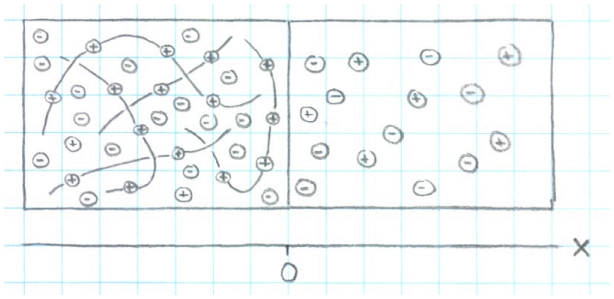
Charge Density Profile Near Interface [pln67]

The relation between densities $n_p^{\pm}, n_s, n_b$ of free and bound ions as described in [pln62] and worked out in [pex56] for the Donnan equilibrium between two chambers reflect bulk properties sufficiently far from the interface.

Near the interface the densities and the electric potential acquire profiles that deviate from the bulk values in characteristic ways:



- bound charges: $n_b(x) = n_b\,\theta(-x)$ (step function),
- mobile charges: $n_+(x)$, $n_-(x)$,
- electric potential: $\psi(x)$,
- Donnan potential: $\Delta\psi = \psi(-\infty) - \psi(+\infty)$,
- charge density: $\rho_e(x) = e_0[n_b(x) + n_+(x) - n_-(x)]$,

Charge neutrality condition: $\displaystyle\int_{-\infty}^{+\infty} dx\,\rho_e(x) = 0.$

Electric dipole moment: $\displaystyle P_e = \int_{-\infty}^{+\infty} dx\,x\,\rho_e(x).$

Poisson equation: $\displaystyle \epsilon\frac{d^2\psi}{dx^2} = -\rho_e(x), \quad \epsilon \doteq \epsilon_r\epsilon_0.$

Solution of Poisson equation [pex57]:

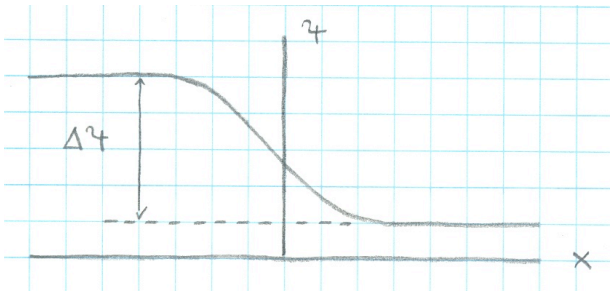
$$\psi(x) = -\frac{1}{2\epsilon}\int_{-\infty}^{+\infty} dx'|x - x'|\rho_e(x'). \tag{1}$$

Donnan potential from electric dipole moment via charge density [pex57]:

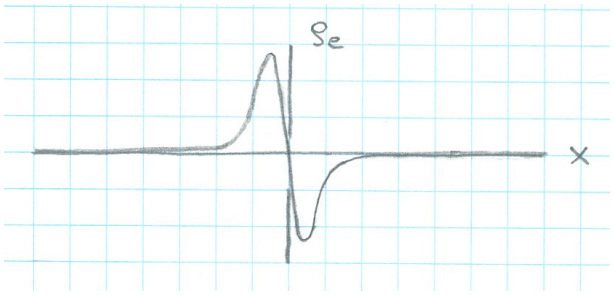
$$\Delta\psi = -\frac{P_e}{\epsilon}. \tag{2}$$

At this stage of the analysis we can infer the charge density profile $\rho_e(x)$ from a model profile $\psi(x)$ for the electric potential or vice versa. The quantitative analysis of a two-parameter model is part of [pex57].

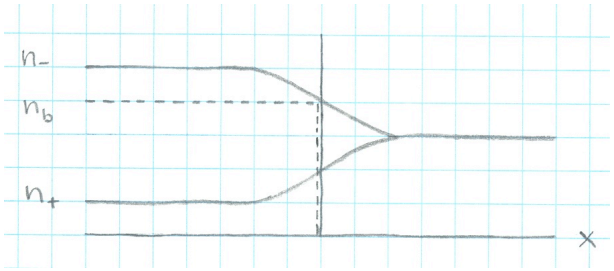
A model electric potential $\psi(x)$ of the shape



will result in a charge density $\rho_e(x)$ in the shape of a double layer:



Further ingredients and assumptions are needed for a quantitative analysis of the densities $n_+(x)$, $n_-(x)$ of mobile ions. However the qualitative shapes of those profiles are no mystery:



[extracted in part from Doi 2013]