Computational Materials Physics

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surface energy and work function

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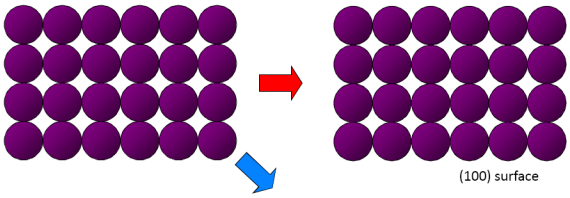
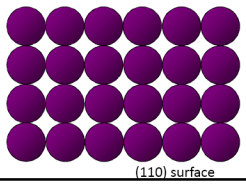
http://molmod.ugent.be
http://www.ugent.be/ea/dmse/en
my talks on Youtube: http://goo.gl/P2b1Hs

surface energy



(100) surface

It costs energy to create a surface. This surface energy depends on :
- the material
- the particular surface



(110) surface

surface energy matters: fracture

It may be seen that high intrinsic surface energy is necessary for a material to have high fracture surface energy (high toughness). Therefore, surface energy is an essential factor in determining the strength of a material. Roughly, if a material with Young's modulus, Y, has a definite yield stress for plastic deformation, σ_y, the fracture surface energy, S_f, is related to the intrinsic surface energy, S_o, by:

$$S_f = (Y/\sigma_y)S_o \qquad (19.2)$$

and the smaller the yield stress is relative to the elastic stiffness, the larger is the fracture surface energy. The ratio can of course be quite large, 100 or more.

Like the other factors that determine strength, the intrinsic surface energy has its basis in electronic structure. This will be discussed in Chapter 20, but S_f is an extrinsic property and will not be discussed further.

"The electronic basis of the strength of materials"
John Gilman (2003)
http://www.cambridge.org/9780521620055

surface energy

Procedure:

- Calculate the total energy per formula unit for the bulk solid (at the theoretical equilibrium geometry !)
- Make a supercell for the surface you want, starting from the bulk equilibrium geometry. Aim for an integer number of formula units in the slab. Keep the cell size fixed, keep a few central layers fixed, optimize the other positions.

$$E_{surf} = \frac{1}{2}\left(E_{slab} - n_{fu}^{slab} E_{bulk}\right)$$

- E_{surf}: per surface area (=surface area at one side of the slab)
- $\frac{1}{2}$: there are two surfaces for a slab
- E_{slab}: for the entire slab
- n_{fu}^{slab}: number of formula units in the slab cell
- E_{bulk}: per fomula unit

surface energy

Example for the (001) surface in fcc Cu (1 fu = 1 Cu atom) :

9-layer slab, 10 au vacuum
a=b=4.859751 au, c=37.490904 au
5 central layers are fixed

- Calculate the total energy per formula unit for the bulk solid (at the theoretical equilibrium geometry !)

E_{bulk} = -3310.05767213 Ry/fu

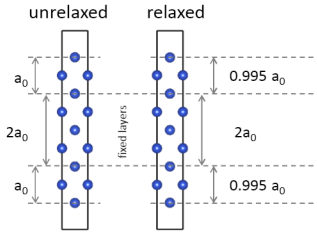
- Make a supercell for the surface you want, starting from the bulk equilibrium geometry. Aim for an integer number of formula units in the slab. Keep the cell size fixed, keep a few central layers fixed, optimize the other positions.

$E_{slab}^{9\,layers}$ = -29790.42467773 Ry/cell

E_{surf} = 2.0 mRy/au^2
97 meV/Å^2
1.6 J/m^2
1550 erg/cm^2

surface energy

- Always verify whether the surface energy is stable with respect to the slab thickness and the vacuum thickness (=is your slab model a good model for a semi-infinite solid ?)
- Effect of the surface on atomic positions :



surface energy

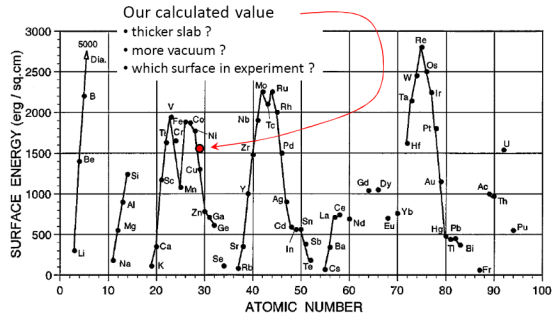


Figure 20.1 Distribution of surface energies in the Periodic Table of the Elements.

work function

work function =
the energy required to remove an electron from a material, and put it in the vacuum close to the material

$W = E(vac) - E_F$

Coulomb potential at the center of the vacuum

```
:VZERO:v0,v0c,v0x  0.44882  0.66645  -0.21763
:FER  : F E R M I - ENERGY(TETRAH.M.)=  0.3313278623
```

for our Cu(001) slab :

W = (0.66645 – 0.33123) Ry
= 0.335 Ry
= 4.56 eV

Work function of elements, in units of electron volt (eV).

Ag	4.26 – 4.74	Al	4.06 – 4.26	As	3.75
Au	5.1 – 5.47	Bi	~4.45	Ba	2.52 – 2.7
Be	4.98	Bi	4.31	C	~5
Ca	2.87	Cd	4.08	Ce	2.9
Co	5	Cr	4.5	Cs	2.14
Cu	4.53 – 5.10	Eu	2.5	Fe	4.67 – 4.81
Ga	4.32	Gd	2.90	Hf	3.9
Hg	4.475	In	4.09	Ir	5.00 – 5.67
K	2.29	La	3.5	Li	2.3
Lu	~3.3	Mg	3.66	Mn	4.1
Mo	4.36 – 4.95	Na	2.36	Nb	3.95 – 4.87
Nd	3.2	Ni	5.04 – 5.35	Os	5.93
Pb	4.25	Pd	5.22 – 5.6	Pt	5.12 – 5.93
Rb	2.261	Re	4.72	Rh	4.98
Ru	4.71	Sb	4.55 – 4.7	Sc	3.5
Se	5.9	Si	4.60 – 4.85	Sm	2.7
Sn	4.42	Sr	~2.59	Ta	4.00 – 4.80
Tb	3.00	Te	4.95	Th	3.4
Ti	4.33	Tl	~3.84	U	3.63 – 3.90
V	4.3	W	4.32 – 5.22	Y	3.1
Yb	2.60 [11]	Zn	3.63 – 4.9	Zr	4.05

http://en.wikipedia.org/wiki/Work_function