



# LEC 4

# PHARMACEUTICAL TECHNOLOGY

## COLLOIDAL DISPERSIONS

3<sup>rd</sup> / 1<sup>st</sup> course

Dr. Ameer S. Sahib

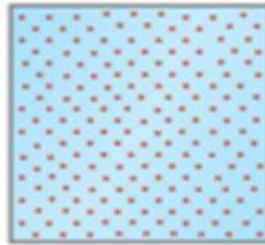
# Dispersed systems

Dispersed systems consist of particulate matter, known as the **dispersed phase**, distributed throughout a **continuous** or **dispersion medium**.

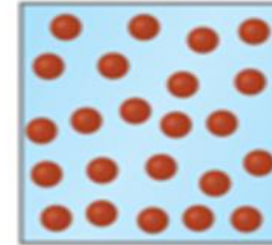
The dispersed material may range in size from particles of atomic and molecular dimensions to particles whose size is measured in millimeters. Accordingly, a convenient means of classifying dispersed systems is on the basis of the mean particle diameter of the dispersed material.

# Types of dispersed systems

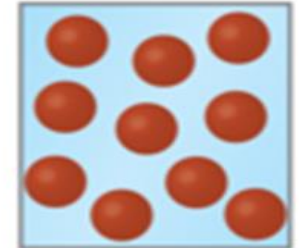
Molecular dispersion	Colloidal Dispersions	Coarse Dispersions
<ul style="list-style-type: none"><li>Particle size <math>&lt; 1\text{ nm}</math></li><li>Invisible in electron microscope and can pass through semi-permeable membrane and ultra-filter.</li><li>Example : Glucose in water (<u>true solution</u>)</li></ul>	<ul style="list-style-type: none"><li>Particles size <math>1\text{ nm} - 0.5\text{ }\mu\text{m}</math> (<math>500\text{ nm}</math>)</li><li>Visible in electron microscope and can pass through filter paper.</li><li>Do not pass through semi-permeable membrane.</li><li>Example: jelly, butter, milk, shaving cream</li></ul>	<ul style="list-style-type: none"><li>Particle size <math>&gt; 0.5\text{ }\mu\text{m}</math></li><li>Visible in ordinary microscope</li><li>Do not pass through a normal filter paper or semi-permeable membrane</li><li>Example: calamine lotion, fine sand in water, red blood cells (<u>Emulsions, suspensions</u>)</li></ul>



solution

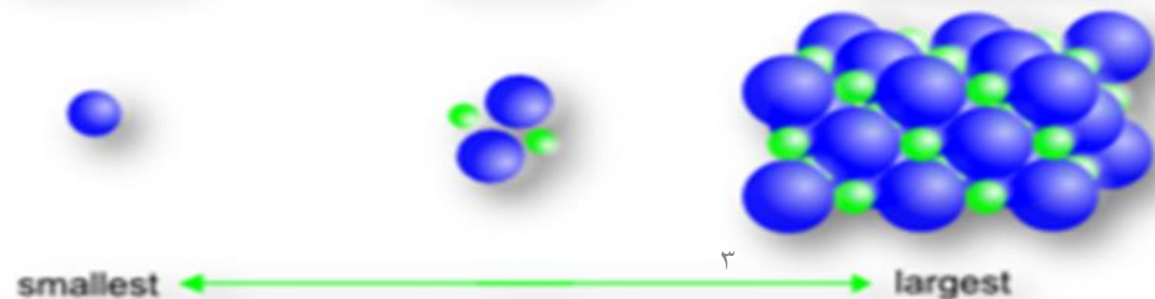


colloid



suspension

1. Molecular dispersions.
2. Colloidal dispersions.
3. Coarse dispersions.



## **Molecular dispersions** (less than 1 nm)

Particles invisible in electron microscope and pass through semipermeable membranes and filter paper. **Particles do not settle down on standing and undergo rapid diffusion** E.g. true solution.

## **Colloidal dispersions** (1 nm - 0.5 $\mu\text{m}$ )

Particles not resolved by ordinary microscope, can be detected by electron microscope. Pass through filter paper but not pass through semipermeable membrane. Particles made to settle by centrifugation. **Diffuse very slowly** E.g. colloidal silver iodide, natural and synthetic polymers, cheese, butter, jelly, paint, milk, shaving cream.

## **Coarse dispersions** ( $> 0.5 \mu\text{m}$ )

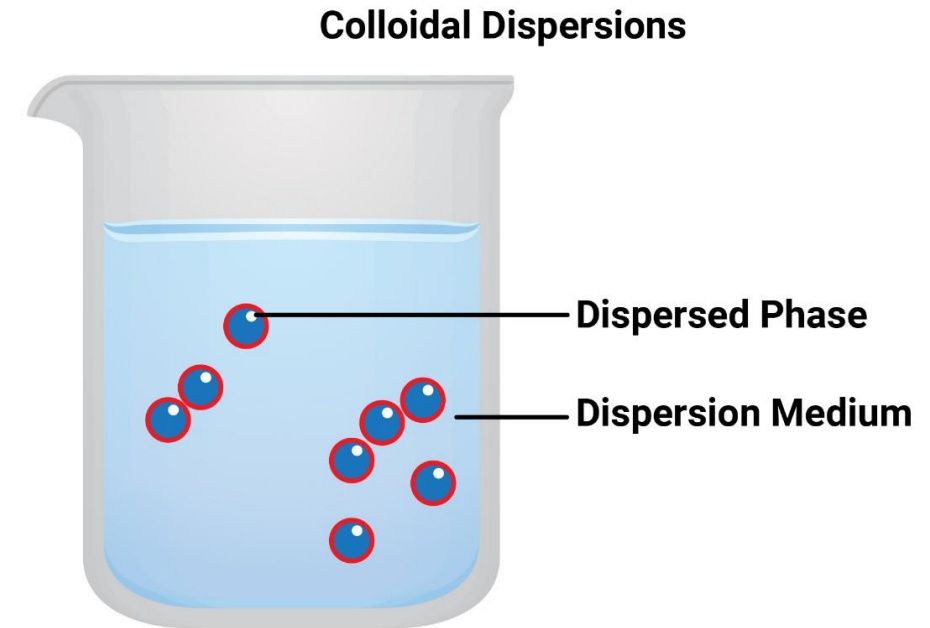
Particles are visible under ordinary microscope. Do not pass through filter paper or semipermeable membrane. **Particles settle down under gravity do not diffuse** E.g. emulsions, suspensions, red blood cells.

# Types of dispersed system

Dispersed phase	Dispersion medium	Type of colloid	Example
Solid	Solid	Solid sol	Gem stones, rubby glass, some alloys
Solid	Liquid	Suspension	Paints, cell fluids
Solid	Gas	Solid aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream, mayonnaise
Liquid	Gas	Liquid aerosol	Fog, mist, cloud
Gas	Solid	Solid foam	Pumice stone, foam rubber, meringue
Gas	Liquid	Liquid foam	Froth, whipped cream, soap lather

# Colloidal dispersions

- Colloid from the Greek word
- Kolla = glue
- Introduced by Thomas Graham
- Colloidal system or colloidal dispersion is a heterogeneous system which is made up of **Dispersed phase** and **Dispersion medium (Continuous phase)**.
- In colloidal dispersion one substance is dispersed as very fine particles in another substance called dispersion medium.

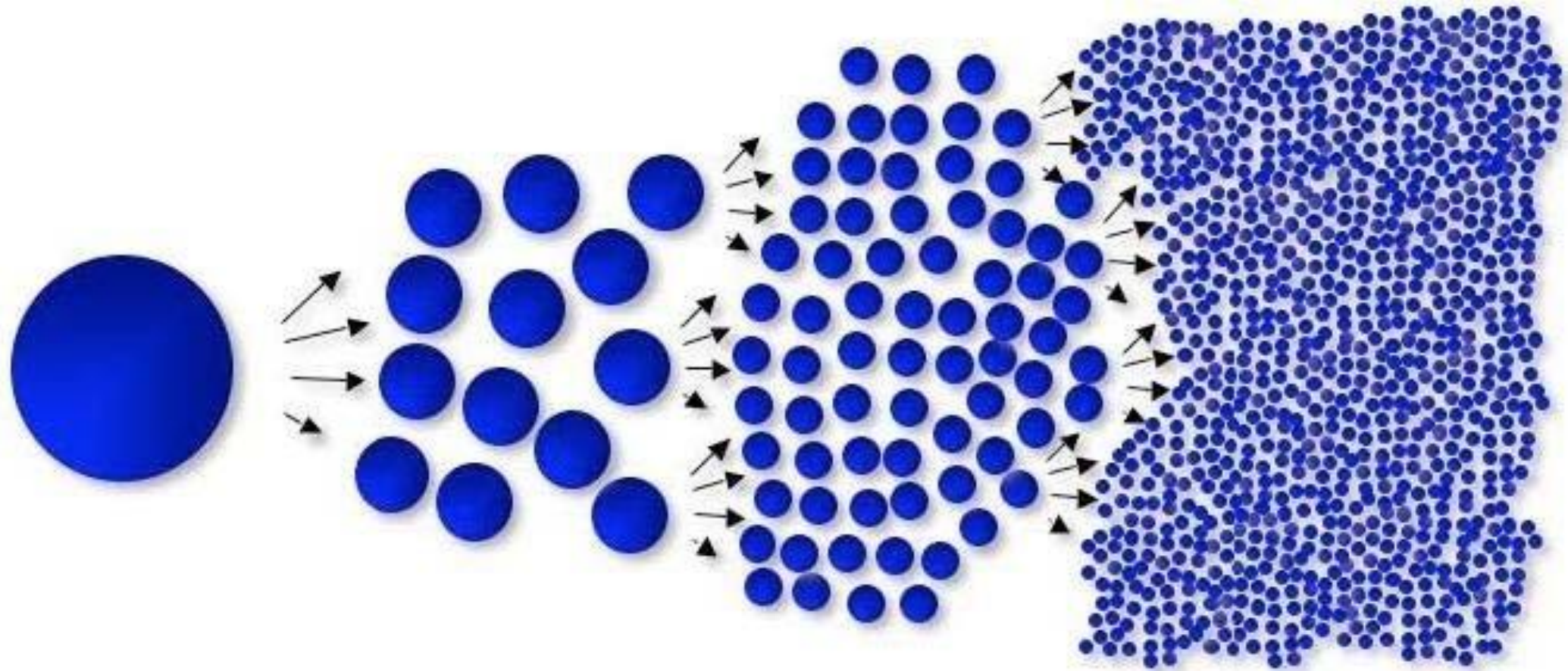


# Characteristics of dispersed phase

## 1) Particle size and surface area

Particles in the colloidal size range possess a surface area that is enormous compared with the surface area of an equal volume of larger particles. Thus, a cube having a 1-cm edge and a volume of 1 cm<sup>3</sup> has a total surface area of 6 cm<sup>2</sup>. If the same cube is subdivided into smaller cubes each having an edge of 100 μm, the total volume remains the same, but the total surface area increases to 600,000 cm<sup>2</sup>. This represents a 10<sup>5</sup>-fold increase in surface area.





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**Particle size**

10 cm

1mm

 $1\mu\text{m}$ 

1 nm

**Surface**

1

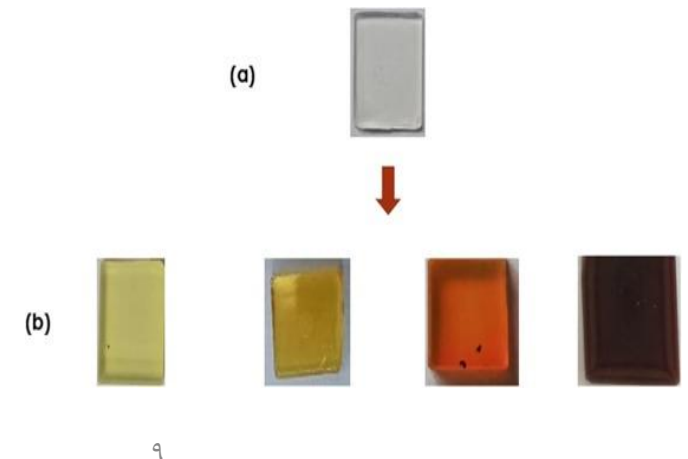
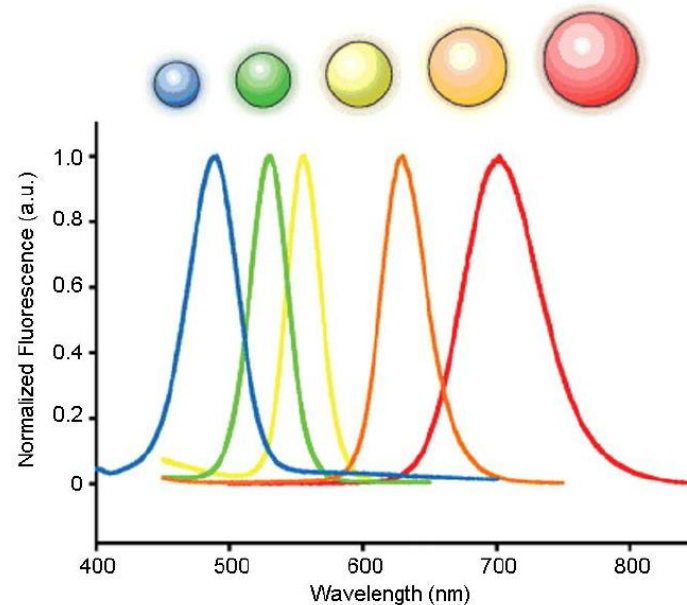
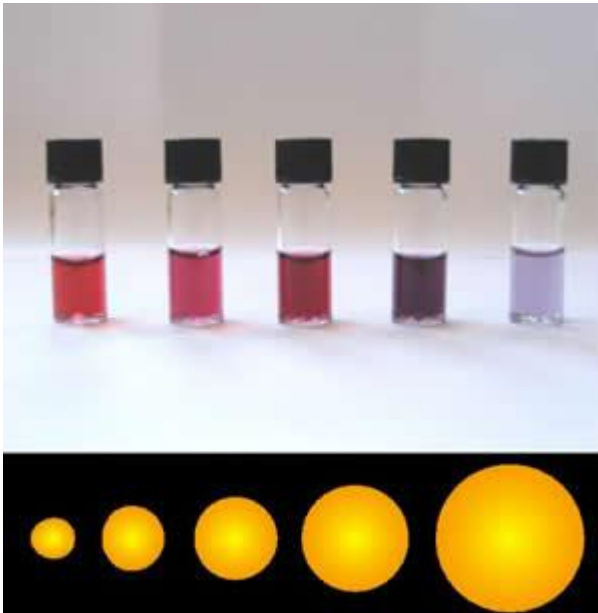
100

100.000

100.000.000

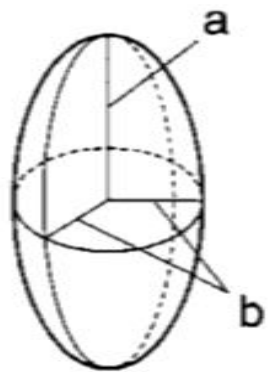


The **color** of colloidal dispersions is related to the size of the particles present. Thus, as the particles in a **red gold sol** increase in size, the dispersion takes on a **blue** color. **Antimony and arsenic trisulfides** change from **red** to **yellow** as the particle size is reduced from that of a coarse powder to that within the colloidal size range.

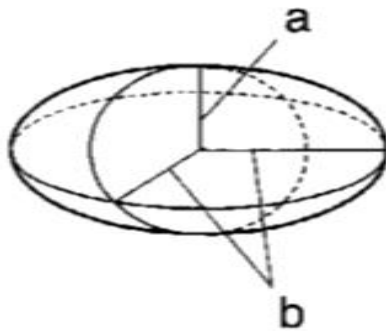


## 2) Shape of colloidal systems

- Many colloidal systems, including emulsions, liquid aerosols and most dilute micellar solutions, contain **spherical particles**,
- Small deviations from sphericity are often treated using **ellipsoidal** models.
- High molecular weight polymers and naturally occurring macromolecules often form random **coils** in aqueous solution.
- Clay suspensions are examples of systems containing **plate-like** particles

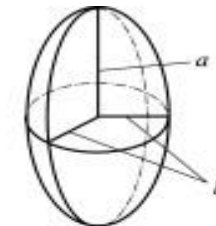


Prolate



Oblate

Model representation of ellipsoids of revolution.



Prolate ellipsoid



Oblate ellipsoid



Rod



Disc



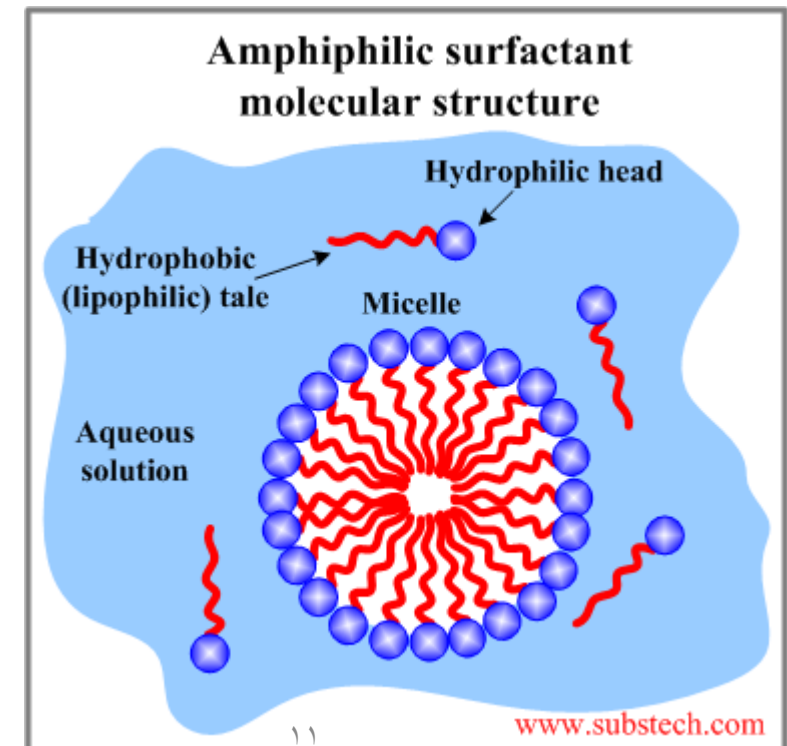
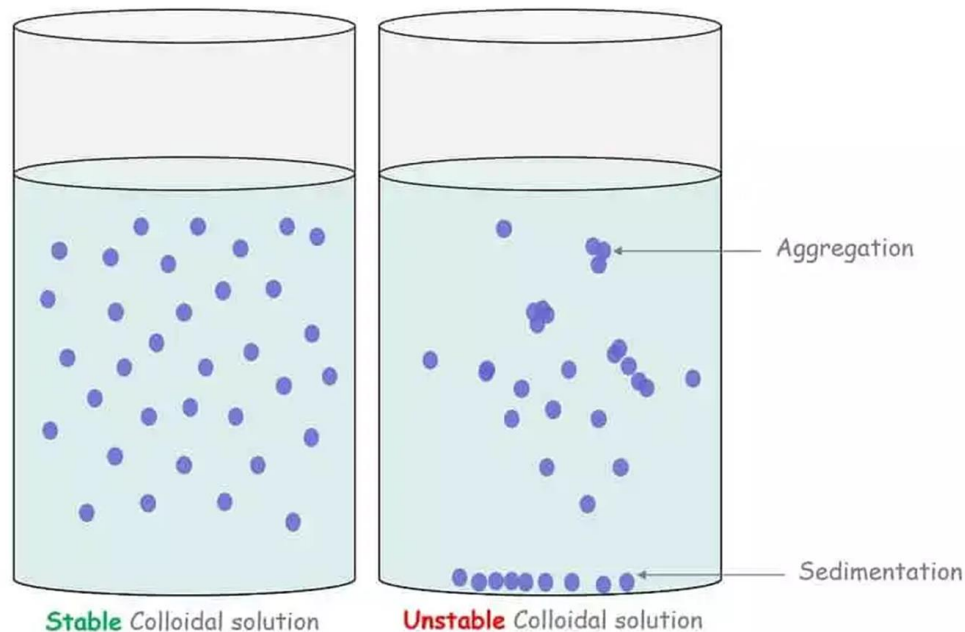
Random coil

**3- Types of colloids** according to the nature of interaction between dispersed phase and dispersion medium divided to:

**A- Lyophilic colloids (solvent attracting) (solvent loving)**

**B- Lyophobic colloids (solvent repelling) (solvent hating)**

**C- Association or amphiphilic colloid is formed by grouping or association of molecules that exhibit both lyophilic and lyophobic properties (surfactant) (e.g. micelles).**



# Lyophilic colloids

- ❑ The particles in a lyophilic system have a **great affinity** for the solvent.
- ❑ If **water** is the dispersing medium, it is often known as a **hydrosol** or **hydrophilic**.
- ❑ **Readily solvated** (combined chemically or physically, with the solvent) and dispersed, even at **high concentrations**.
- ❑ **More viscid**
- ❑ Examples of lyophilic sols include sols of **gum**, **gelatin**, **starch**, **proteins** and certain polymers (rubber) in organic solvents.

- ❑ The sols are quite **stable** as the solute particle surrounded by two stability factors:

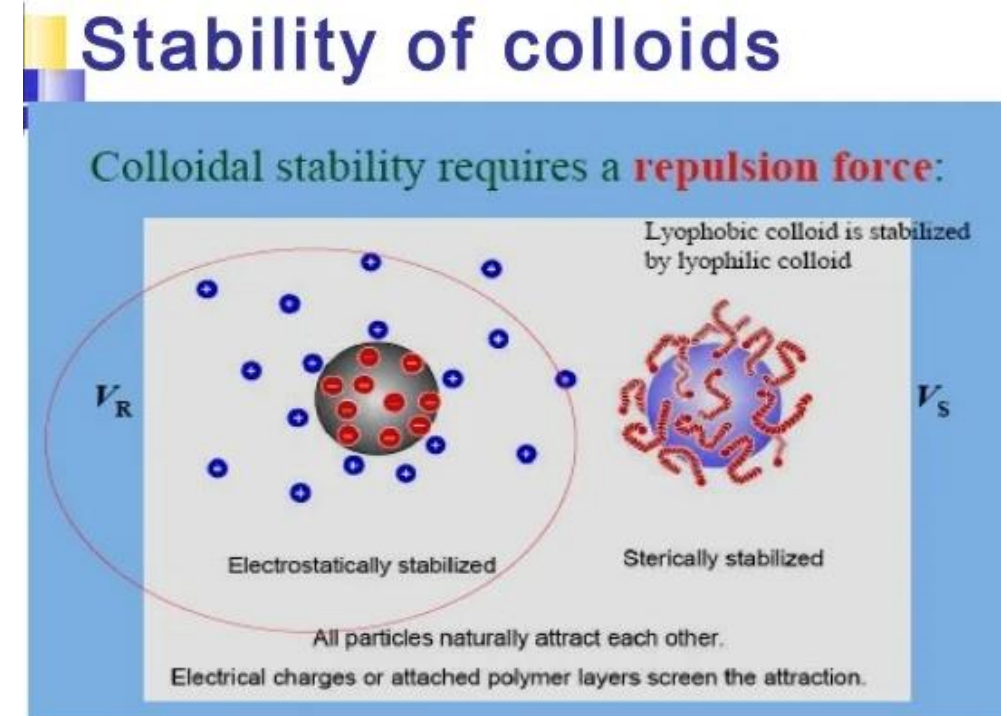
a- negative or positive charge

b- layer of solvent (solvation).

- ❑ The dispersed phase does **not precipitate easily**.

- ❑ If the dispersion medium is separated from the dispersed phase, the sol can be **reconstituted by simple remixing** with the dispersion medium. Hence, these sols are called **reversible sols**.

- ❑ Prepared simply by dispersing the material in the solvent being used e.g. **dissolution of acacia in water**.





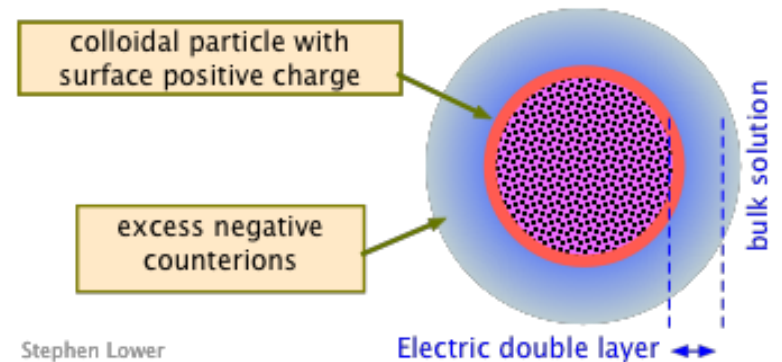
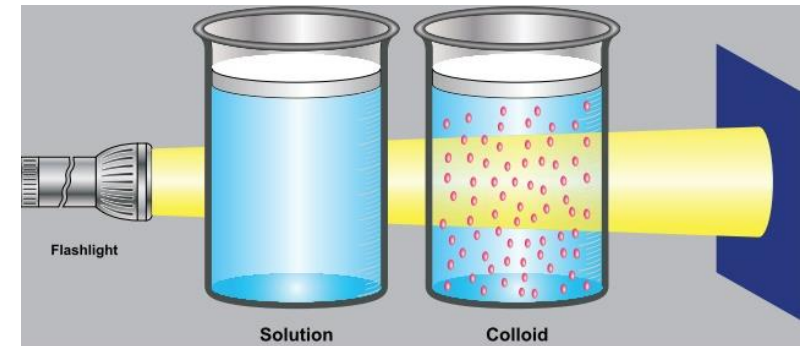
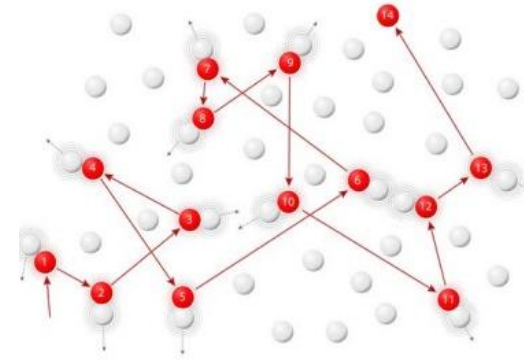
# Lyophobic colloids

- ❑ The particles **resist solvation and dispersion** in the solvent.
- ❑ The **concentration** of particles is usually relatively **low**.
- ❑ **Less viscid**
- ❑ **Less stable** as the particles surrounded **only with a layer of positive or negative charge without solvation**.
- ❑ Once precipitated, it is **not easy to reconstitute** the sol by simple mixing with the dispersion medium. Hence, these sols are called **irreversible sols**.
- ❑ Examples of lyophobic sols include **sols of metals** and their insoluble compounds like sulphides and oxides. e.g. **gold in water**

# Properties of colloids

1. Kinetic properties
2. Optical properties
3. Electrical properties

**Brownian motion**



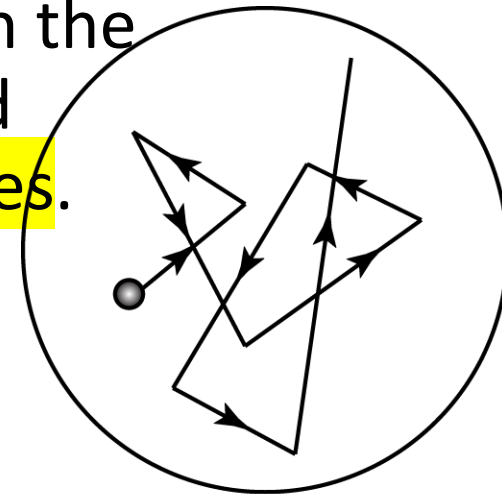
Stephen Lower

# 1 – kinetic properties

- Used to detect **stability** of system, **molecular weight** of particles, **transport** kinetics.
- Includes: Brownian motion, diffusion, osmosis, sedimentation, and viscosity.

**A. Brownian motion :** Colloidal particles are subject to **random** collisions with the molecules of the dispersion medium, with the result that each particle pass in an irregular and complicated zigzag path. **Responsible for the diffusion of colloidal particles.**

- ✓ Particles move against gravitational force.
- ✓ **Brownian motion decreased with increase in size & viscosity.**

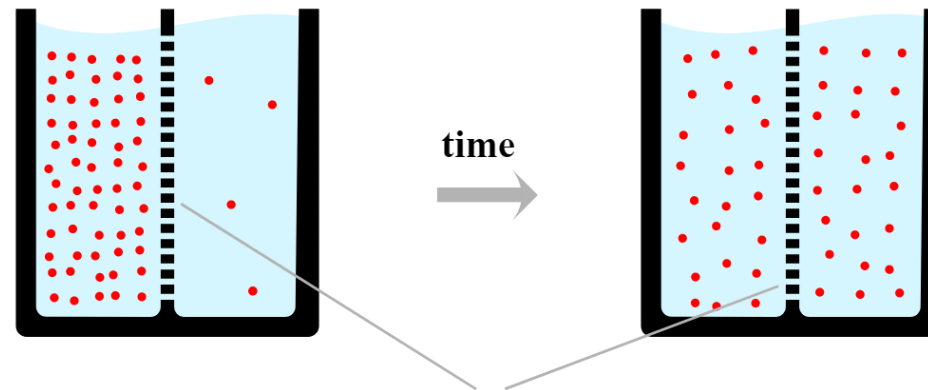


Brownian Movement

## B. Diffusion

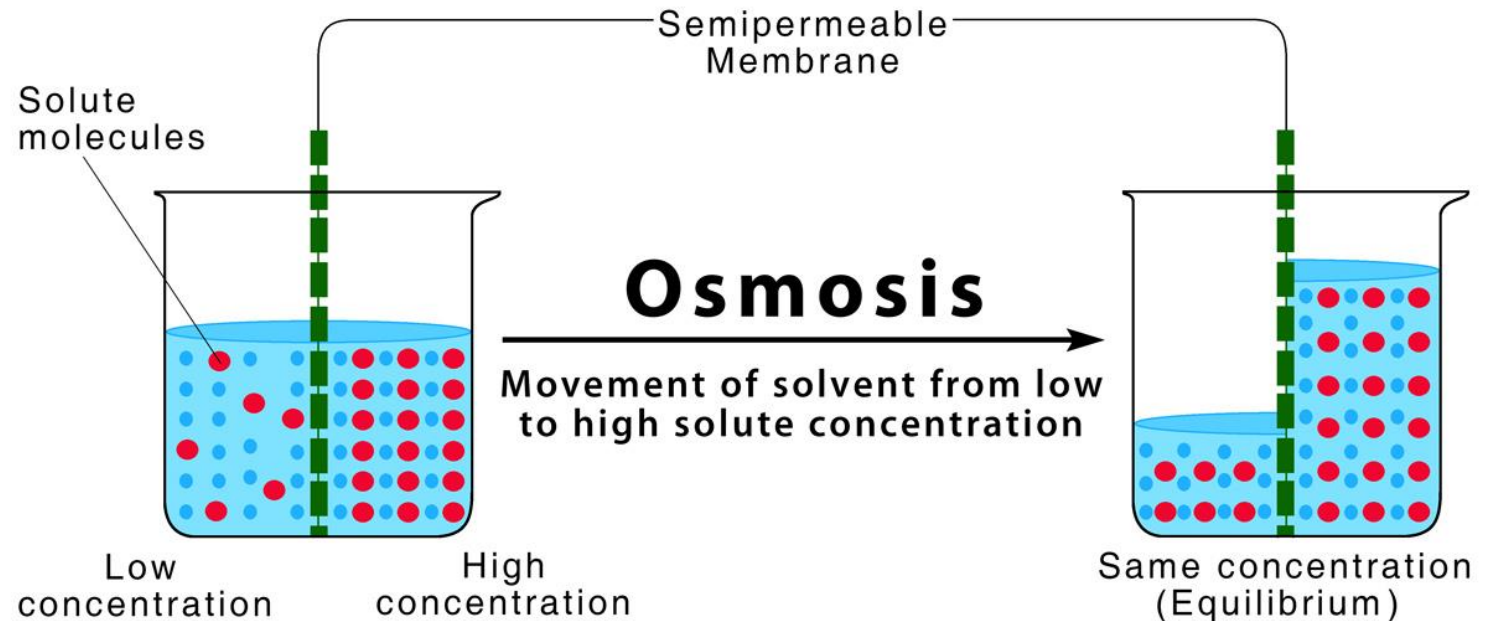
- Particles diffuse spontaneously from a region of **higher concentration** to one of **lower conc.** Until the conc. of the system is uniform throughout.
- Diffusion is a direct result of Brownian motion.
- *Fick's first law* used to describe the diffusion:  
(The amount of substance  $Dq$  diffusing in time  $dt$  across a plane of area  $A$  is directly proportional to the change of concentration  $dc$  with distance traveled)

$$- dq = -DA (dc / dx) dt$$



## C) Osmosis

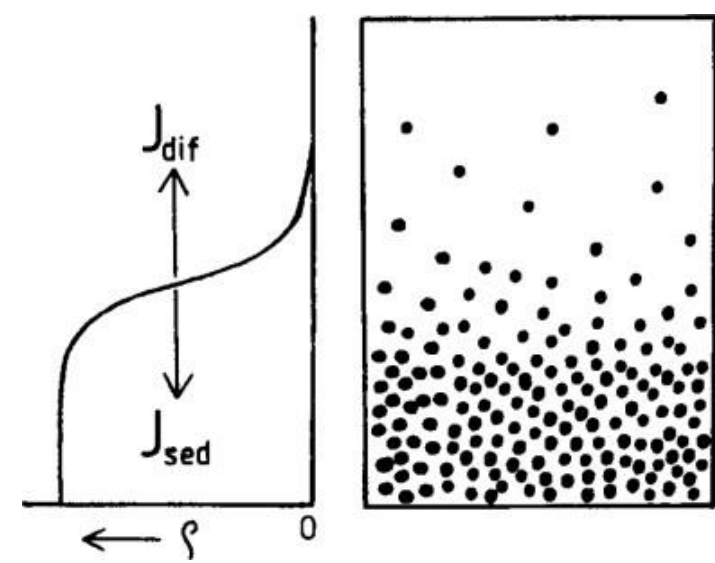
- The usefulness of **osmotic pressure** measurement is limited to a **molecular weight range** of about  $10^4$ - $10^6$  (!?); below  $10^4$  the membrane may be permeable to the molecules under consideration and above  $10^6$  the osmotic pressure will be too small to permit accurate measurement.





## D) Sedimentation

- This is influenced by gravitational force.
- **Stokes law** equation governed this phenomena.
- Colloidal particles have Brownian motion has no sedimentation.



$V$  = rate of sedimentation  
 $d$  = diameter of particles  
 $\rho$  = density of internal phase and external phase  
 $g$  = gravitational constant  
 $\eta$  = viscosity of medium

$$V = \frac{d^2 g (\rho_p - \rho_s)}{18\eta}$$

## E) Viscosity

- ❑ It is the resistance to flow of system under an applied stress. The more viscous a liquid, the greater the applied force required to make it flow at a particular rate.
- ❑ Viscosity affected by many parameters
  - 1. Shape of particle – Spherical ( $\downarrow \eta$ ), Linear shape ( $\uparrow \eta$ )
  - 2. Molecular weight of polymers – proportional to viscosity.

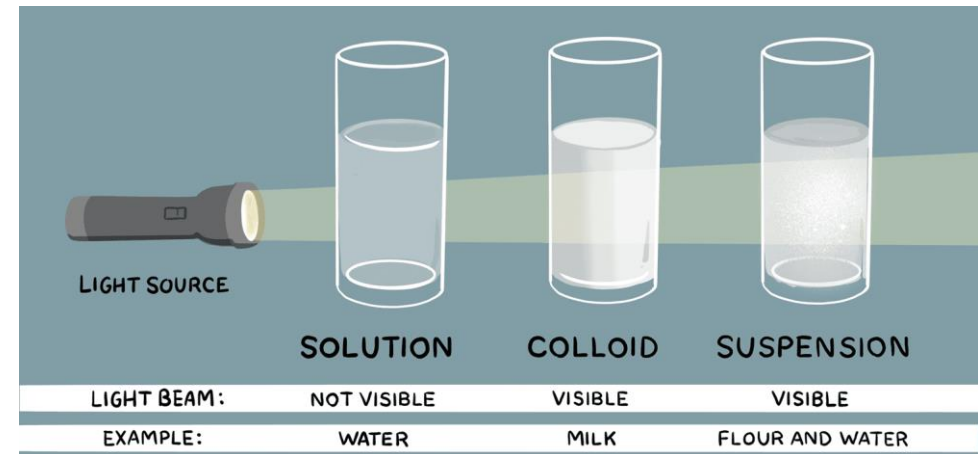
## 2. Optical properties

### Faraday-Tyndall effect

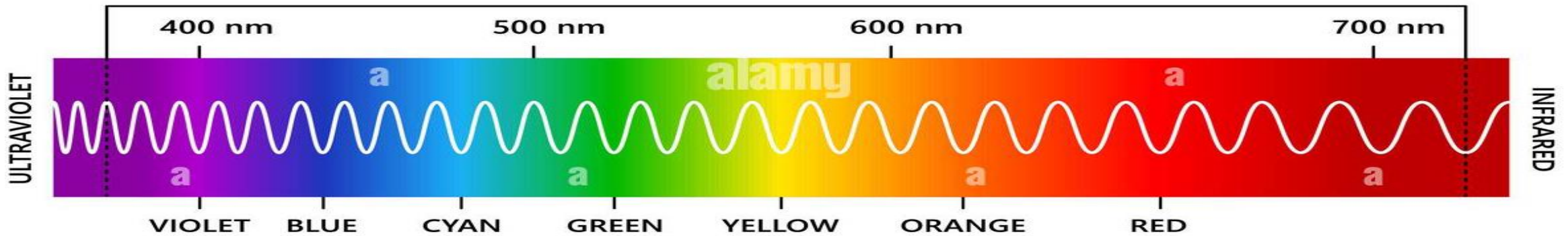
When a beam of light passes through a colloid, colloidal particles scatter the light. The intensity of scattered,  $I_s$ , light is inversely proportional to the fourth power of the wavelength,  $\lambda$  (Rayleigh law):

$$I_s \sim \frac{1}{\lambda^4}$$

- The same effect is noticed when a beam of **sunlight** enters a dark room through a slit when the beam of light becomes visible through the room. This happens due to the scattering of light by particles of dust in the air.



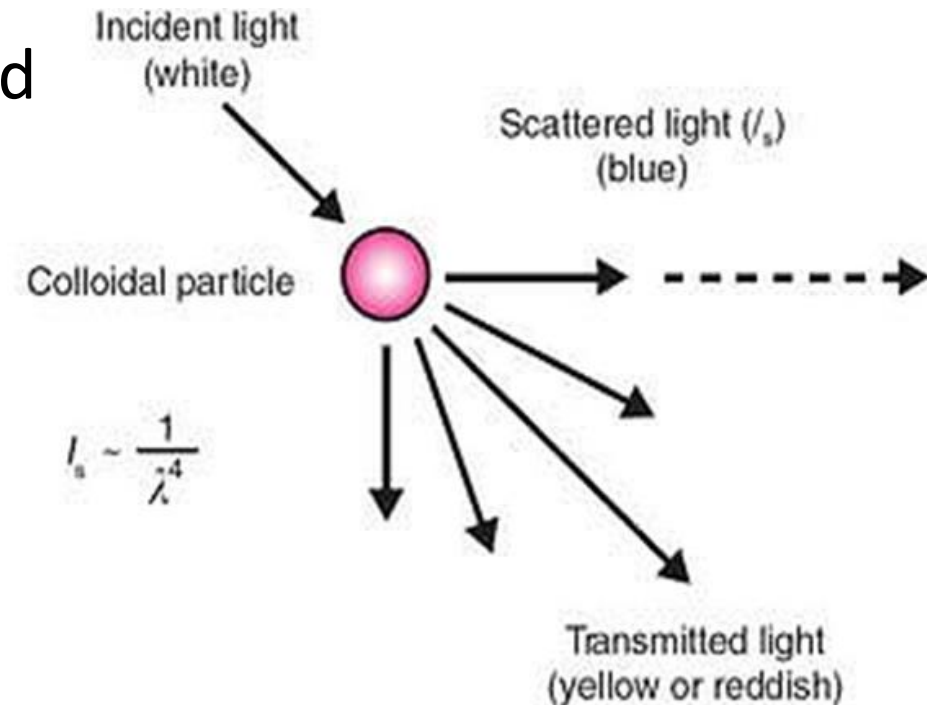
# VISIBLE SPECTRUM



Thus, shorter-wavelength light (blue) ( $\lambda=450\text{nm}$ ) is scattered more intensely than longer-wavelength light (yellow and red), ( $\lambda=650\text{ nm}$ ) and so the scattered light is mostly blue, whereas transmitted light has a yellow or reddish color.

## Why the sky is blue?

This phenomenon is useful to measure **size**, **shape**, **structure** & **molecular weight** of colloids.



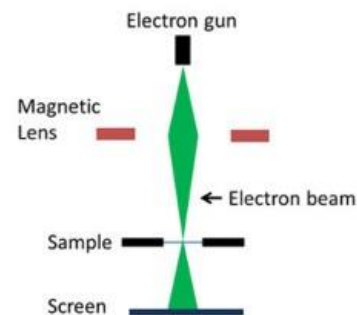
Colloidal particles are too small to be seen in the **light microscope** because its source of radiation is **visible light (400nm-700nm)**, while the **Electron microscope** can be used.

### **Ultra microscope (dark-field microscope):**

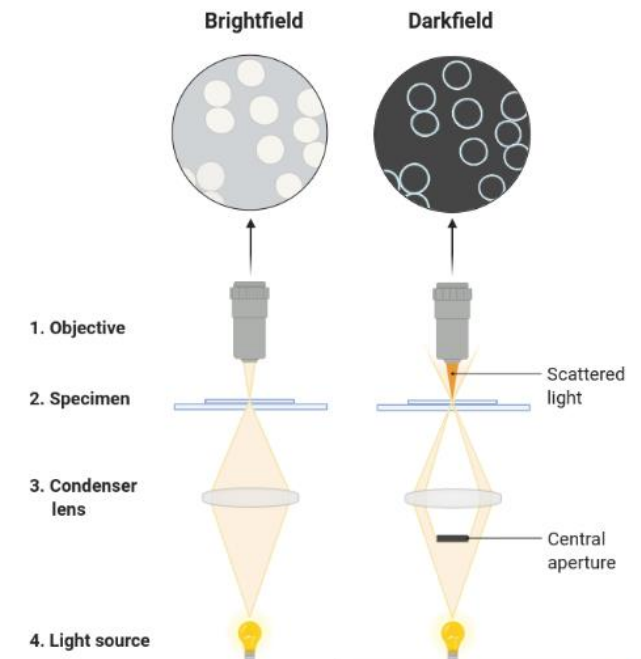
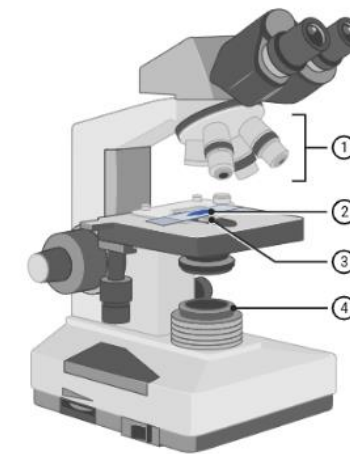
- Used to observe tyndall effect, its wavelength range is **180nm-400nm**.
- Dispersed particles appears bright spots in dark background.
- Used to determine **zeta potential**



### **Electron microscope**



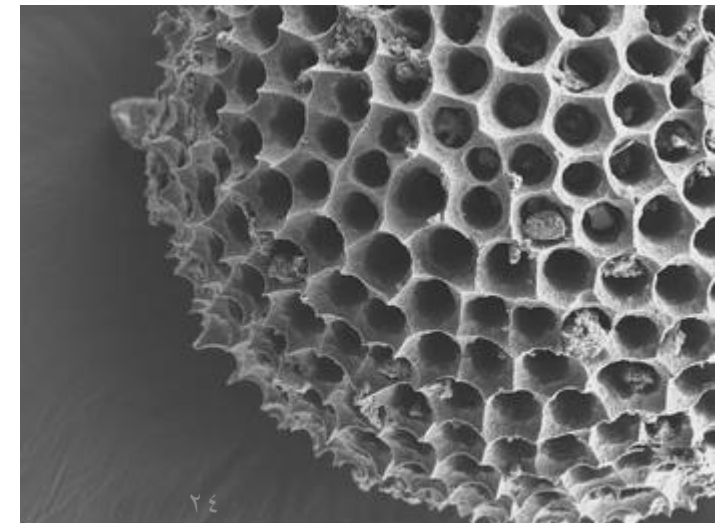
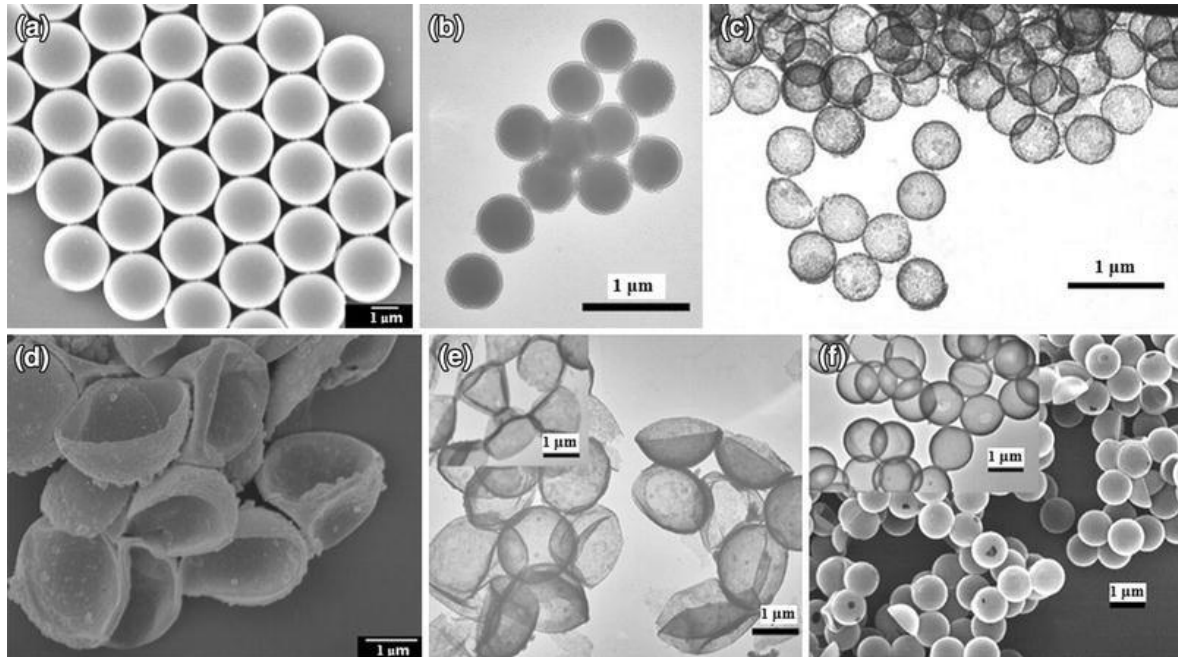
### **Brightfield vs. Darkfield Microscopy**





# Electron microscope:

- Used to measure particle **size, shape, and structure**.
- Radiation source – high energy **electrons** ( $\lambda=0.1\text{\AA}$ )
- As wave-length decreases resolution increases.
- Particle photograph scan can be taken.



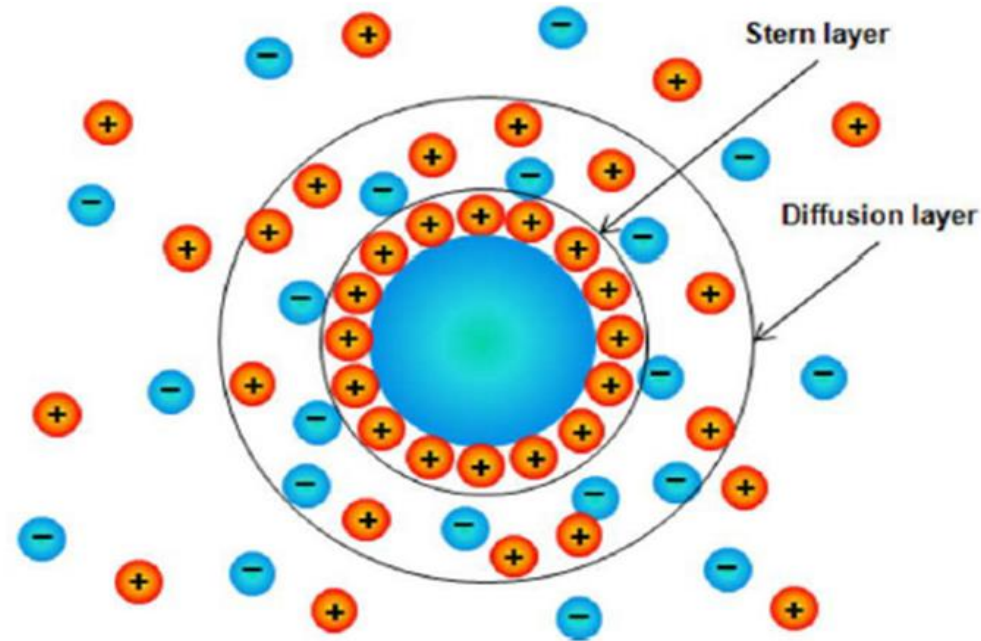
### 3. Electrical properties

#### Electric Double Layer

Particles dispersed in liquid may become charged as a result of:

**Adsorption** of a particular ionic species present in solution.

**Ionization** of groups (such as  $\text{COOH}$ ) that may be situated at the surface of the particle. In this case, the charge depends on  $pK$  and  $pH$ .



As a result, dispersed solid particles usually are surrounded by a double layer of electric charge made of ions.

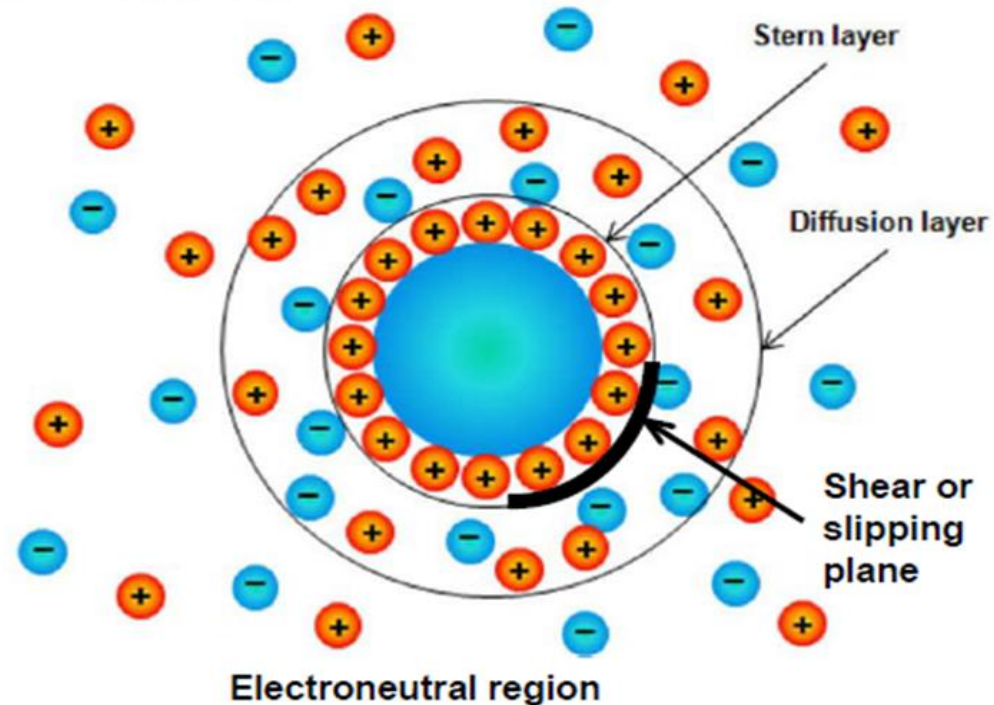


# Nernst and Zeta Potentials

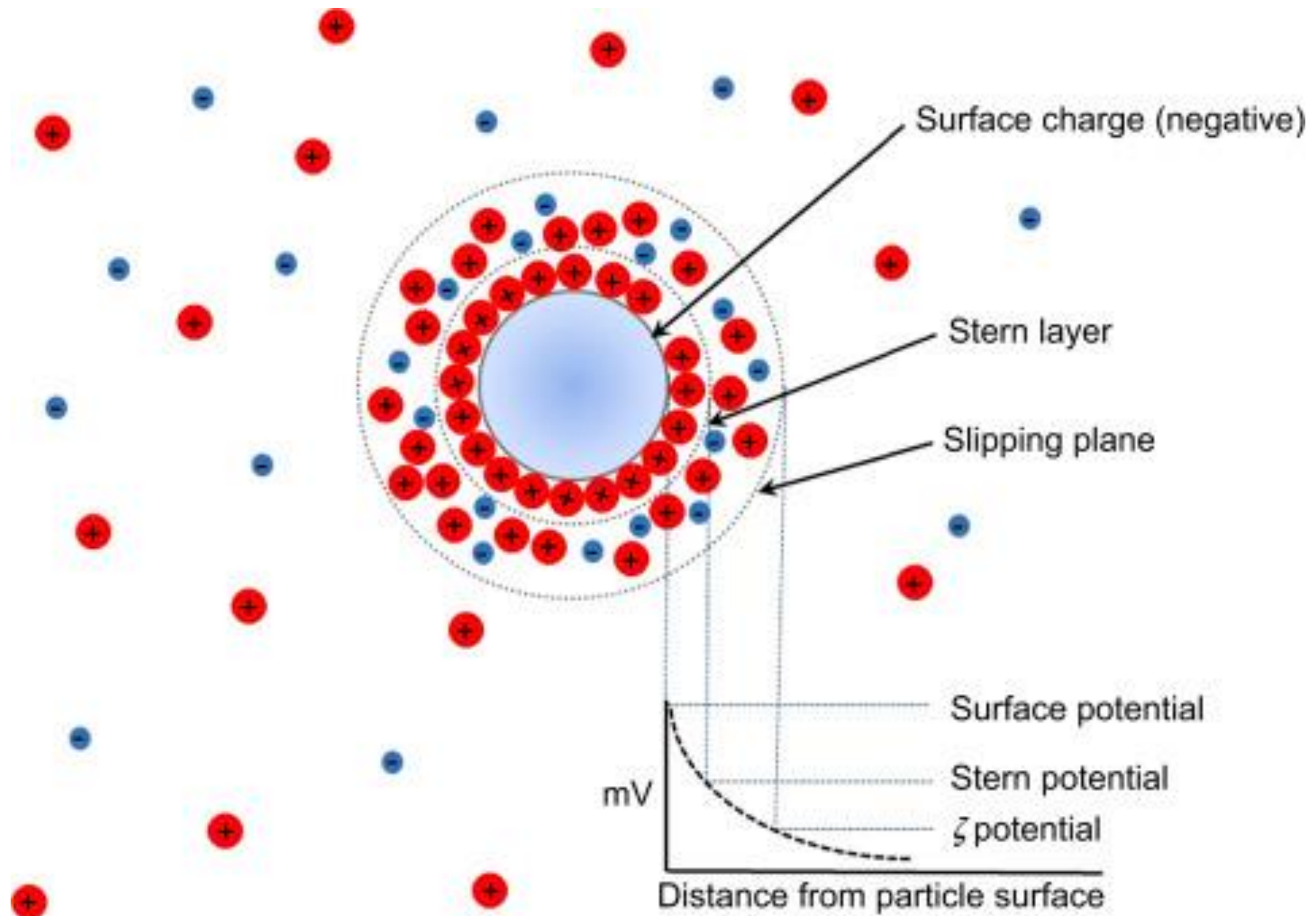
The *electrothermodynamic* (**Nernst**) potential ( $E$ ) is the difference in potential between the actual surface and the electroneutral region of the solution.

The *electrokinetic* (**zeta**) potential ( $\zeta$ ) is the difference in potential between the surface of the stern layer and the electroneutral region of the solution.

The zeta potential is measured to monitor and predict the stability of dispersion systems



- All of the particles of a given colloid take on the same charge (either positive or negative) and thus are repelled by one another.
- **If the charge on the particles is neutralized, they may precipitate out of the dispersion.**



# Physical stability of colloidal systems

- What is the difference between flocculation and coagulation?
- **Flocculation** is large aggregate **temporary** contact rebound or remain **freely dispersed flocs** have an **open structure** in which the particles remain a small distance apart from each other forming a stable colloidal system. This happened by using **flocculating agent**.
- **Coagulation** particles **closely** aggregated, large aggregates sediment out and are **difficult to re-disperse** which will cause destruction of the colloidal system (precipitation). This mostly happened after neutralization of the surface charge of the particles by using **coagulant**.



# How flocculation or coagulation can be brought about?

By addition of Electrolytes. When excess of an electrolyte is added to a sol, the dispersed particles are precipitated. The electrolyte furnishes both positive and negative ions in the medium. The sol particles adsorb the oppositely charged ions and get discharged. The electrically neutral particles then aggregate and settle down as precipitate .

A negative ion (anion) causes the precipitation of a positively charged sol, and *vice versa*.

thank you