Molecular modelling and simulation of adsorption and wetting of structured surfaces

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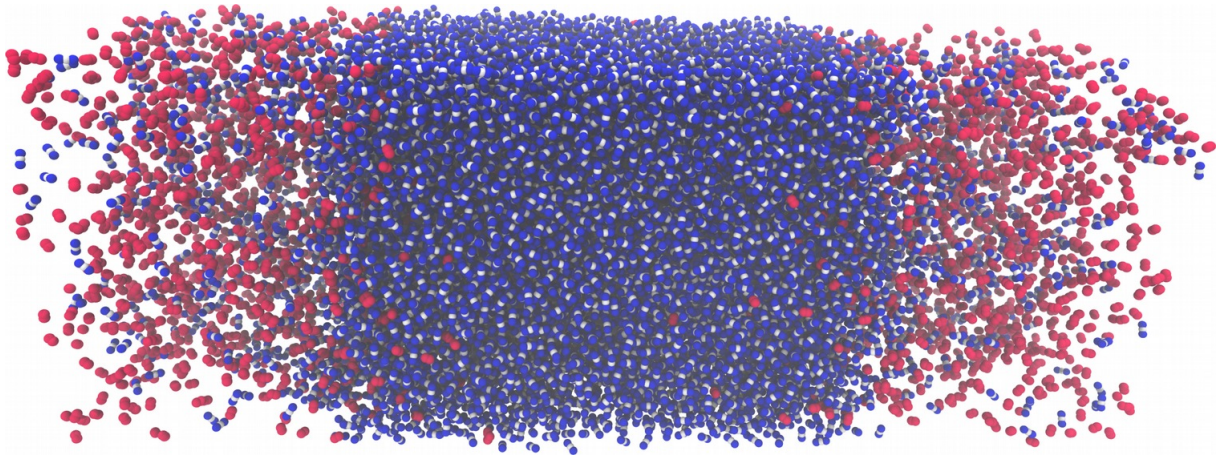
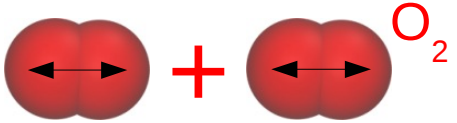
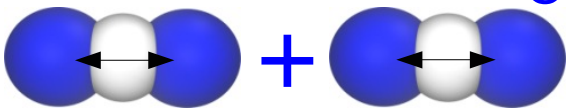
Computational Molecular Engineering

Adsorption at vapour-liquid interfaces

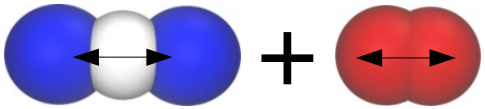




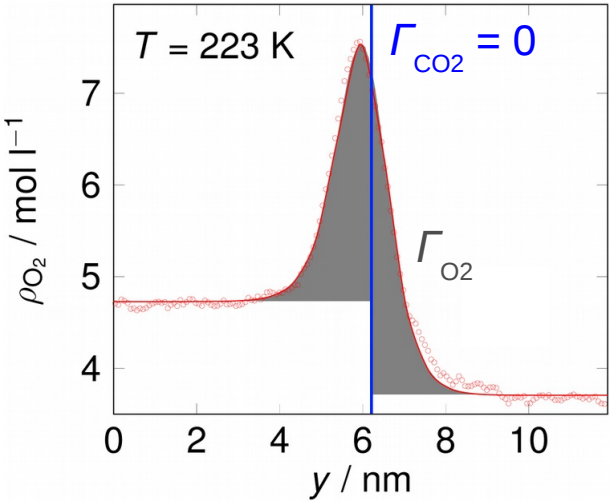
O_2 Vrabec *et al.* (2001)



CO_2 Vrabec *et al.* (2001)



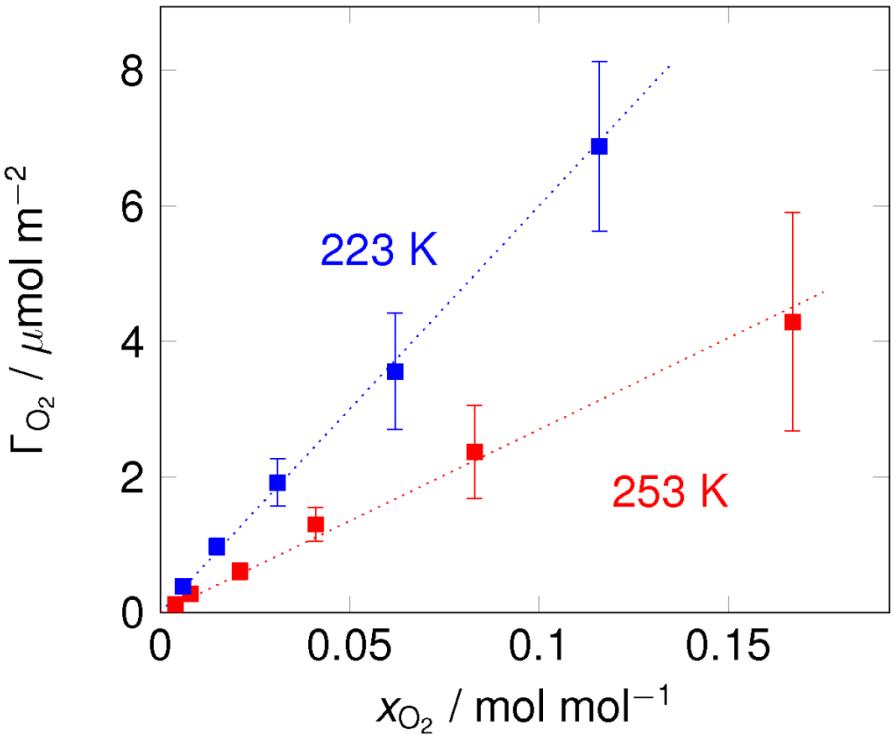
Stoll *et al.* (2003)

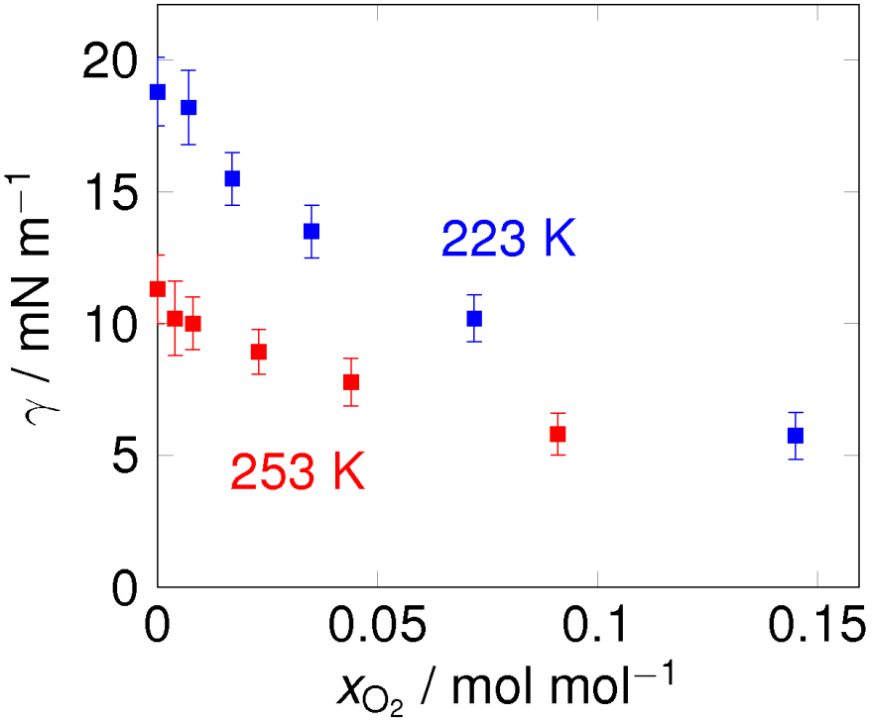


Adsorption at vapour-liquid interfaces

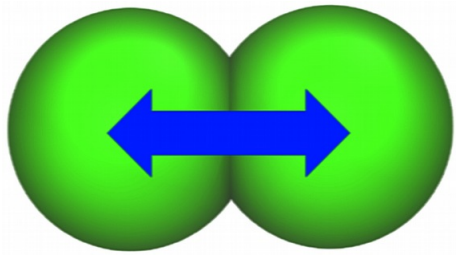
Surface tension and adsorption are related by

$$d\gamma = -\zeta\, dT - \Sigma\, \Gamma_i\, d\mu_i \quad \text{(Gibbs adsorption equation)}$$





Surface tension of real fluids



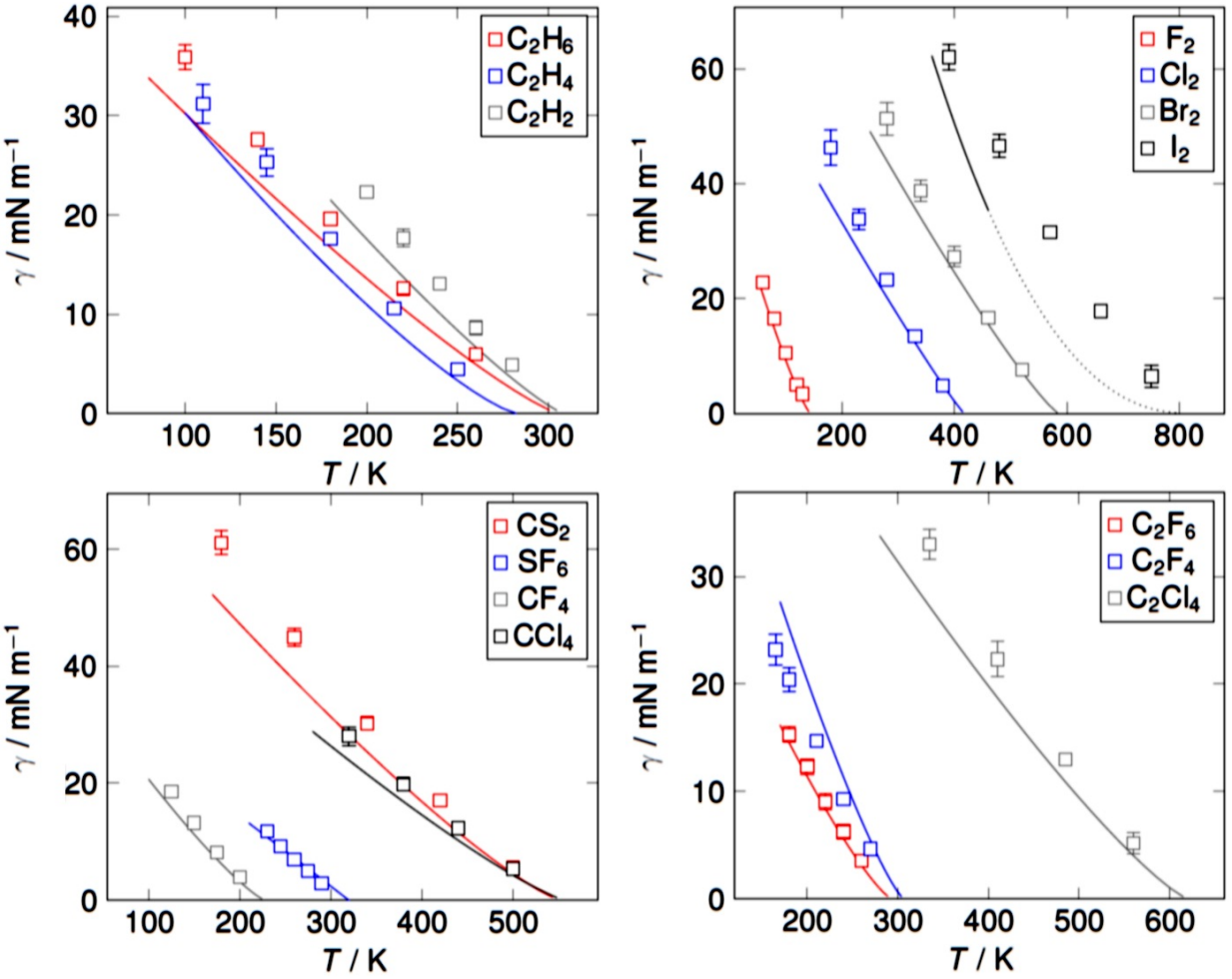
2CLJQ models:

- 2 LJ centres
- Quadrupole

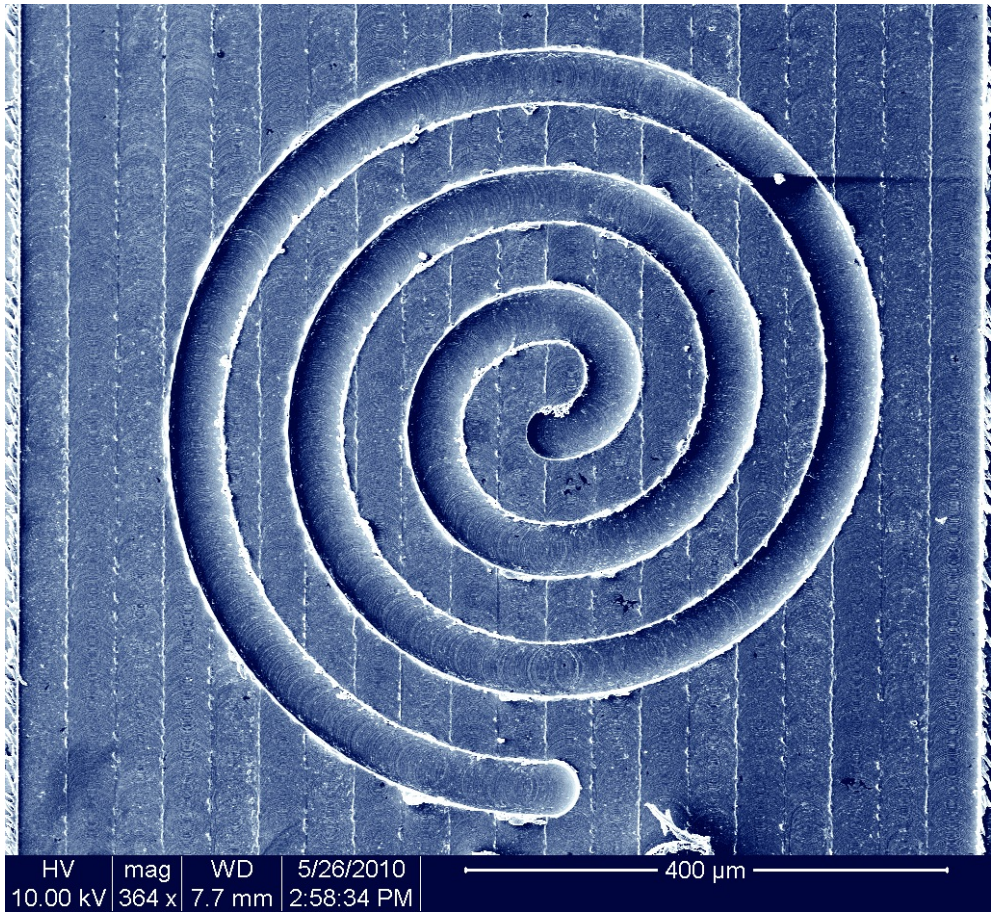
Fit of parameters σ, ε, L, Q to VLE data of 29 fluids by Stoll *et al.*

Deviation:

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



Adsorption at real component surfaces



Titanium components

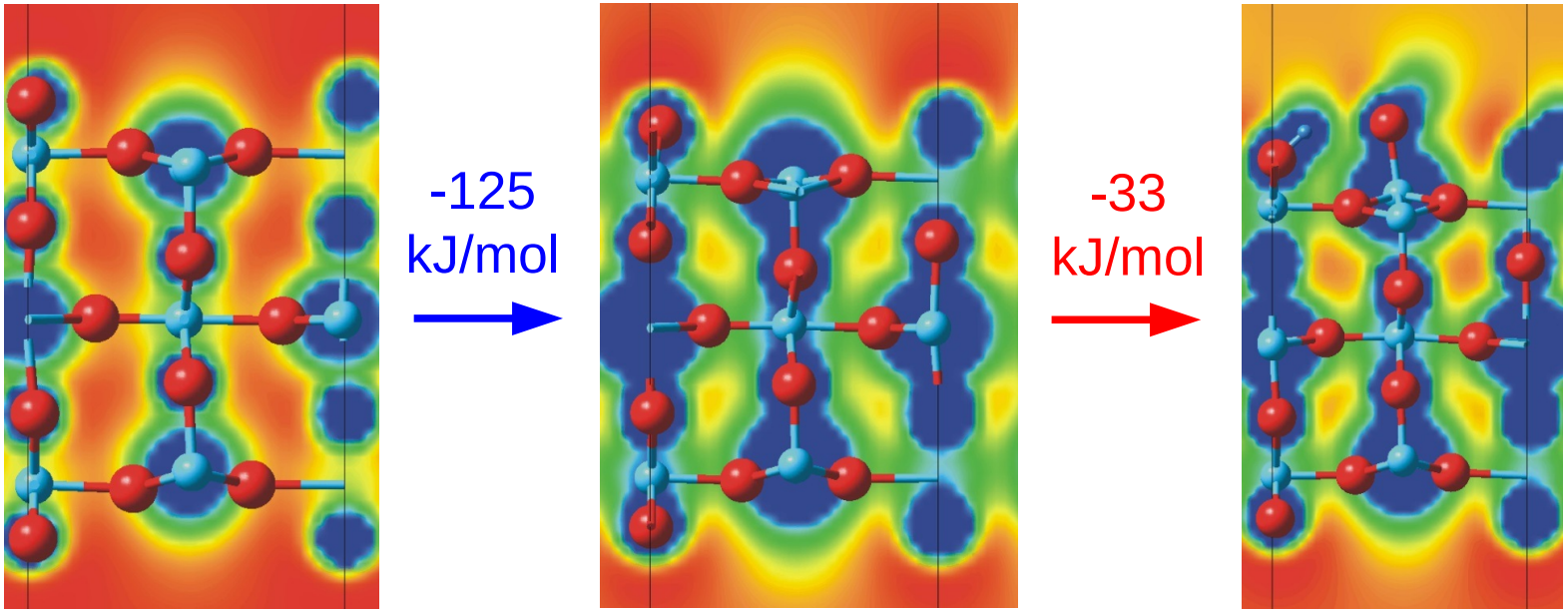
- Covered by oxide layer
- Possibly rough and/or intentionally patterned surface
- Surface may be contaminated with organic matter

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

CRC 926 MICOS Component Surfaces

Quantum mechanical calculations

Computation of the electrostatic potential:



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

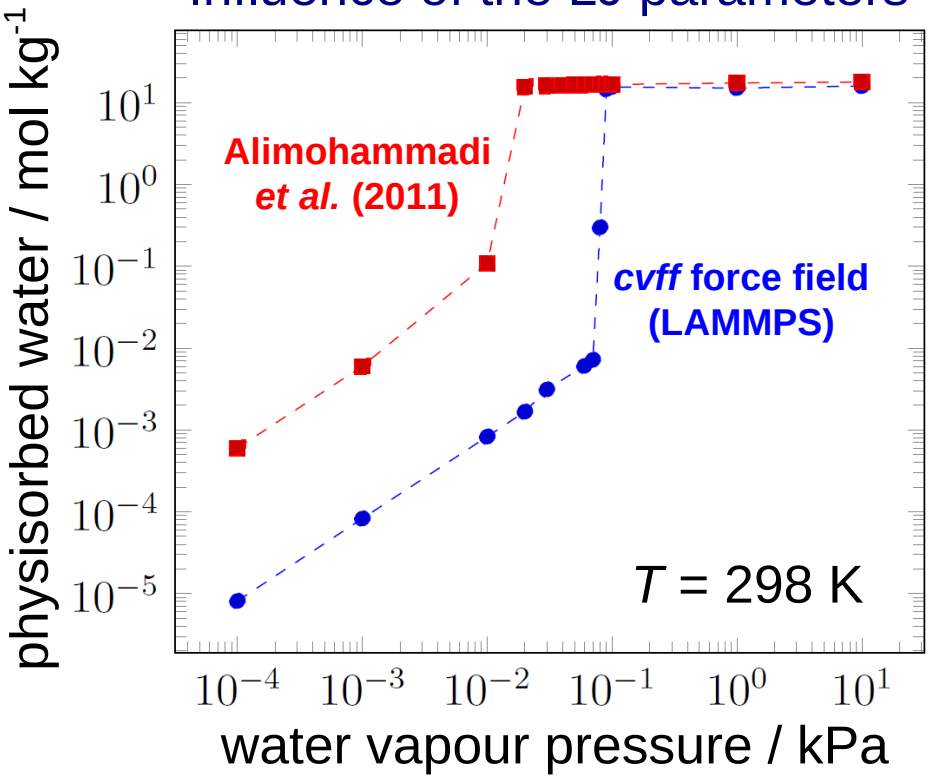
VASP simulation parameters (structure optimization with PBE functional):

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

Adsorption by grand canonical simulation

- Electrostatic grid from VASP
- Lennard-Jones parameters from literature

Influence of the LJ parameters



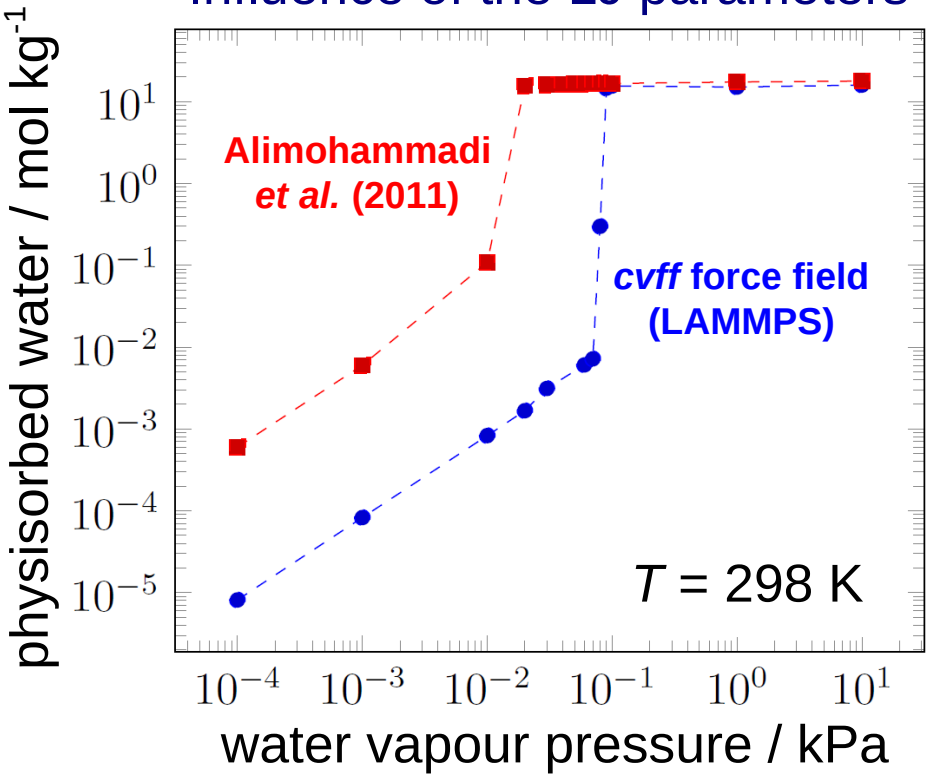
Further open issues:

- Influence of chemisorption on the electrostatic grid
- Influence of organic matter adsorbed at the surface
- Surface roughness and hysterisis effects
- Influence of the water model
- Etc. ...

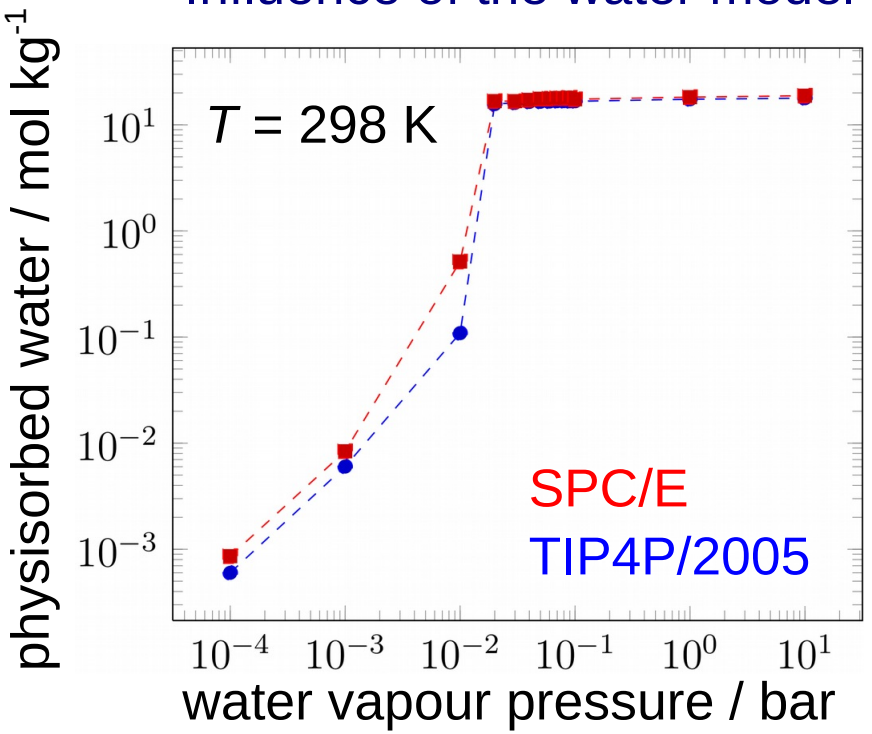
Adsorption by grand canonical simulation

The fluid-solid interaction has a greater impact than the pure fluid model.

Influence of the LJ parameters

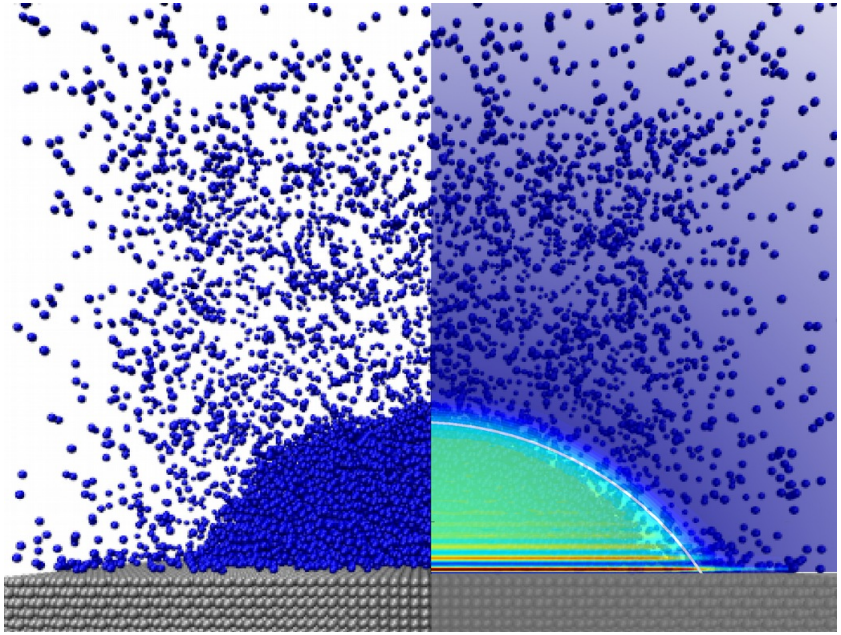


Influence of the water model



Sessile droplet on a planar surface

LJTS fluid (with σ and ε) on a planar LJTS substrate (with $\varepsilon_s = 100\ \varepsilon$):



Correlation of the density profile by

$$\rho(R, y) = f(R) \cdot [h(y) + 1],$$

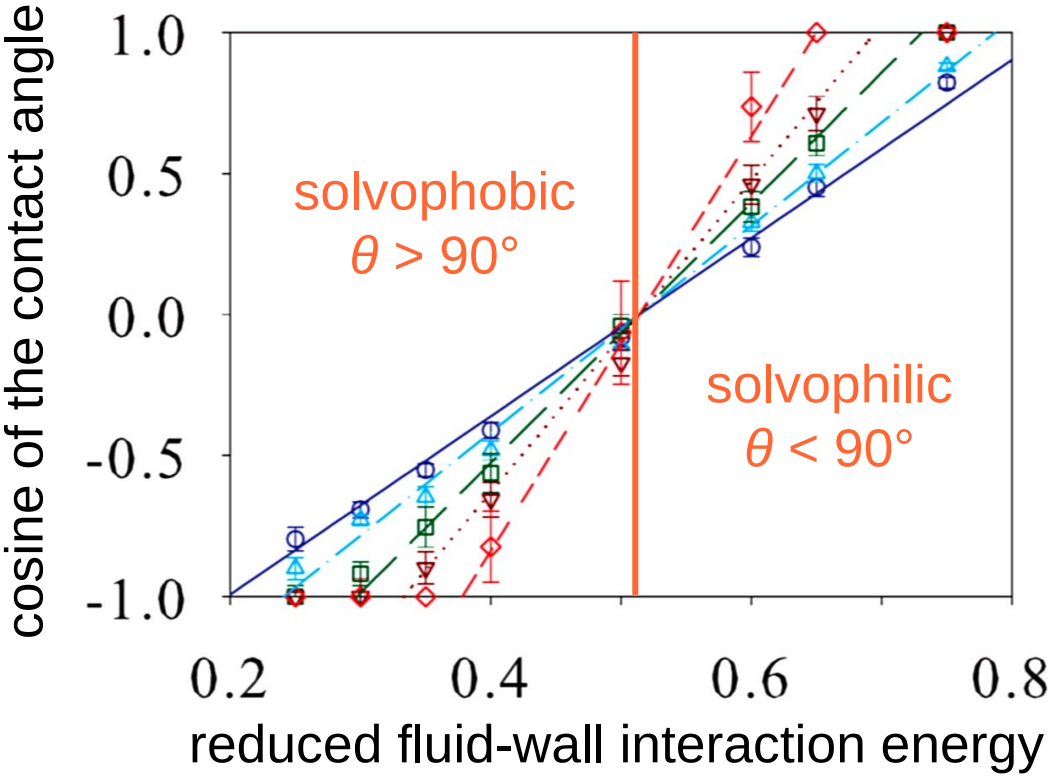
with exponentially decaying oscillations of $h(y)$, in terms of the distance y from the wall,

and a tanh type profile $f(R)$ over the distance R from the droplet centre.

The fluid-solid contact angle is determined at the intersection of the wall surface with the vapour-liquid interface given by the correlation expression.

Influence of the fluid-wall interaction

Variation of the ζ parameter (unlike interaction) on a substrate with $\sigma_s = \sigma$:



$T = 0.7\ \varepsilon$

$T = 0.8\ \varepsilon$

$T = 0.9\ \varepsilon$

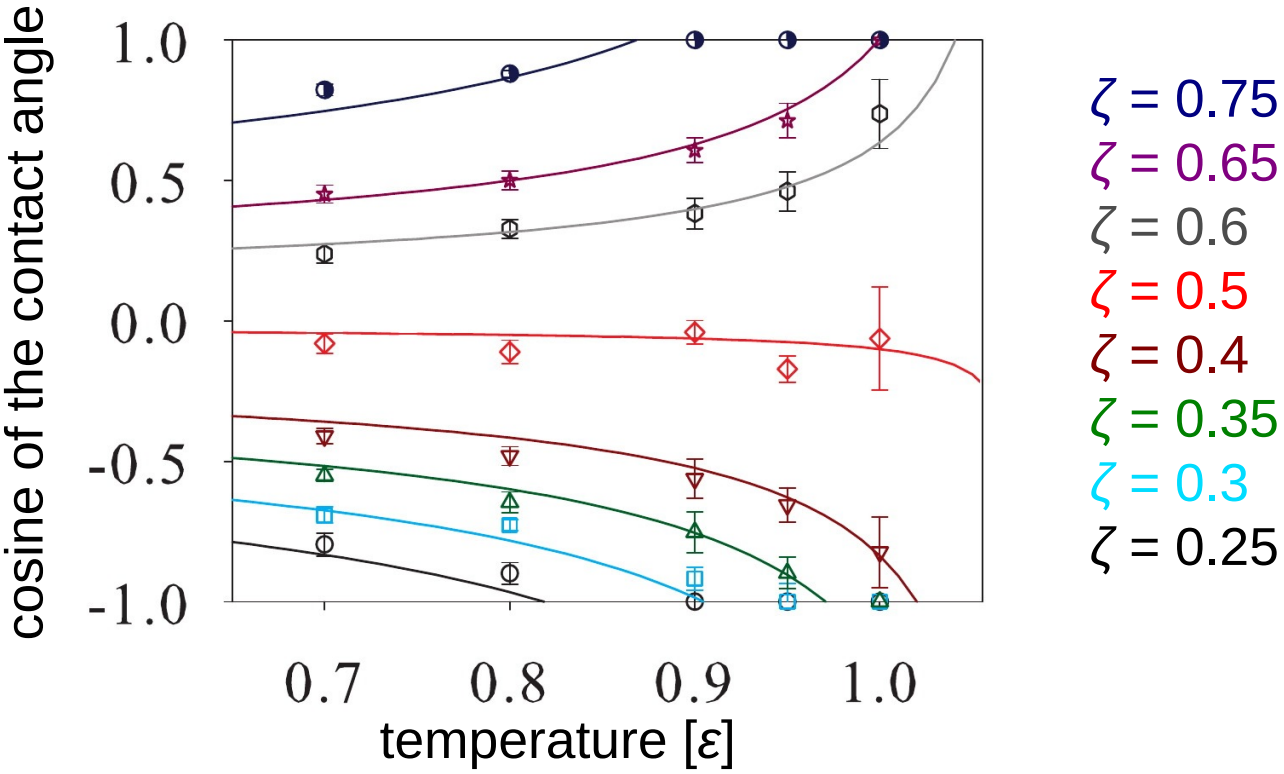
$T = 0.95\ \varepsilon$

$T = 1.0\ \varepsilon$

The transition from solvophilic to solvophobic surfaces is independent of T.

Critical wetting transition

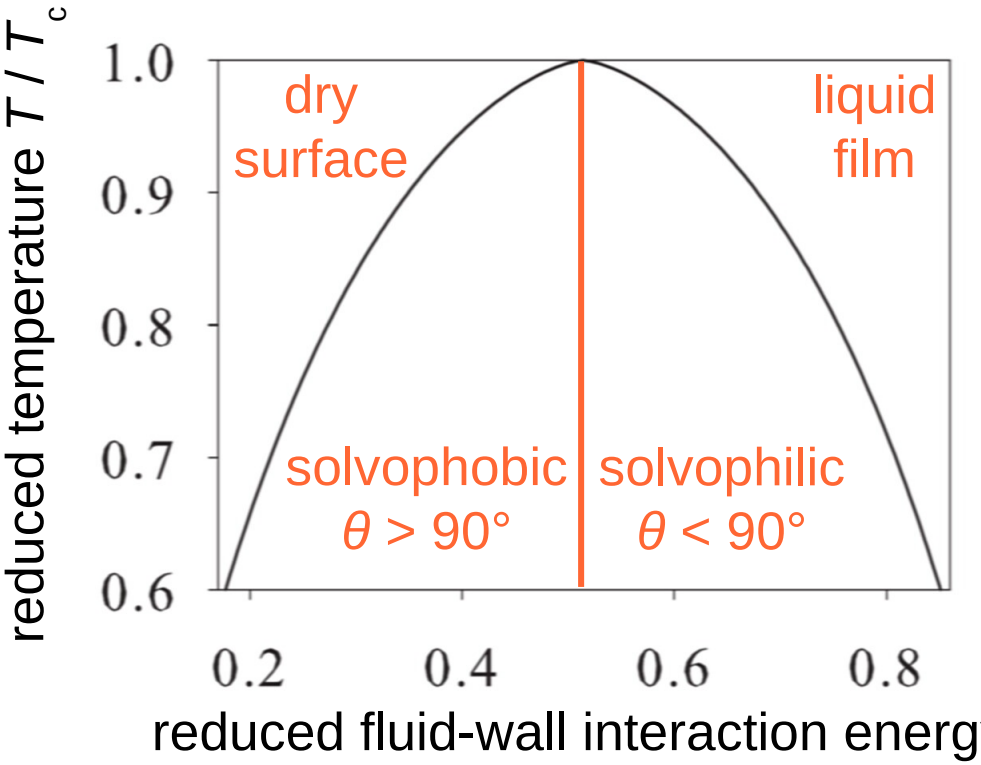
At high temperatures, critical wetting or dewetting is observed ($\sigma_s = \sigma$):



Correlation: $\cos\theta$ proportional to $(1 - T/T_c)^{-2/3} + 1$ as well as $\zeta - \zeta_\perp$.

Critical wetting transition

At high temperatures, critical wetting or dewetting is observed:

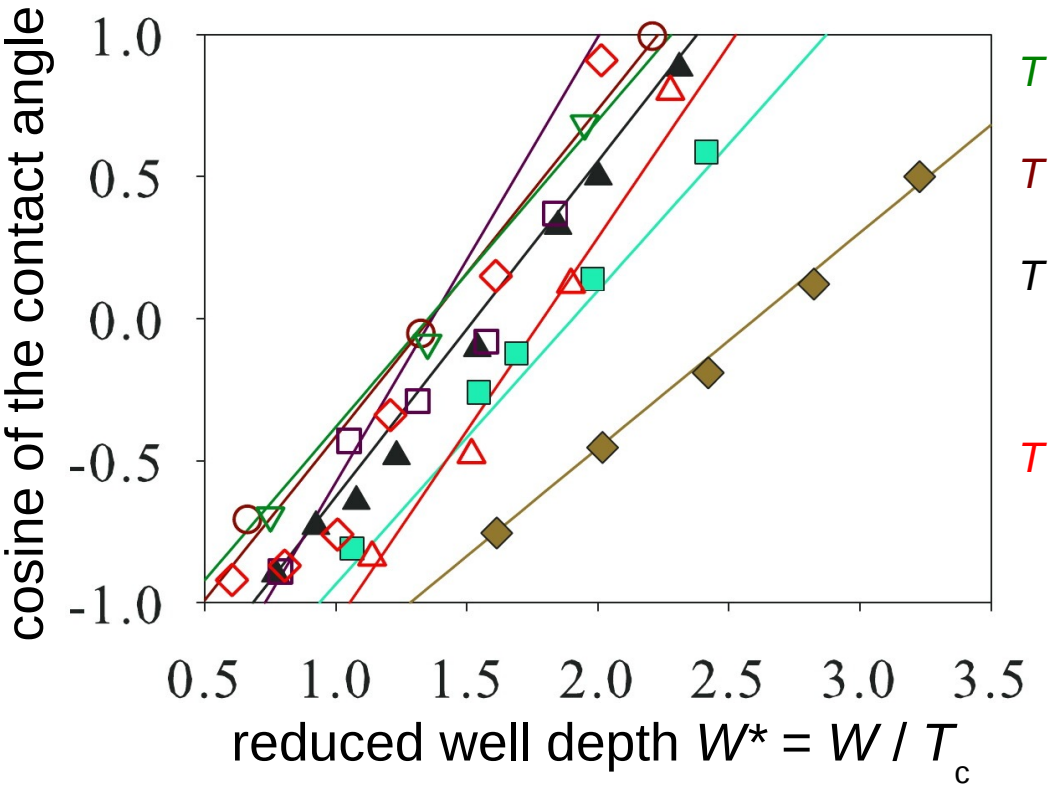


wall with $\sigma_s = \sigma$

Correlation: $\cos\theta$ proportional to $(1 - T/T_c)^{-2/3} + 1$ as well as $\zeta - \zeta_\perp$.

Influence of the substrate model

Wall model and fluid-wall interaction influence the interaction well depth W.



T = 0.7 ε, Grzelak *et al.* (2010)

T = 0.75 ε, Ingebrigtsen and Toxværd (2007)

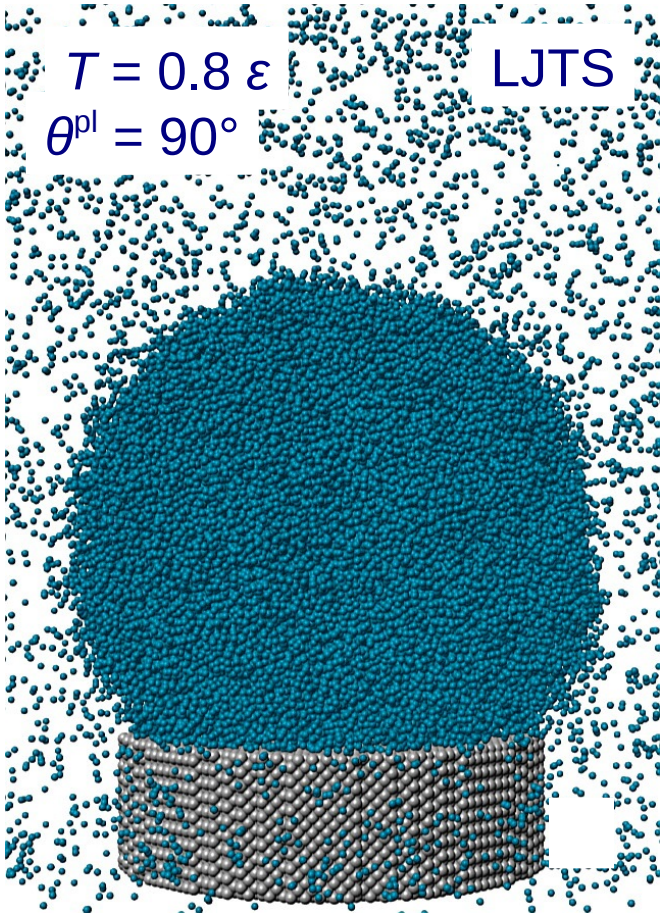
T = 0.8 ε, present work (▲) with $\sigma_s = \sigma$,
(■) with σ_s = 0.8 σ, (♦) with σ_s = 0.64 σ

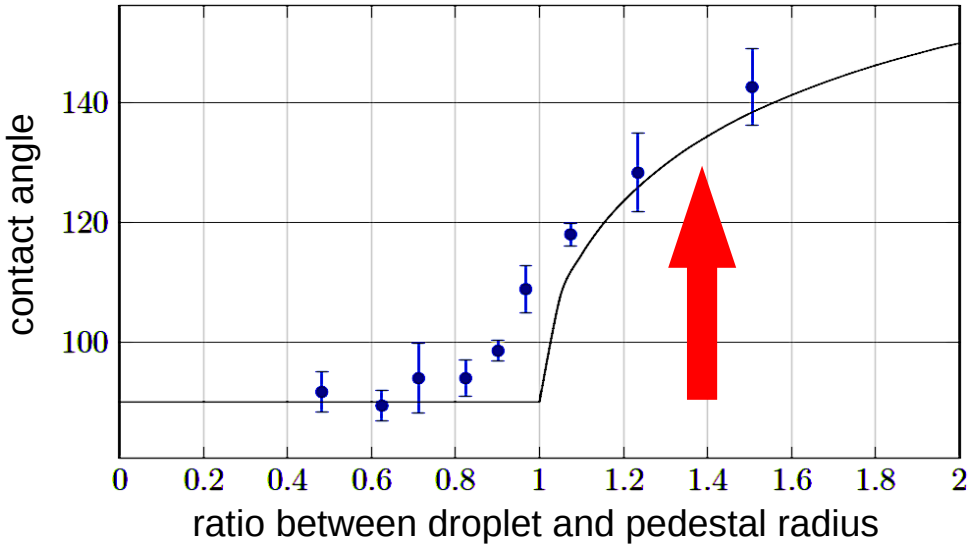
T = 0.9 ε, (Δ) Nijmeijer *et al.* (1990),
(◊) Nijmeijer *et al.* (1992),
and (□) Tang and Harris (1995)

Lines: General correlation $\theta(T^*, W^*, \rho)$ for contact angles of LJ systems.

Patterned surfaces: Epitaxial Cassie state

Epitaxial Cassie state

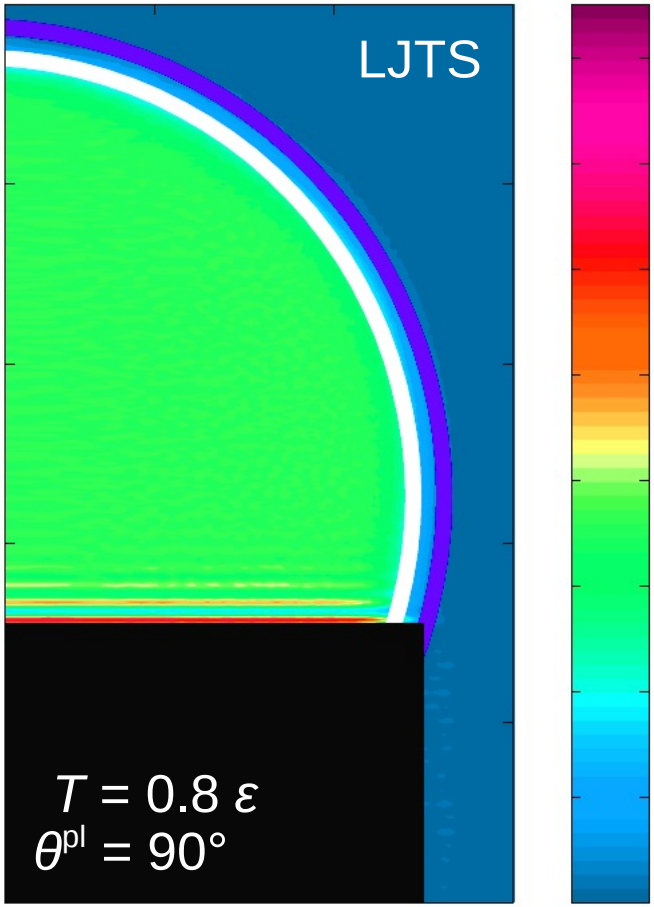


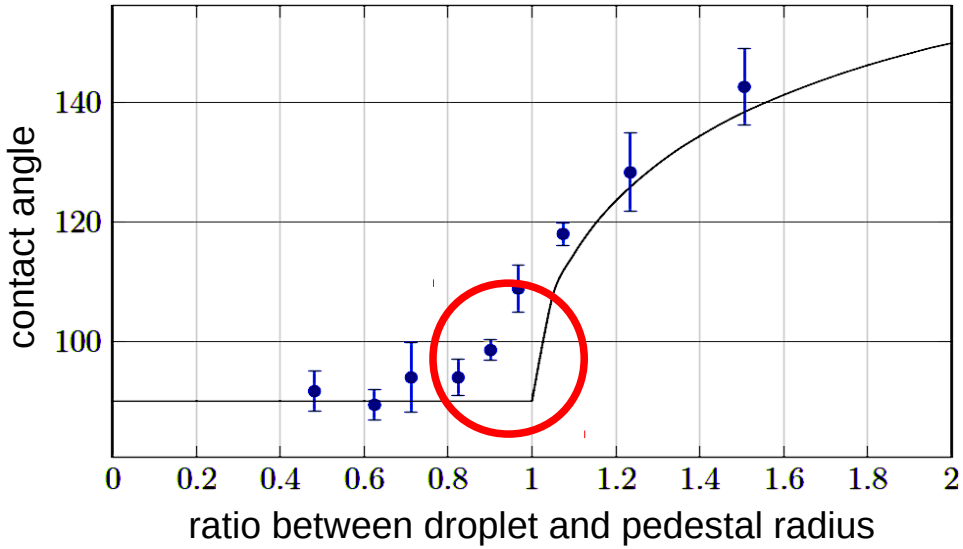


Due to contact line pinning, the contact angle at an edge may significantly exceed the value corresponding to a perfectly planar surface.

Patterned surfaces: Epitaxial Cassie state

Epitaxial Cassie state

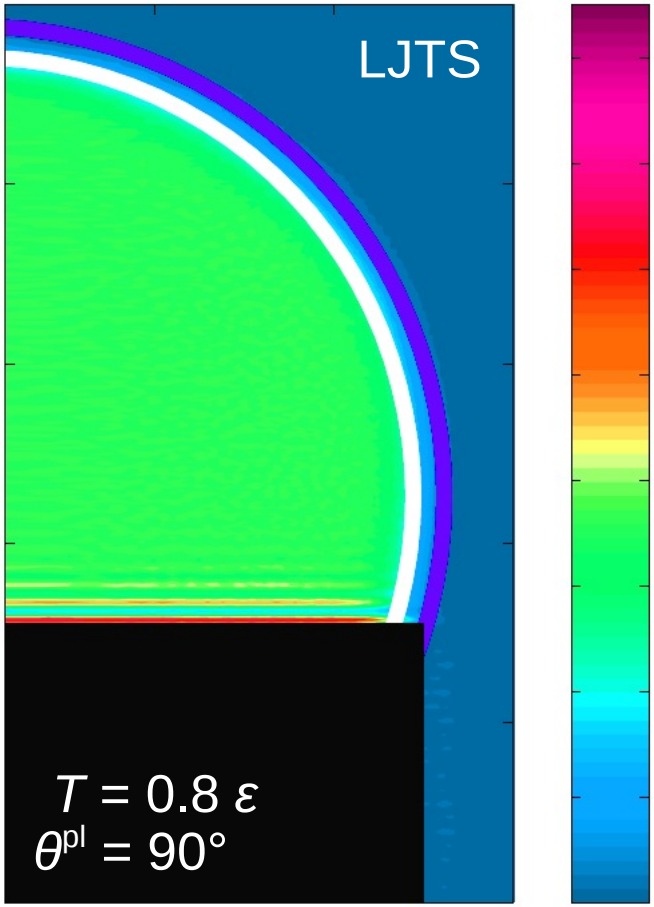


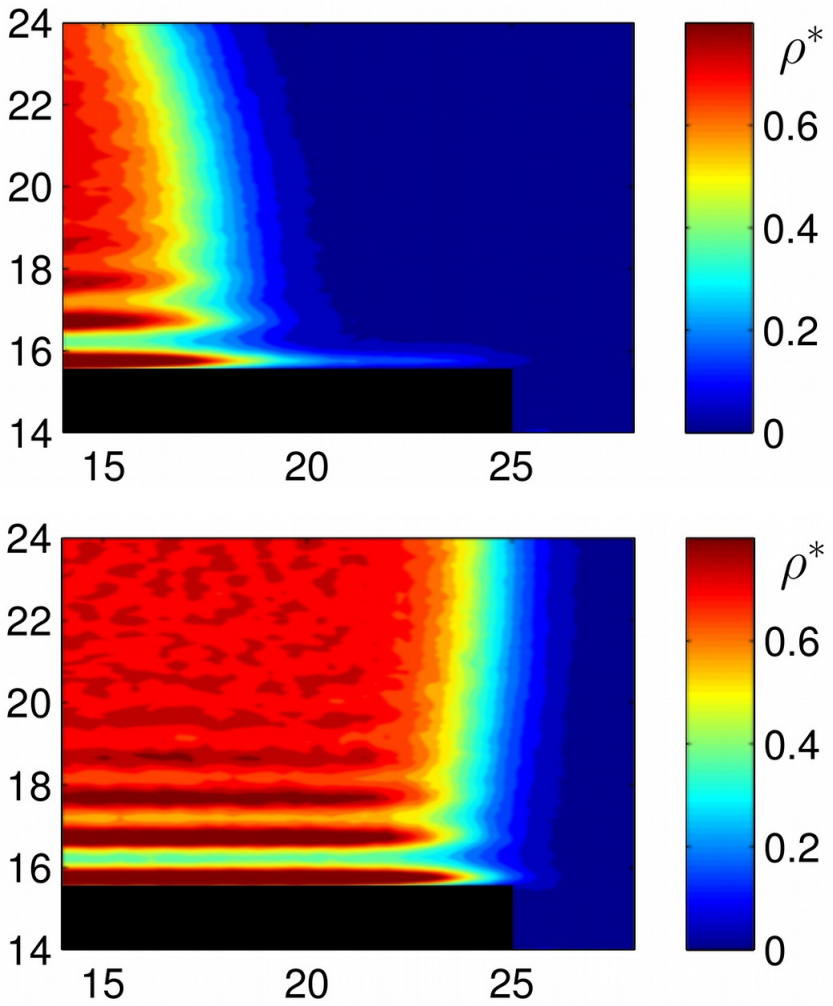


Line pinning does not occur exactly at the edge. The contact line is shifted inward due to the presence of a precursor layer.

Patterned surfaces: Epitaxial Cassie state

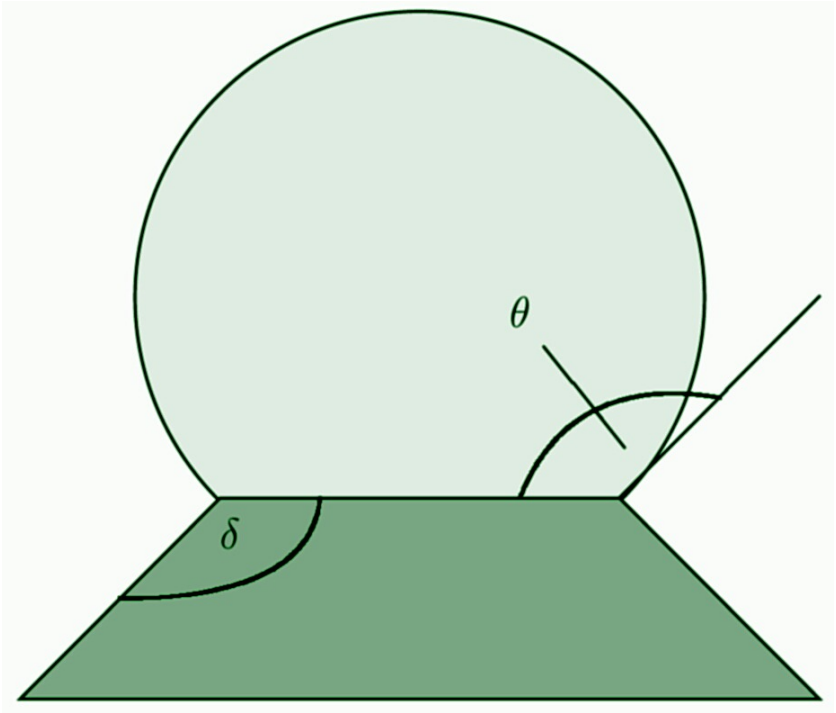
Epitaxial Cassie state





Contact line pinning: Gibbs inequality

Phenomenologically, the range of contact angles that are mechanically stable in the epitaxial Cassie state is given by the Gibbs inequality



$$\theta^{pl} \leq \theta \leq 180° - \delta + \theta^{pl}$$

(with $\theta \leq 180°$).

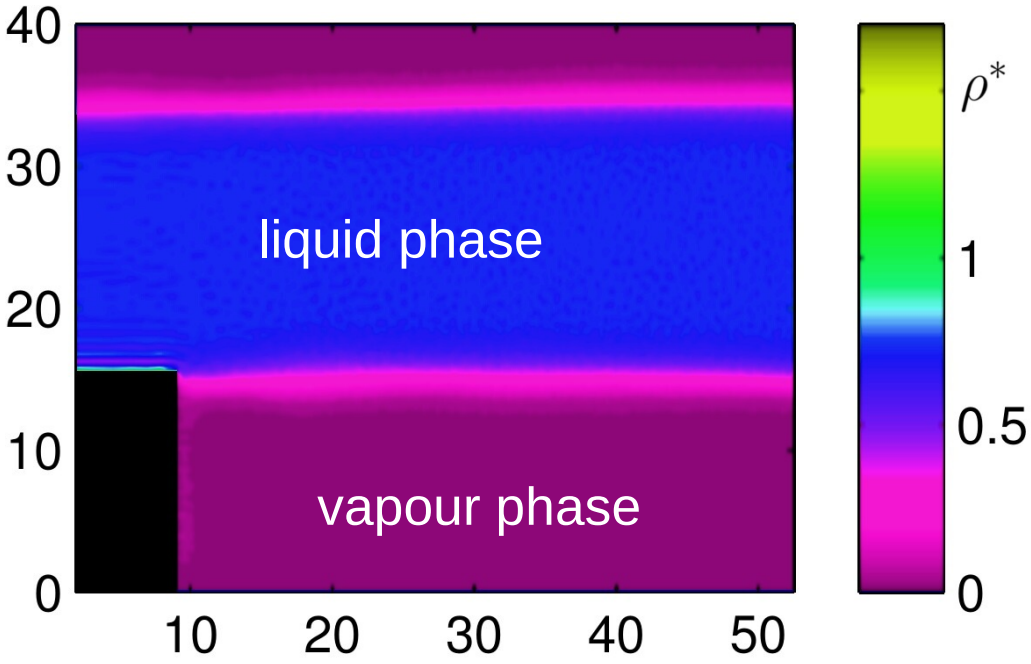
At constant pedestal radius,

- droplet radius R increases with θ,
- R becomes infinite for $\theta \rightarrow 180°$.

To check the Gibbs inequality, the simulation setup has to be altered.

Contact line pinning: Gibbs inequality

Case with $\theta^{max} = 180°$



LJTS potential

$T = 0.8\,\varepsilon$ and $\zeta = 0.4$

$\theta^{pl} = 118°$ and $\delta = 90°$

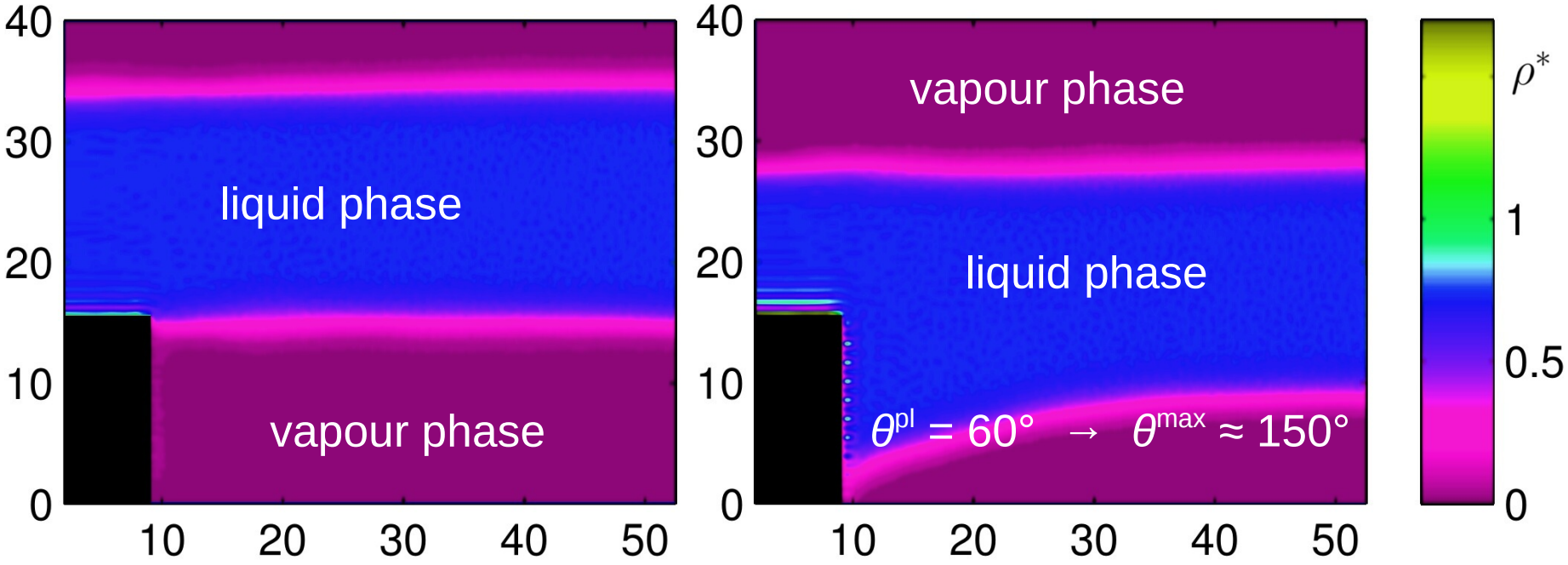
$\theta^{max} \approx 180°$

Present simulation results are in agreement with the Gibbs inequality.

Contact line pinning: Gibbs inequality

Case with $\theta^{max} = 180°$

Case with $\theta^{max} < 180°$



Present simulation results are in agreement with the Gibbs inequality.

Conclusion

- Molecular models for quadrupolar fluids **predict the surface tension** with an average relative deviation of about 20 % from experimental data.
- Even simple molecular fluids can exhibit a significant **surface enrichment**, related to the dependence of the surface tension on composition.
- The fluid-solid **contact angle** was determined and correlated for Lennard-Jones systems in dependence of the substrate density and the fluid-solid interaction well depth.
- Contact **line pinning** at an edge (epitaxial Cassie state) was simulated.