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Colloidal Stability

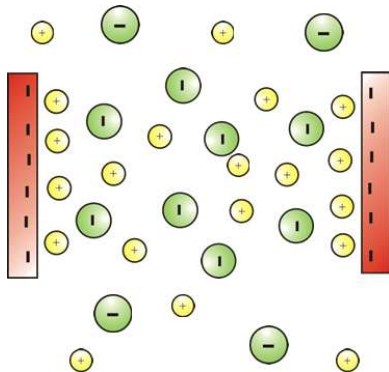
Force & function at the nanoscale



Recap Last lecture

Recall from earlier, the key idea of osmotic pressure which arises due to concentration differences

Due to the charge on the plates there is concentration difference in ions between plates (high) and in bulk (low)



Osmotic pressure pushes fluid between the plate resulting in a repulsive force

We derived the pressure in terms of the potential



$$\Pi = n_0 \frac{z^2 e^2}{k_B T} (V(x))^2$$



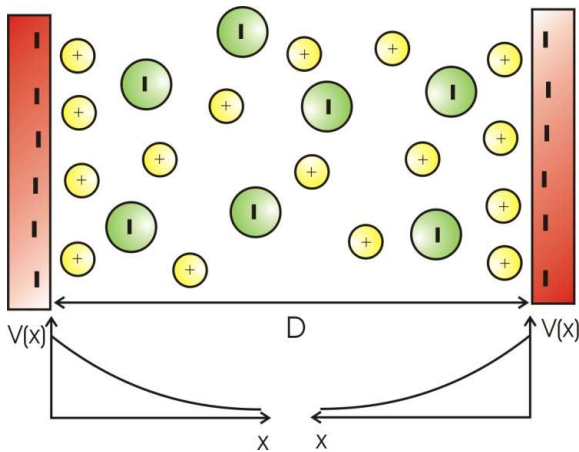
The Debye screening length

Assuming that the potential decays to zero for infinite x , this equation has a solution which is a simple exponential decay

$$V(x) = V_0 \exp(-\kappa x)$$

Where $1/\kappa$ is the Debye screening length

$$\frac{1}{\kappa} = \left(\frac{\epsilon \epsilon_0 k_B T}{2n_0 z^2 e^2} \right)^{1/2}$$



$1/\kappa$ is the distance over which electrostatic interactions are screened in an electrolyte and V_0 is the potential at the surface



12.2 Problem– Two charged surfaces in salt water

A surface is charged to a surface potential of 10 mV and is suspended in water ($\epsilon = 80$) which also has a monovalent salt dissolved in it. $\epsilon_0 = 8.854 \times 10^{-12} \text{ Fm}^{-1}$, $e = 1.602 \times 10^{-19} \text{ C}$, $N_A = 6 \times 10^{23}$, $k_B = 1.38 \times 10^{-23} \text{ m}^2 \text{ kgs}^{-2} \text{ K}^{-1}$, $T = 300 \text{ K}$

Calculate the Debye screening length at room temperature if the salt concentration is

a) 1 mM

b) 100 mM

$$\frac{1}{\kappa} = \left(\frac{\epsilon \epsilon_0 k_B T}{2 n_0 z^2 e^2} \right)^{1/2}$$

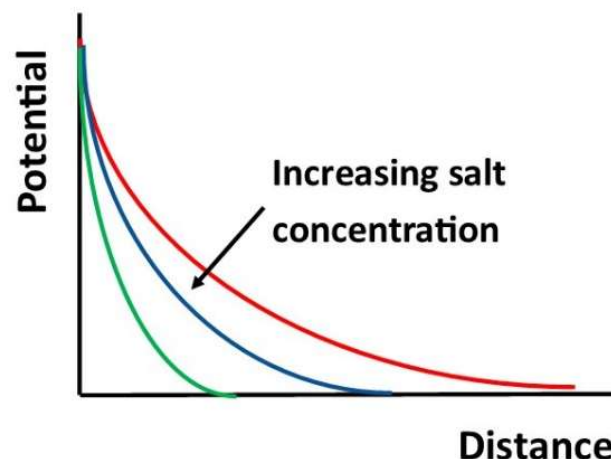


Effect of salt on the decay of potential

κ^{-1} is the Debye screening length and determines the distance over which a charged particle's potential can be felt

$$\kappa^{-1} = \left(\frac{\epsilon \epsilon_0 k_B T}{2 e^2 n_0 z^2} \right)^{0.5} \approx \frac{0.304 \text{ nm}}{\sqrt{[NaCl]}}$$

The electrostatic screening of particles is strongly effected by the concentration of ionic charges in solution

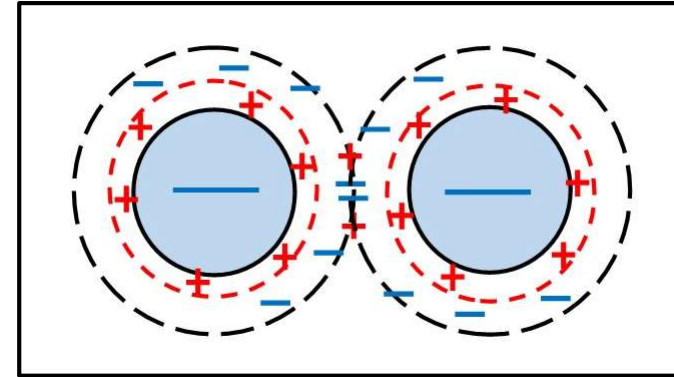


$$\frac{1}{\kappa} = \left(\frac{\epsilon \epsilon_0 k_B T}{2 n_0 z^2 e^2} \right)^{1/2}$$



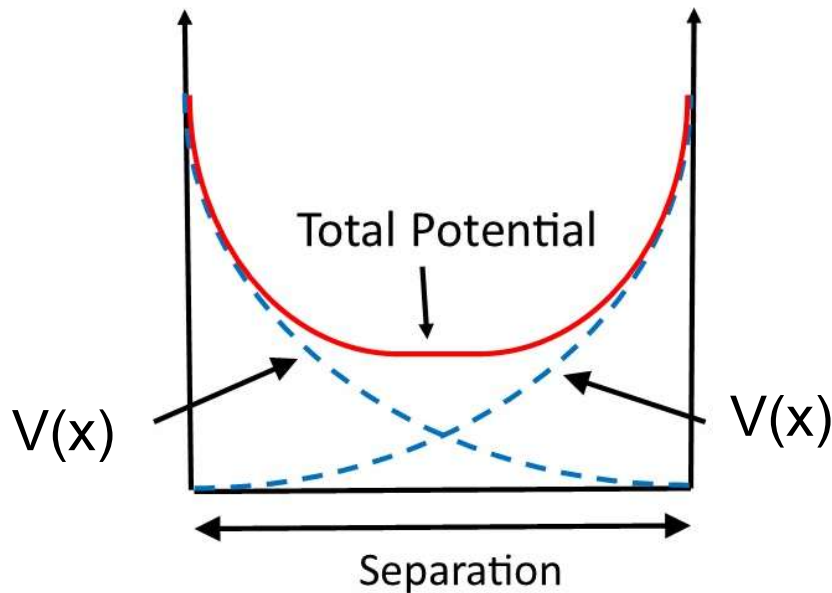
12.3 – Derivation, Repulsion between charged surfaces

As two charged surfaces approach, ions in the fluid move to maintain electrical neutrality



This results in an increase in the concentration of ions in the gap relative to the bulk fluid

$$F = -dU/dD$$

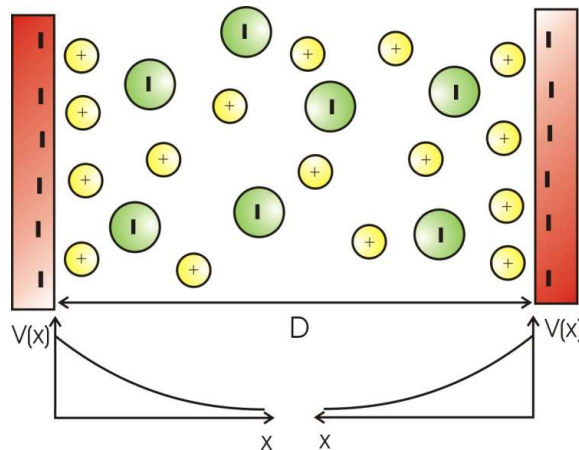




DLVO determining the potential

Recall from earlier that the osmotic pressure due to counterions has the form

$$\Pi = n_0 \frac{z^2 e^2}{k_B T} (V(x))^2$$



If we insert our exponential form for the decay of the potential this gives

$$\Pi = 4n_0 \frac{z^2 e^2 V_0^2}{k_B T} \exp(-\kappa D)$$

where $D=2x$ is the separation between the surfaces



Total pressure between surfaces

The total pressure between two charged surfaces in an electrolyte is

$$P_{tot} = \Pi + P_{dispersion}$$

where $P_{dispersion}$ is the pressure due to attractive dispersion interactions

$$P_{tot} = 4n_0 \frac{z^2 e^2 V_0^2}{k_B T} \exp(-\kappa D) - \frac{A}{6\pi D^3}$$

osmotic pressure

attractive dispersion forces

This is a simplified form of the Derjaguin, Landau, Verwey, Overbeek (DLVO) theory of colloidal stability



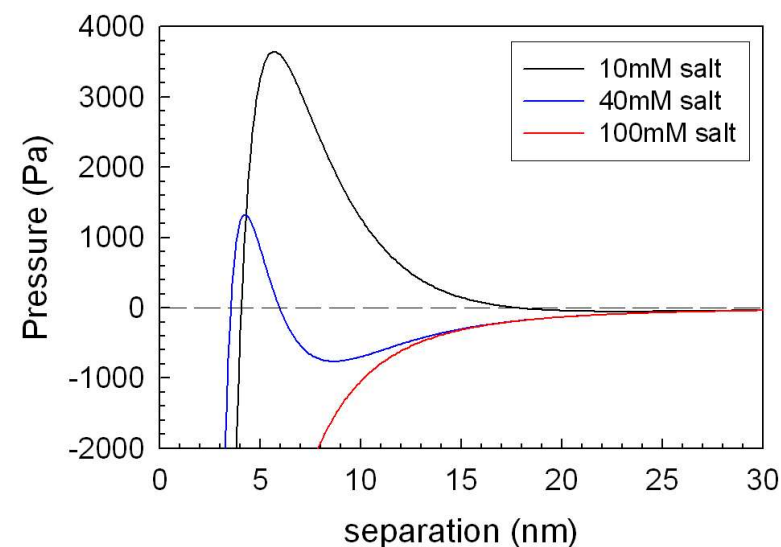
This equation is a simplified version of the DLVO theory – Derjaguin, Landau, Verwey, Overbeek

$$P_{tot} = 4n_0 \frac{z^2 e^2 V_0^2}{k_B T} \exp(-\kappa D) - \frac{A}{6\pi D^3}$$

It controls whether particles come together and stick or stay separate in suspension.

Through changing the amount of salt we can create potential shapes with an energy barrier and even a secondary minimum.

This allows one to manipulate whether particles remain separate or clump together.





Colloidal stability (Overview)

As two charged particles approach, ions in the fluid move to maintain electrical neutrality

This results in an increase in the concentration of ions in the gap relative to the bulk fluid

The concentration difference in ions leads to a chemical potential and subsequent pressure difference between the bulk fluid and the gap.

Assuming the pressure difference is larger than the pressure due to dispersion forces, there will be a flow of liquid into the gap pushing the particles apart.

