

6.7: Ion Distributions Near a Charged Interface

Debye–Hückel Approximation

Describing ions near a negatively charged plane is a way of describing the diffuse layer of cations that forms near the negatively charged interface in lipid bilayers. The simplest approach is to use the Debye–Hückel equation (linearized PBE) in one dimension. x is the distance away from the infinite charged plane with a surface charge density of $\sigma = q/a$.

$$\frac{\partial^2 \Phi(x)}{\partial x^2} = \frac{1}{\lambda_D^2} \Phi(x)$$

Generally, the solution is

$$\Phi(x) = a_1 e^{-x/\lambda_D} + a_2 e^{x/\lambda_D} \quad (6.7.1)$$

Apply boundary conditions:

1. $\lim_{x \rightarrow \infty} \Phi(x) = 0 \therefore a_2 = 0$
2. The electric field for surface with charge density σ (from Gauss' theorem)

$$E = -\frac{\partial \Phi}{\partial x} \Big|_{\text{surface}} = \frac{\sigma}{\epsilon} \quad (6.7.2)$$

Differentiate eq. (6.7.1) and compare with eq. (6.7.2):

$$a_1 = \frac{\sigma \lambda_D}{\epsilon}$$

The electrostatic potential decays exponentially away from the surface toward zero.

$$\Phi(x) = \frac{\sigma \lambda_D}{\epsilon} e^{-x/\lambda_D}$$

Nominally, the prefactor would be the "surface potential" at $x = 0$, but the Debye approximation would significantly underestimate this, as we will see later. Substituting Φ into the Poisson equation gives

$$\rho(x) = \frac{-\sigma}{\lambda_D} e^{-x/\lambda_D} \quad (6.7.3)$$

Ion distribution density in solution decays exponentially with distance. This description is valid for weak potentials, or $x > \lambda_D$. The potential and charge density are proportional as $\Phi(x) = -\lambda_D^2 \rho(x)/\epsilon$; both decay exponentially on the scale of the Debye length at long range.

Note:

Higher ion concentration \rightarrow smaller $\lambda_D \rightarrow$ Double layer less diffuse.

Higher temperature \rightarrow larger $\lambda_D \rightarrow$ Double layer more diffuse.

Note also that the surface charge is balanced by ion distribution in solution:

$$\sigma = - \int_0^\infty \rho(x) dx \quad (6.7.4)$$

which you can confirm by substituting eq. (6.7.3).

Gouy–Chapman Model¹

To properly describe the ion behavior for shorter distances ($x < \lambda_D$), one does not need to make the weak-potential approximation and can retain the nonlinear form of the Poisson–Boltzmann equation:

$$\begin{aligned} \frac{\partial^2 \Phi(x)}{\partial x^2} &= \frac{2zeC_0}{\epsilon} \sinh\left(\frac{ze\Phi(x)}{kT}\right) \\ E &= -\frac{\partial \Phi}{\partial x} \Big|_{\text{surf}} = \frac{4\pi\ell_B\sigma k_B T}{e^2} \end{aligned}$$

In fact, this form does have an analytical solution. It is helpful to define a dimensionless reduced electrostatic potential, expressed in thermal electric units:

$$\underline{\Phi} = \frac{e}{k_B T} \Phi$$

and a reduced distance which is scaled by the Debye length

$$\underline{x} = x / \lambda_D$$

Then the PBE for a 1:1 electrolyte takes on a simple form

$$\nabla^2 \underline{\Phi}(x) = \sinh \underline{\Phi}(x)$$

with the solution:

$$\underline{\Phi}(\underline{x}) = 2 \ln \left(\frac{1 + g e^{-\underline{x}}}{1 - g e^{-\underline{x}}} \right)$$

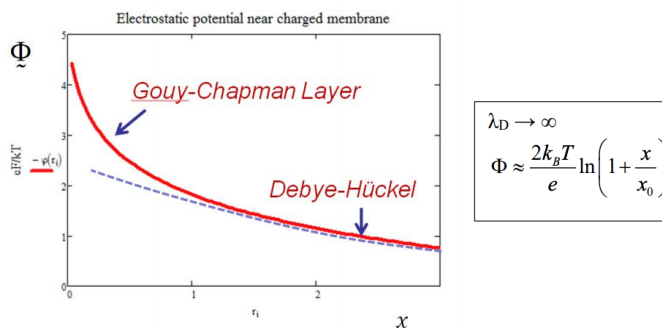
Here g is a constant, which we can relate to the surface potential, by setting x to zero.

$$\exp(-\underline{\Phi}(0)/2) = \frac{1-g}{1+g} = -\tanh(\ln(g)/2)$$

$\underline{\Phi}(0)$ is the scaled surface potential. Using the surface charge density σ we can find:

$$g = -\frac{x_0}{\lambda_D} + \sqrt{1 + \left(\frac{x_0}{\lambda_D}\right)^2} \text{ with } x_0 = \frac{e}{2\pi\ell_B\sigma}$$

Then you can get the ion distribution from Poisson equation: $\rho(x) = \varepsilon \nabla^2 \Phi(x)$.



The **Gouy-Chapman Layer**, which is $x < \lambda_D$, has strong enough ionic interactions that you will see an enhancement over Debye-Hückel.

Stern Layer

In immediate proximity to a strongly charged surface, one can form a direct contacts layer of counterions on surface: the **Stern layer**. The Stern Layer governs the slip plane for diffusion of charged particles. The zeta potential ζ is the potential energy difference between the Stern layer and the electroneutral region of the sample, and governs the electrophoretic mobility of particles. It is calculated from the work required to bring a charge from $x = \infty$ to the surface of the Stern layer.

1. H. H. Girault, *Analytical and Physical Electrochemistry*. (CRC Press, New York, 2004).; M. B. Jackson, *Molecular and Cellular Biophysics*. (Cambridge University Press, Cambridge, 2006), Ch. 11.; M. Daune, *Molecular Biophysics: Structures in Motion*. (Oxford University Press, New York, 1999), Ch. 18.; S. McLaughlin, The electrostatic properties of membranes, *Annu. Rev. Biophys. Biophys. Chem.* 18, 113-136 (1989).

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