Nucleation processes and vapor-liquid interfaces of fluid mixtures

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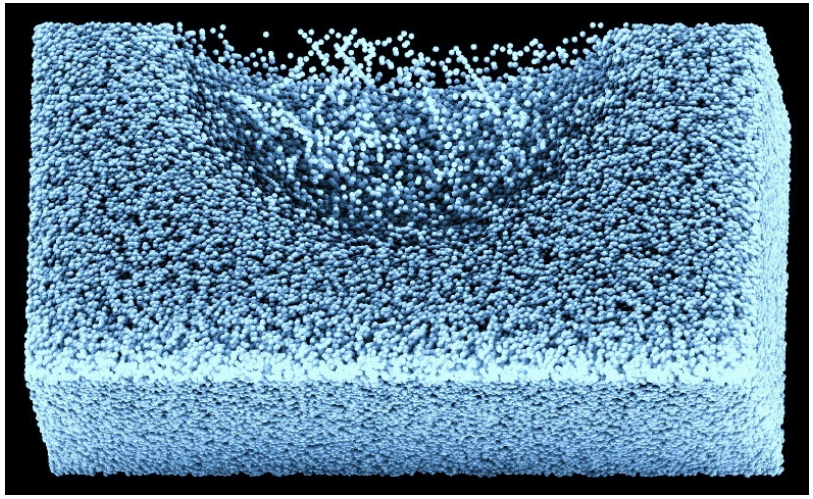
Computational Molecular Engineering

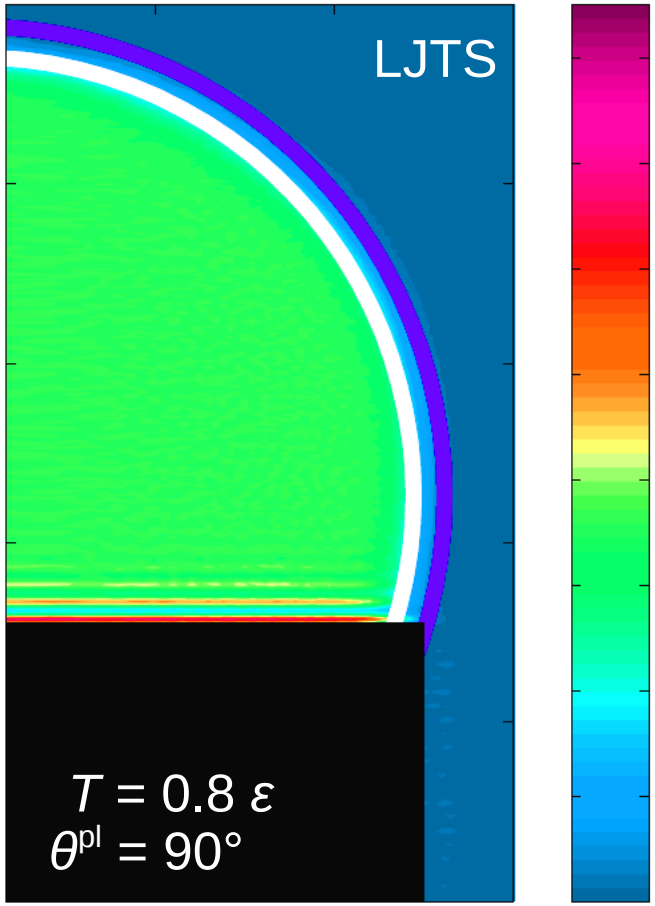
Statistical Mechanics Seminar

UC Berkeley, November 6, 2015

Molecular simulation of fluids at interfaces

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

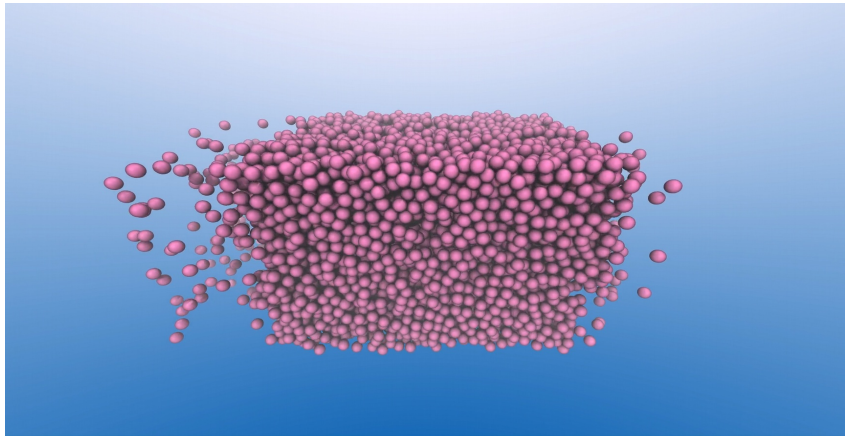


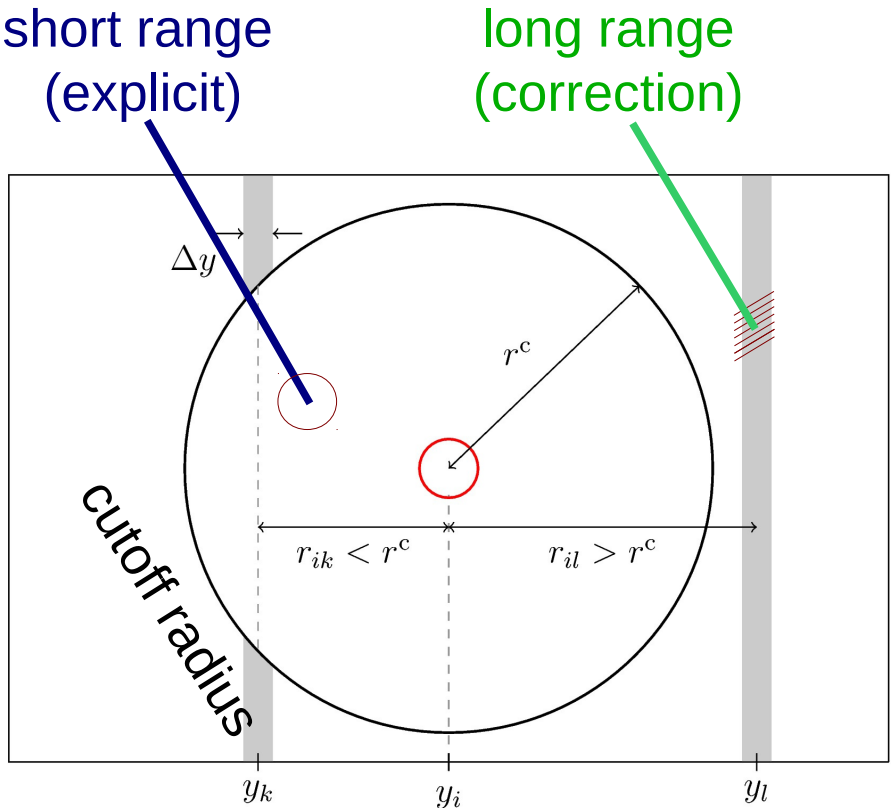


Long-range correction at planar interfaces

For planar interfaces:

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





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

Long-range correction at planar interfaces

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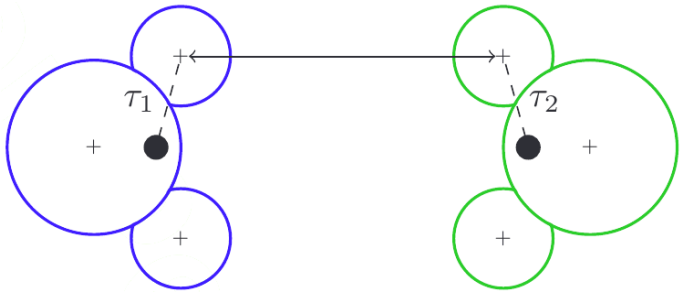
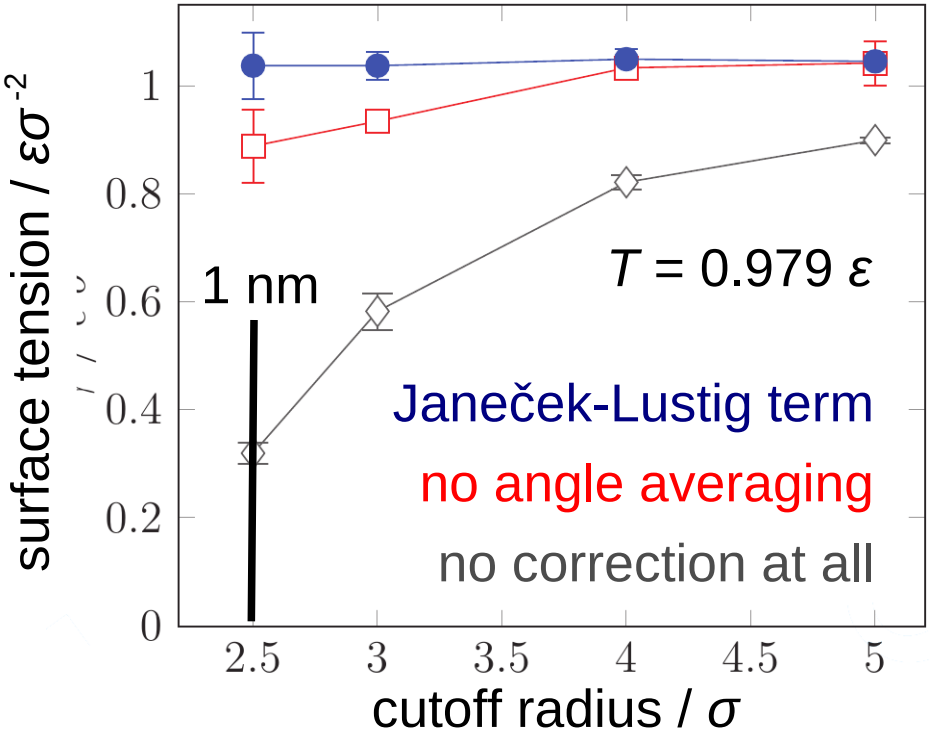
Long-range correction from the density profile, following **Janeček**.



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

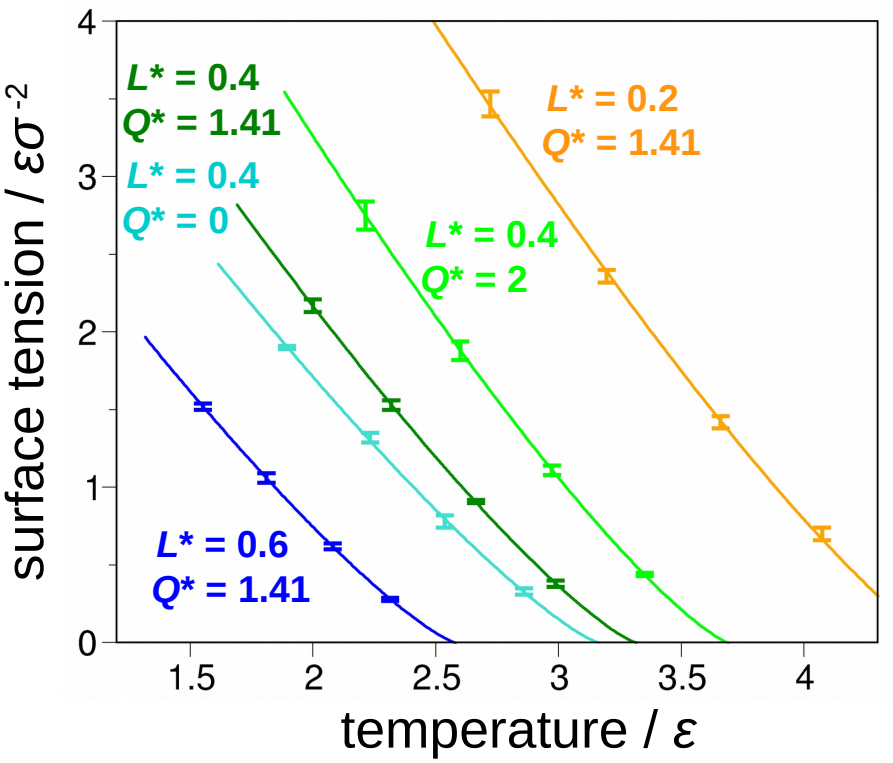
Two-center LJ fluid (2CLJ)

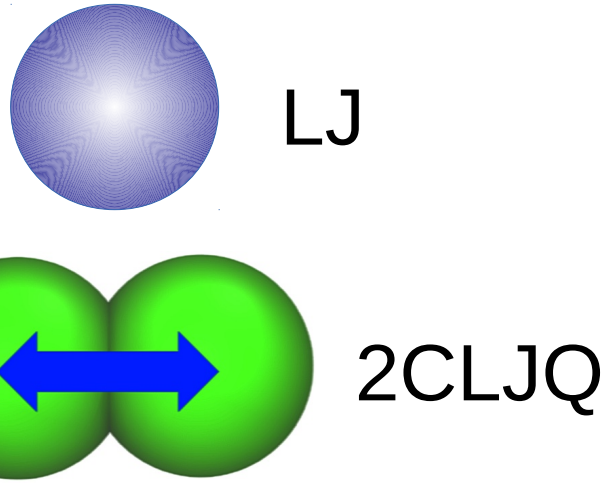


For arbitrary geometries, e.g. the fast multipole method can be employed.

Massively parallel molecular modeling

Two LJ + quadrupole (2CLJQ)

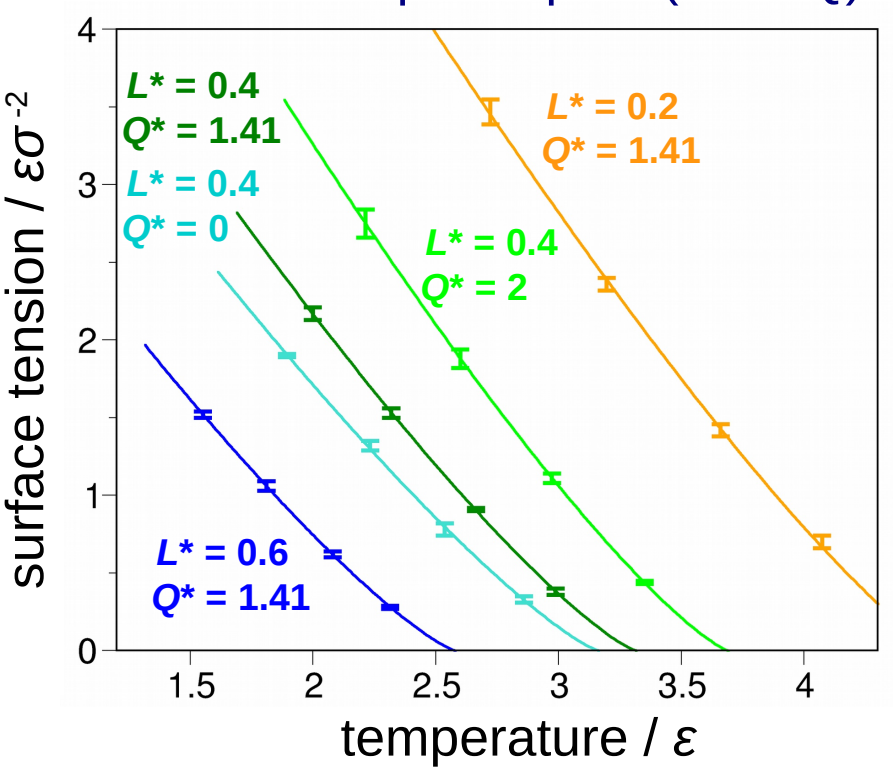




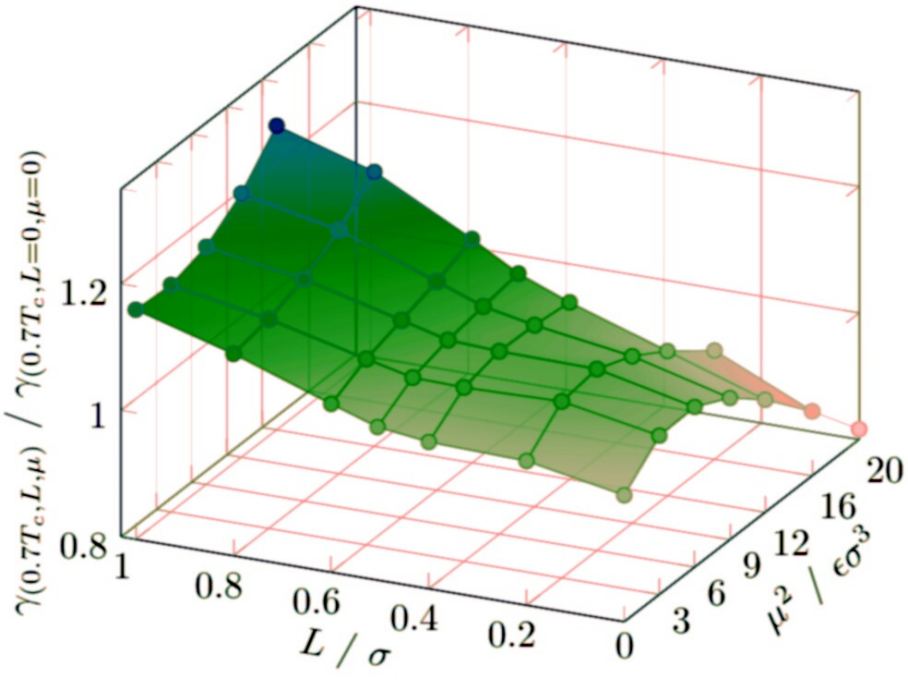
- Systematic exploration of the four-dimensional model parameter space

Massively parallel molecular modeling

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

Parameterization of molecular force fields

Geometry

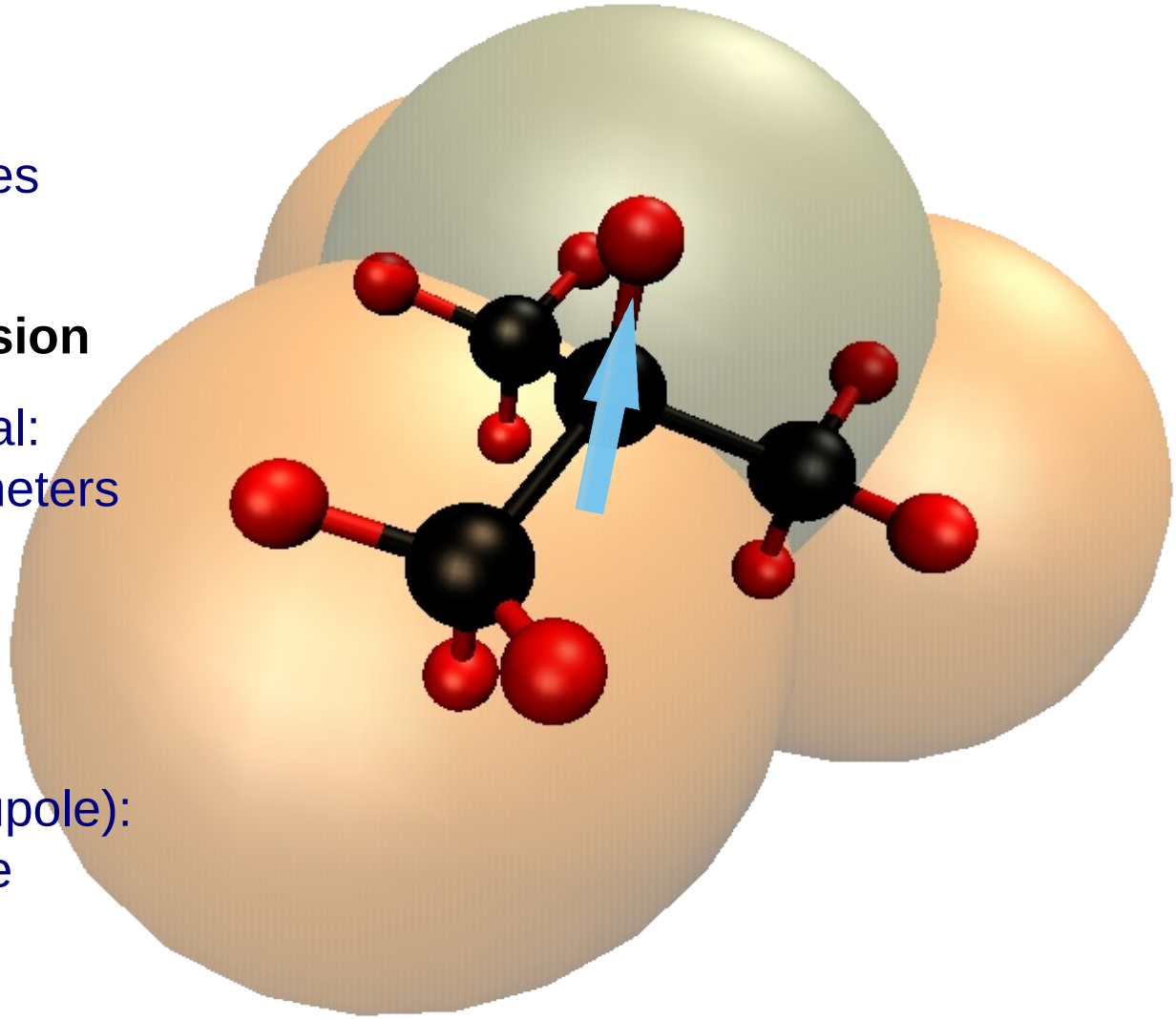
Bond lengths and angles

Dispersion and repulsion

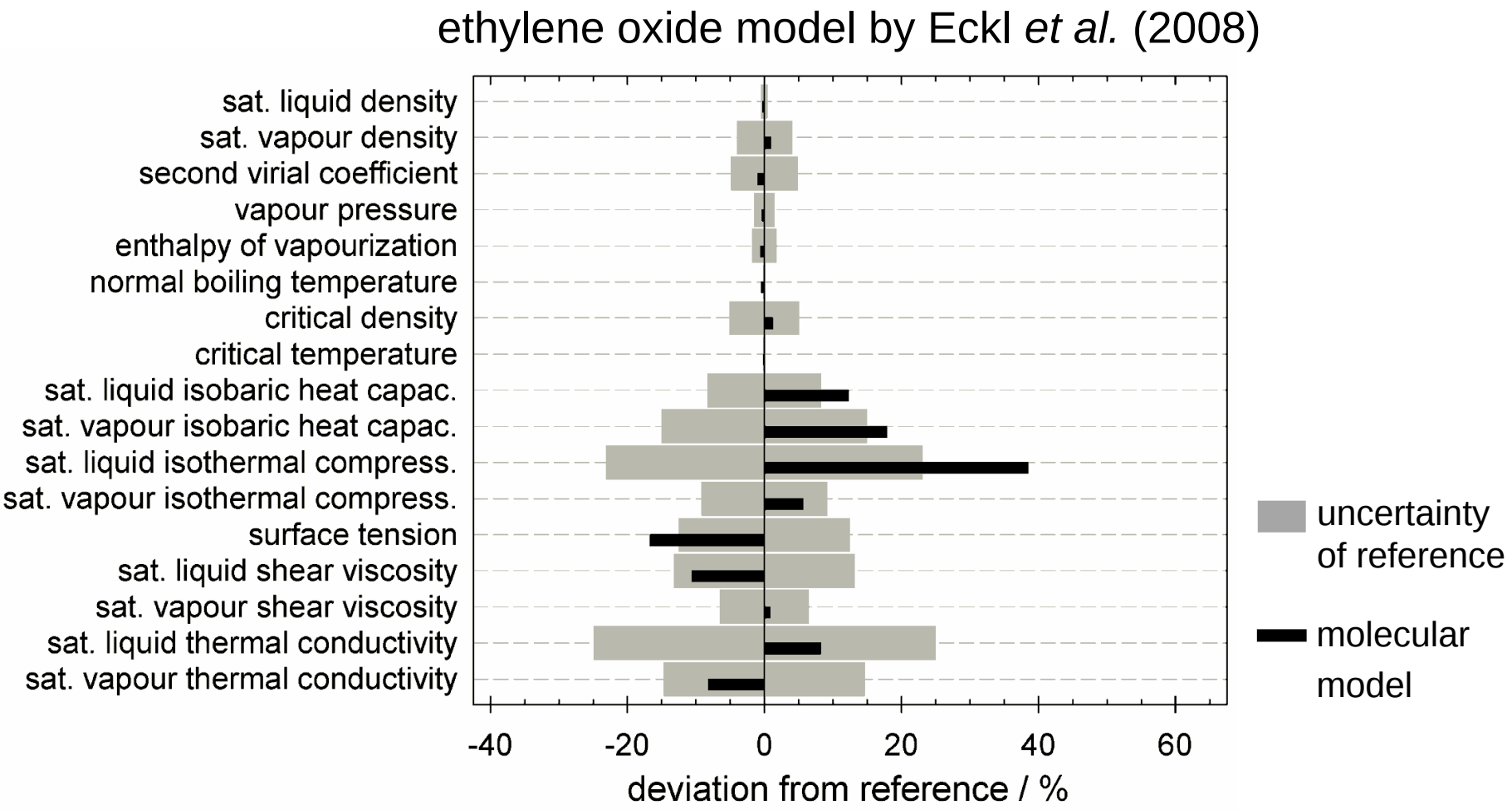
Lennard-Jones potential:
Size and energy parameters

Electrostatics

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

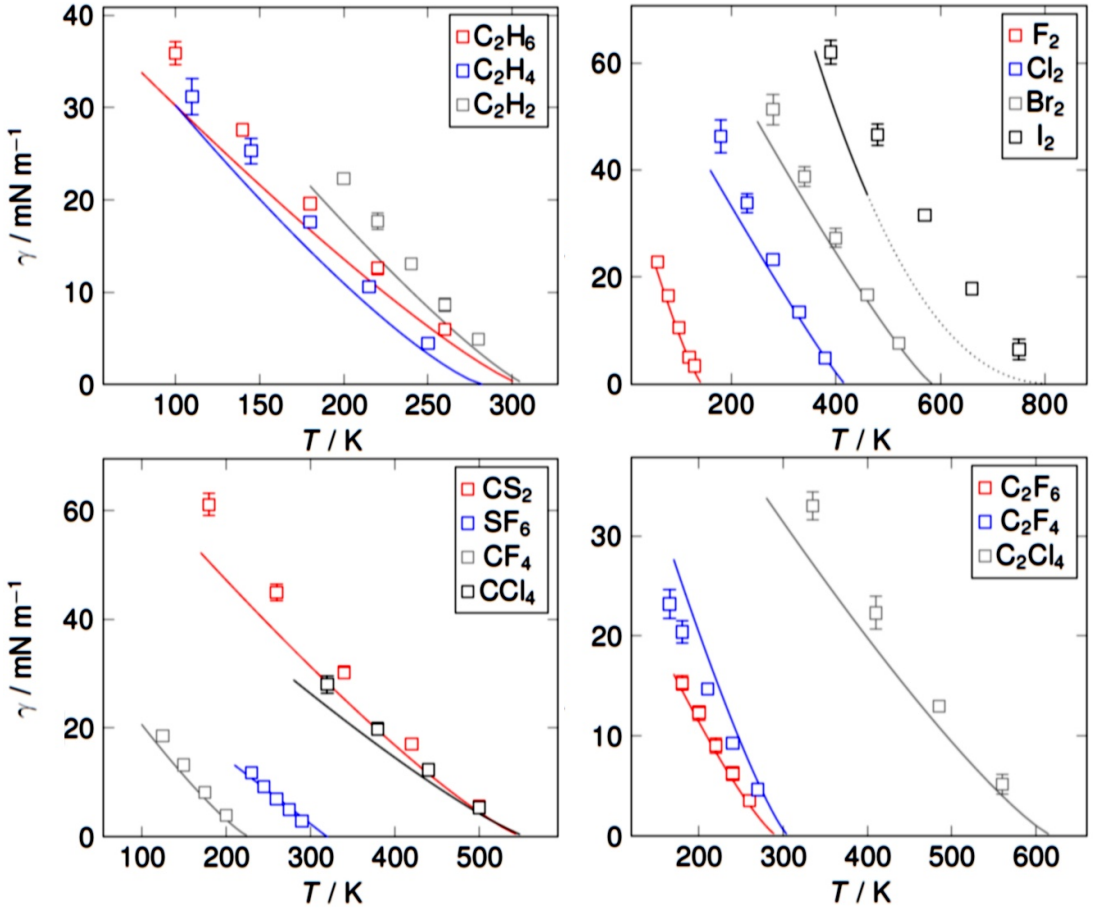


Quantitative reliability of molecular models

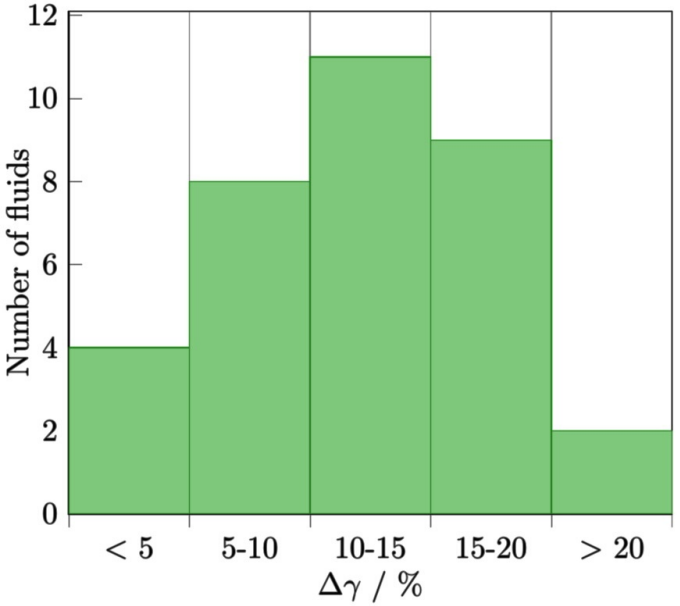


Predictive capacity of literature models

Two LJ + quadrupole (2CLJQ)



Two LJ + dipole (2CLJD)

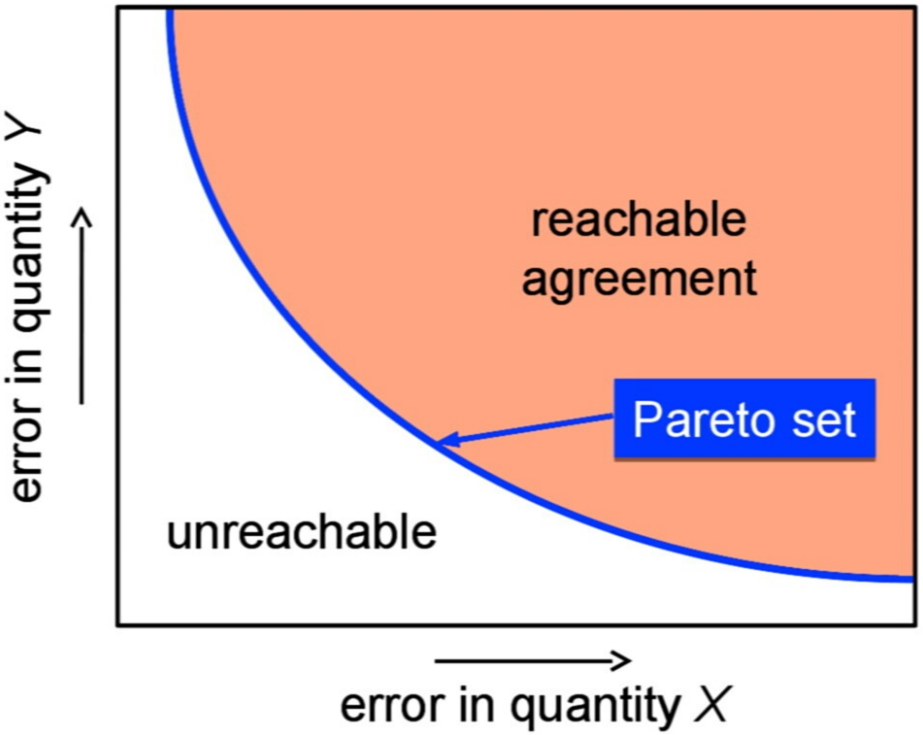


Fit to bulk properties

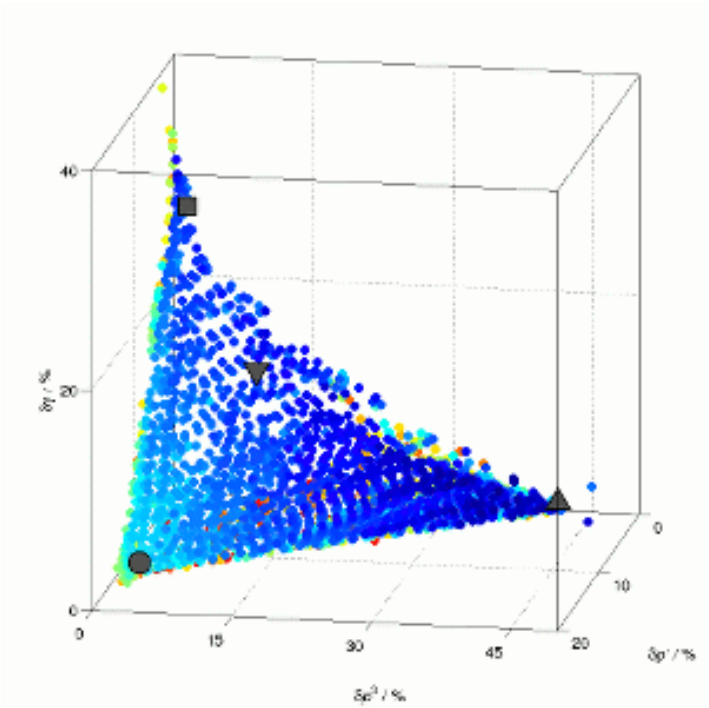
10 to 20 % overestimation of vapor-liquid surface tension

Model tailoring by multicriteria optimization

Pareto optimality criterion



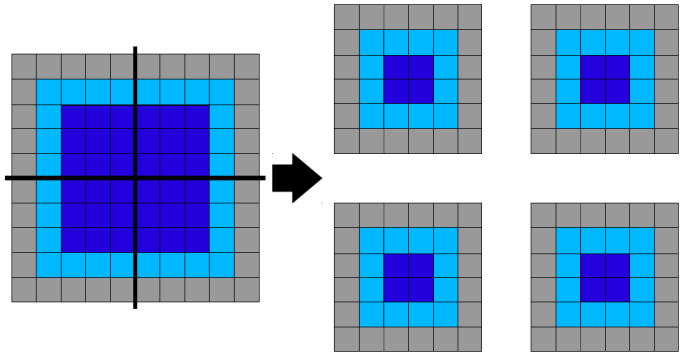
Pareto set for carbon dioxide



Multicriteria optimization requires massively-parallel molecular modeling.

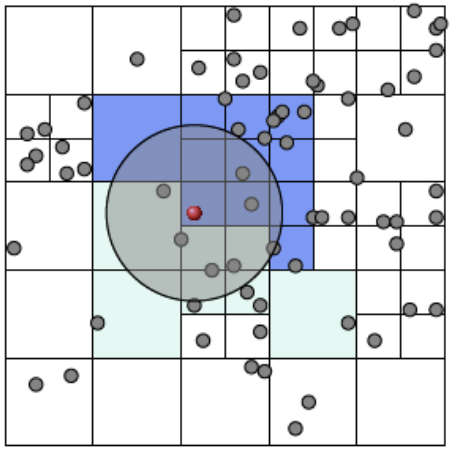
Efficient simulation of large systems

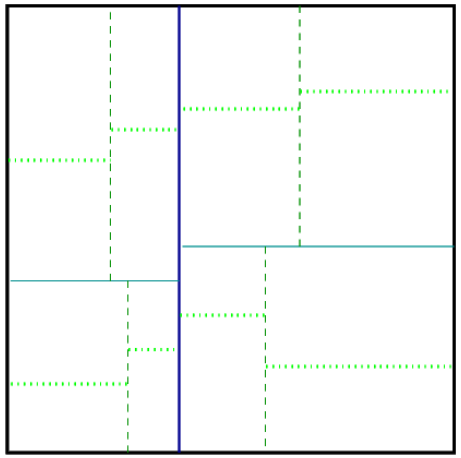
Linked-cell data structure suitable for spatial domain decomposition:



(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

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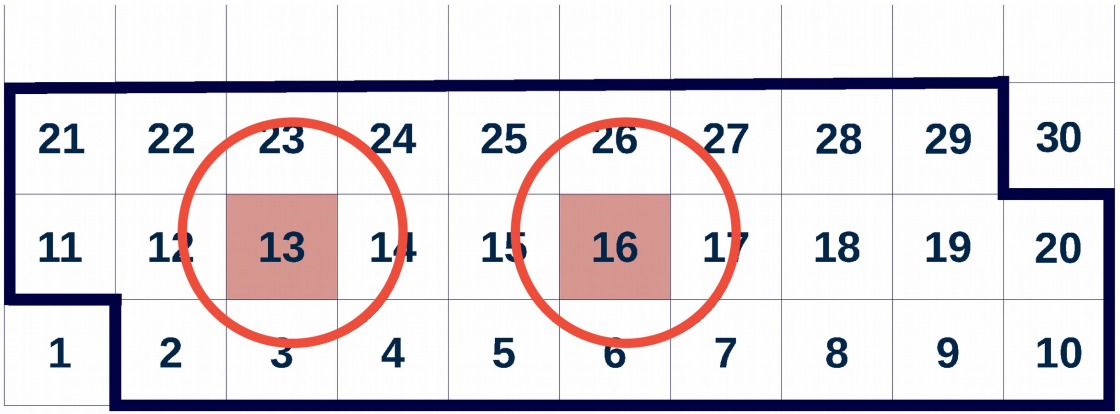
Efficient simulation of large systems

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



hyperthreaded sliding window

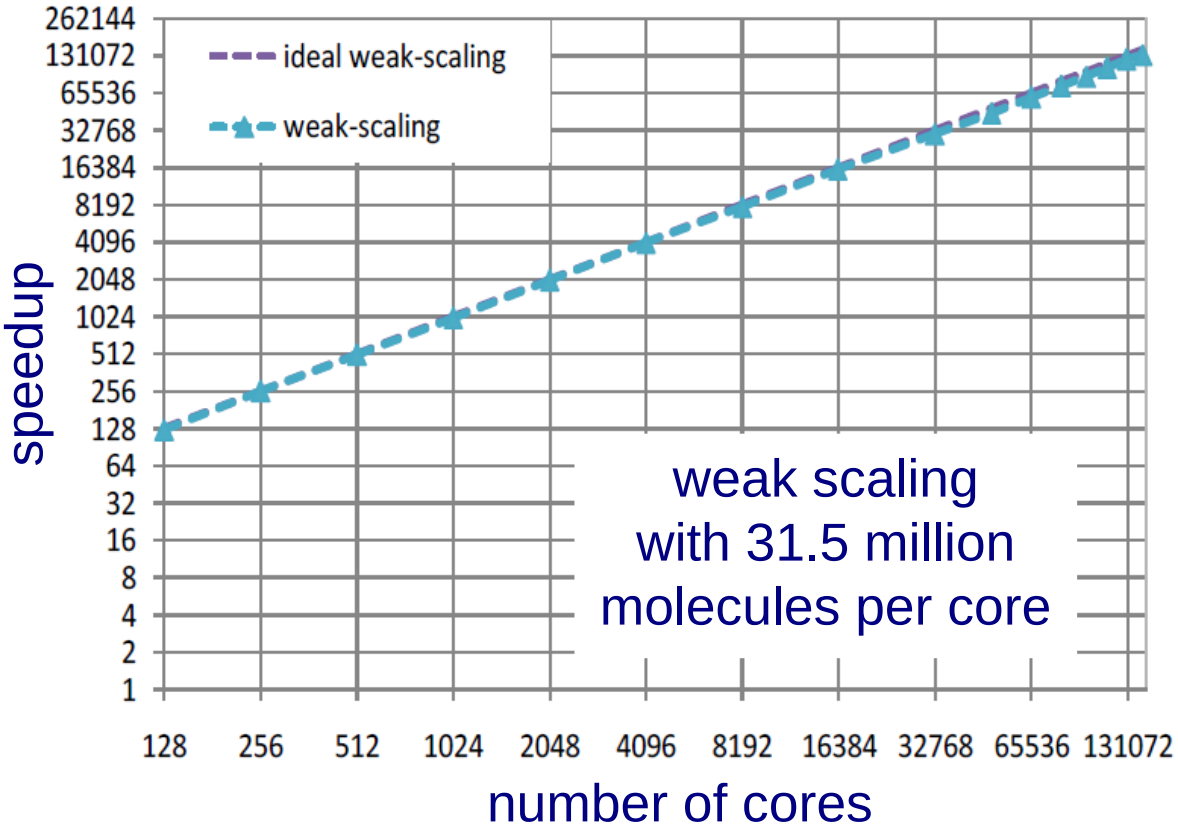
Optionally, forces acting on molecules are only stored until their cell leaves the sliding window.

Efficient vectorization:

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

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

Large-scale MD simulation on SuperMUC



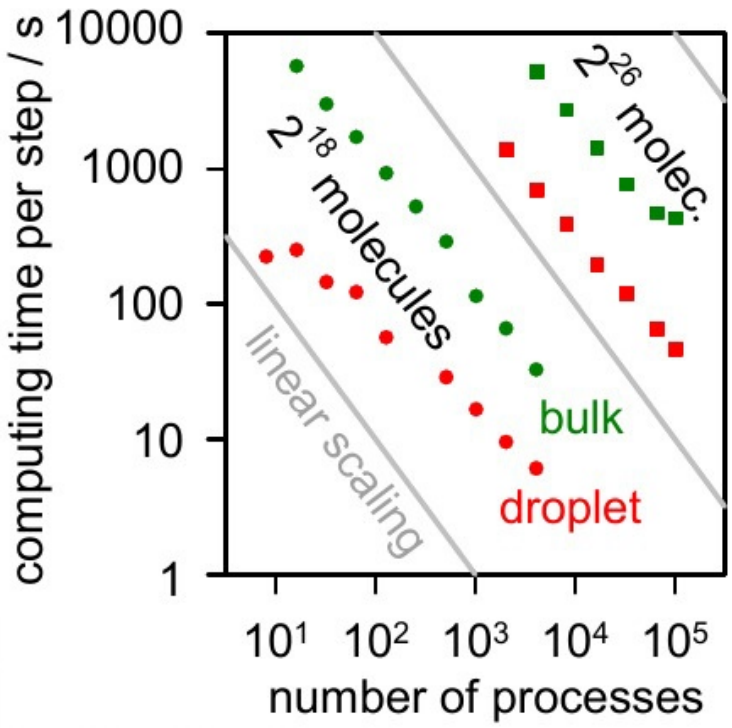
Up to $N = 4 \cdot 10^{12}$ on SuperMUC

large systems "1": molecular dynamics

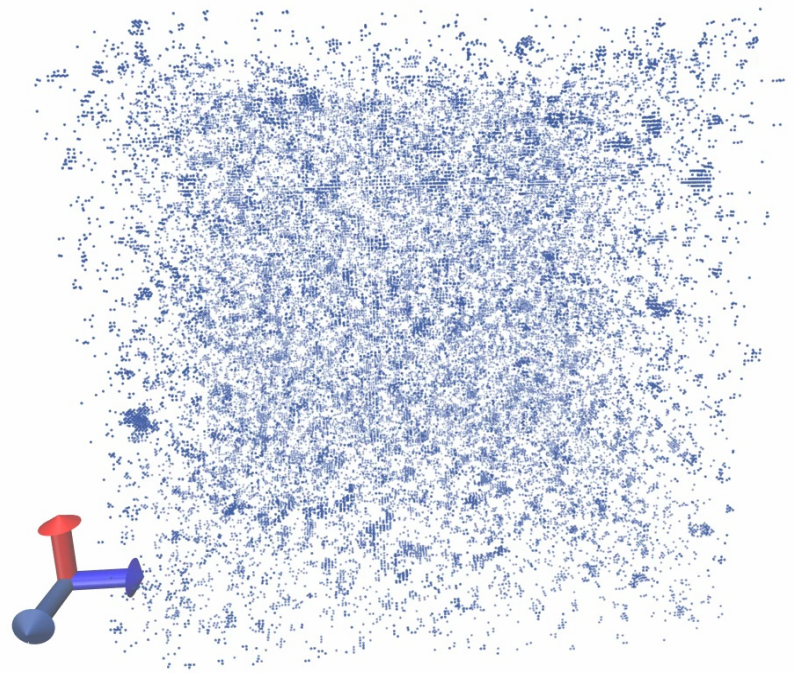
http://www.ls1-mardyn.de/

Large-scale MD simulation on hermit

strong scaling (Amdahl)



homogeneous cavitation

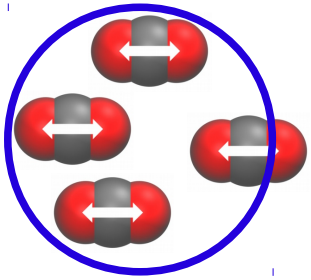


CO_2 (T = 280 K and ρ = 17.2 mol/l), 3CLJQ
25 million molecules on 110 592 cores

Large-scale MD simulation of cavitation

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:

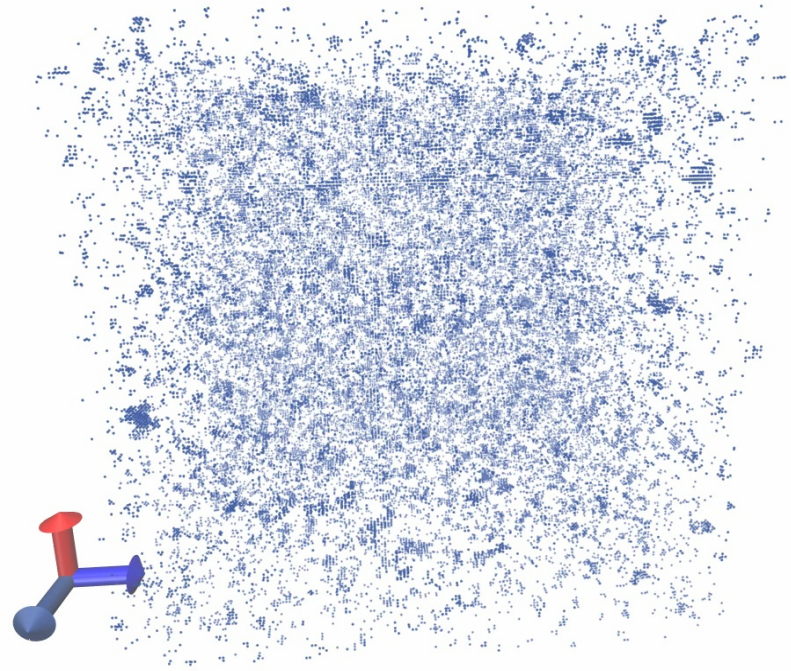


≤ 5 ?

(6 mol/l)

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

homogeneous cavitation



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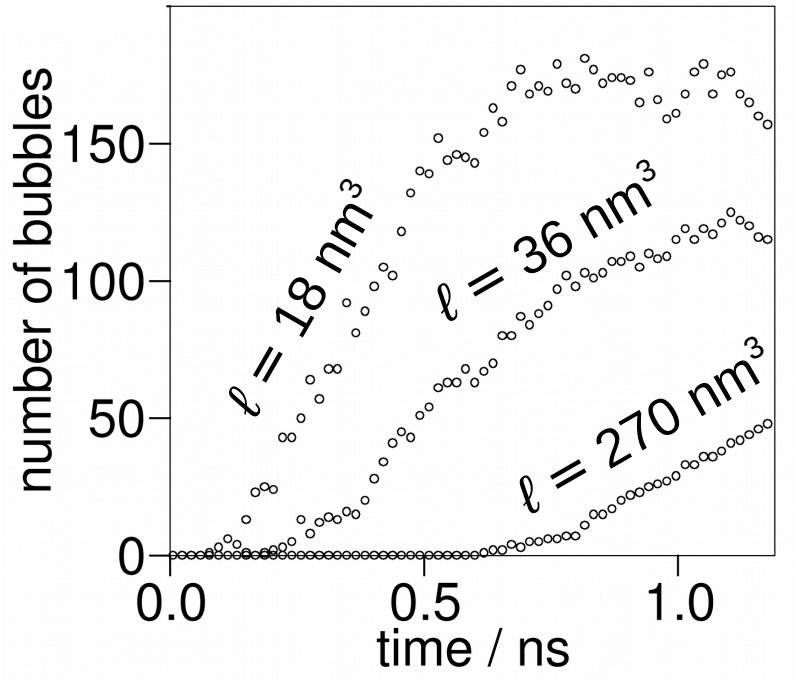
Cavitation in a metastable liquid phase

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

$N = 2.5 \times 10^7$, $V = 2.41 \times 10^{-21}$ m^3, $T = 280$ K

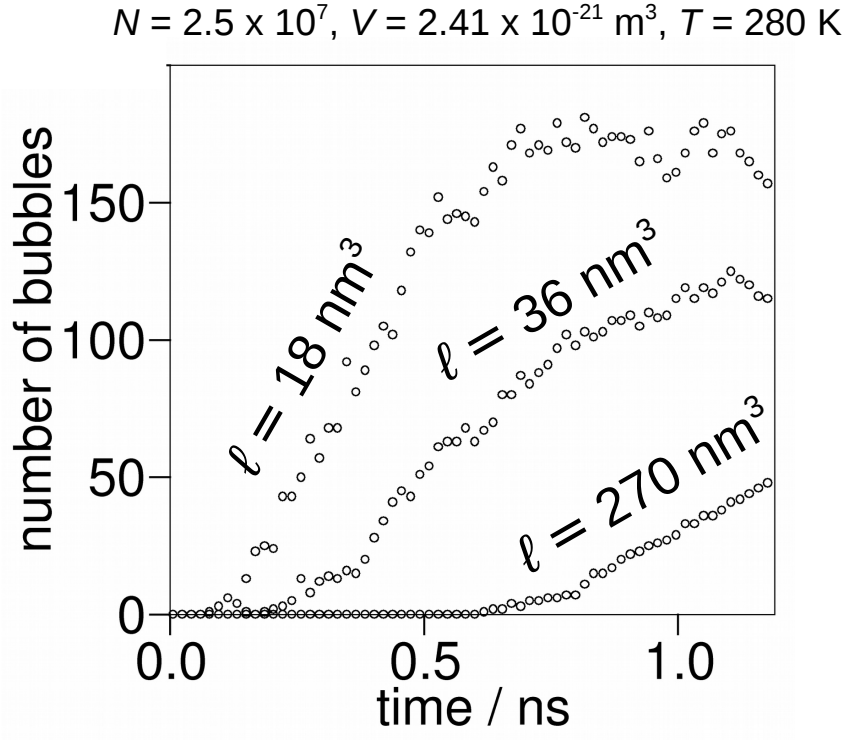


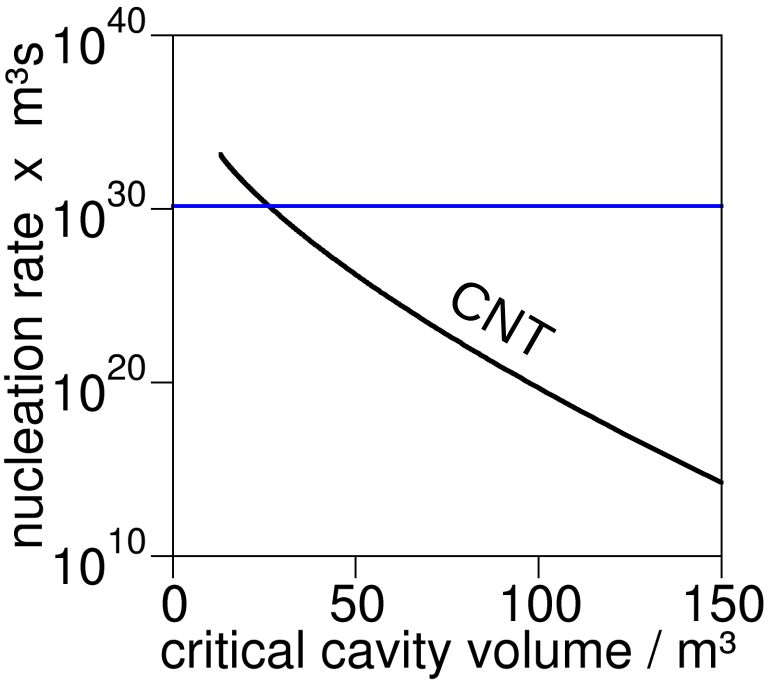
Three consecutive regimes:

- relaxation (equilibration)
- homogeneous cavitation
- growth and aggregation

Cavitation in a metastable liquid phase

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

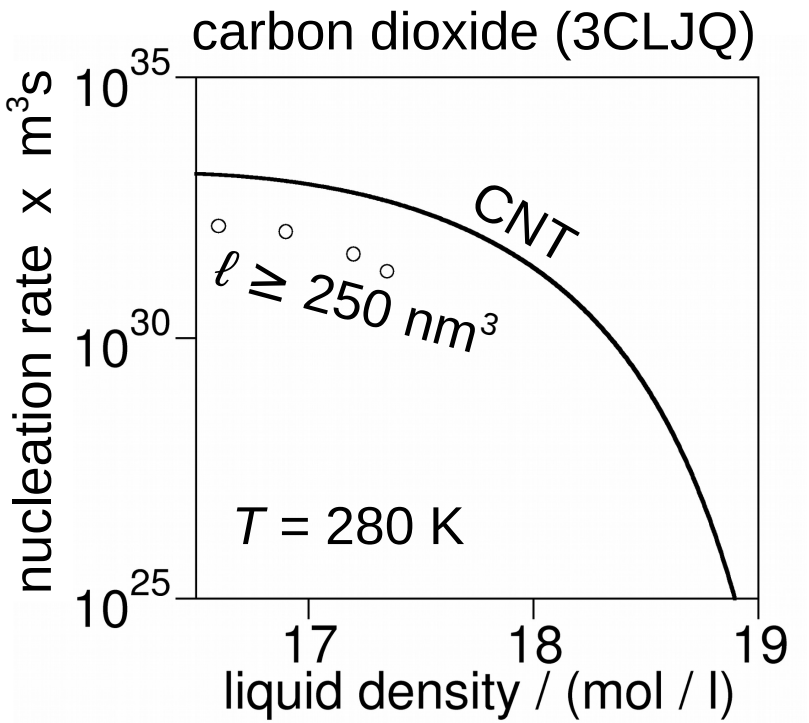


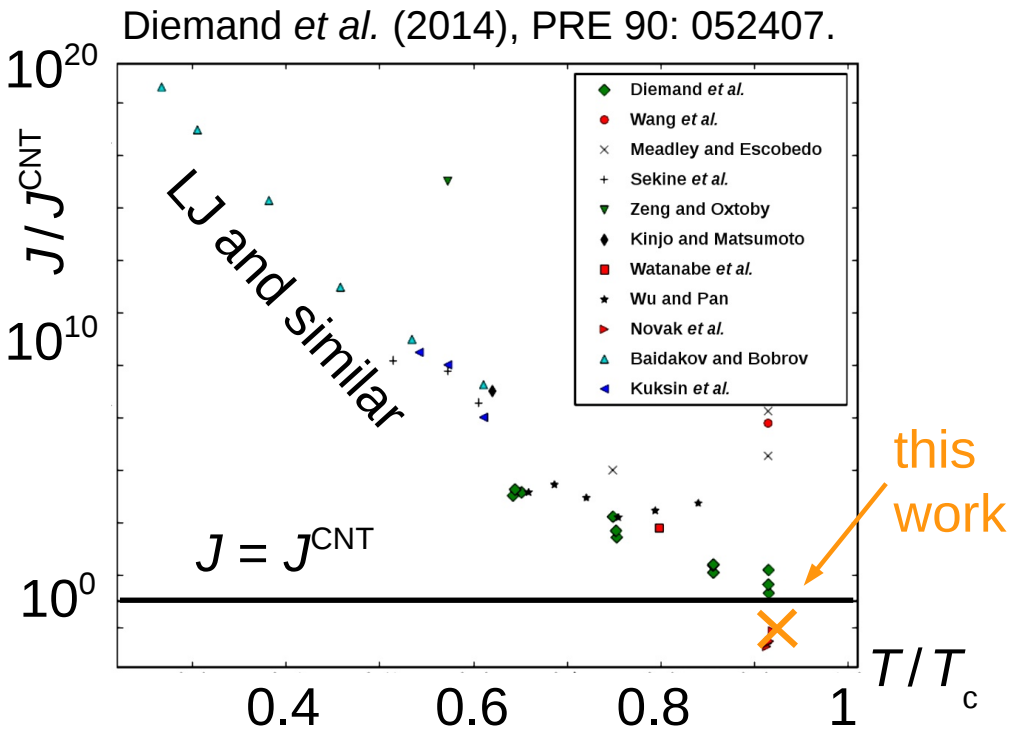


Classical nucleation theory predicts critical cavity sizes from 10 to 30 nm^3.

MD simulation ./. classical nucleation theory

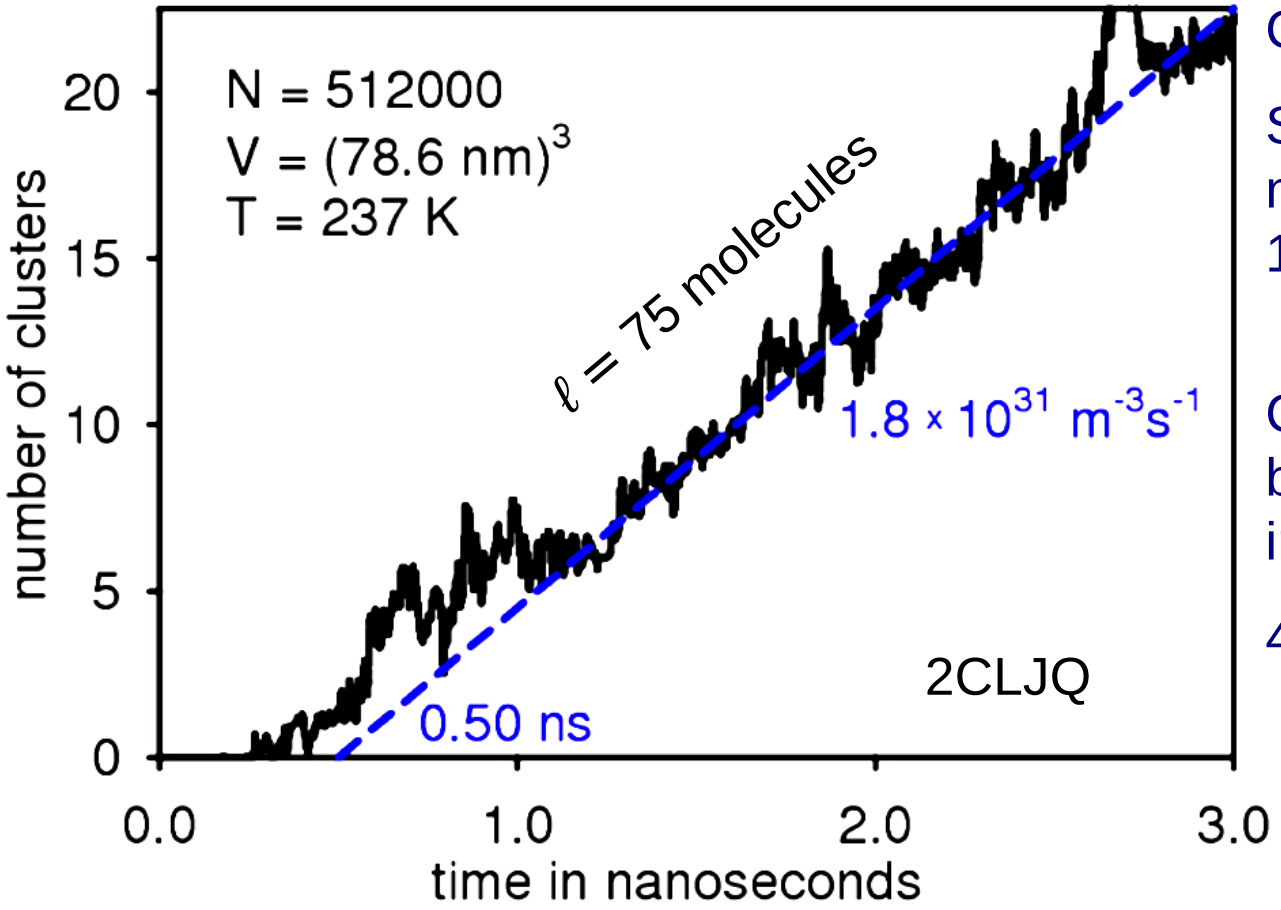
Cavities with a volume greater than 250 nm^3 are sufficiently supercritical.





For cavitation at high temperatures, CNT is a good approximation.

Nucleation in supersaturated vapors



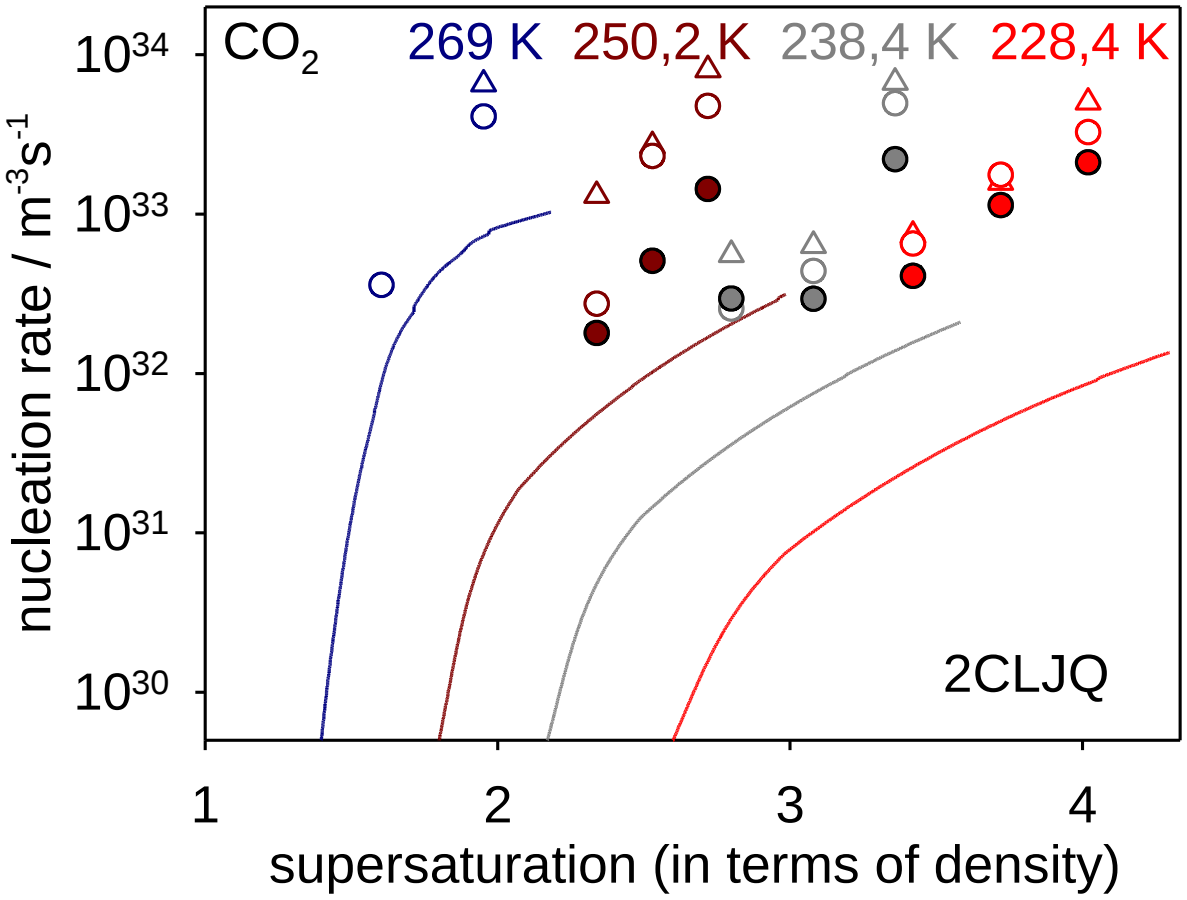
Cluster criterion:

Stillinger type, single neighbor within radius 1.5 σ + L/4, i.e. 5.1 Å.

Critical size predicted by CNT in region of interest:

40 to 60 molecules.

Nucleation in supersaturated vapors



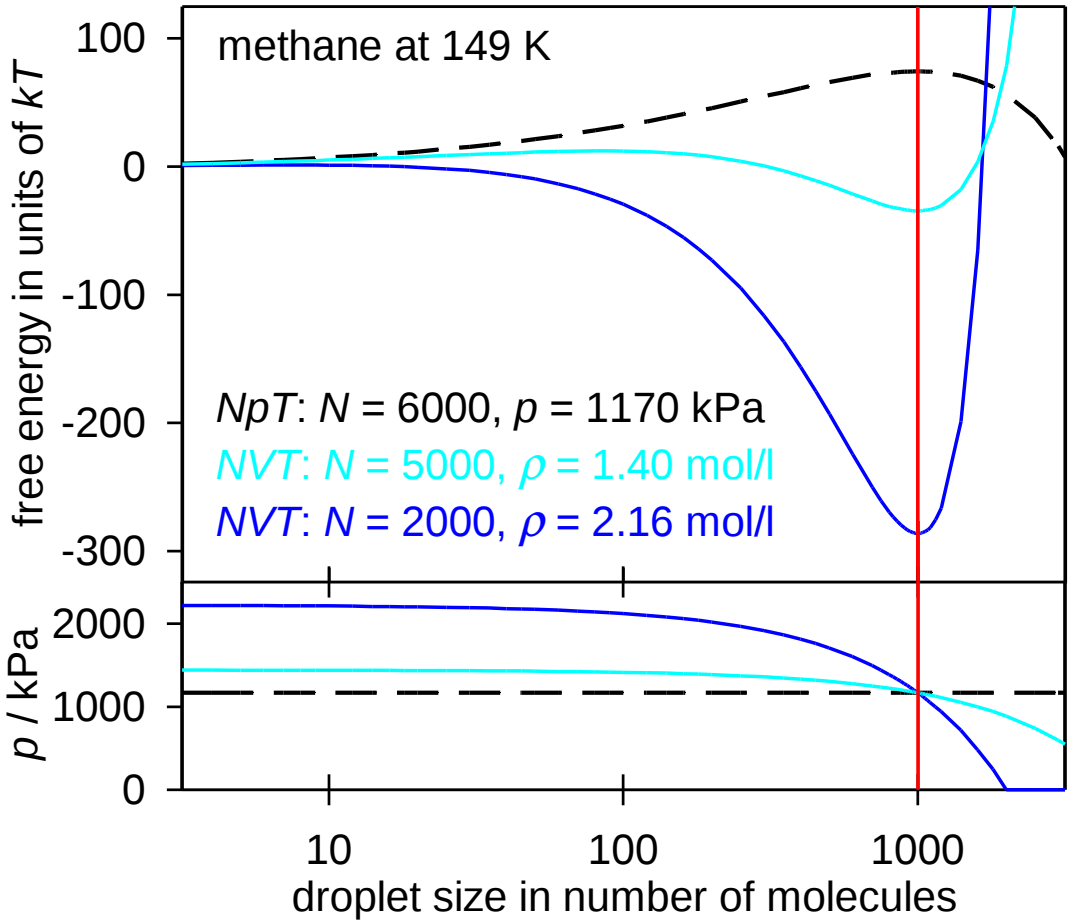
Cluster criterion:

Stillinger type, single neighbour within radius $1.5\,\sigma + L/4$, i.e. 5.1 Å.

— CNT (nonisothermal)

△ ℓ = 50 molecules
○ ℓ = 75 molecules
● ℓ = 250 molecules

Stable and unstable phase equilibria



Equilibrium condition for a nucleus of size j:

$$p = p(T, j)$$

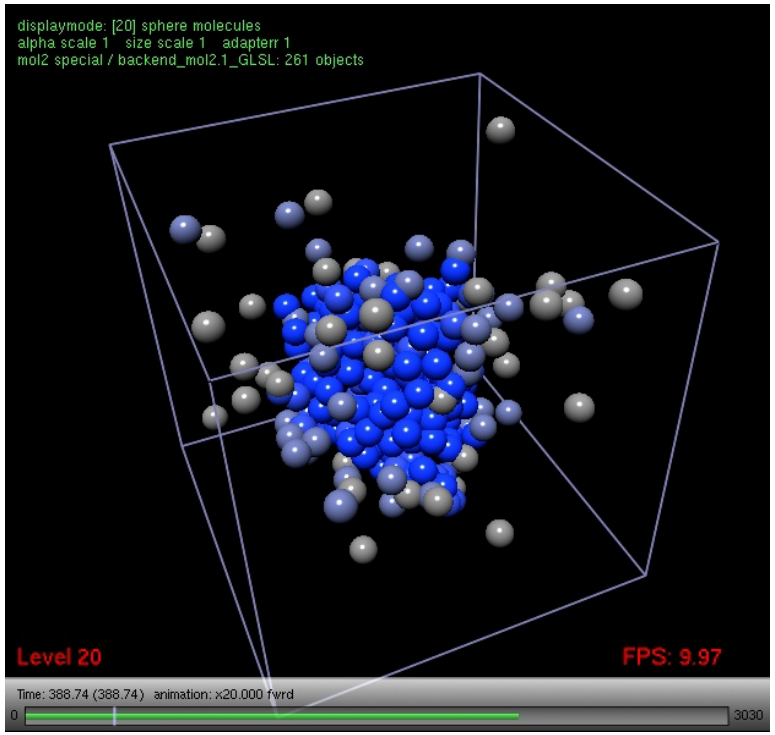
ΔG at constant p and T:

1 unstable equilibrium

ΔF at constant V and T:

(1 unstable equilibrium)
1 stable equilibrium

Molecular simulation of nanodroplets



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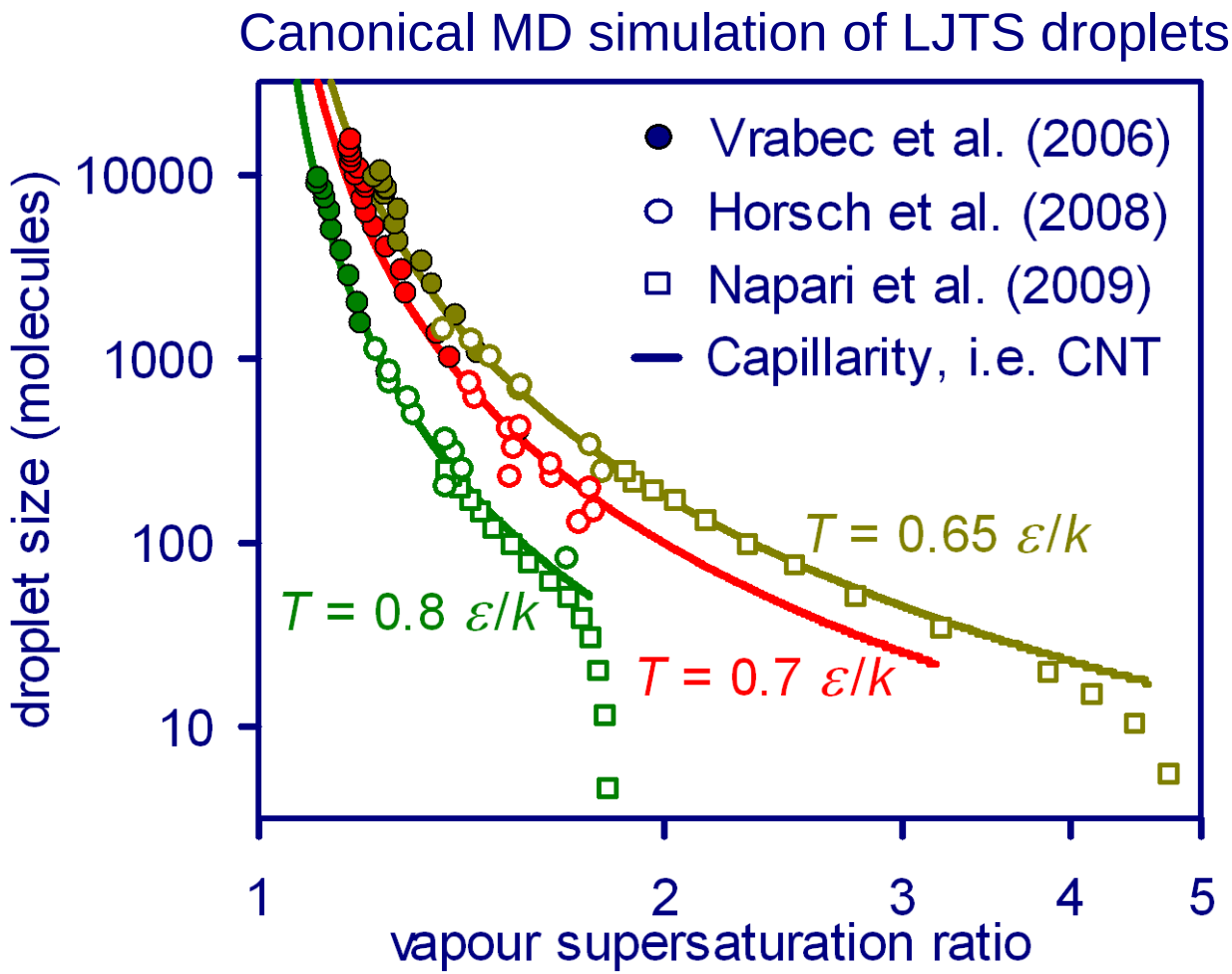


Down to 100 molecules: agreement with CNT ($\gamma = \gamma_0$).

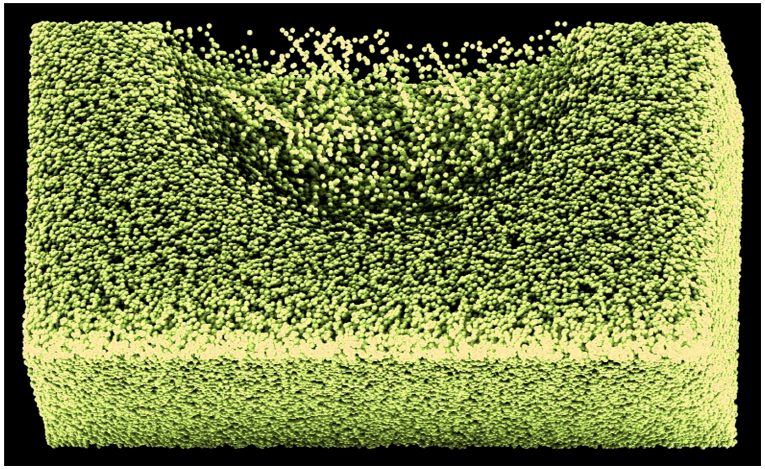
At the spinodal, the results suggest that $R_\gamma = 2\gamma / \Delta p \rightarrow 0$. This implies

$$\lim_{R_\gamma \rightarrow 0} \gamma = 0,$$

as conjectured by Tolman (1949) …

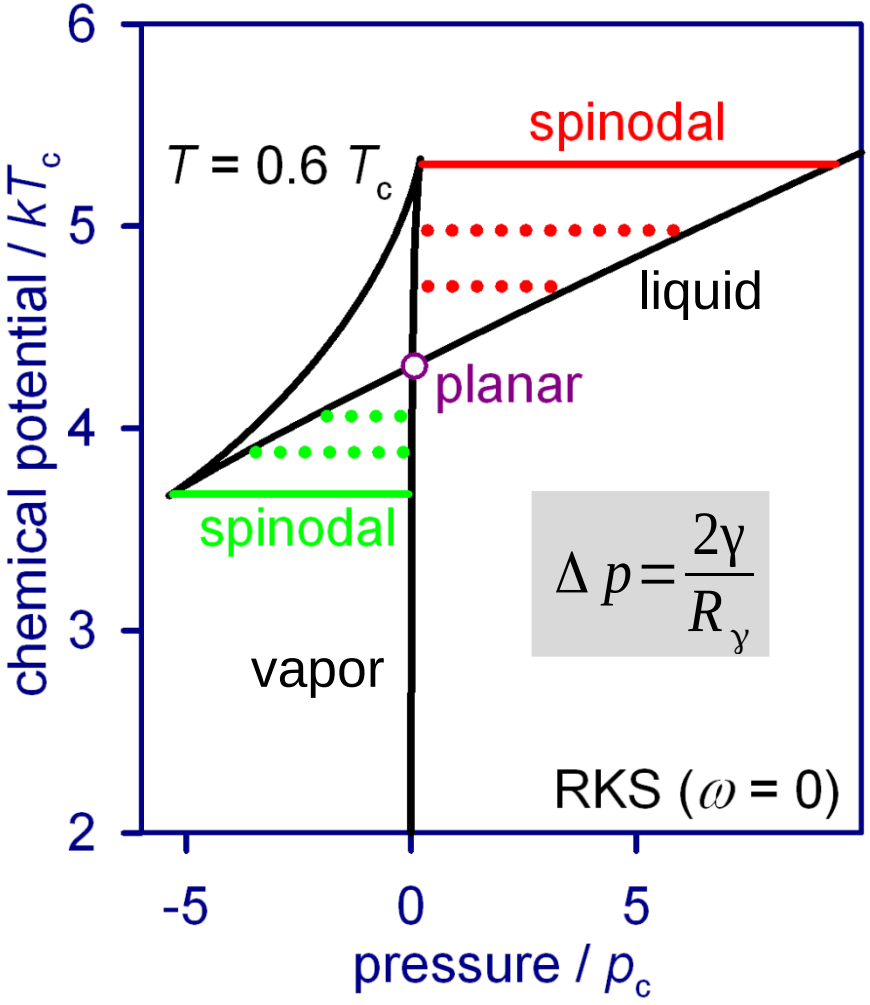
Molecular simulation of nanobubbles

- Droplet + metastable vapor
- Bubble + metastable liquid



Spinodal limit: For the external phase, metastability breaks down.

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



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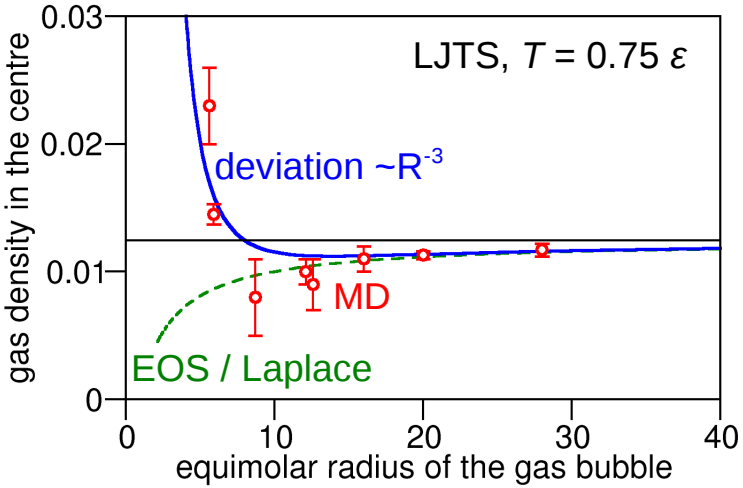

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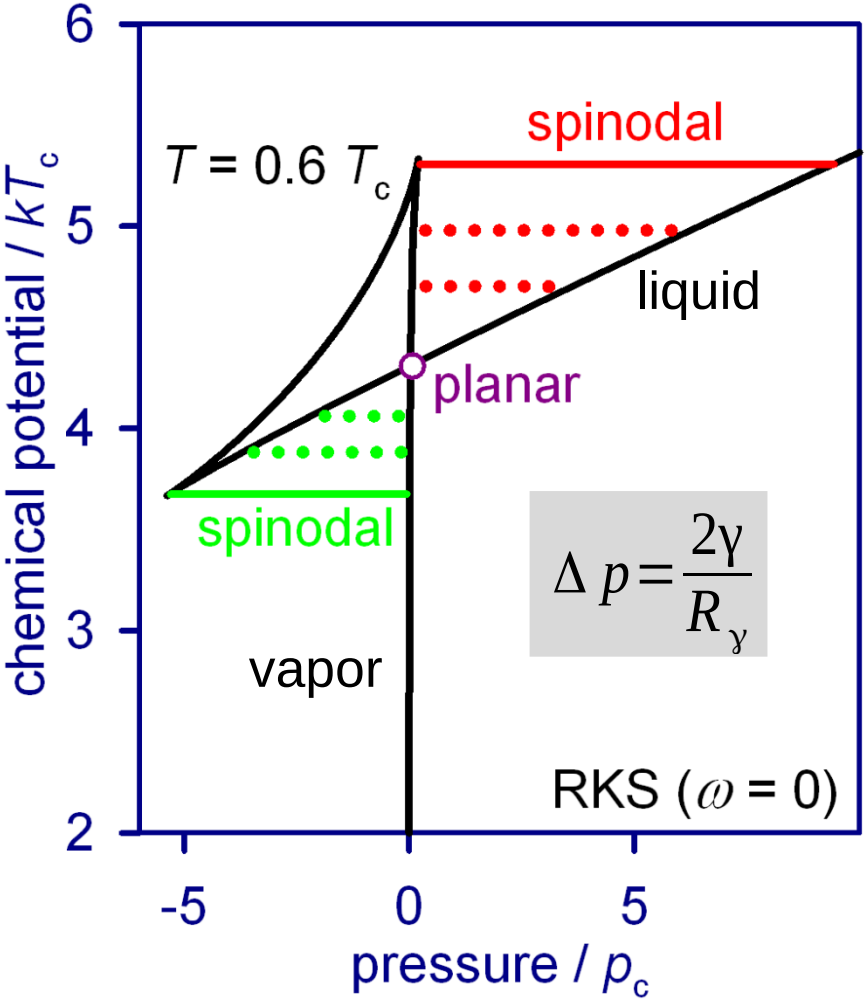
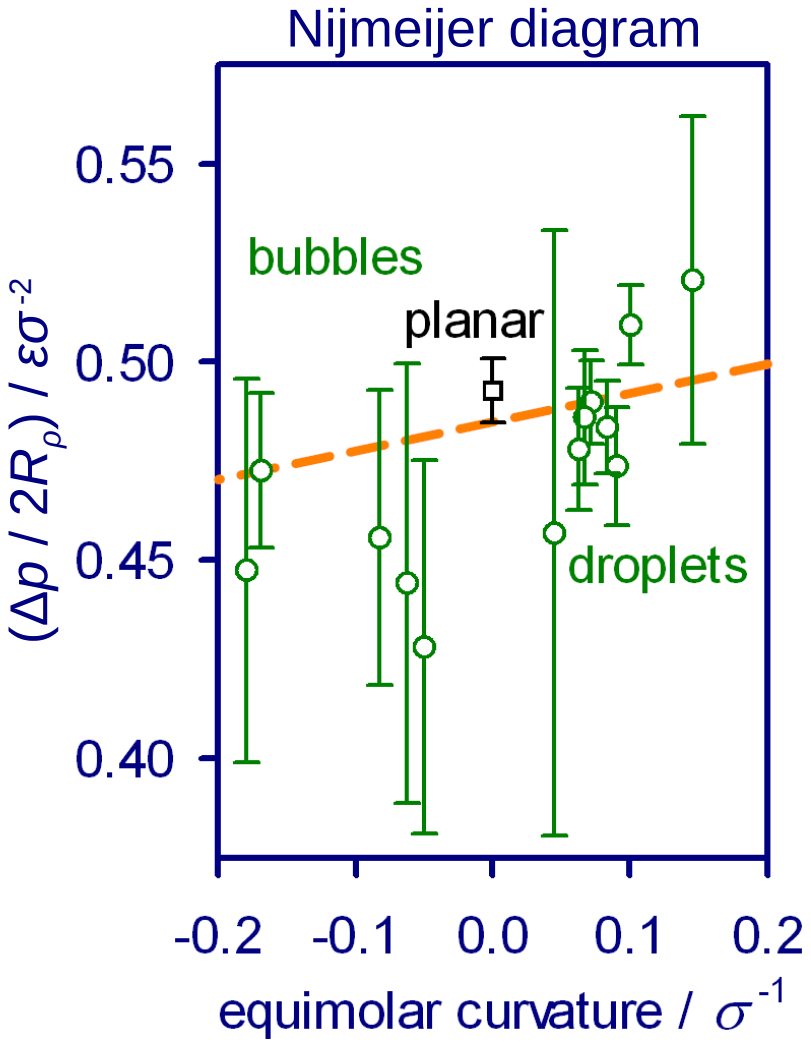


Interpolation to the planar limit



- Convention: Negative curvature (bubbles), positive curvature (droplets).
- Properties of the planar interface, such as its Tolman length, can be obtained by interpolation to zero curvature.
- A positive slope of $\Delta p/2R_\rho$ over $1/R_\rho$ in the Nijmeijer diagram corresponds to a **negative δ**, on the order of -0.1 σ here, conforming that δ is small.
- However, $\boldsymbol{R} \rightarrow \mathbf{0}$ for droplets in the spinodal limit for the surrounding vapor (Napari *et al.*) implies $\boldsymbol{\gamma} \rightarrow \mathbf{0}$.

Breakdown of Tolman's law

The relation obtained by Tolman (1949) for the surface tension of droplets

$$\frac{d\ln R}{d\ln \gamma} = 1 + \frac{1}{2}\left(\frac{\delta}{R} + \left[\frac{\delta}{R}\right]^2 + \frac{1}{3}\left[\frac{\delta}{R}\right]^3\right) \longrightarrow \frac{\gamma}{\gamma_0} = 1 - \frac{2\delta}{R} + O\left(\left[\frac{\delta}{R}\right]^2\right)$$

- accounts for an influence of the radius on the surface tension, but not for *curvature-independent effects* (by construction),
- assumes that the dependence of the surface tension on curvature is *monotonous* (except if the Tolman length δ changes its sign),
- is derived from a thermodynamic approach based on the *Gibbs adsorption equation*, i.e. $d\gamma = -\Gamma\, d\mu$, at constant temperature.

The adsorption equation for macrosystems

A comparison of the total *differential* for the free energy

$$dF = \gamma\, dA - P^{I} dV^{I} - P^{II} dV^{II} - S\, dT + \sum \mu_i dN_i$$

with the *absolute* free energy $F = \gamma A - P^{I} V^{I} - P^{II} V^{II} + \sum \mu_i N_i$ yields:

$$A\, d\gamma = V^{I} dP^{I} + V^{II} dP^{II} - S\, dT - \sum N_i d\mu_i$$

$$0 = V^{I} dP^{I} - S^{I} dT - \sum N_i^{I} d\mu_i$$

$$0 = V^{II} dP^{II} - S^{II} dT - \sum N_i^{II} d\mu_i$$

$$A\, d\gamma = -\eta dT - A \sum \Gamma_i d\mu_i$$

It follows that, at constant temperature,

$$d\gamma = -\sum \Gamma_i d\mu_i .$$

(Gibbs adsorption equation)

The adsorption equation for nanosystems

A comparison of the total *differential* for the free energy

$$dF = \gamma\, dA - P^{I} dV^{I} - P^{II} dV^{II} - S\, dT + \sum \mu_i dN_i$$

with the *absolute* free energy $F = \sigma A - P^{I} V^{I} - P^{II} V^{II} + \sum \mu_i N_i$ yields:

$$A\, d\sigma + (\sigma - \gamma) dA = V^{I} dP^{I} + V^{II} dP^{II} - S\, dT - \sum N_i d\mu_i$$

$$0 = V^{I} dP^{I} - S^{I} dT - \sum N_i^{I} d\mu_i$$

$$0 = V^{II} dP^{II} - S^{II} dT - \sum N_i^{II} d\mu_i$$

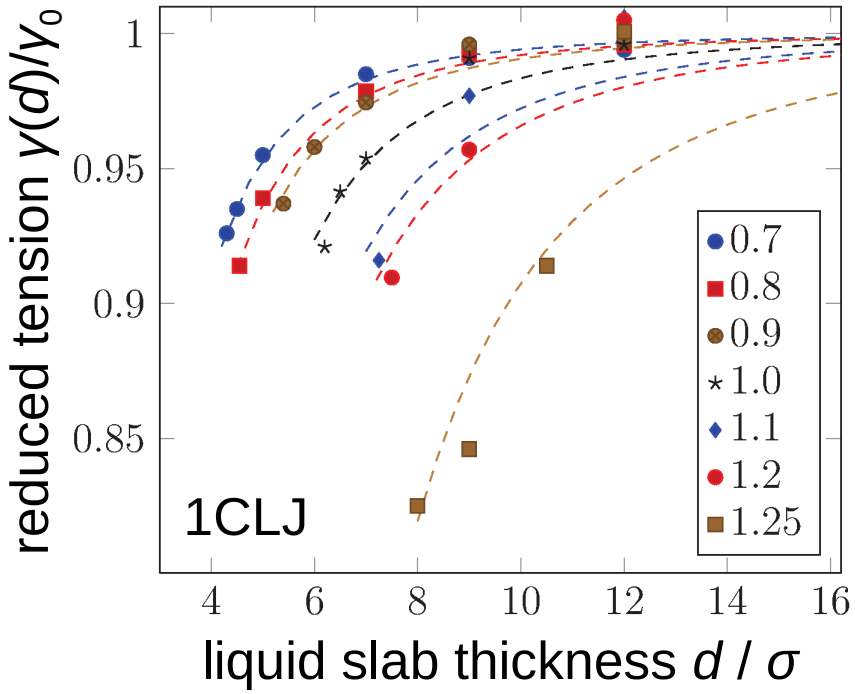
$$A\, d\sigma + (\sigma - \gamma) dA = -\eta\, dT - A \sum \Gamma_i d\mu_i$$

It follows that ...

finite-size effects with $\sigma \neq \gamma$ invalidate the Gibbs adsorption equation.

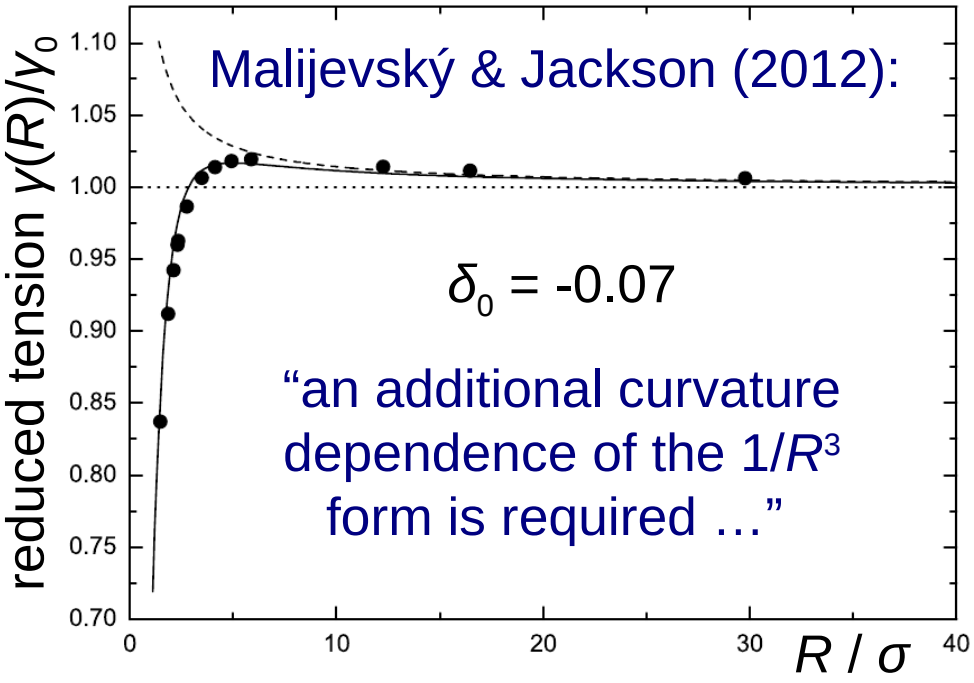
Molecular simulation of thin liquid films

Surface tension of thin films:

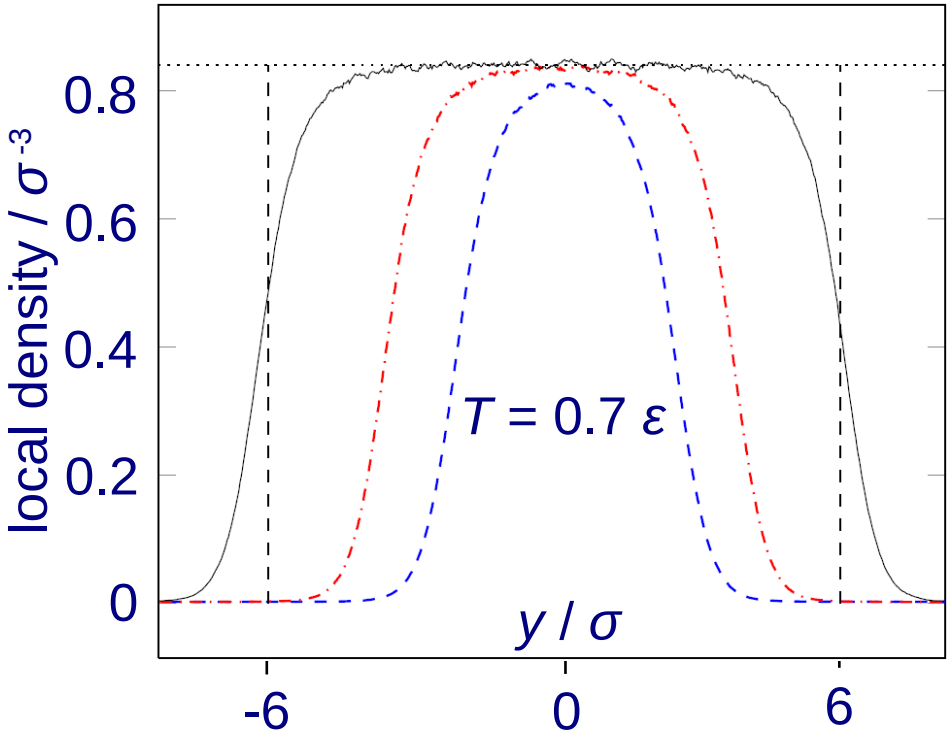


Relation with $\gamma(R)$ for droplets?

δ_0 is small and probably negative

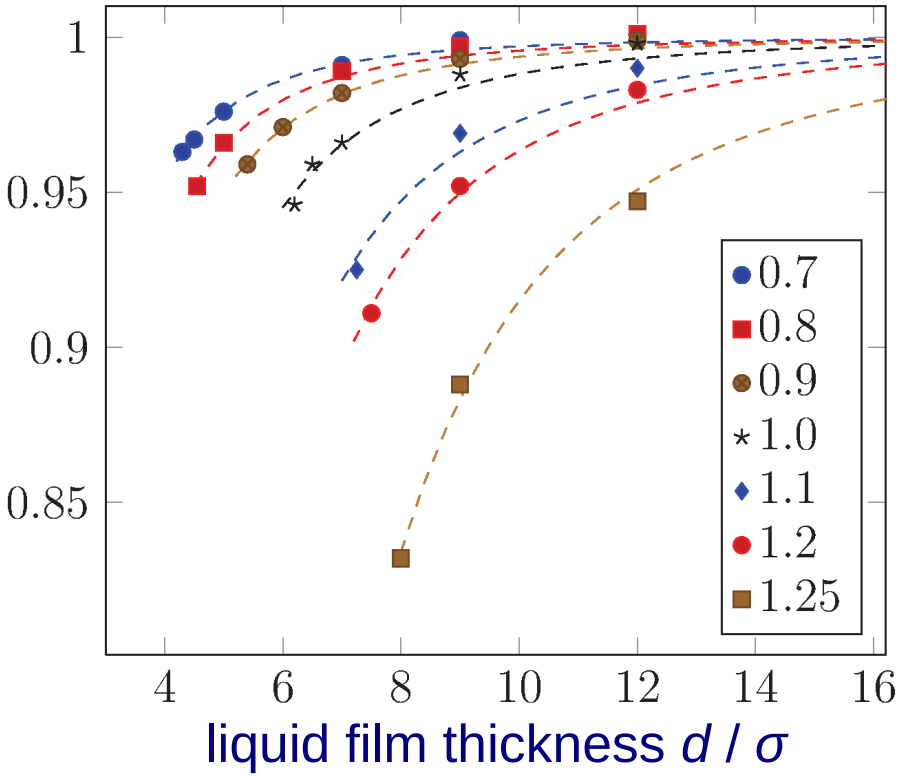


Molecular simulation of thin liquid films

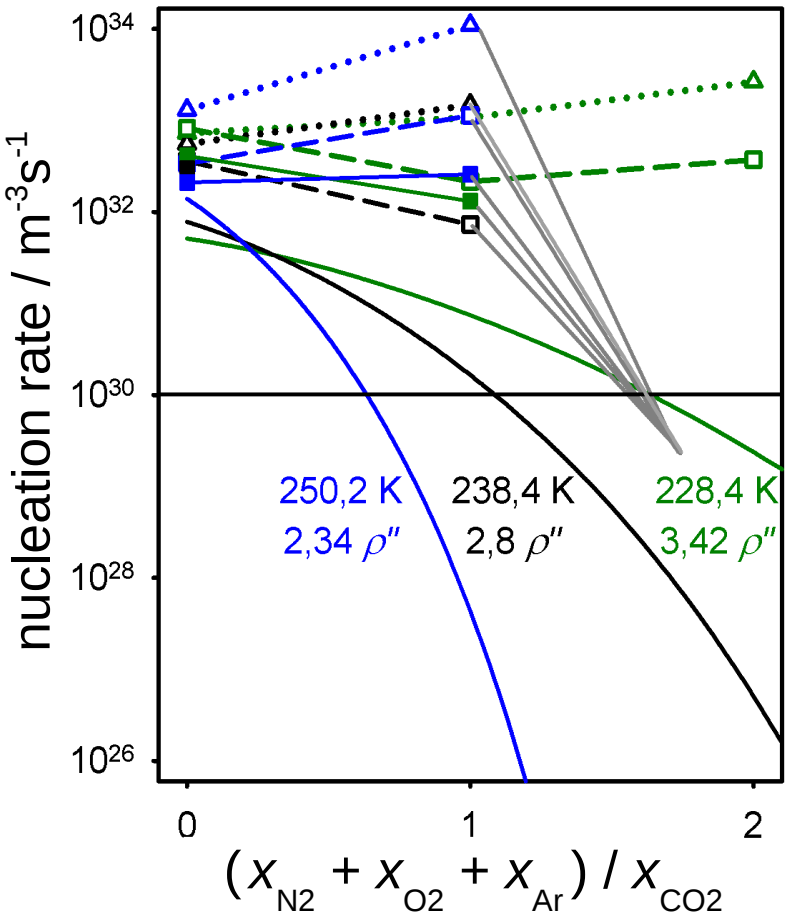


The density in the center of liquid nanofilms deviates from that of the saturated bulk liquid.

By simulating thin liquid films, curvature-independent size effects can be considered.



Nucleation in mixtures: Air + carbon dioxide



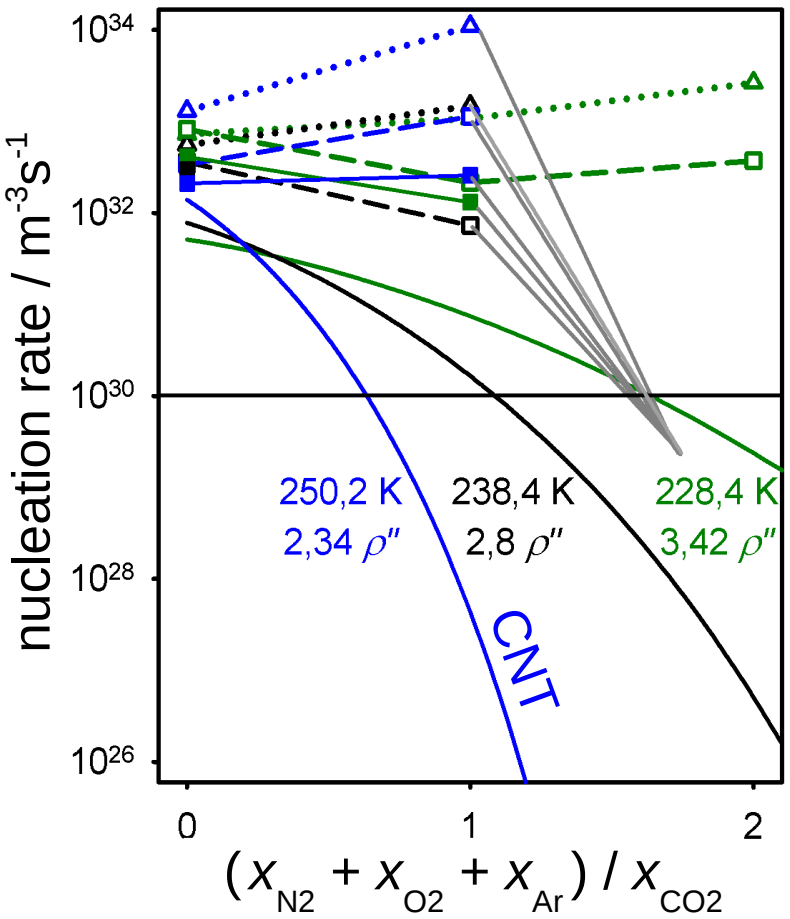
Scenario:

- Vapor contains four components
- Bulk liquid mainly contains CO_2

Results from MD simulation:

△ $\ell = 50$ ▫ $\ell = 100$ ■ $\ell = 150$

The carrier gas effect on nucleation



Scenario:

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

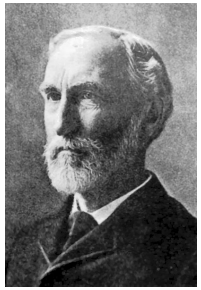
Carrier gas effect (Wedekind *et al.*):

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

— CNT following Wedekind *et al.*

△ $\ell = 50$ □ $\ell = 100$ ■ $\ell = 150$

Interfacial enrichment of carrier gases



„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".

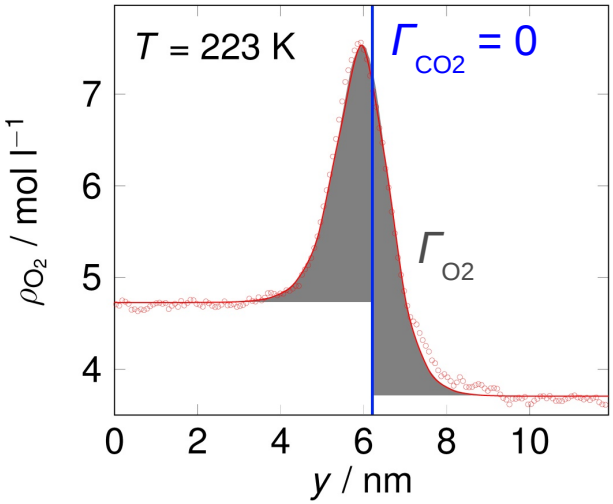
Thermodynamic **excess quantities** are ascribed to this dividing surface

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

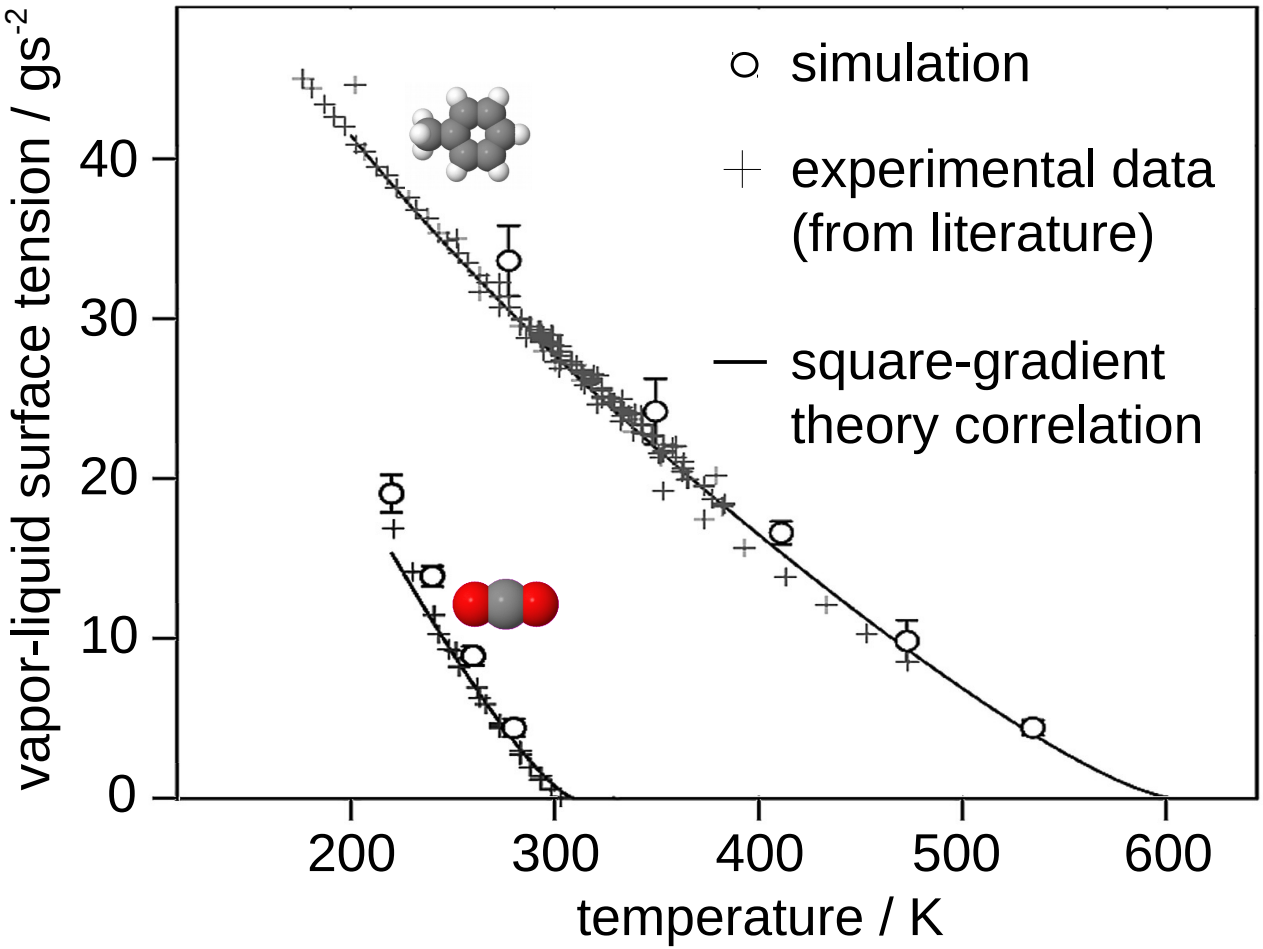
e.g. the surface free energy or the **adsorption**.

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

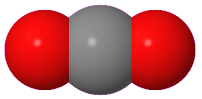
$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{N,V,T}.$$



Case study: Carbon dioxide and toluene

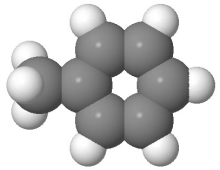


CO_2



3CLJQ
(Merker *et al.*)

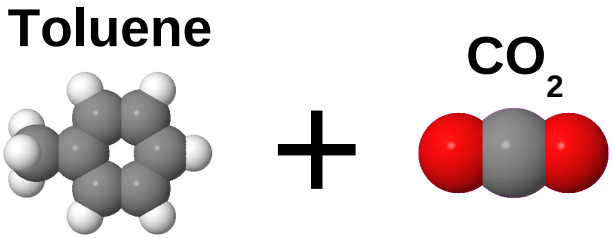
Toluene



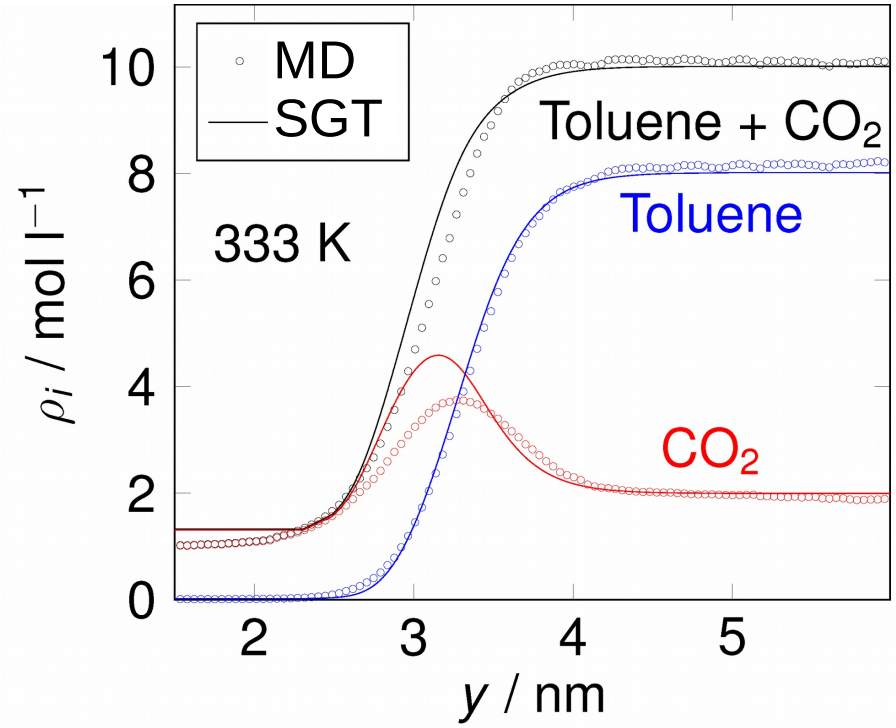
7CLJD+5Q
(Huang *et al.*)

Adjusted to pure component VLE data

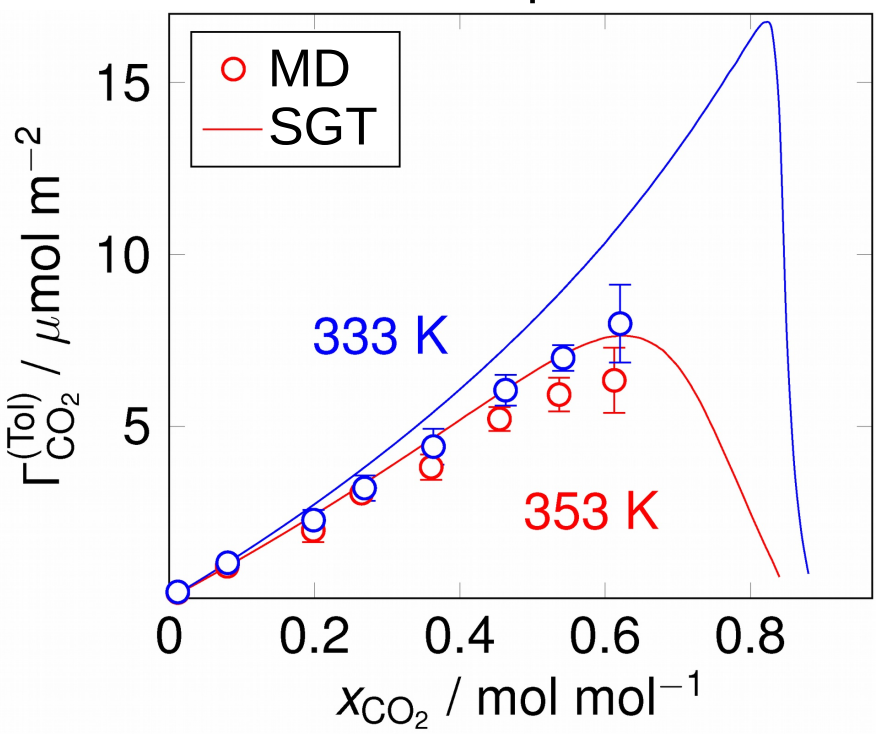
Interfacial enrichment of carrier gases



density profile

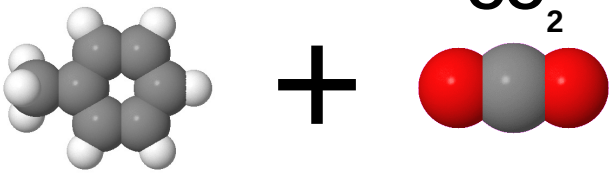


adsorption

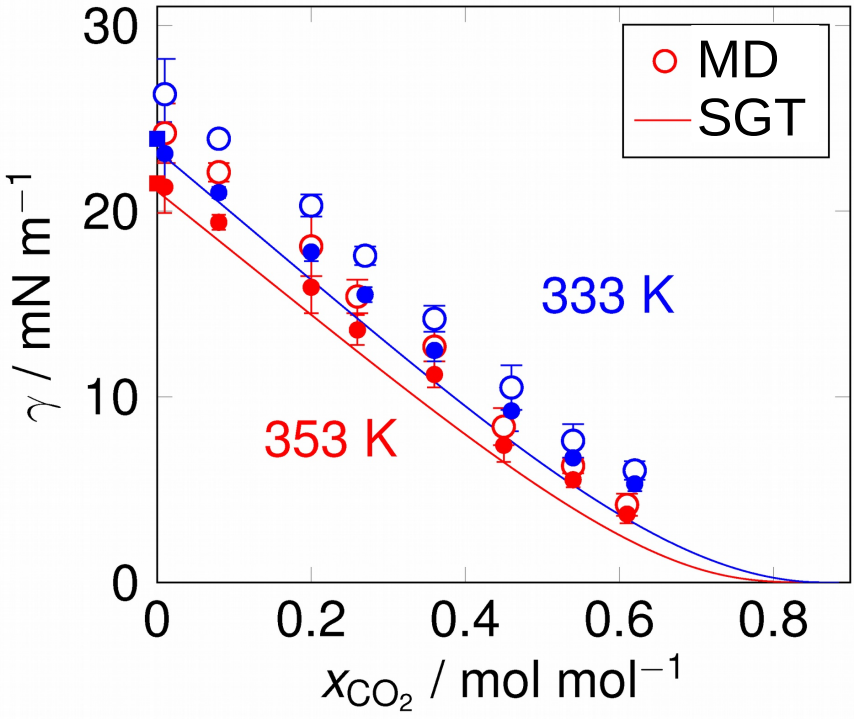


Adsorption effect on the surface tension

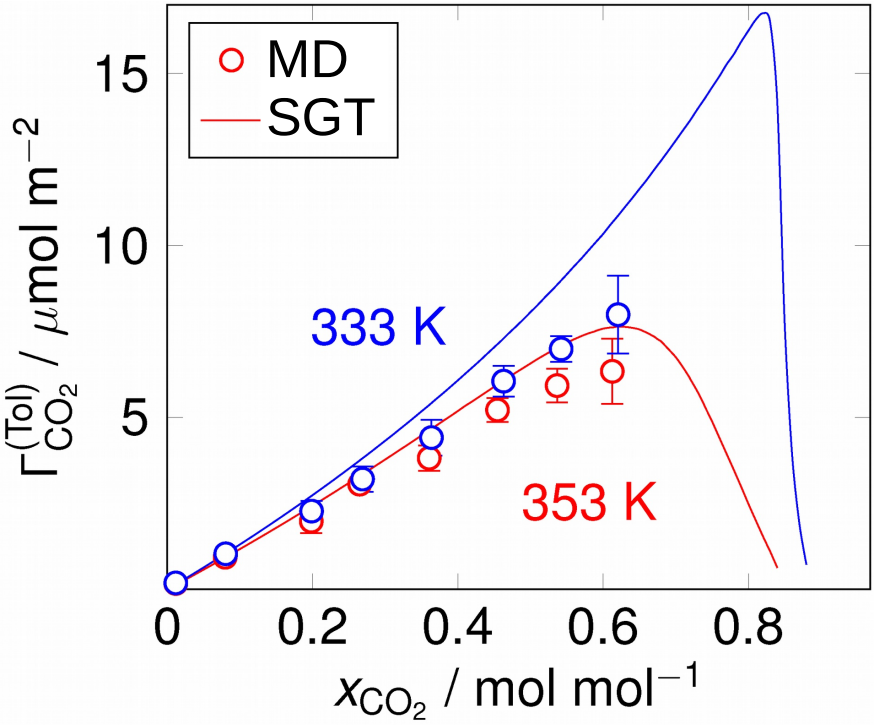
Toluene + **CO_2**



surface tension



adsorption



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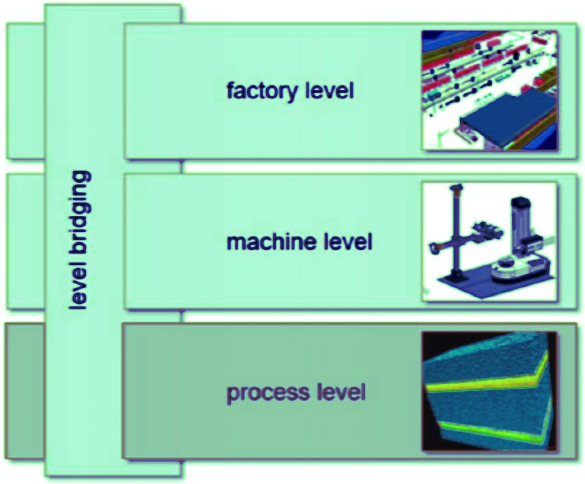

Projects of the German partners are funded by the German Research Foundation (DFG).

Focus: Exchange of doctoral candidates.

IRTG 2057
Physical Modeling for Virtual Manufacturing Systems and Processes

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UC Davis University of California

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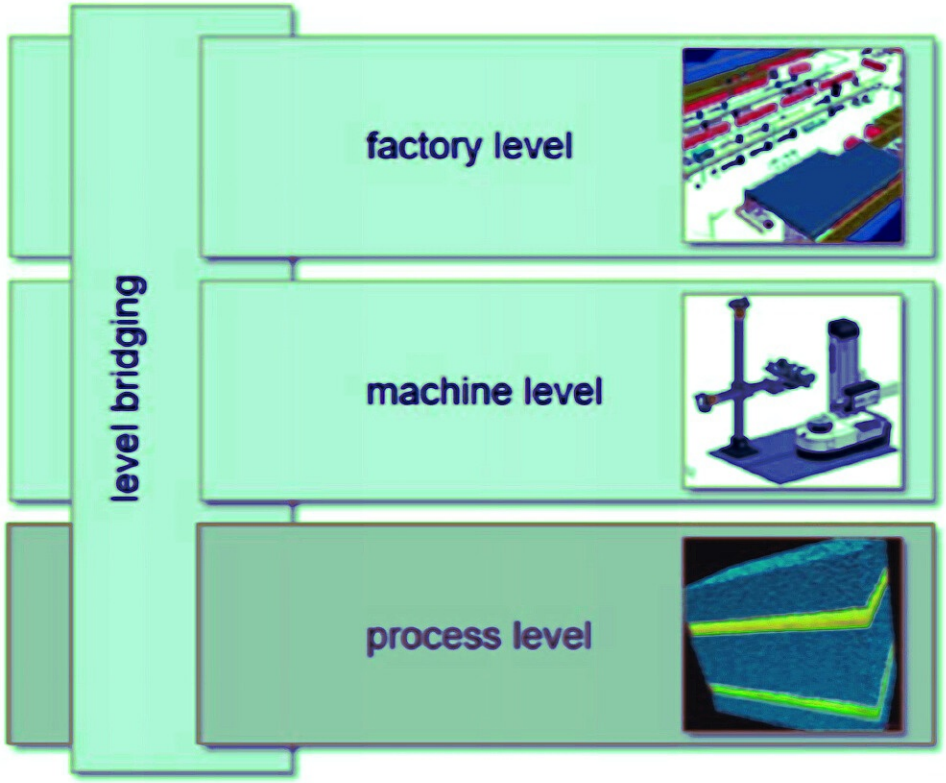

Aim of our subproject:

Investigate elementary processes and properties that are relevant for understanding the role of cutting liquids during machining.

Method: MD simulation.

Technische Universität Kaiserslautern
Berkeley University of California
UC Davis University of California

International Graduate School IRTG 2057

Martin Lautenschläger

Simon Stephan
(from January 2016)

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Technische Universität Kaiserslautern
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Summary

The traditional art of molecular modeling

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 modeling 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**.

Summary

With optimized and validated **molecular models**, e.g. from multicriteria optimization, quantitatively reliable predictions can be made.

Massively parallel MD simulation of large systems makes activated processes like homogeneous nucleation directly accessible. In this way, **over 100 000 cores** of a supercomputer can be used efficiently.

For **pure carbon dioxide**, homogeneous nucleation of bubbles in a metastable liquid and of droplets in a metastable vapor is well described by CNT, without the need for a curvature correction.

The influence of a carrier gas cannot be reduced to its presence in the vapor phase, due to the possibility of **interfacial enrichment**.