# Introduction to Surface/ Interface Chemistry

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# Expectation from the class?

topics:

# syllabus

* Forces & Adsorption
* characterization methods
* imaging methods
* surface chemistry (SAMs)
* grafting polymers
* micropatterning
* biological interfaces

# What is a surface/interface?

boundary between two different phases of solid matter:

* liquid - liquid
* liquid - solid
* solid - solid
* solid - vapor
* liquid - vapor

# What is a surface/interface?

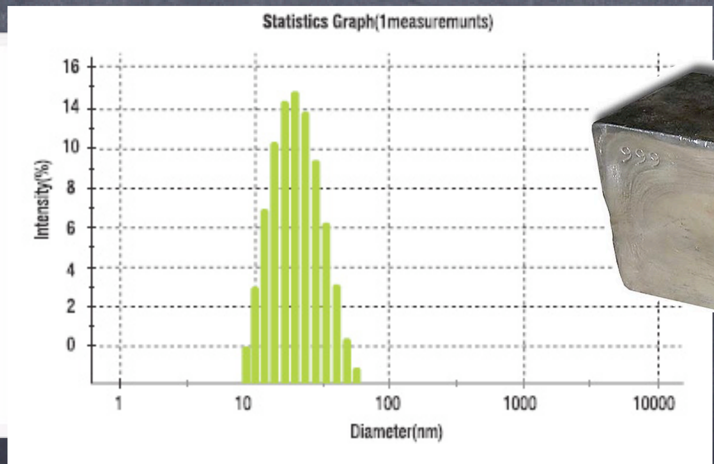
# What is a surface/interface?

common sense: A surface is the shell of a macroscopic object in contact with its environment. An interface is the boundary between two phases.

The surface of an object determines its optical appearance, stickiness, wetting behavior, frictional behavior, and chemical reactivity, etc.

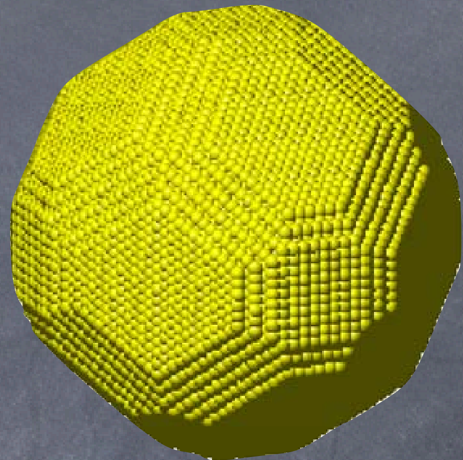
* in large objects with small surface area A to volume V ratio (A/V) the physical and chemical properties are primarily defined by the bulk (inside)
* in small objects with a large A/V-ratio the properties are strongly influenced by the surface

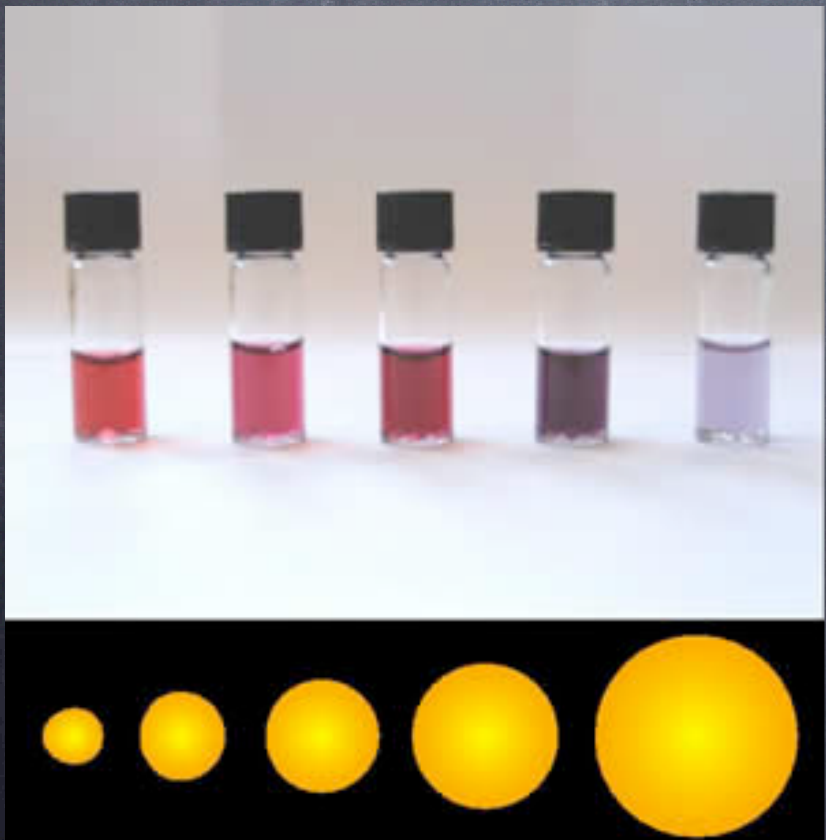
E.g. silver (Ag):

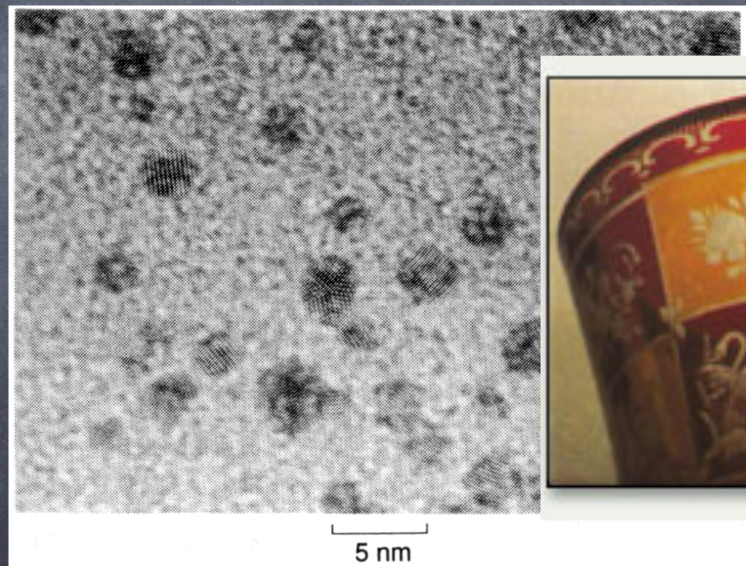



# example: gold nanoparticles

Gold nanoparticles are composed of small crystalline Au clusters with dimensions usually around 2 nm in diameter.
example for material with high A/V ratio, quantum structures (size effects)
surface coating with molecular layer to prevent aggregation (alkylthiols or $PPh_3$)



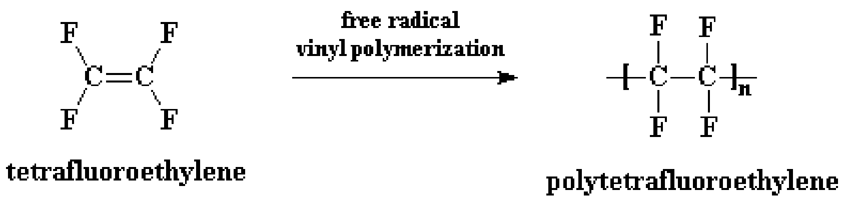


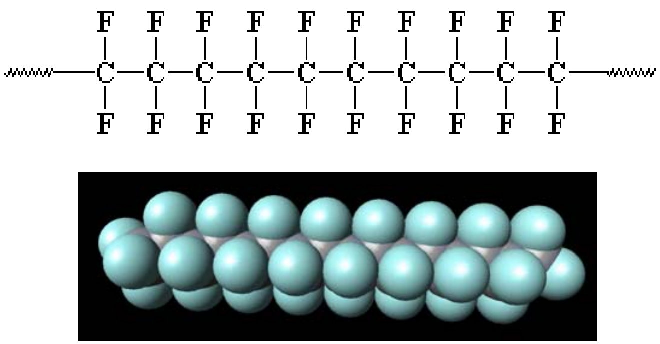



10-nm-diameter particles in "ruby glass,"

# example: teflon frying pan

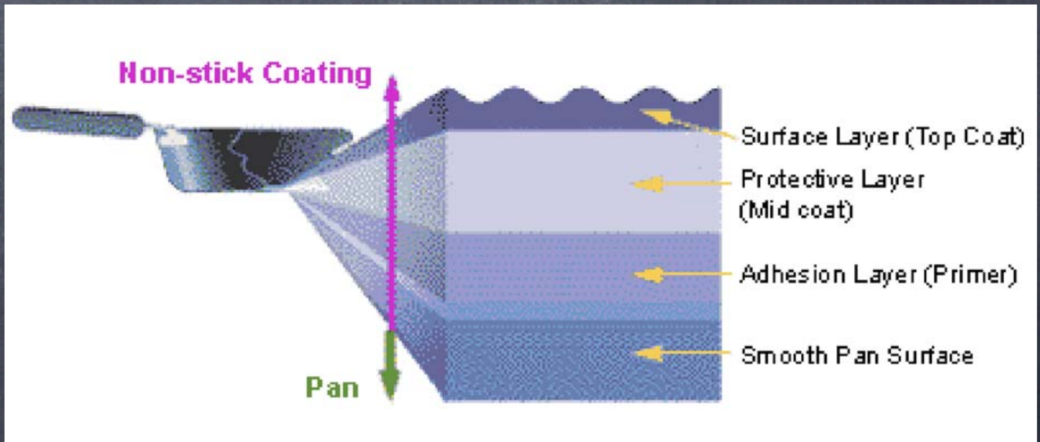
Polytetrafluoroethylene (PTFE, Teflon) is obtained by free radical polymerization of tetrafluoroethylene.



PTFE has very low surface energy (non-sticking), is very apolar, is highly chemically resistant, and shows low friction.

"How does Teflon stick to the frying pan when nothing sticks to Teflon???"

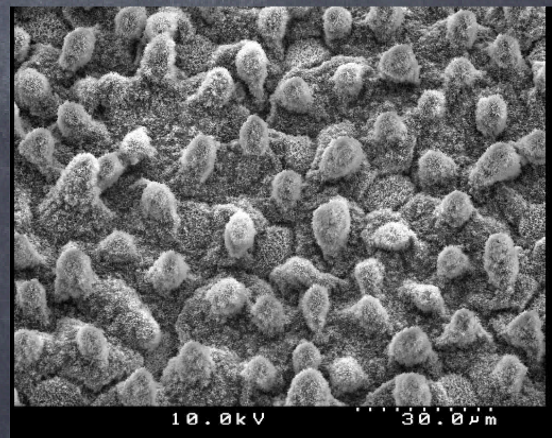


# example: lotus leaf effect

The surface of plant leafs, especially of the lotus flower, can show extreme hydrophobicity to water (large water contact angles > 150°C).

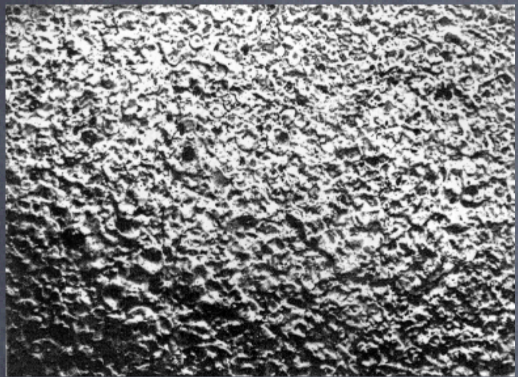
Such hydrophobic surfaces also show a remarkable self-cleaning effect.

explanation:
- hydrophobic material
- surface structure (20-100μm)

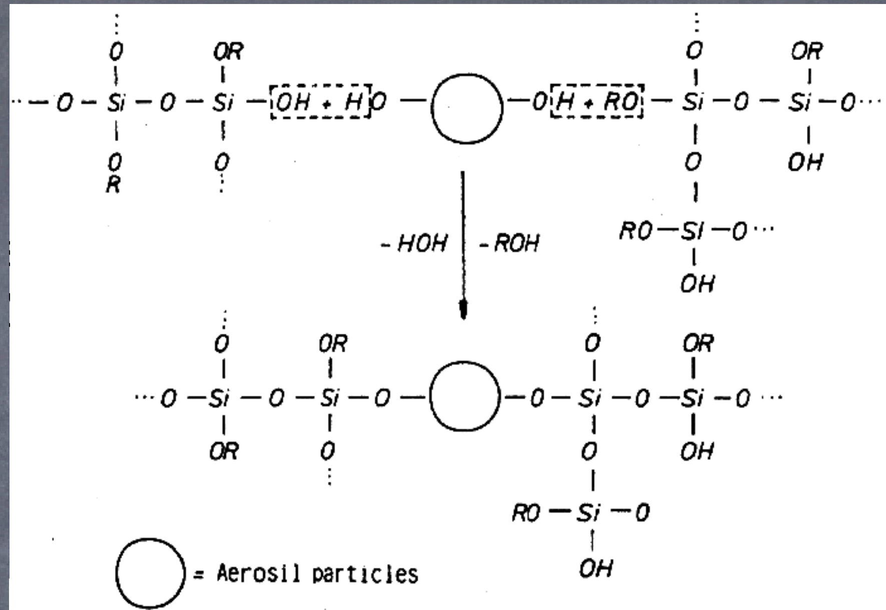


# example: antireflecting surfaces

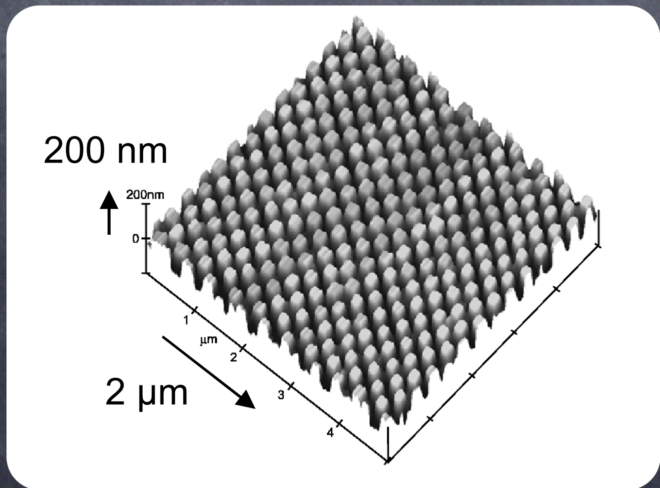
Structured surfaces with feature sizes below the wavelength of visible light (ca. < 200 nm ) show antireflecting behavior.

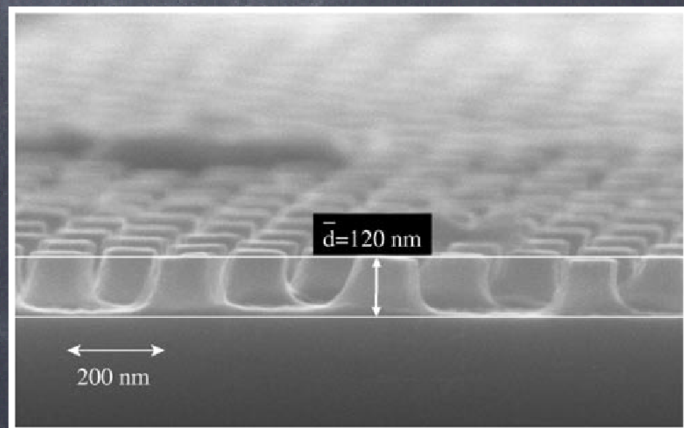


surface roughness from sol-gel cold-spraying process




surface roughness by lithographic patterning and etching

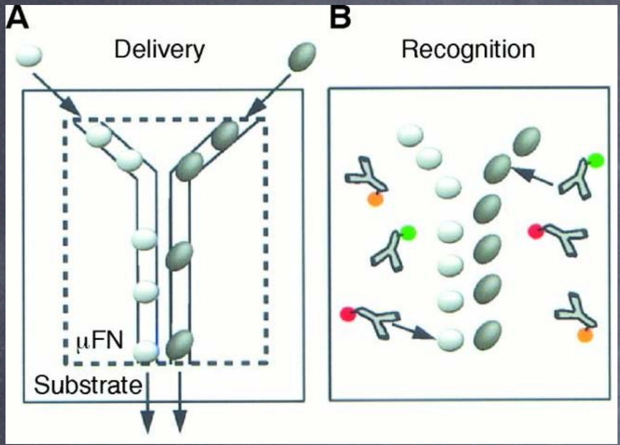


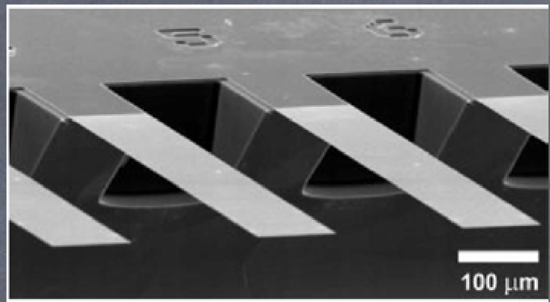
# example: biochips

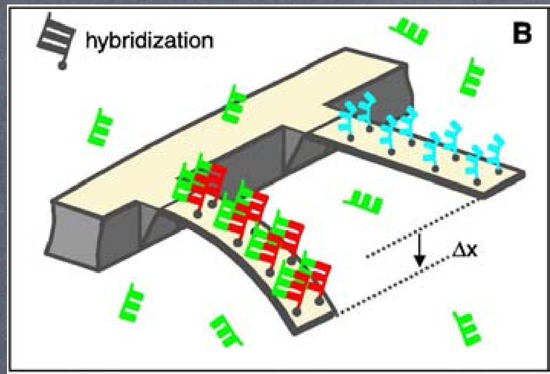
immobilized biomolecules for sensors and diagnostics:

immunoassay in microfluidics

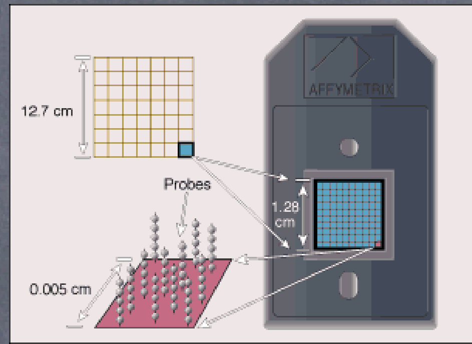


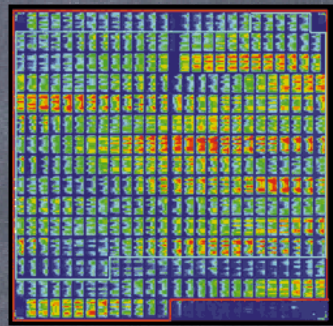

the "chemical nose"



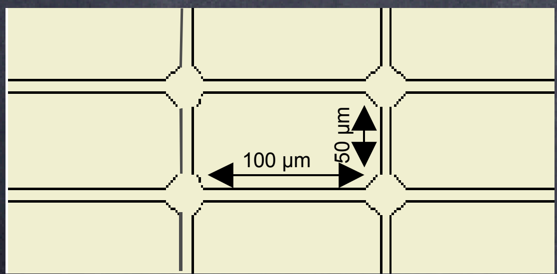

DNA chips



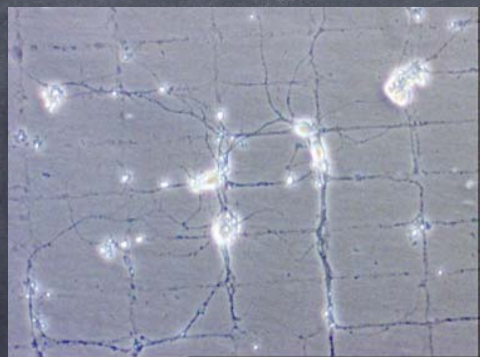



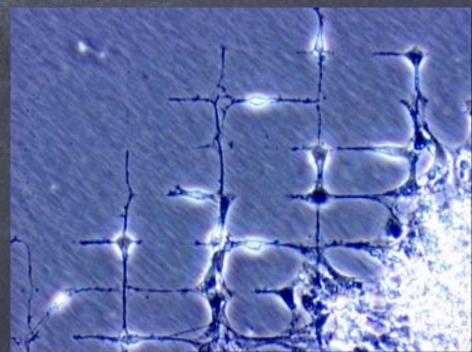
specific surface modification for site-selective adsorption / growth of cells:

Pattern




line width 6 μm, node diameter 14 μm
ECM-gel printed on polystyrene





courtesy of Angela Vogt, MPIP 2002

# important key features of surfaces

- surface material (chemical composition):

-> determines chemical behavior (reactive / inert)
-> physical materials behavior (conducting / insulating)
-> polarity (hydrophilic / hydrophobic)
-> surface structure on a molecular scale
...

- topography ("valleys and hills"):

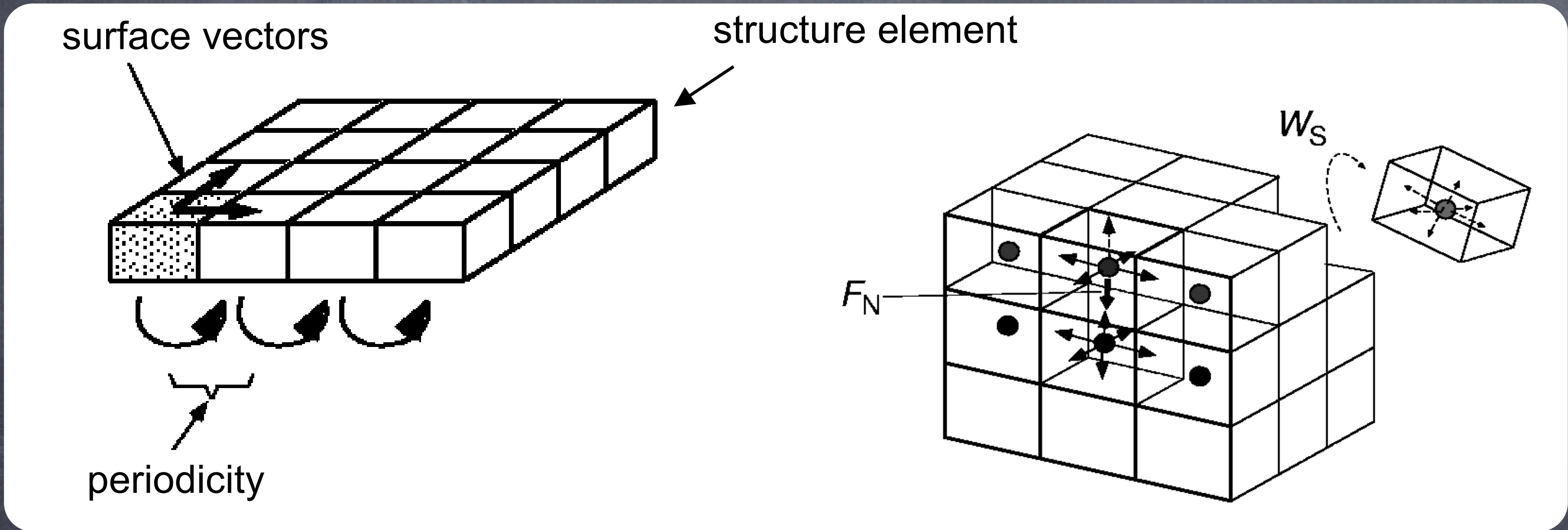
-> determines chemical "reactivity" / kinetics (fast / slow reaction, reactive sites)
-> physical surface behavior (reflectivity, effective wetability)
-> tribological behavior (friction on "rough" or "smooth" surface)
-> surface morphology on a microscopic to macroscopic scale
...

# application examples of surface science

- understanding and design of catalysts (industrial production of $NH_3$ e.g., car exhaust)
- understanding and inhibition of corrosion (ships, cars, buildings)
- modification of surface properties like:
    - friction (tires, bearings)
    - wear (polymer lenses of glasses → ormocers)
    - stickiness (frying pan, adhesive tape)
    - wetting, condensation (scuba diving goggles, outdoor gear, inkjet printing)
    - anti-reflection (picture frames, displays)
    - color (paint)
- chip manufacturing / microelectronics
- hard disks (anti-friction, ultra-smooth,...)
- biological surfaces (biocompatibility, patterned cell growth)
- sensors (chemical, biological)
- microfluidics ...

# schematic representation of a surface

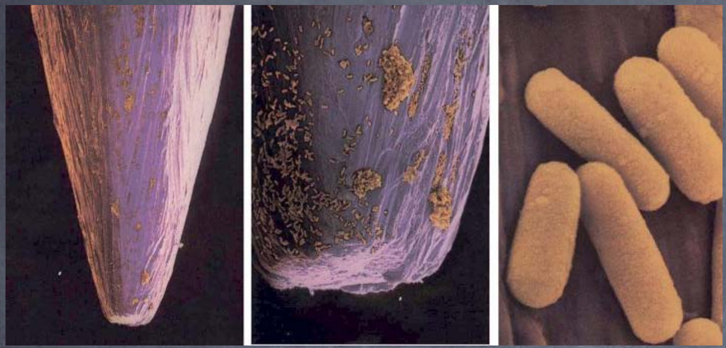
Translational symmetry of structure elements in an ordered surface: idealized crystal lattice




In three dimensions the structure extends to one side of the surface into the bulk.

$F_N$ is the normal force acting onto a surface element towards the bulk, due to missing elements at the exterior.
$W_S$ is the work to transfer a surface element into the gas phase.

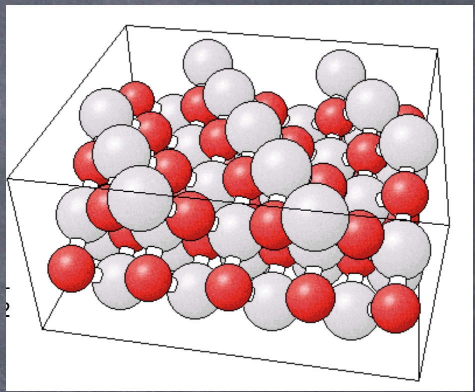
# What is the structure of a surface?



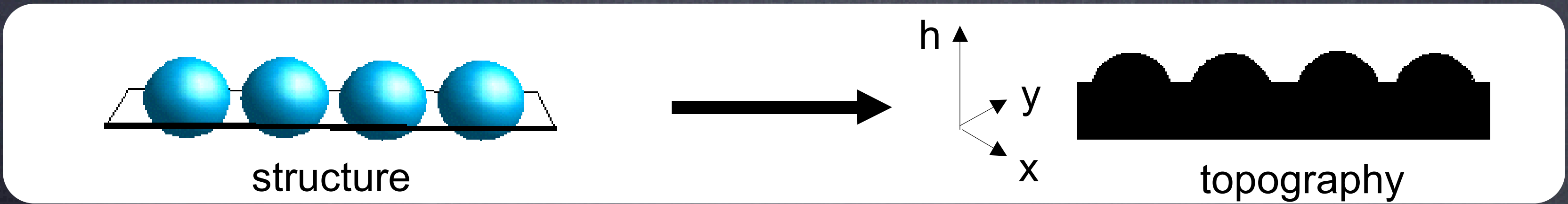
courtesy of Dr. Marx: http://www.siu.edu/~cafs/surface/file1.html

The morphology of a surface is a macroscopic or ensemble property that defines its form and shape.
example: grainy structure of wooden table top

The structure of a surface is given by the atomic and molecular composition and arrangement of the atoms in space.
Geometry of AgBr(111)-(2x1) ->



The topography of a surface is its profile determined by "valley", "planes" and "hills".

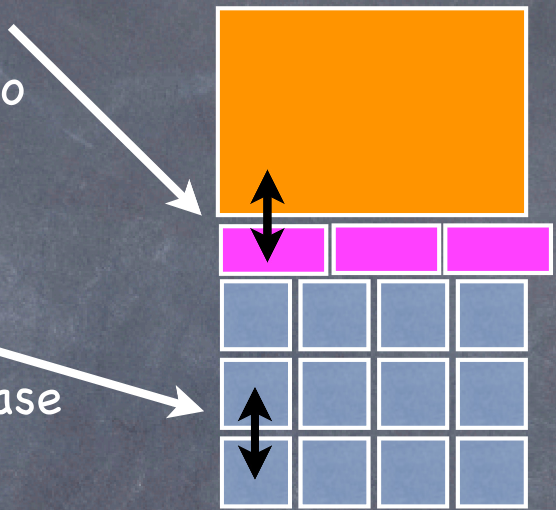


# What is an Interface?

An interface is the separating layer between two condensed phases (usually molecular dimensions).

adhesion: attractive interactions between two different media

cohesion: attractive interactions within a phase (solid or liquid)

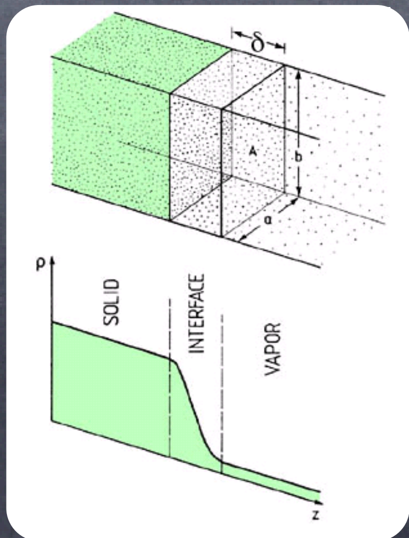


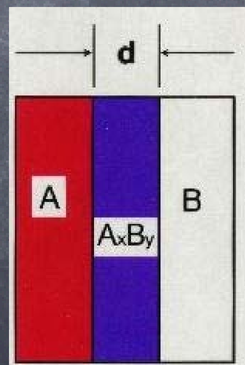
surrounding medium

interfacial region

substrate (solid or liquid)

At the border of a solid or liquid in contact with vapor there is usually no abrupt change in density, but a more or less continuous transition from high density to low density. The interface consists either of evaporating bulk material or condensing material from the gas phase.



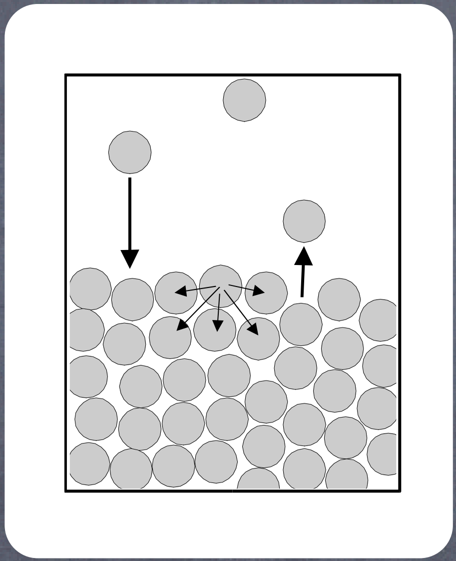



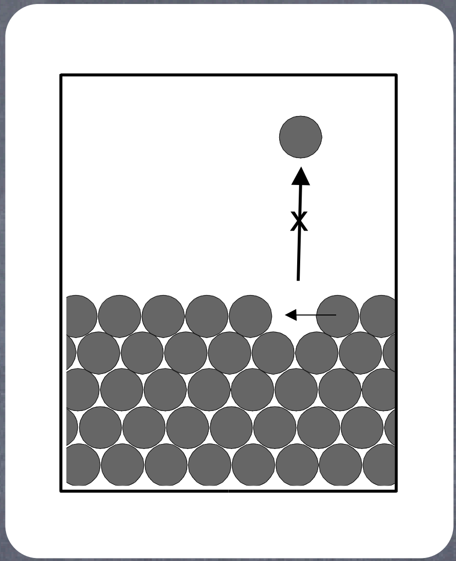

An interphase is a chemical compound composed of the two surrounding phases.

# different surface & interface scenarios

liquid / vapor

solid / vapor (vacuum)



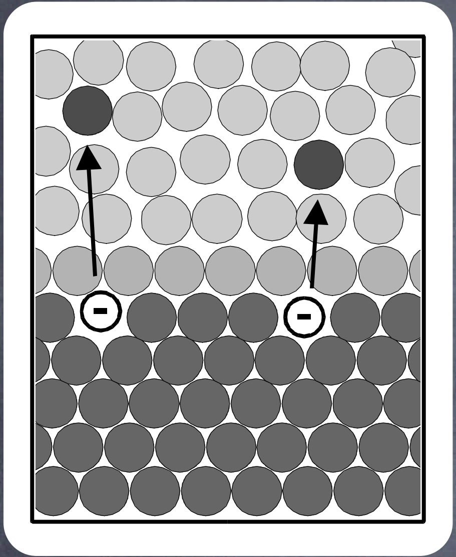


- liquid highly mobile & disordered
- constant evaporation and recondensation at surface

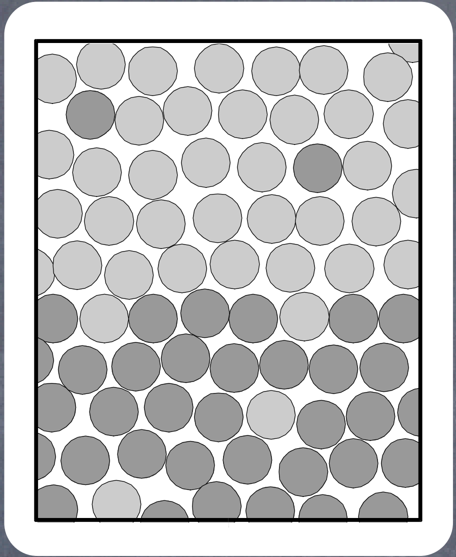
- solid highly immobile
- crystalline solids highly ordered / structured
- usually no evaporation of surface atoms & molecules, only lateral diffusion (depends on T)

# different surface & interface scenarios 2

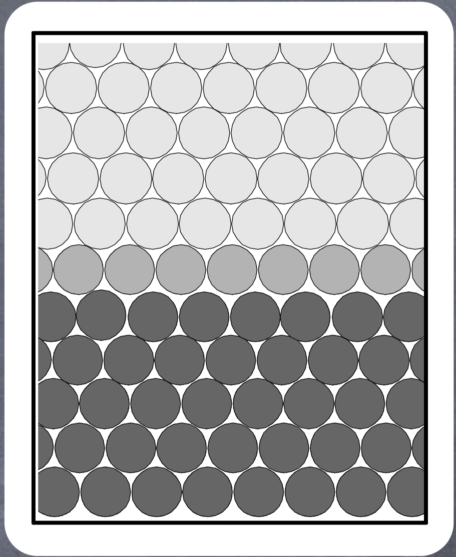
solid / liquid



liquid$_1$ / liquid$_2$



solid$_1$ / solid$_2$



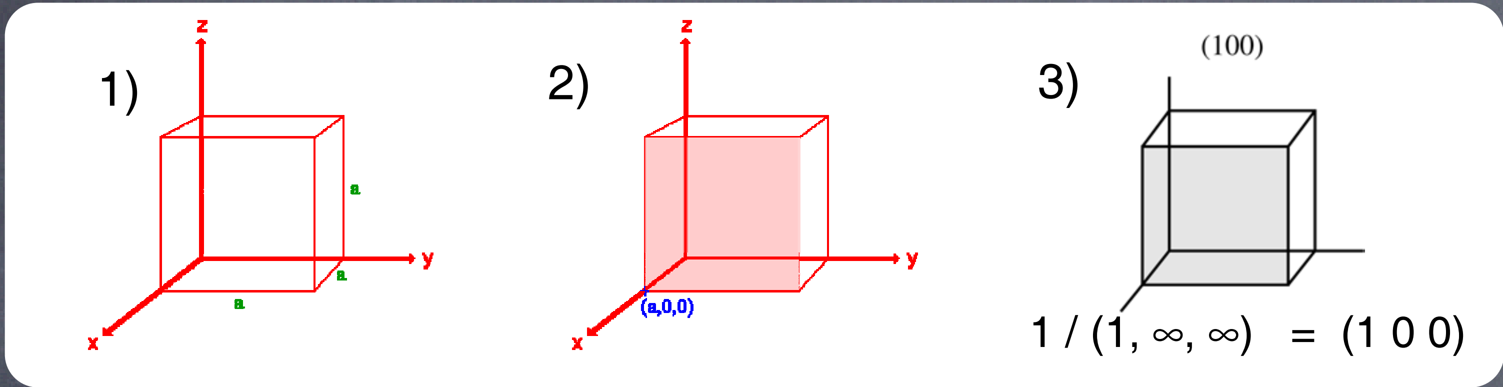
- liquid can dissolve surface atoms → may lead to surface charges
- liquid molecules at the interface can be much higher ordered than in the bulk

- both phases highly mobile → shape of interface is controlled by surface tension
- depending on solubility molecules will migrate from one phase to the other → controlled by chemical potential (partition coeff.)

- if two crystalline solids are in atomic contact the different lattice constants will generate strain @ interface
- if both materials react together new compound will be formed in contact region → interphase
- at high T interdiffusion possible (e.g. Cr & Au)

# crystal planes - Miller indices

The planes of ideal crystals (a cut through the lattice) are closely related to ideal crystal surfaces. To specify a particular plane most commonly Miller indices are used.



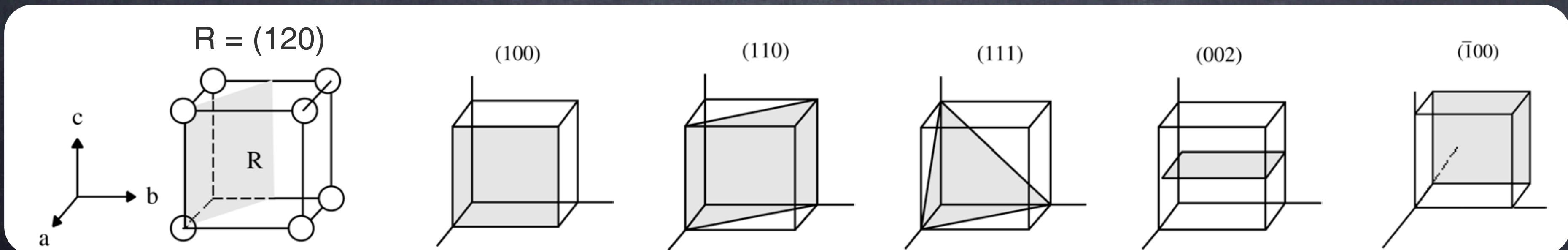

**Procedure:**

1) Identify intercepts of plane on the x−, y−, and z−axes. ⇒ 1 x a, ∞ x b, ∞ x c

   (example: cubic lattice a=b=c, α=β=γ=90°)

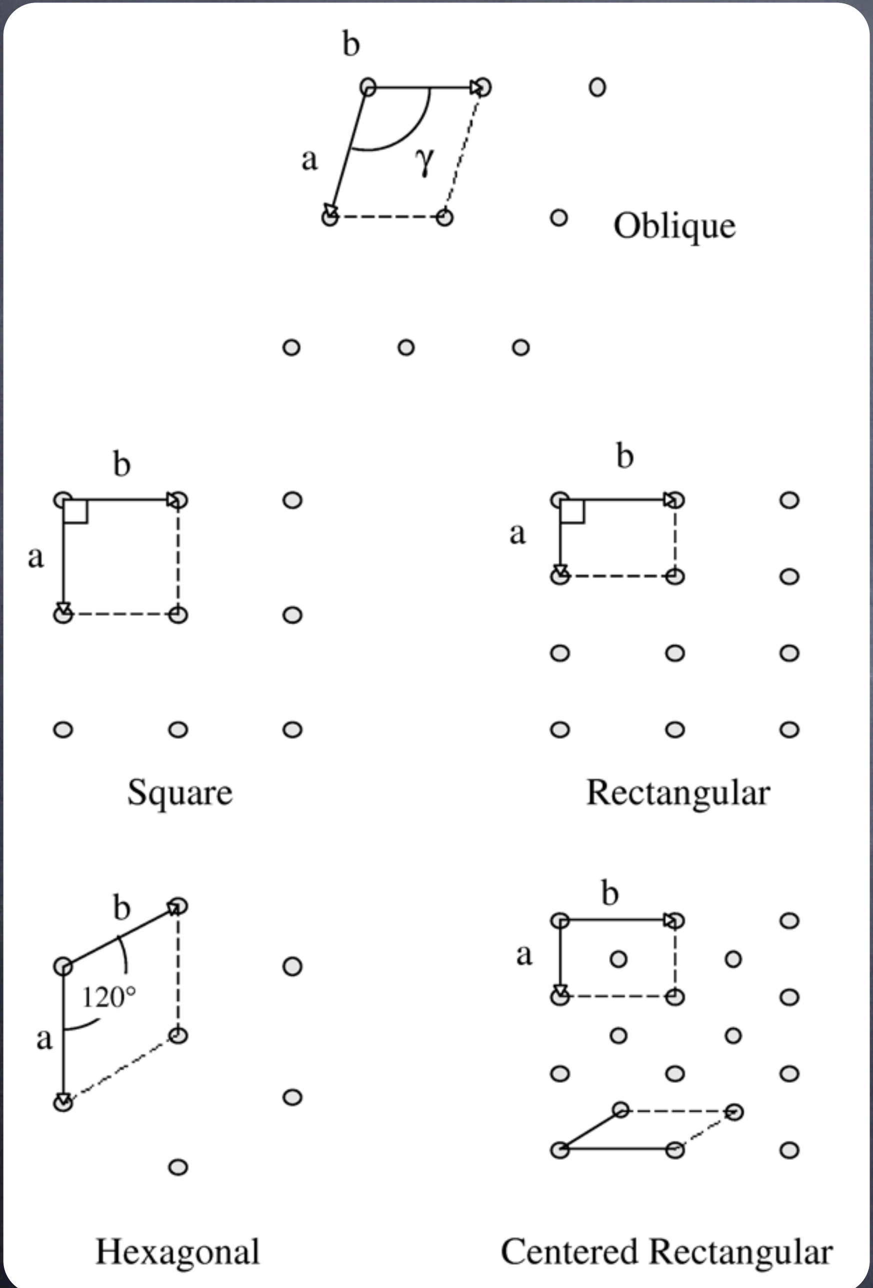
2) Specify intercepts in fractional coordinates of unit cell parameters a, b, c.
   ⇒ (1 x a) / a, (∞ x b) / b, (∞ x c) / c → 1, ∞, ∞

3) Take reciprocal of fractional intercepts, clear fractions.
   ⇒ 1 / (1, ∞, ∞) = (1 0 0) → bar for negative values (h,k,l)

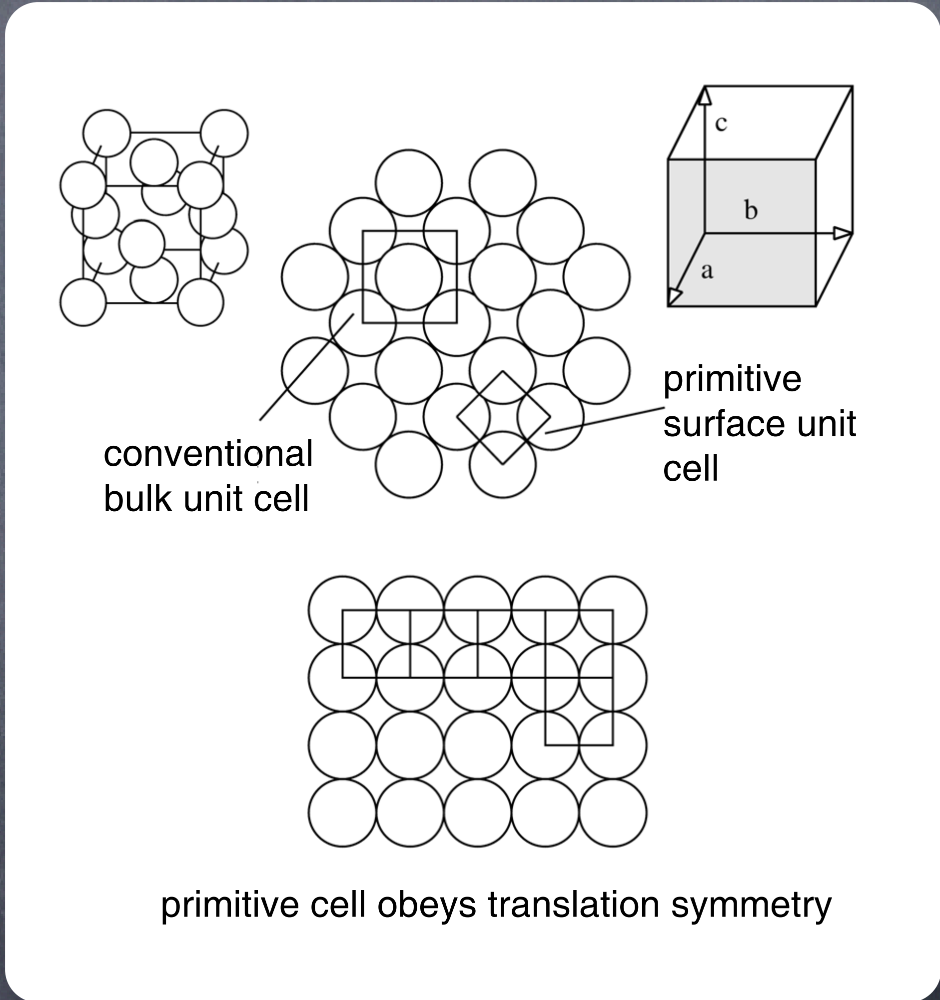


# simple 2D lattices

translation vectors, unit cell vectors: a,b

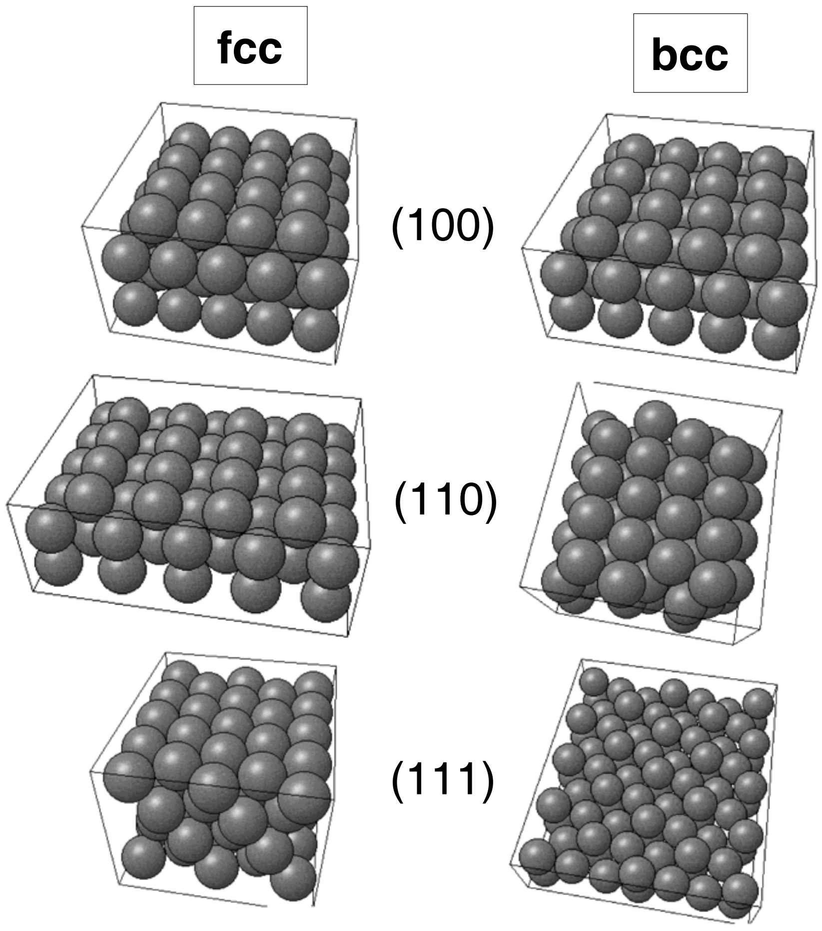



example: Au (100) surface



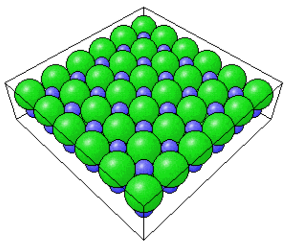
# ideal crystal surfaces

low index surfaces:

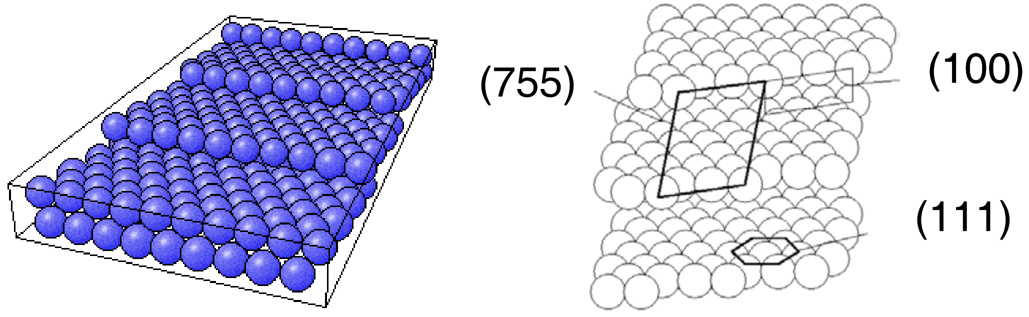



compound surface:

NaCl(100)



high index surfaces:

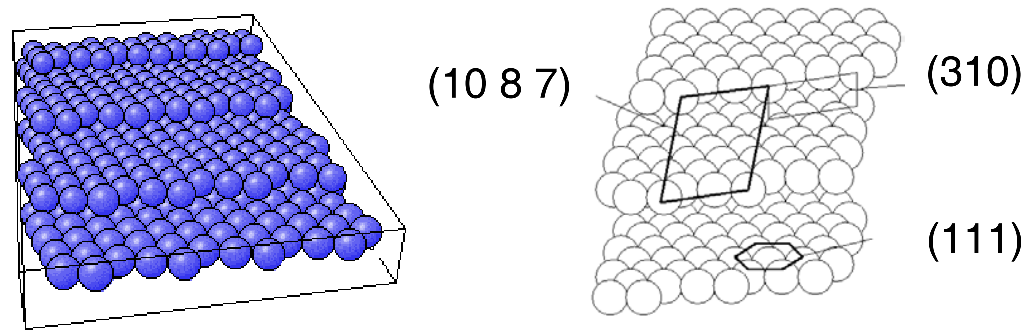



Pt(755) or Pt S–[7(111)x(100)]

stepped surface

(100) step 1 atom high

(111) terrace 7 atoms wide

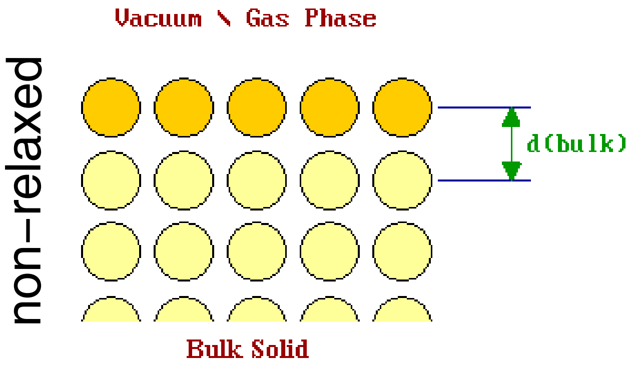



Pt(10 8 7) or Pt S–[7(111)x(310)]

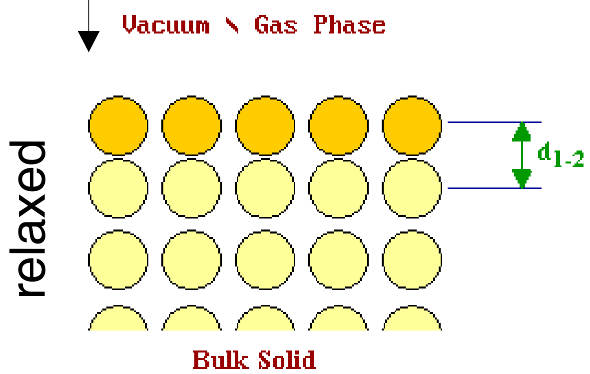
(steps with kinks)

# real crystal surfaces

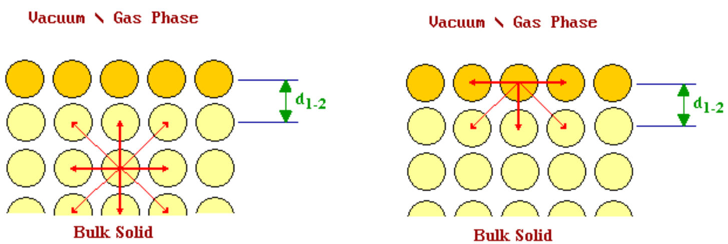
## relaxation:



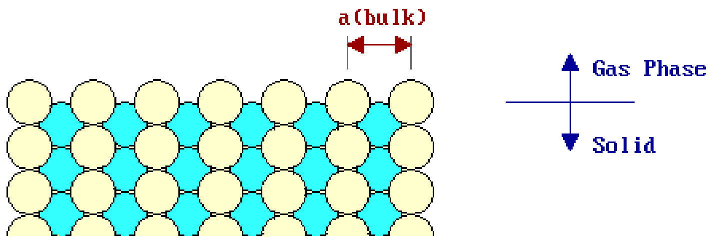

distance change < 10%



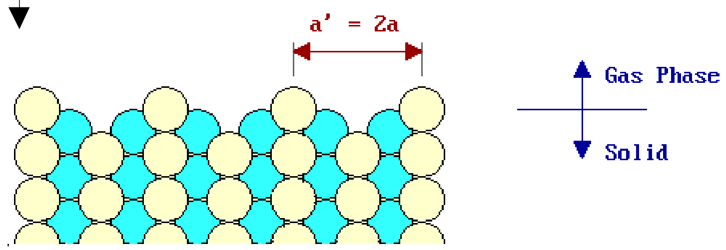

**driving force**:
unbalanced forces compared to bulk




## reconstruction:

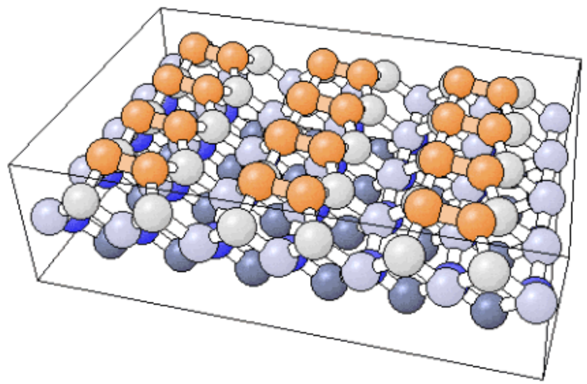



Substantial rearrangement

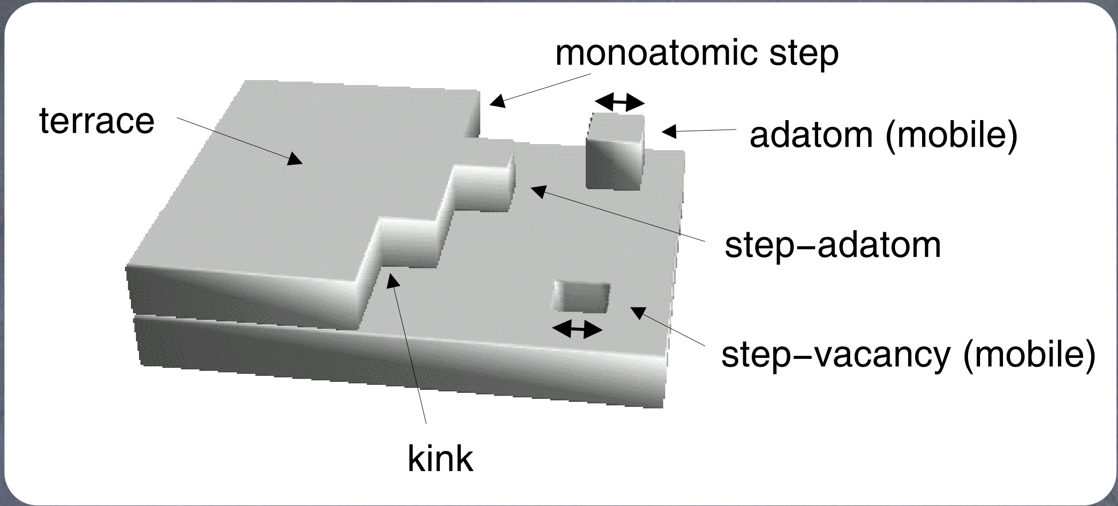



→ satisfying dangling bond

Si(100)–(2x1)



# surface defects and structures



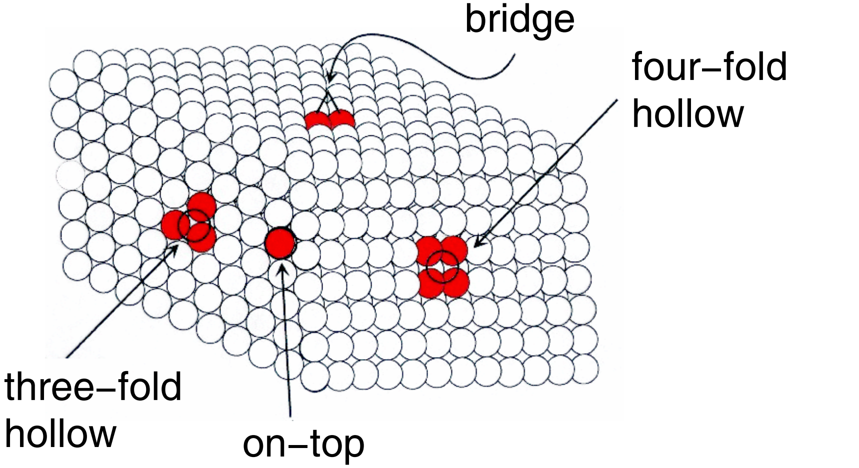

→ surface defects are important for crystal growth:

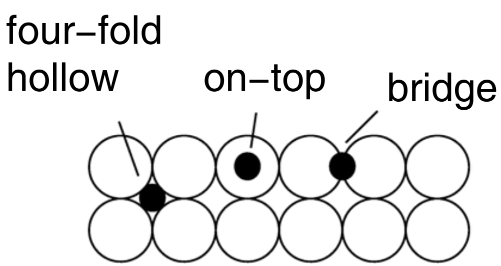
- traps for newly adsorbed atoms / molecules
- restructuring of surfaces happens at defects first

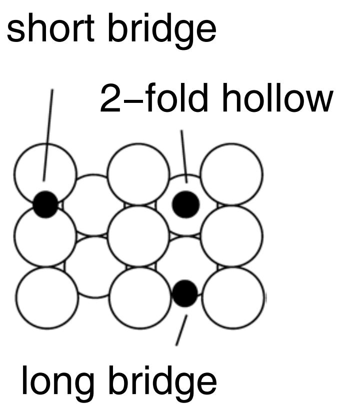
kink−, step−, and terrace−atoms have large equilibrium concentrations on real surfaces
(hard to get perfect surface...)
isolated adatoms ("adsorbed atom") and vacancies are important for atomistic transport (restructuring), but equilibrium concentration is low
(< 1% of monolayer even at $T_{melt}$)

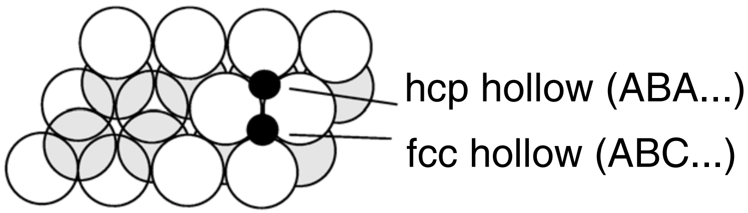
# surface sites and adsorbate structures

Adsorption Sites:

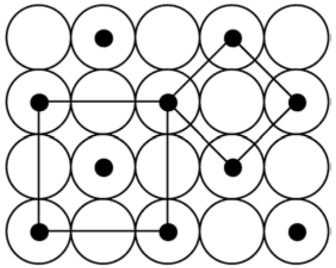


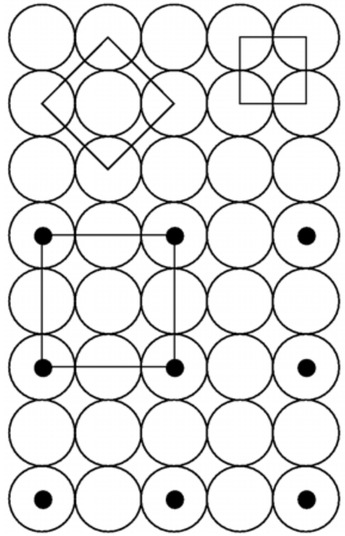



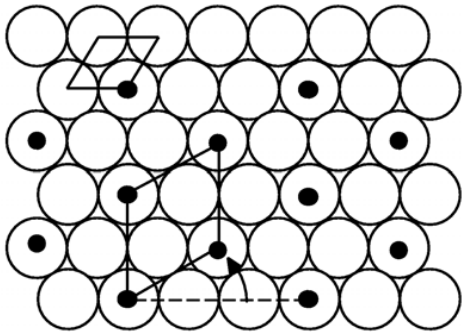

Adsorbate Surface Structures:



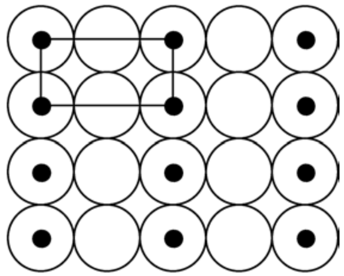
fcc–(100)–c(2x2)
or fcc(100)–(√2x√2)R45



fcc–(100)–p(2x2)
or fcc(100)–(2x2)



fcc(111)–
(√3x√3)R30



fcc–(100)–(2x1)

# Wood's Notation and Matrix Notation

Description of the ordered adlayer (adsorbed atoms and molecules) in terms of the relationship to the underlying ideal crystal plane.

b1=2·a1+0·a2
b2=0·a1+2·a2

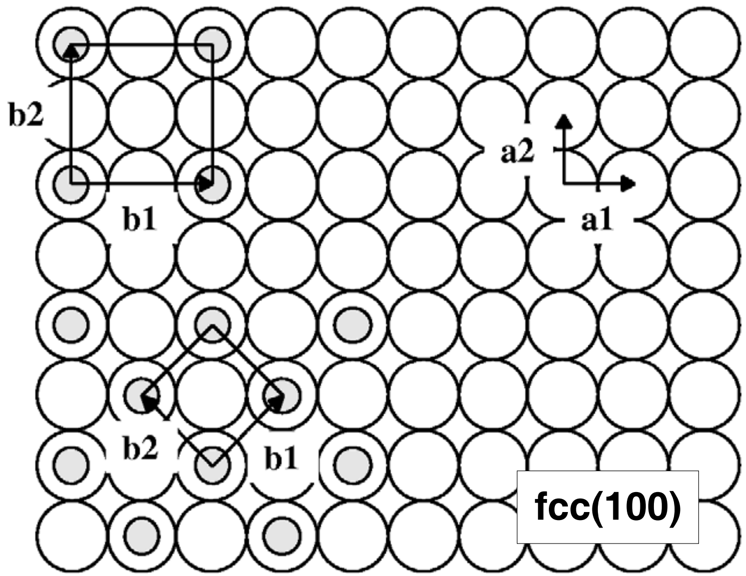
$$\begin{pmatrix} b1 \\ b2 \end{pmatrix} = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix} \begin{pmatrix} a1 \\ a2 \end{pmatrix}$$

p(2x2)

$$M = \begin{pmatrix} 2 & 0 \\ 0 & 2 \end{pmatrix}$$

p(√2x√2)R45

$$M = \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}$$




b1=1·a1+1·a2
b2=-1·a1+1·a2

alternatively:
for p(√2x√2)R45

$$\begin{pmatrix} b1 \\ b2 \end{pmatrix} = \sqrt{2} \begin{pmatrix} \cos 45 & \sin 45 \\ -\sin 45 & \cos 45 \end{pmatrix} \begin{pmatrix} a1 \\ a2 \end{pmatrix}$$

| substrate | plane | centered | mesh ratio | | adsorbate |
|---|---|---|---|---|---|
| Ni | (110) | c | (2x2) | – | O |

(c (2x2): Woods notation)

examples:

| substrate | plane | mesh ratio | | adsorbate | |
|---|---|---|---|---|---|
| Pt | (100) | (2√2x√2)R45 | – | O | ≡ |

((2√2x√2)R45: Woods notation)

| substrate | plane | M= | | adsorbate |
|---|---|---|---|---|
| Pt | (100) | $\begin{pmatrix} 2 & 2 \\ -1 & 1 \end{pmatrix}$ | – | O |

(Matrix notation)