Electric Double Layer and Debye-Huckel Theory

M. Ceriotti - MSE304

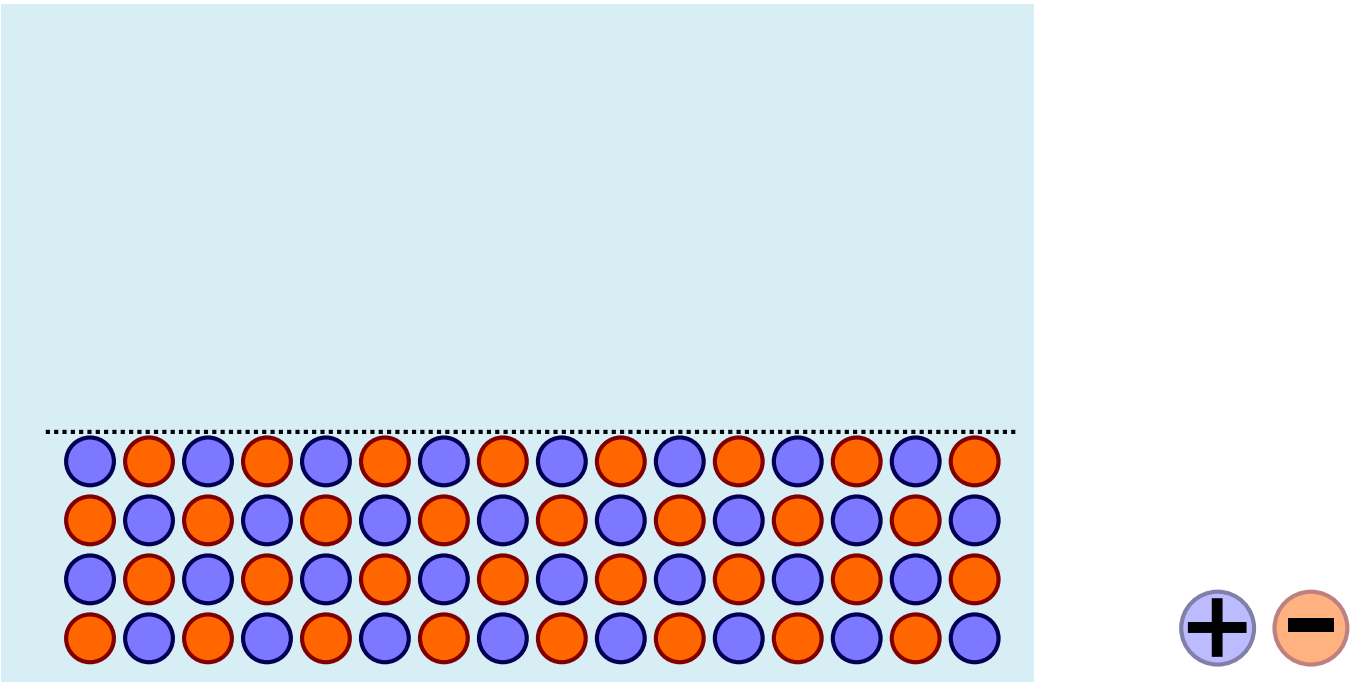
EPFL

Outline

- Chapter 12 of Mulvaney
- Surface charges, electrical double layer
- Zeta potential
- Debye-Hückel theory, screening of charge in solution

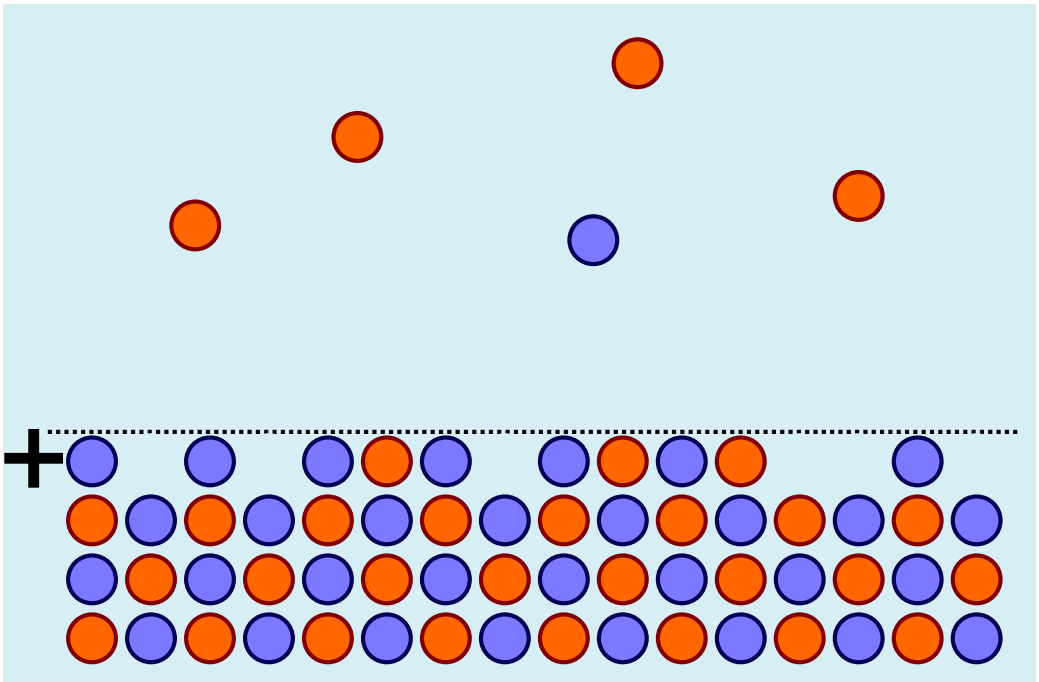
Surface charges

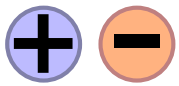
- In aqueous solution there may be accumulation of charge at the solid-liquid interface
  - preferential adsorption or desorption of ions
  - chemical modification of the surface



Surface charges

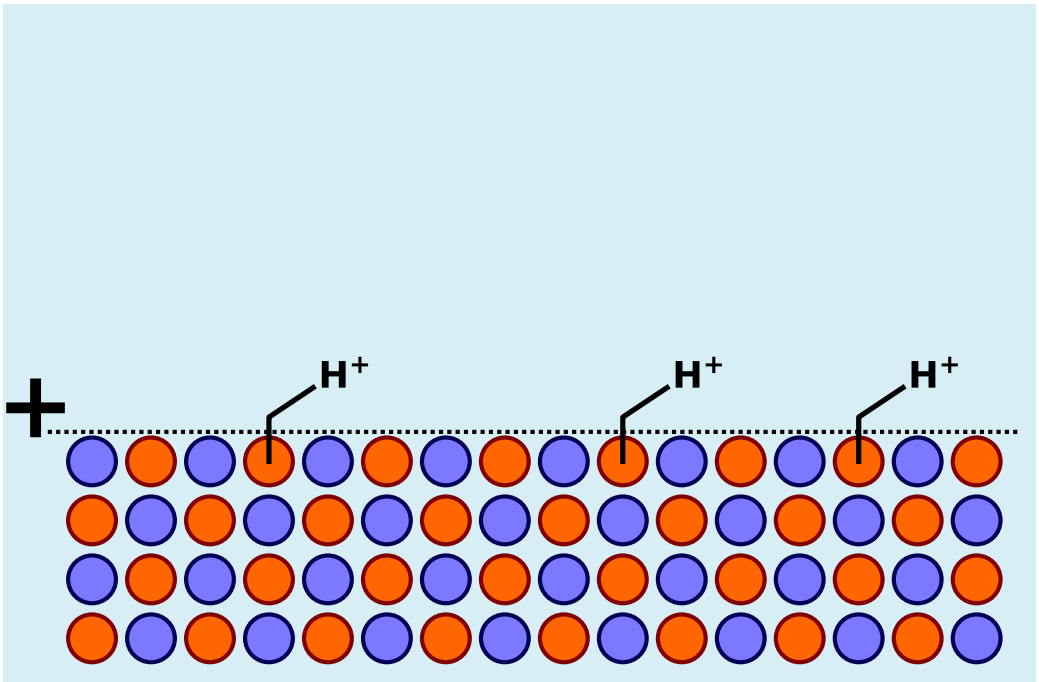
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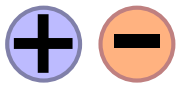




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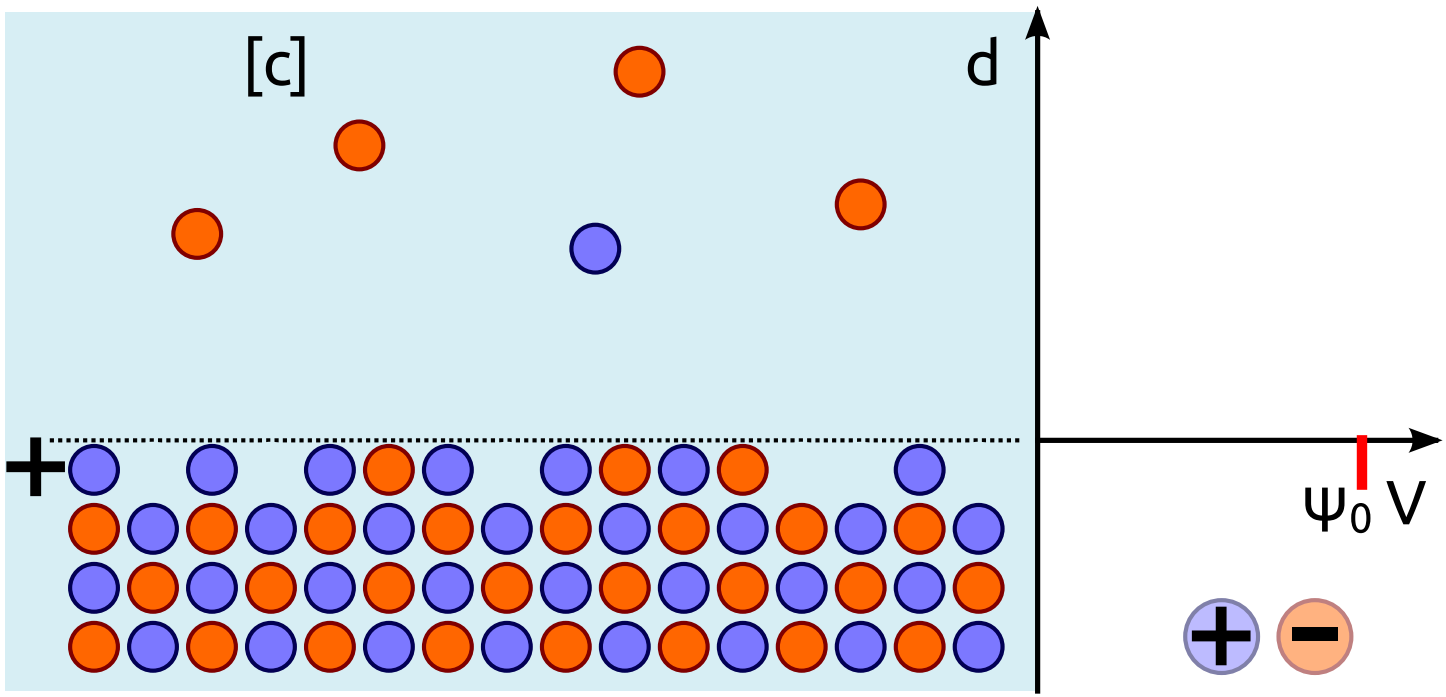
Point of zero charge

- Chemical potential of ions on the surface must equal the chemical potential in solution

$$\mu_+^{sol} = \mu_+^0 + RT \ln c_+, \qquad \mu_+^{surf} = \mu_+^{surf,neut} + z_+ F\psi$$

- "Point of zero charge": concentration leading to zero surface charge

$$-RT \ln c_+^{pzc} = \mu_+^0 - \mu_+^{surf,neut} \qquad \psi = \frac{RT}{z_+ F} \ln \frac{c_+}{c_+^{pzc}}$$



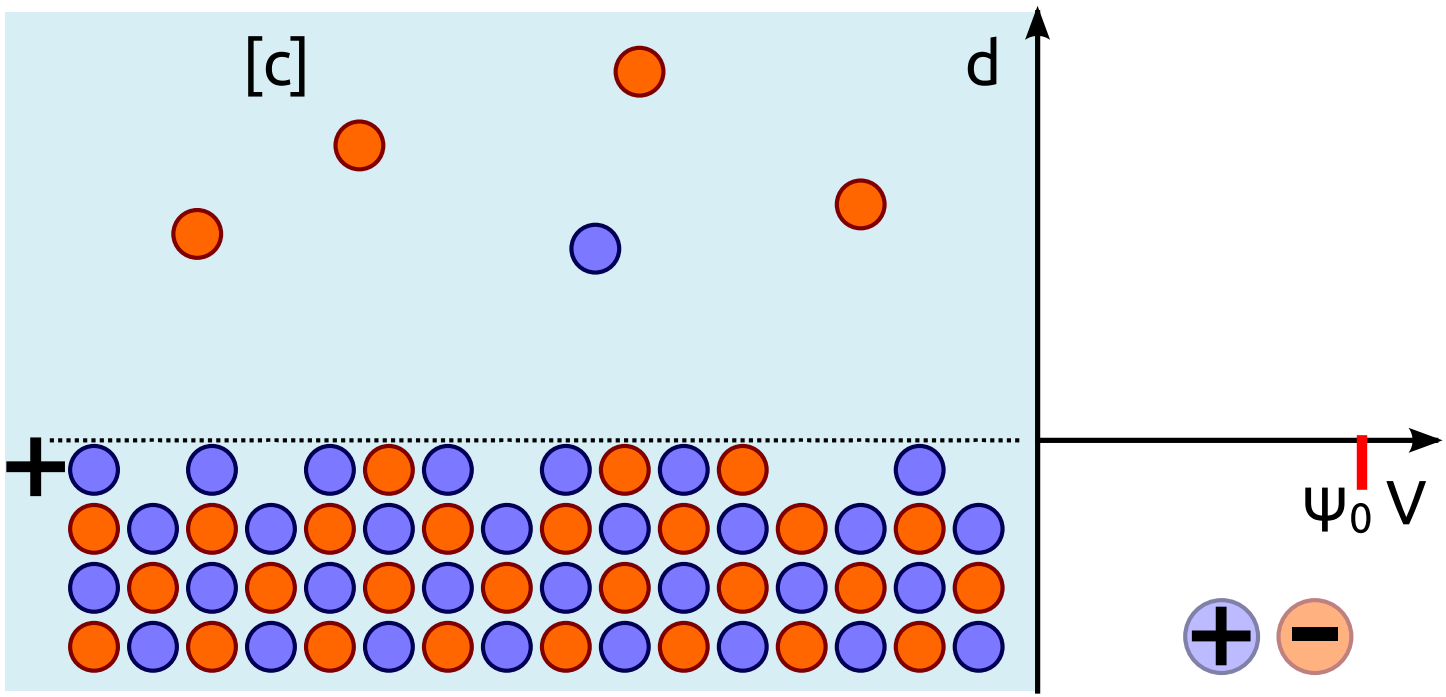
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$$\psi = \frac{RT}{z_+ F} \ln c_+ + \frac{\mu_+^0 - \mu_+^{\text{surf,neut}}}{z_+ F}$$

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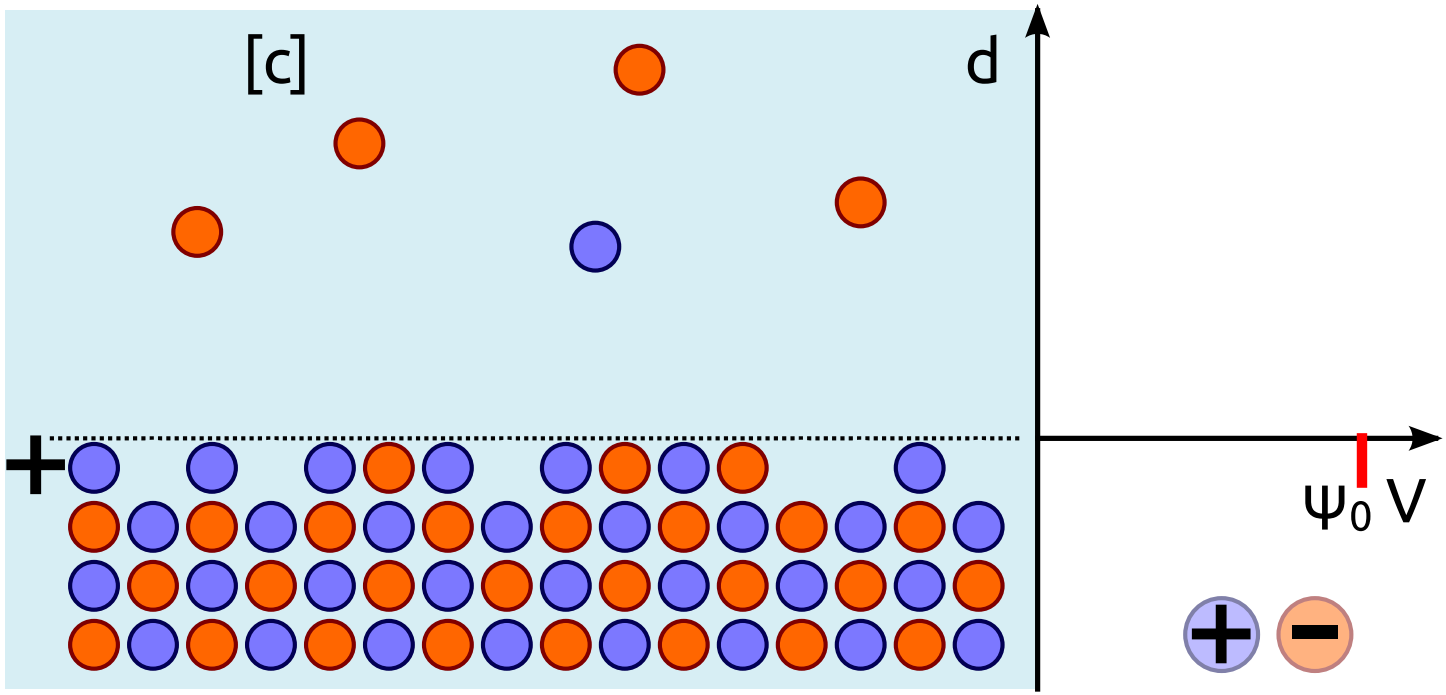
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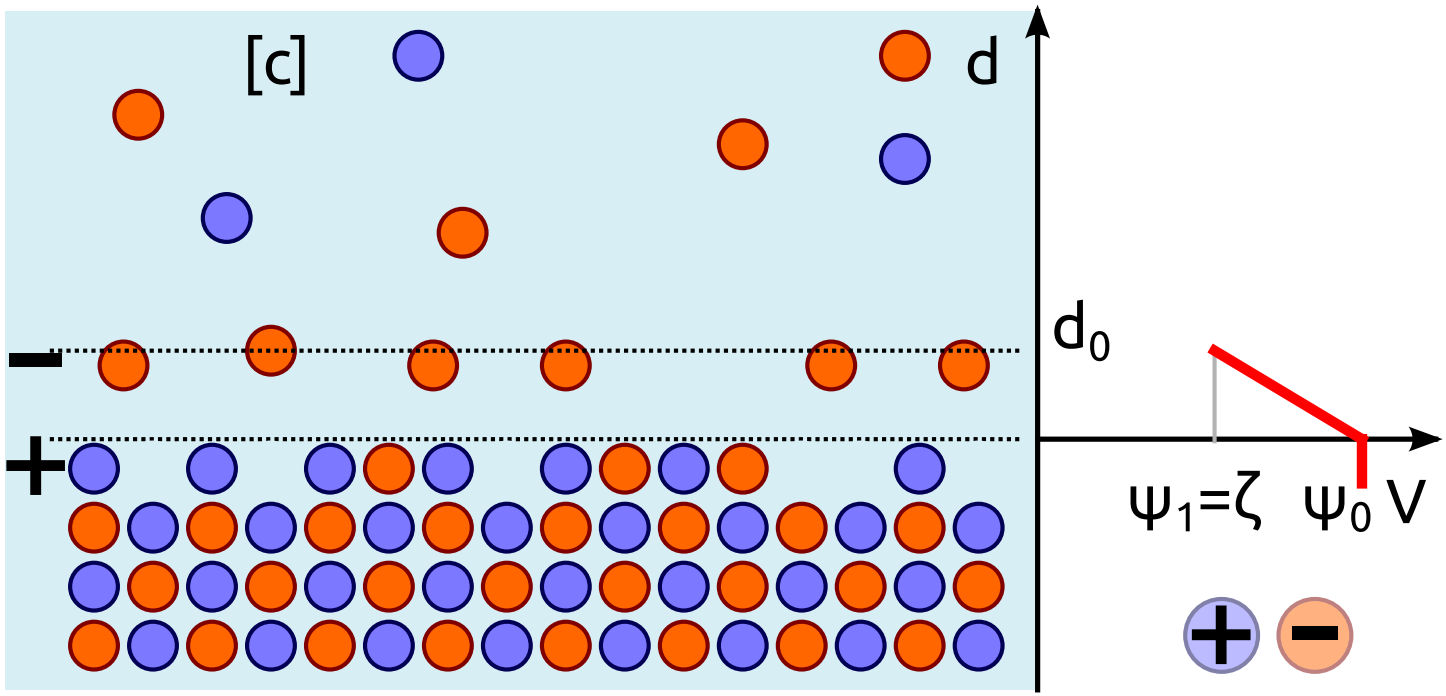
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Electric double layer and the zeta potential

- The very large surface charge leads to the formation of a *Helmoltz layer*, i.e. an accumulation of counter-ions close to the interface
  - Counter-ions are separate from the interface on an atomic scale
  - The double layer can be seen as a capacitor
  - Zeta potential: the potential at the edge of the Helmoltz layer

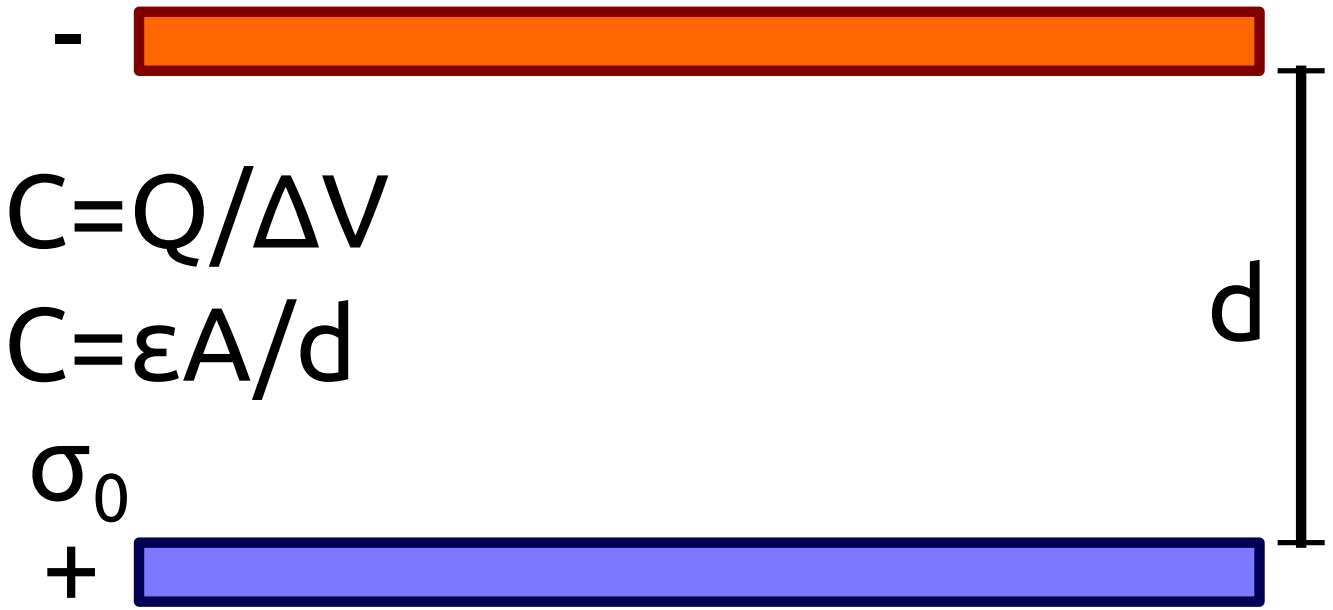


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$$C = \frac{\sigma_0 A}{\psi_0 - \psi_1} = \frac{\epsilon_0 \epsilon_r A}{d_0}$$

  - Zeta potential: the potential at the edge of the Helmoltz layer

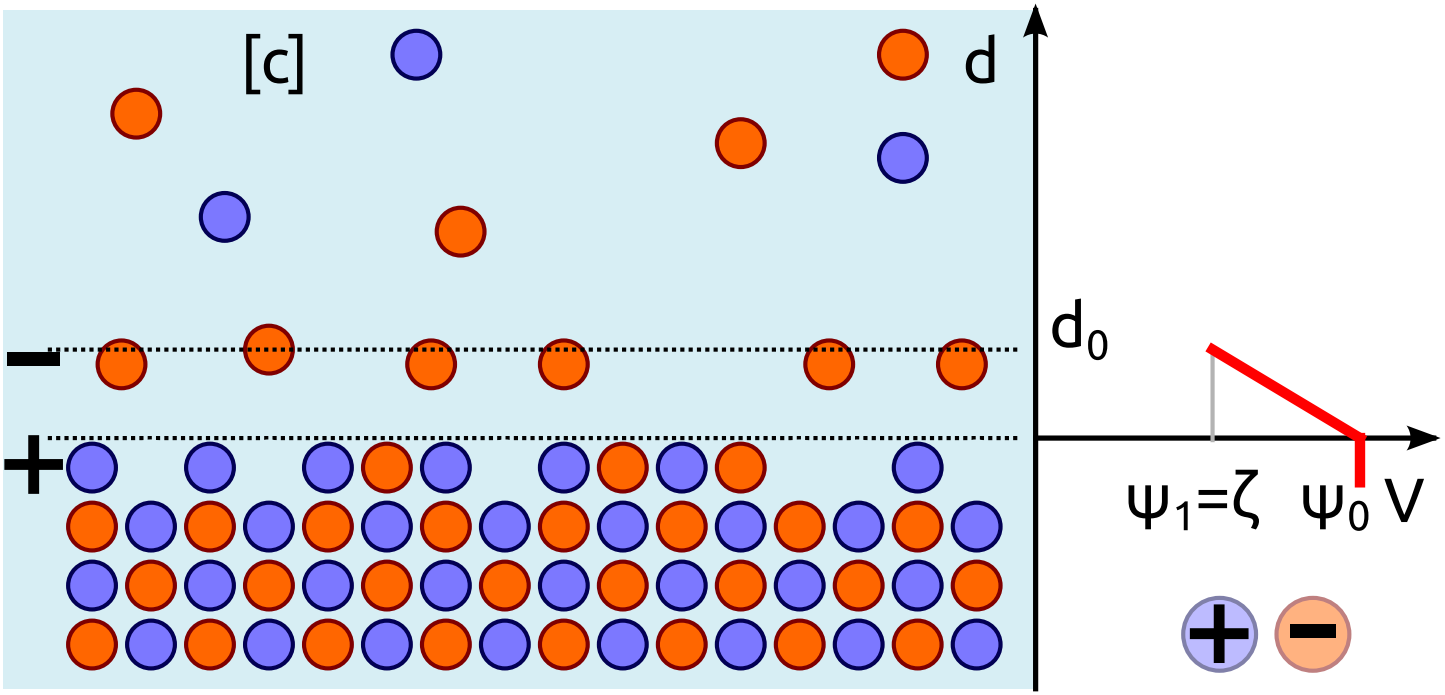


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$$\zeta = \psi_1 = \psi_0 - \frac{d_0 \sigma_0}{\epsilon_0 \epsilon_r}$$

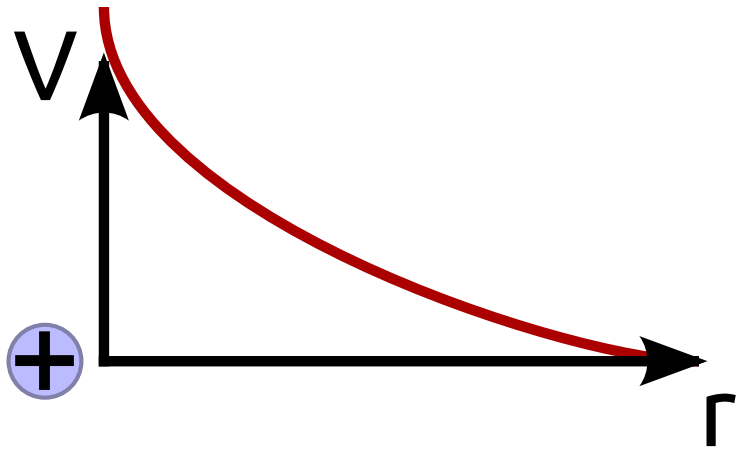
  - Zeta potential: the potential at the edge of the Helmoltz layer



Screening in ionic solutions: Debye-Hückel theory

- Electric potential induced by an ion in a dielectric medium
  - Other ions interact with this potential
  - Mean-field model: ion distribution represented by a Boltzmann density
  - Can be solved analytically if **linearized**

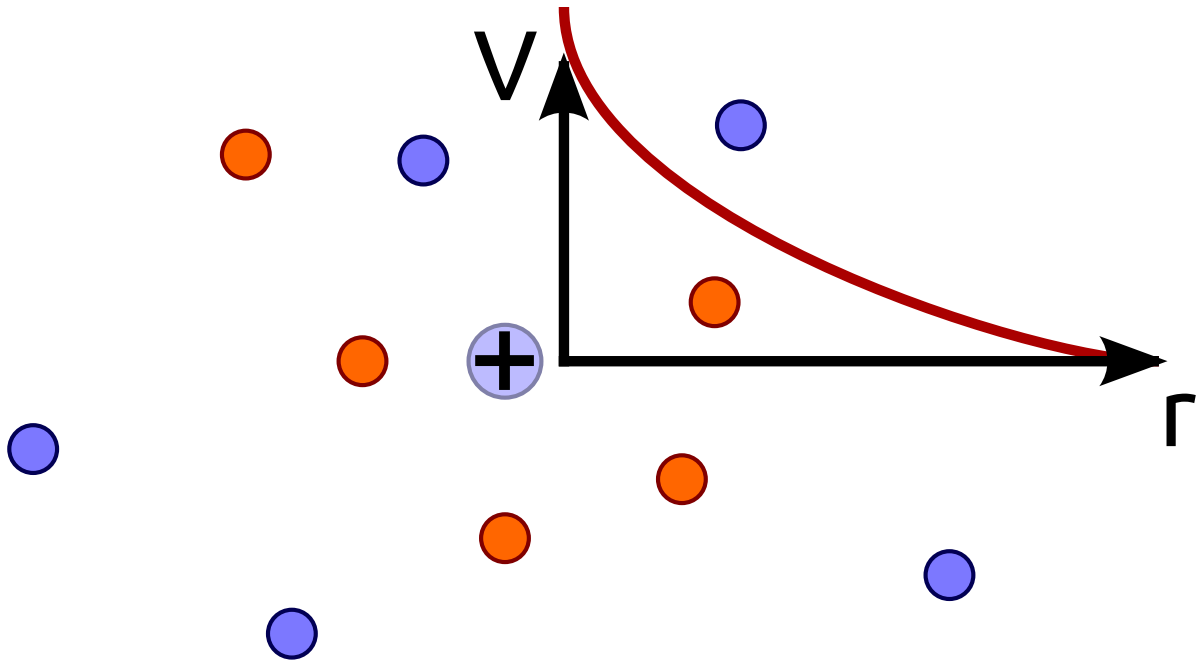
$$\psi_0(r) = \frac{e}{4\pi\epsilon_0\epsilon_r}\frac{z_+}{r}$$



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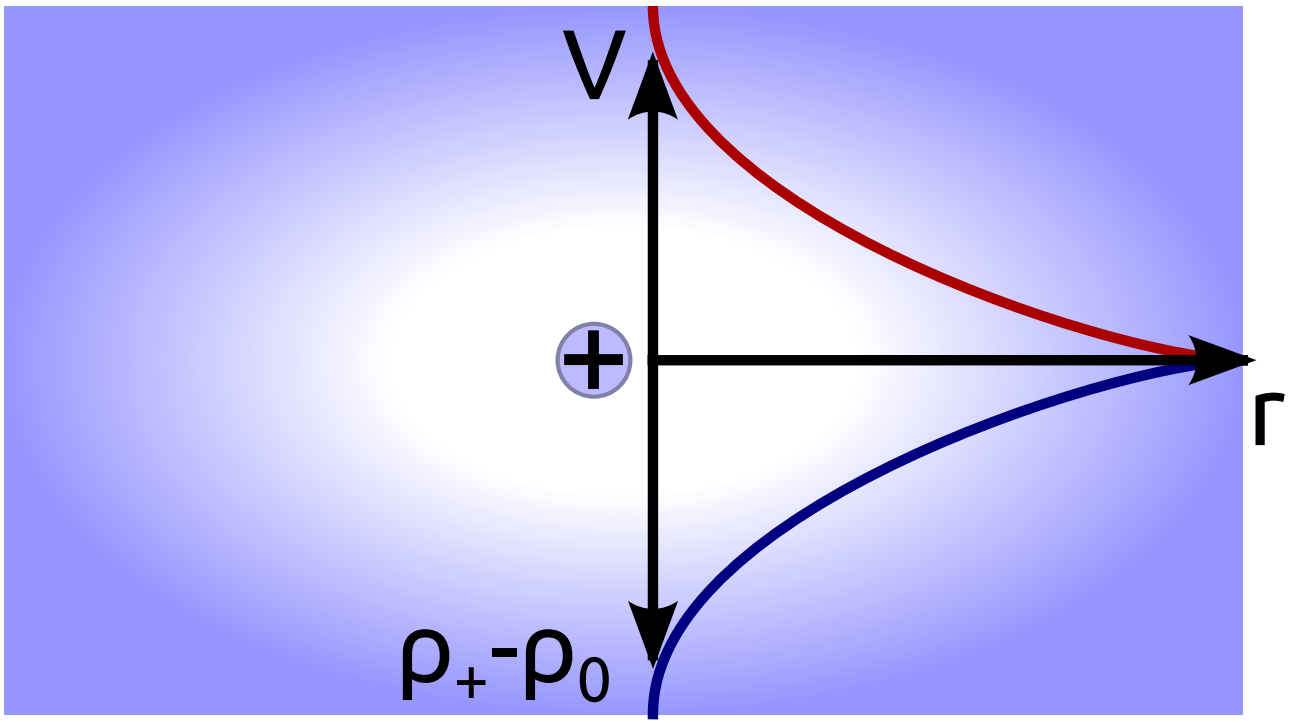
$$U_{\pm}^{0}(r) = ez_{\pm}\psi_0(r) = \frac{e^2}{4\pi\epsilon_0\epsilon_r}\frac{z_{\pm}z_{+}}{r}$$



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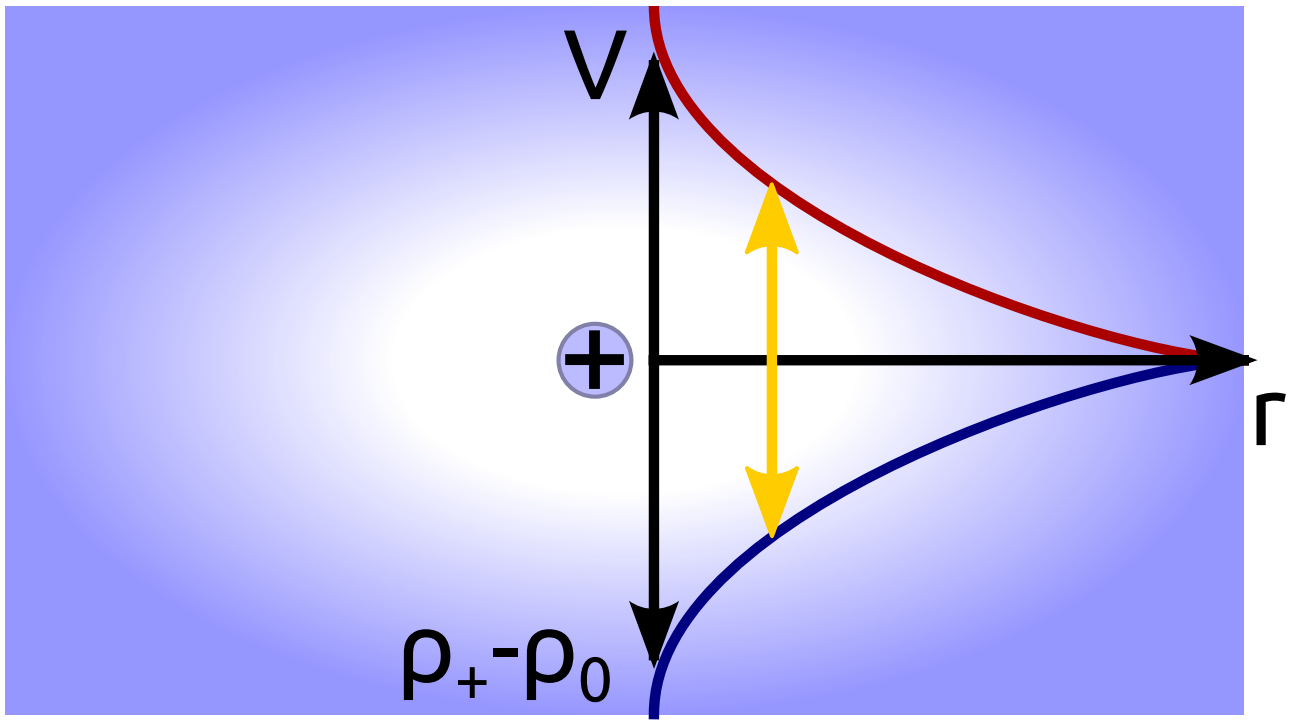
$$\rho_{\pm}(r) = \exp -\frac{ez_{\pm}}{k_B T}\psi(r)$$



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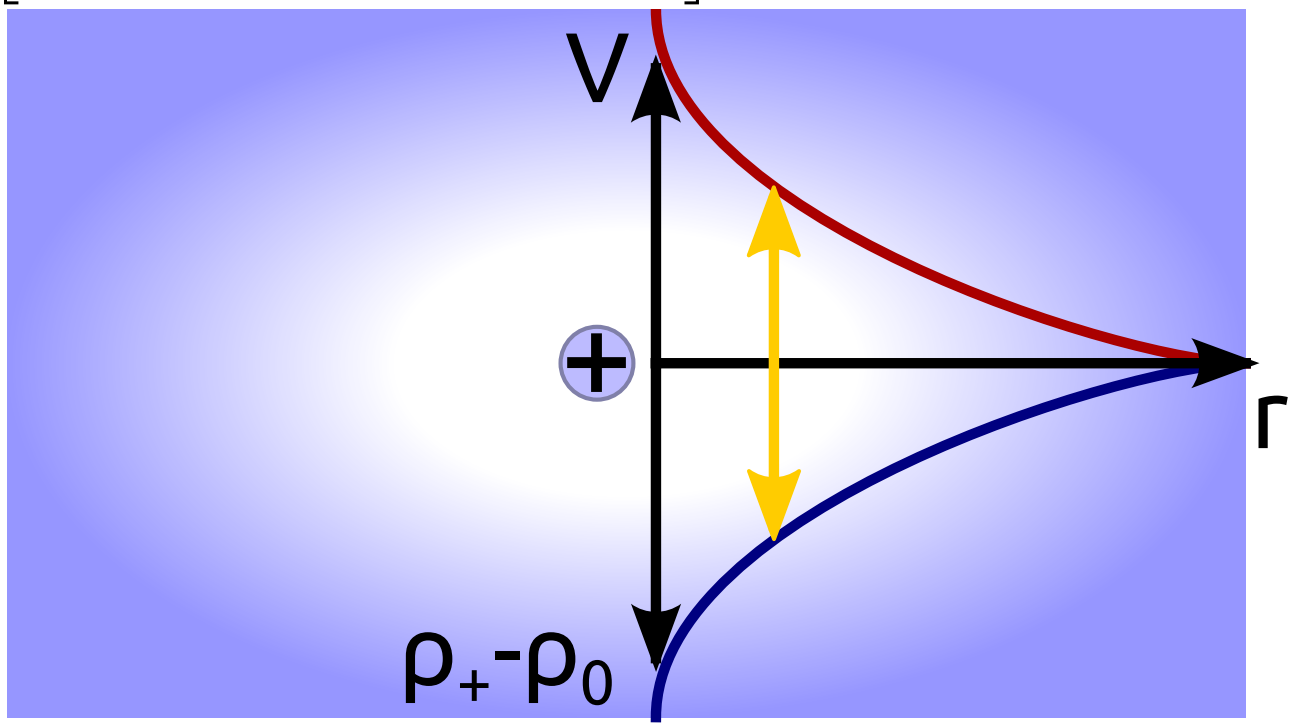
$$\nabla^2\psi = -\frac{\rho}{\epsilon_0\epsilon_r} = -\frac{e}{\epsilon_0\epsilon_r}\left[z_+\rho_+ + z_-\rho_-\right]$$



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$$\nabla^2\psi = -\frac{eC}{\epsilon_0\epsilon_r}\left[z_+ n_+ e^{-\frac{ez_+}{k_BT}\psi} + z_- n_- e^{-\frac{ez_-}{k_BT}\psi}\right] \approx \frac{e}{\epsilon_0\epsilon_r}\frac{eC}{k_BT}\left[n_+ z_+^2 + n_- z_-^2\right]\psi = \kappa^2\psi$$



Solving the Poisson-Boltzmann equation for a ion

- The (radial) Laplacian in spherical coordinates:

$$\frac{\partial^2 \cdot}{\partial x^2} = \frac{\partial}{\partial x}\frac{\partial \cdot}{\partial x} = \frac{\partial}{\partial x}\left(\frac{\partial r}{\partial x}\frac{\partial \cdot}{\partial r}\right) = \left(\frac{\partial r}{\partial x}\right)^2 \frac{\partial^2 \cdot}{\partial r^2} + \frac{\partial^2 r}{\partial x^2}\frac{\partial \cdot}{\partial r} = \frac{x^2}{r^2}\frac{\partial^2 \cdot}{\partial r^2} + \frac{1}{r}\left(1 - \frac{x^2}{r^2}\right)\frac{\partial \cdot}{\partial r}$$

- Solving the Poisson-Boltzmann equation.

Solving the Poisson-Boltzmann equation for a ion

- The (radial) Laplacian in spherical coordinates:

$$\nabla^2 \equiv \frac{\partial^2 \cdot}{\partial r^2} + \frac{2}{r}\frac{\partial \cdot}{\partial r}$$

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- Solving the Poisson-Boltzmann equation.

$$\nabla^2\psi = \psi'' + \frac{2}{r}\psi' = \kappa^2\psi\left(r\right) \quad \longleftarrow \quad \psi\left(r\right) = A\frac{e^{\pm\kappa r}}{r}, \psi' = \left[\pm\kappa - \frac{1}{r}\right]\psi$$

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- Solving the Poisson-Boltzmann equation.

$$\psi'' + \frac{2}{r}\psi' = \frac{\partial}{\partial r}\left[\pm\kappa\psi - \frac{1}{r}\psi\right] + \frac{2}{r}\psi' = \pm\kappa\left[\pm\kappa - \frac{1}{r}\right]\psi - \frac{1}{r}\psi' + \frac{1}{r^2}\psi + \frac{2}{r}\psi' = \psi\kappa^2$$

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- Solving the Poisson-Boltzmann equation.

$$\psi(r) = \frac{e z_+}{4\pi\epsilon_0\epsilon_r}\frac{e^{-\kappa r}}{r}, \qquad \kappa^2 = \frac{e^2 C}{\epsilon_0\epsilon_r}\frac{n_+ z_+^2 + n_- z_-^2}{k_B T}$$

