

ASSIGNMENT - 02

(Q1) The Turkevitch method of gold nanoparticles synthesis.

- In this method, nanoparticles are synthesized by the REDUCTION of Au(III) derivatives.
- This method uses citrate for reducing HAuCl_4 in aqueous condition, in order to synthesize gold nanoparticles. (approx 20nm dimension)
- The size of the nanoparticles synthesized can be altered by controlling reaction time, reducing and stabilizing agents.

Names of the precursors used in this synthesis reaction.

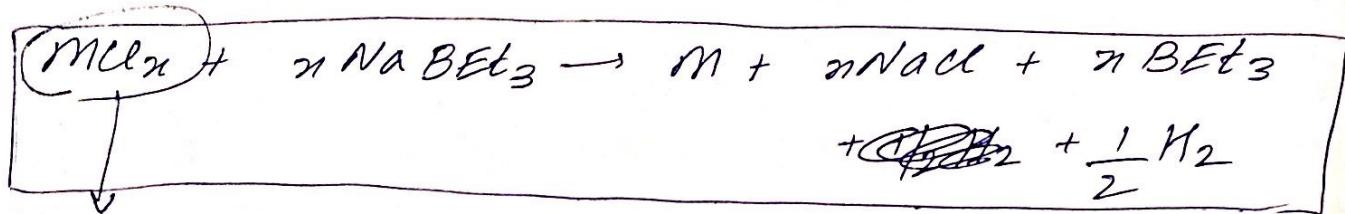
- Chloroauric Acid (HAuCl_4)
- Trisodium Citrate (Na_3Cit)

(Q2) We can use the "salt reduction" method to produce group 6 transition metal nanoparticles.

- This method involves the dissolution of metal salts into aqueous/non-aqueous environments. This is followed by the reduction of metal cations to zero valence states.

○ The nature of metal salts is determined by the type of the reducing agent used.

The chemical reaction is :



Group 6 chloride

○ So in order to produce group 6 nanoparticles, CHLORIDES such as $CrCl_3$, $MoCl_3$, WCl_4 etc are REDUCED with $NaBEt_3$ in Toluene solution at room temperature to produce metal colloids in high yields.

$CrCl_3 \rightarrow$ Chromium(III) chloride

$MoCl_3 \rightarrow$ Molybdenum(II) chloride

$\cancel{NaBEt_3} \rightarrow$ Triethylborane, i.e. $(C_2H_5)_3B$

Q3) (a) For seed-mediated synthesis, we prefer to use a WEAK reducing agent.

→ Weak reducing agents act like an electrostatically stabilizing agent as well as a pH mediator, which helps in the reaction.

→ Ex. of reducing agent: Na_3Cts (Trisodium citrate)

Q4) Given the precursor $\text{Fe}(\text{CO})_5$:

- Nanstructured Fe can be synthesized by
 - sonication
 - Thermal decomposition.
- Of these two approaches, we would favour the Thermal Decomposition method for synthesis.
- This is because in sonication, it is difficult to control the size and distribution of the resulting particle -
This happens due to agglomeration of particles into ^a porous coral-like microstructure hence, with $\text{Fe}(\text{CO})_5$ precursor, we'd prefer to use Thermal Decomposition.

Q5) → SAM's

- SAM's is the acronym for "self Assembled Monolayers".
- These are robust organic molecules that are chemically adsorbed onto solid substrates.
- Most often, they have a polar head that can be bonded to various solid surfaces, and a long hydrophobic tail that extends outwards.

→ Formation of SAM's

- SAM's are formed by the immersion of a substrate in a dilute solution of the molecule, in an organic solvent.
- The resulting film is a dense organization of molecules arranged to expose the end group.
- The durability is dependent on the effectiveness of the anchoring to the substrate surface.

→ Applications of SAM's :

- The end group of a SAM can be functionalised to form precisely arranged molecular arrays for various applications like
 - (1) simple ultra-thin insulators
 - (2) lubricants
 - (3) complex biological sensors.
- Chemical self-assembly use SAM's as the bonding and recognition sites for fabricating complex 3D structures.

Q6) Synthesis of CdS nanoparticle .

A method of synthesis of controlled sized CdS nano particles is by using REVERSE MICELLES .

- In this method, the synthesis of CdS nanoparticles is done by using reverse micelles as nano-reaction vessels. As reverse micelles come into contact, they exchange their contacts.
- For synthesis of CdS, we take reverse micelles containing 2 different precursors
 - One with Cd salt, and
 - One with N₂S
- These solutions are mixed and the exchange of ^{content of} micelles leads to formation of nanoparticles.
- Further, thiol molecules are added to stabilize nanoparticles as they bond to the surface.

Q7)

- (a) Au nanoparticles from HAuCl₄ precursors can be synthesized by using CITRATE - to reduce HAuCl₄ in aqueous condition, to get nanoparticles (with apprx 20 nm dimension)
(as we saw in question 1)

(b) In order to synthesize Fe_3O_4 nanoparticles, we CO-PRECIPITATE a mix of Fe^{2+} and Fe^{3+} precursors in a ratio of 2:1. NH_4OH (ammonium hydroxide) is used as a precipitating agent. Particle size is controlled by varying the reaction temperature.

(Q8)

- ① On the nanometer scale, many material properties become extremely sensitive to its new dimensions. For the bulk material, such properties are generally regarded as intrinsic.
- ② But on the nanometer dimensions, they become a lot more prominent and extrinsic?
- ③ Hence, it's crucial and critical to synthesize uniformly sized/shaped nano crystals.

The uniformity in shape is directly correlated with the homogeneity of their properties

(Q9)

- * Monodispersed nanoparticles: These refer to same-sized particles in a dispersion. Sometimes, it might not be possible to achieve perfect monodispersion and hence, some deviation might be allowed.

(b) If a single nucleation is NOT possible, we can use other methods to control the size and prepare monodisperse nanocrystals, such as :

* Burst Nucleation

- This is similar to ideal single nucleation, but can be performed by having high monomer concentration
- This can be completed in a short period of time.

* Seed mediated Synthesis

- In this method, uniform seed particles are used as NUCLEI.
- Heterogeneous nucleation using these seed particles as nuclei takes place, and this is similar to the single nucleation event.

Q10) We know the equation

$$\boxed{r^* = \frac{2\pi V_m}{RT \ln(s)}}, \text{ where } s = \frac{c}{c_0}$$

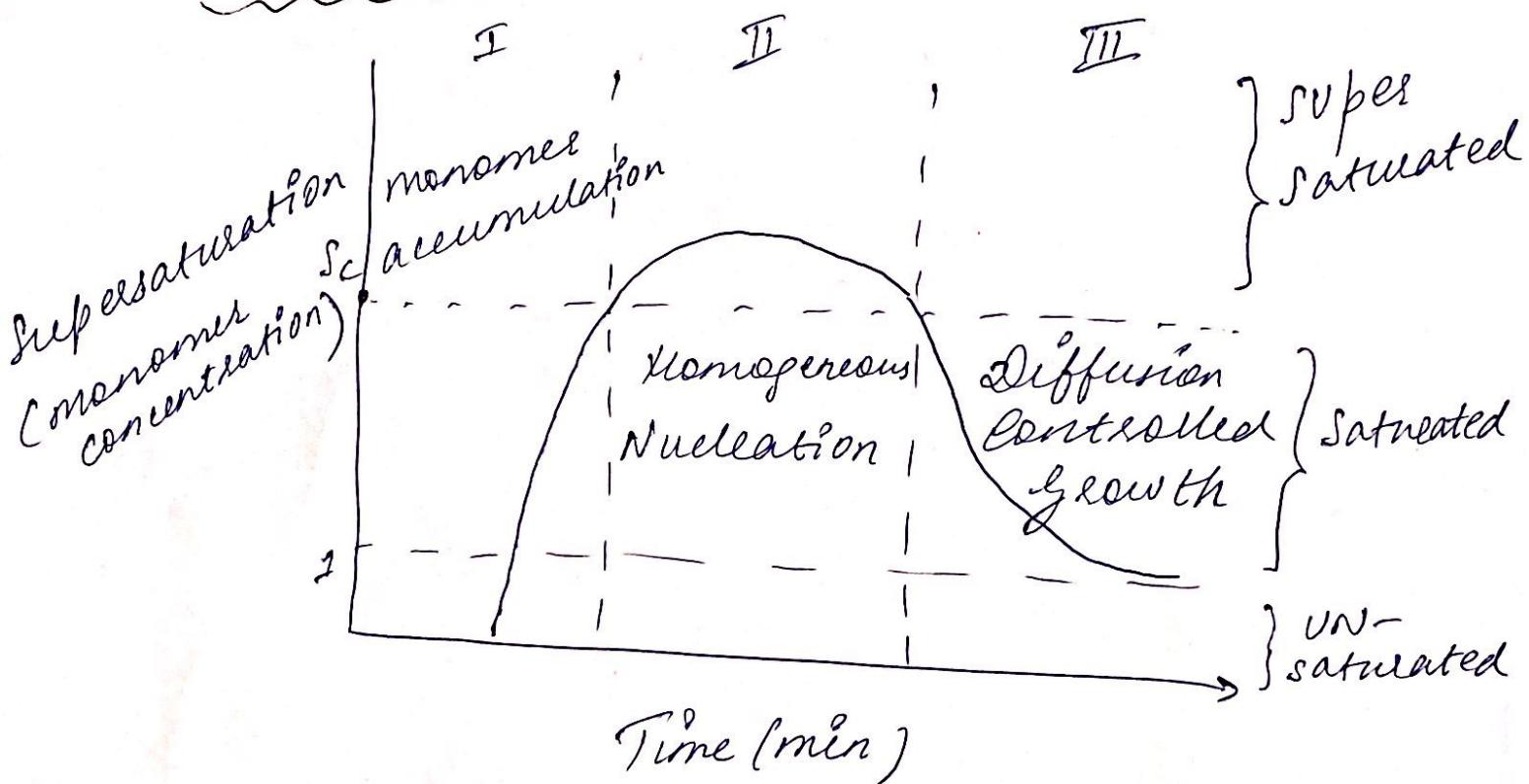
r^* is the critical radius.

V_m → molar volume.

c → equilibrium monomer concentration in crystal.

- * As we can see in the above equation, there is an inverse correlation b/w the monomer concentration (s) and the critical radius/size.
- * Hence, we can prepare smaller nano-particles by increasing the monomers concentration (or the supersaturation), and also the temperature.

Q11) Lamer Plot



where s_c = critical supersaturation.
and I is the saturation level.

* Stage 1 : Prenucleation Phase

- Here, the concentration of the monomers steadily increases upto the supersaturation levels.
Below supersaturation, spontaneous nucleation is impossible.
- The zone below the saturation level is called the stable zone, since it's unsaturated and nucleation is impossible.
- The region b/w saturation and supersaturation is called the metastable zone.
- The zone above the critical supersaturation level is the labile zone (unstable).
Here, spontaneous nucleation is POSSIBLE.

* Stage 2 :

- Here, rapid Nucleation occurs by the aggregation of monomers. The concentration of atoms reaches a critical supersaturation limit, and leads to the formation of critical nuclei.
- Once the limit is reached, the concentration again decreases and once it drops below the critical value, the nucleation stops.

- Hence, nucleation stops as the concentration drops below the critical value. Above that, nucleation happens rapidly.
- Stage 3 : Growth Stage.
- Here, nucleation stops and the number of monomers incorporated into the crystal increases. All the nanocrystals grow almost homogeneously and is hence, called the growth stage.
- The curve remains within the "diffusion controlled growth" region, b/w 1 and sc.

(Q12) We know that

$$\dot{r} = \underbrace{\left(-\frac{V_m}{4\pi k^2} \right)}_{\text{is } \frac{dr}{dt}} \dot{r}_i \quad \text{where} \quad \begin{aligned} \dot{r} &\rightarrow \text{Deposition rate} \\ \dot{r}_i &\rightarrow \text{growth rate} \\ &\text{of particles.} \end{aligned}$$

In the reaction-controlled regime, the availability of monomers is very HIGH, and hence, whenever a reaction site is available, a monomer can be deposited.

\therefore we can say

$$\dot{r} \propto r^2$$

\rightarrow deposition rate

$r^2 \rightarrow$ surface area

Hence, $\dot{r} = \left(\frac{-Vm}{4\pi g^2} \right) \dot{n}$

$\Rightarrow \dot{r} \propto \left(\frac{-Vm}{4\pi g^2} \right) \cdot \text{ct}$

$\Rightarrow \boxed{\dot{r} \propto \frac{-Vm}{4\pi}}$

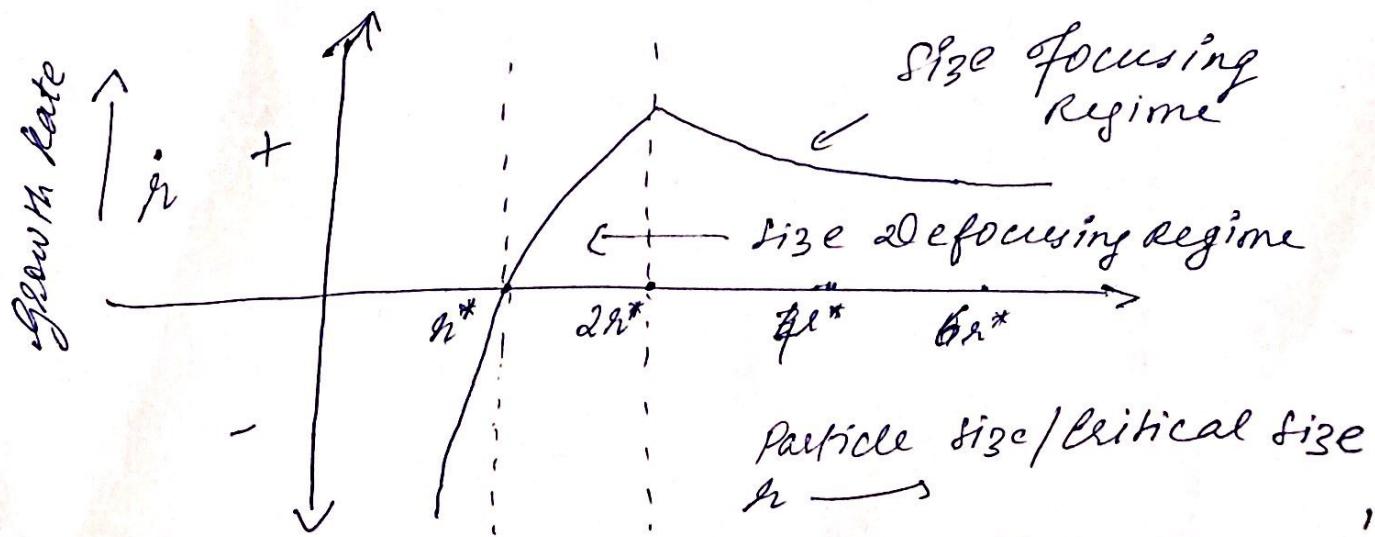
The growth rate is independent of the particle size!

Hence, the proof! :)

Q13)

$$\dot{r} = \frac{2\gamma_{NL} V_m^2 D_{Co}}{RT} \cdot \frac{1}{r} \left(\frac{1}{r^*} - \frac{1}{r} \right).$$

(a) Plotting \dot{r} as a function of particle size (r)



Features of the Growth-rate function:

- * The growth rate converges to 0 as $\delta \rightarrow \infty$.
and diverges to $-\infty$ as $\delta \rightarrow 0$.
- * There exists a maximum in the graph.
The growth rate reaches MAX at $2\delta^*$,
in the graph.
- * Growth rate vanishes at the critical-sized particles (when $\delta = \delta^*$)
- * When $\delta < \delta^*$, the function shows NEGATIVE growth rate, and thus the particles dissociate to monomers.
- * All particles larger than critical size (when $\delta > \delta^*$) grow!

We see 3 zones in the graph:

- * Size-focusing - all particles larger than $2\delta^*$, where larger particles grow slower than smaller particles.
- * Broadening: Particle size b/w δ^* and $2\delta^*$.
larger particles grow FASTER.
- * Ostwald: Particles with $\delta < \delta^*$
dismantle here.

- Q14) During the process, ^{growth} the main parameters affecting the time evolution of particle size is level of supersaturation - 's'.
- In the nanocrystal size evolution, we can see 3 different growth stages, as we saw in Q13.
- ① Size-focusing regime ($r > 2r^*$)
 - Here, the larger particles grow slower than smaller particles.
 - Size distribution becomes narrower.
 - ② Broadening regime ($r^* < r < 2r^*$)
 - Larger particles grow faster than small particles.
 - All particles show +ve growth rate.
 - ③ Oswald ripening: ($r < r^*$)
 - Particles that are smaller than critical size DISMANTLE.
 - The monomers are set free, which get incorporated into larger particles.
- * Now, in order to grow mono-disperse colloidal nanocrystals, we can INTERRUPT the growth before the distribution enters the defocusing window, and much before it enters Oswald ripening regime.

- * We can also keep the size distribution narrow, by adding chemical precursors to maintain high supersaturation values.
- * We can also grow monodisperse samples by hot injection via multiple injections of precursors. (This is known as Distribution focusing)

Q15) The free energy required for nucleation by a factor related to the contact angle of the nucleus, on the foreign surface δ :

$$\Delta G_{\text{net}} = \Delta G_{\text{hom}} f(\delta) = \left(\frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma_{NL} \right) f(\delta)$$

(homogeneous
nucleation)

$f(\delta)$ here is the "contact parameter"

$$f(\delta) = \frac{(\cos \delta + 2)(1 - \cos \delta)^2}{4} < 1.$$

The critical r^* is independent of δ .

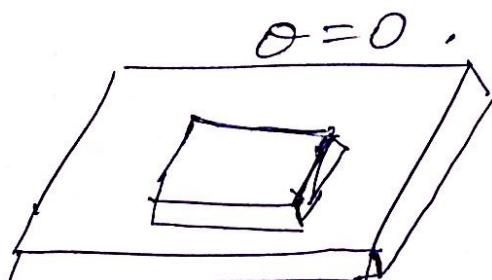
$$r^* = \frac{2 \gamma_{NL}}{\Delta G_v}$$

$$\Delta G^* = \frac{16 \pi \gamma_{NL}^3}{3 \Delta G_v^2} f(\delta).$$

(1) for complete affinity, $\boxed{\theta=0}$

Forms a continuous film.

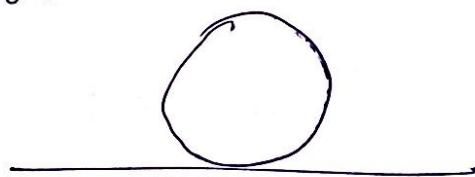
~~Diagram~~



(2) for non-complete affinity, $\boxed{\theta=\pi}$

Forms a perfect sphere

$$\theta=180^\circ$$



Complete Affinity ($\theta=0$)

$$if (\theta)=0 \Rightarrow \underline{\Delta G^* = 0}$$

Since there is complete wetting, nucleation happens spontaneously and no energy barrier exists due to extremely high bonding affinity.

\therefore (1) SPONTANEOUS NUCLEATION
and (2) NO ENERGY BARRIER.

However, we notice differently for $\theta=180^\circ$.

Non complete Affinity ($\delta = 180^\circ$)

$$ef(0) = \frac{(-1+2)(1-(-1))}{4}^2$$

$$\therefore f(0) = \frac{1(2)^2}{4} \Rightarrow f(0) = 1.$$

$$\therefore \Delta G^* = \frac{16\pi \gamma_{NC}^3}{3\Delta C_D r^2}$$

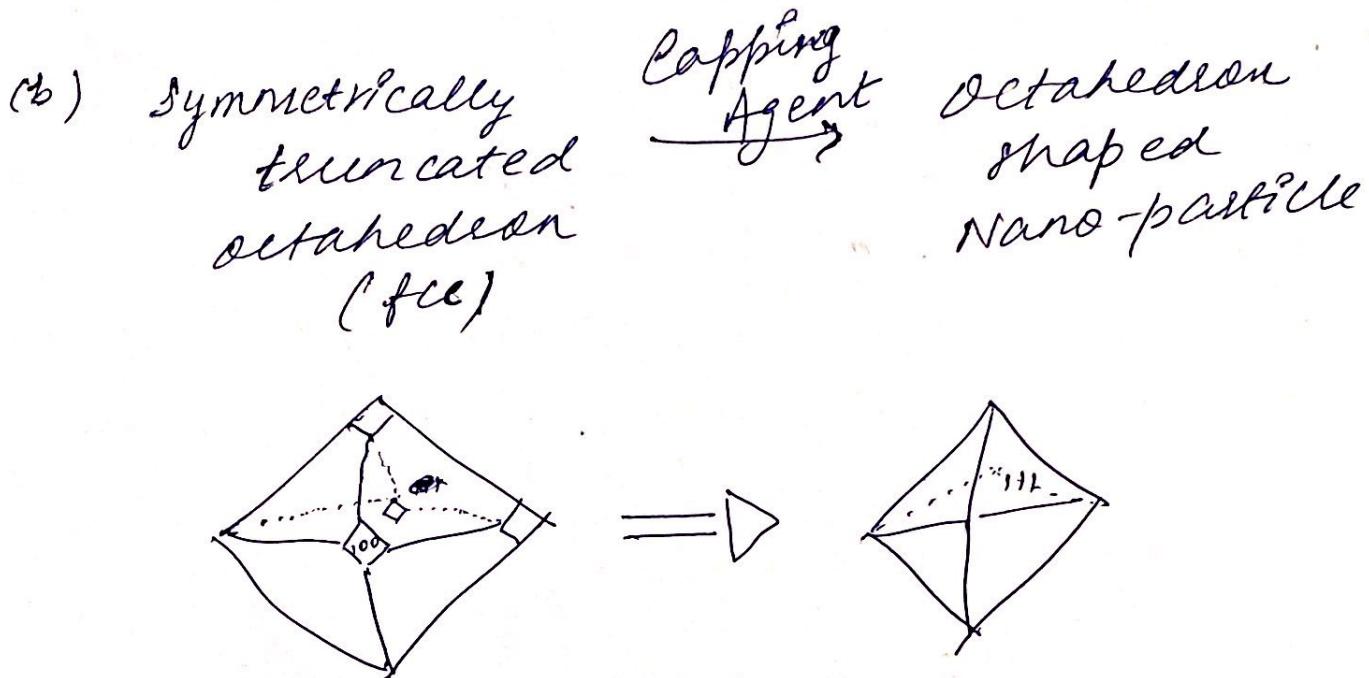
Hence, this is the LARGEST free energy barrier, due to which the nucleation will NOT be spontaneous.

\therefore (1) non-spontaneous nucleation and (2) free energy barriers will be present, with max value as given in the above eqn -

(Q16)

(a) specific molecules that act as terminating and stabilizing agents (or capping agents). allow a higher control over growth rate and nucleation of particles. Hence, smaller regimes can be made into the monomer scale.

These molecules ensure controllable or slow growth rates, prevent interparticle agglomeration and confer stability and processibility for the resulting nano-particles.



- * In case of the truncated octahedron, the $<100>$ faces are NOT blocked by capping agents. Hence, they become smaller as other faces expand and they disappears.
- * Rate of growth 1 to 100 face is given by v_{100} . If we keep this rate higher than v_{111} , the 100 face would gradually disappears and 111 face appears.

Q17) Criteria for preparing ~~Epitaxial~~ epitaxial

(a) 2D layer-by-layer growth:

- * Under a lattice matched or slightly mis-matched with high interfacial bond energies,
 Δy becomes negative
- * Under the above condition, 2D layer-by-layer growth of the deposit occurs under low super-saturation, to suppress 3D nucleation. (Fland - Van-der-Meeve mode)

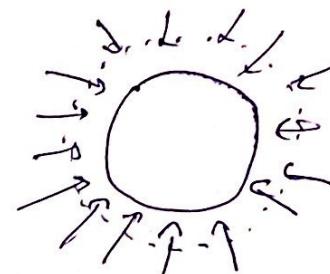
(b) Island Growth of deposits:

- * When the lattice mismatch is HIGH, and the surface energy term of the substrate cannot compensate for the sum of the surface energy of the deposit and interfacial energy, Δy becomes positive
- * Hence, 3D nucleation occurs on high energy sites of substrate under conditions of supersaturation.
- * The deposit forms "3D islands" to minimize strain energy, leads to growth of 3D islands and finally, coalescence.
(Volmer-Weber mode)

(Q18)

(a) Spherical Particles:

- * In the ideal case of a perfectly spherical nanocrystal, each location on the surface of the crystal experiences the same local concentration of monomers, and hence, the same growth rate. Therefore, the overall crystal grows, preserving its shape.

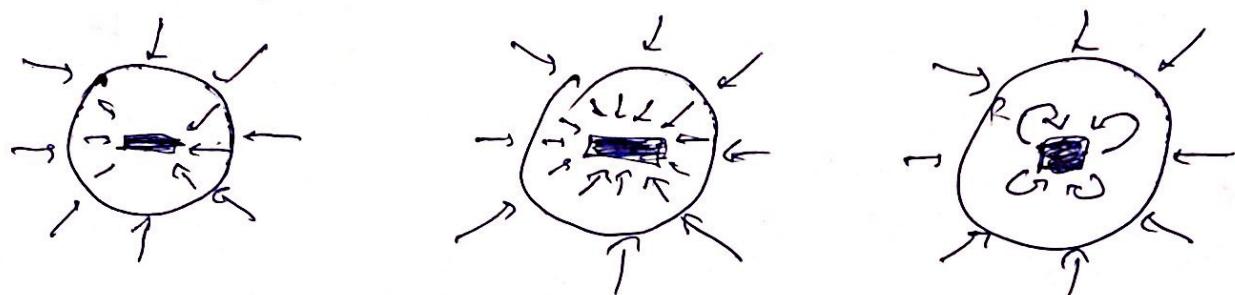


(b) Particles with corners, as a result of faceting:

- * Reactive corners are present and as a result of faceting, these can protrude out in regions of higher monomer concentrations within the diffusion layer.
- * This will cause the area close to the corners to grow much faster than other areas of facets such as the more central regions. This will further deplete the concentration of monomers close to those regions, suppressing the growth factors.
- * As a consequence, branches can start forming which lead to the development of tiny new facets.

(c) Rod-shaped nano-particles:

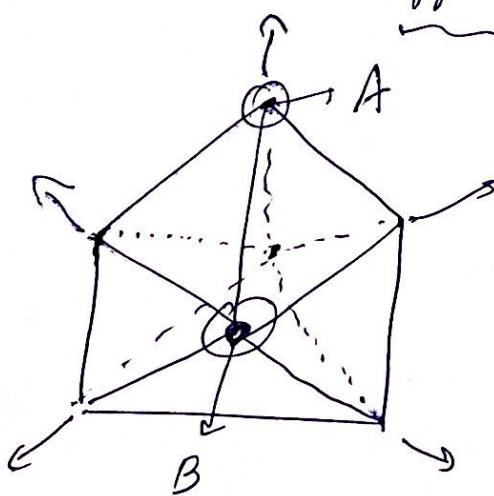
- * Atoms will start detaching from the most unstable facets & will feed other facets. Over time, the overall habit of the crystals will actually evolve towards the shape that minimizes the overall surface energy under the new conditions.
- * For a rod-shaped ~~cystal~~ nano-crystal, this will mean that their aspect ratio would start decreasing.



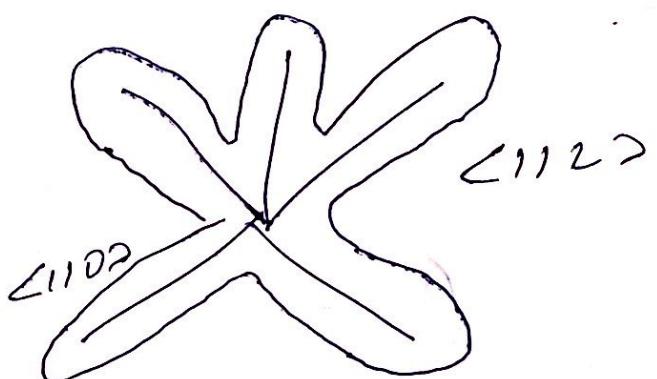
Q13) Formation of Pentapod nanoparticles.

- * Pentapod evolves from pentatwinned decahedral particles. There are 2 different kinds of corners, labelled as A and B. Each of the 5 "type A" corners are formed by the meeting point of two adjacent tetrahedron corners.
- * The "type B" corners are formed at points where all 5 tetrahedrons share their corners.

- * The growth directions along A and B are $\langle 112 \rangle$ and $\langle 110 \rangle$ respectively. A faster growth along $\langle 112 \rangle$ leads to the formation of fine branches.
- * All five "type A" corners ~~are~~ may not be equivalent due to an unequal share of total angular gap, of 7.4, which arises from the defective structure in penta-twinned decahedral particles. This leads to different growth rates and hence, results in different branch lengths!



Decahedron



Pentapod