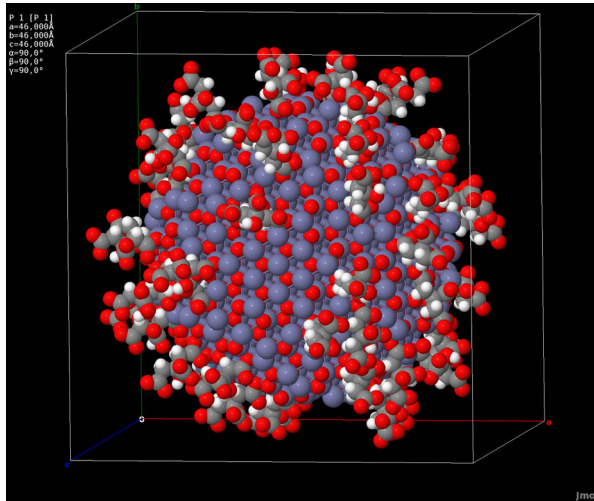
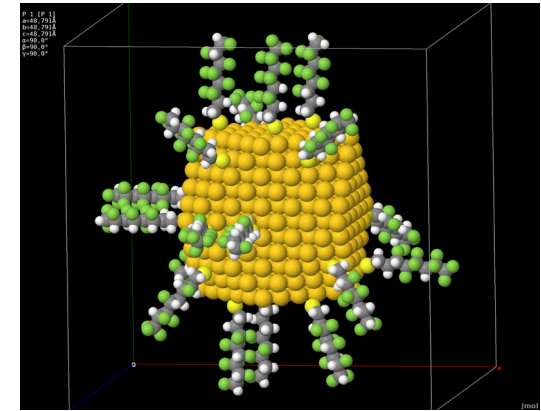


tutorial session XIV

Surface decoration



ZnO
with organic ligand



Gold cuboctahedron
with organic ligands



Goal: cover nanoparticle surface with ligand molecules

Concept:
Build a (general shaped) nanoparticle
(Repair surface)
Decorate surface

Tools

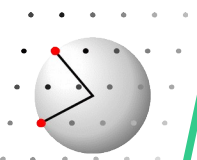
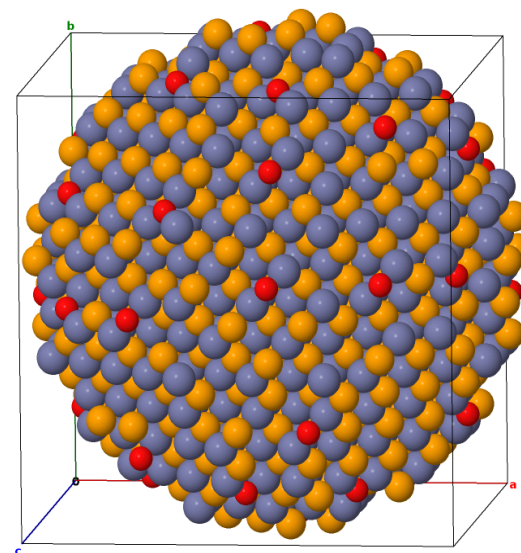
Read menu build a regularly shaped object
(Modify internal structure)

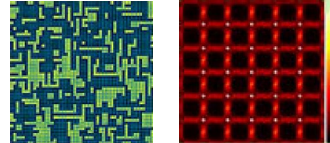
Surface menu builds an **active** surface

Property menu allows to choose **selectively**
needed to **repair**

Decorate menu offers seven attachment scenarios

Lots of internal calculations behind the scenes

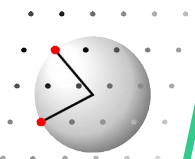
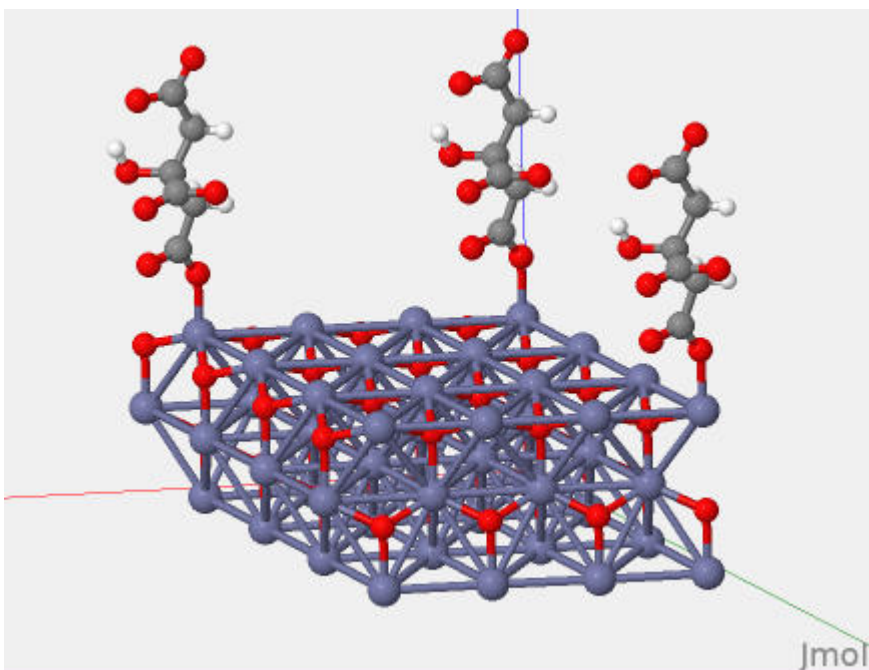


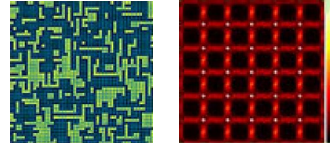


Start discus_suite

Select directory Lectures\14.Decoration\Deco_01

```
suite> @combined.mac zno, flat, normal
```





Surface decoration



```
#
read
    cell CELL/zno.cell,4, 4, 2
#
surface
    set distance,  external, all, 0.55
    boundary hkl, 0, 0, 1, 0.50
exit
purge
#
decorate
    reset
    add citric, normal
    set citric, ligand, CELL/citric.stru, 0.015
    set citric, bond,   Zn,  1,  2.00
    set citric, axis,   3,  16
    set citric, form,   0 , 0, 1
    show
    run
exit
```

Build a ZnO block

**Cut a (001) surface at 0.5Å from origin.
Atoms with 0.55Å are flagged as surface.**

Start decorate menu, reset to default

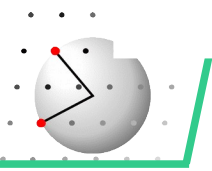
**A scheme „citric“ with the ligand in
„normal“ position is started**

**The actual molecule is „CELL/citric.stru“
at density ~ 0.015 mol/Å²**

**A surface „Zn“ is bonded to ligand atom 1
at distance 2.00Å**

**Ligand atoms 3 and 16 form an axis
that is normal to surface**

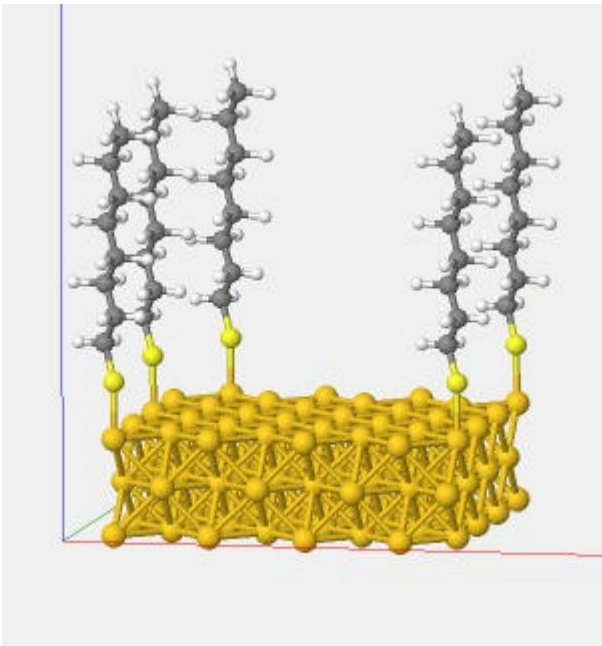
**The decoration is limited to the
{ 0 0 1 } surface**



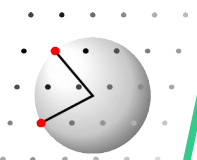
„Normal“ mode

suite> **@combined.mac gold, flat, normal**

Single bond between surface and ligand.
Bond is normal to surface.
Ligand straightened up along axis.

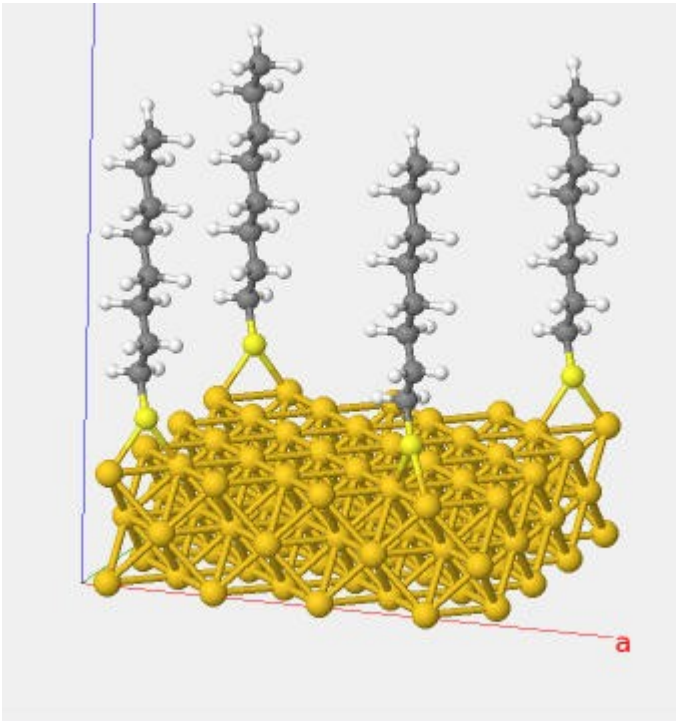


```
decorate
  reset
  add thio, normal
  set thio, ligand, CELL/ligand.stru, 0.015
  set thio, bond, Au, 1, 2.42
  set thio, axis, 2, 20
  set thio, form, 0, 0, 1
  show
  run
exit
# alternatives
decorate
# Make axis automatically
  set thio, axis, auto
# Atoms 17, 18 inherit surface property
  set thio, surface, 17, 18
# Limit to single hkl instead of form
  set thio, hkl, 0, 0, 1
exit
```



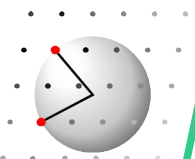
„Bridge“ mode

suite> **@combined.mac gold, flat, bridge**



Two bonds between two surface atoms
to the identical single ligand atom.
Triangle is normal to surface.
Ligand straightened up along axis.

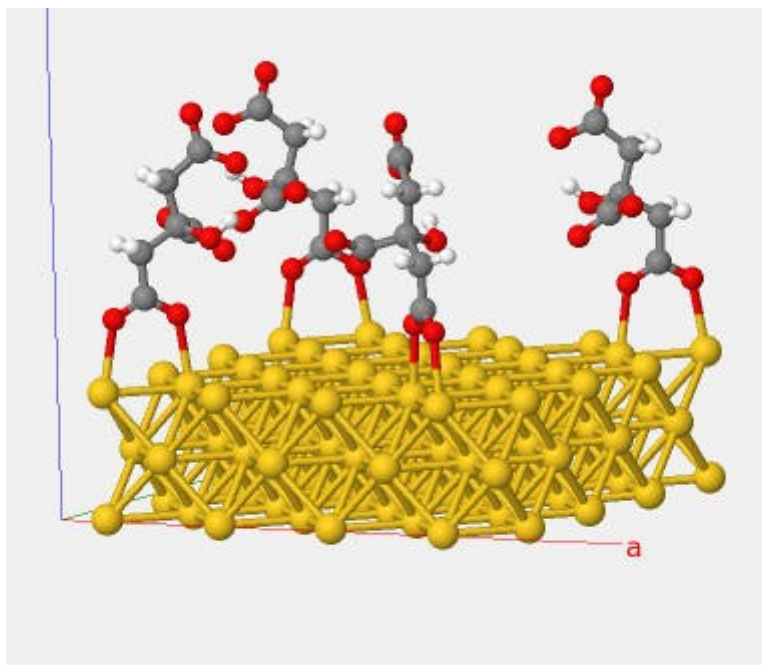
```
decorate
  reset
  add thio, bridge
  set thio, ligand, CELL/ligand.stru, 0.015
  set thio, bond, Au, 1, 2.42
  set thio, axis, 2, 20
  set thio, form, 0, 0, 1
  show
  run
exit
```





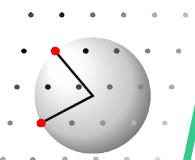
„Bridge“ mode

suite> **@combined.mac gold, flat, double**



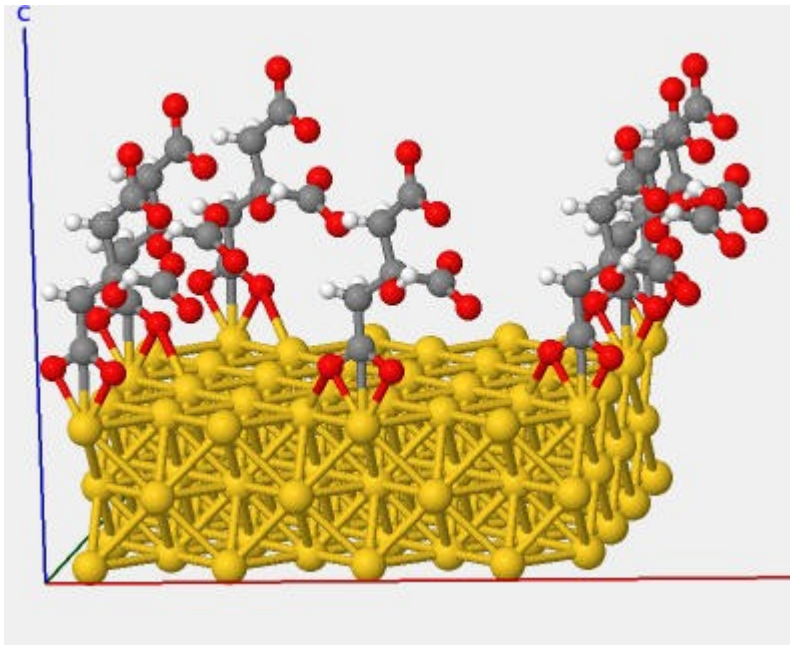
Two bonds between two surface atoms
to two different ligand atoms.
Trapezoid is normal to surface.
Ligand straightened up along axis.

```
decorate
  reset
  add citric, double
  set citric, ligand, CELL/citric.stru, 0.015
  set citric, bond, Au, 1, 2.42
  set citric, bond, Au, 1, 2.41
  set citric, axis, 3, 16
  set citric, form, 0, 0, 1
  show
  run
exit
```



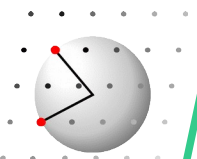
„Bridge“ mode

suite> **@combined.mac gold, flat, chelate**



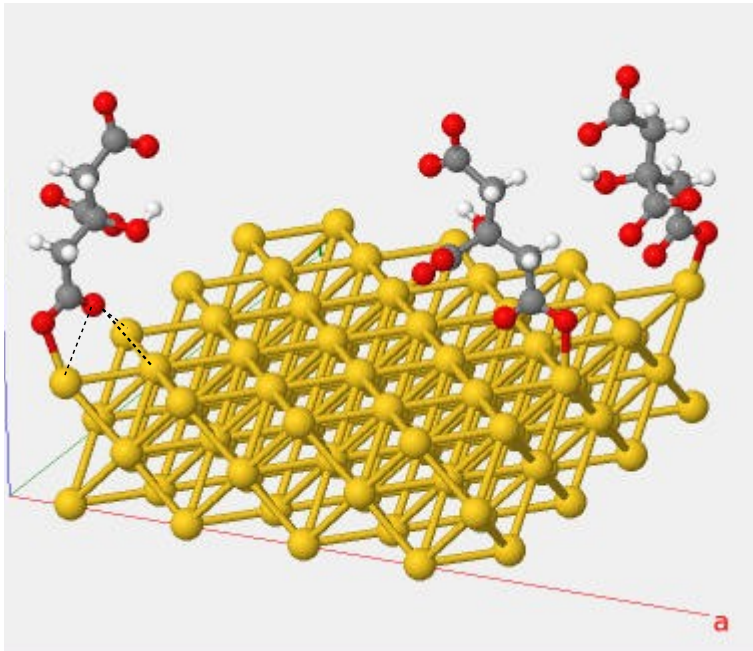
Two bonds between single surface atoms
to two different ligand atoms.
Triangle is normal to surface.
Ligand straightened up along axis.

```
decorate
reset
add citric, chelate
set citric, ligand, CELL/citric.stru, 0.015
set citric, bond, Au, 1, 2.01
set citric, bond, Au, 2, 2.01
set citric, axis, 3, 16
set citric, form, 0, 0, 1
show
run
exit
```



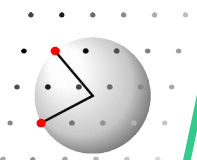
„Bridge“ mode

suite> **@combined.mac gold, flat, multi**



Several bonds between a ligand atom
to several surface atoms.
One single bond between 2nd surface atom
to a ligand atom.
Ligand straightened up along axis.

```
decorate
reset
add citric, multi
set citric, ligand, CELL/citric.stru, 0.015
set citric, bond, Au,Au,Au, 2, 2.70
set citric, bond, Au, 1, 2.00
set citric, axis, 3, 16
set citric, form, 0, 0, 1
show
run
exit
```



„Bridge“ mode

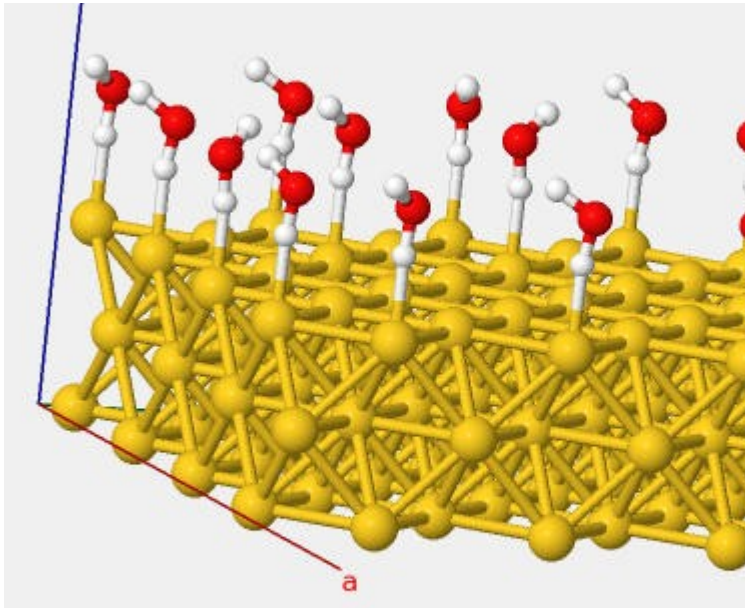
suite> **@combined.mac gold, flat, acceptor**

Surface acts as acceptor.

Ligand (H) placed normal above surface.

Approximately 165° angle in H.

Ligand rotated randomly around A..H bond



```
decorate
  reset
  add water, acceptor
  set water, ligand, CELL/water.stru, 0.045
  set water, bond, Au, 1, 1.92
  set water, form, 0, 0, 1
  set water, surface, 3
  show
  run
exit
```

„Bridge“ mode

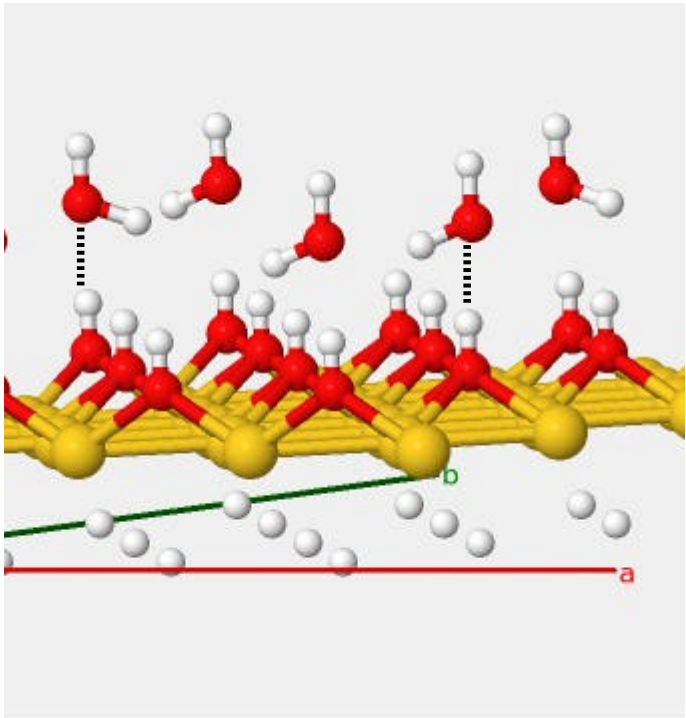
suite> **@combined.mac donor, flat, donor**

Surface acts as donor.

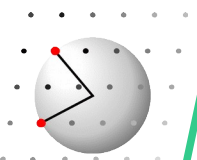
Ligand (O) placed normal above surface.

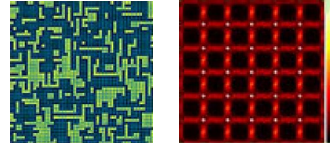
Approximately 165° angle in H.

Ligand rotated randomly around D-H bond



```
decorate
  reset
  add water, donor
  set water, ligand, CELL/water.stru, 0.045
  set water, bond, H, 1, 1.92
  set water, form, 0, 0, 1
  set water, surface, 2, 3
  show
  run
exit
```





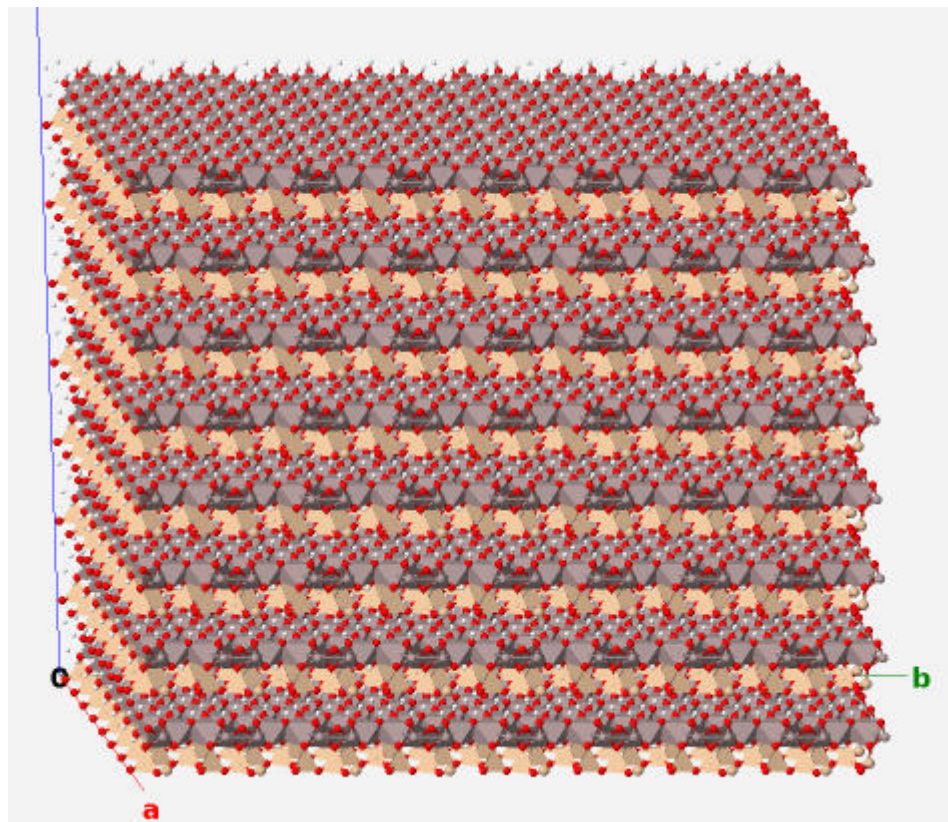
Start discus_suite

Select directory Lectures\14.Decoration\Deco_02

An 8 x 8 x 8 block of Kaolinite

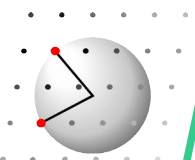
```
suite> @main.mac
```

```
----- > Waiting for <RETURN> :
```



reasonably flat surfaces

No atoms are flagged as *surface atoms*



Start discus_suite

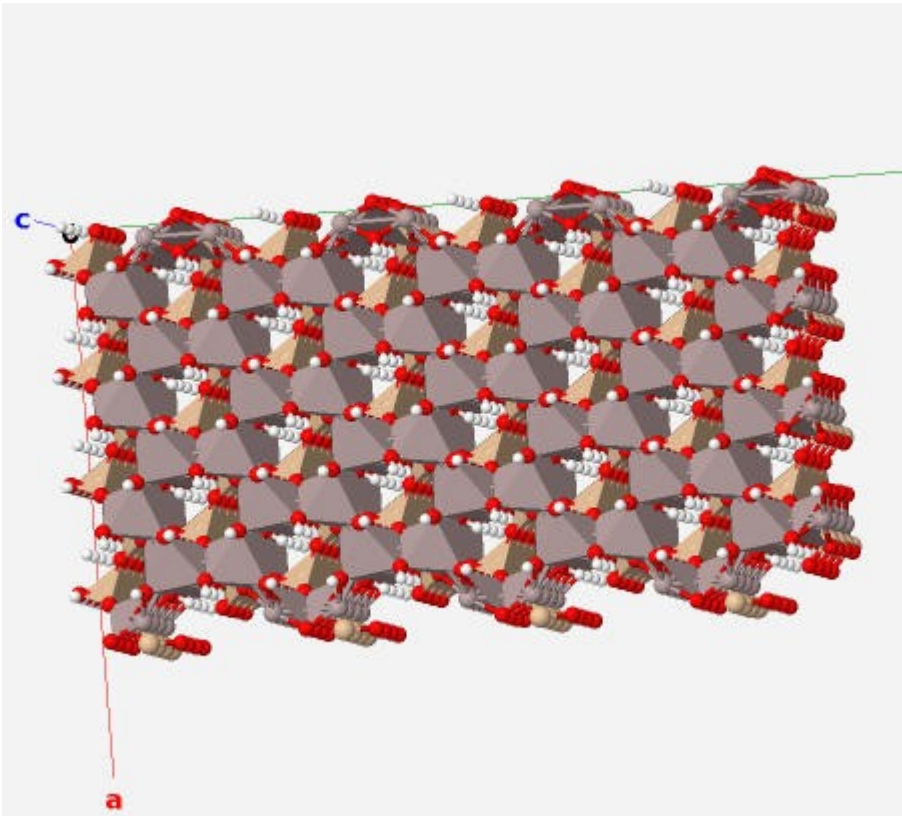
Select directory Lectures\14.Decoration\Deco_02

An 8 x 8 x 8 block of Kaolinite

Cut to ~ 4 x 4 x 4 unit cells at odd distances

```
suite> @main.mac
```

```
----- > Waiting for <RETURN> :
```



corrugated surfaces

Single / non-bonded atoms

Start discus_suite

Select directory Lectures\14.Decoration\Deco_02

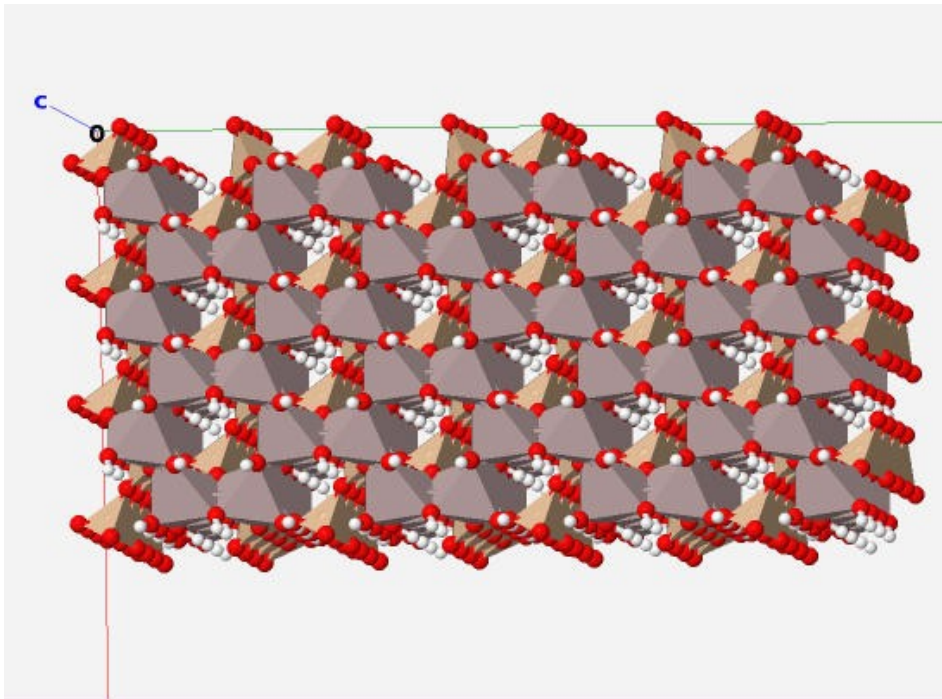
```
suite> @main.mac
```

```
----- > Waiting for <RETURN> :
```

An 8 x 8 x 8 block of Kaolinite

Cut to ~ 4 x 4 x 4 unit cells at odd distances

Applied surface repair steps



Smooth surfaces

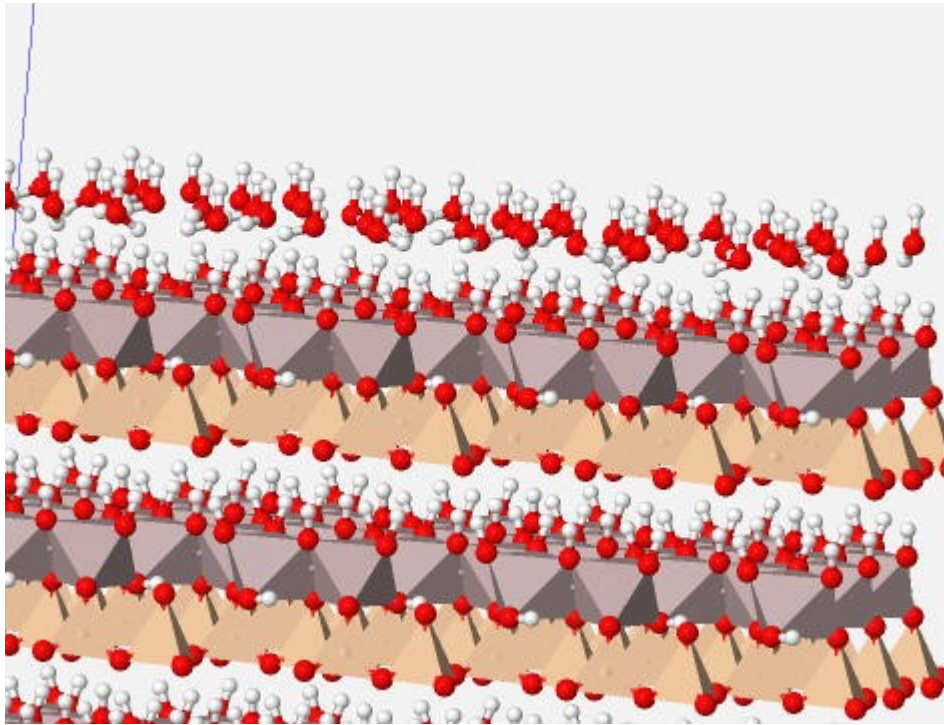
Oxygen terminated surfaces

Start discus_suite

Select directory Lectures\14.Decoration\Deco_02

```
suite> @main.mac
```

```
----- > Waiting for <RETURN> :
```



An 8 x 8 x 8 block of Kaolinite

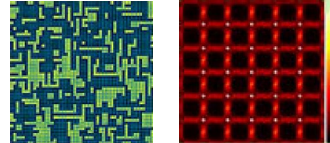
Cut to ~ 4 x 4 x 4 unit cells at odd distances

Applied surface repair steps

Decorated (001) surface with water

Surface acts as donor

Water molecules atop most
surface hydrogen atoms



Start discus_suite

Select directory Lectures\14.Decoration\Deco_02

```
suite> @main.mac
```

```
----- > Waiting for <RETURN> :
```

An 8 x 8 x 8 block of Kaolinite

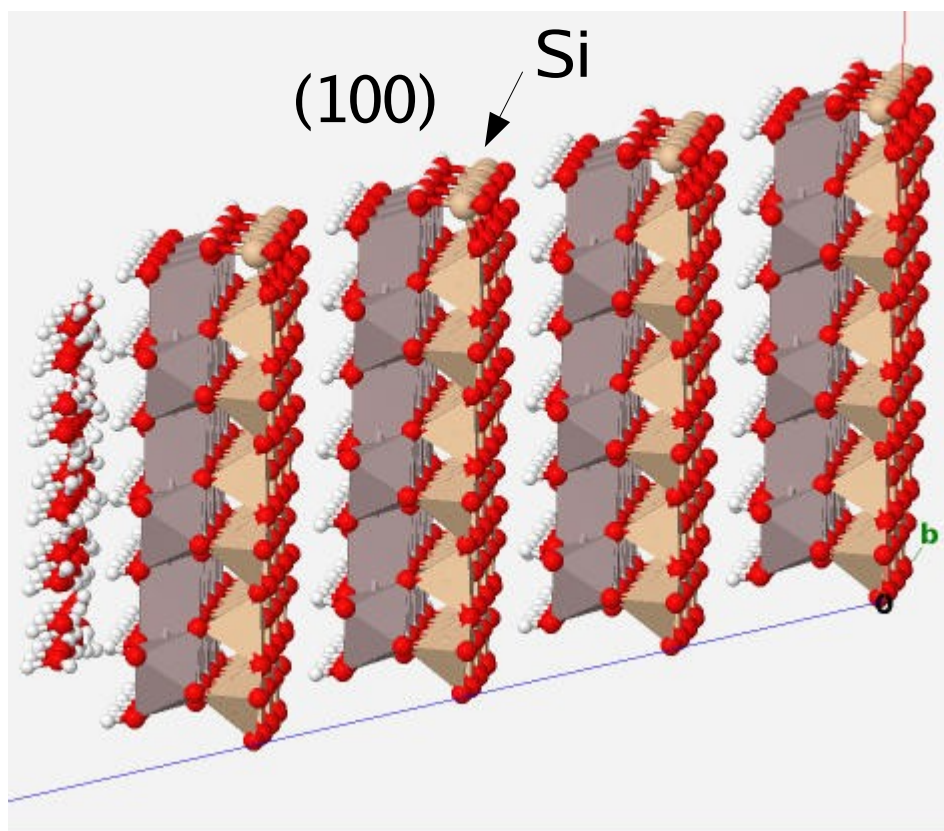
Cut to ~ 4 x 4 x 4 unit cells at odd distances

Applied surface repair steps

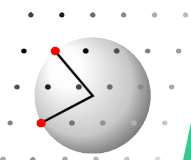
Decorated (001) surface with water

Surface acts as donor

Removed near-surface Oxygen on (100)



Silicon terminated (100)



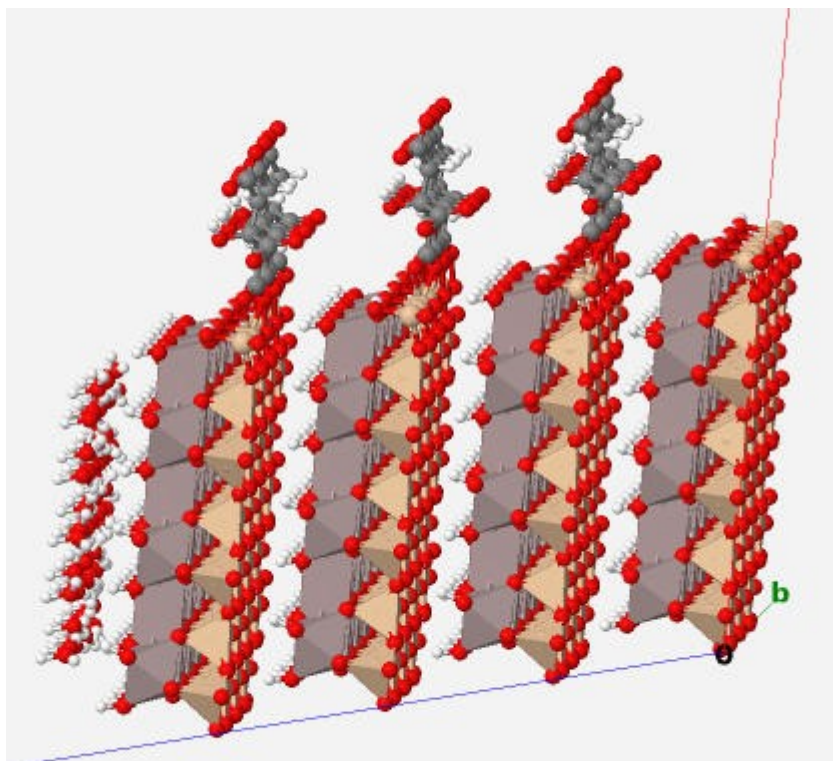


Start discus_suite

Select directory Lectures\14.Decoration\Deco_02

```
suite> @main.mac
```

```
suite>
```



An 8 x 8 x 8 block of Kaolinite

Cut to ~ 4 x 4 x 4 unit cells at odd distances

Applied surface repair steps

Decorated (001) surface with water

Surface acts as donor

Removed near-surface Oxygen on (100)

Decorated (100) surface with citric acid.

Chelate bond scheme

