Quantitatively reliable massively-parallel molecular modelling and simulation of vapour-liquid interfaces

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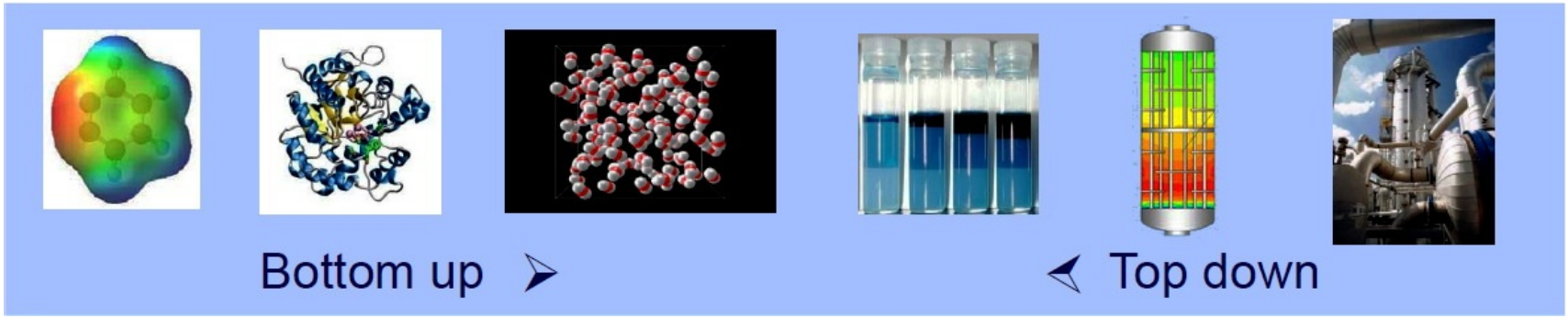
IITK Chemical Engineering Seminar

Computational Molecular Engineering

Computational molecular 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

Force-field models of low-molecular fluids

Geometry

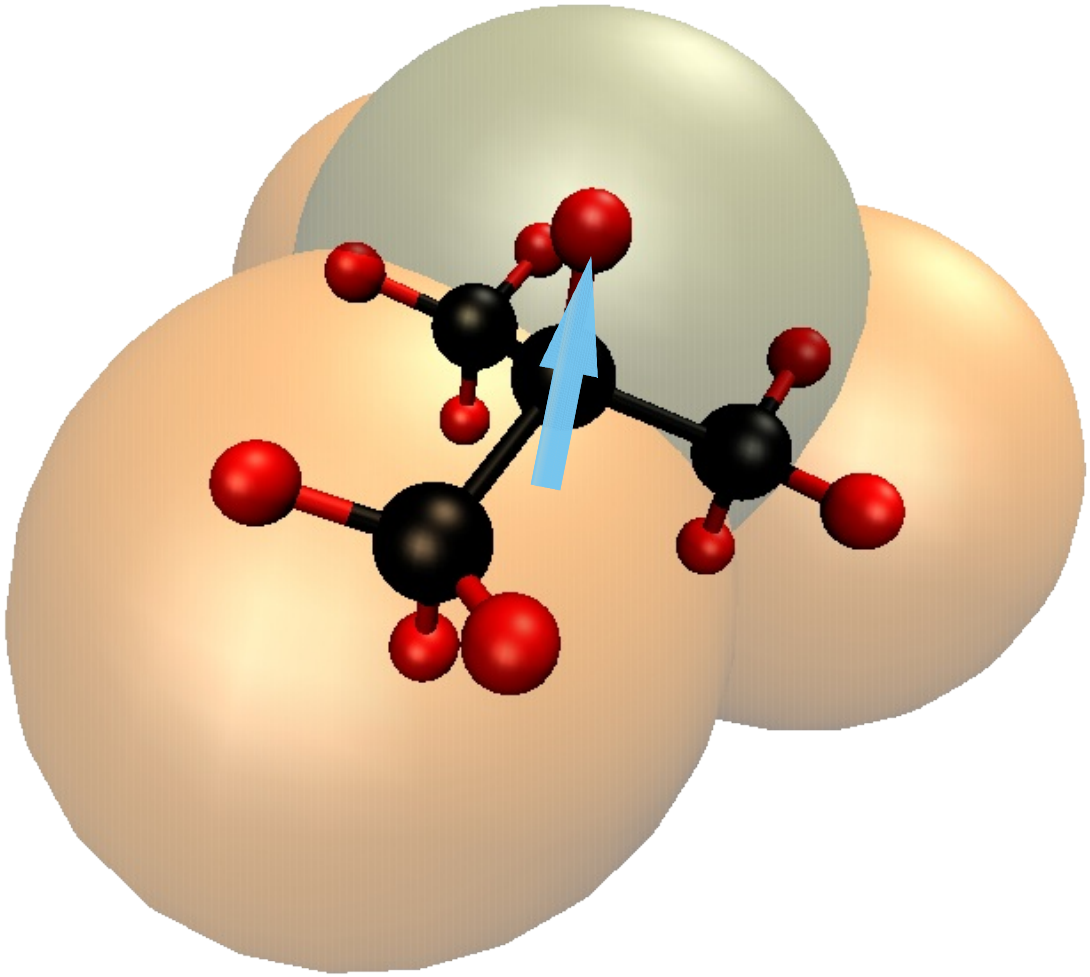
Bond lengths and angles

Dispersion and repulsion

Lennard-Jones potential:
Size and energy parameters

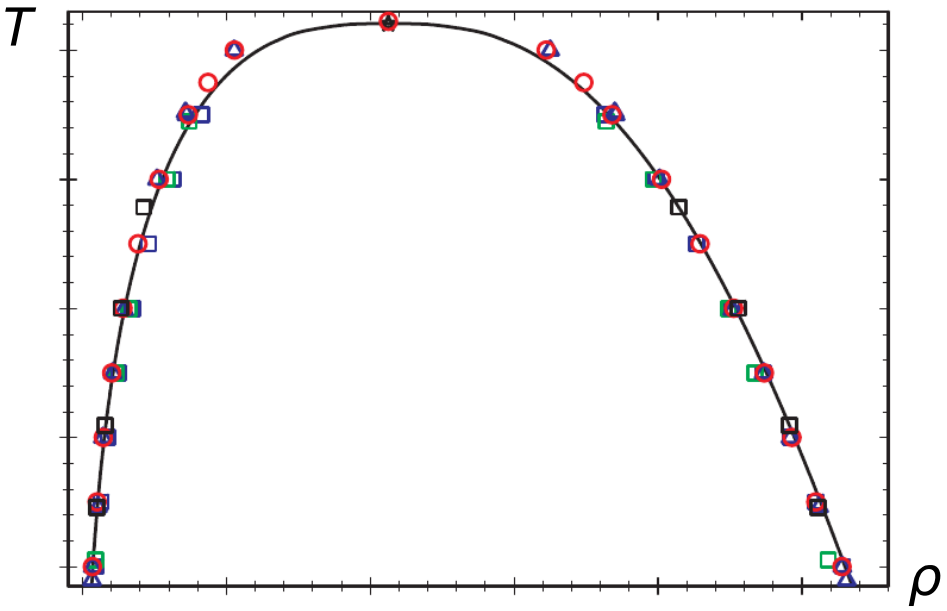
Electrostatics

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



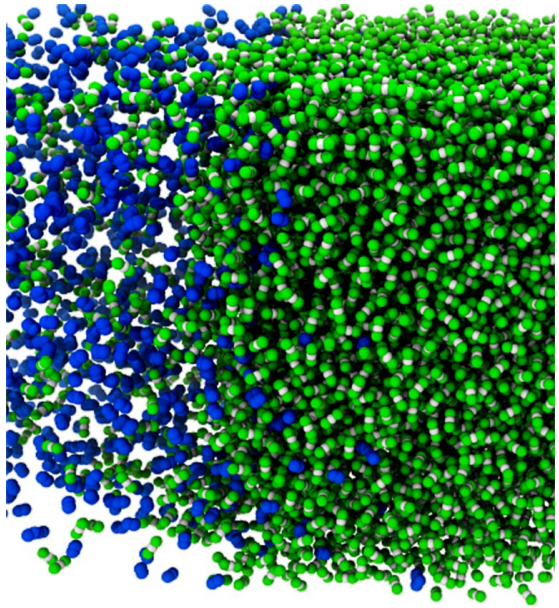
Vapour-liquid equilibria

Bulk properties



vapour pressure, saturated densities, composition, enthalpy of vaporization, etc., by Grand Equilibrium simulation

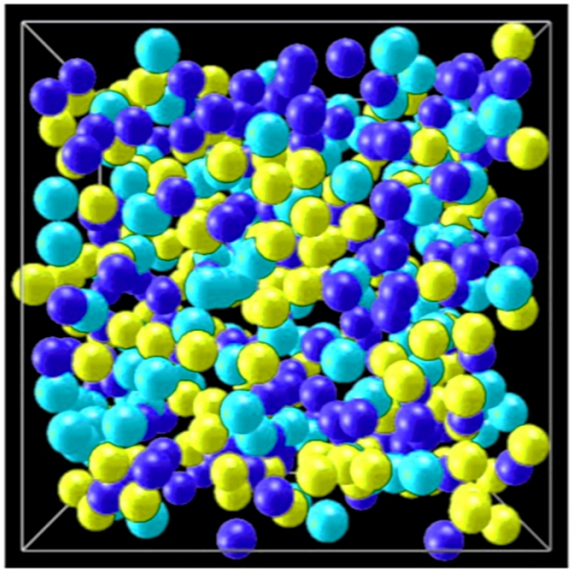
Interfacial properties



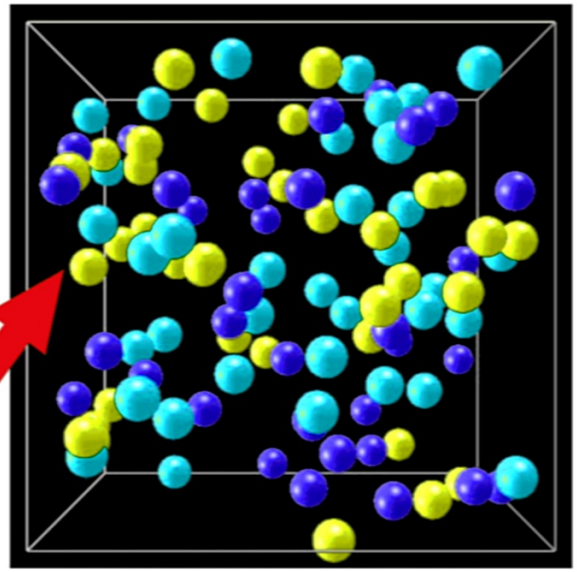
heterogeneous systems with finite-size effects and long-range interactions

Vapour-liquid equilibria: Grand equilibrium

temperature
liquid composition

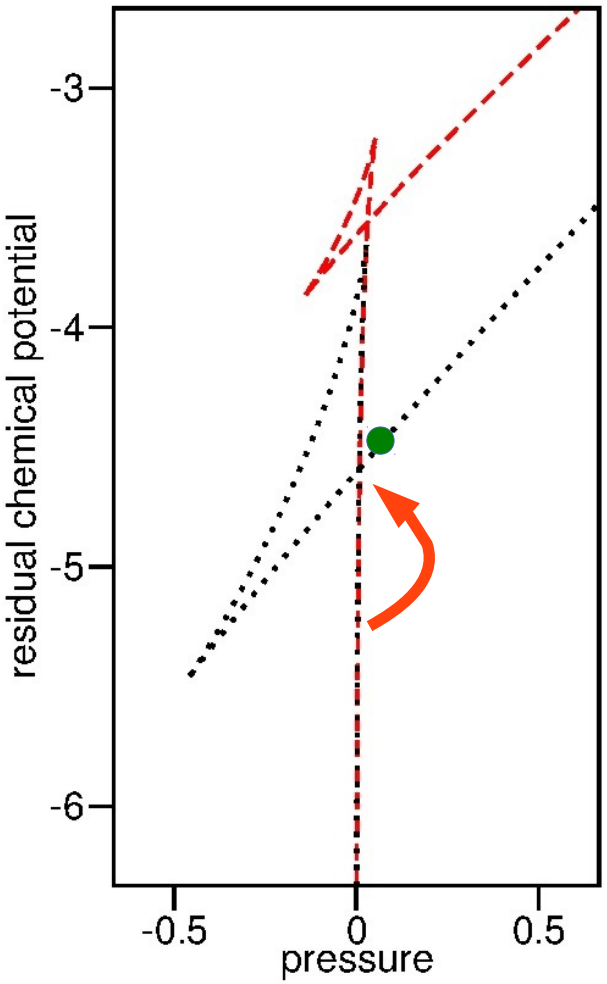


partial molar volumes
chemical potentials



pressure
vapour composition

Vapour-liquid equilibria: Grand equilibrium



Given: Temperature T, liquid composition x

First step: NpT simulation of the liquid phase

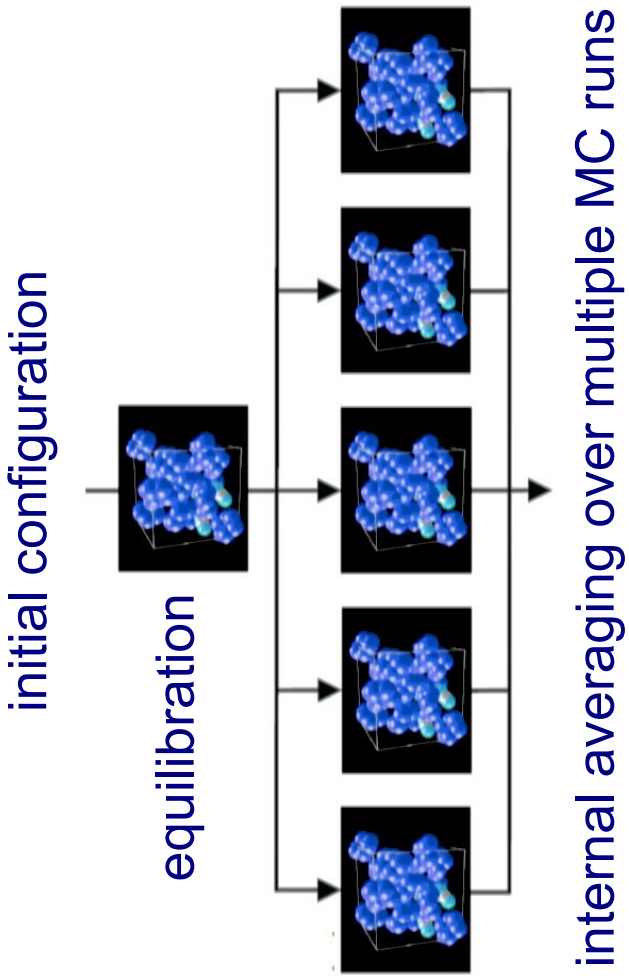
An estimate, which may deviate from $p^{sat}(T)$, is used for p in this simulation. The chemical potential and its first and second derivatives with respect to pressure are determined.

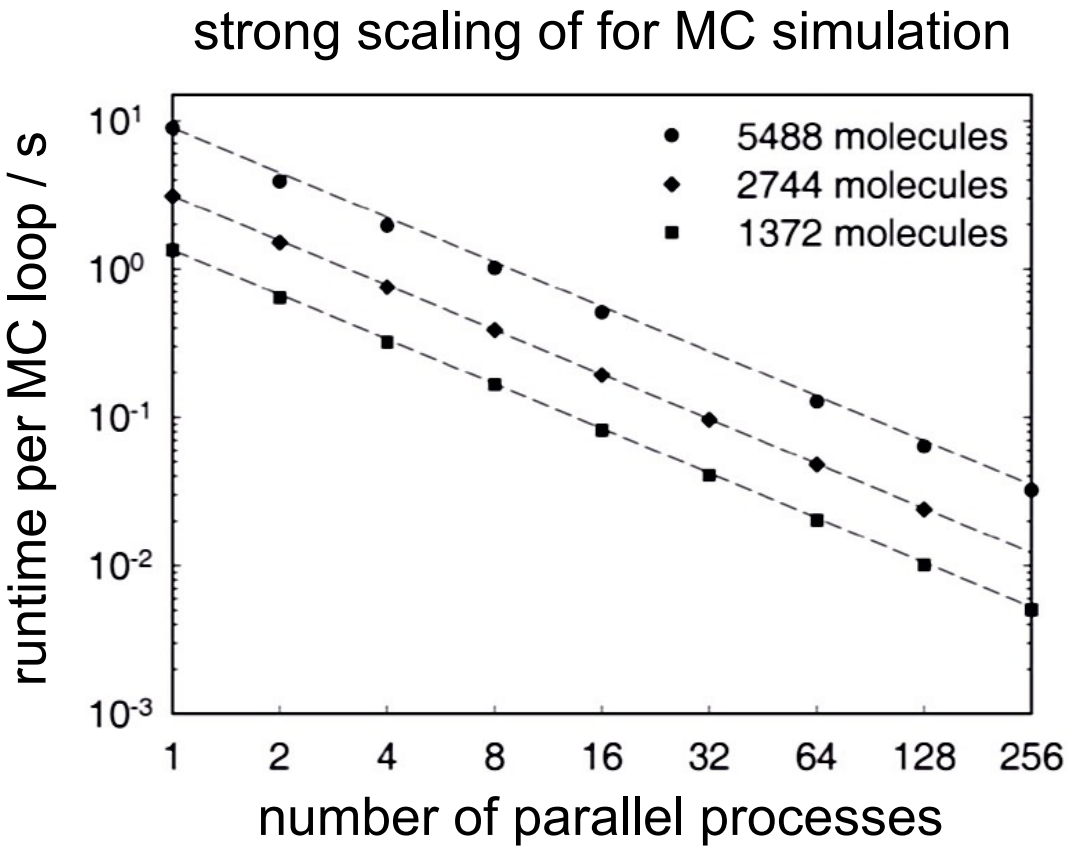
Second step: Pseudo-μVT vapour simulation

Grand-canonical simulation where the value of μ is determined on the fly from the pressure.

Obtained: Pressure p, vapour composition y

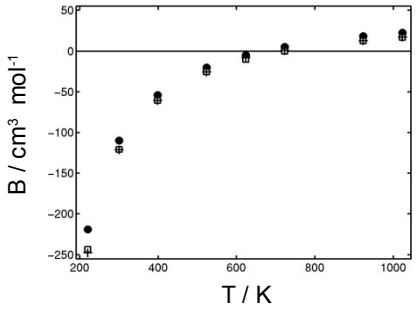
Concurrency of multiple Markov chains



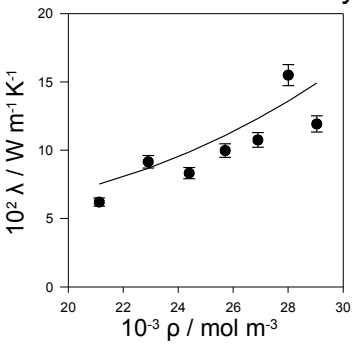


Thermodynamic properties of bulk fluids

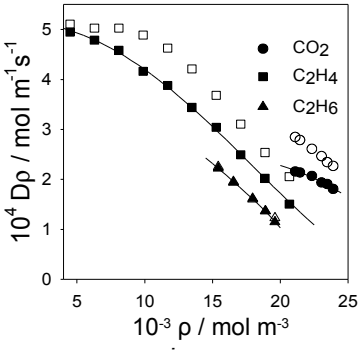
Second virial coefficient



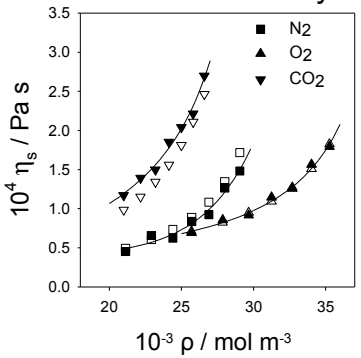
Thermal conductivity



Self-diffusion coefficient



Shear viscosity



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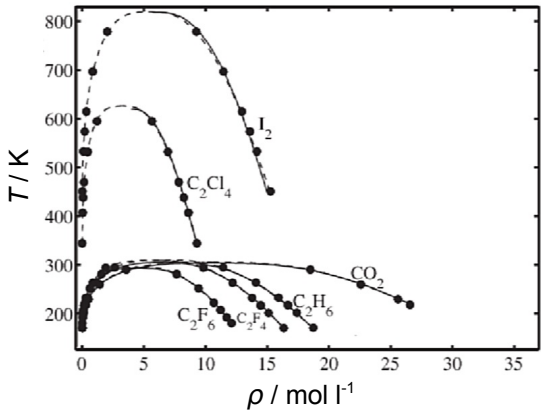
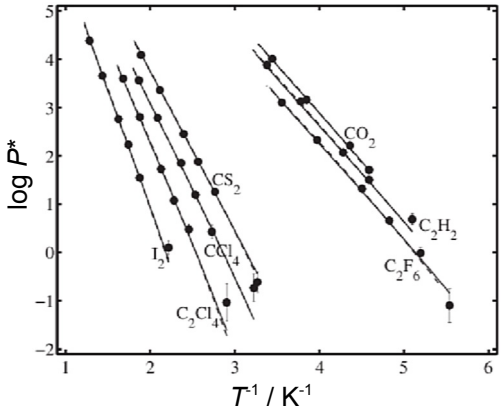
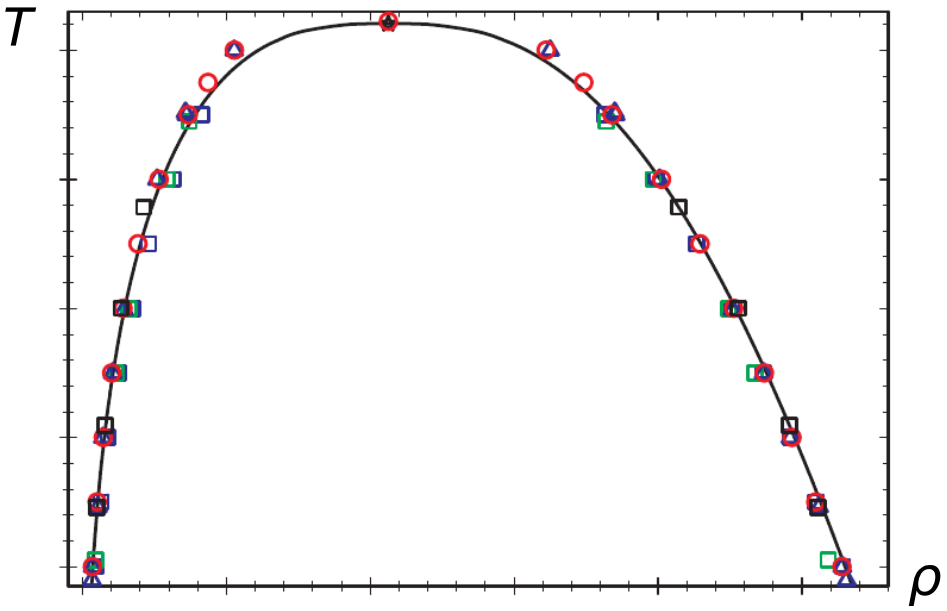
Vapour-liquid equilibira: Saturated densities and vapour pressures





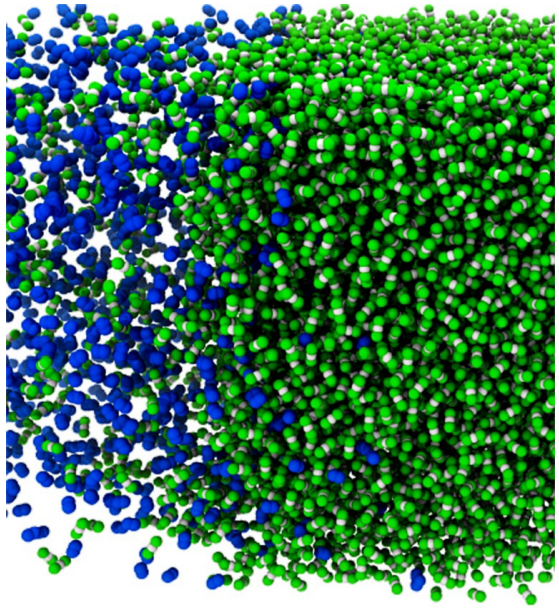
Vapour-liquid interfaces

Bulk properties



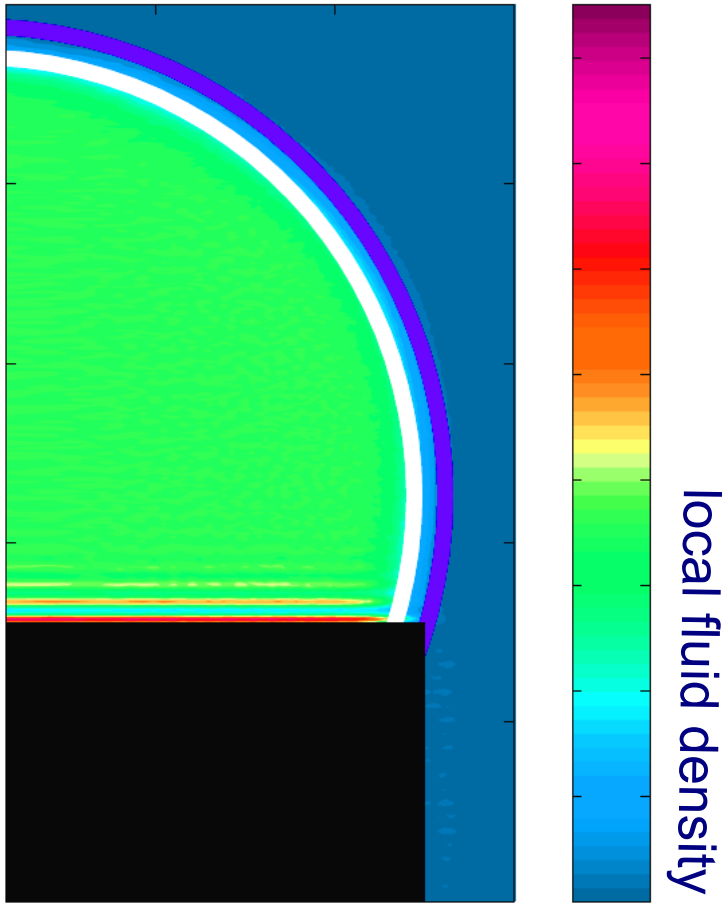
vapour pressure, saturated densities, composition, enthalpy of vaporization, etc., by Grand Equilibrium simulation

Interfacial properties

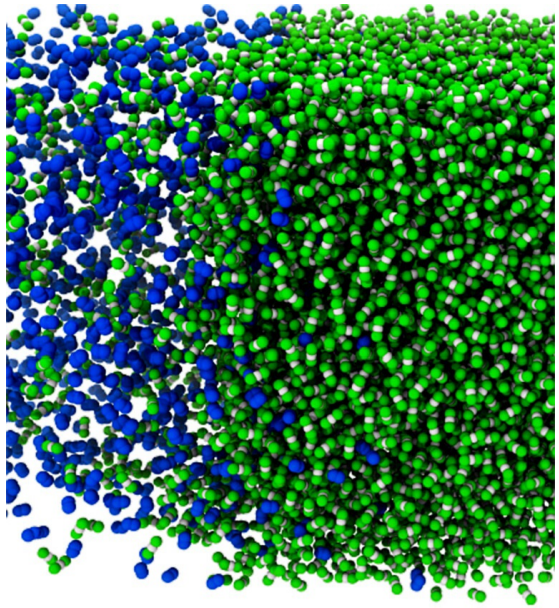


heterogeneous systems with finite-size effects and long-range interactions

Molecular dynamics of fluids at interfaces

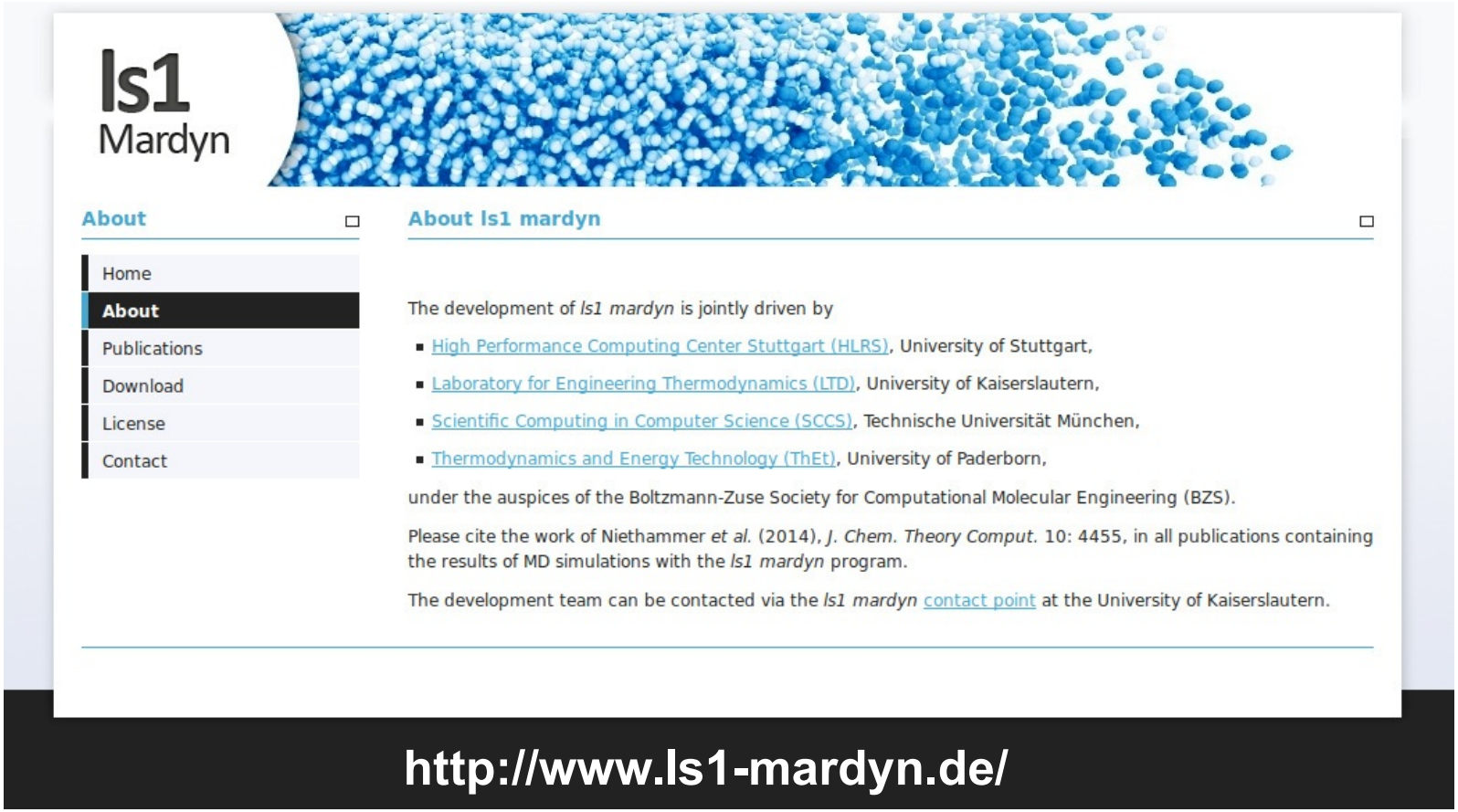


Interfacial properties



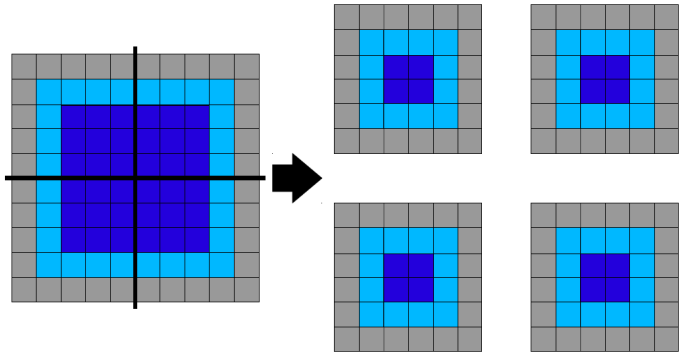
heterogeneous systems with finite-size effects and long-range interactions

Molecular dynamics of large systems



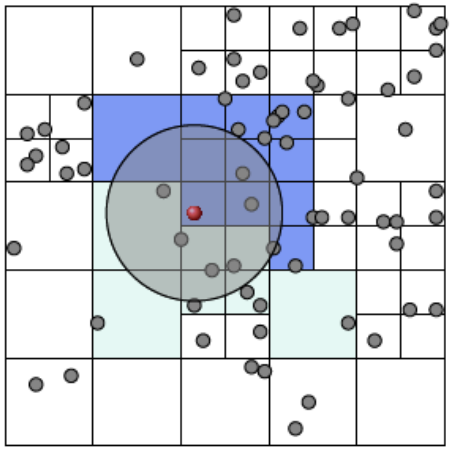
Parallelization by volume decomposition

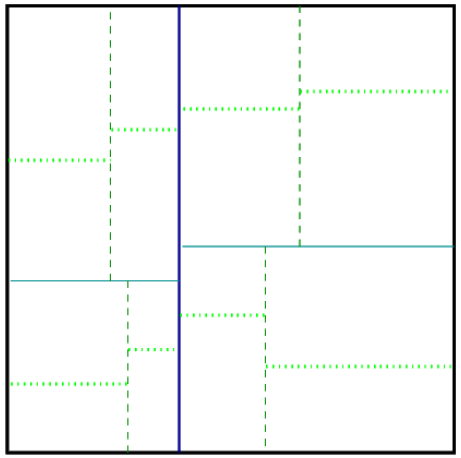
Linked-cell data structure suitable for spatial domain decomposition:



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

Methods for heterogeneous or fluctuating particle distributions:

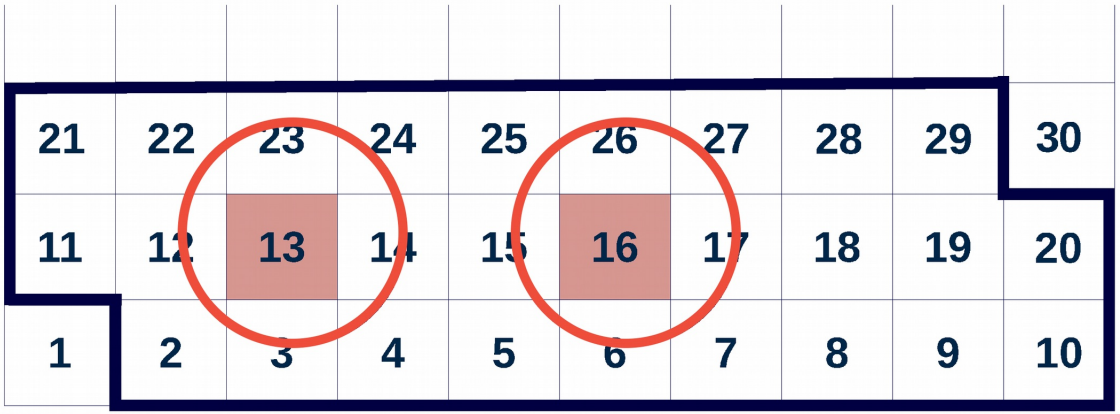




large systems “1”: molecular dynamics http://www.ls1-mardyn.de/

Hyperthreading and vectorization

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



hyperthreaded sliding window

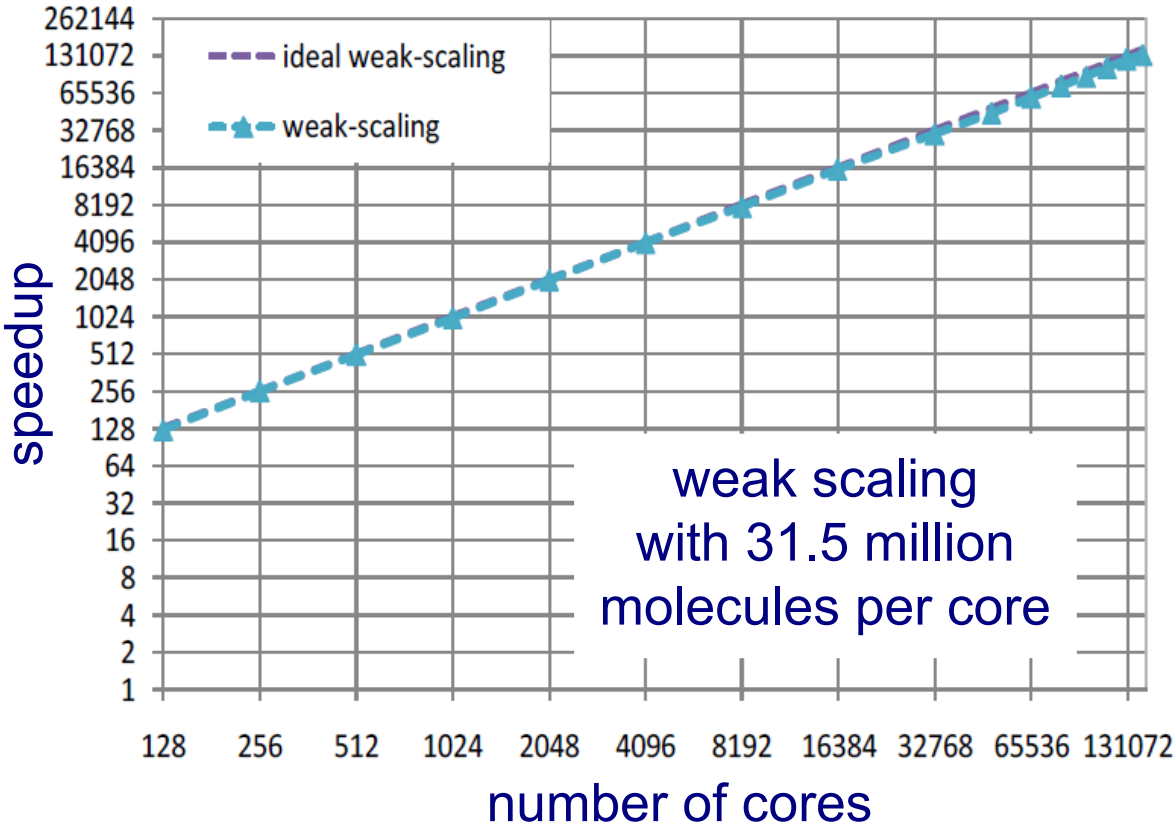
Optionally, forces acting on molecules are only stored until their cell leaves the sliding window.

Efficient vectorization:

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

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

World record with ls1 mardyn on SuperMUC



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

large systems "1": molecular dynamics

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

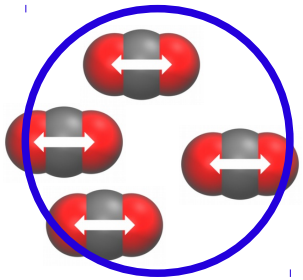
MD simulation of homogeneous cavitation

liquid CO_2 at 220 K and 22.6 mol/l

13 x 10^6 molecules (52 x 10^6 sites)

Scale-up to the entire *hermit* cluster for canonical simulation of cavitation in carbon dioxide.

Evaluation of local density at 180 x 180 x 180 grid points:



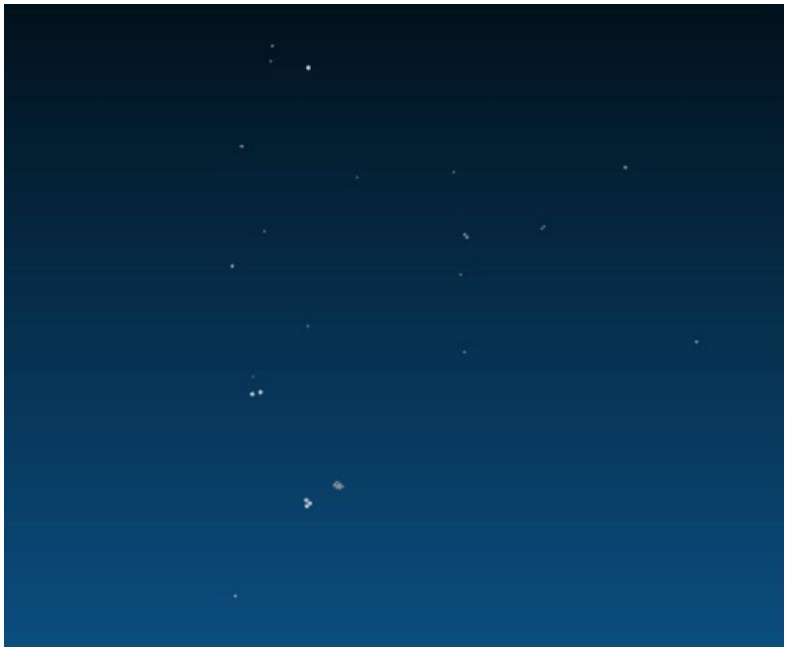
≤ 5 ?

(6 mol/l)

Liquid phase detected for more than 5 neighbours within a radius of 6.9 Å around the grid point.

MD simulation of homogeneous cavitation

liquid CO_2 at 220 K and 23.9 mol/l



Three consecutive regimes:

- relaxation (equilibration)
- homogeneous cavitation
- growth beyond critical size

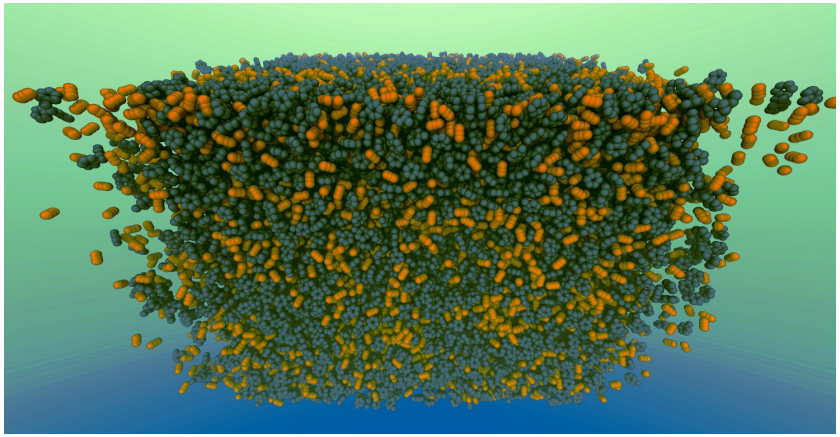
These and other simulations of interfacial phenomena crucially depend on an accurate surface tension.

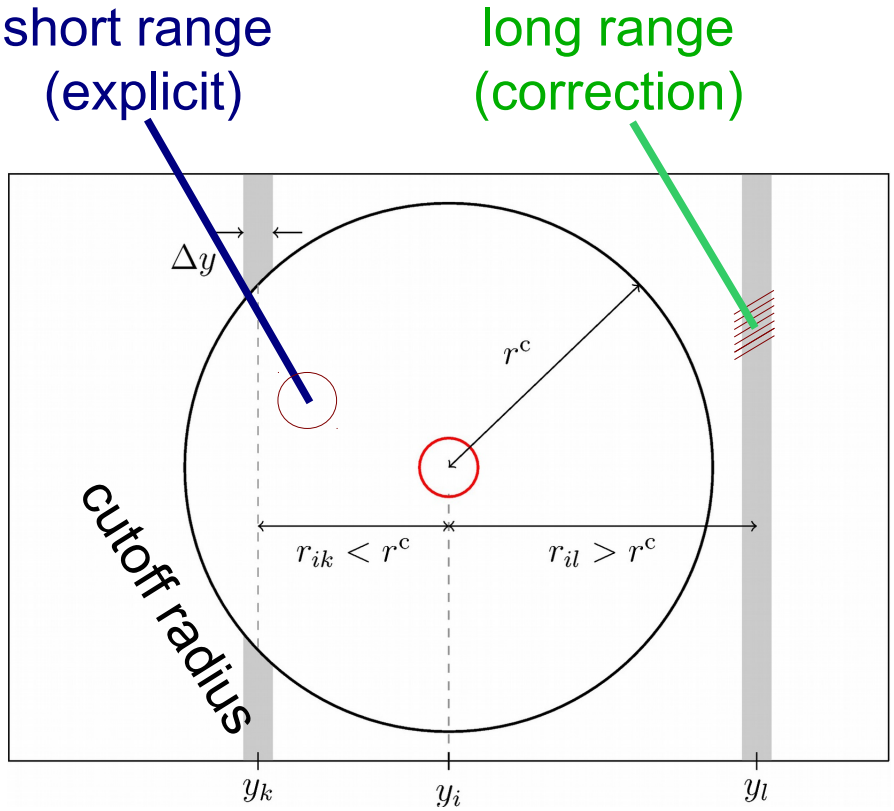
13×10^6 molecules (52×10^6 sites)

Long-range correction at planar interfaces

For planar interfaces:

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



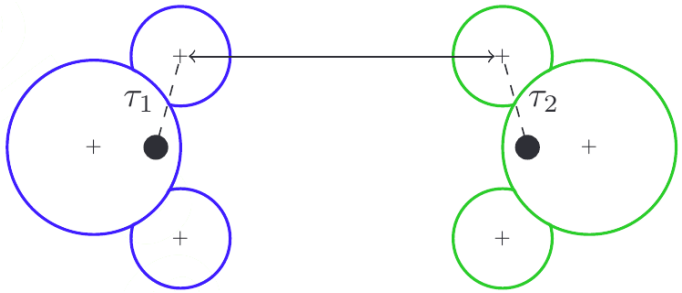


Full evaluation of all pairwise interactions is too expensive ...
... **short-range interactions** are evaluated only for **neighbours**.

Long-range correction at planar interfaces

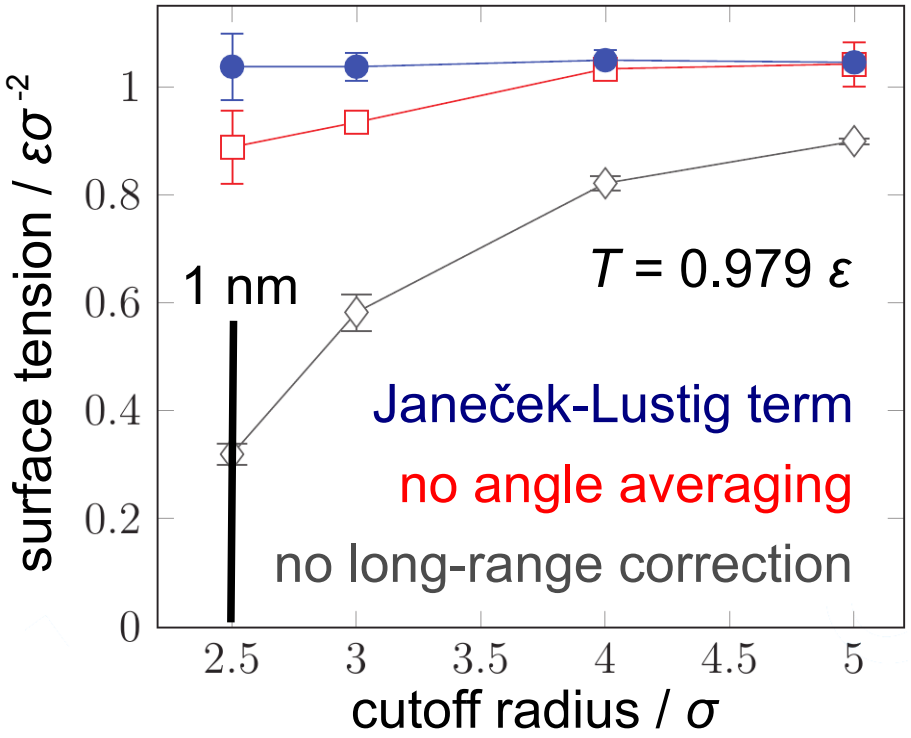
For planar interfaces:

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



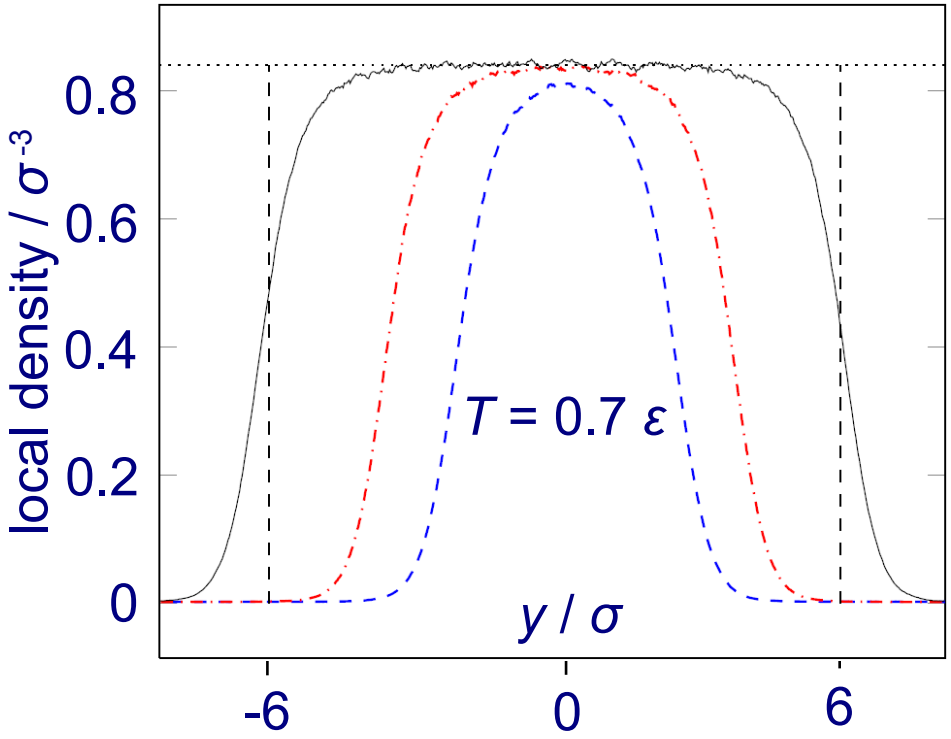
Angle-averaging expression for multi-site models, following **Lustig**.

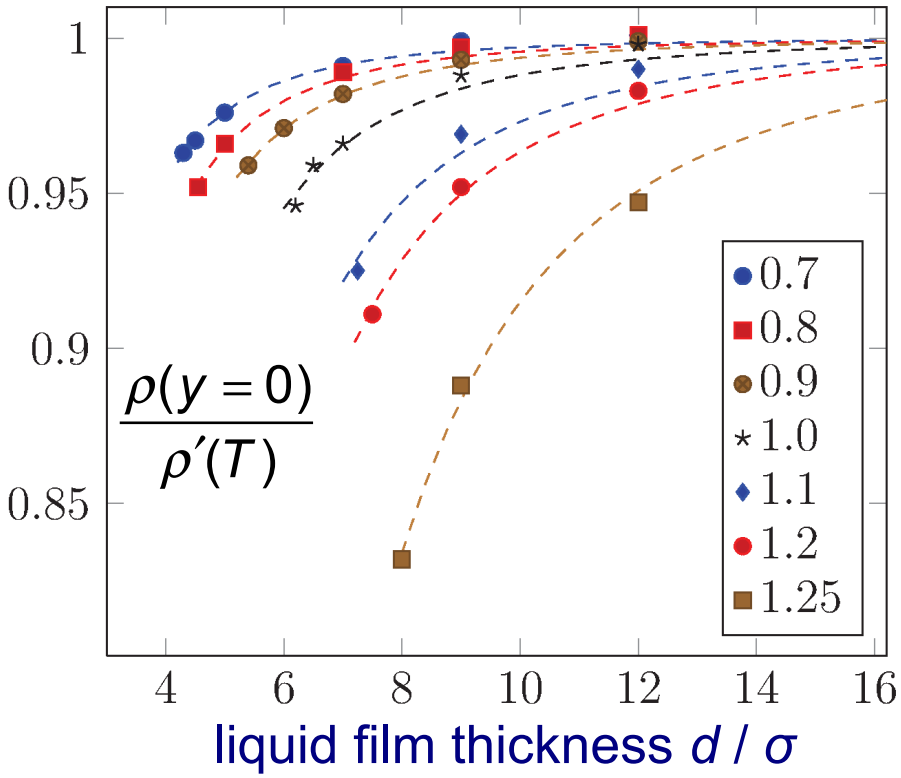
Two-centre LJ fluid (2CLJ)



Dipole and dispersion lead to analogous long-range correction expressions.
The long-range contribution of the quadrupole can be neglected.

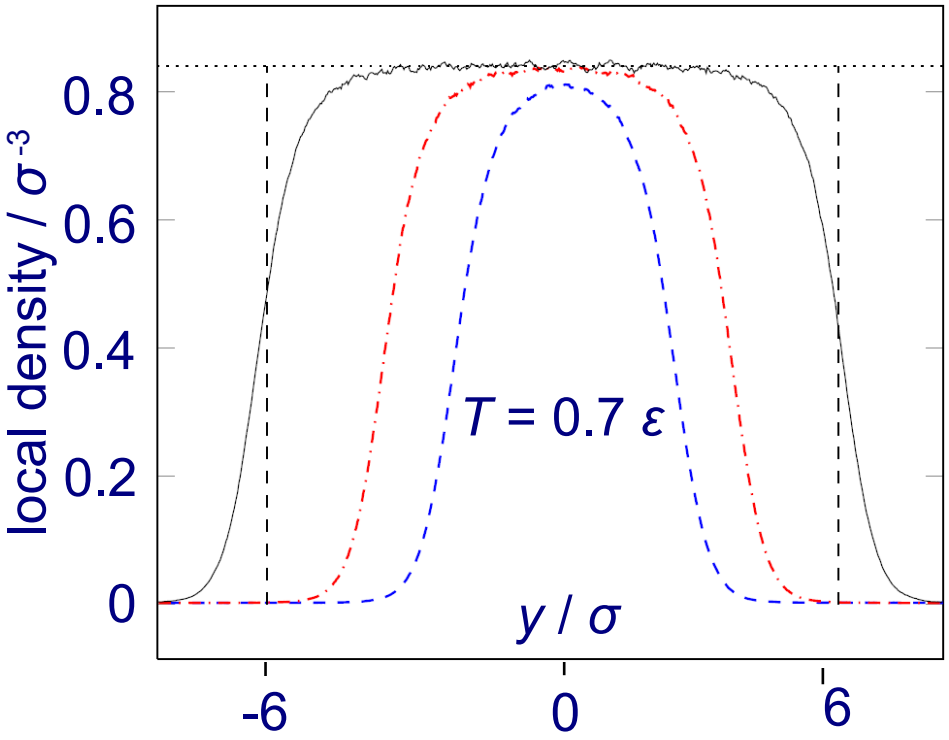
Vapour-liquid interfaces: Finite-size effects



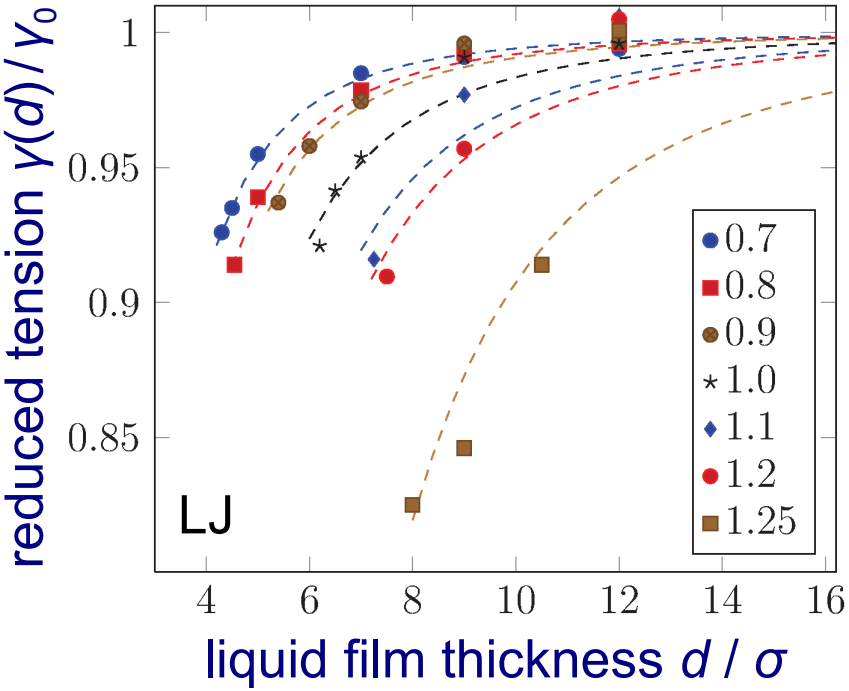


The density at the centre of a liquid nanofilm deviates from that of the saturated bulk liquid at the same temperature (scaling ~ $1/d^3$).

Vapour-liquid interfaces: Finite-size effects

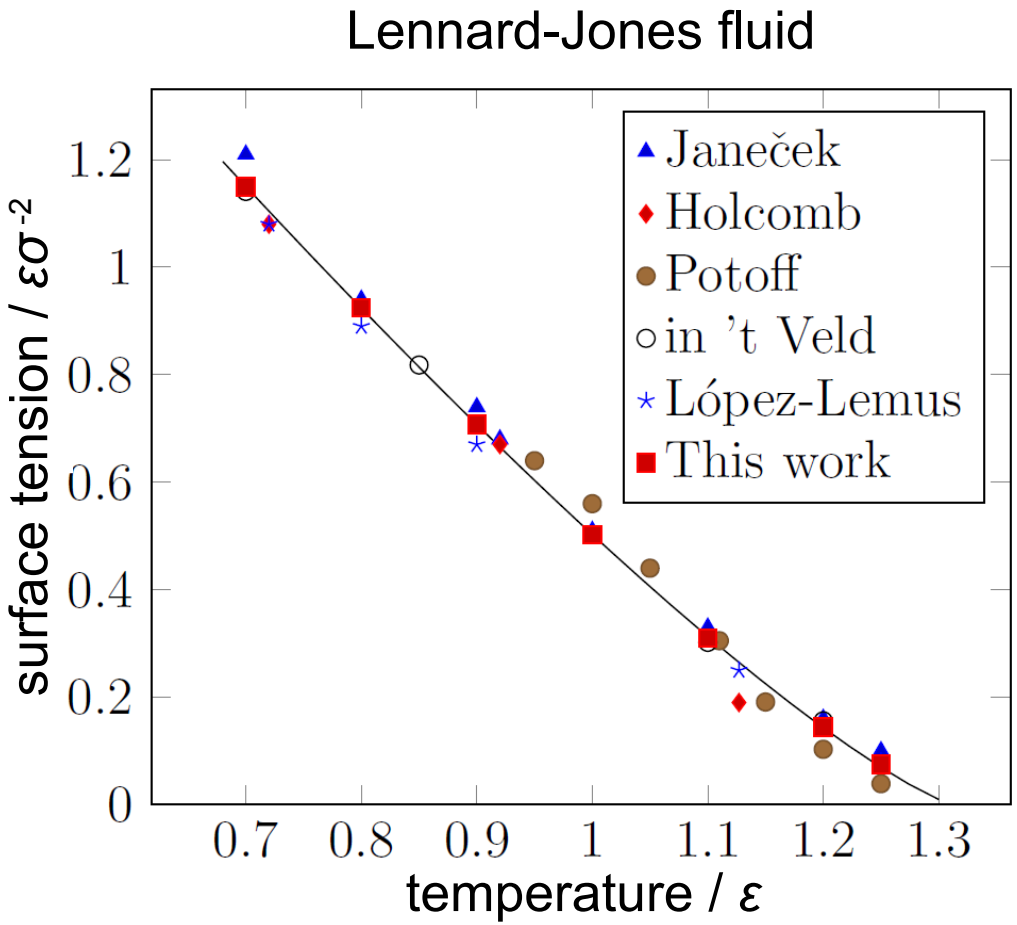


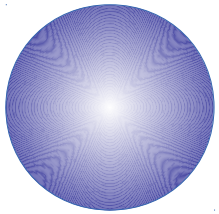
Surface tension of thin films:



The deviation of the surface tension of a nanofilm from the macroscopic value exhibits the same tendency (scaling with $1/d^3$).

Surface tension at high precision

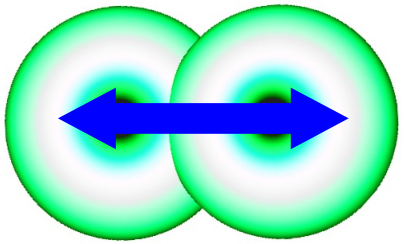




LJ

$$\gamma_0(T) = 2.94 \frac{\varepsilon}{\sigma^2}\left(1-\frac{T}{T_c}\right)^{1.23}$$

Validation of molecular force field models



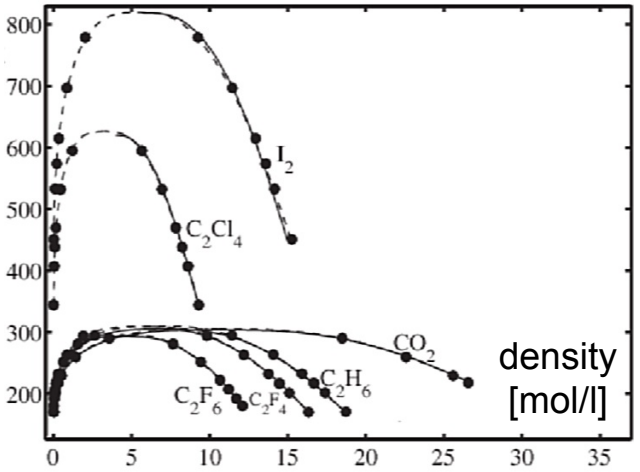
2CLJQ models:

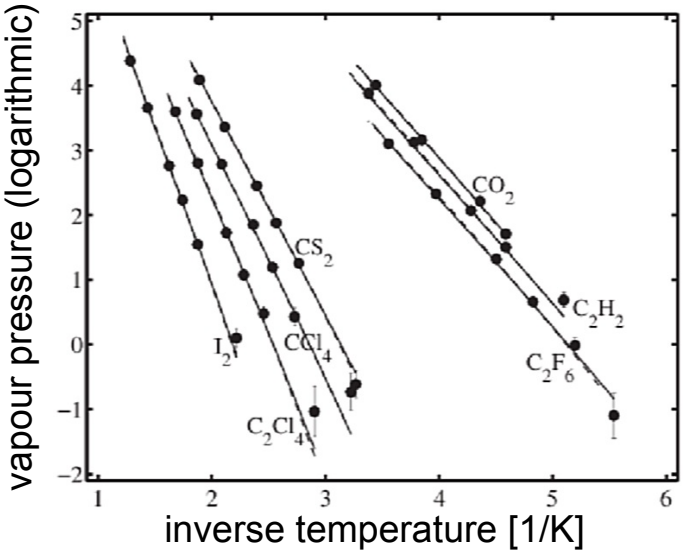
- 2 LJ centres
- 1 quadrupole

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

Deviation:

- $\delta\rho'$ ≈ 1 %
- δP^{sat} ≈ 5 %

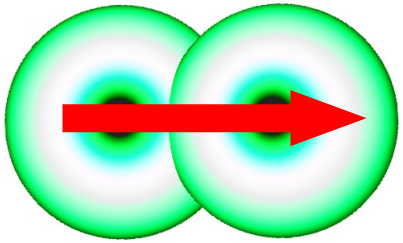




- simulation
— DIPPR correlation

No interfacial properties were considered for the parameterization.

Validation of molecular force field models



2CLJD models:

- 2 LJ centres
- 1 dipole

Fit of parameters σ, ε, L, μ to VLE data of 46 fluids by Stoll *et al.*

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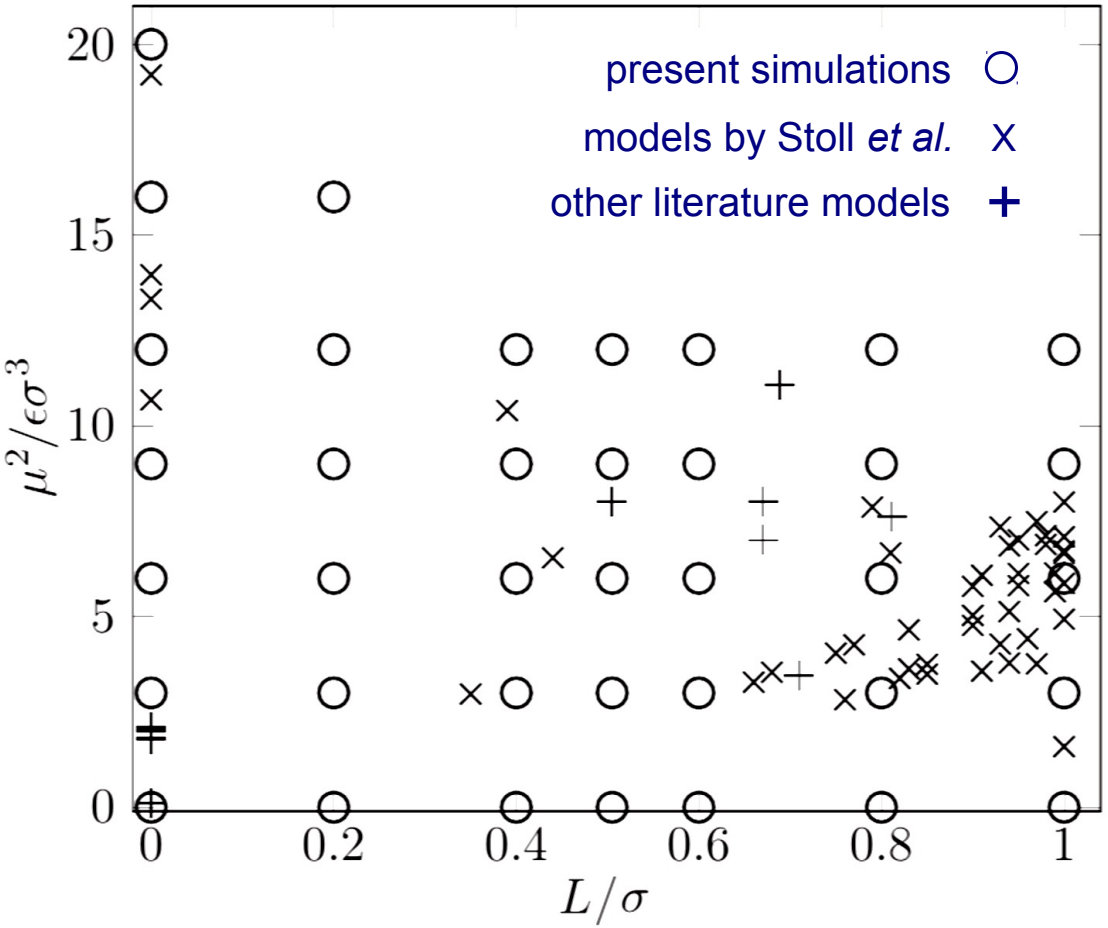
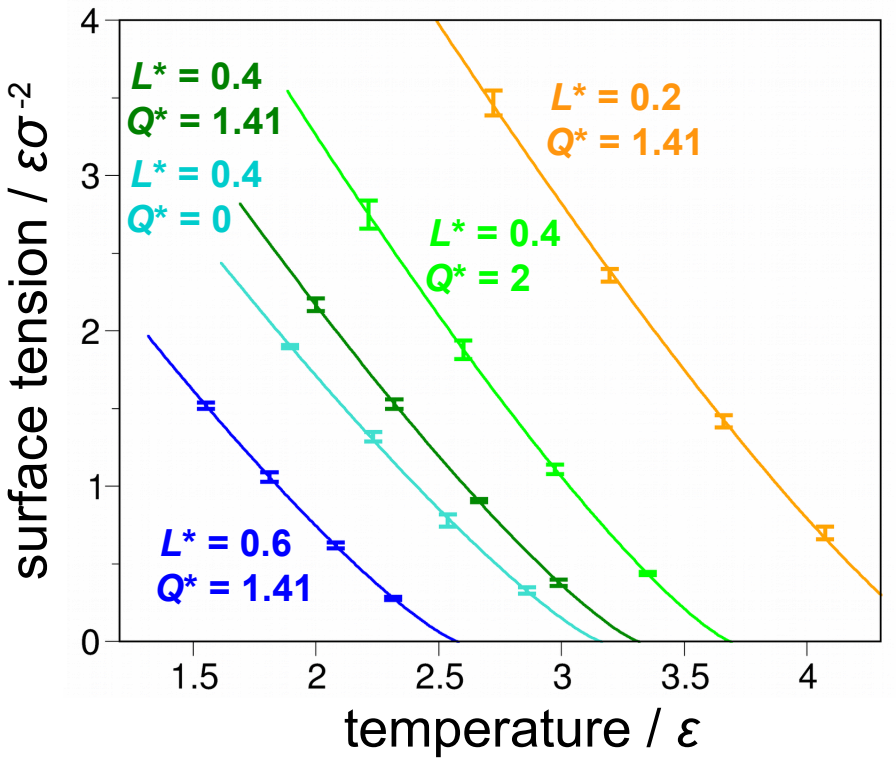
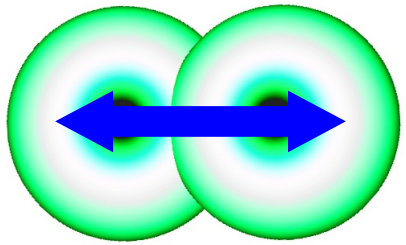


Massively parallel molecular modelling

Two LJ + quadrupole (2CLJQ)





2CLJQ

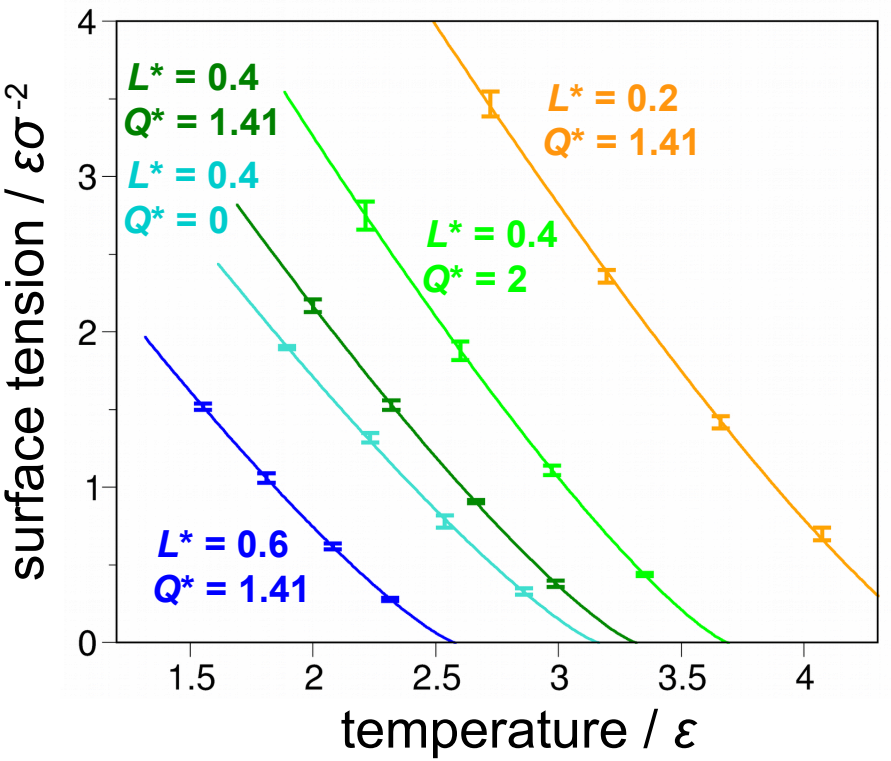
Model parameters:

- LJ size parameter σ
- LJ energy parameter ε
- Elongation L
- Quadrupole moment Q

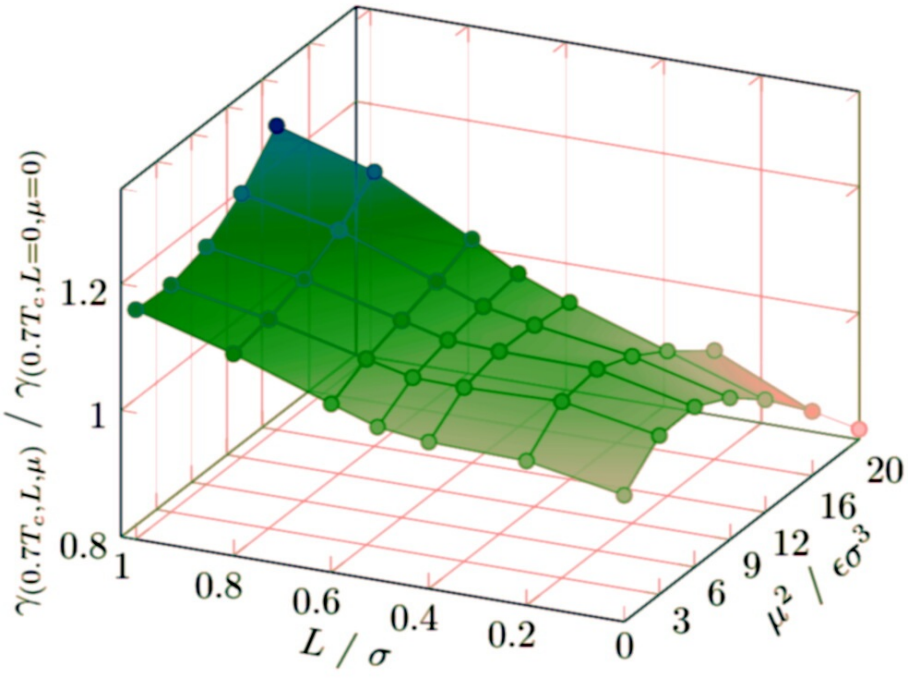
- Systematic exploration of the four-dimensional model parameter space

Massively parallel molecular modelling

Two LJ + quadrupole (2CLJQ)



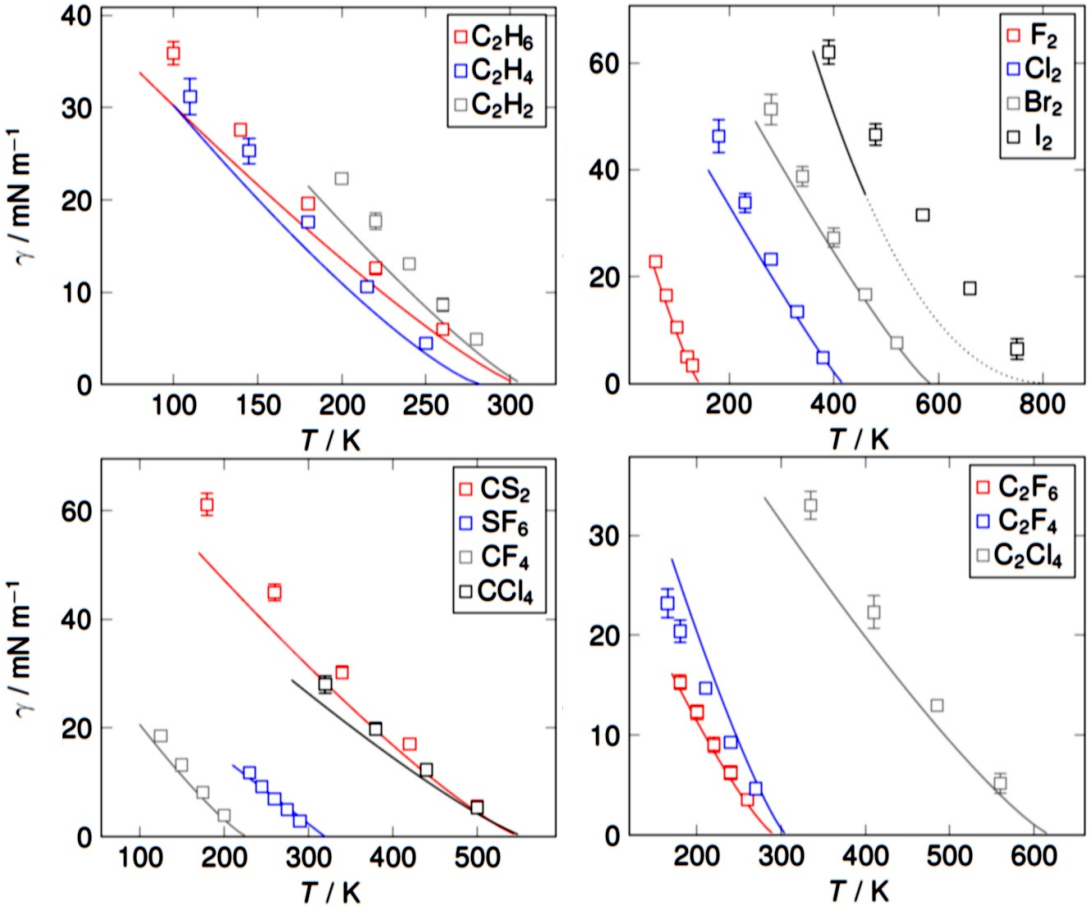
Two LJ + dipole (2CLJD)



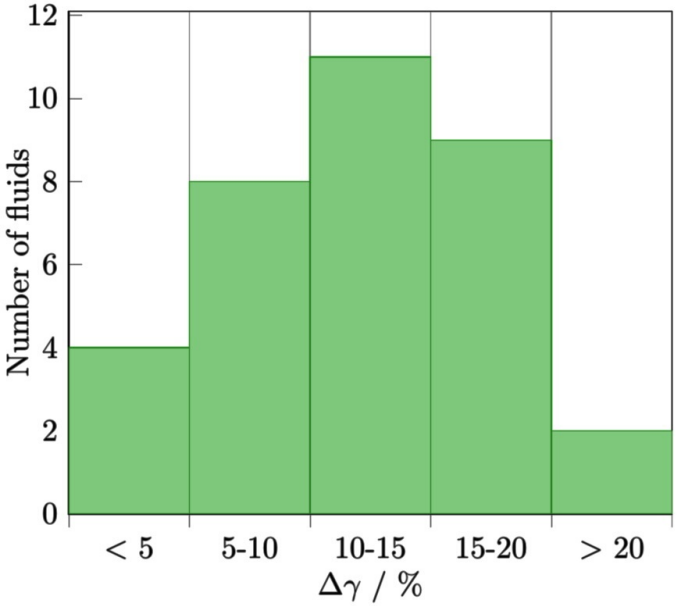
- Systematic exploration of the four-dimensional model parameter space
- Correlation of the surface tension by a critical scaling expression

Validation of molecular force field models

Two LJ + quadrupole (2CLJQ)



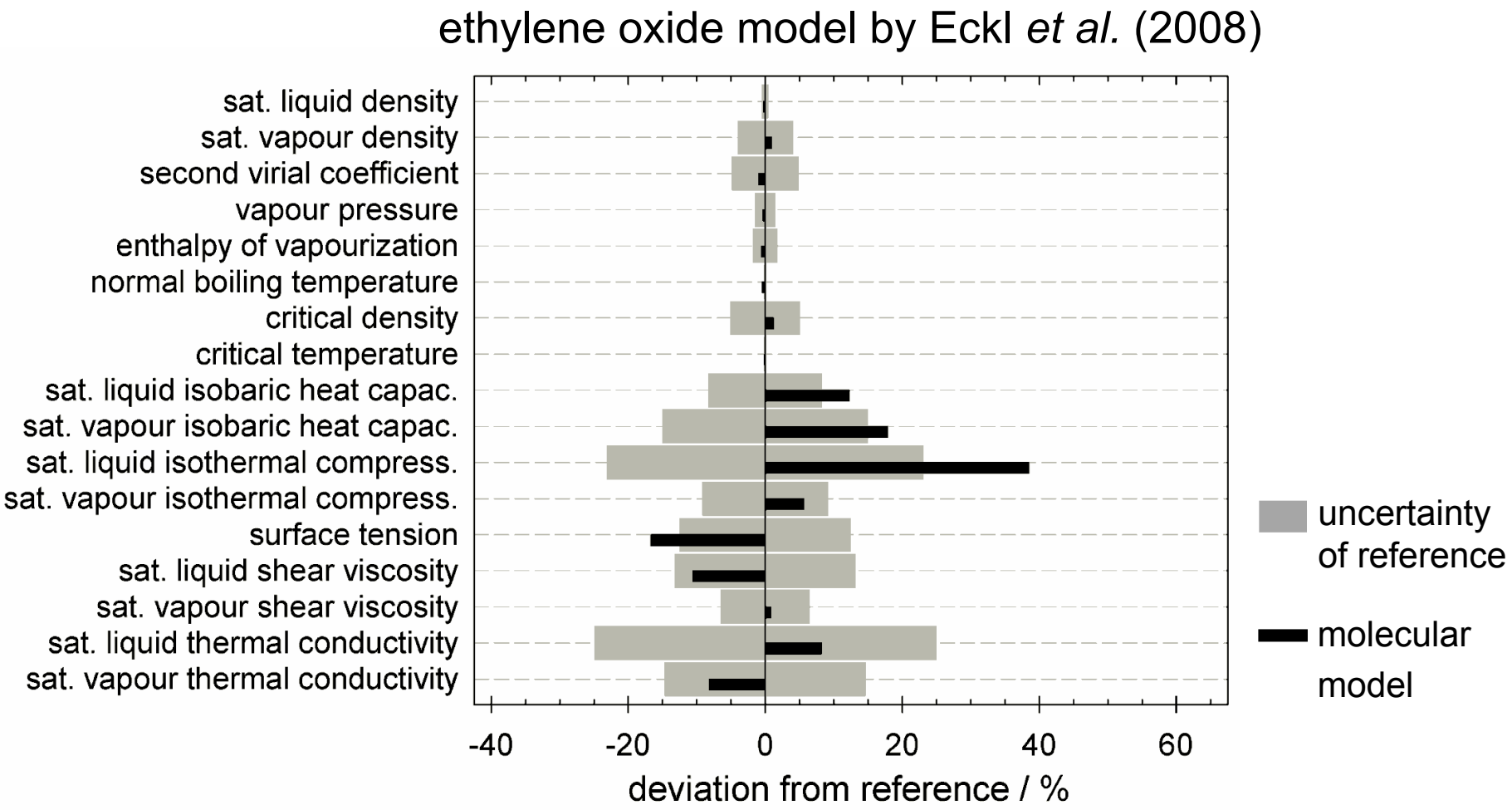
Two LJ + dipole (2CLJD)



Fit to bulk properties

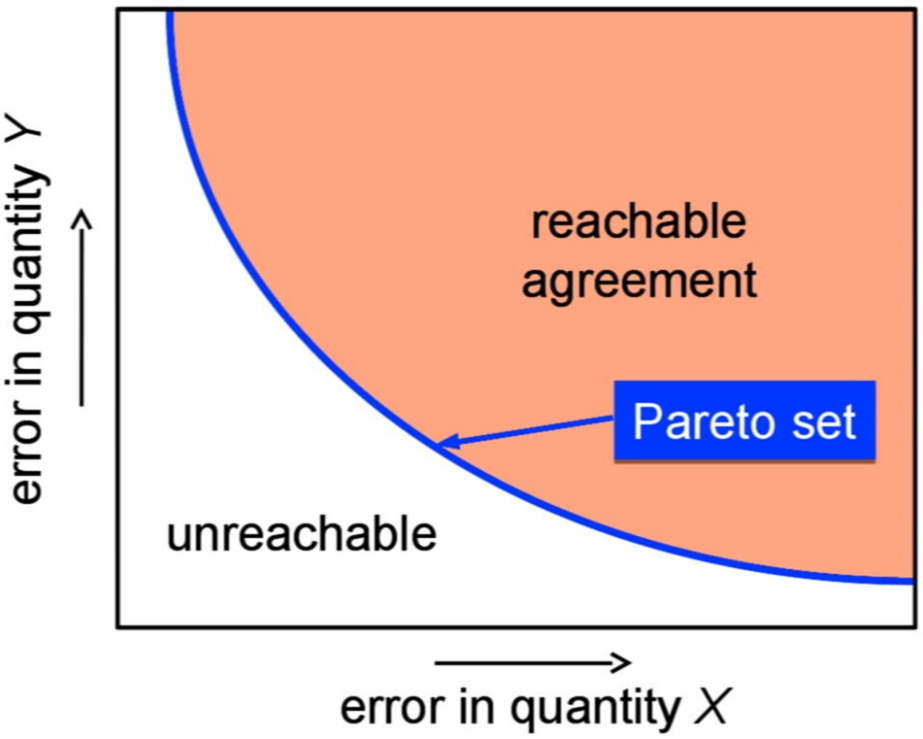
10 to 20 % overestimation of vapour-liquid surface tension

Model optimization with multiple objectives

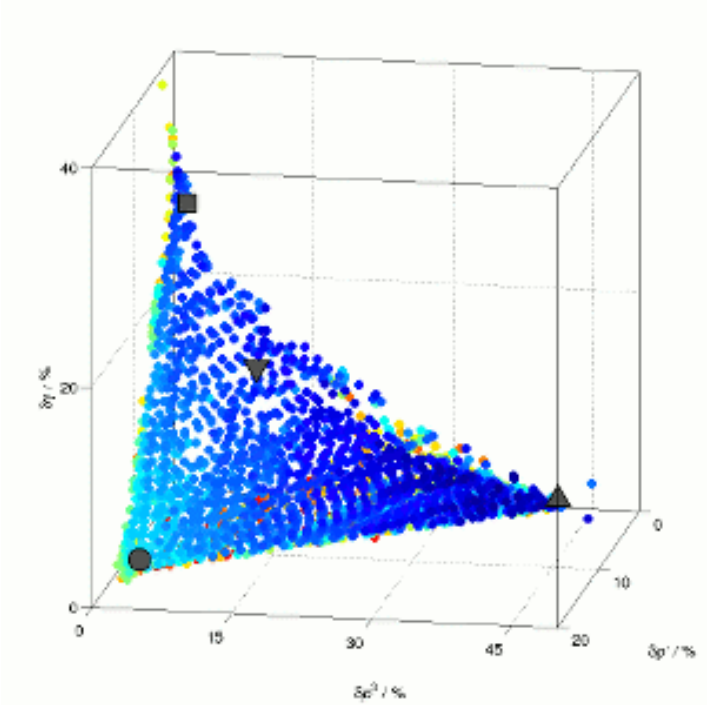


Multicriteria optimization

Pareto optimality criterion



Multiple objectives

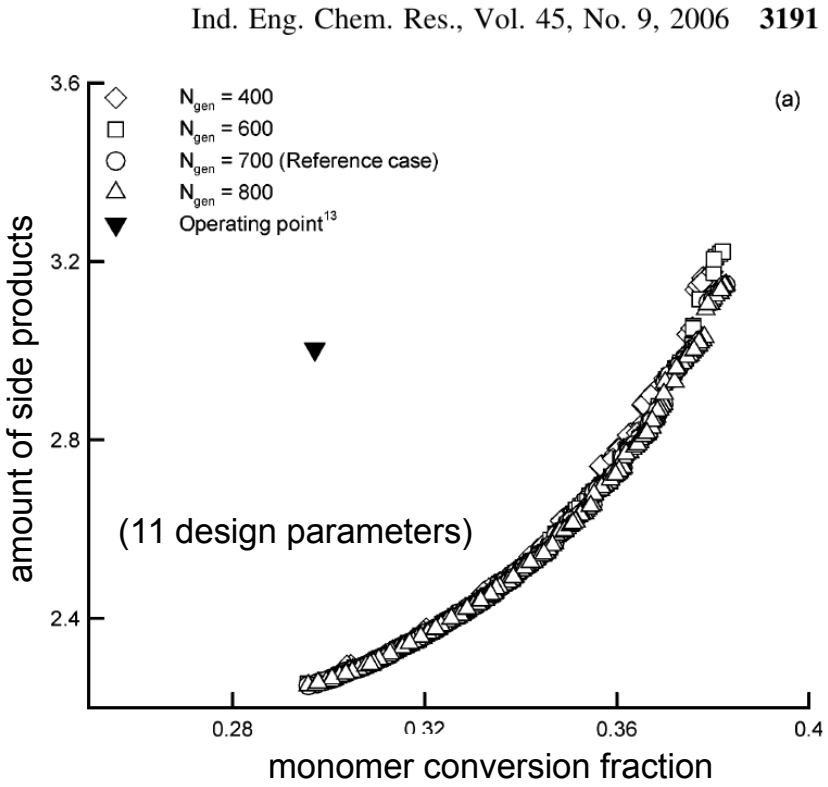


(2CLJQ for carbon dioxide)

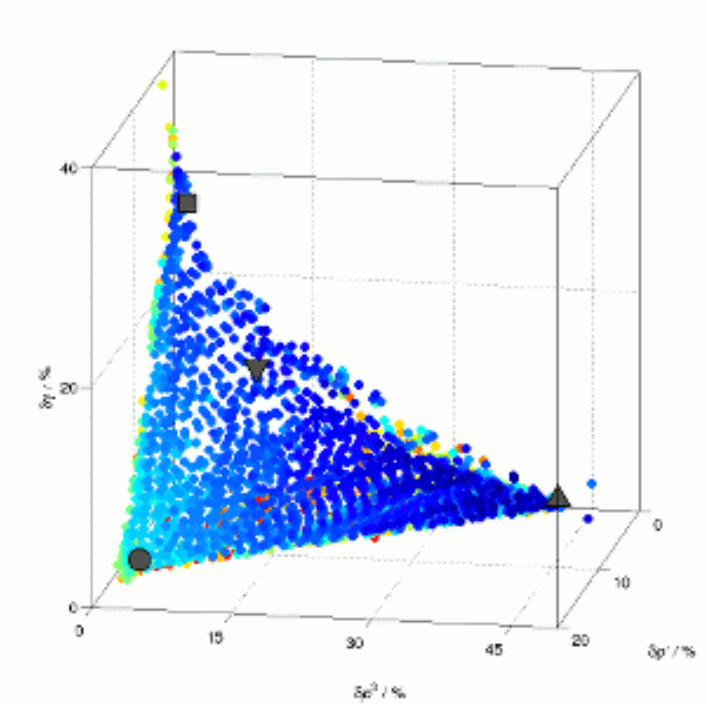
Multicriteria optimization requires massively parallel molecular modelling.

Multicriteria optimization

Literature example: LDPE synthesis



Multiple objectives



(2CLJQ for carbon dioxide)

High-dimensional parameter spaces require stochastic exploration methods.

Parameter space and objective space

p model parameters

(here, $p = 4$)

- LJ size parameter σ
- LJ energy parameter ε
- Model elongation L
- Multipole moment μ or Q

Dimension of Pareto set $d \leq p$.

q optimization criteria

(here, $q = 3$)

- Saturated liquid density ρ'
- Saturated vapour pressure p^s
- Vapour-liquid surface tension γ

Dimension of the Pareto set cannot be greater than $q - 1$.

In general, $d = \min(p, q - 1)$.

(here, $d = 2$)

Computation of the Pareto set

Multicriteria optimization problem

Simultaneously minimized objective functions f_ξ with $\xi \in \{\rho', p^s, \gamma\}$ given by

$$f_\xi = \left\langle \delta \xi^2 \right\rangle_{0.55 T_c^{exp} < T < 0.95 T_c^{exp}} = \lim_{N \to \infty} \frac{1}{N+1} \sum_{i=0}^{N} \left(1 - \frac{\xi^{sim}(T)}{\xi^{exp}(T)} \right)^2_{T/T_c = 0.55 + 0.4 i/N} \quad \text{(here: } N = 9\text{)}.$$

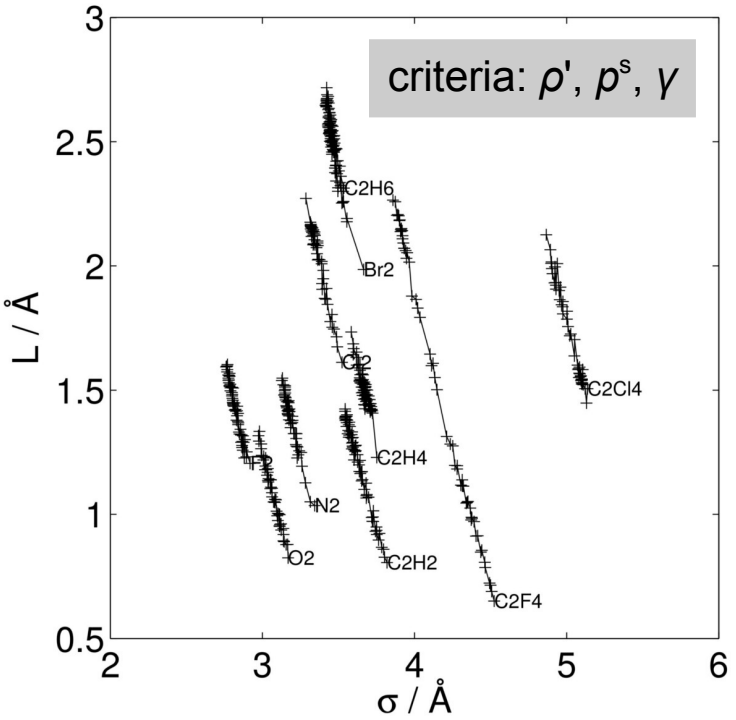
Sandwiching

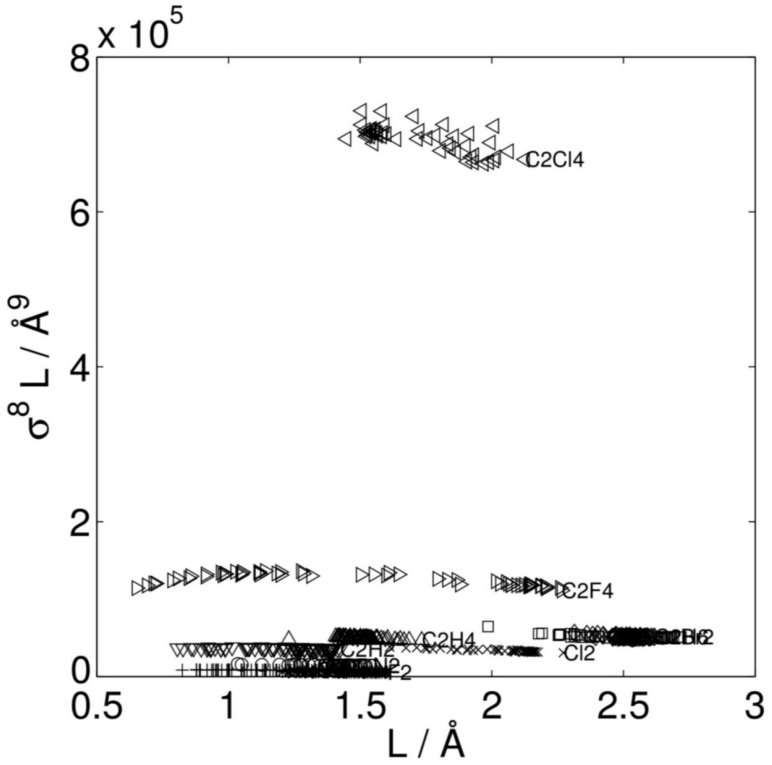
Alternating construction of inner (reachable) and outer (unreachable) approximations, assuming *local convexity* of the Pareto set.

Hyperboxing

In non-convex regions (“hyperboxes”), Pascoletti-Serafini scalarization is employed to obtain a suitable local single-criterion optimization problem.

Invariants of Pareto-optimal models

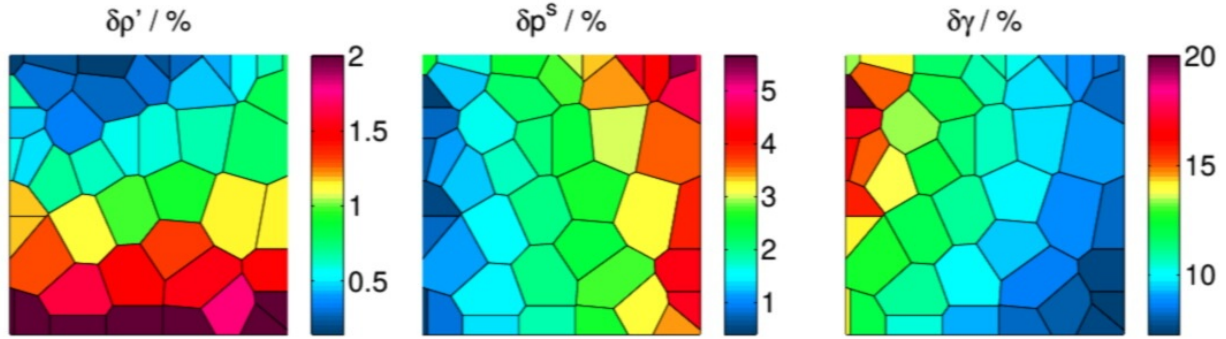




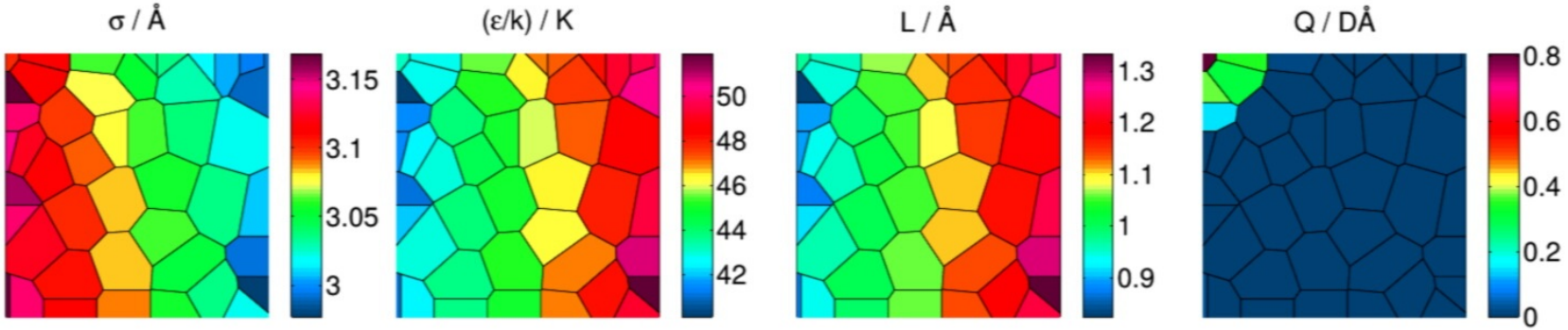
For obtaining a rough approximation of the Pareto set, the dimension of the parameter space can be reduced from four to three (or even two).

Model tailoring by the end user

Representation of objective and parameter spaces by **patch plots**:

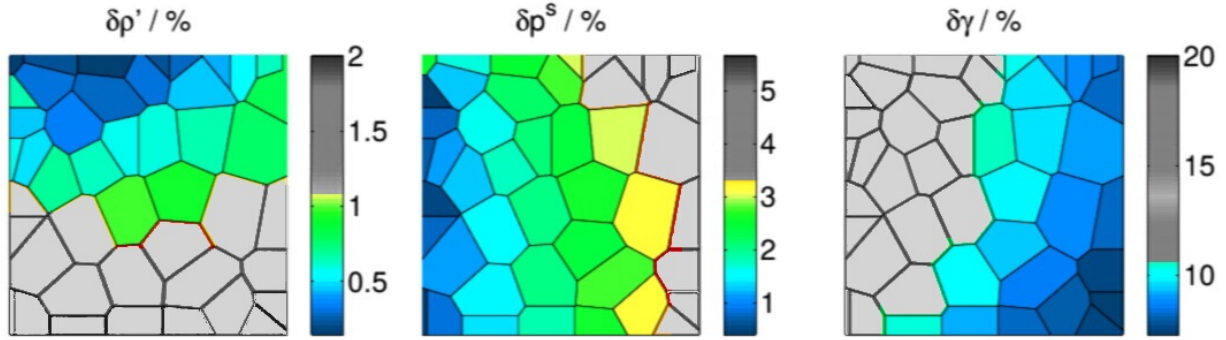


Pareto-optimal 2CLJQ models of molecular oxygen

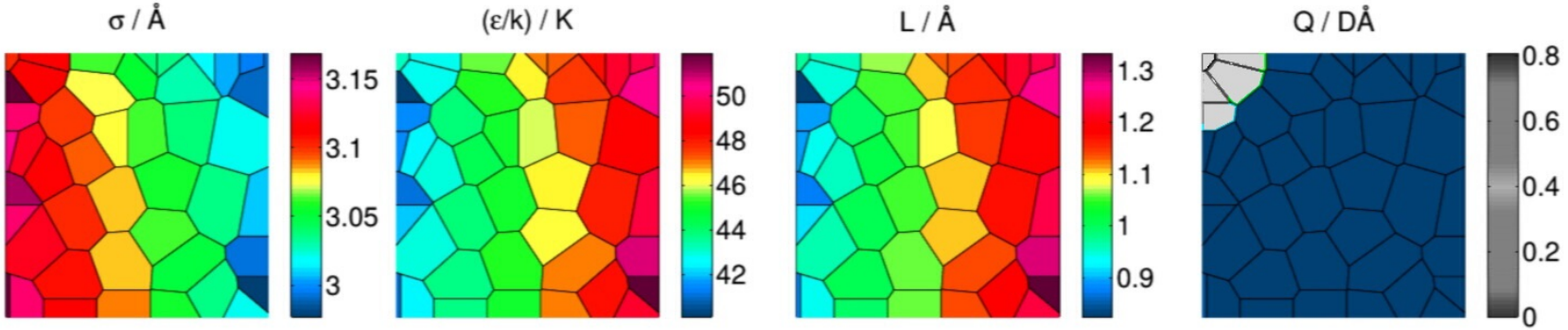


Model tailoring by the end user

For each specific application, accuracy requirements can be specified:

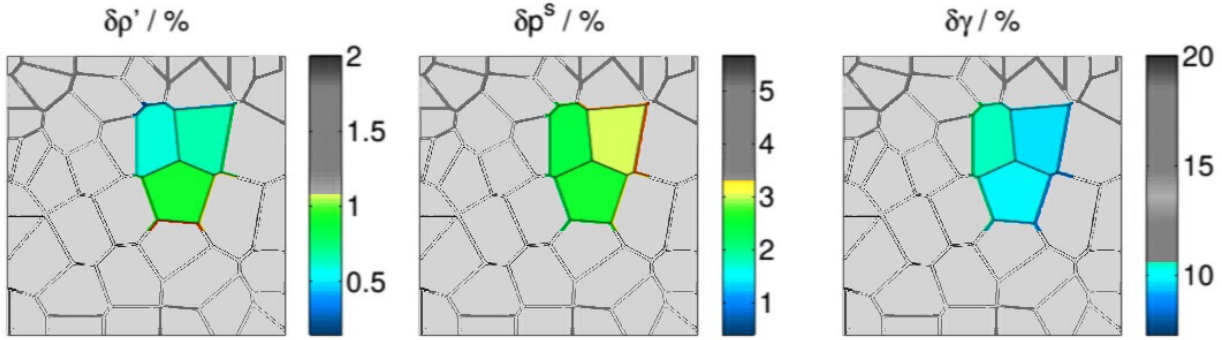


Restrictions imposed on 2CLJ models of molecular oxygen

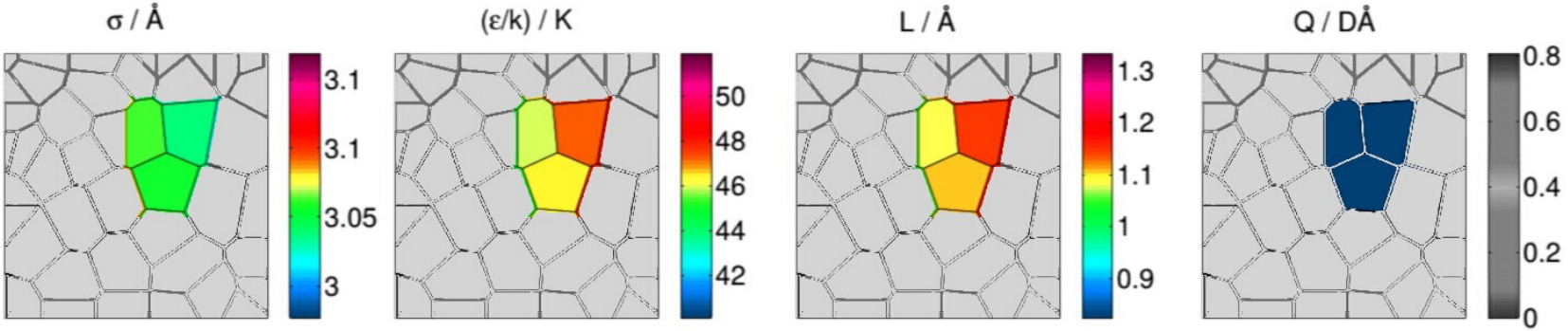


Model tailoring by the end user

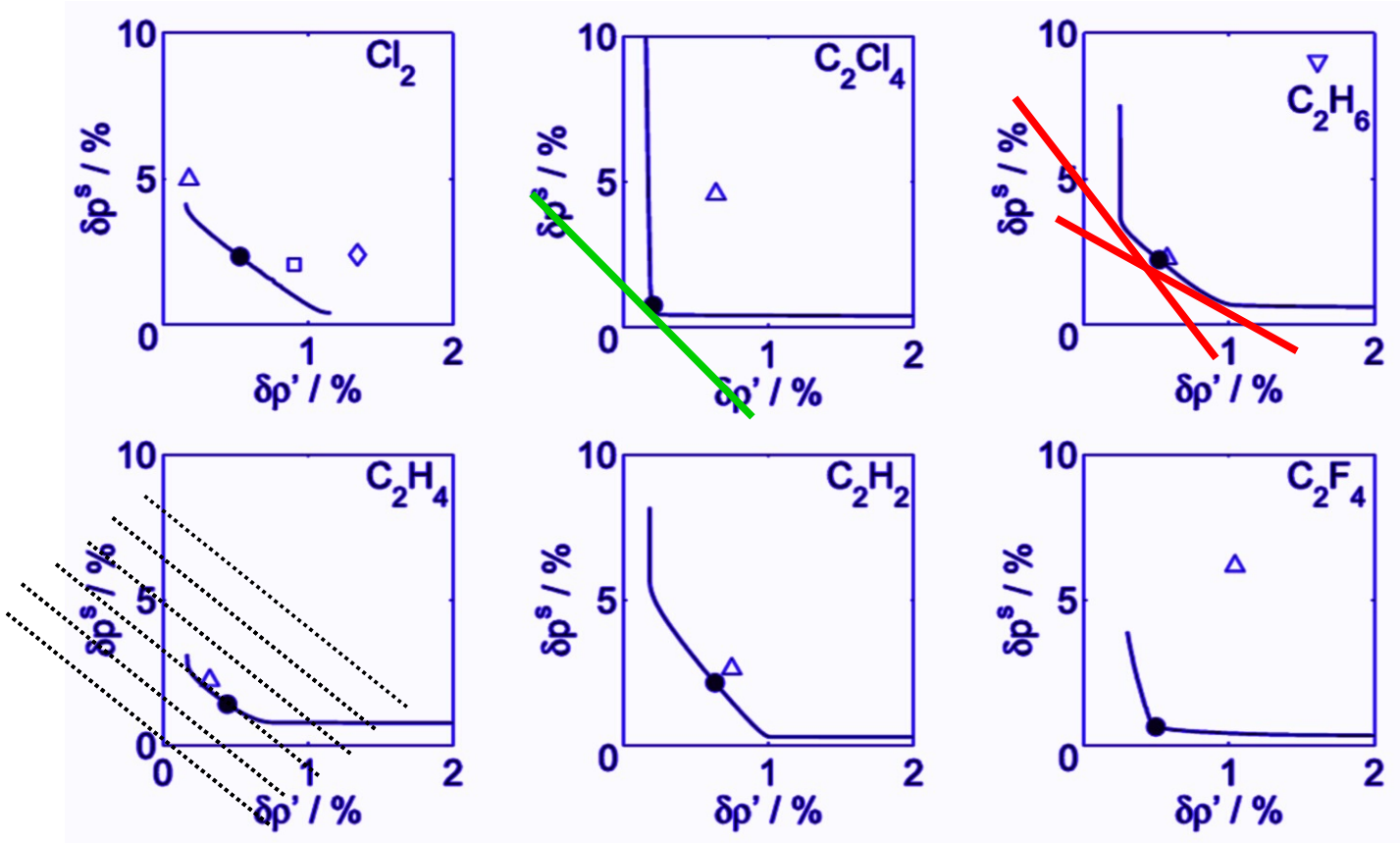
Intersection of the highlighted areas within all replicas of the patch plot:



2CLJ models of molecular oxygen fulfilling all requirements



Overall compromise models: Pareto knee

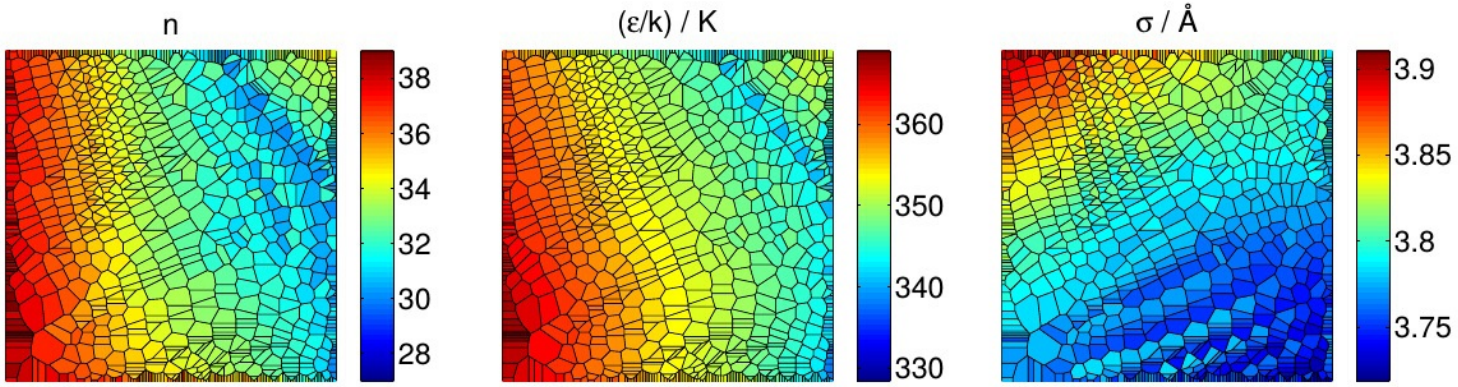


A single-criterion optimization algorithm would often miss the Pareto knee.

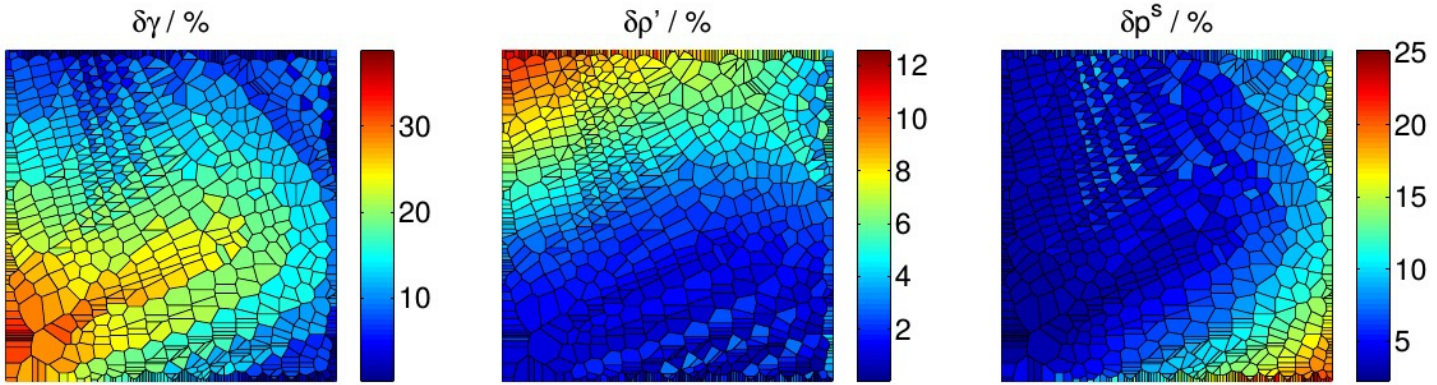
Comparision between model classes

Carbon dioxide: Mie–*n*,6 potential $u(r)=\frac{n}{n-6}\left(\frac{n}{6}\right)^{\frac{6}{n-6}}\epsilon\left[\left(\frac{\sigma}{r}\right)^{n}-\left(\frac{\sigma}{r}\right)^{6}\right]$

parameter space

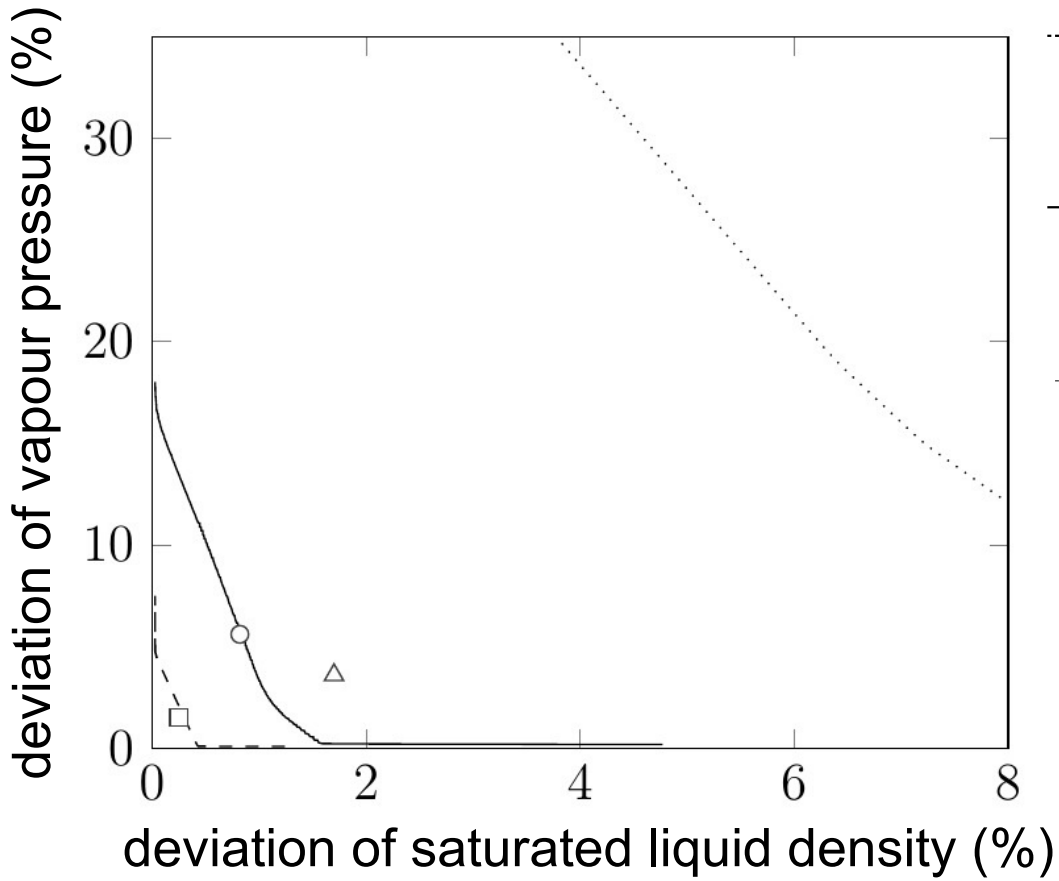


objective space



Comparision between model classes

Carbon dioxide: Mie–*n*,6 potential ./. other model classes



LJ potential (2 parameters)

Mie–*n*,6 potential (3 parameters)

2CLJQ potential (4 parameters)

□ Vrabec *et al.* (2001) 2CLJQ model

△ Avendaño *et al.* (2011) Mie–*n*,*m* model

Summary

The traditional art of molecular modelling

An **expert modelling artist** designs and publishes

- a single optimized model for a particular fluid,
- according to his choice of criteria (often unknown to the public),
- users are passive, they have to live with the artists' decision.

Summary

The traditional art of molecular modelling

An **expert modelling artist** designs and publishes

- a single optimized model for a particular fluid,
- according to his choice of criteria (often unknown to the public),
- users are passive, they have to live with the artists' decision.

Scientific modelling by multicriteria optimization

For established model classes and multiple thermodynamic criteria,

- the dependence of thermodynamic properties on the model parameters is determined and correlated,
- the deviation between model properties and real fluid behaviour is characterized, and the Pareto set is published,
- users can design their own tailored model **with minimal effort**.