Molecular modelling and simulation of electrolyte solutions, biomolecules, and wetting of component surfaces

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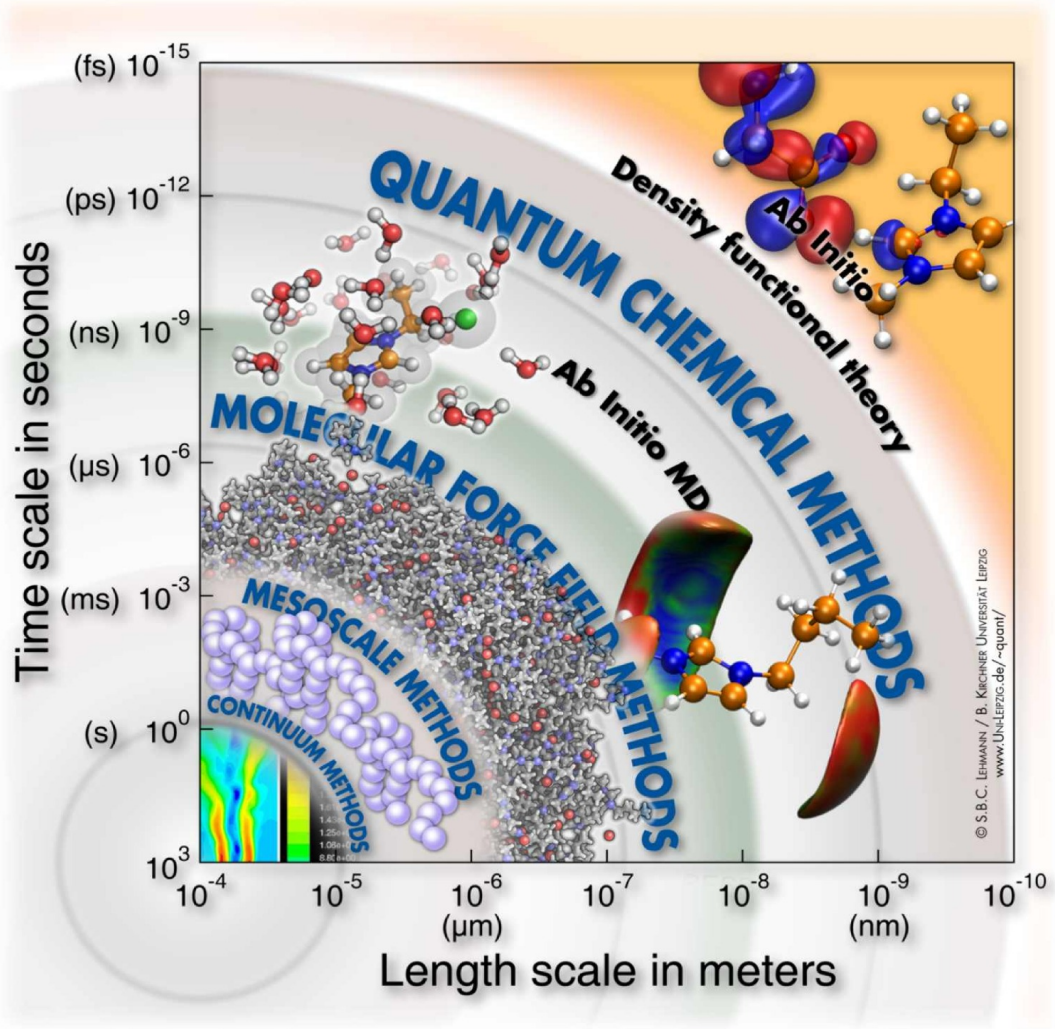
HLRS Results and Review Workshop

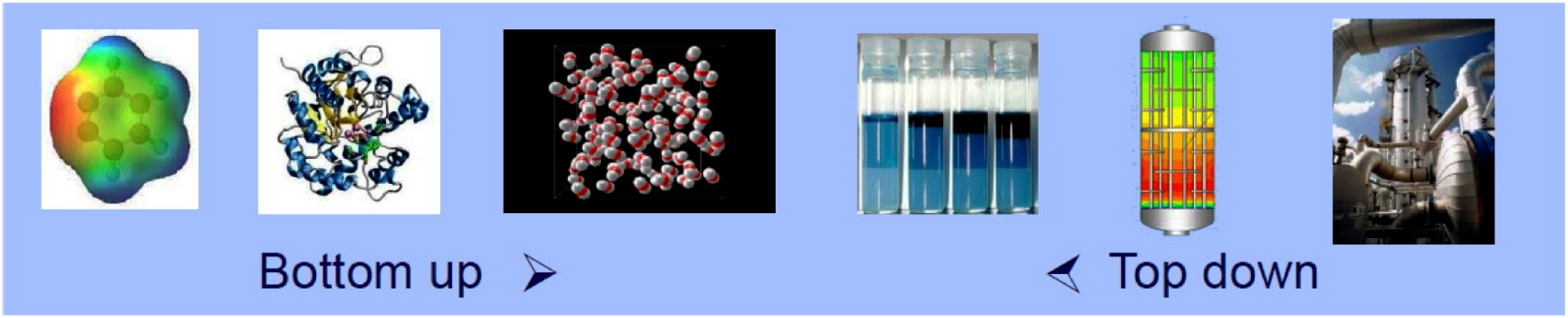
Computational Molecular Engineering

Molecular simulation: Length and time scale



- Classical force fields
- From nano- to microscale
- Molecular-level precision
- Quantitative reliability

Molecular modelling in process engineering



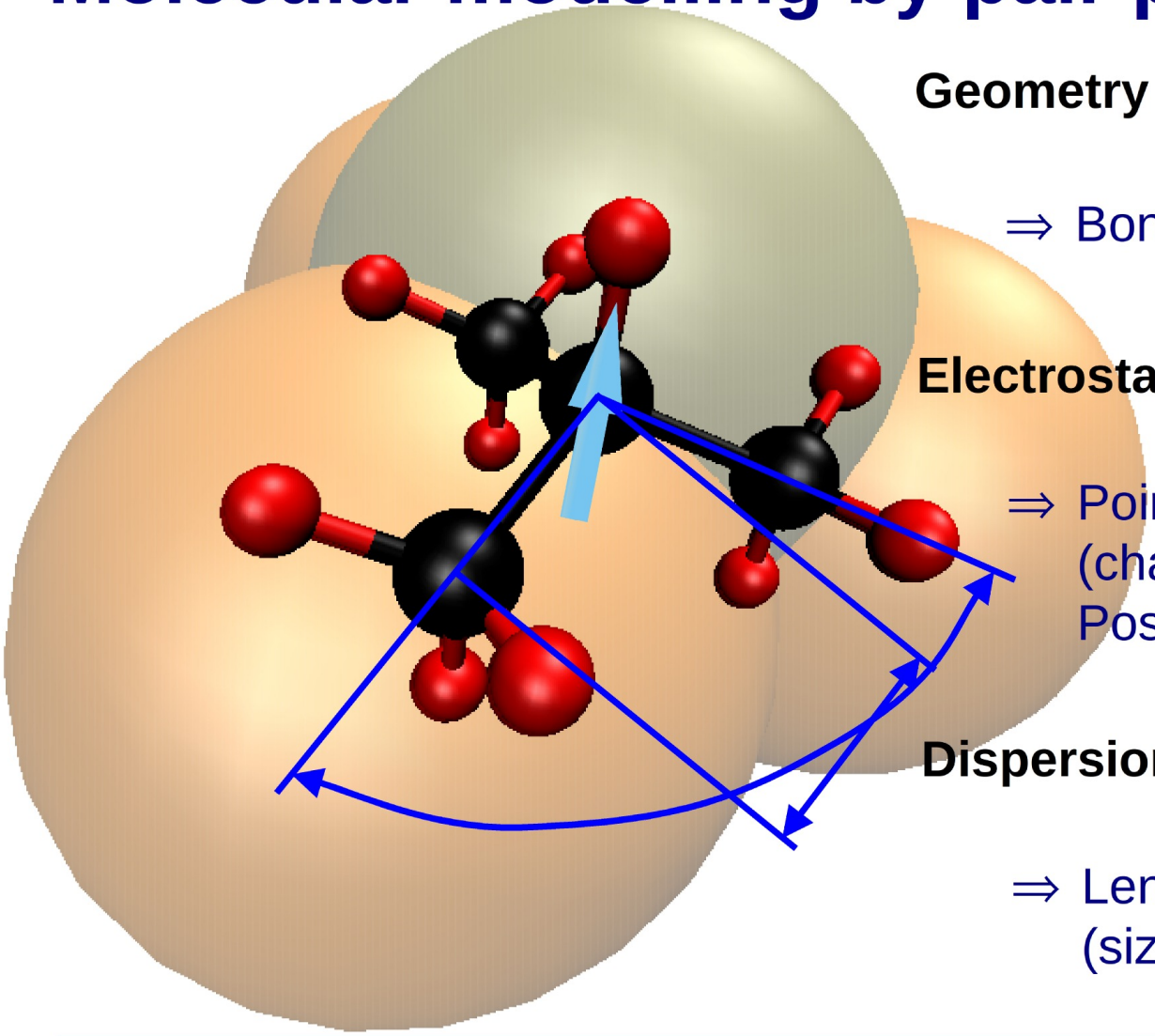
From Physics (qualitative accuracy)

- Physically realistic modelling of intermolecular interactions
- Separate contributions due to repulsive and dispersive as well as electrostatic interactions

To Engineering (quantitative reliability)

- No blind fitting, but parameters of *effective pair potentials* are adjusted to experimental data
- Physical realism facilitates reliable interpolation and extrapolation

Molecular modelling by pair potentials



Geometry

⇒ Bond lengths and angles

Electrostatics

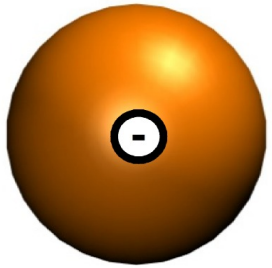
⇒ Point polarities (charge, dipole, quadrupole): Position and magnitude

Dispersion and repulsion

⇒ Lennard-Jones potential: (size and energy parameters)

Modelling aqueous electrolyte solutions

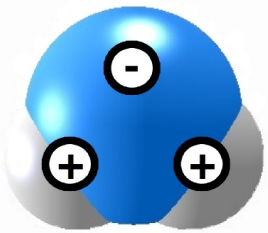
Molecular models:



Ions

1 Lennard-Jones

1 point charge



Water (here: SPC/E)

1 Lennard-Jones

3 partial charges

Literature models:

- Scattering of model parameters

Parameters for Na^+:

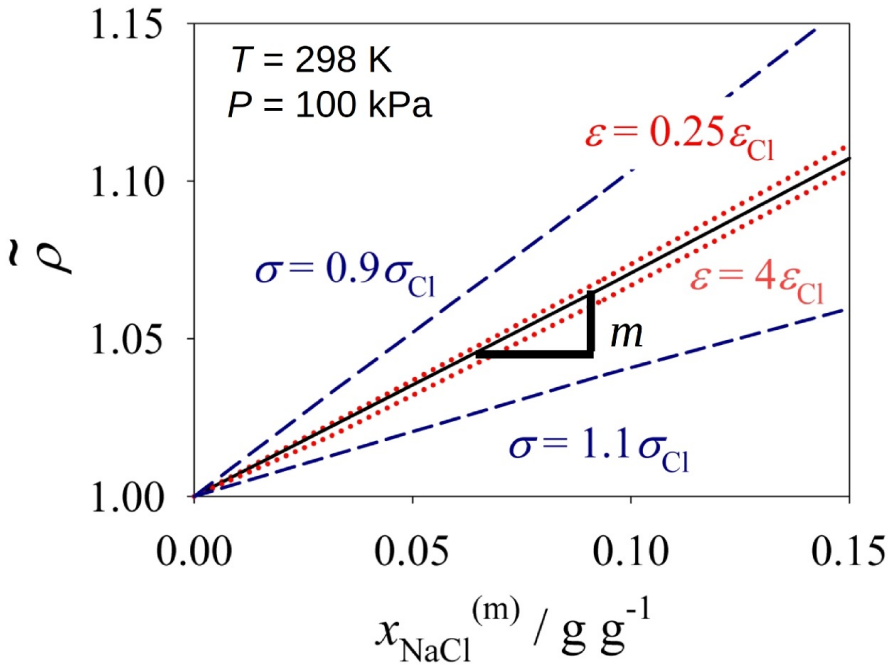
$1.9 < \sigma_{Na+} / Å < 4.1$

$0.06 < \varepsilon_{Na+} / K < 1068.8$

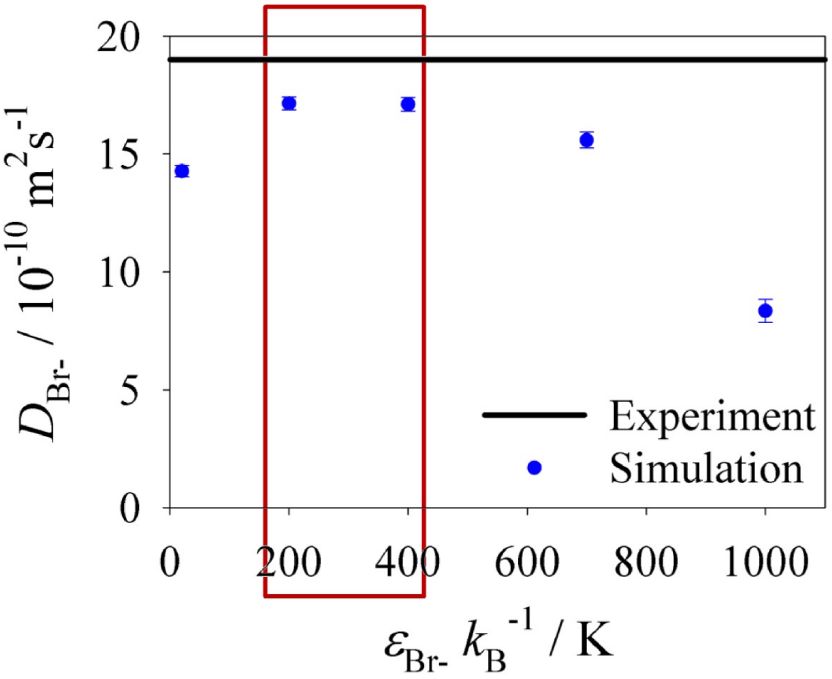
⇨ Large deviation from experimental data!

Adjusting the model to experimental data

Density ratio “solution : pure”



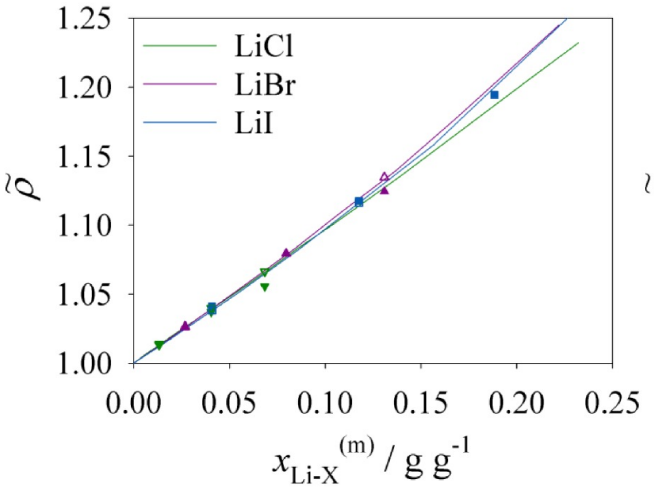
Self-diffusion coefficients

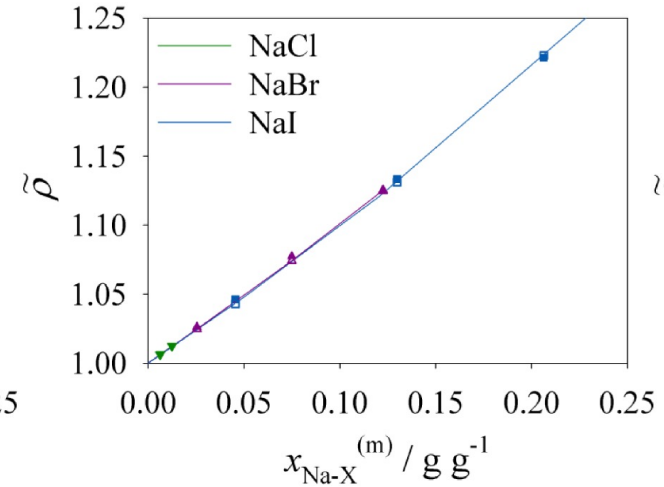


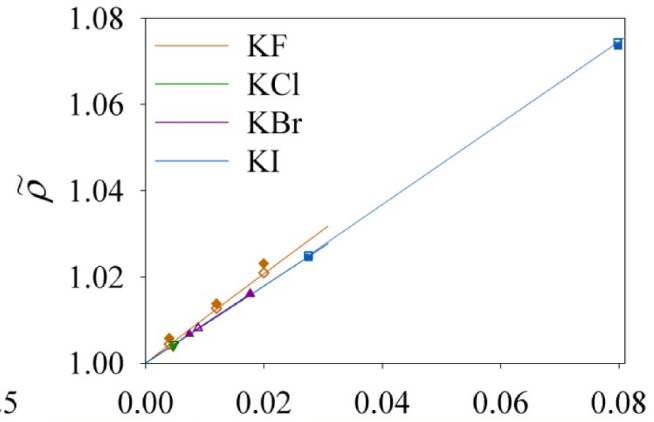
Lennard-Jones size parameter σ

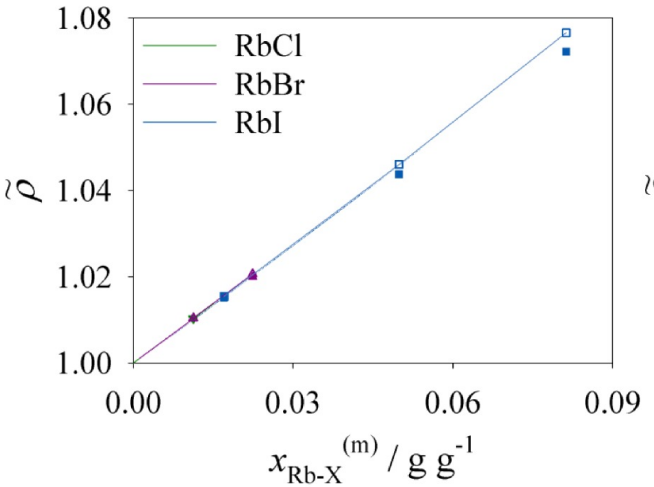
Lennard-Jones energy parameter ε

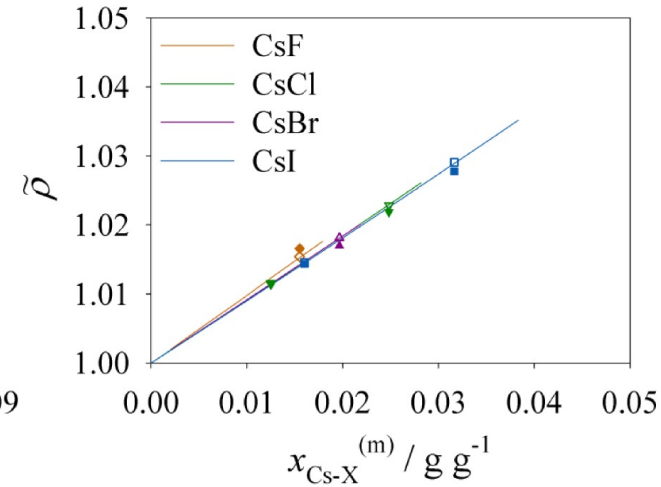
Predicted density of solutions in methanol





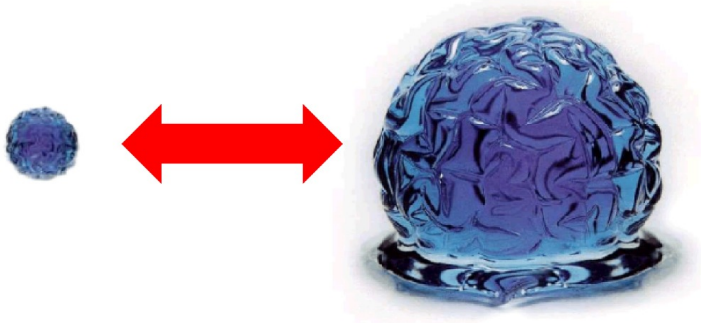






T = 298 K, P = 100 kPa

Molecular simulation of macromolecules



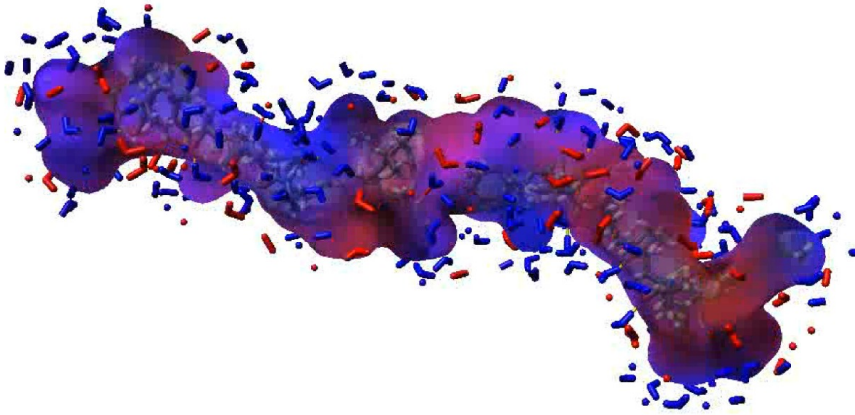
Hydrogels

- Hydrophilic polymer networks
- Transition between swollen and collapsed state permits use as absorber

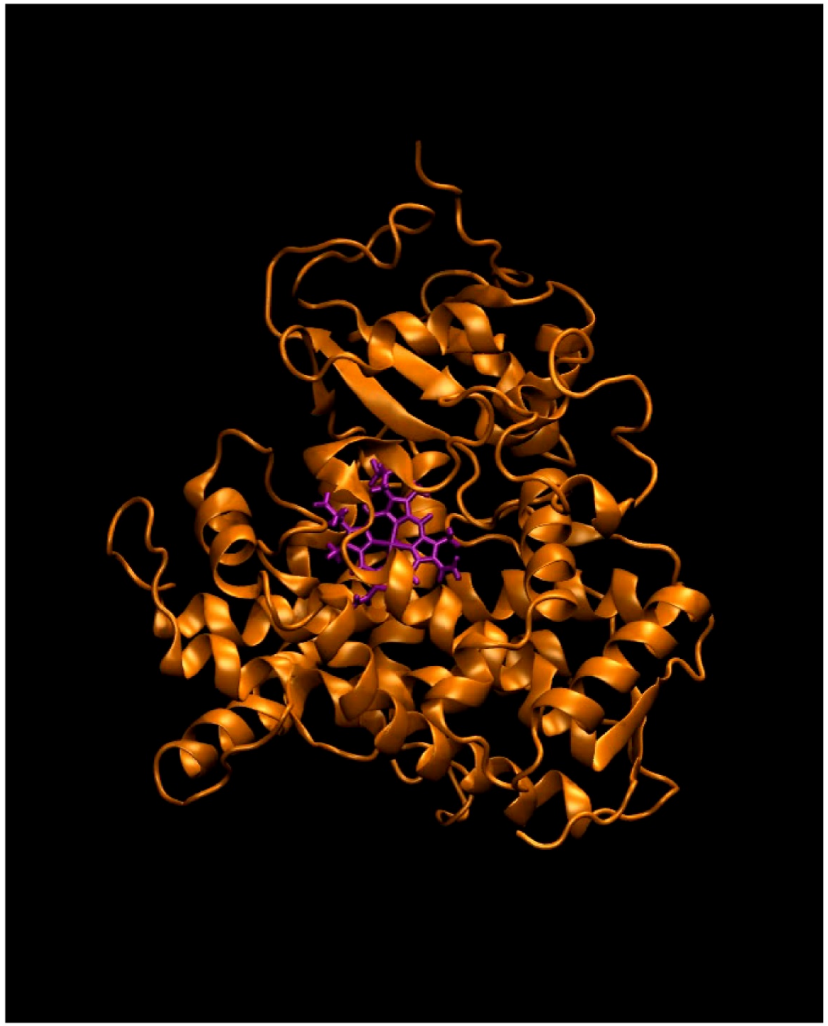
Transition between stretched and collapsed configuration of linear *poly-N-isopropylacyrlamide* chains found by molecular simulation.

The radius of gyration changes by a factor two and can be employed as an order parameter.

Water-polymer interaction can be adjusted to experimental data.



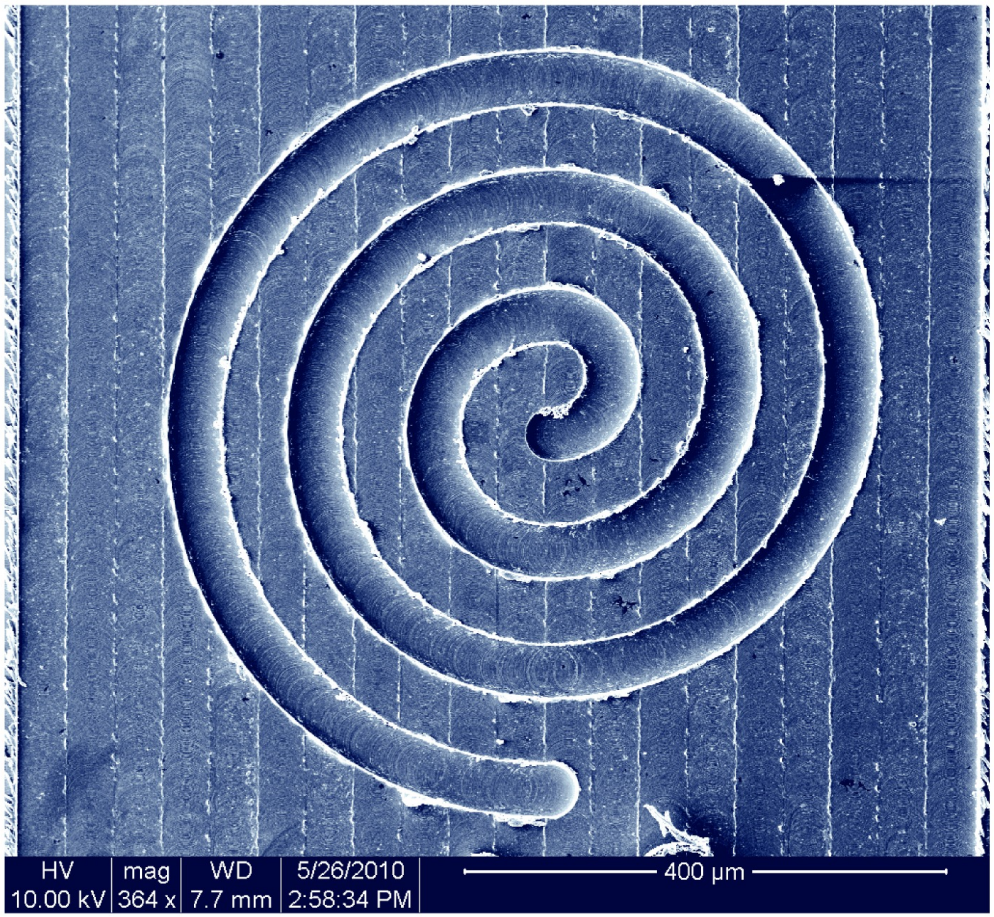
Molecular simulation of biomolecules



Enzymatically catalysed reactions

- Molecular force fields cannot directly predict chemical reactions. However, molecular simulation can cast light on relevant physical mechanisms.
- The enzyme *cytochrome P450 mono-oxygenase* acts as a catalyst for the hydroxylation of organic molecules.
- In a system containing oleic acid and water, the enzyme prefers the aqueous phase. Individual oleic acid molecules remain close to its active centre.

Adsorption at real component surfaces



Titanium components

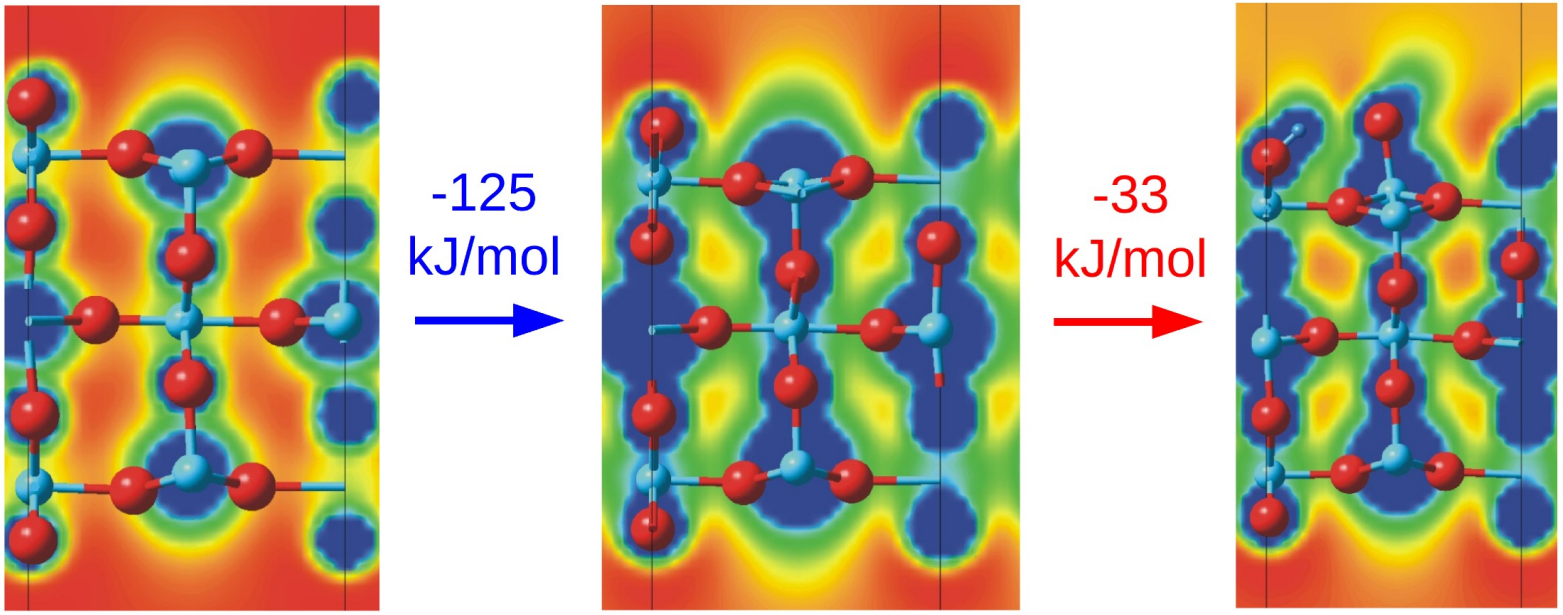
- Covered by oxide layer
- Possibly rough and/or intentionally patterned surface
- Surface may be contaminated with organic matter

First step: Reliable molecular simulation of water adsorbed on a clean and planar surface.

CRC 926 MICOS Component Surfaces

Chemisorption from quantum mechanics

Computation of the electrostatic potential:



dry rutile surface **physisorbed water** **chemisorbed water**

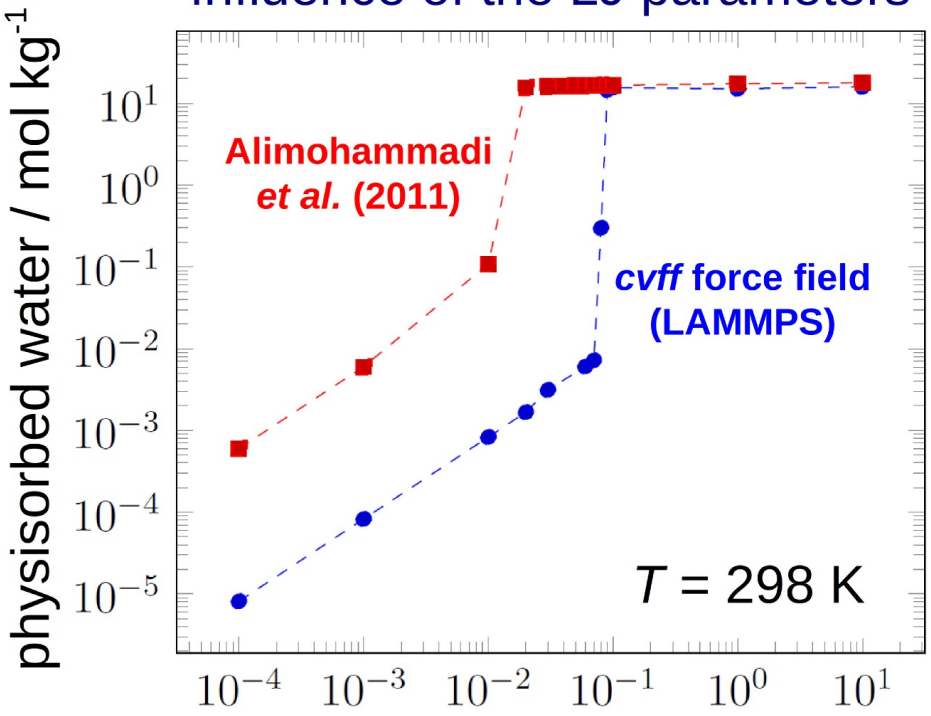
VASP simulation parameters (structure optimization with PBE functional):

Plane-wave cutoff at 282 eV, *k*-point spacing 0.5 $Å^{-1}$, *O s* pseudopotential.

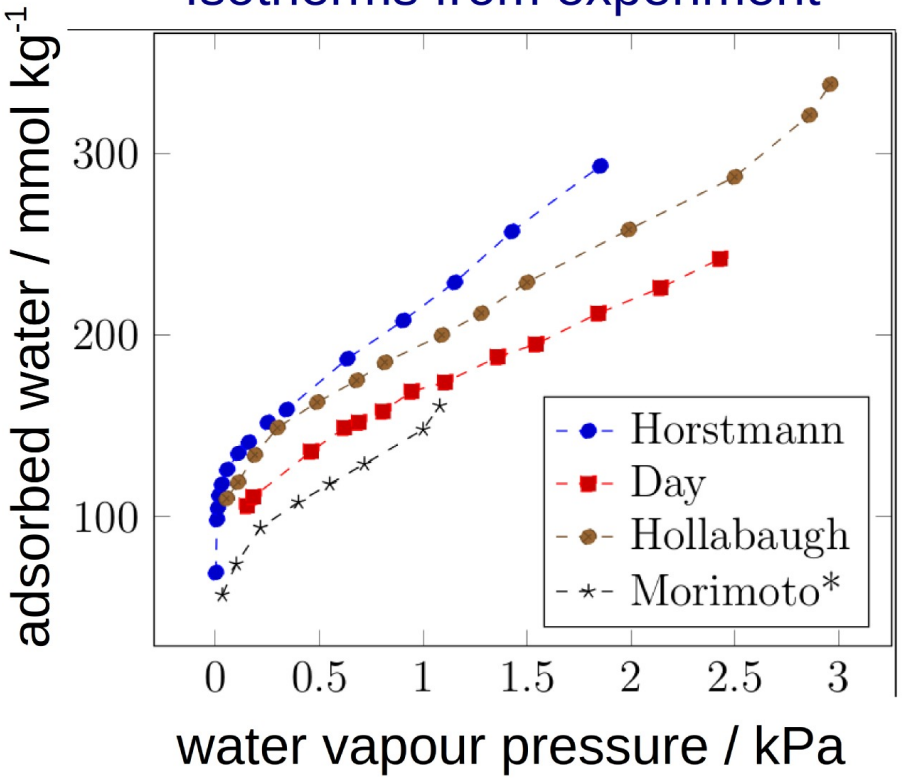
Adsorption: Grand-canonical Monte Carlo

- Electrostatic grid from VASP
- Lennard-Jones parameters from literature

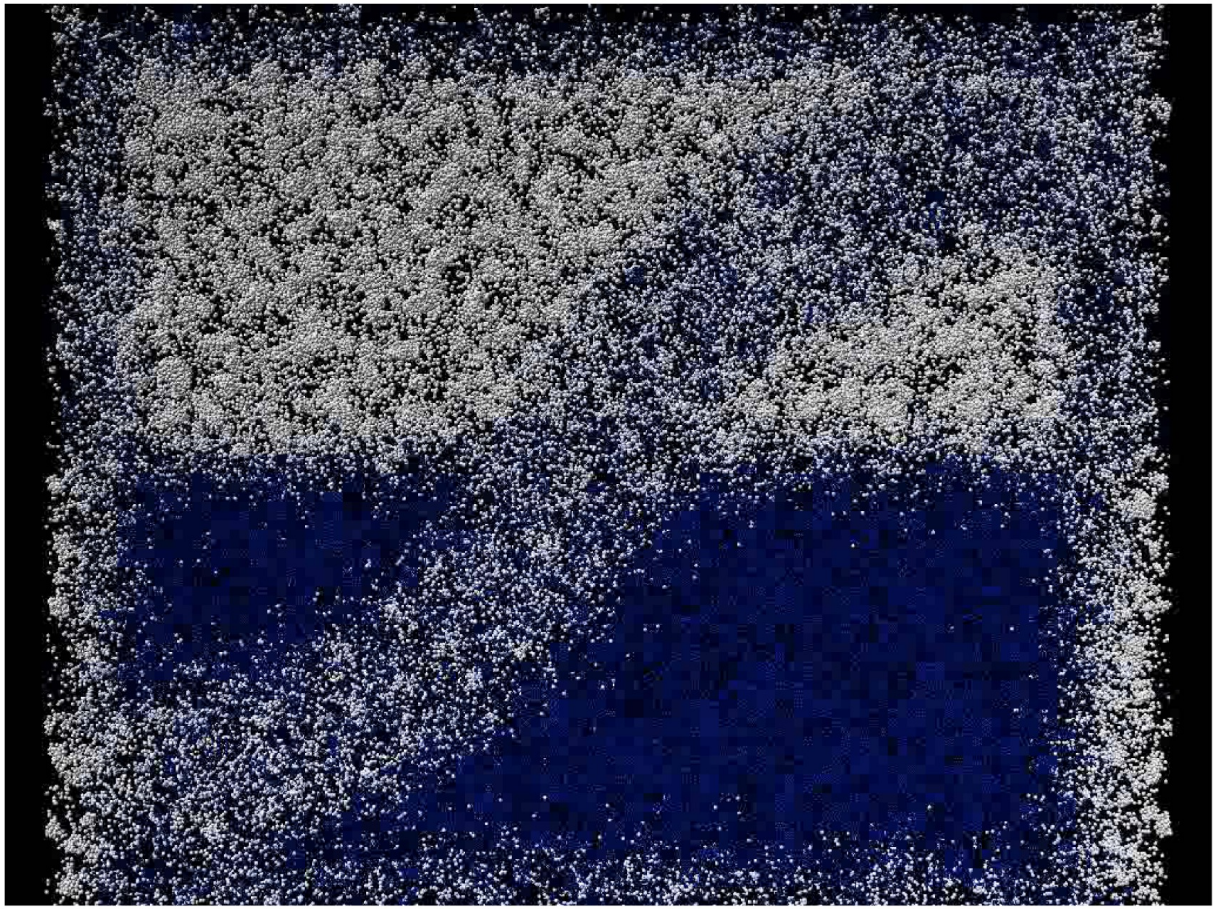
Influence of the LJ parameters



Isotherms from experiment



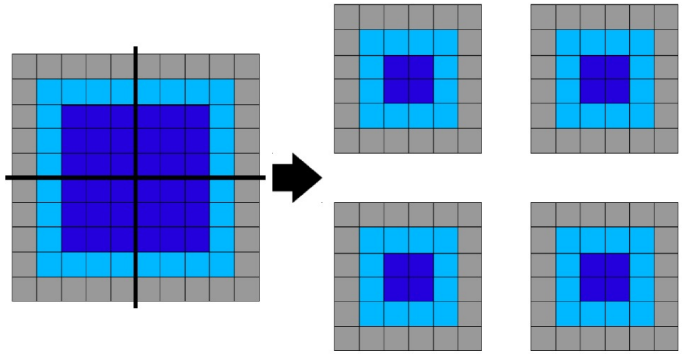
Molecular dynamics with *ls1 mardyn*



MD code for simulations of interfaces, processes, and large systems.

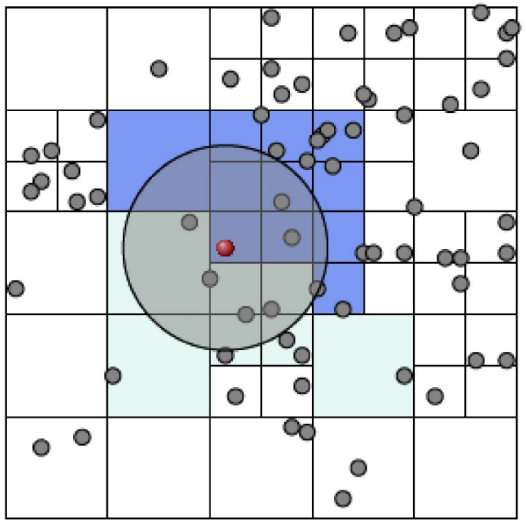
Scalable massively-parallel MD simulation

Linked-cell data structure suitable for spatial domain decomposition:

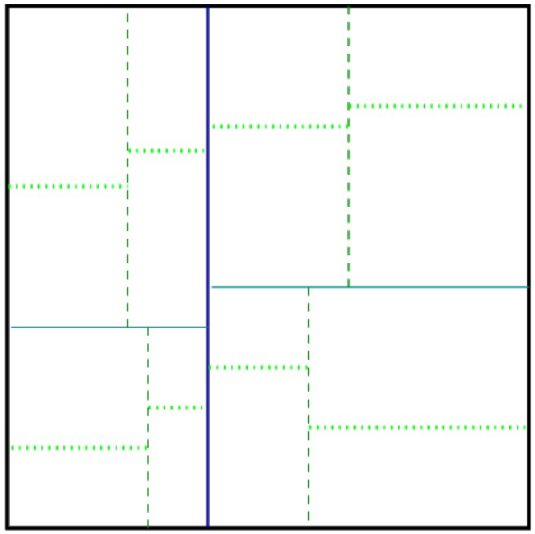


(non-blocking, overlapping MPI send/receive operations)

Methods for heterogeneous or fluctuating particle distributions:



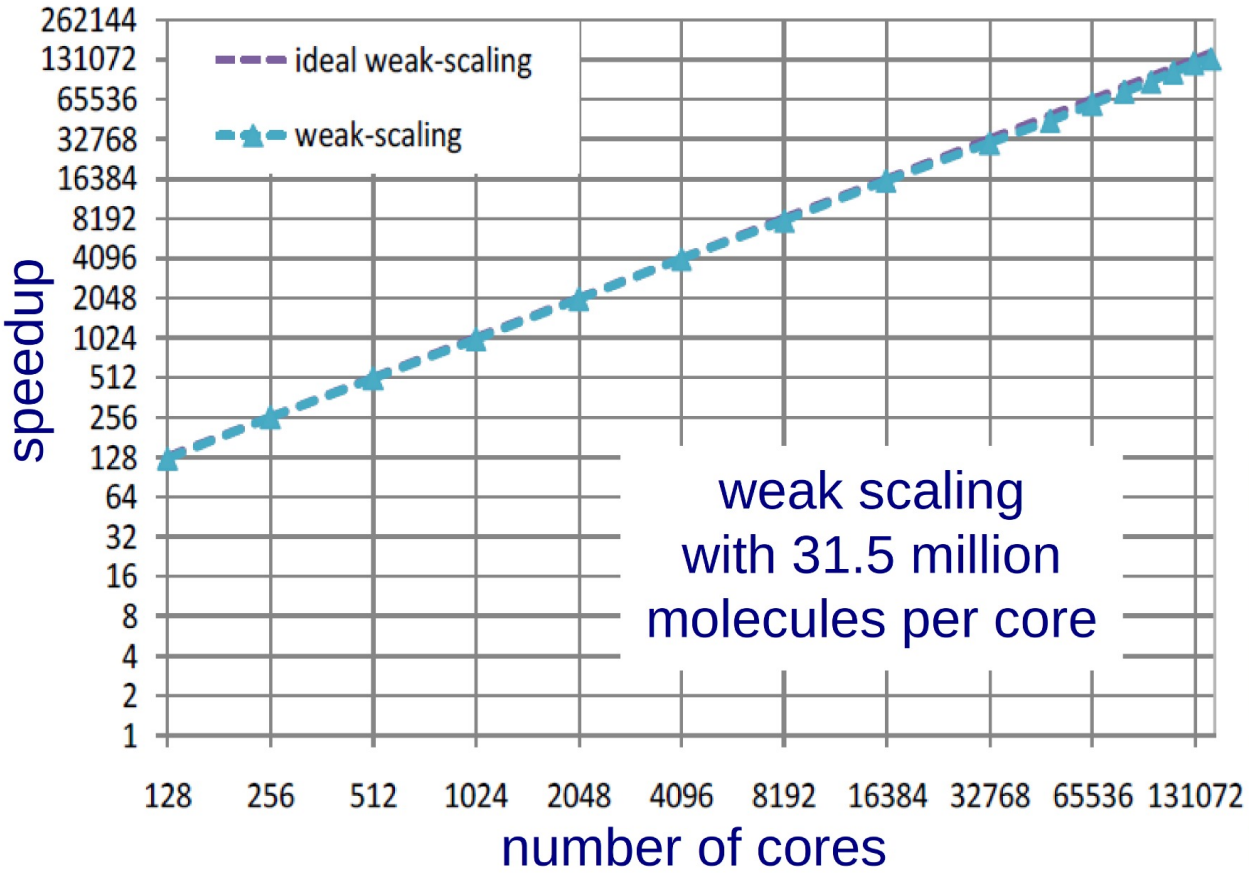
adaptive cells



k-d decomposition

Molecular dynamics world record

Up to $N = 4 \cdot 10^{12}$ molecules on SuperMUC



Conclusion

- By molecular modelling and simulation, processes can be investigated on the molecular length scale, and robust quantitative predictions can be obtained from models with few adjustable parameters.

- With computational resources from the MOCOS grant, molecular models for alkali and halide ions were developed which carry over from aqueous to non-aqueous electrolyte solutions.

- Molecular simulations of complex processes and phenomena, such as conformational transitions for macromolecules and adsorption of water on real component surfaces, were conducted, paving the way to quantitatively reliable models for these systems.

- With *ls1 mardyn*, co-developed by LTD and HLRS (among others), a MD code is available which scales well on modern supercomputing platforms.