

# POLYMERIC NANOMATERIALS AND NANOCOMPOSITES

Prof. Bijay Prakash Tripathi

[MLL718]

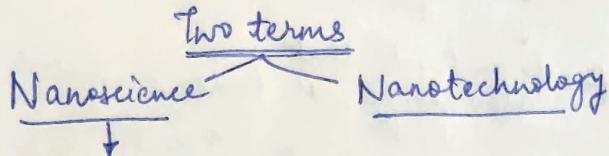
Prof. Anup Kumar Ghosh

# LECTURE-1 (of Prof. B. P. Tripathi)

01/08/2023

\* { NOTE: Before this point,  
see slides uploaded by  
Prof. A.K. Ghosh }

1]



Involves study of  
 synthesis, characterization,  
 modification, and  
 understanding the phenomena at  
 nanoscale

NOTE: Nanoscale : Generally considered

within the range

1 - 100 nm

< 1 is atomic scale

ooooo

length of 5 Si atoms  $\approx$  1 nm  
 (width added together)

(Similarly for  $\sim$  3.5 Gold (Au) atoms )

At this scale we would start getting atomic properties and NOT material properties

NOTE: When transitioning from :

Bulk  $\longrightarrow$  Nanomaterial

$\downarrow$   
 we will observe new properties

NOTE: Nanotechnology : Using nanomaterials to make technology  
 which we then call "nanotechnology"

2]

## Classification

### Zero dimensional

If all x, y, z dimensions are within nanoscale  
 $\downarrow$  (i.e.  $< 100$  nm)

e.g.: Particles, Quantum dots, fullerenes, clusters

they can be Amorphous, Crystalline, Semicrystalline and polycrystalline

### 1-Dimensional

e.g.: Nanotubes & Nanowires

1 dimension is out of nanoscale  
 $\downarrow$  (i.e.  $> 100$  nm)

this means that 2 dimensions of the object are  $> 100$  nm

& thickness is below 100 nm

e.g.: Graphene, MXenes, Silicenes (i.e. 2D silicon)

### 2-Dimensional

all 3 dimensions are out of nanoscale  
 $\downarrow$  (i.e.  $> 100$  nm)

but still show nanoscale phenomena

due to combination of nanomaterial

### 3-Dimensional

NOTE: "4-dimensional" nanomaterials is also a recent concept

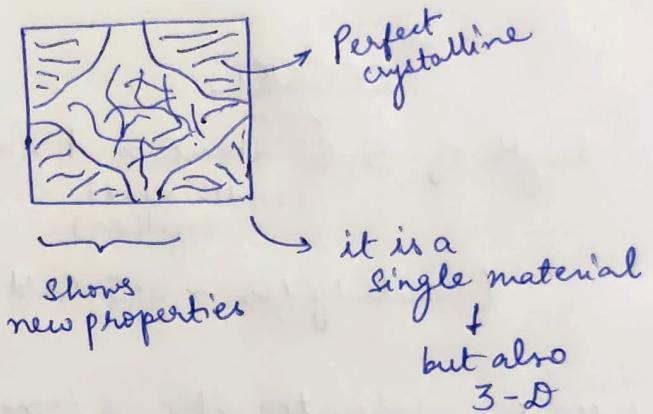
refers to materials that  
also change with time

### 3] Nanostuctures

↓  
Different arrangements of nanomaterials

↓  
thus it is a Bulk nanomaterial  
but shows nanophenomena

eg: Graphene sheets  
+  
Nanotubes



\* Nanostuctures are named using the following system (code):

K D l m n,  
tells Dimensionality of nanostructure  
Dimension      Dimensionality of constituents  
(where,  $l, m, n = 0, 1, 2, 3$ )  
i.e. they can have these values

eg: 0:0 → means:  
0 dimensional nanostucture  
made up of 1 type of 0 dimensional nanomaterial

1D, 0 →   
(made of nanowires and nanoparticles)

2D, 0 →   
(entire 2 dimensional sheet is made up of nanoparticles)

eg: nanofilm made of quantum dots

Similarly:

1D 011 → 1D material  
made up of multiple  
nanowires

3D 012 → 3D nanostucture  
made from dots, wires and sheets

NOTE: Based on this, there are 36 types (categories)  
of nanostuctures possible.

NOTE:  $\text{CH}_3 + \text{CH}_2 \xrightarrow{\text{S H}}$   
↓  
alkyl chain  
(hydrophobic)  
third group  
(it has v. high  
bonding energy  
with gold nanoparticles)

#### 4] Size effect

Surface → it is the outer most layer  
of a material

provides interface  
which regulates the transport

→ i.e.  
more surface area → more interface → More control → More transport

Bulk material → it refers  
to the property → a sum of a  
large no. of molecules

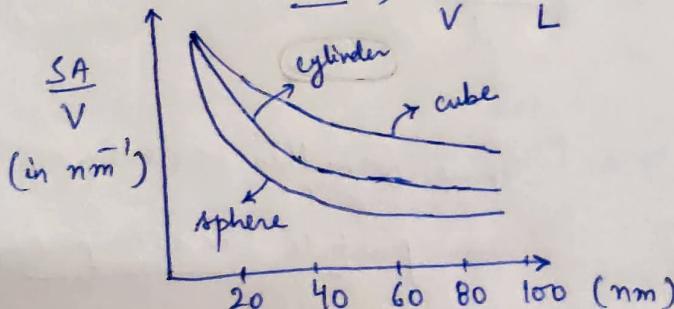
For spherical nanoparticle:

$$\text{Volume, } V = \frac{4}{3}\pi r^3$$
$$\text{Surface area, } SA = 4\pi r^2$$
$$\left. \begin{array}{l} \{ \\ \end{array} \right\} \Rightarrow \frac{SA}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$$

Similarly: cylinder  $\Rightarrow \frac{SA}{V} = \frac{2}{r}$

cube  $\Rightarrow \frac{SA}{V} = \frac{6}{L}$

\* thus, this  
ratio is affected  
by the size of the  
particle

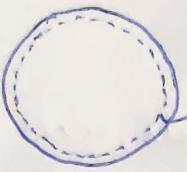


{ decreasing  
size  
↓ leads to  
increase  
in  $\frac{SA}{V}$  }

## LECTURE-2

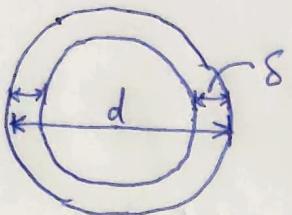
04/08/2023

NOTE:



only particles present in the outer surface are going to matter  
 i.e. it will give most important properties  
 (in terms of properties/behaviour of nanomaterial)

5]



Here,  $\delta$  will be in the range of 0.5 to 1.5 nm

On the surface we see roughness like :

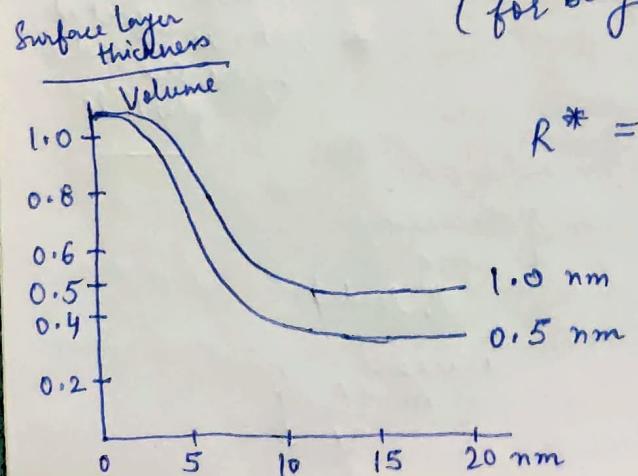
this roughness is the reason for thickness  $\delta$   
 (otherwise we would take surface of perfectly smooth sphere as only the outer 1 atom thick layer)  
 even though this particle (atom) is in the middle it also participates due to electron cloud overlapping

this is why this range is kept 0.5 - 1.5 nm

Based on this :

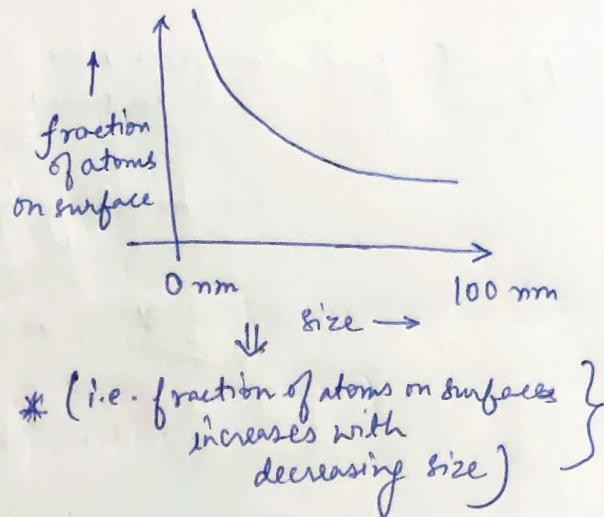
+ we can find critical radius  $R^*$   
 (for being involved in most reactions) as :

$$R^* = 1 - \left( \frac{d - 2\delta}{d} \right)^3$$



Thus, from this we learn that  
 \* particle size is important  
 (since it helps determine thickness)

NOTE:  $\frac{SA}{V} \uparrow \Rightarrow$  decreasing size



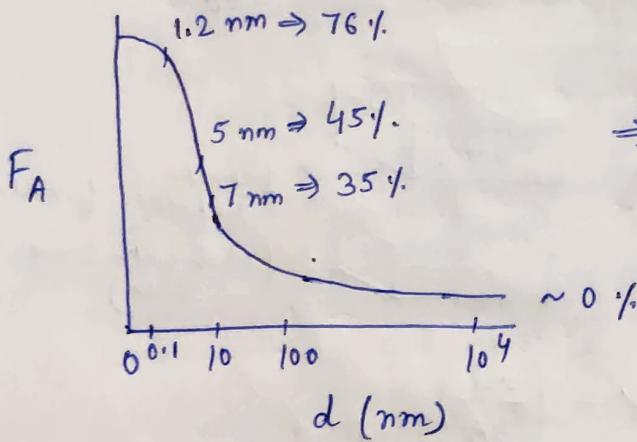
6] For particle  $\rightarrow$  made of  
↓  
radius  $R$        $n$  atoms  
and  
 $r_A$  is atomic radius

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

$$\text{and, } SA = 4\pi R^2 = 4\pi r_A^2 n^{2/3}$$

$\therefore$  fraction of the atoms on the surface :

$$F_A = \frac{4\pi r_A^2 n^{2/3}}{\frac{4}{3}\pi r_A^3 n} = \frac{3}{r_A n^{1/3}}$$



$\Rightarrow$  For 30 nm  $\rightarrow$  5%.  
10 nm  $\rightarrow$  20%  
3 nm  $\rightarrow$  50%

NOTE: Reactions with external molecules can only occur through the atoms present on the surface

NOTE: No. of atoms required to form a particle (e.g. crystal)  
is called "magic number"  
(not covered here, you can read by yourself)

Q  $\rightarrow$  Sphere of Pd (Palladium), of 1 nm radius, and density  
 $\delta_{Pd} = 12.023 \text{ g/cm}^3$ . find no. of atoms of Pd in the sphere.  
and the find no. of atoms on surface.

[H.W.]

7] Surface  $\rightarrow$  gives idea of continuity break

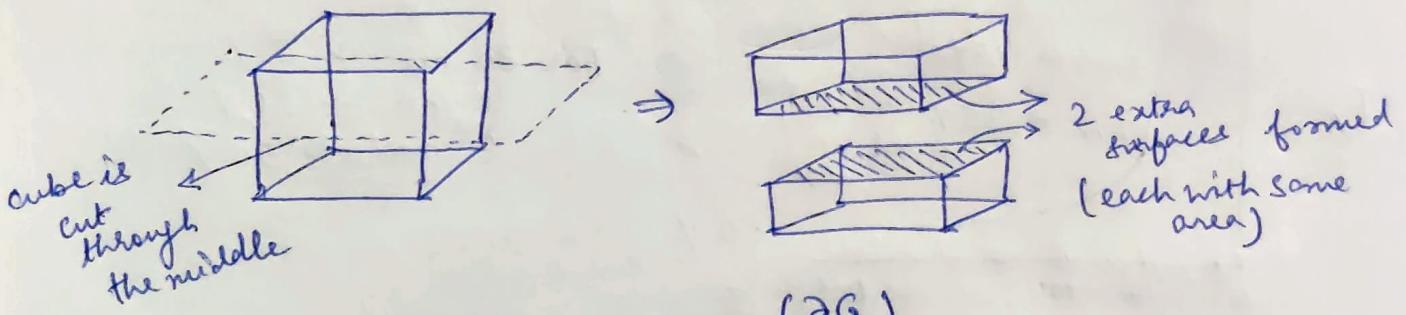
i.e. boundary b/w : Solid - Air/Vapour } external surface  
 Solid - Liquid }  
 Solid - Solid } internal surface  
 eg: grain boundaries  
 (eg: Bubble in water  $\rightarrow$  internal surface)

8] Surfaces have broken bonds

$\therefore$  this requires Energy to form surface  
 (called "Surface Energy")

{as, to break more bonds, requires more energy}

externally  
 if solid-solid  
 is kept together  
 then there is  
 actually  
 always some  
 air in b/w



$$\text{Surface energy, } \gamma = \left( \frac{\partial G}{\partial A} \right)_{n, T, P}$$

$$= \frac{A \beta_A n_B \epsilon}{2A}$$

( $\beta_A$  = # of atoms per unit area)

$n_B$  = # of bonds broken per atom

$\epsilon$  = bond energy per bond )

$$\Rightarrow \boxed{\gamma = \frac{1}{2} \beta_A n_B \epsilon}$$

this is why different materials have different surface energy

9] For FCC  $\Rightarrow$  4 Bonds (100) are broken

$$\therefore \gamma_{100} = \frac{1}{2} \left( \frac{2}{a^2} \right) 4 \epsilon$$

Similarly you can find  $\gamma$  for:  
 $\gamma_{110}, \gamma_{111}$  planes of FCC

10] Total energy of surface:

$$U_{\text{surface}} = \gamma \cdot a$$

↓  
(since  $\gamma$  is energy/area)

For 1 mol of nanomaterial  
 ↓

N no. of nanoparticles :

$$U = N \gamma a$$

$$= \frac{M}{PV} \gamma a$$

$$\Rightarrow U_{\text{mole}} = \boxed{\frac{M}{P} \gamma \left( \frac{a}{V} \right)}$$

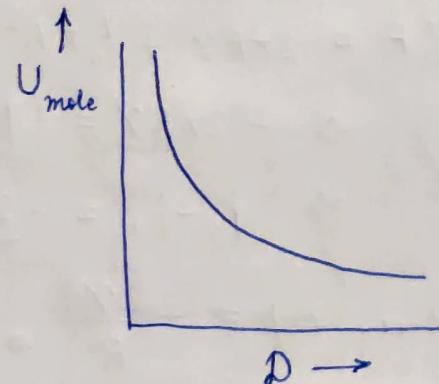
For spherical particles:

$$a = 4\pi r^2 = \pi D^2$$

$$V = \frac{4}{3}\pi r^3 = \frac{\pi D^3}{6}$$

$$\Rightarrow \frac{a}{V} = \frac{6}{D}$$

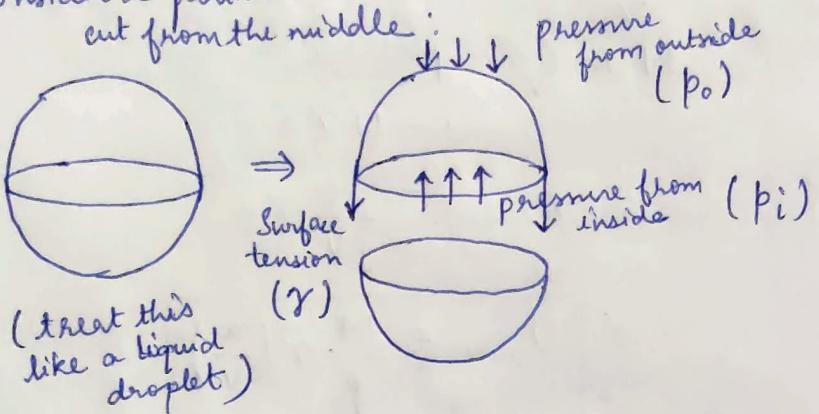
$$\text{Thus, } U_{\text{mole}} = \frac{M}{P} \gamma \cdot \frac{6}{D} = \frac{6M\gamma}{P} \cdot \frac{1}{D}$$



\* NOTE: Since systems with high energy are unstable  
 ↓  
 thus Nanoparticles are unstable  
 (and want to become part of a bulk)

11] \* For particles with size 5 nm and less  
 ↓  
 they are very unstable  
 ↓  
 they have high S.A. → leading to internal pressure

Consider a particle cut from the middle:



thus, the 3 forces are:

$$F_o = p_o \pi R^2$$

$$F_i = p_i \pi R^2$$

$$F_\gamma = 2\pi R \gamma$$

Now, if the system is in equilibrium, the net force should be zero:

$$\text{Total Force} = 0$$

$$\Rightarrow \sum F = 0$$

$$\text{Since, } \sum F = 2\pi R \gamma + p_o \pi R^2 - p_i \pi R^2$$

$$\Rightarrow -2\pi R \gamma = (p_o - p_i) \pi R^2$$

$$\Rightarrow p_o - p_i = -\frac{2\pi R \gamma}{\pi R^2}$$

Hence,

$$\boxed{\Delta p = -\frac{2\gamma}{R}}$$

magnitude ↑  
 ⇒ ∴ when  $R \downarrow$ ,  $\Delta p \uparrow$   
 and thus nanoparticles are unstable

12] For solid & crystalline nanoparticle  
with cubic structure  
(lattice parameter 'a')  
↓  
the Compressibility is given by:

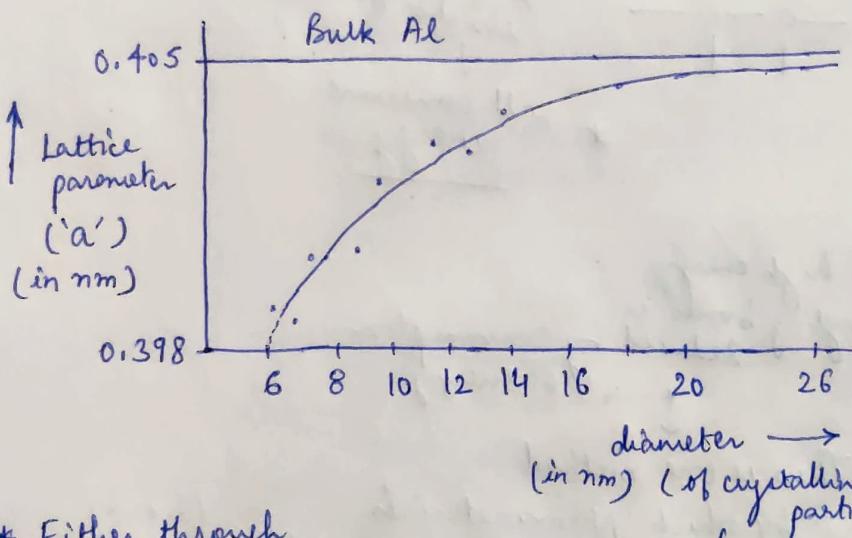
$$\text{compressibility} \leftarrow K = \frac{-1}{V_0} \left( \frac{\partial V}{\partial P} \right)_T$$

here,  $V_0 = a^3$

also,  $\Delta p = -\frac{2\gamma}{R} = -\frac{4\gamma}{d}$

-ve sign shows compression

$$\therefore \Rightarrow \frac{V}{d} = \frac{3}{4K} \frac{\Delta a}{a}$$



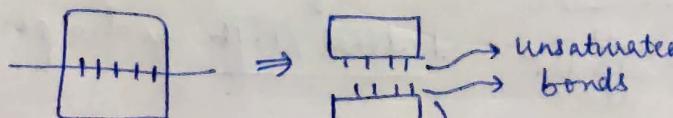
NOTE: The lattice parameter is constant ONLY for bulk materials

- \* Either through external pressure or by self-compression
- ↓  
the size of lattice parameter of nanoparticle can be reduced
- Here, for Al particle

### LECTURE-3

08/08/2023

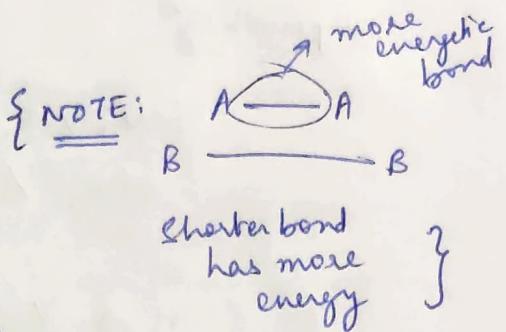
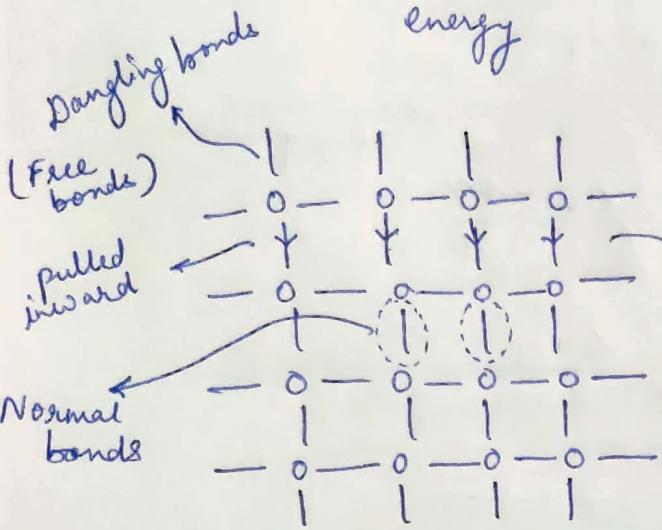
- 13] Nanomaterials are unstable → i.e. more energetic (due to surface energy)



These are called "Dangling bonds"

Dangling bonds are having more energy  
 ↓  
 in order to achieve stability

it will lose energy

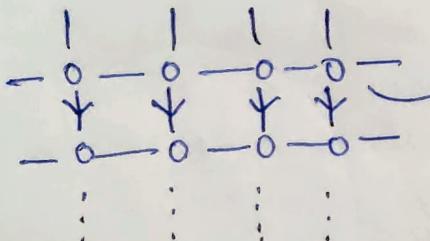


thus to form shorter bond  
 ↓  
 \* will consume energy

Hence the high energy of dangling bonds is reduced by consumption of energy

∴ This is one method by which Nanomaterials can be made more stable

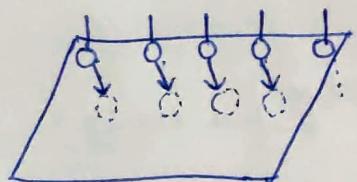
(i.e. by reduction in bond length)



these top atoms will thus shift down ⇒ this is called

"Inward shifting"

NOTE:



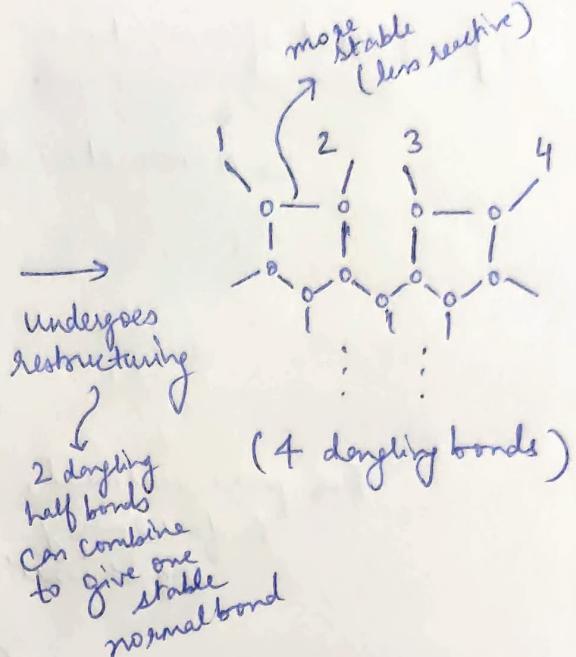
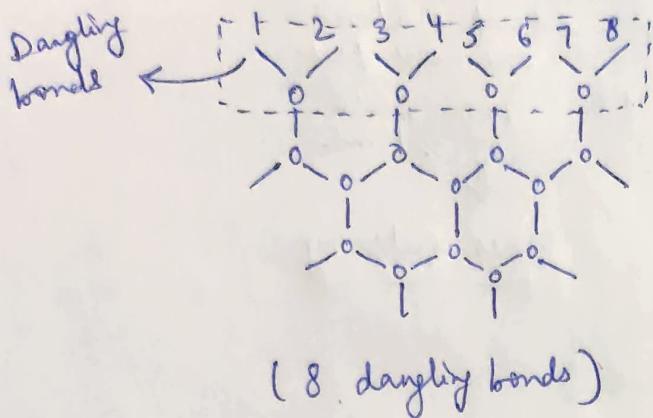
depending on where the vacancy is available

\* NOTE:  
 XPS is used to measure this

(similarly, this could be in another dirn also:  
 eg: ← ← ← )

"Lateral shift" is also possible

## 14] Surface Restructuring

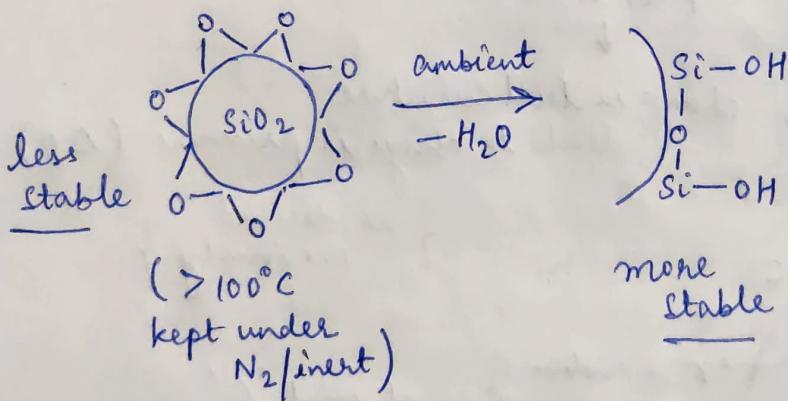


$\therefore$  Surface restructuring

can allow for further consumption of energy  
leading to overall lower energy

( through consumption of dangling bonds )

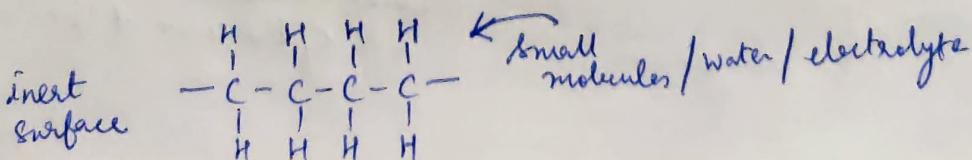
## 15] Taking $\text{Si}-\text{O}-\text{Si}$



\* { this is the mechanism by which  $\text{SiO}_2$  absorbs moisture }

This method of stabilisation is called "Reactive Transformation"

## 16] Adsorption of small molecules also is used to minimize energy:



## 17] Effect of curvature

↓  
In Nanomaterials → surface atoms  
are more free  
than bulk  
atoms

∴ More entropy

For pure material,  
surface energy  
can be written as:

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

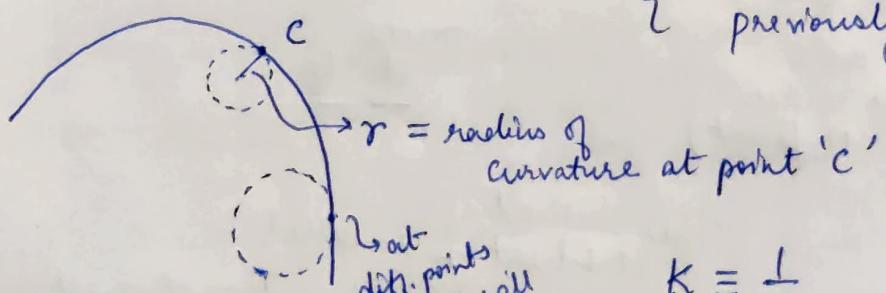
where,  $E^s$  = Internal energy  
 $T$  = Temperature  
 $S^s$  = Surface thermal entropy

Geometry will also  
play an important role

↓  
since geometry  
tells local curvature

and, change in local curvature  
leads to change in pressure ( $\Delta P$ )

{ as derived  
previously }



at  
diff. points  
diff. r will  
be observed

$K = \frac{1}{r}$  → for larger  $r$   
 $K$  will be  
smaller

called  
"Local curvature"  
of the curve at 'c'

$$\left. \begin{array}{l} \text{NOTE: Convex} \Rightarrow K = +ve \\ \text{Concave} \Rightarrow K = -ve \end{array} \right\}$$

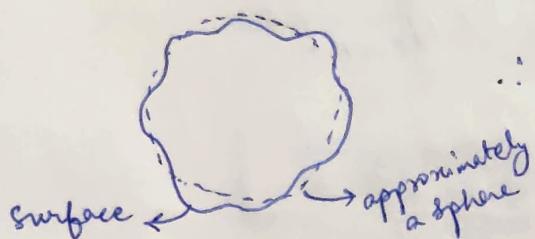
Now, we know:

$$\Delta G = \Delta p V \quad , \text{ where } \Delta p = \frac{2\gamma}{r}$$

$$\Rightarrow \Delta G = 2\gamma \frac{V}{r} \quad \begin{cases} \text{magnitude} \\ \text{i.e.} \end{cases}$$

if local curvature  $\uparrow \Rightarrow \Delta p \uparrow$

\* NOTE: If we synthesize a nanoparticle,  
it won't have a smooth spherical surface



$\therefore$  Local curvature  
will vary depending on  
position on surface

\* NOTE:  
Curvature  
will help  
affect the vacancy  
(conc. on surface)

18] Vacancy conc. can be thus obtained  
from:

$$\Delta G_V^{\text{total}} = \Delta G_V^{\text{bulk}} + \Delta G_V^{\text{excess}} \quad - \textcircled{1}$$

Here,  $\Delta G_V^{\text{excess}} = \frac{\Omega \gamma}{r}$  (i.e. surface) - \textcircled{2}

where,  $\Omega$  = atomic volume  
 $\gamma$  = surface energy  
 $r$  = radius of curvature

Thus, we can write:

$$\Delta G_V^{\text{total}} = \Delta G_V^{\text{bulk}} + \frac{\Omega \gamma}{r} \quad - \textcircled{3}$$

Now, Equilibrium vacancy conc. in nanomaterials is given by:

$$x_V^{\text{Total}} = \exp \left( - \frac{\Delta G_V^{\text{total}}}{k_B T} \right)$$

$$\Rightarrow \chi_v^{\text{Total}} = \exp\left(-\frac{\Delta G_v^{\text{bulk}}}{k_B T}\right) \cdot \exp\left(-\frac{\Omega \gamma}{r k_B T}\right)$$

$$\Rightarrow \chi_v^{\text{Total}} = \chi_v^{\text{bulk}} \exp\left(-\frac{\Omega \gamma}{r k_B T}\right)$$

This can be approximated as:

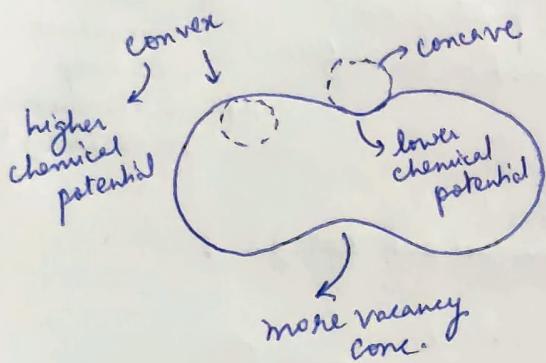
$$\chi_v^{\text{Total}} = \chi_v^{\text{bulk}} \left(1 - \frac{\Omega \gamma}{r k_B T}\right) \quad \leftarrow \begin{matrix} * \\ \text{for convex surface} \end{matrix}$$

OR

$$\chi_v^{\text{Total}} = \chi_v^{\text{bulk}} \left(1 + \frac{\Omega \gamma}{r k_B T}\right) \quad \leftarrow \begin{matrix} * \\ \text{for concave surface} \end{matrix}$$

Thus:

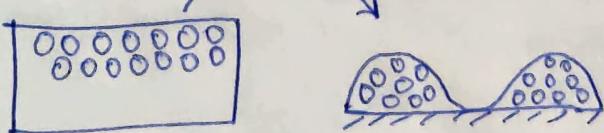
$$(\chi_v)_{\text{concave}} > (\chi_v)_{\text{plane}} > (\chi_v)_{\text{convex}}$$



19] Curvature has strong influence on many properties (such as vacancy cone.)

↓  
another property is  
Chemical Potential

transfer (from flat surface to nanoparticle surface)



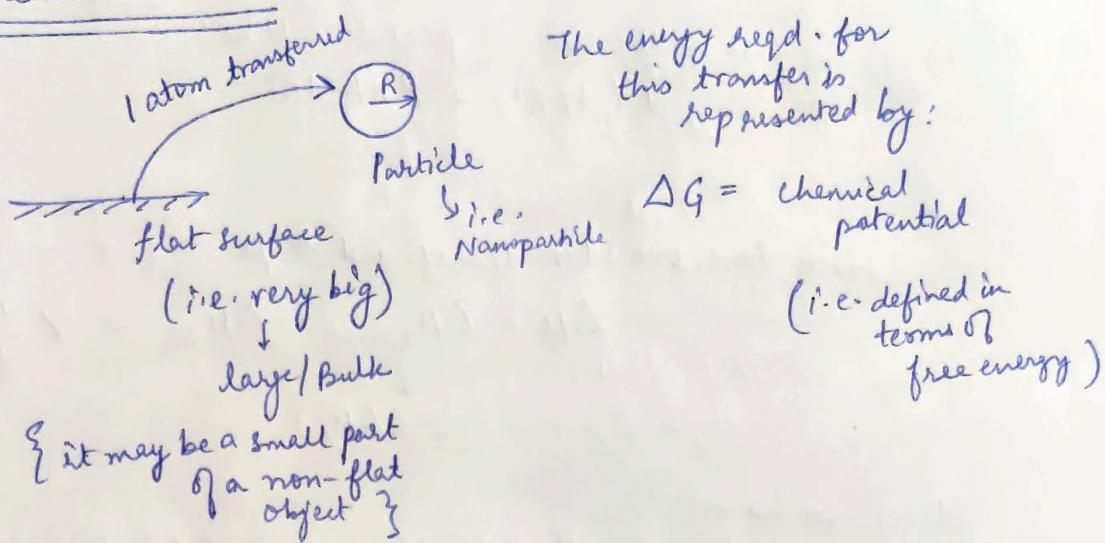
Transfer of an atom  
from flat surface  
to nanoparticle surface

↓  
will involve  
some work

→ this is  
described  
by chemical  
potential

## LECTURE-4

### 20] Chemical Potential



Now, Chemical potential of flat surface,  $\mu_\infty = 0$  (zero)

However if it is smaller (e.g. the nanoparticle shown above)  
then surface will be active

↓  
& transfer will lead to increase in size  $\Rightarrow$  Surface Area ↑  
↓  
Surface Energy ↑

∴ This means that the overall free energy of the whole system (particle + 1 atom) will have increased

We can write change in volume as:

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

(incremental volume)

OR

also called, "atomic volume"

↓ written as

$$\Omega$$

∴ For increment by  $dN$  atoms:  $dV = \Omega dN$

$$\therefore dR = \frac{r}{4\pi R^2}$$

Thus, increase in the area of particle will be:

$$d(4\pi R^2) = 8\pi R dR \\ = \frac{2\pi r}{R}$$

Work done per atom transferred =  $\mu$

$$\therefore \Delta\mu = \Delta\mu_{\text{curved}} - \Delta\mu_{\infty} = \gamma \frac{dA}{dn} \\ (\text{or } \Delta\mu_c)$$

Hence, we have:

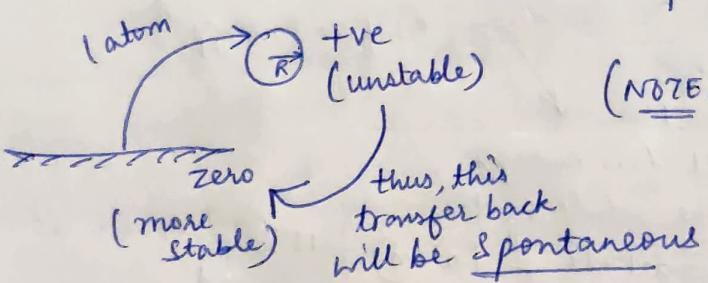
$$\Delta\mu = \gamma \cdot \frac{8\pi R dR}{dV/r} = \gamma 8\pi R dR \frac{r}{dV}$$



$$\therefore \boxed{\Delta\mu = \gamma \frac{2r}{R}}$$

Young-Laplace Equation

$\therefore$  Particle on flat surface  
has zero chemical pot.  
& on the curved surface  
it has +ve chemical  
pot.



(NOTE: This process is called 'Ostwald Ripening')

{  $\therefore$  Transfer from flat to curved particle  
requires some medium/assistance  
i.e. it will not occur by itself }

NOTE: Above was for transfer to spherical surface

$$\text{For cylindrical: } \mu = \gamma \frac{r}{R}$$

21] If we consider transfer into spherical cavity (radius R)



this will have negative curvature

(earlier case had +ve curvature!  $\text{R} \rightarrow$ )

$\therefore$  We obtain:

$$\mu = -\gamma \frac{2\gamma}{R}$$

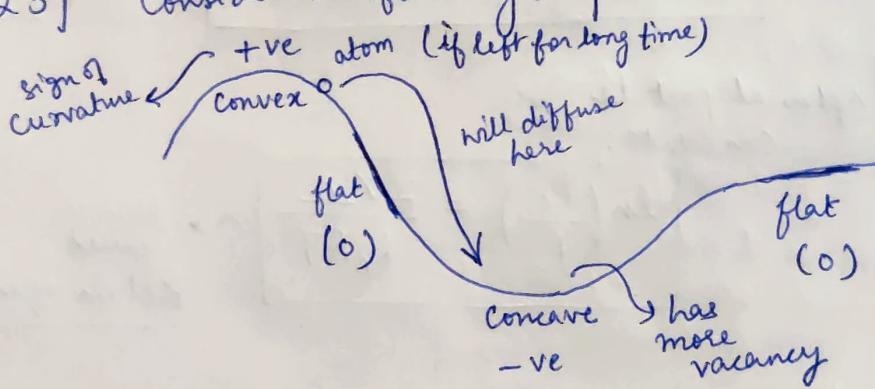
NOTE: However since magnitude is still non-zero thus, it is actually LESS stable than flat surface

(i.e. chemical pot<sup>n</sup> of zero is only the most stable)

22] For curved surfaces  $\Rightarrow$  there are two principle radii

$$\therefore \Delta\mu = \gamma_2 \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

23] Consider the following shape:



Now, chemical pot<sup>n</sup>:

convex > flat > concave

( $\therefore$  Transfer from convex to concave is possible as concave has more vacancies)

The transfer will keep occurring until both convex & concave have zero pot<sup>n</sup>.  
(i.e. they both become flat)

but reverse dir<sup>n</sup> transfer is not possible)

24] We can correlate the Chemical Potential with Pressure / Solubility:

For flat surface:

$$\mu_v - \mu_\infty = -k_B T \ln P_\infty$$

↓  
chemical pot.  
of vapour atom

↓  
Boltzmann  
constant

→ equilibrium  
vapour pressure  
of flat solid surface

For curved surface:

$$\mu_v - \mu_c = -k_B T \ln P_c$$

$$\therefore \text{we can write: } \Rightarrow \mu_c - \mu_\infty = \Delta\mu = k_B T \ln \left( \frac{P_c}{P_\infty} \right)$$

Also, we just saw:

$$\Delta\mu = \gamma_{\text{L}} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

$$\text{thus } \Rightarrow \boxed{\ln \left( \frac{P_c}{P_\infty} \right) = \gamma_{\text{L}} \frac{\frac{1}{R_1} + \frac{1}{R_2}}{k_B T}}$$

→ for general curved surface

For a spherical particle, we can write:

$$\boxed{\ln \left( \frac{P_c}{P_\infty} \right) = \frac{2\gamma_{\text{L}}}{k_B R T}}$$

→ this is called Kelvin equation

25] Also, similarly:

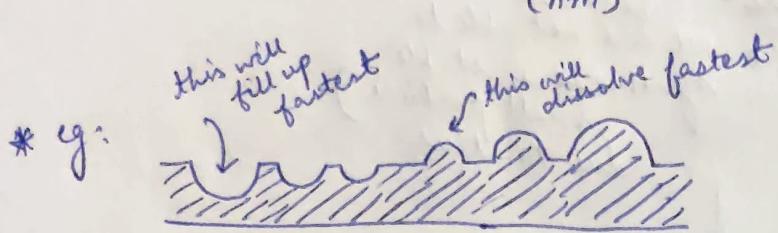
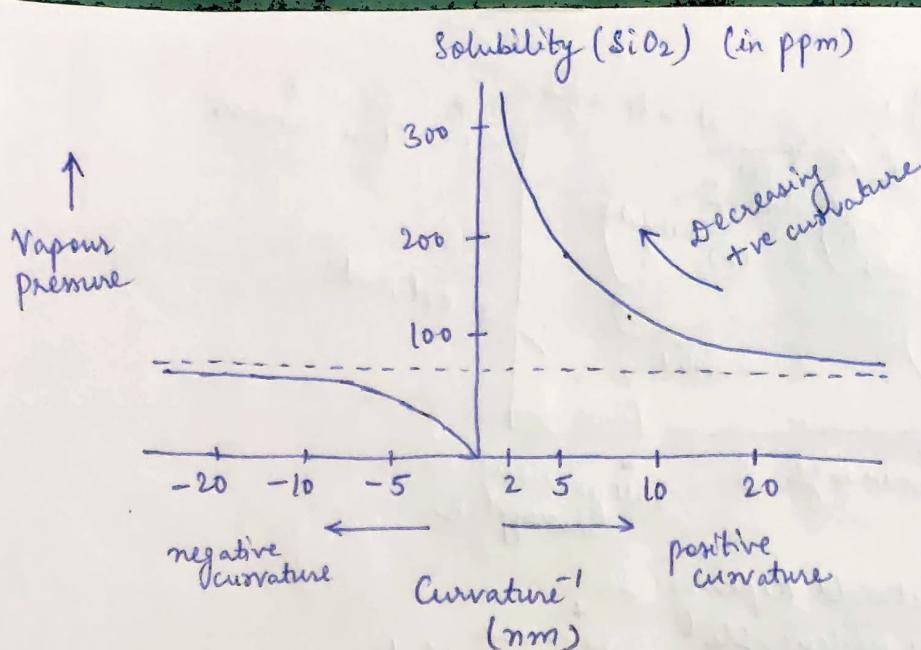
$$\boxed{\ln \left( \frac{S_c}{S_\infty} \right) = \gamma_{\text{L}} \frac{\frac{1}{R_1} + \frac{1}{R_2}}{k_B T}}$$

→ called Gibbs-Thomson relation

where,  $S_c$  is solubility of curved surface

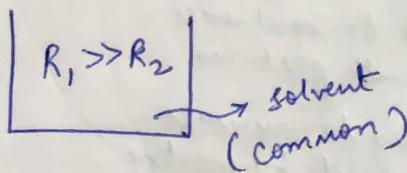
$S_\infty$  is solubility of flat surface

{ Diagram given  
on Next Page }



## 26] Ostwald Ripening

If we take two particles of radii  $R_1$  and  $R_2$   
inside a solvent



Smaller particle will dissolve

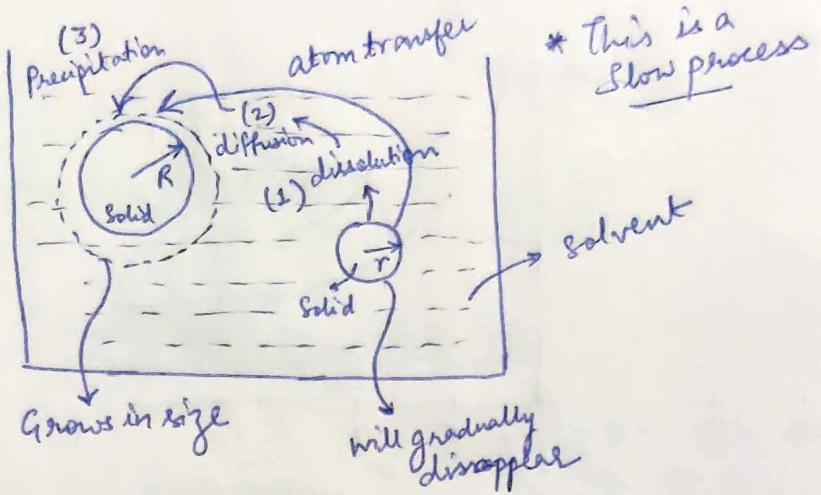
↓ and  
transferred  
to bigger particle

{ if given  
sufficient  
time }

(i.e. smaller particle  
will become smaller  
& bigger particle will become bigger)

{ for the case of  
polydispersity = 1 }

The process of atom transfer takes place in 3 steps as shown:



Thus, Ostwald Ripening

is undesirable

because  
(i.e. we are not able to synthesize a stable small particle)

due to this

the rate of the process can be increased by changing temperature

(since that changes the solubility)

Hence, Ostwald Ripening is a problem for us if we want to synthesize small particles  
we can try to minimize its effect by creating hindrances

## LECTURE 5

25/08/2023

### 27] Stabilization of Nanostructured Materials

there are 2 main methods

i) Electrostatic stabilization



due to charge

ii) Steric stabilization



due to physical barrier