Poisson-Boltzmann Equation for $\psi(x)$ [pln68]

What is the source of model profiles for the electric potential $\psi(x)$ such as used in [pex57]? Consider a scenario with a given profile of bound charges, $n_b(x)$, and the presence of several species $i = 1, 2, \ldots$ of small, mobile ions with yet unknown profiles $n_i(x)$ and charges e_i.

From the condition of chemical equilibrium for each species,

$$\mu_i^{(0)} + k_\mathrm{B}T \ln n_i(x) + e_i\psi(x) = \mu_i^{(0)} + k_\mathrm{B}T \ln n_i^{(s)}, \tag{1}$$

in slight generalization of [pex10] we infer that

$$n_i(x) = n_i^{(s)} e^{-\beta e_i \psi(x)}, \tag{2}$$

where the $n_i^{(s)}$ are uniform ionic densities far away from the bound charges, where $\psi(x) \to 0$. They satisfy the charge neutrality condition, $\sum_i e_i n_i^{(s)} = 0$.

The charge density,

$$\rho_e(x) = e_b n_b(x) + \sum_i e_i n_i(x), \tag{3}$$

slightly generalized from [pln67], substituted into the Poisson equation (see [pln67]) with $n_i(x)$ from (2) yields the Poisson-Boltzmann equation for the profile of the electric potential,

$$\epsilon \frac{d^2}{dx^2}\psi(x) = -e_b n_b(x) - \sum_i e_i\, n_i^{(s)} e^{-\beta e_i \psi(x)}, \tag{4}$$

which has a unique physical solution for given profile $n_b(x)$, asymptotic densities $n_i^{(s)}$, and boundary conditions $\psi(+\infty) = \psi'(+\infty) = 0$.

Debye approximation:

The nonlinear nature of (4) puts an analytic solution out of reach. In the Debye approximation we write $e^{-\beta e_i \psi(x)} \simeq 1 - \beta e_i \psi(x)$, linearizing (4). The linearized Poisson-Boltzmann equation can be brought into the form

$$\frac{d^2}{dx^2}\psi(x) - \kappa^2\psi(x) = -\frac{1}{\epsilon}\, e_b n_b(x), \quad \kappa^2 \doteq \frac{\beta}{\epsilon}\sum_i e_i^2 n_i^{(s)}. \tag{5}$$

[gleaned from Doi 2013]