Debye–Hückel Theory

Mobile charges like Na\(^+\) or Cl\(^-\) ions are very important for the functioning of Biomolecules. In a stationary state, their concentration depends on the local electrostatic field which is produced by the charge distribution of the Biomolecule, which in turn depends for instance on the protonation state and on the conformation. In this chapter, we present continuum models to describe the interaction between a Biomolecule and surrounding mobile charges [17–20].

4.1 Electrostatic Shielding by Mobile Charges

We consider a fully dissociated (strong) electrolyte containing \(N_i\) mobile ions of the sort \(i = 1\ldots\) with charges \(Z_ie\) per unit volume. The charge density of the mobile charges is given by the average numbers of ions per volume:

\[
\varrho_{\text{mob}}(r) = \sum_i Z_i e N_i(r).
\]

The electrostatic potential is given by the Poisson equation:

\[
\varepsilon \Delta \phi(r) = -\varrho(r) = -\varrho_{\text{mob}}(r) - \varrho_{\text{fix}}(r).
\]

Debye and Hückel [21] used Boltzmann’s theorem to determine the mobile charge density. Without the presence of fixed charges, the system is neutral:

\[
0 = \varrho_{\text{mob}}^0 = \sum_i Z_i e N_i^0
\]

and the constant value of the potential can be chosen as zero:

\[
\phi^0 = 0.
\]

The fixed charges produce a change of the potential. The electrostatic energy of an ion of sort \(i\) is
and the density of such ions is given by a Boltzmann distribution:

\[
N_i(r) = \frac{e^{-Z_i e\phi(r)/k_B T}}{e^{-Z_i e\phi^0/k_B T}}
\]  
(4.6)

or

\[
N_i(r) = N_i^0 e^{-Z_i e\phi(r)/k_B T}.
\]  
(4.7)

The total mobile charge density is

\[
\rho_{\text{mob}}(r) = \sum_i Z_i e N_i^0 e^{-Z_i e\phi(r)/k_B T}
\]  
(4.8)

and we obtain the Poisson–Boltzmann equation:

\[
\varepsilon \Delta \phi(r) = -\sum_i Z_i e N_i^0 e^{-Z_i e\phi(r)/k_B T} - \rho_{\text{fix}}(r).
\]  
(4.9)

If the solution is very dilute, we can expect that the ion–ion interaction is much smaller than thermal energy:

\[
Z_i e\phi \ll k_B T
\]  
(4.10)

and linearize the Poisson–Boltzmann equation:

\[
\varepsilon \Delta \phi(r) = -\rho_{\text{fix}}(r) - \sum_i Z_i e N_i^0 e^{-Z_i e\phi(r)/k_B T} - \rho_{\text{fix}}(r).
\]  
(4.11)

The first summand vanishes due to electroneutrality and we find finally

\[
\Delta \phi(r) - \kappa^2 \phi(r) = -\frac{1}{\varepsilon} \rho_{\text{fix}}(r)
\]  
(4.12)

with the inverse Debye length

\[
\lambda_{\text{Debye}}^{-1} = \kappa = \sqrt{\frac{e^2}{\varepsilon k_B T} \sum_i N_i^0 Z_i^2}.
\]  
(4.13)

### 4.2 1−1 Electrolytes

If there are only two types of ions with charges \(Z_{1,2} = \pm 1\) (also in semiconductor physics), the Poisson–Boltzmann equation can be written as

\[
\frac{e}{k_B T} \Delta \phi(r) + \frac{e^2}{\varepsilon k_B T} N^0 (e^{-e\phi(r)/k_B T} - e^{e\phi(r)/k_B T}) = -\frac{e}{\varepsilon k_B T} \rho_{\text{fix}}(r)
\]  
(4.14)