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INTERFACES, COLLOIDS AND GELS *

Course Outline

Nature and relevance of colloidal state; classification and examples; reasons for stability; lyophilic and lyophobic colloids. Gouy-Chapman electrical double layer theory; Poisson-Boltzmann equation; interaction of electrical double layers; DLVO theory for stability of colloids. Preparation methods. Properties.

Clay minerals; clay swelling as an example of electrical double layer properties.

Association colloids; micelles; critical micelle concentration; thermodynamic of micelle formation.

Adsorbed and spread films at liquid-air interfaces; surface pressure; surface pressure isotherms; organisation of adsorbed and spread films.

INTERFACES, COLLOIDS AND GELS

1. Nature and Relevance of Colloids

Colloids are an important class of materials, intermediate between bulk and molecularly dispersed systems.

Definition of a colloid

Colloidal systems consist of a *disperse phase* distributed uniformly in a *finely-divided* state in a *dispersion medium* (the continuous phase).

What do we mean by finely-divided?

At least one of the dimensions of the dispersed phase lies **between 10 Å (1 nm) and 10 000 Å (1 m m).**

Molecularly dispersed solution   Colloidal system   Bulk phase

1 nm to 1 μm
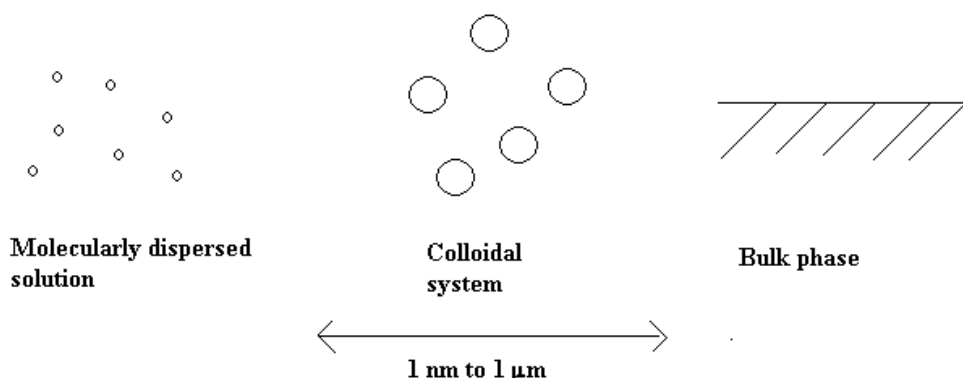
Consequently:

- Colloidal particles are typically many times larger than the molecules of the dispersion medium.

- Colloidal particles have a high surface area to volume ratio compared with bulk materials. A significant proportion of the colloidal molecules lie within, or close to, the interfacial region. Hence, the interfacial region has significant control over the properties of colloids.

e.g. compare the surface areas of a 1cm cube – 6 cm^2 with that available when the cube is broke into smaller cubes of 0.5 m m dimensions (= $(1/5´ 10^{-5})^{3´}$ 6´ 2.5´ 10^{-9}cm^2) = 1.2´ 10^5 cm^2.

Colloidal systems are widespread in their occurrence and have biological and technological significance.

Colloidal Systems

Disperse Phase	Dispersion Medium	Class	Example
Liquid	Gas	Liquid Aerosol	Fog, mist, aerosol sprays
Solid	Gas	Solid Aerosol	Industrial smoke
Gas	Liquid	Foam	Fire-extinguisher, foam, froths
Liquid	Liquid	Emulsion	Milk, butter, mayonnaise, some creams
Solid	Liquid	Sol, Colloidal Suspension	Inorganic colloids, e.g. silver halides
Gas	Solid	Solid Foam	Insulating foam, expanded polymers
Liquid	Solid	Solid Emulsion	Ice cream

Solid	Solid	Solid Suspension	Stained glass, pigmented polymers, pearl
Micelles	Liquid	Association Colloids	Soap, detergents in water
Polymers	Liquid	Gels	Jellies, glue
Biocolloids			
Corpuscles	Serum		Blood
Hydroxy-apatite	Collagen		Bone
Protein structures, thin films of lethecin, etc.			Muscle, cell membranes

NB. Association colloids are formed by surface-active molecules aggregating together to form *micelles*.

Usually, a clear distinction can be made between the dispersed phase and the dispersion medium. Network colloids are an exception. In these, *both phases consist of interpenetrating networks* on the colloidal scale. *Gels* are a typical example.

In *foams*, it is the thickness of the dispersion medium film that has colloidal dimensions.

2. Colloid Stability

A key question is *what factors affect the stability of colloidal dispersions*?

For example, under certain conditions, the colloidal particles will aggregate together to form the condensed phase.
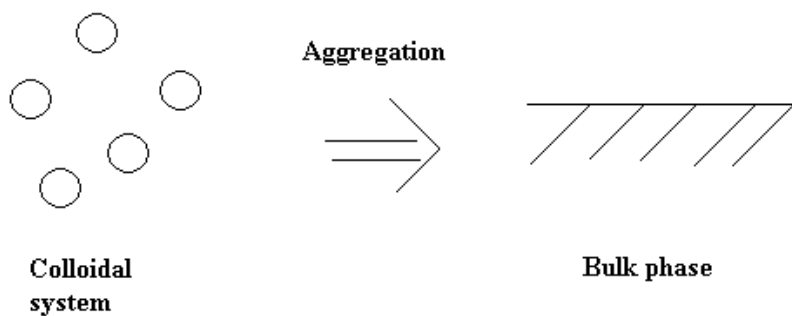
The aggregation process is called:

1. *Coagulation:* aggregate (known as the *coagulum*) is densely packed and the process is *irreversible*.

2. *Flocculation:* aggregate (known as a *floc*) is packed more loosely and the process can be

reversible.

To understand why colloidal dispersions can either be stable, or unstable, we need to consider:
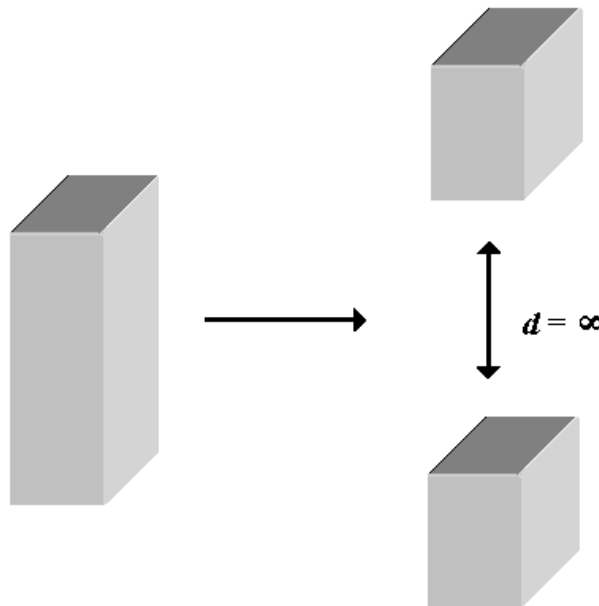
(i) the effect of the large surface area to volume ratio,

(ii) the forces operating between the colloidal particles.

2.1 Creating surfaces

Consider a column of material with a cross sectional area, *A*, clearly split to form two fresh surfaces of total cross sectional area 2*A* and moved apart in a vacuum to infinite separation in a reversible process.

Molecules in the column have attractive forces between them, otherwise they would not be in a condensed state.

\ in splitting the column, work has to be done against these attractive forces. This work, D*W*, is equal to the increase in Gibbs free energy, D*G*.

D *G* μ area of surface created (in this instance, 2A), since the greater the area created, the more intermolecular forces that have to be overcome.

Hence:

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

The proportionality, g , is known as the surface tension, or interfacial tension.

- *The surface tension (or interfacial tension), g , is defined as the work required to create unit area of surface or interface; units N m^{-1}.*

- The surface tension may be considered to arise due to a degree of unsaturation of bonds that occurs when a molecule resides at the surface and not in the bulk.

- The term *surface tension* is used for solid/vapour or liquid/vapour interfaces.

- The term *interfacial tension* is more generally used for the interface between two liquids, two solids or a liquid and solid.

Consequently, it is clear that producing colloidal particles from a bulk material requires work, e.g. we have to grind a bulk material up in order to produce a fine powder. So how can colloidal dispersions remain stable? Why don't the colloidal particles spontaneously aggregate to form bulk material?

If a colloidal dispersion is stable, there must be an *energy barrier* to overcome in order to form the bulk phase; i.e. the system is *metastable*, and the system is under *kinetic* rather than thermodynamic control.

But what is the nature of this energy barrier?

To understand this further, we need to consider the nature of intermolecular forces that exist between molecules, and then the interparticle forces that exist between colloid particles.

2.2 Interparticle Forces

The forces between colloidal particles will be the sum of the forces that exist between molecules.

2.2.1 Intermolecular Forces and Attraction

Molecules without permanent dipoles are attracted to each other by *van der Waals forces* (also known as London dispersion forces). The electron distribution in an atom fluctuates continuously and these fluctuations make the molecule an instantaneous dipole, which induces a dipole in neighbouring molecules and hence they attract each other.
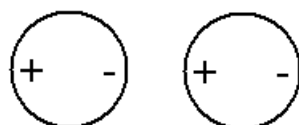
In a hydrogen atom (single e in 1s orbital) the instantaneous dipole moment is;

$$p_1 = a_0 e$$

a_0 = Bohr radius of ground state orbital
e = electron charge

Consider the potential energy between particles, (this is easier than considering the forces between particles, since force is a vector property involving direction, whereas potential energy is a scalar property).

A positive potential energy results from a repulsive force.

A negative potential energy results from an attractive force.

The potential energy of attractive interaction between the two hydrogen dipoles is:

$$V_A(r) = -\frac{\alpha a_0^2 e^2}{(4\pi\varepsilon_0)^2 r^6}$$

$$= -\frac{C_6}{r^6} \quad (2.1)$$

a = polarisability, e $_0$ = permitivitty of free space, r is separation, C_6 is a +ve constant.

When atoms (or particles) are so close that the electron clouds interact with each other – we have Born repulsion which prevents too close an approach. This combination of attraction and repulsion between atoms is summarised in the Lennard-Jones 6-12 potential:

Lennard-Jones 6-12 Potential

$$V(r) = -\frac{C_6}{r^6} + \frac{C_{12}}{r^{12}}$$

C_6 and C_{12} are +ve constants.
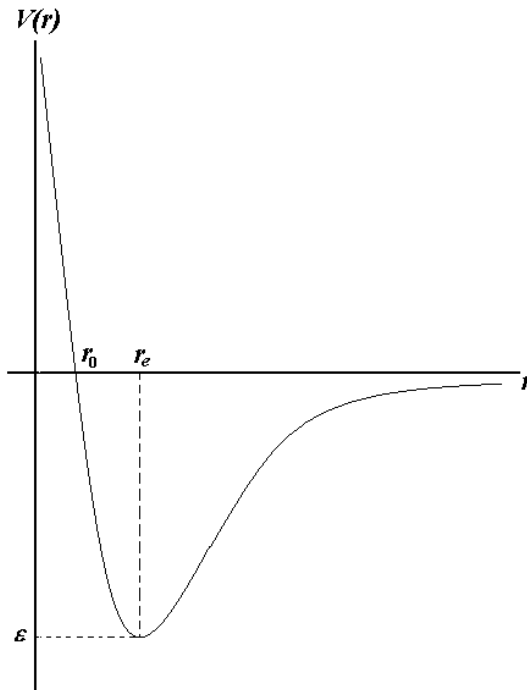
$$V(r) = 4\varepsilon\left\{ -\left(\frac{r_0}{r}\right)^6 + \left(\frac{r_0}{r}\right)^{12} \right\}$$

Also written as:

e = depth of potential well, r_0 = value of r at which $V(r) = 0$,
r_e = value of r at the well minimum = $2^{1/6} r_0$.

2.2.2 Attraction between an atom and a slab

In general: $r^2 = (D + z)^2 + R^2$

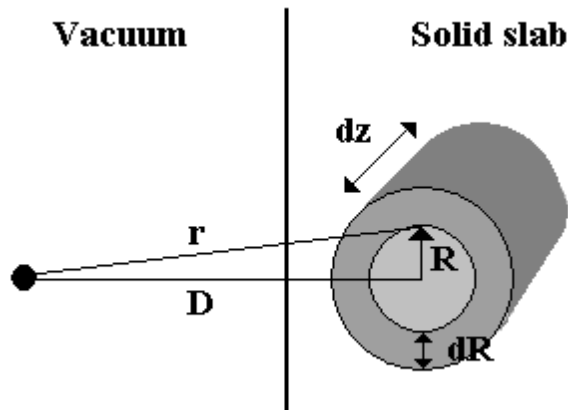We need to sum the potential over all atoms in the slab:

i.e.
$$V_A = -\sum_{i=1}^{n} \frac{C_6}{r_i^6}$$ (2.2)

where n is the number of atoms in the slab.

We can do this by integrating over all the atoms in a small volume of slab of depth, dz and thickness, dR.

The no. of atoms in a small volume, dV = r ' x volume of small slab element = r ' 2p R dR dz

where: r ' = density. This gives:

$$V_A = -C_6 \rho' \int_0^\infty \int_0^\infty \frac{2\pi R}{r^6} dR dz$$

Then, since: $r^2 = (D + z)^2 + R^2$

$$V_A = -C_6 \rho' \int_0^\infty \int_0^\infty \frac{2\pi R}{\left((D+z)^2 + R^2\right)^3} dR dz$$

$$= -\frac{\pi C_6 \rho'}{6D^3}$$ (2.3)

Note that **the potential energy falls off much more slowly** ($1/D^3$) than atom-atom interactions ($1/D^6$).

2.2.3 Attraction between two colloidal particles

Treating the two particles as infinitely large flat plates, then the attraction *per unit surface area* becomes (by integrating 2.3 with respect to D from $D = D$ to ¥):

$$V_A = -\frac{A}{12\pi D^2}$$ (2.4)

Where A is the **Hamaker constant**. A is determined by C_6 and r ' of the material forming the particle and

the nature of the intervening material. Note, ***the potential energy falls off much more slowly*** ($1/D^2$).

For two spherical particles of equal radius a, a distance H apart between centres, the attractive potential becomes:

$$V_A \cong -\frac{Aa}{12H} \quad (2.5)$$

When a fluid fills the intervening space, the attractive force is reduced (but does not become zero) and hence the reduction in Gibbs free energy on aggregation is not so large. In this more typical case, we use the composite Hamaker Constant, A_C, instead of A. A_C is given by:

$$A_C = (A_{11}^{1/2} - A_{22}^{1/2})^2 \quad (2.6)$$

where: A_{11} is the Hamaker constant of the disperse material and A_{22} is the Hamaker constant of the intervening medium (the dispersion medium).

Values of A and A_C are $\sim 10^{-20}$ J.

Assumptions in Hamaker theory

1. ***Pairwise additivity of interactions***: i.e. assumes the total interaction is just the sum of the interaction between pairs of molecules. However, the neighbouring molecules will moderate the interaction between any molecule pair.

2. ***Interaction between fluctuating dipoles is instantaneous***. The electromagnetic wave set up by the moving electrons travels at a finite rate, c. When the wave reaches a neighbouring molecule that is greater than ~ 10 nm away, the original electronic state of the molecule might have changed.

Þ interaction between the molecules will be reduced.

Þ interaction between particles falls off more rapidly if the particles are further than ~ 10 nm apart; e.g. for 2 plates, the interaction is $\mu\, D^{-3}$ instead of D^{-2}, when $D \sim 10$ nm or more. This is known as the ***retardation effect***.

The alternative Lifshitz theory tries to address these assumptions.

- Forces between particles are related to the dielectric properties of the solids and the intervening medium (atomic structure is ignored, so no good at small atomic separations).

- Involves quantum fields, very hard!

- shows that the Hamaker 'constant' actually varies somewhat with the particle separation.

However, the main results of the Hamaker theory still follow, i.e.:

the attractive potential energy between colloid particles falls off far more slowly than the attractive potential energy between molecules.

So why don't all colloidal particles coagulate under the influence of this attractive potential? There must be a repulsive potential, of similar long range order, present.

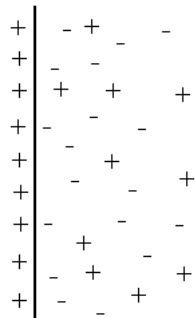### 2.3 Diffuse Electrical Double Layers

Colloids dispersed in water usually carry an electrical charge due to:

1. **Surface group ionisation**: controlled by the pH of the dispersion medium.

2. **Differential solubility of ions**: e.g. silver iodide crystals are sparingly soluble in water and silver ions dissolve preferentially to leave a negatively charged surface.

3. **Isomorphous replacement**: e.g. in kaolinite, Si^{4+} is replaced by Al^{3+} to give negative charges.

4. **Charged crystal surface**: Fracturing crystals can reveal surfaces with differing properties.

5. **Specific ion adsorption**: Surfactant ions may be specifically adsorbed.

Helmholtz first development a model for the electrical double layer in the 1850s for the charge on a metal surface. This charge was balanced by an equal charge in the liquid phase.
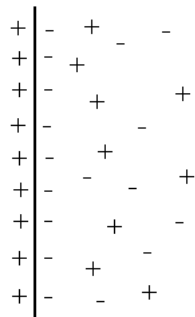
Subsequently it was appreciated that thermal motion of the charges in the dispersion medium would distribute the charges in some manner over a spatial region near the surface.

The model of the electrical double layer in these circumstances is the **Gouy-Chapman model**.

2.3.1 Gouy-Chapman Electrical Double Layer Model

A flat surface is considered. The charge on that surface influences the ion distribution in nearby layers of the electrolyte. The electrostatic potential, y , and the volume charge density, r , which is the excess of charges of one type over the other, are related by the Poisson equation:

$$d^2 y / dx^2 = -\rho / (\varepsilon_o \varepsilon_r) \quad (2.7)$$

e_r = relative permitivitty (dielectric constant) of electrolyte.

The ion distribution in the charged surface region is determined by (i) temperature and (ii) the energy required, w_i, to bring the ion from an infinite distance away (where y = 0) to the region where the electrostatic potential is y . This distribution is given by a Boltzmann equation:

$$n_i = n_i^0 \exp\left(-w_i / k_B T\right) \quad (2.8)$$

n_i^0 = no of ions of type i per unit volume of bulk solution.

$w_i = z_i e y$, the energy expended in bringing an ion from an infinite distance from the surface to a point where the potential is y .

z_i = valency of ion species i.

The volume charge density at y is: $\rho = \sum_i n_i z_i e = \sum_i n_i^0 z_i e \exp\left(-z_i e \psi / k_B T\right)$

Thus the combination of this with the Poisson equation gives the **Poisson-Boltzmann equation**:

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\varepsilon_0 \varepsilon_r} \sum_i n_i^0 z_i e \exp\left(-z_i e \psi / k_B T\right) \quad (2.9)$$

When $k_B T >> (|z_i e y|)$, the exponential can be expanded and only the first two terms retained. This is called the **Debye-Hückel approximation**.

$\exp(x) = 1 + x + x^2/2! + x^3/3! + x^4/4! + \ldots$, hence:

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\varepsilon_0 \varepsilon_r}\left[\sum_i z_i e n_i^0 - \sum_i z_i^2 e^2 n_i^0 \psi / k_B T\right]$$

but $\sum_i z_i e n_i^0 = 0$ (preservation of electroneutrality)

$$\frac{d^2\psi}{dx^2} = \sum \frac{z_i^2 e^2 n_i^0}{\varepsilon_0 \varepsilon_r k_B T}\psi$$

i.e. $\frac{d^2\psi}{dx^2} = \kappa^2 \psi$

Þ $y = y_0 \exp(-k x)$ (2.10)

y_0 is the potential at the plate surface, k is the **Debye-Hückel parameter**; it has units of (length)$^{-1}$.

1/k is the distance at which the potential, y , has dropped to (1/e) of its value at the solid surface, y$_0$, and this distance is called the **double layer thickness or Debye length**.

$$\kappa = \left(\frac{e^2 \sum n_i^0 z_i^2}{\varepsilon_0 \varepsilon_r k_B T}\right)^{1/2}$$
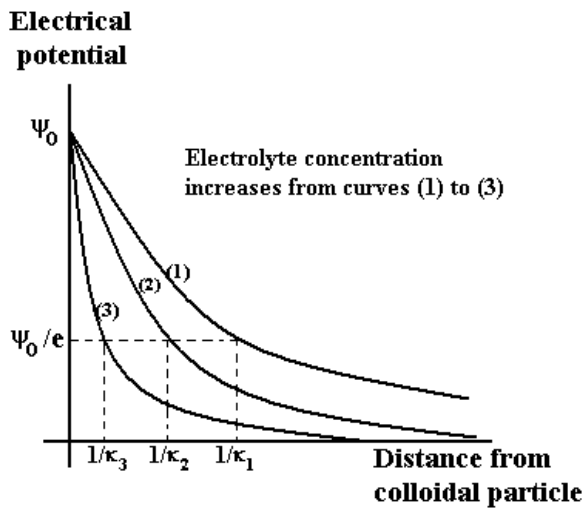
$$\kappa^2 = \left(\frac{2000F^2}{\varepsilon_0\varepsilon_r RT}\right)I \quad (2.11)$$

F = Faraday's constant = eN_A = 96.485 x 10^3 C mol^{-1};

$$I = \frac{1}{2}\Sigma\left(c_i z_i^2\right)$$
, the ionic strength of the electrolyte; c_i = conc^n in mol dm^{-3}.

$\kappa = 3.288\,I^{\frac{1}{2}}$ nm^{-1} for an aqueous phase at 25 ° C.

As the concentration of ions increases, the double layer thickness decreases.

If the Debye-Hückel approximation is not valid (i.e. $k_B T$ is not $>> |z_i e\psi|$), then for $z{:}z$ symmetrical electrolytes i.e $|z_i| = |z_+| = |-z_-| = z$, Equation 2.9 can be written as:

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\varepsilon_0\varepsilon_r}\left[n^0 ze\exp\left(-ze\psi/k_BT\right) - n^0 ze\exp\left(ze\psi/k_BT\right)\right]$$

$$= \frac{n^0 ze}{\varepsilon_0\varepsilon_r}\left[\exp\left(ze\psi/k_BT\right) - \exp\left(-ze\psi/k_BT\right)\right]$$

Trig relations: $\quad \sinh(x) = \frac{1}{2}\left[\exp(x) - \exp(-x)\right] \quad \cosh(x) = \frac{1}{2}\left[\exp(x) + \exp(-x)\right]$,

$$\backslash \quad \frac{d^2\psi}{dx^2} = \frac{2n^0 ze}{\varepsilon_0\varepsilon_r}\left[\sinh\left(\frac{ze\psi}{k_BT}\right)\right]$$

or $\quad 2n^0 ze\left[\sinh\left(\frac{ze\psi}{k_BT}\right)\right] - \frac{d^2\psi}{dx^2}\varepsilon_0\varepsilon_r = 0 \quad\quad (2.12)$

This can be solved to give:

$$\tanh(ze\,\psi / 4k_B T) = \tanh(ze\,\psi_0 / 4k_B T)\exp(-\kappa x) \qquad (2.13)$$

Case 1. Potential, y_0, is low

For very low potentials, then $\tanh(x) \sim x$, so 2.13 reduces to equation 2.10:

$$y = y_0 \exp(-k\,x) \quad (2.10)$$

Case 2. Far from a plate of high potential, y_0

Far out in the double layer, where the potential, y, is low, using $\tanh(x) \sim x$ gives:

$$\psi = \frac{4k_B T}{ze}\tanh(ze\,\psi_0 / 4k_B T)\exp(-\kappa x)$$

Then if y_0 is high, $\tanh(x) \sim 1$ and we have:

$$\psi = \frac{4k_B T}{ze}\exp(-\kappa x) \qquad (2.14)$$

Comparing equations 2.10 and 2.14, we see that far from a flat plate of high potential, the potential seems to have arisen from a plate of potential **$4k_B T/ze$**, irrespective of the actual y_0 value.

2.3.2 Double Layer Overlap

- The apparent stability of colloids with an electric double layer at their surfaces is due to the **_repulsive potential energy generated when the double layers overlap_**.

- As the two charged surfaces approach each other, the ion concentration between the surfaces increases due to the requirement to maintain electrical neutrality and so a **_greater osmotic pressure_** is generated.

For mathematical simplification, consider this situation applied to flat plates. Assume that the electrical potential between the two plates is additive and that overlap is small enough to have constant charge between the plates.

The mean excess osmotic pressure, $\overline{\pi}$, developed between the plates is

$$\overline{\pi} = \pi_p - \pi_{bulk}$$

where: p $_p$ = osmotic pressure between plates, p $_{bulk}$ = osmotic pressure in bulk dispersion.

Osmotic pressure, p, is given by: $\pi = n k_B T$, where n = number of ions per unit volume. Hence, at the mid-point between the plates, we have:

$$\pi_p = k_B T \left[(n_+ + n_-)_m \right]$$

$$= k_B T \left[n^0 \exp\left(\frac{ze\psi}{k_B T}\right) + n^0 \exp\left(-\frac{ze\psi}{k_B T}\right) \right]$$

$$= 2n^0 k_B T \cosh\left(\frac{ze\psi}{k_B T}\right)$$

where: $(n_+ + n_-)_m$ = number of positive and negative ions at the mid-point between plates.

$$\backslash \ \overline{\pi} = k_B T \left[(n_+ + n_-)_m - 2n^0 \right]$$

$$= 2n^0 k_B T \left[\cosh\left(\frac{ze\psi}{k_B T}\right) - 1 \right] \quad (2.15)$$

If the electrical potential at the mid-point between the plates is small, we can use just the first two terms in the series expansion of $\cosh(x) = 1 + x^2/2! + x^4/4! + ..$ to give:

$$\overline{\pi} = \frac{n^0 z^2 e^2}{k_B T} \psi_m^2 \quad (2.16)$$

At the mid-point between the plates, $\psi_m = 2\psi$, and using equation 2.14 for y , then:

$$\psi_m = \frac{8k_B T}{ze} \exp\left(-\kappa \frac{D}{2}\right)$$

where: D = distance between plates.

$$\backslash \ \overline{\pi} = 64 k_B T n^0 \exp\left(-\kappa D\right) \quad (2.17)$$

The repulsive potential energy per unit area due to the overlap of the flat plate electrical double layers, V_R, is the work done when the plates are brought closer to each other from an infinite separation. The opposition to this closer movement is provided by $\overline{\pi}$. Hence:
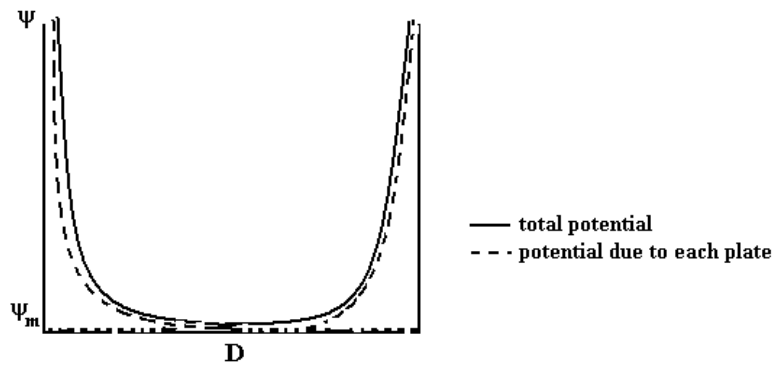
$$V_R = -\int_\infty^D \overline{\pi} \, dD$$

$$= -64 k_B T n^0 \int_0^D \exp\left(-\kappa D\right) dD$$

$$= \frac{64 k_B T n^0}{\kappa} \exp\left(-\kappa D\right) \quad (2.18)$$

Since k = $(2 e^2 n^0 z^2 / e_0 e_r k_B T)^{1/2}$ for a symmetric electrolyte, *as the concentration of ions increases, the repulsion due to double layer overlap decreases*.

Overlap of Ionic Double Layers
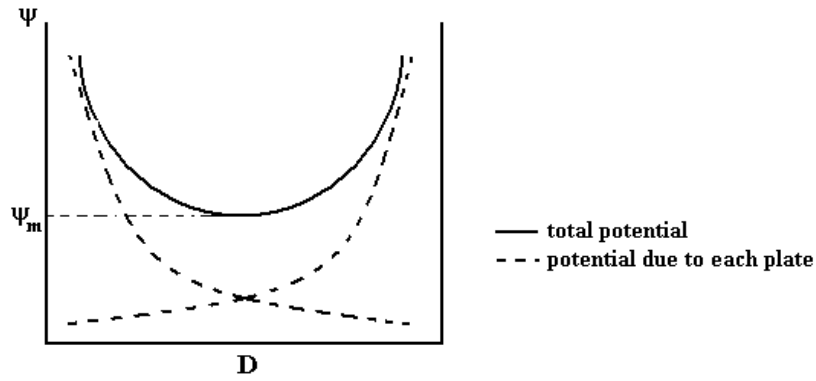
Increased ionic concentration leads to:

2.4 Total Potential Energy of Interaction: DLVO Theory

DLVO theory (named after Deryagin, Landau, Verwey and Overbeek) states that the expressions for the attractive potential energy, V_A, (Equation 2.4) and repulsive potential energy, V_R, (Equation 2.18) can be combined to give the total interaction energy function, V_T, i.e.:

$$V_T = V_A + V_R$$

$$= -\frac{A}{12\pi D^2} + \frac{64n^0 k_B T}{\kappa} \exp(-\kappa D) \quad (2.19)$$
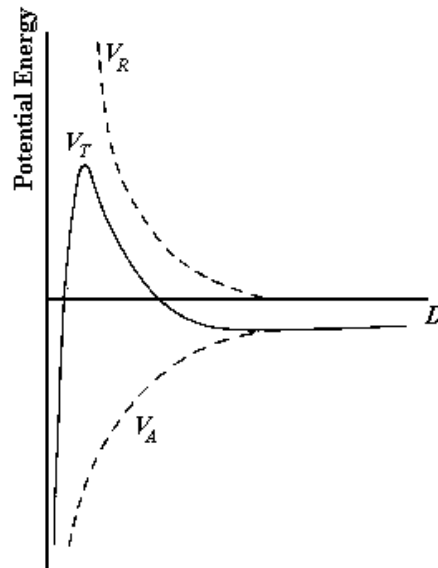
The form of equation 2.19 is such that the van der Waals attraction always dominates at both small and large separations. In between, however, the behaviour depends critically upon the ionic strength, I, and hence the electrolyte concentration, of the dispersion.
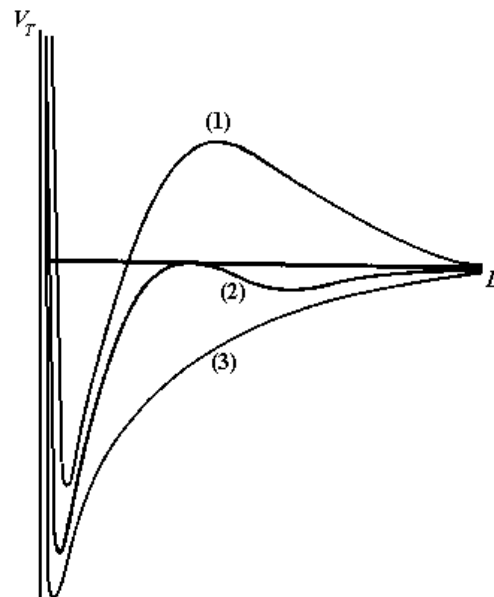
Curve 1: Low I values: primary minimum and maximum Þ stable colloidal dispersion.

Curve 2: Intermediate I values: primary minimum, primary maximum and secondary minimum Þ colloidal dispersions can be stable or unstable.

Curve 3: High I values: only primary minimum Þ unstable colloidal dispersion.

The concentration of electrolyte at which coagulation becomes rapid is the ***critical coagulation concentration* (c.c.c.)**. The condition for rapid coagulation can be considered to be that the primary maximum in the total potential energy curve is tangential to the x-axis, i.e.

$$V_T = 0 \quad \text{and} \quad dV_T / dD = 0$$

$$\text{Þ} \quad V_T = -\frac{A}{12\pi D^2} + \frac{64n^0 k_B T}{\kappa} \exp\left(-\kappa D\right) = 0$$

$$\text{and} \quad \frac{dV_T}{dD} = \frac{2A}{12\pi D^3} - 64n^0 k_B T \exp\left(-\kappa D\right) = 0$$

These two equations are satisfied if $\kappa D = 2$. This gives the concentration of ions, $n^0(c.c.c.)$ at the critical coagulation concentration as:

$$n^0(c.c.c.) \propto z^{-1/6} A^{-2} \quad (2.20)$$

Hence as the valency of counter ion increases from 1 to 3 we expect the c.c.c values to be in the ratio of $1:2^{-6}: 3^{-6}$: (1:0.0156: 0.0014).

2.5 Schulze-Hardy Rule

The Schulze-Hardy rule, which has been known since the end of the nineteenth century, states that c.c.c values are determined by the *counter ion valency*.

Electrolyte Valency	As$_2$S$_3$ sol *-ve charged*		Fe(OH)$_3$ sol *+ve charged*	
	c.c.c. / millimole dm^{-3}		*c.c.c.* / millimole dm^{-3}	
Mono	LiCl	58	NaCl	9.25
	NaCl	51	1/2BaCl$_2$	9.65
	KNO$_3$	50	KNO$_3$	12
Di	MgCl$_2$	0.72	K$_2$SO$_4$	0.205
	MgSO$_4$	0.81	MgSO$_4$	0.22
	ZnCl$_2$	0.69	K$_2$Cr$_2$O$_7$	0.195
Tri	AlCl$_3$	0.093		
	1/2Al$_2$(SO$_4$)$_3$	0.096		
	Cl(NO$_3$)$_3$	0.080		

Note the following.

1. Similar electrolytes have similar c.c.c. values.

2. Effectiveness of the electrolyte in coagulating the dispersion increases when multivalent ions are contained.

3. *Counter ion valency* is the important factor in determining c.c.c.

For the As$_2$S$_3$ sol, the c.c.c. values above are in the ratio 1:0.015: 0.0018, as the counter ion valency increases from 1 to 3. This is in excellent agreement with the DLVO theory which states that the ratios should be $1:2^{-6}: 3^{-6}$ (1:0.0156: 0.0014).

Colloids can be broadly divided into two classes.

Lyophilic (solvent loving)

- easily dispersed by the addition of a suitable dispersing medium.

- usually thermodynamically stable, and D *G* of formation is negative.

Lyophobic, (solvent hating)

- require vigorous mechanical agitation to be dispersed.

- thermodynamically unstable, but are often metastable due to charge stabilisation through the presence of surface charges.

2.6 Other Factors affecting Colloidal Stability

Effect of polymers (very long chain molecules).

2.6.1 Steric Stabilisation due to adsorbed polymer

- The polymer *adsorbs* on to the colloidal particles, forming a protective sheath around the colloidal particle of thickness, d .
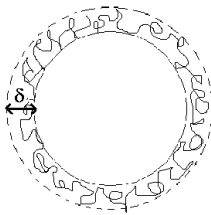
- If colloidal particles are closer than a distance, 2d , apart, then the adsorbed polymer chains will overlap and hinder the closer approach of the colloidal particles.
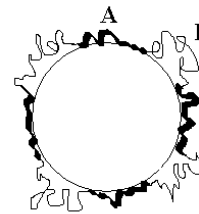
Þ *steric stabilisation*.
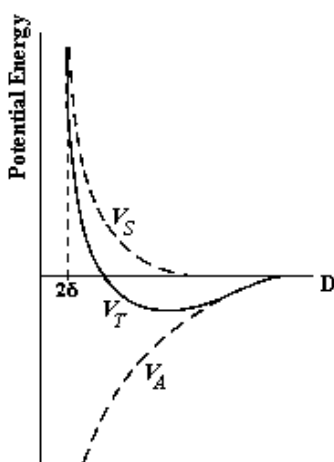
The steric potential, V_s, may be considered to arise mainly from two contributions:

  i. *Entropic term* (always repulsive) due to loss of conformational entropy of polymer chains as they overlap one another.

  ii. *Enthalpic term*. Depends upon extent to which polymer segments prefer to be next to solvent compared to themselves (depends on Flory-Huggins parameter which you will encounter next year in Prof. Richard's Polymer Course).

The ideal polymer for steric stabilisation is a *diblock copolymer*, AB.

- One component (A) adsorbs strongly onto the colloidal particles.

- The other component (B) likes to be immersed in solvent (maximises d).

Alternatively the polymer can be *chemically grafted* onto the colloidal surface.

Advantages of Steric over Charge Stabilisation

Steric Stabilisation

Steric Stabilisation	*Charge Stabilisation*
Insensitive to electrolyte	Coagulates on addition of electrolyte
Effective in both aqueous & non-aqueous dispersions	Effective mainly in aqueous dispersions
Effective at high and low colloid concentrations	Ineffective at high colloid concentrations
Reversible flocculation possible	Coagulation usually irreversible

Can reserve the term *flocculation* for colloidal particles in the presence of polymers.

2.6.2 Depletion Flocculation

- The polymer is **not adsorbed,** but remains free in the dispersion medium.

- As the colloidal particles come closer together, the intercolloidal region consists of a region that is depleted in polymer.
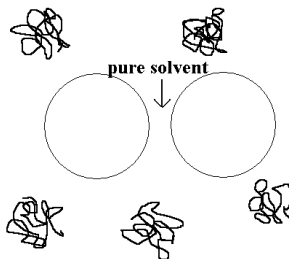
\ a polymer concentration gradient, and hence an osmotic pressure, exists.

Solvent between the colloidal particles then tends to diffuse out to reduce the concentration gradient, causing the colloidal particles to *aggregate*.

This is known as *depletion flocculation*.

2.6.3 Bridging Flocculation

A high molecular weight (i.e. very long chain) polymer is present in a *very small amount* (i.e. p.p.m.) and *adsorbs* onto the colloidal particles.

The two ends of the polymer may adsorb onto different colloidal particles and then draw them together, leading to **bridging flocculation**.

This flocculation mechanism can be highly effective; e.g. in water purification, addition of a few p.p.m. of a high molecular weight polyacrylamide results in the flocculation of any remaining particulate matter.

2.7 Summary

The use of polymers in colloidal dispersions to either stabilise (steric stabilisation) or flocculate (bridging or depletion) colloidal dispersions is now widespread. There is much interest in producing so-called 'smart' colloids, which are system-responsive colloids that are reversibly flocculating depending upon the conditions, i.e. temperature, pH, dispersion medium etc.

3. Preparation Methods

Two broad methods of preparing colloids:

1. breaking down bulk matter into colloidal dimensions known as *dispersion methods* and

2. building up molecular aggregates to colloidal sizes known as *condensation methods*.

3.1 Dispersion methods:

Comminution, emulsification, suspension and aerosol methods

- generally involve the grinding (solids) or shaking (liquids) of the material in the presence of a suitable dispersing agent to stop aggregation.

3.2 Condensation methods

Includes precipitation processes, vapour condensation and chemical reaction to produce an insoluble colloidal dispersion.

Examples of the latter include the oxidation of thiosulphate under acid conditions to produce colloidal sulphur:

$$S_2O_3^{2-} + H_2O \rightarrow S + SO_4^{2-} + 2H^+ + 2e^-$$
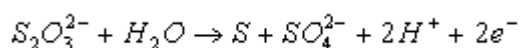
and the reaction of silver nitrate with alkali halides to produce silver halide sols.

In forming lyophobic colloids, a stabilising mechanism, e.g. charge or steric, must operate so that the

colloid particles remain dispersed.

To produce a colloidal dispersion by condensation, the supply of molecules must run out whilst the particles are in the colloidal size range.

This is achieved by:

    i. having dilute solutions
   ii. ensuring that a very large number of *nuclei* are formed in as short a time as possible.

Consider the precipitation process more fully:

$$nA_{(aq)} \ \circledR \ A_{n(s)}$$
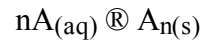
- The precipitating colloidal material must be *supersaturated*, i.e. formation of the bulk phase is thermodynamically favourable.

- At the initial stages of forming the colloidal dispersion by building up molecular aggregates, the small aggregates, or *nuclei*, will have *very large surface area to volume ratios.*

The creation of surfaces/interfaces requires work.

Hence these nuclei are *unstable* relative to larger aggregates, and they will tend to dissociate before they can grow to larger sizes.

(shown by Gibbs Thomson equation)

This will be true for all nuclei up to a certain critical size, *r**. Nuclei with this size, *r**, are termed *critical nuclei*.
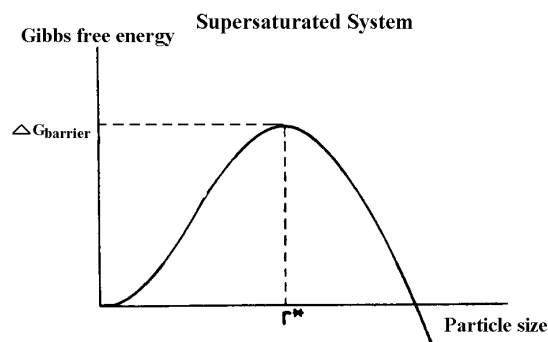
Consequently, an energy barrier exists to the formation of the new phase.

So how does the new phase form?

In any thermodynamic system, *statistical fluctuations* about the normal state occur.

Þ new phase will be able to form provided a positive free energy fluctuation occurs that is equal to, or larger than, the magnitude of this energy barrier, D $G_{barrier}$.

This process is known as *nucleation*.

After the nucleation process, *growth* of the critical nuclei to colloidal (and more typically macroscopic) sizes occurs*.*

Colloidal dispersions can sometimes be made *monodisperse*, i.e. the distribution in particle size is very small.

E.g. if the supersaturation is achieved rapidly (i.e. reaction producing insoluble material is fast, or the system is suddenly cooled) then the rate at which critical nuclei are formed (termed the *nucleation rate*) is also fast.

The fast nucleation rate means material is used up rapidly, so the concentration then quickly drops.
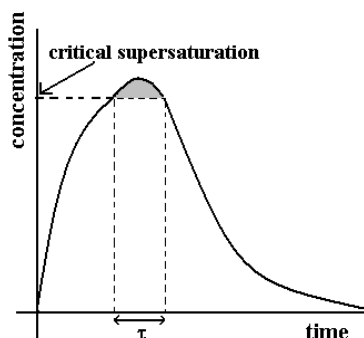
New nuclei can only form

during time t .

No nuclei can then be produced (supersaturation is too low) and the nuclei then grow to colloidal dimensions at all the same rate

Þ colloidal particles have very similar sizes.

Inorganic colloids, and polymer latexes produced by polymerisation of monomers in emulsions, can be monodisperse.

4. Clays, the Swelling of Clays and Direct Measurement of Repulsive Forces

Clays are soils where the particles have a radius less than ~2 m m. The term *clay mineral* refers to a specific group of silicate minerals. In terms of tonnage, clays are second only to oil in use. Clay minerals are used in the ceramic industry to make bricks, china and pottery. Clays are extensively used as fillers in paper, paint, polymers etc.

The essential feature of clay minerals is the existence of *extensive sheets of silicon bonded with oxygen combined with flat sheets of metal (usually Al or Mg) oxides*. Layered crystals are formed. This basic structure is exhibited by talc, pyrophyllite and kaolinite. The first two can be modified to produce vermiculite, mica and montmorillonite.

4.1 Crystal Structure of Clay Minerals

Basic structure

Silica layer: Oxygen atoms are arranged tetrahedrally around a central silicon, the bonds between Si and O being equally ionic and covalent in character. These tetrahedra link together to form hexagonal rings that repeat in two dimensions forming a sheet.

Alumina layer: Aluminium and oxygen (and hydroxyl) form octahedra with the Al at the centre, and the octahedra link together to form a sheet.

In kaolinite, the alumina octahedra are on top of the silica tetrahedra, with the apical oxygens from the silica layer being shared between both layers.

Kaolinite crystals:

- silica-alumina double sheets are bonded to one another, partly by van der Waals forces and partly by hydrogen bonding between OHs in the octahedral layer and O in the adjacent silica tetrahedral layer.
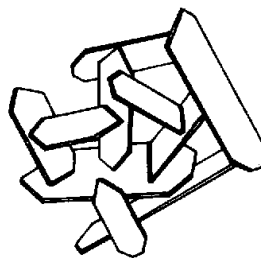
- usually hexagonal.
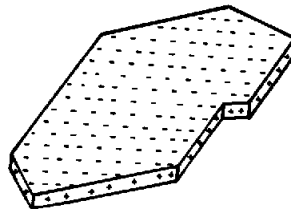
- Negative charges occur on the basal planes due to Al substituting for Si in the tetrahedral layer.

- The edges are positively charged due to the dissociation:

$$>\text{Al-OH} ® >\text{Al}^+ + \text{OH}^- .$$
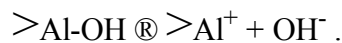
  This process is readily reversed at high pH.

- Edge to face attraction leads to 'house of cards' arrangement of kaolinite platelets.

Kaolinite is called a 1:1 non-swelling clay; 1 silica layer to 1 alumina layer; double sheets do not separate from each other under normal circumstances.

There are two forms of clay minerals of the 2 to 1 type (2 silica sheets to 1 of alumina or magnesia).

Pyrophyllite - alumina central layer

Talc - magnesia central layer

Only van der Waals forces between basal oxygen planes hold the successive tri-layers together and hence pyrophyllite and talc can easily be cleaved along these planes.

Replacement of ¼ of the Si atoms by Al atoms in pyrophillite results in the formation of *muscovite mica*.

- A large negative charge is produced on each sheet, which is balanced by K^+ ions fitting in hexagonal holes of the silica sheet.

- The bonding between the triple layers is greatly increased.

- Mica crystals are very large and easily cleaved to produce atomically smooth surfaces.

Montmorillonite is obtained when one in six of the Al atoms in pyrophillite is replaced by Mg^{2+}.

- The excess negative charge generated in each triple sheet is compensated by cations in the inter-triple sheet region.

- Dry montmorillonite absorbs water between the triple sheets (interlayer region); about 4 layers of water molecules being adsorbed in each interlayer.

- the clay mineral swells and cation exchange can take place between the ions in solution and those in the interlayer when the triple sheets separate.

- If the interlayer cations are Na^+ and Li^+, interplate repulsion is greater and separation is easier.

Vermiculite is derived from talc by replacing 1/6 of the tetrahedral silicons by aluminium. The balancing cation is often magnesium.

4.2 Clay Swelling

The swelling of clay minerals by water clearly has important implications in civil engineering and in the manufacture of ceramic products.

In montmorillonite and vermiculite, the sheets are held together by the alternating layers of bridging cations (Na^+, K^+ or Ca^{2+}). In the presence of water these ions dissociate and a double layer repulsion is generated between the triple sheets.

Empirical relation between the thickness of the water interlayer, d_w /nm, and the concentration, c, of monovalent electrolyte solution in which the clay mineral is immersed:

$$d_w \simeq 1.14\left(1 + c^{-\frac{1}{2}}\right) \quad (4.1)$$

and which is valid for $0.01 < c/\text{mol dm}^{-3} < 0.25$.

4.3 Direct Measurement of Forces Between Surfaces.

The ability to cleave mica to produce *atomically smooth surfaces* allows the measurement of forces between surfaces using the surface force balance first developed by Tabor but subsequently improved by Israelachvili.

Mica, silver coated on one surface, is stuck to transparent quartz discs which have a half-cylindrical cross section. The half cylinders are mounted in a surface force balance apparatus so that they have a *crossed cylinder configuration*.
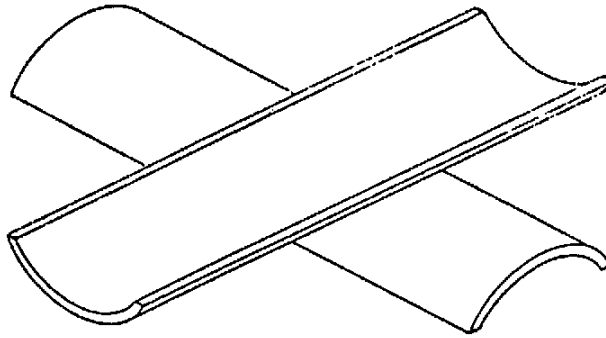
FIGURE 1. Arrangement of crossed cylinders. Molecularly smooth mica sheets about 3 μm thick are glued to cylindrical glass formers of radius of curvature about 1 cm. The back surfaces of the mica are lightly silvered so that the separation between the surfaces may be studied by multiple beam interferometry.
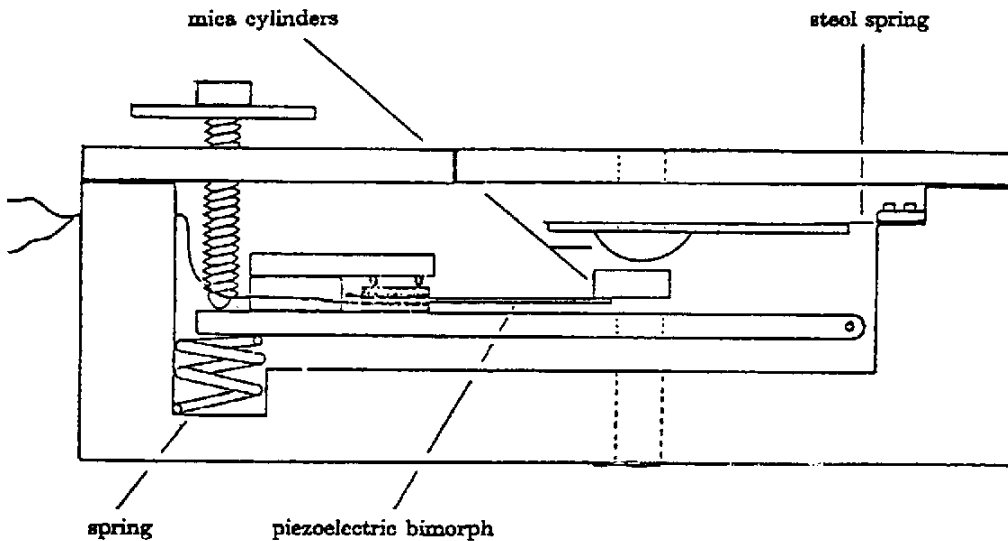

FIGURE 2. Apparatus supporting the mica surfaces. The lower surface can be moved upwards coarsely by the screw thread on the left. The fine adjustment is carried out by means of the piezoelectric transducer. The upper surface is supported on a short metal spring. At a critical separation the two surfaces jump together.

White light is passed through the cylinder attached to the leaf spring, multiply reflected between the silvered cylinders and then collected by the spectrometer. Only certain wavelengths (i.e. fringes of equal chromatic order) are transmitted, and the *shift in wavelength of these fringes gives the change in separation of the two cylinders.*

The lower cylinder can be accurately translated to the upper cylinder by the micrometers. *If the fringe orders indicate that the distance travelled is less than that imparted by the micrometers, then the leaf spring has bent this distance differential due to repulsive forces.*

Since the spring constant is known the repulsive force can be calculated.

When immersed in water, the potassium counter ions at the mica surface dissociate to form a diffuse double layer and the interaction between these can be accurately measured.

At large separations the data follows the curve for the constant potential case, at closer distances the constant charge calculations, are more appropriate. But the overall decay of the repulsion potential is

exponential as predicted by theory. If the two cylinders approach each other sufficiently closely, they jump into adhesive contact due to the attractive van der Waals forces.

5 Association Colloids

Certain *amphiphilic* molecules (i.e. molecules which have *both a hydrophillic region and a hydrophobic region*), exhibit a sharp change in the behaviour of certain properties when this property is plotted as a function of concentration
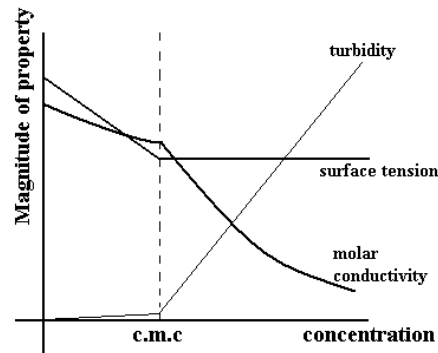


The process can be understood as follows:

At low concentrations these molecules dissolve in water and form a true solution but with *an excess of the molecules at the air-water interface*. This enables the non-polar tail to avoid contact with the water whilst the polar head group remains in contact. Consequently, these materials are known as *surfactants* (i.e. they are surface-active).

Schematic diagram of surfactant molecule
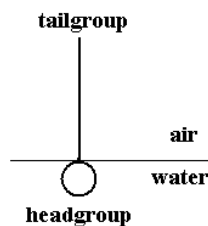
As the concentration increases the interface becomes packed with surfactant until a *complete monolayer* is formed.

Schematic diagram
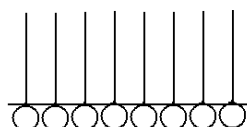
At this fairly distinct concentration, the *c.m.c.*, further addition of surfactant causes them to aggregate into *micelles*. Micelles are *association colloids*.

In water the micelle structure can be schematically drawn as:
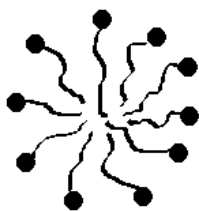
- The polar head groups populate the exterior of the micelle increasing the interaction with water.

- The hydrocarbon tails are in the interior of the micelle reducing unfavourable interactions with water.

- The micelles are generally spherical but at higher concentrations cylinders or lamellar structures may be formed.

disc-like   lamellar   spherical vesicle
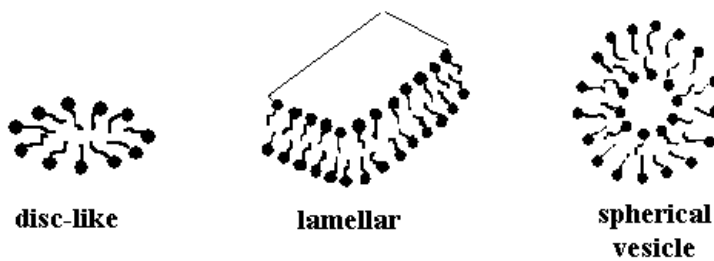
Surfactants which display this behaviour include ionic (anionic, cationic) and non-ionic molecules.

Surfactant	Name	Headgroup	c.m.c./mol dm^{-3}
Anionic $C_{12}H_{25}OSO_3Na$	Sodium dodecyl sulphate	$-OSO_3^-$	8.1×10^{-3}
Cationic + $C_{10}H_{21}N(CH_3)_3Br$	Decyl trimethyl ammonium Bromide	$-\overset{+}{N}Me_3$	6.8×10^{-2}
Non-ionic $R_n(O\ CH_2CH_2)_mOH$	Polyethylene oxides	$-(O\ CH_2CH_2)_mOH$	8.7×10^{-5} (for m=6; n=12)

Soap molecules (sodium or potassium salts of organic acids) are well-known example of surfactants, e.g. sodium stearate, $CH_3(CH_2)_{16}COO^-Na^+$, potassium oleate, $CH_3(CH_2)_7CH=CH(CH_2)_7COO^-K^+$.

Analysis of the thermodynamics of micellisation shows that it is accompanied by an *increase in the entropy* of the system; this increase is the major contributor to the negative D G^o. This phenomenon is rationalised in the following way.

Below the c.m.c., the hydrocarbon tail constitutes a cavity in the water structure, this cavity is lined by water molecules which differ in their organisation from that of the bulk water. The water becomes more *'structured'*. Furthermore, the hydrocarbon tail is less free to move in the solvated molecule because of the surrounding water.

On micelle formation, the bulk structure of water is restored and *the entropy of the water increases*. In the micelle core, which is essentially liquid hydrocarbon, there is greater freedom for movement and *so the entropy associated with the hydrocarbon tails also increases*.

The head groups are little affected by micellisation since *they are surrounded by water molecules at all stages* of the process. However, *interactions between headgroups* (within the same micelle) will determine *the size and shape of the micelle*. These interactions will result in some of the hydrocarbon core being exposed to water because the surface cannot be covered by a close-packed arrangement of polar head groups.

5.1 Influencing Factors on C.M.C.

Head group and chain length

$$\text{Log (c.m.c.)} = b_0 - b_1 m_c \quad (5.1)$$

m_c = no of carbon atoms in hydrocarbon chain, b_0 and b_1 are constants for particular surfactants.

	b_0	b_1
Na Carboxylates	2.41	0.341
K Carboxylates	1.92	0.29
Alkyl ammonium chlorides	1.25	0.265

Note the head group influences b_0 and b_1.

Branching, double bonds in the hydrocarbon increase the c.m.c.

Counter ion

Changing the valency of the counter ion has a strong influence on the c.m.c. in the same way as they influence the critical coagulation concentration.

Temperature and Pressure

For ionic surfactants below a certain temperature, known as the *Krafft point*, the surfactant comes out of solution and there are no micelles present.

For non-ionics increasing the temperature causes the formation of large aggregates which separate out as a distinct phase at the *cloud point*. This is attributed to the reduction in hydrogen bonding solvation between head groups and water.

Organic Molecules

Organic molecules can influence c.m.c. behaviour markedly and in ionic surfactants may frequently be present as impurities. Sodium dodecyl sulphate often contains dodecanol as a hydrolysis product.

The micellar phenomenon of *solubilisation* is very important, whereby lipophiles are apparently solubilised in water by the addition of surfactants.

Þ *detergent action* of surfactants.

Dirt on clothing is a mixture of soil and oil, on dishes it is denatured proteins, fats and sugars. The surfactant adsorbs on to the exposed surfaces and the shearing action of the washing process lifts the dirt from the surface, the fresh dirt surfaces become covered in surfactant that then disperses the dirt in the aqueous phase. Other additives in the detergent adsorb on to the clean surface to block redeposition of dirt.

Solubilisation of non-polar material into micelle core