

(Q1) * Properties that are INDEPENDENT of the size or volume of the material are referred to as Intensive Properties.

* Unique properties of nanomaterials arise mainly from their small sizes, leading to quantum confinement effects and large surface area to volume ratio.

* Examples of intensive properties are

- melting point
- electrical conductivity and magnetism
- Ionization Potential
- Electron affinity

These properties ~~do~~ do not depend on size, but they become size-dependent for nanomaterials.

(Q2) * Two broad features that arise from the small size of nanomaterials and give rise to unique properties are

- (1) Quantum Confinement Effects : confinement of electrons, phonons and photons at the nanoscale level
- (2) Large Surface area to volume ratio -- give rise to properties like melting point and solubility .

(Q3)

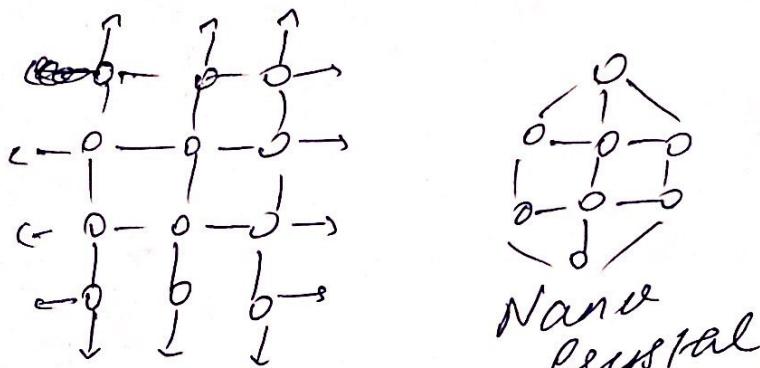
- * According to GLEITER's Definition, when the characteristic size (D) - (diameter, thickness, length) of the building blocks of micro-structures becomes comparable or LESS than the length scale of the physical phenomena (like mean free path length of electrons, coherent length), that is when the SIZE effects on the material properties begin to appear.
- * Since the length scale of most of the physical phenomena lies in the nanometer scale, the nanomaterials show the size/shape-dependent properties.

(Q4)

- * At the nanoscale level, due to quantum confinement, many properties of materials drastically change from those observed in bulk materials. At the same time, the FRACTION OF SURFACE ATOMS become significant with respect to the total number of atoms. in the NP.
- * Hence, the surface-interface effects also play very significant roles in the properties of ~~non-~~ nanomaterials.

- * The surface of an object becomes increasingly important as its size decreases. The surfaces play a crucial role in phenomena like shape of nanoclusters, catalysis etc.
- * Also, many important processes like nucleation, growth etc. occurs at the INTERFACE b/w different phases. Hence, nanoscale properties are very sensitive to surface area, surface energy etc.

* For example, in nanocrystals, surface atoms have strained bonds, hence, fraction of surface to bulk atoms is very high!



Hence, due to dominance of strained surface bonds, they have LOWER melting points.

Q5) * Full shell clusters are built up of hcp and ccp atoms. Hence, number of shells per atom is $10n^2 + 2$, completely covering the $(n-1)^{th}$ shell.

$$\text{Hence, total no. of atoms} = 1 + \sum_{i=1}^n 10i^2 + 2$$

where n is number of shells.

$$\therefore 1 + 10 \sum_{i=1}^n i^2 + 2 \sum_{i=1}^n 1$$

$$= 1 + 10 \underbrace{\frac{n(n+1)(2n+1)}{6}} + 2n .$$

Given that, number of shells is 4.
 $\therefore n = 4$.

$$\therefore 1 + \frac{10(4)(5)(9)}{6} + 2(4)$$

$$= 1 + 300 + 8 = \underline{\underline{309}}$$

Hence, % of surface atoms is

$$\frac{309 - 147}{309} \times 100 \leftarrow$$

52.43%

Q6)

(a) spherical particle of radius R.

(i) Volume of particle $= \frac{4}{3} \pi R^3$.

Total surface Area $= 4 \pi R^2$

$$\frac{\text{Area}}{\text{Volume}} = \frac{4\pi R^2}{\frac{4}{3}\pi R^3} = \boxed{\frac{3}{R}} .$$

(ii) Surface atoms to Total Atoms.

The total no. of atoms scales linearly.

With the volume

$$\Rightarrow N_A \propto \frac{4}{3} \pi R^3 . \quad \text{--- (1)}$$

For surface atoms, we need to find the no. of atoms in the subshell which will scale linearly with the volume of the subshell, given by $\frac{4}{3}\pi(R-2r)^3$.

$$\therefore N_s \propto \frac{4}{3}\pi(R^3 - (R-2r)^3) \quad \text{(2)}.$$

\therefore from (1) and (2),

$$\begin{aligned} \frac{N_s}{N_v} &= \frac{R^3 - (R-2r)^3}{R^3} \\ &= \frac{R^3 - (R^3 - 8r^3 - 3R^2(2r) + 3R(4r^2))}{R^3} \\ &= \frac{R^3 - (R^3 - 8r^3 - 6R^2r + 12Rr^2)}{R^3} \\ &= \frac{R^3 - R^3 + 8r^3 + 6R^2r - 12Rr^2}{R^3} \\ &= \frac{8r^3}{R^3} + \frac{6r}{R} - \frac{12r^2}{R^2}. \end{aligned}$$

$\therefore r \ll R$, we can neglect these terms!

$$\therefore \boxed{\frac{N_s}{N_v} \approx \frac{6r}{R}}.$$

(b) We have seen above that

$$\frac{N_s}{N_0} = \frac{6\pi}{R}$$

for a gold nanoparticle,

$$R = 0.179 \text{ nm}.$$

∴ we substitute that value in above formula,

$$\frac{N_s}{N_0} = \frac{6 \times 0.179}{R} = \frac{1.074}{R} \underset{\sim}{=} \frac{1}{R}.$$

Hence, $\frac{N_s}{N_0}$ is $\frac{1}{R}$, where R is in nm.

(c) For gold, $\frac{N_s}{N_0} \underset{\sim}{=} \frac{1}{R}$

$$\Rightarrow N_s \underset{\sim}{=} \frac{N_0}{R}.$$

Given that, $N_0 = 8000$ atoms

$R = 5 \text{ nm}$ (particle radius)

$$\therefore N_s = \frac{8000}{5} = \boxed{\frac{1600 \text{ atoms}}{\text{at the surface}}}.$$

Q7)

- * Surface atoms have a much smaller coordination numbers than the bulk atoms and hence, they have several unsaturated coordinations or dangling bonds.
- * A surface atom has unsatisfied bonds, which makes it chemically VERY ACTIVE.
- * Hence, the dominance of surface atoms leads to a heightened chemical reactivity. The chemical activity INCREASES as the particle size reaches a few nm. And a dramatic manifestation of this is the auto ignition of fine metal powders in air.

Hence, even though Al is used for safety in cooking pan, Al powder is used as ROCKET FUEL due to low particle size and heightened chemical activity.

Q8)

- * The melting point DECREASES and solubility INCREASES with decrease in size of nanoparticles.

Melting Point

- * The reason for the decrease in melting point is that as the particle size decreases in nano-scale, the surface to volume ratio INCREASES. So there are more atoms on the surface, as opposed to the bulk.
- * The melting point is dependent on the Thermal energy that must be supplied in order to BREAK the solid crystal lattice, and subsequently convert into a liquid.
- * But if less number of particles constitute the lattice, \therefore less thermal energy will be supplied. Hence, the ^{solid} lattice will convert into liquid EARLIER and the melting point will be LOWERED.
Hence, we see a depression in melting point.

Solubility

- * As particle size decreases, the solubility increases.

$$\text{At eqbm, } M_p(\text{sol}) = M_s + \frac{2\pi s L}{f r} \quad \text{---(1)}$$

for a spherical particle
of radius r .

For a bulk solid,

$$\mu_s(\text{sol}) = \mu_s - \textcircled{2}.$$

∴ the surface term is negligible,

$$\text{from D, } \textcircled{2} \Rightarrow \mu_p(\text{sol}) - \mu_s(\text{sol}) = \frac{2\gamma_{SL}}{f_2} \rightarrow \textcircled{3}.$$

In case of a diluted solution, chemical potential can be expressed as a function of the solute mole fraction.

$$\mu_i^o(\text{sol}) = \mu^o + RT \ln x_i - \textcircled{4}.$$

Putting $\textcircled{3}$ in $\textcircled{4}$,

$$RT \ln \left(\frac{x_p}{x_s} \right) = \frac{2\gamma_{SL}}{f_2}$$

$$\Rightarrow x_p = x_s e^{\frac{2\gamma_{SL}}{f_2 RT}},$$

Hence, as x decreases,

the solubility INCREASED.

Also, the Ostwald-Freudlich equation, derived from the Kelvin equation,

$$p \times \frac{RT}{M} \ln \frac{s_s}{s_\infty} = \frac{2\gamma_{SL}}{R}.$$

$$\Rightarrow \boxed{\ln(s_s) \propto 1/x}$$

Hence, s_s increases as x decreases

Q9)

- * Sintering or Firing is the process of pressing and heating of powdered materials close to their melting point, for compacting the powder particles to create a solid shape. It creates ~~per~~ materials with very uniform contents.
- * Sintering is done in order to improve the mechanical, electrical and thermal properties of powdered materials. These materials have very rough surfaces and sharp tips. Such nanoscale surface protrusions have melting temperatures well below their bulk melting temperature.
Hence,
* When these powdered particles are heated to high temperatures close to melting point, the nanoscale protrusion on the surface MELT → without melting the whole particle – and diffuse to the neighbouring particles.
- * This leads to a reduction of the surface energy by decreasing the solid-vapor interface. Hence, Sintering is related to nanoscience in this manner.

Q10)

- * small particles are MORE soluble than the larger ones. The smaller the particle is, the more the dissolution is energetically favoured.
- * Thus, molecules passed into solution from smaller particles prefers to recondensate onto larger particles, rather than coming back to the smaller ones.
- * This leads to the growth of larger particles (both size and relative number) at the expense of the smaller ones, which tend to shrink and ~~fully~~ fully dissolve, and to decrease the solute concentration in the solution.
- * This peculiar time evolution of the particle size distribution is known as Ostwald Ripening.

Q11) * A hydrophobic surface repels water. If the drop spreads, the phenomenon is called "wetting". If the drop shrinks, it is called "non-wetting". This is measured by the CONTACT ANGLE of water droplets on the surface.

- * Superhydrophobicity occurs when the contact angle is GREATER than 150° .

In such a scenario, the water droplet does NOT wet the surface and very easily rolls off. Hence, it makes the surface "self-clearing".

- * Here are the conditions for a super hydrophobic self-clearing surface:

- ① Dynamic contact angles are measured during growth (advancing θ_{ad}) and shrinkage (θ_{sd}). Roll off angle is θ_R .
- ② Superhydrophobic surfaces show $\boxed{\theta_R < 5^\circ}$.
- ③ Perfect hydrophobicity is shown when the drop touches at a single point.
i.e. $\theta_{ad}/\theta_{sd} = \frac{180^\circ}{180^\circ}$.
- ④ Superhydrophobic surfaces have $\boxed{\theta_{ad} - \theta_{sd} < 10^\circ}$.

And as we've already seen in the definition,

$$\boxed{\text{Contact Angle} > 150^\circ}$$

Q12)

- * The Wenzel and Cassie-Baxter models are used to account for the change in effective contact angle. Both account for surface roughness, but Cassie-Baxter comes into play when air is trapped WITHIN the rough textured surface.

- * According to Wenzel's model,

$$\underline{\cos \theta_w = s \cos \theta_y}.$$

θ_w - apparent contact angle.

θ_y - young's contact angle.

s - roughness factor.

For a hydrophobic surface, $\theta_y > 90^\circ$.
As $s > 1$, $\cos \theta_w$ would become more negative, ~~and~~ thereby INCREASING the apparent contact angle.

- * According to Cassie-Baxter Model.

$$\cos \theta_{CB} = f_1 \cos \theta_{y1} + f_2 \cos \theta_{y2}$$

θ_{CB} - apparent contact \angle .

f_1 - surface fraction of phase 1

f_2 - " " of phase 2

θ_{y1} - young's contact \angle of phase 1

θ_{y2} - " " of phase 2

And, ~~$f_1 + f_2 = 1$~~ .

* Let us assume that the liquid is water, and vapour is air.

$$\therefore \theta_2 = 180^\circ, f_2 = 1 - f_1.$$

Putting these in above eqn,

$$\cos \theta_{CB} = \underbrace{f_s(1 + \cos \theta_3)}_{\sim} - 1.$$

\therefore As per Cassie-Baxter model, reducing f_s and increasing amount of air increases the water-repelling tendency of the surface, irrespective of whether it is hydrophobic or hydrophilic.

Q13)

(a) Square Pillars - s mm side
 h mm high
 d mm apart,
in a square array.

Let us consider n square blocks along the length and breadth of the array.

\therefore the dimensions are:

$$n(\text{width} + \text{spacing}) * n(\text{width} + \text{spacing})$$

$$n * n(s+d) * n(s+d) = \underbrace{n^2(s+d)^2}_{\sim}.$$

\therefore Projected area of ~~the~~ flat square array is $n^2(s+d)^2$.

Hence,
 The surface area of top of the pillars +
 surface area of remaining substrate
 is also equal to the projected area,
 which we have gotten as $\underline{\underline{n^2 (std)^2}}$.

Now,
 hs is the surface area of each open side.
 There are 4 open sides in each pillar.

$$\therefore \text{surface area of open sides} \\ = \underline{\underline{4hs}} \text{ (one pillar)}.$$

$$\text{Total no of square blocks} = n^2.$$

$$\therefore \text{for all pillars, surface area of} \\ \text{open sides} = \underline{\underline{(4hs)n^2}}.$$

Hence, we now compute the roughness factor as :

$$R = \frac{\text{Surface area at TOP} \\ + \\ \text{Surface area of remaining substrate} \\ + \\ \text{Surface area of open sides}}{\text{Projected Area}}$$

$$\Rightarrow \lambda = \frac{n^2(s+dl)^2 + (4hs)n^2}{n^2(s+dl)^2}$$

$$\Rightarrow \boxed{f_2 = 1 + \frac{4hs}{(s+dl)^2}}$$

$$\therefore f_1 = fs = \frac{n^2(\text{width} \times \text{width})}{n^2(\text{width} + \text{spacing})^2}$$

$$\Rightarrow \boxed{f_1 = \frac{s^2}{(s+dl)^2}}.$$

Hence, $f_2 = 1 - f_1$

$$\Rightarrow \boxed{f_2 = 1 - \frac{s^2}{(s+dl)^2}}$$

(b) The roughness factor for the given geometry is :

$$\boxed{\lambda = 1 + \frac{4hs}{dl^2}} \quad (\text{as derived in previous part})$$

Given: $dl = 150 \mu\text{m}$

$$h = 10 \mu\text{m}$$

$$s = 50 \mu\text{m}$$

$$\therefore \lambda = 1 + \frac{4(150)(10)}{(150)^2} = \underline{\underline{1.0889}}$$

Hence, for Wenzel,

$$\cos \theta^* = 1.0889 \cos 114^\circ$$

$$\Rightarrow \boxed{\theta^* = 116^\circ} \rightarrow \text{Wenzel theta}$$

For Cassie-Baxter model:

$$f_1 = \frac{s^2}{d^2} = 0.111$$

$$f_2 = 1 - 0.111 = 0.889.$$

$$\therefore \cos \theta^* = 0.111 \cos 114^\circ + 0.889$$

$$\Rightarrow \boxed{\theta^* = 159.6^\circ} \rightarrow \text{Cassie-Baxter theta}$$