# Interfacial properties of fluids by computational molecular engineering

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Computational Molecular Engineering

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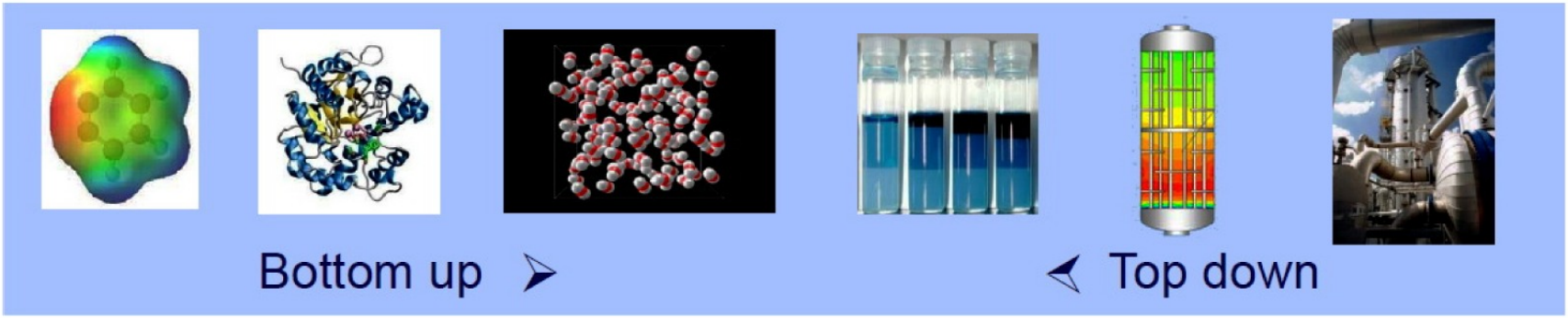
I3MS Seminar

# Computational molecular engineering



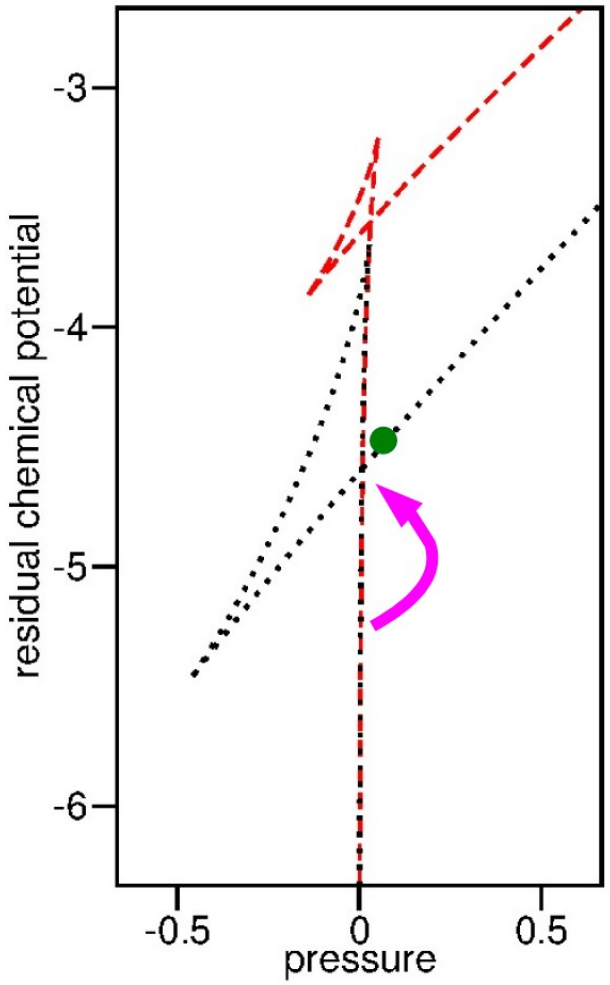

## From Physics (qualitative accuracy)

- 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

# Vapour-liquid equilbiria: 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.

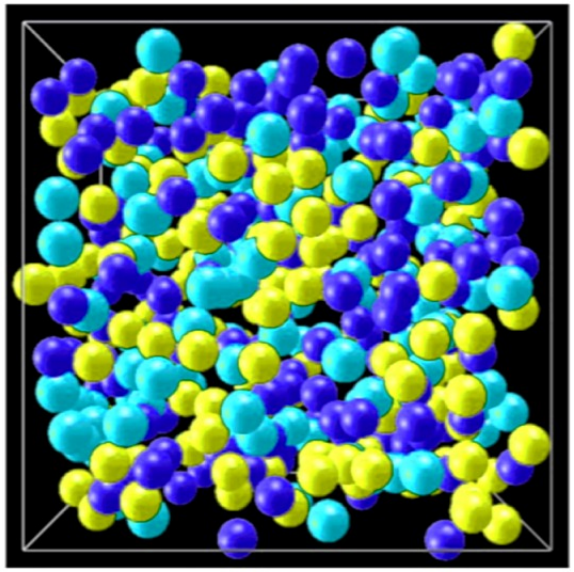
Second step: Pseudo-$\mu VT$ vapour simulation

Grand-canonical simulation where the value of $\mu$ is determined on the fly from the pressure.

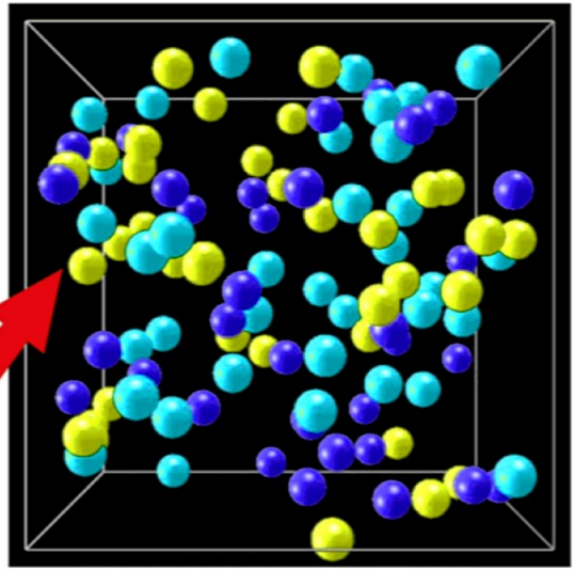
Obtained: Pressure $p$, vapour composition $y$

# Vapour-liquid equilbiria: Grand Equilibrium

temperature
liquid composition



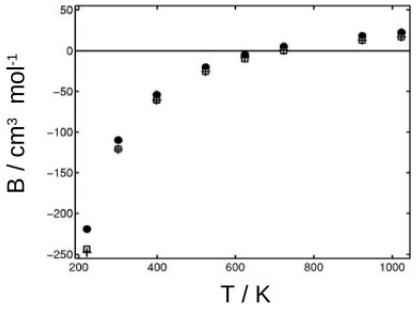
partial molar volumes
chemical potentials



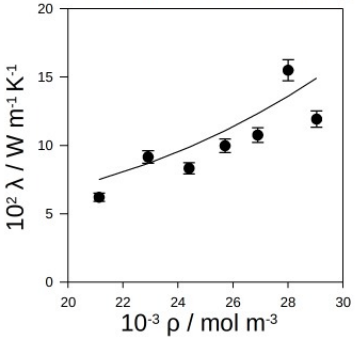
pressure
vapour composition

# Simulation of bulk properties with ms2

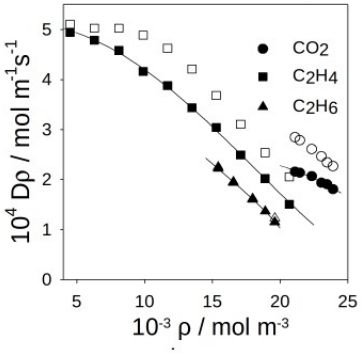
Second virial coefficient



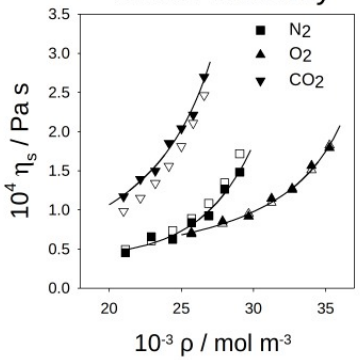

Thermal conductivity




Self-diffusion coefficient

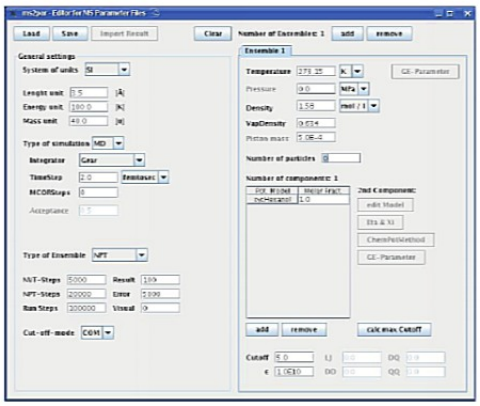



Shear viscosity



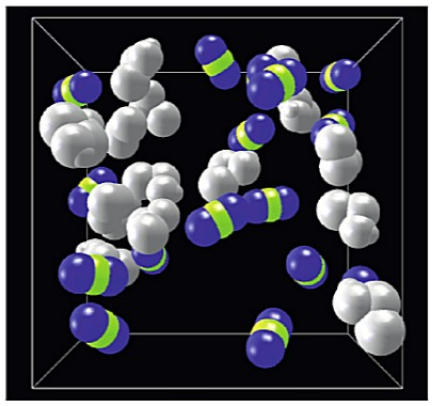

*ms2* is freely available for academic use – register at http://www.ms-2.de/

***ms2par***



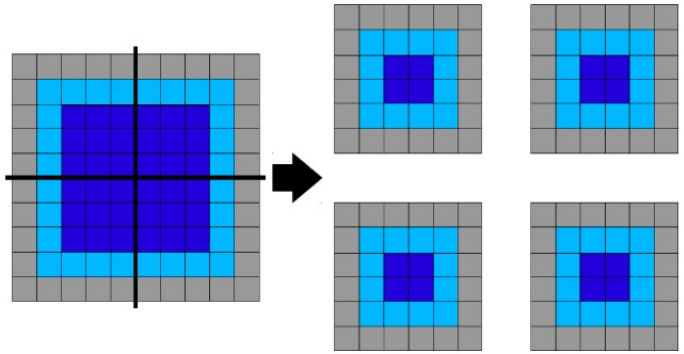
***ms2chart***

***ms2molecules***



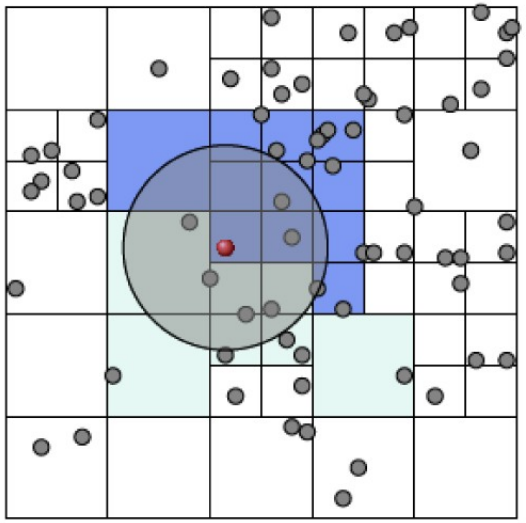
# Scalable MD simulation with *ls1 mardyn*

Linked-cell data structure suitable for spatial domain decomposition:

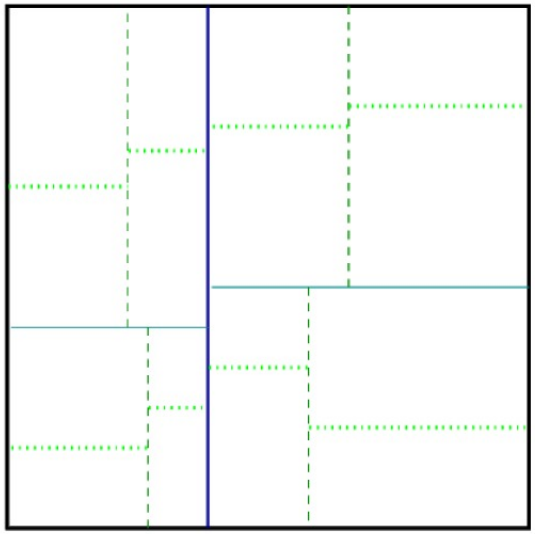


(non-blocking, overlapping MPI send/receive operations)

Methods for heterogeneous or fluctuating particle distributions:



adaptive cells



*k*-d decomposition

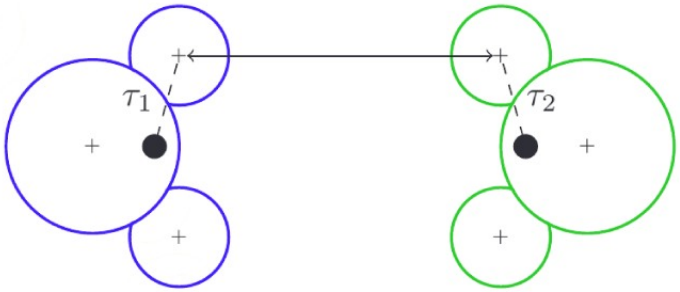
# Long-range correction: Planar geometry

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

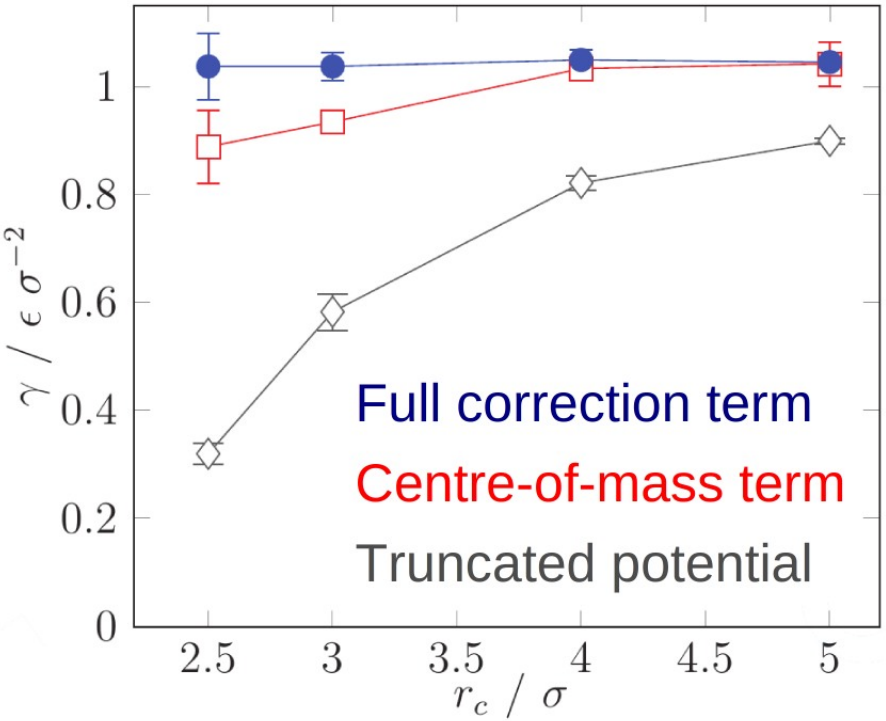
$$\Delta U_i = 2\pi \int_0^L dy\, \rho(y) \int_R^\infty dr\, u(r) r$$

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

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




Two-centre LJ fluid (2CLJ)




For complex geometries, a version of *ls1* applies the fast multipole method.

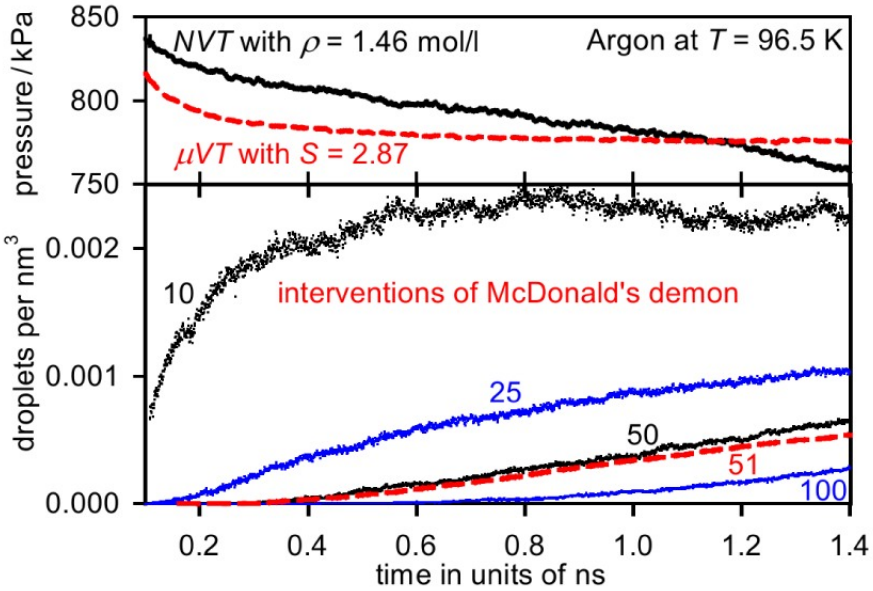
# MD simulation of nucleation

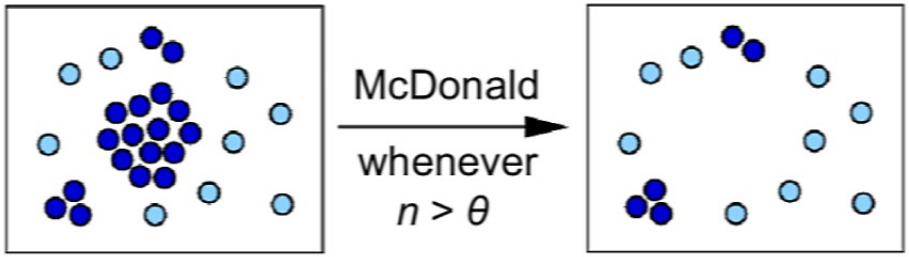
Yasuoka-Matsumoto method:

- 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.

# Intervention rate and nucleation rate

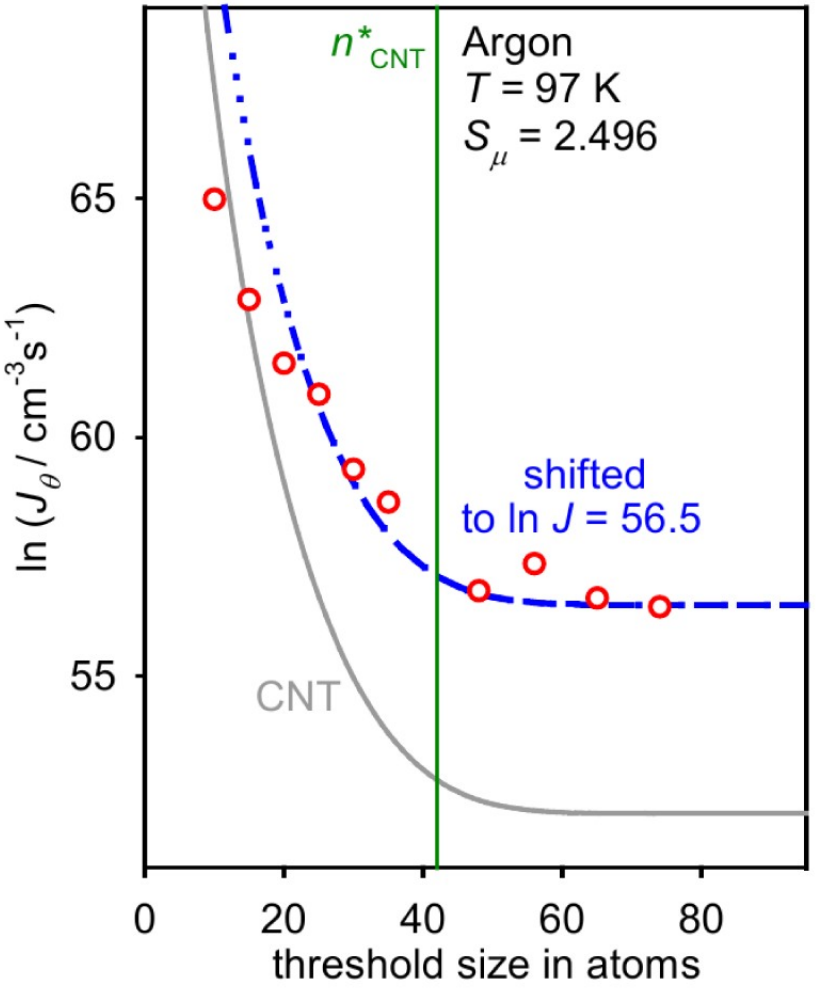
Not all of the removed clusters would have grown to macroscopic size

$$J = J_\theta q(\theta).$$

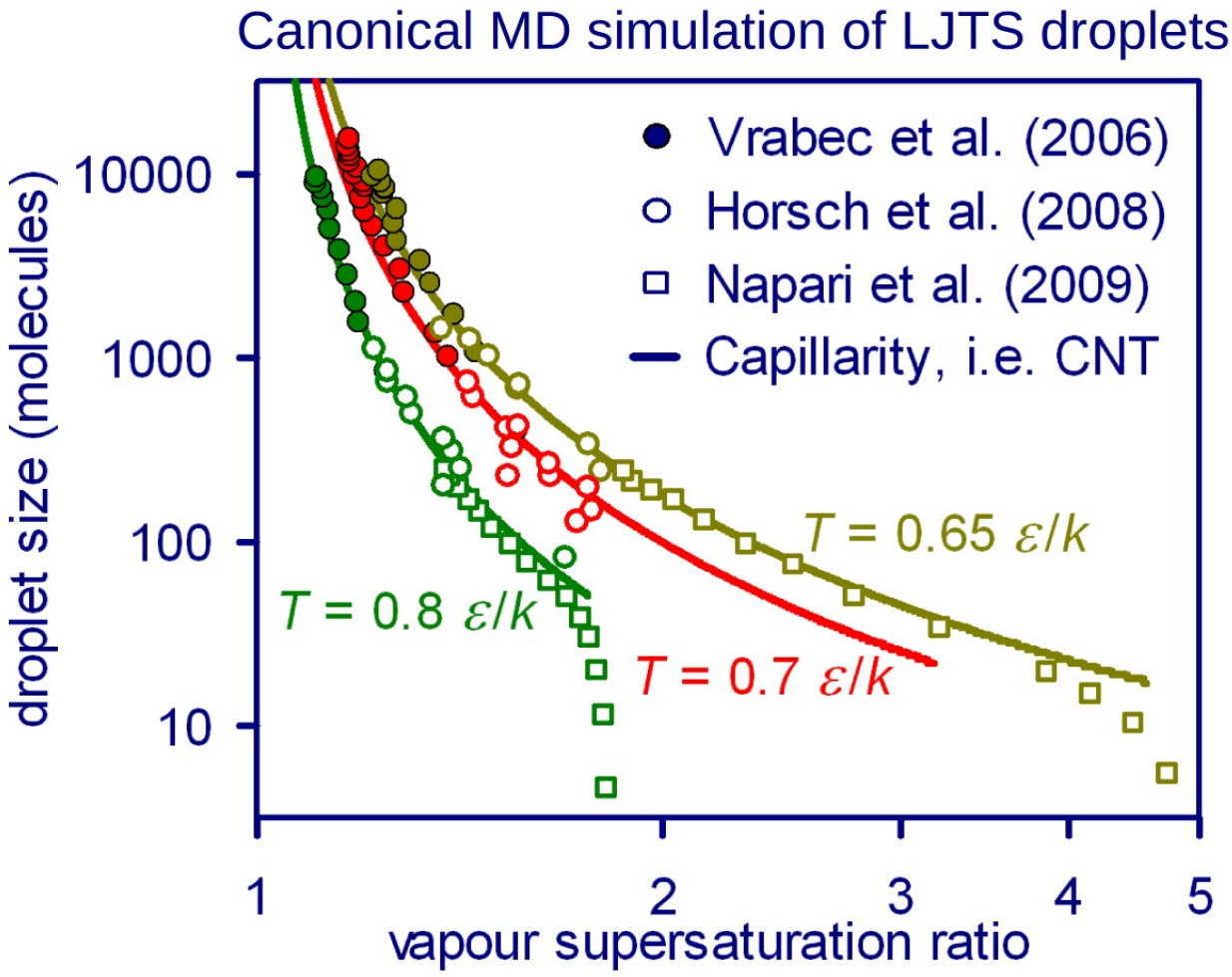
The probability for a droplet to grow from size $\theta$ to infinity is

$$q(\theta) = \frac{\int_1^\theta dn \exp(2F/T)}{\int_1^\infty dn \exp(2F/T)},$$

and for the critical nucleus it is approximately $q(n^*) \approx 1/2$.



# Equilibrium vapour pressure of a droplet



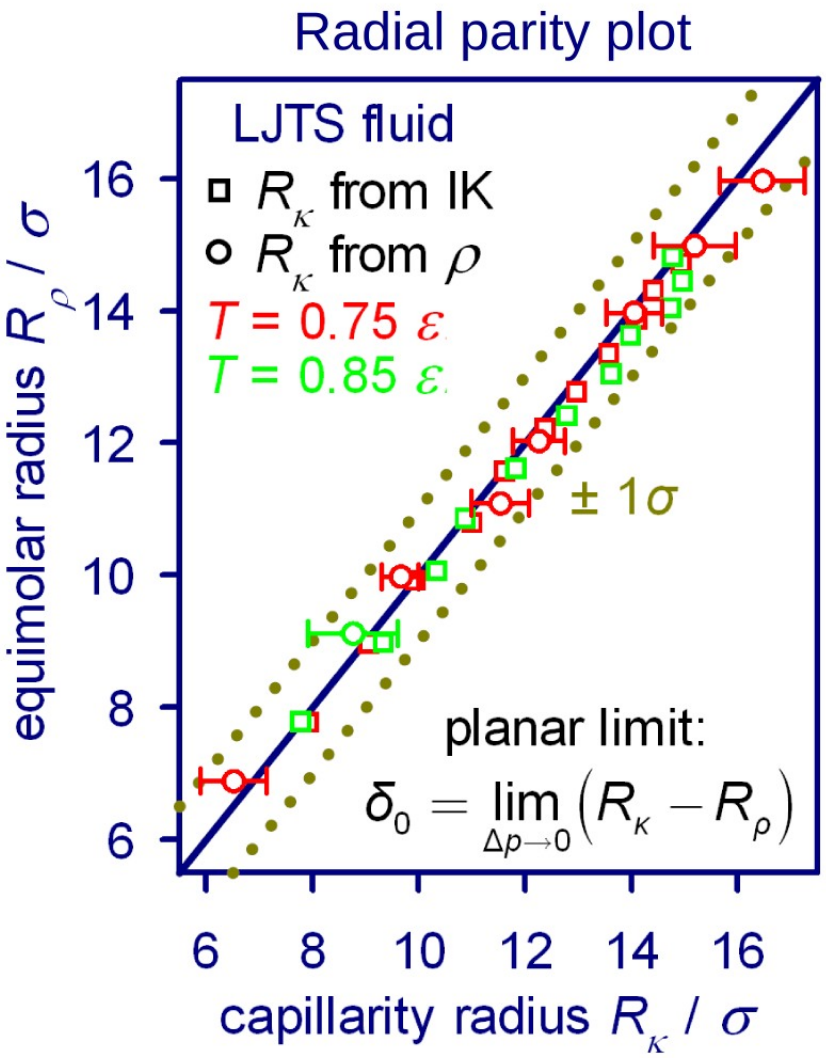

Down to 100 molecules: agreement with CNT ($\gamma = \gamma_0$).

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) …

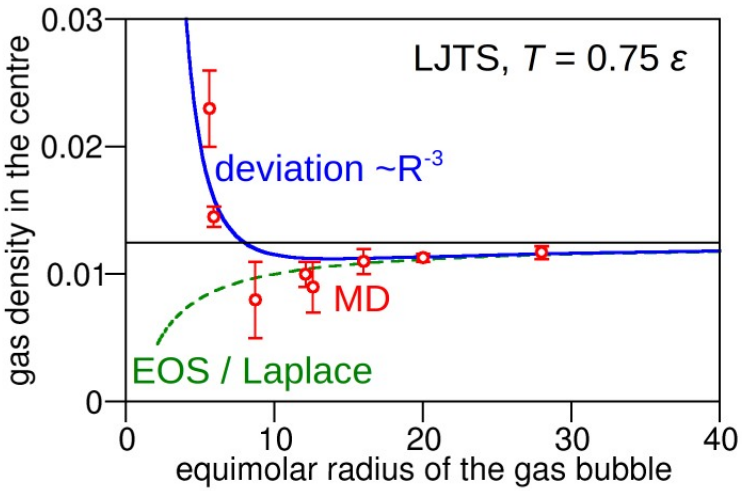
# Tolman length in the planar limit




- The deviation between the equimolar radius and the capillarity radius is consistently found to be smaller than $\sigma$ / 2.
- The curvature dependence of $\gamma$ is weak: The deviation from the planar surface tension is smaller than 10 % for radii larger than 5 $\sigma$.

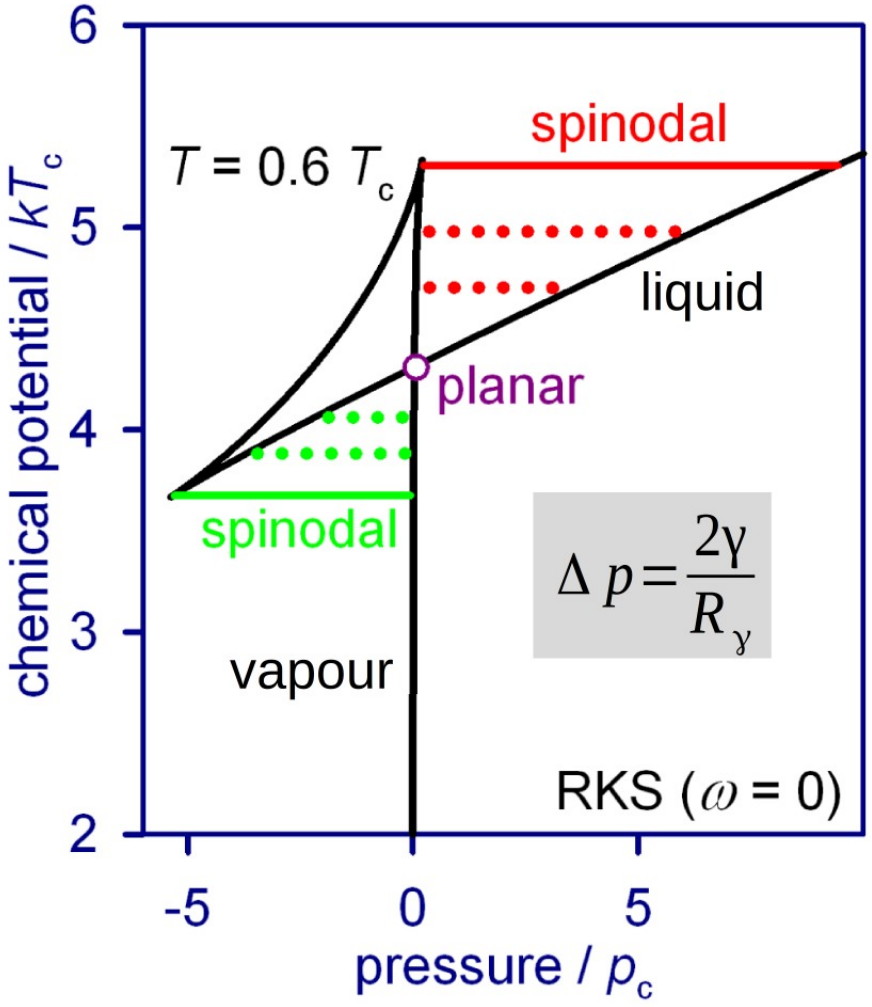
# Nanoscopic gas bubbles in equilibrium

- Droplet + metastable vapour
- Bubble + metastable liquid



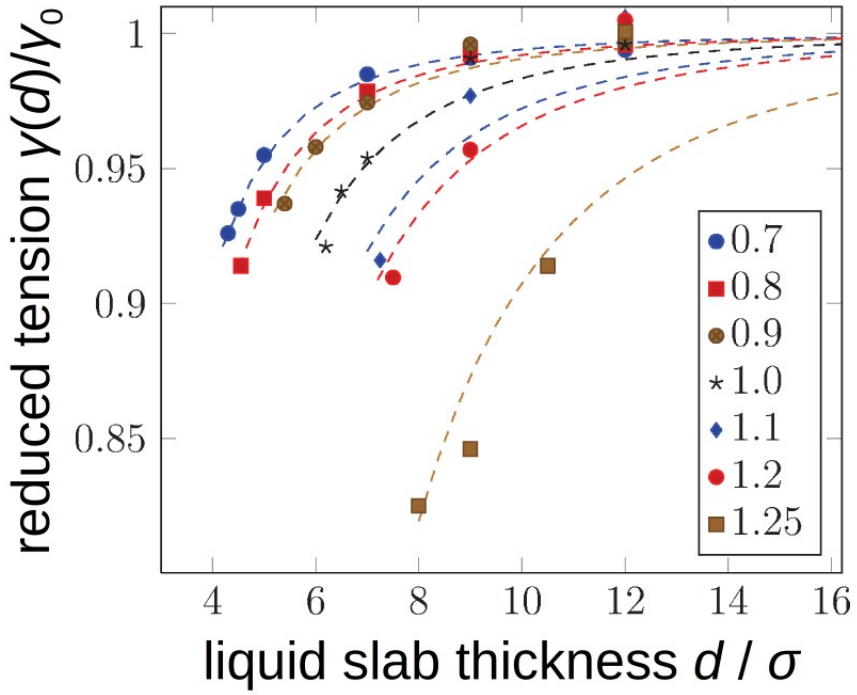

Spinodal limit: For the external phase, metastability breaks down.

Planar limit: The curvature changes its sign and the radius $R_\gamma$ diverges.



# A curvature-independent size effect

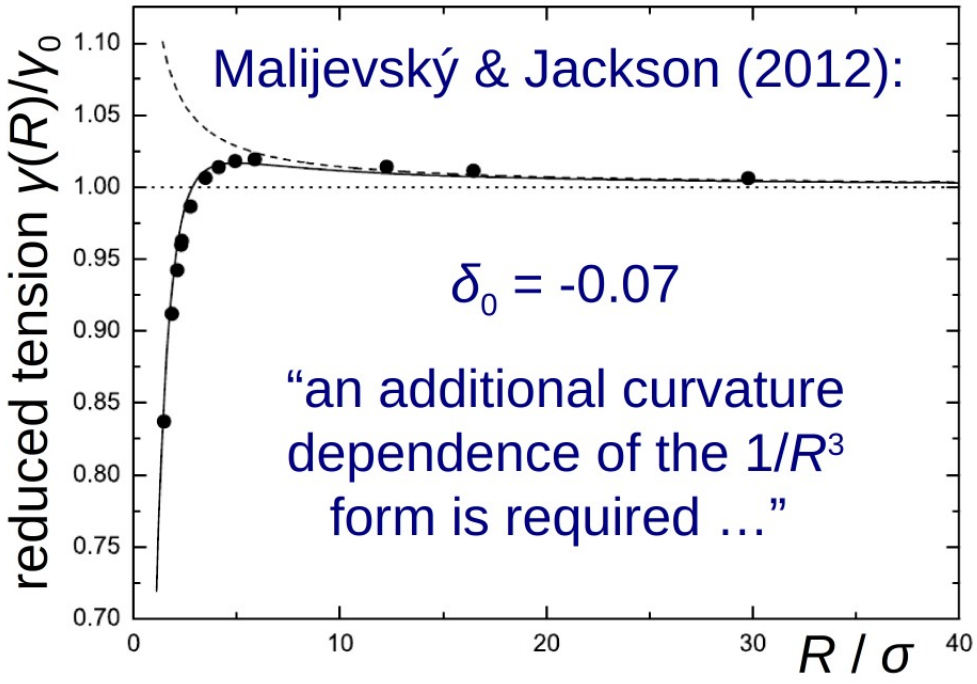
Surface tension for thin slabs:




Correlation: $\frac{\gamma(d, T)}{\gamma_0(T)} = 1 - \frac{b(T)}{d^3}$

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

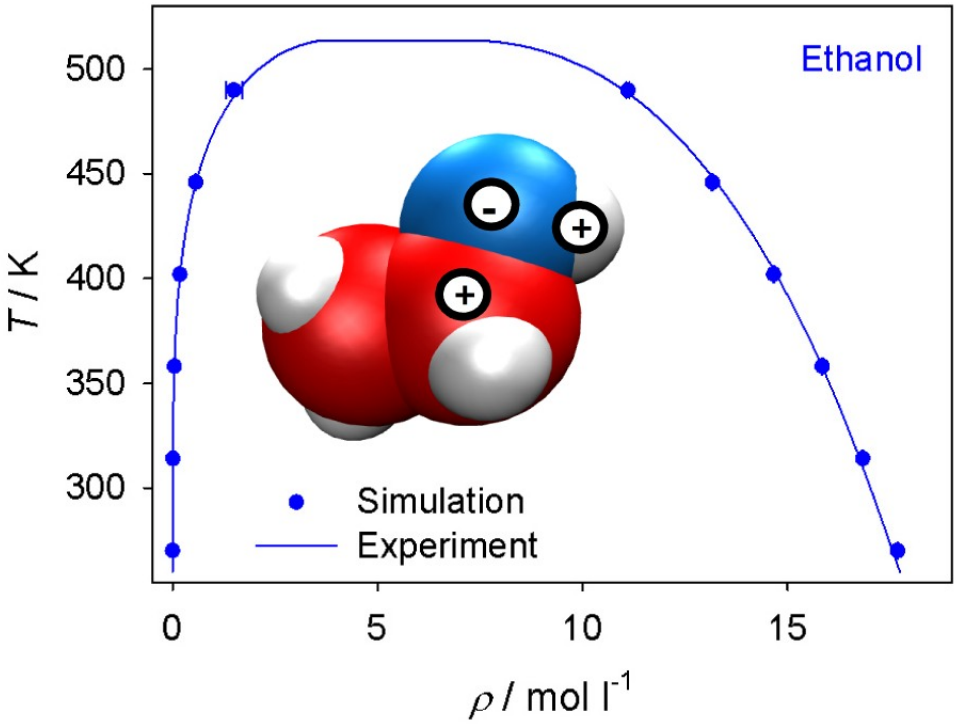
$\delta_0$ is small and probably negative

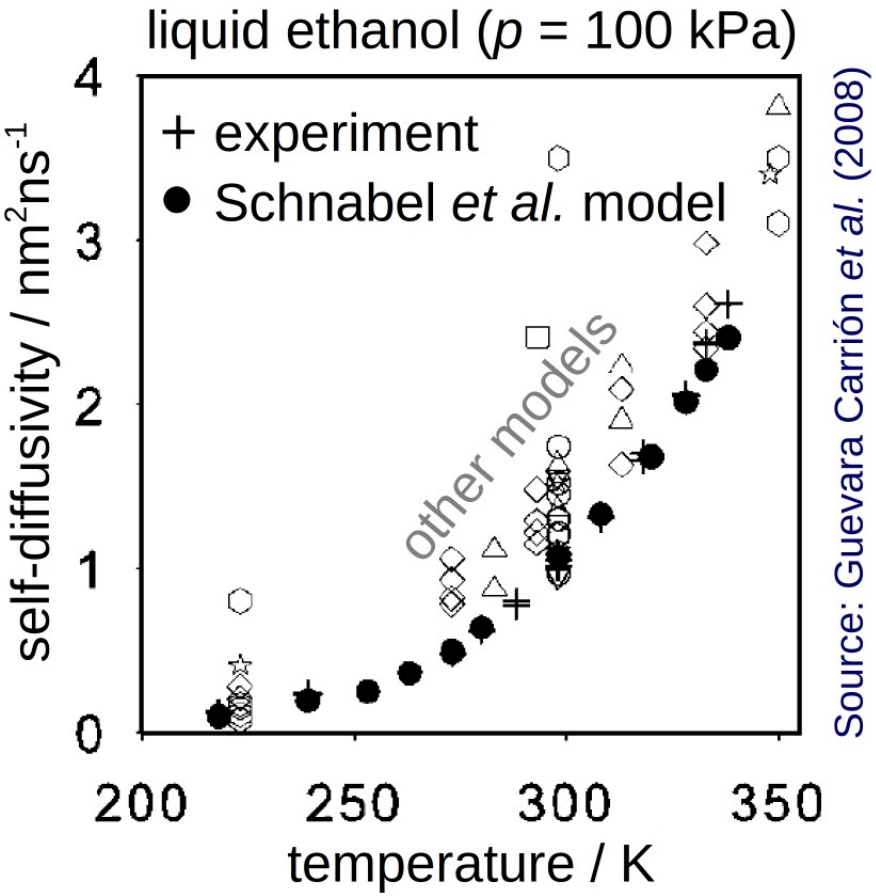


# Modelling hydrogen bonding fluids

Model parameters are adjusted to VLE data

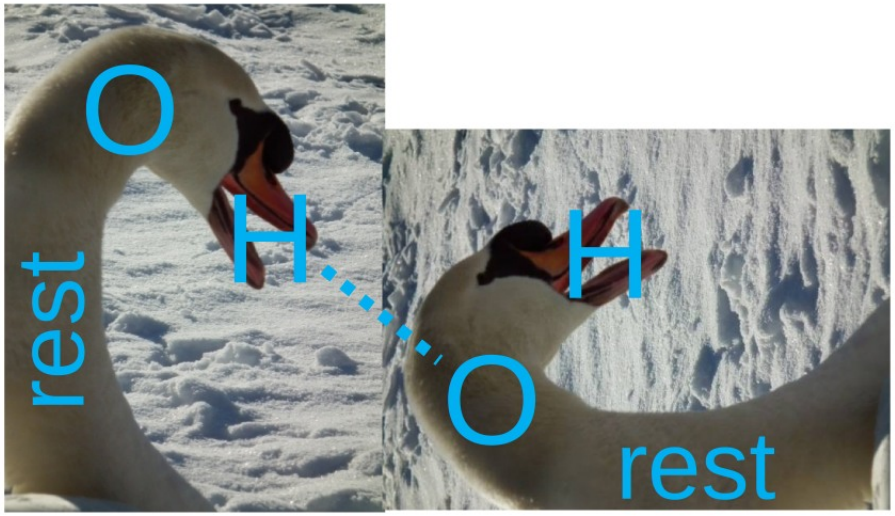
vapour-liquid equilibrium

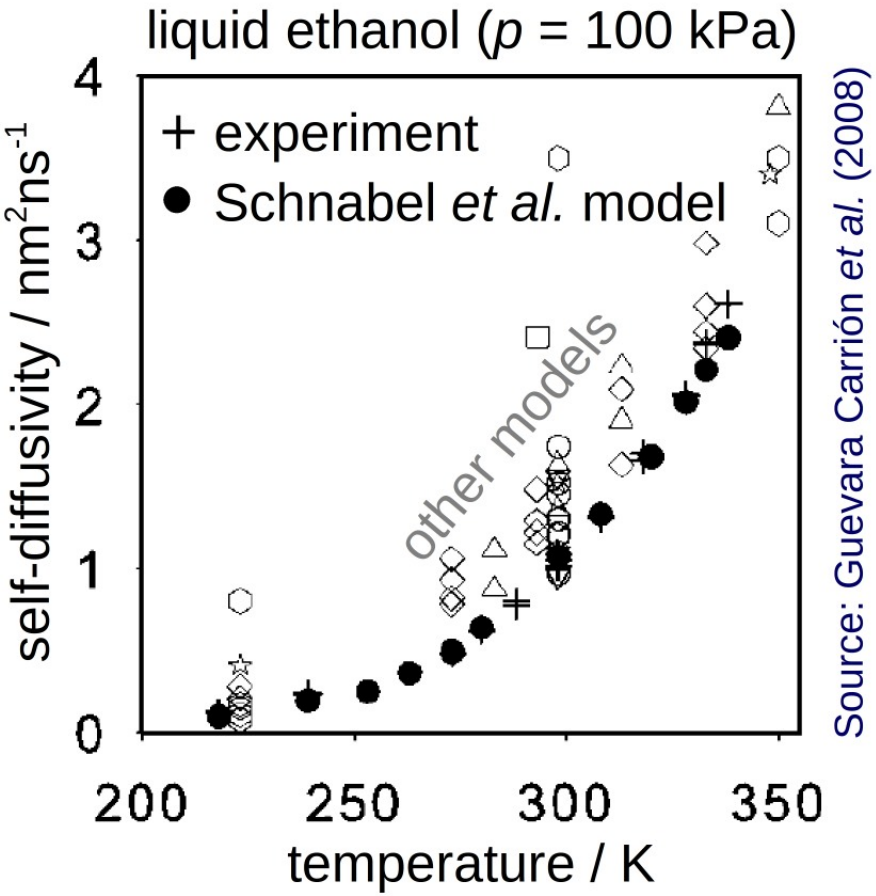


# Modelling hydrogen bonding fluids

simple “beak” approach

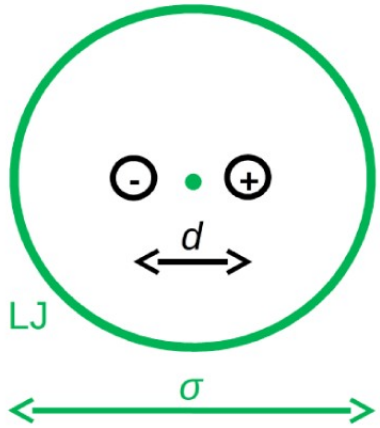


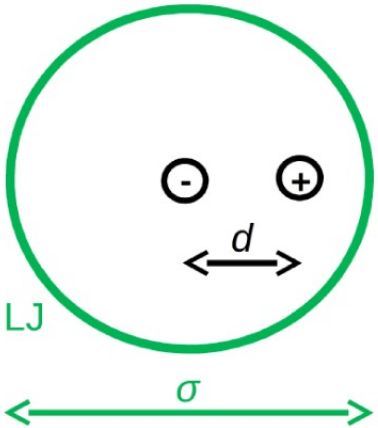



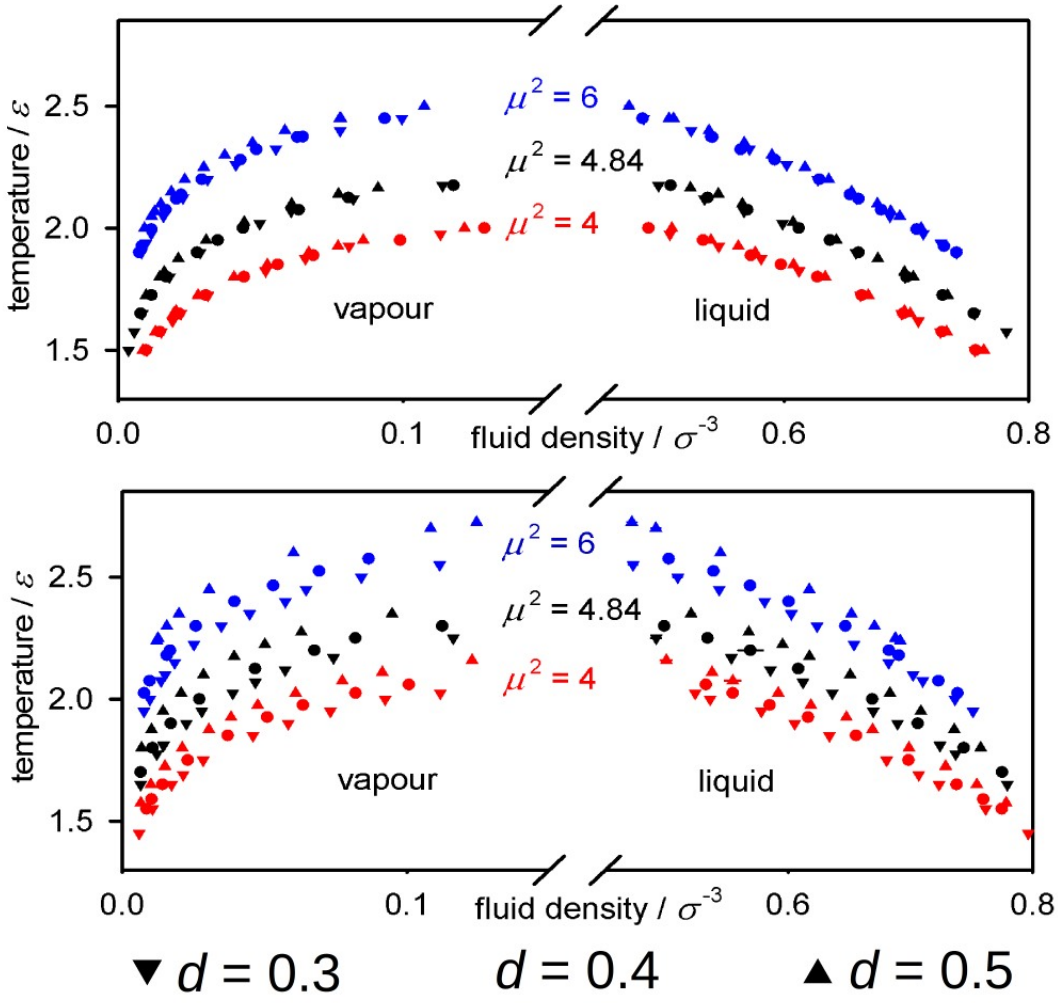

Oxygen: LJ with negative charge

Hydrogen: Positive charge (no LJ)

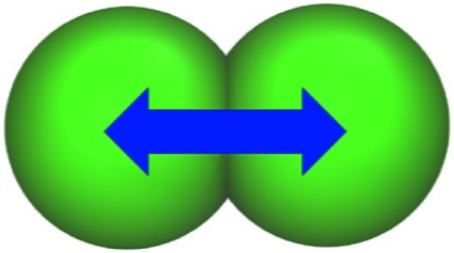
# Polarity and hydrogen bonding



# Surface tension of quadrupolar fluids



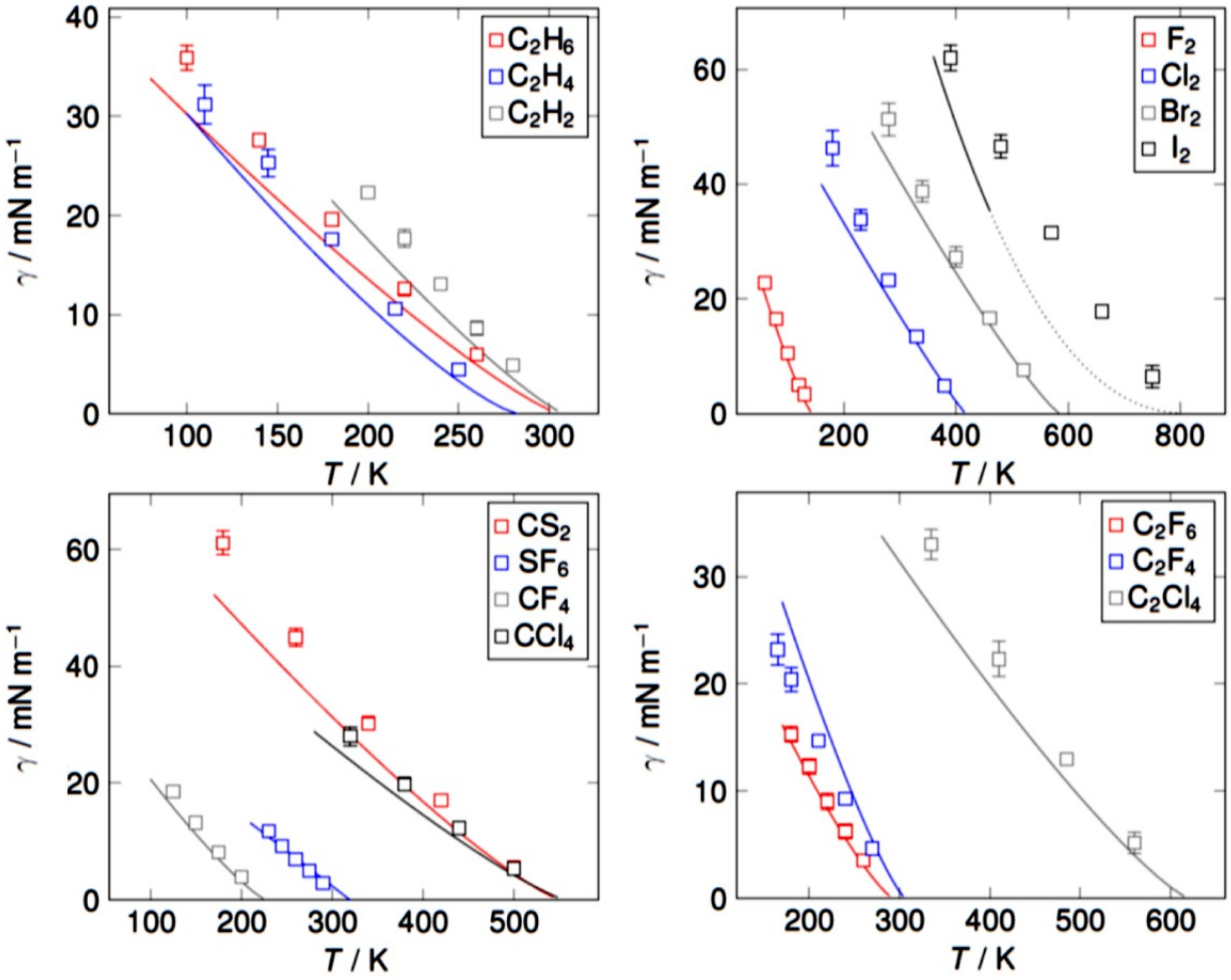
2CLJQ models:

- 2 LJ centres
- Quadrupole

Fit of parameters $\sigma$, $\varepsilon$, $L$, $Q$ to VLE data of 20 fluids by Stoll *et al.*

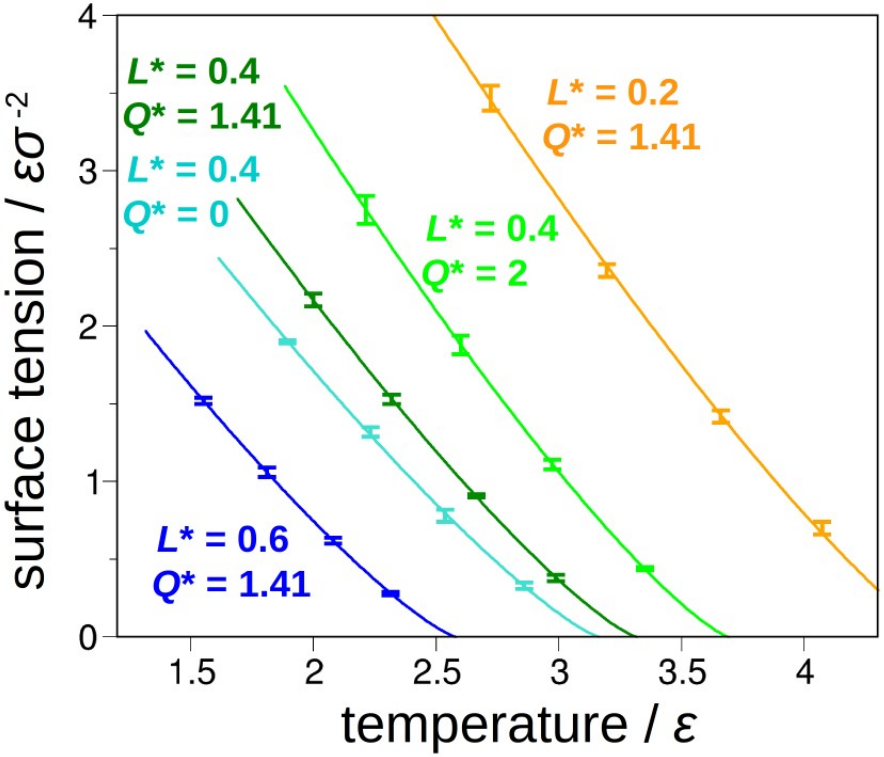
Deviation:

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

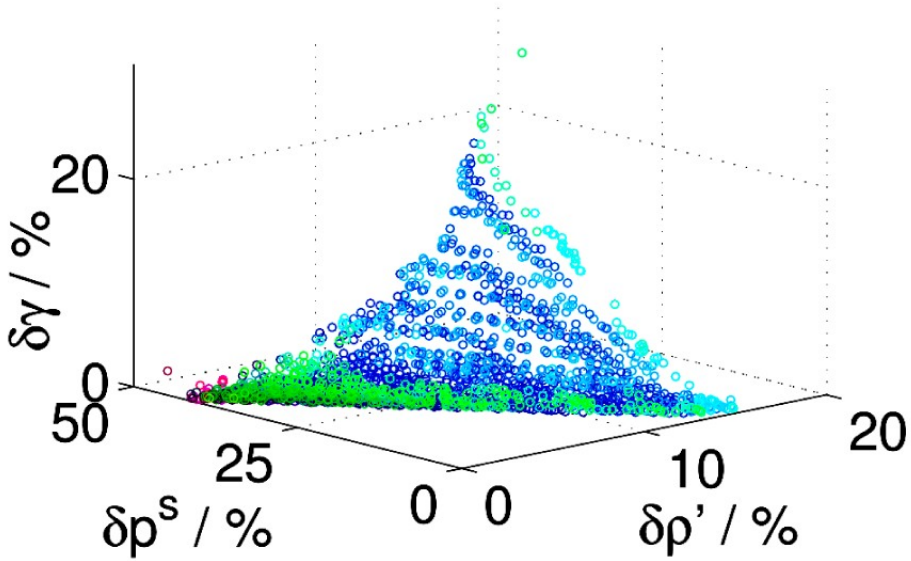


# Multi-criteria model optimization

Two-centre LJ + quadrupole



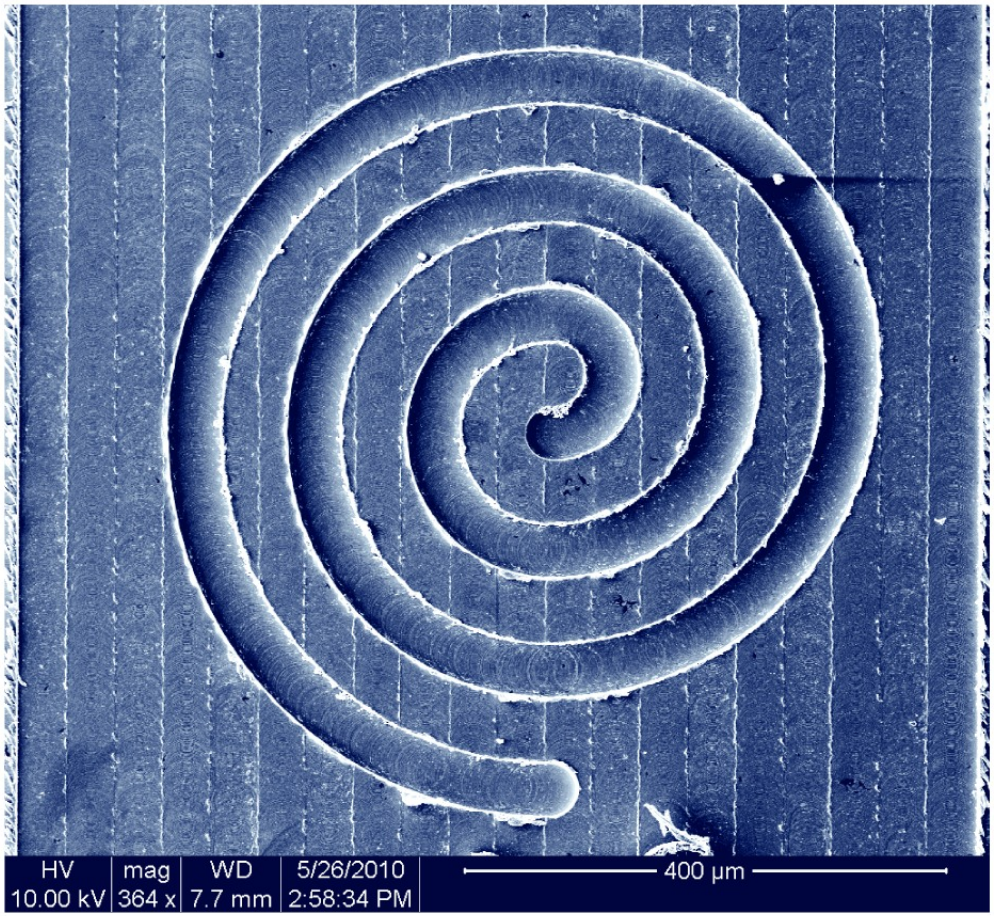

Pareto front for carbon dioxide




«Good compromises» found, e.g. decreasing $\delta\gamma$ from 20 % to 5 % ...

Correlation: Critical scaling $\gamma = A(1 - T/T_c)^{1.24}$ with two parameters.

# Adsorption at real component surfaces




**Titanium components**

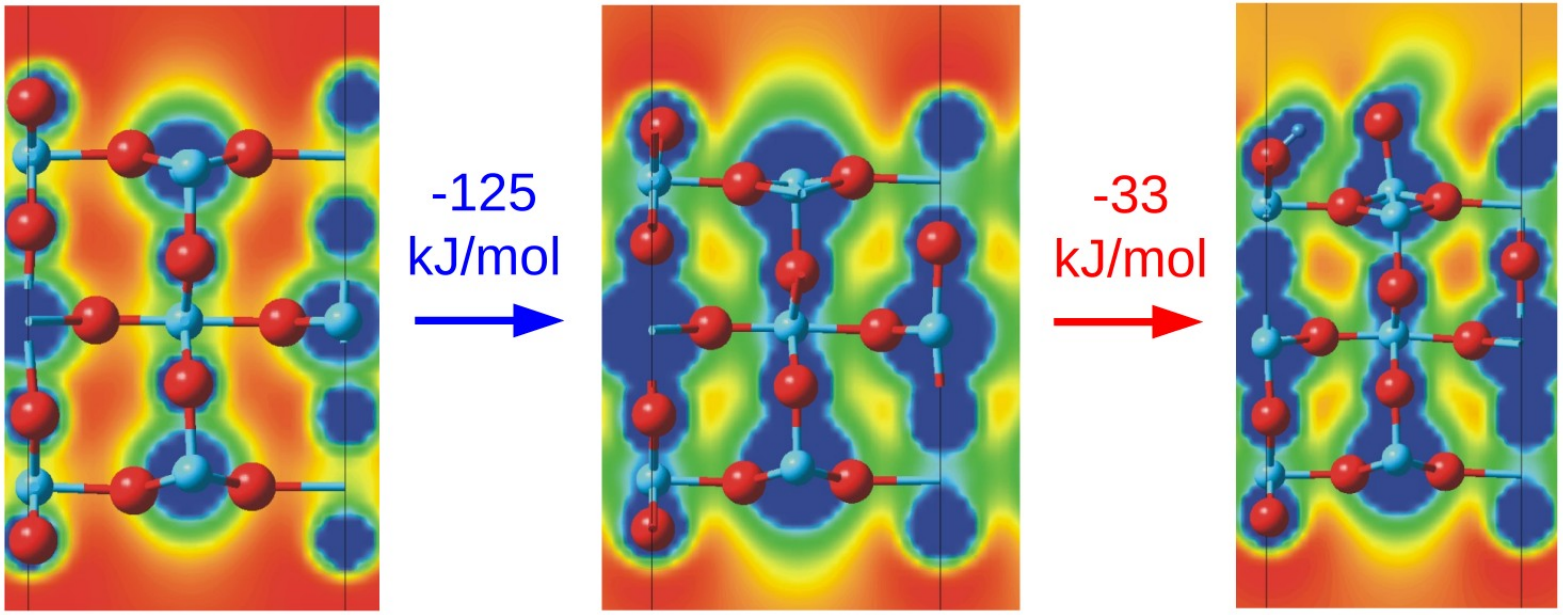
- Covered by oxide layer
- Possibly rough and/or intentionally patterned surface
- Surface may be contaminated with organic matter

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

CRC 926 MICOS Component Surfaces

# Quantum mechanical simulation

Computation of the electrostatic potential:



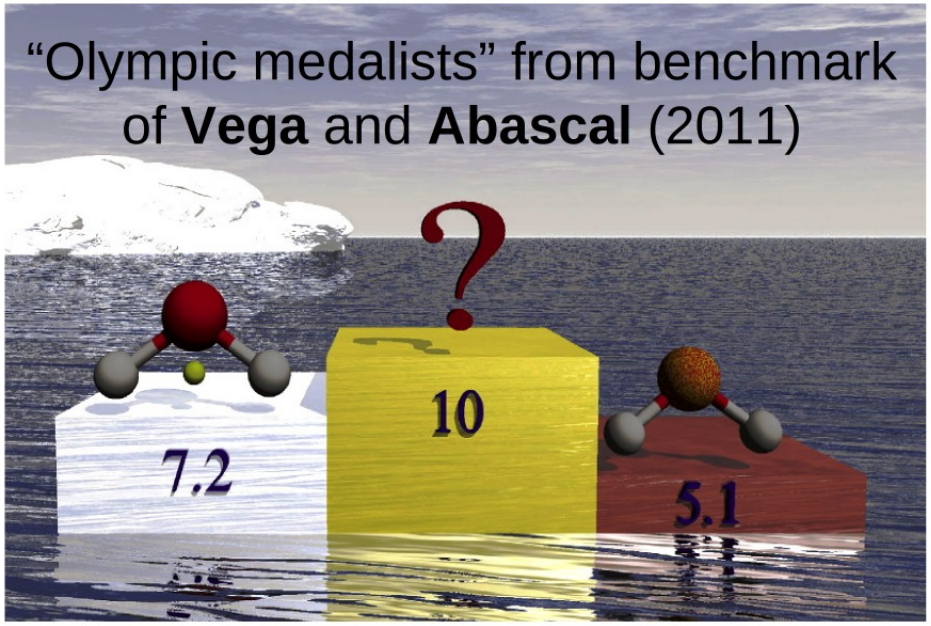

**dry rutile surface** **physisorbed water** **chemisorbed water**

VASP simulation parameters (structure optimization with PBE functional):

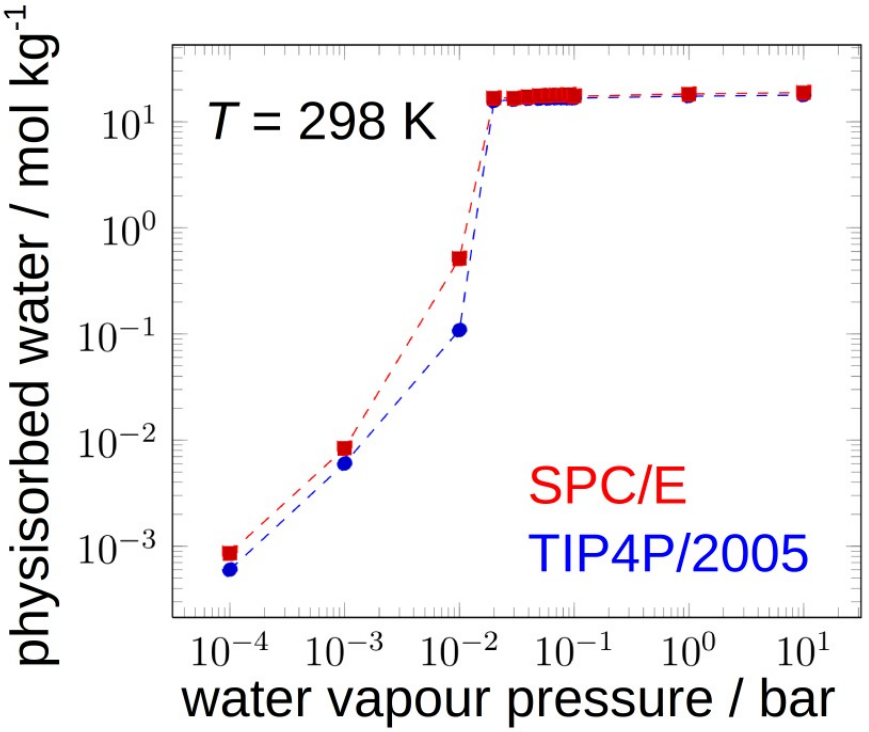
Plane-wave cutoff at 282 eV, *k*-point spacing 0.5 $Å^{-1}$, *O s* pseudopotential.

# Influence of the water model

Available water models do not capture all properties equally well.

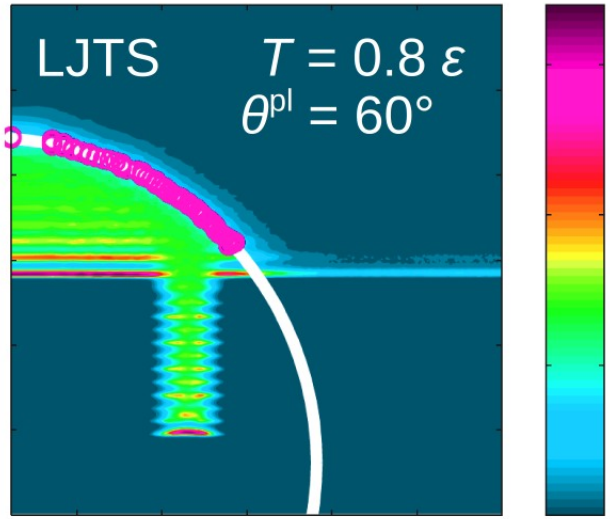



**TIP4P/2005** **SPC/E**




In the present case, the choice of the water model is relatively insignificant.

# Patterned surfaces: Wenzel state



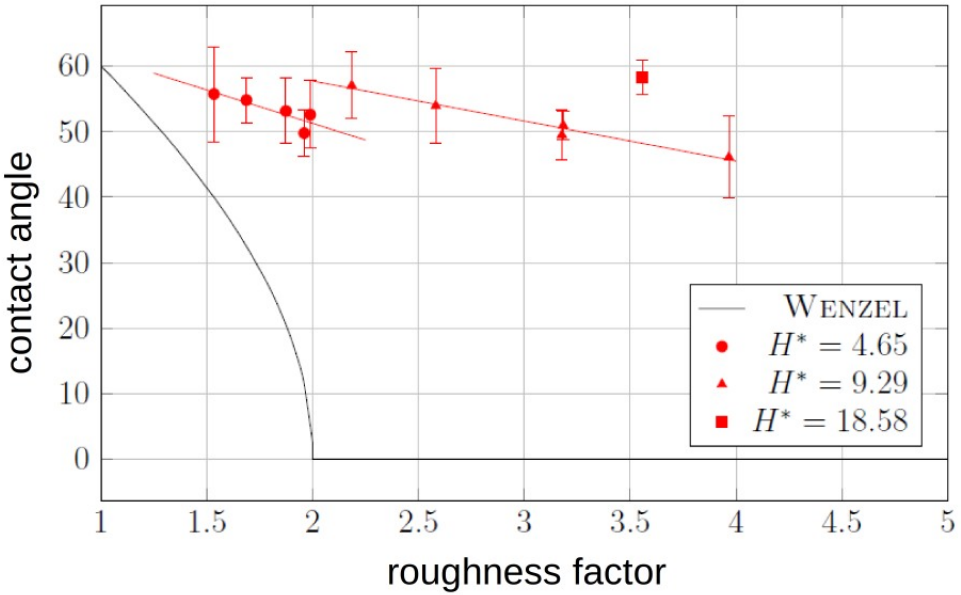

According to Wenzel, the roughness factor

$$f^{ro} = \frac{\textit{actual surface area}}{\textit{projected planar surface area}}$$

characterizes wetting of structured surfaces if the rough sites are entirely filled with liquid.

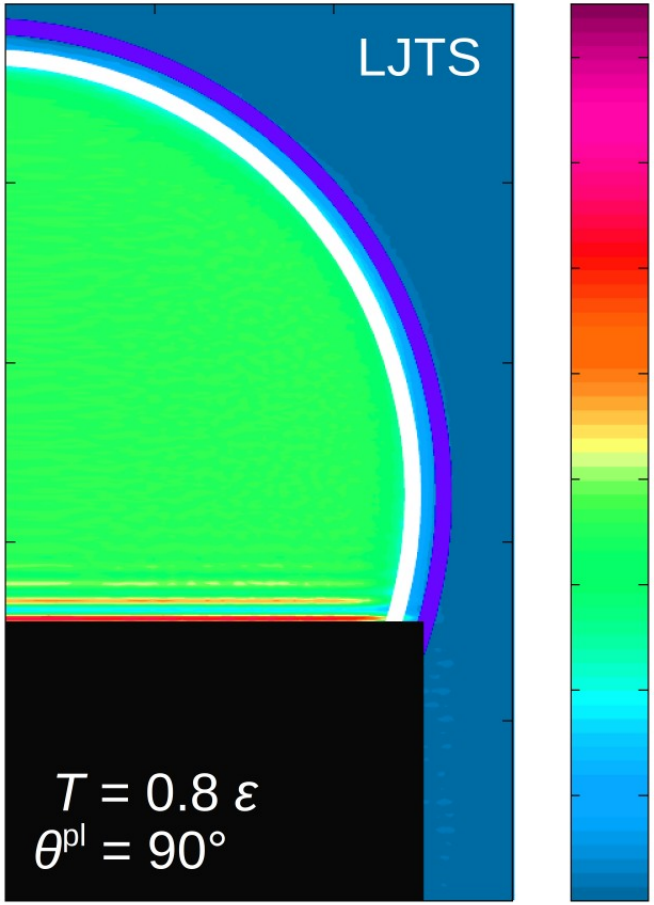
Wenzel's "law" assumes

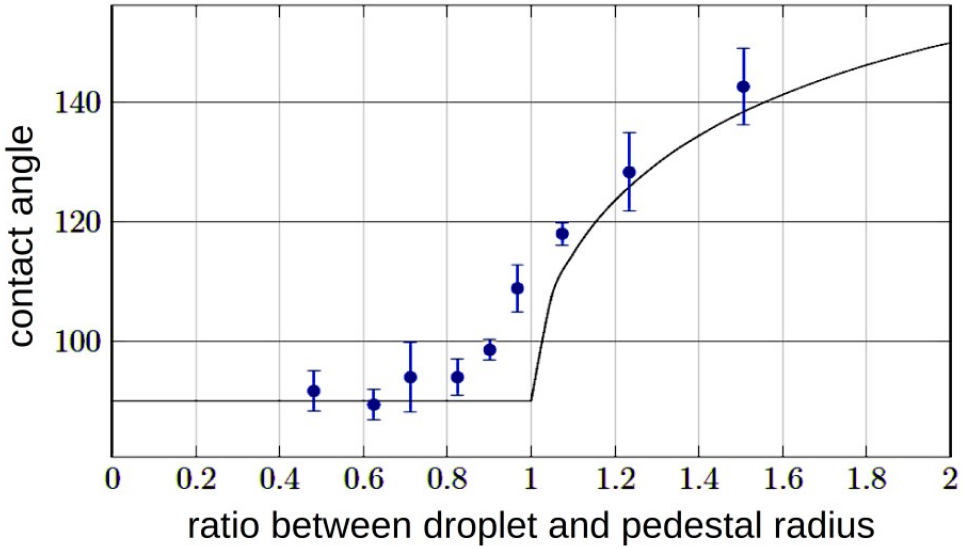
$$\cos\theta^{ro} = \frac{\gamma_{vs}^{ro} - \gamma_{ls}^{ro}}{\gamma_{vl}} = \frac{f^{ro}\left(\gamma_{vs}^{pl} - \gamma_{ls}^{pl}\right)}{\gamma_{vl}} = f^{ro}\cos\theta^{pl}.$$

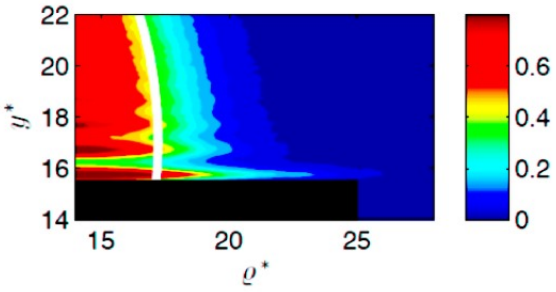


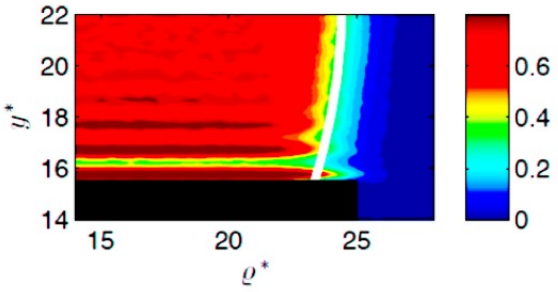
# Patterned surfaces: Contact line pinning

## Epitaxial Cassie state



# Conclusion

- Computational molecular engineering combines massively-parallel **molecular simulation** with quantitatively reliable **molecular modelling**.
- Non-equilibrium MD simulation of large systems, employing Maxwellian dæmons, yields insights on **processes at interfaces**, e.g. nucleation.
- For nanoscopic systems with interfaces, the size dependence of the **surface tension** is relevant. Beside Tolman's law for the influence of curvature, a **curvature-independent size effect** has to be considered.
- 2CLJQ models from previous work **predict the surface tension** well, with $\delta\gamma \approx 20$ %. Multi-criteria optimization can further improve them.
- Phenomena at **real component surfaces**, such as contact line pinning and characterizing adsorbed organic matter, remain challenging.