3.3 Abnormal titration curves of coupled residues

Let us consider a simple example of a model protein with only two titrable sites of the same type. The free enthalpies of the four possible states are

$$\Delta G(AH, AH) = \Delta G_1' + \Delta G_2' + E_{1,2}^{1,1} - E_{1,2}^{0,0}$$

$$\Delta G(A-, AH) - \Delta G(AH, AH) = -\Delta G_{1,int}$$

$$\Delta G(AH, A-) - \Delta G(AH, AH) = -\Delta G_{2,int}$$

$$\Delta G(A-, A-) - \Delta G(AH, AH) = -\Delta G_{1,int} - \Delta G_{2,int} + W_{12} =$$
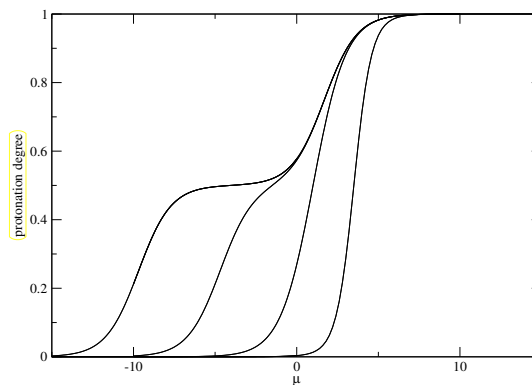
$$= -\Delta G_2' - \Delta G_1' + E_{1,2}^{0,0}$$

The grand partition function is

$$\Xi = 1 + e^{-\beta(-\Delta G_{1,int}+\mu)} + e^{-\beta(-\Delta G_{2,int}+\mu)} + e^{-\beta(-\Delta G_{2,int}-\Delta G_{1,int}+2\mu+W)}$$

The average protonation values are

$$\overline{s_1} = \frac{1 + e^{-\beta(-\Delta G_{2,int}+\mu)}}{\Xi}$$

$$\overline{s_2} = \frac{1 + e^{-\beta(-\Delta G_{1,int}+\mu)}}{\Xi}$$

Figure 40: abnormal titration curves

two interacting residues , neutral state (AH,AH) ,$\Delta G_{1,intr} = \Delta G_{2,intr} = 1.0$, $W = -5, 0, 5, 10$

Part II
Protein Electrostatics and Solvation

Biological macromolecules contain chemical compounds with certain electrostatic properties. These are often modelled using localized electric multipoles (partial charges, dipoles ...) and polarizabilities.

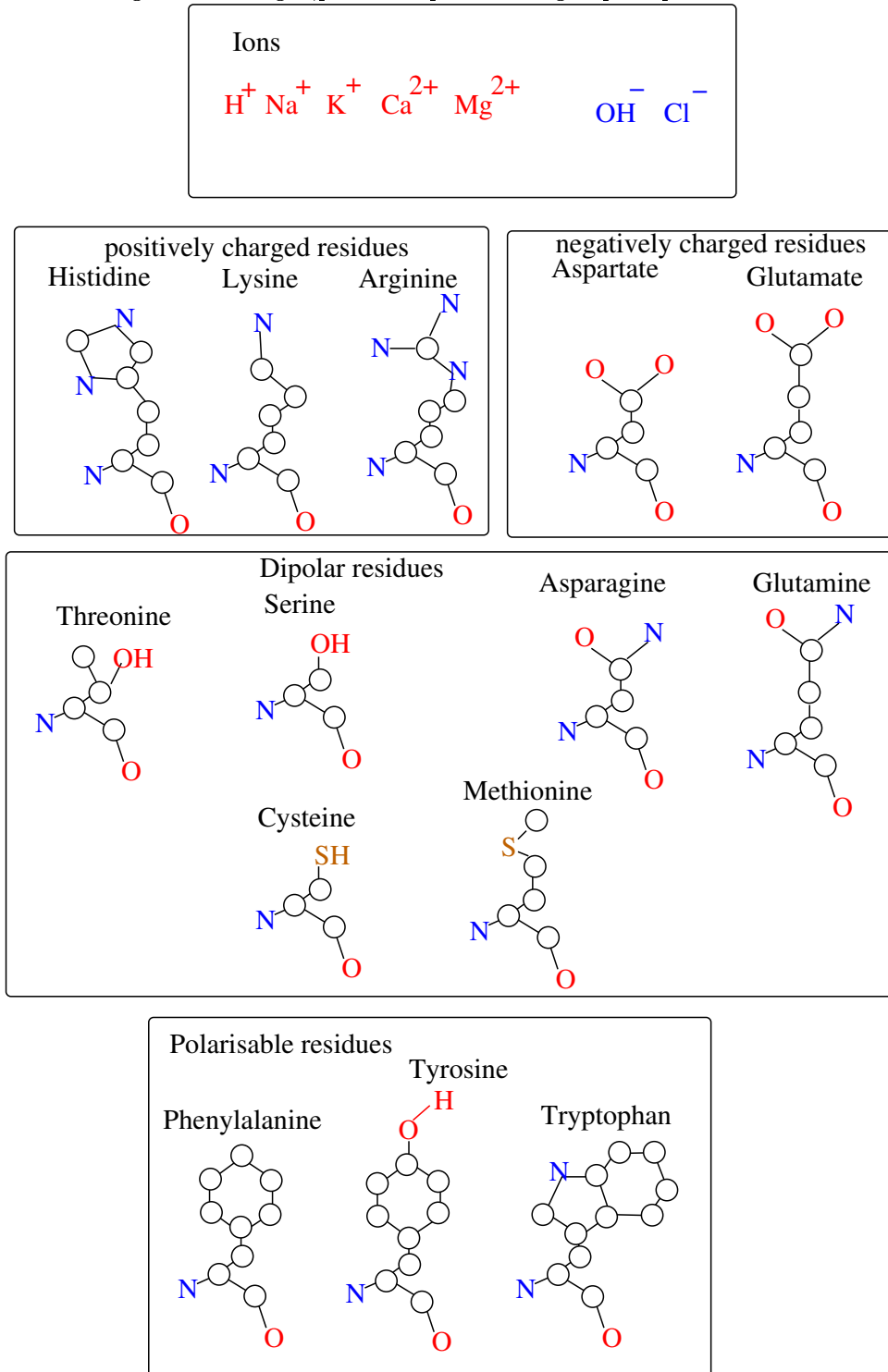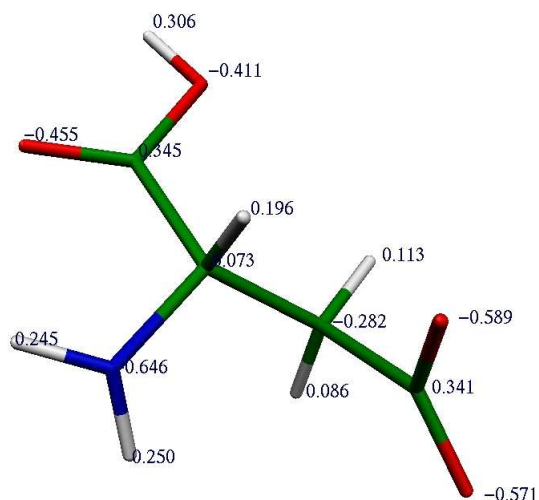Figure 41: charged,polar and polarizable groups in proteins

Figure 42: Mulliken charge analysis for Aspartate

4   Implicit continuum solvent models

Since an explicit treatment of all solvent atoms and ions is not possible in most cases the effect of the solvent on the protein has to be approximated by implicit models. In solution a protein occupies a conformation $\vec{\gamma}$ with the Boltzmann probability

$$P(X,Y) = \frac{e^{-U(X,Y)}}{\int dX dY e^{-U(X,Y)}}$$

where X stands for the coordinates of the protein (including the protonation state) and Y for the coordinates of thesolvent. The potential energy can be formally split into three terms

$$U(X,Y) = U_{prot}(X) + U_{solv}(Y) + U_{prot,solv}(X,Y)$$

The mean value of a physical quantity which depends only on the protein coordinates $Q(X)$ is

$$\overline{Q} = \int dX dY \quad Q(X)P(X,Y) = \int dX \quad Q(X)\widetilde{P}(X)$$

where we define a reduced probability distribution for the protein

$$\widetilde{P}(X) = \int dY \quad P(X,Y)$$

which is represented by introducing a **_potential of mean force_**

$$\widetilde{P}(X) = \frac{e^{-W(X)/kT}}{\int dX \quad e^{-W(X)/kT}}$$

$$e^{-W(X)/kT} = e^{-U_{prot}(X)/kT} \int dY \quad e^{-(U_{solv}(Y)+U_{prot,solv}(X,Y))/kT}$$

$$= e^{-(U_{prot}(X)+\Delta W(X))/kT}$$

where ΔW accounts implicitly but exactly for the solvents effect on the protein. In the following we discuss implicit solvent models which treat the solvent as a dielectric continuum. In response to the partial charges of the protein q_i polarization of the medium produces an electrostatic reaction potential ϕ^R.

If the medium behaves linearly (no dielectric saturation) the reaction potential is proportional to the charges

$$\phi_i^R = \sum_j f_{ij} q_j$$

Let us now switch on the charges adiabatically by introducing a factor

$$q_i \to q_i \lambda \qquad 0 < \lambda < 1$$

The change of the free energy is

$$dF = \sum_i \phi_i q_i d\lambda = \sum_{i \neq j} \frac{q_i q_j \lambda}{4\pi\epsilon r_{ij}} d\lambda + \sum_{ij} f_{ij} q_j q_i \lambda d\lambda$$

and thermodynamic integration gives the change of free energy due to Coulombic interactions

$$\Delta F_{elec} = \int_0^1 \lambda d\lambda \left(\sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon r_{ij}} + \sum_{ij} f_{ij} q_j q_i \right)$$

$$= \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{4\pi\epsilon r_{ij}} + \frac{1}{2} \sum_{ij} f_{ij} q_j q_i$$

The first part is a property of the protein and hence included in U_{prot}. The second part is the mean force potential

$$\Delta W_{elec} = \frac{1}{2} \sum_{ij} f_{ij} q_i q_j$$

4.1   Example: Charges in a protein

An important example is an ion pair within a protein ($\epsilon_r = 2$) which is surrounded by water ($\epsilon_r = 80$). We study an idealized model where the protein is represented by a sphere.

Figure 43: Ion pair in a protein
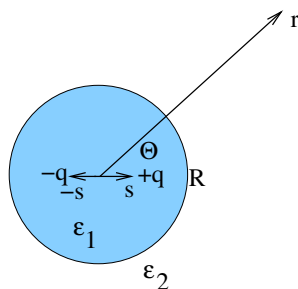
We will first treat a single charge within the sphere. A system of charges can then be treated by superposition of the individual contributions.

Using polar coordinates (r, θ, φ) the potential of a system with axial symmetry (no dependence on φ)can be written with the help of Legendre polynomials as

$$\phi = \sum_{n=0}^{\infty} (A_n r^n + B_n r^{-(n+1)}) P_n(\cos\theta)$$

The general solution can be written as the sum of a special solution and a harmonic function. The special solution is given by the multipole expansion

$$\frac{q}{4\pi\epsilon_1 |\vec{r} - \vec{s}_+|} = \frac{q}{4\pi\epsilon_1} \frac{1}{r} \sum_{n=0}^{\infty} \left(\frac{s}{r}\right)^n P_n(\cos\theta)$$

Since the potential has to be finite at large distances, outside it has the form

$$\phi_2 = \sum_{n=0}^{\infty} B_n r^{-(n+1)} P_n(\cos\theta)$$

and inside the potential is given by

$$\phi_1 = \sum_{n=0}^{\infty} (A_n r^n + \frac{qs^n}{4\pi\epsilon_1} r^{-(n+1)}) P_n(\cos\theta)$$

At the boundary we have two conditions

$$\phi_1(R) = \phi_2(R) \rightarrow B_n R^{-(n+1)} = A_n R^n + \frac{qs^n}{4\pi\epsilon_1} R^{-(n+1)}$$

$$\epsilon_1 \frac{\partial}{\partial r} \phi_1(R) = \epsilon_2 \frac{\partial}{\partial r} \phi_2(R) = 0$$

$$\rightarrow -\frac{\epsilon_2}{\epsilon_1}(n+1) B_n R^{-(n+2)} = n A_n R^{n-1} - (n+1)\frac{qs^n}{4\pi\epsilon_1} R^{-(n+2)}$$

from which the coefficients can be easily determined

$$A_n = \frac{qs^n}{4\pi\epsilon_1} R^{-1-2n} \frac{(\epsilon_1 - \epsilon_2)(n+1)}{n\epsilon_1 + (n+1)\epsilon_2}$$

$$B_n = \frac{qs^n}{4\pi\epsilon_1} \frac{(2n+1)\epsilon_1}{n\epsilon_1 + (n+1)\epsilon_2}$$

The potential inside the sphere is

$$\phi_1 = \frac{q}{4\pi\epsilon_1 |\vec{r} - \vec{s}_+|} + \phi^R$$

with the reaction potential

$$\phi^R = \sum_{n=0}^{\infty} \frac{qs^n}{4\pi\epsilon_1} R^{-1-2n} \frac{(\epsilon_1 - \epsilon_2)(n+1)}{n\epsilon_1 + (n+1)\epsilon_2} r^n P_n(\cos\theta)$$

and the electrostatic energy is given (without the infinite self energy) by

$$\frac{1}{2}q\phi(s, \cos\theta = 1)$$

$$= \frac{q}{2}\sum_{n=1}^{\infty}\frac{qs^n}{4\pi\epsilon_1}R^{-1-2n}\frac{(\epsilon_1 - \epsilon_2)(n+1)}{n\epsilon_1 + (n+1)\epsilon_2}s^n$$

which for $\epsilon_2 >> \epsilon_1$ is approximately

$$\frac{q^2}{2}\frac{1}{4\pi R}(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1})\sum\left(\frac{s}{R}\right)^{2n} = -\frac{q^2}{2}\frac{1}{4\pi R}(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2})\frac{1}{1 - s^2/R^2}$$

Consider now two charges $\pm q$ at symmetric positions $\pm s$. The reaction potentials of the two charges add up to

$$\phi^R = \phi_+^R + \phi_-^R$$

and the electrostatic free energy is given by

$$\frac{-q^2}{4\pi\epsilon_1(2s)} + \frac{1}{2}q\phi_+^R(s) + \frac{1}{2}q\phi_-^R(s) + \frac{1}{2}(-q)\phi_+^R(-s) + \frac{1}{2}(-q)\phi_-^R(-s)$$

from comparison we find

$$\frac{q^2}{2}f_{++} = \frac{1}{2}q\phi_+^R(s) = -\frac{q^2}{2}\frac{1}{4\pi R}(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2})\frac{1}{1 - s^2/R^2}$$

$$\frac{(-q)^2}{2}f_{--} = \frac{1}{2}(-q)\phi_-^R(-s) = -\frac{q^2}{2}\frac{1}{4\pi R}(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2})\frac{1}{1 - s^2/R^2}$$

$$\frac{(-q)q}{2}f_{-+} = \frac{1}{2}(-q)\phi_+^R(-s) = \frac{(-q)}{2}\sum_{n=1}^{\infty}\frac{qs^n}{4\pi\epsilon_1}R^{-1-2n}\frac{(\epsilon_1 - \epsilon_2)(n+1)}{n\epsilon_1 + (n+1)\epsilon_2}(-s)^n$$

$$\approx \frac{-q^2}{2}\frac{1}{4\pi R}(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1})\sum_{n=0}^{\infty}(-)^n\left(\frac{s}{R}\right)^{2n} = -\frac{(-q^2)}{2}\frac{1}{4\pi R}(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2})\frac{1}{s^2/R^2 + 1}$$

$$\frac{q(-q)}{2}f_{+-} = \frac{1}{2}q\phi_-^R(s) = \frac{(-q)q}{2}f_{-+}$$

and finally solvation energy

$$W_{elec} = \sum_{n=1}^{\infty}\frac{q^2 s^n}{4\pi\epsilon_1}R^{-1-2n}\frac{(\epsilon_1 - \epsilon_2)(n+1)}{n\epsilon_1 + (n+1)\epsilon_2}(s^n - (-s)^n)$$

$$W_{elec} \approx -q^2\frac{1}{4\pi R}(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2})\frac{1}{1 - s^2/R^2} - \frac{(-q^2)}{2}\frac{1}{4\pi R}(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2})\frac{1}{s^2/R^2 + 1}$$

$$= \frac{q^2}{4\pi R}(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2})\frac{2}{1 - s^4/R^4}$$

If the extension of the system of charges in the protein is small compared to the radius $s << R$ the multipole expansion of the reaction potential converges rapidly. Since the total charge of the ion pair is zero the monopole contribution (n=0)

$$W_{elec}^{(1)} = \frac{Q^2}{8\pi R}(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1})$$

vanishes and the leading term is the dipole contribution (n=1)

$$W_{elec}^{(2)} = \frac{p^2}{4\pi\epsilon_1 R^3}\frac{(\epsilon_1 - \epsilon_2)}{\epsilon_1 + 2\epsilon_2}$$

5   Debye-Hückel theory

5.1   electrostatic shielding by mobile charges

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

$$\rho_{mob}(\vec{r}) = \sum_i Z_i e \overline{N}_i(\vec{r})$$

The electrostatic potential is given by solution of the Poisson equation

$$\epsilon\Delta\phi(\vec{r}) = -\rho(\vec{r}) = -\rho_{mob}(\vec{r}) - \rho_{fix}(\vec{r})$$

Debye and Hückel used Boltzmann's theorem to determine the mobile charge density. Without the presence of fixed charges the system is neutral

$$0 = \rho_{mob}^0 = \sum_i Z_i e N_i^0$$

and the constant value of the potential can be chosen to be zero.

$$\phi^0 = 0$$

The fixed charges produce a change of the potential. The electrostatic energy of an ions of sort i is

$$W_i = Z_i e \phi(\vec{r})$$

and the density of such ions is given by a Boltzmann distribution

$$\frac{N_i(\vec{r})}{N_i^0} = \frac{e^{-Z_i e\phi(\vec{r})/kT}}{e^{-Z_i e\phi^0/kT}}$$

or

$$N_i(\vec{r}) = N_i^0 e^{-Z_i e\phi(\vec{r})/kT}$$

The total mobile charge density is

$$\rho_{mob}(\vec{r}) = \sum_i Z_i e N_i^0 e^{-Z_i e\phi(\vec{r})/kT}$$

and we obtain the Poisson-Boltzmann equation

$$\epsilon\Delta\phi(\vec{r}) = -\sum_i Z_i e N_i^0 e^{-Z_i e\phi(\vec{r})/kT} - \rho_{fix}(\vec{r})$$

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

$$Z_i e\phi \ll kT$$

and linearize the Poisson-Boltzmann equation

$$\epsilon\Delta\phi(\vec{r}) = -\rho_{fix}(\vec{r}) - \sum_i Z_i e N_i^0 (1 - \frac{Z_i e}{kT}\phi(\vec{r}) + \cdots)$$

The first summand vanishes due to electroneutrality and we find finally

$$\Delta\phi(\vec{r}) - \kappa^2\phi(\vec{r}) = -\frac{1}{\epsilon}\rho_{fix}(\vec{r})$$

with the inverse Debye length

$$\lambda_{Debye}^{-1} = \kappa = \sqrt{\frac{e^2}{\epsilon kT}\sum_i N_i^0 Z_i^2}$$

5.2   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

$$\frac{e}{kT}\Delta\phi(\vec{r}) + \frac{e^2}{\epsilon kT}N^0(e^{-e\phi(\vec{r})/kT} - e^{e\phi(\vec{r})/kT}) = -\frac{e}{\epsilon kT}\rho_{fix}(\vec{r})$$

which after substitution

$$\widetilde{\phi}(\vec{r}) = \frac{e}{kT}\phi(\vec{r})$$

takes the form

$$\Delta\widetilde{\phi}(\vec{r}) - \kappa^2\sinh(\widetilde{\phi}(\vec{r})) = -\frac{e}{\epsilon kT}\rho_{fix}(\vec{r})$$

and with the scaled radius vector $\vec{r}' = \kappa\vec{r} \to \widetilde{\phi}(\vec{r}) = f(\vec{r}') = f(\kappa\vec{r})$
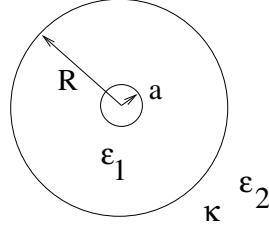
$$\Delta f(\vec{r}') - \sinh(f(\vec{r}')) = -\frac{e}{\kappa^2\epsilon kT}\rho_{fix}(\kappa^{-1}\vec{r}')$$

5.3   Charged sphere

We consider a spherical protein (radius R) with a charged sphere (radius a) in its center.

Figure 44: simple model of a charged protein

For a spherical problem we only have to consider the radial part of the Laplacian and the linearized Poisson-Boltzmann equation becomes outsides the protein

$$\frac{1}{r}\frac{d^2}{dr^2}\left(r\phi(r)\right) - \kappa^2\phi(r) = 0$$

which has the solution

$$\phi_2(r) = \frac{c_1 e^{-\kappa r} + c_2 e^{\kappa r}}{r}$$

Since the potential should vanish at large distances we have $c_2 = 0$. Inside the protein $(a < r < R)$ solution of the Poisson equation gives

$$\phi_1(r) = c_3 + \frac{Q}{4\pi\epsilon_1 r}$$

At the boundary we have the conditions

$$\phi_1(R) = \phi_2(R) \rightarrow c_3 = \frac{c_1 e^{-\kappa R}}{R} - \frac{Q}{4\pi\epsilon_1 R}$$

$$\epsilon_1 \frac{\partial}{\partial r}\phi_1(R) = \epsilon_2 \frac{\partial}{\partial r}\phi_2(R) \rightarrow -\frac{Q}{4\pi R^2} = c_1\epsilon_2 \left(-\frac{e^{-\kappa R}}{R^2} - \kappa\frac{e^{-\kappa R}}{R}\right)$$

which gives the constants

$$c_1 = \frac{Q e^{\kappa R}}{4\pi\epsilon_2(1 + \kappa R)}$$

and

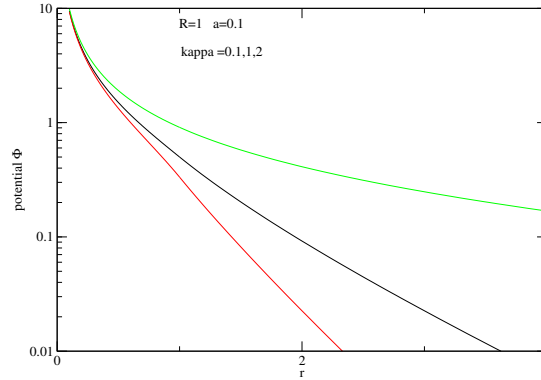$$c_3 = -\frac{Q}{4\pi\epsilon_1 R} + \frac{Q}{4\pi\epsilon_2 R(1 + \kappa R)}$$

together we find the potential inside the sphere

$$\phi_1(r) = \frac{Q}{4\pi\epsilon_1}\left(\frac{1}{r} - \frac{1}{R}\right) + \frac{Q}{4\pi\epsilon_2 R(1 + \kappa R)}$$

and outside

$$\phi_2(r) = \frac{Q}{4\pi\epsilon_2(1 + \kappa R)}\frac{e^{-\kappa(r-R)}}{r}$$

Figure 45: charged sphere in an Electrolyte
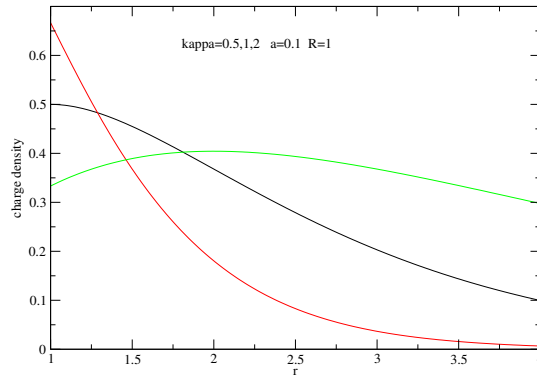
The ion charge density is given by

$$\rho_{mob}(r) = \epsilon_2 \Delta \phi_2 = \epsilon_2 \kappa^2 \phi_2$$

hence the ion charge at distances between r and $r + dr$ is given by

$$\kappa \frac{Q}{(1 + \kappa R)} r e^{-\kappa(r-R)} dr$$

This function has a maximum at $r_{max} = 1/\kappa$ and decays exponentially at larger distances.

Figure 46: charge density around the charged sphere

Let the charge be concentrated on the surface of the inner sphere. Then we have

$$\phi_1(a) = \frac{Q}{4\pi\epsilon_1} \left(\frac{1}{a} - \frac{1}{R} \right) + \frac{Q}{4\pi\epsilon_2 R(1 + \kappa R)}$$

Without the medium ($\epsilon_2 = \epsilon_1, \kappa = 0$) the potential would be

$$\phi_1^0(a) = \frac{Q}{4\pi\epsilon_1 a}$$

hence the solvation energy is

$$W = \frac{1}{2}Q\phi^R = \frac{1}{2}Q(\phi_1(a) - \phi_1^0(a)) = \frac{Q^2}{8\pi R}\left(\frac{1}{\epsilon_2(1 + \kappa R)} - \frac{1}{\epsilon_1}\right)$$

which for $\kappa = 0$ becomes the well known Born formula

$$W = -\frac{Q^2}{8\pi R}\left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2}\right)$$

and for $a \rightarrow R$,$\epsilon_1 = \epsilon_2$ gives the solvation energy of an ion in solution

$$\Delta G_{sol} = W = -\frac{Q^2}{8\pi\epsilon}\frac{\kappa}{(1 + \kappa R)}$$
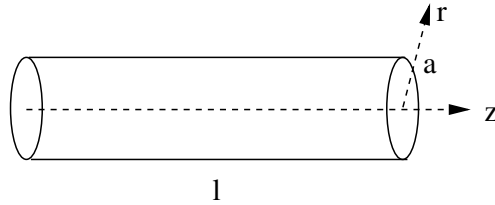
5.4 Charged cylinder

Next we discuss a cylinder of radius a and length $l \ll a$ carrying the net charge Ne uniformly distributed on its surface .

$$\sigma = \frac{Ne}{2\pi al}$$

Outside the cylinder this charge distribution is equivalent to a linear distribution of charges along the axis of the cylinder with a 1-d density

$$\frac{Ne}{l} = 2\pi a\sigma = \frac{e}{b}$$

Figure 47: charged cylinder model

Outside the cylinder the linear BPE becomes using cylindrical coordinates

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d}{dr}\right)\phi(r) = \kappa^2\phi(r)$$

Substitution $r \rightarrow x = \kappa r$ gives the equation

$$\frac{d^2}{dx^2}\phi(x) + \frac{1}{x}\frac{d}{dx}\phi(x) - \phi(x) = 0$$

The solution of this equation are the modified Bessel functions of order zero denoted as $I_0(x)$ and $K_0(x)$. For large values of x

$$\lim_{x \rightarrow \infty} I_0(x) = \infty \qquad \lim_{x \rightarrow \infty} K_0(x) = 0$$

and hence the potential in the outer region has the form

$$\phi(r) = C_1 K_0(\kappa r)$$

Inside the cylinder surface the electric field is given by Gauss' theorem

$$2\pi r l \epsilon_1 E(r) = Ne$$

$$E(r) = -\frac{d\phi(r)}{r} = \frac{Ne}{2\pi\epsilon_1 rl}$$

and hence the potential inside is

$$\phi(r) = C_2 - \frac{Ne}{2\pi\epsilon_1 l}\ln r$$

The boundary conditions are

$$\phi(a) = C_1 K_0(\kappa a) = C_2 - \frac{Ne}{2\pi\epsilon_1 l}\ln a$$

$$\epsilon_1 \frac{d\phi(a)}{dr} = -\frac{Ne}{2\pi al} = \epsilon_2 \frac{d\phi(a)}{dr} = \epsilon_2 C_1(-\kappa K_1(\kappa a))$$

from which we find

$$C_1 = \frac{Ne}{2\pi al \epsilon_2 \kappa K_1(\kappa a)}$$

and

$$C_2 = \frac{Ne}{2\pi al \epsilon_2 \kappa} \frac{K_0(\kappa a)}{K_1(\kappa a)} + \frac{Ne}{2\pi\epsilon_1 l}\ln a$$

The potential then is outside

$$\phi(r) = \frac{Ne}{2\pi al \epsilon_2 \kappa} \frac{K_0(\kappa r)}{K_1(\kappa a)}$$

and inside

$$\phi(r) = \frac{Ne}{2\pi al \epsilon_2 \kappa} \frac{K_0(\kappa a)}{K_1(\kappa a)} + \frac{Ne}{2\pi\epsilon_1 l}\ln a - \frac{Ne}{2\pi\epsilon_1 l}\ln r$$

For small $\kappa a \to 0$ we can use the asymptotic behaviour of the Bessel functions

$$K_0(x) \to \ln\frac{2}{x} - \gamma + \cdots \qquad \gamma = 0.577\cdots$$

$$K_1(x) \to \frac{1}{x} + \cdots$$

to have approximately

$$C_1 \approx \frac{Ne}{2\pi al \epsilon_2 \kappa}\kappa a = \frac{Ne}{2\pi l \epsilon_2}$$

$$C_2 \approx \frac{Ne}{2\pi l \epsilon_2}(\ln\frac{2}{\kappa a} - \gamma) + \frac{Ne}{2\pi\epsilon_1 l}\ln a$$

The potential outside is

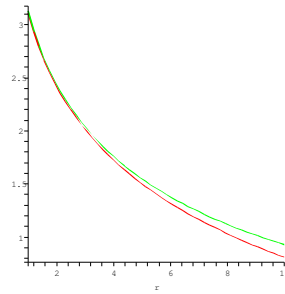$$\phi(r) = -\frac{Ne}{2\pi l \epsilon_2}(\gamma + \ln\frac{\kappa}{2} + \ln r)$$

and inside

$$\phi(r) = \frac{Ne}{2\pi l \epsilon_2}(\ln\frac{2}{\kappa a} - \gamma) + \frac{Ne}{2\pi \epsilon_1 l}\ln a - \frac{Ne}{2\pi \epsilon_1 l}\ln r$$

$$= \frac{Ne}{2\pi l}\left(-\frac{\gamma}{\epsilon_2} - \frac{1}{\epsilon_2}\ln\frac{\kappa}{2} + \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2}\right)\ln a - \frac{1}{\epsilon_1}\ln r\right)$$

Outside the potential consists of the potential of the charged line ($\ln r$) and an additional contribution from the screening of the ions.

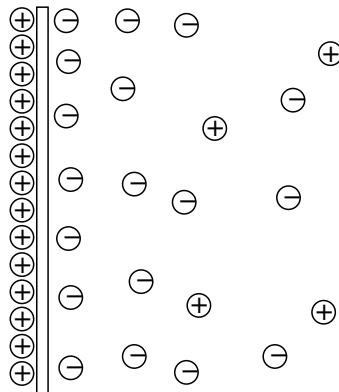Figure 48: Potential of a charged cylinder with unit radius a=1

The function $K_0(\kappa r)/(\kappa K_1(\kappa))$ and its approximation by $-\ln\frac{\kappa}{2} - \ln r - \gamma$ is shown for $\kappa = 0.05$

5.5   Charged membrane (Goüy-Chapman double layer)

We approximate the surface charge of a membrane by a thin layer charged with a homogeneous charge distribution.

Figure 49: Gouy-Chapman double layer

Gouy (1910) and Chapman (1913) derived the potential similar to Debye-Hückel theory. For a 1-1 electrolyte (NaCl for example) the 1-dimensional Poisson-Boltzmann equation has the form (with transformed variables as above)

$$\frac{d^2}{dx^2}f(x) - \sinh(f(x)) = g(x)$$

where the source term $g(x) = -\frac{e}{\kappa^2 \epsilon kT}\rho(x/\kappa)$ has the character of a Delta-function centered at $x = 0$. Consider an area A of the membrane and integrate along the x-axis:

$$\int dA \int_{-0}^{+0} \rho(x)dx = \sigma_0 A$$

$$\int dA \int_{-0}^{+0} dx \quad g(x) = -\frac{e}{\kappa^2 \epsilon kT}\int dA \int_{-0}^{+0} \kappa dx' \rho(x')$$

$$= -\frac{e}{\kappa \epsilon kT}\sigma_0 A$$

Hence we identify

$$\rho(x) = \sigma_0 \delta(x) \qquad g(x) = -\frac{e\sigma_0}{\kappa \epsilon kT}\delta(x)$$

The PB equation can be solved analytically. But first we study the linearised homogeneous equation

$$\frac{d^2}{dx^2}f(x) - f(x) = 0$$

with the solution

$$f(x) = f_0 e^{\pm x}$$

or going back to the potential

$$\phi(x) = \frac{kT}{e}f_0 e^{\pm \kappa x} = \phi_0 e^{\pm \kappa x}$$

The membrane potential is related to the surface charge density. Let us assume that on the left side (x<0) the medium has a dielectric constant of ϵ_1 and on the right side ϵ. Since in one dimension the field in a dielectric medium does not decay we introduce a shielding constant κ_1 on the left side and take the limit $\kappa_1 \to 0$ to remove contributions not related to the membrane charge. The potential then is given by

$$\phi(x) = \begin{cases} \phi_0 e^{-\kappa x} & \text{x>0} \\ \phi_0 e^{\kappa_1 x} & \text{x<0} \end{cases}$$

and ϕ_0 is determined from the b.c.

$$\epsilon \frac{d\phi}{dx}(+0) - \epsilon_1 \frac{d\phi}{dx}(-0) = -\sigma_0$$

which gives

$$-\epsilon \kappa \phi_0 - \epsilon_1 \kappa_1 \phi_0 = -\sigma_0$$

In the limit $\kappa_1 \to 0$ we find

$$\phi_0 = \frac{\sigma_0}{\epsilon\kappa}$$

For $x < 0$ the potential is constant and for $x > 0$ the charge density is

$$\rho(x) = -\epsilon\frac{d^2\phi(x)}{dx^2} = -\sigma_0\kappa e^{-\kappa x}$$

which adds up to a total net charge per unit area of

$$\int_0^\infty \rho(x)dx = -\sigma_0$$

hence the system is neutral and behaves like a capacity of

$$\frac{\sigma_0 A}{\phi_0} = \epsilon\kappa A = \epsilon\frac{A}{L_{Debye}}$$
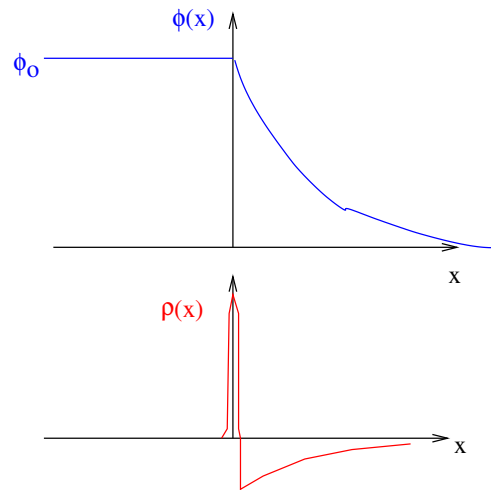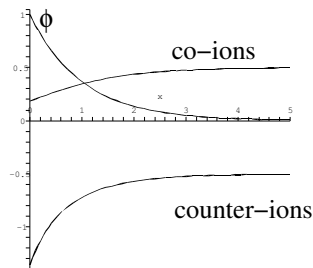
per area

Figure 50: electrolytic double layer

Figure 51: charge density of counter- and co-ions

The solution of the nonlinear homogeneous equation can be found multiplying the equation with $\frac{df(x)}{dx}$

$$\frac{df}{dx}\frac{d^2f}{dx^2} = \sinh(f)\frac{df}{dx}$$

and rewriting this as

$$\frac{1}{2}\frac{d}{dx}\left(\frac{df}{dx}\right)^2 = \frac{d}{dx}\cosh(f)$$

which can be integrated

$$\left(\frac{df}{dx}\right)^2 = 2\left[\cosh(f) + C\right]$$

The constant C is determined by the asymptotic behaviour

$$\lim_{x\to\infty} f(x) = \lim_{x\to\infty}\frac{df}{dx} = 0$$

and obviously has the value $C = -1$.

Making use of the relation

$$\cosh(f) - 1 = 2\sinh(\frac{f}{2})^2$$

we find

$$\frac{d}{dx}f(x) = \pm 2\sinh\left(\frac{f(x)}{2}\right)$$

Separation of variables then gives

$$\frac{df}{2\sinh(f/2)} = \pm dx$$

with the solution

$$f(x) = 2\ln\left(\pm\tanh\left(\frac{x}{2} + \frac{C}{2}\right)\right)$$

For $x > 0$ only the plus sign gives a physically meaningful result. The constant can be related to the potential at the membrane surface via

$$C = arctanh\left(e^{f(0)/2}\right) = \frac{1}{2}\ln\left(\frac{1 + e^{f(0)/2}}{1 - e^{f(0)/2}}\right)$$

to give

$$f(x) = 2\ln\left(\tanh\left(\frac{x}{2} + \frac{C}{2}\right)\right) = 2\ln\left(\frac{1 - e^{-x-C}}{1 + e^{-x-C}}\right)$$

The integration constant is again connected to the surface charge density by

$$\frac{d\phi}{dx}(0) = -\frac{\sigma_o}{\epsilon}$$

and from

$$\frac{d}{dx}\phi(x) = \frac{kT}{e}\frac{d}{dx}f(\kappa x) = \frac{kT}{e}\kappa f'(\kappa x)$$

we find

$$\frac{\sigma_0}{\epsilon} = -\frac{kT}{e}\kappa f'(0)$$

Now the derivative is

$$f'(x) = \frac{1 - (\tanh(\frac{x}{2} + \frac{C}{2}))^2}{\tanh(\frac{x}{2} + \frac{C}{2})}$$

and especially

$$f'(0) = \frac{1 - \tanh(\frac{C}{2})^2}{\tanh(\frac{C}{2})}$$
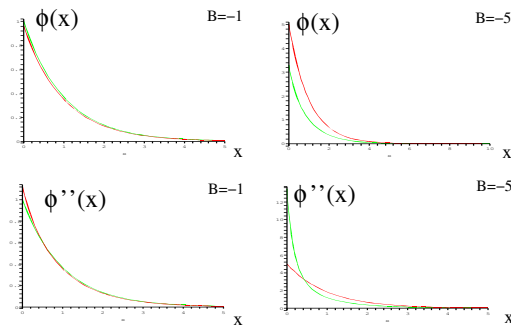
and we have to solve the equation

$$\frac{1 - t^2}{t} = -\frac{e\sigma_0}{kT\kappa\epsilon} = B$$

which yields[6]

$$t = -\frac{B}{2} - \frac{\sqrt{B^2 + 4}}{2}$$

$$C = 2\text{arctanh}\left(-\frac{B}{2} - \frac{\sqrt{B^2 + 4}}{2}\right)$$

Figure 52: Comparison of full and linearized 1-dim PB equation for fixed surface charge σ

Linearisation can be applied roughly if $|f(0)| < 1$ or $|e\phi(0)| < kT$

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[6]the second root leads to imaginary values