Reliable molecular modelling and massively-parallel molecular simulation

SkaSim

CRC 926 MICOS Component Surfaces

Martin Horsch, Max Kohns, Kai Langenbach, Stephan Werth, Hans Hasse

Lehrstuhl für Thermodynamik
Technische Universität Kaiserslautern

Stuttgart, 18th June 2015
Collaborative Research Centre 716

Computational Molecular Engineering

Reliable molecular modelling and massively-parallel molecular simulation

SFB 716 “A1” memo

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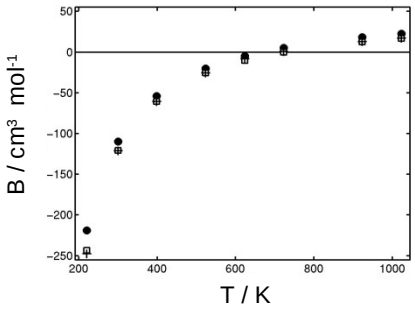
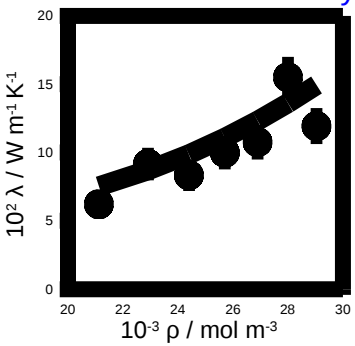
Computational Molecular Engineering

Homogeneous systems in equilibrium: ms2

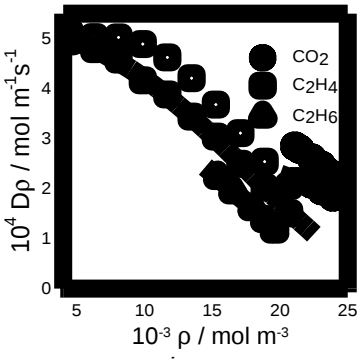
Second virial coefficient



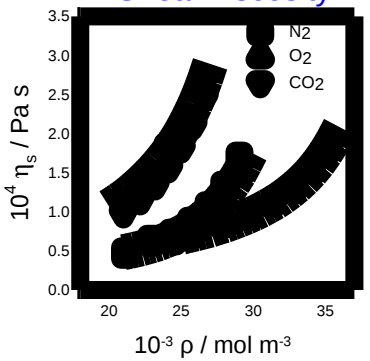
Thermal conductivity



Self-diffusion coefficient

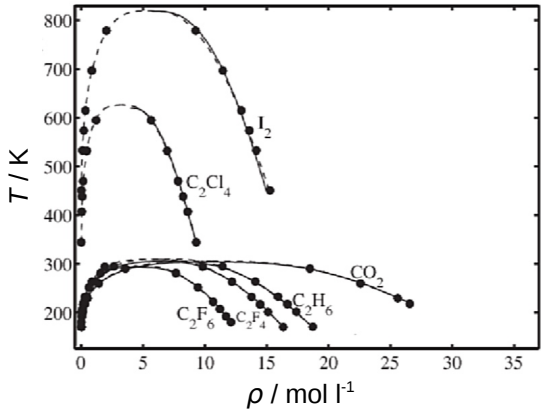


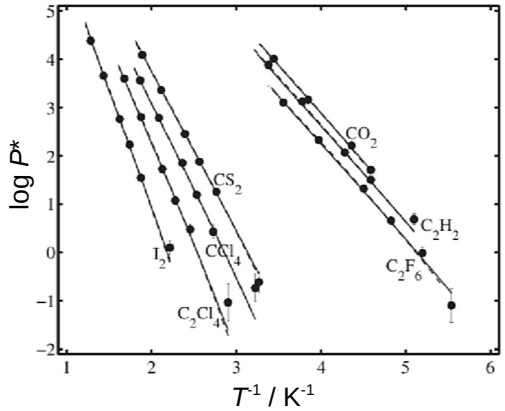
Shear viscosity



transport properties from equilibrium MD simulation

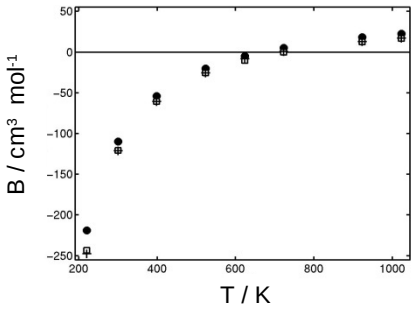
Vapour-liquid equilibira: Saturated densities and vapour pressures



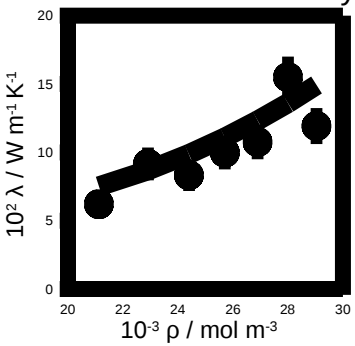


Homogeneous systems in equilibrium: ms2

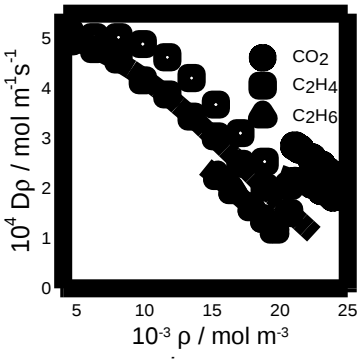
Second virial coefficient



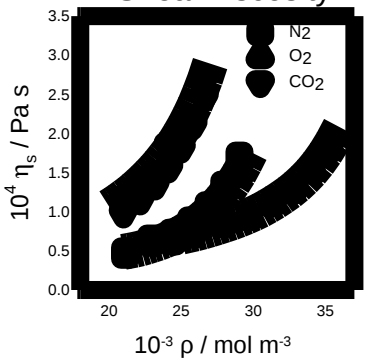
Thermal conductivity



Self-diffusion coefficient

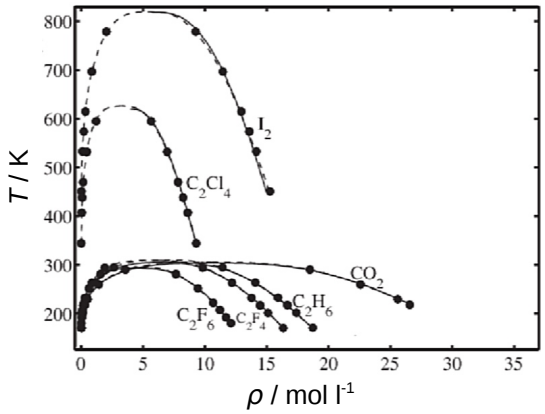


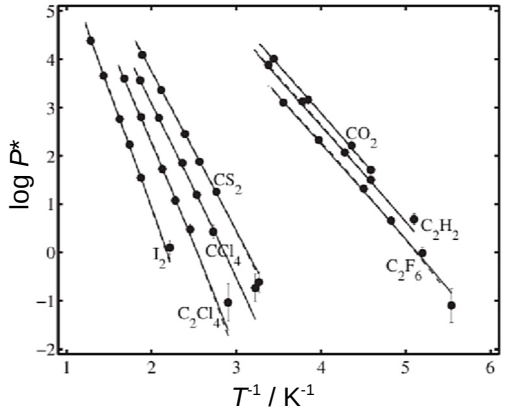
Shear viscosity



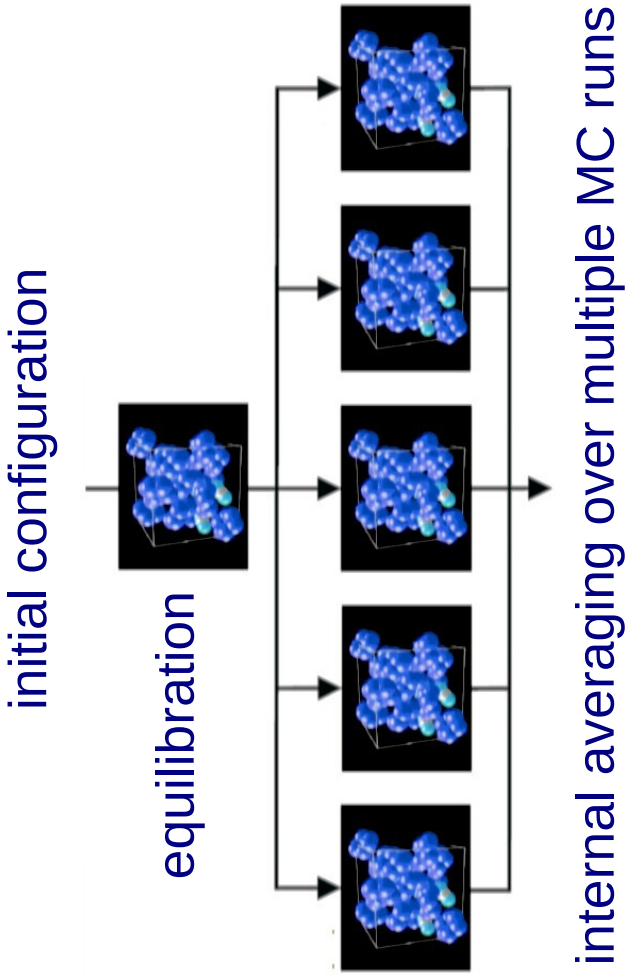
ms2 is freely available for academic use – register at http://www.ms-2.de/

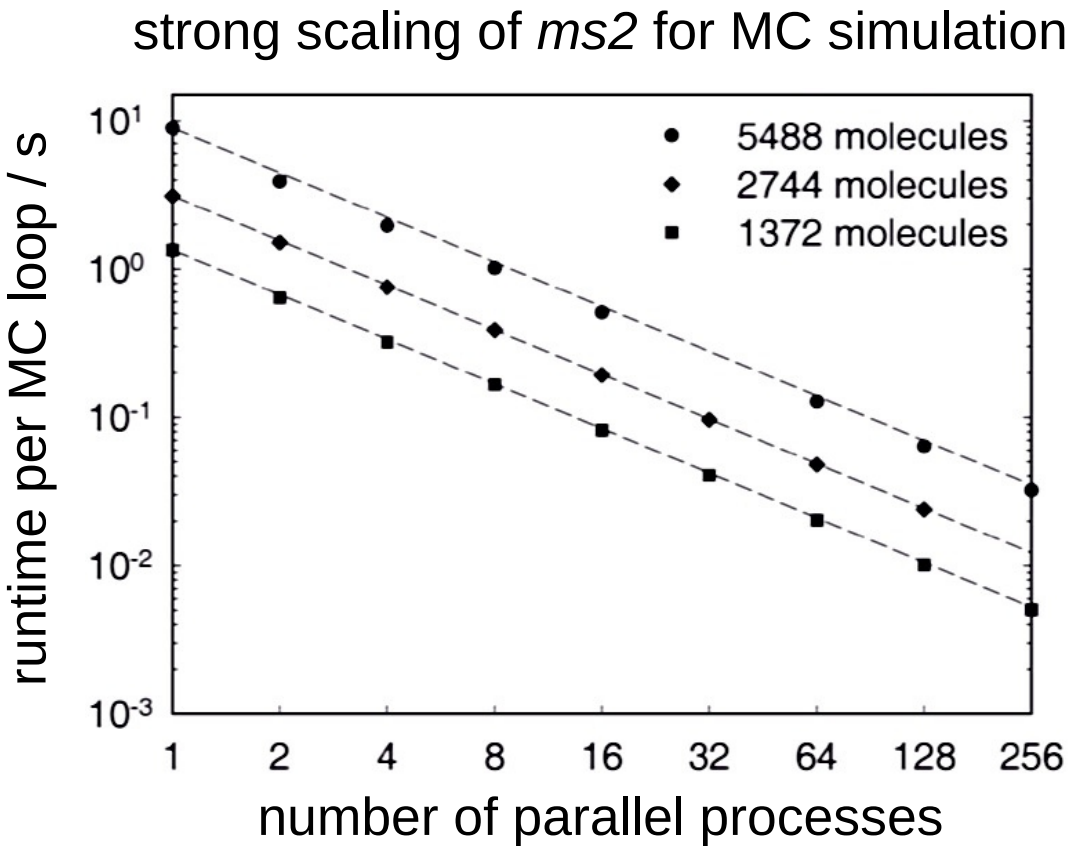
Vapour-liquid equilibira: Saturated densities and vapour pressures





Parallel sampling of configurations





Force fields for low-molecular fluids

Geometry

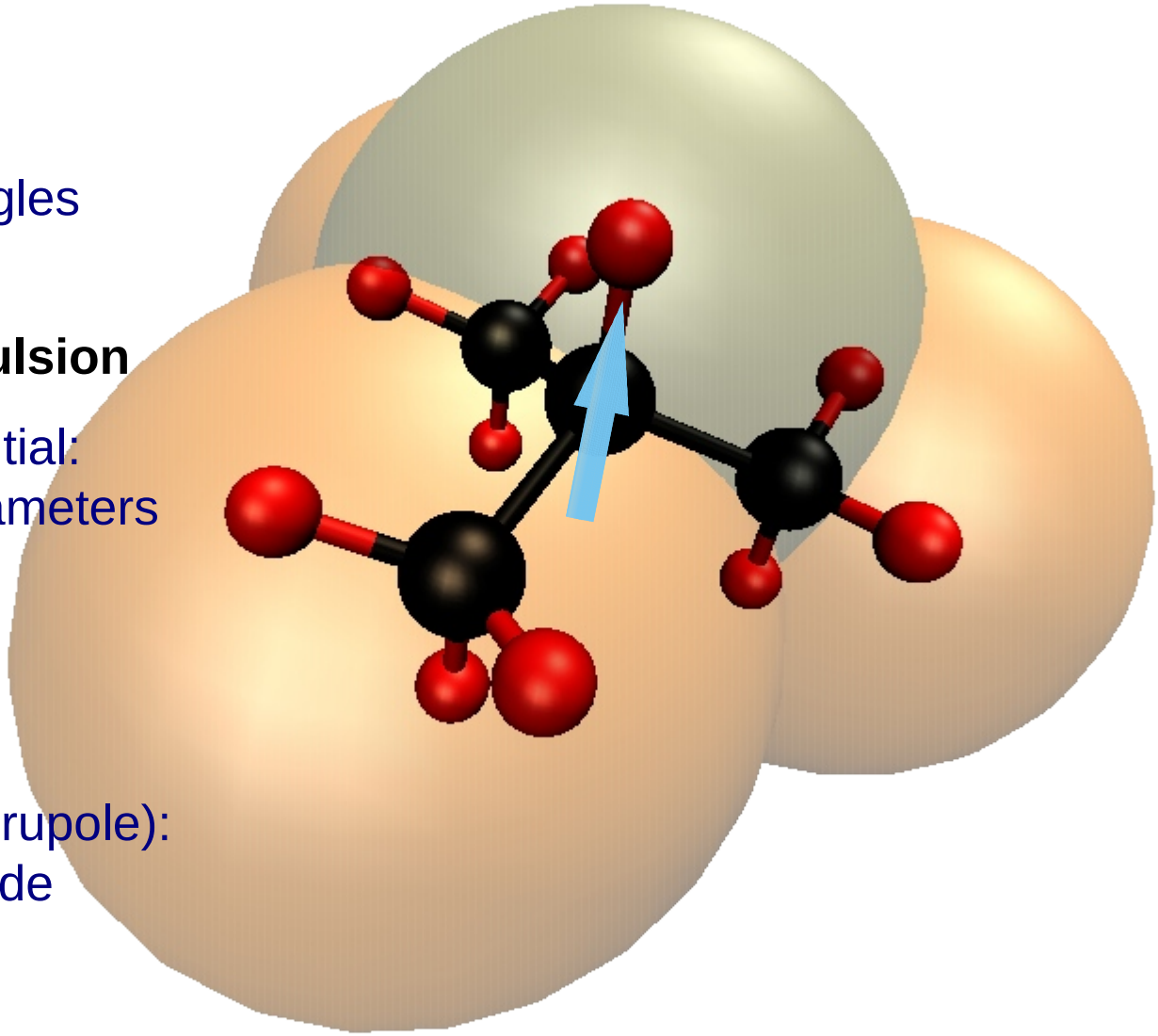
Bond lengths and angles

Dispersion and repulsion

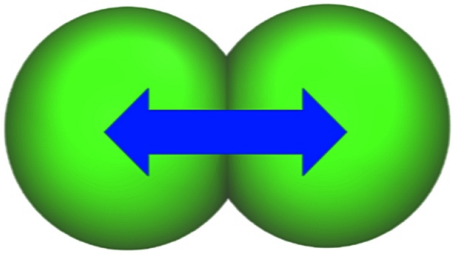
Lennard-Jones potential:
Size and energy parameters

Electrostatics

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



Parameterization of molecular models



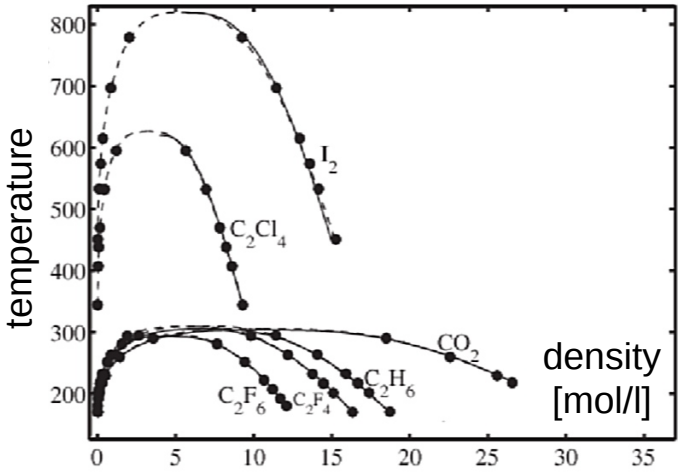
2CLJQ models:

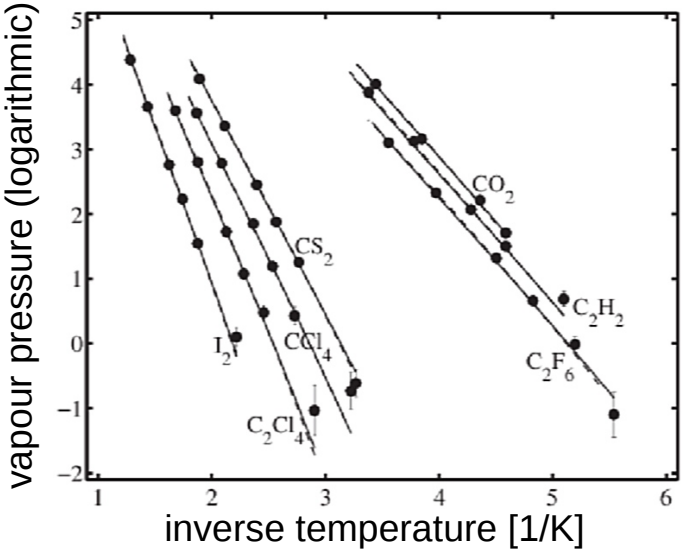
- 2 LJ centres
- Quadrupole

Fit of parameters σ, ε, L, Q to VLE data of 29 fluids by Stoll *et al.*

Deviation:

- $\delta\rho' \approx 1$ %
- $\delta P^{sat} \approx 5$ %

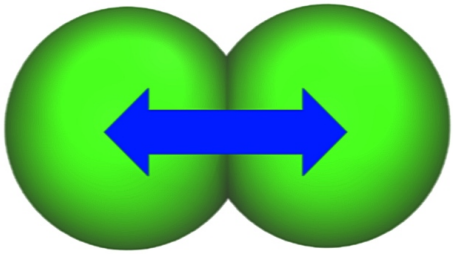




- simulation
— DIPPR correlation

No interfacial properties were considered for the parameterization.

Model validation and predictive simulations



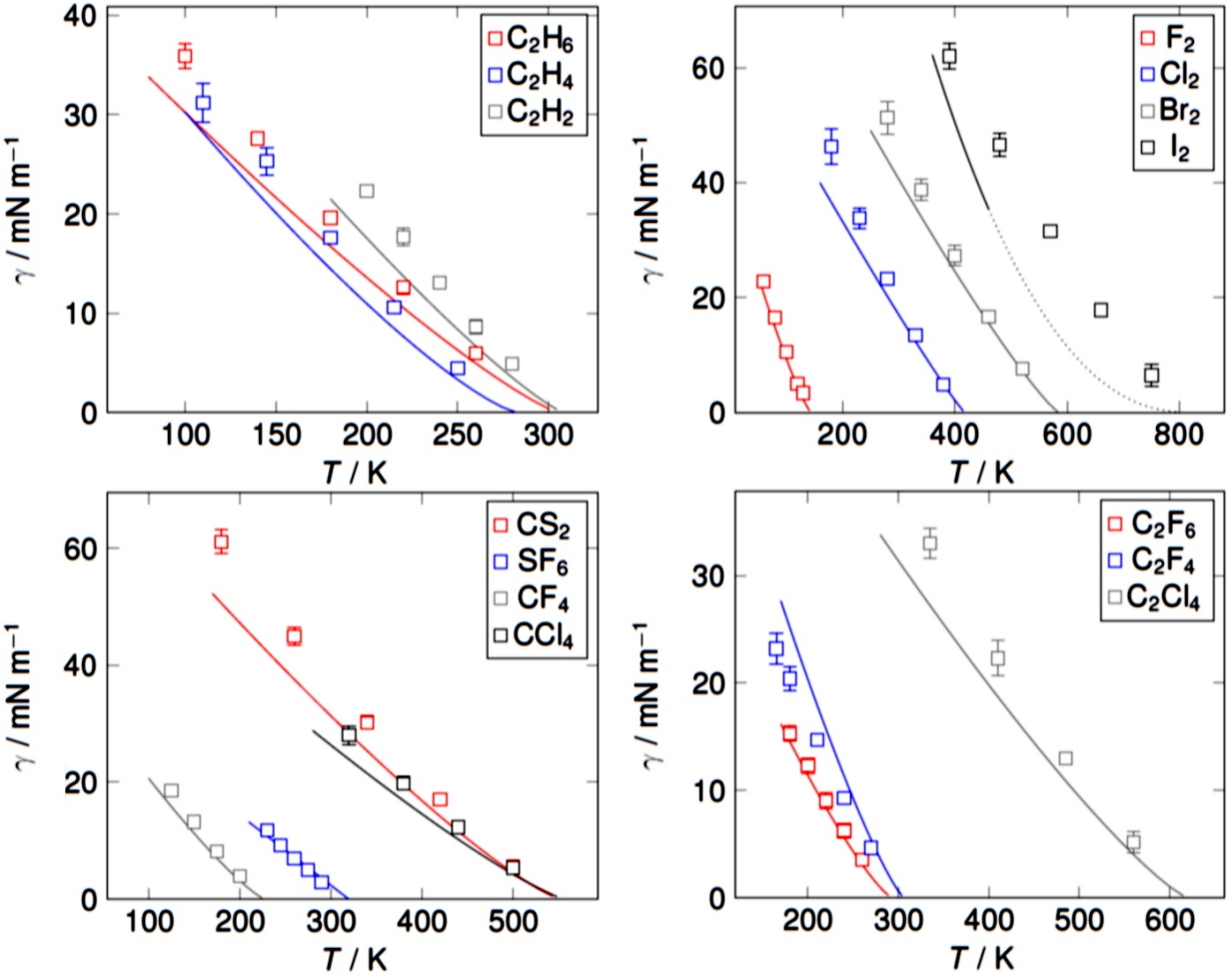
2CLJQ models:

- 2 LJ centres
- Quadrupole

Fit of parameters σ, ε, L, Q to VLE data of 29 fluids by Stoll *et al.*

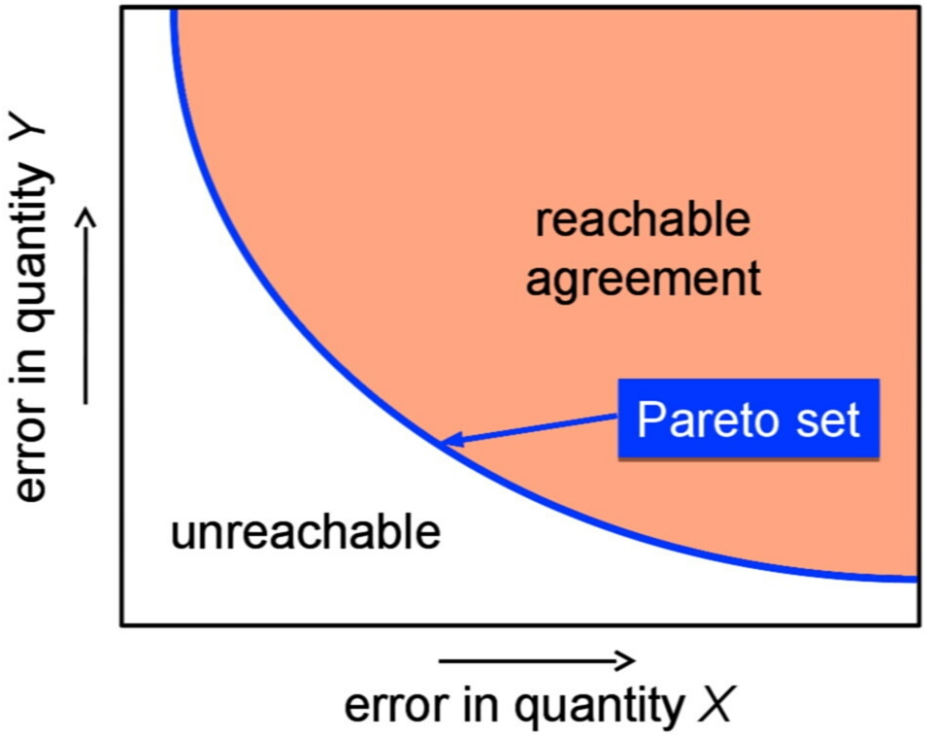
Deviation:

- $\delta\gamma \approx 10 - 20$ %

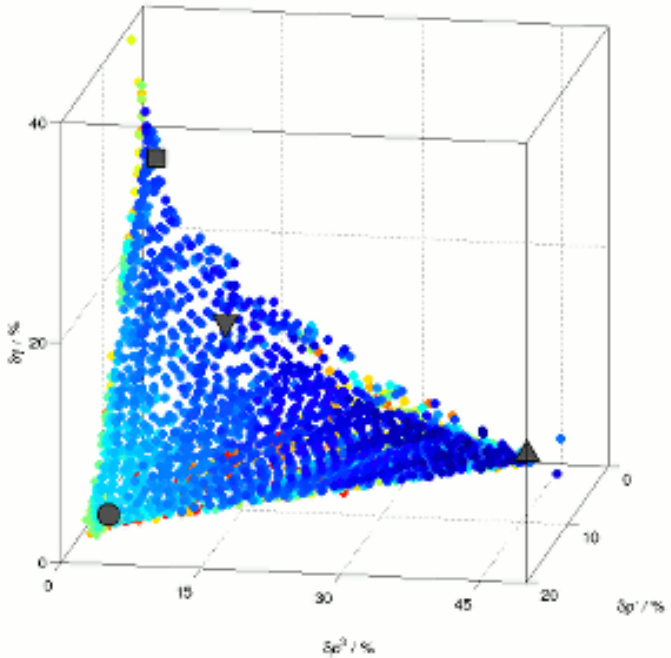


Model tailoring by multicriteria optimization

Pareto optimality criterion



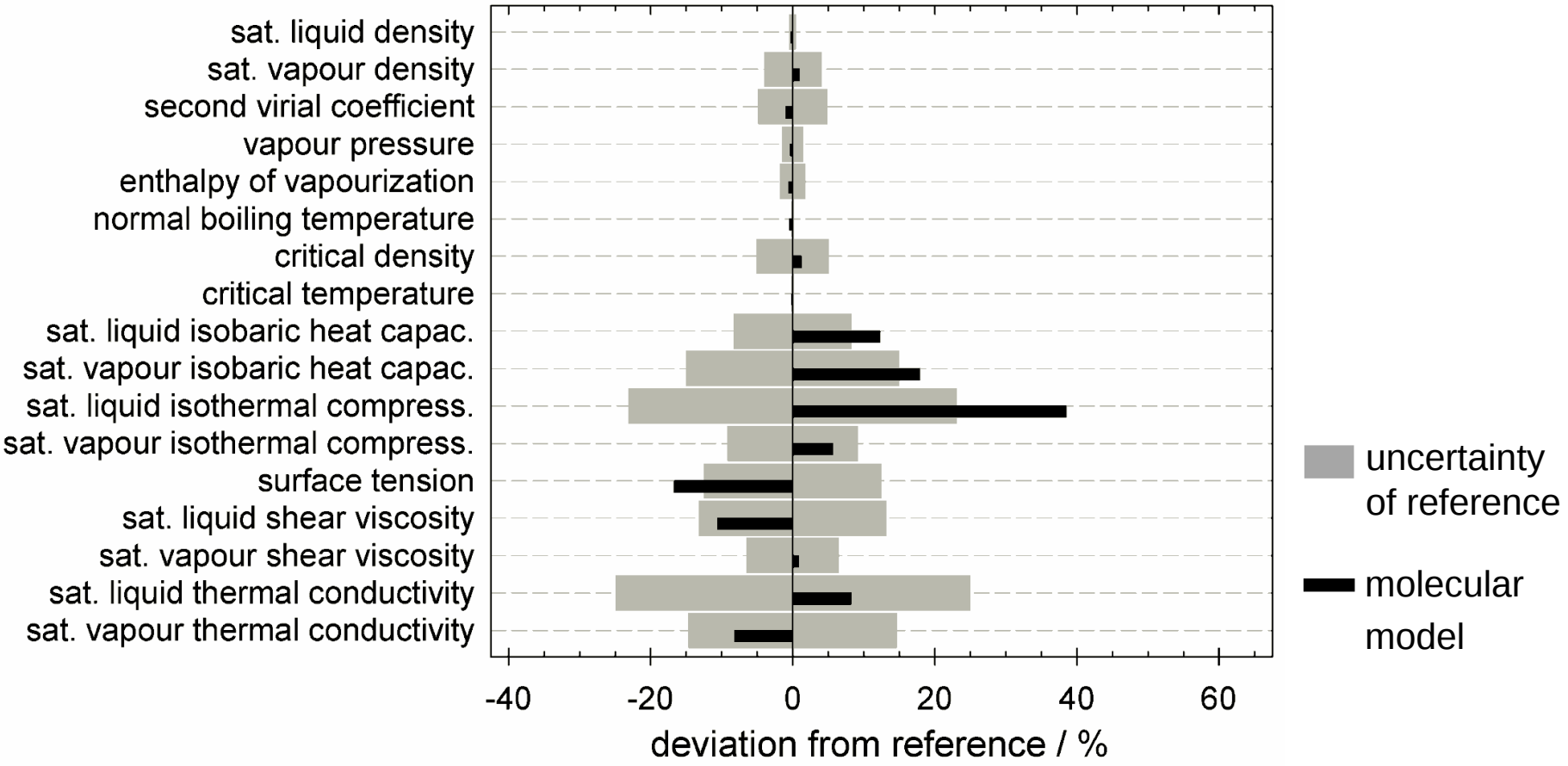
Pareto set for carbon dioxide



Multicriteria optimization requires massively-parallel molecular modelling.

Quantitative reliability of molecular models

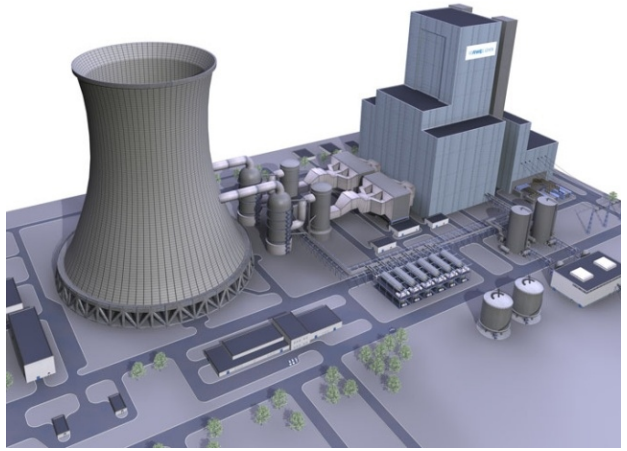
ethylene oxide model by Eckl *et al.* (2008)

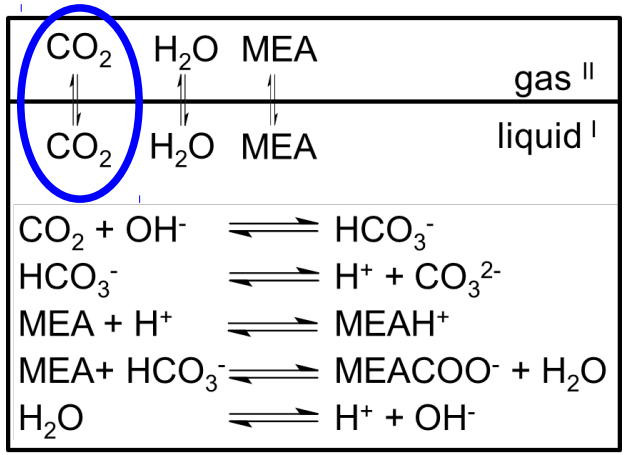


Case study: Analogy between CO_2 and N_2O

Engineering application scenario:

- Gas cleaning by reactive absorption
- Physical gas solubility of CO_2
  - Key property
  - Sometimes impossible to determine





Case study: Analogy between CO_2 and N_2O

Engineering application scenario:

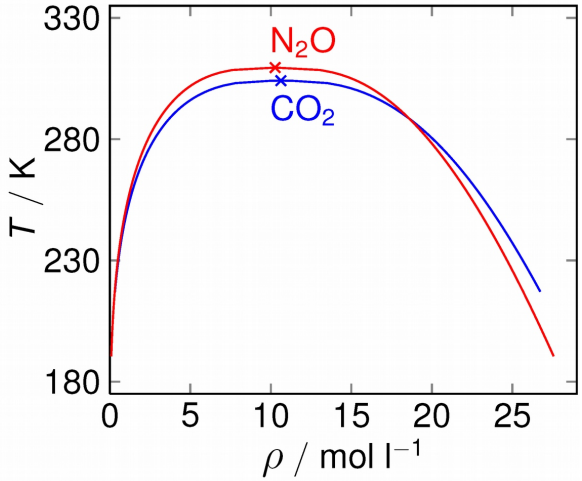
- Gas cleaning by reactive absorption
- Physical gas solubility of CO_2
  - Key property
  - Sometimes impossible to determine

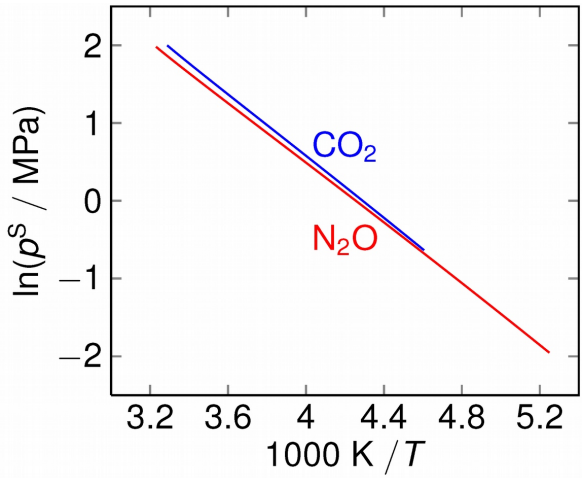
Henry's law: $Py_i = H_i x_i$

Rule of thumb for Henry's law coefficients:

- Analogy with nitrous oxide
- Assumption:

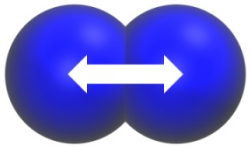
$$R_H = \frac{H_{N_2O,water}}{H_{CO_2,water}} = \frac{H_{N_2O,aqueous\ solution}}{H_{CO_2,aqueous\ solution}} = \text{const.}$$



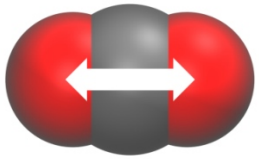


Force field for the pure fluids

Solutes

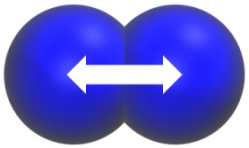


CO_2 (Vrabec *et al.*)

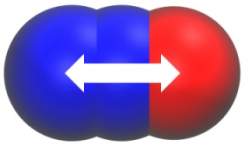


CO_2 (Merker *et al.*)

new molecular models

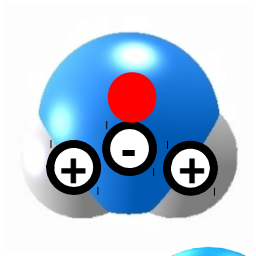


N_2O two-site model

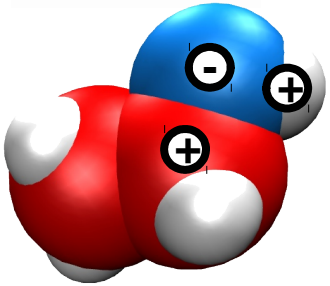


N_2O three-site model

Solvents



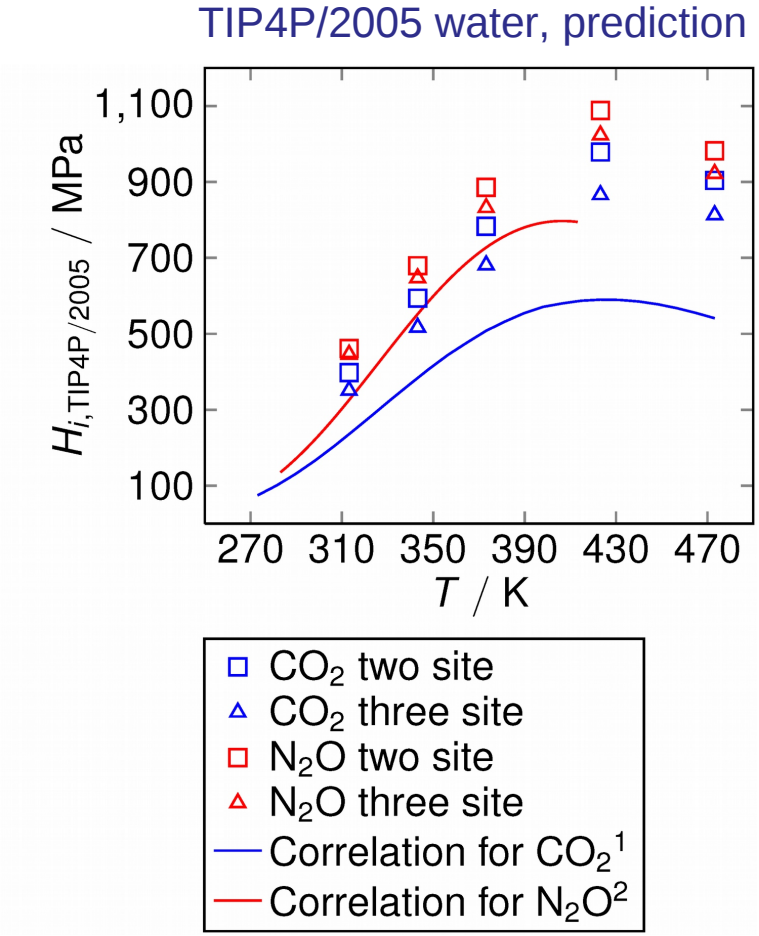
Water (TIP4P/2005)



Ethanol (Schnabel *et al.*)

Do mixed solvents containing water and ethanol behave as predicted by the CO_2-N_2O analogy?

Physical solubility in pure water



- Lorentz-Berthelot combining rule:

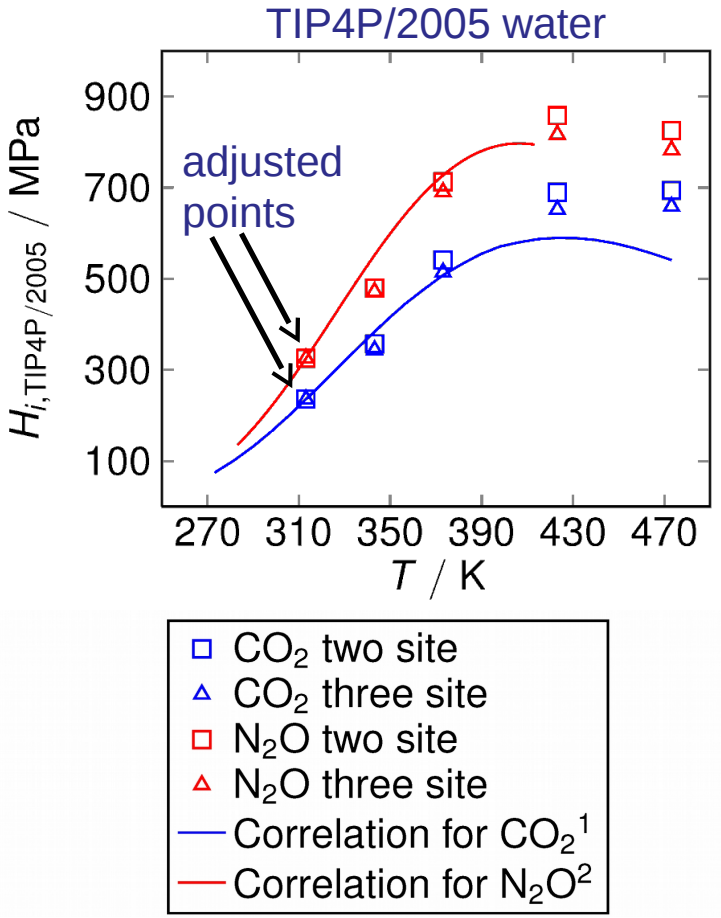
$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}$$

- Overestimation of Henry's law constant in all cases
- Adjustment of a binary interaction parameter necessary

1) Rumpf and Maurer, Ber. Bunsenges. Phys Chem. 97 (1993) 85.
2) Penttilä *et al.*, Fluid Phase Equilib. 311 (2011) 59.

Physical solubility in pure water



- Modified Lorentz-Berthelot combining rule:

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

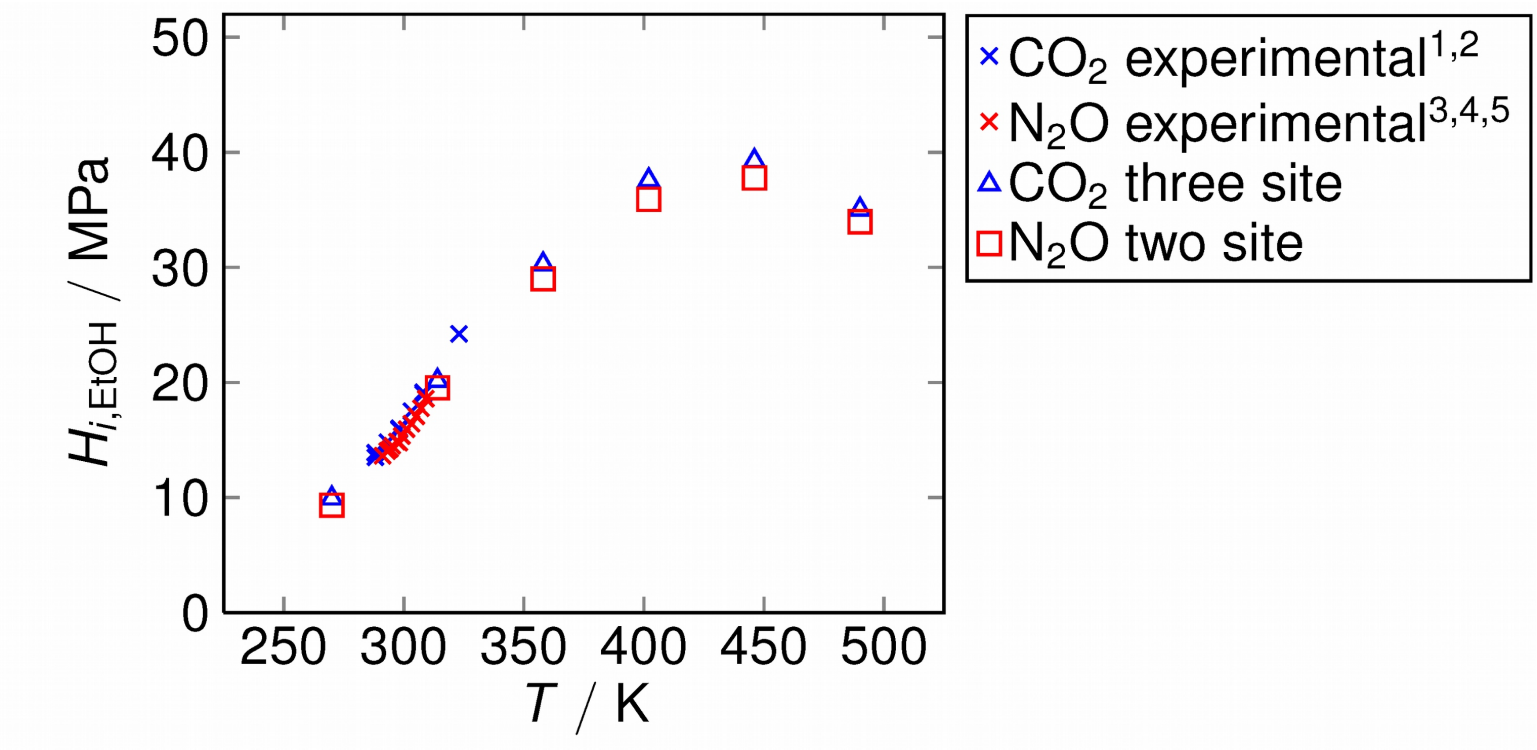
$$\epsilon_{AB} = \xi_{AB}\sqrt{\epsilon_A \epsilon_B}$$

- Temperature dependence is well captured by all models
- Best agreement for two-site model of N_2O and three-site model of CO_2

1) Rumpf and Maurer, Ber. Bunsenges. Phys Chem. 97 (1993) 85.
2) Penttilä *et al.*, Fluid Phase Equilib. 311 (2011) 59.

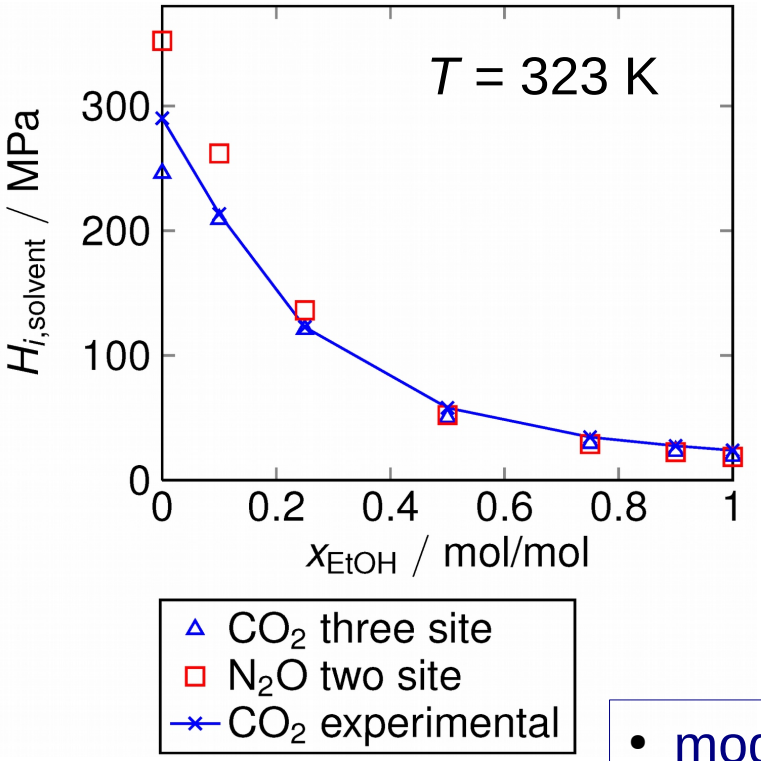
Solubility in pure ethanol

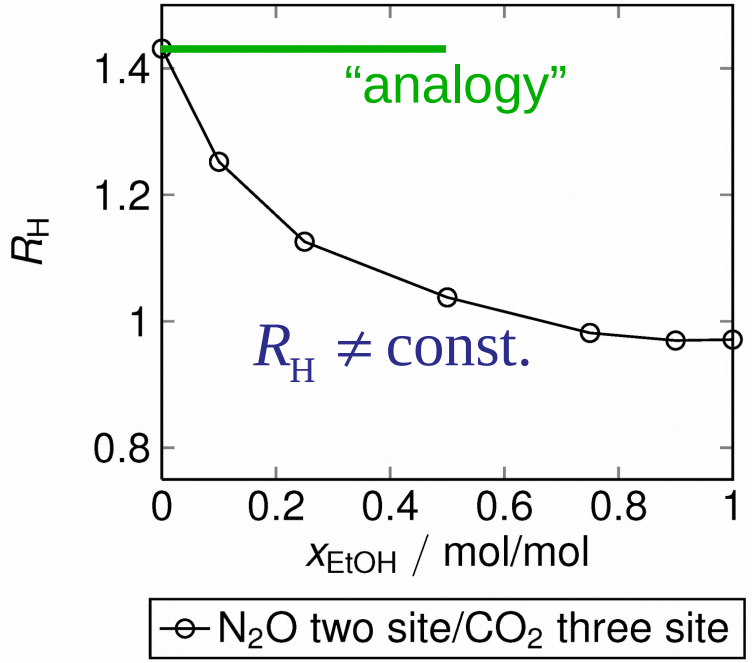
Predictive simulations, i.e. $\xi_{ab} = 1$ in all cases



1) Postigo and Katz, J. Solution. Chem. 16 (1987) 1015; 2) Dalmolin et al., Fluid Phase Equilib. 245 (2006) 193; 3) Kunerth, Phys. Rev. 19 (1922) 512; 4) Sada et al., Ind. Eng. Chem. Fundam. 14 (1975) 232; 5) Hsu and Campbell, Aerosol Age 9 (1964) 34.

Physical solubility in the mixed solvent



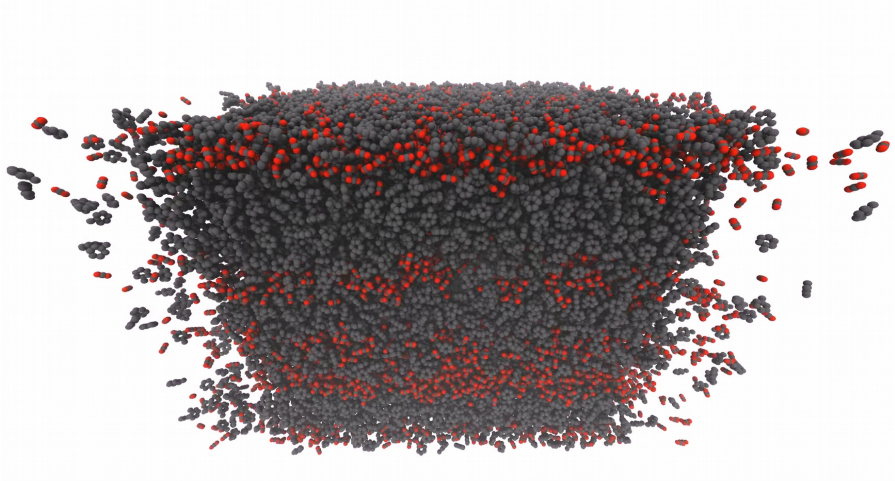


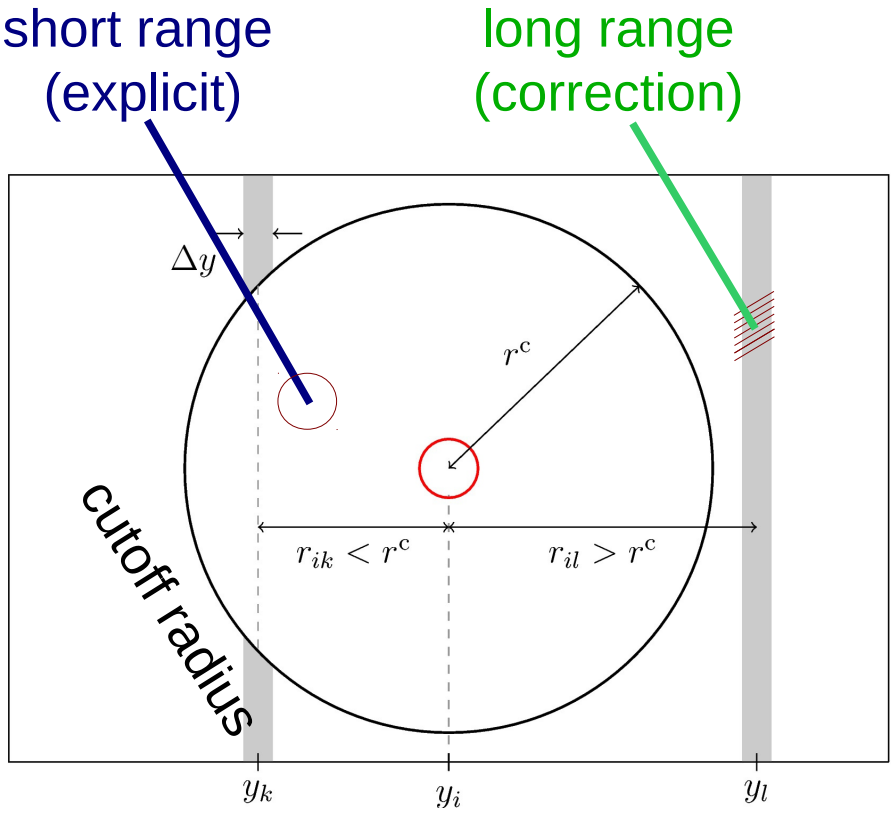
- models adjusted to solubility in pure water
- validated for pure EtOH (both), mixture (CO_2)
- predictive use: breakdown of the "analogy"

Efficient simulation of fluids at interfaces

For planar interfaces:

Long-range correction from the density profile, following **Janeček**.



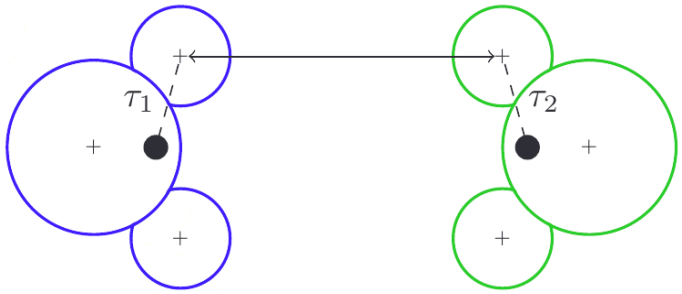


Full evaluation of all pairwise interactions is too expensive ...
... instead, **short-range interactions** are evaluated for **neighbours**.

Efficient simulation of fluids at interfaces

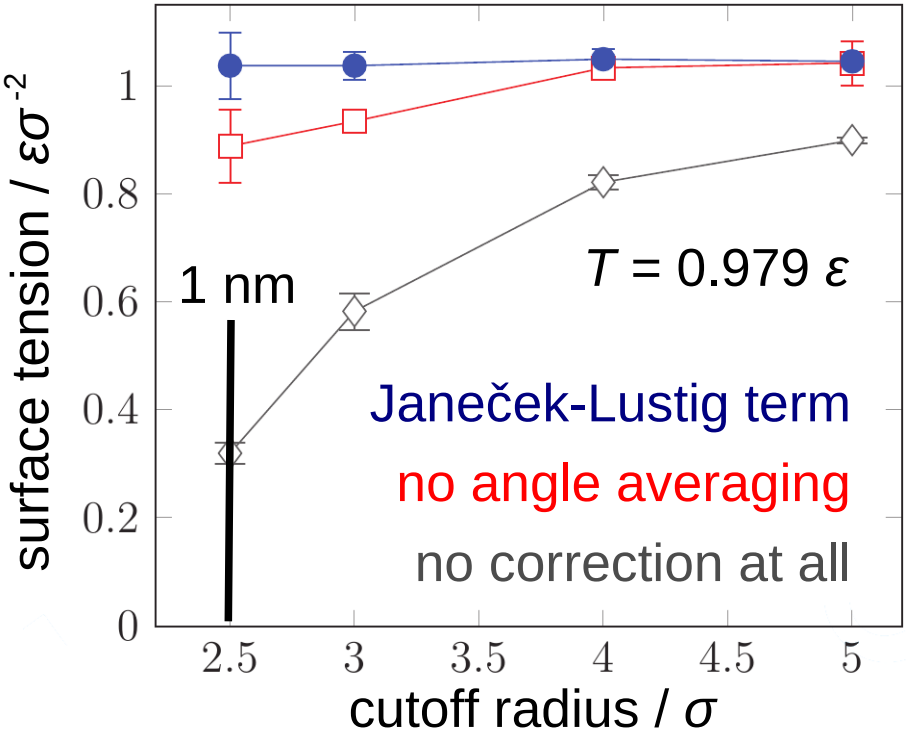
For planar interfaces:

Long-range correction from the density profile, following **Janeček**.



Angle-averaging expression for multi-site models, following **Lustig**.

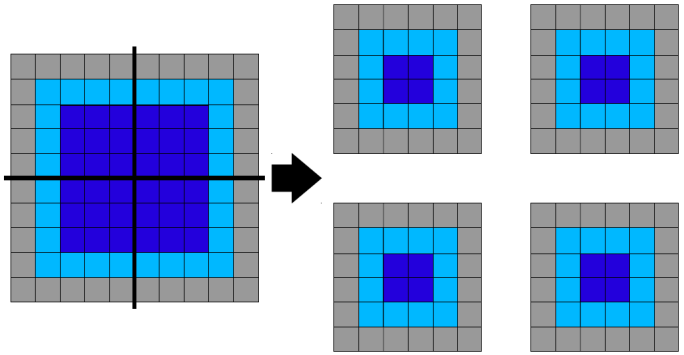
Two-centre LJ fluid (2CLJ)



For arbitrary geometries, e.g. the fast multipole method can be employed.

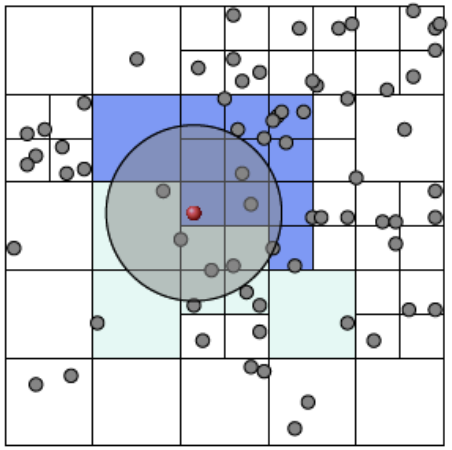
Efficient simulation of large systems

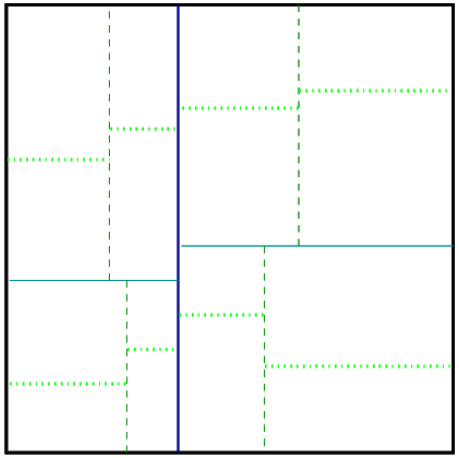
Linked-cell data structure suitable for spatial domain decomposition:



(non-blocking, over-lapping MPI send/ receive operations)

Methods for heterogeneous or fluctuating particle distributions:





large systems “1”: molecular dynamics **http://www.ls1-mardyn.de/**

Efficient simulation of large systems

Memory-efficient implementation based on the linked-cell data structure:

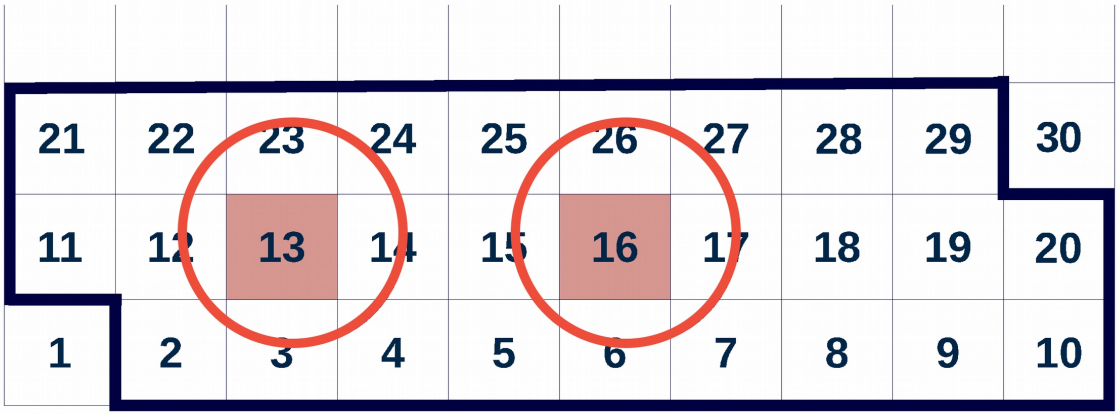
sliding window

Optionally, forces acting on molecules are only stored until their cell leaves the sliding window.

large systems “1”: molecular dynamics **http://www.ls1-mardyn.de/**

Efficient simulation of large systems

Memory-efficient implementation based on the linked-cell data structure:



hyperthreaded sliding window

Optionally, forces acting on molecules are only stored until their cell leaves the sliding window.

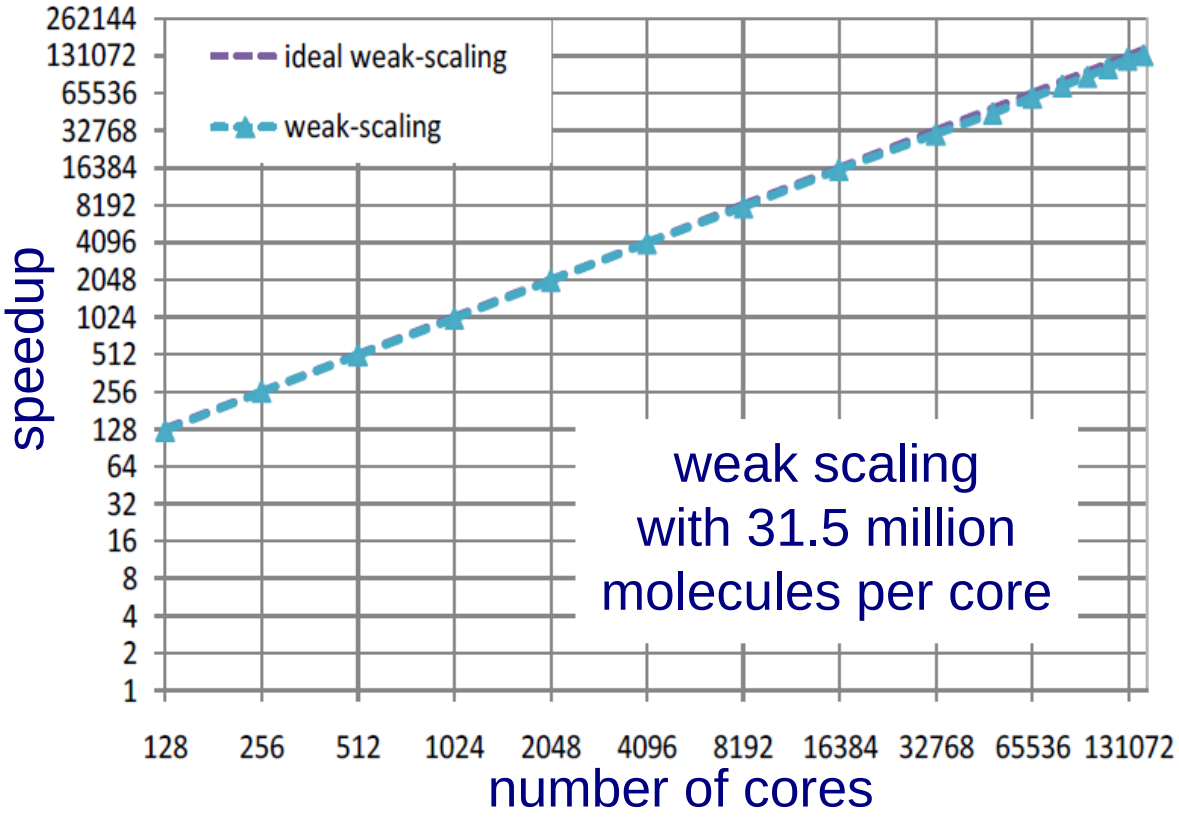
Efficient vectorization:

- Optimization by hand, using advanced vector extensions (AVX).
- Conversion from array of structures (AoS) to structure of arrays (SoA).

large **s**ystems “**1**”: **m**olecul**ar dyn**amics **http://www.ls1-mardyn.de/**

Large-scale MD simulation on SuperMUC

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

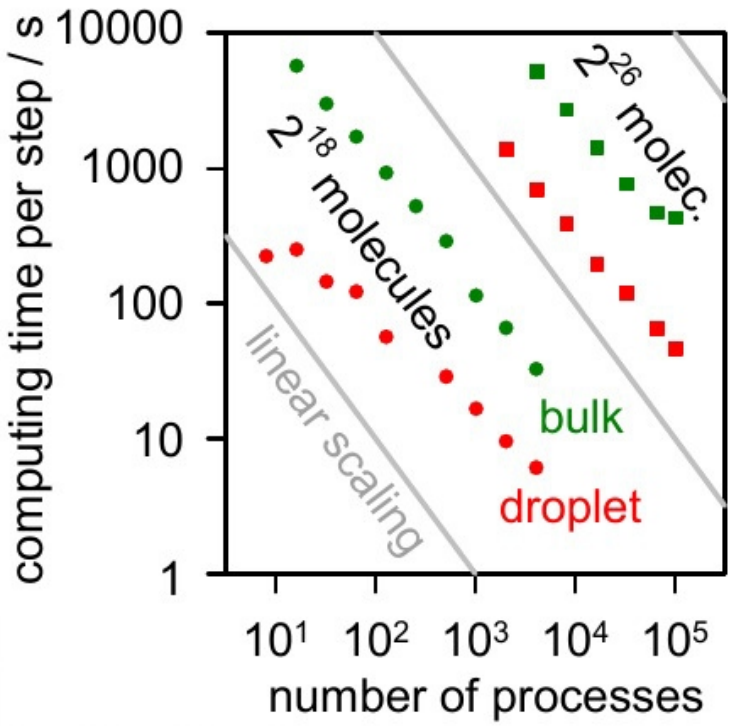


large systems "1": molecular dynamics

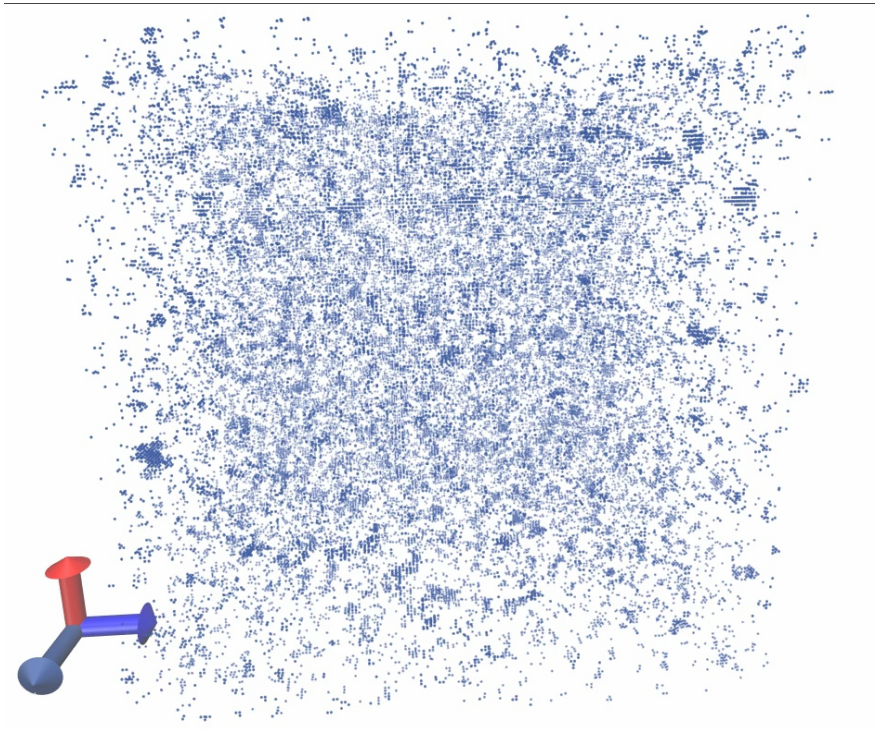
http://www.ls1-mardyn.de/

Large-scale MD simulation on hermit

strong scaling (Amdahl)



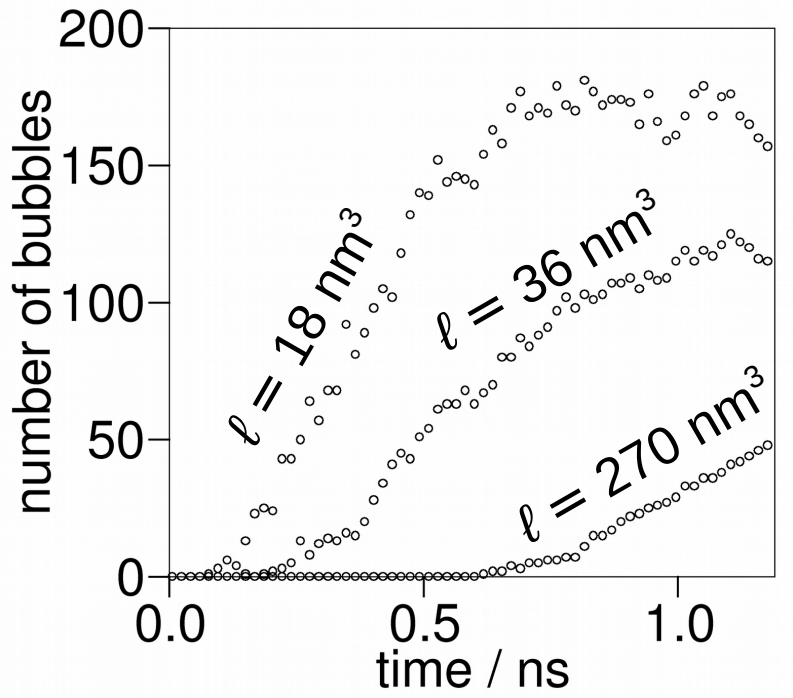
homogeneous cavitation

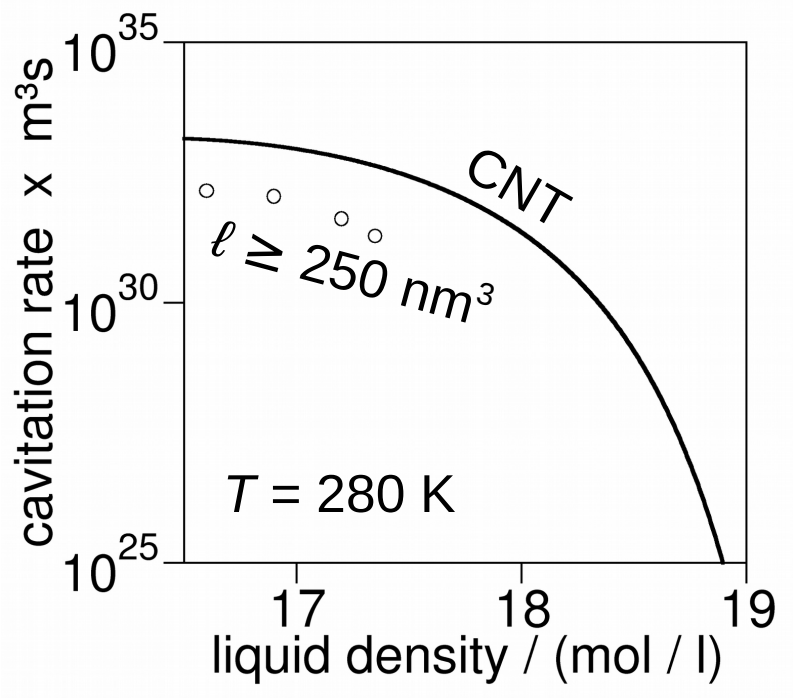


CO_2 (T = 280 K and ρ = 17.2 mol/l), 3CLJQ
25 million molecules on 110 592 cores

MD simulation of cavitation processes

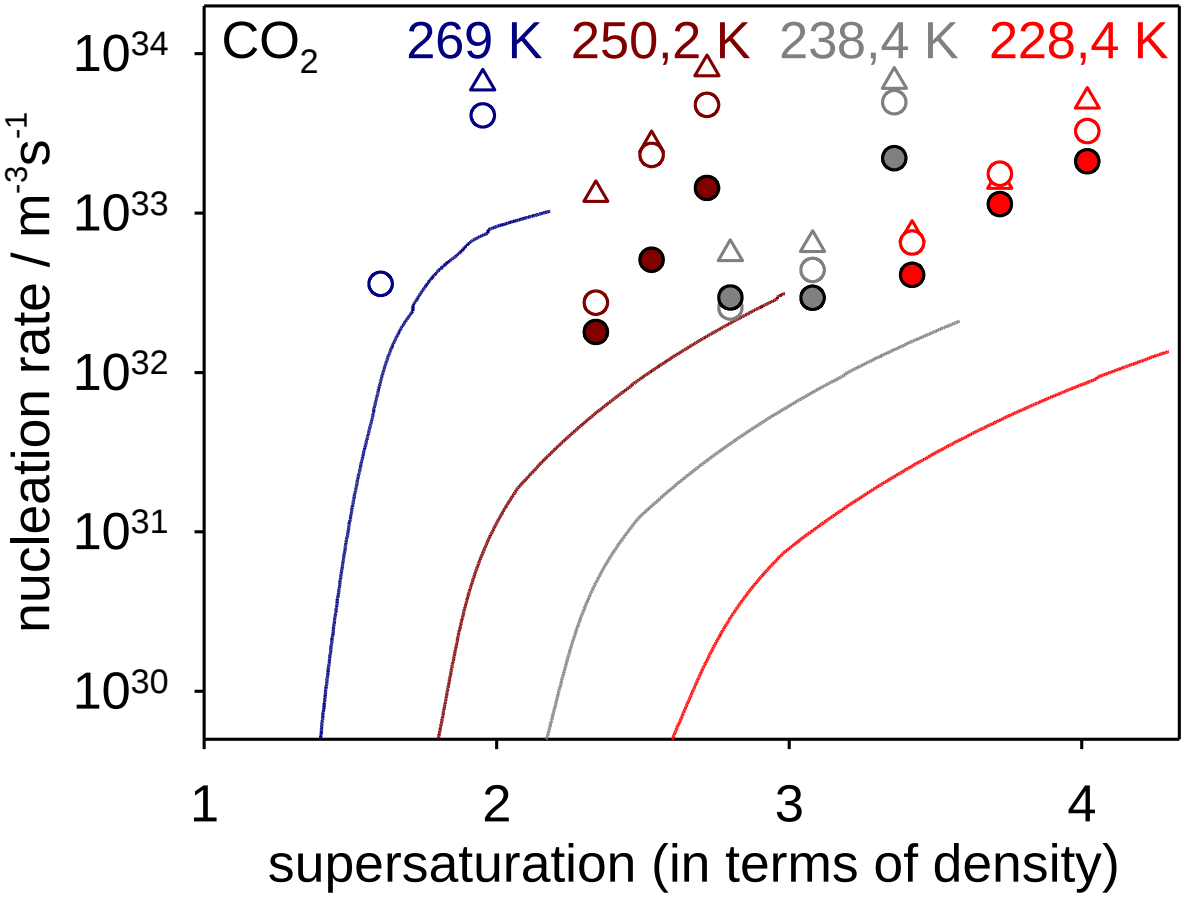
Yasuoka-Matsumoto method: Count nuclei exceeding a threshold size ℓ.





Classical nucleation theory predicts critical cavity sizes from 5 to 100 nm^3.

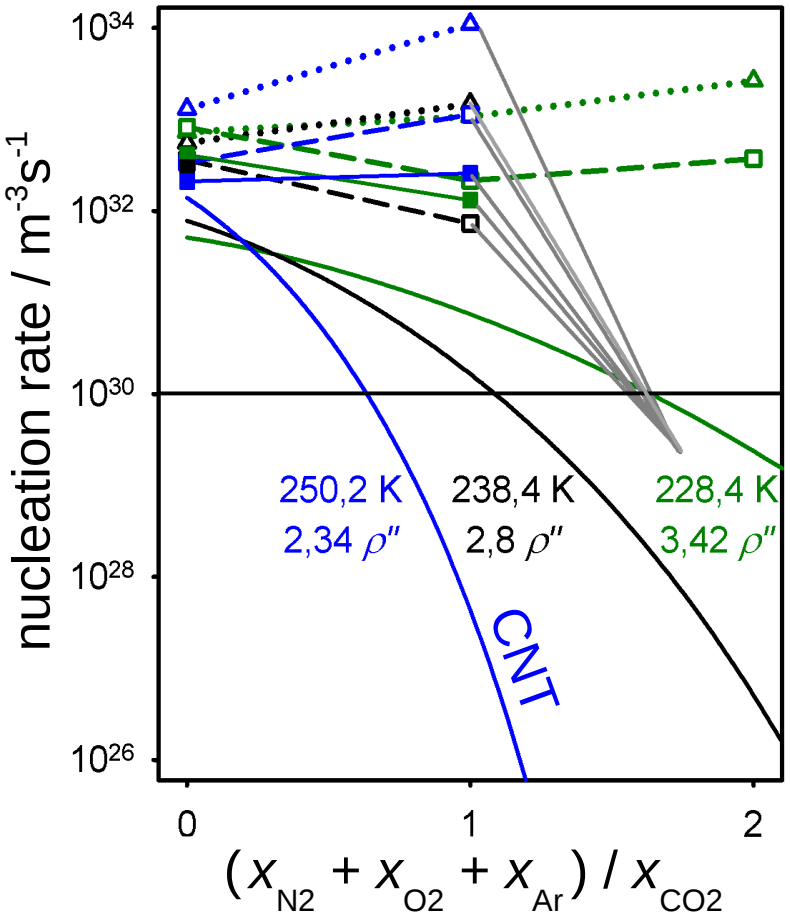
MD simulation of nucleation in vapours



— Classical nucleation theory (CNT)

△ ℓ = 50 molecules
○ ℓ = 75 molecules
● ℓ = 300 molecules

The air pressure effect on CO_2 nucleation



Scenario:

- Vapour contains *k* components
- Liquid phase is approximately pure
- Other *k* – 1 components: Carrier gas

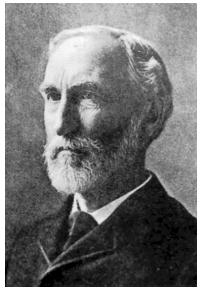
Carrier gas effect (Wedekind *et al.*):

- Thermalization → *J* increases
- Greater pressure → *J* decreases

— CNT following Wedekind *et al.*

△ ℓ = 50 ▫ ℓ = 100 ▪ ℓ = 150

Fluid mixtures: Interfacial thermodynamics



„take some point […] and **imagine a geometrical surface** to pass through this point and all other points which are similarly situated […] called the dividing surface“.

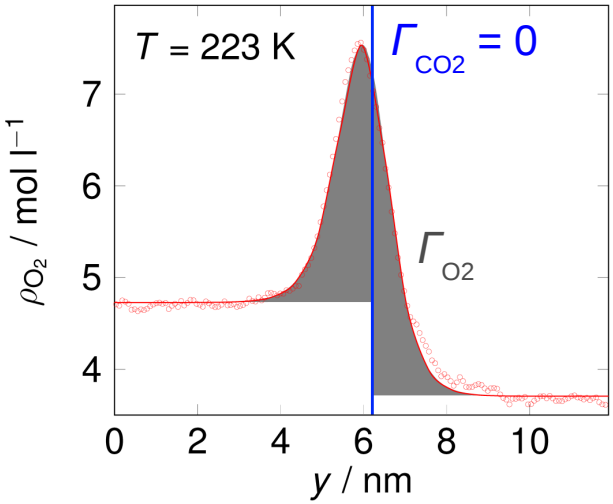
Thermodynamic **excess quantities** are ascribed to the interface

$$X^{\text{System}} = X^{I} + X^{II} + X^{E},$$

e.g. surface free energy or adsorption.

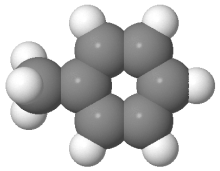
Beside absolute excesses, there are **differential quantities**, such as the surface tension

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{N,V,T}.$$



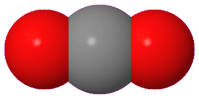
Case study: Adsorption at fluid interfaces

Toluene



7CLJD+5Q
(Huang *et al.*)

CO_2



3CLJQ
(Merker *et al.*)

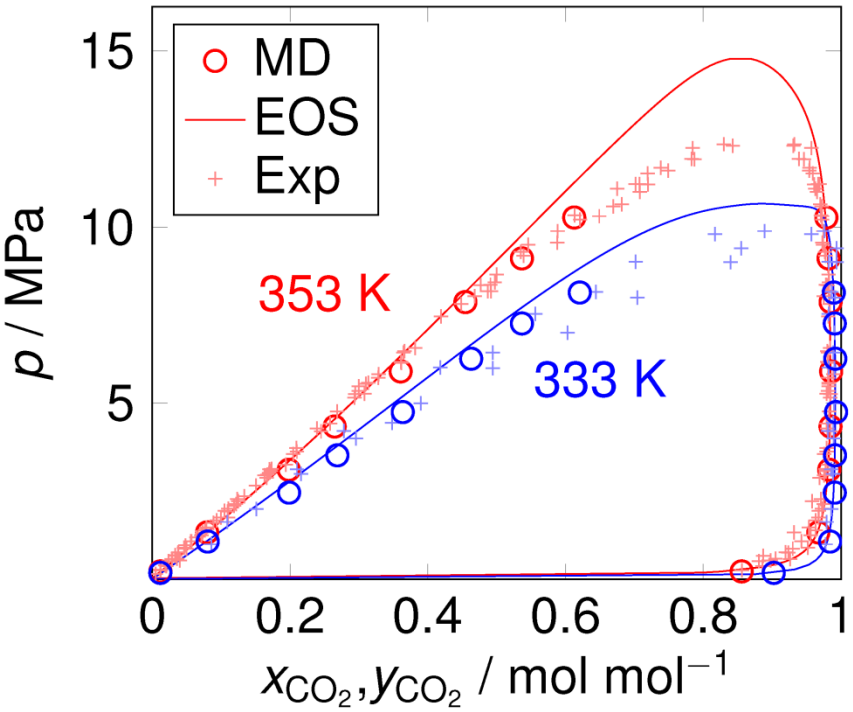
unlike interaction by modified Lorentz-Berthelot rule

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2} \qquad \epsilon_{AB} = \xi_{AB}\sqrt{\epsilon_A \epsilon_B}$$

with $\varepsilon_{AB} = 0.95$

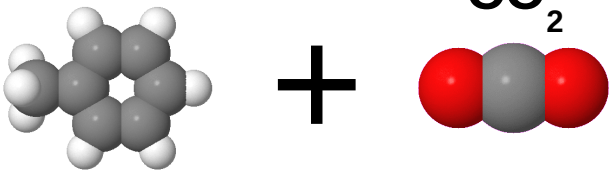
adjusted to Henry's law coefficients

vapour-liquid equilibrium

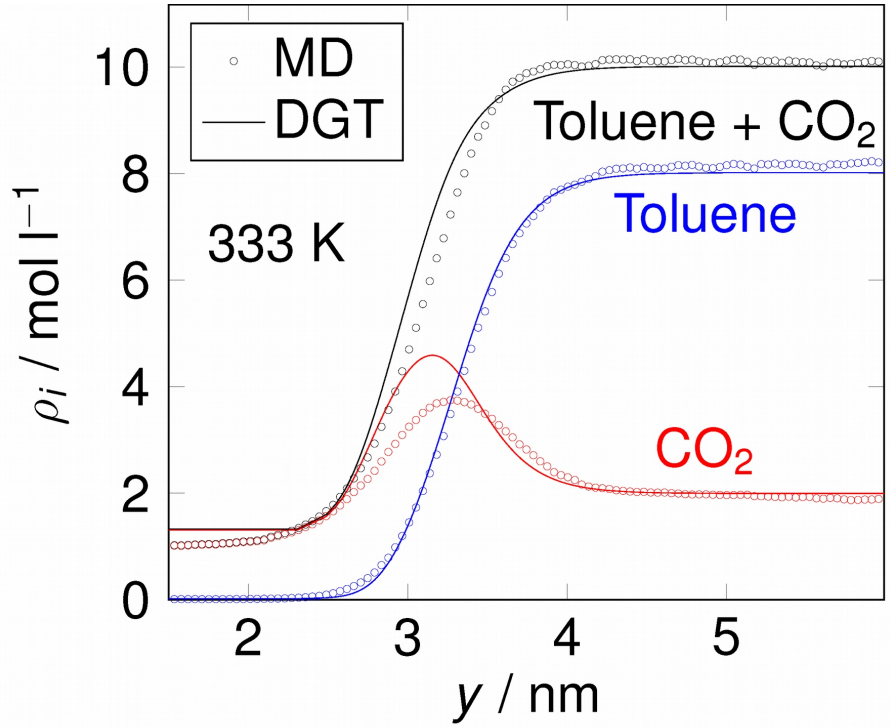


Case study: Adsorption at fluid interfaces

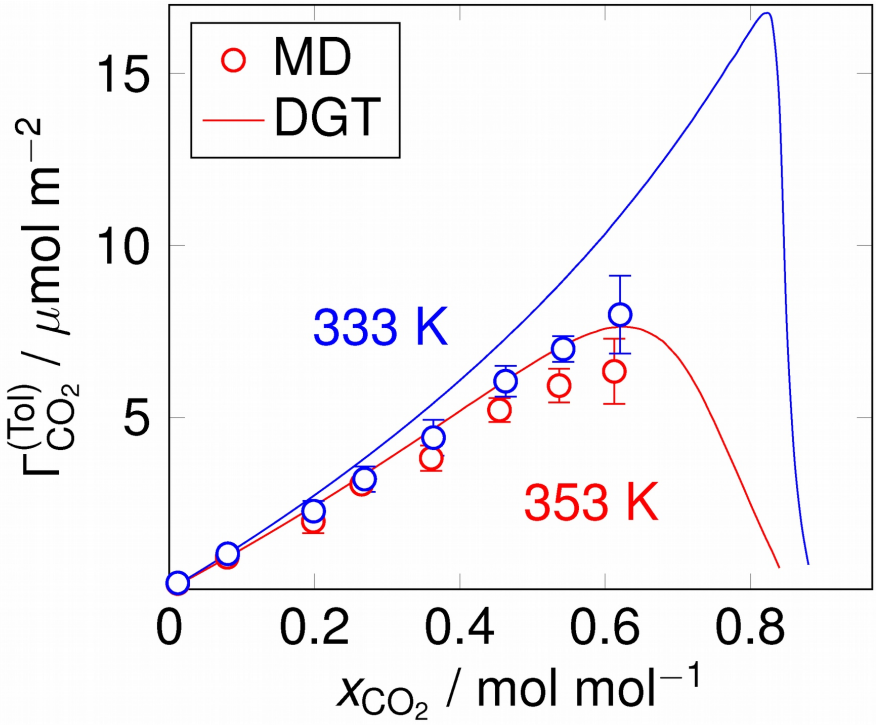
Toluene + **CO_2**



density profile

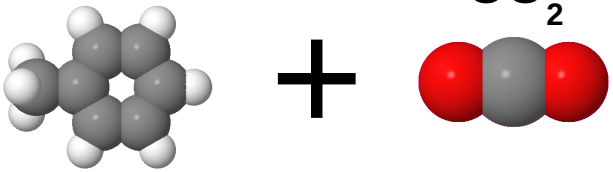


adsorption

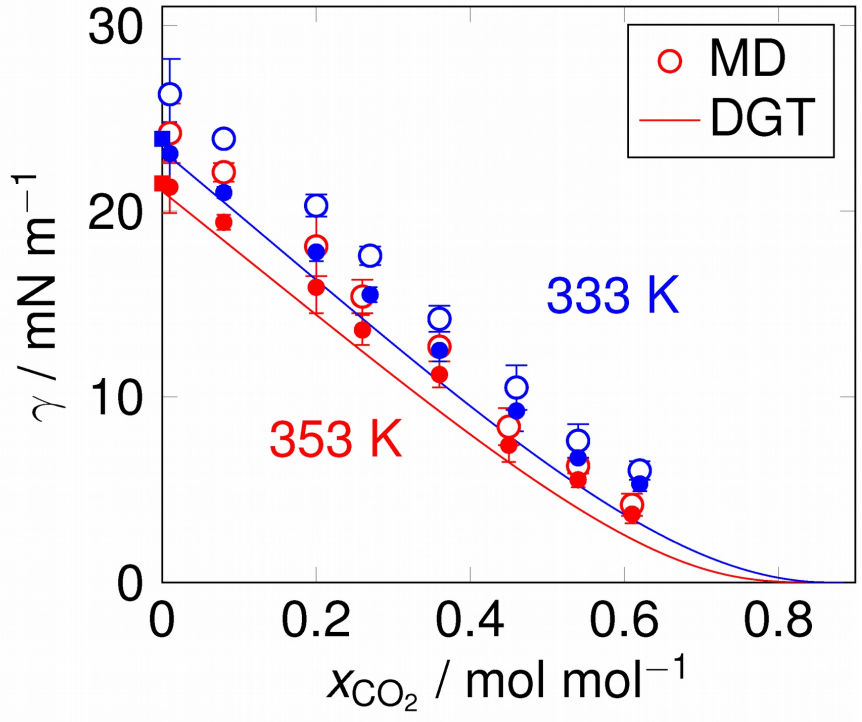


Case study: Adsorption at fluid interfaces

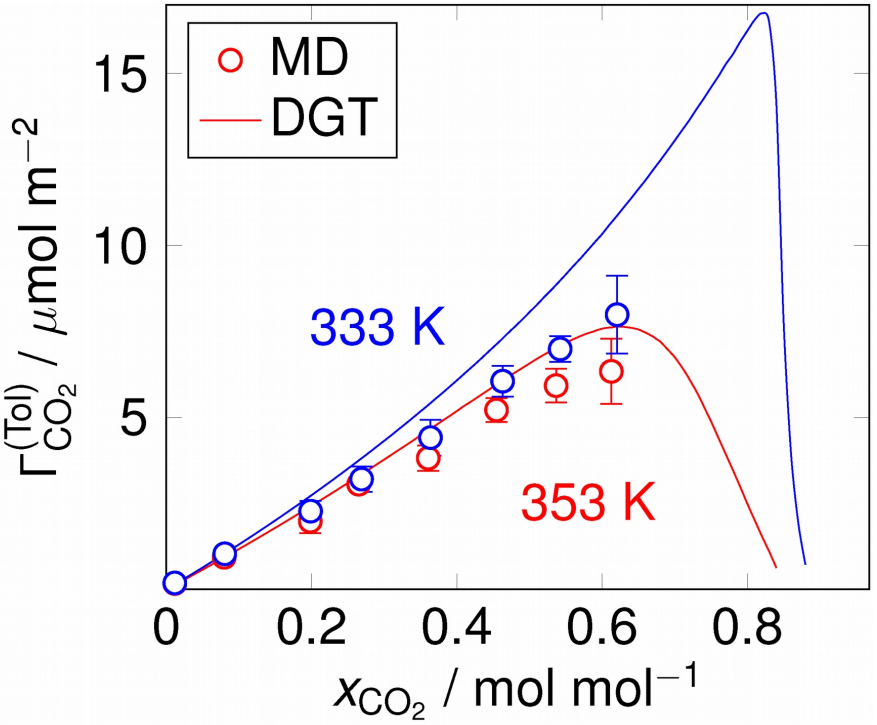
Toluene + **CO_2**



surface tension



adsorption



Conclusion

By massively-parallel molecular modelling, the thermodynamic behaviour of model classes (e.g. 2CLJD, 2CLJQ) can be characterized and used to tune molecular models to an application by **multicriteria optimization**.

Validated molecular models enable **reliable predictions** for thermo-dynamic properties by which empirical rules of thumb become obsolete.

By massively-parallel molecular simulation, complex activated processes like **cavitation** in metastable liquids and **nucleation** in supersaturated vapours can be investigated at molecular resolution.

Adsorption of light-boiling components at vapour-liquid interfaces of fluid mixtures can be determined and related to the surface tension.