Computational molecular engineering by massively-parallel molecular simulation

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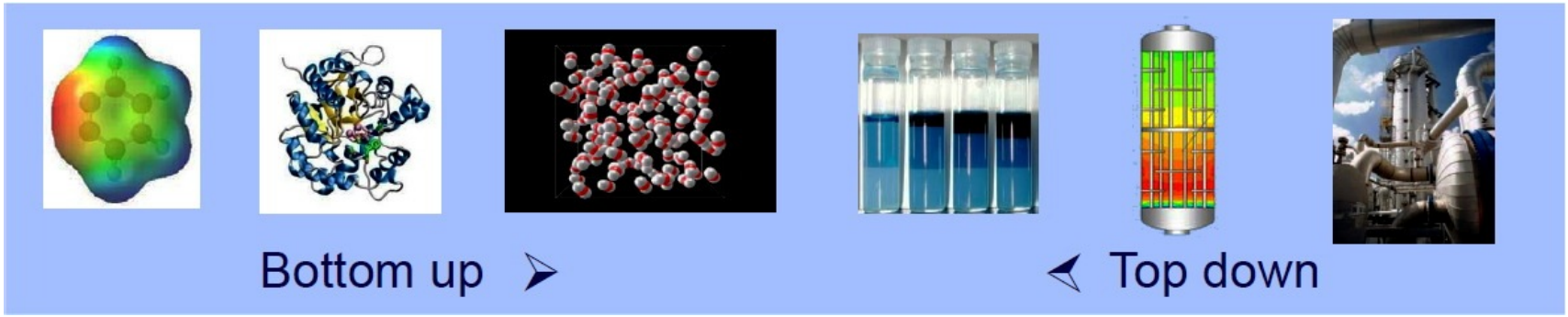
Daresbury, Cheshire, 11th September 2014
CECAM Workshop

Computational Molecular Engineering

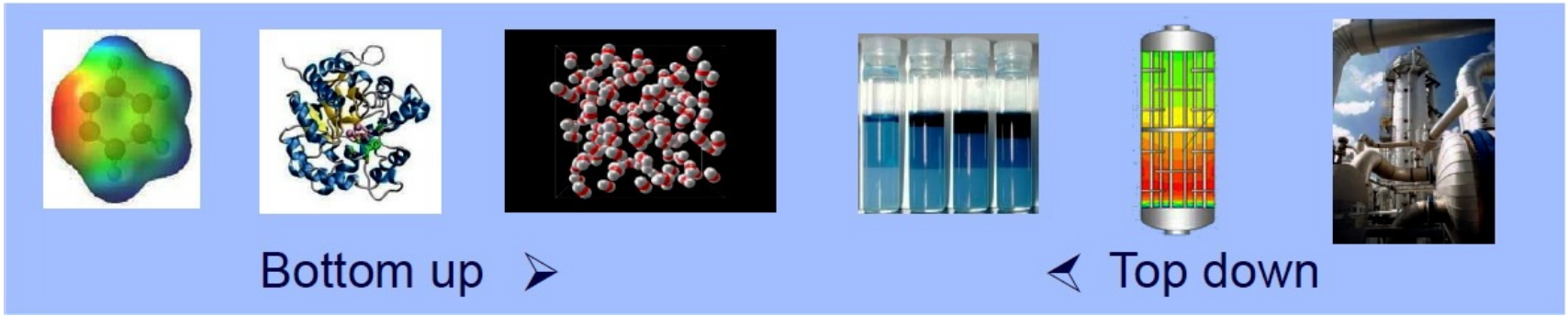
Computational Molecular Engineering



From Physics
(qualitative accuracy)

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

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

Molecular models of real fluids

Geometry

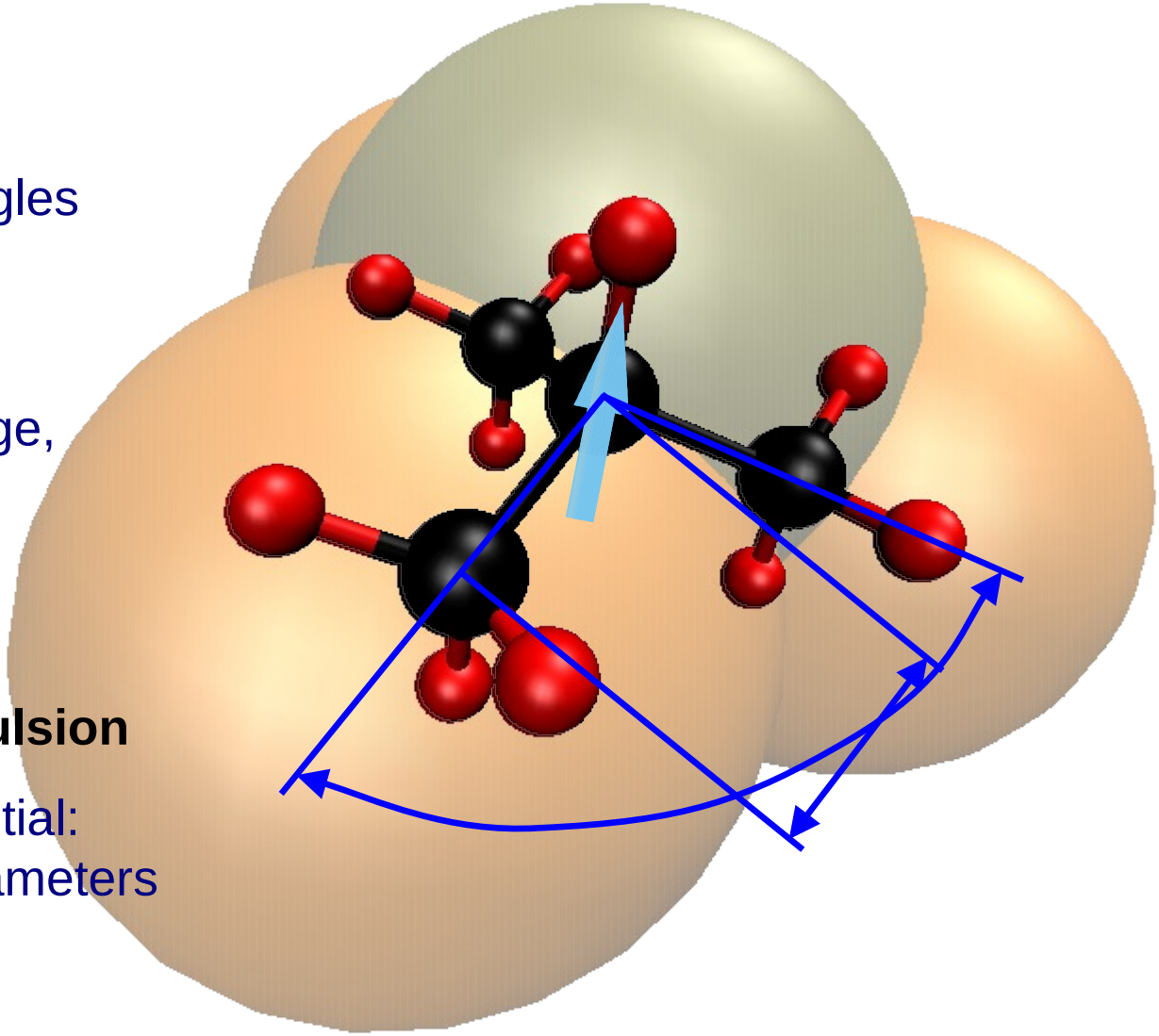
Bond lengths and angles

Electrostatics

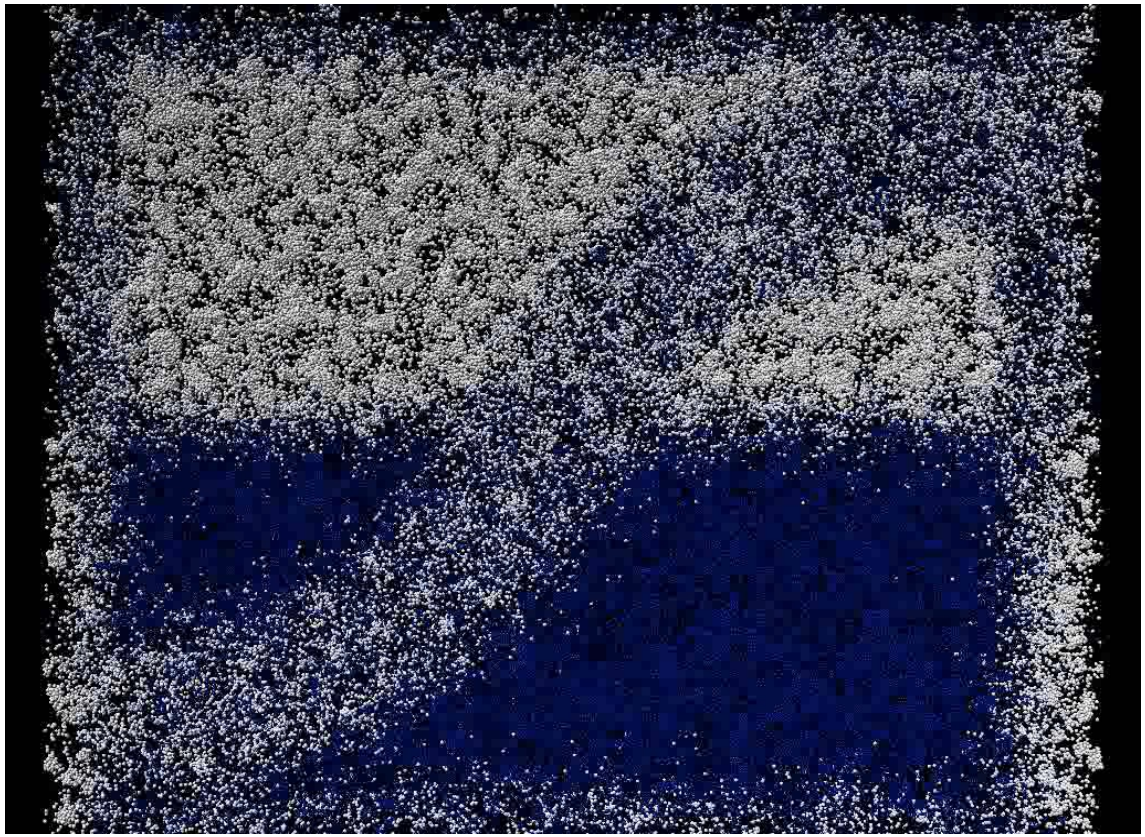
Point polarities (charge, dipole, quadrupole): Position and magnitude

Dispersion and repulsion

Lennard-Jones potential: Size and energy parameters



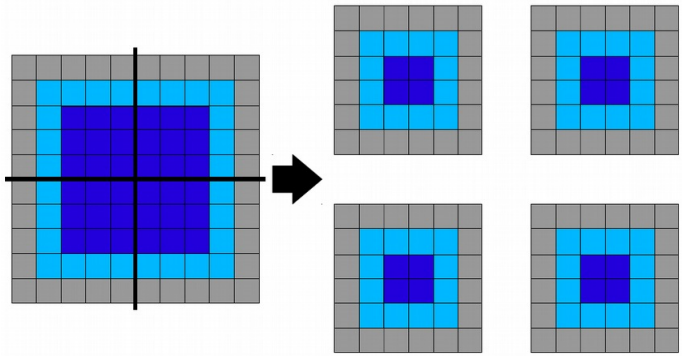
Molecular dynamics with *ls1 mardyn*



large systems 1: molecular dynamics

Scalable data structures in *ls1 mardyn*

Linked-cell data structure suitable for spatial domain decomposition:



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

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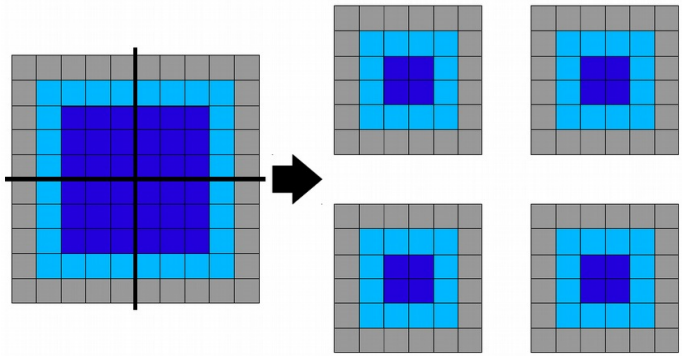
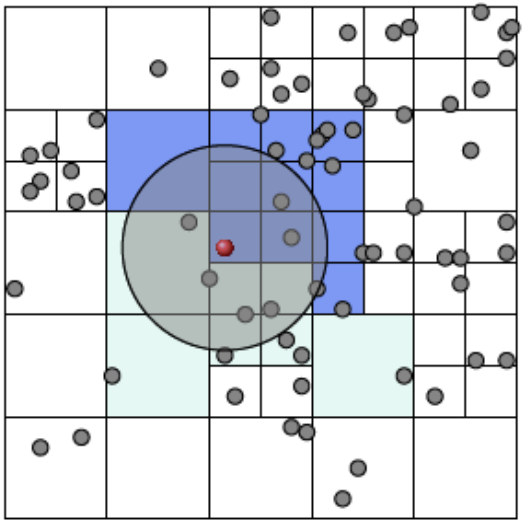
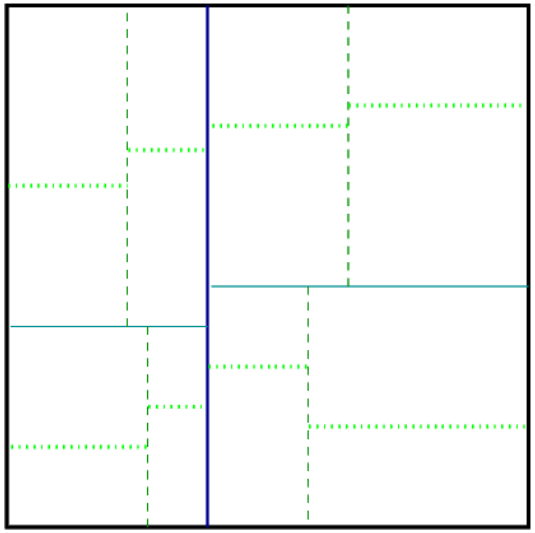


(non-blocking, overlapping MPI send/receive operations)

Methods for heterogeneous or fluctuating particle distributions:





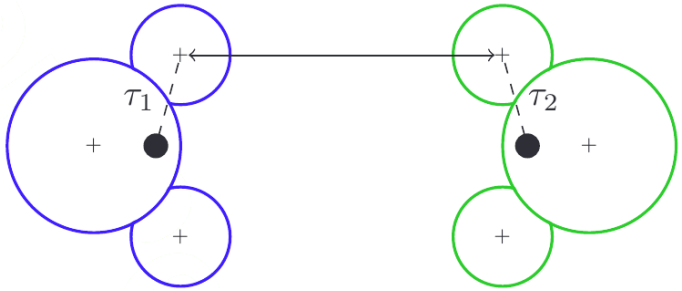
Long-range correction at planar interfaces

Correction from the **density profile**, following Janeček (2006):

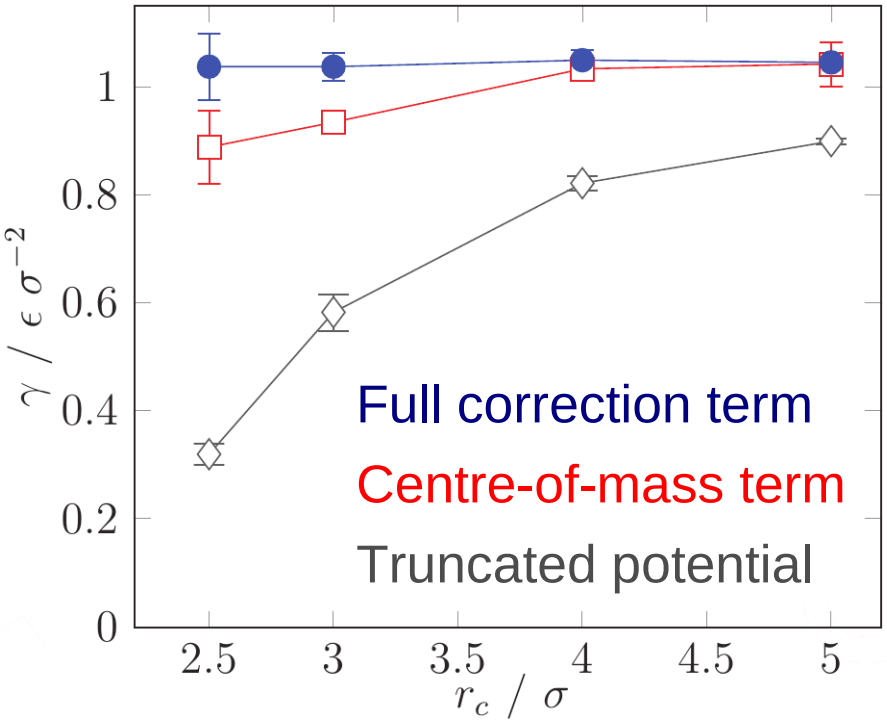
$$\Delta U_i = 2\pi \int_0^L dy\, \rho(y) \int_R^\infty dr\, u(r) r$$

with $R = \max(r_c, \Delta y)$

Angle-averaging expression for multi-site models (Lustig, 1988):

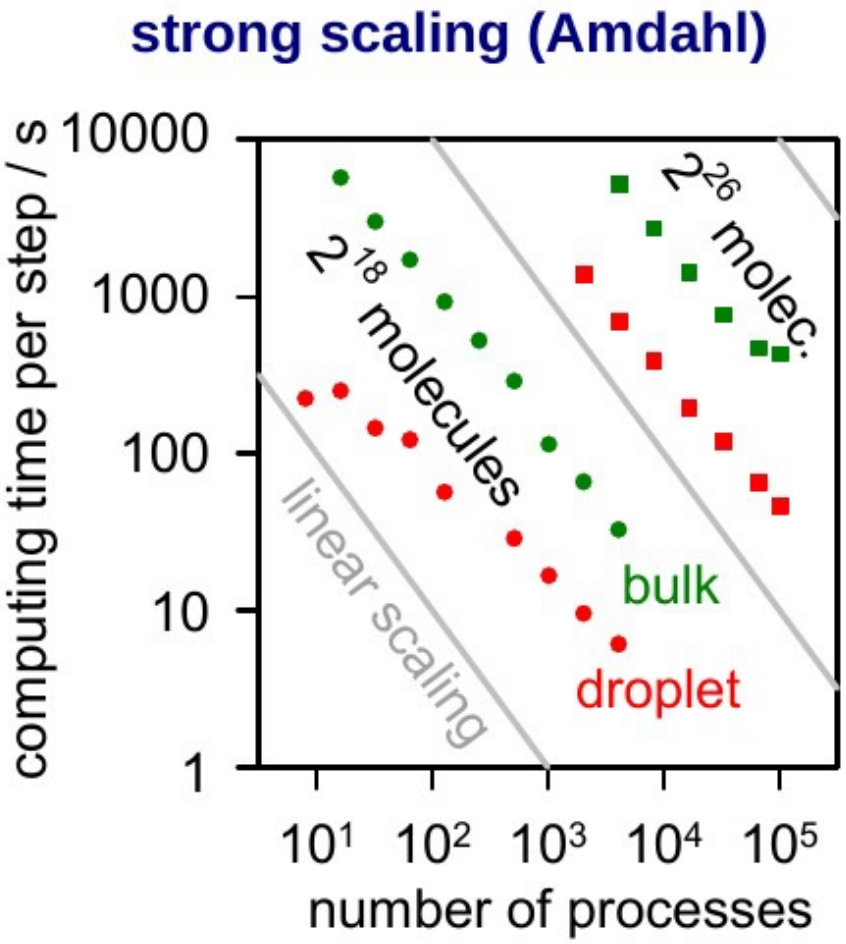


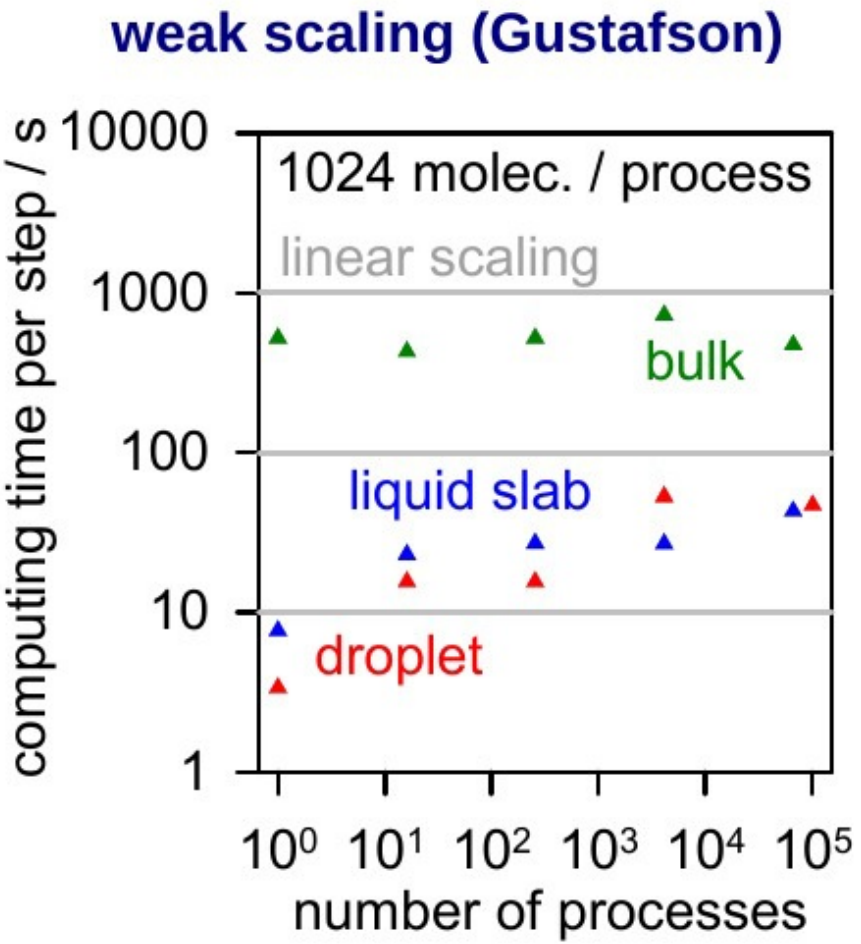
Two-centre LJ fluid (2CLJ)



For arbitrary geometries, FMM is implemented in a version of *ls1 mardyn*.

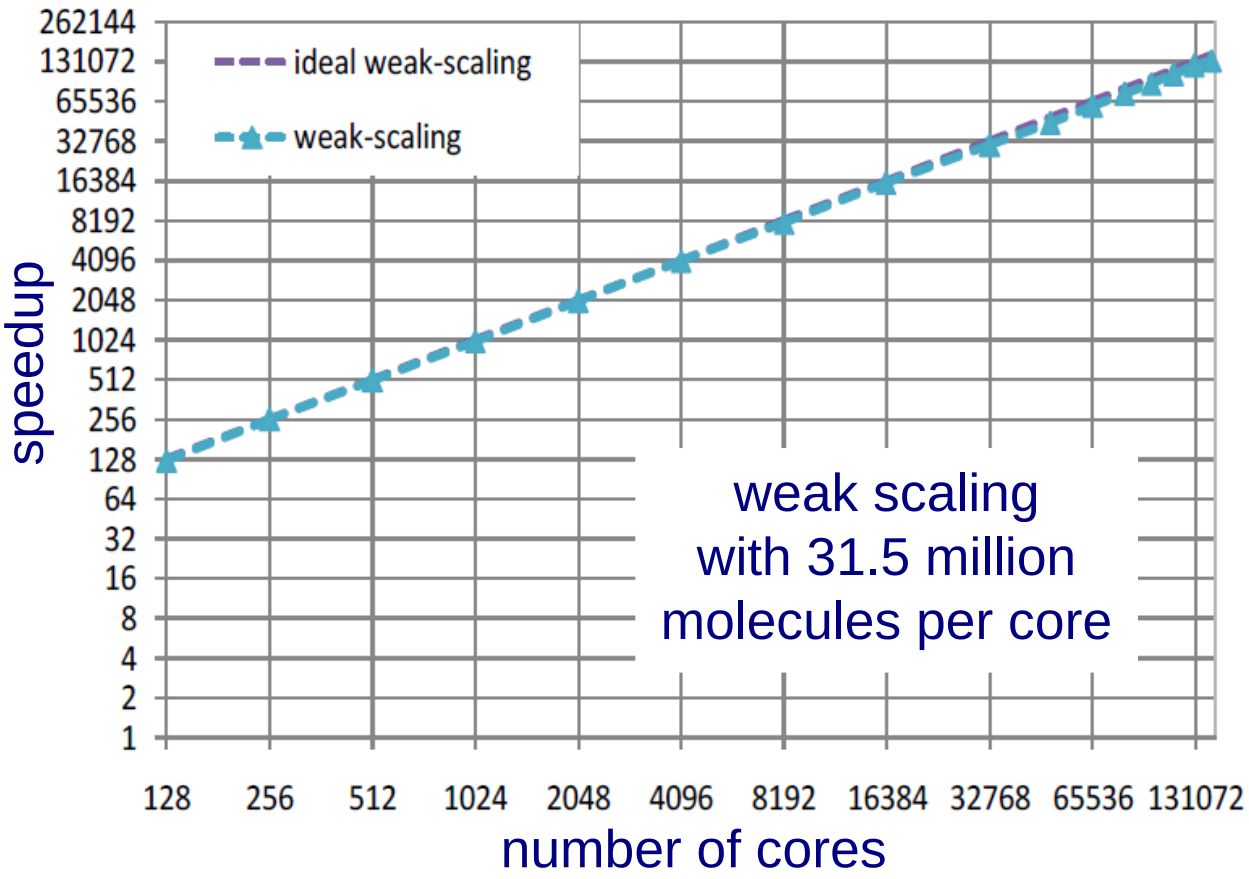
Scalability of *ls1 mardyn* on *hermit* (HLRS)



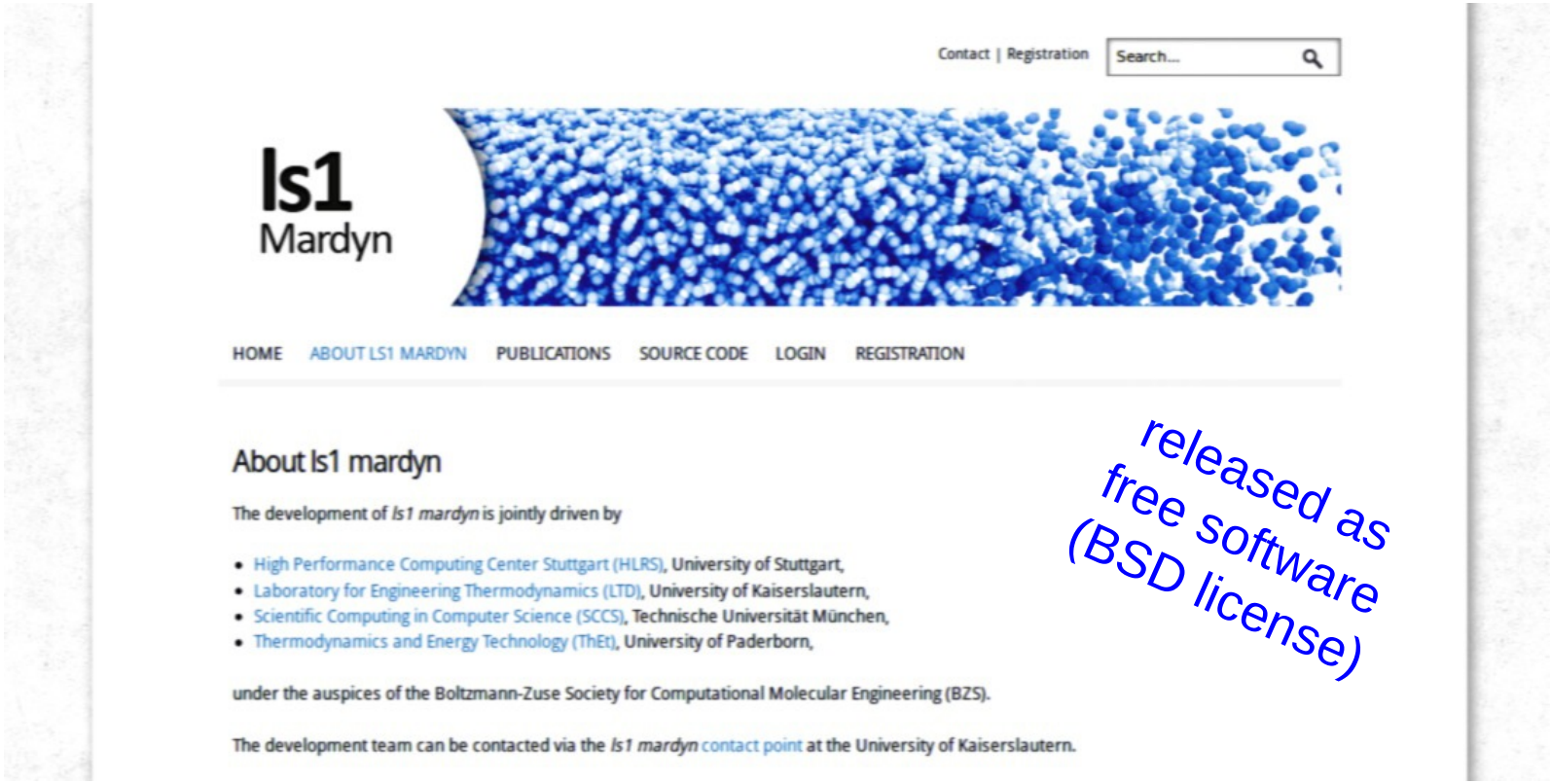


MD world record on *SuperMUC* (LRZ)

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



Free release of the *ls1 mardyn* program

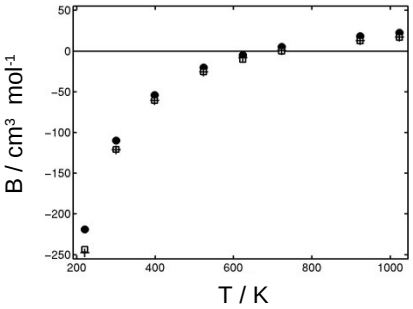


released as free software (BSD license)

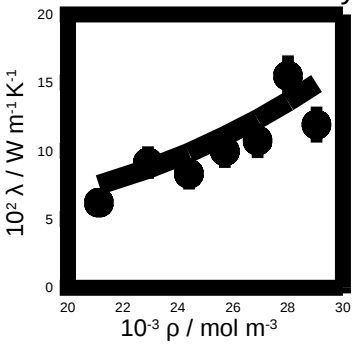
Download *ls1 mardyn* on the www.ls1-mardyn.de website.

Simulation of bulk properties with *ms2*

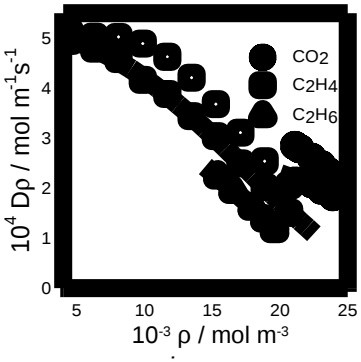
Second virial coefficient



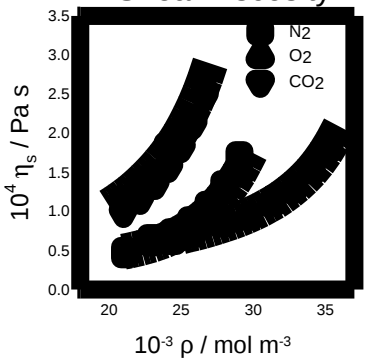
Thermal conductivity



Self-diffusion coefficient

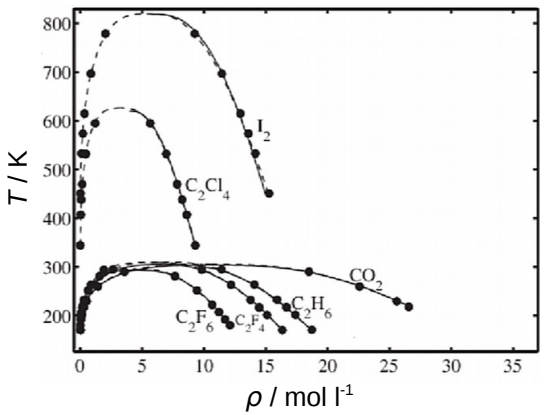


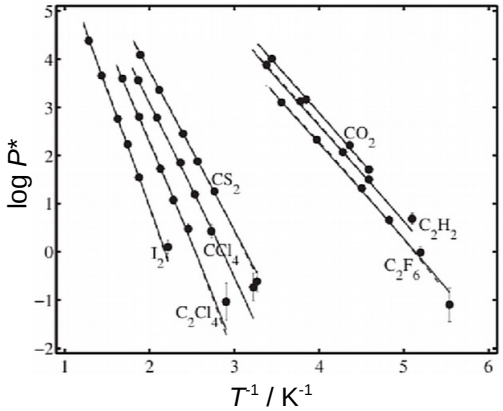
Shear viscosity



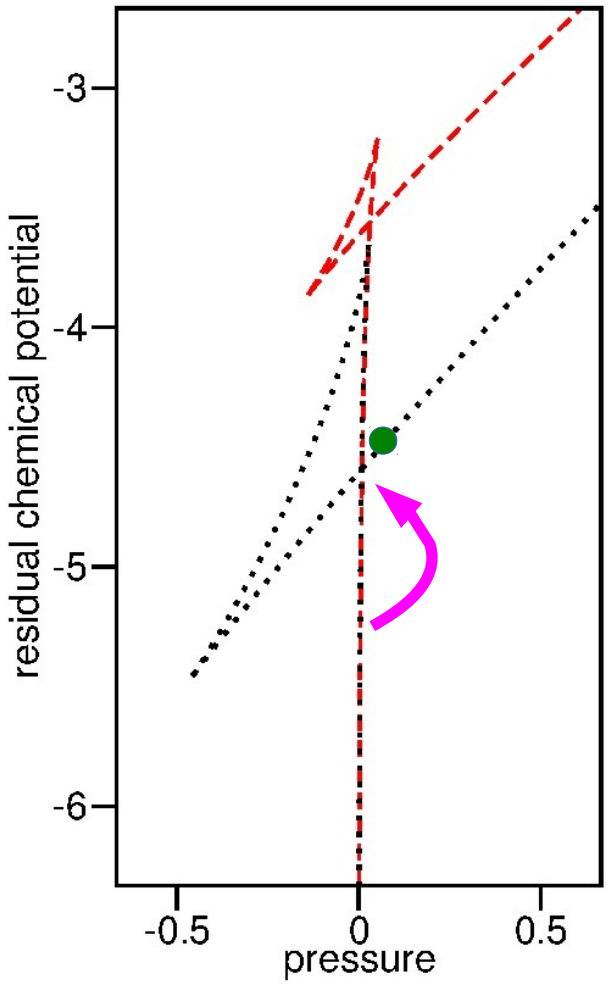
ms2 is freely available for academic use: register at www.ms-2.de

Vapour-liquid equilibira: Saturated densities and vapour pressures





Grand equilibrium simulation



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.

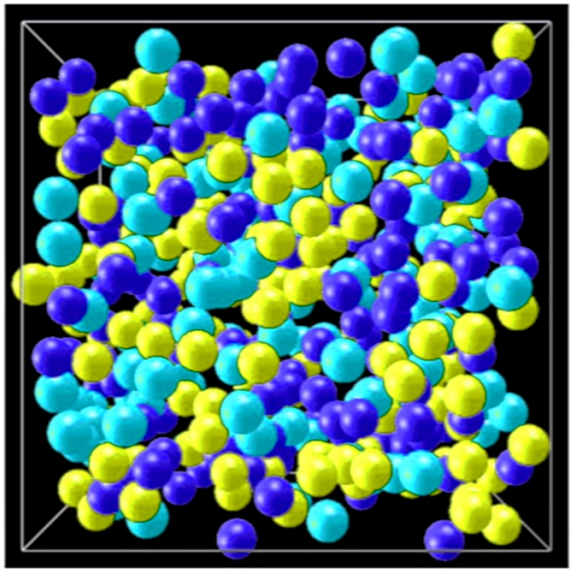
Second step: Pseudo-μVT vapour simulation

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

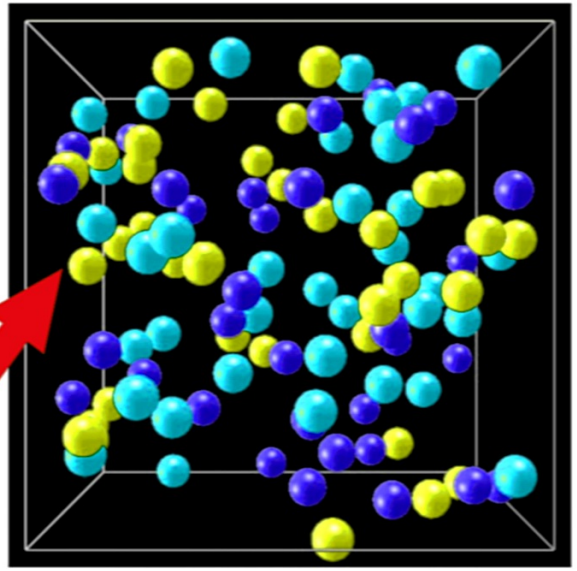
Obtained: Pressure p, vapour composition y

Grand equilibrium simulation

temperature
liquid composition

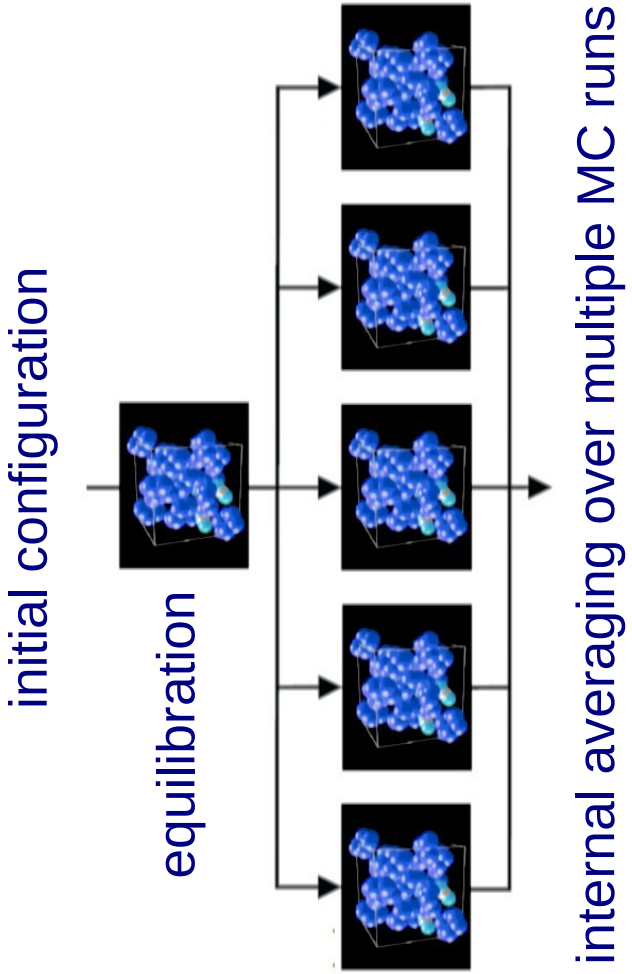


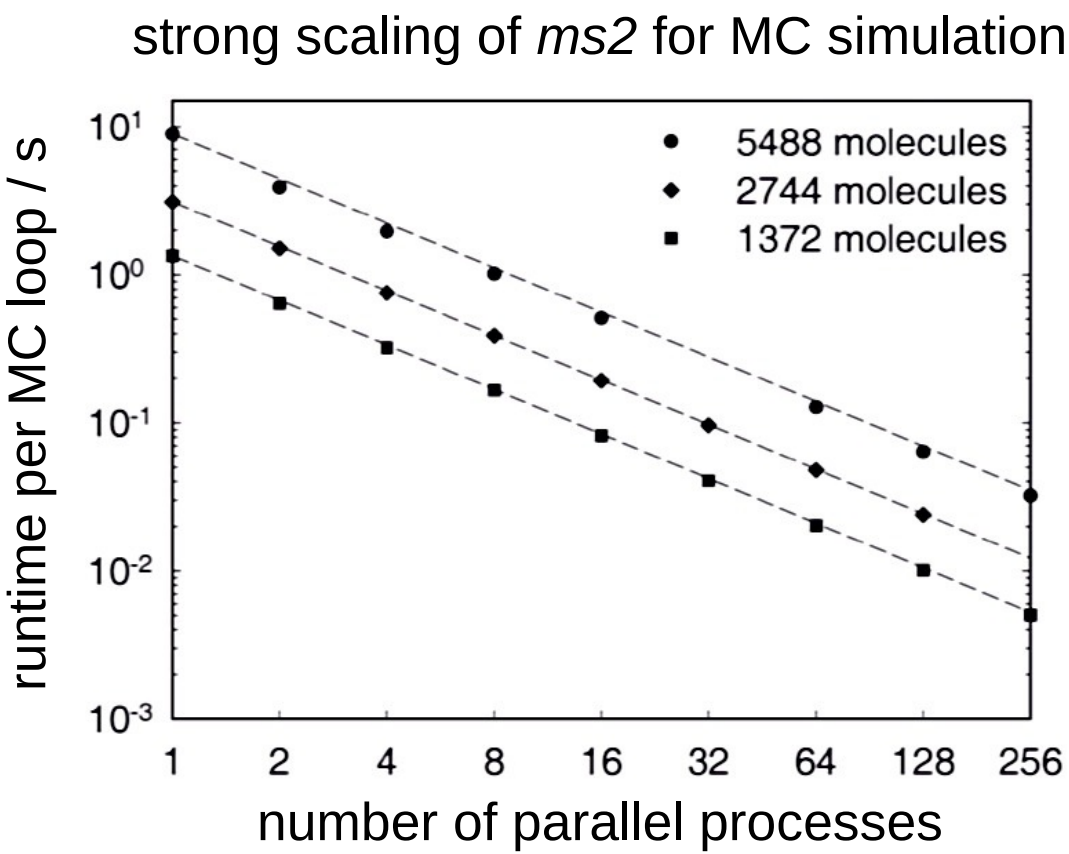
partial molar volumes
chemical potentials



pressure
vapour composition

Parallel sampling of multiple Markov chains





Fluctuations and thermodynamics

From highly performant molecular simulations, not only ensemble averages, but also higher-order fluctuations are accurately determined.

Massieu potential $\Phi = \frac{A}{T} = -\ln Z_{NVT}$

m^{th} order energy fluctuation
n^{th} order virial expression

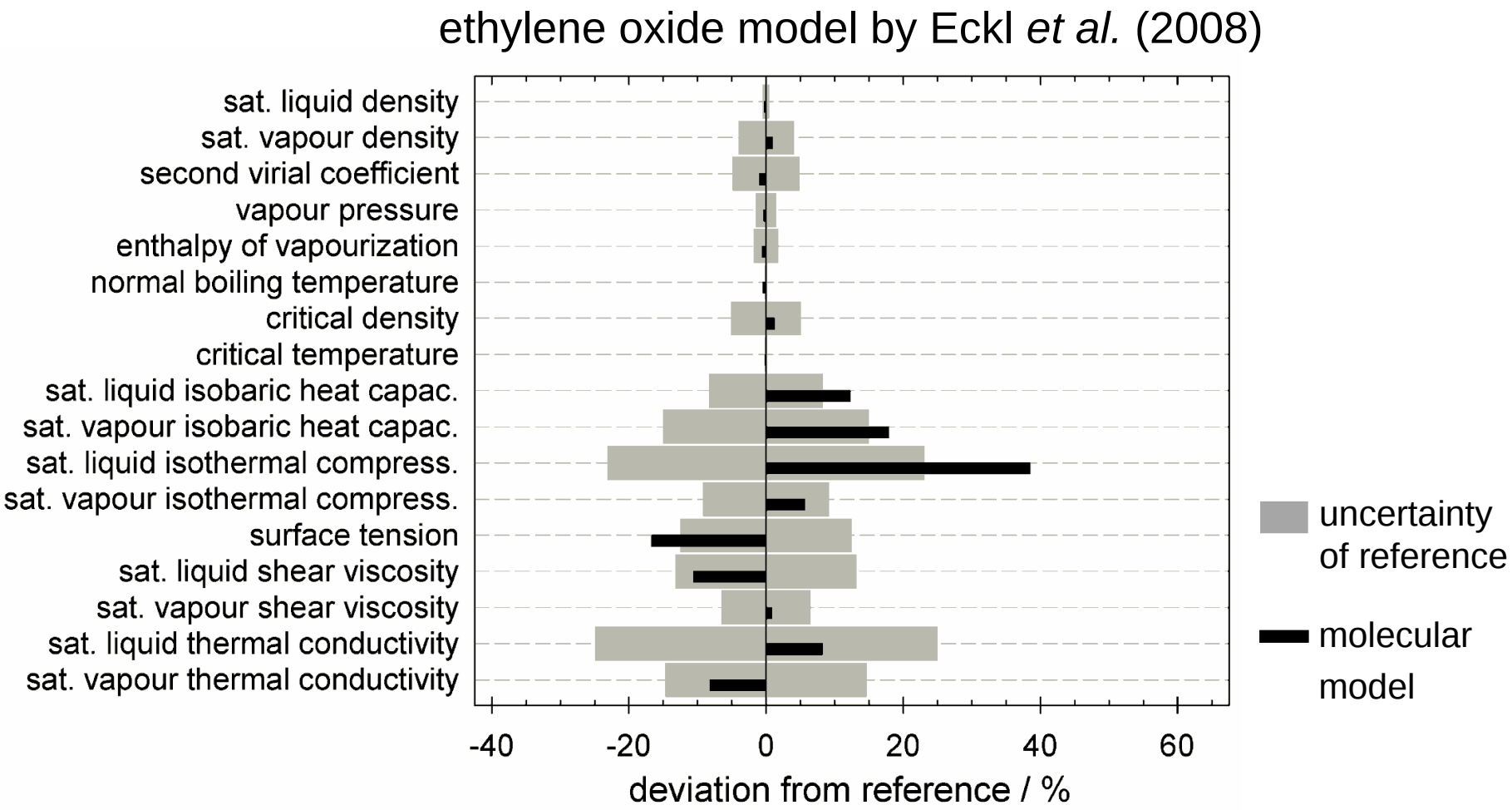
Higher-order derivatives $\Phi_{mn} = \left(\frac{\partial^{m+n} \Phi}{\partial \beta^m \partial \rho^n} \right) = \Phi_{mn}^{id} + \Phi_{mn}^{conf}$

Energy fluctuations $\Phi_{30}^{conf} = \frac{1}{NT^3} \left(\langle U_{pot}^3 \rangle - 3 \langle U_{pot}^2 \rangle \langle U_{pot} \rangle + 2 \langle U_{pot} \rangle^2 \right)$

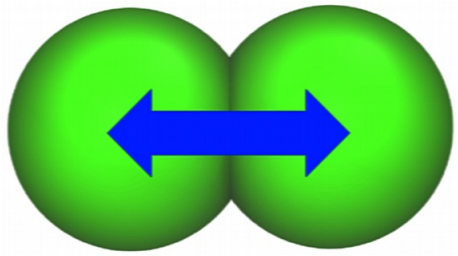
The derivatives of the Massieu potential can be applied for:

- Extrapolating simulation results (on the basis of less simulations)
- Parameterizing equations of state (further improving extrapolation)

Quantitatively reliable molecular modelling



Molecular models of quadrupolar fluids



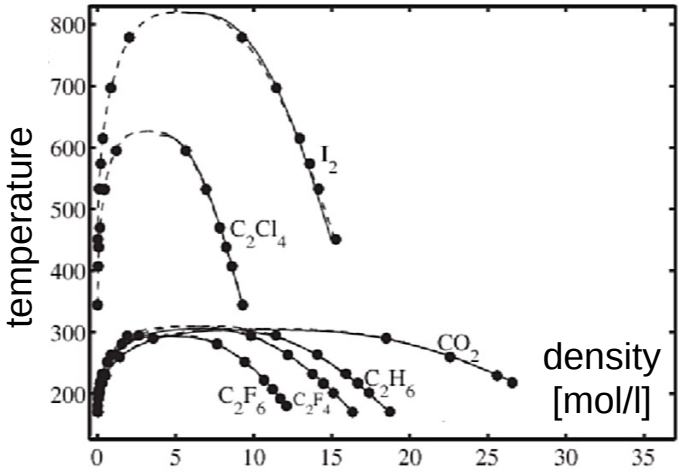
2CLJQ models:

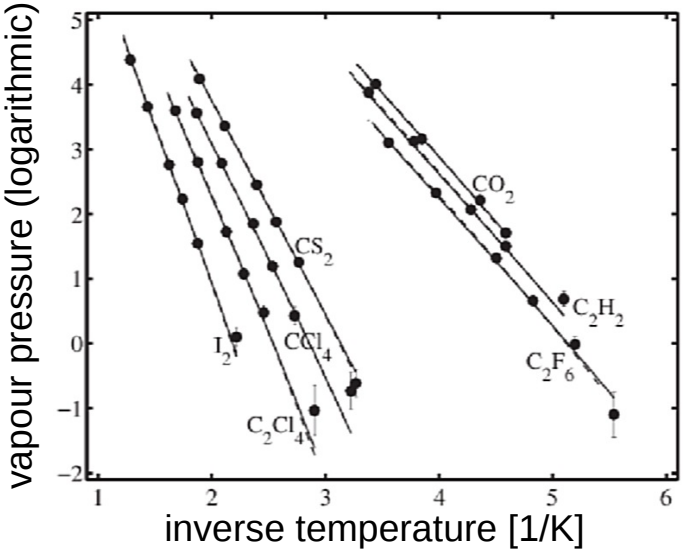
- 2 LJ centres
- Quadrupole

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

Deviation:

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

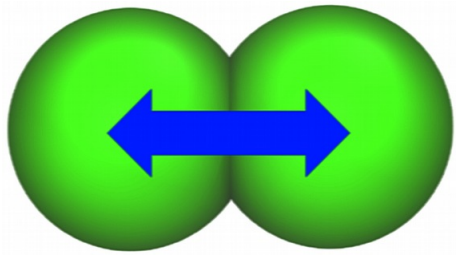




- simulation
— DIPPR correlation

No interfacial properties were considered for the parameterization.

Surface tension of real fluids



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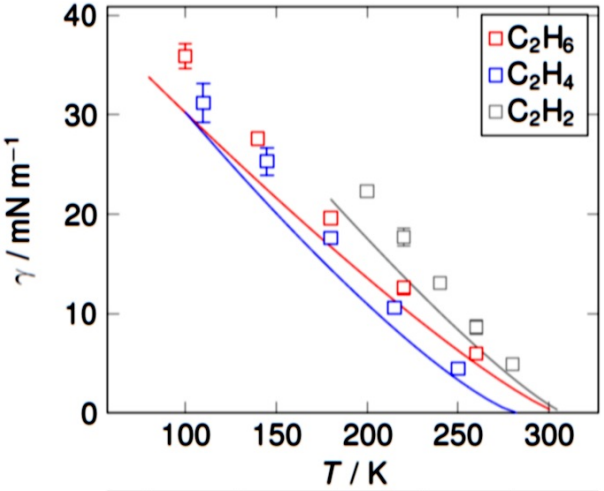
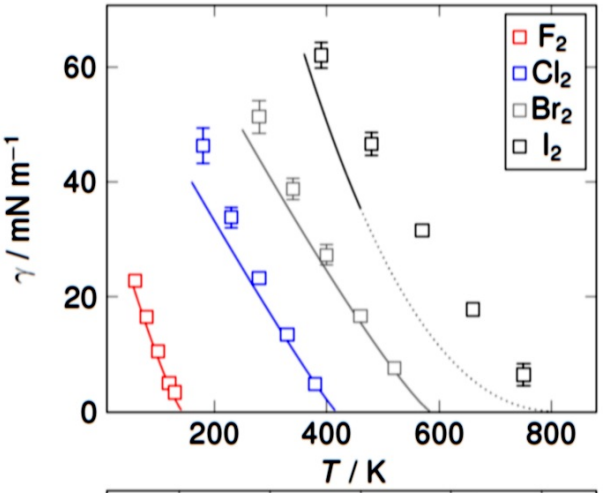
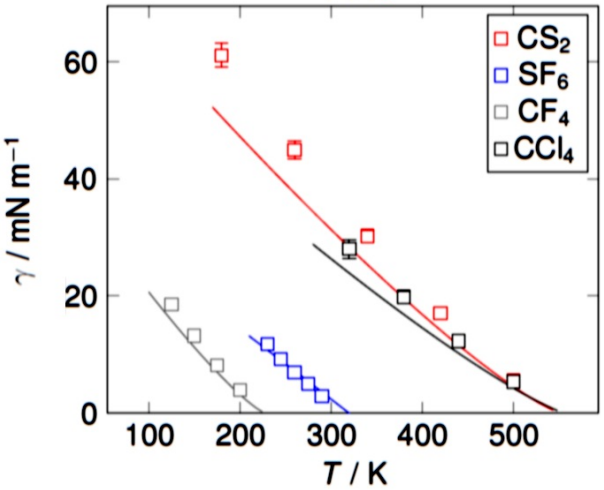
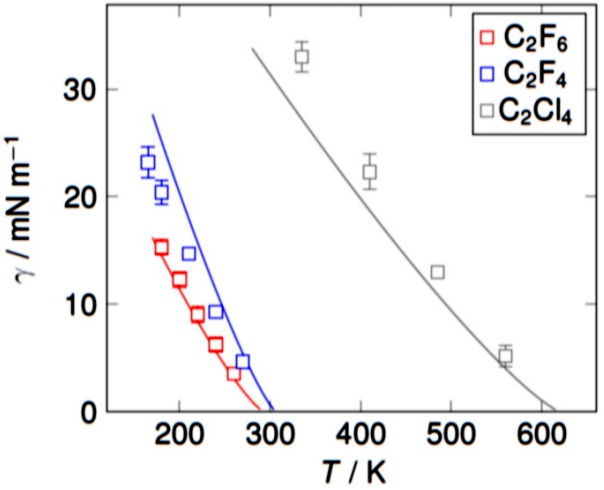


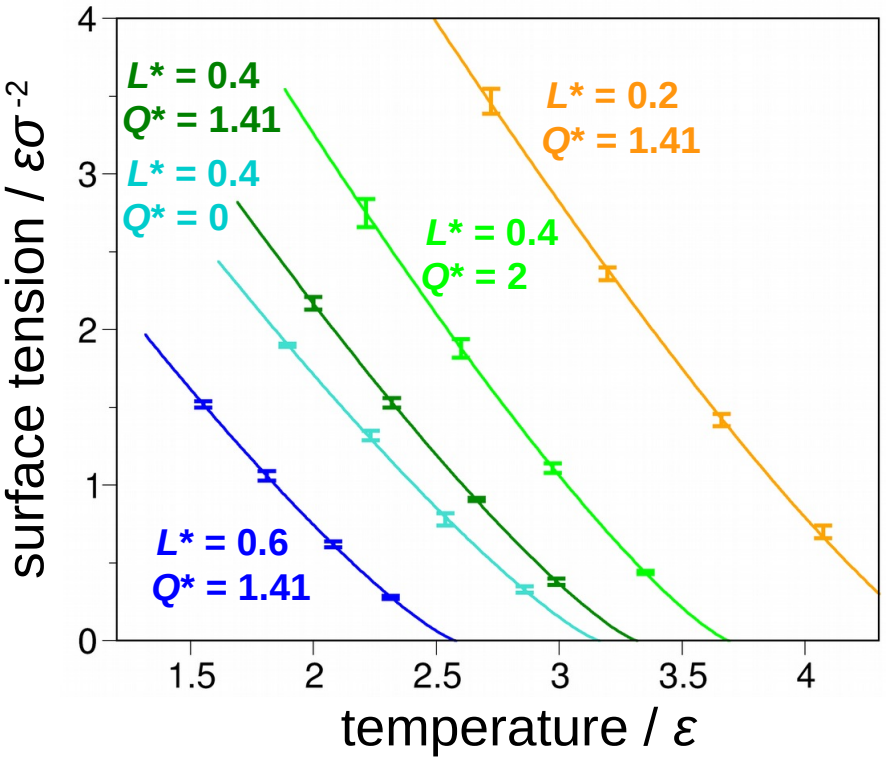




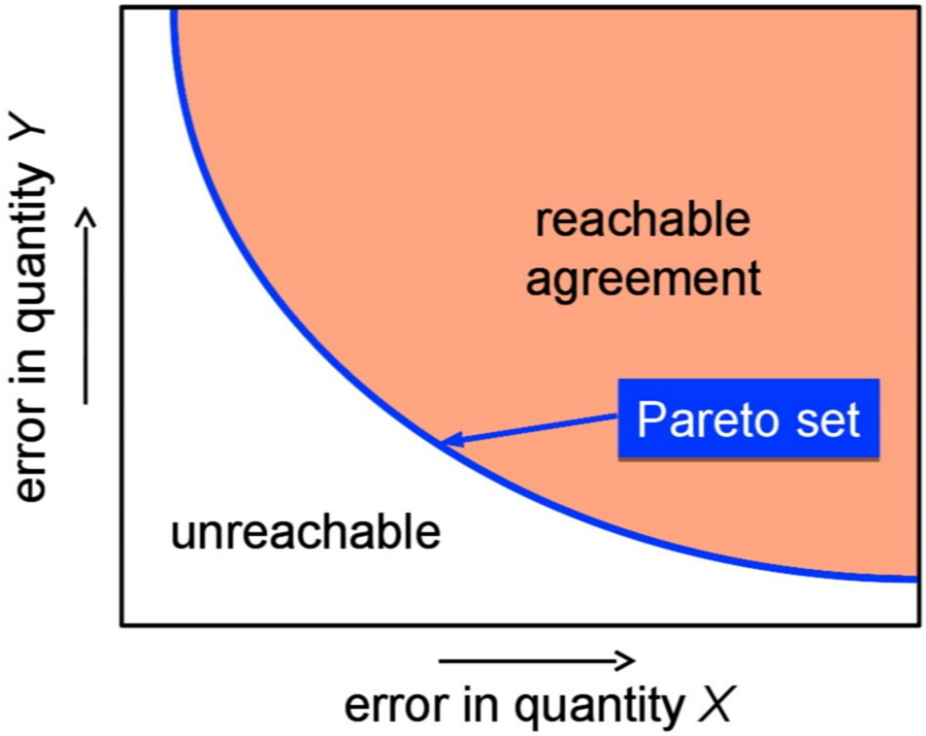


Modelling by multi-criteria optimization

Two-centre LJ + quadrupole



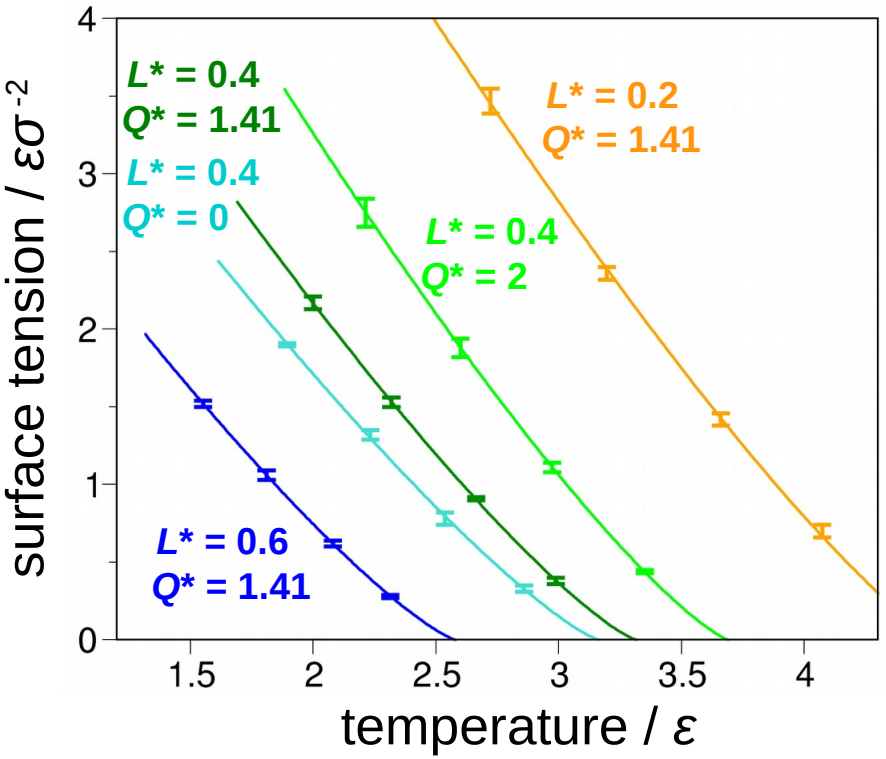
Pareto optimality criterion



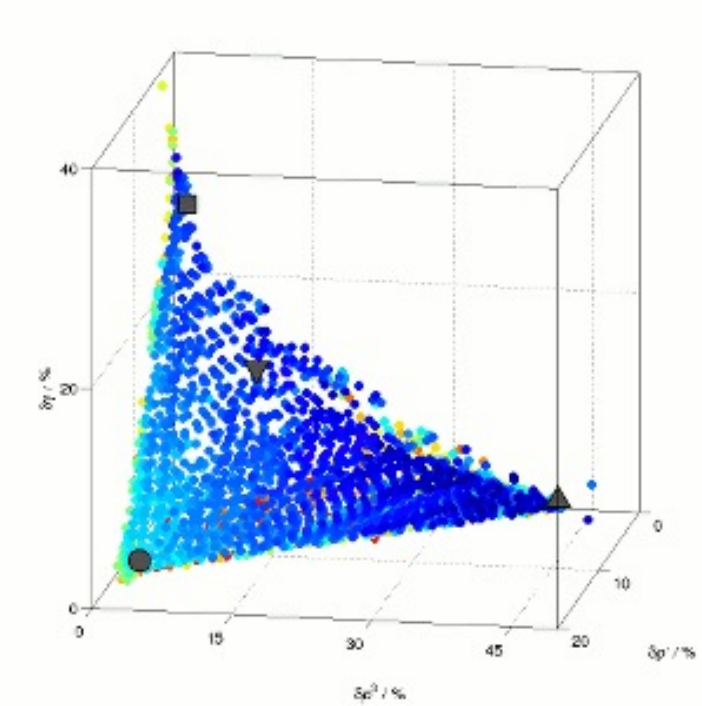
Surface tension: Critical scaling $y = A(1 - T/T_c)^{1.24}$ with two parameters.

Modelling by multi-criteria optimization

Two-centre LJ + quadrupole



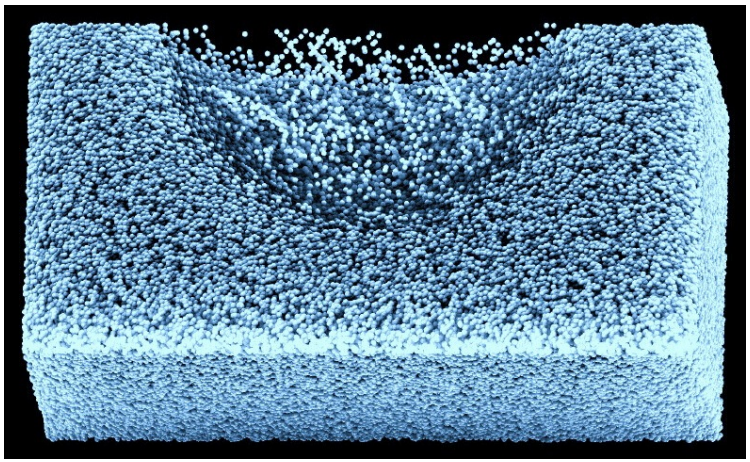
Pareto front for carbon dioxide

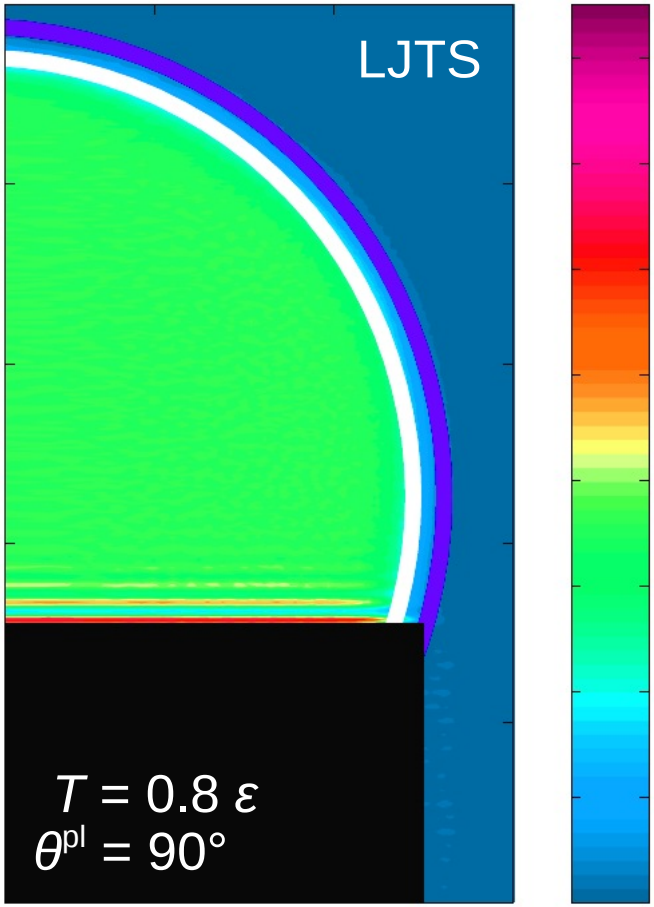


Multi-criteria optimization requires massively-parallel molecular modelling.

MD simulation of fluids at interfaces

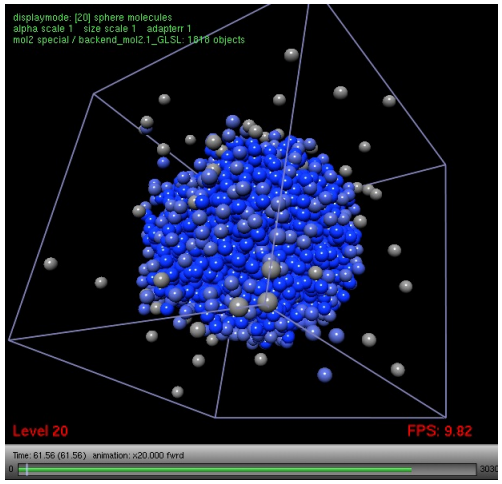
- Adsorption (fluid-fluid and fluid-solid)
- Vapour-liquid surface tension
- Curved vapour-liquid interfaces
- Contact angle and contact line pinning

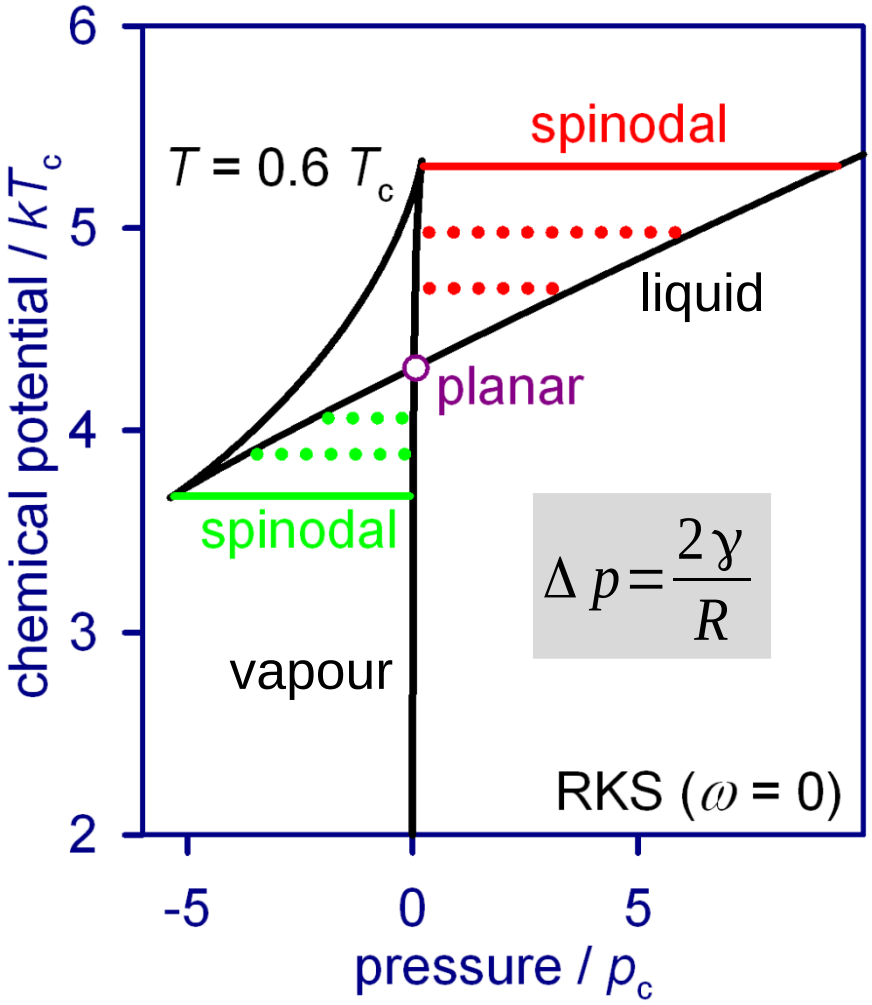




Thermodynamics of curved interfaces

- Droplet + metastable vapour
- Bubble + metastable liquid

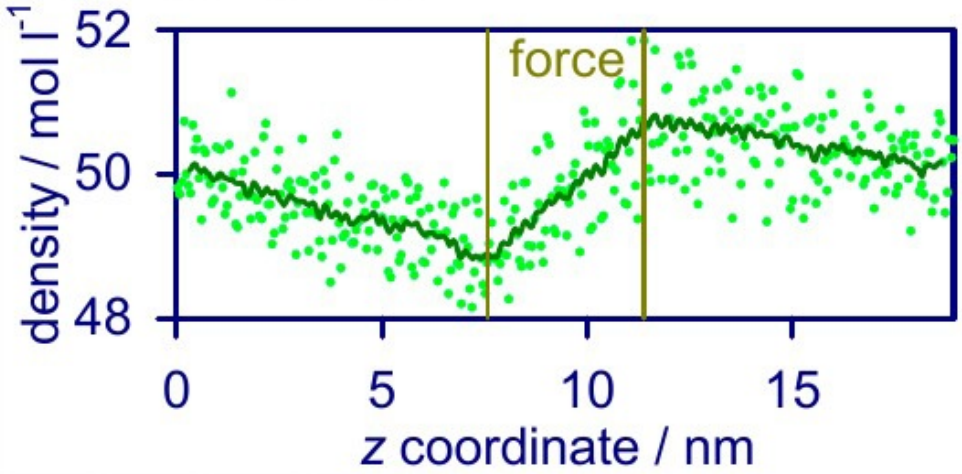




Planar limit: The curvature changes its sign, and the radius diverges.

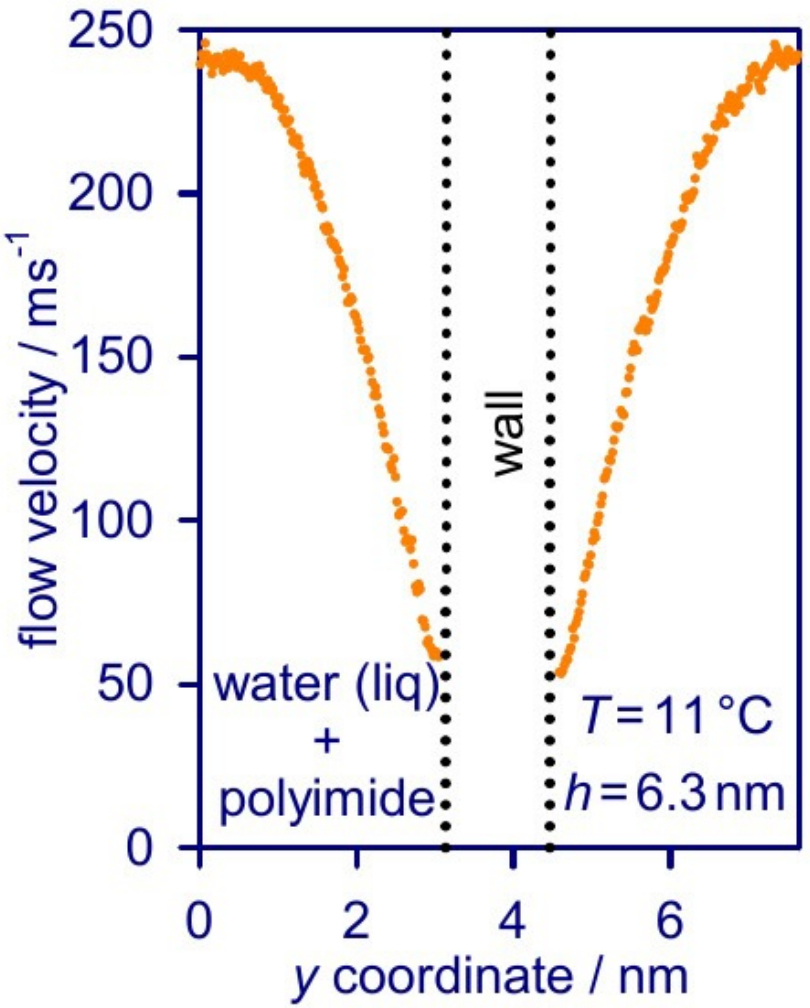
Large length and time scales required.

Transport at interfaces in nanofluidics

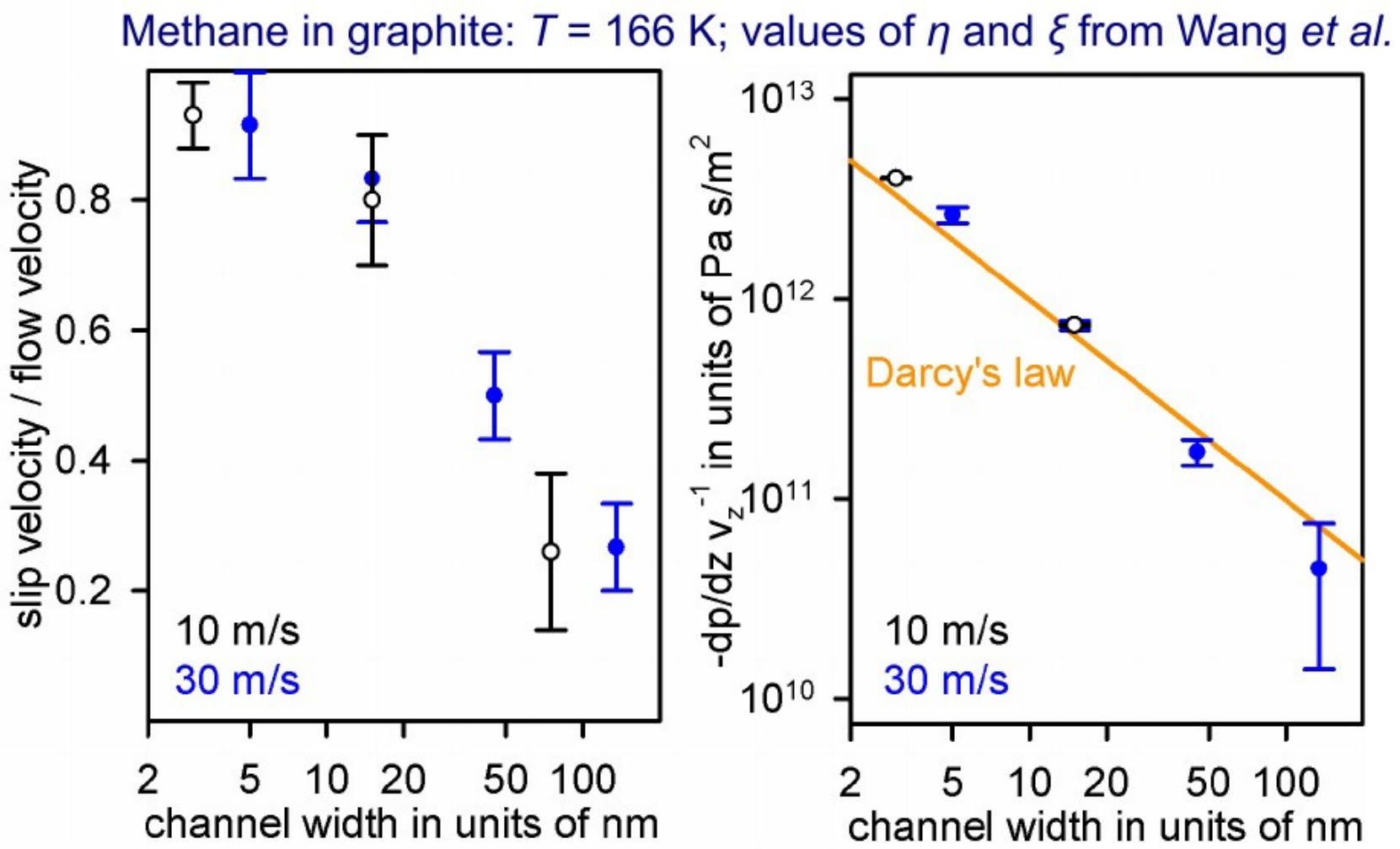


The accelerating force is only applied to the fluid molecules within a specified control volume.

It overcompensates the pressure drop, so that (equivalent) density, pressure, and chemical potential gradients are actually present.



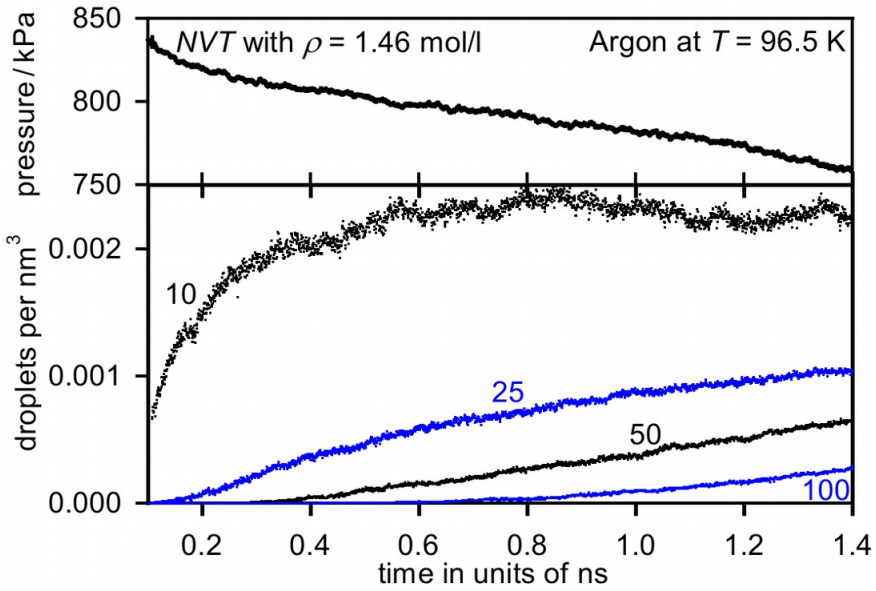
From nanofluidics to microfluidics



MD simulation of nucleation

Yasuoka-Matsumoto method:

- Canonical MD simulation
- Limited time interval for nucleation
- Conditions change over time



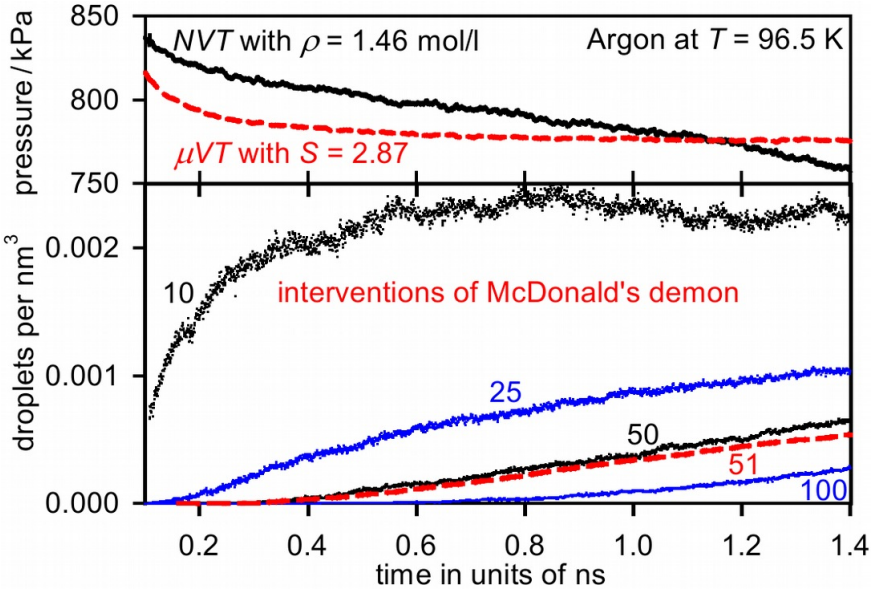
NEMD simulation of nucleation

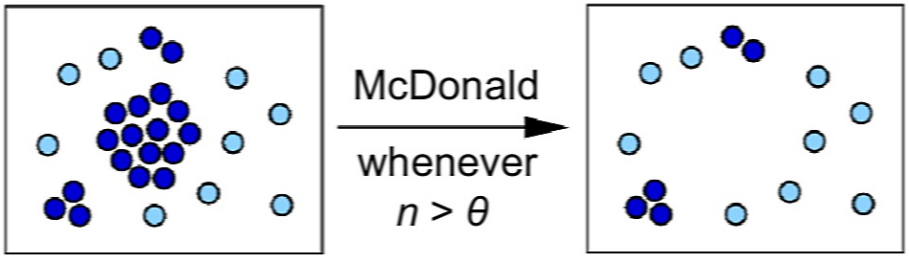
Yasuoka-Matsumoto method:

- Canonical MD simulation
- Limited time interval for nucleation
- Conditions change over time

Alternative approach:

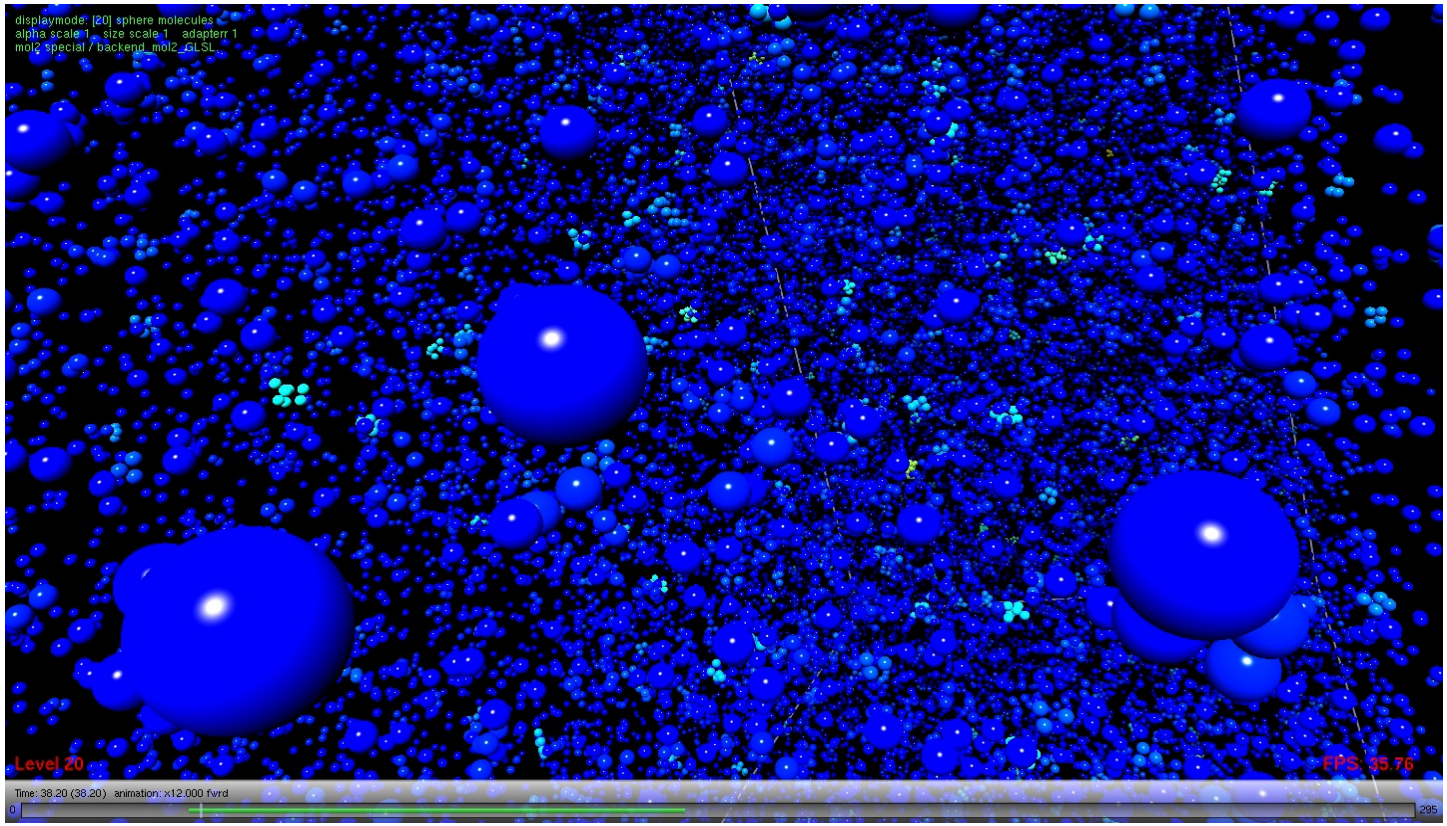
- Grand-canonical MD simulation



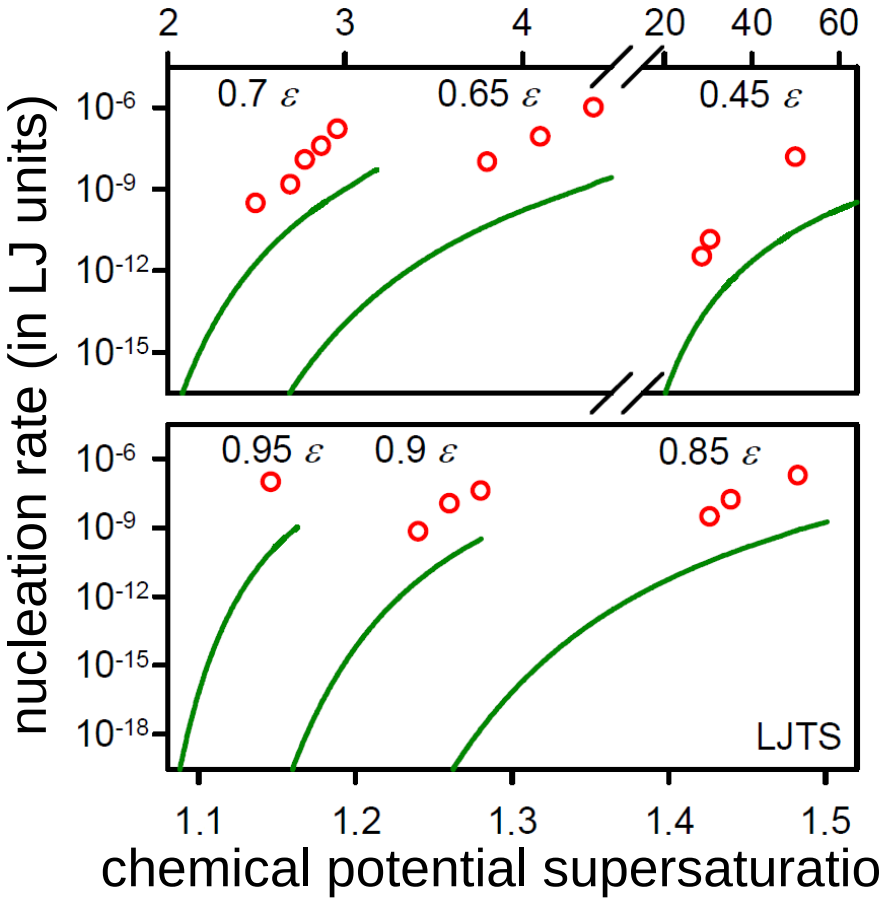


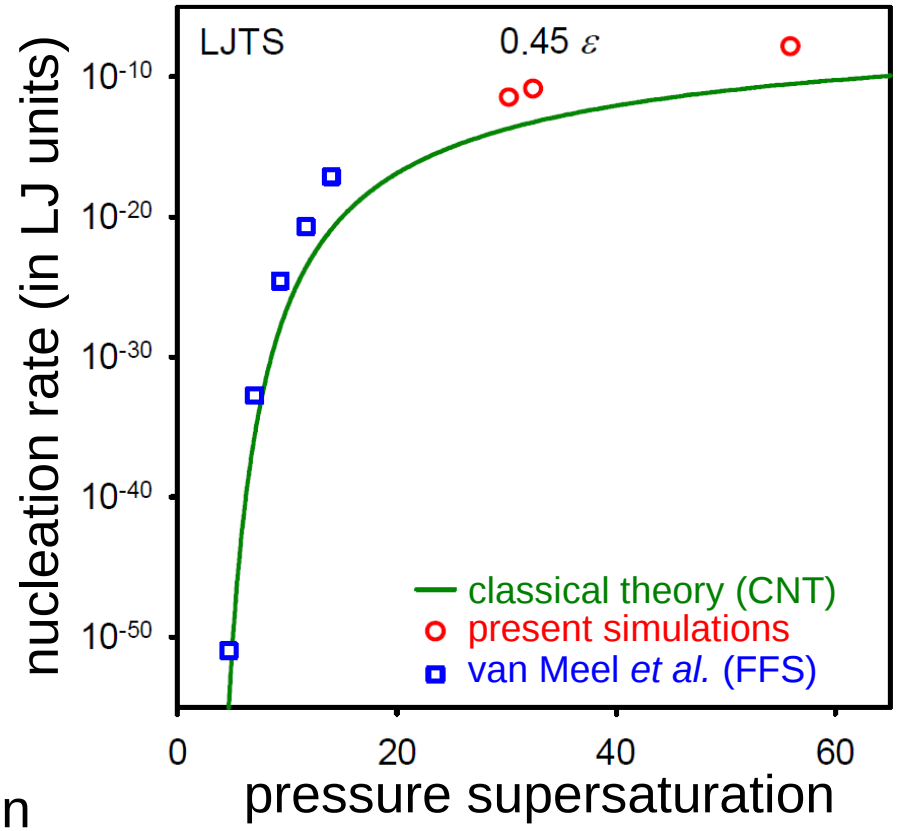
Thermodynamic conditions of the supersaturated state are maintained.

NEMD simulation of nucleation



Nucleation rates from NEMD simulation





Bridging large length and time scales is crucial for capturing rare events.

Conclusion

- Computational molecular engineering combines massively-parallel **molecular simulation** with quantitatively reliable **molecular modelling**.
- Performant and scalable molecular simulation codes were presented: ***ls1 mardyn*** for large heterogeneous systems, ***ms2*** for bulk properties.
- 2CLJQ models from previous work **predict the surface tension** well, with $\delta\gamma \approx 20$ %. Multi-criteria optimization can further improve them.
- Non-equilibrium MD simulation of large systems, employing Maxwellian dæmons, yields insights on **processes at interfaces**, e.g. nucleation.
- The transition **from nano- to microsystems** for the length and time scale can now be accomplished by highly performant MD simulation.