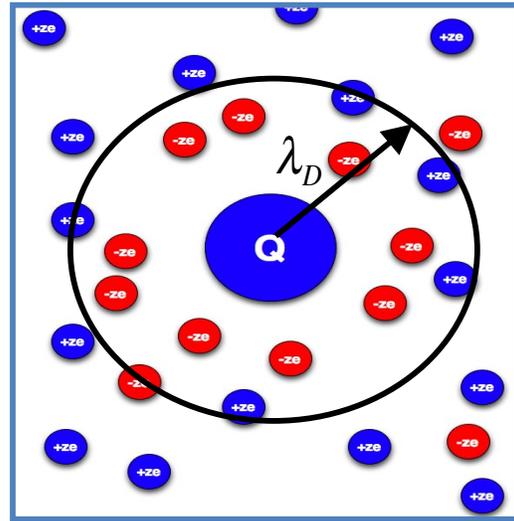


Estimating the Debye length

The Debye length is the distance over which a charge Q is shielded by the ions in a solution. What this means, referring to the picture at right, is that the excess ionic charge within the sphere of radius λ_D is approximately equal to charge $-Q$, thus canceling out the field of the $+Q$ of the original charge at distances further than λ_D . There is excess ionic charge in this sphere because, if Q is positive, negative ions are attracted into the sphere and positive ions are repelled from the sphere, leaving an excess of negative charge in the sphere.



How do we estimate this excess charge? To do this we need to estimate the concentrations of positive and negative ions inside the sphere and multiply by the volume of the sphere. To estimate the concentrations we assume that the ions are in thermal equilibrium. We then know that the relative probability of finding an ion at a point where the potential is V , compared with what it is where the potential is zero (far away from charge Q) is given by the Boltzmann factor. For a positive ion with charge Ze (here e is the fundamental charge and Z is an integer giving the charge state) the Boltzmann factor is $\exp[-ZeV / k_B T]$. For a negative ion with charge $-Ze$ the Boltzmann factor is $\exp[+ZeV / k_B T]$. These factors make sense in that if V is positive, as it would be in the region surrounding a positive charge Q , then the probability of finding a positive ion is decreased and the probability of finding a negative ion is increased.

Let's say that far from Q the concentrations of positive and negative ions are equal to some ambient concentration c_0 , which we measure in units of number of ions per cubic meter. Near the charge Q the concentrations of positive and negative ions will be given by the formulas $c_{\pm} = c_0 \exp[\mp ZeV / k_B T]$ incorporating the Boltzmann factors we discussed. The excess concentration of ionic charge will then be given by the difference of the positive and negative ion charge densities $\rho = Zec_0 (\exp[-ZeV / k_B T] - \exp[+ZeV / k_B T])$. Each ion contributes a charge of magnitude Ze .

We are now going to make an approximation that can only be verified later. We are going to assume the potential energy ZeV is much smaller than the thermal energy $k_B T$. This will allow us to replace the exponential factors by something simpler. Specifically, if the exponent is small, $\exp[x] \approx 1 + x$. This gives the much simpler expression for the ionic charge density, $\rho \approx -2Z^2 e^2 c_0 V / (k_B T)$. The charge density is negative if V is positive as we expect. We are now going to make another simplifying assumption. We will ignore the fact that the potential varies continuously throughout the

volume of the sphere, and we will replace it with a “typical value”, $V = k_c Q / \kappa \lambda_D$, which is the value of the potential a distance λ_D from a positive charge Q . Note, we have included in this estimate the relative dielectric constant κ , which describes the effect of the polarization of the solvent’s molecules in reducing the potential. The result then for the excess charge density is $\rho \approx -2Z^2 e^2 c_0 k_c Q / (\lambda_D \kappa k_B T)$. (whew!!)

Our last steps are to estimate the ionic charge inside a sphere of radius λ_D to be

$Q_i = \frac{4\pi}{3} \lambda_D^3 \rho \approx -\frac{8\pi}{3} \lambda_D^2 Z^2 e^2 c_0 k_c Q / (\kappa k_B T)$, and then to demand that the ion charge be equal and opposite to the original charge, $Q_i = -Q$. This then gives an approximate formula for the Debye length,

$$\lambda_D^2 \approx \frac{3\kappa k_B T}{8\pi Z^2 e^2 c_0 k_c}.$$

A more precise theory not making the simplifying assumption that potential is uniform inside the sphere gives for the Debye length,

$$\lambda_D^2 = \frac{\kappa k_B T}{4\pi Z^2 e^2 c_0 k_c}.$$