6.5: Poisson–Boltzmann Equation

Poisson–Boltzmann Equation[1]

The **Poisson–Boltzmann Equation** (PBE) is used to evaluate charge distributions for ions around charged surfaces. It brings together the description of the electrostatic potential around a charged surface with the Boltzmann statistics for the thermal ion distribution. Gauss' equation relates the flux of electric field lines through a closed surface to the charge density within the volume: $\nabla \cdot \bar{E} = \rho/\varepsilon$. The Poisson equation can be obtained by expressing this in terms of the electrostatic potential using $\bar{E} = -\nabla\Phi$

$$-\nabla^2\Phi = \frac{\rho}{\varepsilon} \tag{6.5.1}$$

Here ρ is the bulk charge density for a continuous medium.

We seek to describe the charge distribution of ions about charged surfaces of arbitrary geometry. The surface will be described by a surface charge density σ. We will determine $\rho(r)$, which is proportional to the number density or concentration of ions

$$\rho(r) = \sum_i z_i e C_i(r) \tag{6.5.2}$$

where the sum is over all ionic species in the solution, and z_i is the ion valency, which may take on positive or negative integer values. Drawing from the Nernst equation, we propose an ion concentration distribution of the Boltzmann form

$$C_i(r) = C_{0,i} e^{-z_i e\Phi(r)/k_BT} \tag{6.5.3}$$

Here we have defined the bulk ion concentration as $C_0 = C(r\to\infty)$, since $\Phi \to 0$ as $r \to \infty$. Note that the ionic composition is taken to obey the net charge neutrality condition

$$\sum_i z_i C_{0,i} = 0 \tag{6.5.4}$$

The expressions above lead to the general form of the PBE:

$$-\nabla^2\Phi = \frac{e}{\varepsilon}\sum_i z_i C_{0,i}\exp[-z_i e\Phi/k_BT] \tag{6.5.5}$$

This is a nonlinear differential equation for the electrostatic potential and can be solved for the charge distribution of ions in solution for various boundary conditions. This can explain the ion distributions in aqueous solution about a charged structure. For instance:

- Surface (membrane) $\dfrac{\partial^2\Phi}{\partial x^2} = \dfrac{e}{\varepsilon}\sum_i z_i C_{0,i} e^{-z_i e\Phi(x)/k_BT}$
- Sphere (protein) $\dfrac{1}{r^2}\dfrac{\partial}{\partial r} r^2 \dfrac{\partial\Phi}{\partial r} = \dfrac{e}{\varepsilon}\sum_i z_i C_{0,i} e^{-z_i e\Phi(x)/k_BT}$
- Cylinder (DNA) $\dfrac{1}{r}\dfrac{\partial}{\partial r} r \dfrac{\partial\Phi}{\partial r} + \dfrac{\partial^2\Phi}{\partial z^2} = \dfrac{e}{\varepsilon}\sum_i z_i C_{0,i} e^{-z_i e\Phi(x)/k_BT}$

These expressions only vary in the form of the Laplacian ∇^2. They are solved by considering two boundary conditions: (1) $\Phi(\infty) = 0$ and (2) the surface charge density $\sigma/\epsilon = -\nabla\Phi$. We will examine the resulting ion distributions below.

In computational studies, the interactions of a solute with water and electrolyte solutions are often treated with "implicit solvent", a continuum approximation. Solving the PBE is one approach to calculating the effect of implicit solvent. The electrostatic free energy is calculated from $\Delta G_{\text{elec}} = \frac{1}{2}\sum_i e z_i \Phi_i$ and the electrostatic potential is determined from the PBE.

As a specific case of the PBE, let's consider the example of a symmetric electrolyte, obtained from dissolving a salt that has positive and negative ions with equal valence $(z_+ = -z_- = z)$, resulting in equal concentration of the cations and anions $(C_{0,+} = C_{0,-} = C_0)$, as for instance when dissolving NaCl. Equation (6.5.2) is used to describe the interactions of ions with the same charge (co-ions) versus the interaction of ions with opposite charge (counterions). For counterions, z and Φ have opposite signs and the ion concentration should increase locally over the bulk concentration. For co-ions, z and Φ have the same sign and we expect a lowering of the local concentration over bulk. Therefore, we expect the charge distribution to take a form

$$\begin{aligned} \rho &= -zeC_0\left(e^{ze\Phi/k_BT} - e^{-ze\Phi/k_BT}\right) \\ &= -2zeC_0 \sinh\left(\frac{ze\Phi}{k_BT}\right) \end{aligned} \tag{6.5.6}$$

Remember: $2\sinh(x) = e^x - e^{-x}$. Then substituting into eq. (6.5.1), we arrive at a common form of the PBE[2]

$$\nabla^2\Phi = \frac{2zeC_0}{\varepsilon}\sinh\left(\frac{ze\Phi}{k_BT}\right) \tag{6.5.7}$$

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1. M. Daune, *Molecular Biophysics: Structures in Motion*. (Oxford University Press, New York, 1999); M. B. Jackson, *Molecular and Cellular Biophysics*. (Cambridge University Press, Cambridge, 2006).
2. Alternate forms in one dimension:

$$\frac{\partial^2\Phi}{\partial x^2} = \frac{e}{\varepsilon}C_0 2\sinh\left(\frac{e\Phi}{k_BT}\right) = \frac{k_BT}{e}\frac{1}{\lambda_D^2}\sinh\left(\frac{e\Phi}{k_BT}\right) = \frac{4\pi k_BT}{e}\ell_B C_0 \sinh\left(\frac{e\Phi}{k_BT}\right)$$
