

# Lecture 11

## Electrical Double Layer at Solid-Electrolyte Interface

### 11.1 The Poisson-Boltzmann equation

In Lecture 8 we have seen the Poisson equation as the governing equation for electrostatic problem in dielectric media. The Poisson equation is also applicable to model the distribution of ions in a electrolyte solution near the electrodes, where the solvated ions are mobile due to highly screening electrostatic interaction between individual ions in a high-permittivity environment. If both the electric potential and the concentration are small, the concentration of ions  $i$  at position  $r$ ,  $c_i(r)$ , follows the Boltzmann distribution, such that:

$$c_i(r) = c_{i,0} \exp\left(\frac{-E_i}{k_B T}\right) = c_{i,0} \exp\left(\frac{-ez_i\psi(r)}{k_B T}\right) \quad (11.1)$$

where  $c_{i,0}$  is the bulk number concentration (unit:  $\text{m}^{-3}$ ) of the ion when  $\psi = 0$ ,  $z_i$  is the valence of ion,  $k$  is the Boltzmann constant and  $T$  is the temperature. therefore a cation (positively charged) is depleted while an anion (negatively charged) accumulates in the region where  $\psi > 0$ . Insert Equation 11.1 into the Poisson equation we get the Poisson-Boltzmann equation of electrolytes

$$\begin{aligned} \nabla^2\psi &= -\sum_i \frac{z_i e \rho_i}{\epsilon_0 \epsilon_r} \\ &= -\frac{e}{\epsilon_0 \epsilon_r} \sum_i z_i c_{i,0} \exp\left(-\frac{ez_i\psi}{k_B T}\right) \end{aligned} \quad (11.2)$$

Here we only consider the simplest 1D case, where an infinitely-large plate electrode is inserted into the electrolyte solution.  $\nabla^2\psi$  is now simplified as  $d^2\psi/dx^2$ , where  $x$  is the coordinate perpendicular to the plate. Consider the following boundary conditions (Figure 11.1):

- $\psi = 0$  when  $x \rightarrow \infty$
- $\frac{d\psi}{dx} = 0$  when  $x \rightarrow \infty$

- $\psi = \psi_0$  when  $x = 0$

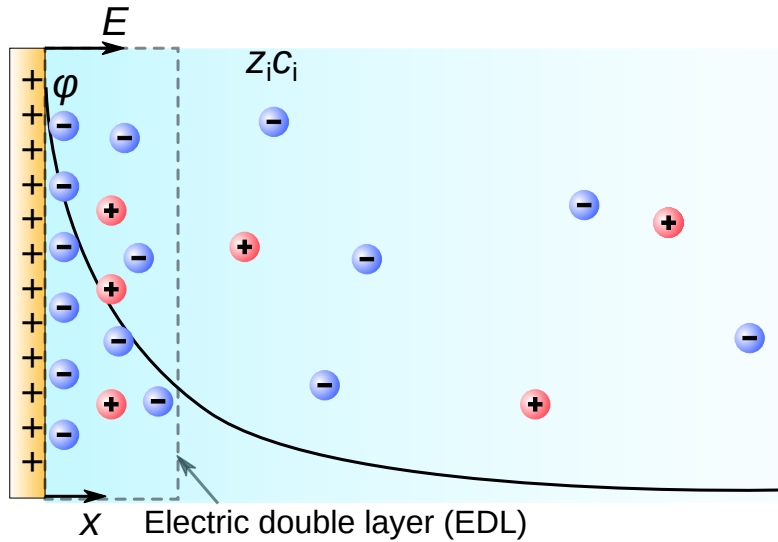


Figure 11.1: Scheme of the concentration of electrolyte near a charged interface. The region of electric double layer is shown.

From Gauss's law we know the surface charge on the conducting plate  $\sigma_M$  is related to  $d\psi/dx$  at  $x = 0$ :

$$\begin{aligned}
 \sigma_M &= - \int_0^{\infty} \rho dx \\
 &= \epsilon_0 \epsilon_r \left. \frac{d\psi}{dx} \right|_0^{\infty} \\
 &= -\epsilon_0 \epsilon_r \left. \frac{d\psi}{dx} \right|_{(x=0)}
 \end{aligned}
 \tag{11.3}$$

Although the Poisson-Boltzmann equation (Equation 11.2) is mostly calculated numerically due to the nonlinear term on the right hand side, it is still possible to obtain an analytical solution after certain approximation / simplifications. We will introduce two of such approaches, namely the Debye-Hückel approximation and the Gouy-Chapman solution in this lecture to reveal some fundamental properties of the electrolyte interface.

## 11.2 Debye-Hückel approximation

The Debye-Hückel (DH) approximation considers that the electrical potential of ions  $z_i e \psi$  is much smaller than  $k_B T$ . In this case the exponential parts is expanded using Taylor series

to the first order, and the charge density in the electrolyte solution becomes:

$$\begin{aligned}
 \rho &= \sum_i z_i e c_{i,0} \exp\left(-\frac{z_i e \psi}{k_B T}\right) \\
 &= \sum_i z_i e c_{i,0} \left(1 - \frac{z_i e \psi}{k_B T}\right) \\
 &= -\psi \sum_i \frac{z_i^2 e^2 c_{i,0}}{k_B T}
 \end{aligned} \tag{11.4}$$

By defining  $\kappa = \left[ \sum_i \frac{z_i^2 e^2 c_{i,0}}{\epsilon_0 \epsilon_r k_B T} \right]^{1/2}$ , the Debye-Hückel approximation is written as:

$$\nabla^2 \psi = \kappa^2 \psi \tag{11.5}$$

In the 1D case, the solution to 11.5 is:

$$\psi = \psi_0 \exp(-\kappa x) \tag{11.6}$$

which indicates the electrical potential decays exponentially. The characteristic length of  $\psi$  is thus  $\kappa^{-1}$ . If  $\psi_0 > 0$ , the cations are depleted and the anions are accumulated at the interface, forming a structure called the **electrical double layer** (EDL).  $\kappa^{-1}$  characterizes the thickness of the EDL, and is also frequently referred as the Debye length  $\lambda_D$ .

In chemistry the molar concentration  $M_{i,0}$  (in mol·L<sup>-1</sup>) is usually used instead of the number concentration  $c_{i,0}$  in the original DH approximation.  $\kappa$  in this case is written as:

$$\begin{aligned}
 \kappa &= \left[ \frac{1000 e^2 N_a}{\epsilon_0 \epsilon_r k_B T} \sum_i z_i^2 M_{i,0} \right]^{1/2} \\
 &= \left[ \frac{1000 e^2 N_a}{\epsilon_0 \epsilon_r k_B T} \right]^{1/2} \sqrt{2I}
 \end{aligned} \tag{11.7}$$

where  $I = 1/2 \sum_i z_i^2 M_{i,0}$  is the **ionic strength** of the electrolyte solution. At 25 °C the Debye length can be approximated with  $\kappa = 0.431/\sqrt{2I}$  nm if  $I$  is in mol·L<sup>-1</sup>. For example 10 mM KCl solution has a Debye length of 3.05 nm. There are several aspects influencing the Debye length  $\kappa^{-1}$ :

- The permittivity of the solvent  
 $\kappa^{-1} \propto \epsilon_r^{1/2}$ : the larger  $\epsilon_r$  is, the longer the Debye length.
- The ionic strength  
 $\kappa^{-1} \propto I^{-1/2}$ : the larger  $I$  is, the shorter the Debye length.

The Double layer also have capacitance: the higher  $\psi_0$  is, the more charges accumulates at the electrode plate. In the DH approximation,  $\sigma_M = -\epsilon_0 \epsilon_r \frac{d\psi}{dx}(x=0) = \epsilon \epsilon_r \kappa \psi_0$ , therefore

the differential capacitance per area  $C_{\text{DH}}$  is:

$$\begin{aligned} C_{\text{DH}} &= \frac{d\sigma_{\text{M}}}{d\psi_0} \\ &= \frac{d(\varepsilon\varepsilon_r\kappa\psi_0)}{d\psi_0} \\ &= \frac{\varepsilon_0\varepsilon_r}{\kappa^{-1}} \end{aligned} \quad (11.8)$$

which resembles a parallel plate capacitance with relative permittivity  $\varepsilon_r$  and thickness  $\kappa^{-1}$ .

### 11.3 Gouy-Chapman solution

The DH approximation can only be valid when  $z_+e\psi/k_{\text{B}}T \ll 1$ , i.e.  $\psi \ll 25$  mV at 300 K, which is not the case for most electrochemical reactions. However there is one situation where analytical solution in 1D is still available, known as the Gouy-Chapman solution, where the electrolyte only contains one salt with  $z_+ = -z_- = z$ . The Poisson-Boltzmann equation in GC assumption is written as:

$$\begin{aligned} \frac{d^2\psi}{dx^2} &= -\frac{zc_0e}{\varepsilon_0\varepsilon_r} \left[ \exp\left(-\frac{ze\psi}{k_{\text{B}}T}\right) - \exp\left(\frac{ze\psi}{k_{\text{B}}T}\right) \right] \\ &= \frac{2zc_0e}{\varepsilon_0\varepsilon_r} \sinh\left(\frac{ze\psi}{k_{\text{B}}T}\right) \end{aligned} \quad (11.9)$$

The solution to the GC equation is:

$$\frac{\tanh(ze\psi/4k_{\text{B}}T)}{\tanh(ze\psi_0/4k_{\text{B}}T)} = \exp(-\kappa x) \quad (11.10)$$

The charge on the conducting plate is:

$$\sigma_{\text{M}} = \sqrt{8k_{\text{B}}T\varepsilon_0\varepsilon_r c_0} \sinh\left(\frac{ze\psi_0}{2k_{\text{B}}T}\right) \quad (11.11)$$

And the capacitance from the GC solution is:

$$C_{\text{GC}} = \sqrt{\frac{2z^2e^2\varepsilon_0\varepsilon_r c_0}{k_{\text{B}}T}} \cosh\left(\frac{ze\psi_0}{2k_{\text{B}}T}\right) = \frac{\varepsilon_0\varepsilon_r}{\kappa^{-1}} \cosh\left(\frac{ze\psi_0}{2k_{\text{B}}T}\right) \quad (11.12)$$

Unlike  $C_{\text{DH}}$ ,  $C_{\text{GC}}$  depends on both  $\kappa^{-1}$  and  $\psi_0$ , and increases rapidly with  $\psi_0$ . Nevertheless, when  $\psi_0 \rightarrow 0$ , we have  $C_{\text{GC}} \approx C_{\text{DH}}$ . For a 1:1 electrolyte solution with concentration of 1 M and  $\psi_0 = 50$  mV,  $C_{\text{GC}}$  is  $\sim 330 \mu\text{F}\cdot\text{cm}^{-2}$ . This is a considerably large capacitance, which is not possible to achieve using even high-permittivity solid statics. For instance such capacitance is equivalent to that in a 10.4 pm thick  $\text{SiO}_2$  ( $\varepsilon_r = 3.9$ ) layer or 2.2 Å thick  $\text{TiO}_2$  ( $\varepsilon_r = 80$ ) layer, both are thinner than even one single lattice. Therefore the electrolyte EDL has been used for creating supercapacitors<sup>1</sup> and gating materials in solid state transistors.<sup>2</sup> However, practical considerations should also be given, since a higher electrolyte concentration also leads to larger leakage current in supercapacitors.

## References

- (1) Conway, B. E. *J. Electrochem. Soc.* **1991**, *138*, 1539.
- (2) Lee, J.; Panzer, M. J.; He, Y.; Lodge, T. P.; Frisbie, C. D. *J. Am. Chem. Soc.* **2007**, *129*, 4532–4533.