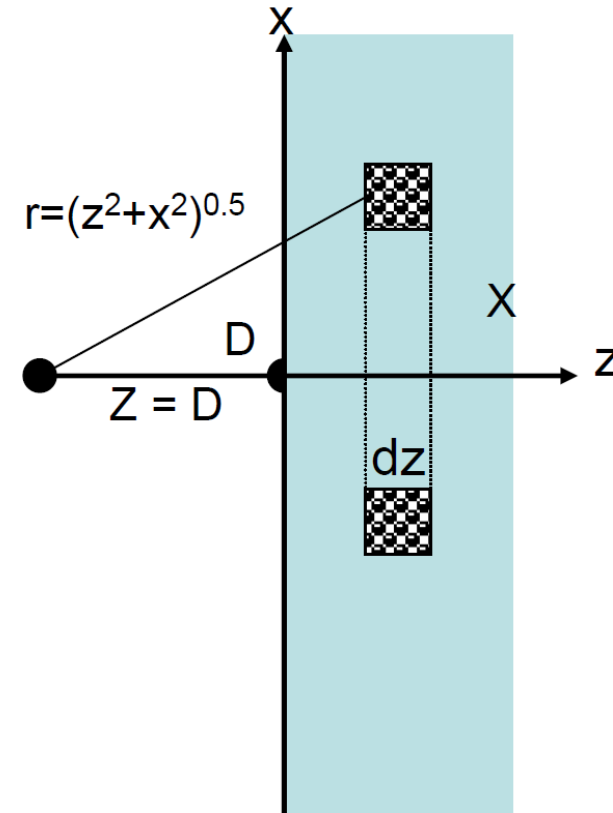# Interactions between particles

In this course we shall consider three types of interaction between particles.

- Van der Waals interaction

- Electrical interactions

- Interactions due to polymers/surfactants

Van Der Waals Interactions between Macroscopic Bodies

- The van der Waals interaction between molecules is of the form $w(r)$ = $-C/r^n$. Then assuming additivity, the interaction of a molecule with a surface is the sum of its interactions with all the molecules in the body.

Van Der Waals Interactions between Macroscopic Bodies

Between a sphere and a plate the van der Waals interaction is given by

$$W(D) = -\pi^2 C \rho^2 R / 6D = -AR / 6D$$

- Note that the interaction decays as 1/D, very much slower than the $1/r^6$ dependence of the intermolecular pair potential.

- For two equally sized spheres the same analysis yields **W(D)=-AR/12D**

- for parallel surfaces we obtain **W(D)=-A/12D²**

Exercise

- Use Excel to calculate the van der Waals energy between 2 silica spheres of radius 1 micron and 10 nm in a vacuum and in water.

- Hamaker constant silica = 6.5×10^{-20} J

- Hamaker constant water = 8×10^{-20} J

Plot your data over the range 500 nm to 0.5 nm and scale the energy axis by the thermal energy kT, i.e. divide the energy by kT

Impinging air jets may be used to clean particles from surfaces. The kinetic energy per unit volume (J/m³) of an air jet at a surface, E_r, may be written as:

$$E_r = \frac{\rho v^2}{2} kd^{-1.3}$$

Where:
ρ = density of air (1.3 kg/m³), v = air velocity
k = proportionality constant (0.4 mm$^{1.3}$)
d = distance from the jet nozzle (10 mm).

For a sphere adhered to a flat surface (A_{11} = 1x10^{-19} J),

(1) What size of particle (diameter) could a hurricane force
    wind (v = 15 m/s) remove from a surface?
(2) What size of particle can be removed at v = 340 m/s
    (speed of sound)?
(3) What air velocity would be required to remove a
    1 mm particle and a 100 nm particle?

Areas where Intermolecular Forces are important

- The Gecko's ability to walk on walls is NOT due to the traditionally (mis)understood vacuum theory:

  - It is due to van der Waals attractive forces between spatulae (1 billion) on the Gecko's leg and the wall

  https://www.youtube.com/watch?v=gzm7yD-JuyM&feature=related

Many observed phenomena in nature have their basis in intermolecular forces!

Short-range forces have long-range (macroscopic) effects. Identifying & quantifying intermolecular forces is key to the successful design of stable/unstable systems as required

Problems with Hamaker Approach

- Is additivity correct? Will neighbouring atoms affect the interaction?
- Assumption is interaction between fluctuating dipoles is instantaneous. OK is atoms are close but not when further away (eg 100nm)
- An alternative approach is the Lifshitz theory, which treats matter as a continuum. It is considered to be more accurate but in effect it is an alternative way to calculate the Hamaker constant. The basic relation remains the same.
- What about if we are in a solvent?

Solvent Effects

Previous results were in vacuum.

Presence of a solvent between particles
will affect the overall Hamaker constant:
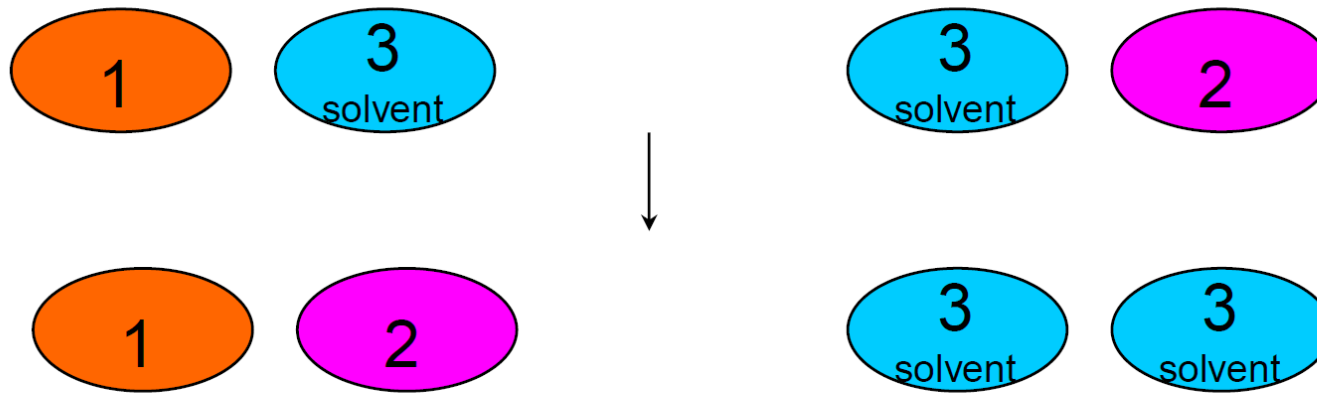
$$V_R \propto A$$

$$A_{effective} = A_{132} = A_{final} - A_{initial}$$

$$A_{132} = A_{12} + A_{33} - A_{23} - A_{13}$$

$$A_{12} \approx (A_{11} A_{22})^{1/2}, etc...$$

Net result:

$$A_{132} = \left(A_{11}^{1/2} - A_{33}^{1/2}\right)\left(A_{22}^{1/2} - A_{33}^{1/2}\right)$$

If particles are the same reduces to...

$$A_{131} = \left(A_{11}^{1/2} - A_{33}^{1/2}\right)^2$$

- If particles are the same…
  - A_{eff} is always positive -- i.e attractive.
  - If A's are similar, attraction is weak.

- If particles are different…
  - A_{eff} is positive if $A_{33}>A_{11},A_{22}$ or $A_{33}< A_{11},A_{22}$ attractive.
  - A_{eff} is *negative* if $A_{11}<A_{33}<A_{22}$ i.e. repulsive interaction if the solvent Hamaker constant is intermediate to those of the particles. Intermolecular Forces Magic Trick - YouTube

Interactions between particles

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Charged Surfaces

- Charges can originate from 3 different source

1 Dissolution of soluble ions, mainly metal ions, such as in clays

2 Adsorption of ions to surfaces, generally anions, e.g. Iodide in silver iodide

3 Adsorption of surfactants or polyelectrolyte

Charged Surfaces

- When you have a charged surface, for the condition of electrical neutrality to be met there must be ions of opposite charge, counter ions, present somewhere in the solution. From an enthalpic point of view, it is favourable for the ions to be as close to the charged surface as possible, as they are in a crystal, from an entropic viewpoint however, it is favourable for the ions to be as far as possible. In reality something in between happens and an **electrical double layer** is formed.

# The electrical double layer
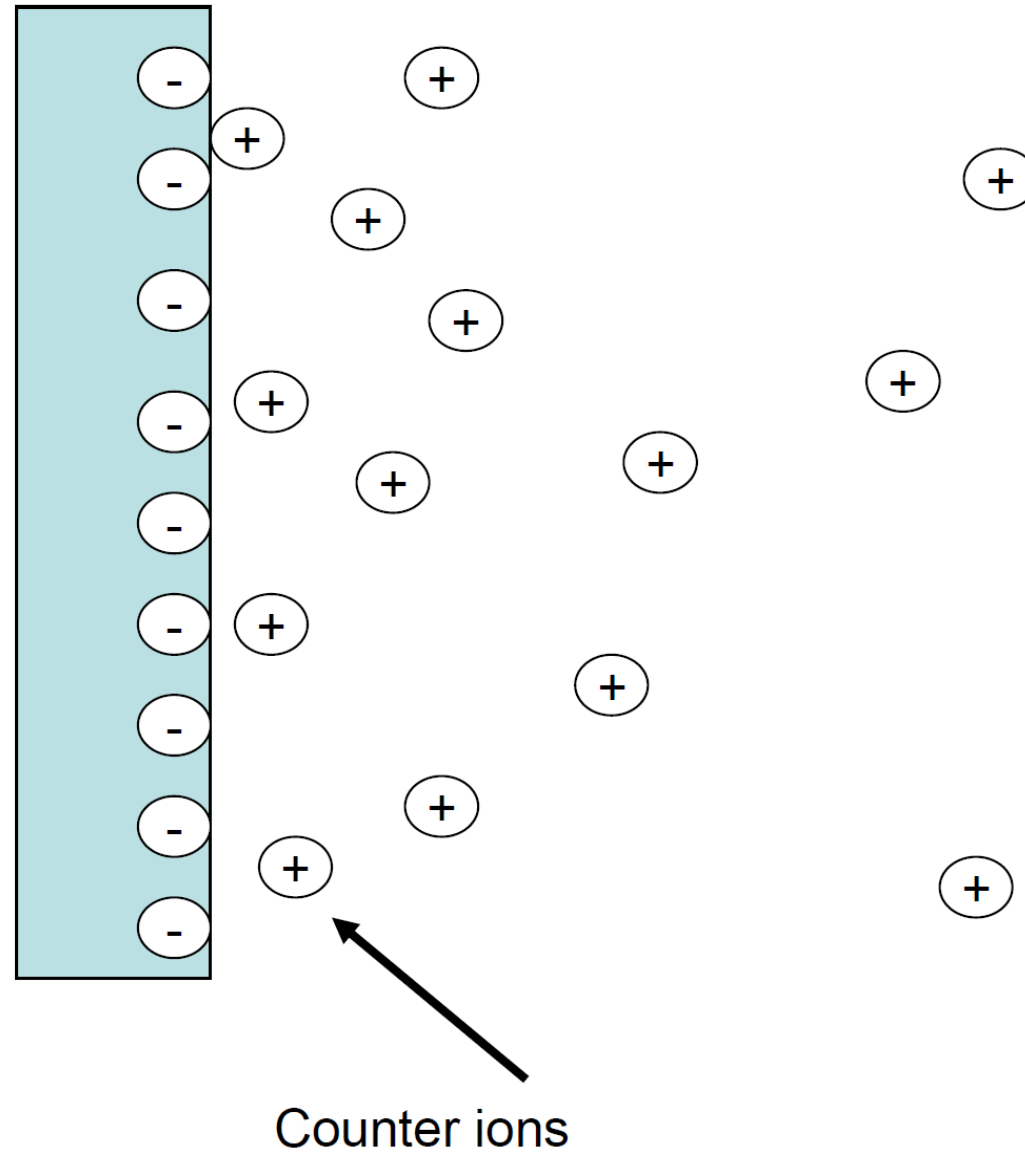
Counter ions

Charged Surfaces

- A Charged Surface in Water

For the case where only counter-ions are
present in solution, the chemical potential
may be written as

$$\mu = ze\psi = kT \log \rho - - - - - - 2.1$$

where ψ is the electrostatic potential, ρ the
number density of ions of valency z at any
point x between two surfaces and e is the
charge on an electron. Since only
differences in potential are physically
meaningful, we may set the potential at
the mid plane between two particles $\psi_0 = 0$
where $x=0$ and $(d\psi/dx)_0 = 0$ by symmetry
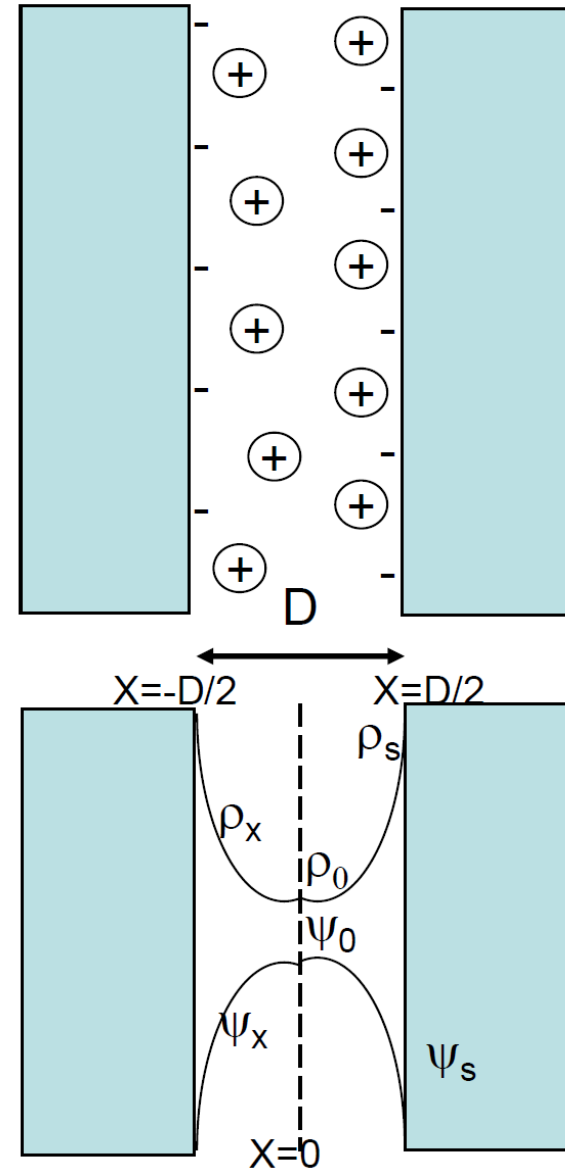
Charged Surfaces

- From the equilibrium requirement that the chemical potential be uniform throughout, eqn. 2.1 gives us the expected *Boltzmann* distribution of counter-ions at any point x

$$ze\rho_x = -\varepsilon\varepsilon_0 \left(\frac{d^2\psi}{dx^2} \right) - - - - - - 2.3$$

- This when combined with the Boltzmann Distribution gives the *Poisson-Boltzmann* Equation

$$\rho_{(x)} = \rho_0 e^{-\frac{ze\psi(x)}{kT}} - - - - - - 2.2$$

$$\frac{d^2\psi}{dx^2} = -\frac{ze\rho_{(x)}}{\varepsilon_0} = \left(\frac{-ze\rho_0}{\varepsilon_0} \right) e^{-\frac{ze\psi(x)}{kT}} - - - - -2.4$$

- One further equation is required and that is the classic *Poisson equation* for the net excess charge density at any point x

- When solved this gives us the potential, ψ, electric field, E=dψ/dx and counter-ion density at any point x in the gap between the surfaces.

Charged Surfaces

- The above discussion has been for a charged surface in pure water, in practice there are of course electrolyte ions present in solution that significantly affect matters, Firstly the structure of the double layer is somewhat modified and secondly, as we shall see the range of the double layer is affected. This in turn affects the interactions between charged surfaces
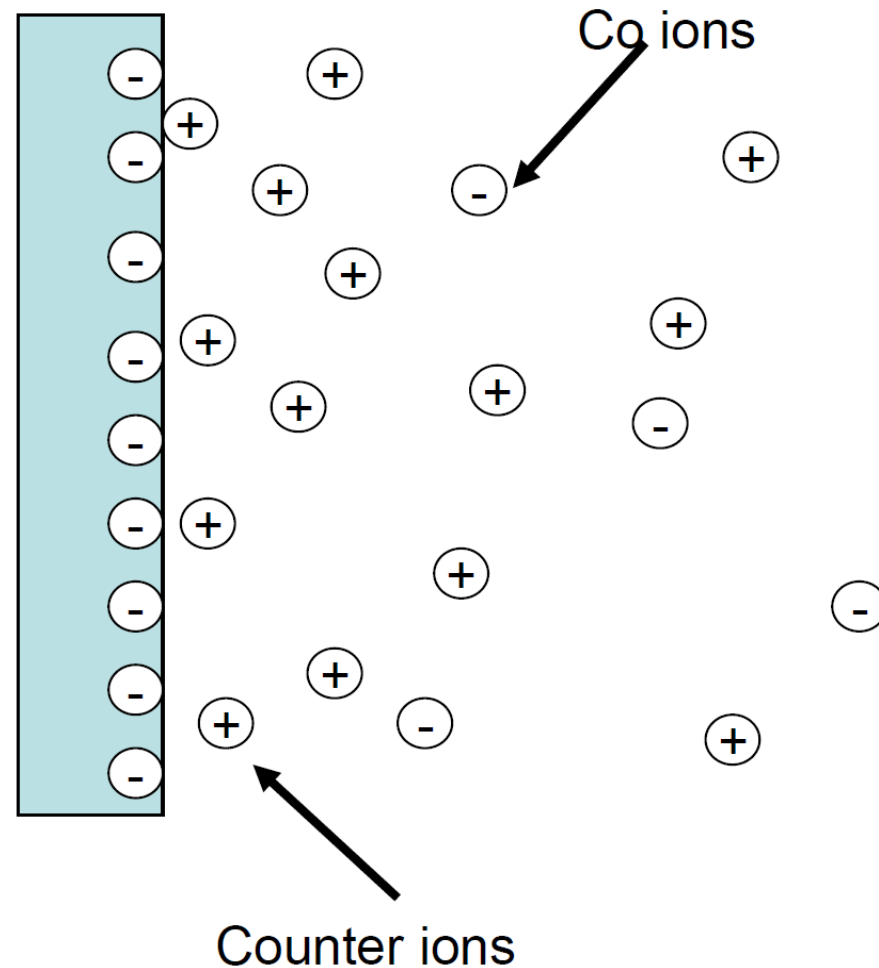
Charged surfaces

Let us consider an isolated surface or two surfaces apart, in contact with an electrolyte solution. For convenience we shall now say the x=0 at the surface rather than the midplane.

Thus equation 2.2, the *Boltzmann* Equation becomes

$$\rho_{xi} = \rho_{\infty i} e^{-z_i e \psi_x / kT} \quad ------2.5$$

While at the surface, x=0, the contact values of ρ and ψ are related by

$$\rho_{0i} = \rho_{\infty i} e^{-z_i e \psi_0 / kT} \quad -----2.6$$

Combining equation 2.6, with the *Poisson* Equation (2.3) gives

$$d^2\psi / dx^2 = -\frac{1}{\varepsilon \varepsilon_0} \sum_i z e \rho_{\infty i} e^{-ze\psi_x / kT} \quad ----2.7$$

Charged Surfaces

- This equation can either be solved exactly, (See Stokes and Evans) or more simply by making some assumption. We shall do the later!

  For the approximate solution we shall say the $ze\psi << kT$. We can therefore expand the exponential

and only the first two terms retained. This is called the **_Debye-Hückel approximation._**

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

hence:

$$\frac{d^2\psi}{dx^2} = -\frac{1}{\varepsilon_0}\sum_i ze\rho_{\infty i}(1 - ze\psi/kT) - - - - - 2.8$$

Charged Surfaces

- The electro-neutrality condition means that the sum of the positive and negative ion charges is zero

$$\sum_i ze\rho_{\infty i} = 0 - - - - - - 2.9$$

- This leads to the cancellation of the 1st term in eqn 2.8 leaving

$$d^2\psi \Big/ dx^2 = \frac{\psi}{\varepsilon_0 kT} \sum_i (ze)^2 \rho_{\infty i}) - - - - - 2.10$$

It is convenient to lump all the constants in eqn 2.10 into a single constant κ, such that

$$\kappa^2 = \sum_i (z_i e)^2 \rho_{\infty i} / \varepsilon_0 \varepsilon_r kT - - - - -2.11$$

So that equation 2.10 becomes

$$\frac{d^2\psi}{dx^2} = \kappa^2 \psi - - - - 2.12$$

Charged Surfaces

Using the boundary condition that $\psi \rightarrow \psi_0$ as $x \rightarrow 0$ and $\psi \rightarrow 0$ as $x \rightarrow \infty$ we can solve eqn 2.12 to give

$$\psi_{(x)} = \psi_0 \exp(-\kappa x) - - - - -2.13$$

- Note that the quantity $1/\kappa$ has dimensions of length and is defined as the *Debye screening length* or the thickness of the electrical double layer. For water in a 1:1 electrolyte such as sodium chloride at say 10^{-3} M, the Debye length is 10 nm, but at 10^{-1}M it is only 1nm.
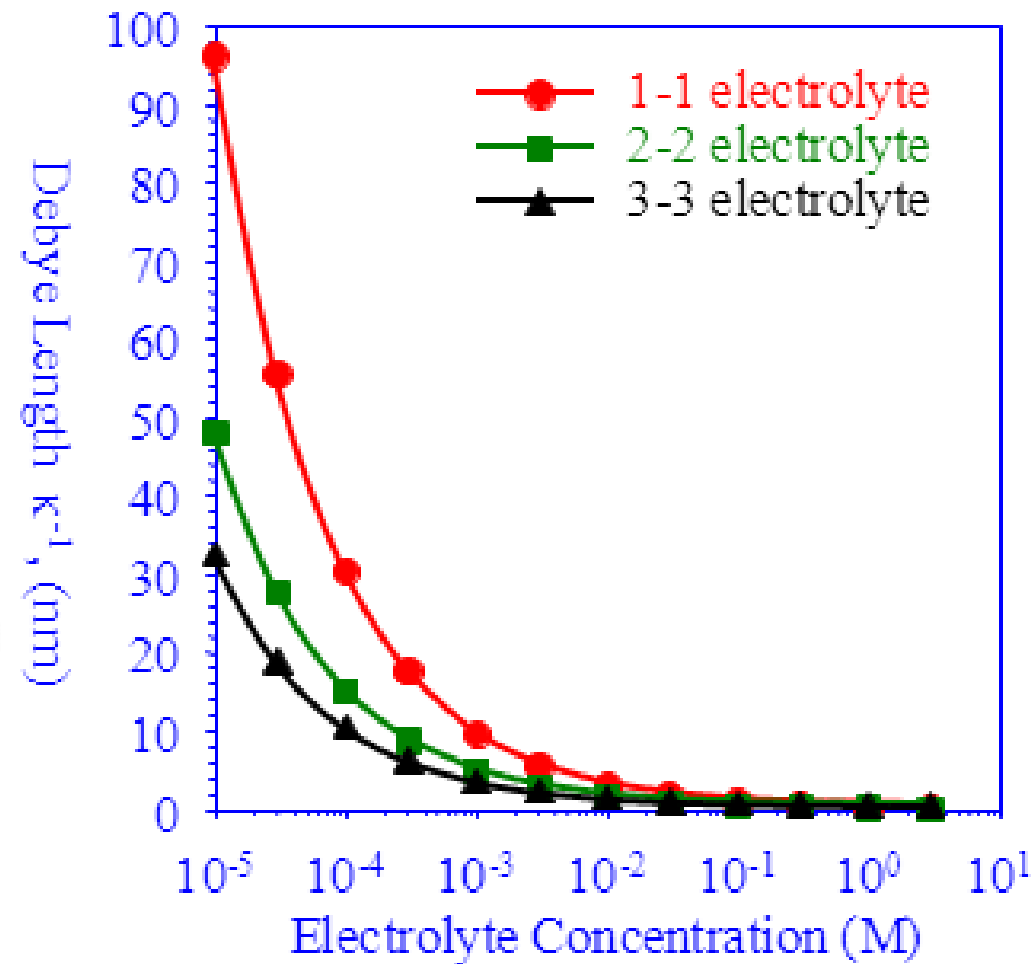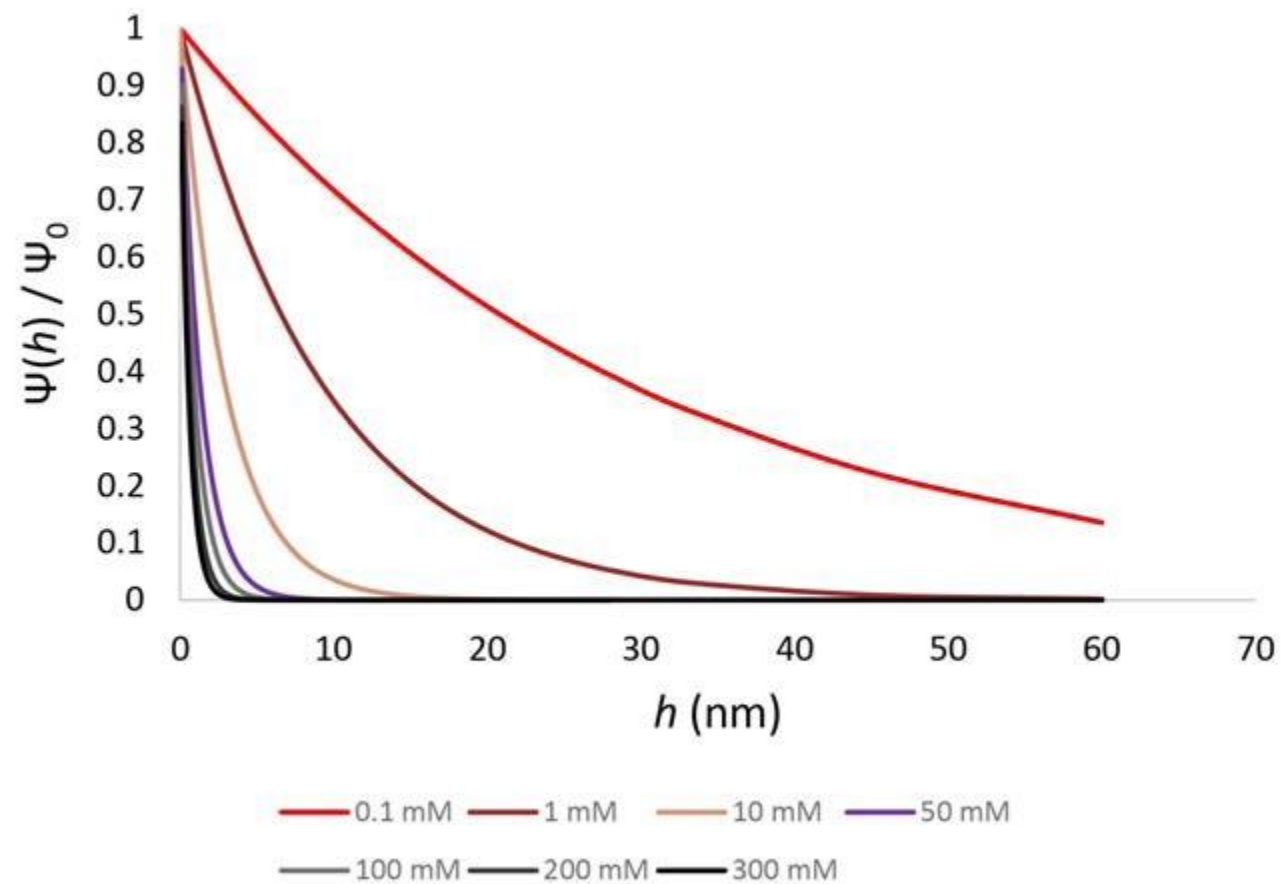
Overlapping double layers

- **The repulsive potential between two charged surfaces**

- The repulsive potential between two charged surfaces has two origins, firstly the electrostatic interaction. The electric field emanating from the charged surfaces exerts a force on the ions between the surfaces F_{el}, such that

$$F_{el} = \rho \frac{d\psi}{dx} \text{---------------} 2.18$$
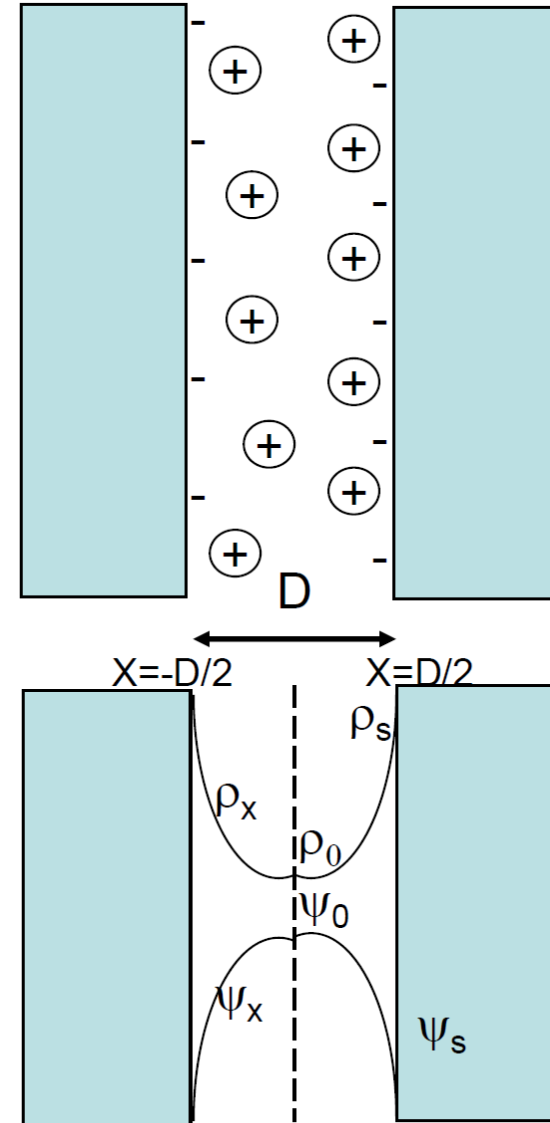
Charged Surfaces

- A Second force present in the electrolyte between the plates has an origin that is less obvious. Due to the double layer, the concentration of ions close to a surface is larger than that in the bulk, this gives rise to an osmotic pressure difference between the double layer and the bulk which for an electrolyte is given by

$$\Pi_{osm} = 2kT\rho_{i\infty} -----2.19$$

- The total repulsive force is simply a sum of these two terms, i.e.

$$F_{rep} = F_{el} + F_{osm} = \rho\frac{d\psi}{dx} + \frac{d\Pi_{osm}}{dx} ----2.20$$

- At the mid point between two surfaces $d\psi/dx = 0$ so the only force operating is the osmotic force. Thus the repulsive force is simple the difference in the osmotic pressure at the midpoint between the two surfaces and the bulk solution

$$F_{rep} = kT(\rho_{D/2,cations} + \rho_{D/2,anions} - 2\rho_{i.0}) ----2.21$$

Charged Surfaces

- We can use the Boltzmann equation, 2.5 to relate the local concentration of ions to the potential at the mid-plane $\psi_{D/2}$ by,

- Where z is the valency of the ion irrespective of sign.

$$\rho_i = \rho_{\infty i} e^{-z_i e \psi_{D/2}/kT}$$

- *Substituting into equation 2.21 give*

$$F_{rep} = \rho_{i\infty} kT \left| \exp\left(-ze\psi_{D/2}/kT\right) + \exp\left(+ze\psi_{D/2}/kT\right) - 2 \right| ----2.22$$

- Or

$$F_{rep} = 2\rho_{i,\infty} kT \left[\cosh\left(ze\psi_{D/2}/kT\right) - 1 \right] ----2.23$$

Charged Surfaces

- We can relate the potential at the mid-plane, $\psi_{D/2}$ to the surface potential ψ_O using the analysis presented earlier for the variation of the potential away from a surface. A proper analysis by inserting eqn 2.14 into eqns 2.23 and 2.24 can only be achieved using a numerical integration, however we can consider a simpler case where D/2 is large, so that $ze\psi_{D/2} <<kT$. We can then expand eqn 2.23 as a power series $\cosh(x) = 1+x2/2! + x4/4! + ..$ to obtain:

$$F_{rep} = \rho_{i,0}kT\left(ze\psi_{D/2}\middle/kT\right)^2 ----2.24$$

We recall that κ is given by

$$\kappa^2 = \sum_i (z_i e)^2 \rho_{\infty i} / \varepsilon_0 \varepsilon_r kT ----2.11$$

We obtain

$$F_{rep} = \frac{\kappa^2 \varepsilon_0 \varepsilon_R}{2}\psi_{D/2}^2 ------------2.25$$

This still contains $\psi_{D/2}$ which is unknown. We now say that the potential at $\psi_{D/2}$ between two particles is simply twice that from each individual surface. Using the Debye Huckel Approx, eqn 2.13 for ψ we obtain

Charged Surfaces

$$F_{rep} = 2\kappa^2 \varepsilon_0 \varepsilon_R \psi_0^2 \exp(-\kappa D /) ----- 2.26$$

- What we are really after is the energy of interaction between two charged surfaces so that it can be compared to the van der Waals Energy, *i.e.*

$$W_{REP}(D) = -\int F_{REP} dD ---- 2.27$$

- We can now integrate eqn 2.26 to give

$$W(D)_{rep} = 2\kappa \varepsilon_R \varepsilon_0 \psi_0^2 \exp[-\kappa D] --- 2.28$$

- For spheres of radius R the equivalent equation is

$$W(D)_{rep} = 2\kappa \varepsilon_R \varepsilon_0 R \psi_0^2 \exp[-\kappa D] --- 2.29$$

TOTAL INTERACTION BETWEEN PARTICLES

- The total interaction between charged particles, *i.e.* taking into account van der Waals interactions is simply the sum of the van der Waals and double layer interactions,*i.e.*

$$W(D)_{Tot} = -\frac{AR}{12D} + 2\kappa\varepsilon_R\varepsilon_0 R\psi_0^2 \exp[-\kappa D] - - - 2.30$$

https://www.youtube.com/watch?v=5uuQ77vAV_U&feature=related

- This summation is known as the DLVO theory after the people who came up with the idea, Derjaguin and Landau in Soviet Union and Verwey and Overbeek in the Netherlands.

- **Use this equation to explore the nature of the interaction between colloidal particles. Take ψ_0 to vary from 0 to 100 mV, κ to vary form 0.1 to 10^{-5} M NaCl, and R to vary between 10 nm and 1.0 μm.**

Electrokinetic phenomena

- The zeta potential is determined by measuring the electrophoretic mobility of the particle, u_e, which is the velocity of the particle, v in an electric field E, i.e

$$u_E = \frac{v}{E}$$

- The mobility is a function of the zeta potential, ζ, the viscosity of the suspending medium and the ratio of the particle radius to the electrical double layer thickness (κR)

$$u_E = \frac{4\pi\varepsilon_0\varepsilon_R\zeta}{\eta} f(\kappa R)$$

Where ε_R is the dielectric constant. For large κR, $f(\kappa R)$ =1.5, i.e. large particles and high electrolyte and for small κR, $f(\kappa R)$ =1, i.e. small particles dilute electrolyte.

Zeta Potential