MOLECULAR SIMULATIONS OF DIFFUSION IN ZEOLITES AND IN AMORPHOUS POLYMERS

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APPLICATIONS

Zeolites

- Adsorption separations
- Industrial catalytic processes
- Ion exchange
- Detergents
- Gas storage

Polymers

- Membrane separations
- Packaging materials
- Biomedical devices

Performance is governed by sorption and diffusion phenomena which depend on molecular-level structure and interactions.

MOLECULAR MODELS

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

"united atom" representation for alkanes:
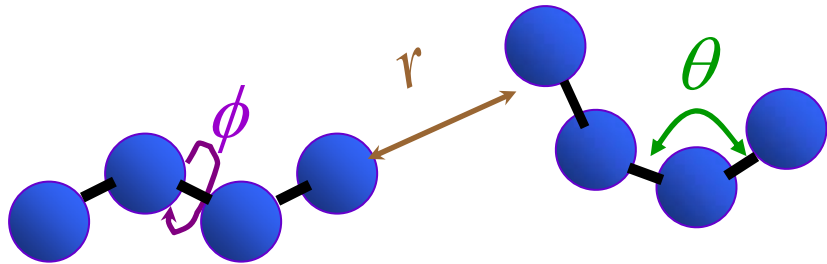
Lennard-Jones (dispersion attraction and excluded volume interactions):

$$\mathcal{V}_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$
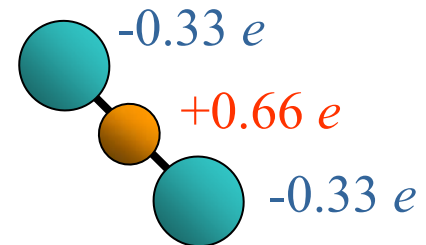
Polar molecules (e.g., CO_2):

In addition, Coulomb interactions between partial charges: $\mathcal{V}_C(r) = \dfrac{z_i z_j e^2}{4\pi\varepsilon_o r}$
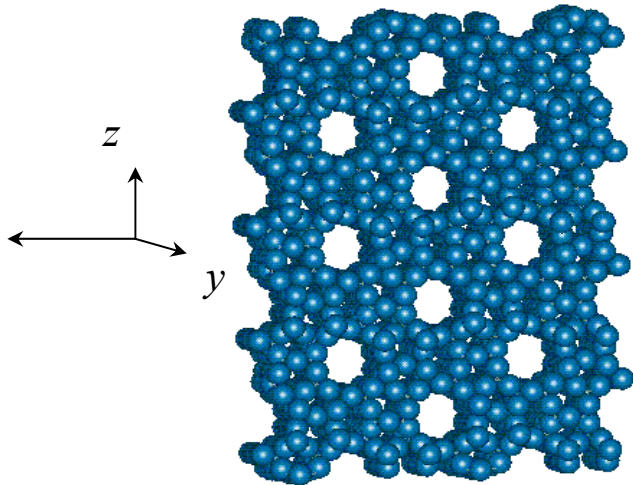
Bond angle bending:

$$\mathcal{V}_\theta(\theta) = \frac{1}{2}k_\theta(\theta - \theta_o)^2$$

Dihedral angle torsion:

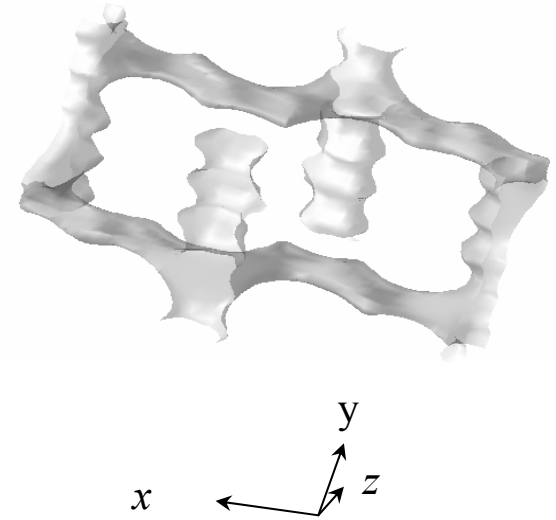$$\mathcal{V}_\phi(\phi) = \sum_{k=0}^{5} c_k \cos^k(\phi)$$

-0.33 e

+0.66 e

-0.33 e

MOLECULAR MODELS

Silicalite
$Si_{96}O_{192}$

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.

MOLECULAR MODELS

Amorphous Polymers: Represented by same types of force fields as small organic molecules.

C_{6000} polyethylene
24 polymer chains
192000 interaction sites
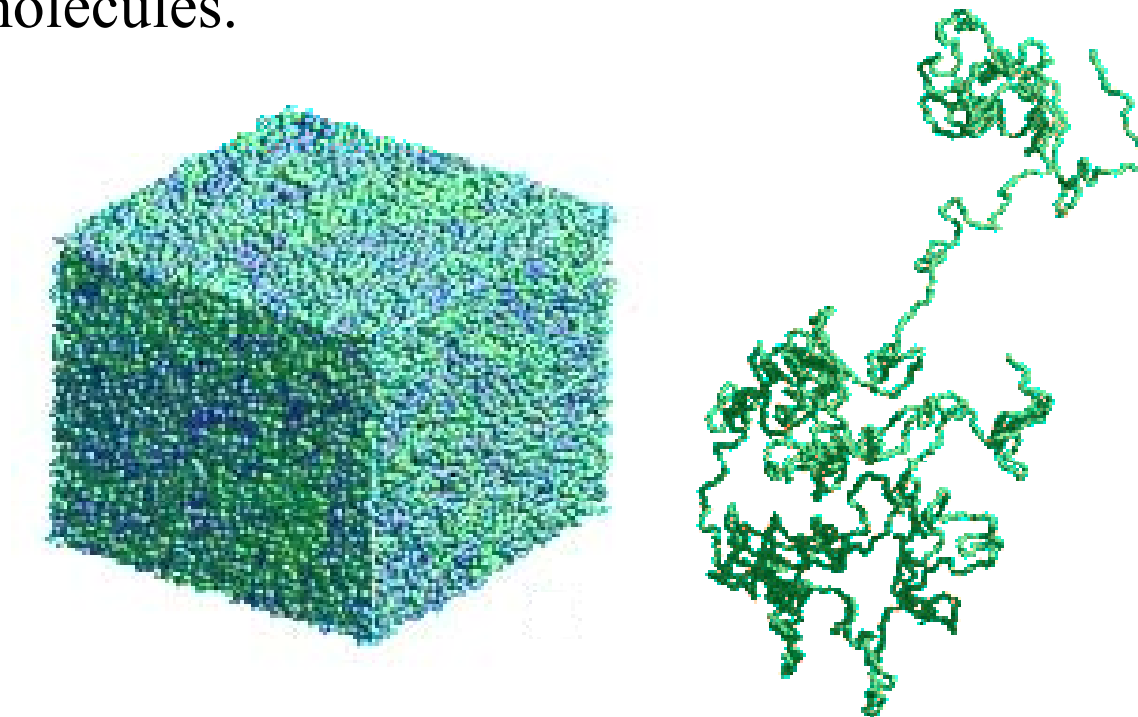
Thoroughly equilibrated using specially designed algorithms, e.g., connectivity-altering Monte Carlo
N. Karayiannis, V.G. Mavrantzas, DNT, *Phys. Rev. Lett.* **88**, 105503 (2002).

PVT behavior, packing, segmental dynamics, accessible volume distribution validated against experiments.
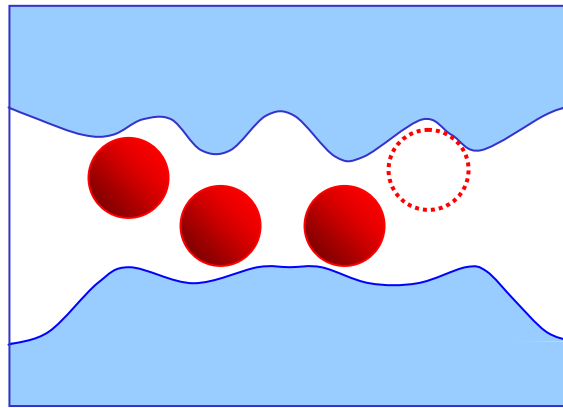
PREDICTION OF SORPTION ISOTHERMS

Grand Canonical Monte Carlo (GCMC) Simulation:

Sorbate fugacity

Sorbate-zeolite system simulated under constant V_s, T, f
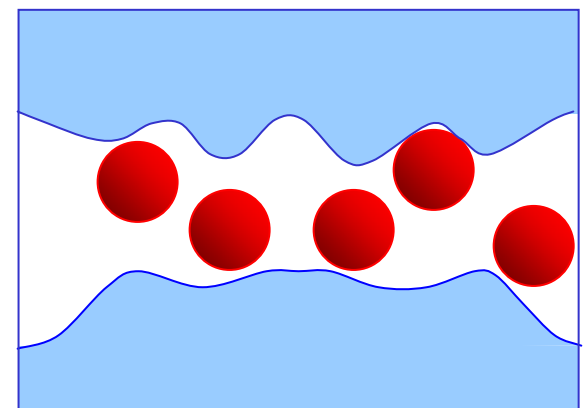
Elementary moves attempted:
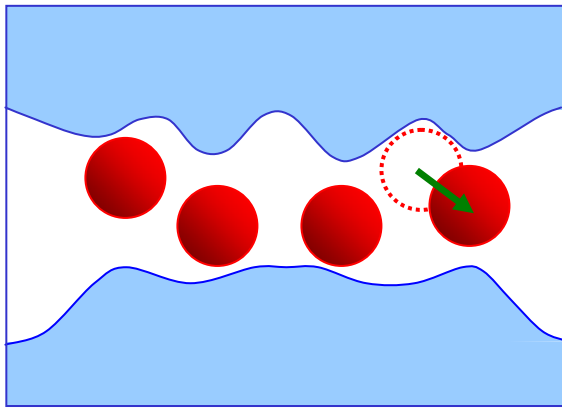
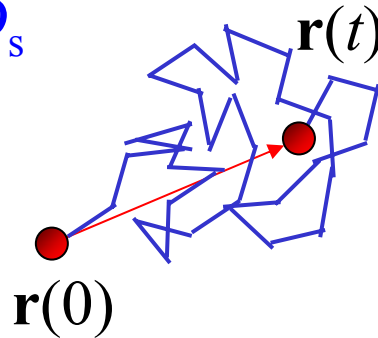displacement   removal   addition

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.

$$<N> = f(V_s, T, f) \rightarrow \text{Equilibrium adsorption isotherm at } T$$

PREDICTION OF DIFFUSIVITY:
Molecular Dynamics (MD) Simulations

Self-Diffusivity D_s

$\mathbf{r}(t)$

$\mathbf{r}(0)$

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

(Albert Einstein, 1905)

Transport Diffusivity D_t

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

(Adolf Fick, 1855)

flux, mol m⁻² s⁻¹
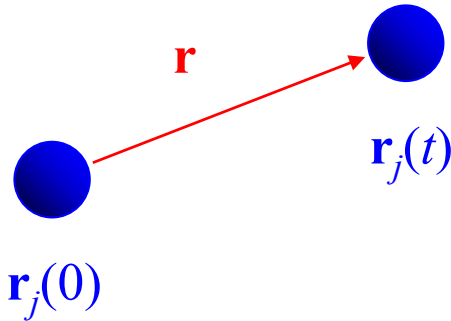
concentration, mol m⁻³

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

r

$\mathbf{r}_j(t)$

$\mathbf{r}_j(0)$

Self-part of the van Hove correlation function:

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

Self-part of the intermediate scattering function:

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

Incoherent scattering function:

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

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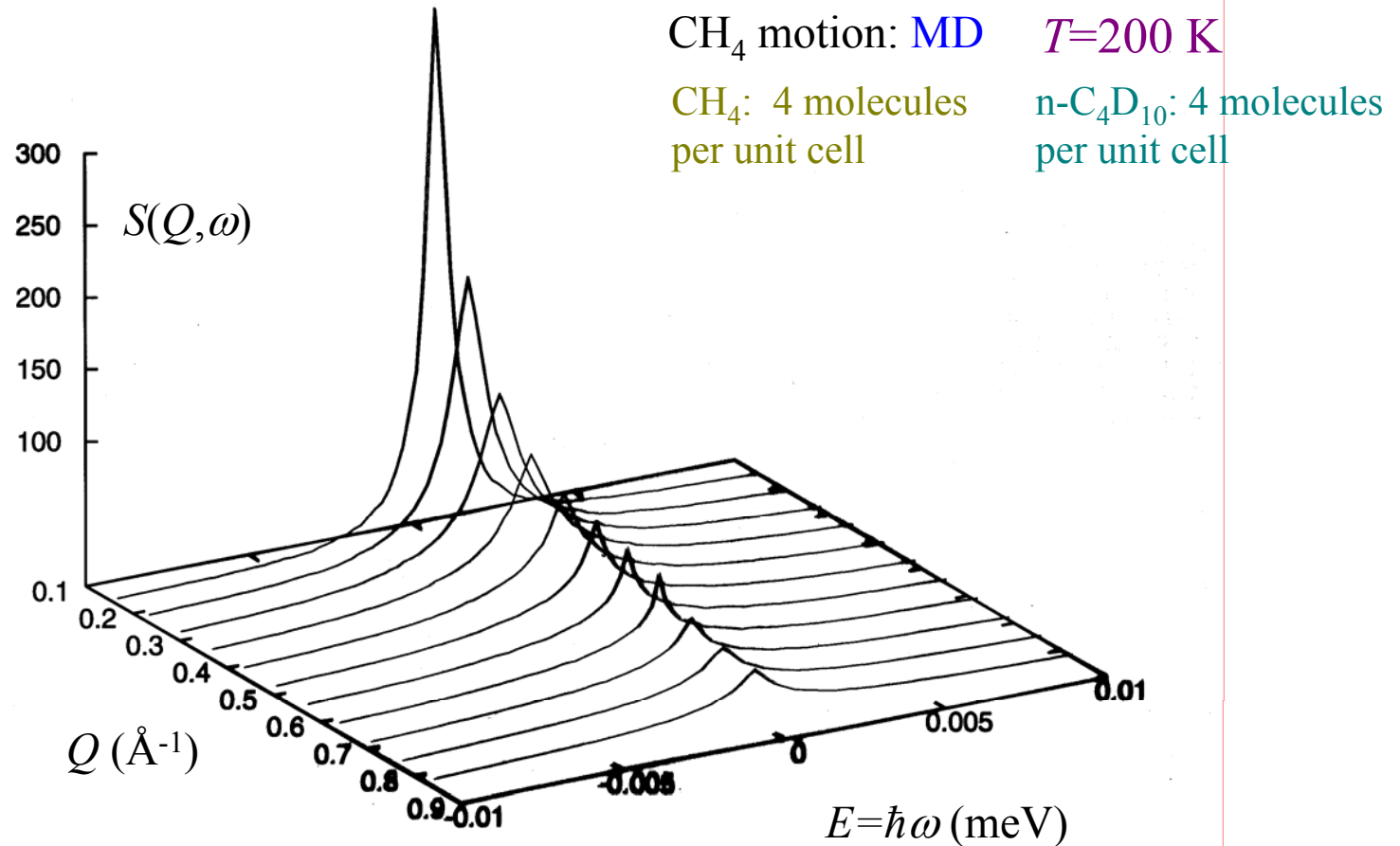
$$I_s(Q,t) = \exp(-D_s Q^2 t)$$

Gaussian in Q, exponential in 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

CH_4 motion: MD T=200 K

CH_4: 4 molecules per unit cell

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

$S(Q,\omega)$

Q (Å^{-1})

$E=\hbar\omega$ (meV)

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)

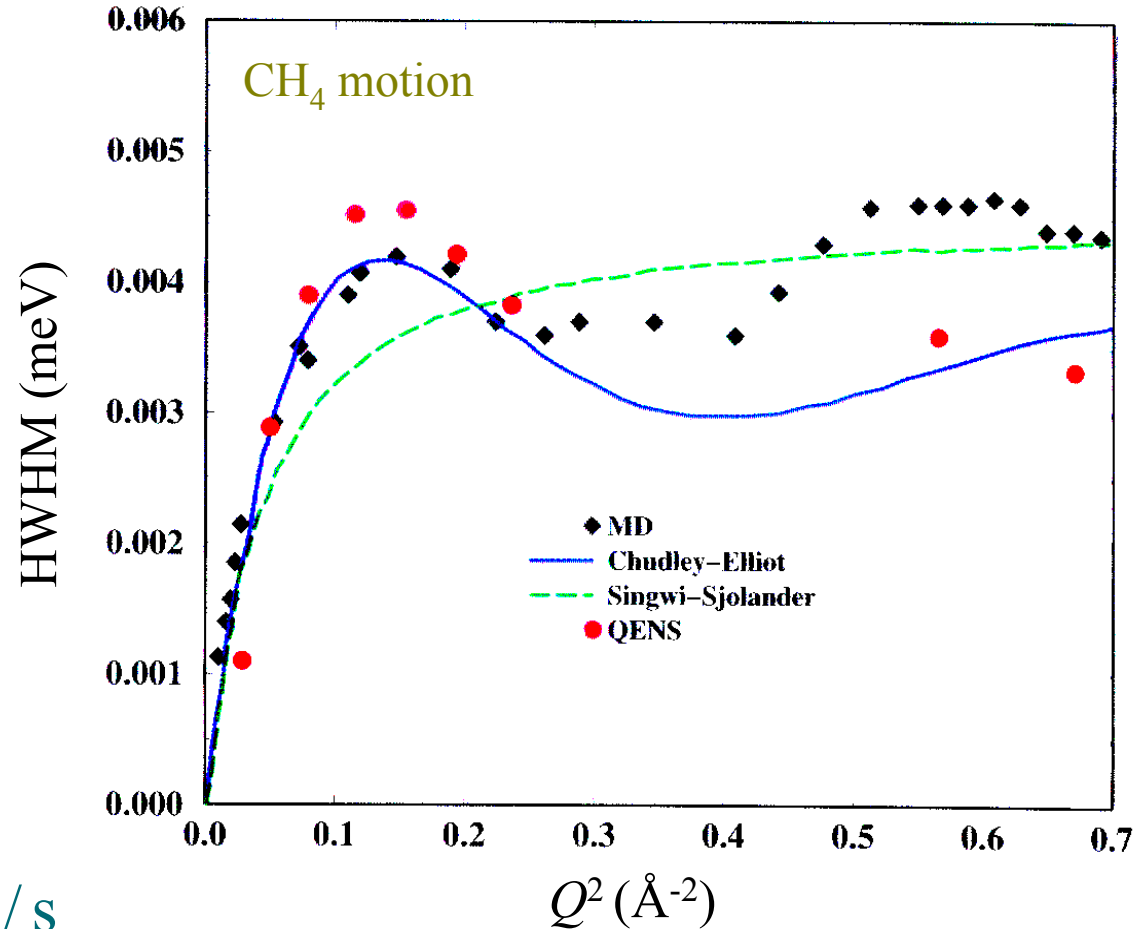# SCATTERING FUNCTION LINE SHAPE ANALYSIS: METHANE – n- BUTANE MIXTURES IN SILICALITE

T=200 K

CH_4: 2 molecules per unit cell

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

MD:

$$D_{s,CH_4} = 1.8 \times 10^{-5} \, cm^2 / s$$

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

CH$_4$ motion

MD
Chudley–Elliot
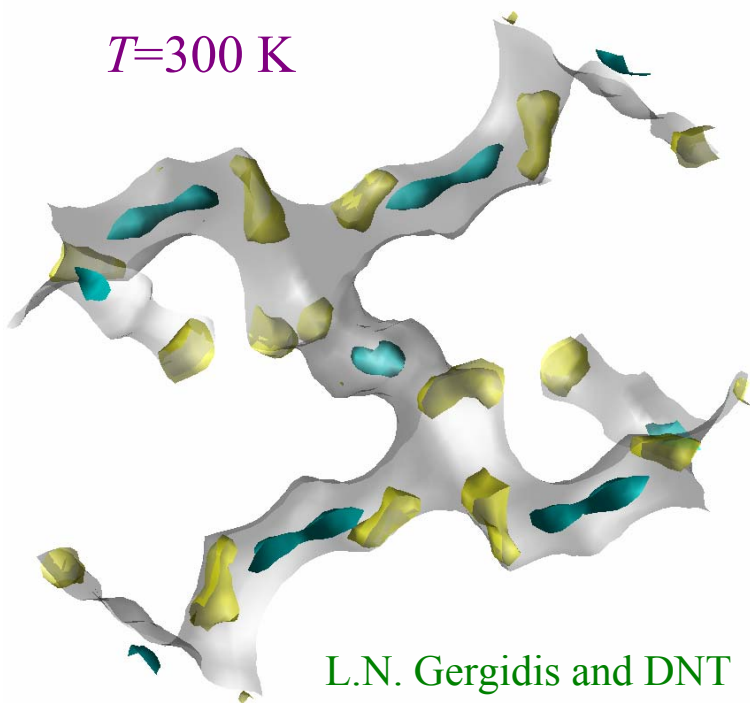Singwi–Sjolander
QENS

DIFFUSION OF METHANE – n-BUTANE MIXTURES IN SILICALITE

Distribution in the pores

CH$_4$: 4 molecules per unit cell

n-C$_4$H$_{10}$: 9 molecules per unit cell

T=300 K

Methane self-diffusivity
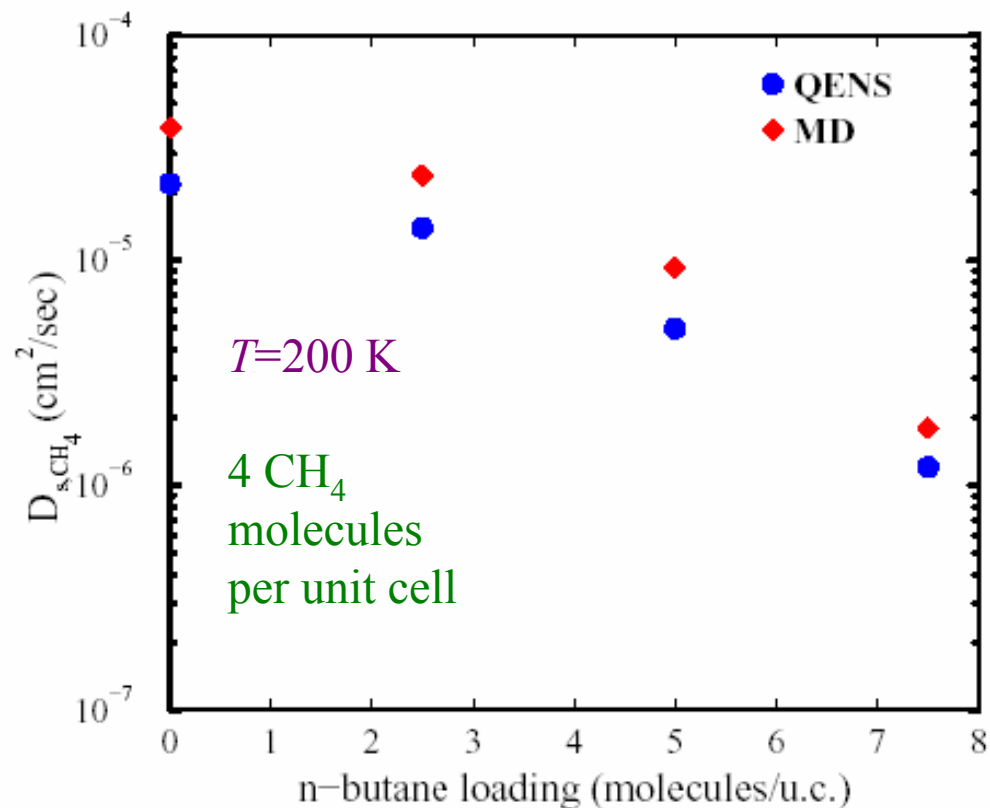
T=200 K

4 CH$_4$ molecules per unit cell

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)

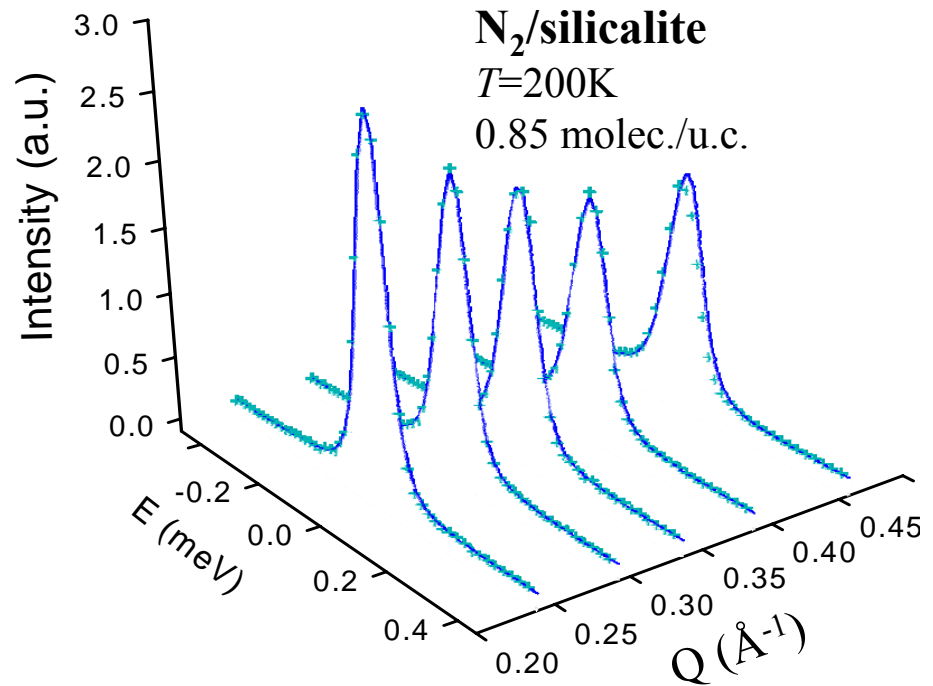# D_t , D_o MEASUREMENT AND SIMULATION

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:

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

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

N$_2$/silicalite
T=200K
0.85 molec./u.c.

Intensity (a.u.)

E (meV)

Q (Å^{-1})

Equilibrium MD Simulation, duration ≤ 10ns

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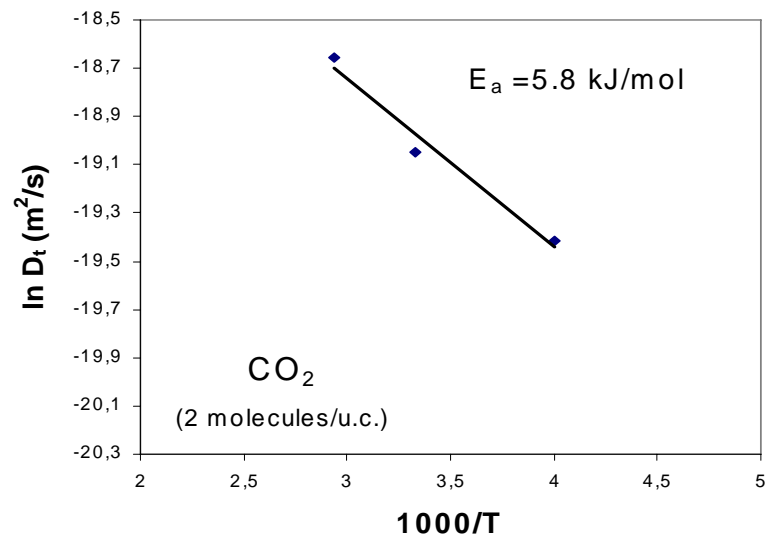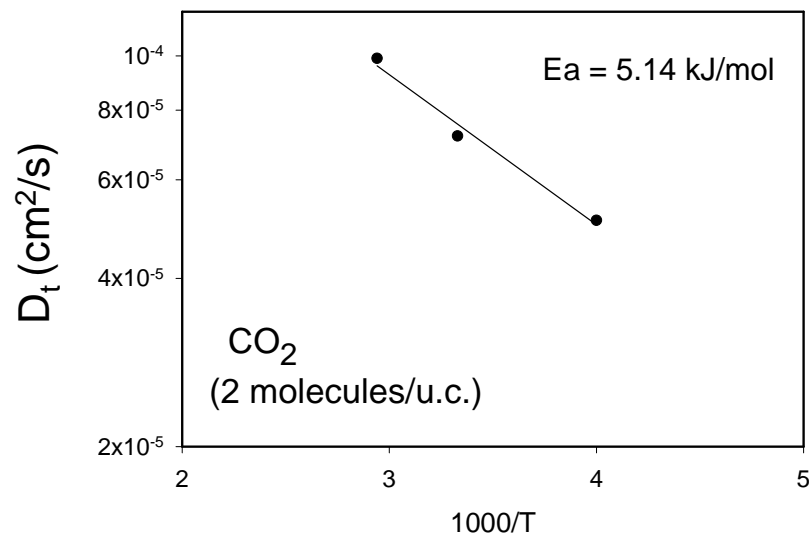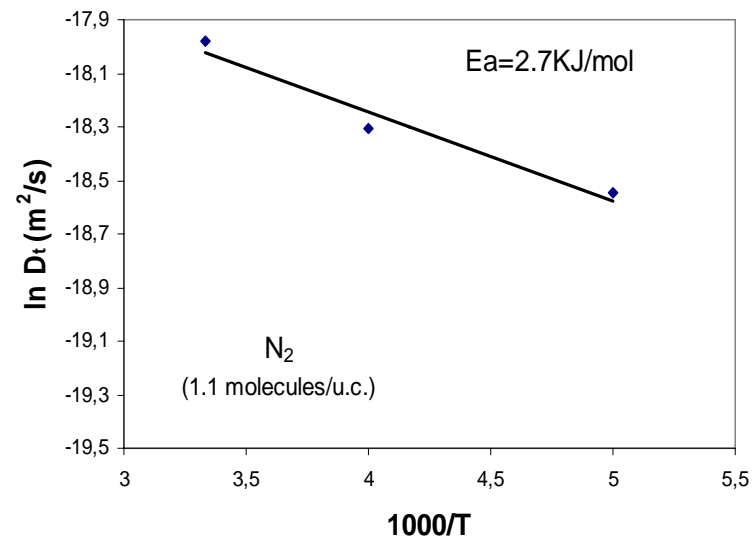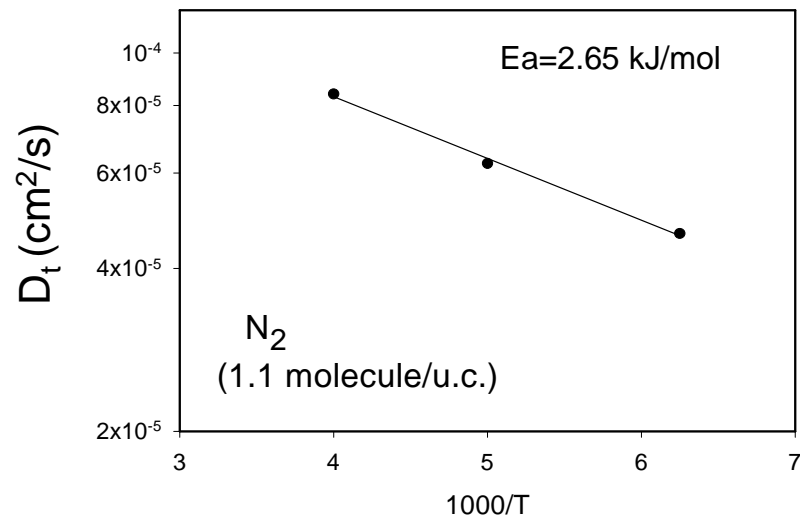
Molecular velocities
Green-Kubo

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
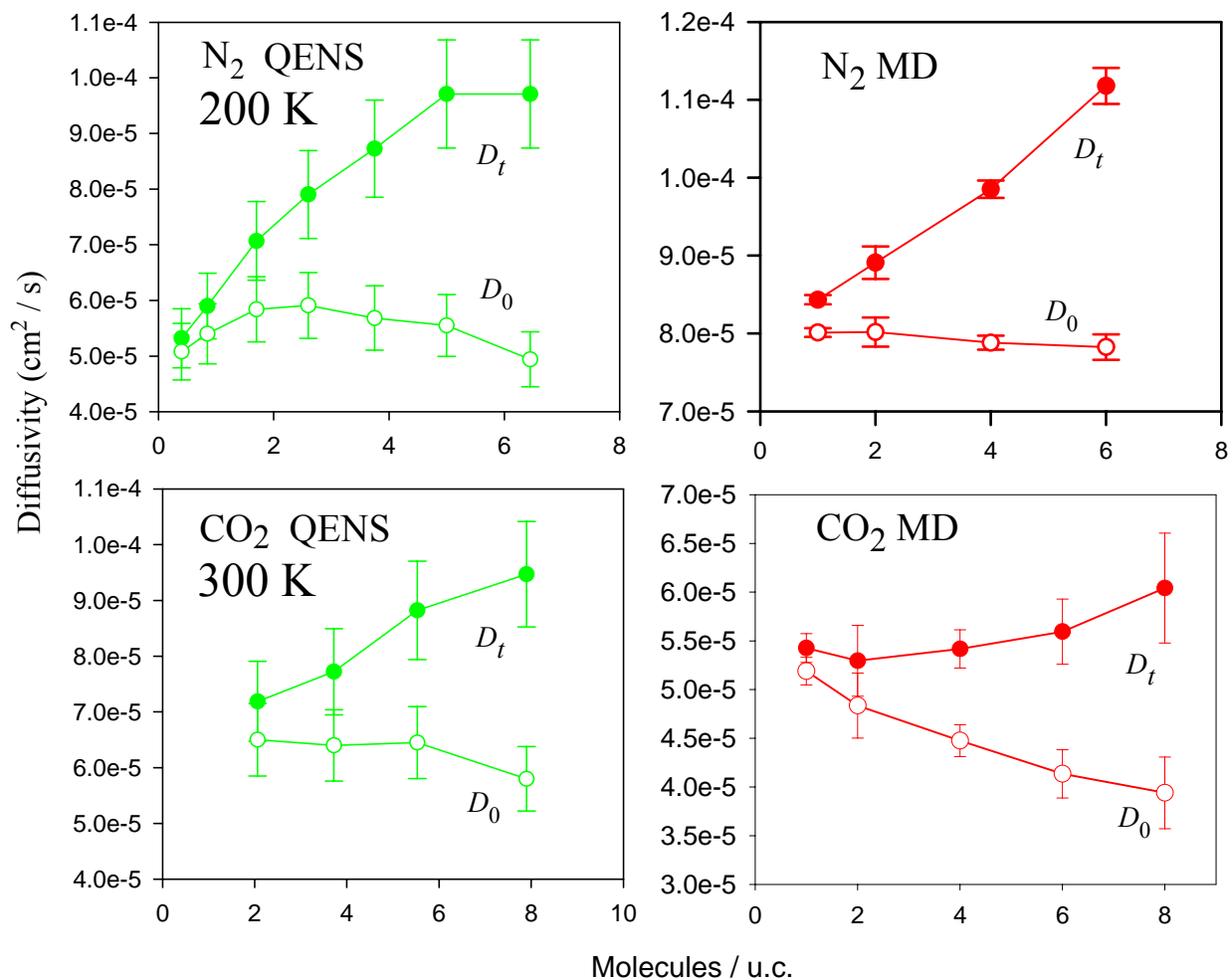
TRANSPORT OF N_2 AND CO_2 IN SILICALITE
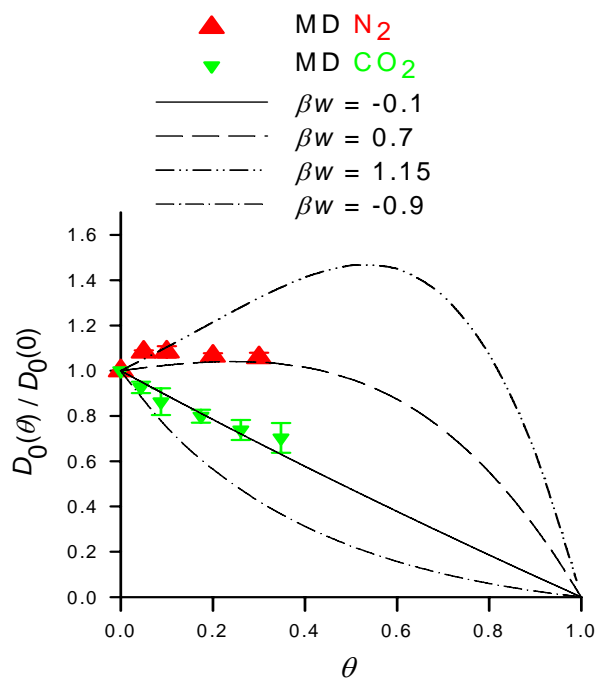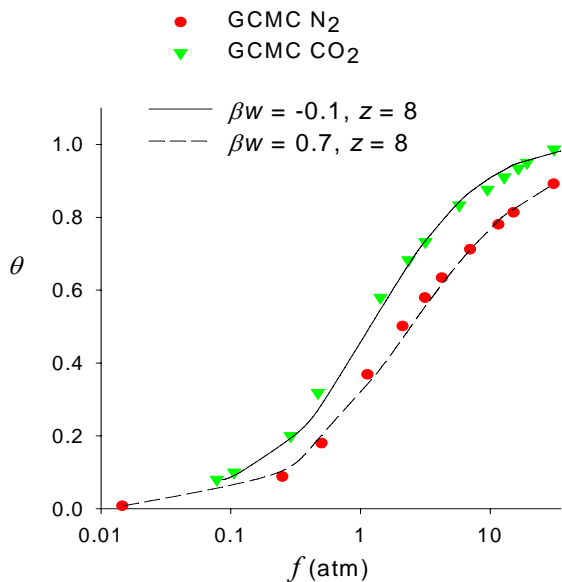

QENS experiment (H. Jobic)   MD (Athens)

ANALYTICAL MODEL FOR $D_0(\theta)$

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

- 3D-lattice of uniform **z**
- fraction of occupied sites θ

Effective jump rate of molecules surrounded by **j** *neighbors in the lattice*

Quasichemical isotherm

$$\Gamma(\theta) \propto \Gamma(j)\, P(j)$$

Individual jump rate

nearest-neighbor interactions **w**

QC: $\quad \dfrac{D_0(\theta)}{D_0(0)} = \left[\dfrac{\zeta(w,z)+1}{2-2\theta}\right]^{-z}\left[1+\dfrac{\zeta(w,z)-1+2\theta}{2-2\theta}\exp(2\beta w/z)\right]^{z-1}$

Langmuir: $\quad \dfrac{D_0(\theta)}{D_0(0)} = 1-\theta$

G K. Papadopoulos, H. Jobic, D. N. Theodorou, J. *Phys. Chem. B* **2004**, 108, 12748

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

GAS PERMEABILITY OF AMORPHOUS POLYMERS

Basic question: How do the solubility and diffusivity of small molecules in polymers depend on chemical constitution and temperature?

Common diffusion mechanism: Sequence of elementary "jumps" between accessible volume clusters within the polymer. Jumps are infrequent events.

ELEMENTARY DIFFUSIONAL JUMP

Transition-State Theory provides an estimate of the rate constant $k_{0 \to 1}$ in terms of the energies and eigenfrequencies at $0, \dagger$.

†: Saddle point of $\mathcal{V}(\mathbf{r})$

1: Local minimum of $\mathcal{V}(\mathbf{r})$
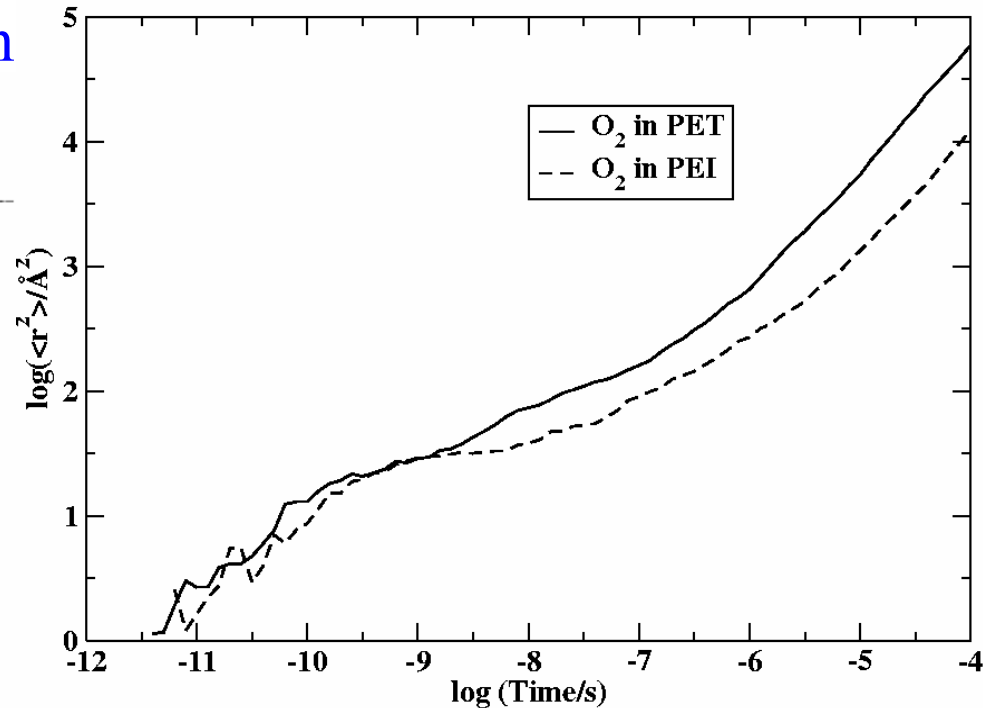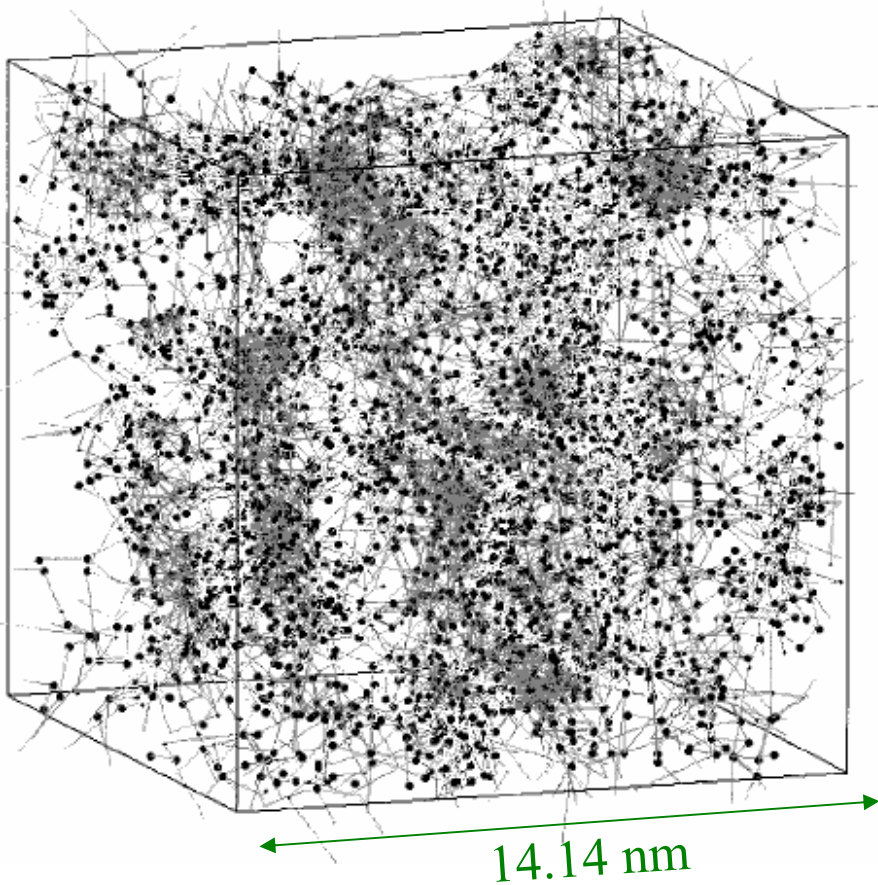
0: Local minimum of $\mathcal{V}(\mathbf{r})$
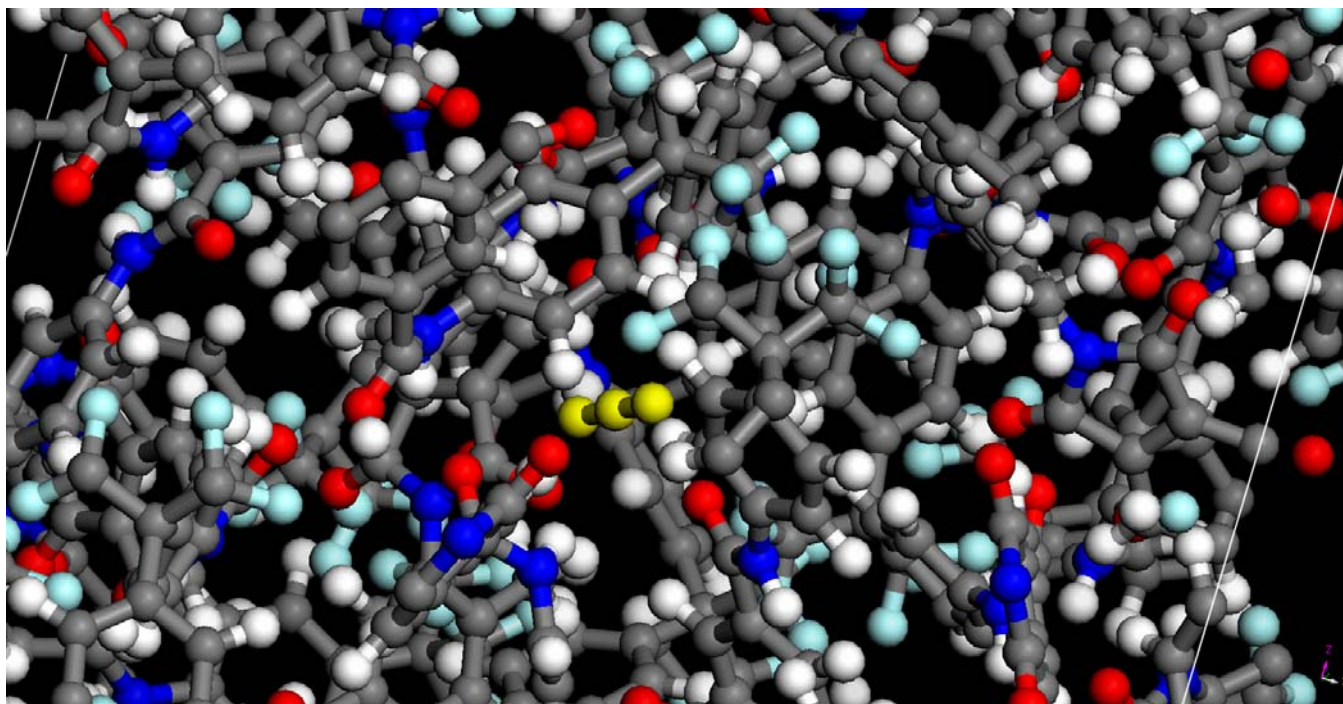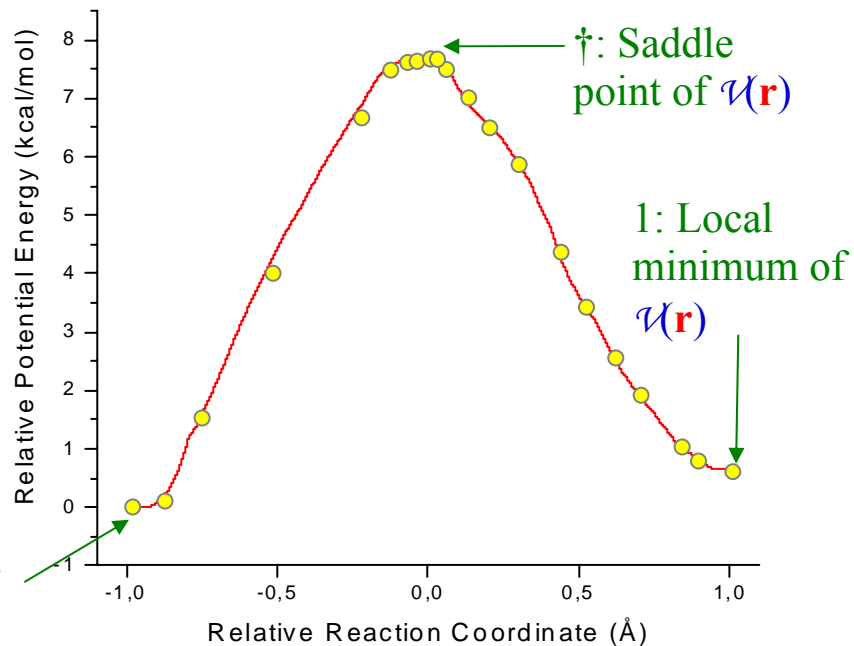
CO_2 in PAI, 300 K

N. Vergadou

Diffusion: Sequence (Poisson process) of uncorrelated elementary jumps in a disordered network of sorption sites
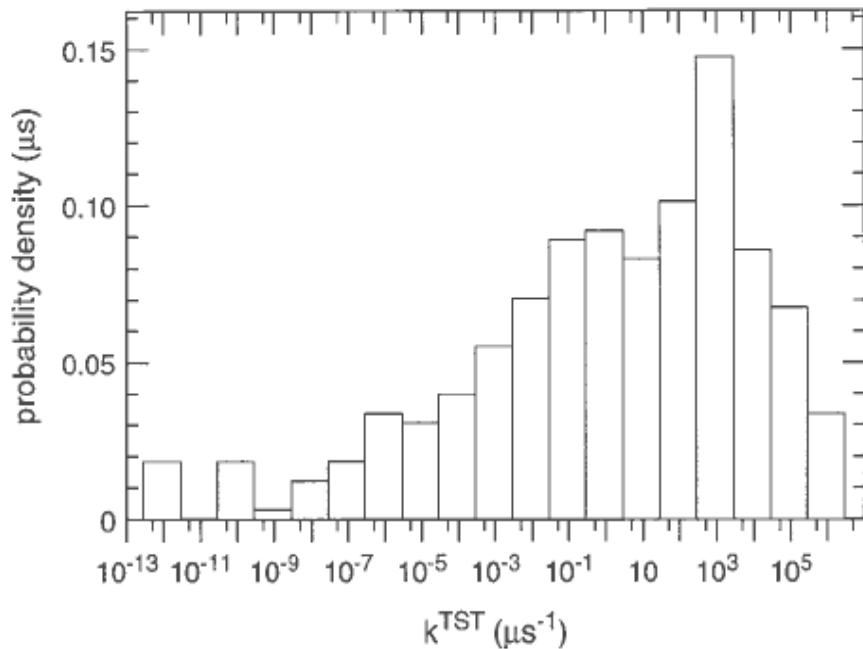
Kinetic Monte Carlo simulation

14.14 nm

Self-diffusivity D_s:

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

M.L. Greenfield and DNT, *Macromolecules* **34**, 8561 (2001)
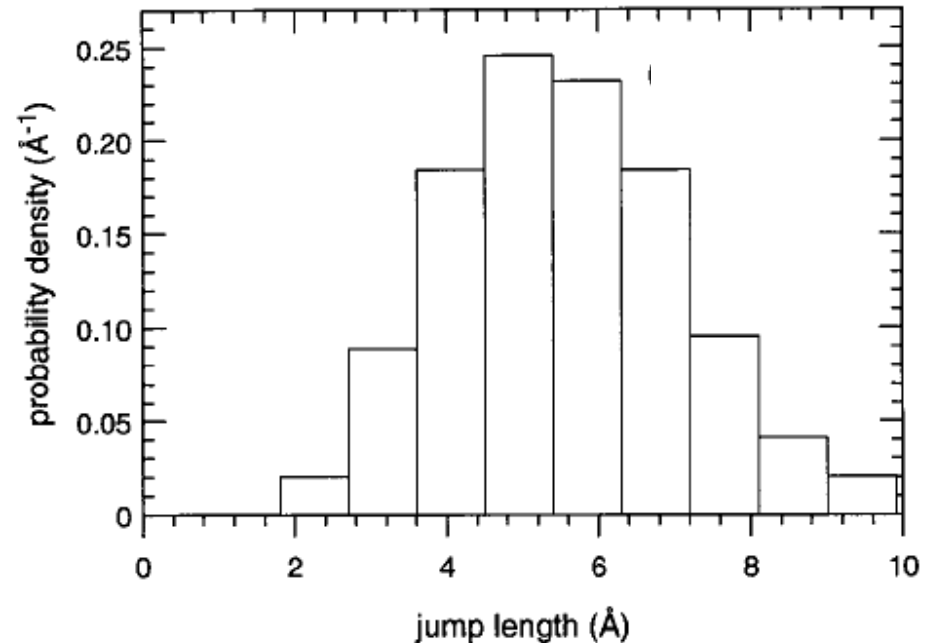
ORIGIN OF ANOMALOUS DIFFUSION IN GLASSY POLYMERS

$$\langle r^2 \rangle \propto t^n \ , \ \ n < 1$$

Penetrant motion in the glassy matrix exhibits great dynamic heterogeneity

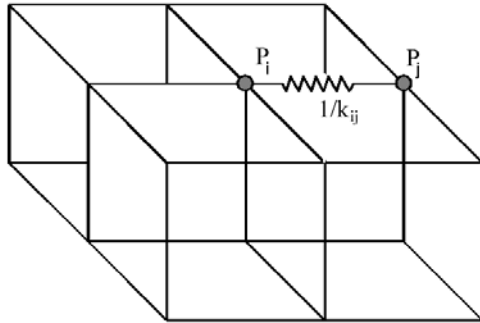Distribution of rate constants for elementary jumps.

Distribution of elementary jump lengths.

CH$_4$/glassy atactic polypropylene

M.L. Greenfield and DNT, *Macromolecules* **31**, 7068 (1998)

# SIMPLE INVESTIGATION OF THE EFFECTS OF DYNAMIC HETEROGENEITY

Simple cubic lattice of sites.

Random assignment of intersite transition rate constants $k_{i \rightarrow j}$ from a distribution.

Calculation of D_s through Kinetic Monte Carlo simulation (KMC) and Effective Medium Approximation (EMA).

$k_{i \rightarrow j}$ Distribution Functions:

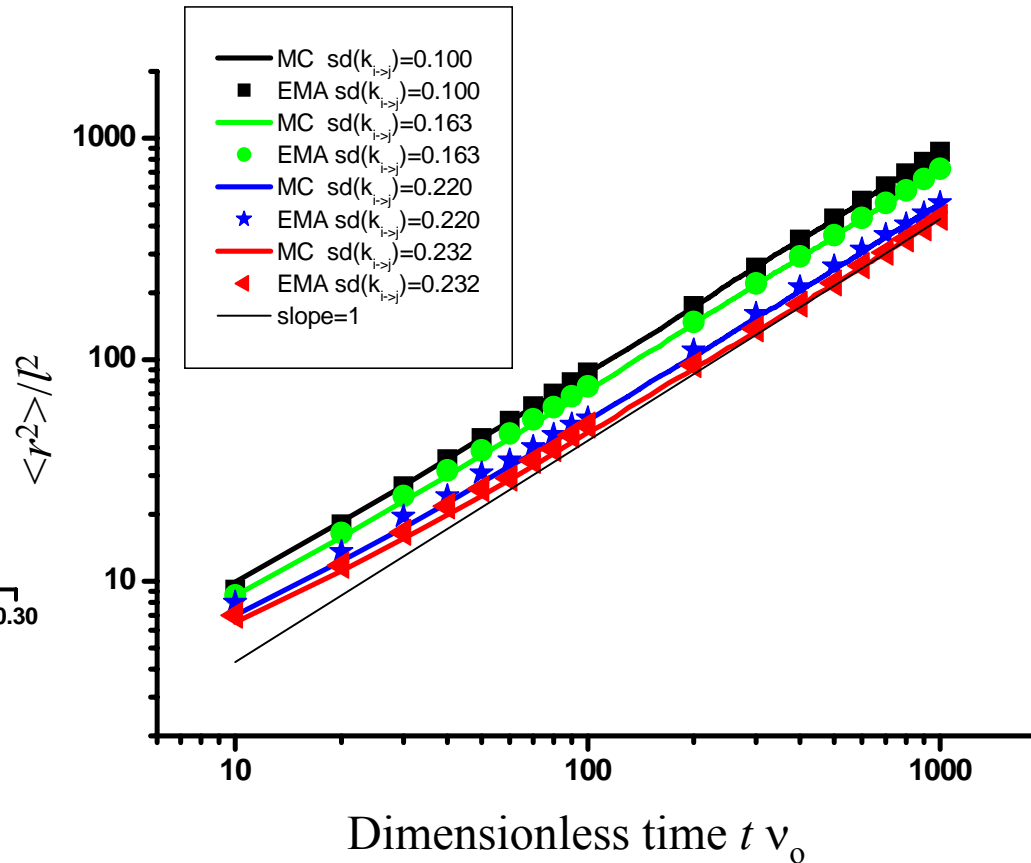• Same mean, $\nu_o/6$

• Various standard deviations, $sd(k_{i \rightarrow j})$

• Truncated Gaussian distribution of barrier heights.

N. Ch. Karayiannis, V. G. Mavrantzas and D. N. Theodorou, *Chem. Eng. Sci.* **56,** 2789 (2001)
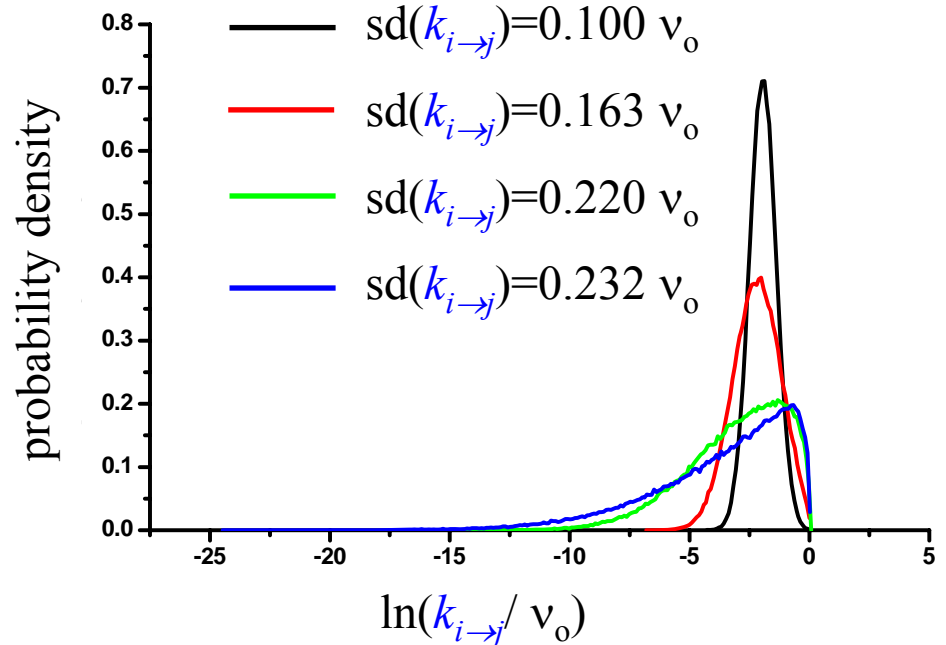
Diffusion coefficient as a function of the width of the jump-rate constant distribution
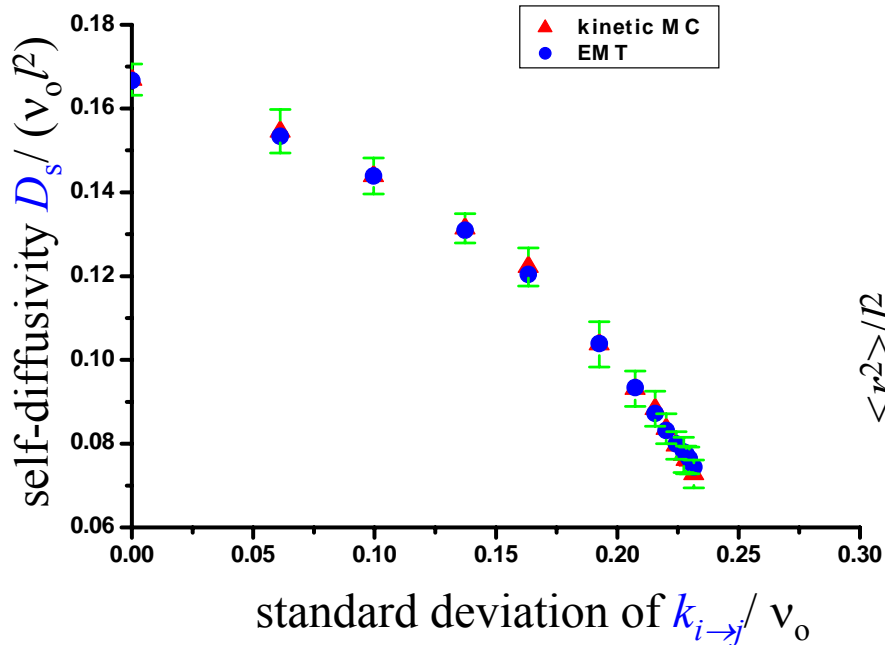
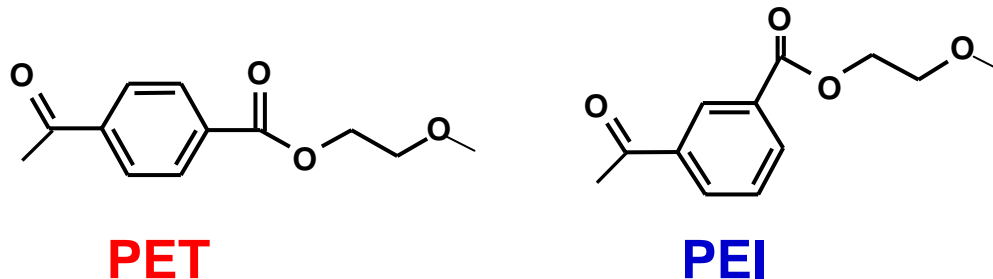**Mean square displacement (msd) as a function of time (KMC& EMA)**

Time-dependent Effective Medium Approximation (EMA):
K.W. Kehr, K. Mussawisade, T. Wichmann, in J. Kärger, P. Heitjans, and R. Haberlandt (Eds.) *Diffusion in Condensed Matter*, Vieweg: Wiesbaden (1998), p 265-305.
Long time limit: S. Kirkpatrick, *Phys.Rev.Lett*., 27, 1722-1725 (1971).

APPLICATION: O_2 DIFFUSIVITY IN PET, PEI

PET   **PEI**

Polyester	ρ (imposed in simulation) (g/cm^3)	ρ (experimental) (g/cm^3)	D_s (calculated) (10^{-9} cm^2/sec) Gusev-Suter, 1993	D_s, (experimental) (10^{-9} cm^2/sec)
PET	1.335	1.336 (1.333)	9.6	9.5 (6.5)
PEI	1.356	1.356 (1.346)	5.4	2.7

Lower permeability of PEI is mainly due to its smaller segmental mobility. The latter is attributable to the different mode of connection of phenyl groups within the chains.

N. Ch. Karayiannis, V.G. Mavrantzas, and DNT, *Macromolecules* **37**, 2978 (2004).

DYNAMICS OF PHENYL RINGS IN PET, PEI
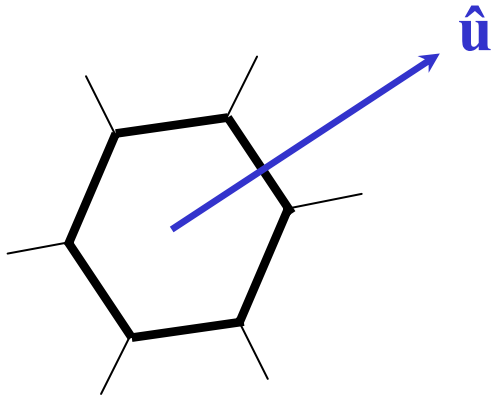
$$M_{\mathbf{u}}(t) = <\mathbf{u}(t) \cdot \mathbf{u}(0)>$$
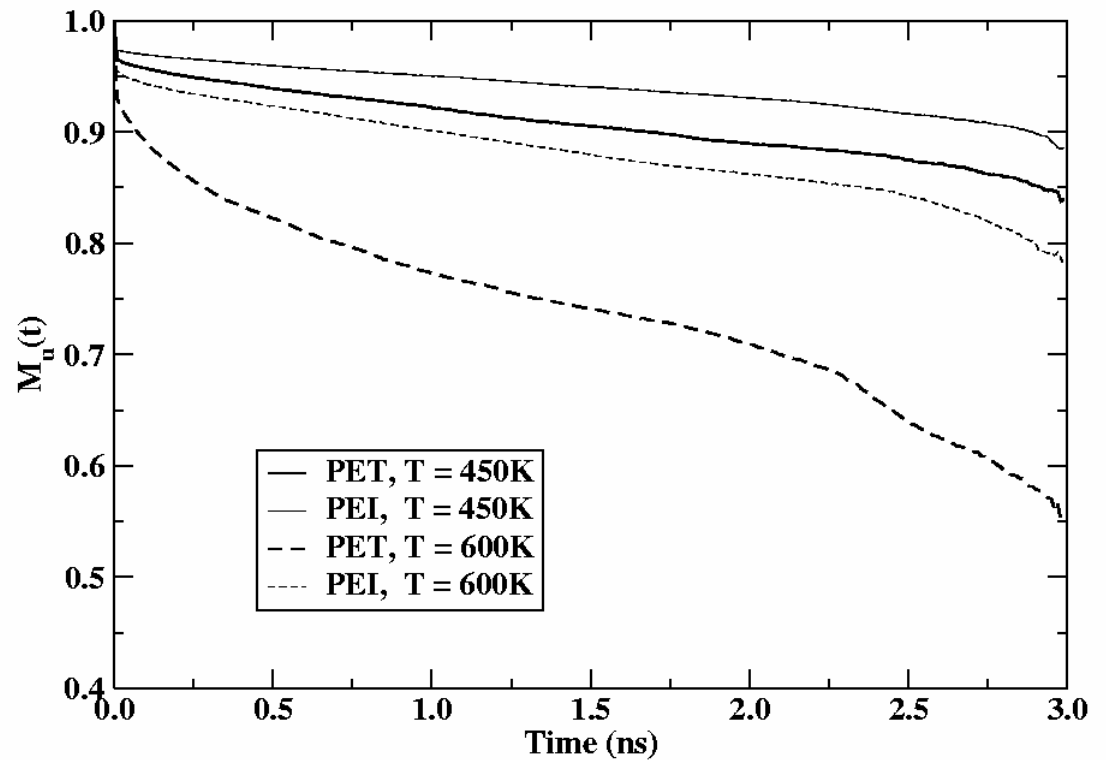
Segmental mobility higher in PET.

CONCLUSIONS

- Molecular simulations are useful in elucidating mechanisms and predicting rates of diffusion in separation materials.

- Molecular simulations aid in the interpretation of diffusion measurements.

- Broad spectra of length and time scales present in technologically important separation materials necessitate the development of hierarchical modelling and simulation approaches.

ACKNOWLEDGEMENTS

3.A Monte Carlo Algorithm

1. Construction of **3D lattice** with **periodic boundary conditions**. Each **site** represents a **macrostate**.

2. Assignment of the **energy** (E_i) and calculation of the **occupancy probability** (p_i^{eq}) for each **site**.

3. Assignment of the **barrier energy** (E_{ij}), calculation of the **activation energy** and the **rate constant** for each **transition.**

    $$k_{i \to j} = v_o \exp\left[-\frac{E_{ij} - E_i}{k_b T} \right]$$
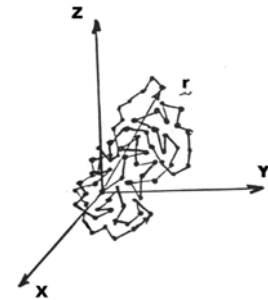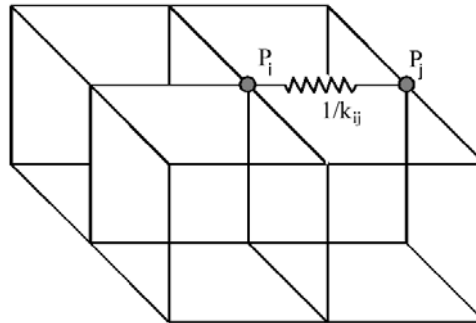
4. Distribution of a large number of **penetrant walkers** on the **lattice sites**. <u>There are no interactions between the walkers.</u>

5. Track down the **trajectories** for all walkers for a long period of time.
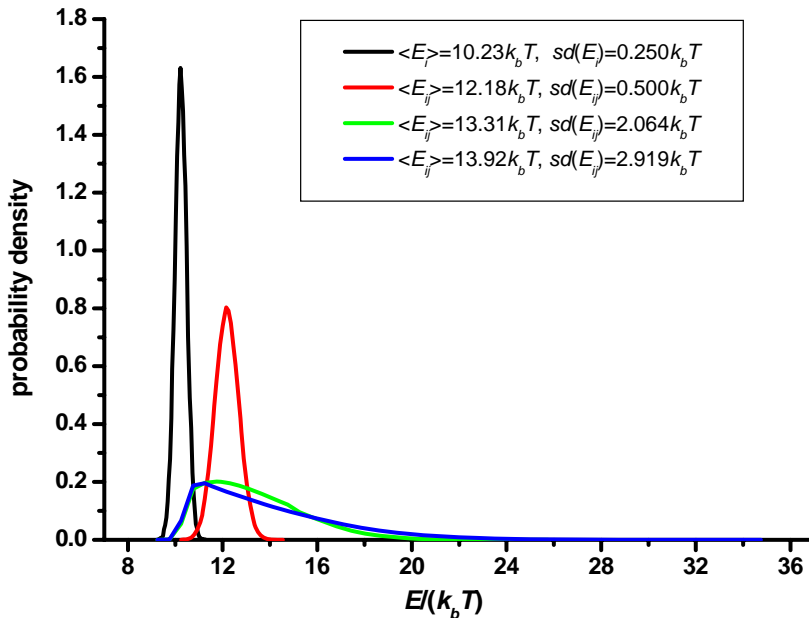
6. Calculate **penetrant diffusivity** (**_D_**) according to **Einstein's relation**:

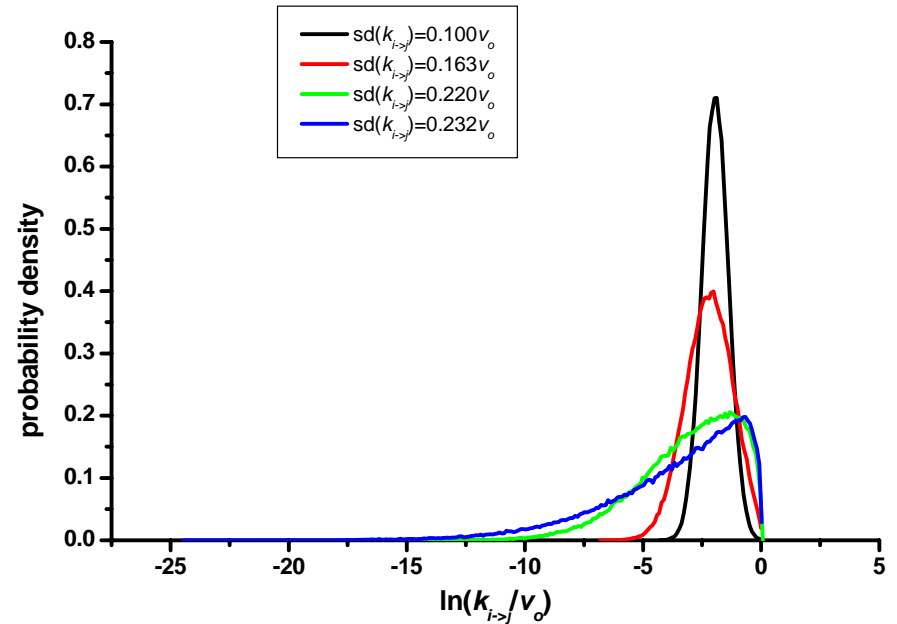 $$D = \lim_{t \to \infty} \left\{ \frac{\langle r(t) - r(0) \rangle^2}{6t} \right\}$$

3.Γ Results

N. Ch. Karayiannis, V. G. Mavrantzas and D. N. Theodorou, *Chem. Eng. Sci.* 56, 2789 (2001)

Energy distributions

Legend:
- $\langle E_i \rangle = 10.23 k_b T$, $sd(E_i) = 0.250 k_b T$
- $\langle E_{ij} \rangle = 12.18 k_b T$, $sd(E_{ij}) = 0.500 k_b T$
- $\langle E_{ij} \rangle = 13.31 k_b T$, $sd(E_{ij}) = 2.064 k_b T$
- $\langle E_{ij} \rangle = 13.92 k_b T$, $sd(E_{ij}) = 2.919 k_b T$

probability density vs $E/(k_b T)$

Jump Rate constants distributions

Legend:
- $sd(k_{i \rightarrow j}) = 0.100 v_o$
- $sd(k_{i \rightarrow j}) = 0.163 v_o$
- $sd(k_{i \rightarrow j}) = 0.220 v_o$
- $sd(k_{i \rightarrow j}) = 0.232 v_o$

probability density vs $\ln(k_{i \rightarrow j}/v_o)$

Rate constant distribution of elementary CH$_4$ jumps in atactic PP ✡
[*Greenfield & Theodorou, 1998*]

(a) between macrostates

probability density (μs) vs k^{TST} (μs^{-1})
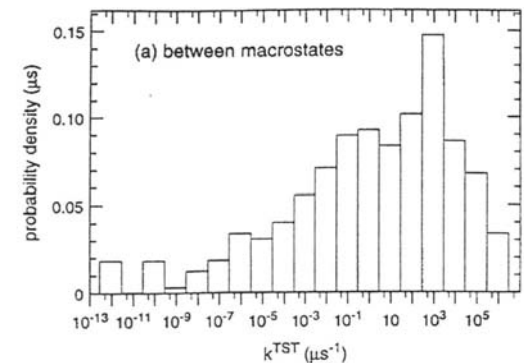
Duration of the "anomalous diffusion" phenomenon as a function of the width of the jump rate constant distribution
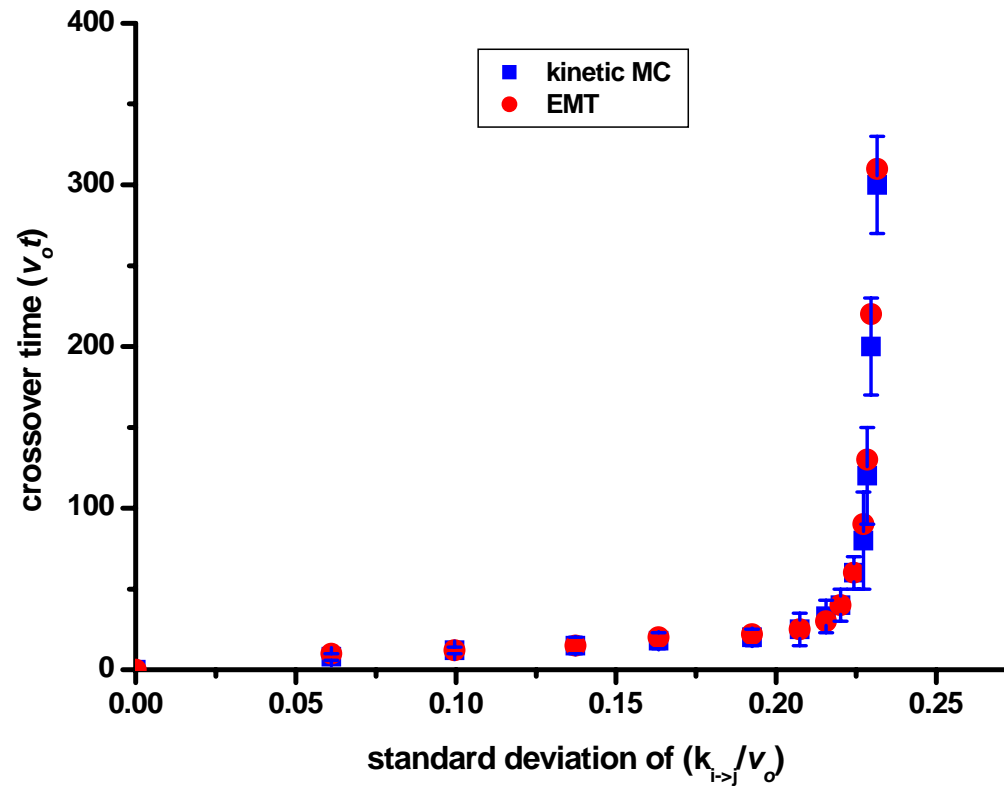
3.B Time dependent Effective Medium Theory

Application of t-d E.M.T. to calculate mean square displacement in time. [*Argyrakis et al., 1995*]

The **effective rate constant** $\overline{k}_{eff}$ **(Laplace space) is calculated from:**

$$\int_{k\,min}^{k\,max} \frac{k_{ij} - \overline{k}_{eff}(s)}{1 - \frac{2}{z}\left[s\overline{G}(0,s) - 1\right]\dfrac{k_{ij} - \overline{k}_{eff}(s)}{\overline{k}_{eff}(s)}}\rho(k_{ij})dk_{ij} = 0$$

where:

$\rho(k_{ij})$: **probability distribution function of k_{ij},**

z : **lattice coordination number ($z = 6$),**

$\overline{G}(0,s)$: **initial site occupancy probability [*Horner et al., 1995*]:**

$$\overline{G}(0,s) = (\frac{1}{2\pi})^3 \frac{1}{\overline{k}_{eff}} \int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi} \frac{dw_1 dw_2 dw_3}{\dfrac{s}{\overline{k}_{eff}} + 6 - 2\cos w_1 - 2\cos w_2 - 2\cos w_3}$$

Mean Square Displacement (Laplace space) is calculated using:
$$<r^2>(s) = \frac{\overline{k}_{eff}(s)}{p_{av}^{eq}}\frac{l^2}{s^2}z$$

Diffusivity is calculated from:
$$D = \frac{k_{eff}}{p_{av.}^{eq}}l^2, \quad k_{eff} = \lim_{s\to 0}\overline{k}_{eff}(s)$$

ZEOLITES

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

MATERIAL PROPERTIES

Sorption thermodynamics
- Henry's law constants
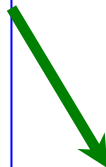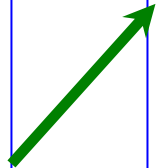- Sorption isotherms

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

MODEL AND POTENTIAL ENERGY FUNCTION

Rigid zeolite framework: O-atoms = Lennard-Jones spheres at positions determined by X-ray diffraction in Pnma-HZSM-5 (D.H. Olson *et al*. *J. Phys. Chem*. **85**, 2238 (1981).

$\mathcal{V} = \mathcal{V}\big($positions of all sites constituting the sorbate molecules$\big) =$

Conformational energy of individual sorbate molecules ← flexible alkanes

+

Zeolite/sorbate Lennard-Jones interactions

+

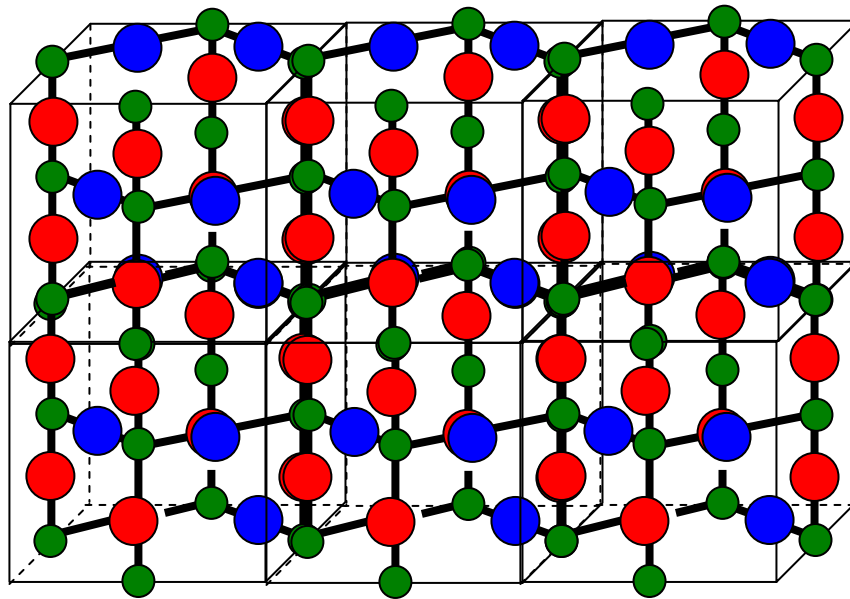Zeolite/sorbate Coulomb interactions

+

Sorbate/sorbate Lennard-Jones interactions

+

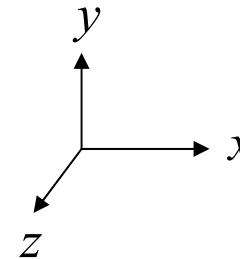Sorbate/sorbate Coulomb interactions

aromatic sorbates, N_2, CO_2
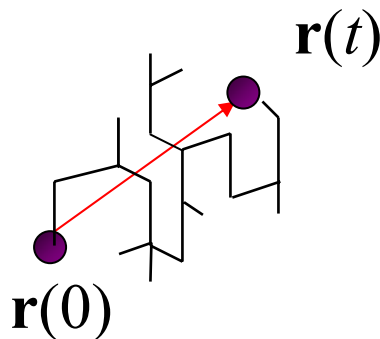
DIFFUSIVITY FROM RATE CONSTANTS: KINETIC MONTE CARLO

Methane/Silicalite sorption states

- 🔴 straight channel
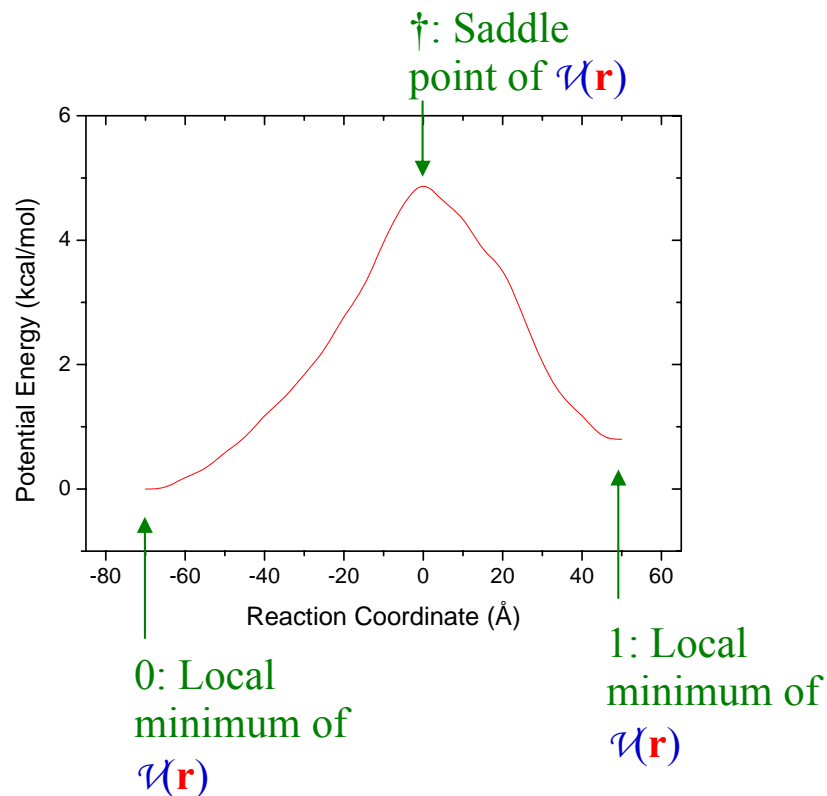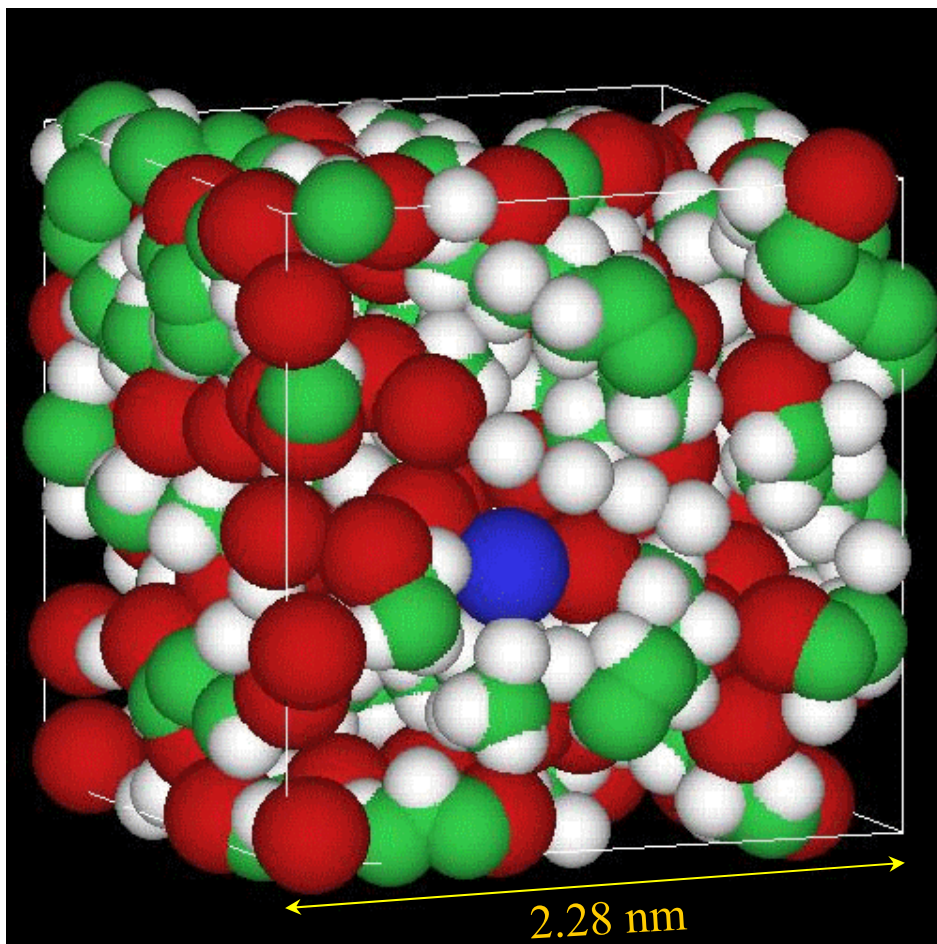- 🔵 zig-zag channel
- 🟢 intersection

Poisson process: Succession of uncorrelated jumps between sorption states, with rate constants known from atomistic analysis.
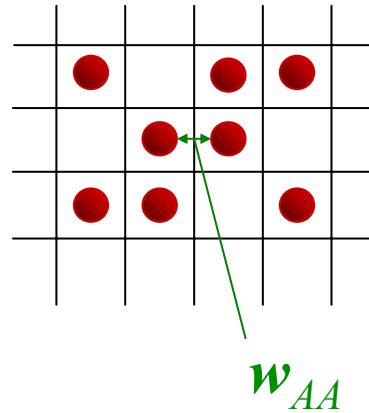
$$\mathbf{r}(t)$$

$$\mathbf{r}(0)$$

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

(Einstein, 1905)

ELEMENTARY DIFFUSIONAL JUMP

2.28 nm

†: Saddle point of $\mathcal{V}(\mathbf{r})$

0: Local minimum of $\mathcal{V}(\mathbf{r})$

1: Local minimum of $\mathcal{V}(\mathbf{r})$

Transition-State Theory provides an estimate of the rate constant $k_{0\to 1}$ in terms of the energies and eigenfrequencies at 0, †.

M.L. Greenfield and DNT, *Macromolecules* **31**, 7068 (1998)

QUASICHEMICAL MODEL OF SORPTION

- **Regular lattice of sites**
- z **coordination number**
- w **nearest-neighbor interactions**
- **Quasichemical approximation (QC)**

$$w_{AA} \qquad w = \frac{z w_{AA}}{2}$$
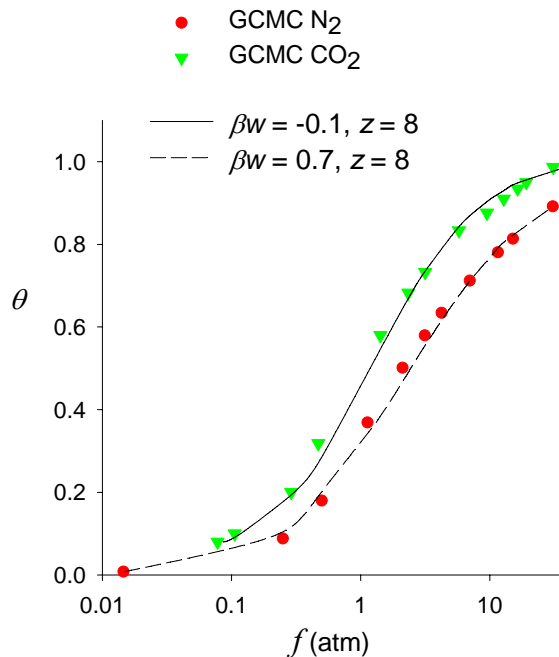
QC isotherm: $\quad bf = \dfrac{\theta}{1-\theta}\left(\dfrac{2-2\theta}{\zeta(w,z)+1-2\theta}\right)^{z}$

$$\zeta(w,z) = \left\{1-4\theta(1-\theta)[1-\exp(-2\beta w/z)]\right\}^{1/2}$$

Langmuir isotherm: $\quad bf = \dfrac{\theta}{1-\theta}$

Legend:
- ● GCMC N_2
- ▼ GCMC CO_2
- —— βw = -0.1, z = 8
- – – – βw = 0.7, z = 8
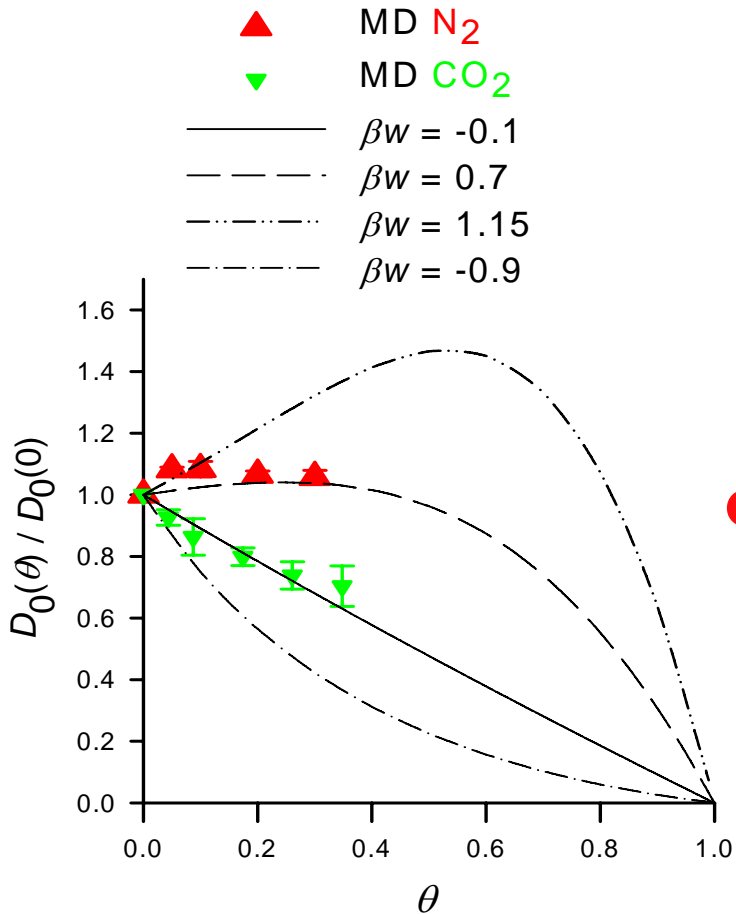
θ vs f (atm)

ANALYTICAL MODEL FOR $D_0(\theta)$

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

Lattice model of uniform z.

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

Overall effective jump rate is a function of the individual jump rates of a molecule and the probabilities of being surrounded by i neighbours.
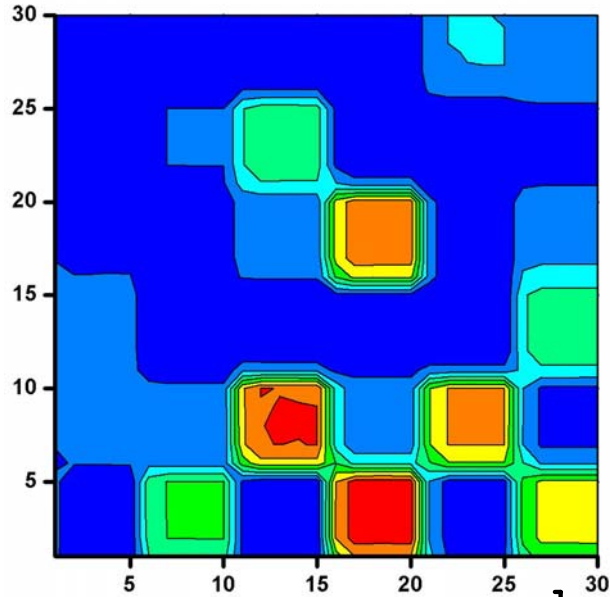

Legend:
- ▲ MD N_2
- ▼ MD CO_2
- —— $\beta w = -0.1$
- – – – $\beta w = 0.7$
- –··–··– $\beta w = 1.15$
- –·–·– $\beta w = -0.9$

Axes: $D_0(\theta) / D_0(0)$ vs θ

QC: $$\frac{D_0(\theta)}{D_0(0)} = \left[\frac{\zeta(w,z)+1}{2-2\theta}\right]^{-z}\left[1 + \frac{\zeta(w,z)-1+2\theta}{2-2\theta}\exp(2\beta w/z)\right]^{z-1}$$
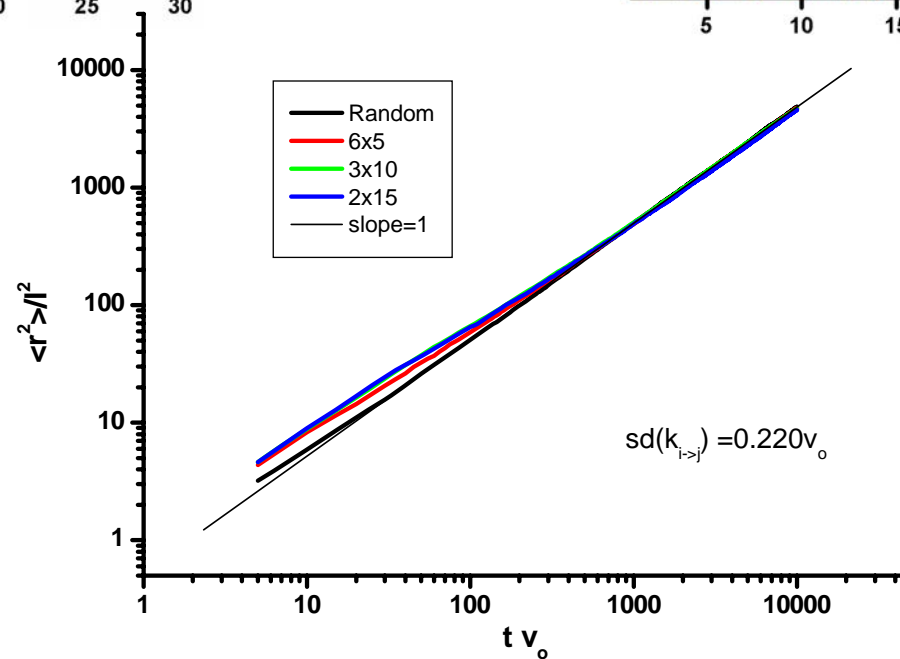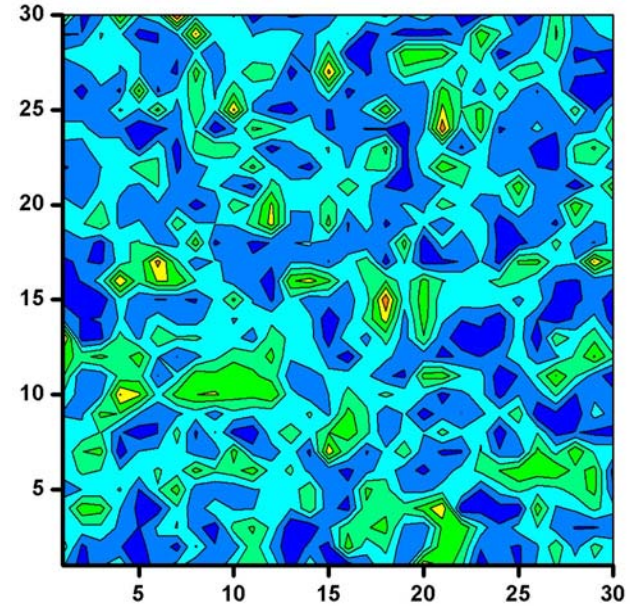
Langmuir: $$\frac{D_0(\theta)}{D_0(0)} = 1-\theta$$

Comparison between random and spatially correlated lattices
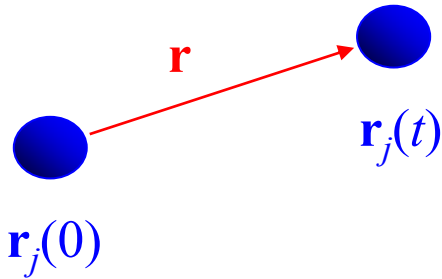
Spatially correlated lattice

Random lattice

INCOHERENT QENS SPECTRA FROM MD

$$\frac{d\sigma^2}{d\Omega dE} \propto \sigma_{inc} S_{inc}(Q,\omega) + \sigma_{coh} S_{coh}(Q,\omega)$$

r

$\mathbf{r}_j(t)$

$\mathbf{r}_j(0)$

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

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

inc

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi} \iint d\mathbf{r}dt \, \exp\{i(\mathbf{Q}\cdot\mathbf{r} - \omega t)\} G(\mathbf{r},t)$$

coh

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