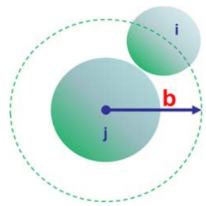
6.8: Ion Distributions Near a Charged Sphere

Ion Distributions Near a Charged Sphere[1]



Now let's look at how ions will distribute themselves around a charged sphere. This sphere could be a protein or another ion. We assume a spherically symmetric charge distribution about ions, and a Boltzmann distribution for the charge distribution for the ions (i) about the sphere (j) of the form

$$\rho(r)=\sum_i e z_i C_{0,i} e^{-z_i e \Phi_j(r)/k_B T} \tag{6.8.1}$$

$\Phi_j(r)$ is the electrostatic potential at radius r which results from a point charge $z_j e$ at the center of the sphere. Additionally, we assume that the sphere is a hard wall, and define a radius of closest approach by ions in solution, b. The PBE becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Phi}{dr}\right)=\frac{1}{\varepsilon}\sum_i e z_i C_{0,i} e^{-z_i e \Phi_j(r)/k_B T}$$

To simplify this, we again apply the Debye–Hückel approximation $(ze\Phi \ll k_B T)$, expand the exponential in eq. , drop the leading term due to the charge neutrality condition, and obtain

$$\rho(r)=-\sum_i C_{0,i} z_i^2 e^2 \Phi_j(r)/k_B T \tag{6.8.2}$$

Then the linearized PBE is in the Debye–Hückel approximation is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\Phi}{dr}\right)=\kappa^2\Phi \tag{6.8.3}$$

As before: $\kappa^2=\lambda_D^{-2}=2e^2 I/\varepsilon k_B T$. Solutions to eq. (6.8.3) will take the form:

$$\Phi=A_1\frac{e^{-\kappa r}}{r}+A_2\frac{e^{\kappa r}}{r} \tag{6.8.4}$$

To solve this use boundary conditions:

1. $A_2=0$, since $\Phi\to 0$ at $r=\infty$.
2. The field at the surface of a sphere with charge $z_j e$ and radius b is determined from

$$4\pi b^2 E(b)=\frac{z_j e}{\varepsilon} \tag{6.8.5}$$

Now, using

$$E(b)=-\frac{d\Phi}{dr}|_{r=b} \tag{6.8.6}$$

Substitute eq. (6.8.4) into RHS and eq. (6.8.5) into LHS of eq. (6.8.6). Solve for A_1.

$$A_1=\frac{z_j e e^{\kappa b}}{4\pi\varepsilon(1+\kappa b)}$$

So, the electrostatic potential for $r\geq b$ is

$$\Phi(r) = \underbrace{\frac{z_j e}{4\pi\varepsilon_0 r}}_{\text{vacuum}} \frac{e^{-\kappa(r-b)}}{\varepsilon_r(1+\kappa b)} \tag{6.8.7}$$

Setting $r = b$ gives us the surface potential of the sphere:

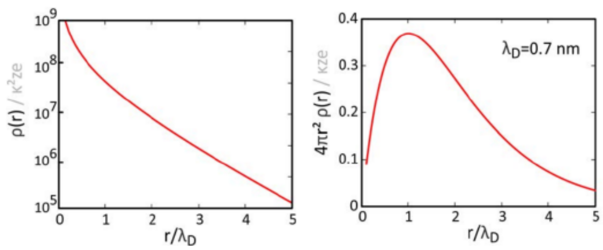
$$\Phi(b) = \frac{z_j e}{4\pi\varepsilon b(1+\kappa b)}$$

Note the exponential factor in eq. (6.8.7) says that Φ drops faster than r^{-1} as a result of screening. Now substitute eq. (6.8.7) into eq. (6.8.2) we obtain the charge probability density

$$\rho(r) = \frac{-\kappa^2 z_j e}{4\pi r} \frac{e^{-\kappa(r-b)}}{1+\kappa b} \tag{6.8.8}$$

We see that the charge density about ion drops as $e^{-\kappa(r-b)}/r$, a rapidly decaying function that emphasizes the strong tendency for ions to attract or repel at short range. However, the charge density between r and $r+dr$ is $4\pi r^2 \rho(r)$ and therefore grows linearly with r before decaying exponentially: $re^{-\kappa(r-b)}$. We plot this function to illustrate the thickness of the "ion cloud" around the sphere, which is peaked at $r = \lambda_D$. Additionally, note, that the charge distribution around that ion is equal and opposite to the charge of the sphere "j".

$$\int_b^\infty \rho(r) 4\pi r^2 dr = -z_j e$$



It is also possible to calculate radial distribution functions for ions in the Debye–Hückel limit.[2] The radial pair distribution function for ions of type i and j, $g_{ij}(r)$, is related to the potential of mean force W_{ij} as

$$g_{ij}(r) = \exp[-W_{ij}(r)/k_B T] \tag{6.8.9}$$

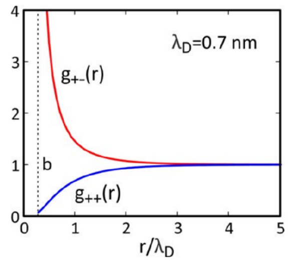
If only considering electrostatic effects, we can approximate W_{ij} as the interaction energy $U_{ij}(r) = z_i e \Phi_j(r)$. Using the Debye–Hückel result, eq. (6.8.7),

$$U_{ij}(r) = \frac{z_i z_j e^2}{4\pi\varepsilon(1+\kappa b)} \frac{e^{-\kappa(r-b)}}{r}$$

Let's look at the form of $g(r)$ for two singly charged ions with $\lambda_D = 0.7\ nm$, $\epsilon = 80$, and $T = 300\ K$. The Bjerrum length is calculated as $\ell_B = e^2/4\pi\epsilon k_B T = 0.7\ nm$. Since the Debye–Hückel holds for $ze\Phi \ll k_B T$, we can expand the exponential in eq. as

$$g_{ij}(r) = 1 - \chi_{ij} + \frac{1}{2}\chi_{ij}^2 + \cdots$$

where we define $\chi_{ij} = U_{ij}(r)/k_B T = \ell_B e^{-\kappa(r-b)} r^{-1} (1+\kappa b)^{-1}$. The resulting radial distribution function for co- and counterions calculated for $b = 0.15\ nm$ are shown below.



Readings

1. M. Daune, *Molecular Biophysics: Structures in Motion*. (Oxford University Press, New York, 1999), Ch. 16, 18.
2. D. A. McQuarrie, *Statistical Mechanics*. (Harper & Row, New York, 1976), Ch. 15.

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1. See M. Daune, *Molecular Biophysics: Structures in Motion*. (Oxford University Press, New York, 1999), Ch. 16.; D. A. McQuarrie, *Statistical Mechanics*. (Harper & Row, New York, 1976), Ch. 15.; Y. Marcus, Ionic radii in aqueous solutions, Chem. Rev. 88 (8), 1475-1498 (1988).
2. See D. A. McQuarrie, Statistical Mechanics. (Harper & Row, New York, 1976), Ch. 15.