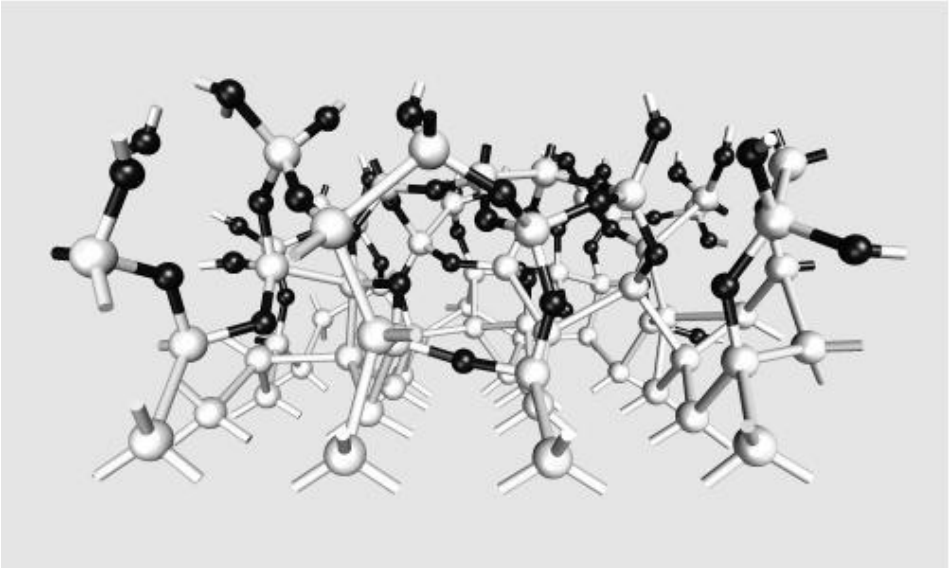
Computational Chemistry II Chapter 8 2023

Solid-solid and solid-liquid interphases

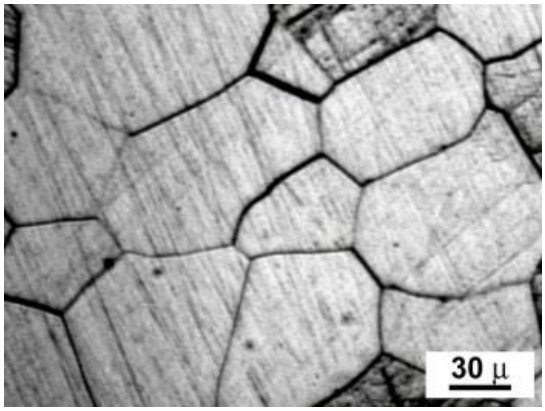
The modelling of solid interphases is rather difficult since the interphases atomic structure is mostly unknown and the reorganization barriers in solid systems are very large. This means that the interphase is at best on a good local minima. On the other hand the grain boundaries are very important for materials macroscopic properties.

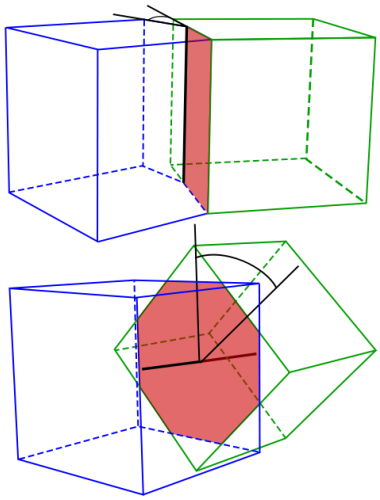
Example: Si|SiO2 interphase.



Grain boundaries

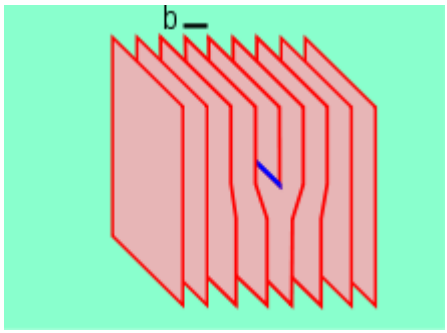
Every real material consists of grains and real materials are full of grain boundaries. We can assume that each grain is a single crystal in which the atoms are perfectly oriented. The grain size varies a lot but is usually on the micrometre scale. Typically, the grains have irregular shapes. Now the grain boundaries can be classified with the tilt and twist angles





Schematic representations of a tilt boundary (top) and a twist boundary between two idealized grains.

Atoms in these ideal boundaries will relax to minimize the interaction energy. The simplest grain boundary is the one with only tilt. If the angle is small boundary can be described with a dislocation. There will be an extra atomic layer in the systems and after some layer again a new layer. As one can imagine the interphase structure can be complex and on atomic level they have not been modelled much. The grain boundaries will also move (slowly) since the atoms will diffuse. Often this movement is not wanted. One can add some impurities (atoms) to prevent the boundaries to move. (Zener pinning)



There has been very little ab initio modelling of grain boundaries. I found one interesting article A.L-S.Chua et al. Nature Mat. 9 (2010), 418.

Abstract

Recent years have seen great advances in our ability to predict crystal structures from first principles. However, previous algorithms have focused on the prediction of bulk crystal structures, where the global minimum is the target. Here, we present a general atomistic approach to simulate in multicomponent systems the structures and free energies of grain boundaries and heterophase interfaces with fixed stoichiometric and non-stoichiometric compositions. The approach combines a new genetic algorithm using empirical interatomic potentials to explore the configurational phase space of boundaries, and thereafter refining structures and free energies with first-principles electronic structure methods. We introduce a structural order parameter to bias the genetic algorithm search away from the global minimum (which would be bulk crystal), while not favouring any particular structure types, unless they lower the energy. We demonstrate the power and efficiency of the algorithm by considering non-stoichiometric grain boundaries in a ternary oxide, SrTiO3.

One the other hand there has been some publications using empirical models. A good example is: D.E. Spearot and D.L. McDowell, J. Eng. Mater. Technol. **131**, 041204 (2009).

Solid liquid interphase – water molecules on a surface

The real solid water interphase has not been studied much with ab initio methods. The reason is simple – the calculations are time consuming. On the other hand single and few water molecules has been studied quite a lot. The water molecule will bound to almost any surface. It mostly stable but on for example transition metal oxide surfaces (like TiO2) the water molecules can dissociate. We look first the simple metal surfaces. Compared to many other molecules the water is more problematic since it form easily hydrogen bonds. Then the cluster structures depend both one the interaction with the surface and the hydrogen bonds.

A good article is: S.Meng, E.G.Wang and S.Gao, Phys. Rev. B 69, 195404 (2004)

With small amount of water the situation is simple. The water molecules are usually oxygen toward the metal. If there are more molecules they form hydrogen bonds. The O-O distance is seldom close to the M-M distance so the molecules in clusters are usually not on certain specific positions (like top, bridge or hollow).

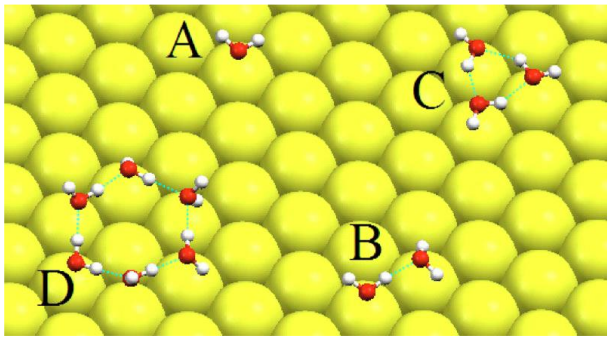
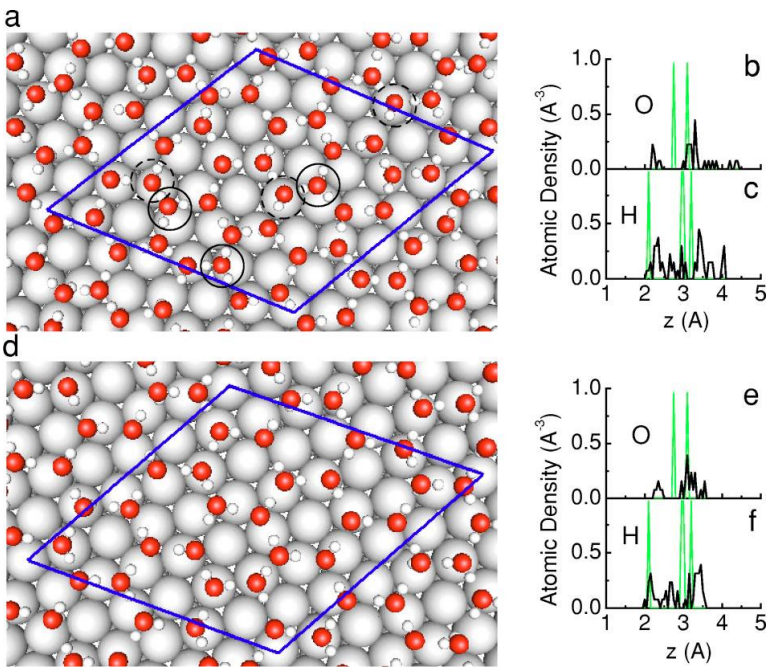


Figure: water clusters on Pt(111) surface

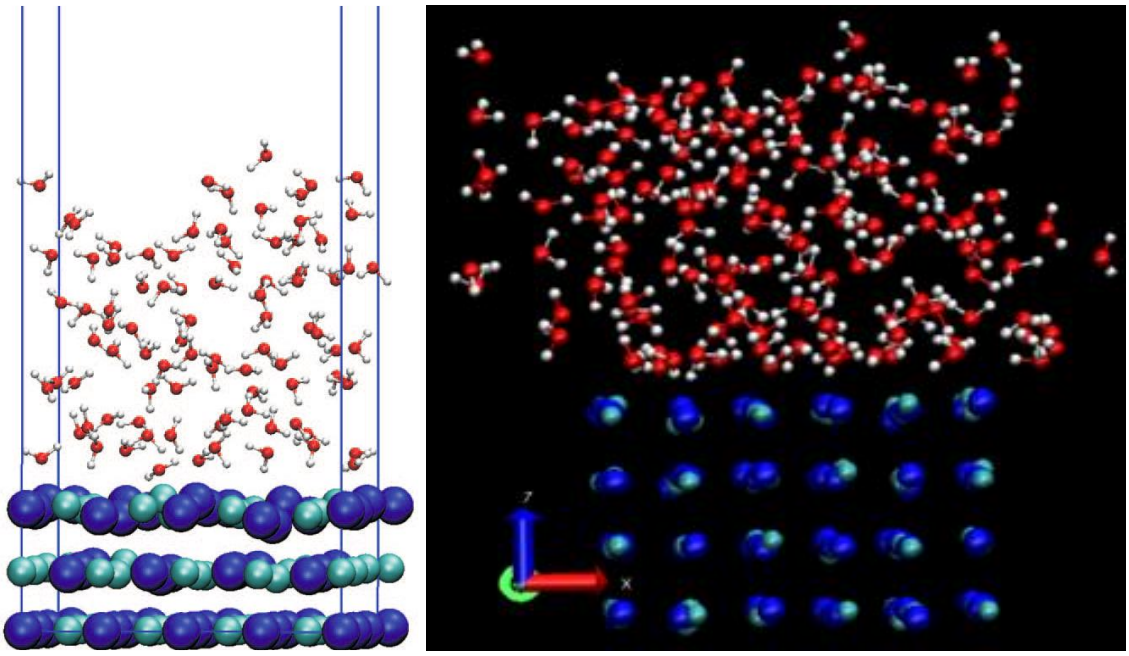
But when there are more waters the over layer structure can be complex.



The surface cell is √39x√39*R*16.1° Note that the waters are not exactly on the Pt atoms and this is the main reason to the large unit cell. Also the water layer is smooth. There is quite a bit of variation in the height.

Liquid water solid interphase

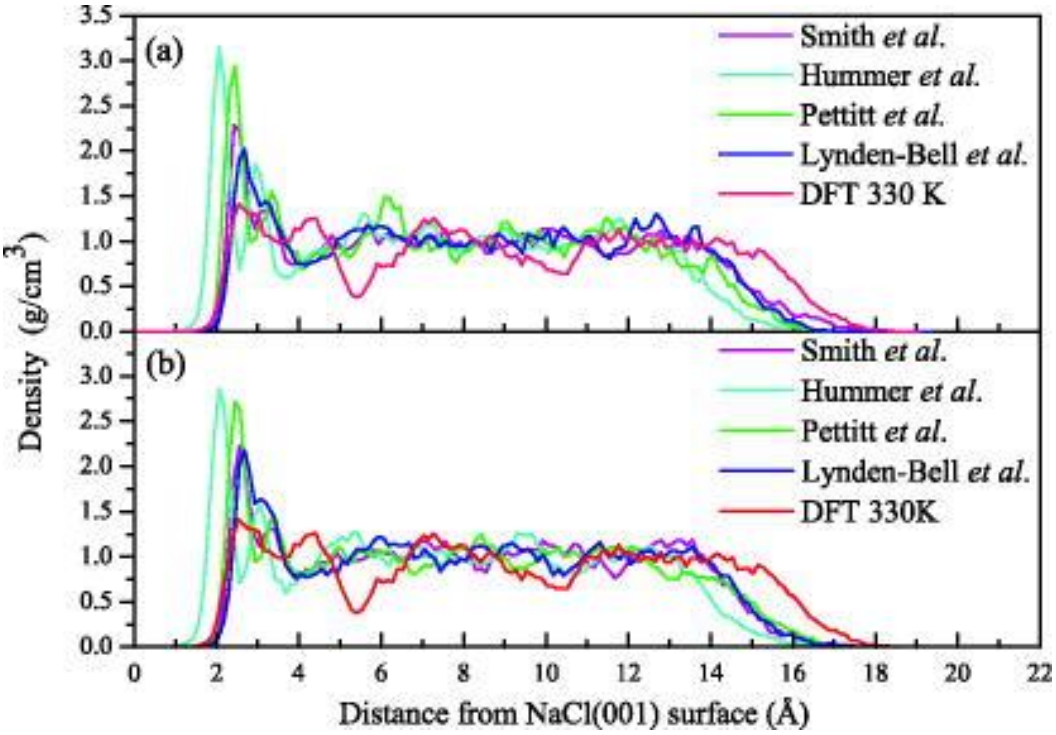
As said earlier there are very few ab initio studies of liquid solid interphase. One of the studied systems is water-NaCl. The system is relatively simple. There is a slab of NaCl and on top of that some layers of water. The NaCl is naturally ionic so the water molecules will orient strongly near to the surface.



Lähde: L.-M. Liu M. Krack and A. Michaelides, J. Chem. Phys. 130, 234702, (2009) and J-C Chen, P. Spijker, B. Reischl, N. Holmberg, K. Laasonen and A. S. Foster, 'ab initio Kinetic Monte Carlo simulations of dissolution at the NaCl-water interface', PCCP, 16, 22545-22554, (2014).

Next there are some plots of vertical density profile with both empirical and ab initio simulations. The first layer is clear but it varies a lot form model to model. Note that in the first picture the DFT results are very noisy. In the second picture the DFT simulations are much longer and the systems is also larger. The second DFT simulations shows that the maximum density is rather low (ca. 1.6 g/cm3) compared to many of the empirical models (2.0-3.0 g/cm3)

Figure 1: Density profiles with several ion models near the NaCl surface. Figure (a) is with TIP3P water model and (b) with SPC/E model. From: L.-M. Liu M. Krack and A. Michaelides, J. Chem. Phys. 130, 234702, (2009)).



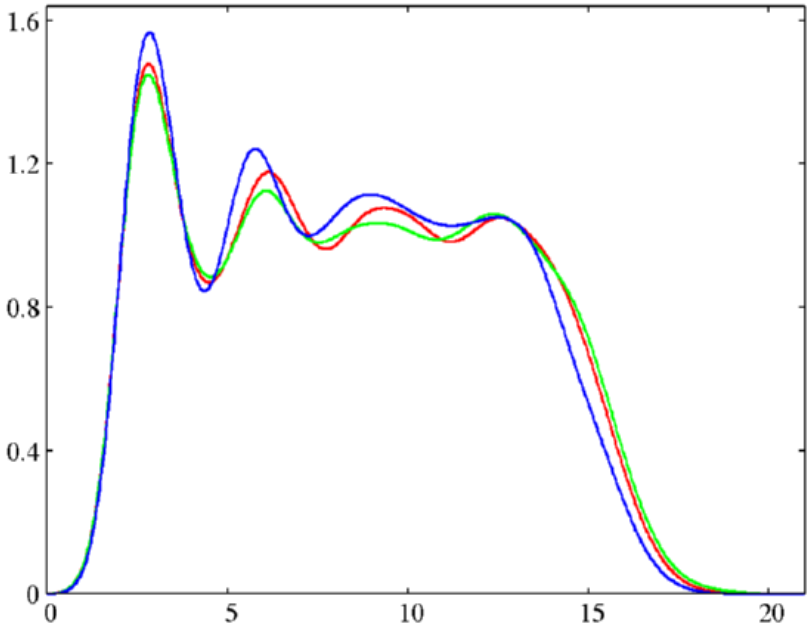
Liquid water on NaCl(100) surface

PBE (4x4) cell

PBE (3x3) cell

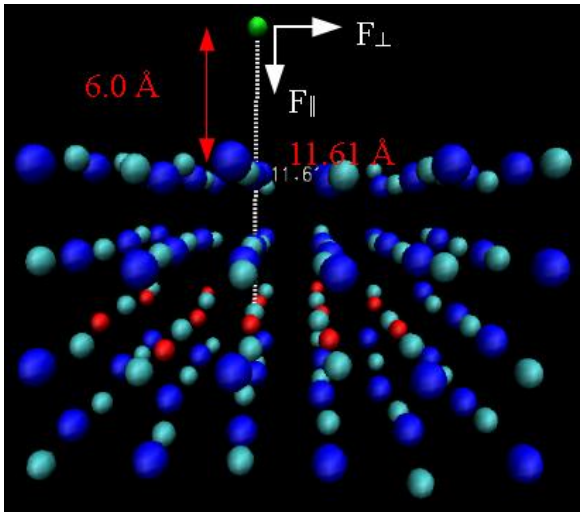
BLYP (4x4) cell

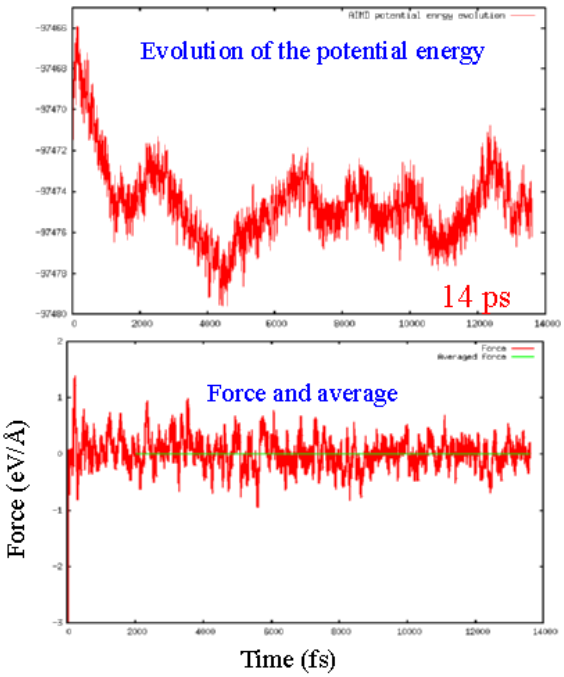
Chen et al. PCCP (2014)



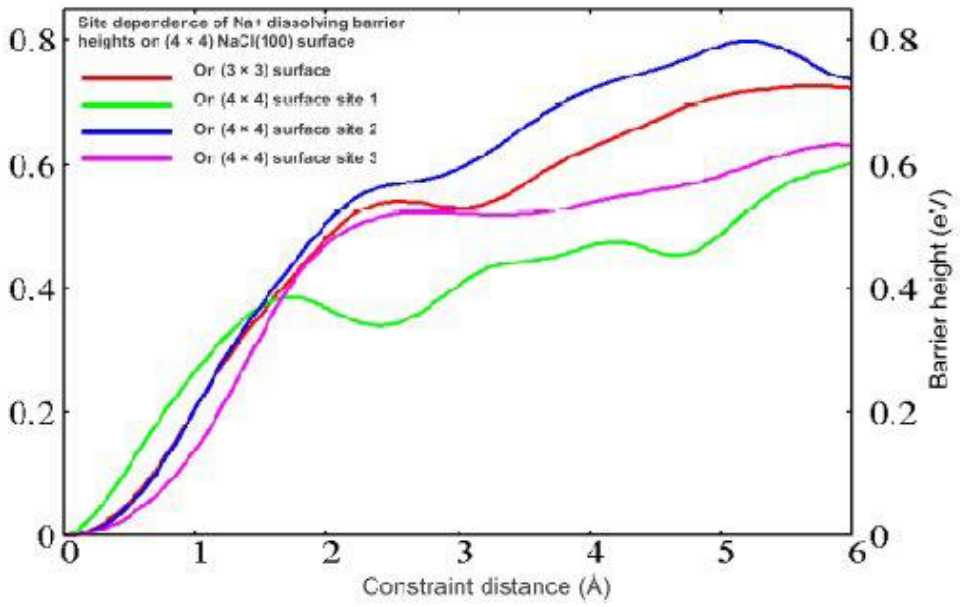
The structure of water is interesting but also the Na and Cl dissociation can be studied (Chen et al. PCCP (2014). Computationally the atoms can be pulled from the surface and the force acting to the atom can be computed. This force is rather noisy so relatively long simulations are needed.

$$\Delta G = \int_{d0}^{d1} \langle f_{cons}(x) \rangle \, dx$$

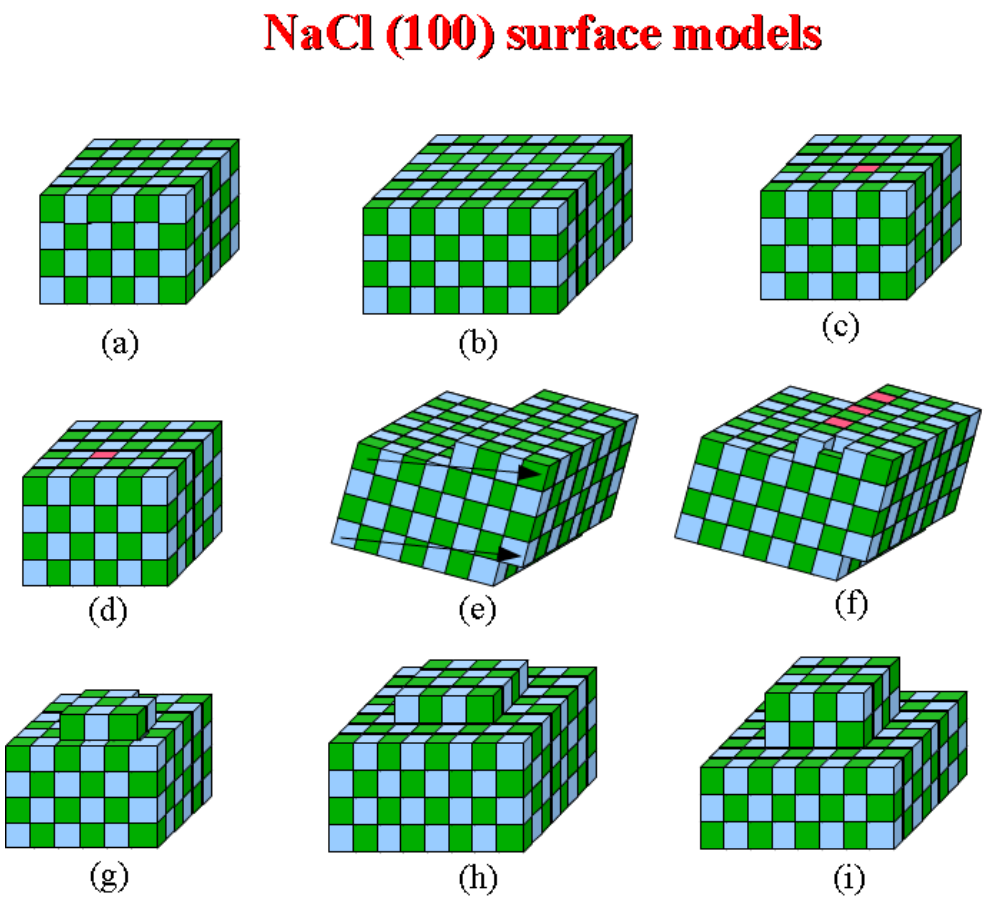




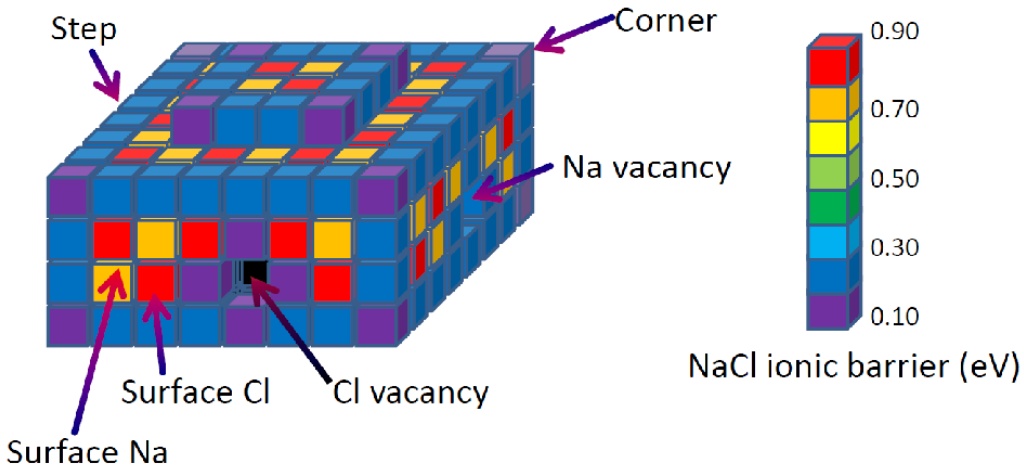
After the simulation, one can compute the reaction barriers. Below the barrier have been tested with different equivalent sites.



Also different surface sites can be studied. We have studied flat surface, sites near vacancy, step sites and corner sites.



The important observation is that the barriers are very different

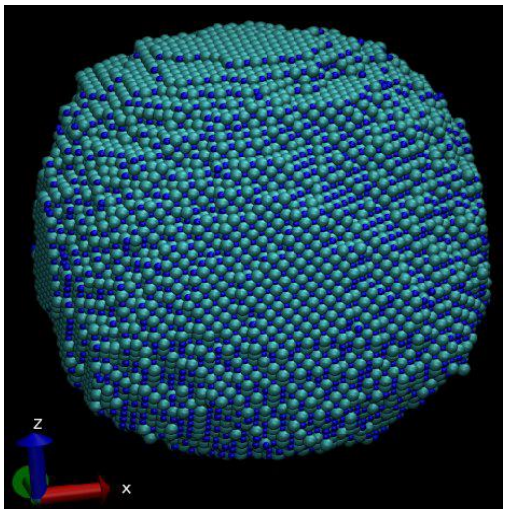


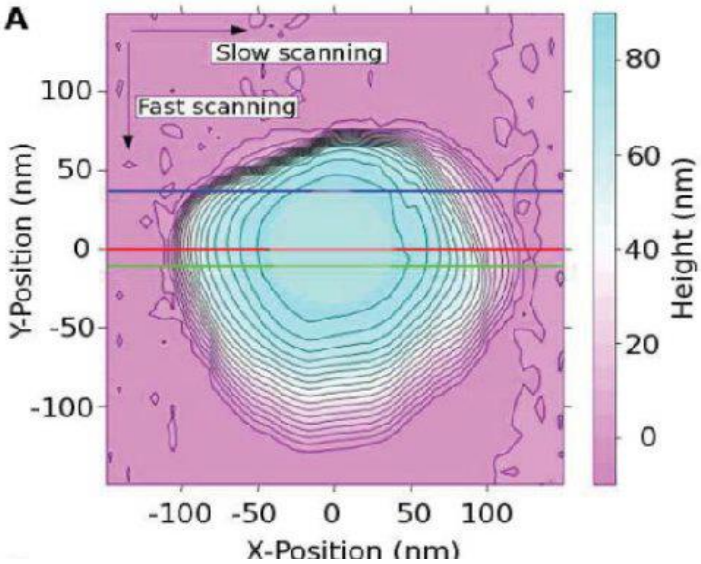
It is rather obious that the corner atoms dissociates easily and also the steps atoms dissolves much easier than surface atoms. We have also made a Kinetic Monte Carlo model for this system. With the KCM model systems of thousands of atoms can be studied.

system	Barrier (eV)	System	Barrier (eV)
Flat Cl-	0.75	Corner Cl-	0.17
Flat Na+	0.78	Corner Na+	0.05
Step Cl-	0.23	Vacancy Cl-	0.27
Step Na+	0.26	Vacancy Na+	0.10

The KCM predict that cube of NaCl will become round. On the left there is the simulation result and on the right an experimental picture of the NaCl particle in humid atmosphere. The structure is same but the size is different (simulation 14 nm and exp 160 nm)

(Exp: A. Bruzewicz, A. Checco, B. M. Ocko, E. R. Lewis, R. L. McGraw and S. E. Schwartz, JCP 134 (2011) 2011)

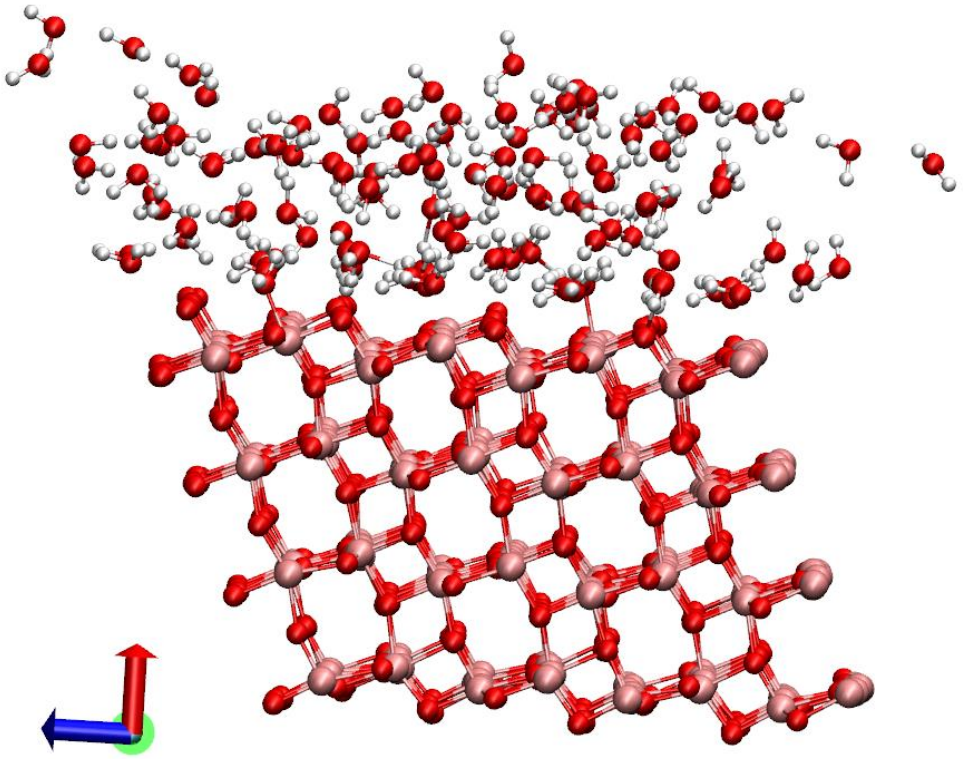




D=14 nm

TiO2 – water interphase has been modelled

We study a collection of water molecules interacting with a perfect TiO2(110) surface using *ab initio* molecular dynamics simulations. No water dissociation is observed. When we zoom in on the interface zone we see that water molecules can jump away from the first layer and go into the second layer. More details can be found in Liu *et al*, *Phys. Rev. B.* **82**, 161415(R) (2010)



Electrochemical modelling

Another very interesting field of water solid interphase modelling is the modelling of electrochemical reactions. The reactions are relatively “easy”, like hydrogen evolution

Hydrogen evolution reaction (HER)

$2H_3O^+ + 2e^- \rightarrow H_2 + 2\,H_2O$

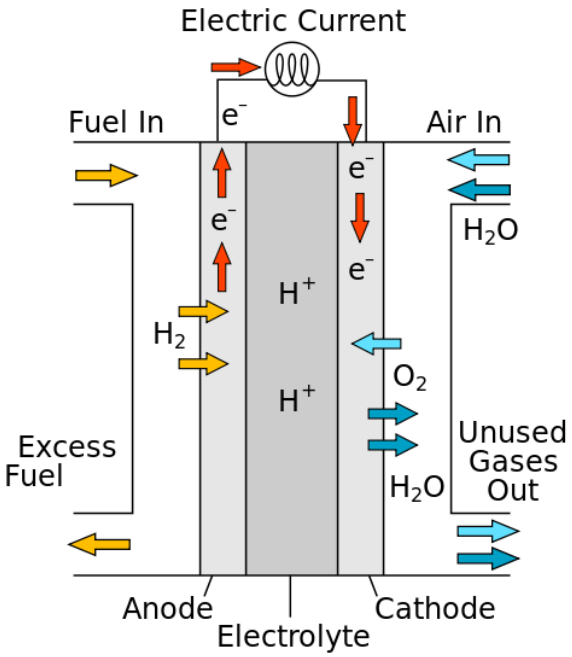
Detailed reaction

$H_3O^+ + e^- \rightarrow H^* + H_2O$ (Volmer)

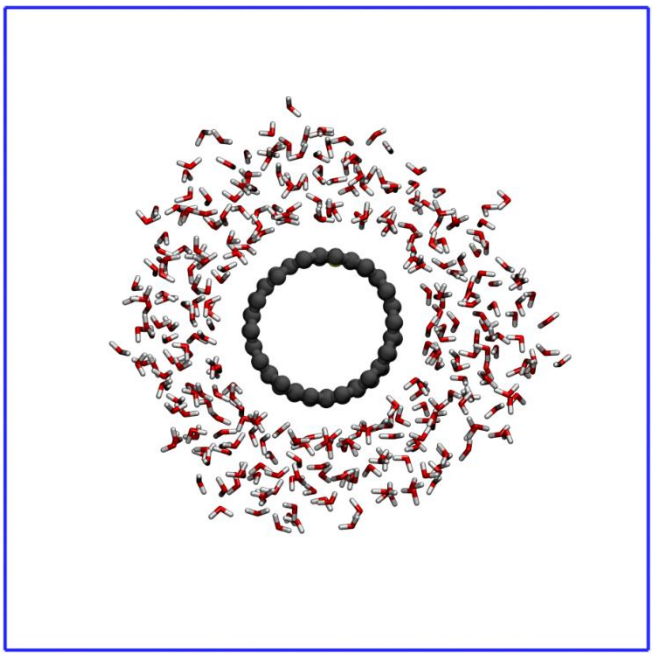
$2H^* \rightarrow H_2$ (Tafel)

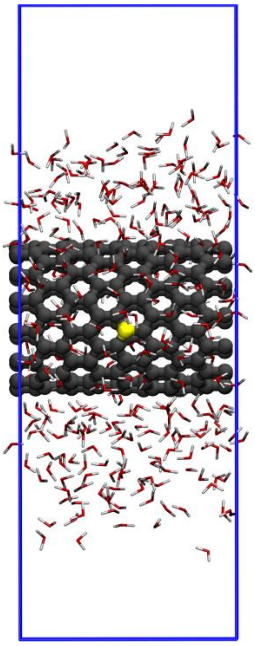
$H^* + H_3O^+ + e^- \rightarrow H_2 + 2\,H_2O$ (Heyrovsky)

(H* = H bonded to catalyst)

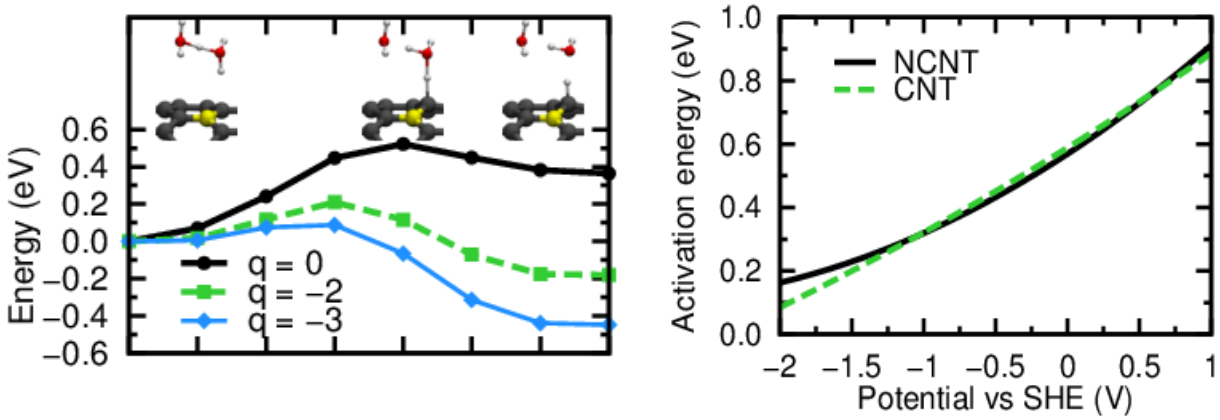


We have done some modelling with Carbon Nanotubes (CNT) as catalyst. Naturally the CNT has to be in water. Then the hydrogen reaction need to be modelled. An extra problem but the key in electrochemistry is the voltage in the system. This makes the catalyst to be charged and this has a big effect to the reactivity. The charge is easy to include to the computations (but it is not easy to find the relation between the voltage and charge). The next step is to compute the barriers with some charged systems.

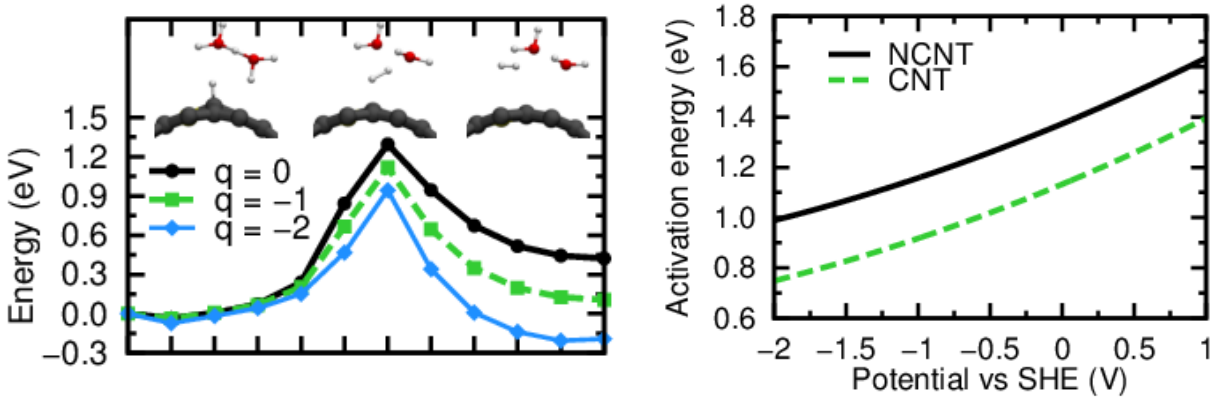




The Volmer reaction (H+(aq) + e -> H-CNT) and its activation energy. Note that the activation energy a rather smooth but sensitive function of the potential. These barriers have been done with the NEB method, where only few waters are allowed to move. The NEB method is not ideal since the results are sensitive to the choice of the flexible waters. The usage of constrained AIMD is also possible. The two systems are pure CNT and N doped CNT (NCNT)



The Heyrovsky reaction (H+(aq) + H-CNT + e -> H2 + CNT) and its activation energy. Note that the Heyrovsky barrier is much higher so the Heyrovsky reaction is the rate limiting step. The potential range is realistic since around -1.7 V water start breaking. The Heyrovsky reaction barrier is rather high so the CNT or NCNT are not good catalyst for HER. The best catalyst for HER is Pt and also that has been studied computationally.



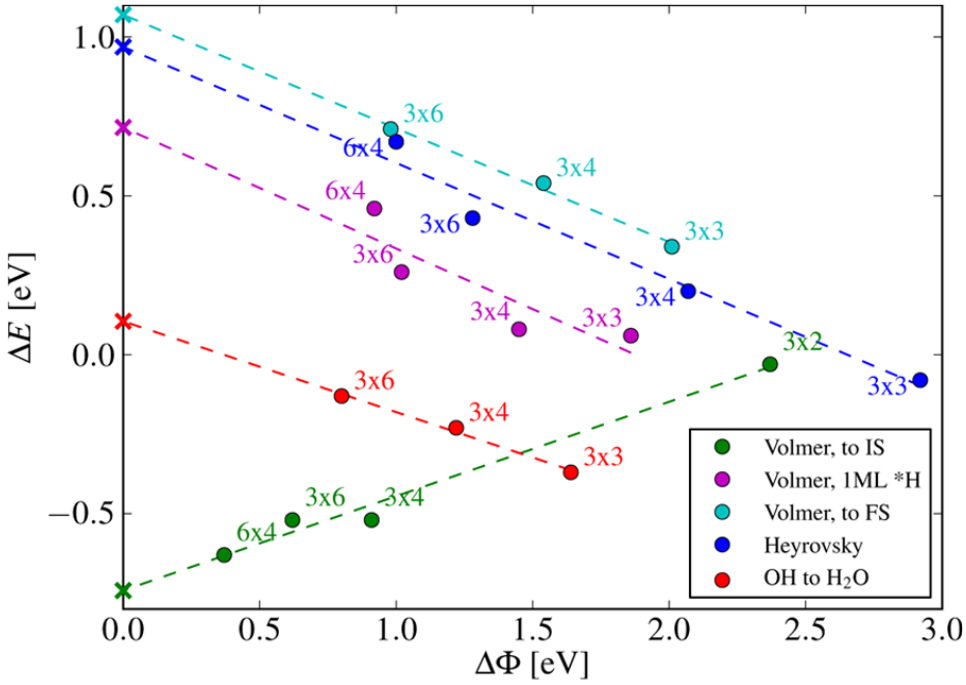
The atomic level electrochemical modelling has another challenge since there is an electron transfer eg. from H+ to the surface and this will cause a rather large charge to the electric field. The experiments are done at constant potential and the discrepancy need to be corrected.

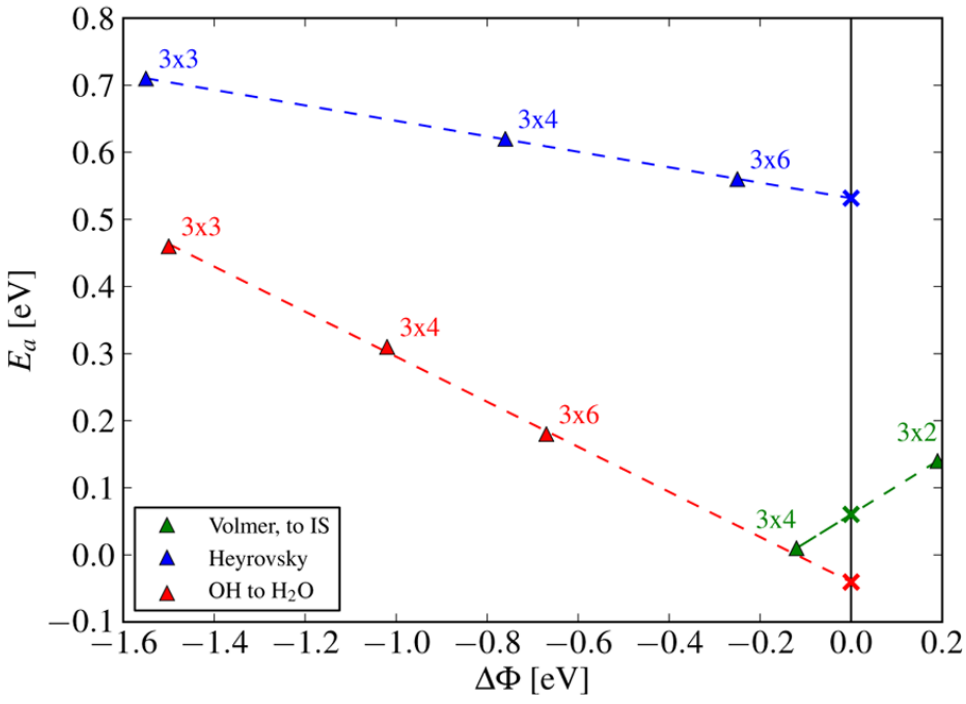
Below are some results on Pt(111) surface (From Chan and Norskov: J. Phys. Chem. Lett. 2015, 6, 2663−2668. The ΔE is the reaction energy and E_a is the reaction

barrier. The dots are computed values and the extrapolation to Δϕ=0 is done with equation (a capacitor correction)

$$E_2(\phi_1) - E_1(\phi_1) = E_2(\phi_2) - E_1(\phi_1) + \frac{1}{2}(q_2 - q_1)(\phi_2 - \phi_1)$$

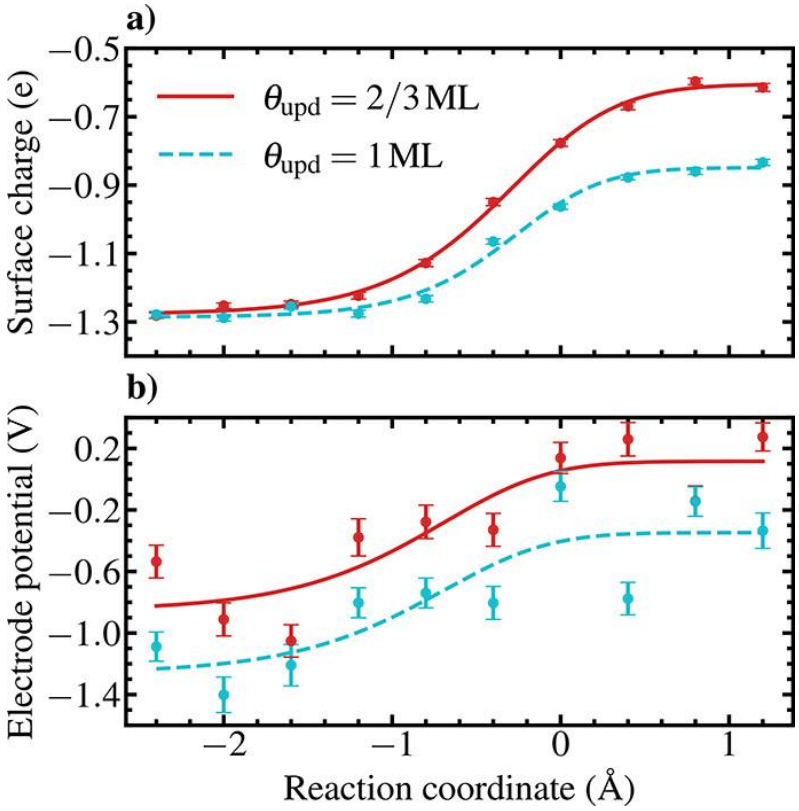
where E_1 and E_2 are the energies of interest. The ϕ is the work function of the system and q is the charge change in the system. In very big system the $\phi_2 = \phi_1$ and $q_2 = q_1$.



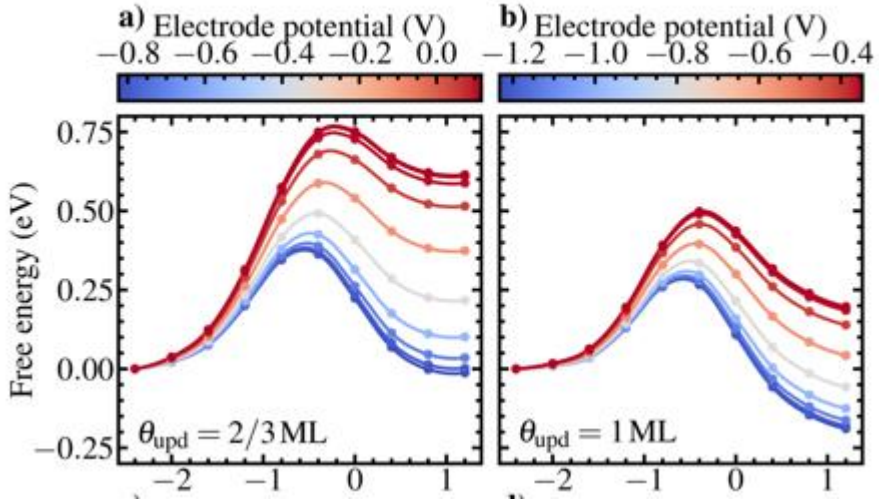


As one can see in this case the extrapolation work well. Note that the corrections are large. In real experiments, the system is very large and the applied potential is constant.

The charge and potential can be computed for any systems. Below is these values form H+ approaching Pt(111) surface (from Kronberg and Laasonen, ACS Catal. 2021, 11, 13, 8062-8078). Note that the potential is quite noisy.



This capacitor correction is important since it change the barrier and reaction energy of the hydrogen adsorption on the surface. Below is a figure



NEB vs. Constraint AIMD

As said above the NEB method can be used to study the reactions but the Thermodynamical integration method is more realistic. We have done HER reactions with NEB and Const-AIMD with doped carbon nanotubes. (From: Kronberg, Lappalainen and Laasonen, Revisiting the Volmer-Heyrovský hydrogen evolution mechanism on a nitrogen doped carbon nanotube: Constrained molecular dynamics versus the nudged elastic band method, Phys.Chem.Chem.Phys. 22, 10536-10549 (2020).)

In this example the main result is that the barriers are similar but the reaction energies are very different. This is due to the fact that the NEB started from the initial state and the final stated was not so optimal.

Table 1 Activation and reaction (free) energies of the Volmer-Heyrovský mechanism as determined using CI-NEB and constrained MD with thermodynamic integration. The margins of error of the constrained MD results correspond to 95 % confidence intervals based on standard errors obtained using block averaging and accounting for error propagation.

Method	Reaction	$E^{\ddagger}$ / $A^{\ddagger}$ (eV)	ΔE / ΔA (eV)
CI-NEB, PBE	Volmer	0.96	0.74
	Heyrovský	1.60	0.83
CI-NEB, PBE0	Volmer	1.16	0.68
	Heyrovský	1.83	0.71
Constr. MD, PBE	Volmer (restr.)	0.32 ± 0.03	-0.52 ± 0.04
	Volmer	0.73 ± 0.02	-0.08 ± 0.05
	Heyrovský	1.56 ± 0.04	-0.15 ± 0.07

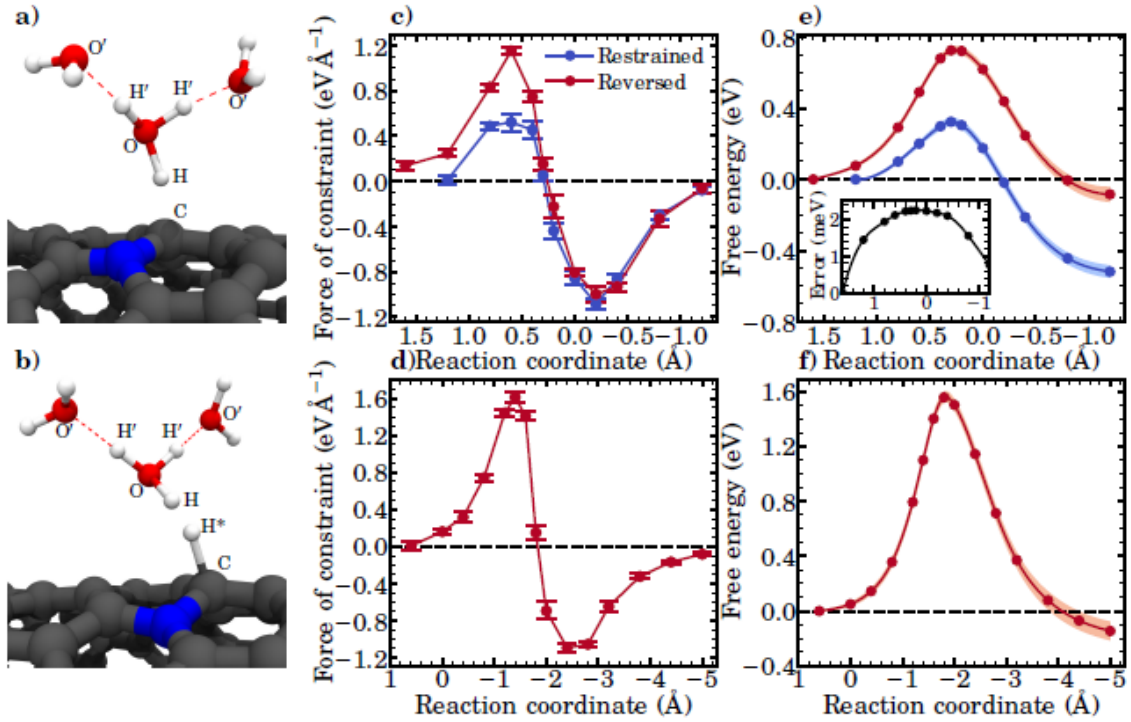
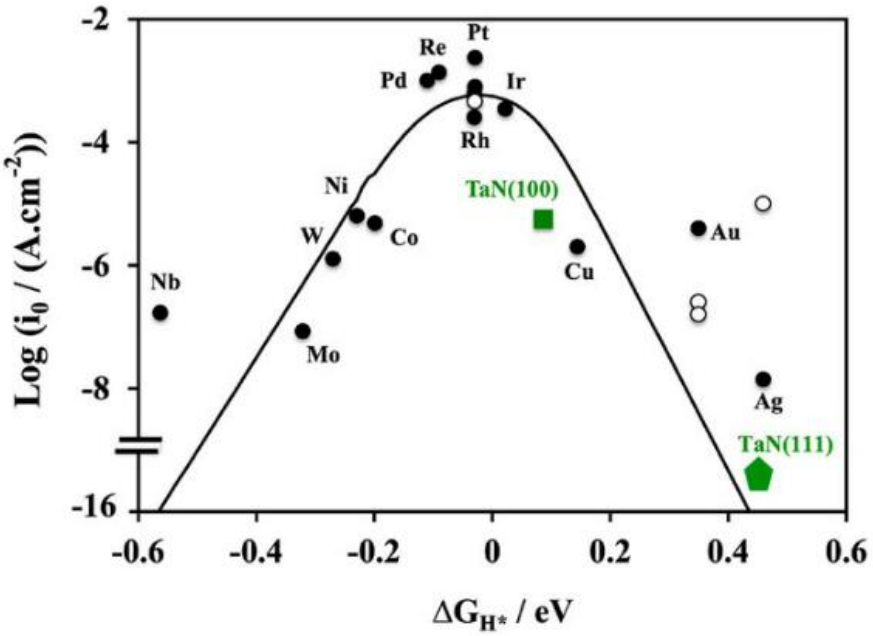


Figure 4.3. Snapshots from the constrained DFT-MD trajectories of the a) Volmer and b) Heyrovský transition states. Carbon, nitrogen, hydrogen and oxygen atoms are colored gray, blue, white and red, respectively. Most water molecules have been excluded for clarity. Forces of constraint and thereof obtained free energy profiles for the c,e) Volmer and d,f) Heyrovský reactions including margins of error at a 95 % confidence level. The effect of applying ancillary OH′ restraints to control Grotthuss shuttling is shown in c and e. The inset in e also displays the free energy error along the reversed Volmer reaction caused by using the bare Lagrange multiplier to approximate the true mean force (2.32). The legend in c applies also to panels d–f.

Fast screening of electrochemical systems

The methods above are very time consuming and faster methods are sometimes useful. We can estimate the hydrogen adsorption rate by only looking the hydrogen binding energy.



The $\Delta G_H(n)$ is

$$\Delta G_H(n) = E(n) - E(n-1) - \frac{1}{2}E(H_2) + 0.24\,eV + eU$$

where the E(n) is a system with n hydrogens, E(H2) is the energy of H2 molecules and U it the potential. This calculation does not need any barrier calculation or water thus it is very fast. It is very useful for screening and it has been used a lot (or too much).

Example: doped NiP2 surface. We have set a H atoms on different postions on NiP2 surface. Usually the first H atom binds strongly and we have need to test the second hydrogen. Green square means that there are no hydrogens in the optimal window (-0.1 – 0.1 eV), Blue square means that there are 1-2 hydrogens in the optimal window.

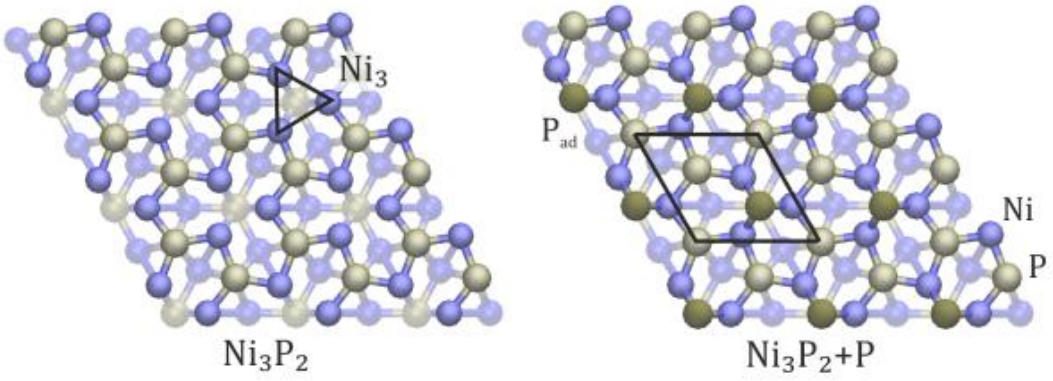


Figure 1: A surface representation of the Ni_3P_2 and Ni_3P_2+P terminations of Ni_2P. In this and all remaining figures, the hydrogen atoms are indicated by white, the phosphorus atoms by yellow-brown, the Ni atoms by deep blue, and the metal atoms by teal. The pshophorus adatom is marked by P_{ad}.

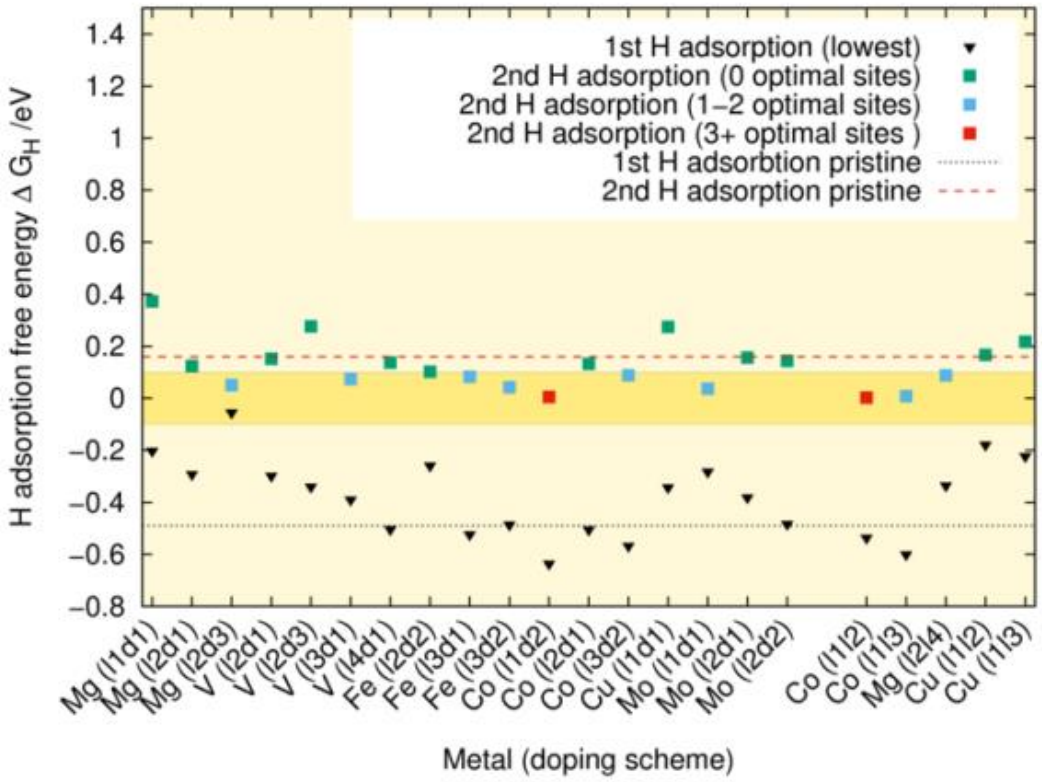


Figure 5: Hydrogen adsorption free energies (ΔG_H) for Mg-, V-, Fe-, Co-, Cu-, and Mo-doped Ni_3P_2 terminated Ni_2P. The triangles indicate ΔG_H values for the first hydrogen adsorption, whereas the squares signify ΔG_H values for the second hydrogen adsorption. The deep yellow band highlights the ± 0.1 eV region around the optimal $\Delta G_H = 0$ value.