

4xx Mem 5 - Charged plate in an electrolyte

The phosphate group of a phospholipid carries a negative charge which may be balanced by the positive charge borne by many lipid-head groups. An exception is the serine group, which is electrically neutral, leaving the phospholipid negative overall. Thus, a bilayer made from the common phospholipids may have a negative surface charge density. For an area per head-group of 0.5 nm^2 in the bilayer plane, this charge density could be as high as 0.3 C/m^2 if each lipid carried a single electron charge ($1.6 \times 10^{-19} \text{ C}$). Overall, the membrane and its environment is electrically neutral, so that positive counterions must be present in the media adjacent to the membrane. In this lecture, we examine the distribution of mobile ions surrounding a charged object with fixed geometry.

Poisson-Boltzmann equation

We first develop a mean field description of charge distributions that includes the effects of temperature. We'll need Gauss' law, which has the integral form

$$\int \mathbf{E} \cdot d\mathbf{A} = (1/\epsilon) \int \rho_{\text{ch}} dV, \quad (1)$$

and differential form

$$\nabla \cdot \mathbf{E} = \rho_{\text{ch}}/\epsilon, \quad (2)$$

where ϵ is the permittivity of the medium (in vacuum, $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2$). The charge density ρ_{ch} is not a number density - it's the charge per unit volume (in C/m^3 in MKSA units). The integrals in Eq. (1) are performed over a closed surface with area $\int dA$ and enclosed volume $\int dV$.

Now, electric field \mathbf{E} and potential ψ are related by $\mathbf{E} = -\nabla\psi$. Replacing \mathbf{E} by $-\nabla\psi$ permits Eq. (2) to be recast in a form called Poisson's equation

$$\nabla^2\psi = -\rho_{\text{ch}}/\epsilon. \quad \text{Poisson's equation} \quad (3)$$

The charge distribution reflects a competition between energy and entropy: mobile positive ions cluster near a negatively charged bilayer at low temperature, but roam further afield at high temperature. The density of counterions at a given position is proportional to the Boltzmann factor with a potential energy evaluated at that position. We assume for now that only one species of mobile ion is present, each ion with charge q experiencing a potential energy $V(\mathbf{r}) = q\psi(\mathbf{r})$. Defining ρ_0 to be the **number** density of ions at the reference point $\psi = 0$, the *Boltzmann* expression for the density profile is

$$\rho(\mathbf{r}) = \rho_0 \exp(-q\psi(\mathbf{r})/k_B T). \quad (4)$$

Here, the electrostatic potential ψ represents an average over local fluctuations in the ion's environment. This form for $\rho(\mathbf{r})$ can be substituted into the *Poisson* expression of

Eq. (3) using $\rho_{ch}(\mathbf{r}) = q\rho(\mathbf{r})$ to give the Poisson-Boltzmann equation, which is a differential equation in ψ

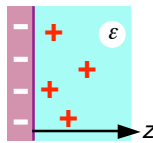
$$\nabla^2\psi = - (q\rho_0/\varepsilon) \exp(-q\psi/k_B T). \quad \text{Poisson-Boltzmann equation} \quad (5)$$

Eq. (5) can easily be generalized to include more than one species of charge.

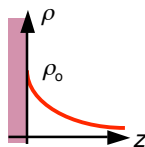
Charged plate with one counterion species

In most introductory physics courses, the integral form of Gauss' Law is used to find the electric field from a large flat plate carrying a charge density σ_s in the absence of counterions in the surrounding medium. One finds that the magnitude of the electric field must be $E = |\sigma_s| / 2\varepsilon$, independent of the distance from the plate. Since the electric field is the (negative) derivative of the potential, $\mathbf{E} = -\nabla\psi$, a constant value for E implies that the magnitude of ψ must grow linearly with z as $\sigma_s z / 2\varepsilon$. As usual, the location where the potential vanishes can be chosen arbitrarily.

Now, let's add counterions to one side of the plate, taking the plate to be negative and the counterions positive:



At low temperature, the counterions cluster near the plate, their density ρ falling with distance z from the plate



We choose the origin of the z -axis to lie at the plate boundary, where we fix $\psi = 0$. If the field is independent of direction parallel to the plate, the only non-vanishing part of $\nabla^2\psi$ is $d^2\psi / dz^2$ and Eq. (5) reads

$$d^2\psi / dz^2 = -(q\rho_0/\varepsilon) \exp(-q\psi / k_B T). \quad (6)$$

It is useful to incorporate the constants $q / k_B T$ into the potential to render it unitless through the definition

$$\Psi(z) \equiv q\psi(z) / k_B T, \quad (7)$$

such that Eq. (6) becomes

$$d^2\Psi / dz^2 = -\rho_0(q^2 / \varepsilon k_B T) e^{-\Psi}. \quad (8)$$

The combination $q^2 / \varepsilon k_B T$ in this equation has units of *[length]* and appears in the

Bjerrum length ℓ_B :

$$\ell_B \equiv q^2 / 4\pi\epsilon k_B T. \quad (9)$$

Through q and ϵ , the quantity ℓ_B depends upon the properties of the counterions and the medium, not on the charge density of the plate. For instance, the Bjerrum length of a single electron charge in air at room temperature is 58 nm, dropping to 0.7 nm in water where the permittivity is eighty times that of air. At this point, we introduce yet another parameter K , which has the units of $[length]^{-1}$, by

$$K^2 \equiv 2\pi\ell_B\rho_o, \quad (10)$$

to further simplify the appearance of the Poisson-Boltzmann equation:

$$d^2\Psi / dz^2 = -2K^2 e^{-\Psi}. \quad (11)$$

To solve Eq. (11), we first multiply both sides by $d\Psi/dz$ and then use the following two relations

$$(d\Psi/dz) \cdot (d^2\Psi/dz^2) = (1/2) \cdot d[(d\Psi/dz)^2]/dz \quad (12)$$

$$e^{-\Psi} (d\Psi/dz) = -d(e^{-\Psi})/dz, \quad (13)$$

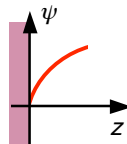
to rewrite the equation as

$$d[(d\Psi/dz)^2]/dz = 4K^2 d(e^{-\Psi})/dz. \quad (14)$$

Integrating this expression over z and taking the square root of the result gives

$$d\Psi/dz = 2K e^{-\Psi/2}, \quad (15)$$

where the positive root is chosen to correspond to



The integration constant that should appear in Eq. (15) has been set equal to zero permitting the electric field, which is proportional to $d\Psi/dz$, to vanish at the large values of Ψ expected as $z \rightarrow \infty$. Eq. (15) can be integrated easily by rewriting it as

$$\int e^{\Psi/2} d\Psi = 2K \int dz, \quad (16)$$

which gives

$$e^{\Psi/2} = K(z + \chi), \quad (17)$$

where the integration constants have been rolled into the factor χ .

We have now established that the functional form of $e^{-\Psi}$ is $[K(z + \chi)]^{-2}$, allowing us to generate an expression for the charge density from $\rho = \rho_o e^{-\Psi}$:

$$\rho(z) = \rho_0 / [K(z + \chi)]^2 = 1 / [2\pi\ell_B (z + \chi)^2]. \quad (18)$$

The integration constant is fixed by the value of the surface charge density σ_s . For the system to be electrically neutral, the integral over the positive charge density $\int q\rho dz$ must equal σ_s in magnitude (recall ρ is a number per unit volume); in symbols

$$-\sigma_s = (q / 2\pi\ell_B) \int dz / (z + \chi)^2, \quad (19)$$

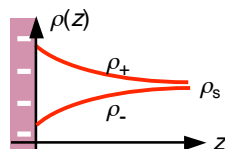
where the integral covers $0 \leq z \leq \infty$. The solution to this equation requires the distance χ to be

$$\chi = q / (-2\pi\ell_B\sigma_s) = 2\epsilon k_B T / (-q\sigma_s), \quad (20)$$

which is positive because q and σ_s have opposite signs here. There are several features to note about the form of the number density of counterions. First, the density falls like the square of the distance from the plate, with half of the counterions residing within a distance χ of the plate. Second, from Eq. (20), the width of the distribution grows linearly with temperature, as the counterions venture further into the surrounding medium.

Charged plate in a salt bath

Both the interior of a cell and the environment surrounding it contain various organic compounds as well as ions released from salts such as NaCl, which we will refer to as "bulk" salts or ions. The effect that a negatively charged bilayer has on these bulk ions depends upon their charge: the density of positive ions is enhanced near the plate while negative mobile ions are depleted. The distributions are shown schematically in the figure, where $\rho_+(z)$ and $\rho_-(z)$ are the number densities of positive and negative ions carrying charges $+q$ and $-q$, respectively.



The effect of the electrolyte is to "screen" the charge of the plate, which then modifies the distribution of counterions. We don't have time to cover this in lectures, but the system is treated in Sec. 9.2.3 of *Mechanics of the Cell*.