Lahore College for Women University
Lahore

Nanotechnology & Nanostructures (Lecture # 9)

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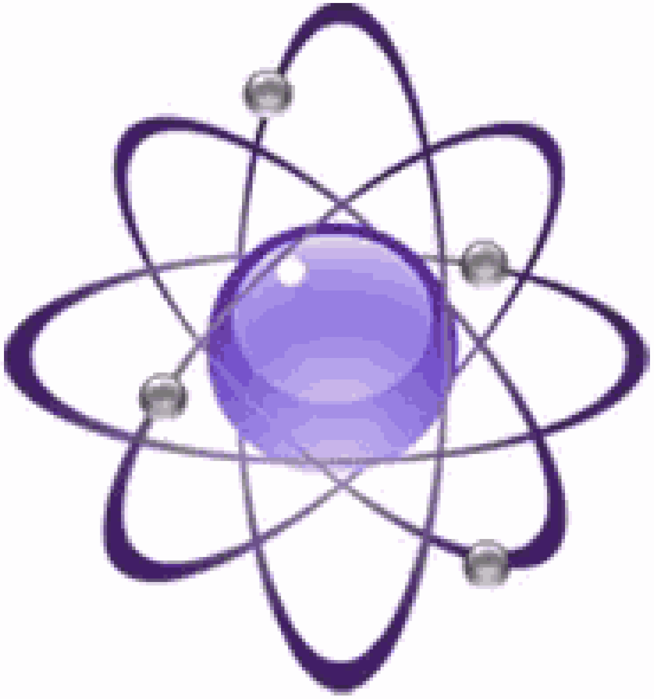
- Physics Department

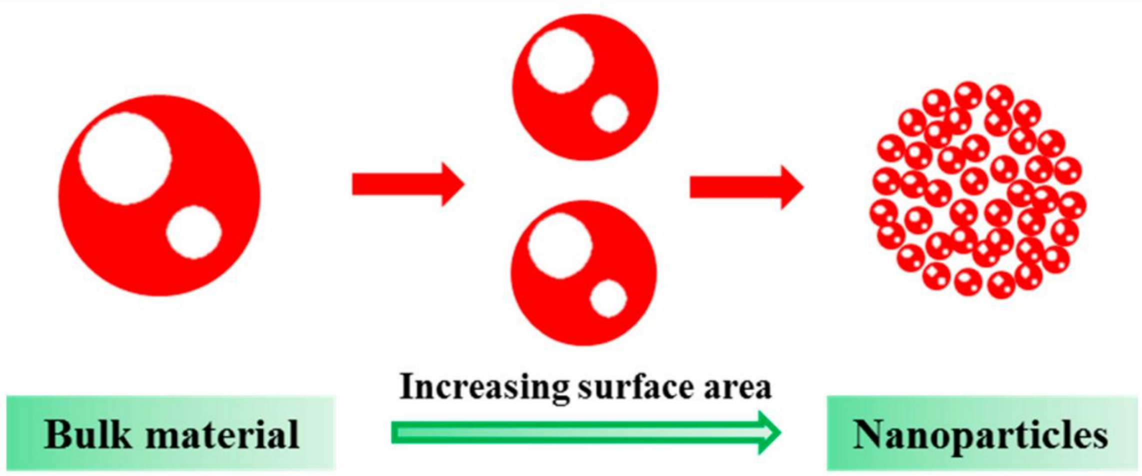
Size Effects:

1. Surface-to-Volume Ratio versus Shape
2. Magic Numbers
3. Surface Curvature
4. Strain Confinement
5. Quantum Effects



1.Surface-to-Volume Ratio versus Shape

- Major difference between nanomaterials and larger-scale materials is that nanoscale materials have an extraordinary large surface area to volume ratio.



- Almost all properties of the thin layer of atoms that lie in the surface or interface of things behave in a different way than those in the interior. Surfaces, you could say, have their own properties.

- At the macro scale (bulk), the fraction of atoms that lie on the surface is minuscule. On the micron scale (micro) it is still tiny. But approach the nanoscale and it takes off.

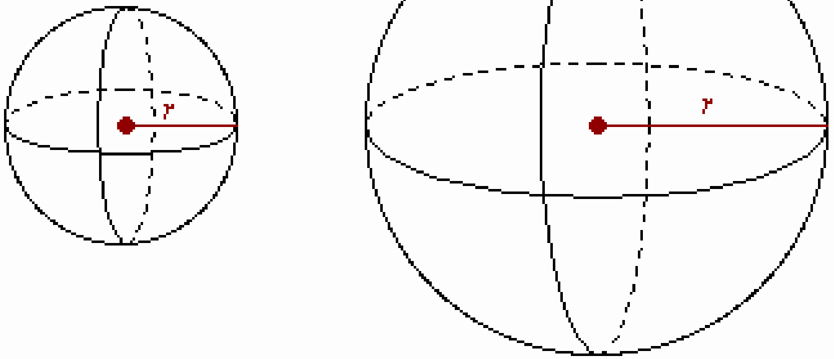
- This inverted the surface area to volume ratio for nanomaterials and its effects on nanomaterials properties is a key feature of nanoscience and nanotechnology.

Shapes of Nano Material

A nanomaterial's shape is of great interest because various shapes will produce a distinct surface-to-volume ratios and therefore different properties.

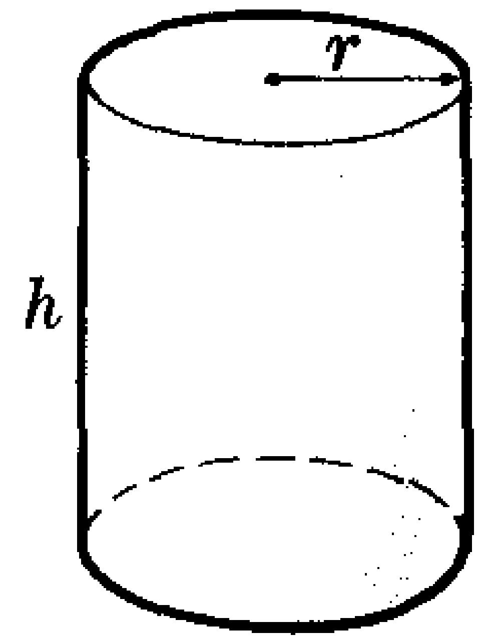
1.The surface-to-volume ratio of a sphere of radius r is given by:

$$\frac{A}{V} = \frac{4\pi r^2}{\frac{4\pi r^3}{3}} = \frac{3}{r}$$



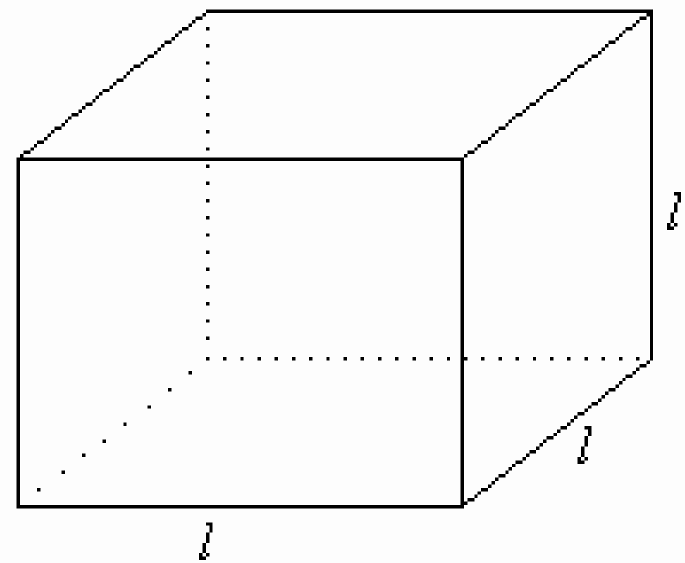
2. The surface-to-volume ratio of a cylinder of radius r and height H is given by:

$$\frac{A}{V}=\frac{\pi r^2 H}{2\pi r H}=\frac{2}{r}$$



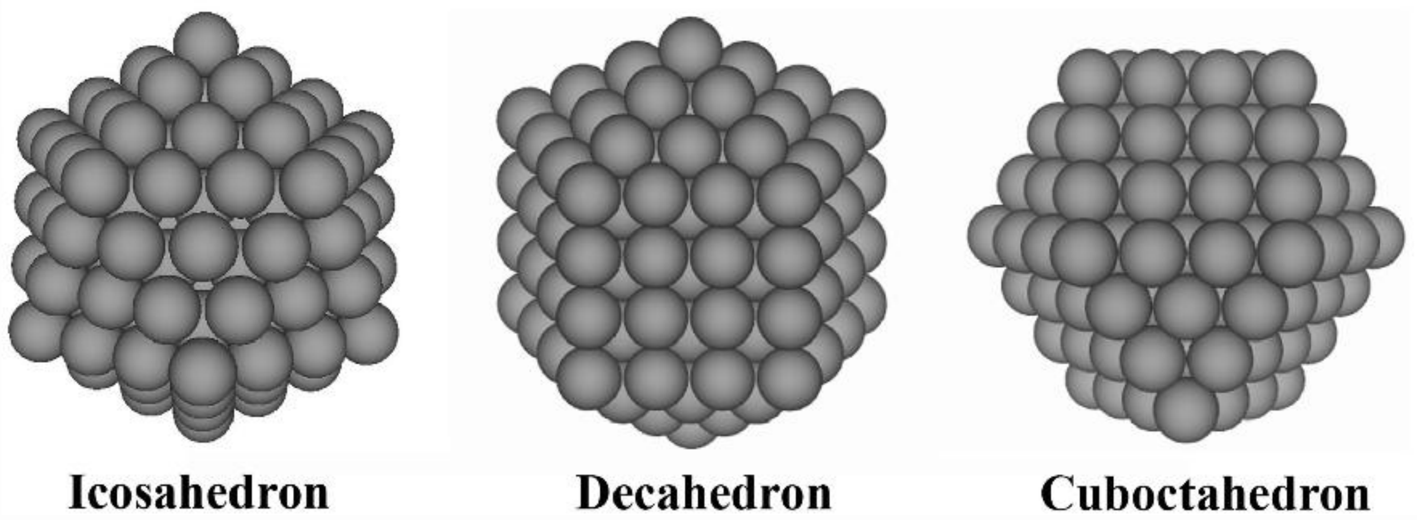
3. The surface-to-volume ratio of a cube of length L is given by:

$$\frac{A}{V} = \frac{6L^2}{L^3} = \frac{6}{L}$$



2. Magic Numbers

Nanoparticles have a “structural magic number”, that is, the optimum number of atoms that leads to a stable configuration while maintaining a specific structure.



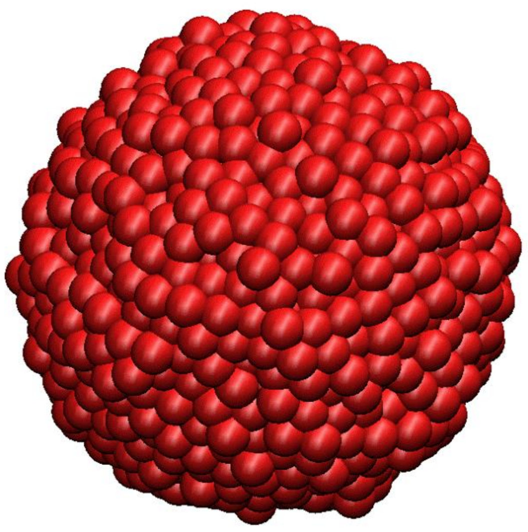
- If the crystal structure is known, then the number of atoms per particle can be calculated. For a decrease in particle radius, the surface to volume ratio increases. Therefore the fraction of atoms increases as the particle size goes down.

- For spherical nanoparticles, the number of surface and bulk atoms is given as:

$$V = \frac{4\pi}{3} r_A^3 n$$

$$A = 4\pi r_A^2 n^{2/3}$$

where V =volume of the nanoparticle.
A =surface area of the nanoparticle.
r_A=atomic radius.
n =number of atoms.



The fraction of atoms F_A (=A/V) on the surface of a spherical nanoparticle can be given by:

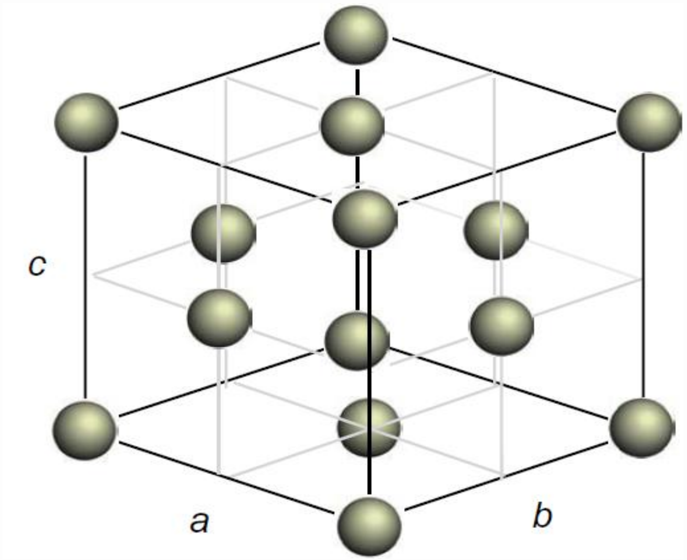
$$F_A = \frac{3}{r_A n^{1/3}}$$

Face-centered cubic (FCC) structure.

•In addition to the shape of the particle, we have to take into consideration the crystal structure.

•Assume a nanoparticle with a face-centered cubic (FCC) structure.

•This crystal structure is of practical importance because nanoparticles of gold (Au), silver (Ag), nickel (Ni), aluminum (Al), copper (Cu)and platinum (Pt) exhibit such a structure.



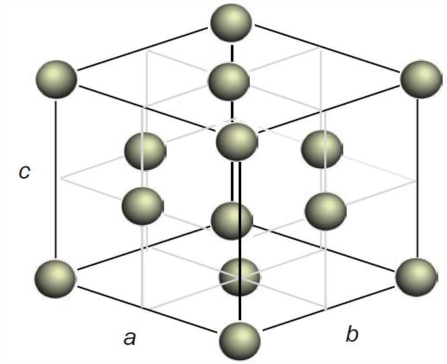
Clearly, the 14 atoms are all surface atoms. If another layer of atoms is added so that the crystal structure is maintained, a specific number of atoms must be introduced. In general, for n layers of atoms added, the total number of surface atoms can be given by:

$$N^{S}_{Total} = 12n^2 + 2$$

The total number of bulk (interior) atoms can be given by:

$$N^{B}_{Total} = 4n^3 - 6n^2 + 3n - 1$$

Thus, above two equations relate the number of surface and bulk atoms as a function of the number of layers. These numbers are called **structural magic numbers**.



Equilibrium shape of nano crystalline particles

Equilibrium (**minimum**) shape of nanocrystalline particles is determined by:

$$\sum A_i \gamma_i = \text{minimum}$$

Where
γ_i is the surface energy per unit area A_i of exposed surfaces, if edge and curvature effects are negligible.

Cubo-octahedron

- Among the possible shapes, the smallest FCC nanoparticle that can exist is a **cubo-octahedron (dual octahedron)**, which is a14-sided polyhedron. This nanoparticle has 12 surface atoms and one bulk atom.

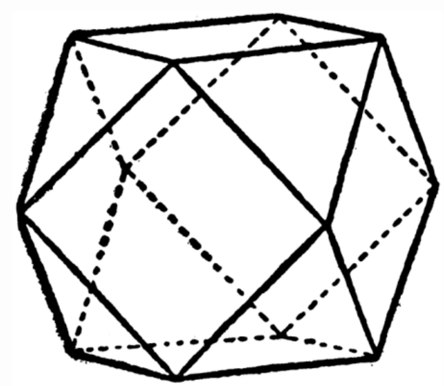
- If additional layers of atoms are added to the cubo-octahedral nanoparticle such that the shape and crystal structure of the particle are maintained, a series of structural magic numbers can be found.

In cubo-octahedral nanoparticle, for n layers of atoms added, the total number of surface atoms can be given by:

$$N_{Total}^{S} = 10n^2 - 20n + 12$$

whereas the total number of bulk (interior) atoms can be given by:

$$N_{Total}^{B} = \frac{1}{3}\left(10n^3 - 15n^2 + 11n - 3\right)$$



3. Surface Curvature

- All solid materials have finite sizes. The atomic arrangement at the surface is different from that within the bulk because the surface atoms are not bonded in the direction normal to the surface plane.

- If the energy of each bonded atom is $\varepsilon/2$ (the energy is divided by 2 because each bond is shared by two atoms), then for each surface atom not bonded there is an excess internal energy of $\varepsilon/2$ over that of the atoms in the bulk.

- In addition, surface atoms will have more freedom to move and thus higher entropy. These two conditions are the origin of the **surface free energy** of materials.

For a pure material, the surface free energy γ can be expressed as:

$$\gamma = E^S - TS^S$$

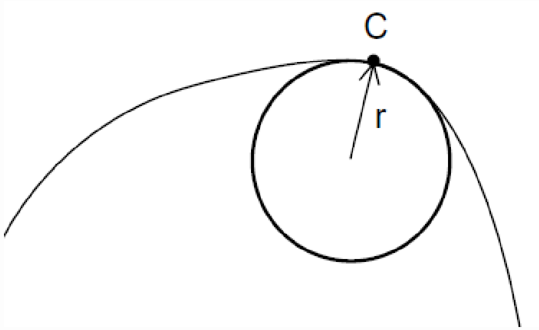
where E^S =internal energy.
T = Temperature.
S^S = surface thermal entropy.

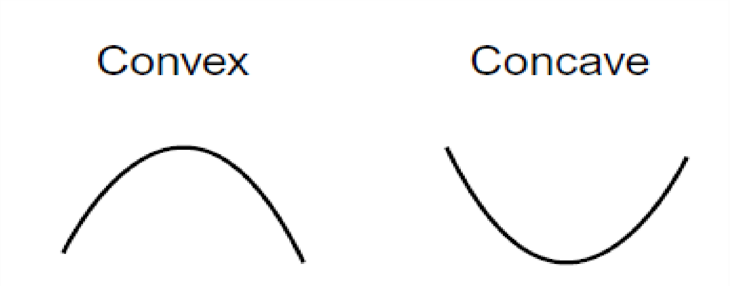
Geometry of the surface

•The **geometry of the surface** (specifically its local curvature) will cause a change in the system's pressure.

• These pressure effects are normally called **capillarity effects** due to the fact that the initial studies were done in fine glass tubes called capillaries.

•For the concept of surface curvature, consider the 2-D curve shown in Figure. A circle of radius r just touches the curve at point C.





- The radius r is called the radius of curvature at C, whereas the reciprocal of the radius is called the local curvature of the curve at *C*.

$$k = 1/r$$

- The local curvature may vary along the curve. By convention, the local curvature is defined as positive if the surface is convex and negative if concave.

Gibbs free energy

As the total energy (Gibbs free energy) of a system is affected by changes in pressure, i.e. variations in surface curvature will result in changes in the **Gibbs free energy** given by:

$$\Delta G = \Delta PV = \frac{2\gamma V}{r}$$

•When two nanoparticles are in contact with each other, the neck region between the nanoparticles has a concave surface, which results in reduced pressure.

• As a consequence, atoms readily migrate from convex surfaces with positive curvature (high positive energy) to concave surfaces with negative curvature (high negative energy), leading to the coalescence of nanoparticles and elimination of the neck region.

•In other words, nanoparticles exhibit a high tendency to sintering, even at room temperature, due to the curvature effect.

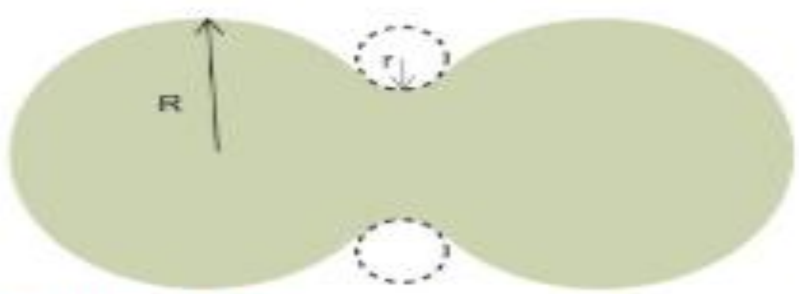


FIGURE 6.26

Schematic showing the sintering process of two nanoparticles. R is the radius of the convex surface and r is the radius of the concave surface.

Lattice parameter

One other important physical property of a material is its lattice parameter. To understand the effects of scale on the lattice parameter, we consider the Gauss-Laplace formula given by:

$$\Delta P = \frac{4\gamma}{d}$$

where ΔP = difference in pressure between the interior of a liquid droplet and its outside environment

γ = surface energy.

d= diameter of the droplet.

$$\frac{\gamma}{d} = \frac{3K}{4}\frac{\Delta a}{a}$$

Since the surface energy increases as the particle size decreases, because the radius of curvature decreases, last equation reveals that the lattice parameter is reduced for a decrease in particle size.

Thank you