Molecular modelling of adsorption on real component surfaces

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TU Kaiserslautern and Materials Design

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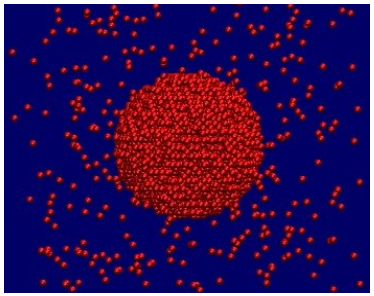
MedeA Users Group Meeting

Computational Molecular Engineering

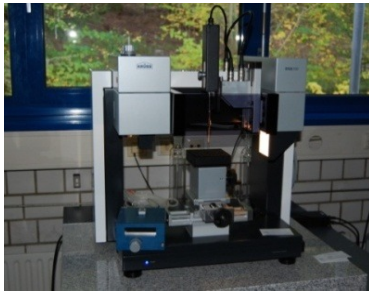
Collaborative Research Centre (SFB) 926

CRC 926 MICOS Component Surfaces

"Microscale Morphology of Component Surfaces (MICOS)"

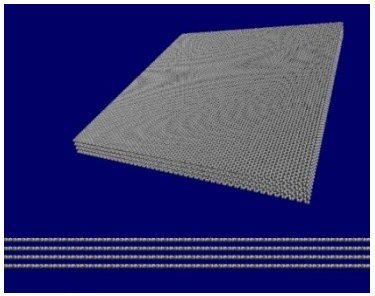


fluid model

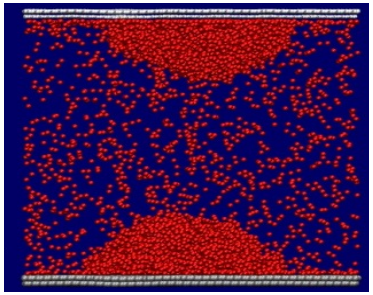


experiment

Morphology-property relations (MEB)
Surface-generation morphology-property relations (OMEB)

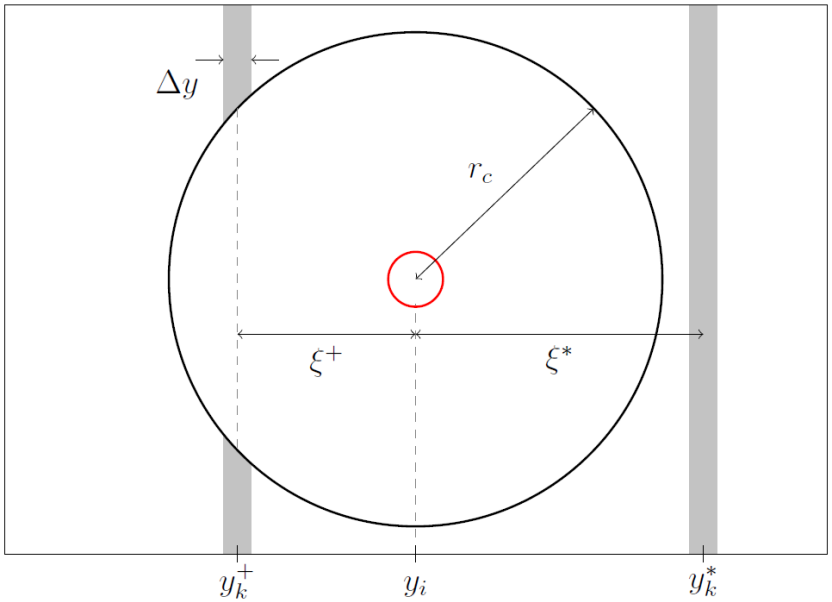


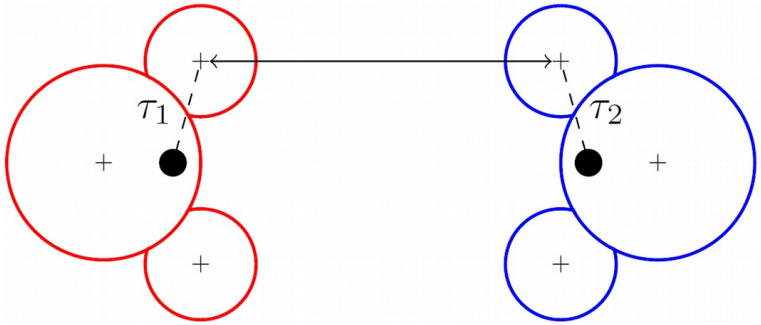
wall model

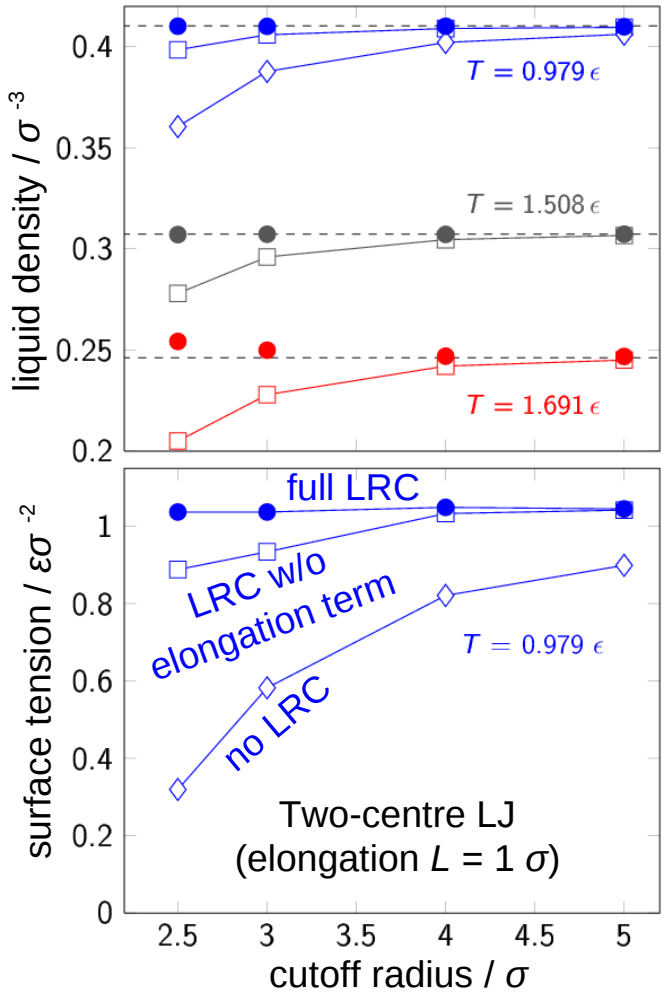


fluid-wall interaction model

Long-range correction for planar interfaces

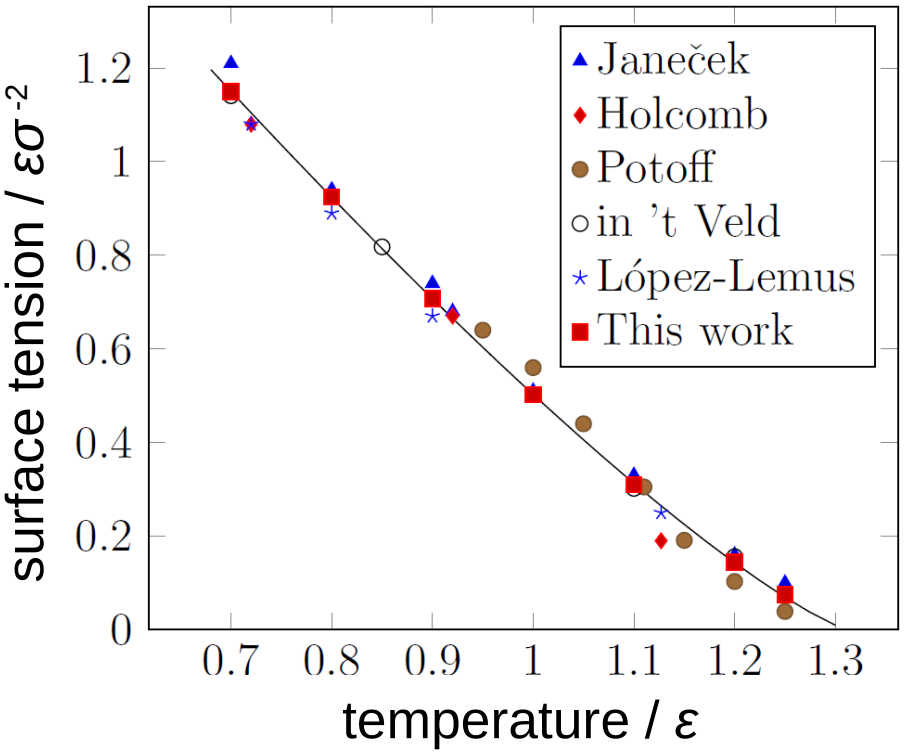






Surface tension of planar interfaces

Lennard-Jones fluid



Correlation: Universal critical scaling $\gamma = A(1 - T/T_c)^B$ with $B \approx 1.24$.

Surface tension of planar interfaces

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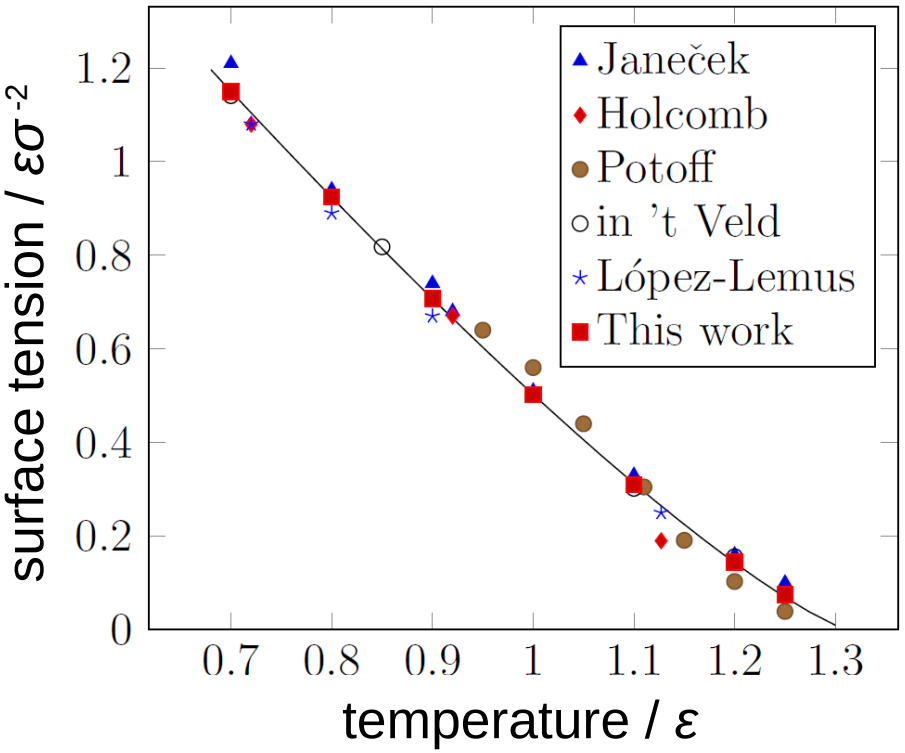
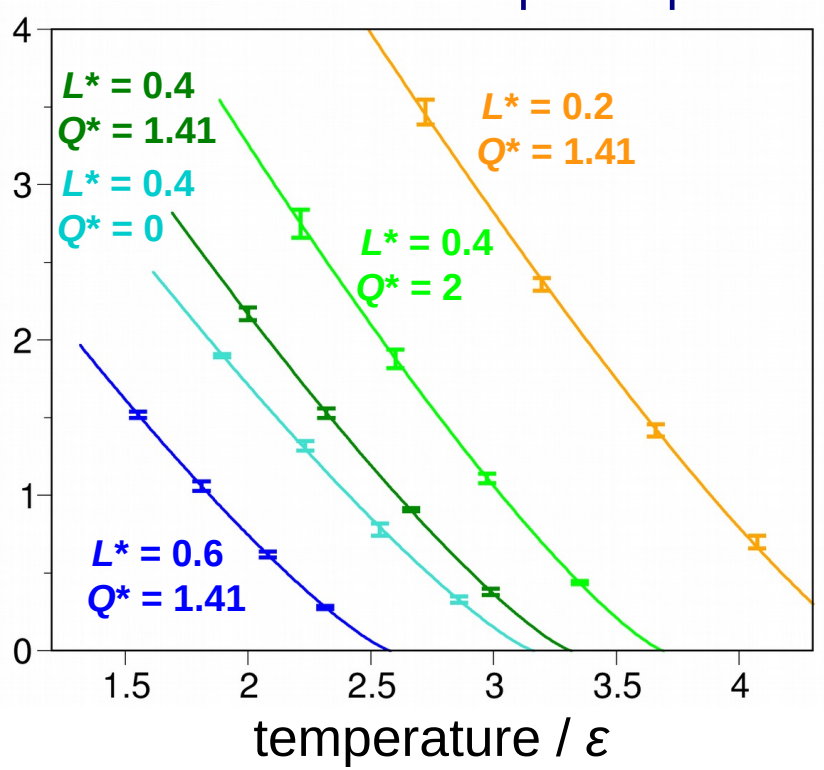
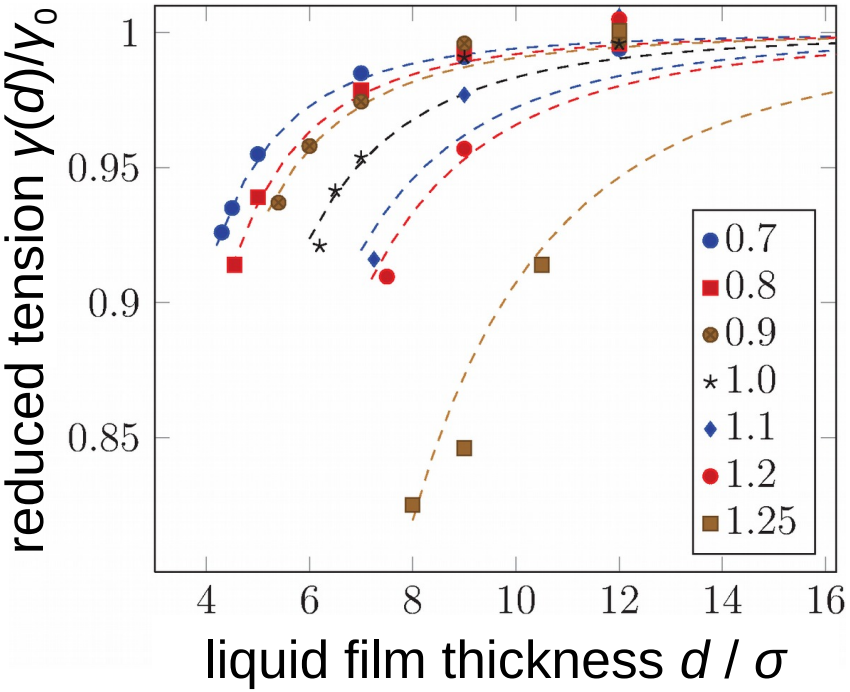


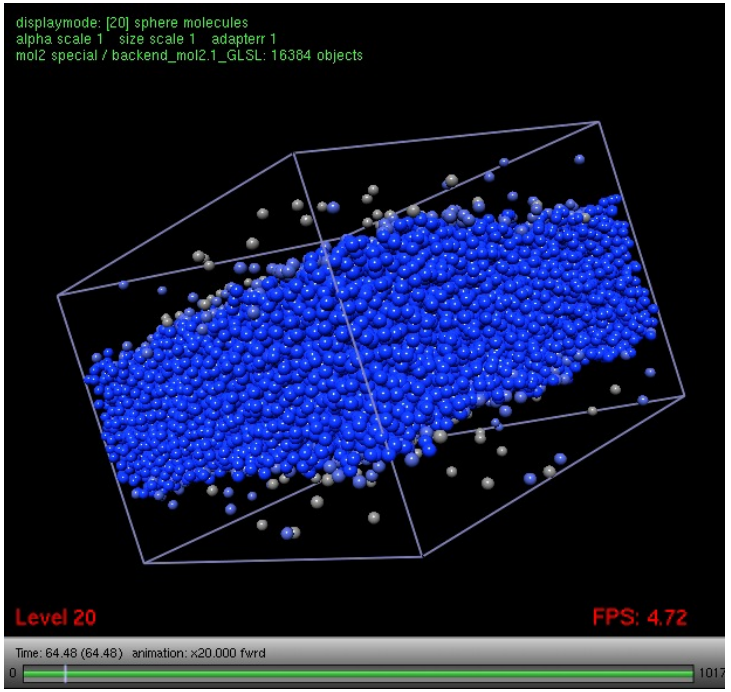
Two-centre LJ + quadrupole



Correlation: Universal critical scaling $\gamma = A(1 - T/T_c)^B$ with $B \approx 1.24$.

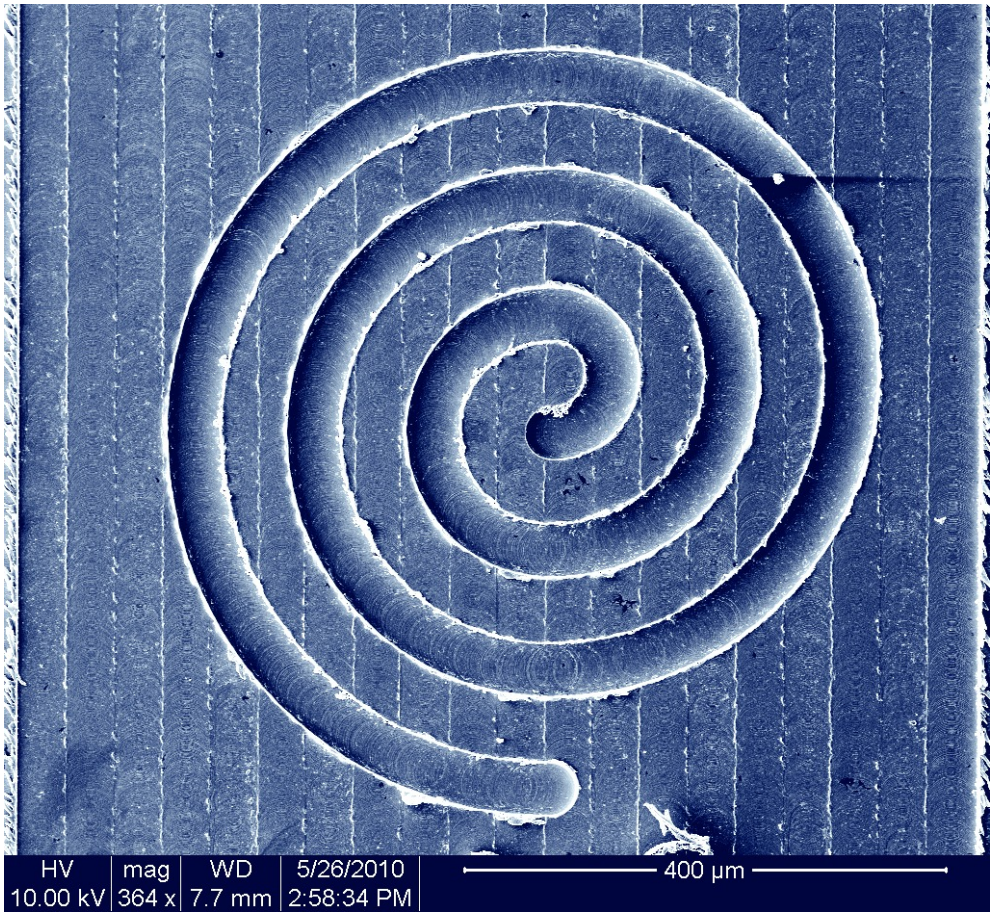
Surface tension of thin liquid films





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

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.

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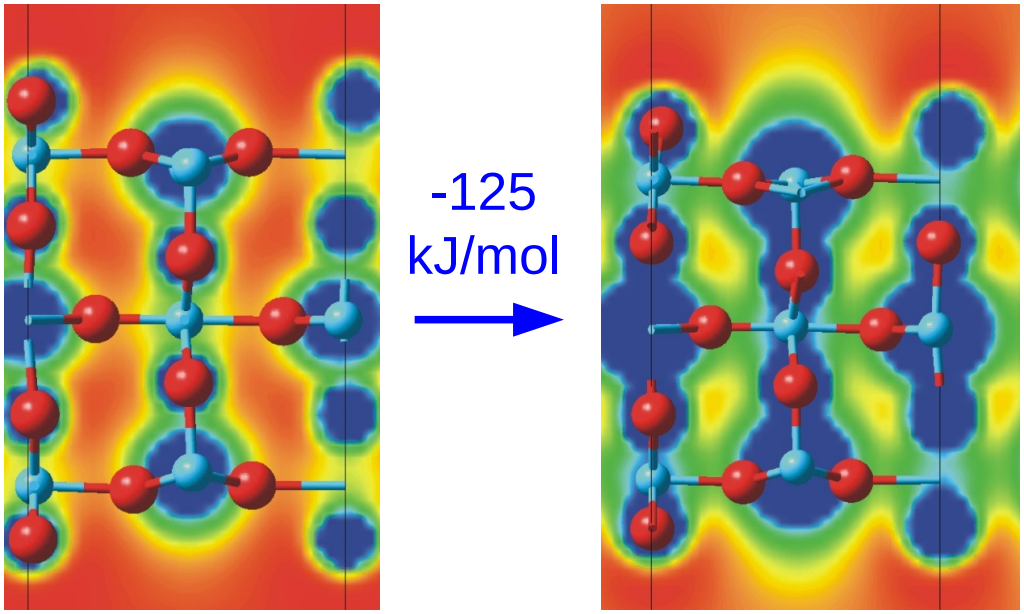
Quantum chemical simulations (VASP)

Computation of the electrostatic potential:



dry rutile surface **physisorbed 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.

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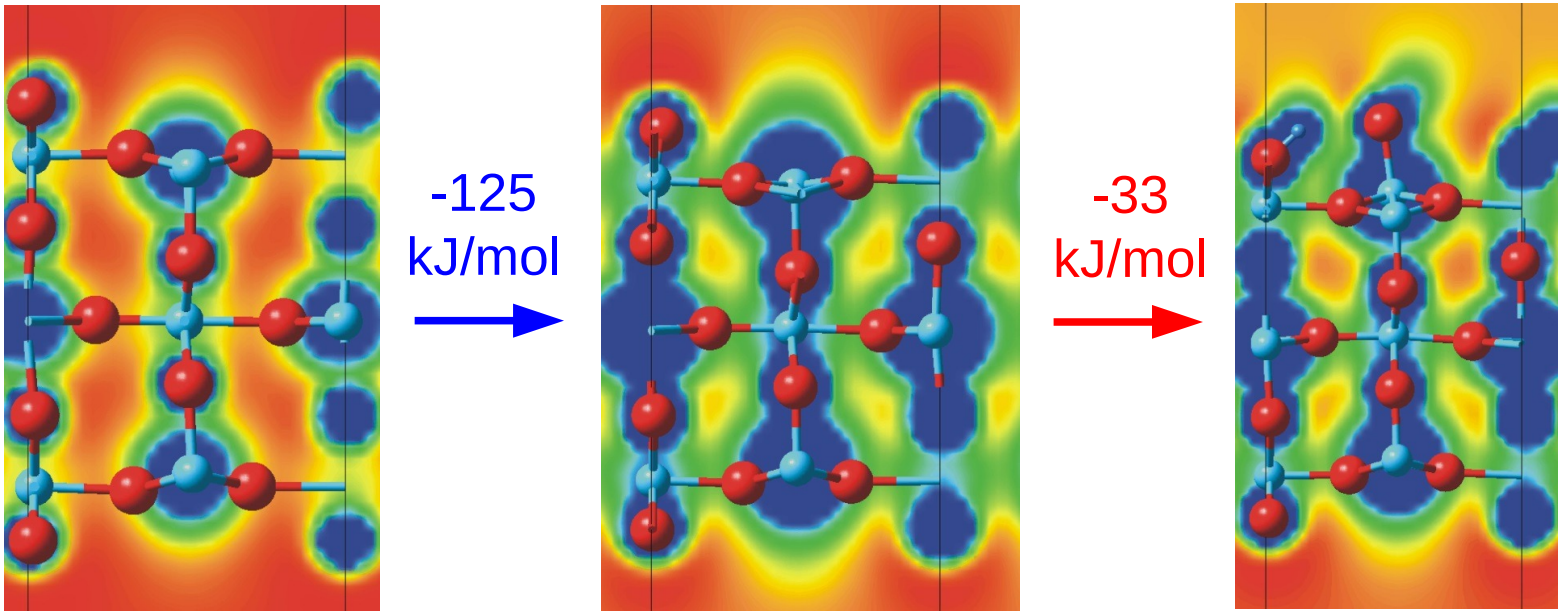


dry rutile surface **physisorbed water** **chemisorbed water**

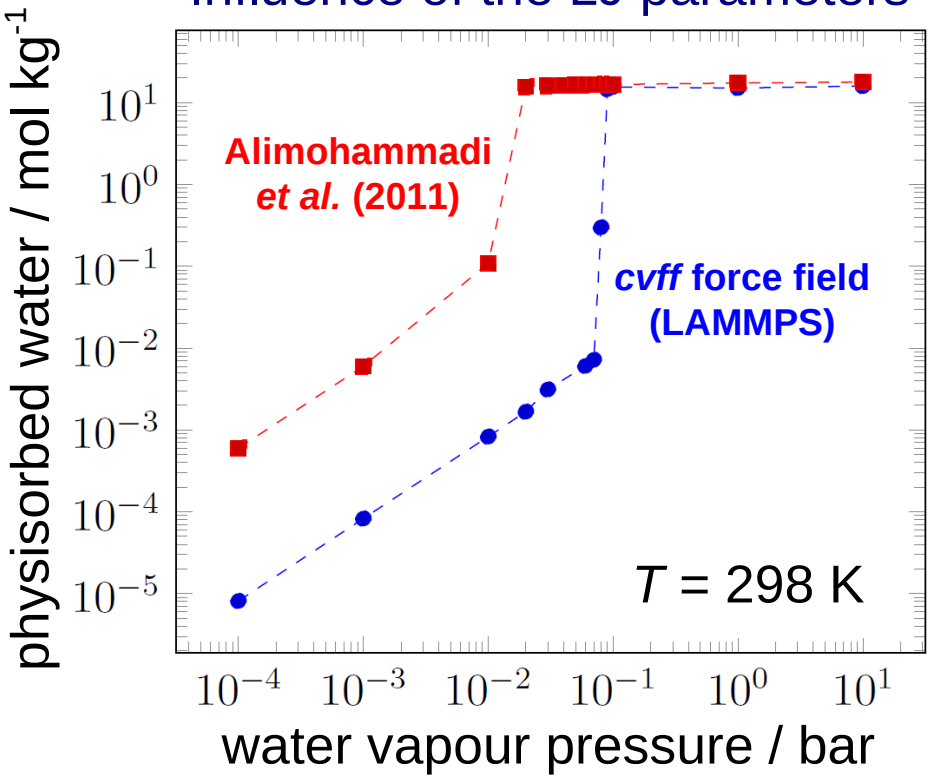
VASP simulation parameters (structure optimization with PBE functional):

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

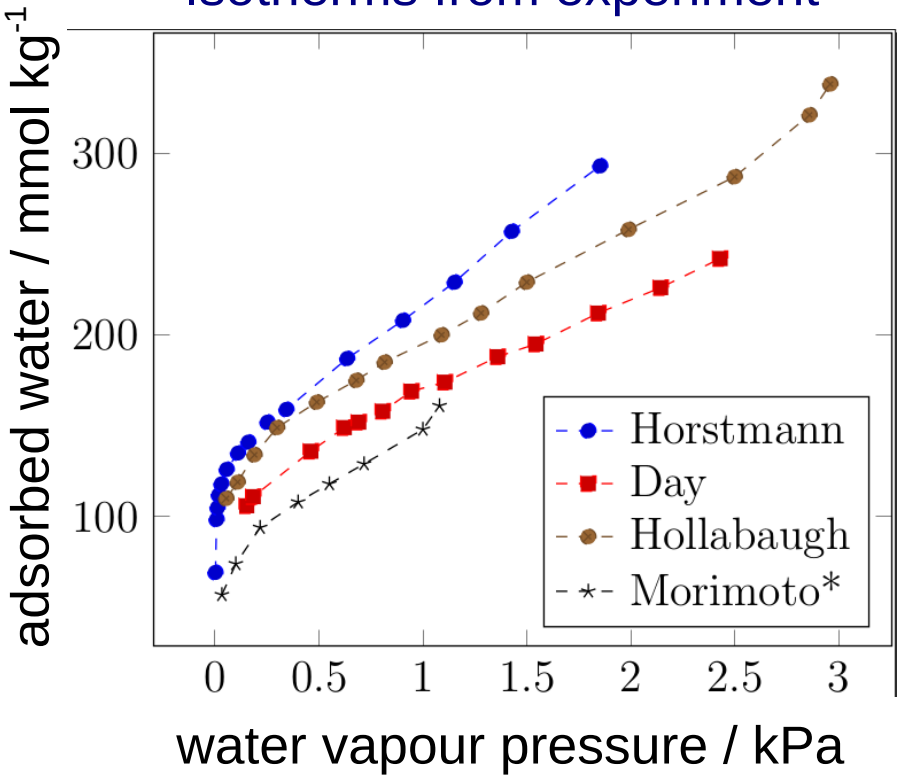
GCMC simulation of physisorption (Gibbs)

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

Influence of the LJ parameters



Isotherms from experiment



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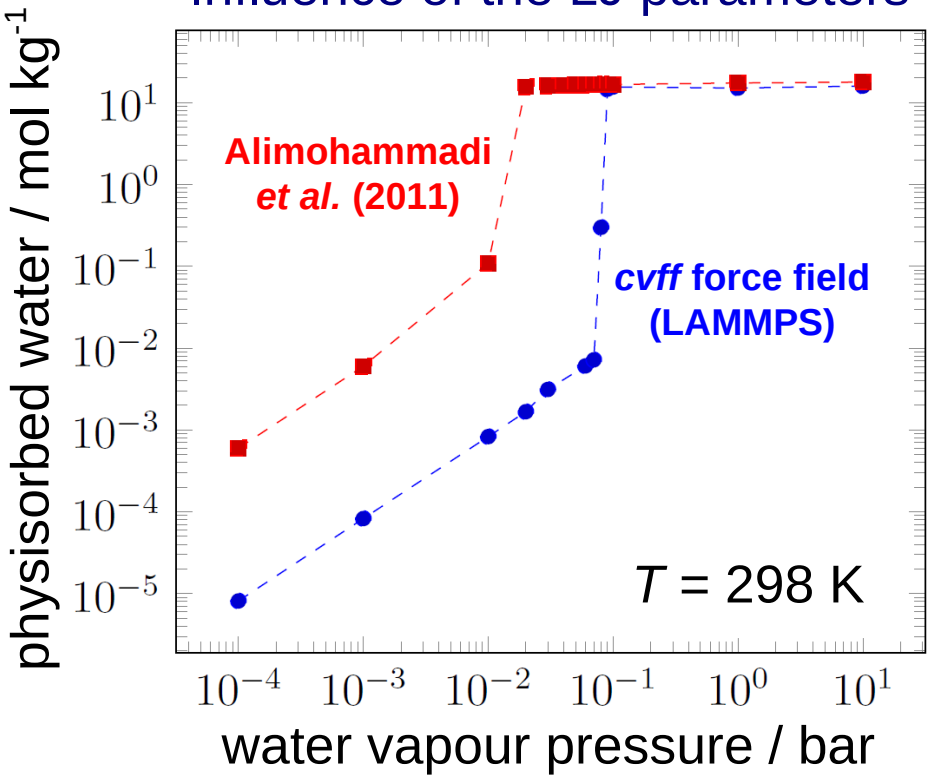
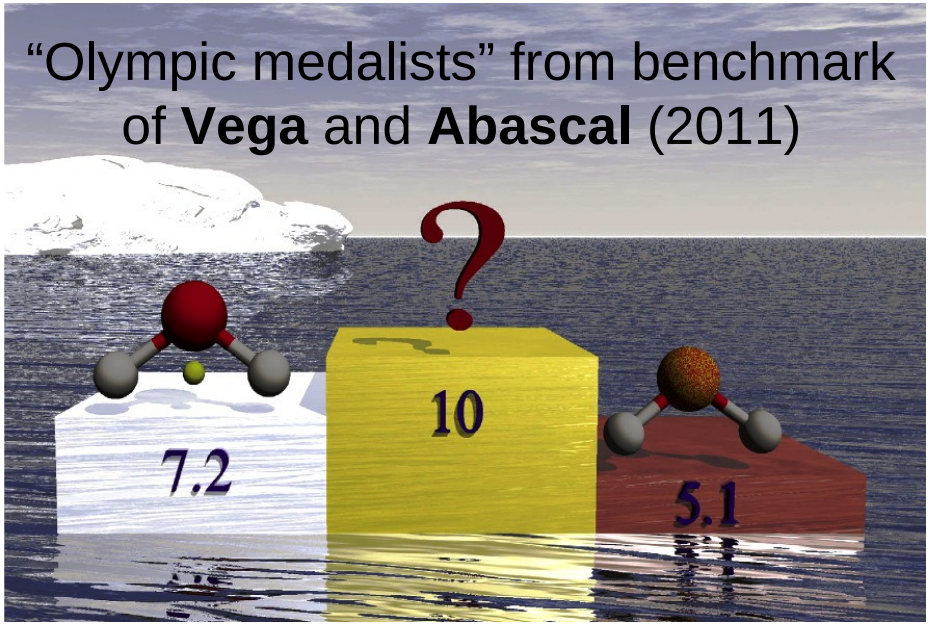


Further open issues:

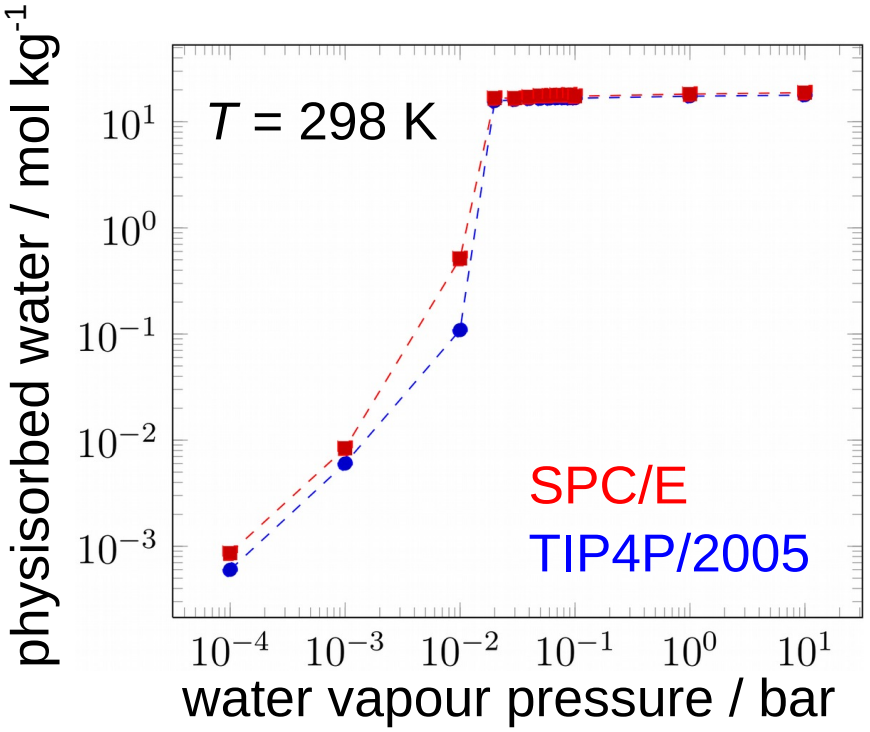
- Influence of chemisorption on the electrostatic grid
- Influence of organic matter adsorbed at the surface
- Long-range interaction with the titanium substrate
- Influence of the water model
- Etc. ...

Influence of the water model

Available water models do not capture all properties equally well.



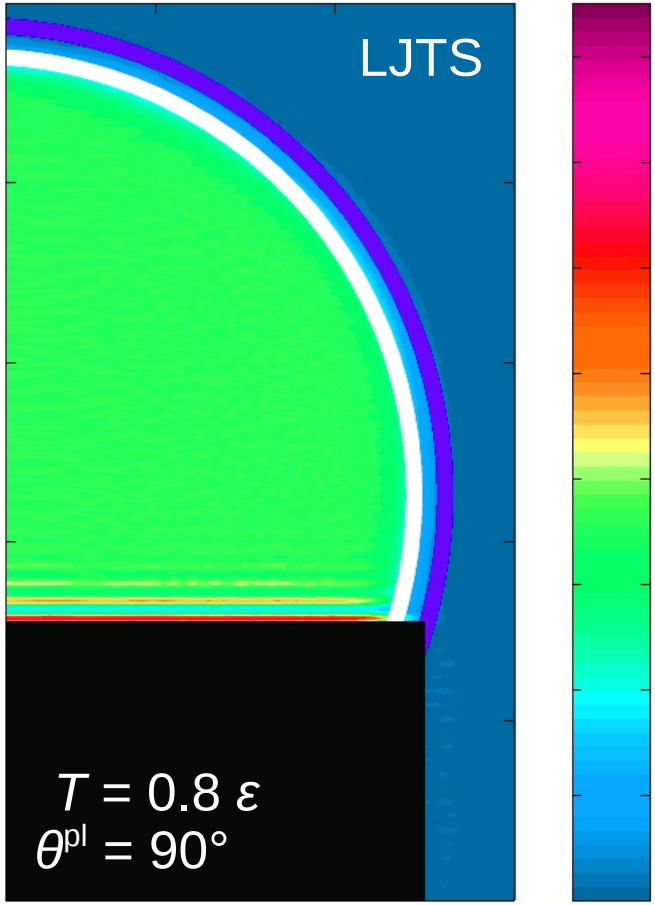
TIP4P/2005 **SPC/E**

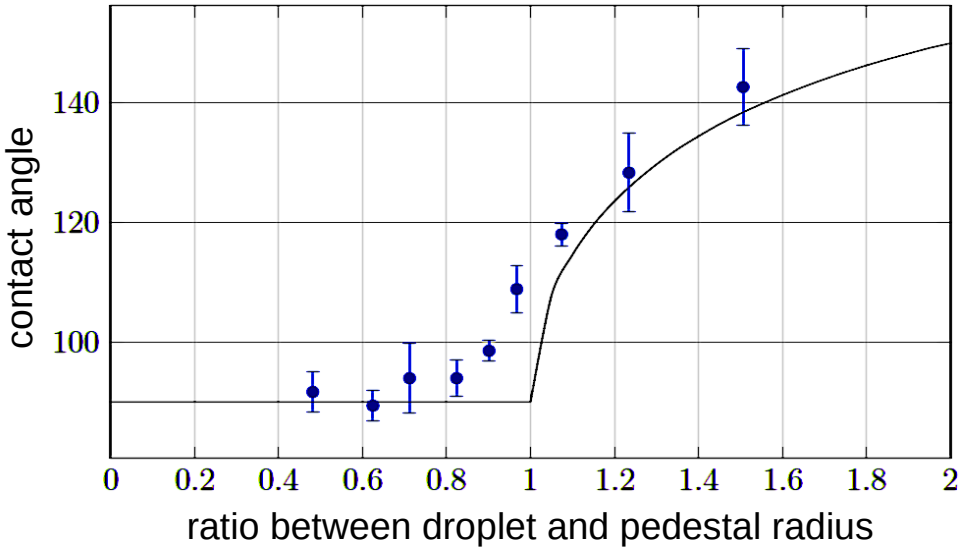


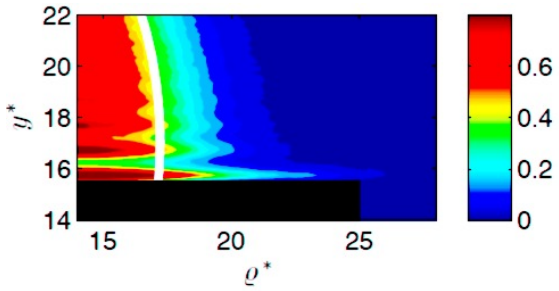
In the present case, the choice of the water model is relatively insignificant.

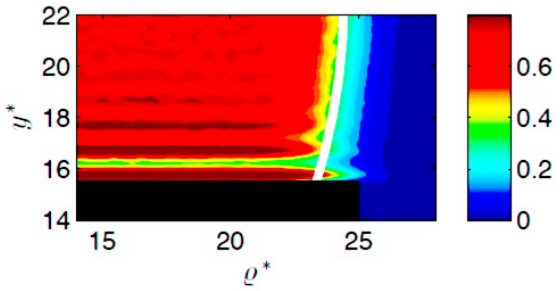
Contact line pinning

Epitaxial Cassie state

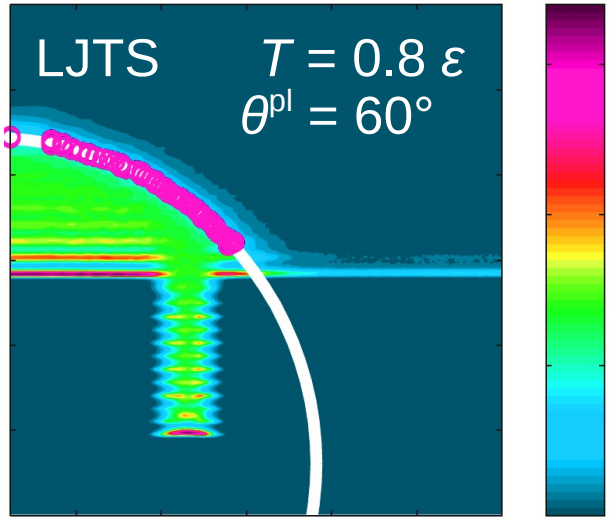








Wenzel's „law“ for rough surfaces



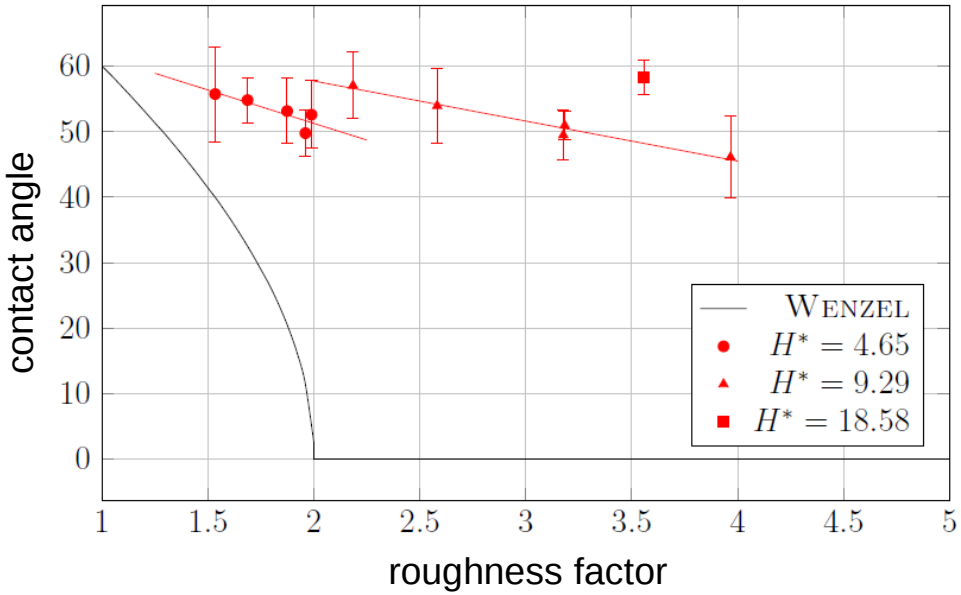
According to Wenzel, the roughness factor

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

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

Wenzel's “law” assumes

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



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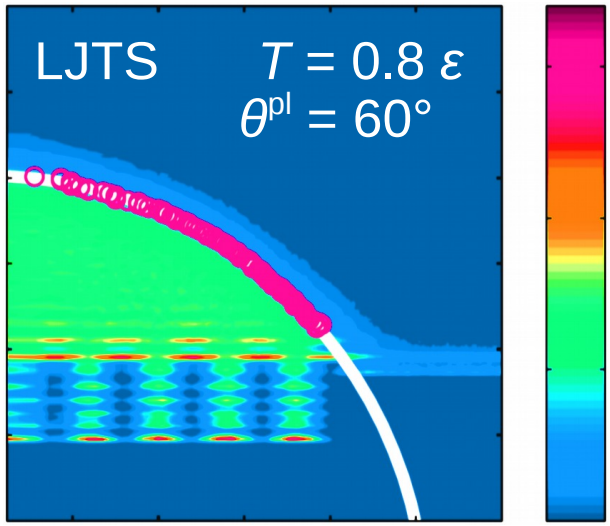

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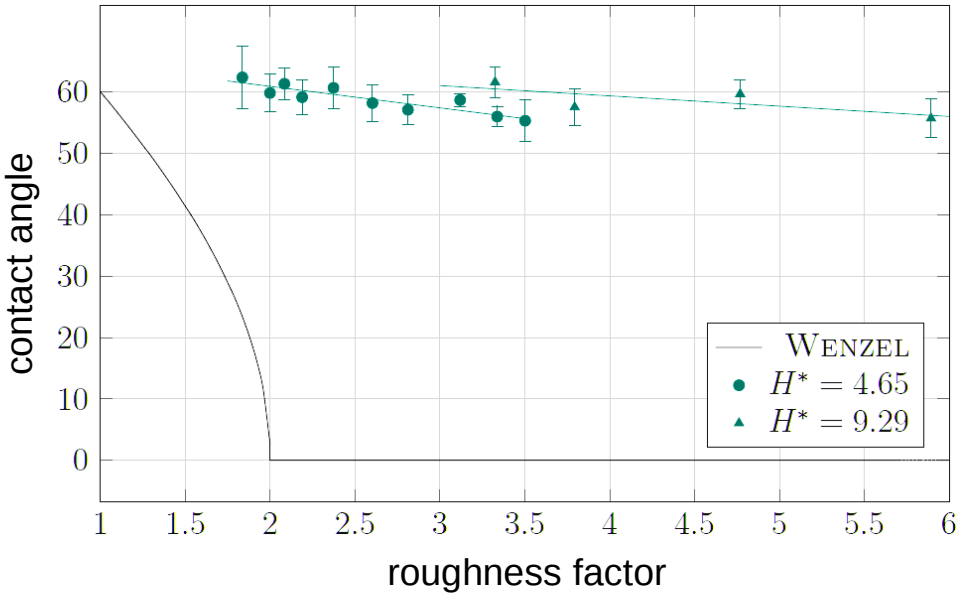

Conclusion

- Long-range interactions affect fluids at interfaces more significantly than the bulk phases, and sufficiently large systems need to be considered to account for both finite-size effects and the macroscopic limit.

- By quantum chemical computations with *MedeA VASP* and grand-canonical MC simulations with *MedeA GIBBS*, chemisorption and physi-sorption of water on a titania substrate was investigated.

- A quantitatively reliable molecular modelling approach requires a consistent treatment of both physisorption and chemisorption.

- Roughness and manufactured patterns of the surface can have a significant impact on static and dynamic wetting properties, which is not captured correctly by simple phenomenological theories.