11}	56.13	55.7
6	6.10×10^{-6}	5.93×10^{-6}	6.07×10^{-11}	6.07×10^{-11}	65.87	66.0
7	1.23×10^{-5}	1.22×10^{-5}	1.53×10^{-12}	1.29×10^{-12}	75.77	76.7
8	2.43×10^{-5}	2.49×10^{-5}	3.67×10^{-13}	3.25×10^{-13}	85.82	86.6
9	4.61×10^{-5}	4.73×10^{-5}	8.59×10^{-14}	8.41×10^{-14}	95.81	96.1

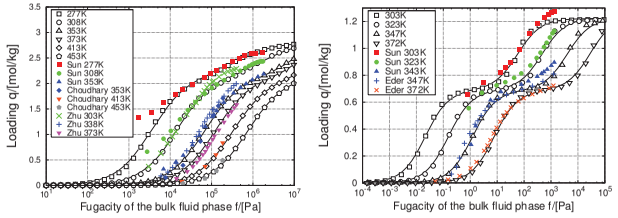
relation	Sim.	Exp.
$Q = \alpha \mathrm{CN} + \beta$	$\alpha = 9.93$	$\alpha = 10.1$
$-\Delta S = \gamma \mathrm{CN} + \delta$	$\gamma = 11.65$	$\gamma = 11.99$
$-\ln(K_\infty) = AQ + B$	$A = 0.141, B = 16.54$	$A = 0.143, B = 16.4$

Simulations from: Dubbeldam, Calero, Vlugt, Krishna, Maesen, Smit, J. Phys. Chem. B, 2004, 108, 12301.

Experiments from: Arik, Denayer, Baron, Microporous Mesoporous Materials, 2003, 60, 111-114.

Linear Alkanes

ethane (C_2) heptane (C_7)



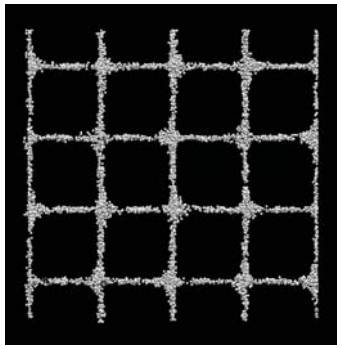
Dual Site Langmuir model

$$\Theta(P) = \frac{\Theta_A b_A P}{1 + b_A P} + \frac{\Theta_B b_B P}{1 + b_B P}$$

Dubbeldam, Calero, Vlugt, Krishna, Maesen, Smit
J. Phys. Chem. B, 2004, 108, 12301

Commensurate Freezing of n-heptane (1)

Center of mass position butane (C_4)

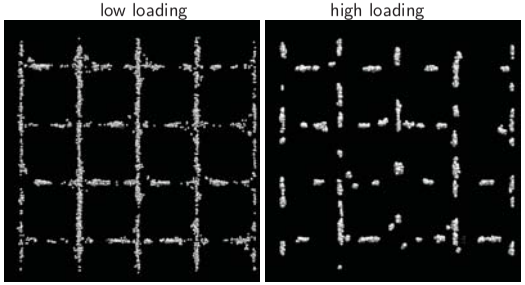


Maesen, Smit, Nature, 1995, 374, 42-44.
Vlugt, Krishna, Smit, J. Phys. Chem. B, 1999, 103, 102-1118.

Commensurate Freezing of n-heptane (2)

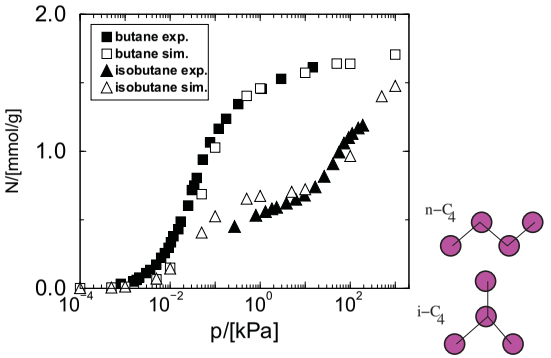
Center of mass position heptane (C_7)

low loading high loading



Maesen, Smit, Nature, 1995, 374, 42-44.
Vlugt, Krishna, Smit, J. Phys. Chem. B, 1999, 103, 102-1118.

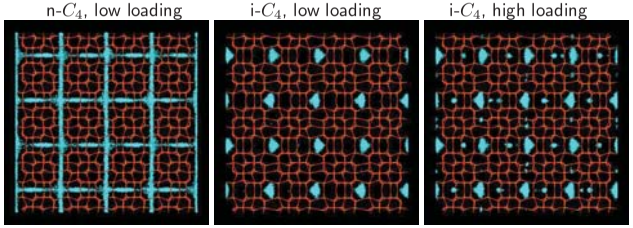
Adsorption of Isobutane in MFI (1)



Vlugt, Zhu, Kapteijn, Moulijn, Smit, Krishna,
J. Am. Chem. Soc., 1998, 120, 5599

Adsorption of Isobutane in MFI (2)

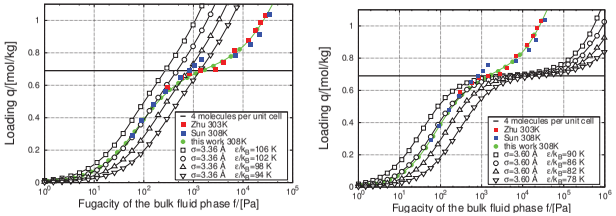
n-C_4, low loading | i-C_4, low loading | i-C_4, high loading



Vlugt, Zhu, Kapteijn, Moulijn, Smit, Krishna,
J. Am. Chem. Soc., 1998, 120, 5599

Influence of σ_{O-CH_x} (Isobutane in MFI)

5% too low | 5% too large

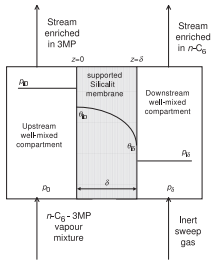


Dubbeldam, Calero, Vlugt, Krishna, Maesen, Smit
J. Phys. Chem. B, 2004, 108, 12301.

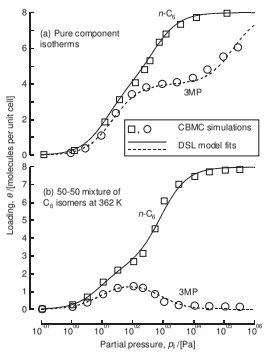
Membrane Permeation (1)

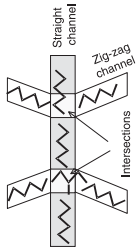
Flux	$n-C_6$	$i-C_6$	selectivity
pure	179	136	1.3
50%-50%	46	1.9	24

Experiments by J. Falconer, Univ. Colorado



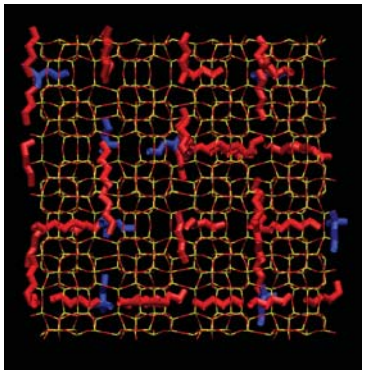
Membrane Permeation (2)





Simulation Snapshot

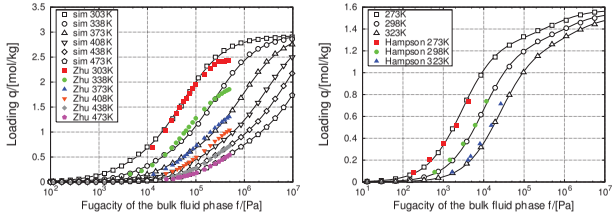
blue = branched (i-C_6) red = linear (n-C_6)



Other Zeolite Frameworks

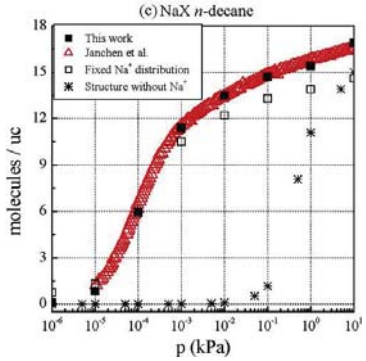
Simulated using the same force field as for MFI

DDR (ethane, C_2) | TON (ethane, C_2)



Dubbeldam, Calero, Vlugt, Krishna, Maesen, Smit
J. Phys. Chem. B, 2004, 108, 12301.

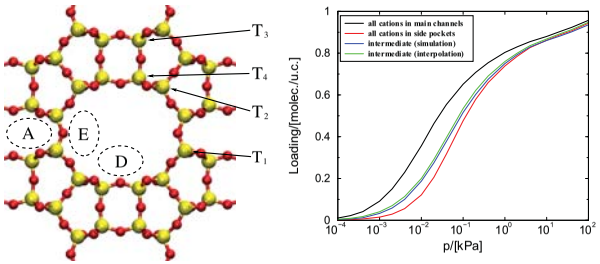
Zeolites with Non-Framework Cations



Calero, Dubbeldam, Krishna, Smit, Vlugt, Denayer, Martens, Maesen,
J. Am. Chem. Soc., 2004, 126, 11377.

Location of Cations Important for MOR-type Zeolite

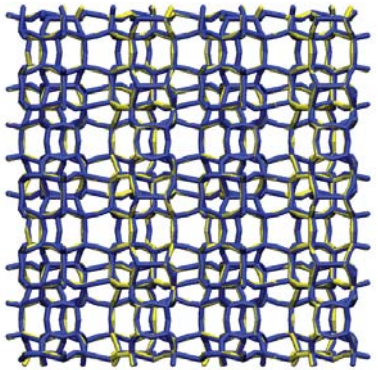
Butane in Na^+-MOR; cations located both in main channels and side pockets



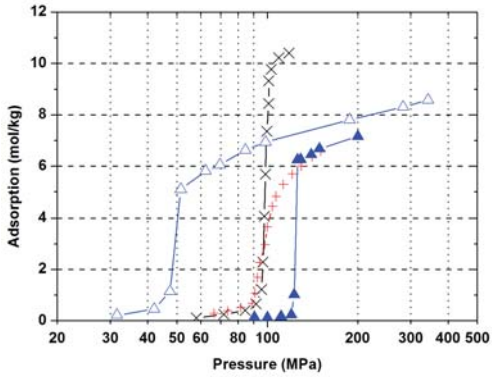
S. Ban, T.J.H. Vlugt
Journal of Chemical Theory and Computation, 2009, 5, 2858-2865.

Two Structures of MFI-type Zeolite

Van Koningsveld and Olson



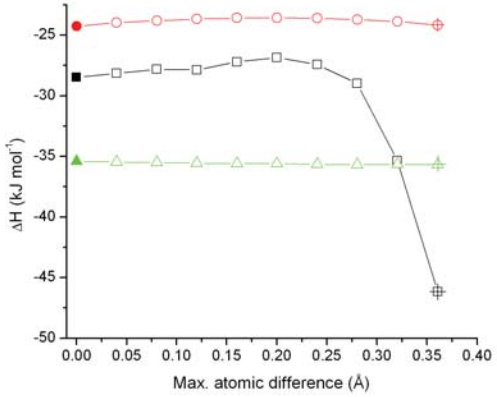
Adsorption of Water in Silicalite



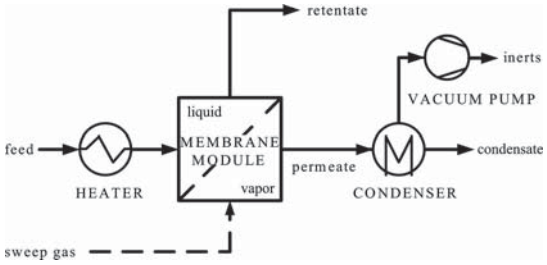
J.M. Castillo, D. Dubbeldam, T.J.H. Vlugt, B. Smit, S. Calero
Molecular Simulation, 2009, 35, 1067-1076.

Transforming van Koningsveld into Olson

Heat of adsorption for CO_2, water and propane



Separation of Water/Alcohol Mixtures (1)



J. Kuhn, J.M. Castillo, J. Gascon, S. Calero, D. Dubbeldam, T.J.H. Vlugt,
F. Kapteijn, J. Gross, J. Phys. Chem. C, 2009, 113, 14290-14301.

Experimental data from: J. Kuhn, K. Yajima, T. Tomita, J. Gross, F. Kapteijn
J. Membr. Sci., 2008, 321, 344-349.

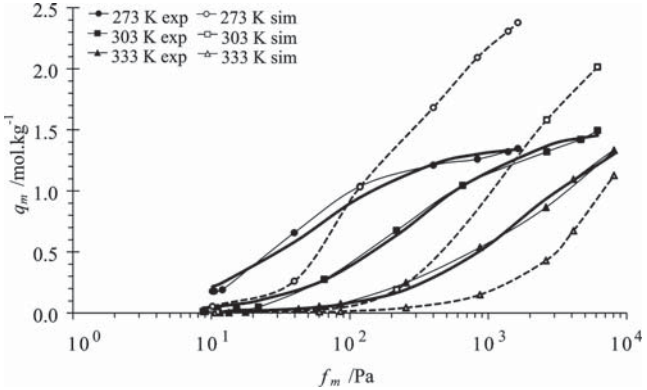
Separation of Water/Alcohol Mixtures (2)

- Hydrophobic, high silica DD3R membrane (NGK insulators, Japan)
- Experimentally: $\alpha_{w,e} = 1500$ and $\alpha_{w,m} = 9$
- Membrane flux follows from Maxwell-Stefan equations:

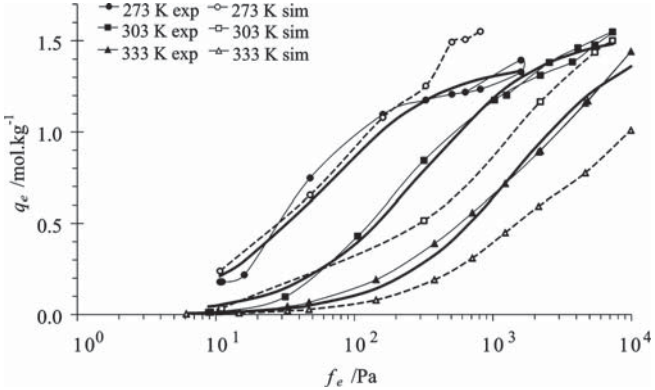
$$N_i \approx -\frac{\rho_z D_{iM}}{\delta}\left[\langle\Gamma_{ii}\rangle\,\Delta q_i + \langle\Gamma_{ij}\rangle\,\frac{q_i^{\mathrm{sat}}}{q_j^{\mathrm{sat}}}\Delta q_j\right]$$

- Quantitative force field for water/alcohols in all-silica zeolites?
- Separation mechanism?

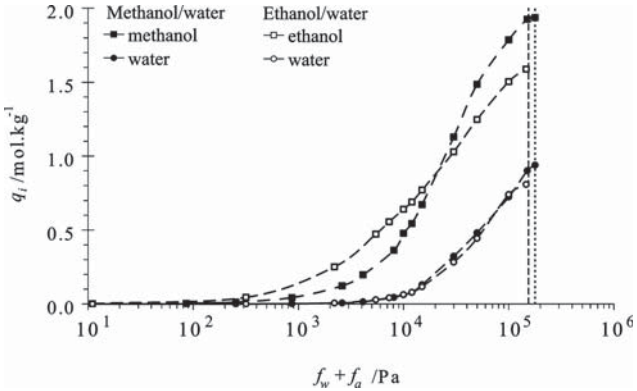
Adsorption Isotherms of Methanol on DDR-type Zeolite



Adsorption Isotherms of Ethanol on DDR-type Zeolite



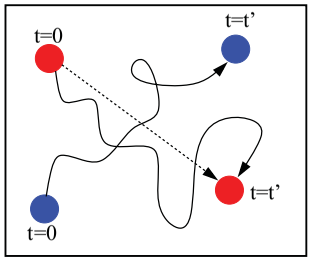
Mixture Adsorption Isotherms; $f_w/(f_w + f_a) = 0.2$



Intermezzo: Self Diffusion

Average mean-squared displacements of **individual** molecules

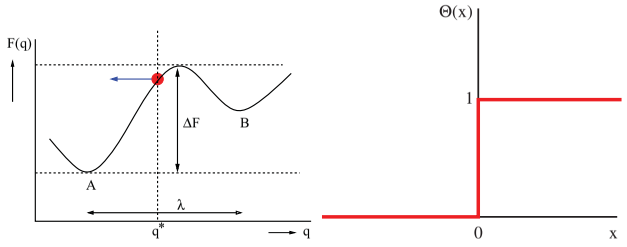
$$D_{\alpha,\mathrm{self}} = \frac{1}{2N}\lim_{t\to\infty}\frac{d}{dt}\left\langle\sum_{i=1}^{N}\left(r_{i\alpha}(t) - r_{i\alpha}(0)\right)^2\right\rangle$$



Dynamically Corrected Transition State Theory

MD does not work well when free energy barrier ΔF is large

$$k_{A\to B} = \underbrace{\frac{\langle\delta(q^* - q)\rangle}{\langle\theta(q^* - q)\rangle}}_{P_{\in A}(q^*)} \times \underbrace{\frac{\langle\dot{q}(0)\delta(q^* - q(0))\,\theta(q(t) - q^*)\rangle}{\langle\delta(q^* - q(0))\rangle}}_{R(t)}$$



Permeation of Pure Components: Water/Alcohols

T [K]	q_i^{feed} [mol·kg^{-1}]	q_i^{perm} [mol·kg^{-1}]	D_i^s [m^2·s^{-1}]
Water			
348	0.87	0.004	$3.61 \pm 0.01 \times 10^{-10}$
360	0.97	0.003	$6.10 \pm 0.04 \times 10^{-10}$
373	1.11	0.002	$5.89 \pm 0.04 \times 10^{-10}$
Methanol			
348	2.46	0.09	$3.36 \pm 0.01 \times 10^{-11}$
360	2.39	0.05	$3.55 \pm 0.01 \times 10^{-11}$
373	2.36	0.03	$4.80 \pm 0.02 \times 10^{-11}$
Ethanol			
348	1.49	0.23	$< 3 \times 10^{-14}$ *
360	1.42	0.15	$< 3 \times 10^{-14}$ *
373	1.39	0.10	$< 3 \times 10^{-14}$ *

* Free energy barrier for diffusion $\Delta F \approx 17\ k_B T$

Permeation of Water/Methanol and Water/Ethanol Mixtures

component	N_i^{exp} [mol·m^{-2}·s^{-1}]	N_i^{pred} [mol·m^{-2}·s^{-1}]	$y_i^{\text{perm,exp}}$ [-]	$y_i^{\text{perm,pred}}$ [-]
methanol/water				
water	0.023	0.40	0.63	0.69
methanol	0.013	0.19	0.37	0.31
methanol/water				
water	0.015	0.25	0.996	0.998
ethanol	0.59×10^{-4}	4.9×10^{-4}	0.004	0.002

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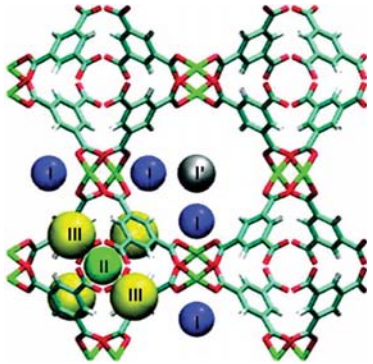
Metal Organic Framework Cu-BTC (HKUST-1)

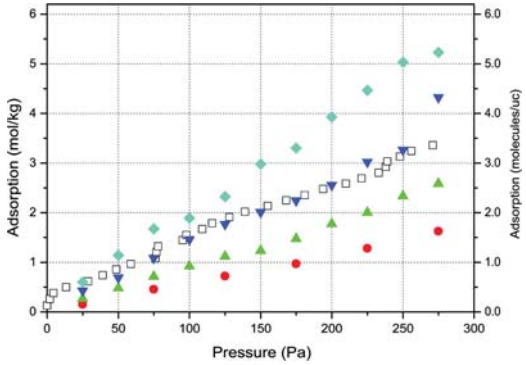
Cu metal center, Benzene Tricarbolylate linker molecules



J.M. Castillo, T.J.H. Vlugt, S. Calero, J. Phys. Chem. C, 2008, 112, 15934-15939.

Adsorption of Water in Cu-BTC

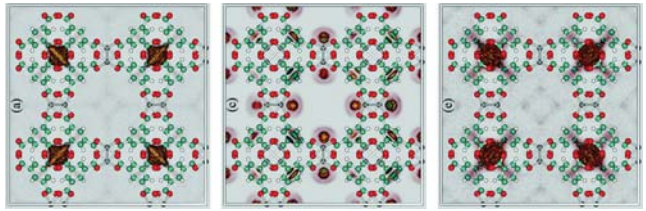
high sensitivity to values of framework charges (differences of 2%)



J.M. Castillo, T.J.H. Vlugt, S. Calero, J. Phys. Chem. C, 2008, 112, 15934-15939.

Adsorption Sites of Methane, Water, CO_2 in Cu-BTC

methane water CO_2



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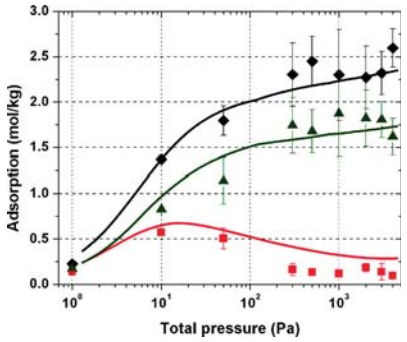
Separation of Xylene Isomers in MIL-47 (1)

adsorption: ortho > para > meta



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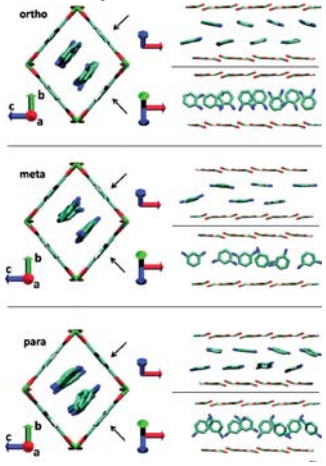
Separation of Xylene Isomers in MIL-47 (2)



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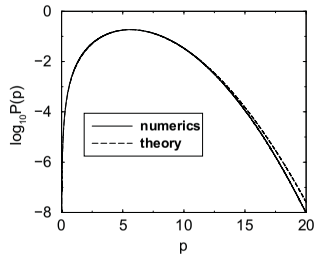
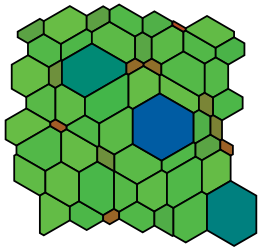
- J. Kuhn (TU Delft)
- J. Gross (TU Delft)
- F. Kapteijn (TU Delft)

Local Pressure Statistics in Static Granular Matter





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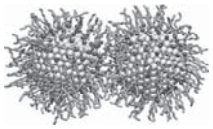
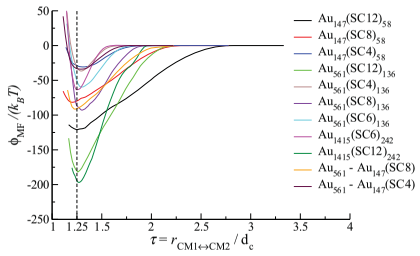
Self-Assembly of Nanocrystals





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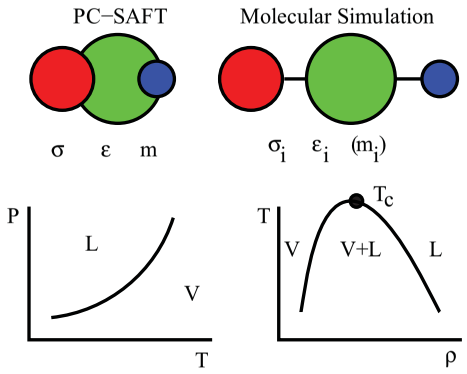
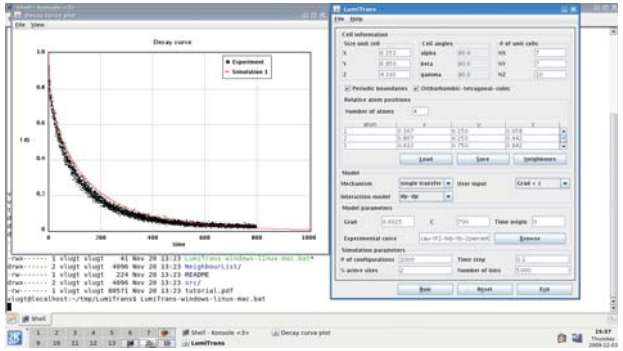
Better Force Field Fitting for VLE Computations



Prof. Joachim Gross and Thijs van Westen

Modeling of Luminescence Decay Curves for Downconversion



Prof. Andries Meijerink (Utrecht University) and J.M. Castillo Sanchez

Questions?