

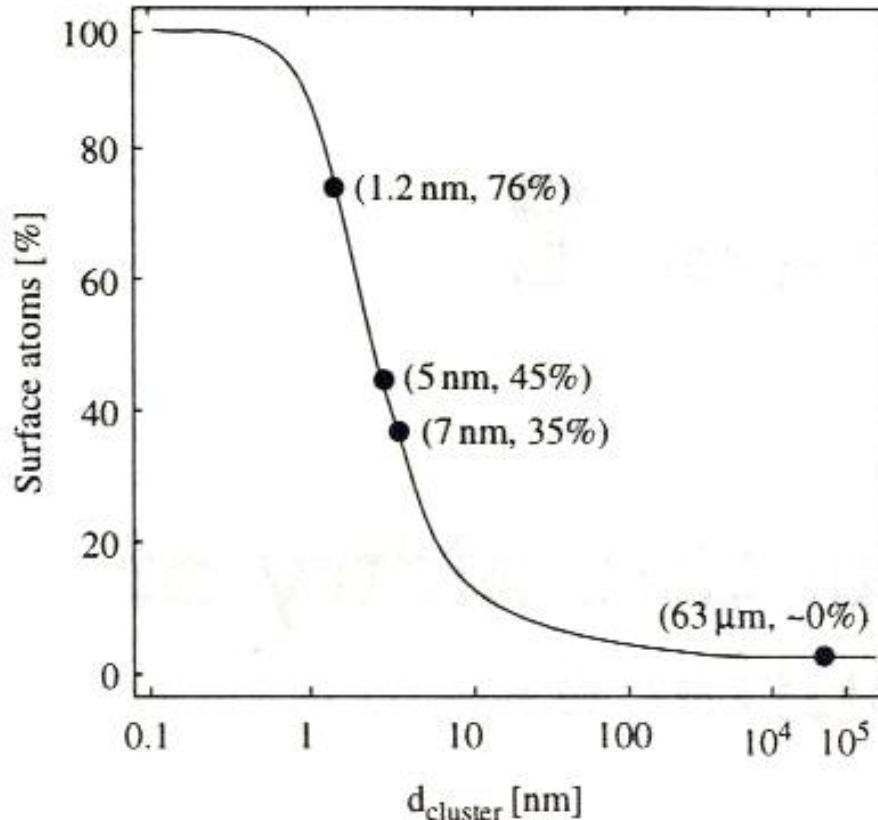
# Surface Energy and Thermodynamic Potentials\*

February 17<sup>th</sup>, 2020

# Question...

Is it the same surface energy and surface tension?

# Percentage of surface atoms changes with cluster diameter



**Fig. 2.1.** The percentage of surface atoms changes with the palladium cluster diameter.  
[C. Nützenadel, A. Züttel, D. Chartouni, G. Schmid, and L. Schlapbach, *Eur. Phys. J.* **D8**, 245 (2000).]

For 1 g of Sodium Chloride, the original 1 g cube is successively divided into smaller cubes.

**Table 2.1.** Variation of surface energy with particle size.<sup>22</sup>

<i>Side</i> (cm)	<i>Total surface area</i> (cm <sup>2</sup> )	<i>Total edge</i> (cm)	<i>Surface energy</i> (J/g)	<i>Edge energy</i> (J/g)
0.77	3.6	9.3	$7.2 \times 10^{-5}$	$2.8 \times 10^{-12}$
0.1	28	550	$5.6 \times 10^{-4}$	$1.7 \times 10^{-10}$
0.01	280	$5.5 \times 10^4$	$5.6 \times 10^{-3}$	$1.7 \times 10^{-8}$
0.001	$2.8 \times 10^3$	$5.5 \times 10^6$	$5.6 \times 10^{-2}$	$1.7 \times 10^{-6}$
$10^{-4}$ (1 µm)	$2.8 \times 10^4$	$5.5 \times 10^8$	0.56	$1.7 \times 10^{-4}$
$10^{-7}$ (1 nm)	$2.8 \times 10^7$	$5.5 \times 10^{14}$	560	170

## Comments:

- ✓ Due to the vast surface area, all nanostructured materials possess a huge surface energy and, thus are thermodynamically unstable or metastable.
- ✓ Goal: to overcome the surface energy, and to prevent the nanomaterials from growth in size, driven by the reduction of overall surface energy.

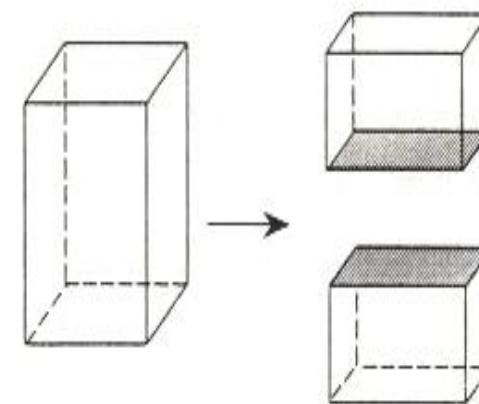


Fig. 2.2. Schematic showing two new surfaces being created by breaking a rectangular solid into two pieces.

# Surface Energy

- ✓ Definition: energy required (or produced) to create a unit area of a new surface, therefore,

$$\gamma = (\delta G / \delta A)_{n_i, T, P}$$

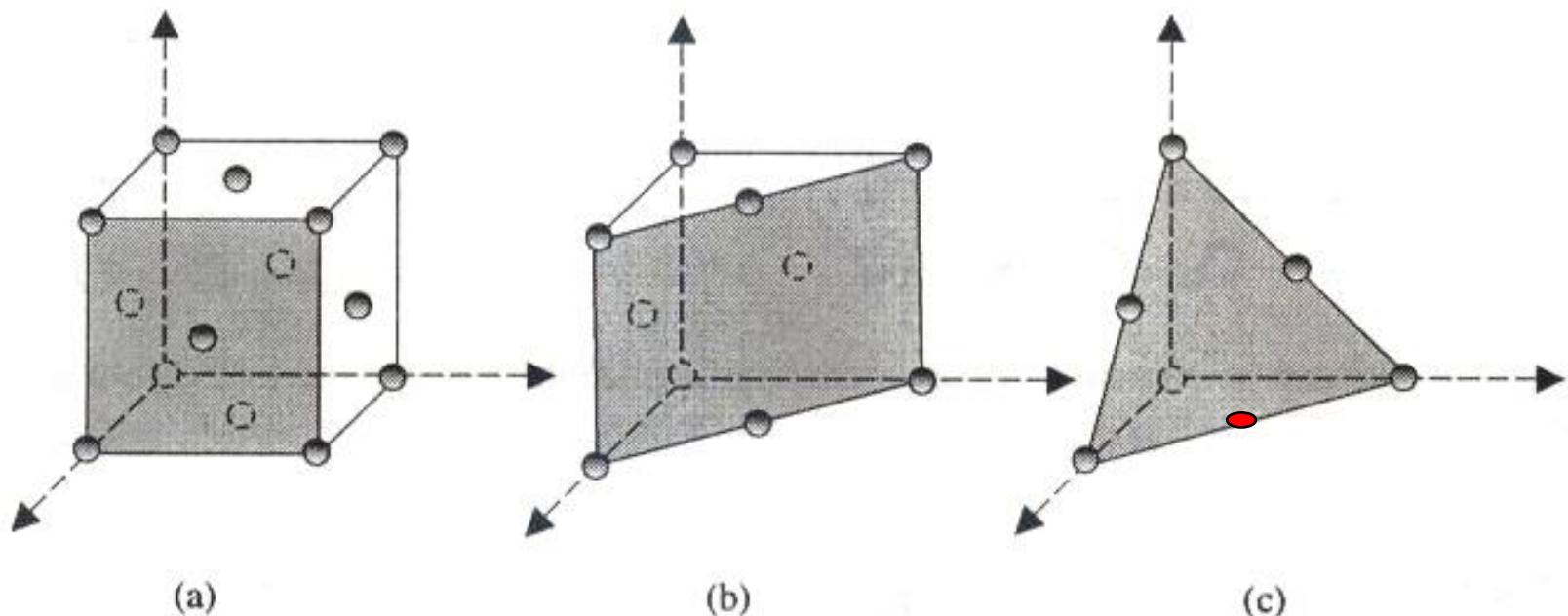
- ✓ G: Gibbs free energy of the surface
- ✓ A: Surface area of the particles
- ✓ Surface area can be increased by cutting a particle into two halves. The molecules of the newly created surface possess fewer nearest neighbors or coordination numbers, and thus have dangling or unsatisfied bonds. Due to the dangling bonds on the surface, surface atoms or molecules are under an inwardly directed force and the bond distance between molecules and the sub-surface molecules becomes smaller. An extra force or energy is required to pull the surface to its original positions.

# Surface Energy

This energy is defined as surface energy,  $\gamma$

$$\gamma = N_b \varepsilon \rho_a / 2 = (\partial G / \partial A)_{n_i, T, P}$$

- ✓  $N_b$ : number of broken bonds  
 $\gamma_{la}$
- ✓  $\varepsilon$ : bond strength
- ✓  $\rho_a$  = number of atoms or molecules per unit surface area density
- ✓ The above equation is very crude model and does not account for interactions between higher order neighbors.



**Fig. 2.3.** Schematic representing low index faces of a face-centered cubic (fcc) crystal structure: (a) {100}, (b) {110} and (c) {111}.

# Surface Energy

- ✓ For FCC structure with lattice constant  $a$ , each atom will have a coordination number 12, and each atom on the surface  $\{100\}$  has 4 broken bonds, on  $\{110\}$  5 broken bonds and on  $\{111\}$  3 broken bonds. Therefore,

$$\gamma = N_b \varepsilon \rho_a / 2 \quad \text{If } a=1, \varepsilon=1$$

$$\gamma_{\{100\}} = 2/a^2 \cdot 4 \cdot \varepsilon \cdot 1/2 \quad \gamma_{\{100\}} = 4$$

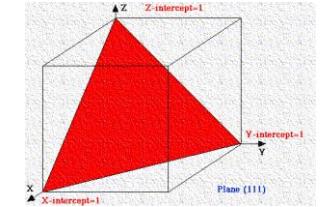
$$\gamma_{\{110\}} = 2/2^{0.5}a^2 \cdot 5 \cdot \varepsilon \cdot 1/2 \quad \gamma_{\{110\}} = 3.52$$

$$\gamma_{\{111\}} = 2/3^{0.5}\varepsilon a^2 \quad \gamma_{\{111\}} = 1.16$$

$$\gamma_{\{100\}} = \frac{4\epsilon}{a^2}$$

$$\gamma_{\{110\}} = \frac{5}{2^{0.5}} \frac{\epsilon}{a^2}$$

$$\gamma_{\{111\}} = 2(3)^{0.5} \frac{\epsilon}{a^2}$$



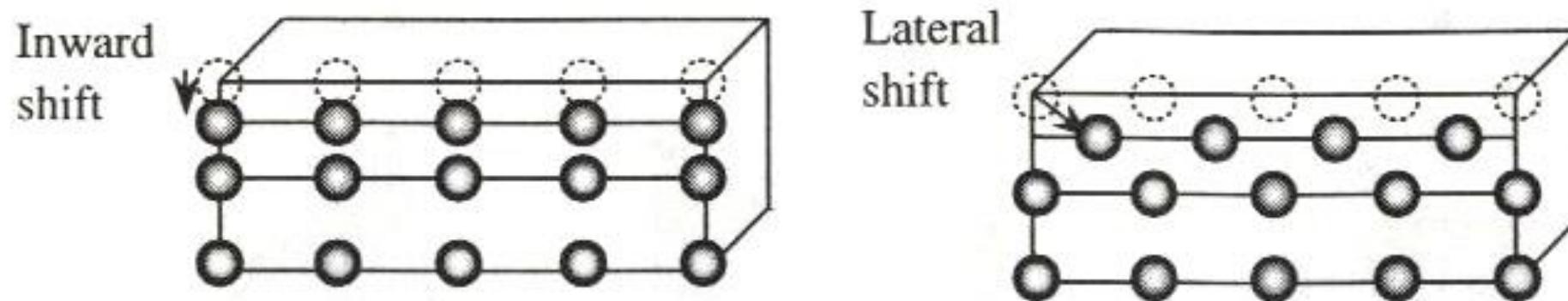
<http://chemistry.bd.psu.edu/jircitano/Miller.html>

According to Eqn (1), the lower Miller index facets have low surface energy. System is stable only when it is in a state with the lowest Gibbs free energy. Therefore, a crystal is often surrounded by low index surfaces.

# Surface energy reduced by

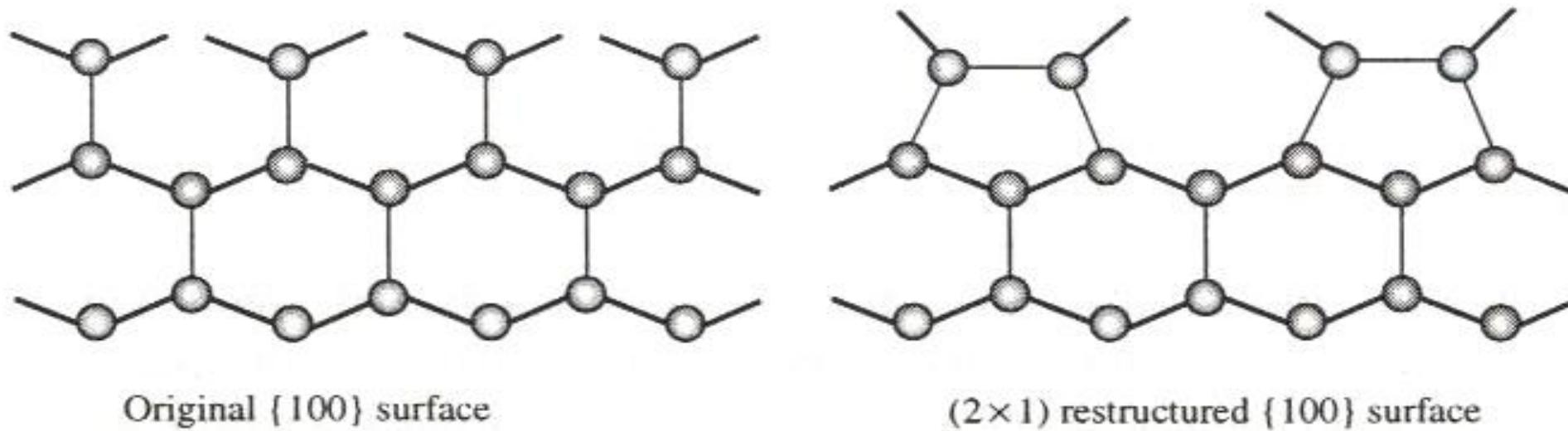
- Surface relaxation: surface atoms or ions shift inwardly.
- Surface restructuring through combining surface dangling bonds into strained new chemical bonds
- Surface adsorption through chemical or physical adsorption of terminal chemical species by forming chemical bonds or weak attraction forces such as electrostatic or van der Waals forces.
- Composition segregation or impurity enrichment on the surface through solid-state diffusion.

# Surface energy reduction by surface relaxation



**Fig. 2.4.** Schematic showing surface atoms shifting either inwardly or laterally so as to reduce the surface energy.

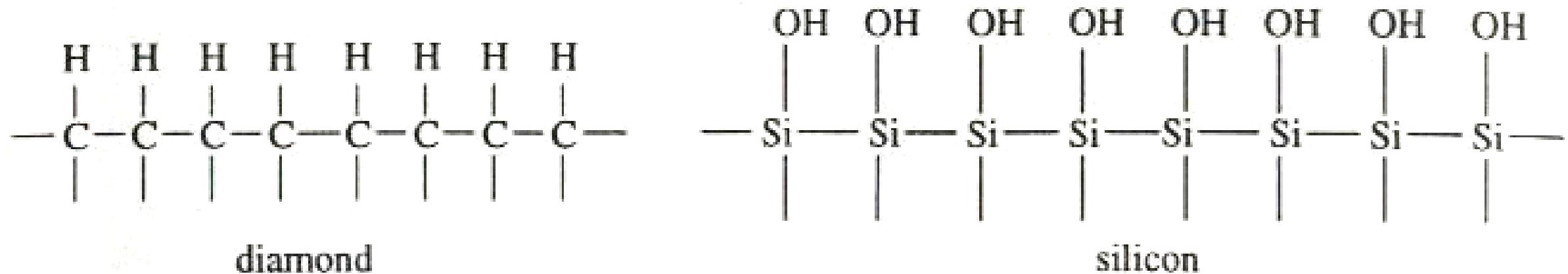
# Surface energy reduction by restructuring



**Fig. 2.5.** Schematic illustrating the  $(2 \times 1)$  restructure of silicon  $\{100\}$  surface.

The restructured  $\{100\}$  faces have the lowest surface energy among  $\{111\}$ ,  $\{110\}$  and  $\{100\}$  faces.

# Surface energy reduction by chemical or physical adsorption



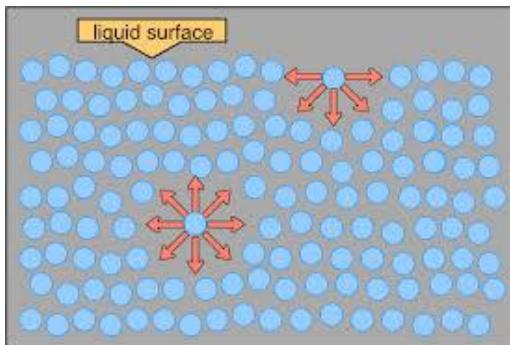
**Fig. 2.6.** Schematic showing the surface of diamond is covered with hydrogen and that of silicon is covered with hydroxyl groups through chemisorption before restructuring.

# Surfaces...

...and you

## ***Importance of surfaces***

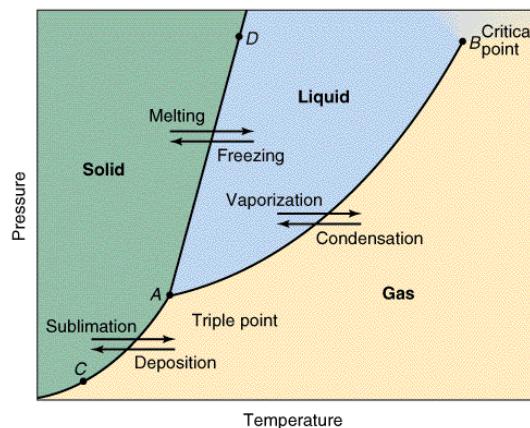
- What is a surface?
- Surface structure
- Surface processes
- Surface interfaces
- Surfaces in nature
- Measuring surfaces
- Modifying surfaces



# Surfaces Defined

- Discontinuity between material phases:

- Solid / air
- Solid / liquid
- Solid / solid
- Liquid / air
- Liquid / liquid
- Liquid / solid

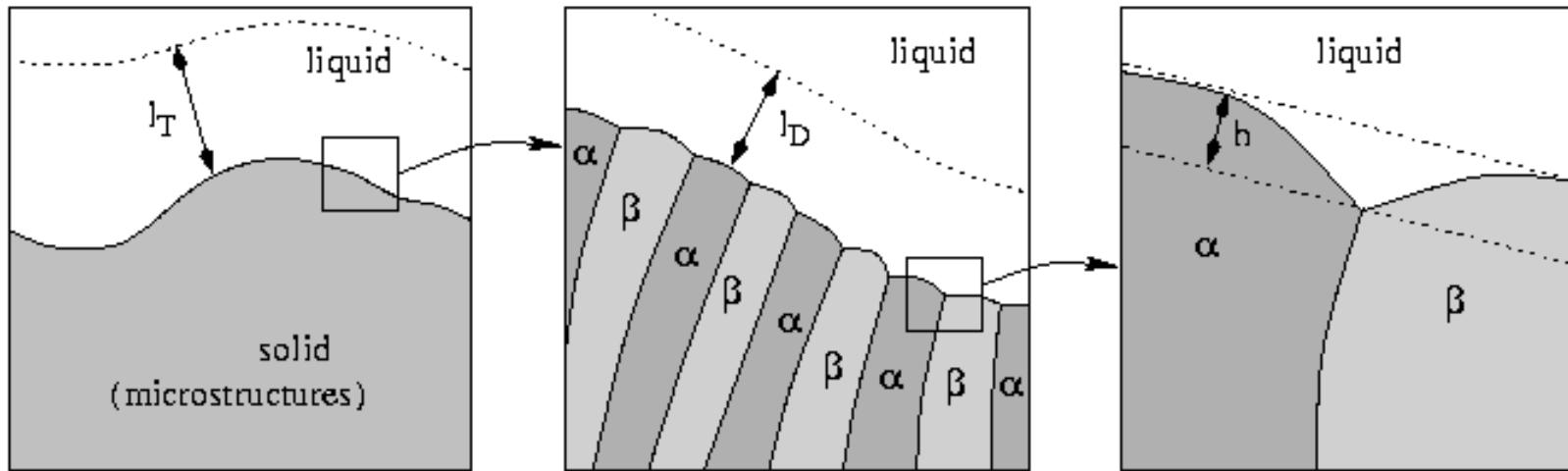


- Molecules and colloids / particles have surfaces, surface charges, etc. This is what drives proteins to spontaneously fold (surface energy with water).

- Surfaces exist at phases. Free energy must be minimized
- Energy drives most surface reactions

Passivation  
Oxidation  
Adsorption of hydrocarbon and water  
Reconstruction and reorientation

# Heterogeneous *Surface Structure*



Different length scales involved during solidification. In the left image the thickness of the temperature diffusion layer (largest scale). In the middle image the mass diffusion layer is shown; at this scale the microstructures in the solid region can be seen. In the image at right the height deviations of the interface on the smallest scale.

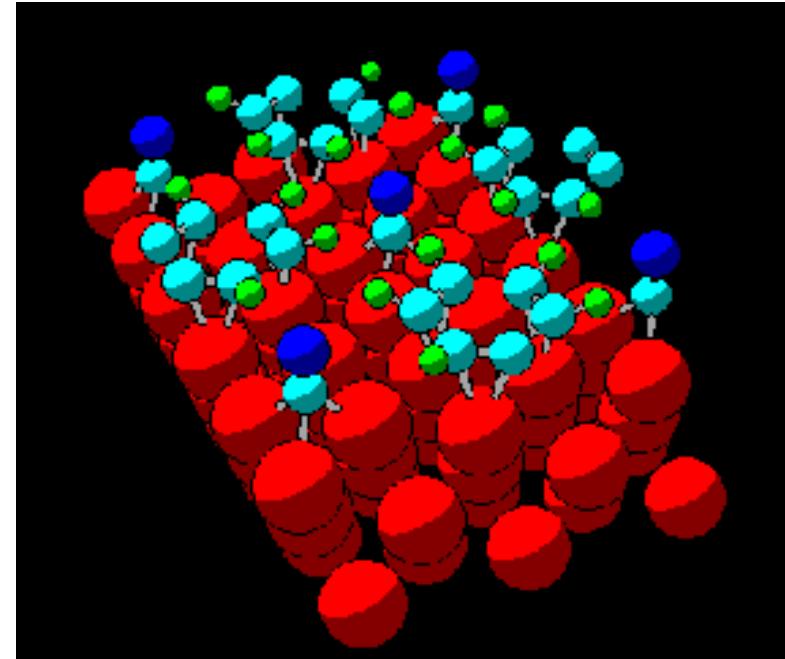
[http://www.uni-regensburg.de/Fakultaeten/nat\\_Fak\\_I/Mat8/Ist/spp/projectSPP1095solidification.html](http://www.uni-regensburg.de/Fakultaeten/nat_Fak_I/Mat8/Ist/spp/projectSPP1095solidification.html)

# *Real Surfaces Explained*

- Discontinuities create an interface
- Dangling bonds, attractive / repulsive forces, unit cell cleavage planes
- Interfaces often form passivation layers
- Surfaces can scatter electrons
- Materials can fail at interfaces
  - Can be cohesive / adhesive failures

# Surface Structure Database

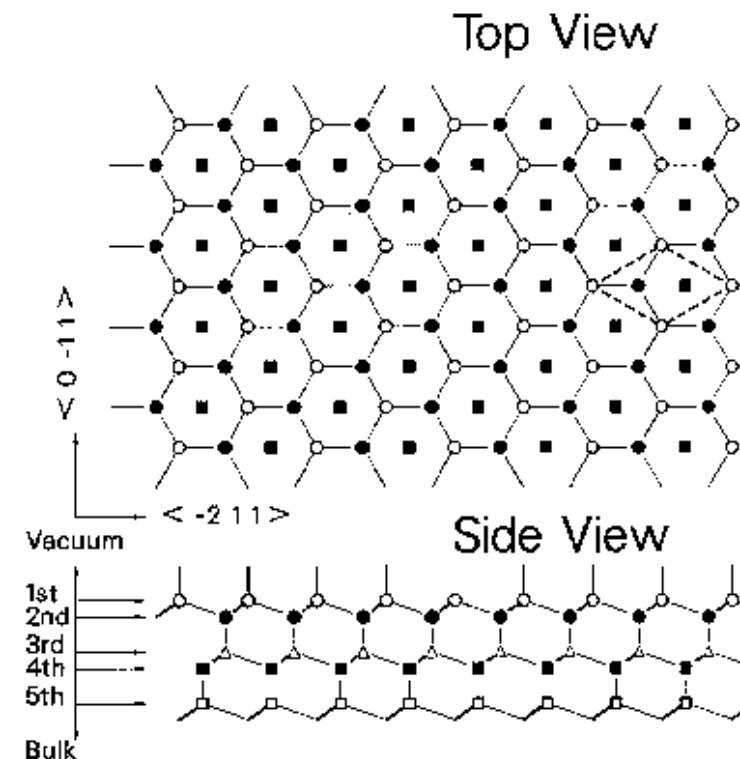
- The Surface Structure Database (SSD) is the only complete critical compilation of reliable crystallographic information now available on surfaces and interfaces. SSD brings instant access to detailed *text and graphical* displays of over 1250 experimentally-determined atomic-scale structural analyses.



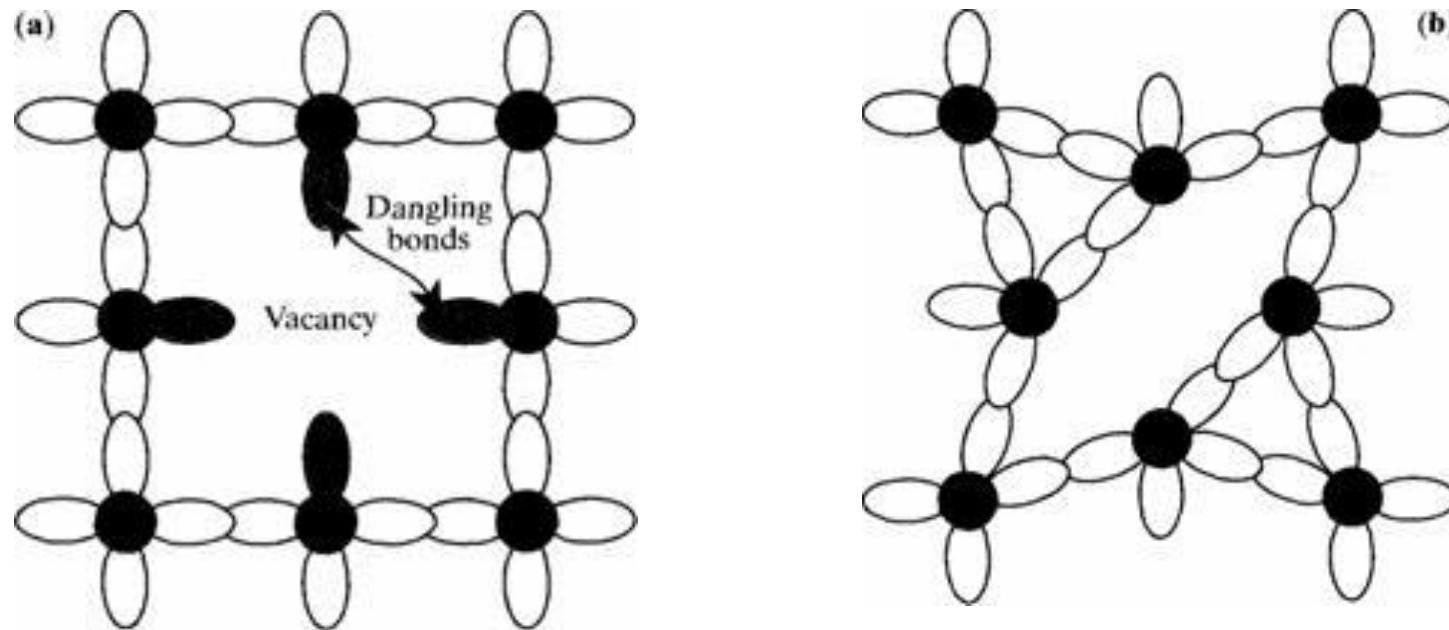
<http://www.nist.gov/srd/nist42.htm>

# Silicon Surface Planes

- Model of the ideal surface for Si{111}1x1.  
The open and closed circles represent Si atoms in the first and second layers, respectively.  
Closed squares are fourth-layer atoms exposed to the surface though the double double-layer mesh.  
The dashed lines indicated the surface 1x1 unit-cell.



# Si Surface *Reconstruction*



Schematic diagram of a covalent semiconductor with (a) an unrelaxed vacancy involving four dangling bonds and (b) a relaxed vacancy with no dangling bonds

[http://www.mtmi.vu.lt/pfk/funkc\\_dariniai/sol\\_st\\_phys/defects.htm](http://www.mtmi.vu.lt/pfk/funkc_dariniai/sol_st_phys/defects.htm)

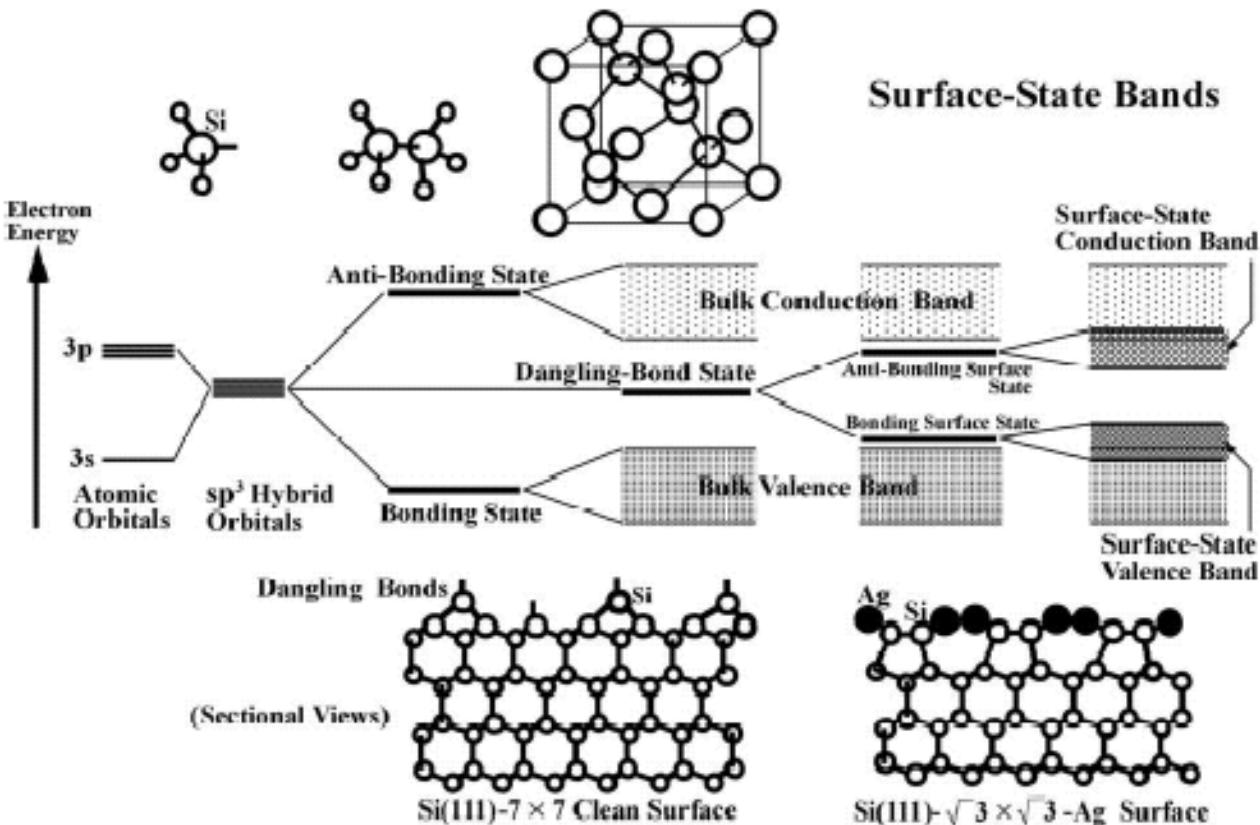


Fig. 6. A schematic illustration of energy diagram of atoms, molecules, and also in bulk and at surface of a silicon crystal. The valence electrons of an isolated Si atom are in 3p and 3s atomic orbitals. These orbitals are ‘hybridized’ into  $sp^3$  orbitals when the atoms arrange in tetrahedral structures like in a diamond-lattice crystal and in SiH<sub>4</sub> molecules. When the atoms make bonds with the neighbouring atoms, the energy level of the orbitals splits into anti-bonding and bonding states. Furthermore, in the crystal the atomic orbitals overlap with each other between the neighbouring sites, the energy levels broaden into bands, conduction band and valence band, between which an energy gap opens. This is an electronic state in the bulk crystal of Si. The Si atoms on the topmost surface layer of the crystal, however, have dangling bonds, of which energy level is similar to the unpaired  $sp^3$  hybrid orbitals, locating within the band gap. The dangling-bond state split into anti-bonding and bonding states when foreign atoms bond to the topmost Si atoms. These states are created only in the surface layer, surface electronic states. When the adsorbate adsorption induces a surface superstructure, the surface states become bands due to the overlap of surface states among the periodic atomic sites on the surface. These are surface-state bands. They have characters different from the bands in the bulk crystal because the atoms in the surface superstructure arrange in a way completely different from in the bulk crystal.

# Surface Processes

- ***Passivation***
  - Oxide formation
  - Adventitious carbon
- ***Reconstruction***
  - Crystalline
  - Polymer orientation
- ***Adsorption*** of gases and water vapor
  - Both can lead to surface passivation

# ***Surface Free Energy***

The net effect of this situation is the presence of free energy at the surface. The excess energy is called surface free energy and can be quantified as a measurement of energy/area. It is also possible to describe this situation as having a line tension or surface tension which is quantified as a force/length measurement. Surface tension can also be said to be a measurement of the cohesive energy present at an interface. The common units for surface tension are dynes/cm or mN/m. These units are equivalent. Solids may also have a surface free energy at their interfaces but direct measurement of its value is not possible through techniques used for liquids. Polar liquids, such as water, have strong intermolecular interactions and thus high surface tensions. Any factor which decreases the strength of this interaction will lower surface tension. Thus an increase in the temperature of this system will lower surface tension. Any contamination, especially by surfactants, will lower surface tension. Researchers should be very cautious about the issue of contamination. [http://www.ksvinc.com/surface tension.htm](http://www.ksvinc.com/surface_tension.htm)

# **Surface *Energetics***

The unfavorable contribution to the total (surface) free energy may be minimized in several ways:

- 1. By reducing the amount of surface area exposed – this is most common / fastest**
  
- 2. By predominantly exposing surface planes which have a low surface free energy**
  
- 3. By altering the local surface atomic geometry in a way which reduces the surface free energy**

# **How do Molecules *Bond* to Surfaces?**

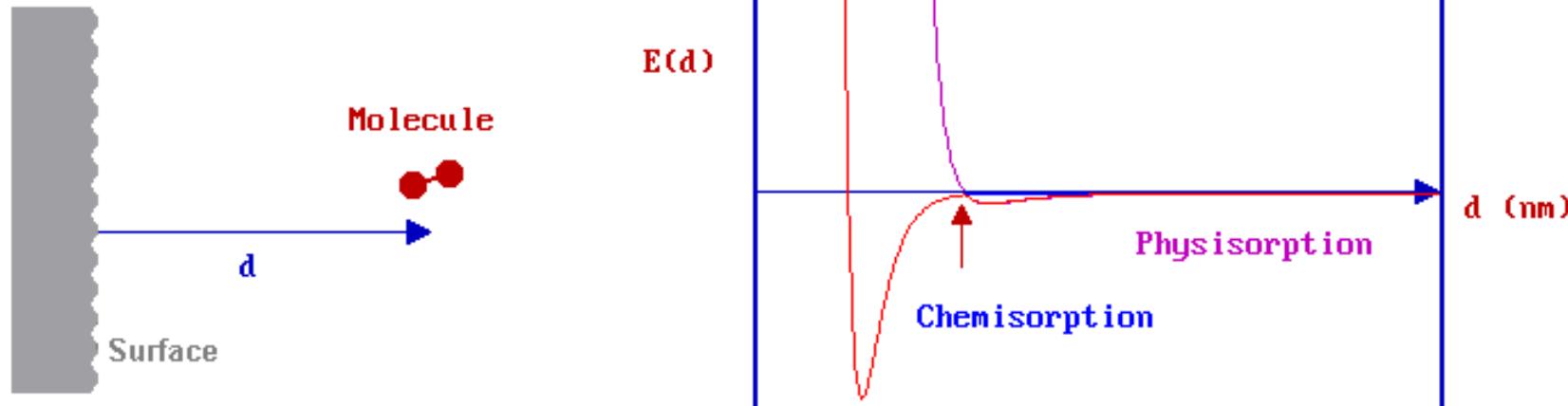
- There are two principal modes of adsorption of molecules on surfaces:
- **Physical adsorption ( Physisorption )**
- **Chemical adsorption ( Chemisorption )**
- The basis of distinction is the nature of the bonding between the molecule and the surface. With:
- ***Physical adsorption*** : the only bonding is by weak Van der Waals - type forces. There is no significant redistribution of electron density in either the molecule or at the substrate surface.
- ***Chemisorption*** : a chemical bond, involving substantial rearrangement of electron density, is formed between the adsorbate and substrate. The nature of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character.

<http://www.chem.qmul.ac.uk/surfaces/scc/>

# **Adsorption / Self Assembly Processes on Surfaces**

- Physisorption
  - Physical bonds
- Chemisorption
  - Chemical bonds
- Self-Assembled Monolayers (SAMs)
  - Alkane thiols on solid gold surfaces
  - Self assembly of monolayers

# Chemi / Physi - *Adsorption*



The graph above shows the PE curves due to physisorption and chemisorption separately - in practice, the PE curve for any real molecule capable of undergoing chemisorption is best described by a combination of the two curves, with a curve crossing at the point at which chemisorption forces begin to dominate over those arising from physisorption alone. The minimum energy pathway obtained by combining the two PE curves is now highlighted in red. Any perturbation of the combined PE curve from the original, separate curves is most likely to be evident close to the highlighted crossing point.

# *Forces at Interfaces*

- Van Der Val's forces
- Surface tension
- Interfacial bonding
- Hydrophobic / hydrophilic interactions
- Surface reconstruction / reorientation
- Driven by, or are part of '**excess surface free energy**' which must be ***minimized***.

# ***Importance of Interfaces***

- Chemical reactions occur at interfaces
  - Particularly corrosion
- Scattering energy
  - Electrons
  - Light
  - Phonons
- ***An interface is actually two surfaces***

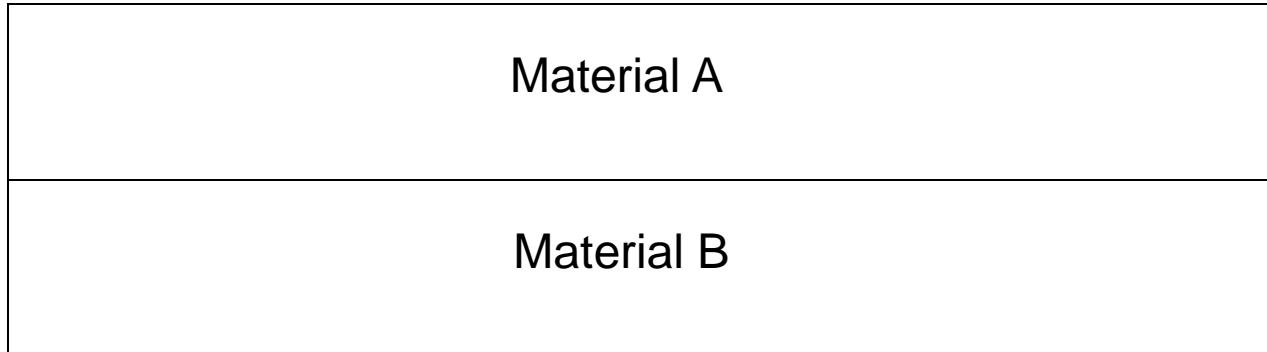
# ***Defects at Interfaces***

- Missing atoms
  - Defects and holes
- Extra atoms
  - Surface segregation
- Dangling bonds
  - Disrupted electronic properties
- Dimensional issues
  - Lattice mismatch / shelves

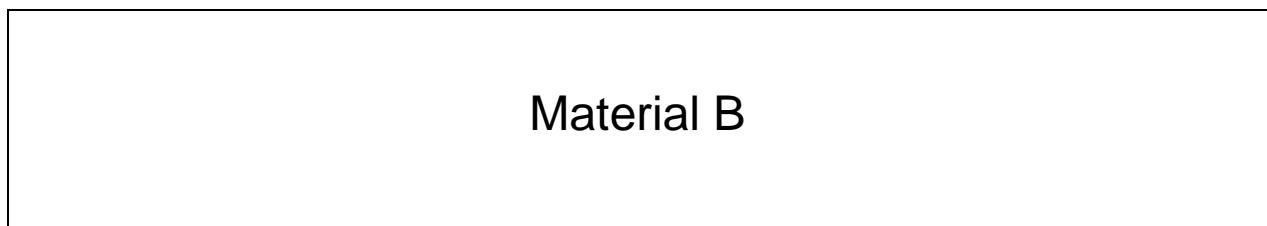
# **Cohesive / Adhesive *Failure at Interfaces***

- Cohesive failure occurs within a layer
- It can be from material weakness
- Or simply less strong than adhesion
- Adhesive failure occurs between layers
- It can arise from contamination, or poor adhesion, or simply the strength of adhesion was greater than the material

# Cohesive Failure



Material fails cohesively within B

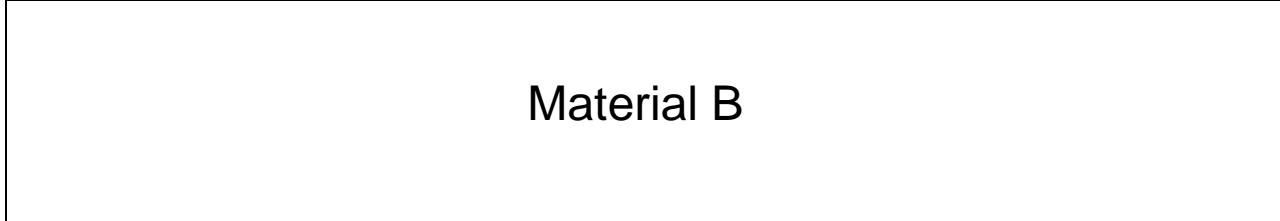


# Adhesive Failure



Material A

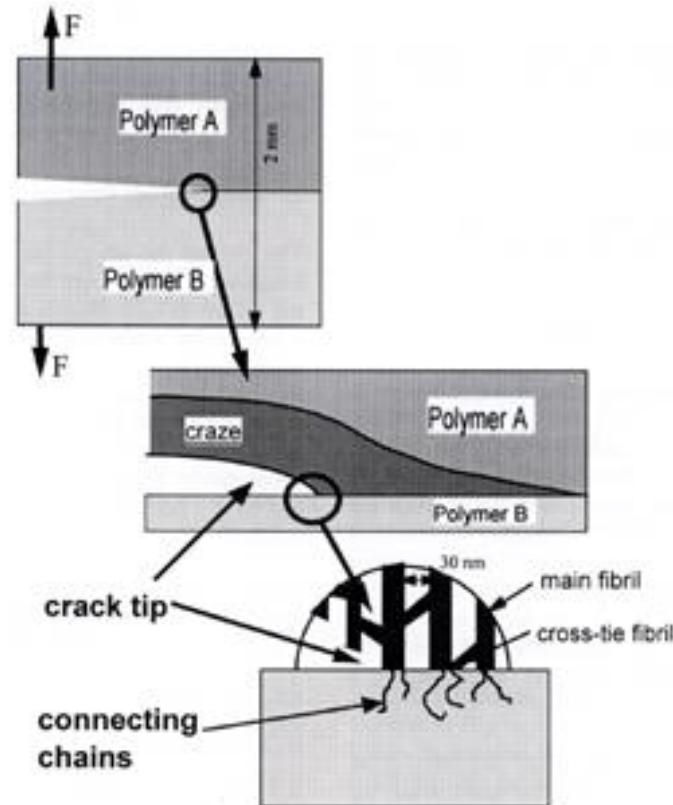
Material fails adhesively between A and B



Material B

# Adhesive Failure (Craze)

Schematic representation of the structure at the crack tip in a crazing material are shown at three length scales. It is assumed that only material A crazes. The whole of the craze consists of lain and cross-tie fibrils.



# **Surface *Reactions***

- Oxidation
- Surface diffusion
- Diffusion and oxidation
- Adventitious carbon bonding
  - Hydrocarbons from the atmosphere
- Surface rearrangement
  - Polymers may reorient to minimize energy

# A *Typical* Surface

Hydrocarbon layer of about 15 to 20 Angstroms

Oxide layer of about 15 to 20 Angstroms

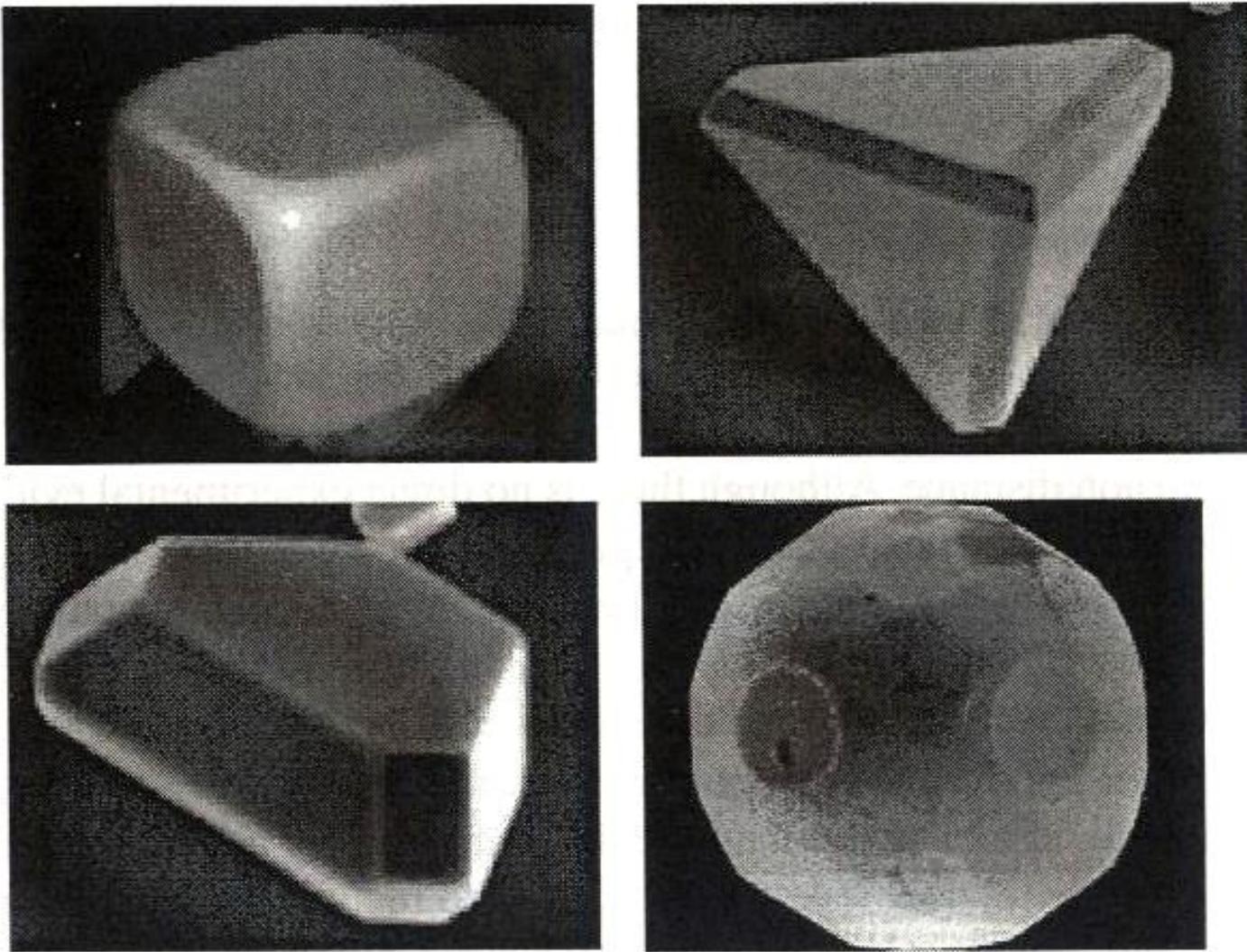
Solid material like silicon or aluminum

Hydrocarbons and water rapidly adsorb to a metal or Silicon surface. Oxides form to a thickness of about 15 To 20 Angstroms, and hydrocarbons to a similar thickness. This is part of the normal surface passivation process.



# Reduction of surface energy for a nanoparticle:

- One is to reduce the total surface area. That is, surface tends to become spherical.
- For crystalline particle, facets forms because they have smaller surface energy than a spherical surface does. Since facets with a lower Miller Index have a lower surface energy than that with a higher Miller Index. Therefore, crystal is often surrounded by low index surfaces.



**Fig. 2.7.** Examples of single crystals with thermodynamic equilibrium shape. (Top-left) Sodium chloride, (top-right) silver, (bottom-left) silver, and (bottom-right) gold. Gold particles are formed at 1000°C and some facets have gone through roughening transition.

# Crystal Growth with Nonfacets

- At certain high temperature, the equilibrium crystal surfaces may not be smooth, and difference in surface energy of various crystal facets may disappear. Such a transition is called surface roughening or roughening transition. Most nanoparticles grown at elevated temperature are spherical in shape (not facets).
- Kinetic factors (processing or crystal growth conditions) may also prevent formation of facets.

# Mechanisms for reduction of overall surface energy

Combining individual nanostructures together to form large structures so as to reduce the overall surface area, which includes:

- **Sintering**: individual structures merge together which occurs at 70% of  $T_m$ . Replacing solid-vapor interface by solid-solid interface and becomes polycrystalline.
- **Ostwald ripening**: A large one grows at the expense of the smaller one until the latter disappears completely, and becomes a single crystal. It occurs at relatively low temperature.
- **Agglomeration** of individual nanostructures through chemical bonds and physical attraction forces at interfaces without altering the individual nanostructures. The smaller the particles, the greater the bonding forces are.

# Thermodynamic potentials

Thermodynamic potentials are state functions that, together with the corresponding equations of state, describe the equilibrium behavior of a system as a function of so-called "natural variables". The natural variables are a set of appropriate variables that allow to compute other state functions by partial differentiation of the thermodynamic potentials.

Source: [https://itp.uni-frankfurt.de/~gros/Vorlesungen/TD/5\\_Thermodynamic\\_potentials.pdf](https://itp.uni-frankfurt.de/~gros/Vorlesungen/TD/5_Thermodynamic_potentials.pdf)

# Review

The Laws of Thermodynamics

<https://www.youtube.com/watch?v=8N1BxHgsoOw>

Thermodynamic Potentials Part 1

<https://www.youtube.com/watch?v=EgbrBJ3-OH4>

Thermodynamic Potentials Part 2

<https://www.youtube.com/watch?v=VVDaR6oczJU>

# Thermodynamic equations

Name	Formula
Internal Energy	$U$ (depends on the system)
Helmotz Free Energy	$F = A = U - TS$
Enthalpy	$H = U + PV$
Gibbs Free Energy	$G = U + PV - TS = H - TS$
Landau Potential	$\Omega = U - TS - \sum_i \mu_i N_i$

Where:  $T$ = temperature,  $S$ = entropy,  $P$ = pressure,  $V$ =Volume,  $N_i$  is the number of particles and  $\mu$  is the chemical potential

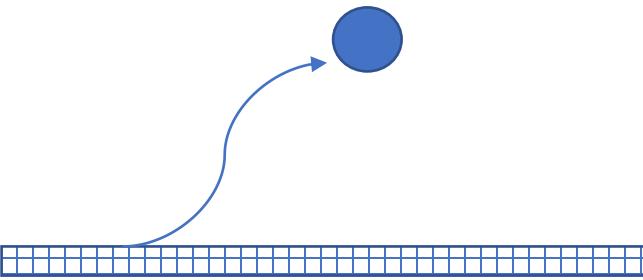
Helmholtz free energy is often represented by  $F$  (particularly in physics), although IUPAC prefers the symbol  $A$  (which is used primarily in chemistry).

It can be shown that the knowledge of one of the thermodynamic potentials based on their natural variables allows obtaining all the thermodynamic variables of the system. This is possible by using the **four Maxwell relationships for thermodynamics**, partial derivative equations that relate state variables to thermodynamic potentials.

Each thermodynamic potential, under this point of view, is not only a physical quantity to which a value (real number) that we can eventually measure, but more properly must be seen as a mathematical functional dependence, which contains all the information of the system.

This is why we talk about the "natural variables" of each potential: they are the magnitudes that play the role of independent variables in the function associated with the potential

# Chemical Potential and Surface Tension



Flat surface  
Migration of chemical species  
from a flat surface to a  
spherical particle

$$dV = 4\pi R^2 dR = \Omega dn$$

$$\Omega = \frac{dV}{dn}$$

NOTE: Here **Omega is the atomic volume** not the Landau Potential

$$\Delta\mu = \mu_c - \mu_\infty = \gamma \frac{dA}{dn} = \gamma 8\pi R dR \frac{\Omega}{dV}$$

NOTE:  $\mu_c$  is the chemical potential  
gamma is the surface energy  
 $n$  is the number of particles

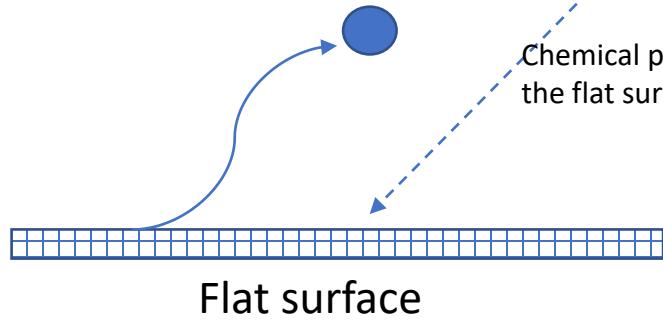
Similar to the Young-Laplace eqn

# Chemical Potential and Surface Tension

$P_{\infty}$  is the equilibrium vapor pressure of the flat surface

$$\mu_v - \mu_\infty = -kT \ln P_\infty$$

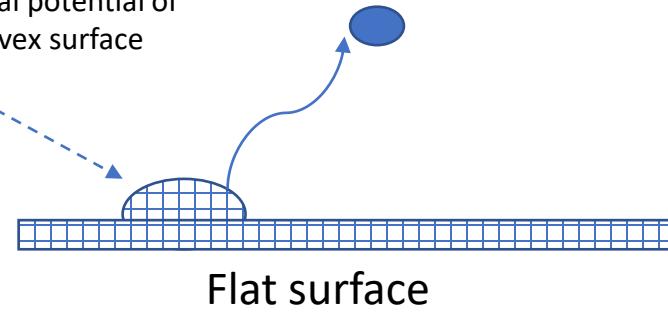
Chemical potential of the flat surface



Evaporation of an atom form from a flat surface to the environment

$$\mu_v - \mu_c = -kT \ln P_c$$

Chemical potential of the convex surface



Evaporation of an atom form from a flat surface to the environment

If we combine with equation 1 from the previous slide:

For a spherical particle

The vapor pressure of the particle increases as the radius of the particle decreases

# Chemical potential and its effect on vapor pressure

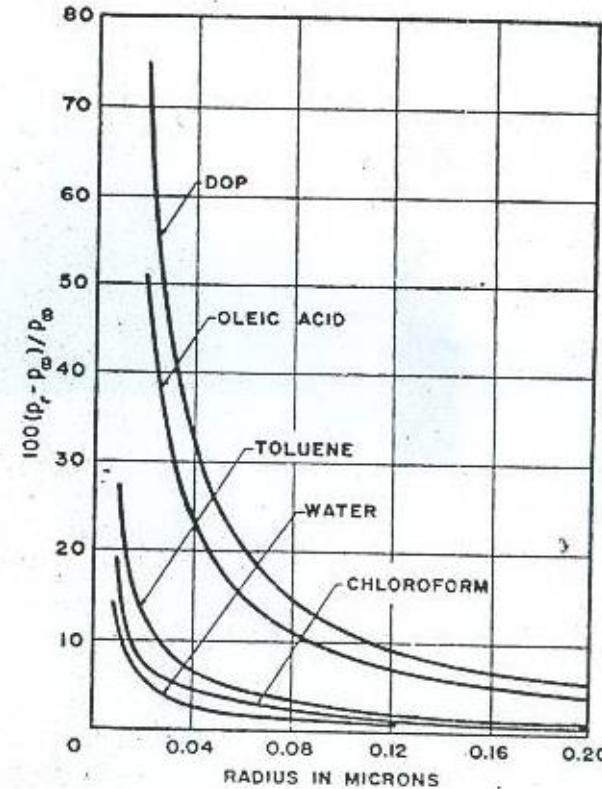


Fig. 2.12. Vapor pressure of a number of liquids as a function of droplet radius. [V.K. La Mer and R. Gruen, *Trans. Faraday Soc.* 48, 410 (1952).]

# Chemical potential and its effect on solubility

Similarly, for solubility:

$$\ln\left(\frac{S_c}{S_\infty}\right) = \gamma\Omega \frac{R_1^{-1} + R_2^{-1}}{kT}$$

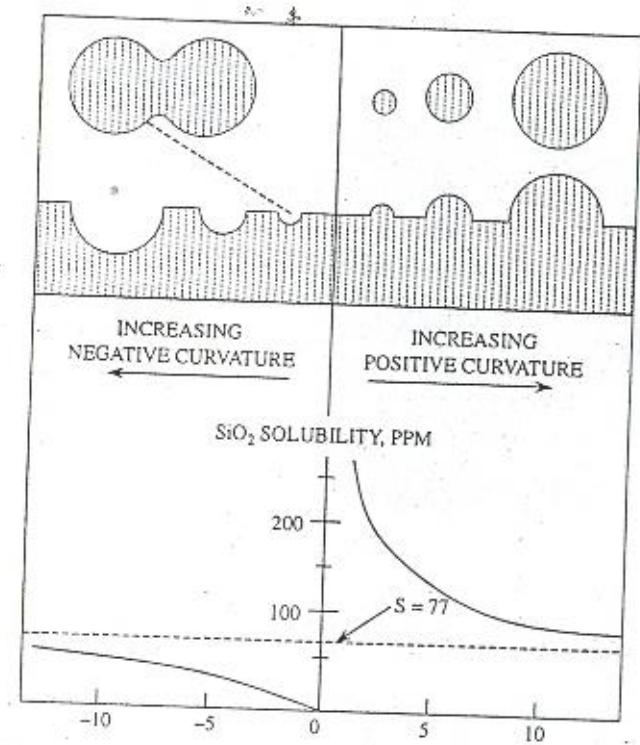
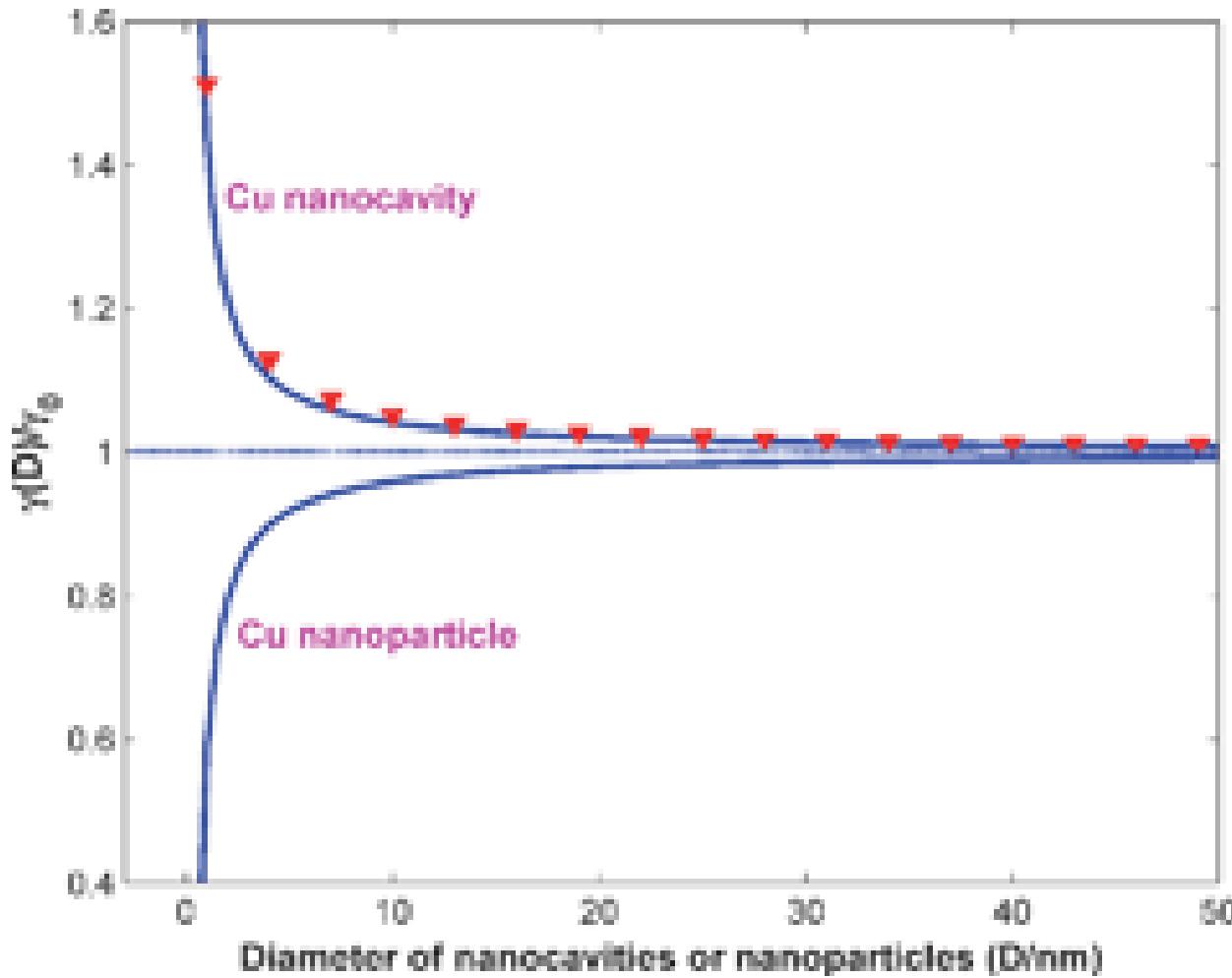


Fig. 2.11. Variation in solubility of silica with radius of curvature of surface. The positive radii of curvature are shown in cross-section as particles and projections from a planar surface; negative radii are shown as depressions or holes in the surface, and in the crevice between two particles. [R.K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979.]



#### Modeling size effects on the surface free energy of metallic nanoparticles and nanocavities

Shiyun Xiong,<sup>a</sup> Weihong Qi,<sup>\*ab</sup> Yajuan Cheng,<sup>a</sup> Baiyun Huang,<sup>c</sup> Mingpu Wang<sup>ab</sup> and Yejun Li<sup>a</sup>; Physical Chemistry Chemical Physics Journal, Issue 2, 2011  
<https://pubs.rsc.org/en/content/articlelanding/2011/cp/c0cp02102d#!divAbstract>

# Ostwald Ripening Phenomenon

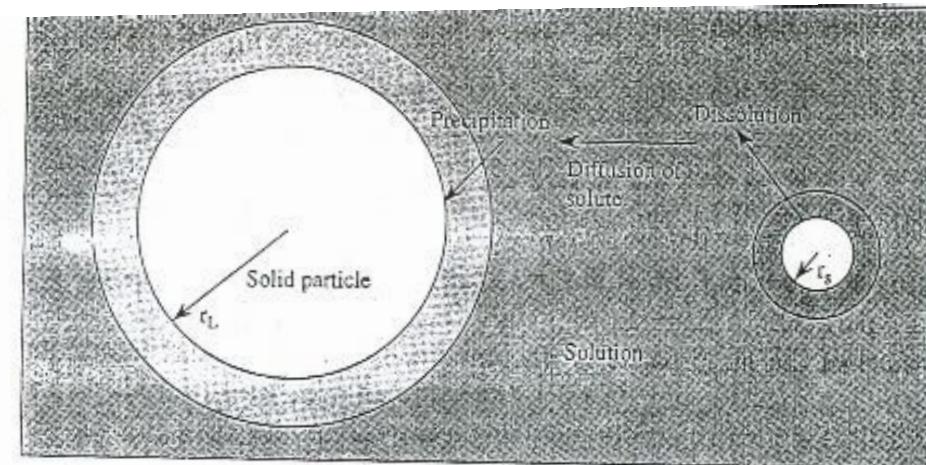


Fig. 2.13. Schematic illustrating the Ostwald ripening processing. Smaller particle has a larger solubility or vapor pressure due to its larger curvature, whereas the larger particle possesses a smaller solubility or vapor pressure. To maintain the local concentration equilibrium, smaller particle would dissolve into the surrounding medium; solute at proximity of smaller particle diffuses away; solute at proximity of larger particle would deposit. The process would continue till disappearance of the smaller particle.

$$\Delta\mu = 2\gamma\Omega \left( \frac{1}{R_1} - \frac{1}{R_2} \right)$$

Surface stress and surface energy of Al nanoclusters computed based on DFT calculation. The surface energy/stress-particle radius curves were drawn based on the data presented in ref. 29.

