CORRELATING MOLECULAR MODELLING AND EXPERIMENTAL DIFFUSIVITIES IN ZEOLITES

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OUTLINE

1. Introduction.
2. Models and Methods.
3. Self-diffusion of methane – *n*-butane mixtures in silicalite-1.
4. Transport diffusivity of N_2 and CO_2 in silicalite-1.
5. *n*-alkanes in silicalite-1: Chain length dependence of self-diffusivity and activation energy.
6. Computer reconstruction of beds of zeolite crystals and simulation of long-range diffusion therein.

6. Summary

ZEOLITES

STRUCTURE

- framework geometry
- framework charge distribution
- size, shape, flexibility, and charge distribution of sorbed molecules

MATERIAL PROPERTIES

Sorption thermodynamics

- Henry's law constants
- Sorption isotherms

Intracrystalline transport

- Self-diffusivities
- Transport diffusivities

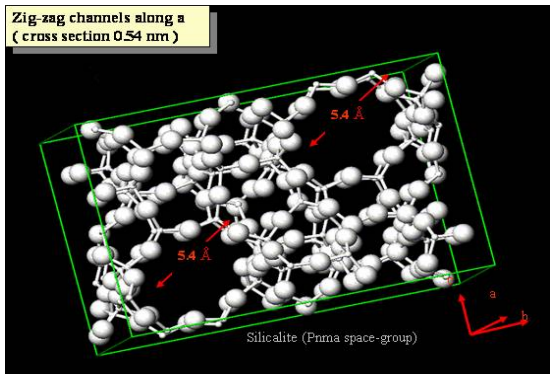
MICROSCOPIC ASPECTS

- Siting of sorbate molecules
- Conformational changes upon sorption
- Modes and characteristic times of sorbate motion

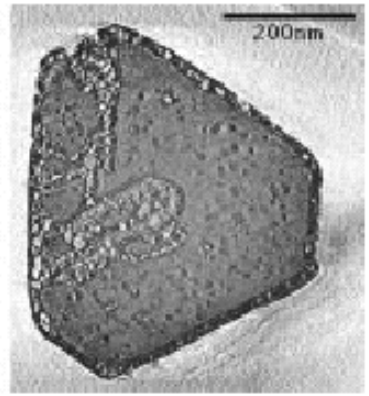
PERFORMANCE

Selectivity and rates in sorption separation and catalytic applications

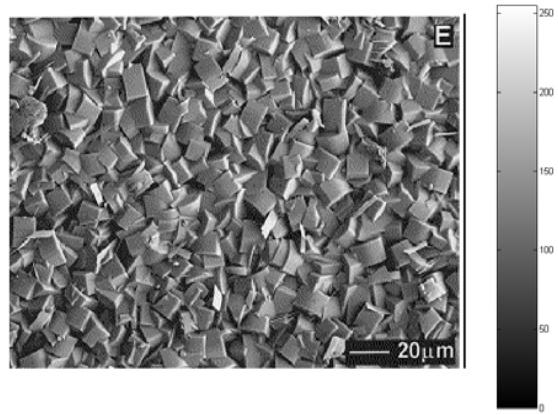
STRUCTURE AND TRANSPORT IN ZEOLITE MATERIALS MAY BE GOVERNED BY WIDE RANGE OF LENGTH SCALES



0.1 - 10 nm:
Configurational diffusion in zeolite nanopores



10 nm – 1 μm:
Defects, pore blocking in zeolite crystals



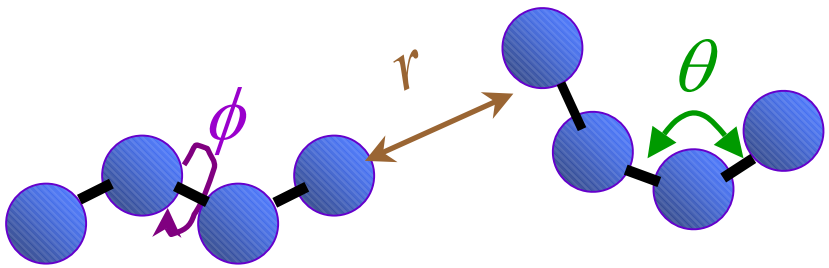
1 μm – 1 m: Molecular, Knudsen, surface diffusion in particles and beds

Prediction of performance in applications requires hierarchical modelling approaches that can address a wide range of length and time scales.

MOLECULAR MODELLING

Sorbates: Use "molecular mechanics" force fields that give good predictions for fluid-phase properties

"united atom" representation for alkanes:



Bond angle bending:

$$V_\theta(\theta) = \frac{1}{2} k_\theta (\theta - \theta_o)^2$$

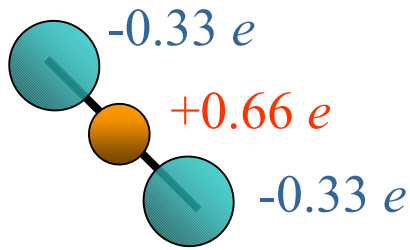
Lennard-Jones (dispersion attraction and excluded volume interactions):

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

Dihedral angle torsion:

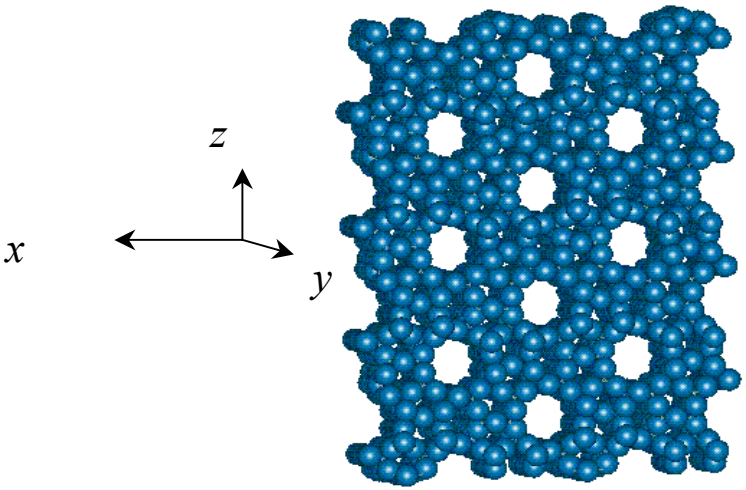
$$V_\phi(\phi) = \sum_{k=0}^{5} c_k \cos^k(\phi)$$

Polar molecules (e.g., CO_2):



In addition, Coulomb interactions between partial charges: $V_C(r) = \dfrac{z_i z_j e^2}{4\pi\varepsilon_o r}$

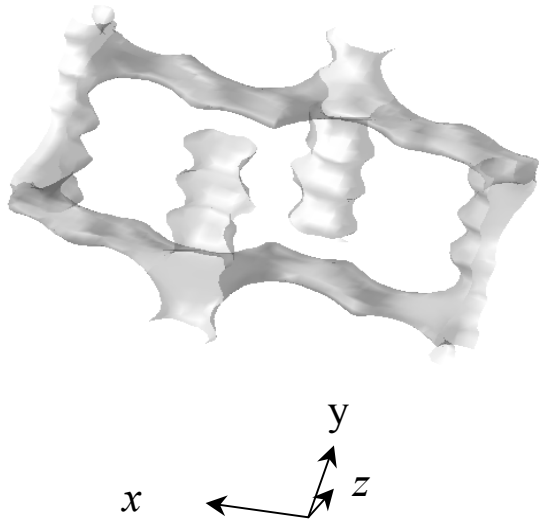
MOLECULAR MODELS



Silicalite-1
$Si_{96}O_{192}$

Pnma
a = 20.07 Å
b = 19.91 Å
c = 13.42 Å

(2 × 2 × 4
unit cells shown)



Zeolites: Represented as sets of framework atoms and counterions at their crystallographically known positions.

Lennard-Jones and Coulomb interactions with sites on sorbate molecules. Partial charges on framework from DFT calculations.

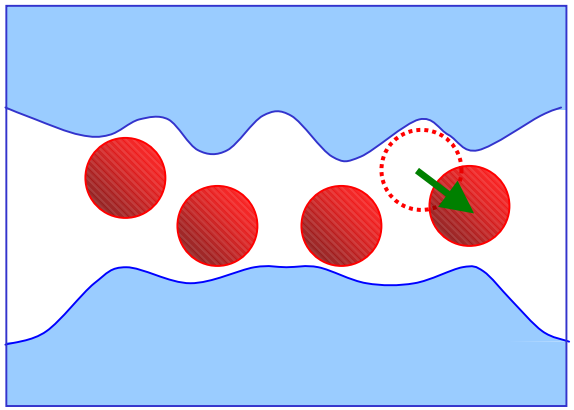
Rigid framework model allows pretabulation of the zeolite field experienced by sorbate sites: 100 fold savings in CPU time.

PREDICTION OF SORPTION ISOTHERMS

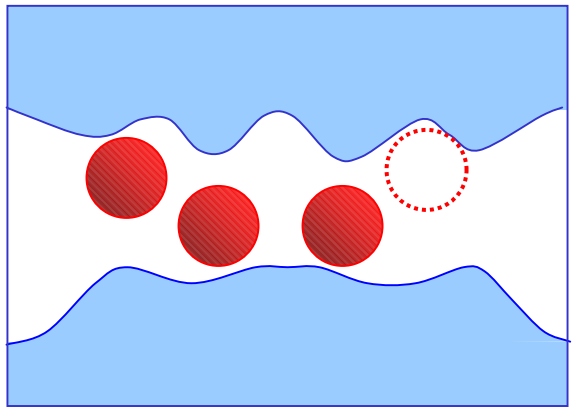
Grand Canonical Monte Carlo (GCMC) Simulation:

Sorbate-zeolite system simulated under constant V_s, T, f ← Sorbate fugacity

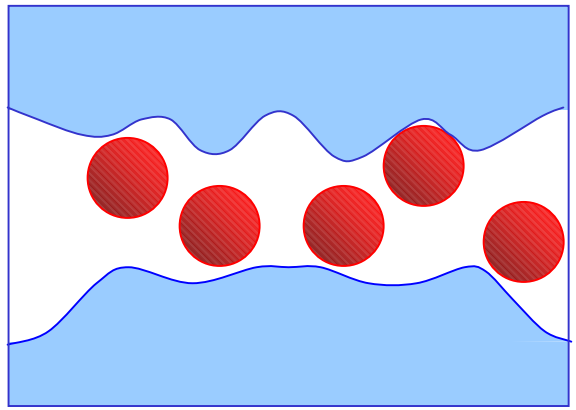
Elementary moves attempted:



Sorbate molecule displacement



Sorbate molecule removal



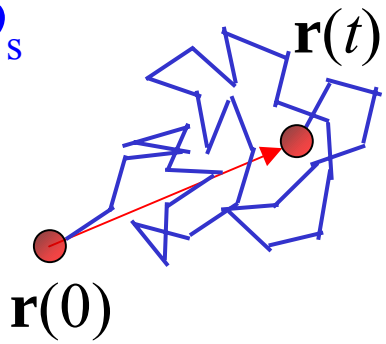
Sorbate molecule addition

Move acceptance criteria designed so that the sequence of configurations generated samples the equilibrium probability distribution of the grand canonical ensemble at prescribed V_s, T, f.

$\langle N \rangle = f(V_s, T, f)$ → Equilibrium adsorption isotherm at T

PREDICTION OF DIFFUSIVITY:
Molecular Dynamics (MD) Simulations

Self-Diffusivity D_s



$$D_s = \lim_{t\to\infty} \frac{<[\mathbf{r}(t)-\mathbf{r}(0)]^2>}{6t}$$

(Einstein, 1905)

Transport Diffusivity D_t

$$\mathbf{J} = -D_t \nabla c$$

flux, mol m^{-2} s^{-1}

concentration, mol m^{-3} crystal

Corrected Diffusivity D_o

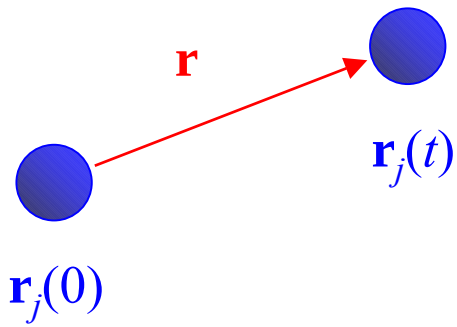
L.S.Darken, *Trans. AIME* **1948**, *174*, 184

sorbate fugacity

$$D_t = D_o \left.\frac{\partial \ln f}{\partial \ln c}\right|_T$$

$$\lim_{c\to 0} D_s(c) = \lim_{c\to 0} D_t(c) = \lim_{c\to 0} D_o(c)$$

INCOHERENT QENS SPECTRA FROM MD



Self-part of the van Hove correlation function:

$$G_s(\mathbf{r},t) = \frac{1}{N}\left\langle \sum_{j=1}^{N} \delta\left[\mathbf{r} + \mathbf{r}_j(0) - \mathbf{r}_j(t)\right]\right\rangle$$

Hydrodynamic limit
(isotropic self-diffusion over large r, t):

$$G_s(r,t) = \frac{1}{(4\pi D_s t)^{3/2}} \exp\left[-\frac{r^2}{4D_s t}\right]$$

Gaussian in r

Self-part of the intermediate scattering function:

$$I_s(\mathbf{Q},t) = \int G_s(\mathbf{r},t)\, \exp(i\mathbf{Q}\cdot\mathbf{r})\, \mathrm{d}^3 r$$

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

Gaussian in Q, exponential in t

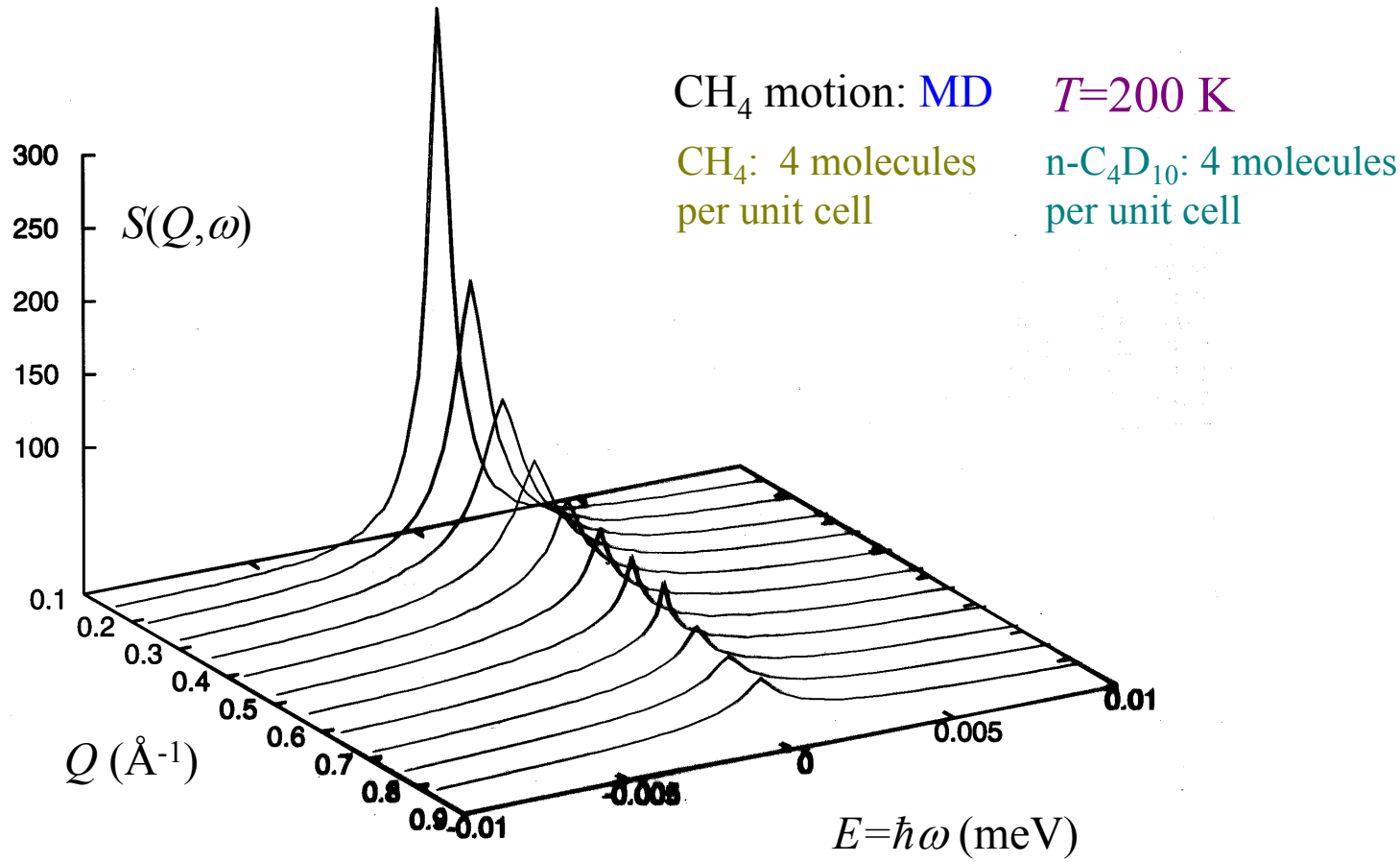
Incoherent scattering function:

$$S_s(\mathbf{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} I_s(\mathbf{Q},t)\, \exp(-i\omega t)\, \mathrm{d}t$$

$$S_s(\mathbf{Q},\omega) = \frac{1}{\pi}\frac{D_s Q^2}{\omega^2 + \left(D_s Q^2\right)^2}$$

Lorentzian in ω
HWHM=$D_s Q^2$

DIFFUSION OF METHANE – n-BUTANE MIXTURES IN SILICALITE



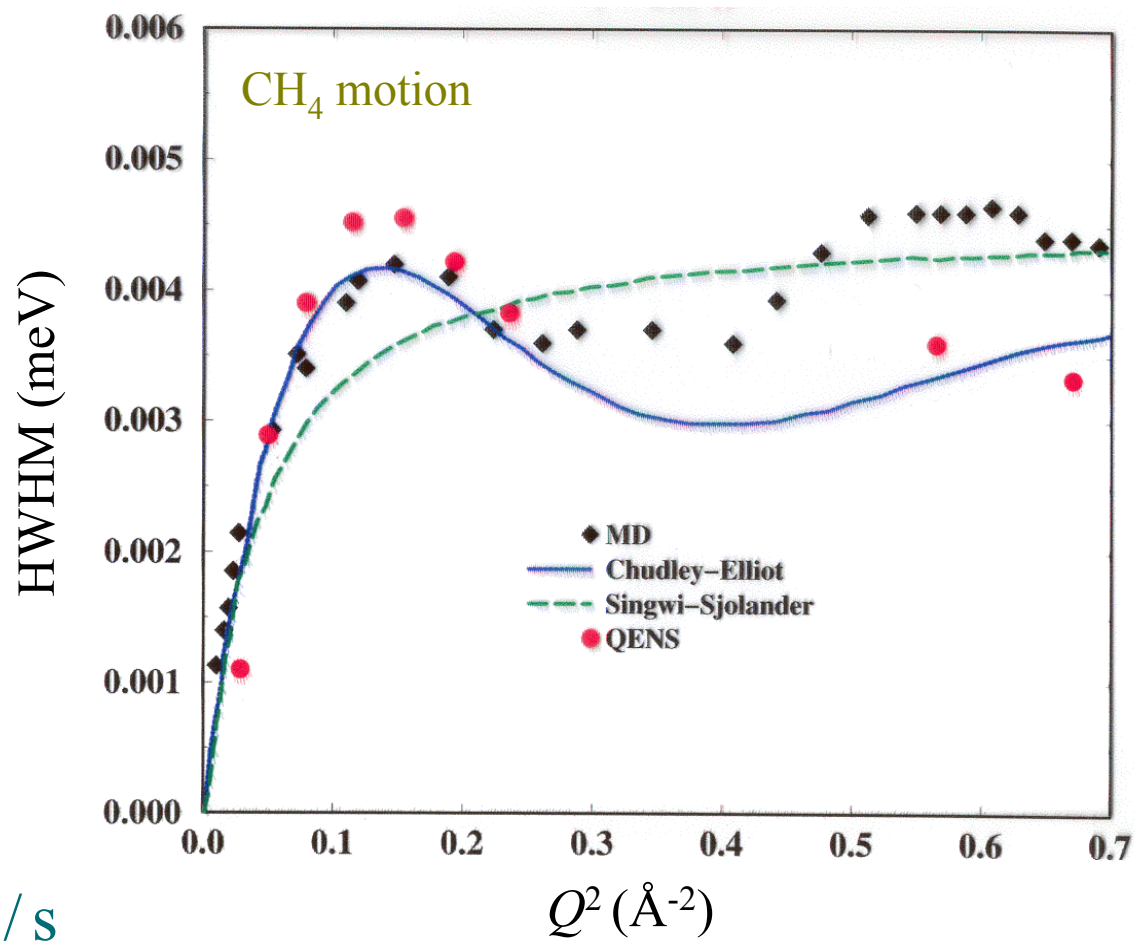
L.N. Gergidis and DNT *J. Phys. Chem.*, **103**, 3380-3390 (1999)
L.N. Gergidis, DNT, and H. Jobic *J. Phys. Chem.*, **104**, 5541-5552 (2000)

SCATTERING FUNCTION LINE SHAPE ANALYSIS: METHANE – n- BUTANE MIXTURES IN SILICALITE

T=200 K

CH_4: 2 molecules per unit cell

n-C_4D_{10}: 4 molecules per unit cell



MD:

$$D_{s,CH_4} = 1.8\times10^{-5}\,cm^2/s$$

$$D_{s,n\text{-}C_4D_{10}} = 4.1\times10^{-6}\,cm^2/s$$

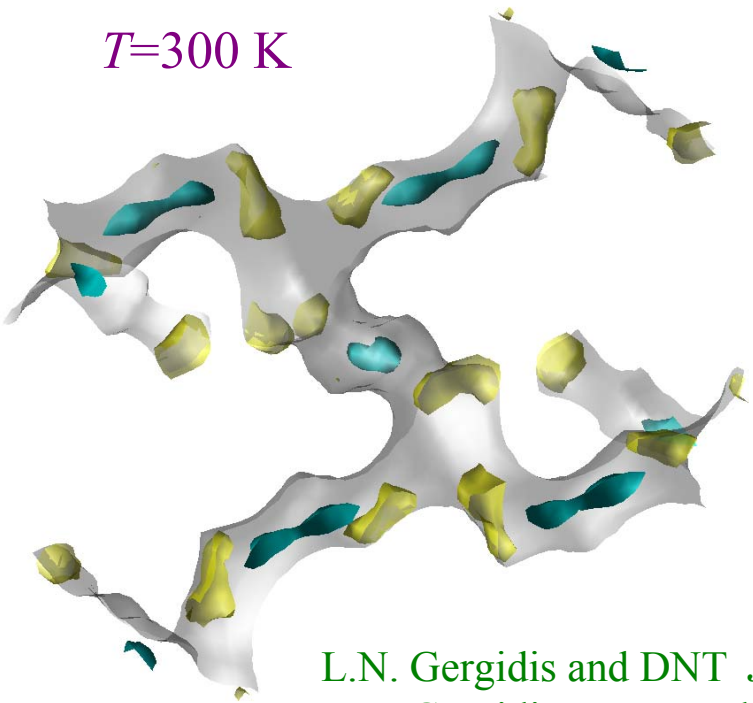
DIFFUSION OF METHANE – n-BUTANE MIXTURES IN SILICALITE

Distribution in the pores

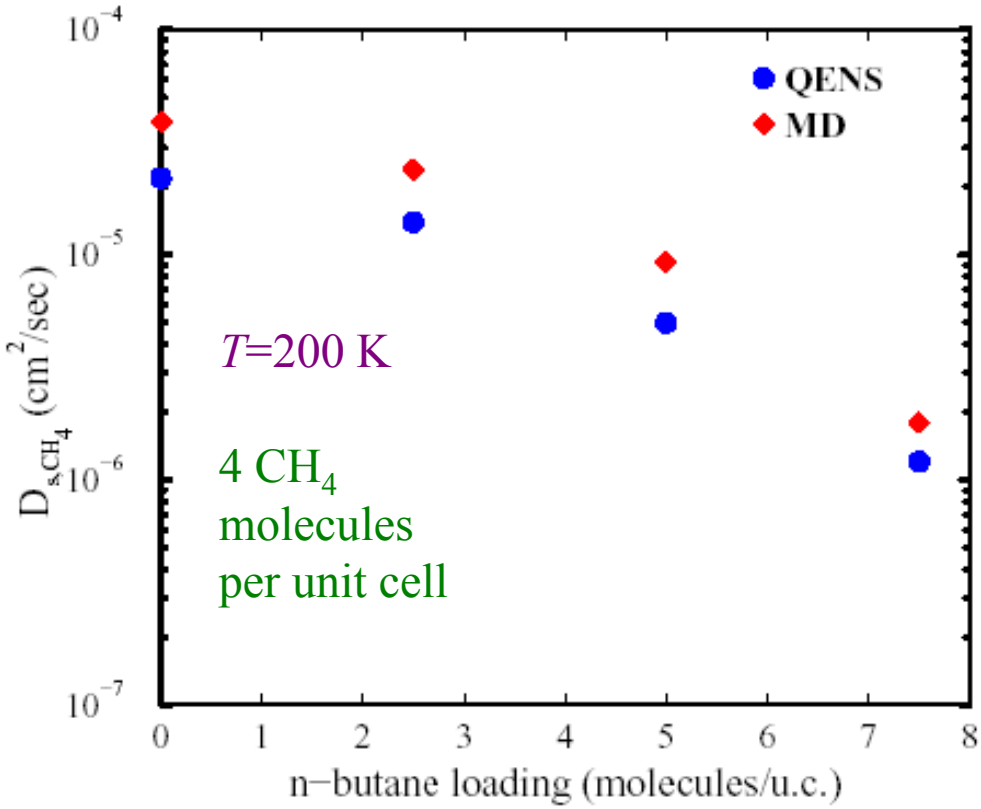
CH_4: 4 molecules per unit cell

n-C_4H_{10}: 9 molecules per unit cell

T=300 K



Methane self-diffusivity



L.N. Gergidis and DNT *J. Phys. Chem.*, **103**, 3380-3390 (1999)
L.N. Gergidis, DNT, and H. Jobic *J. Phys. Chem.*, **104**, 5541-5552 (2000)

D_t , D_o MEASUREMENT AND SIMULATION

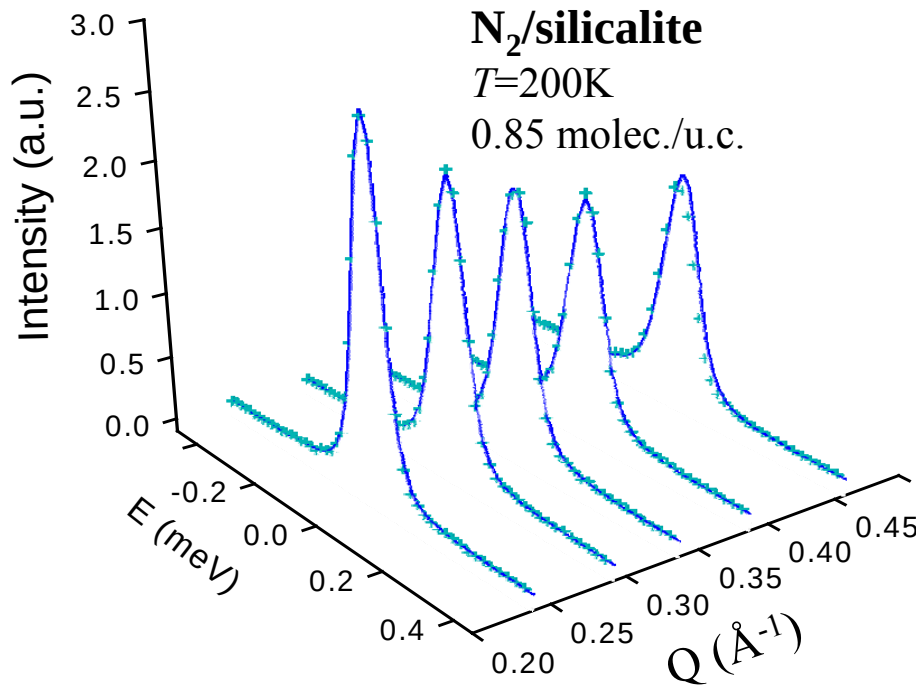
Coherent Quasielastic Neutron Scattering (QENS)

Dr. Hervé Jobic, Institut de Recherches sur la Catalyse, CNRS, Villeurbanne, France:
IN6 spectrometer, ILL, Grenoble

Coherent Scattering Function (isotropic motion) at low Q:

$$S_{\text{coh}}(\mathbf{Q},\omega) = \frac{S(Q)}{\pi}\frac{D_t Q^2}{\omega^2 + (D_t Q^2)^2}$$

D_t extracted from slope of HWHM wrt Q^2 at low Q.



Equilibrium MD Simulation, duration ≤ 10ns

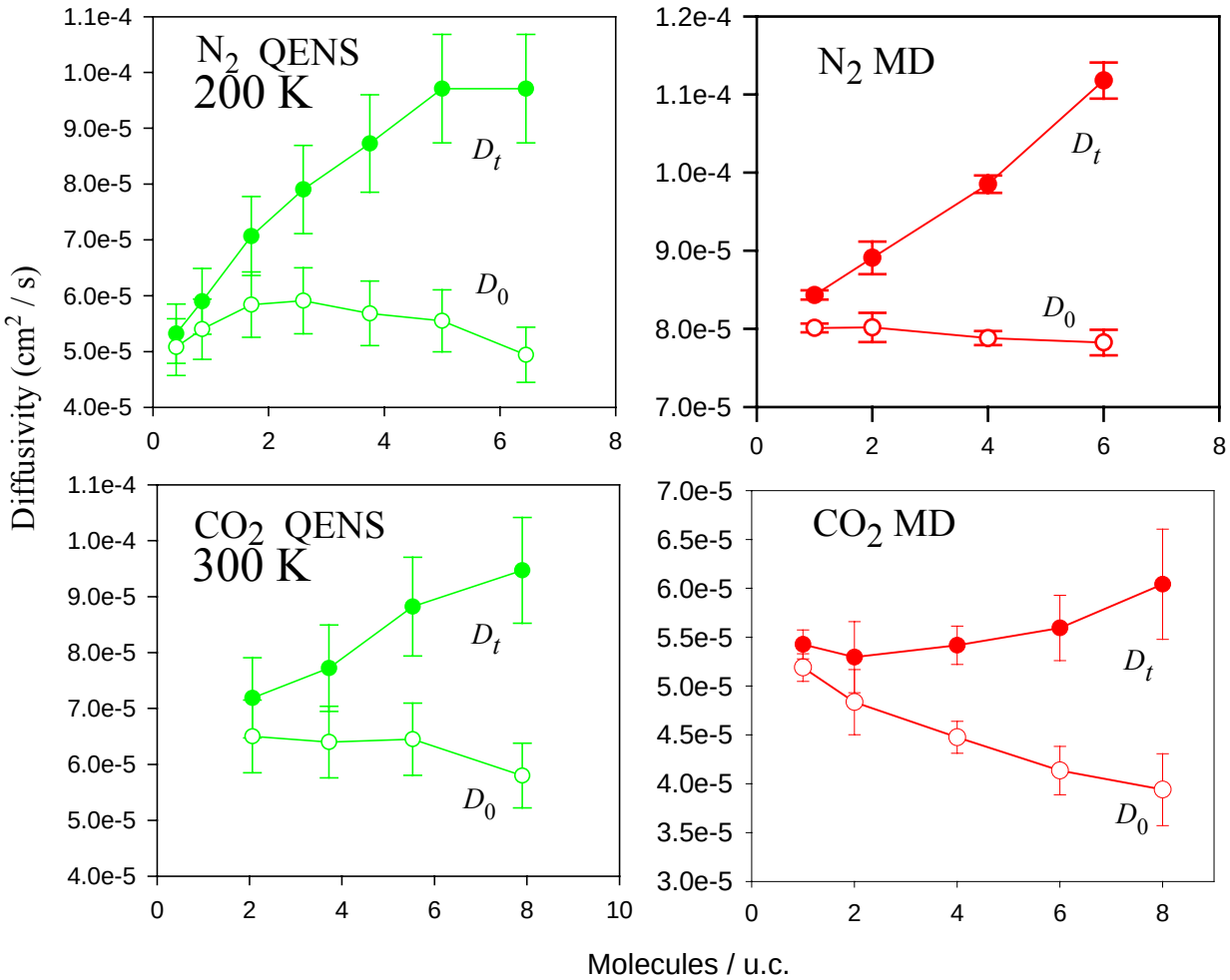
$$D_o = \frac{1}{3N}\int_0^\infty dt \sum_{i=1}^{N}\sum_{j=1}^{N} < \mathbf{v}_i(t)\cdot\mathbf{v}_j(0) > = \frac{d}{dt}\lim_{t\to\infty}\frac{N}{6}\left\langle\left[\mathbf{R}_{\text{cm}}(t) - \mathbf{R}_{\text{cm}}(0)\right]^2\right\rangle$$

Molecular velocities
Green-Kubo

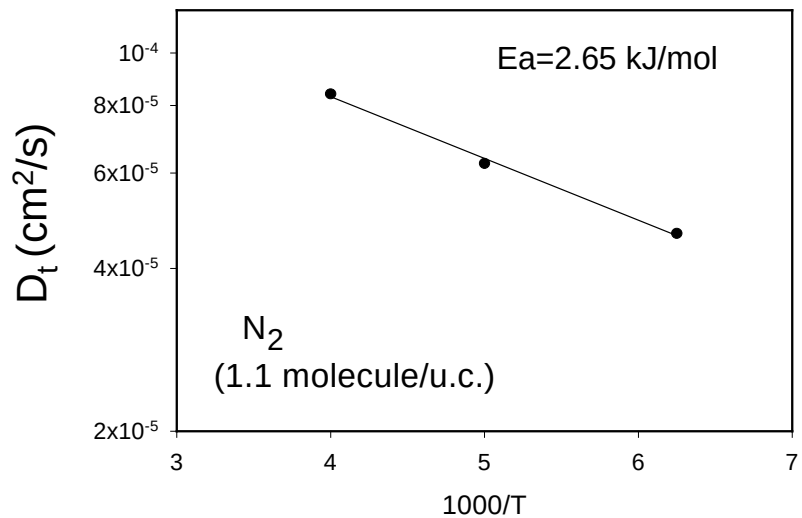
Center of mass of swarm of N molecules: Einstein

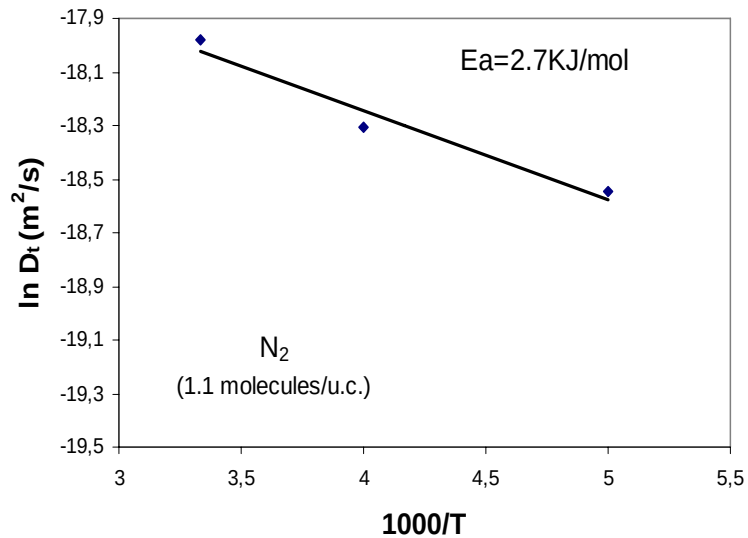
TRANSPORT DIFFUSIVITY OF N_2 AND CO_2 IN SILICALITE-1: COHERENT QENS MEASUREMENTS AND MD SIMULATIONS

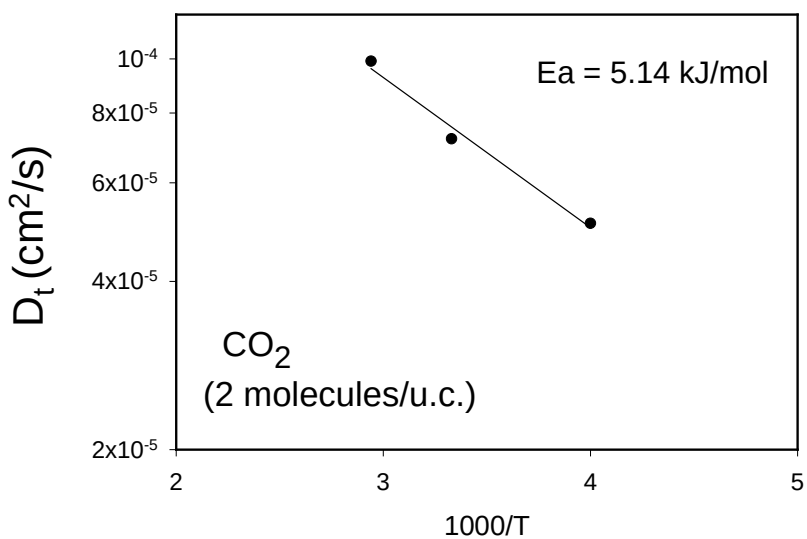
G. K. Papadopoulos, H. Jobic, DNT, *J. Phys. Chem. B*, **108**, 12748 (2004)

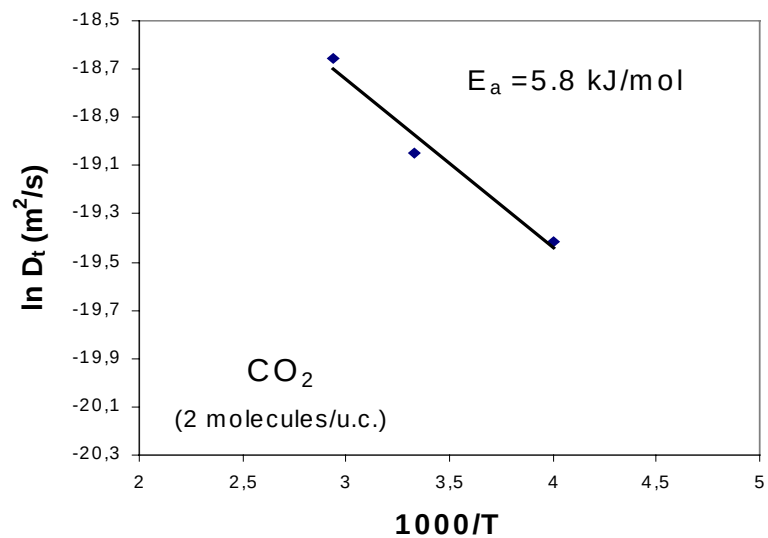


TRANSPORT OF N_2 AND CO_2 IN SILICALITE







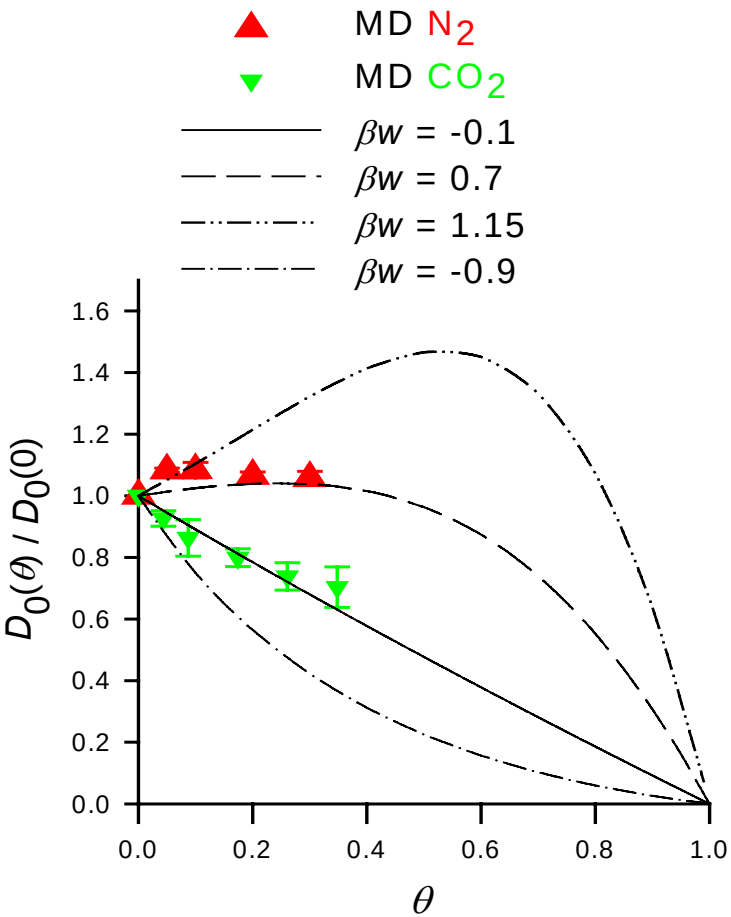


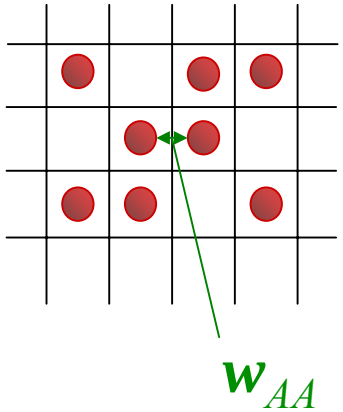
QENS experiment (H. Jobic)

MD (Athens)

ORIGIN OF DIFFERENT θ-DEPENDENCE OF D_0 OF N_2 AND CO_2 IN SILICALITE-1

D.A. Reed and G. Ehrlich, *Surface Sci.*, **102,** (1981) 588.





- **Regular lattice of sites**
- z **coordination number**
- w_{AA} **nearest-neighbor interactions**
- **Quasichemical approximation**

$$w = \frac{z w_{AA}}{2}$$

Molecular jumps with fixed attempt rate. Attempt to jump into an occupied site unsuccessful.

Decreasing trend of $D_0(\theta)$ for CO_2 explained in terms of stronger, attractive sorbate-sorbate interactions in that system.

G.K. Papadopoulos, H. Jobic, DNT, *J.Phys.Chem. B*, **108**, 12748 (2004).

RATIOS OF PURE GAS PERMEABILITIES THROUGH MFI MEMBRANES AT 300 K

Experiments: Supported Membrane Permeation

Y. Yan, M.E. Davis, G.R. Gavalas, *Ind. Eng. Chem. Res*. **34**, 1652 (1995).

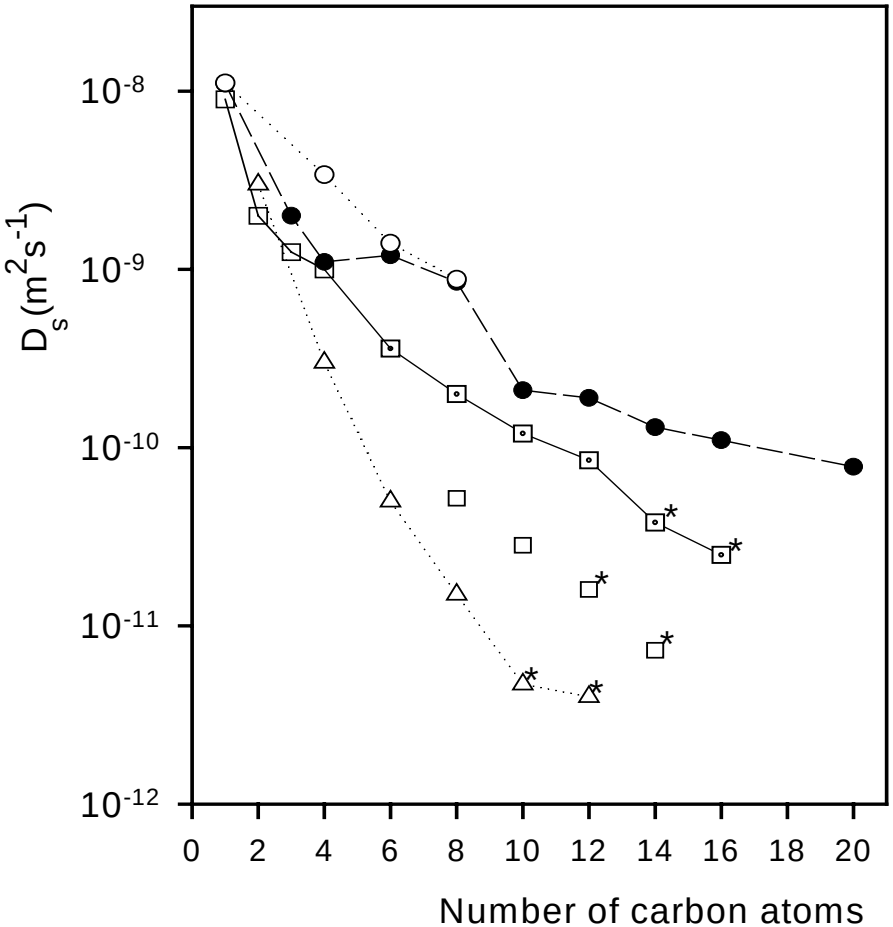
Simulations: Equilibrium NVE MD and GCMC

K. Makrodimitris, G.K. Papadopoulos, DNT, *J. Phys. Chem. B* **777**, 105 (2001).

Sorbates	Experiments	Simulations
CH_4/N_2	1.2	1.6
CO_2/CH_4	2.3	2.2
CO_2/N_2	2.8	3.4

SELF-DIFFUSIVITY OF *n*-ALKANES IN SILICALITE-1

T=300 K, low occupancy



(○) MD simulations [F. Leroy, B. Rousseau, and A.H. Fuchs, *Phys. Chem. Chem. Phys.* 6 (2004) 775]

(●) hierarchical simulations [E.J. Maginn, A.T. Bell, and DNT, *J.Phys.Chem.* 100 (1996) 7155]

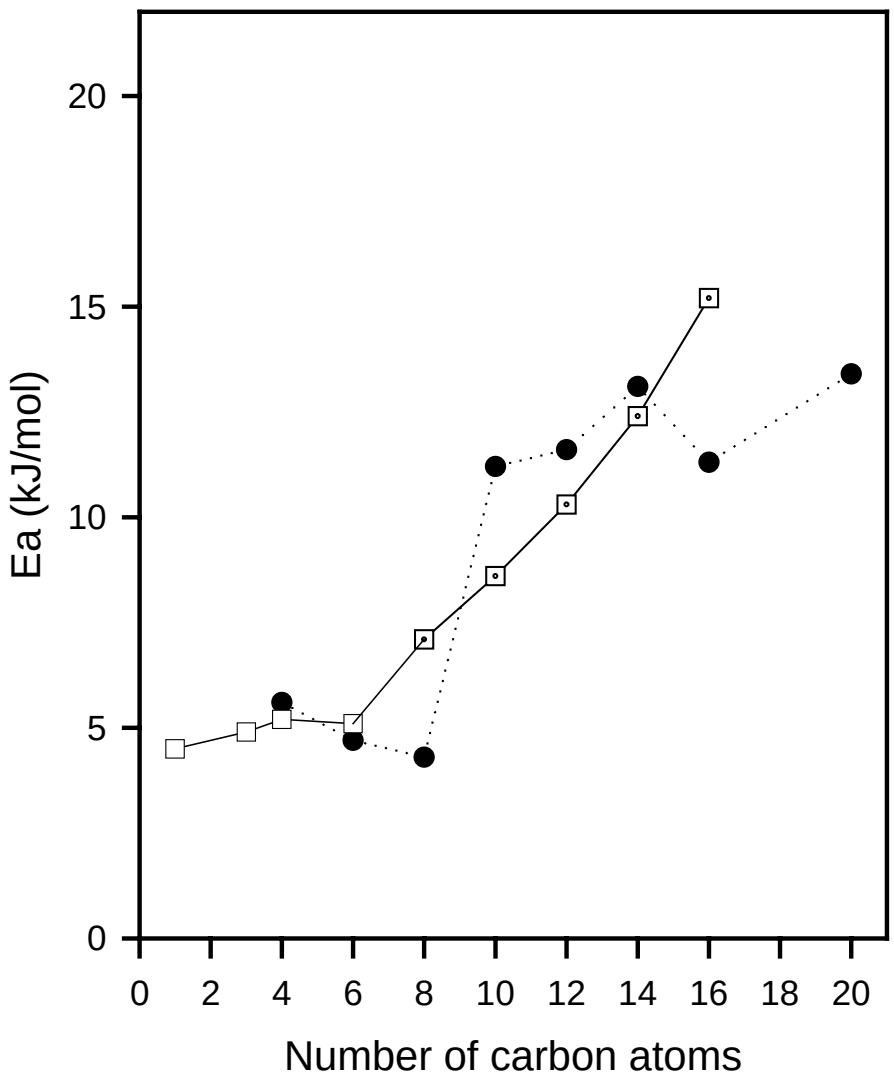
(□) QENS in Na-ZSM-5 [H. Jobic, *J. Mol. Catal. A-Chem.* 158 (2000) 135-142]

(□) QENS in silicalite-1 [H. Jobic and DNT, *J. Phys. Chem.* 110 (2006) 1964].

(Δ) PFG NMR [H. Jobic, W. Schmidt, C.B. Krause, and J. Kärger, J., *Micropor. Mesopor. Mater.* 90, 299(2006)].

Asterisked symbols: extrapolation to 300 K.

ACTIVATION ENERGY FOR SELF-DIFFUSION: ALKANES IN SILICALITE-1



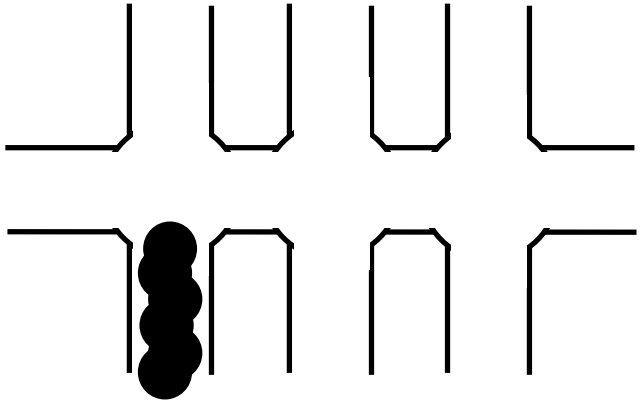
low occupancy

(●) hierarchical simulations [E.J. Maginn, A.T. Bell, and DNT, *J.Phys.Chem.* 100 (1996) 7155]

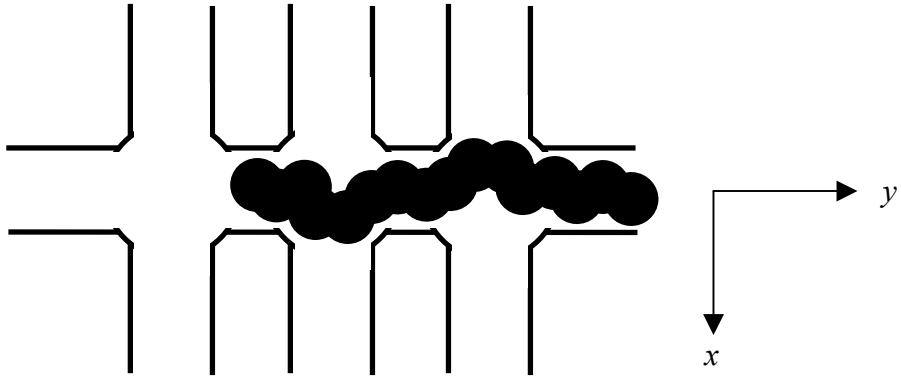
(□) QENS in ZSM-5 [H. Jobic, *J. Mol. Catal. A-Chem.* 158 (2000) 135-142]

(□) QENS in silicalite-1 [H. Jobic and DNT *J. Phys. Chem.* 110 (2006) 1964].

POSSIBLE EXPLANATION OF CHAIN LENGTH-DEPENDENCE OF E_a



n-hexane sorbed in a Z coarse-grained conformation in silicalite-1



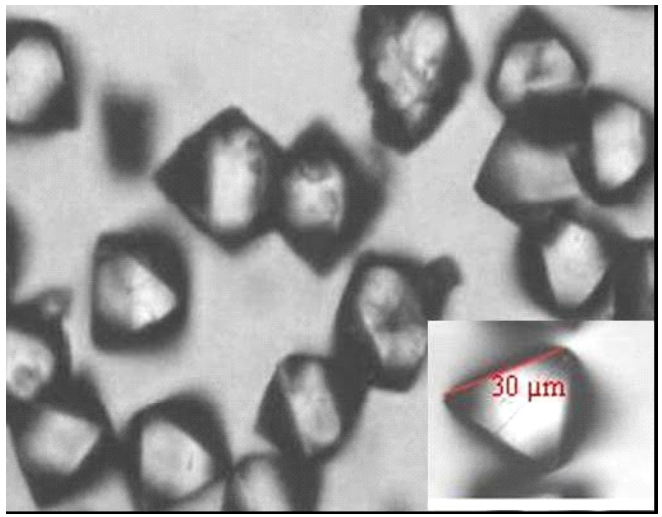
n-hexadecane sorbed in a SISIS coarse-grained conformation within silicalite-1

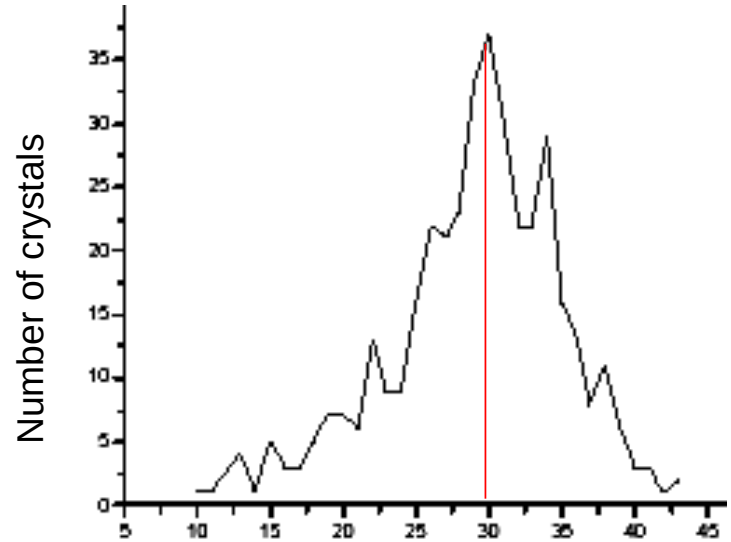
$n<8$: Jumps across more spacious, energetically less favorable intersection regions

$n>8$: Conformational rearrangement accompanies translation along S channels

PARTICLE-BASED COMPUTER RECONSTRUCTION

Experimental input





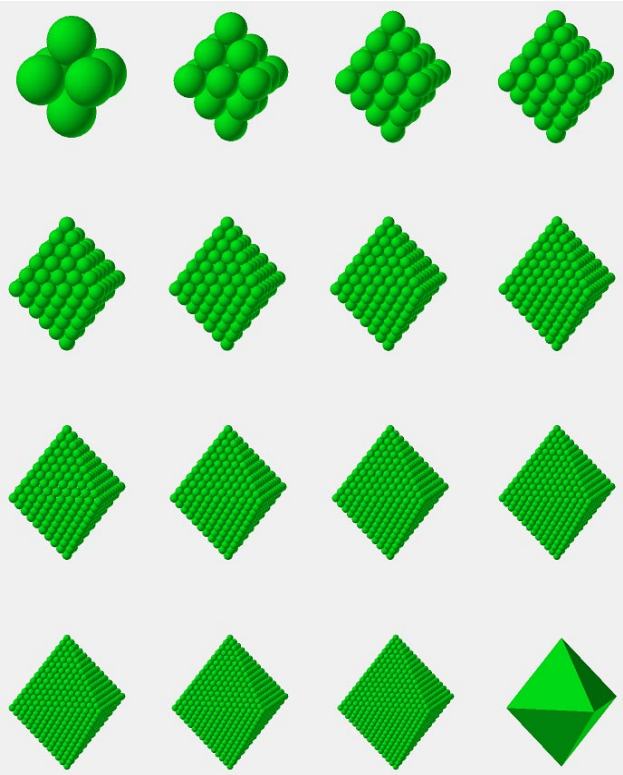
$\rho_{crystal}$ =1530 kg / m^3

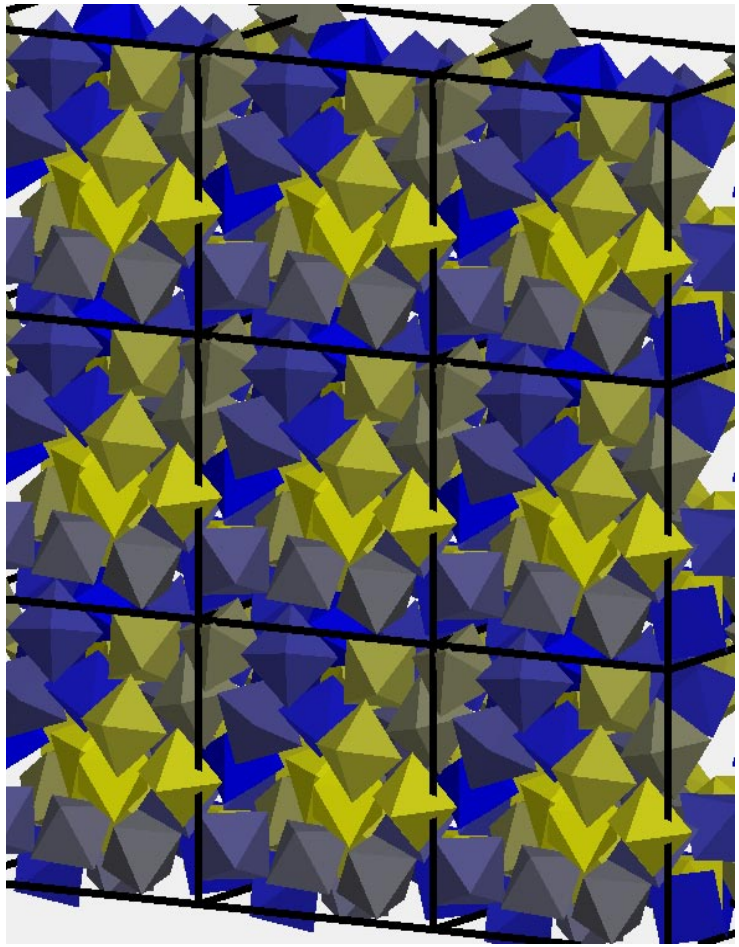
ρ_{bed} = 590 kg / m^3

Bed of NaX zeolite crystals: Dr. S.Vasenkov , Prof. Dr. J. Kärger, U. Leipzig

PARTICLE-BASED COMPUTER RECONSTRUCTION

Application: bed of NaX crystals





Sequence of energy minimizations at fixed porosity, using progressively higher generations for the representation of particles.

SIMULATION OF "LONG-RANGE" DIFFUSIONAL PROCESSES IN INTERCRYSTALLINE SPACE

Track long trajectories of individual sorbate molecules by kinetic MC simulation:

- Translational motion with constant speed $\bar{u}$
- Intermolecular collisions with mean free path λ
- Diffuse reflections upon collision with solid surfaces

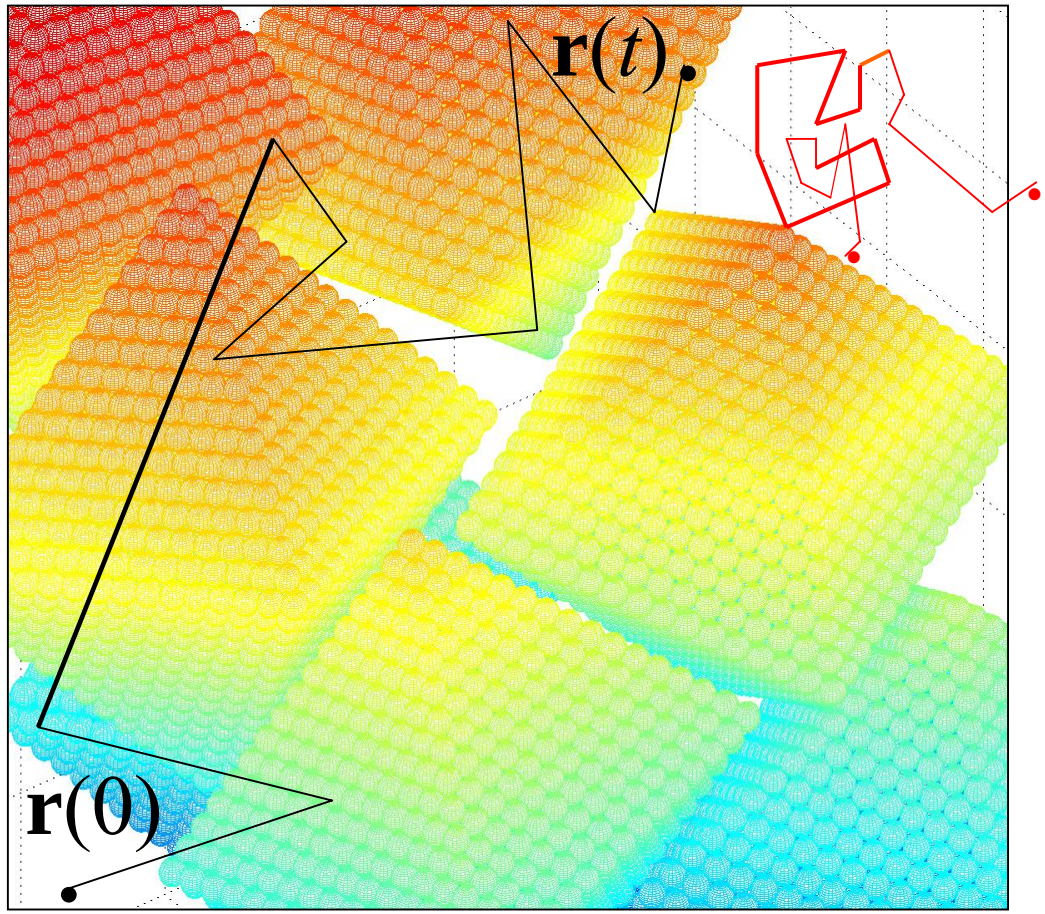
$$\lambda = \frac{k_B T}{\sqrt{2}\pi\sigma^2 P}$$

$$\bar{u} = \sqrt{\frac{8 k_B T}{\pi m}}$$

Effective Diffusivity:

$$D = \lim_{t\to\infty} \frac{\left\langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \right\rangle}{6t}$$

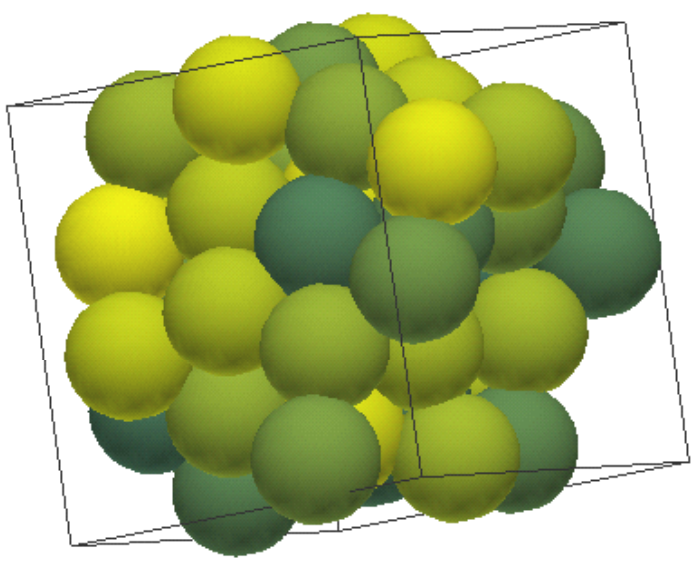
Measurements: O. Geier, S. Vasenkov, J. Kärger, *J. Chem. Phys.* **2002**, *117*, 1935-1938

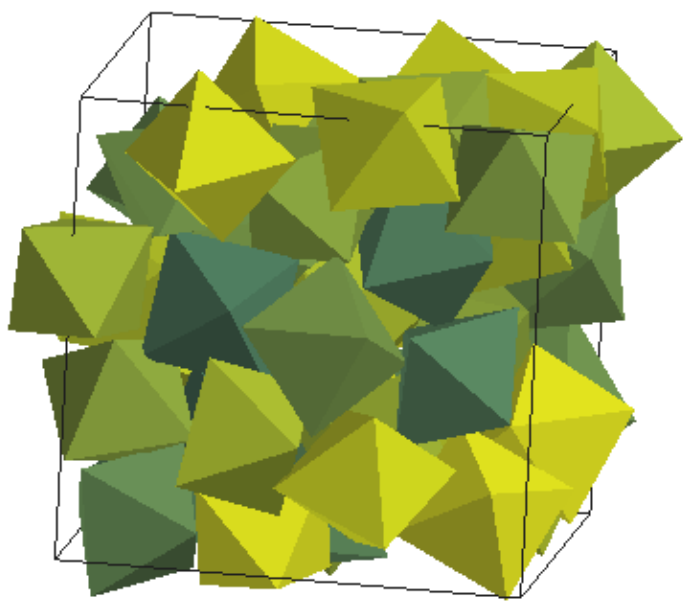


LONG-RANGE DIFFUSION IN CRYSTAL BEDS

Ethane in two model beds:

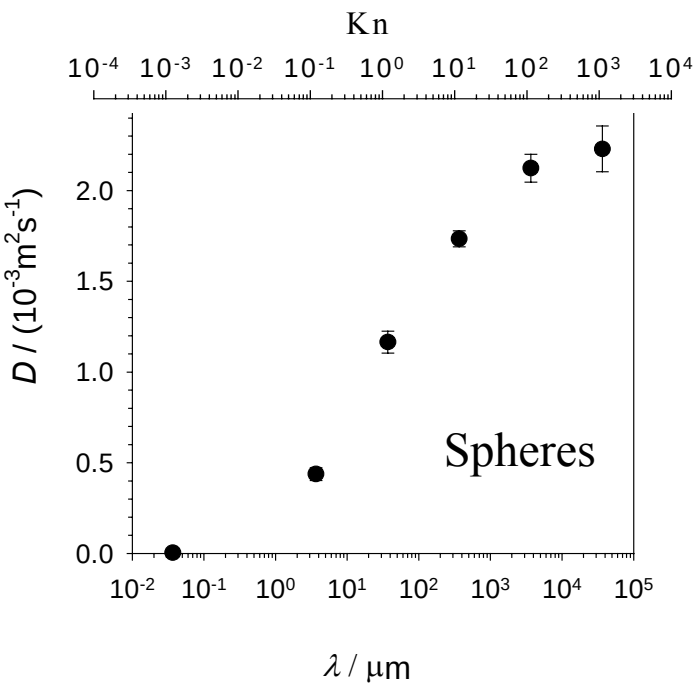
Crystal geometry	Simulation box length (μm)	Particle size (μm)	ϕ	Genera-tion
Spherical	116.740	28.969 (diameter)	0.60	0
Octahedral	116.740	29.996 (edge)	0.60	15

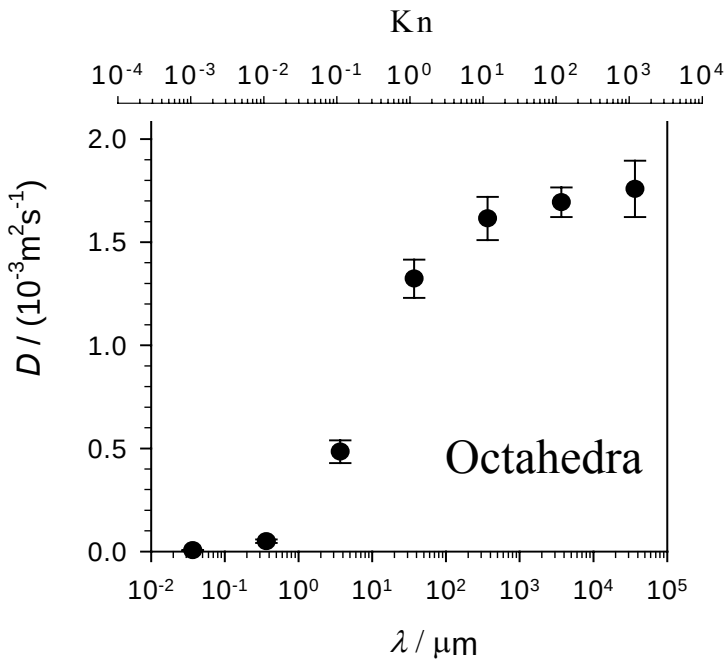




TRANSITION FROM MOLECULAR TO KNUDSEN DIFFUSION WITH INCREASING λ

Ethane in NaX bed, 295 K, $\phi = 0.60$





Molecular diffusion regime

$$D = D_b = \frac{D_{0b}\phi}{\eta_b}$$

η_b ← tortuosity factor

$$D_{0b} = \frac{1}{3}\bar{u}\lambda$$

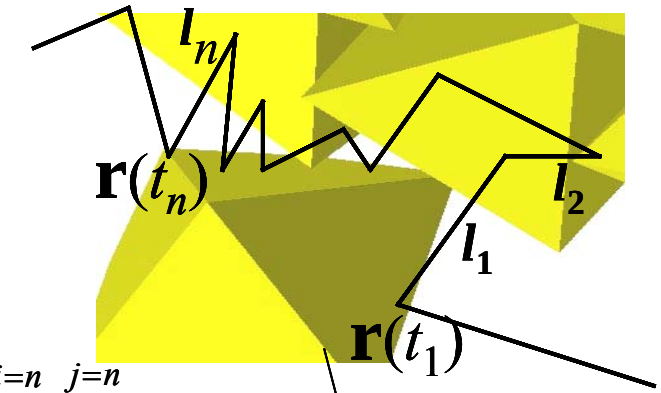
Knudsen regime

$$D = D_K = \frac{D_{0K}\phi}{\eta_K}$$

$$D_{0K} = \frac{1}{3}\bar{u}\, l_{ss}$$

l_{ss} ← **mean solid-to-solid path length**

DERJAGUIN CORRECTION TO THE KNUDSEN DIFFUSIVITY



$$D_{0K} = \frac{\langle \mathbf{r}^2 \rangle}{6t}$$

$$\langle \mathbf{r}^2 \rangle = \left\langle \sum_{i=1}^{i=n} l_i^2 + 2\sum_{i=1}^{i=n} \sum_{j=i+1}^{j=n} l_i l_j \cos\gamma_{ij} \right\rangle$$

Consecutive lengths not correlated
Lengths and orientations mutually independent

$$\langle \mathbf{r}^2 \rangle = n\langle l^2 \rangle + 2n\langle l \rangle^2 \sum_{k=1}^{\infty} \langle \cos\gamma_k \rangle$$

l_{SS}

$$D_{0K} = \frac{1}{3}\bar{u}\langle l \rangle \left[\frac{\langle l^2 \rangle}{2\langle l \rangle^2} - \beta \right]$$

$$\beta = -\sum_{k=1}^{\infty} \langle \cos\gamma_k \rangle$$

TORTUOSITY FACTORS FROM EXPERIMENT AND SIMULATION

ϕ	d_s (μm)	l_{ss} (μm)	η_K/η_b PFG NMR*	η_K/η_b simulation	β	$\frac{\langle l^2 \rangle}{2\langle l \rangle^2}$	η_K/η_b corrected
0.60 (sph)	26.51	26.35	-	1.55	0.309	0.935	0.97
0.60 (oct)	24.49	24.32	4.8-10	2.04	0.298	0.849	1.12

$$d_s = \frac{4V_{void}}{S}$$

l_{ss}=mean solid-to-solid path length

*O. Geier, S. Vasenkov, J. Kärger, *J. Chem. Phys.* **2002**, *117*, 1935-1938

CONCLUSIONS

- Molecular simulations are useful in elucidating mechanisms and predicting rates of diffusion in zeolitic materials.
- Molecular simulations aid in the interpretation of diffusion measurements.
- Broad spectra of length and time scales present in technologically important zeolitic materials necessitate the development of hierarchical modelling and simulation approaches.

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