

## Colloids

Originally derived from a *GREEK* word – ***KOLLA*** means ***GLUE***

### Definition:

Colloidal dispersions – *discontinuous particle phase* (dispersed phase) distributed uniformly in a finely divided state in a *continuous phase* (dispersion medium).

Staudinger – particles with  $10^3$  to  $10^9$  atoms.

Dimension of disperse phase

1 nm – 1  $\mu$ m

### Historical data:

Selmi (1845) - described pseudosolution i.e particles that are larger than the usual molecules.  
- first to investigate colloidal system systematically e.g. preparation of colloidal sulphur, silver chloride and prussian blue, albumin and starch solutions.

Michael Faraday (1857) - investigation of optical properties of gold sol (*Faraday sols* ~ 3 nm radius). Prepared by reduction of a gold chloride solution with phosphorus.

Thomas Graham (1861) - classical experiment e.g. rate of diffusion from different substances.

Coined the term “Colloid” (glue like) to describe Selmi’s pseudosolution. Displayed a low rate of diffusion and lack of crystallinity therefore the particles must be very large at least 1 nm. On the other hand, failure of the particle to sediment under the influence of gravity explained that the particles have an upper limit of about 1 micron.

Tyndal (1869) - light scattered by colloidal particles is polarised.

Ostwald - *Any dispersed system consists of a homogeneous medium and particles, and both of the medium and the particles can either be solid, liquid, or gaseous.*

*Association colloids:*

James Mcbain - found that the osmotic pressure of alkali metal fatty acid salt displays a pronounced break in the concentration beyond which the osmotic pressure coefficient remains constant. The aggregate structure he called micelles. G. S.

Hartly proposed a spherical structure. William Harkins – cylindrical. Mcbain – flat laminar.

Derjaguin-Landau and Verwey-Overbeek (1945)

– Provide DVLO theory that explains the quantitative relationship between the attractive van der Waals forces (coagulation) and the repulsive electrostatic forces which stabilize the colloidal dispersion.

### **General description for the size of colloidal particles:**

- Smaller than coarse
- Filterable
- Larger than small molecules.
- Can scatter light
- 1 nm – 1000 nm

### **Colloidal state**

Marriage of several disciplines  
or  
crossed-disciplinary subjects

One substance distributed **uniformly, homogeneously** in one another.

**Substance can be**

- solid
- liquid
- gas

**True solution**

made of dissolution of matter.  
Typically in molecular dimension.

Colloidal system, solute is considerably larger than the solvent.

#### **Colloidal suspension response to environment**

- Thermodynamics
- Temperature
- Pressure
- pH of solution
- Electrolyte

#### **Sizes?**

- In micron or submicron
- Larger than the solvent
- May floc to form larger particles
- Larger particle may breakdown into smaller ones.

#### **Industrial and technological significances**

- Telecommunication
- Ceramics
- Oil industries.
- Paint industries.

#### **Biological Significances**

- Cell and cell adhesion / interaction
- Drug delivery system
- Digestion system
- Synovial fluid (joint lubrication)

#### **Food industries.**

- Ice-cream
- Chocolate
- Dough making / Bread
- Confectionaries
- Butter
- Fizzer drinks

## **Cosmetics and pharmaceutical industries**

- Vitamines
- Mineral supplement
- Cream
- shampoos

## **Type of Colloidal Systems**

*Colloidal suspensions or sols* (dispersion of solid in liquid)

– in the form of various soups and sauces. Paints, inks clay particles and delta formation. Called lyophobic colloids.

Emulsions - dispersion of liquid in liquid such as milk, mayonnaise cosmetics and pharmaceutical, w/o and o/w emulsion.

Solid dispersions – solid in solid dispersion such as in some gem stones, concrete, alloy.

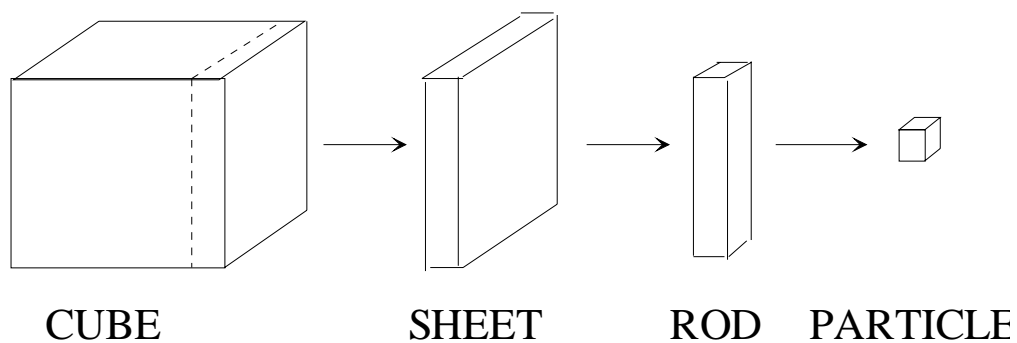
Aerosols – liquid dispersion in gases such as fog, mist deodorants.

Macromolecules – Gels, DNA, protein. Also called lyophilic colloids. Exhibit thermodynamic stability.

Association colloids – soap bubbles, foams, biological membrane, micelles, vesicles and liquid crystals.

Colloidal particles are normally associated with providing a large surface area. The colloidal particles size characteristic forms an intrinsic property of a colloidal system. For example, a typical micellar solution containing 0.1 M surfactant has  $\sim 4 \times 10^4 \text{ m}^2$  of micellar-water interfacial area per liter of solution.

### Simple approach to make colloidal particles

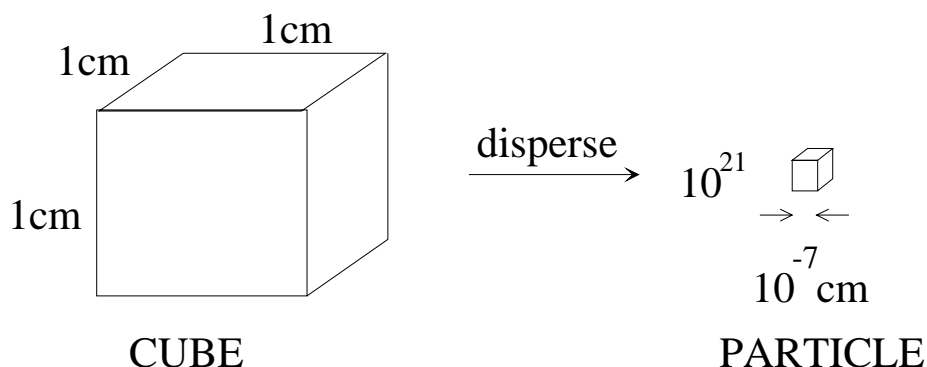


SHEET  $\longrightarrow$  e.g. thin film, clay.

ROD  $\longrightarrow$  e.g. gels

PARTICLE  $\longrightarrow$  e.g. gold sols, micelles.

Say we have a cube with  $1 \times 1 \times 1$  cm then disperse into  $10^{21}$  small cubic particles.



Now, we start with a cube.

$$\text{Total volume} = 1 \text{ cm}^3$$

Then make  $10^{21}$  particles of side  $10^{-7}$  cm.

$$\begin{aligned} \therefore \text{Area of small particle} &= \text{no. of faces} \times \text{area of one face} \\ &= 6 \times 10^{-14} \text{ cm}^2 \end{aligned}$$

$$\begin{aligned} \text{Total area by these particles} &= 6 \times 10^{-14} \times 10^{21} \text{ cm}^2 \\ &= 6 \times 10^7 \text{ cm}^2 \end{aligned}$$

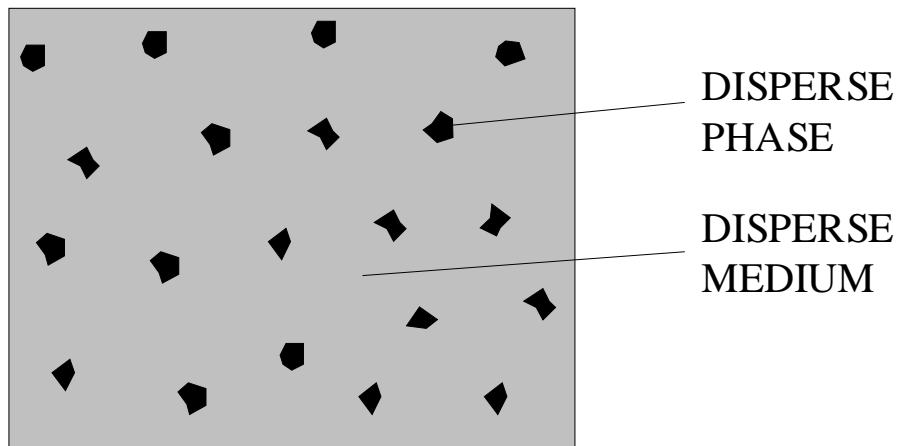
Therefore an increase by  $10^7$

This also tells us that molecules at surface are very important!

- because it may affect the properties of the system.

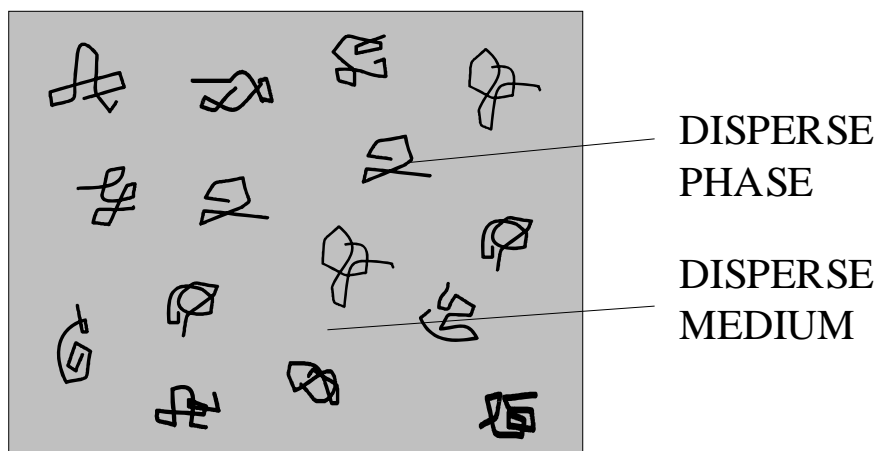
e.g solubility, free energy

## LYOPHOBIC AND LYOPHILIC COLLOID



### **Lyophobic colloid:**

Discrete particles of one material suspended in another.  
Interface is well defined.



### **Lyophilic colloid:**

Solution of high molecular weight substance (protein, polymer, etc.) in liquid medium. No clear defined interface.

## Types of colloidal system:

Name	Disperse phase	Disperse medium	Examples
Colloidal sol	Solid	Liquid	Ink, paint.
<i>Emulsion</i>	Liquid	Liquid	Mayonaise, emulsion, fat digestion, biomembrane.
<i>Foam</i>	Gas	Liquid	Fire extinguisher, vacuoles
<i>Aerosol</i>	Solid	Gas	Smoke, volcanic smoke, pollen.
	Liquid	gas	Fog, mist, hairspray.
<i>Solid dispersion</i>	Solid	Solid	Wood, bone, pearl, opal, composite, alloy, glasses.
<i>Solid emulsion</i>	Liquid	Solid	Bitumin, ice-cream.
<i>Solid foam</i>	Gas	Solid	Styrofoam, zeolites, fruits, bread

### *Compare with*

macromolecular colloids:-

In the case of gel – macromolecules dissolve in solvent e.g water as in GLUE

Association colloids:-

Soaps / detergents dissolve in solvent (water) as in washing-up liquid.

### Other definitions

1. *Disperse medium / continuous phase* It refers to the medium.  
e.g. water, oil, gas, solid etc.
2. *Discontinuous phase* – small particles as colloid.
3. *Monodisperse* – all particles similar size.
4. *Polydisperse* – range of sizes

## Lyophilic and lyophobic sols

Lyophobic	Lyophilic
Solvent hating e.g. $\text{AgCl}_{(s)}$ in water	Solvent loving e.g. proteins in aq. Solution, microemulsion droplets
Dispersed by vigorous mechanical agitation or by an external energy	Dispersed by adding a suitable solvent
Technological and agricultural materials.	Biological colloid e.g. protein, polysaccharide
Subjected to van der Waals forces (attractive), thermodynamically unstable	Thermodynamically stable

Very complex phenomena

– cannot be classified accordingly

QUESTION: 17<sup>th</sup> July 2007

Discuss emulsion preparation and stability in mayonnaise.

The mayonnaise:



3 egg yolks  
 1 cup olive oil  
 The juice of a lemon  
 Salt & white pepper to taste

#### PREPARATION:

Mayonnaise can be made with a whisk or egg beater, but is much easier to make with a blender.

Lightly beat the yolks, then begin to add the olive oil in a slow stream, beating all the while. The mixture should emulsify and become creamy. When you have beaten in about half the oil, beat in the lemon juice -- the mixture will thin considerably. Slowly add the remaining oil, continuing to beat, until your mayonnaise is again fluffy and creamy. Season to taste with a pinch of salt and a little freshly ground white pepper.

You'll find this is much richer than commercially prepared mayonnaise, which usually contains vegetable oil instead of olive oil. If you want to make your mayonnaise zestier, beat in a pinch or so of ground mustard (at the beginning), or perhaps a pinch of horseradish or ground cayenne -- assuming that what you'll be serving it with will go with these flavors. Or try using vinegar instead of lemon juice.

The mayonnaise is an emulsion between vitellus (egg yolk) and oil, which means that the particles of the yolks are dispersed in the oil. Beating the egg consist in breaking down the proteins bond such they mix more easily with the water and the lipids coming from the oil. To facilitate the preparation of mayonnaise salt ( $\text{Na}^+$ ,  $\text{Cl}^-$ ) is added to the mixture to increase the electrostatic forces and lemon juice can also be added to decrease the pH of the mixture.

## Preparation of Colloidal suspensions

### 1) Dispersion

- Grinder (solid)
- High speed stirring (solid and liquid)
- Sonication

*These are essentially mechanical but nonetheless effective.*

### 2) Condensation methods.

- Dissolution and precipitation  
e.g. a)– to precipitate the solid from the solvent by sudden mixing with a second liquid which is immiscible with the first but a non solvent for the

solid. – many water insoluble dyes and pigments –  
pouring their solutions in concentrated  $\text{H}_2\text{SO}_4$  into  
large volume of water.

b) - pouring a dissolved wax in ethanol into hot  
water – opalescent paraffin wax sol.

- Condensation from vapour  
e.g. mist – spontaneous condensation of  
supersaturated vapour as T drops below  
condensation point.
- Chemical reactions  
Producing an insoluble product  
e.g.  $2\text{Fe}^{3+} + 3\text{H}_2\text{O} \longrightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+$

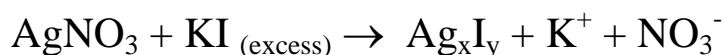
## Colloid Stability

Consider LYOPHOBIC sol:

Small solid particles (1-100 nm)

e.g. AgI, CdS, Au

Preparation :



Usually the value of  $y > x$

Thus, we have negatively charged sols

Say, typical  $x = 100$  and  $y = 200$

Hence overall charge = - 100

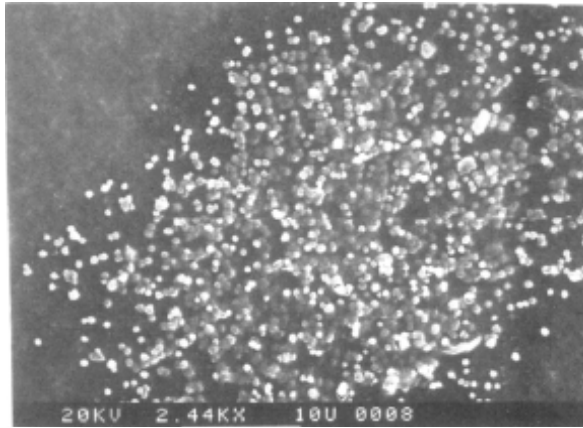
### **Definition of colloidal stability**

- no change in particle size with time.
- Instability normally will lead to FLOCCULATION

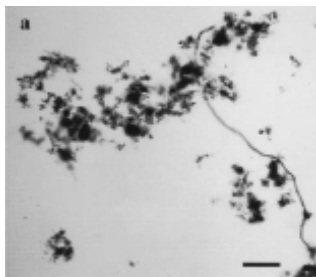
**i.e. a process when small particles clump to gether but do not fuse into new particle.**

### **Colloidal Stability**

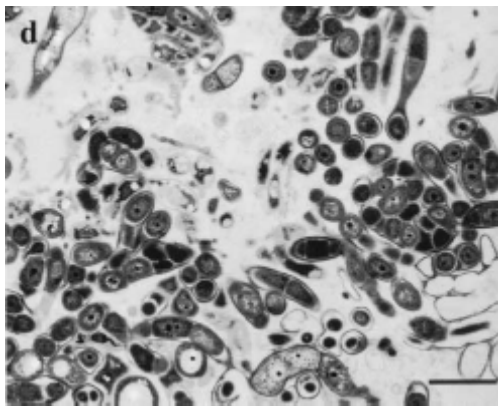
- Particles in a dispersion may adhere together and form aggregates of increasing size which may settle out due to gravity
- An initially formed aggregate is called a FLOC and its formation FLOCCULATION - this process is reversible (DEFLOCCULATION)
- If the aggregate changes to a much denser form it is said to undergo COAGULATION - this process is irreversible
- In the 1940s Derjaguin, Verway, Landau and Overbeek developed a theory which dealt with colloidal stability DVLO.



Hydrous aluminium hydroxide at pH 7.5 *Environ. Sci. Technol.* **1991**, *25*, 1766-1773



100 micron, light microscope



1 micron, TEM

*J. ENVIRON. QUAL.*, VOL. 32, NOVEMBER-DECEMBER 2003 2100-2108

## DVLO Theory

- It says that the stability of a colloidal system is determined by the sum of the electrical double layer repulsive and van de Waals attractive forces which the particles experience as they approach one another

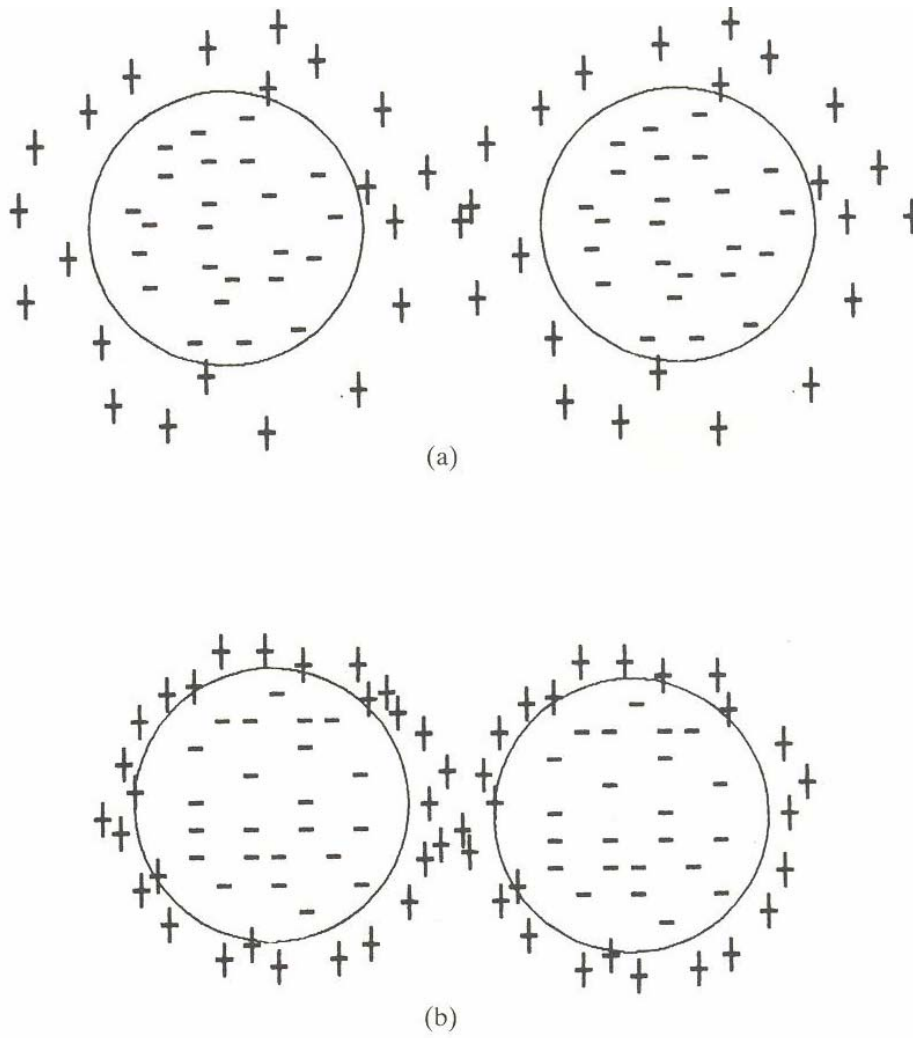
- The theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together
- But if the particles collide with sufficient energy to overcome that barrier, the attractive force will pull them into contact where they adhere strongly and irreversibly together.

## **Maintaining Colloidal Stability**

For colloidal stability, the repulsive forces between particles must be dominant

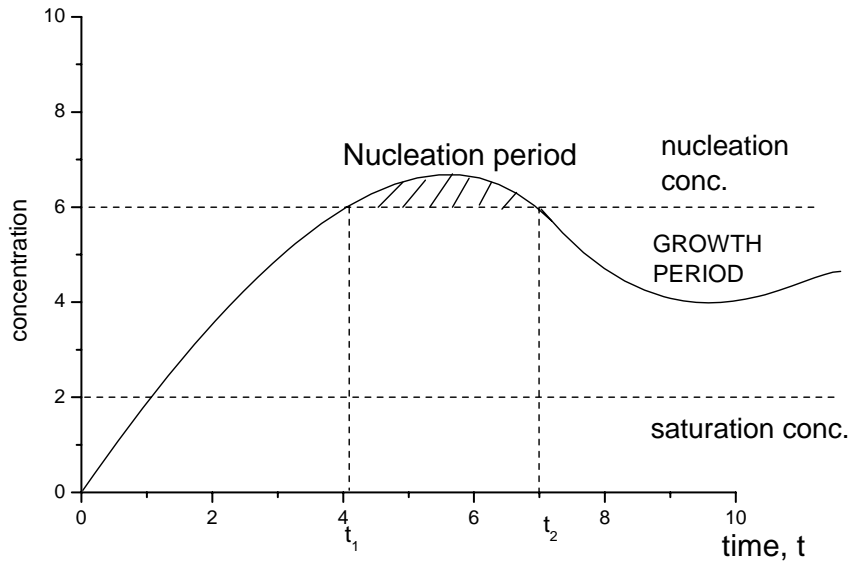
There are two fundamental mechanisms that affect colloidal stability:

- Steric repulsion.
- Electrostatic (Charge) repulsion.



**Figure 3.2** Interaction of charged particles in (a) low and (b) high ionic strength solutions, showing the effect on the range of double-layer repulsion.

## Preparation of Mono disperse Colloids



The La Mer diagram formation of nuclei –  $t_1 \rightarrow t_2$  allowing for a short period

must allow growth on nuclei  $t > t_2$

Increase the concentration of the required material get supersaturation  $\rightarrow$  formation of nuclei .Then grow into final particles ( $t_1-t_2$ )

Solution concentration thereby reduced!

Growth occurs when concentration maintained between the saturation and nucleation.

e.g : Preparation of metal carbonates.

## COAGULATION and FLOCCULATION

No clear distinction between the two processes.

Both involve “aggregation”

i.e the gathering together of suspended particulates to form larger ones.

Principally concerned with lyophobic colloids since their most stable TD state is one where all the particles are condensed!

Attempts for the distinction between these processes.

1) In terms of the resultant of aggregate size

Purchas 1968 , Kirk-Othmer 1980 and Perry & Green 1984.

**Coagulation** – addition of reagent that cause aggregation of colloidal particles

**Flocculation** – gentle agitation that promotes collisions between these small aggregates to form “floc”

i.e : large enough to settle

2) Classification on the basis of mechanisms

La Mer & Healy 1963,1966

## Widespread acceptance

Akers 1972, O'Melia and Weber 1972, Ubehend 1976

### About Coagulation and Flocculation.....

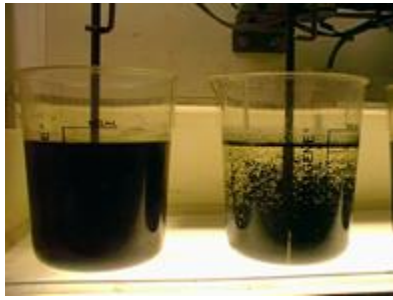
In wastewater treatment operations, the processes of coagulation and flocculation are employed to separate suspended solids from water. Although the terms coagulation and flocculation are often used interchangeably, or the single term "flocculation" is used to describe both; they are, in fact, two distinct processes. Knowing their differences can lead to a better understanding of the clarification and dewatering (making cake solid sludge) operations of wastewater treatment.

Finely dispersed solids (colloids) suspended in wastewaters are stabilized by negative electric charges on their surfaces, causing them to repel each other. Since this prevents these charged particles from colliding to form larger masses, called flocs, they do not settle. To assist in the removal of colloidal particles from suspension, chemical coagulation and flocculation are required. These processes, usually done in sequence, are a combination of physical and chemical procedures. Chemicals are mixed with wastewater to promote the aggregation of the suspended solids into particles large enough to settle or be removed.

Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Cationic coagulants provide positive electric charges to reduce the negative charge (zeta potential) of the colloids. As a result, the particles collide to form larger particles (flocs). Rapid mixing is required to disperse the coagulant throughout the liquid. Care must be taken not to overdose the coagulants as this can cause a complete charge reversal and restabilize the colloid complex.

Flocculation, is the action of polymers to form bridges between the flocs. and bind the particles into large agglomerates or clumps. Bridging occurs when segments of the polymer chain adsorb on different particles and help particles aggregate. An anionic flocculant will react against a positively charged suspension, adsorbing on the particles and causing destabilization either by bridging or charge neutralization. In this process it is essential that the flocculating agent be added by slow and gentle mixing to allow for contact between the small flocs and to agglomerate them into larger particles. The newly formed agglomerated particles are quite fragile and can be broken apart by shear forces during mixing. Care must also be taken to not overdose the polymer as doing so will cause settling/clarification problems. Anionic polymers themselves are lighter than water. As a result, increasing the dosage will increase the tendency of the floc to float and not settle.

Once suspended particles are flocculated into larger particles, they can usually be removed from the liquid by sedimentation, provided that a sufficient density difference exists between the suspended matter and the liquid. Such particles can also be removed or separated by media filtration, straining or floatation. When a filtering process is used, the addition of a flocculant may not be required since the particles formed by the coagulation reaction may be of sufficient size to allow removal. The flocculation reaction not only increases the size of the floc particles to settle them faster, but also affects the physical nature of the floc, making these particles less gelatinous and thereby easier to dewater.



sludge clarification.

The term **clarification** can also mean any process (typically an industrial process) that removes suspended solids from water to make the water clear.

**HYDROFLOC™ polymers can be used in a number of industries, for various applications. Aqua Ben has extensive experience in the following industries:**

Industry	Application
Mining & Mineral Industry	Ore leaching, flotation treatment, tailings treatment
Sand & Gravel Production	Clay removal, dewatering, water recycling
Sewage & Municipal Wastes	Sludge thickening, settling, clarification and dewatering
Potable Water Treatment	Clarification
Food Industry	Clarification and dewatering
Raw Water Treatment	Clarification
Sugar Industry	Juice clarification, dewatering
Metal Plating / Anodizing Industry	Clarification and settling
Septic and Grease Trap Wastes	Dewatering

**SOILFLOC™** is a water-soluble, linear polyacrylamide (**PAM**) polymer that was designed to be used for **erosion control, soil structure improvement and dust abatement**. **SOILFLOC™** works by aggregating soil particles, increasing pore space and infiltration capacity, resulting in soils that are less susceptible to raindrop and scour erosion. **SOILFLOC™** is **environmentally safe and non-toxic**. A variety of PAM products have been approved by NSF International for potable water clarification. They will naturally degrade with UV light and are consumed by microbiological attack. This product is compatible with almost all irrigation systems. PAM products are now registered throughout the western United States.

MSDS and TDS available upon request.

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### **WHERE TO USE**

- Irrigated Agriculture
  - Construction Sites
  - Landscaping
  - Hydroseeding
  - Stormwater Runoff
- 

### **BENEFITS**



- **Reduces soil loss by up to 95%**
- **Improves water infiltration into soils**
- Reduces runoff turbidity and sediment runoff
- Reduces hardening and crusting of irrigated soils
- Reduces pesticide and fertilizer loss from water run-off
- \*Environmentally Safe \*Non-toxic \*Biodegradable
- No bioaccumulation in crops
- Aids in plant growth on high-grade slopes
- Less soil reshaping and spreading
- Cost effective and time saving
- Suitable for surface, mechanical and drip irrigation systems

## **MECHANISM of AGGREGATION**

1- Charge neutralization by double-layer compression  
reduction of repulsive potential obtained by addition of  
polyvalent ions of opposite sign to that of the surface charge.

2- Action of material of high molecular weight

e.g polymer ,starch, gelatine – to produce “ Bridging effect “

3- Entrapment of smaller particles

e.g : additional of a hydrolysing metal salt in water treatment of alkalinity – formation of gelatinous ppt of metallic hydroxide may entrap suspended turbid particles.

***Coagulation*** : aggregation process in which member particles are not in direct physical contact but are separated from each other by a thin film – estimated thickness  $< 0.1$  mm.

***Flocculation*** : aggregation process which is characterized by the action of a bonding agent, usually a high MW polymer that physically bridges primary particles together into large units.

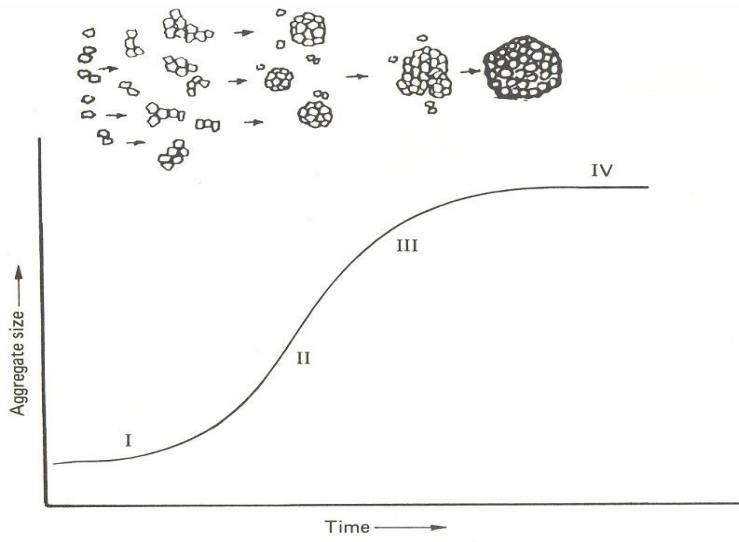


Figure 1.4 Schematic diagram showing the course of aggregation process in a stirred vessel.

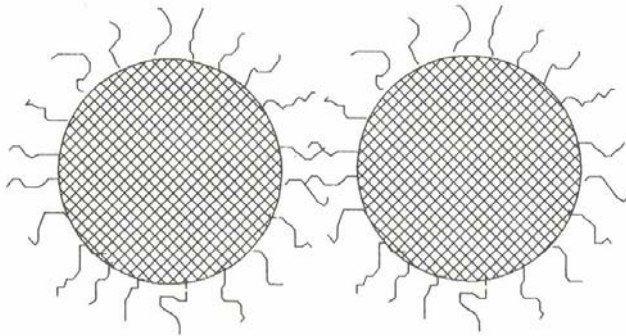


Figure 3.3 Prevention of particle contact by terminally adsorbed polymer chains – steric stabilization.

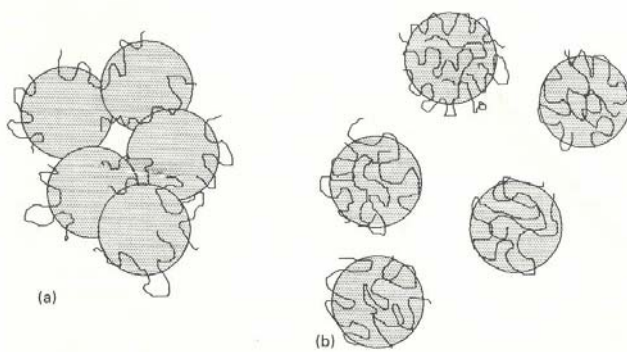


Figure 3.4 Schematic diagram showing (a) bridging flocculation and (b) restabilization by adsorbed polymer.

## PARTICLE AGGREGATION

Particles collide and adhere to one another – aggregation

It has been suggested that at least there are 4 stages of aggregation

Stage I >> formation of doublets

a slow process

growth is due to binary collision between primary particles of equal size

Stage II >> growth is rapid

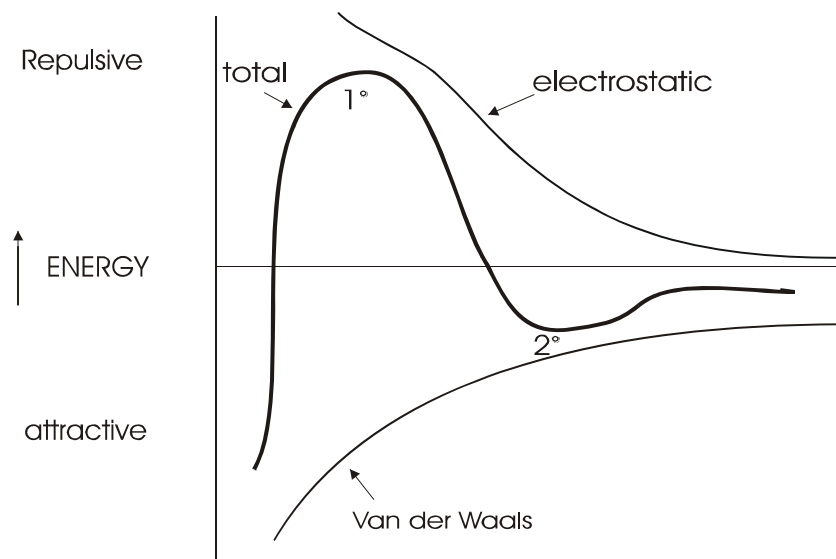
Stage III >> the rate of increase in aggregate size decreases

Stage IV >> stable aggregate size

### **IDEALISED PAIR POTENTIAL ENERGY DIAGRAM**

Total free energy of interaction between two colloidal particles – identical

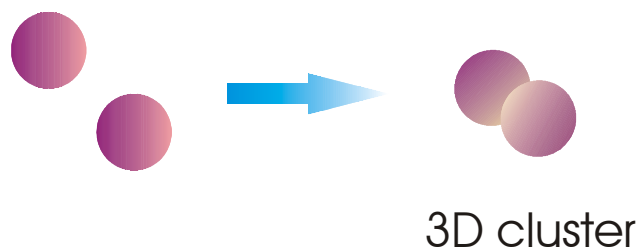
$$\begin{aligned}\Delta G = & \Delta G_{aH} \text{ (van der Waals)} + \Delta G_{rep} \text{ (electrostatic)} \\ & + \Delta G_{rep} \text{ (short range)} + \Delta G_{rep} \text{ (steric)} \\ & + \Delta G \text{ (other effects)}\end{aligned}$$



1° Primary maximum ( prevents flocculation )

2° Secondary minimum ( assists flocculation )

## Flocculation / aggregation



Reversibility dependent upon mechanism

Dependent upon balance between a number of forces

Attractive – Van der Waals

Repulsive – electrostatic

### Attractive Force

Every atom is a fluctuating dipole

i.e : electrons surrounding a nucleus do not constitute a spatially and temporally uniform screen

creates an attraction between atoms

>> Van der Waals or dispersion energy ( *electronic oscillations* )

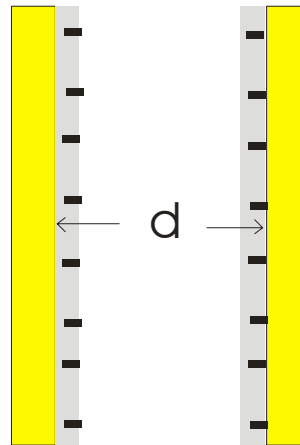
Approximately additive:

Play an important part in the interaction between particles in colloidal dimension to cause flocculation.

### Hamaker (1937)

For the case of parallel flat plates, separated by a distance  $d$ , the interaction energy per unit area is;

$$E_{aH} = -\frac{A}{12\pi d^2}$$



where  $A$  is the Hamaker constant for the interacting media.

$A$  is in the order of  $10^{-19} - 10^{-20}$  J.

A negative sign indicates an attractive energy.

For a spherical particles with radii  $a_1$  and  $a_2$

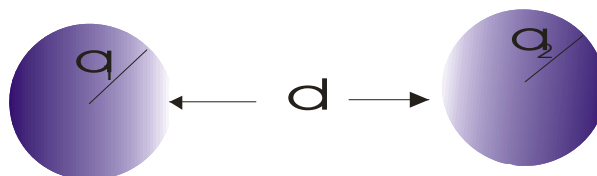
$$E_{aH} = -\left(\frac{A}{6d}\right)\left(\frac{a_1 a_2}{a_1 + a_2}\right)$$

For the case of identical spheres in a medium

$$E_{aH} = \frac{Aa}{12d}$$

Where  $d$  is the distance of maximum approach

Holds for  $a > d$



**Note : for atoms,  $E_{aH} \propto \frac{1}{d^6}$**

Hamaker constant is also called Van der Waals constant.  
 $E_{aH}$  is always negative because its value at infinity is zero,  
decreases as the particles approach each other.

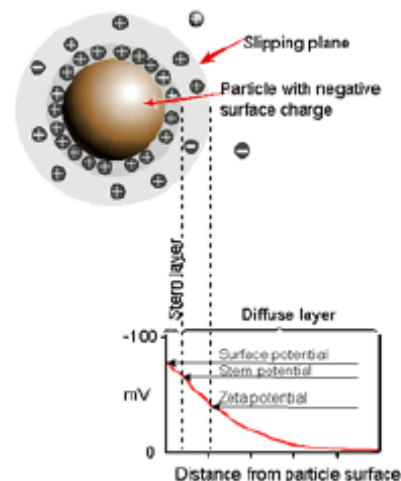
$A$  becomes inaccurate at separations greater than about 10% of the particle radius.

## REPULSIVE FORCE

Practically all particles in aqueous suspensions carry a net surface charge.

- ionization of surface groups
- specific adsorption of ions

Charges can be associated to the surface or attracted to the surface.



The nature of electrical double layer formed can greatly influence the interaction between charged particles.

### At Low Ionic Strength ;

The diffuse layer of counterions around the particles extends to a considerable distance when particles approach each other, the DL is less extensive, need to be really close in order to experience the repulsion.

### **At High Ionic Strength ; (high electrolyte concentration)**

DL is less extensive , need to be really close in order to experience the repulsion.

**Electrical Potential** is now an important quantity when considering particles interaction.

Region? Inner boundary of the Diffused Layer

and just outside the closely associated counterions. i.e : Stern layer

Can be experimentally measured by **Zeta Potential**,  $\zeta$  for to spherical particles, radii  $a_1$  and  $a_2$  , zeta potential  $\zeta_1$  and  $\zeta_2$ , the electrical interaction energy.

$$E_{rep} = \frac{64a_1a_2}{a_1+a_2} \varepsilon \pi \left( \frac{kt}{zq} \right)^2 \gamma_1 r_2 \exp(-\kappa d)$$

where,  $\varepsilon$  - permittivity of the medium

$z$  – valency of the ions

$q$  – elementary charge

$\gamma_1$  – dimensionless function ,

The interaction decreases exponentially with separation distance

, with a decay length.  $\frac{1}{\kappa}$  .

$\kappa$  is **Debye- Huckel** parameter.

$\frac{1}{\kappa} \propto$  ionic strength.

For aqueous electrolyte at 25° C ,

$$\kappa = 2.3 \times 10^9 \left( \sum c_i z_i^2 \right)^{1/2} \text{ units, m}^{-1}$$

Where  $c_i$  is molar concentration.

Solution	$1/\kappa$ distance
Water ( deionized )	1 $\mu m$
1-1 electrolyte	30 nm in $10^{-4}$ M solution
-same-	3nm in $10^{-2}$ M solution

NB : The effective thickness of DL

$$\frac{1}{\kappa} = \left[ \frac{\epsilon_r \epsilon_o}{4\pi F^2 \sum c_i z_i^2} \right]^{1/2}$$

$\epsilon_o$  = permittivity volume

F = Faraday constant

For identical particles  $a_1 = a_2$

$$E_{rep} = 32\pi\epsilon a_1 \left[ \frac{kT}{zq} \right]^2 \gamma_1^2 \exp(-\kappa d)$$

for small values of zeta potential

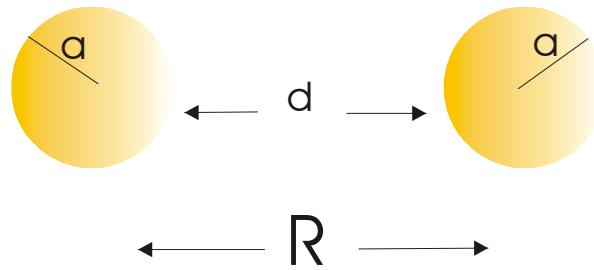
$$E_{rep} = 2\pi\epsilon a_1 \zeta^2 \exp(-\kappa d)$$

**Lyklema (1968) – Two Spherical Particles**

For small particle,  $\frac{a}{1/\kappa} \ll 1$

we have a relatively thick electrical double layer ,

$$E_{rep}^s = \frac{\epsilon a^2 \psi_o^2}{R} \exp(-\kappa d)$$



For large particle ,  $\frac{a}{(1/\kappa)} \gg 1$

Thus , relatively thin electrical double layer

$$E_{rep}^l = \frac{\epsilon a \psi_o^2}{2} \ln(1 + \exp(-\kappa d))$$

$E_{rep}$  is always +ve , its valuent  $\infty$  is zero and increases as particles approach each other. Added salts cause a decrease in *zeta potential* , reduces the repulsion , increases in  $\kappa$  .

Effect more pronouce with highly charged ions thus multivalent ions are expected to have a greater effect on colloid stability.

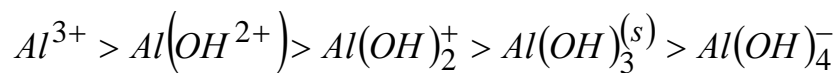
$E_{rep}$  Depends on :

- ❖ Size and shape of the dispersed particles
- ❖ Separations distances
- ❖ Surface potential  $\psi_o$  i.e zeta potential
- ❖  $\epsilon$ , the dielectric constant of the dispersing liquid.
- ❖ The effective thickness of the electrical double layer

**Note:**

Examples of most commonly use inorganic flocculants : iron and aluminium compounds.

Their effectiveness could be explained in terms of the highly charge  $Fe^{3+}$  and  $Al^{3+}$  ions.



—————> sequence of hydrolysis as PH increases <—————>

The hydrolysis products adsorbed by many particles due to positively charge , can cause charge neutralisation and reversal.



## Mechanisms Affecting Dispersion Stability

**Steric Stabilization** - this involves polymers added to the system adsorbing onto the particle surface and causing repulsion

It is a simple process requiring just the addition of a suitable polymer

However it can be difficult to subsequently flocculate the system if required

The polymer can be expensive and in some cases undesirable (e.g. when a ceramic slip is cast the polymer has to be burnt out causing shrinkage and possible defects).

## Mechanisms Affecting Dispersion Stability

Electrostatic or Charge Stabilization - this is the effect on particle interaction due to the distribution of charged species in the system

Stabilization or flocculation of a system may be modified simply by altering the concentration of ions in a system

It is a reversible process

It is potentially inexpensive

Zeta Potential is a very good index of the magnitude of the interaction between colloidal particles and Zeta

Potential measurements are used to assess the stability of colloidal systems.

26<sup>th</sup> july

## Zeta Potential

The zeta potential is the overall charge a particle acquires in a specific medium.

- The magnitude of the zeta potential gives an indication of the **potential stability** of the colloidal system
- If all the particles have a large negative or positive zeta potential they will repel each other and there is dispersion stability
- If the particles have low zeta potential values then there is no force to prevent the particles coming together and there is dispersion instability
- Stable and unstable aqueous dispersions is generally taken at between +30 or -30 mV

## The Influence of Zeta Potential

### *Zeta Potential and pH*

The most important factor that affects zeta potential is pH

A zeta potential value quoted without a definition of its environment (pH, ionic strength, concentration of any additives) is a meaningless number

Imagine a particle in suspension with a negative zeta potential. If more alkali is added to this suspension then the particles tend to acquire more negative charge

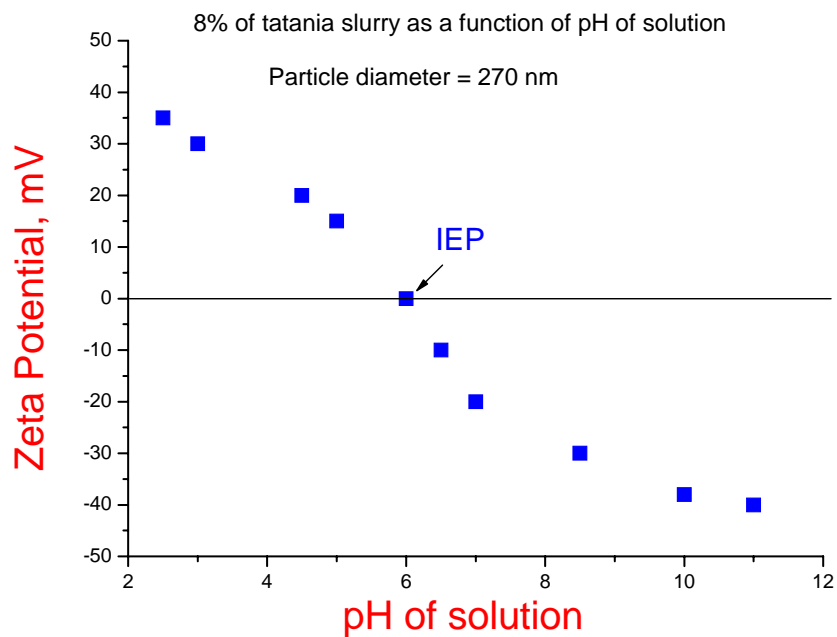
If acid is added to this suspension then a point will be reached where the charge will be neutralized

Further addition of acid will cause a build up of positive charge

In general, a zeta potential versus pH curve will be positive at low pH and lower or negative at high pH

The point where the curve passes through zero zeta potential is called the isoelectric point.

Considered normally where the colloidal system is least stable .



The isoelectric point (IEP) at pH = 6.0.

This is a characteristic of the particle surface and depends on the type of the metal oxide bond, the particle crystal structure, (rutile vs. anatase for titania) and on the type and level of impurities or other soluble species bonded to the titania particle surface.

## Electrical Charge at Colloid Surface

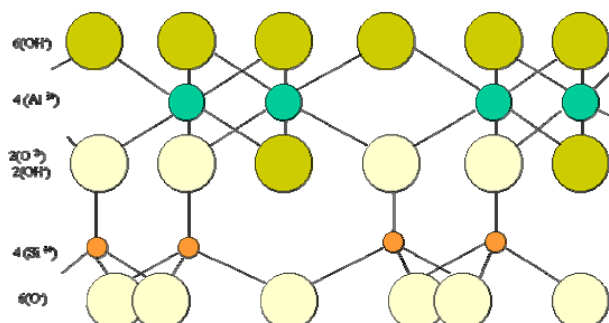
Most colloids possess surface charge

e.g : clay minerals

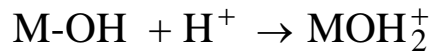
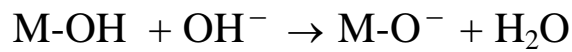
other such as –

COOH , -OSO<sub>3</sub>H , NH<sub>2</sub>

Diagrammatic Representation of Kaolinite



For metal oxides – mostly have surface layer of metal hydroxide which is amphoteric :



Charge surfaces create

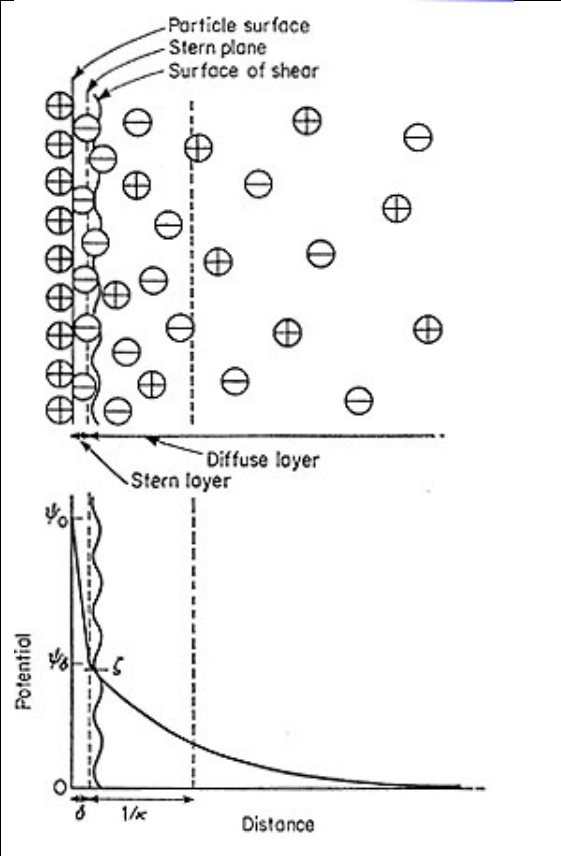
electrostatic potential

→ Addition of salt results in

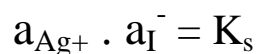
compression in DDL

so, it is important for colloid

stability.



Consider suspension of AgI in water



Can modify the activities of  $\text{Ag}^+$  ( or  $\text{I}^-$  ) by addition of

$\text{AgNO}_{3(\text{aq})}$  or  $\text{KI}_{(\text{aq})}$

Other ion then adjusts itself to keep  $K_s$  constant by forming solid.

Net charge on surface thus the electrostatic potential  $\propto$  the

balance between  $\text{Ag}^+$  and  $\text{I}^-$ .

In practice ,  $I^-$  preferentially adsorbed!!

$Ag^+$  and  $I^-$  are called *potential determining ion (p.d.i)* for AgI system.

For metal oxides:



## BROWNIAN MOTION

To explain the continuous jiggling motion of particles or suspended particles in solution.

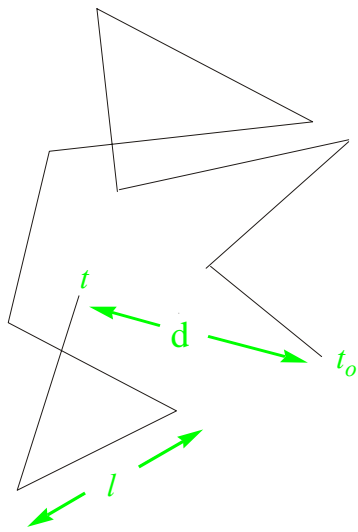
Found by Robert Brown –19<sup>th</sup> century

Implication – Brownian motion is responsible for the diffusion process

Driving force for solute to attain **uniformity**

In a gas phase ,

A molecule will move at high speed, in 1 second it might cover hundreds of meters. However it doesn't go anywhere because its movement is **random**.

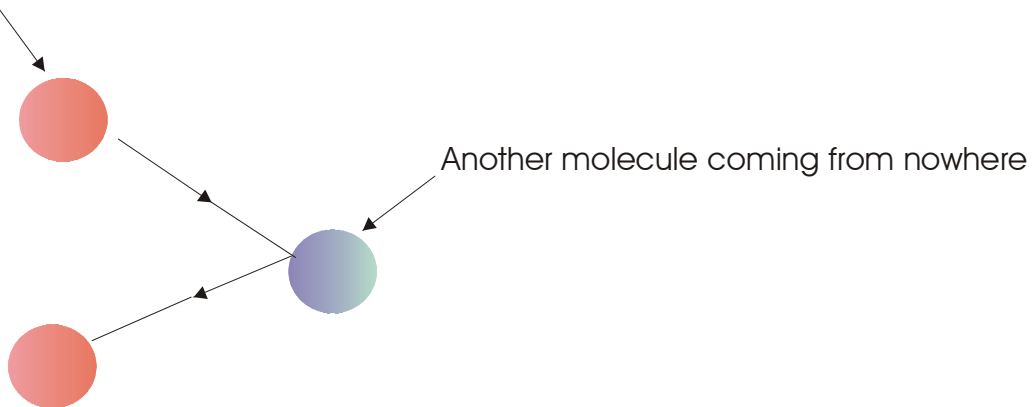


$d = \text{displacement}$   
 $l = \text{mean free path}$

Random path

## IN GAS PHASE

$\infty$  r  
 molecule



Given ,

$$\langle d^2 \rangle = N^c l^2$$

where;  $\langle d^2 \rangle$  - mean-square displacement per sec.

$N^c$  - no of collisions per sec  
 $l$  - mean free path

In dilute gas;

$$\langle d^2 \rangle = \frac{\langle \mu \rangle^2}{N^c}$$

$$\begin{aligned} \langle d^2 \rangle^{1/2} &= \sqrt{N^c} \cdot l \\ &= \frac{\langle \mu \rangle}{\sqrt{N^c}} \end{aligned}$$

The value of  $\langle \mu \rangle$  is normally high.

### PARTICLE IN A BOX

Say, for N identical molecules mean- square velocity

$$\langle V_x^2 \rangle = \frac{1}{N} \sum_{i=1}^N v_{xi}^2$$

molecular velocity

$$V_{i,tot}^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2$$

now, we have

$$\langle v^2 \rangle = \frac{\sum_{i=1}^N v_i^2}{N}$$

$$\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle \quad \text{assume all equal recall,}$$

$$P = \frac{Nm}{V} \langle v^2 \rangle$$

thus,

$$PV = \frac{1}{3} Nm \langle v^2 \rangle$$

recall an ideal gas equation,

$$PV = nRT = \frac{N}{N_A} RT \quad (\text{n- no of moles})$$

then,

$$RT = \frac{N_A}{N} \cdot \frac{1}{3} Nm \langle v^2 \rangle$$

so,

$$RT = \frac{1}{3} N_A m \langle v^2 \rangle$$

We can now relate this equation with previous translational  $E_{kin}$

$$E_{kin} = \frac{1}{2} mv^2$$

$$RT = \frac{2}{3} \cdot N_A \cdot \left( \frac{1}{2} m \langle v^2 \rangle \right)$$

$$E_{kin,trans} = \frac{3}{2} RT \quad \text{for one mole of gas}$$

Can also deduce

$$\langle v^2 \rangle = \frac{3RT}{M}$$

so, root mean-square velocity

$$\langle v^2 \rangle^{1/2} = \left( \frac{3RT}{M} \right)^{1/2}$$

How to measured if a molecule moves N steps after time t?

e.g; 1. one steps



possible path = +ve or -ve  
left or right

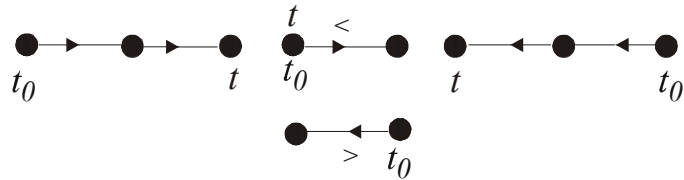


$\therefore$  2 possible location  $d_i$ ,  
Since there is equal probability to move left or right, it mean  
displacement  $\langle d \rangle$  always **zero**.

$$\langle d^2 \rangle = 1 \quad (\text{mean-square displacement})$$

e.g : 2) two steps

Possible path :



Mean of displacement = 0

Possible location = +2      0,0      -2

$\langle d^2 \rangle = 2$  (no .of steps)

Calculation :

Mean displacement

$$\langle d \rangle = \frac{\sum_i^{paths} d_i}{no.paths}$$

Mean-square displacement

$$\langle d^2 \rangle = \frac{\sum_i^{paths} d_i^2}{no.of\ paths}$$

e.g: for  $N$  with direction length of ,  $l$

$$\langle d^2 \rangle = Nl^2$$

Root mean-square displacement

$$\sqrt{\langle d^2 \rangle} = \sqrt{Nl^2}$$

$$\langle d^2 \rangle = \sqrt{Nl}$$

Can be applied to measure end-to-end random polymer unit with  $N$  monomer units.