Nano structured materials-synthesis, properties, self assembly and applications by Prof. A.K. Ganguli, Chemistry Department, IIT Delhi, New Delhi.

Module 3 Lecture7, 8 and 9:

Problem:

Self-assembly 1:

- 1. What is self-assembly? Give a natural example.
- 2. What are the forces which are responsible for self-assembly?
- 3. What are the nonbonding interactions? Explain with examples.
- 4. What are the types of self-assembly?
- 5. What are the common factors that affects self-assembly?
- 6. Define the packing factor in self-assembly?
- 7. How does the shape of the assembly change with packing factor?

Self-assembly 2:

- 1. Why is self-assembly important in nanomaterials?
- 2. Give an example of template based self-assembly?
- 3. How can you program a self-assembly? Explain with example.
- 4. What is convective assembly and capillary assembly?
- 5. How does the temperature important for capillary assembly?

Self-assembly 3:

- 1. What is Langmuir-Blodgett technique?
- 2. What are the different types of molecular deposition on hydrophobic surface?
- 3. Draw the different molecular arrangement at air-water interface at different surface pressure.
- 4. What is the importance of surface energy change in nanoparticle assembly at liquid-liquid interface? How does it depend on the interfacial tensions?
- 5. Why does smaller nanoparticles form less stable assembly at liquid-liquid interface?
- 6. Write the net enthalpy change in SAM formation at liquid-solid interface.

Module 3 Lecture7, 8 and 9:

Solution:

Self-assembly 1:

- 1. A process where all the components spontaneously form stable, well-shaped, ordered aggregates. As example, bubble formation is a self-assembly.
- 2. weak intermolecular interactions, non-covalent interactions (hydrogen bonding, electrostatic, ion dipole, Van der Waal forces, supramolecular assembly etc.), weak covalent interactions like coordinate bonds.
- 3. ion-dipole, Hydrogen bond, dipole-dipole, ion-induced dipole, dipole-induced dipole, London forces. See details of the energy and examples in module 3 lecture 7, at 23:12 mins.
- Static self-assembly where systems are at global or local equilibrium and it does not dissipate energy. As an example molecular crystal formation.
 Dynamic self-assembly where system dissipate energy resulting interactions.
- 5. external forces, gravitational attraction, external electromagnetic fields, magnetic, Capillary and entropic interactions.
- 6. Relative volume fraction of amphiphilic systems, $P = v/(a_0 l_c)$
 - \mathbf{v} : the volume of the hydrophobic chain.
 - \mathbf{a}_0 : the polar head surface area at the critical micelle concentration (cmc).
 - l_c : the chain length.
- 7. P=1 bilayer sheet, 1>P>0.5 bilayer sphere, 0.5>P>0.33 cylindrical micelle, P<0.33 micelles.

Self-assembly 2:

- 1. optoelectronic device size reduction, optical switches, hydrophobic surfaces, sensors etc.
- 2. Gold nanoparticles assembly on CNTs.
- 3. single stranded DNA functionalized nanoparticles can binds complementary DNA strand functionalized nanoparticles. One can program different nanoparticles with different DNA strands which can be assembled.
- 4. In convective assembly, convective flow of solvent induced by evaporation at the contact line of the droplet leads to the formation of 2D layer of packed particles. In capillary assembly, geometrical confinement and capillary forces are responsible for the assembly where receding contact angle Θ_{rec} is less the 20°.
- 5. recirculation flow (J_r) has to be compensated by the evaporation of the solvent. For that T_s has to be greater than T_c .

Self-assembly 3:

- 1. Programmed self-assembly of amphiphiles at the water –air interface and transferring on a substrate is called Langmuir-Blodgett technique.
- 2. Z-type, Y-type and X-type deposition on hydrophobic surface.
- 3. 3. gaseous 2D phase of the molecules becomes extended 2D phase then condensed 2D phase and finally collapse as the surface pressure increases.



4. The reduction in the total free energy of the system is important for adsorption of nanoparticles to liquid-liquid

interface

$$\Delta E = -\frac{\pi a^2}{\gamma_{o/w}} \left(\gamma_{o/w} - (\gamma_{p/w} - \gamma_{p/o}) \right)^2$$

 $\gamma_{o/w}$, $\gamma_{p/w}$ and $\gamma_{p/o}$ are the interfacial tensions at the **oil–water**, particle–water and particle–oil interfaces

 ΔE = Surface energy reduction of a particle of radius (a) at the interface

5. *E* depends on a^2

The energy gain is smaller and the assembly is less stable for smaller nanoparticles than for larger ones

6.

 $\Delta H_{\rm r} = -D - (\Delta H_{\rm sol} + \Delta H_{\rm dil}) - (E_{\rm S} - E_{\rm SAM})$

D : the binding energy of the SAM molecules with the solid ΔH_{sol} and ΔH_{dil} : the enthalpies of dissolution and dilution E_{s} and E_{sAM} : the surface energies of bare solid and SAM