Molecular Dynamics - Computer Simulations

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Scope of the talk

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1 Our profile

Our aim: Computer simulations and analytical theory are used to get insight into the underlying microscopic processes that lead to measured macroscopic phenomina.

Check theories and help to understand surprising experimental results.

Future prospects of our students: Computer simulations are wanted by many institutes all over the world.

E.g. Announcments of positions by CCP5 for PhD students and postdocs.

For our departments website see:

http://www.uni-leipzig.de/~mdc/

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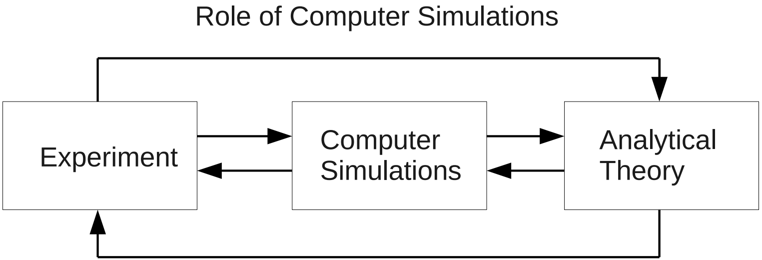
Simulations in Natural Science

Simulation on the computer is nowedays a standard tool!



Computer simulations form a bridge between theory and experiment.

Classical picture of the world - the Laplace demon

"An intelligent being who, at a given moment, knows all the forces that cause a nature to move and the positions of the objects that it is made from, if also it is powerful enough to analyze this data, would have described in the same formula the movements of the largest bodies of the universe and those of the lightest atoms. Although scientific research steadily approaches the abilities of this intelligent being, complete prediction will always remain infinitely away."

Laplace, 1820

With computer simulations we are close to be this demon! At least for some hundred particles.

In reality, the atoms and molecules do not follow classical physics but, for most practical systems the classical picture is sufficient.

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MD and MC simulations

- There are many kinds of computer simulations.
- The most common ones are Molecular Dynamics (MD) and Monte Carlo (MC)
- In MC, situations of the system are created randomly but, with the correct probability distribution.
- In MD the trajectories of typically some thousands of particles are numerically calculated from Newtons secons law.
- This is our favorite method in connection with analytical theory.

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The finite system size

The simulations usually include only few hundreds or thousands of particles.

- How can that be a model for a real liquid?
- For example in cubic lattice of 8x8x8 = 512 particles 296 are situated at the surface. These are 58 per cent.
- Surface effects will be dominating!
- This is a tiny droplet. Smaller then most real droplets.
- This is not a bulk fluid!
- Compromise: Artifical periodicity.

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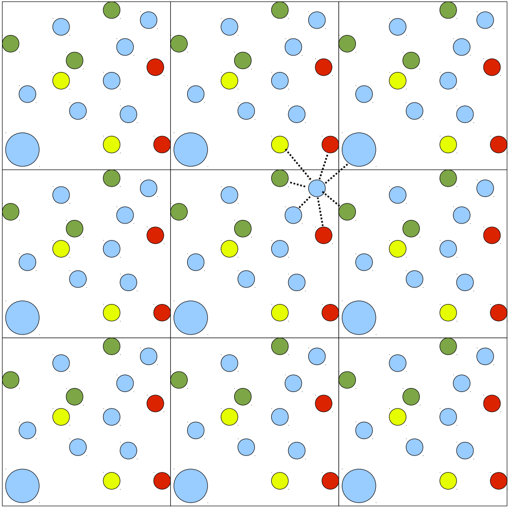

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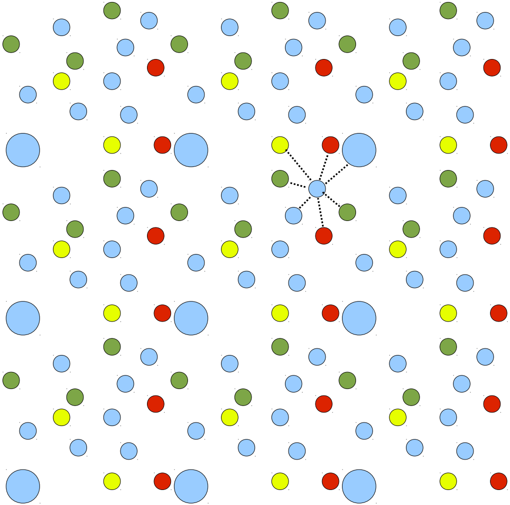

What can we learn from the trajectory?

How do we analyze the trajectory? Here are some examples!

Structural quantities:

- The pair correlation function
- The chemical potential.

Dynamical quantities:

- The self diffusion coefficient.
- The Velocity Auto Correlation Function (VACF)

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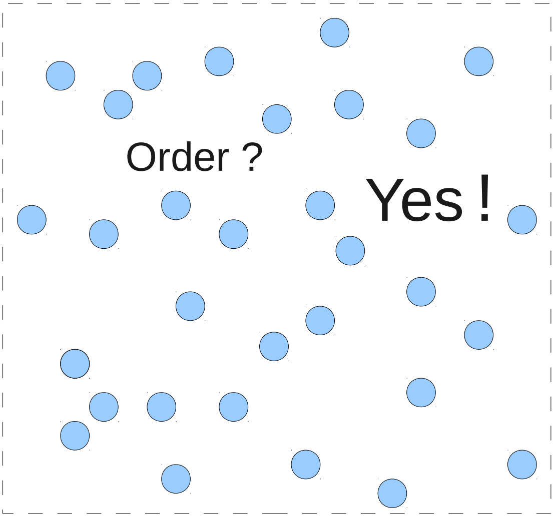
Is there order in an irregular fluid ???



The Radial Distribution Function

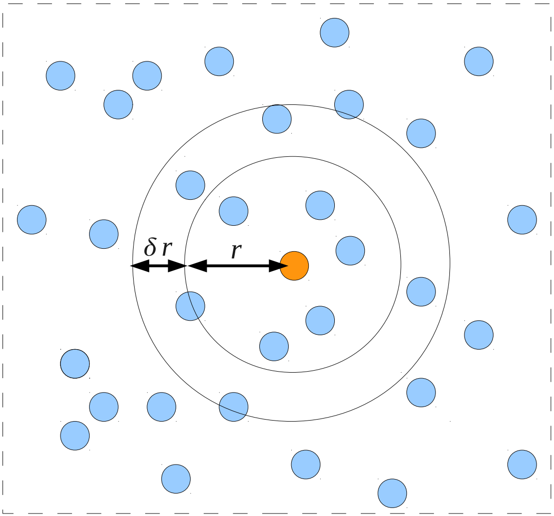
Look at a given particle.

Assume a spherical shell of radius r and thicknes δr and volume δV around it.

Count the number δN of other particles the center of which is situated within the shell.

These are $\delta N = 5$ in the following example.

The Radial Distribution Function



The Radial Distribution Function

The Radial Distribution Function $g(r)$ is defined as the average density in the shell divided by the average density in the system.

$$g(r) = \frac{1}{n}\frac{\delta N}{\delta V}. \tag{1}$$

n is the average density of blue particles in the system.

If their would be total randomness, then we would have $g(r) = 1$ for all r. This is not the case, even in the dilute neutral system.

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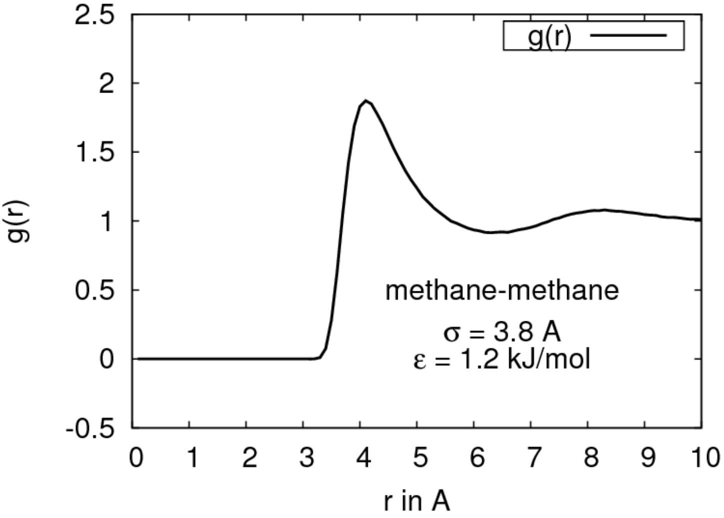
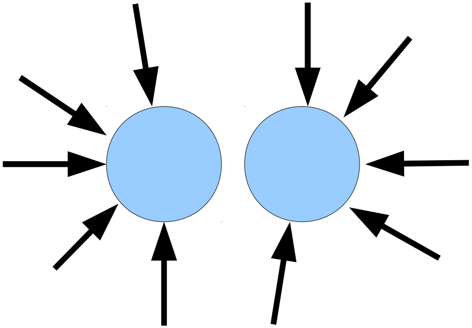


The Radial Distribution Function

Particles prefer to be close to each other!



Reason: Mutual screening against other particles.

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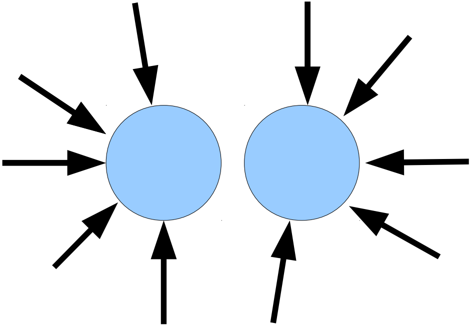

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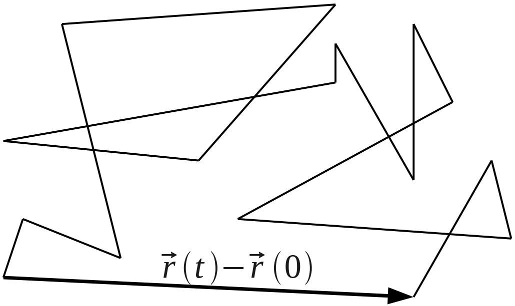
The Self Diffusion Coefficient

Self-diffusion is the shift of single particles by irregular thermal motion.



Like a drunken guy searching his house.

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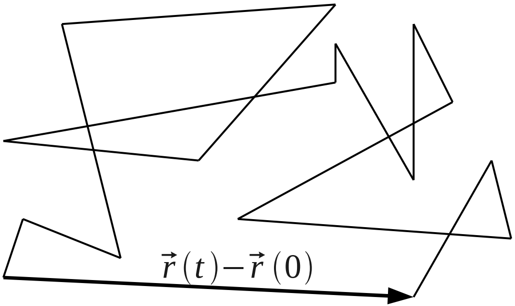

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The Self Diffusion Coefficient

Einsteins law: The square of the distance between a particles initial site at $t = 0$ and that to later time is proportional to the travel time t (at large times).

$$D_S = \lim_{t\to\infty} \frac{\sum_{i=1}^{N}(\vec{r}_i(t) - \vec{r}_i(0))^2}{6Nt} \tag{2}$$

Faster convergence if we use

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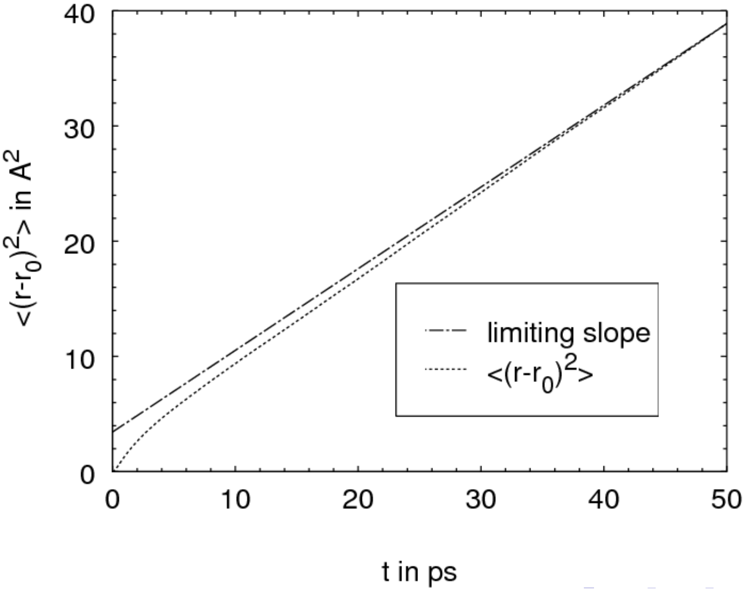
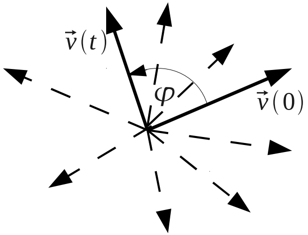


VACF - the particles memory

If we compare many times the velocity $\vec{v}(0)$ of a particle at time t with the velocity $\vec{v}(t)$ of the same particle at time t



many angles φ and different sizes are possible.

In average $< \vec{v}(t) \cdot \vec{v}(0) >= 0$ if there is no memory.

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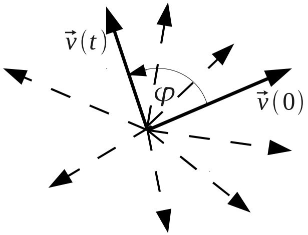

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- For a free flight the velocity will remain constant.

$$< \vec{v}(t) \cdot \vec{v}(0) >= [v(0)]^2$$

- For a one dimensional harmonic oscillator $v(t) = v(0) \cos \omega t$

$$< v(t)v(0) >= [v(0)]^2 \cos \omega t$$

- Normally the VACF $\Phi(t)$ is defined as

$$\Phi(t) = \frac{< \vec{v}(t) \cdot \vec{v}(0) >}{[v(0)]^2} \quad (4)$$

Hence, $\Phi(0) = 1.0$.

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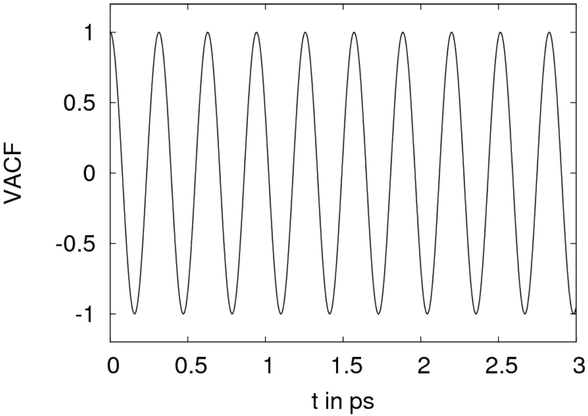

The VACF will not vanish for long times.

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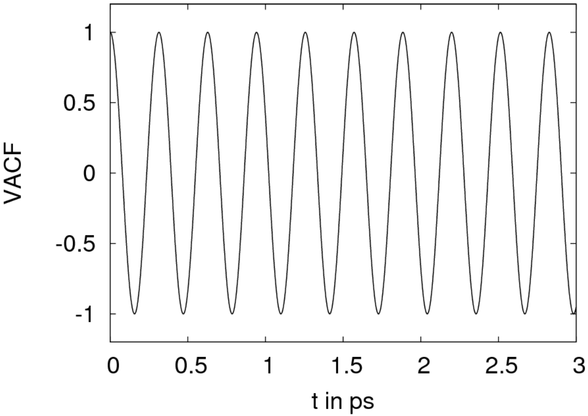

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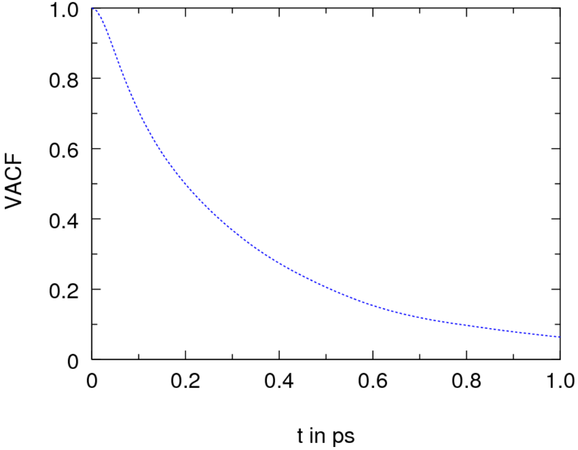
Example: A methane molecule within a dense gas.



The particle hits other methane and looses its memory at long times.

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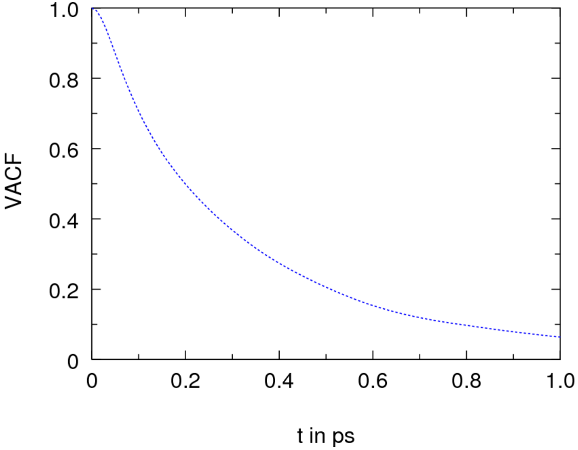

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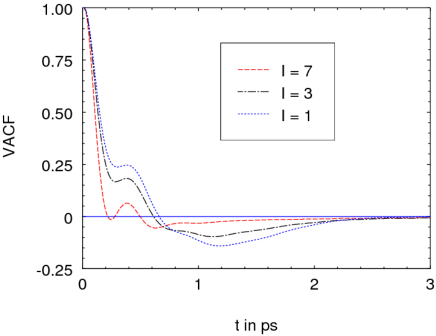

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Many conclusions about the particle dynamics are possible

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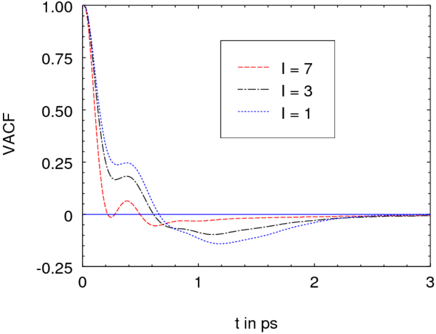

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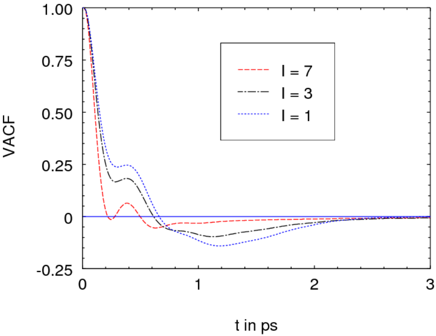

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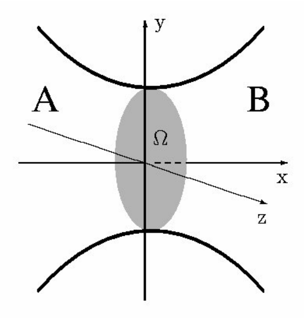
The principle will be demonstrated for a bottleneck in a porous solid and a diffusing particle.

Stream through the dividing surface



The principle of TST

Probability density to find a particle within the transition state multiplied by the particle velocity yields the stream. The number of passing particles per time unit is

$$\frac{\mathrm{d}N}{\mathrm{dt}} = \int_{\Omega} j(\vec{s})\,\mathrm{d}\Omega = \int_{\Omega} n(\vec{s})\,v_x(\vec{s})\,\mathrm{d}\Omega$$

Integration over the dividing surface Ω.

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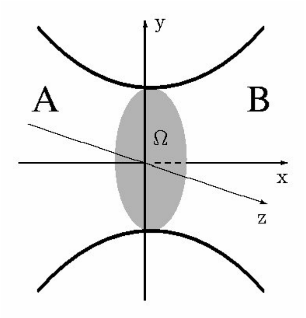

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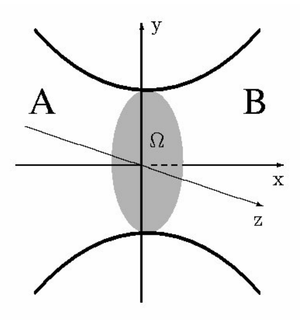

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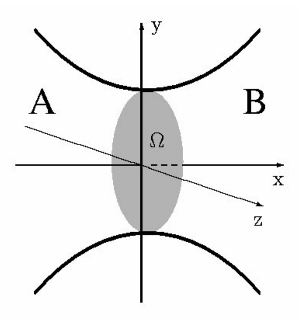

The principle of TST

Probability density to find a particle within the transition state multiplied by the particle velocity yields the stream. The number of passing particles per time unit is

$$\frac{\mathrm{d}N}{\mathrm{dt}} = \int_\Omega j(\vec{s})\,\mathrm{d}\Omega = \int_\Omega n(\vec{s})\,v_x(\vec{s})\,\mathrm{d}\Omega$$

Integration over the dividing surface Ω.

3 Transition State Theory

Otherwise the total number of particles in state A is

given by the partition function $N = \int_A n(\vec{s})\,\mathrm{dV}.$

Hence, the rate is

$$\frac{1}{N}\frac{\mathrm{dN}}{\mathrm{dt}} = \frac{\int_\Omega n(\vec{s})\,v_x(\vec{s})\,\mathrm{d}\Omega}{\int_A n(\vec{s})\,\mathrm{dV}}$$

Replacing $v_x(\vec{s})$ by the average particle velocity in x–direction

$$\int_0^\infty v_x\,f(v_x)\,\mathrm{d}v_x = < v_x >_+ = \sqrt{\frac{k_B T}{2\pi m}}$$

the rate cofficient k is

$$k = \frac{1}{N}\frac{\mathrm{d}N}{\mathrm{d}t} = < v_x >_+ \frac{\int_\Omega n(\vec{s})\,\mathrm{d}\Omega}{\int_A n(\vec{s})\,\mathrm{d}V}$$

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3 Transition State Theory

In this basic formula of TST the partition function ratio

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is the key quantity that must be evaluated.
In MD the evaluation of the numerator is done by considering a volume δV, which is a sheet of thickness δ over Ω. Hence,

$$\int_\Omega n(\vec{s})\,\mathrm{d}\Omega = \lim_{\delta\to 0}\frac{1}{\delta}\int_{\delta V} n(\vec{s})\,\mathrm{d}V$$

$$k = < v_x >_+ \lim_{\delta\to 0}\frac{1}{\delta}\frac{\int_{\delta V} n(\vec{s})\,\mathrm{d}V}{\int_A n(\vec{s})\,\mathrm{d}V}$$

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- Applicability of the diffusion equation in porous materials
- Local Boltzmann distribution in the pores
- D_S increasing with increasing concentration
- Influence of the cations on diffusion of neutral molecules
- D_S decreasing with increasing temperature
- Role of the lattice flexibility in MOF's

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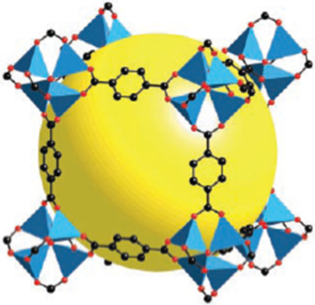
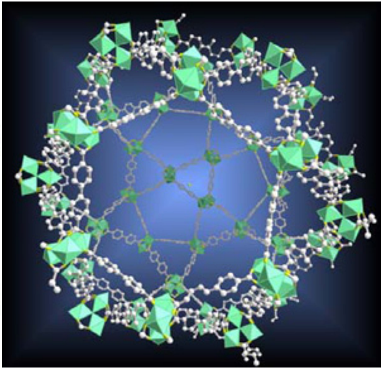
5 Metal Organic Frameworks (MOF)





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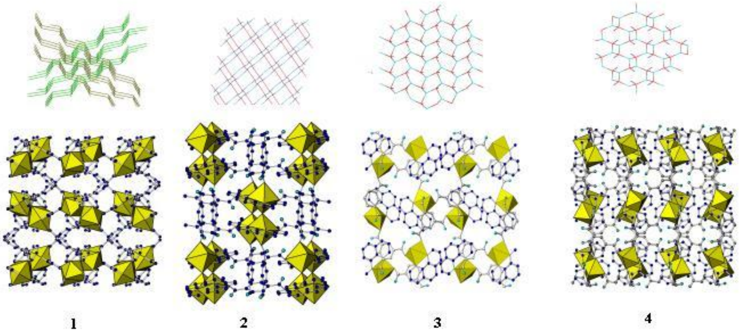

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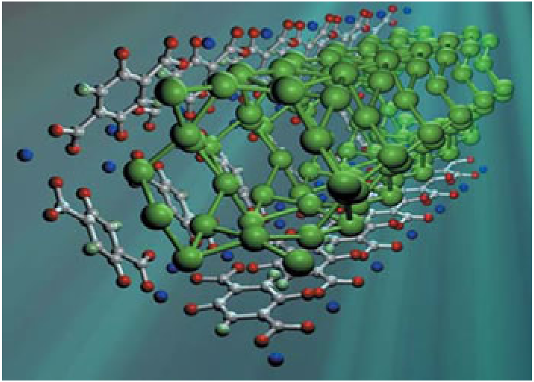

- Ethane in Zn(tbip)
- Diffusion of CH_4 and H_2 in ZIF-8

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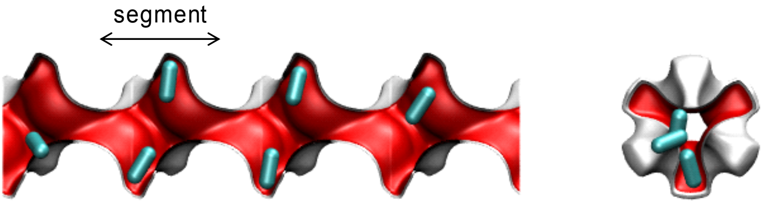
6 Selected applications from the last 2 years

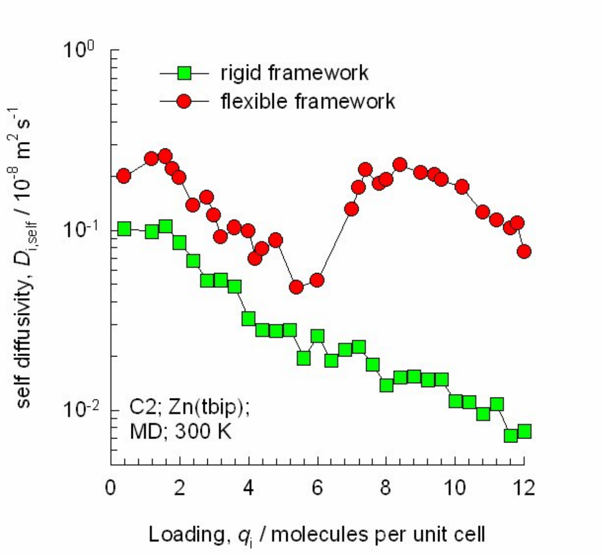
- Ethane in Zn(tbip)
- Diffusion of CH_4 and H_2 in ZIF-8

6.1 Diffusion of Ethane in Zn(tbip)

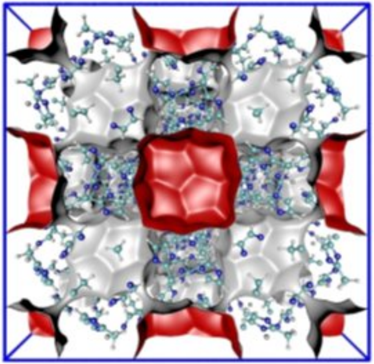
Snapshots of C2 in Zn(tbip)

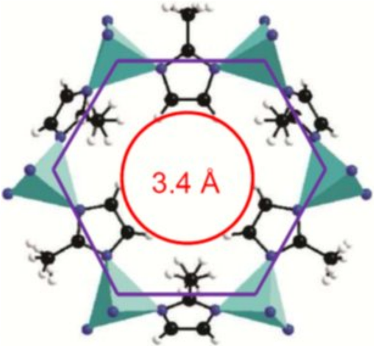


6.1 Diffusion of Ethane in Zn(tbip)



ZIF's are Zeolitic Imidazolate Frameworks. ZIF-8 has a cubic structure similar to zeolites of type LTA.

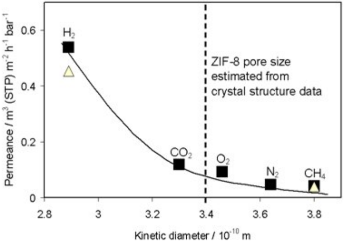


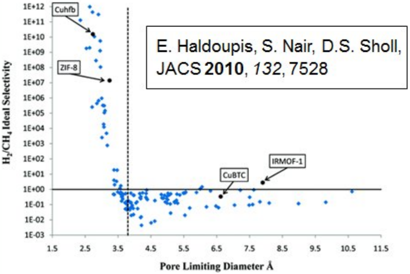


6.2 Diffusion of CH_4 and H_2 in ZIF-8

Membrane diffusion versus simulation with rigid lattice:

Evaluation of ZIF Membrane Separation Performance



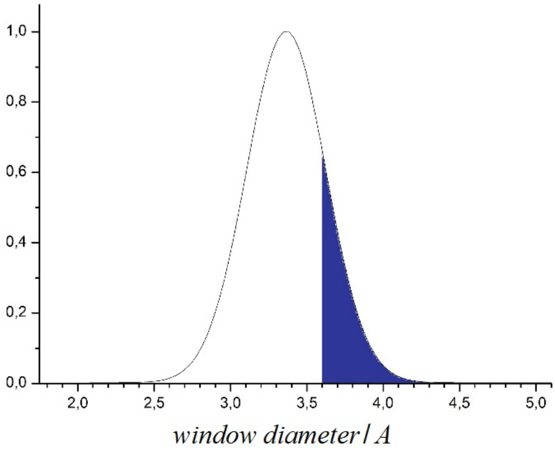


- Separation of Small Molecules
- Separation Factors up to 16 (H_2 / CH_4)
- Reasonable Permeances
- Good Thermal and Chemical Stability

Sharp Cut-offs as Predicted by Sholl and Co-workers have never been Observed
$\Rightarrow$ Framework Dynamics have to be Considered in Simulations

6.2 Diffusion of CH_4 and H_2 in ZIF-8

Probability distribution of the window diameter in ZIF-8



7 DFG projects

Two projects are running from which we have students position

- International research training group (IRTG 1056)
- Priority Program SPP 1362, Metal Organic Frameworks

8 International partnerships

- Chulalongkorn University Bangkok, Thailand (Prof. S. Hannongbua (dean), Dr. O. Saengsawang, Dr. R. Channajaree)
- Prof. P. Bopp (University of Bordeaux, France)
- Prof. D. Theodorou (University Athens/Patras, Greece)
- University of Sassari, Italy, (Prof. Suffritti, Prof. Demontis)
- Prof. S. Auerbach, University of Amhurst, USA

Thanks!

Thank you for your attention!