Metal Oxidation

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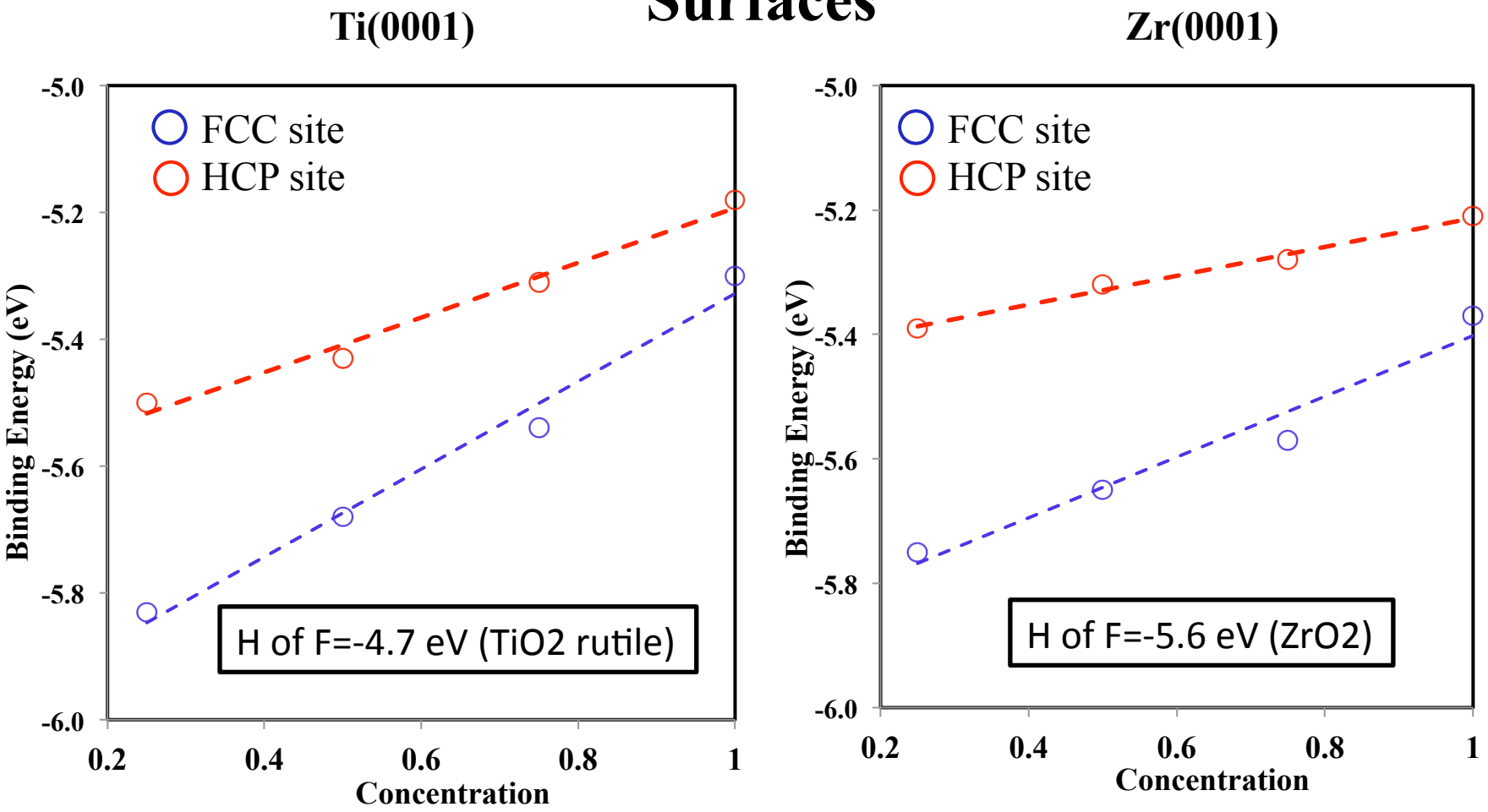
Thursday Nov 19, 2012

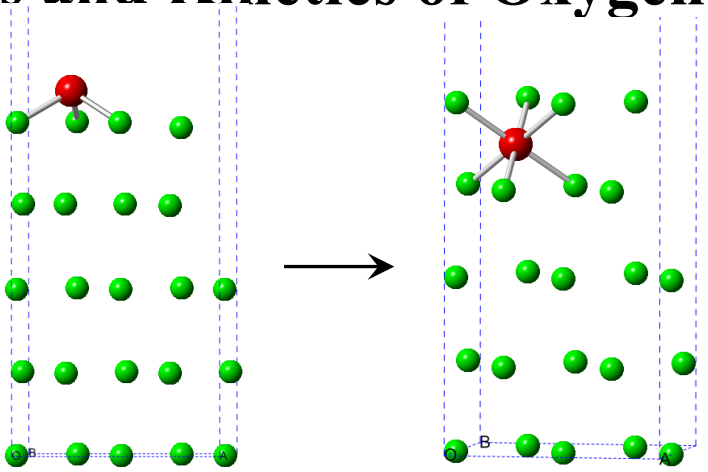
CALTECH-INTEL

Oxygen Binding Energy of Ti(0001) and Zr(0001) Surfaces



Surface coverage

The Effect of Surface Oxygen Concentration on the Thermodynamics and Kinetics of Oxygen Penetration (Zr)



Concentration	Reactant	TS	Product (unit: eV)
25 %	0.0		0.68
50 %	0.0	~1.9	0.39
75 %	0.0	~1.5	0.06
100 %	0.0	~1.0	-0.65

Thermodynamically unfavorable for O to penetrate below 100%

Will look at additional layers below the surface

eFF Effective Core Potentials (ECP)

eFF-ECP describes core-valence Pauli interaction, proportional to the overlap between two wave-packets,

$$E_{core-val} \propto S^2$$

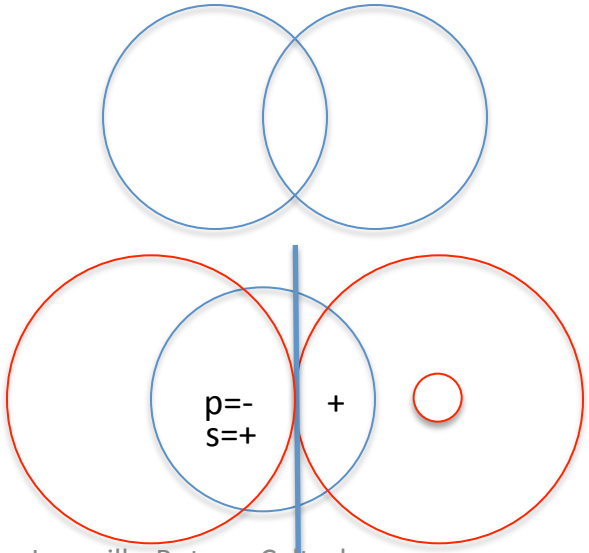
Two types of ECPs developed (and supported in LAMMPS):

1. s-s overlap (e.g. Na, C, Al, Si) – 3 parameters

$$E = a\,exp\left(-\frac{br^2}{c+s^2}\right)$$

2. s-p overlap (e.g. C, N, O) – 6 parameters

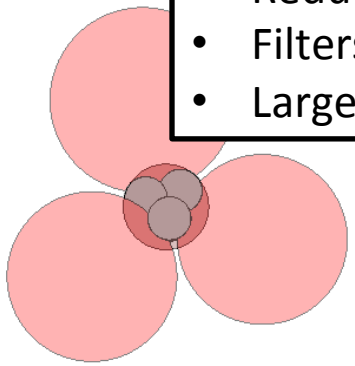
$$E = a\left(\frac{2}{b/s+s/b}\right)\left(r-cs\right)^2 exp\left[-\frac{d\left(r-cs\right)^2}{e+s^2}\right]$$

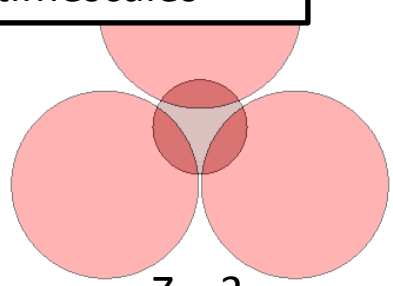


eFF-ECP e.g. atom representations

- Reduced number of DOF
- Filters high-frequency core vibrations
- Larger systems and longer timescales

Aluminum





Aluminum core pseudoparticle with valence electrons

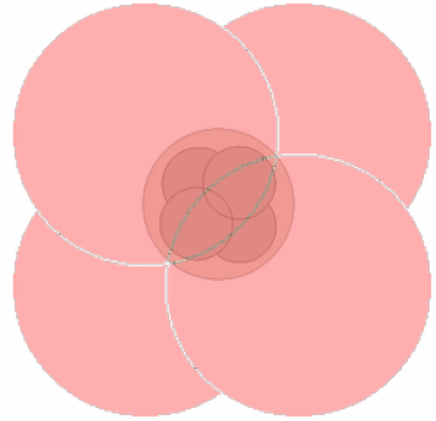
Z = 13

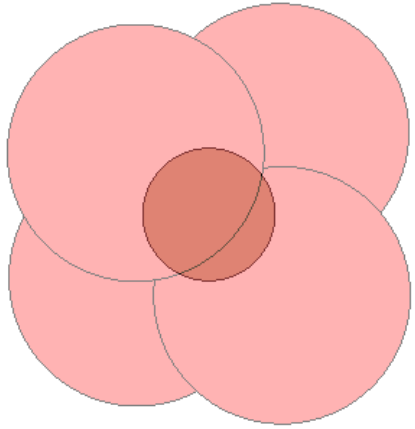
Core+Valence: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

Z = 3

Valence: $3s^2\ 3p^1$ (4 particles per Al)

Silicon





Silicon core pseudoparticle with valence electrons

Z = 14

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

15 particles per Si!

Z = 4

$3s^2\ 3p^2$ (5 particles per Si)

Si eFF-ECP Pseudopotentials

$$E_{core-elec} = \sum_{i,j} \frac{Z_i Z_j}{R_{ij}} Erf\left(\frac{\sqrt{2} R_{ij}}{\sqrt{s_{core,i}^2 + s_{elec,j}^2}} \right)$$

$$E_{core-core} = \sum_{i<j} \frac{Z_i Z_j}{R_{ij}} Erf\left(\frac{\sqrt{2} R_{ij}}{\sqrt{s_{core,i}^2 + s_{core,j}^2}} \right)$$

$$E_{core-nuc} = \sum_{i,j} \frac{Z_i Z_j}{R_{ij}} Erf\left(\frac{\sqrt{2} R_{ij}}{\sqrt{s_{core,j}^2}} \right)$$

$$E_{Pauli_{SS}} = a\, Exp\left(\frac{-b\, r^2}{c + s^2} \right)$$

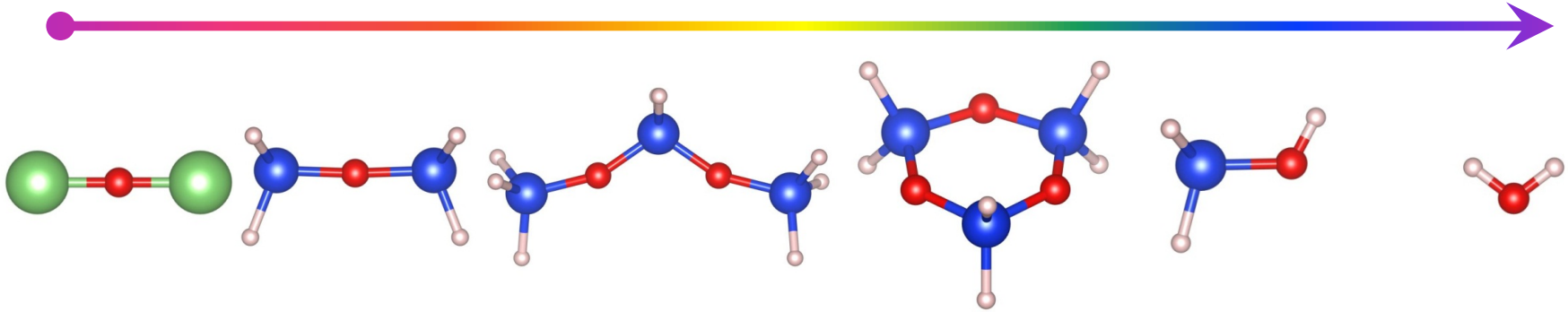
$$E_{Pauli_{SP}} = a\left(\frac{2}{b/s + s/b} \right)(r - cs)^2 \exp\left[-\frac{d(r - cs)^2}{e + s^2} \right]$$

Multicore interactions supported

- SS-SS
- SS-SP
- SP-SP

O-ECP in lone pairs with ionic vs. covalent bonding

From ionic to covalent bonds



Li_2O	$H_3Si\text{-}O\text{-}SiH_3$	$H_3Si\text{-}O\text{-}SiH_2\text{-}O\text{-}SiH_3$	$(O\text{-}SiH_2)_3$	SiH_3OH	H_2O
(<Li-O-Li = 180°)	(<Si-O-Si = 177.9°)	(<Si-O-Si = 158.5°)	(<Si-O-H = 131.7°)	(<Si-O-H = 119.2°)	(<H-O-H = 104.5°)
eFF-ECP: 180°	eFF-ECP: 179.8°	eFF-ECP: 158.0°	eFF-ECP: 121.1°	eFF-ECP: 115.7°	eFF-ECP: 104.6°

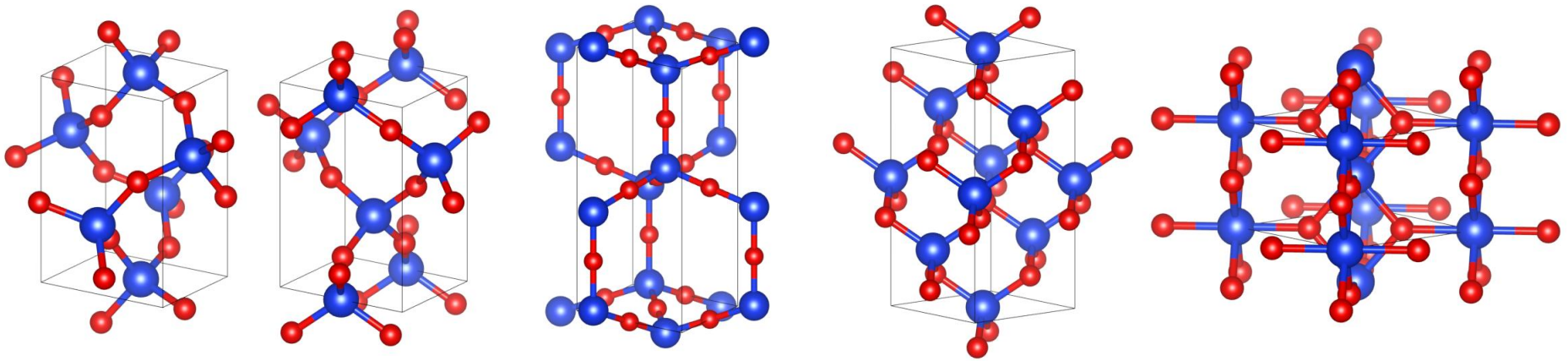
Decreasing Oxygen-centered angle increases covalent bonding (larger repulsion with lone pairs). Focus of ECP is on geometries (angles and bond lengths).

bond length (pm)	Li_2O	$H_3Si\text{-}O\text{-}SiH_3$	$H_3Si\text{-}O\text{-}SiH_2\text{-}O\text{-}SiH_3$	$(O\text{-}SiH_2)_3$	SiH_3OH	H_2O
bond type	Li-O	Si-O	Si-O	Si-O	Si-O	H-O
Expt.	161.0	163.7	164.4/163.5	165.9	165.9	96.1
eFF-ECP	163.2	165.4	165.0/165.2	171.6	167.3	127.4

O-ECP flexibility of Si-O-Si angle in SiO_2

$$(\alpha\text{-quartz} \xrightarrow{846\ K} \beta\text{-quartz} \xrightarrow{1140\ K} \beta\text{-tridymite} \xrightarrow{2010\ K} \beta\text{-cristobalite}) \xrightarrow{7.5\sim8.5\ GPa} \text{stishovite}$$

Ground state



140.2°	**150.3°**	**180.0°**	**106.3°**	**98.4°/130.8°**
129.3°	**139.0°**	**179.8°**	**98.6°**	**99.9°/130.0°**

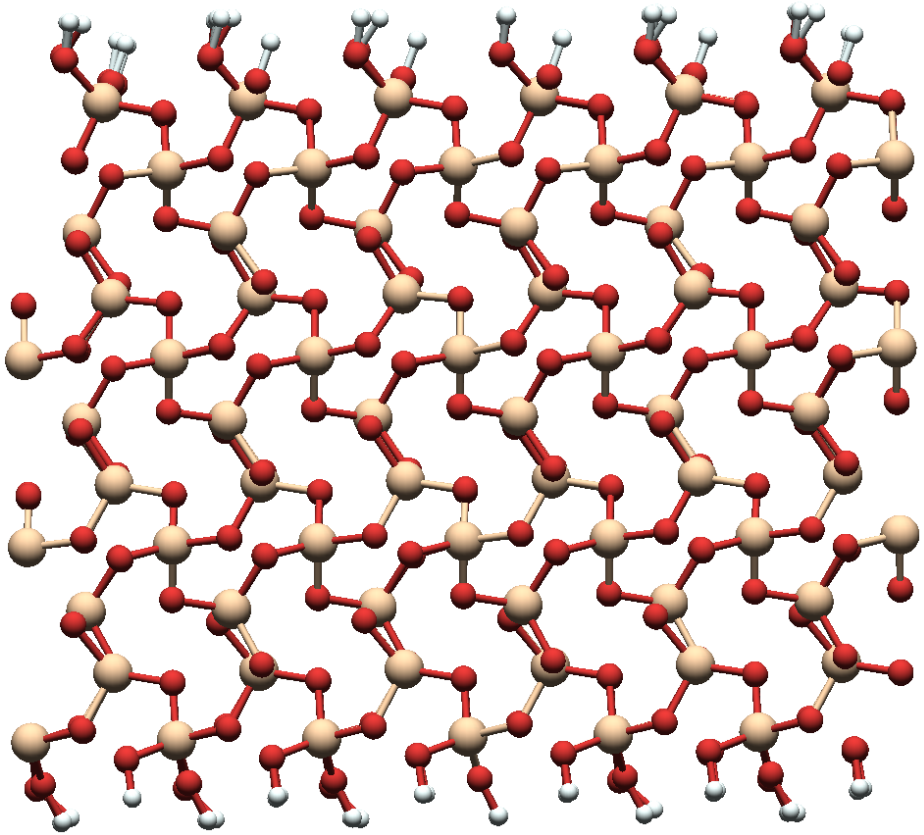
Si-O-Si angle from **PBE** and **eFF-ECP**

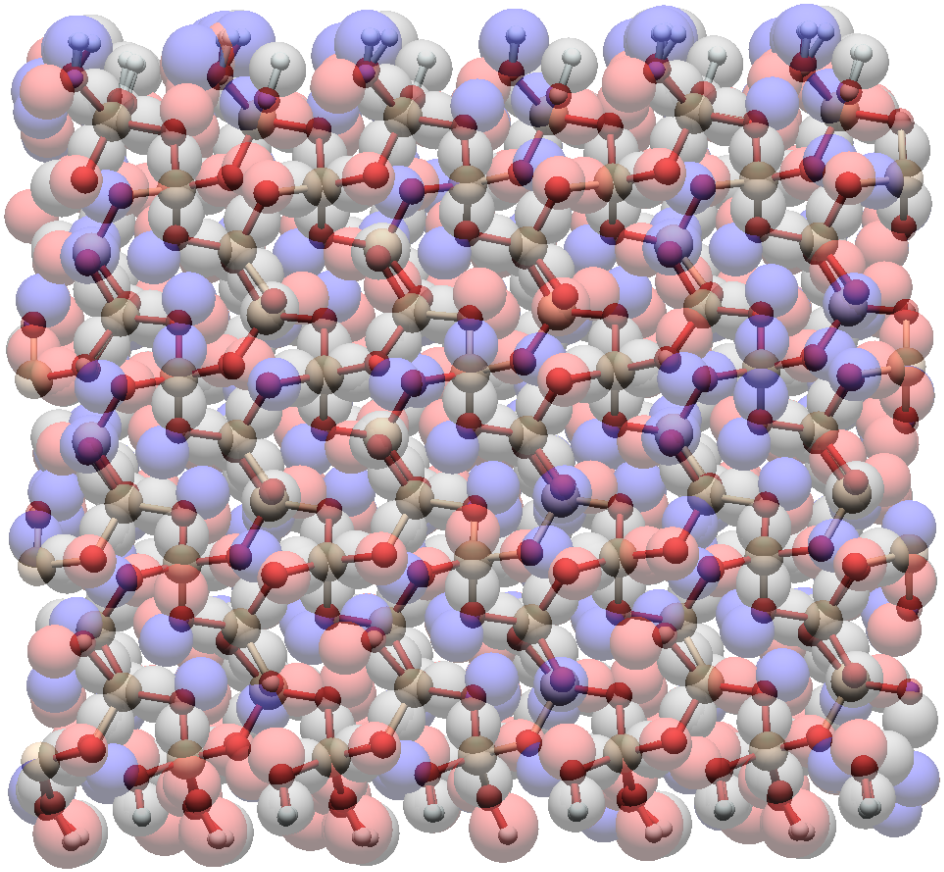
Si-O bonds in silica possess mixed ionic and covalent nature, and cause a wide range of Si-O-Si angles adopted in various phases. eFF-ECP is able to capture such subtle changes, which demonstrates its capability of describing lone pairs.

Silica Slab Equilibration at 300 K

- Alpha-quartz (001) surface was used, with hydrogen saturating all dangling bonds at both surfaces (oxygen terminated).
- The slab was constructed with dimensions of 46.3 x 48.1 x 42.5 Bohr (the last value is the thickness), with z direction non-periodic and of vacuum.
- Currently we are running nvt equilibration at 300 K (for ~0.1 ps), and the structure is stable.

Snapshot of Silica Slab at 300 K





Next

- Kinetic rates as a function of surface/layer coverage, for both Ti and Zr
- Dynamics with ReaxFF on Ti and Zr oxidation
- kMC approach
- SiO2 dielectric breakdown