Module 7: "Surface Thermodynamics"

Lecture 35:""

The Lecture Contains:

Previous Next

Charge Density

Till now we have calculated potential as a function on distance. In this section we will calculate surface charge density as a function of surface potential. Surface Charge density (s) can be defined as charge per unit area.

$$\sigma = \frac{q}{A}$$

System as a whole is electrically neutral. Thus,

$$\sigma + \int_0^{\infty} \rho dx = 0 \tag{9.19}$$

Where the integral term is the net charge per unit area and ρ is the charge density.

Also from Poisson equation we have,

$$\frac{d^2\Psi}{dx^2} = -\frac{\rho}{\varepsilon}$$

Substituting ρ from equation (9.20) in equation (9.19) we have,

$$\sigma = \varepsilon \int_0^\infty \frac{d^2\Psi}{dx^2} dx$$

$$\sigma = \varepsilon \left(\frac{d\Psi}{dx}\right)_0^\infty$$

dψ/dx is zero at infinity so

$$\frac{d\Psi}{dx} \to 0 \quad x \to 0$$

$$\sigma = -\varepsilon \left(\frac{d\Psi}{dx}\right)_0 \qquad (9.20)$$

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dψ/dx is zero at infinity so

$$\frac{d\Psi}{dx} \to 0 \quad x \to \infty$$

$$\sigma = \varepsilon \left(\frac{d\Psi}{dx}\right)_0 \qquad (9.21)$$

Previous Next

This is a general expression of s in terms of ψ. Knowing the function of ψ we can calculate dψ/dx at zero. For symmetric electrolyte we have calculated ψ in Gouy Chapman theory. Thus,

$$\left.\frac{d\Psi}{dx}\right|_{x=0} = \left(\frac{2kTn_0}{\varepsilon}\right)^{\frac{1}{2}}\left[\exp\left(\frac{-ze\Psi_0}{2kT}\right) - \exp\left(\frac{ze\Psi_0}{2kT}\right)\right] \tag{9.22}$$

The value of 2kT/e at 25°C will be

$$\frac{2kT}{e} = \frac{2\times(1.38\times10^{-23})\times 298}{1.6\times10^{-19}}$$

$$51.4\text{mV}$$

If we also assume surface potential to be small or Debye-Huckel (DH) approximation to be valid following condition must be satisfied

$$\frac{ze\Psi_0}{2kT} < 1$$

$$\Psi_0 < \frac{2kT}{ze} \approx \frac{51}{z}\text{mV}$$

So, for z =1, ψ<50mV and for z = 2, ψ<26. For low potential we have

$$\left.\frac{d\Psi}{dx}\right|_{x=0} = -k\Psi_0$$

Thus,

$$\sigma = \frac{\varepsilon\Psi_0}{K^{-1}}$$

In the case of and similar fluid based systems, direct measurement of the surface charge is impossible due to small sizes of the objects. Instead,measurement yields information for calculation surface charge.

Force Between Two Particles

In the sections earlier we have discussed only one charged surface in an electrolyte. In practical situation there will be more than one charge surface. In this section we will calculate force per unit area between two charged particles in an electrolyte. Consider two parallel plates placed in an electrolyte separated by distance d as shown in figure below. Bulk concentration of electrolyte is no. We will look at the steady state situation. We take a case when both the surfaces have same surface potential ψ_o.

Electrical force per unit charge is given by gradient of potential.

$$F' = \frac{d\Psi}{dx}$$

Thus force per unit volume is given by product of charge density and potential gradient.

$$\text{Force per unit volume} = -\frac{d\Psi}{dx}\rho$$

$$\text{Force on an ion of charge } (ze) = -\frac{d}{dx}(ze\Psi)$$

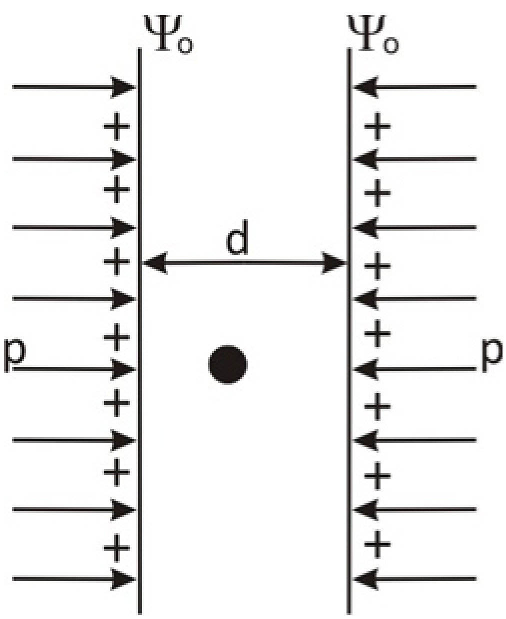

Fig. 9.2: Force between two particles.

Since we are looking at static and steady state, the forces must balance. Thus from Navier Stroke equation we have,

$$\rho_d \frac{D^1 v}{Dt} \nabla p - \nabla \emptyset + \nabla^{2\frac{F}{v}} \qquad (9.23)$$

F is for electric body force per unit volume here equal to $-\frac{d\Psi}{dx}\rho$