Surface Energy and Thermodynamic Potentials*

February 17th, 2020

* Based on a presentation from the author´s book

Question…

Is it the same surface energy and surface tension?

Percentage of surface atoms changes with cluster diameter

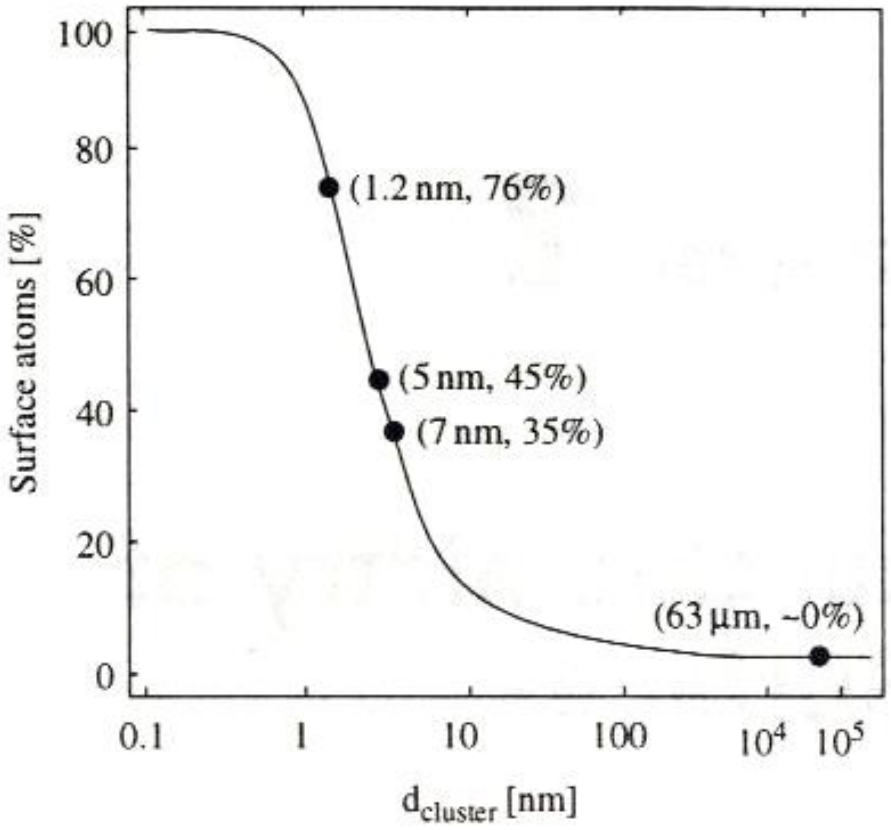


Fig. 2.1. The percentage of surface atoms changes with the palladium cluster diameter. [C. Nützenadel, A. Züttel, D. Chartouni, G. Schmid, and L. Schlapbach, *Eur. Phys. J.* **D8**, 245 (2000).]

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.[22]

Side (cm)	*Total surface area* (cm^2)	*Total edge* (cm)	*Surface energy* (J/g)	*Edge energy* (J/g)
0.77	3.6	9.3	7.2×10^{-5}	2.8×10^{-12}
0.1	28	550	5.6×10^{-4}	1.7×10^{-10}
0.01	280	5.5×10^{4}	5.6×10^{-3}	1.7×10^{-8}
0.001	2.8×10^{3}	5.5×10^{6}	5.6×10^{-2}	1.7×10^{-6}
10^{-4} (1 μm)	2.8×10^{4}	5.5×10^{8}	0.56	1.7×10^{-4}
10^{-7} (1 nm)	2.8×10^{7}	5.5×10^{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.

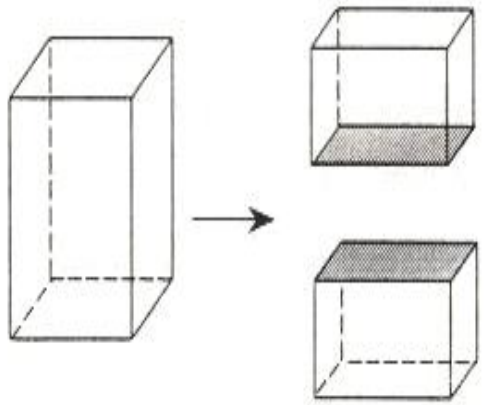


Fig. 2.2. Schematic showing two new surfaces being created by breaking a rectangular solid into two pieces.

Surface Energy

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

$$\gamma = (\partial G / \partial A)_{ni,\, T,\, P}$$

- G: Gibs 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, γ

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

- ✓ N_b: number of broken bonds

γ_{la}

- ✓ ε: bond strength
- ✓ ρ_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.

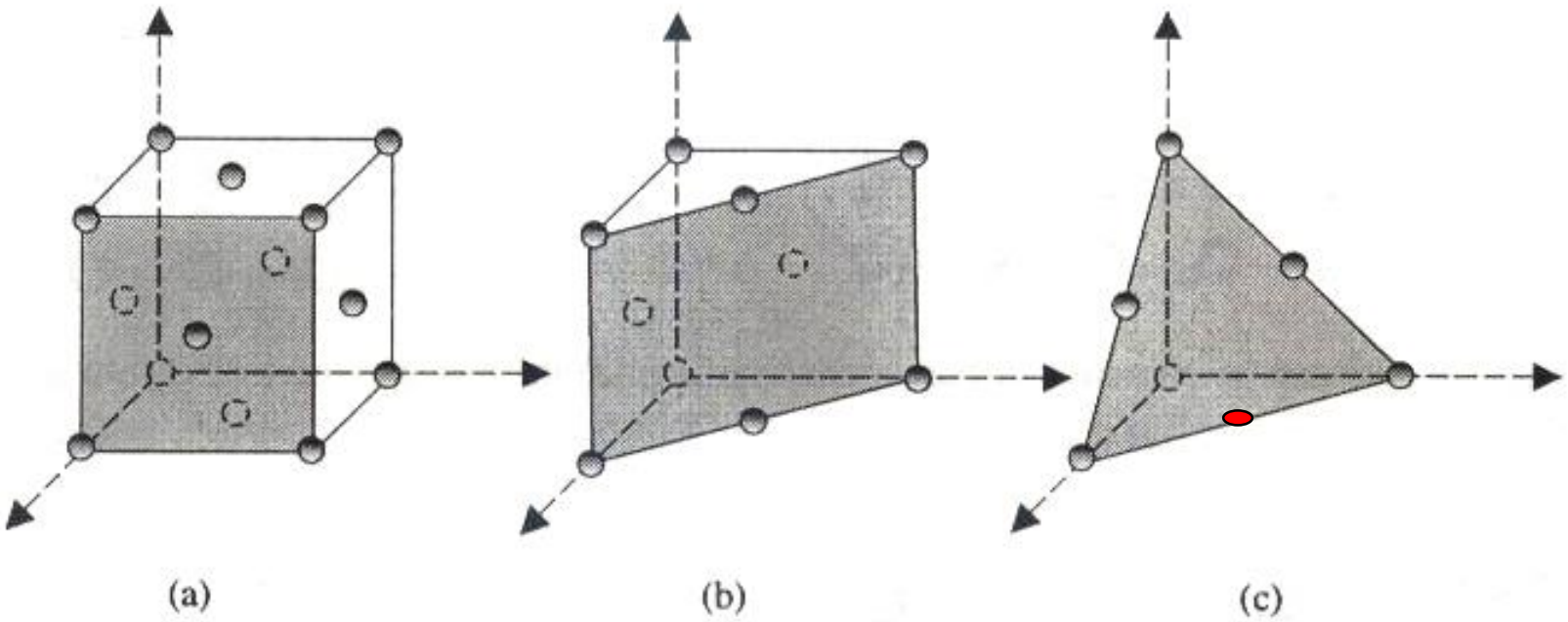


Fig. 2.3. Schematic representing low index faces of a face-centered cubic (fcc) crystal structure: (a) {100}, (b) {110} and (c) {111}.

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,

$$\gamma = N_b \, \varepsilon \, \rho_a / 2$$

If a=1, ε=1

$$\gamma_{\{100\}} = 2/a^2 . \; 4 . \; \varepsilon . \; 1/2$$

$\gamma_{\{100\}} = 4$

$$\gamma_{\{110\}} = 2/2^{0.5}a^2 . \; 5 . \; \varepsilon . \; 1/2$$

$\gamma_{\{110\}} = 3.52$

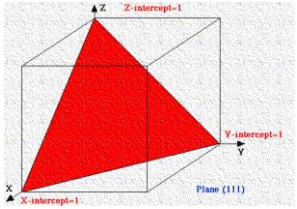
$$\gamma_{\{111\}} = 2/3^{0.5}\varepsilon a^2$$

$\gamma_{\{111\}} = 1.16$

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

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

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



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.

http://cmacd.myweb.cs.uwindsor.ca/Teaching/553-class/59-553_Notes3.pdf

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

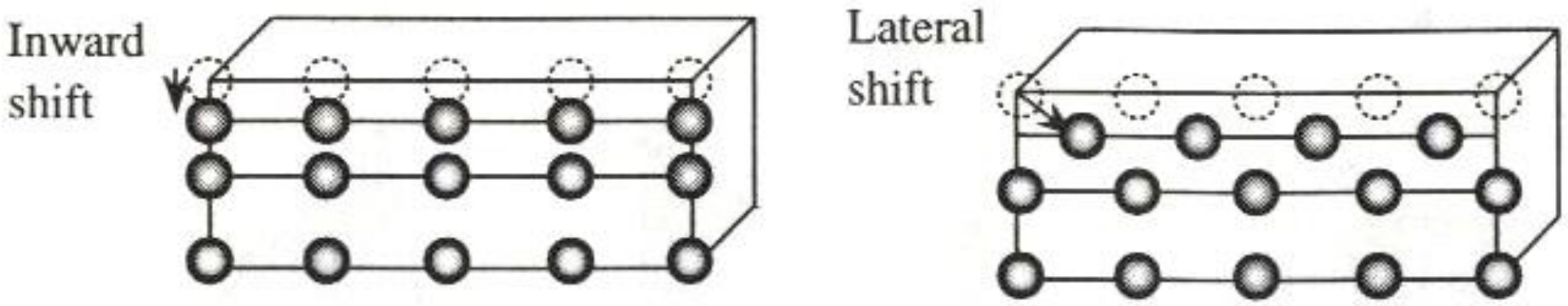


Fig. 2.4. Schematic showing surface atoms shifting either inwardly or laterally so as to reduce the surface energy.

Surface energy reduction by restructuring

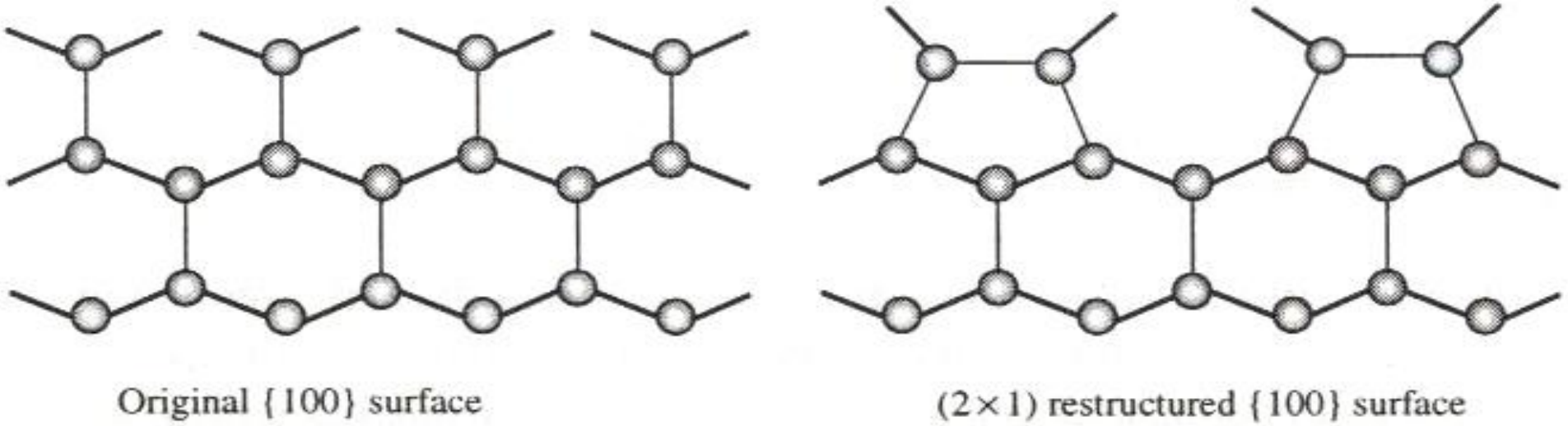


Fig. 2.5. Schematic illustrating the (2 × 1) restructure of silicon {100} surface.

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

Surface energy reduction by chemical or physical adsorption

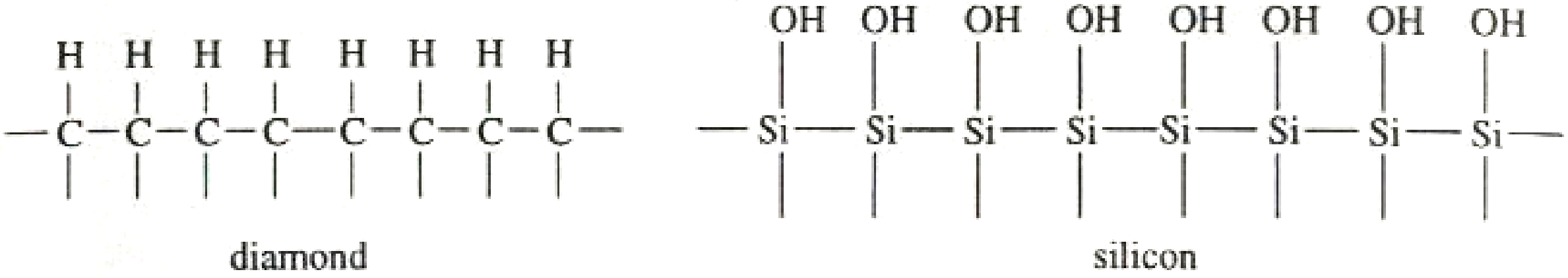


Fig. 2.6. Schematic showing the surface of diamond is covered with hydrogen and that of silicon is covered with hydroxyl groups through chemisorption before restructuring.

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.

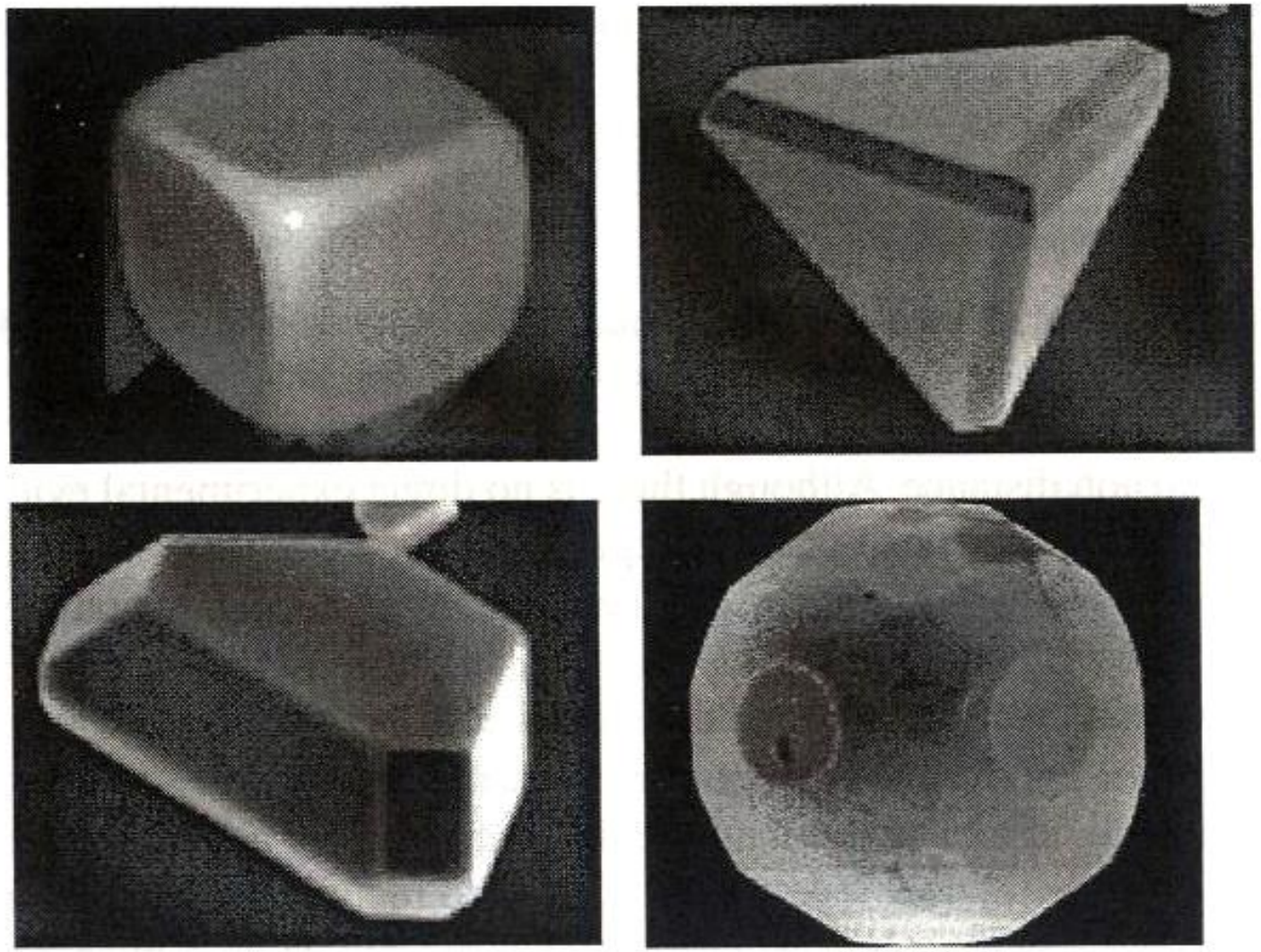


Fig. 2.7. Examples of single crystals with thermodynamic equilibrium shape. (Top-left) Sodium chloride, (top-right) silver, (bottom-left) silver, and (bottom-right) gold. Gold particles are formed at 1000°C and some facets have gone through roughening transition.

Crystal Grown 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

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	$\boxed{\Omega} = U - TS - \sum_i \mu_i N_i$

Where: T= temperature, S= enthropy, P= pressure, V=Volume, N_i is the number of particles and μ is the chemical potential

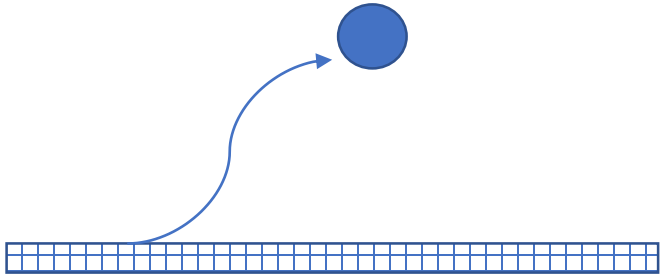
Helmholtz free energy is often represented by F (particularly in physics), although IUPAC prefers the symbol A (which is used primarily in chemistry).

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: Miu is the chemical potential
gamma is the surface energy
n is the number of particles

$$\Delta\mu = 2\gamma \frac{\Omega}{R}$$

Similar to the Young-Laplace eqn

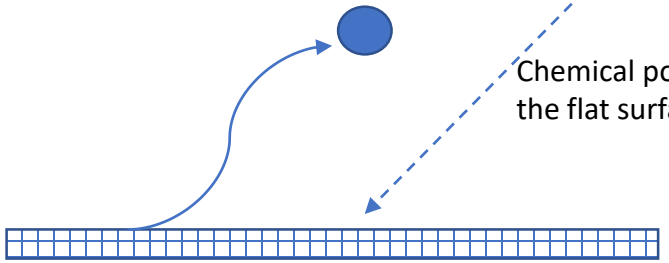
(1) $$\Delta\mu = \gamma\Omega\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Chemical Potential and Surface Tension

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

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

Chemical potential of the flat surface



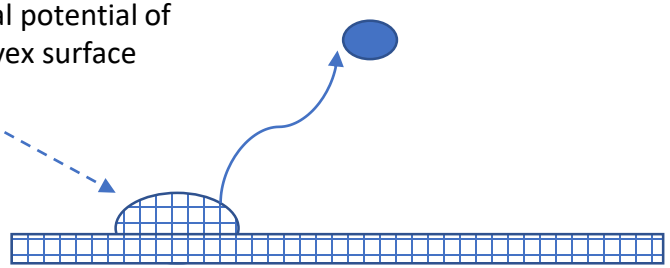
Flat surface

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

Pc is the equilibrium vapor pressure of the curved surface

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

Chemical potential of the convex surface



Flat surface

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

$$\Delta\mu = \mu_c - \mu_\infty = \Delta\mu = kT \ln\left(\frac{P_c}{P_\infty}\right)$$

If we combine with equation 1 from the previous slide:

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

For a spherical particle

$$\ln\left(\frac{P_c}{P_\infty}\right) = \frac{2\gamma\Omega}{kRT}$$

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

Chemical potential and its effect on vapor pressure

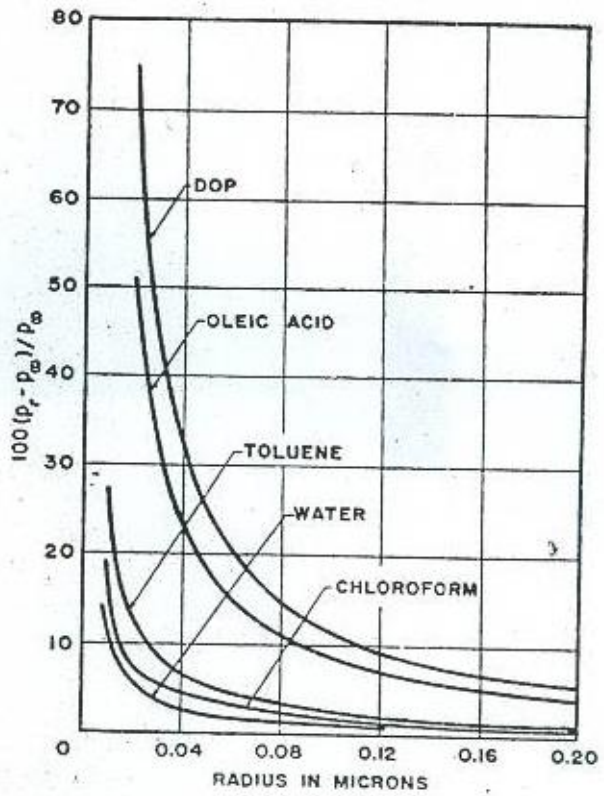


Fig. 2.12. Vapor pressure of a number of liquids as a function of droplet radius. [V.K. La Mer and R. Gruen, *Trans. Faraday Soc.* 48, 410 (1952).]

Similarly, for solubility:

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

$$\ln\left(\frac{S_c}{S_\infty}\right) = \frac{2\gamma\Omega}{kRT}$$

Chemical potential and its effect on solubilty

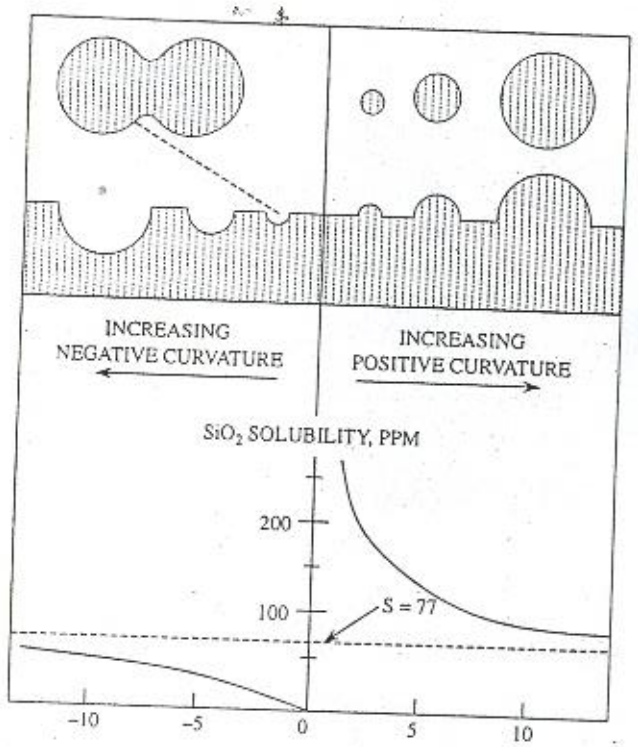
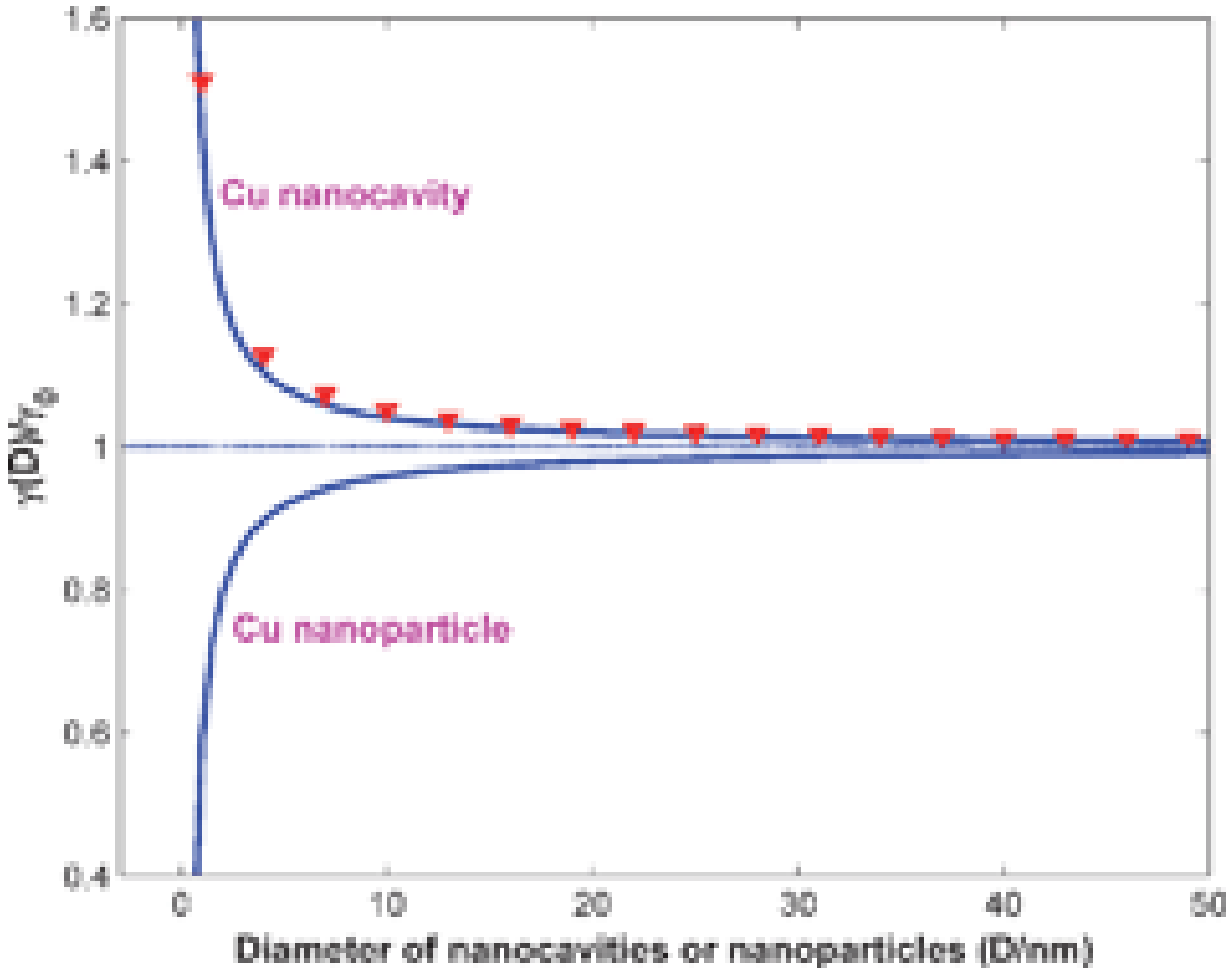


Fig. 2.11. Variation in solubility of silica with radius of curvature of surface. The positive radii of curvature are shown in cross-section as particles and projections from a planar surface; negative radii are shown as depressions or holes in the surface, and in the crevice between two particles. [R.K.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

Let us discuss these behaviors



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

Shiyun Xiong,[a] Weihong Qi,*[ab] Yajuan Cheng,[a] Baiyun Huang,[c] Mingpu Wang[ab] and Yejun Li[a] ; Physical Chemistry Chemical Physics Journal, Issue 2, 2011

https://pubs.rsc.org/en/content/articlelanding/2011/cp/c0cp02102d#!divAbstract

Ostwald Ripening Phenomenon

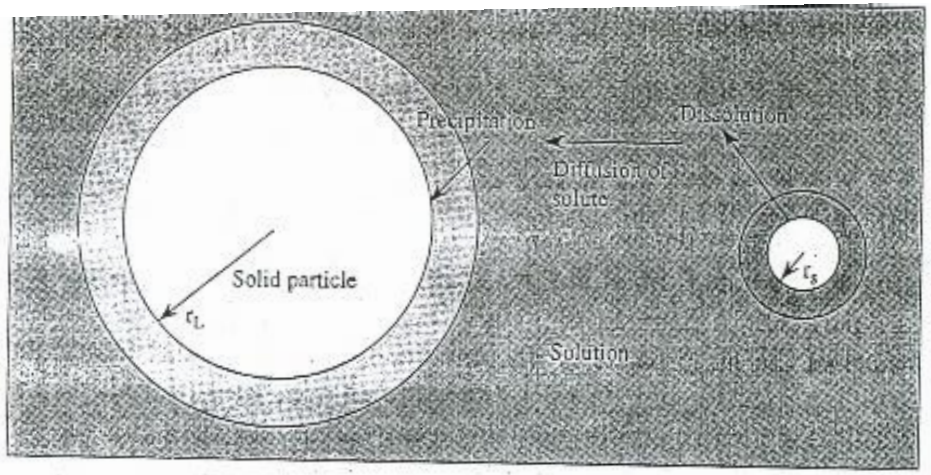
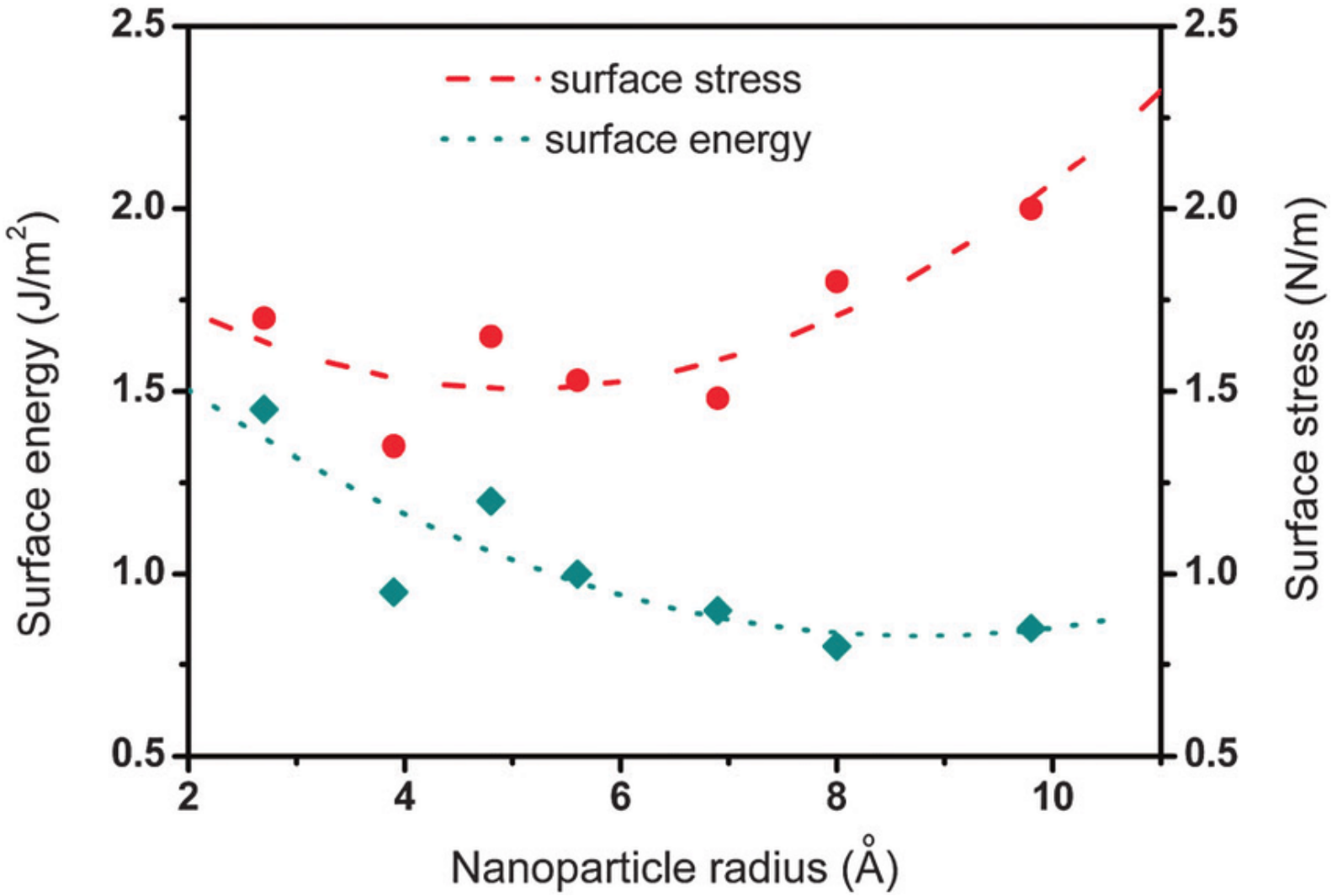


Fig. 2.13. Schematic illustrating the Ostwald ripening processing. Smaller particle has a larger solubility or vapor pressure due to its larger curvature, whereas the larger particle possesses a smaller solubility or vapor pressure. To maintain the local concentration equilibrium, smaller particle would 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.



Wu, Jianbo & li, Panpan & Pan, Yung-Tin & Warren, Steven & Yin, Xi & Yang, Hong. (2012). ChemInform Abstract: Surface Lattice-Engineered Bimetallic Nanoparticles and Their Catalytic Properties. Chemical Society reviews. 41. 10.1039/c2cs35189g.