

나노소재의 이해와 응용

2024-2

4. Synthesis of Nanomaterials - II

(Chemical Methods)

4. Synthesis of Nanomaterials II (Chemical Methods)

4.1 Introduction

Advantages of Chemical Synthesis

- Simple techniques
 - Inexpensive, less instrumentation compared to many physical methods
 - Low temperature (<350 °C) synthesis
 - Doping of foreign atoms (ions) possible during synthesis
 - Large quantities of the materials can be obtained
 - Variety of sizes and shapes are possible
 - Materials are obtained in the form of liquid but can be easily converted into dry powder or thin films
 - Self assembly or patterning is possible
- ➡ The instrumentation involved in the chemical synthesis can be relatively simple and inexpensive as compared to many physical methods.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

- As in many cases nanoparticles synthesized by chemical method form what is known as ‘**colloids**’
- A class of materials, in which two or more phases (solid, liquid or gas) of same or different materials co-exist with the dimensions of at least one of the phases less than a micrometre (μm) is known as **colloids**
- Colloids may be particles, plates or fibres

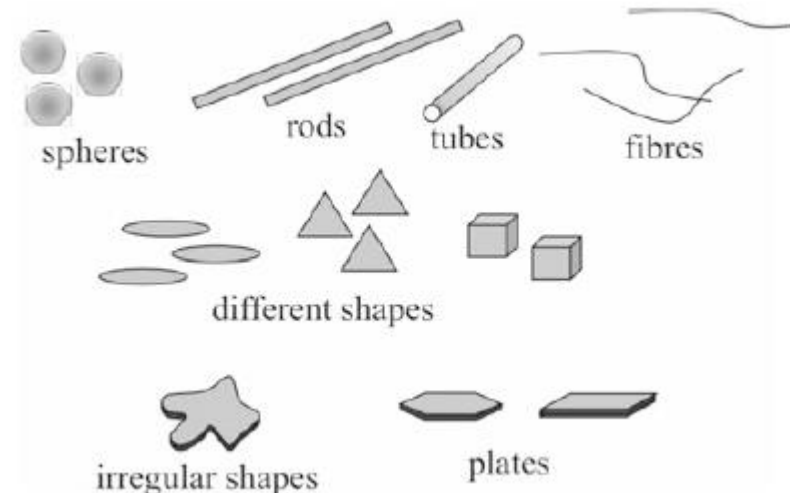


Fig. 4.1 Different shapes of colloids

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

- Nanomaterials are a subclass of colloids, in which one of the dimensions of colloids is in nanometer(nm) range.

- Examples of Colloids:

liquid in gas (fog), liquid in liquid (fat droplets in milk), solid in liquid (tooth paste), solid in solid (tinted glass), gas in liquid (foam)



Foam



Milk



Smoke



Detergents



Gel



Blood



Paint



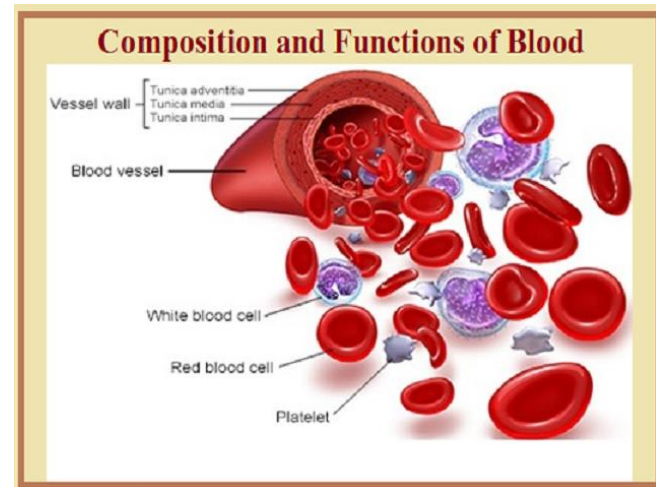
Cosmetics

Examples of Colloids that we meet daily

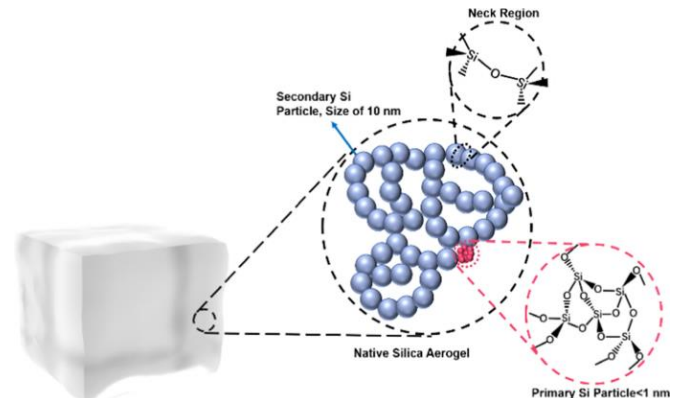
4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

- Organic and inorganic materials can be dispersed into each other to form colloids.
- Several examples exist even of bio-colloids. Blood and bones are good examples of bio-colloids. Blood has corpuscles dispersed in serum and bone has colloids of calcium phosphate embedded in collagen.



- Colloids may even form networks. For example aerogels are a network of silica colloidal particles, pores of which are filled with air.



4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.1 Interactions of Colloids and Medium

- Colloids are particles with large surface to volume ratio
 - Correspondingly there are large number of atoms/molecules on the surface of a colloidal particle, which do not have as many neighbors as those for an atom/molecule inside the interior.
 - Therefore atoms on the surface are in a highly reactive state, which easily interact to form bigger particles or tend to coagulate.
 - It is thus necessary to understand the stability of colloids
 - > how the colloids dispersed in a medium can remain as separated particles.
- ➡ We consider the inorganic spherical colloids of equal size, dispersed in a liquid medium

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.1 Interactions of Colloids and Medium

Brownian motion

When fine particles are dispersed in a liquid medium, it is known that any of various physical phenomena in which some quantity is constantly undergoing small, random fluctuations.

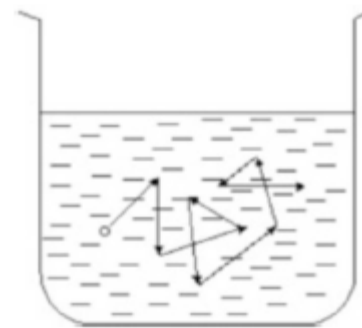


Fig. 4.2 Brownian motion of colloidal particles

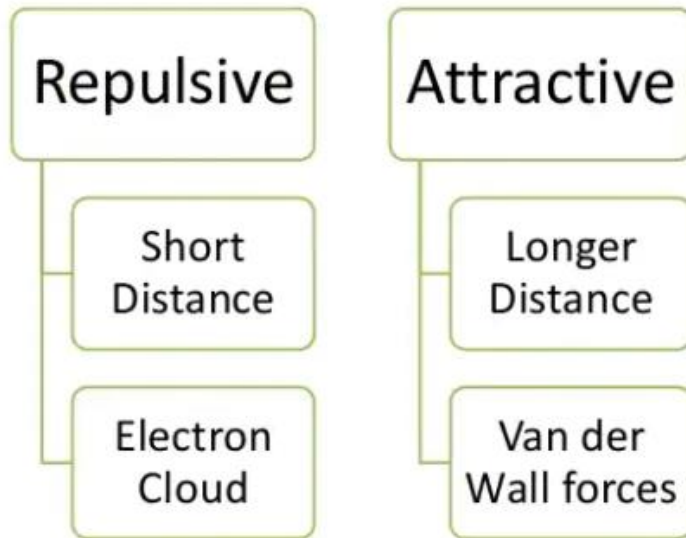
- If we are able to tag a particle in the solution, it would appear as if it is making random motion.
- All other particles also execute random motion, hitting each other and changing direction of motion in solution -> Distance travelled between successive collisions is random too.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.1 Interactions of Colloids and Medium

Type of Interaction



- Interactions of such constantly and randomly moving particles with each other and with liquid in general would be quite complex

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.1 Interactions of Colloids and Medium

Type of Interaction

Consider for example the van der Waals interaction (see Chap. 2) between two atoms or molecules

Two parts in the interaction viz. attractive and repulsive parts given by

$$dG_1 = \left(\frac{A}{R^{12}} \right) - \left(\frac{B}{R^6} \right)$$

where dG_1 is the interaction energy,
 A and B are constants and R is the
distance between two particles

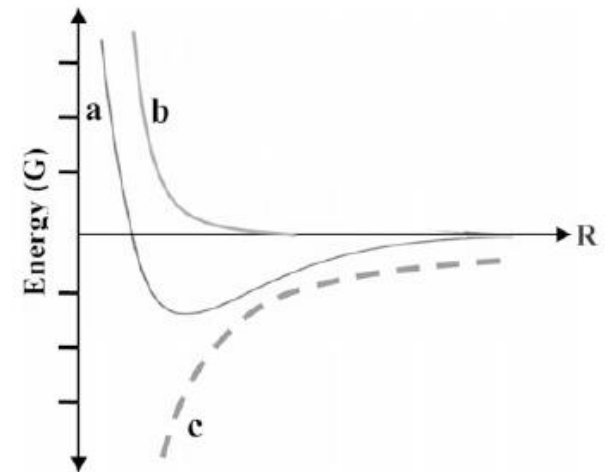


Fig. 4.3 Van der Waals interaction: (a) Resulting energy, (b) **Repulsive energy** and (c) **Attractive energy**

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4.2 Colloids and Colloids in Solutions

4.2.1 Interactions of Colloids and Medium

Type of Interaction

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- The first term is repulsive interaction (Born repulsive interaction) effective only at short distance
 - ➔ Repulsive part arises due to repulsion between electron clouds in each atom
- The second term represents long range attractive interaction (van der Waals attraction)
 - ➔ Attractive part is due to interaction between fluctuating or permanent dipoles of atoms/molecules

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.1 Interactions of Colloids and Medium

Concept of Free Energy

- Free energy of a body is a measure of ability to do work.
- A body always tends to attain the state of lower energy by releasing ‘free energy’ and is given by Gibb’s free energy

$$G = H - TS$$

where G is the energy absorbed or released by a body, H – enthalpy, T – temperature and S is entropy.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.1 Interactions of Colloids and Medium

Concept of Free Energy

- In order to understand the meaning of surface free energy, consider that a cylinder with cross section 'A' and length '2l' into two equal pieces
- Work has to be done in order to break the cylinder into two pieces and separate them by a distance R.

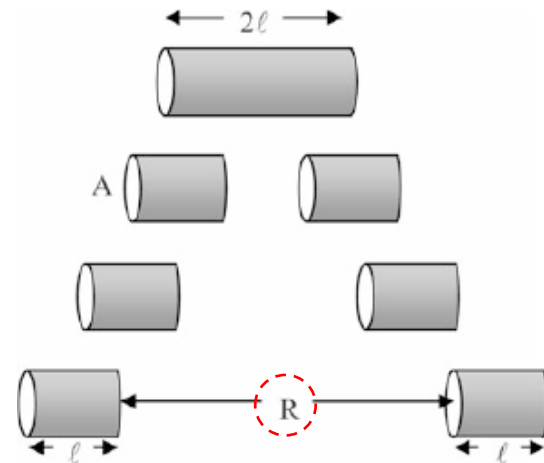


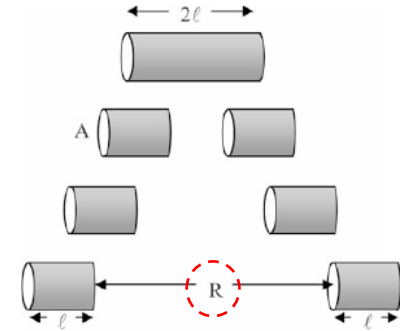
Fig. 4.4 A cylinder with cross section A and length $2l$ has been cut into two pieces of equal length

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4.2 Colloids and Colloids in Solutions

4.2.1 Interactions of Colloids and Medium

Concept of Free Energy



- Energy increases as the distance between the two pieces increases.
- The two pieces keep on attracting each other due to intermolecular forces at the broken interface. Therefore, more and more energy has to be supplied in order to separate them.
- Interfacial energy is related to the surface tension ‘ γ ’.
- Surface tension ” is along the normal to surface and is expressed as force per unit length (N/m or Joule/m²).
- Surface free energy is given by

$$\Delta W = \Delta G - 2\gamma A$$

where W is the work done to break the cylinder, ”–surface tension and A is the surface area. (Factor ‘2’ arises because while creating two surfaces, surface area would be $2A$ for two surfaces)

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.1 Interactions of Colloids and Medium

Concept of Free Energy

- The surface free energy per unit volume would increase with separation R between two particles (Fig. 4.5)

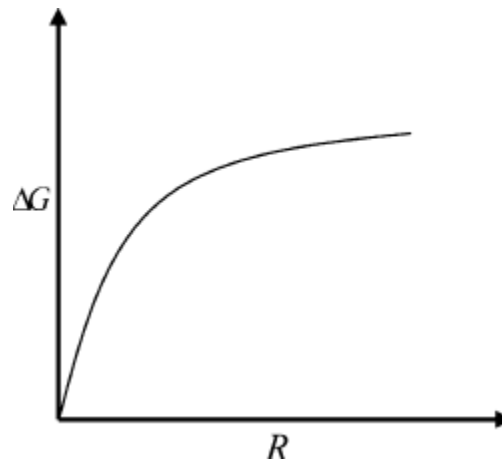
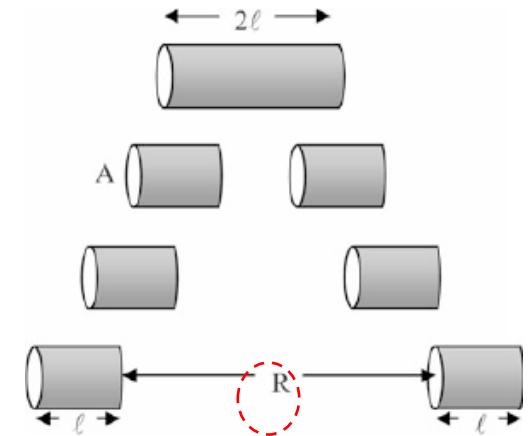


Fig. 4.5 Change in surface free energy with separation R between two pieces of the cylinder



4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.1 Interactions of Colloids and Medium

Concept of Free Energy

- The force of attraction would increase in vacuum as shown in Fig. 4.6

In a liquid the force of attraction would reduce in general.

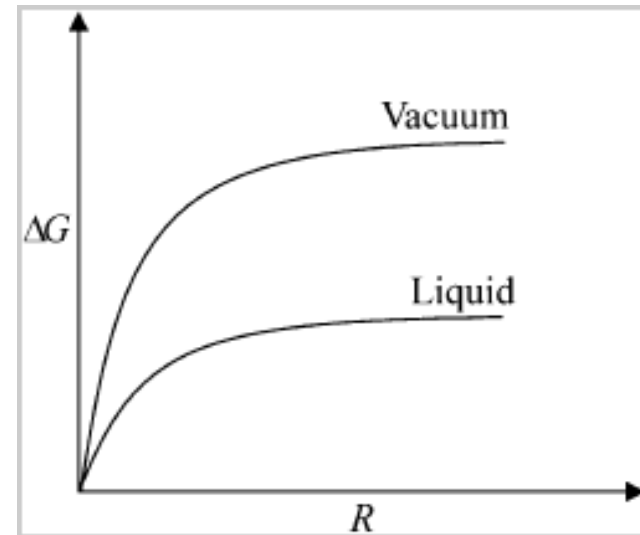


Fig. 4.6 Change in surface free energy with separation R between two pieces of the cylinder shown in Fig. 4.4, placed in vacuum or liquid

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.3 Colloid in a Medium

- Consider now a situation, in which inorganic spherical colloids are immersed in a liquid (and do not dissolve)
- The attractive interactions between the colloids get modified through the change of Hamaker constant as A_H

$$A_H = \left(\sqrt{A_{1v}} - \sqrt{A_{2v}} \right)^2$$

where A_{1v} is the Hamaker constant for particle of inorganic solid under consideration, in vacuum and A_{2v} is Hamaker constant of colloid of medium in vacuum.

- In general the effect of liquid medium is to reduce the Hamaker constant of colloid particle. Hence the attractive force between colloid particles will in general reduce.

*Hamaker constant

The Hamaker constant is a coefficient accounting for the van der Waals interaction between two materials, and it has a strong correlation with various physical phenomena, such as liquid wettability, adhesion, friction, adsorption, colloidal stability, polymer flow, and deformation

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.4 Effect of Charges on Colloids

- Colloids in liquid may be positively charged, negatively charged or even neutral. But in most of the cases they are charged.
- There are various sources for colloids by which they acquire charges on their surfaces viz. through composition of colloidal material, properties of dispersing medium including the type and concentration of dissolved ions in the solution.
- In any case as soon as there are some charges on particles, ions of opposite charges accumulate around them.
- Oppositely charged ions are known as *counter ions*. This accumulation of counter ions leads to formation of an electric double layer.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.4 Effect of Charges on Colloids

- Helmholtz considered that the situation is like that in a parallel plate condenser, where there are opposite charges as plates separated by a medium (for example air as shown in Fig. 4.8)
- Due to their Brownian motion, counter ions are not fixed nor are colloidal particles at rest. They execute their own Brownian motion and form a dynamic double layer around them (Fig. 4.9)

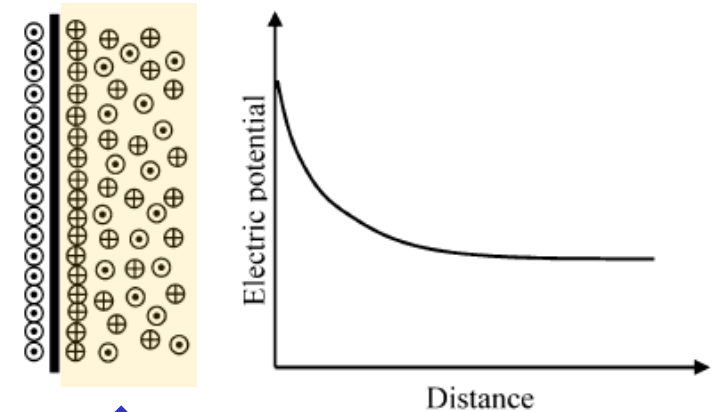


Fig. 4.8 Double layer of charges and fall of electrical potential from negatively charged plate with positive ion accumulation

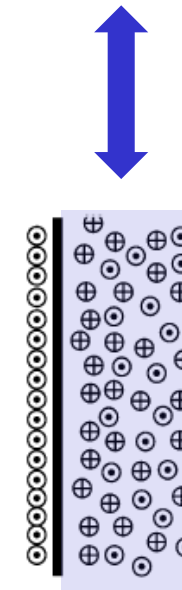


Fig. 4.9 Diffuse double layer because of Brownian motion

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.4 Effect of Charges on Colloids

- The changes occur when concentrations of charges on colloid and local ionic charges in solution contribute to double layer change
- The concentration of electrolyte would strongly affect the electric potential curve
- Consider now a situation in which two charged colloidal particles come closer with their electric double charge layers
- As they approach each other force of repulsion increases, It is easy to see that the difference in concentrations of double layer charges would play an important role

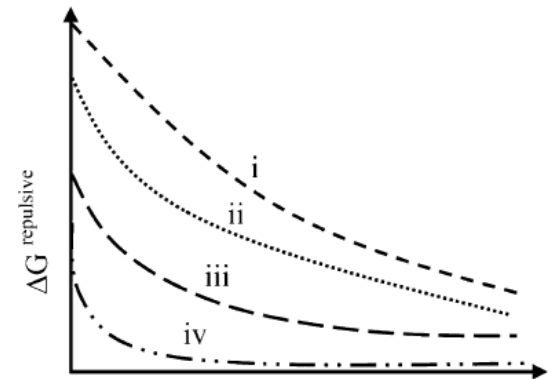


Fig. 4.10 Effect of concentration on change of potential from a particle. Curves **i, ii, iii** and **iv** refer to increasing electrolyte concentrations

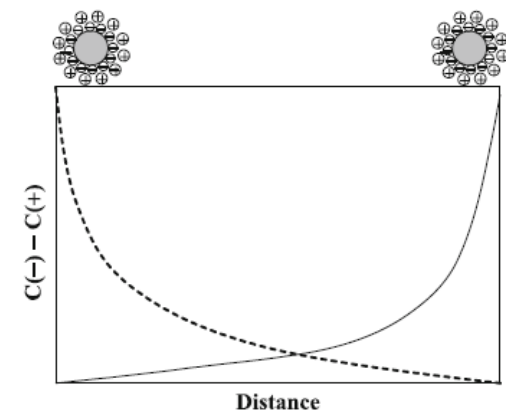
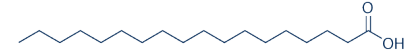


Fig. 4.11 Colloid-colloid interaction with electric double charge layer

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions



Stearic acid is a saturated fatty acid with an 18-carbon chain

4.2.5 Stearic Repulsion

- Stability of colloids can be increased by creating Stearic hindrance or repulsion
- By adsorbing some layers of a different material on colloidal particles e.g. polymer or organic molecules on inorganic colloidal particles, it is possible to reduce the attractive forces between them

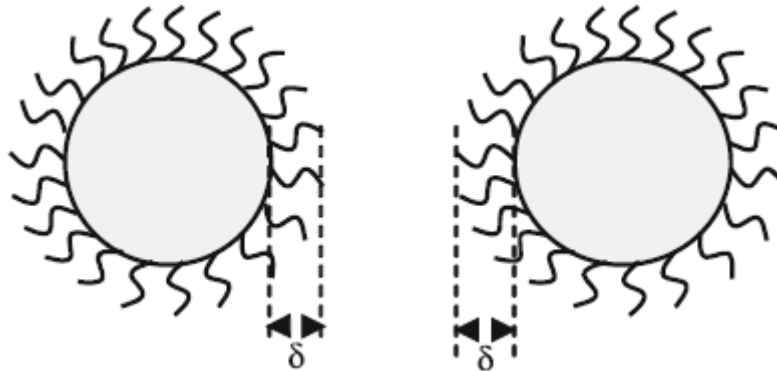
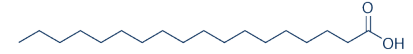


Fig. 4.12 Colloids with coatings. Separation between the particles, each coated with coating of thickness δ , increases by 2δ

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions



Stearic acid is a saturated fatty acid with an 18-carbon chain

4.2.5 Stearic Repulsion

- With addition of adsorbed layers, the effective sizes of the particles change which helps them to stay at a longer distance from each other, reducing the attractive interaction.
- If the coating materials is similar in properties to that of the solvent, the effect of coating would be negligible

➡ This idea is the basis of ‘capped nanoparticles’

- The colloids interact with each other dynamically and are affected by van der Waals forces, colloid-colloid interaction mediated through dispersing medium, electric double layer and Stearic interactions.
- If the repulsive forces are strong enough, colloids would be stabilized. Otherwise ripening, coagulation, or network formation may take place

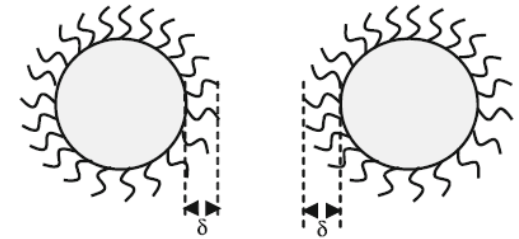


Fig. 4.12 Colloids with coatings. Separation between the particles, each coated with coating of thickness δ , increases by 2δ

4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.6 Synthesis of Colloids

Colloids

- phase separated submicrometre particles in the form of spherical particles or particles of various shapes and sizes like rods, tubes, plates.
- They are the particles suspended in some host matrix
- Metal, alloy, semiconductor and insulator particles of different shapes and sizes can be synthesized in aqueous or non-aqueous media.
- Colloidal particles in liquids are stabilized as discussed above by Coulombic repulsion, which arises due to similar charges they may have acquired on their surfaces.
- In some cases surface passivating molecules may be used which provide sufficient steric hindrance inhibiting coalescence or aggregation

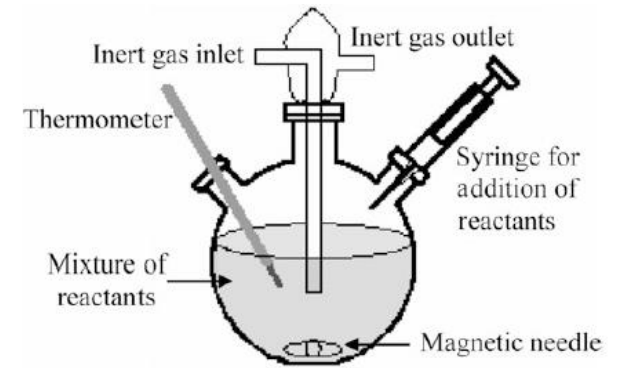
4. Synthesis of Nanomaterials II (Chemical Methods)

4.2 Colloids and Colloids in Solutions

4.2.6 Synthesis of Colloids

Synthesis of Colloids (Nano or micro particles)

- Synthesis of colloids is a very old method
- Making nanoparticles using colloidal route goes back to nineteenth century when M. Faraday synthesized gold nanoparticles by wet chemical route.
- The particles are so stable that even today the colloidal solution made by him can be seen in the British Museum in London
- Chemical reactions in which colloidal particles are obtained are carried out in some glass reactor of suitable size
- Glass reactor usually has a provision to introduce some precursors, gases as well as measure temperature and pH during the reaction. It is usually possible to remove the products at suitable time intervals.
- Reaction is usually carried out under inert atmosphere like argon or nitrogen gas so as to avoid any uncontrolled oxidation of the products



4. Synthesis of Nanomaterials II (Chemical Methods)

4.3 Nucleation and Growth of Nanoparticles

- Synthesis of nanoparticles of different shapes and sizes may appear as a complex process
- ➡ The process of nucleation is a ‘bottom-up’ approach in which atoms and/or molecules come together to form a solid.

The nucleation process can be spontaneous

Homogenous nucleation is said to take place when it involves the nucleation around the constituent atoms or molecules of the resultant particles.

Heterogeneous nucleation can take place on a foreign particle like dust, deliberately adding seed particles, templates, or the walls of the container

4. Synthesis of Nanomaterials II (Chemical Methods)

4.3 Nucleation and Growth of Nanoparticles

- Various routes of nucleation processes

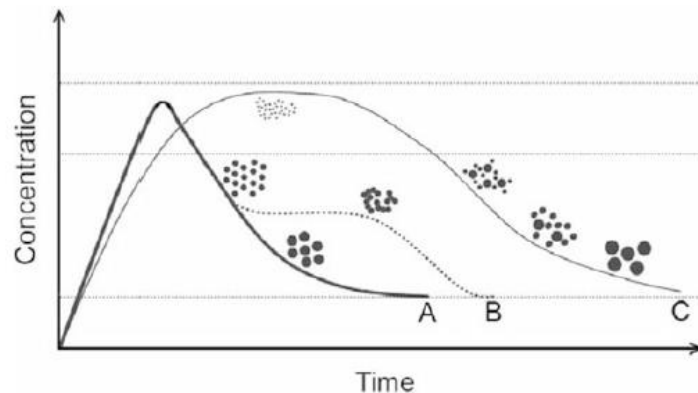


Fig. 4.14 Nucleation and growth of nanoparticles (LaMer diagram). All the dots appearing in the sketch are small/big nanoparticles

- A:** fast nucleation takes place as the solute concentration approaches super saturation
- B:** If the nuclei acquire atoms quickly by diffusion through solution thus reducing the solute concentration, particles of uniform size are formed in a relatively shorter time compared to aggregated particles
- C:** the nucleation proceeds for a long time bringing in smaller and larger nuclei to co-exist when super-saturation region exists over a longer period and then the solute concentration decreases (Ostwald ripening process)

4. Synthesis of Nanomaterials II (Chemical Methods)

4.3 Nucleation and Growth of Nanoparticles

Formation of nucleus

- The size of a nucleus is determined by both the free energy change occurring during the formation of the solid (from a liquid), as well as the surface energy of the nucleus.

<Homogeneous Nucleation>

A stable nucleus (of a critical radius r^*) needs to be formed so that it can grow into a larger stable particle

- Let us refer to particles of radii smaller than r^* as embryos; the energy for such an embryo formation (G_r) is given by:

$$\Delta G_r = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$$

where r is the radius of the embryo, G_v is the free energy change per unit volume between the liquid and solid, and γ_{SL} is the interfacial free energy of the liquid and solid.

- Below the melting temperature (T_m) of the solid, ΔG_v is negative, whereas the surface free energy, or surface tension γ_{SL} is positive.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.3 Nucleation and Growth of Nanoparticles

- The two energies compete with each other with increasing value of the embryo radius r .
- Differentiating Eq. (4.9) with respect to r and equating it to zero at $r = r^*$, we obtain:

$$4\pi r^{*2} \Delta G_v + 4\pi (2r^*) \gamma_{SL} = 0$$

➔
$$r^* = \frac{-2\gamma_{SL}}{\Delta G_v}$$

- After the critical size r^* , the free energy starts decreasing and the growth begins.

- The energy G_v depends on latent heat of fusion and the degree of undercooling
- Undercooling is a result of faster cooling rate than required for the equilibrium cooling. Some finite time is required in any system so that atoms/molecules adjust themselves and acquire the position of minimum energy.

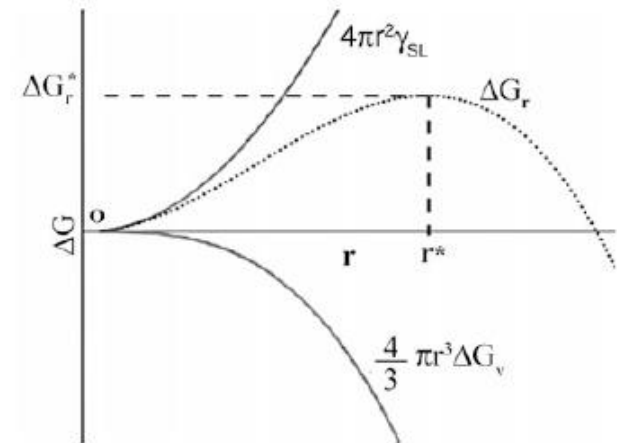


Fig. 4.15 Nucleation process

4. Synthesis of Nanomaterials II (Chemical Methods)

4.3 Nucleation and Growth of Nanoparticles

- The undercooling temperature is given as:

$$\Delta T = T - T_m$$

where T_m is equilibrium melting temperature, T – bulk temperature, and ΔH_f is the heat of fusion per unit volume

$$\Delta G_v = \frac{\Delta H_f \Delta H}{T_m}$$

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

$$r^* = \frac{-2\gamma_{SL} T_m}{\Delta H_f \Delta H}$$

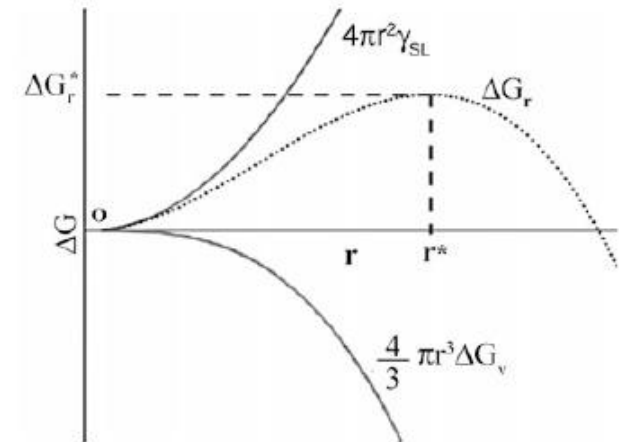


Fig. 4.15 Nucleation process

- If ΔG_v is the total free energy of the nucleus of radius r , number of clusters n_r can be obtained using

$$n_r = N e^{\left(\frac{-\Delta G_v}{kT}\right)}$$

where N is the total number of atoms and k is Boltzmann constant.

4. Synthesis of Nanomaterials II (Chemical Methods)

4.3 Nucleation and Growth of Nanoparticles

<Heterogeneous Nucleation>

- When the nucleation occurs on some foreign particle or surface (e.g. of the container wall or substrate), heterogeneous nucleation is said to occur
- This lowers the energy necessary for the nucleation of a particle.
- Consequently the critical size or radius r^* for nucleation is smaller in heterogeneous nucleation than that for homogeneous nucleation.

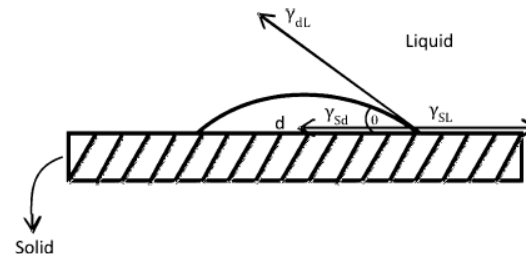


Fig. 4.16 Nucleation on a solid surface

- Consider a solid substrate on which a drop of liquid forms, γ_{sd} , γ_{SL} and γ_{dL} are the interfacial surface tensions between substrate and liquid drop, surface and liquid and the drop and liquid respectively

$$\Delta G = V\Delta G_v + A_{dL}\gamma_{dL} - \pi r^2\gamma_{dL} \cos \theta$$

where V is the volume of the liquid drop; it may be noted that there is change in the volume free energy G_v as discussed with reference to homogeneous nucleation

4. Synthesis of Nanomaterials II (Chemical Methods)

4.3 Nucleation and Growth of Nanoparticles

<Heterogeneous Nucleation>

- the critical radius r^* which is given as

$$r^* = \frac{-2\gamma dL}{\Delta G_v}$$

- In general, once the nuclei with critical radii r^* are generated, stable nuclei and particle growth starts by addition of atoms or molecules from the solute.



Nucleation of carbon dioxide bubbles around a finger

Next

**4. Synthesis of Nanomaterials - II
(Chemical Methods)**