Modelling Reactive Electrified Interfaces: From DFT to Force Fields

Stephan N. STEINMANN

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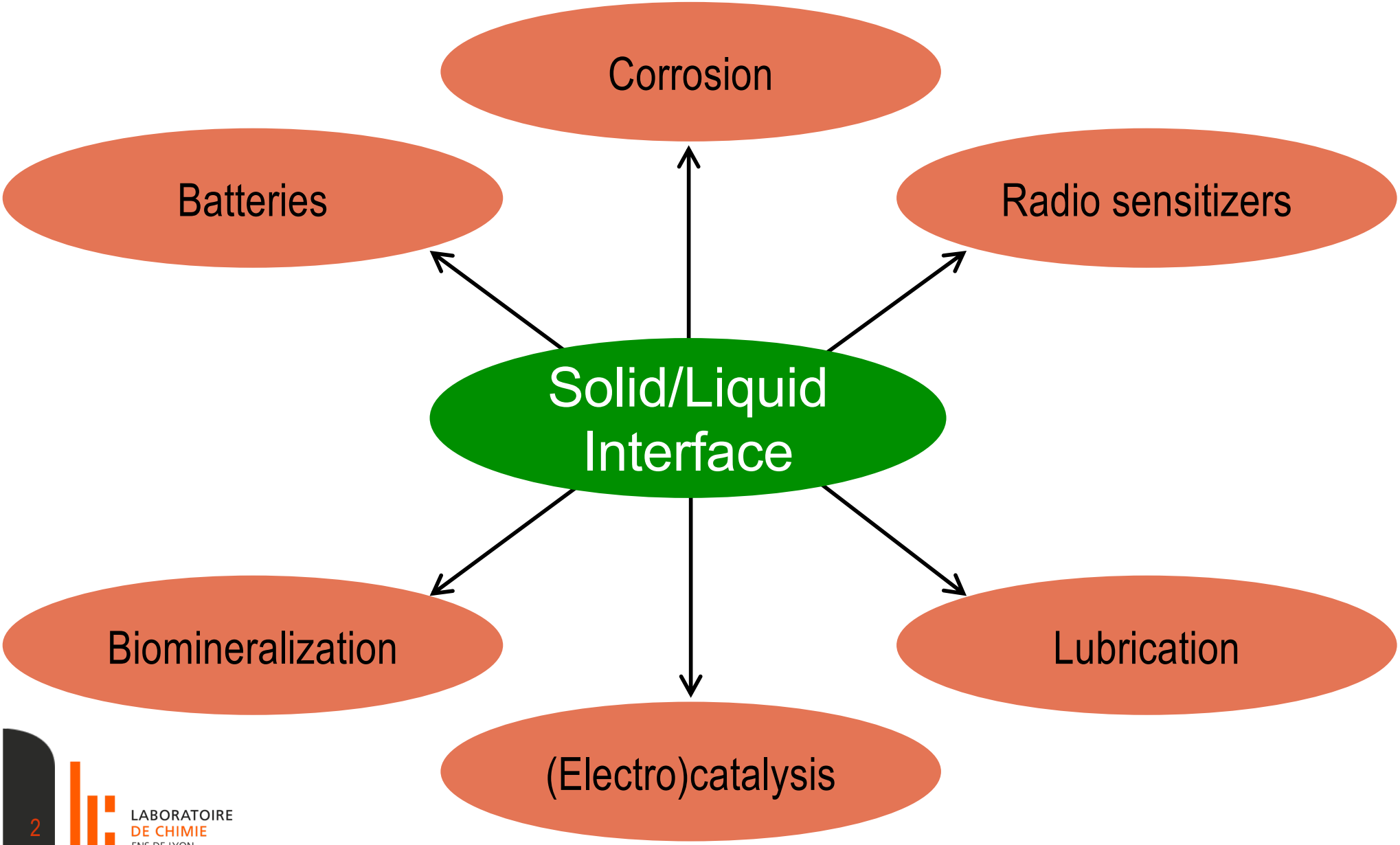
Importance of Solid/Liquid Interfaces



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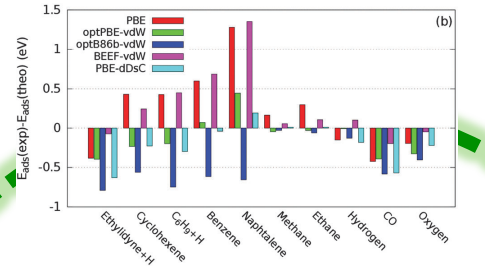
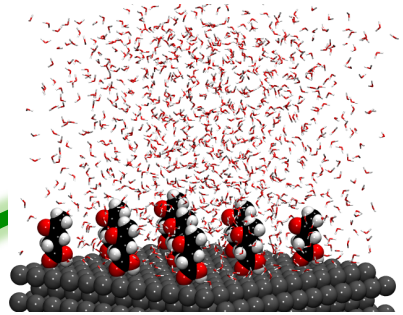
Gautier, Steinmann, Fleurat-Lessard, Michel, Sautet, *PCCP*. **2015**, *17*, 28921.

The Wishlist



Accurate energies

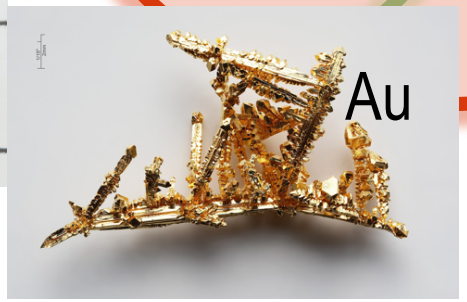


Steinmann, Michel, Sautet PCCP, 2016, 18, 31850.

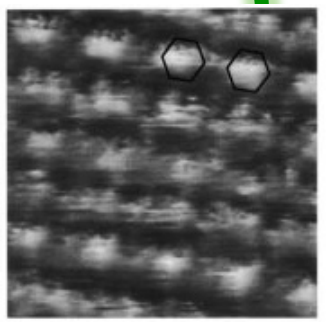
Phase space sampling

Solid Liquid Interfaces

Metal surfaces



Benchmark data



Osawa and co-workers, *Langmuir* **1998**, *14*, 6992.

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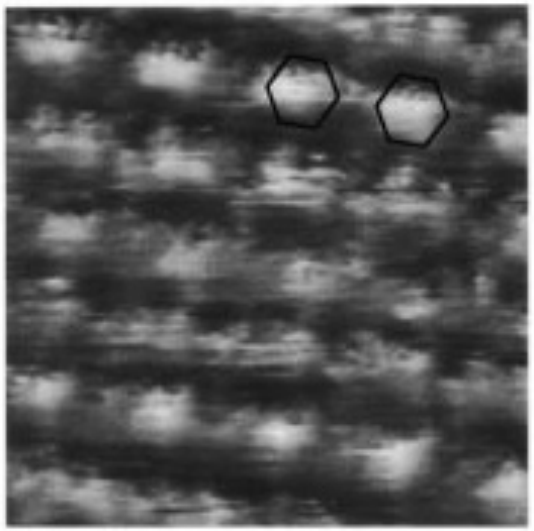
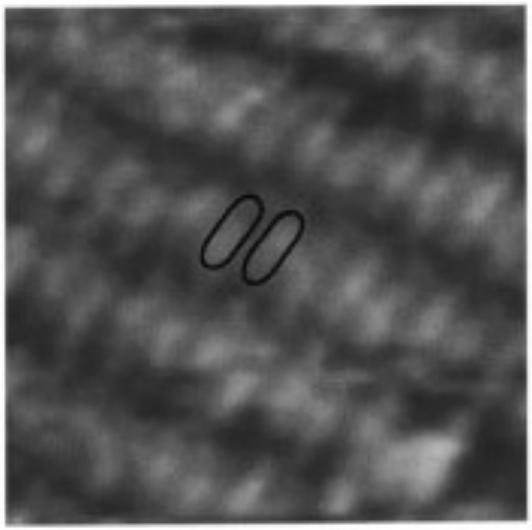
Wikipedia

System for Method Validation: Pyridine@Au(111) Experimental Data

< -0.5 V
No pyridine[1,3]

5x5 nm^2





1.5 V:
No pyridine[2]

0.1 V vs SHE (**flat**) 0.6 V vs SHE (**vertical**)

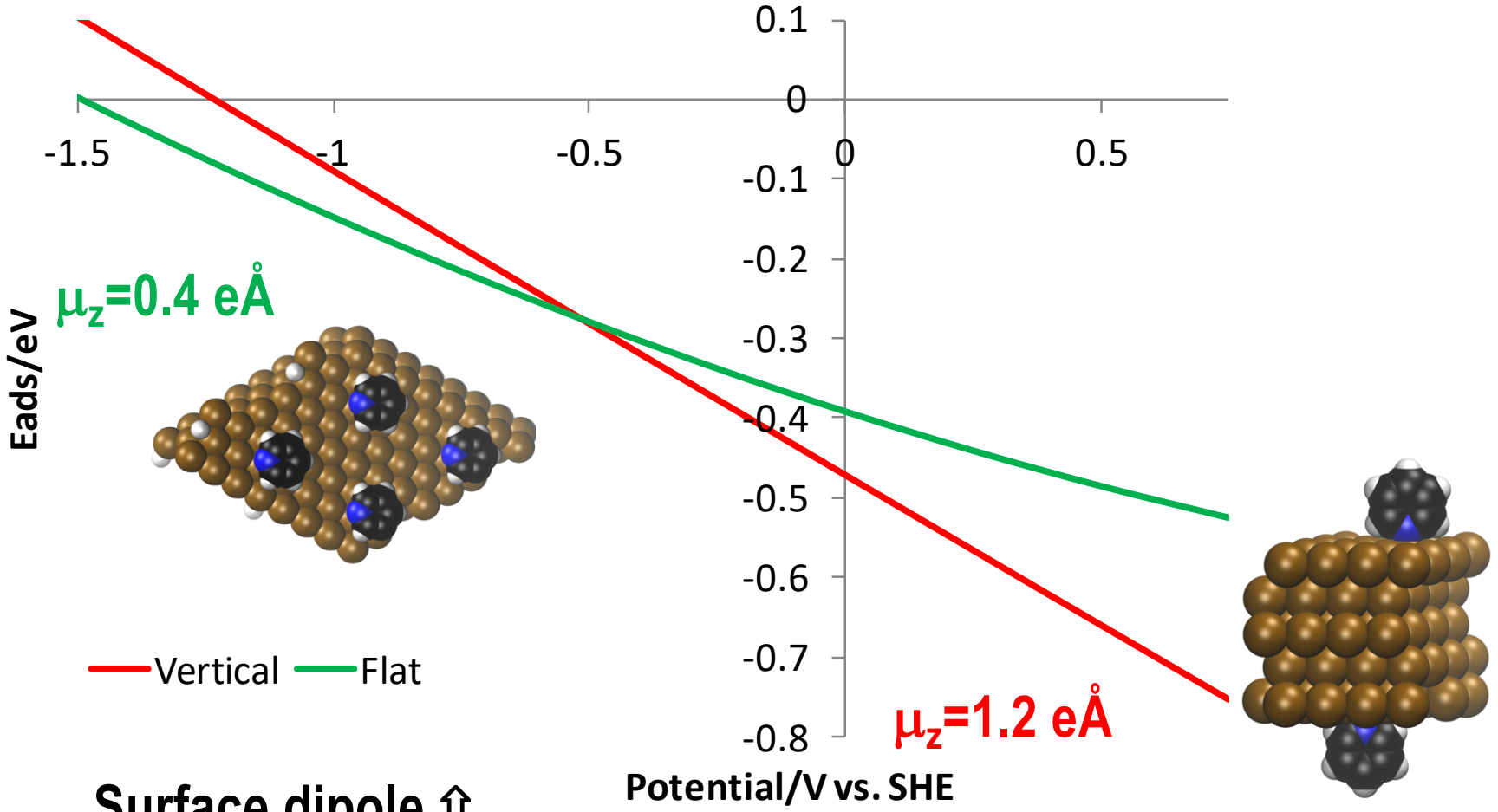
-0.15 to 0.15 V
Flat[1,2,3]

0.4 to 0.5 V
Vertical[1,2,3]

[1] Wieckowski and co-workers, *J. Electroanal. Chem*. **1993** *355* , 147.
[2] Wieckowski and co-workers, *Langmuir* **1990** *6,* 974.
[3] Osawa and co-workers, *Langmuir* **1998**, *14,* 6992.

Pyridine@Au(111)
Homogenous Background Countercharge

Neurock et al., *PRB* 2006, 73, 165401; Filhol, *PCCP* 2011, *13*, 7675.



Surface dipole ⇧

Potential dependence ⇧

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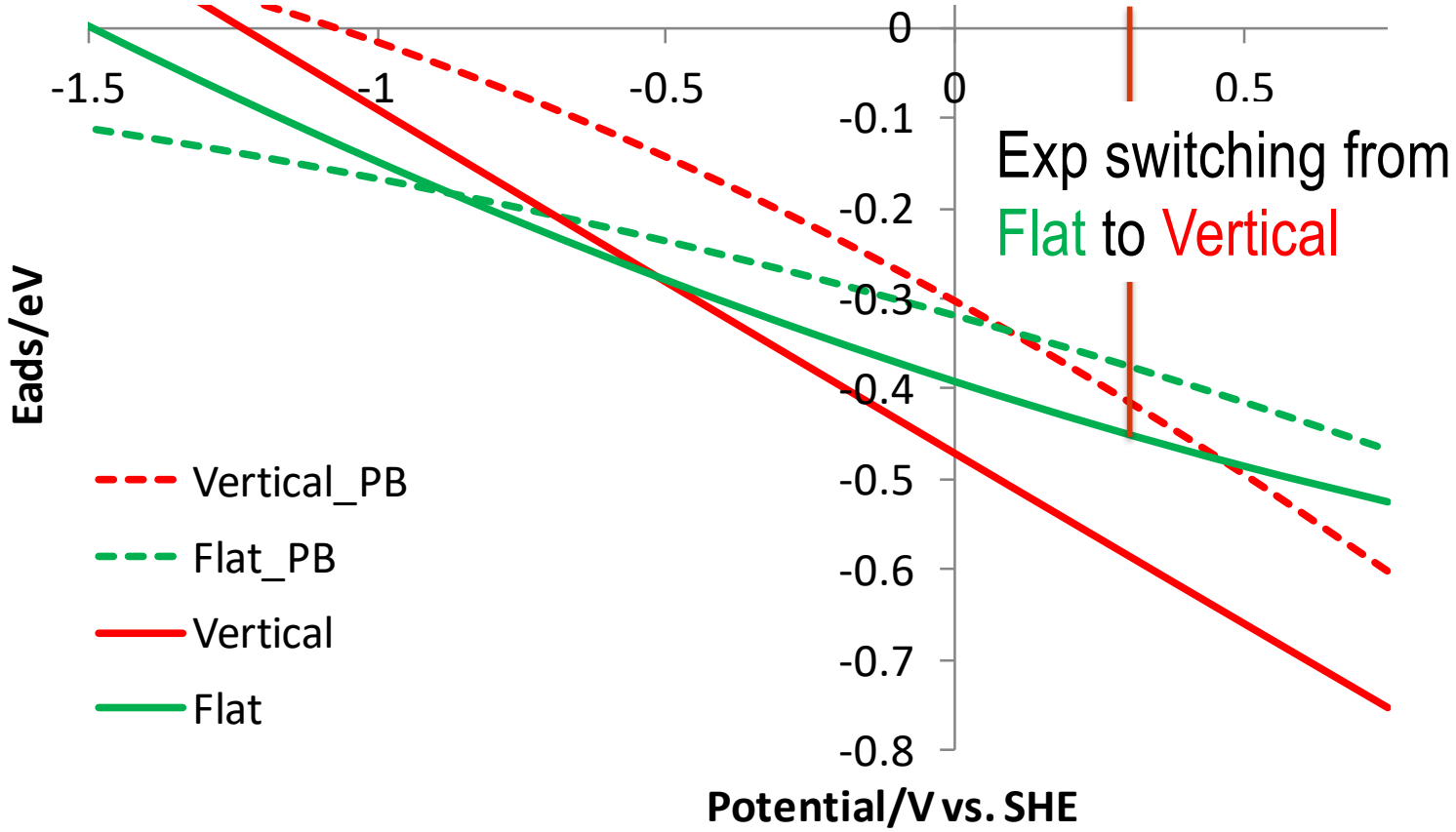
Steinmann and Sautet, *JPCC*, **2016**.

Pyridine@Au(111)

Solid: Homogeneous background (SC)

Broken: Boltzmann distribution of an electrolyte (PB)



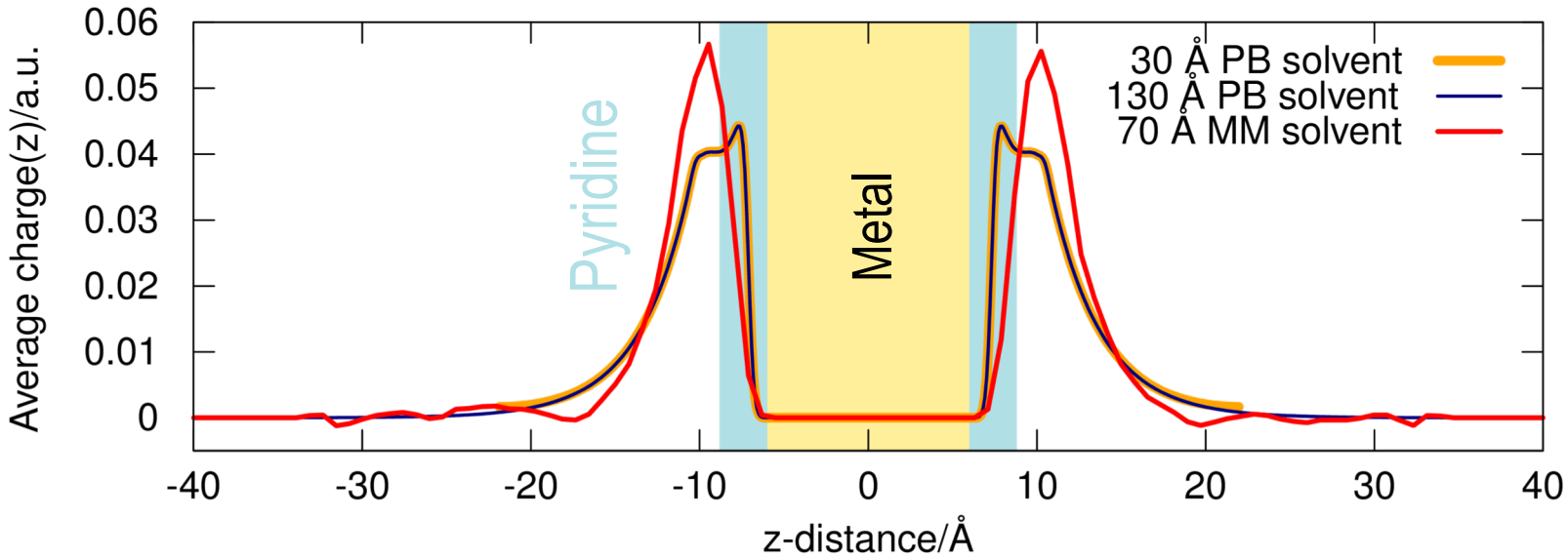
Electrolyte distribution improves agreement

Steinmann and Sautet, *JPCC*, **2016**.

QM/MM

QM: Metal surface+adsorbate

MM: Electrolyte



Comparison of PB with MM Electrolyte (1 M)

✓ Distributions are remarkably similar

✗ PB electrolyte looses fine structure and approaches the surface too closely

Accuracy of implicit solvent models for metal surfaces unknown

Steinmann, Michel, Sautet PCCP, 2016, 18, 31850.

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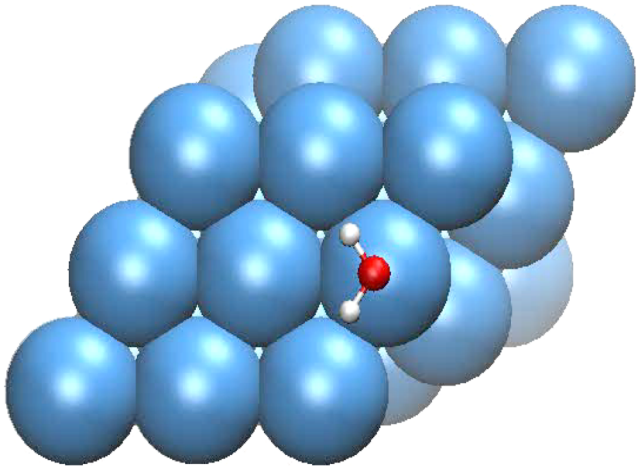
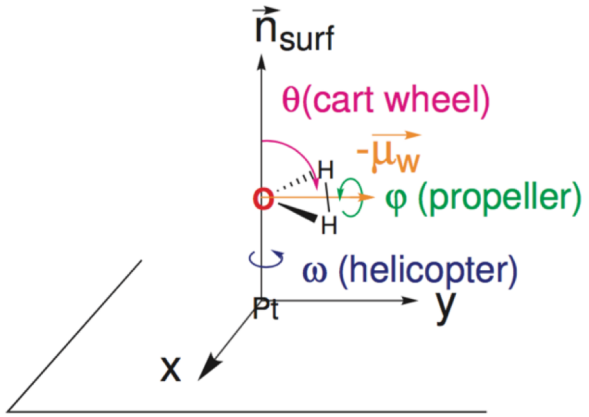
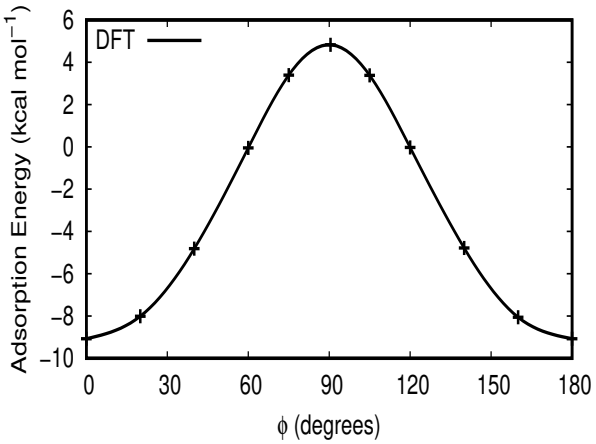
How to assess different force fields?





propeller



PBE-dDsC, 400 eV cutoff, 4 layers, VASP.

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Which force fields are available?

1987: Spohr-Heinzinger:

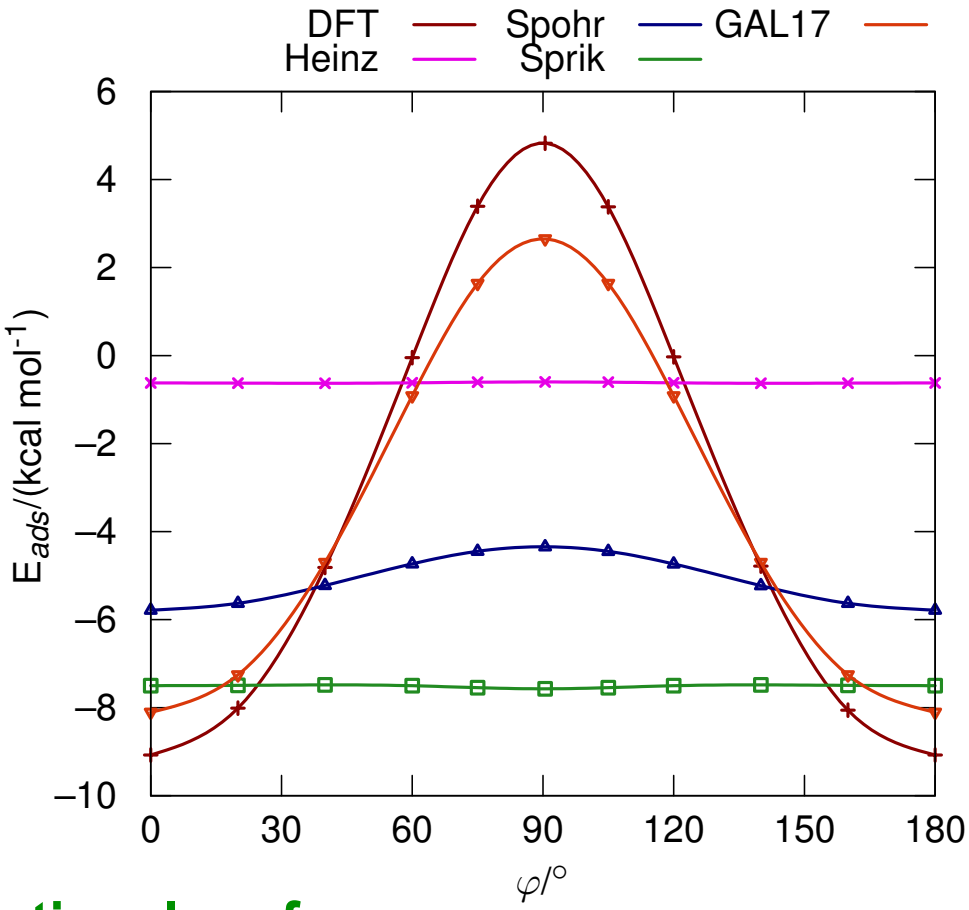
Problem: H-repulsion too weak

1991: Siepmann-Sprik

Problem: NO H-repulsion

2009: METAL (Heinz)

Problem: NO H-repulsion



GAL17 qualitatively correct orientational preference

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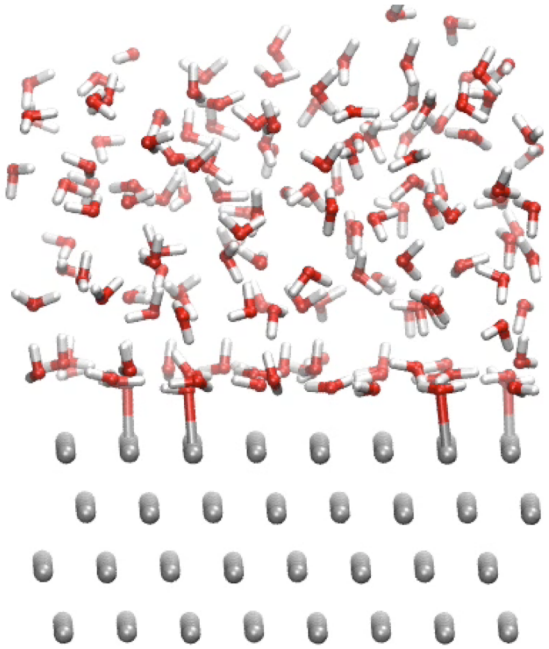
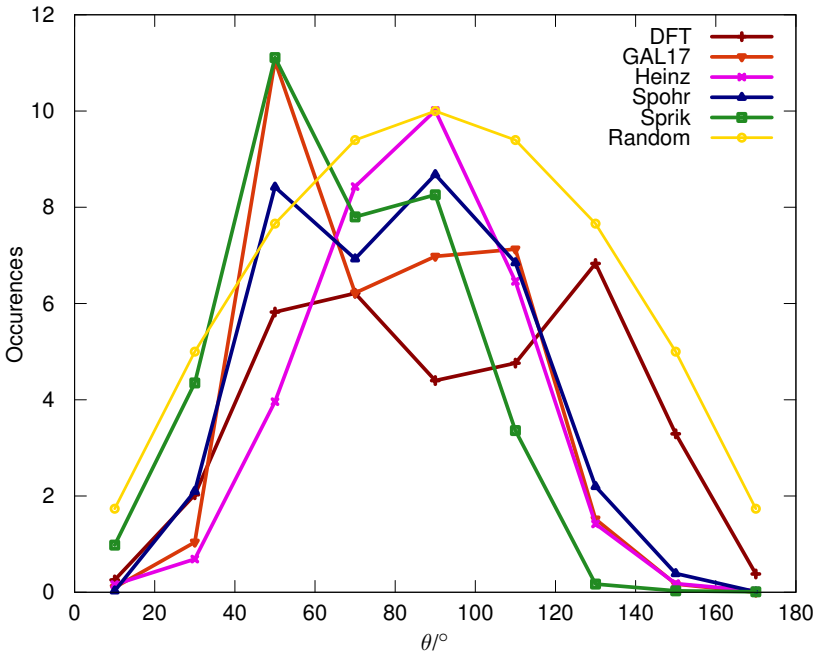
Steinmann, Ferreira de Morais, Goetz, Fleurat-Lessard, Iannuzzi, Sautet, Michel, *J Chem Theory Comput*. **2018**, 14, 3238.

GAL17: Solid/liquid interface



1 ns MM: 2 CPUh
10 ps QM: 140'000 CPUh
(2 months real time on 96 CPUs)



Orientations in 1st layer (10 ps)

10 ps are not enough for convergence

Competition between water-water and Pt/water delicate

No definite answers about the "true" structure (yet)

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Conclusions

Pyridine adsorption: Electrolyte description is non-trivial

Standard force fields are inaccurate for Metal/Water

GAL17 is a novel Water/Pt(111) force field with improved accuracy
Available in AmberTools18

The community needs more
Method development and validation

Acknowledgements

Paul Clabaut and Ruben Staub

Carine Michel

Paul Fleurat-Lessard

Philippe Sautet

Andreas Götz

Marcella Iannuzzi

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