Excercise : Constrained MD: H_2@TiO_2 [110]

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Constrained MD: Adsorption of H_2O on TiO_2 [110]

general remarks (1)

- this excercise consists of 3 steps which unfold if you untar the file h2o_on_tio2.tgz
  `tar zxvf h2o_on_tio2.tgz`
  1. $\longrightarrow$ std_relaxation: geometry relaxation using Hellmann-Feynman forces and a conjugate gradient algorithm
  2. $\longrightarrow$ constrMD_microcanonical: constrained MD (fixing the geometry of the water molecule) in a microcanonical emsemble (i.e. without coupling to the thermostat):
  3. $\longrightarrow$ constrMD_canonical: constrained MD (fixing the geometry of the water molecule) in a canonical emsemble
- while the geometry of the H_2O molecule slightly changes using standard relaxation, the input geometry (d_{O-H} and $\angle$ HOH) is enforced to be kept fixed using the constrained MD method

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general remarks (2)

for all calculations of this excercise, use:

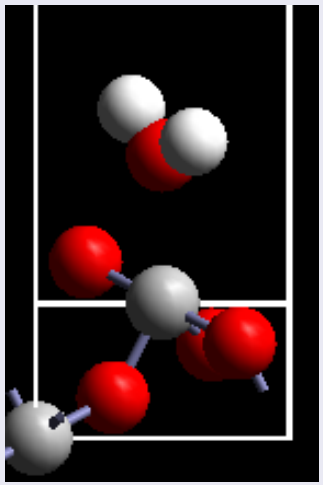
- PAW-PBE pseudopotentials (`potpaw_PBE_54.tar.gz`)
- an orthorhombic unit cell with vacuum width of 11.82Å and the same starting configuration:
  - H_2O is placed 3.18Åabove the surface Ti atom
  - the d_{O-H} is slightly elongated (1.03Å instead of 0.97Å),
  - $\angle$ is sightly increased as well (102.21° instead of 102.18°) to show the effects of constraint vs. relaxation)
- the bottom layer of the TiO_2 slab is kept fixed to account for the small slab thickness and to reduce the computing time.
- a $5 \times 5 \times 1$ Monkhurst-Pack k-mesh:

Constrained MD: H_2O @ TiO_2 [110]: standard geometry relaxation

POSCAR

```
TiO2+H2O
1.00000000000000
4.61949 0.00000 0.00000
0.00000 4.61949 0.00000
0.00000 0.00000 14.7788
Ti O H
2 5 2
Selective
Direct
0.00000 0.00000 0.00000 F F F
0.50000 0.50000 0.10000 T T T
0.30374 0.30374 0.00000 F F F
0.69625 0.69625 0.00000 F F F
0.19625 0.80374 0.10000 T T T
0.80374 0.19625 0.10000 T T T
0.50000 0.50000 0.31500 T T T
0.37720 0.62280 0.35881 T T T
0.62280 0.37720 0.35881 T T T
```

Input Geometry for all runs



- use Selective dynamics
- fix the position of bottom layer of the slab `F F F`
- positions of the H_2O atoms (atoms # 7, 8, 9)

Adsorption of H_2O on TiO_2 [110]: standard relaxation

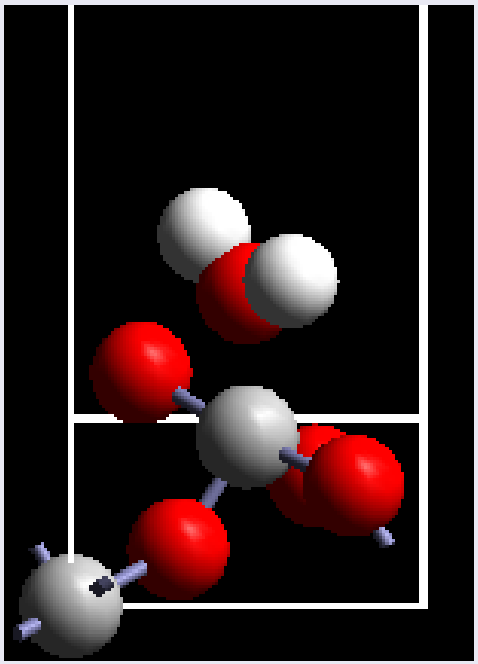
INCAR

```
SYSTEM = H2O_TiO2
ENMAX = 400
ISMEAR = 2
SIGMA = 0.05
EDIFF = 1e-6
EDIFFG = -0.05
IBRION = 2
POTIM = 0.5
NSW = 200
```

standard relaxation

- E_{cutoff}: default value
- max. force on the relaxed atoms: 0.05 eV/AA
- BZ integration: MP
- ionic relaxation: CG-algorithm

relaxed structure



d_{Ti-O}	2.23Å
d_{O-H}	0.97Å
$\angle$ HOH	111.8°

- H_2O remains upright
- no rotation
- $\angle$ HOH is increased by 9.6°
- d_{O-H} adopts its equilibrium value

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- all MDs run for 100 steps (100 fs), to keep the run-time at a reasonable level. This is not sufficient to reach equilibration
- VASP has to be compiled with -Dtbdyn

ICONST

```
R 7 8 0
R 7 9 0
A 8 7 9 0
```

- in the file `ICONST` the constraints to the system are defined:
- `R` fix d_{O-H} of H_2O
- `A` fix the HOH bond angle
- `0` 'status': 0 indicates a constraint to the atoms

Constrained MD: Adsorption of H_2O on TiO_2 [110]

INCAR

```
SYSTEM = H2O_TiO2
ENMAX = 400
ISMEAR = 2
SIGMA = 0.05
ISMEAR = 0
EDIFF = 1e-6
EDIFFG = -0.05
IBRION = 0
POTIM = 1.
MDALGO = 1
ANDERSEN_PROB = 0.9
TEBEG = 10; TEEND = 10
NSW = 100
```

- IBRION = 0: use MD
- POTIM = 1: step size: 1fs
- MDALGO = 1: use the Andersen Thermostat
- ANDERSEN_PROB = 0.9A collision probability with the thermostat canonical ensemble
- ANDERSEN_PROB =0.0 for microcanonical ensembles
- NSW run-time of the MD: 100 fs

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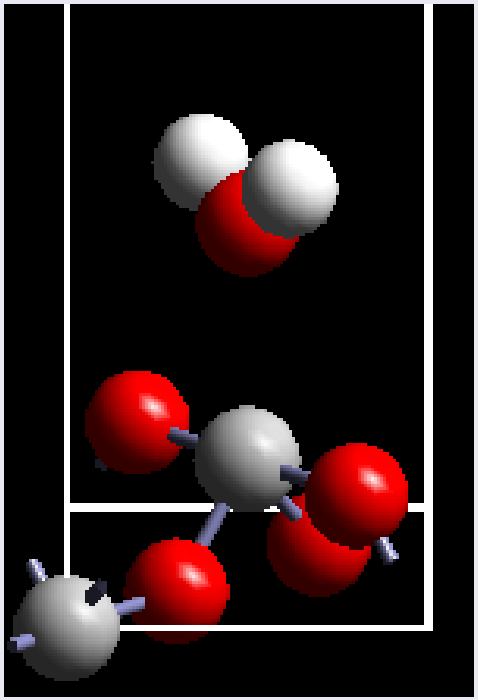
REPORT

- for all advanced MD runs, VASP writes all MD-related output to a file REPORT:
- the used Thermostat
- the number of steps to reach convergence of the SHAKE algorithm
- the constraint variables
- E_{tot} and the contributions of E_{pot}, E_{kin} and E_{const}
- T

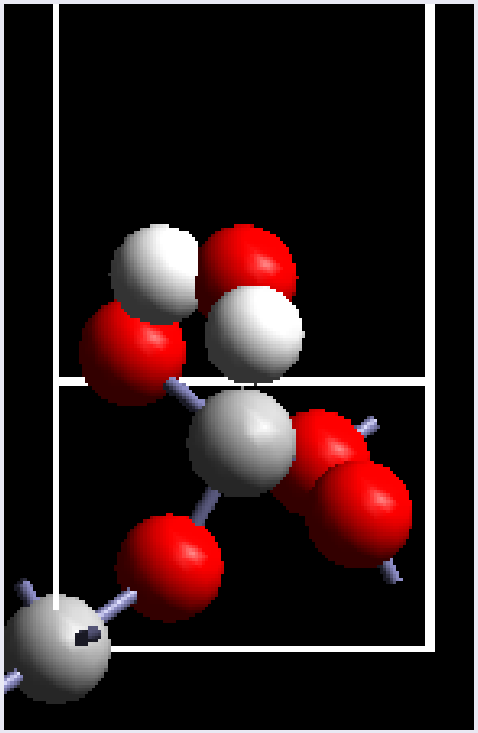
canonical ensemble: snapshot after 100 steps



d_{Ti-O}	3.19Å
d_{O-H}	1.03Å
$\angle$ HOH	102.2°

- H_2O remains upright
- slight rotation around z
- due to the low T (10K), the geometry is almost unchanged: H_2O is still at a large distance to the slab, therefore there are almost no changes in the the TiO_2 surface layer

microcanonical ensemble: snapshot after 100 steps



d_{Ti-O}	3.12Å
d_{O-H}	1.03Å
$\angle$ HOH	102.21°

- due the conservation of the total energy of the system, the decrase of E_{pot} leads to an increase of E_{kin} and hence an increase of T ($T = \frac{1}{3k_B TN_{ions}} \sum_{i=1}^{N(ions)} E_{kin}(i)$)
- H_2O tilts (almost parallel to the surface)
- the surface layer is pushed inwards