Debye length

The Debye length λ_D can be calculated from the following equation:

$$\boxed{\lambda_D = \left(\frac{N_A e^2}{\varepsilon \varepsilon_0 k T} \sum_i z_i^2 c_i^\infty \right)^{-1/2}}$$

where:

N_A Avogadro number [6,022 10^23 (mol-1)]
e charge of an electron [1,6 10-19 (C)]
ε_0 permittivity of free space [8,85 10-12 (F/m)]
ε dielectric constant (water ~80)
kT thermal energy → Boltzman constant x absolute T (in K) [k= 1,38 10-23 J/K]
z_i valence number of the specie *i*
c_i^∞ is the concentration of the ion *i* expressed in mol/m^3.

In aqueous medium at 298K we have that

$$\frac{N_A e^2}{\varepsilon \varepsilon_0 k T} = 5.404 \cdot 10^{15}\, m/mol$$

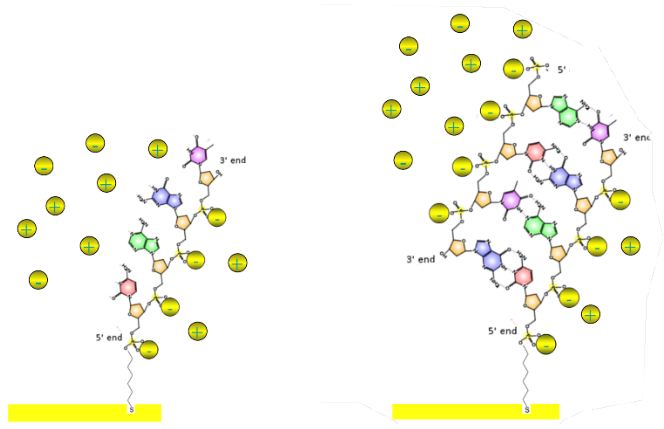
Therefore we can calculate the Debye length as

$$\boxed{\lambda_D = \left(5.404 \cdot 10^{15} \sum_i z_i^2 c_i^\infty \right)^{-1/2}}$$ **at 298 K**

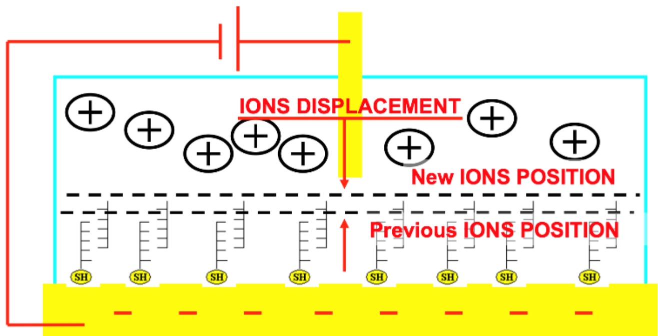
Capacitance measurements of single strand DNA

Ion distribution of:

a)DNA probe on the solid substrate b)hybridized DNA probe+target on the solid susbtrate



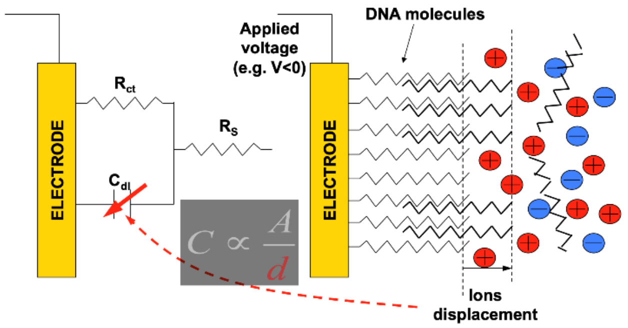
The formation of a hybridized DNA probe/target complex causes a certain ion displacement in solution



Ion planes are formed at the interface when electrodes immersed in solution are polarized

Single strand DNA can thus be detected with capacitance measurements.

The Capacitance DNA Detection



Unlabeled ssDNA may be detected with capacitance measurements as due to charge displacement

We can model the electrochemical interface as a parallel circuit involving a resistance and a capacitance, plus a further resistance in series. The first resistance (Rct) is the electrode resistance, and the parallel capacitance Cdl takes into account the layering phenomena related to the Helmholtz layers.

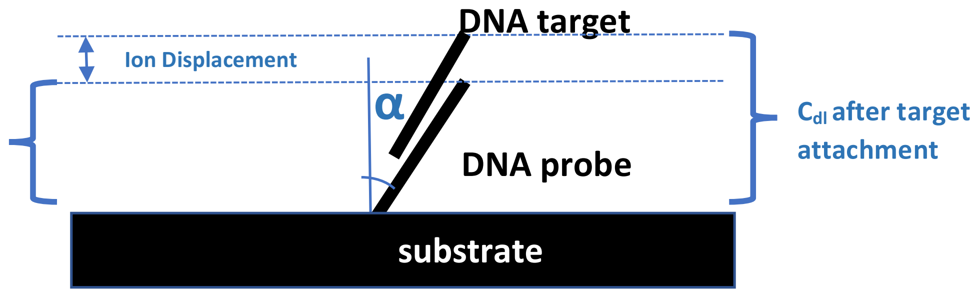
In a first approximation the **equivalent capacitance** of DNA can be computed as

$$C_{dl} = \varepsilon_{DNA}\varepsilon_0 \frac{A}{d} \qquad \textbf{(1)}$$

where $\varepsilon_{DNA} = 2.5$, A is the electrode area, d is the ions distance from the electrodes computed as

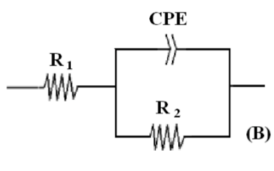
$$\mathbf{d = n\ l\ cos(\alpha)} \qquad \textbf{(2)}$$

where n is the number of bases of single strand DNA, l is the vertical rise per base pair and α is the angle with respect to the vertical axis.



It is worth noting that Eq. (1) shows a capacitance that does not depend on the frequency. However, measurements performed on DNA immobilized on gold electrodes show a certain frequency dependence. Clearly, such dependence is not expressed by Eq. (1). Thus, the constant phase element (CPE) better describes a layering capacitance that manifests such a frequency trend. The CPE is an equivalent component used in electrochemistry for describing capacitor with non-ideal behaviour.

Consequently, **the equivalent circuit of the electrochemical interface** can be re-drawn as:



Where R1 is the solution resistance, R2 is the electrode resistance and CPE is the constant phase element (i.e. non ideal capacitor) used to describe the capacitance for layering effects.

Using the definition of CPE, it is possible to write

$$Z_{CPE} = \frac{1}{C_p(j\omega)^{\alpha}} \qquad (1)$$

Where α describes the non-ideality of the capacitor and can have values between 0 and 1 (for α=1 we have the case of the ideal capacitor)

Using Eulero formulas

e^{jx}= cos x + j sen x

e^{-jx}= cos x - j sen x

x=π/2 → $e^{j\pi/2}$= j

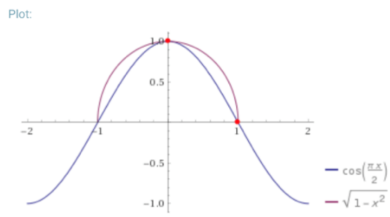
it is possible to write

$$\frac{1}{j^{\alpha}} = j^{-\alpha} = e^{-\left(\frac{\pi}{2}\right)j\alpha} = \cos(\frac{\pi}{2}\alpha) - j\sin(\frac{\pi}{2}\alpha) \qquad (2)$$

By substituting in eq. (1) we get:

$$Z_{CPE} = \frac{\cos\left(\frac{\pi}{2}\alpha\right)}{C_p\omega^{\alpha}} - j\frac{\sin\left(\frac{\pi}{2}\alpha\right)}{C_p\omega^{\alpha}}.$$

In between -1 and 1 it is possible to approximate $cos\ (\frac{\pi}{2}\alpha\ )\ \cong \sqrt{1-\alpha^2}$ and $sen\ (\frac{\pi}{2}\alpha\ )\ \cong \alpha$



such that we finally get:

$$\boxed{Z_{CPE} = \frac{1}{C_p(j\omega)^{\alpha}} \cong \frac{1}{\omega^{\alpha}C_p}\sqrt{1-\alpha^2} - j\frac{1}{\omega^{\alpha}C_p}\alpha}$$

Since Z= R-jX (R=resistance, X= reactance), we can observe that:

$$R_{CPE} \cong \frac{1}{\omega^{\alpha}C_P}\sqrt{1-\alpha^2}$$
$$X_{CPE} \cong \frac{\alpha}{\omega^{\alpha}C_P}$$

$\omega = 2\pi f$

By definition $X_{CPE} = \frac{1}{\omega C_{CPE}}$, so we can write:

$$C_{CPE} \cong \frac{C_p}{\alpha \cdot \omega^{1-\alpha}}$$
$$C_p = C_{CPE} \cdot \alpha \cdot \omega^{1-\alpha}$$