

6.6: Debye–Hückel Theory

Since it is nonlinear, it is not easy to solve the PBE, but for certain types of problems, we can make approximations to help. The **Debye–Hückel approximation** holds for small electrostatic potential or high temperature conditions such that

$$\frac{ze\Phi}{k_B T} \ll 1$$

This is the regime in which the entropy of mixing dominates the electrostatic interactions between ions. In this limit, we can expand the exponential in eq. (6.5.5) as $\exp[-ze\Phi/k_B T] \approx 1 - ze\Phi/k_B T$. The leading term in the resulting sum drops because of the charge neutrality condition, eq. (6.5.4). Keeping the second term in the expansion leads to

$$\nabla^2 \Phi = \kappa^2 \Phi \quad (6.6.1)$$

where

$$\kappa^2 = \frac{2e^2}{\epsilon k_B T} I$$

and the ionic strength, I , is defined as

$$I = \frac{1}{2} \sum_i C_{0,i} z_i^2$$

Looking at eq. (6.6.1), we see that the Debye–Hückel approximation linearizes the PBE. It is known as the Debye–Hückel equation, or the linearized PBE. For the case of the 1:1 electrolyte solution described by eq. , we again obtain eq. (6.6.1) using $\sinh(x) \approx x$ as $x \rightarrow \infty$, with

$$\kappa^2 = \frac{2z^2 e^2 C_0}{\epsilon k_B T} = 8\pi z^2 C_0 \ell_B$$

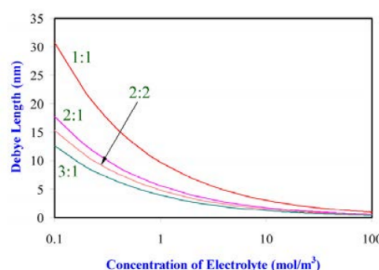
The constant κ has units of inverse distance, and its inverse is known as the **Debye length** $\lambda_D = \kappa^{-1}$. The Debye length sets the distance scale over which the electrostatic potential decays, i.e., the distance over which charges are screened from one another. For the symmetric electrolytes

$$\lambda_D = \kappa^{-1} = \sqrt{\frac{\epsilon k_B T}{2z^2 e^2 C_0}} \quad (6.6.2)$$

As an example: 1:1 electrolytes in H_2O : $\epsilon = 80$; $z_+ = -z_- = 1$; $T = 300 \text{ K}$ leads to

$$\begin{aligned} C_0 = 100 \text{ mM} & \quad \lambda_D = 9.6 \text{ \AA} \\ C_0 = 10 \text{ mM} & \quad \lambda_D = 30.4 \text{ \AA} \\ \lambda_D(\text{\AA}) & \approx 3.04 \cdot [C_0(\text{M})]^{-1/2} \end{aligned}$$

The Debye approximation holds for small electrostatic potentials relative to $k_B T$ ($r > \lambda_D$). For instance, it's ok for ion distribution about large protein or vesicle but not for water in a binding pocket.



The variation of Debye length with concentrations of electrolytes. Reprinted from P. Ghosh
<http://nptel.ac.in/courses/103103033/module3/lecture3.pdf>.

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