The electrified interface.

- The interface between two dissimilar interfaces is electrified. Almost all surfaces carry an excess electric charge.
- Hence when two dissimilar phases come into contact, charge separation occurs in the interfacial region which results in the generation of an interfacial potential difference or electric field.
- How does this happen?

Bottom line: an electrical double layer is set up at M/S interface.
Electro-neutrality is valid in bulk solution.

- Consider a metal electrode in contact with an aqueous solution containing salt (e.g. KCl (aq)).
- The solution contains solvated charged ions and solvent dipoles.
- Forces experienced by ions and solvent molecules in bulk of solution are isotropic: spherical symmetry operates. Ions and water molecules (on a time average) experience forces which are position and direction independent.
- There is no net alignment of solvent dipoles, and positive and negative ions are equally distributed throughout any volume element of the solution.
- Electroneutrality operates in bulk solution region very far from electrode surface.

Electroneutrality breaks down in surface region.

- What about the solution region next to the electrode surface?
- In this region forces experienced by ions and solvent dipoles are no longer isotropic and homogeneous. The forces are anisotropic because of the presence of the electrode phase.
- New solvent structure, different from that of the bulk, develops because of the phase boundary.
- Electroneutrality breaks down on the solution side of the interface.
- There will be a net orientation of solvent dipoles and a net excess charge in any volume element of the solution adjacent to the electrode surface.
- The solution side of the interface becomes electrified.
Interfacial charge separation generates high interfacial E-field.

- Once the solution side of the interface becomes electrified (acquires a net or excess charge), an electric field will operate across the phase boundary.
- Since the metallic phase contains charged particles, the latter will respond to this E field.
- The free electrons will move away from or move towards the interface depending on the direction of the E field.
- Thus a net charge will be induced on the metal, which will be equal in magnitude and opposite in sign to that on the solution side of the phase boundary.
- Thus charge separation occurs across the M/S interface, and this gives rise to an interfacial potential difference.
- Typically the potential difference is ca. 1.0 V. However the spatial dimensions of the interface region are very small, typically 1 nm thick. Thus the electric field strength present at the M/S interface will be typically $10^7$ Vcm$^{-1}$ which is very large.

Electrified interface.

- Formal definition.
  - Term electrified interface used to describe the arrangement of charges and oriented solvent dipoles at the interface between an electrode and an electrolyte solution.
- We now present some simple approximate models to describe the properties of the electrified interface.
- We examine three simple models:
  - Helmholtz compact layer model
  - Gouy-Chapman diffuse layer model
  - Stern model
- A key idea which we develop involves the representation of interfacial structure in terms of an electrical equivalent circuit element (specifically a single capacitor or series of capacitors).
- We initially adopt a simple pictorial description. This will be followed by a more quantitative mathematical analysis.
Simple representation of electrode/solution interphase region: Helmholtz compact layer model.

Structure of thin double layer region modelled as a parallel plate capacitor with a plate separation of molecular dimension.

\[ C_{DL} = C_H = \frac{\varepsilon_0 \varepsilon_r}{x_H} \]

Numerical calculations Using the Helmholtz Model.

We need the following relationships from basic physics.

\[ E = \frac{\Delta \phi}{x_H} \]

Electrical field Strength (V/m)

\[ \sigma = C_H \Delta \phi \]

Surface charge density on metal (C/m²)

\[ \varepsilon_0 = \text{permittivity of vacuum} = 8.854 \times 10^{-12} \text{ F/m} \]

\[ \varepsilon_r = \text{dielectric constant of solution} \]

\[ \varepsilon_r (\text{bulk}) \approx 78 \]

\[ \varepsilon_r (\text{Helmholtz}) \approx 5 - 6 \]

• A fundamental problem is assigning a value for the dielectric constant of the solvent in the thin Helmholtz region.
  • Solvent structure in this region differs considerably from that of the bulk solution.
  • Have considerable dielectric saturation effects and so dielectric constant will be much lower than that associated with the bulk solution.
  • The dielectric constant may also vary rapidly with distance in interface region.
Potential Distribution in Helmholtz Compact Layer.

Potential distribution obtained using the Poisson-Boltzmann equation which relates charge density $\rho$ and electrostatic potential $\phi$.

$$\frac{d^2 \phi}{dx^2} = -\frac{\rho}{\varepsilon_0 \varepsilon_r}$$

Radius of solvated ion $= x_H$

Ions treated as point charges. Hence can assume that excess charge density between electrode surface and OHP is zero, hence $\rho = 0$.

$$\phi(x) = \phi_M - \frac{\phi_M - \phi_S}{x_H} x$$

Simple models are not always good ones.

- The simple Helmholtz picture is not complete since it predicts:
  - The double layer capacitance is a constant independent of ion concentration and electrode potential
  Whereas:
  - Experiment indicates that the double layer capacitance varies with both of these quantities in a definite manner.
- A more elaborate model is required.
The diffuse double layer.

- How does a 3-D distribution of charge arise?
- We have neglected the disordering effect of the thermal motion of the ions in the solution. This opposes the ordering tendency due to operation of electrostatic forces in the interface region.
- Thermal and electrostatic forces results in an equilibrium. The excess charge density \( s_S \) counterbalancing the excess charge density \( s_M \) on the metal, is at a maximum close to the electrode surface. It diminishes in an approximate exponential manner with increasing distance from the electrode surface, giving rise to a diffuse space charge layer adjacent to the electrode.
- Detailed analysis indicates that the thickness of the diffuse layer region will depend both on the potential applied to the electrode, and on the concentration of ions present in the electrolyte solution.

Gouy-Chapman model of diffuse double layer.

In the Gouy-Chapman model of the interface region, it is assumed that the excess charge density on the solution side of the interface can be represented in terms of a three dimensional space charge.
**Gouy-Chapman model of diffuse double layer.**

At potential of Zero charge:
\[ \theta_0 = 0 \]

Charge density in diffuse layer
\[ \sigma_d = -4\varepsilon_0 e^z L_D \sinh[\theta_0] \]

Excess positive charge density
\[ \sigma_M = -\sigma_d \]

Excess negative charge density
\[ \phi_0 = \frac{\varepsilon_0 e^z}{L_D} \]

**Diffuse layer thickness.**

The diffuse layer thickness is called the Debye Length and is given the symbol \( L_D \). In many books this is denoted as \( 1/\kappa \). For a \( z,z \) electrolyte the Debye length is given by the expression across. Evaluation of the constants gives a useful expression for computation.

\[ L_D \approx \left( \frac{\varepsilon k T}{2z^2 e^z} \right)^{1/2} = \frac{\varepsilon_0 e z L_D}{2z^2 F^2 e^z} \]

Note that the Debye Length increases as the ionic concentration decreases. The diffuse layer thickness will be greatest for the most dilute solutions.

(1,1) electrolyte, water \( \varepsilon_r = 78 \), \( T = 298K \)
Stern model of the interface region.

- Neither the Helmholtz compact layer model nor the Gouy-Chapman diffuse layer model is totally satisfactory.
- In the GC model the solvated ions are modelled as point charges. This neglect of ion size is unrealistic. In reality the solvated ion can only approach the electrode surface to a distance equal to its solvated radius $a$.
- Hence a more logical approach is to combine the features of the Helmholtz and Gouy-Chapman models. This was done by Stern.

The Stern model is as follows. Next to the electrode we have a region of high electric field and low dielectric constant ($\varepsilon_r$ value ca. 6) with a row of firmly held counter ions. Beyond that there is an ionic atmosphere (the diffuse layer) where there is a balance between the ordering electrostatic force and disordering thermal motions. The dielectric constant increases rapidly with distance in this region.

- The electrical potential varies linearly with distance (ca. hydrated ion radius) within the inner compact layer and decreases in an approximate exponential manner with distance within the diffuse layer, decaying to zero in the bulk solution.

Stern model of solid/solution interphase region.

\[
\frac{1}{C_{DL}} = \frac{1}{C_H} + \frac{1}{C_D}
\]

The smaller of the two capacitances will determine the overall capacitance. If $C_H$ and $C_D$ are of very different size then the term containing the larger one may be neglected.

The diffuse layer capacitance will predominate when the solution concentration is low.
A reasonable model of the electrode/solution interface.

The electrode/solution interface is modelled as a series arrangement of two capacitors. This is an equivalent circuit representation of the interface.

\[ C_{DL} \quad C_H \quad C_D \]

Series arrangement of capacitors.

From basic physics:

\[ \frac{1}{C_{DL}} = \frac{1}{C_H} + \frac{1}{C_D} \]

Total capacitance

Diffuse layer

The Poisson-Boltzmann equation (I).

From classical electrostatics we use the Poisson equation which relates the dielectric displacement vector \( \mathbf{D} \) and the local volume density of charge \( \rho \) (the number of charges per unit volume).

\[ \nabla \cdot \mathbf{D} = \rho \]

\[ \mathbf{D} = \varepsilon \mathbf{E} \]

\[ \nabla \cdot (\varepsilon \mathbf{E}) = \rho \]

Divergence operator

Electric field vector \( \mathbf{E} \) can be related to the electrostatic potential \( \phi \) using basic physics:

\[ \mathbf{E} = -\nabla \phi \]

Gradient operator

This is the form of the Poisson equation which relates the charge density and the electrostatic potential.
The Poisson-Boltzmann equation (II).

We now need to evaluate the charge density $\rho$. The volume density of charge is obtained by adding together the product of the charge $q_j$ and concentration $c_j$ of each ionic species $j$ in the solution next to the electrode surface.

$$\rho = \sum_j q_j c_j = \sum_j z_j^+ e c_j$$

We use the Boltzmann equation of statistical mechanics to obtain a relationship between the local counterion concentration $c_j$ and the bulk concentration $c^\infty_j$. To do this we need to evaluate the work $w_j$ done in bringing the ion from a reference point at infinity, up to a point distance $r$ from the electrode surface. We assume that this work is purely electrical in nature.

$$w_j(r) = q_j \phi(r) = z_j e \phi(r)$$

The Poisson-Boltzmann equation (III).

We are now in a position to write down the PB equation. This is a fairly complicated equation to solve from first principles. The exact form of the differential equation depends on the geometry. We shall assume a $z,z$ electrolyte such as KCl or NaCl. The geometry determines the form that the $\nabla^2$ operator takes. A planar geometry is used for macroelectrodes, whereas a spherical geometry is adopted for ultramicroelectrodes.

$$\nabla^2 \phi = -\frac{\rho(r)}{\varepsilon} = -\frac{1}{\varepsilon} \sum_j z_j e c_j(r)$$

Debye Length, $z,z$ electrolyte

$$L_D = \frac{1}{k} = \frac{1}{z e} \sqrt{\frac{\varepsilon k_B T}{2 e^2}}$$

$$z_j e c^\infty_j \exp\left[\frac{z_j e \phi(r)}{k_B T}\right]$$

$z,z$ valent electrolyte

$$d^2 \phi(s) = -\frac{z e c^\infty}{\varepsilon} \left[ \exp\left[\frac{z e \phi}{k_B T}\right] - \exp\left[\frac{z e \phi}{k_B T}\right] \right]$$

The PB equation is solved for $\phi$. Planar geometry

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) \phi = -\frac{z e c^\infty}{\varepsilon} \left[ \exp\left[\frac{z e \phi}{k_B T}\right] - \exp\left[\frac{z e \phi}{k_B T}\right] \right]$$

Spherical geometry
The Poisson Boltzmann equation (IV).

- The PB equation fully describes the pertinent electrical properties of the diffuse layer. However, it can only be solved analytically for a few special situations. For the most general cases a numerical solution has to be adopted.
- The PB equation for flat planar surfaces can be rigorously solved for z, z electrolytes.
- This cannot be done rigorously for spherical surfaces. Approximate solutions of varying degrees of accuracy have been produced.
- A reasonable approach valid both for planar and spherical interfaces involves the Debye-Huckel approximation, which results in the transformation of the PB equation into a linear form as indicated across. This approximation will be valid provided that the potential at the surface of the electrode is not too large.

\[ \frac{\nabla^2 \phi}{\kappa^2 \phi} \approx k_B T \]

**Planar geometry**

**DH approximation**

\[ \frac{d^2 \phi}{dx^2} \approx \kappa^2 \phi \]

Approximate form of potential distribution

\[ \phi = \phi_0 \exp[-\kappa x] = \phi_0 \exp\left[-\frac{x}{L_D}\right] \]

**Poisson/Boltzmann equation : planar surface**

\[ \frac{d^2 \Theta}{dx^2} - \frac{1}{2} \sinh[2\Theta] = 0 \]

Neglect compact layer

\[ \chi = 0 \quad \Theta = \Theta_0 \]

\[ \chi \to \infty \quad \Theta \to 0 \]

Normalised potential

\[ \Theta = \frac{ze \chi}{2k_B T} \]

\[ \Theta_0 = \frac{ze \phi_0}{2k_B T} \]

Normalised distance

**Variation of electrostatic potential with distance in the diffuse layer region.** The potential is effectively exponentially decaying with distance from solid surface.

**Full solution of PB equation**

**Large surface potential**

\[ \Theta = 2 \tanh^{-1}[\exp(-\chi)] \]

**Small surface potential**

Debye-Huckel approximation

\[ \chi = \frac{x}{L_D} \]

**Thickness of Diffuse layer**

\[ \Theta_0 = 1 \]

\[ \Theta_0 > 5 \]
Charge density in diffuse layer region.

\[ \sigma_D = \int_0^\infty \rho(x) \, dx = \frac{1}{k} \int_0^\infty \rho(\chi) \, d\chi \]

For a \( z, z \) electrolyte the local charge density \( \rho \) is given by

\[ \rho = \frac{zec^z}{k} \left( \exp[-2\theta] - \exp[2\theta] \right) \]

\[ \sigma_D = -\frac{2zec^z}{k} \int_0^\infty \sinh[2\theta] \, d\chi \]

\[ = \frac{2zec^z}{k} \left[ \frac{\sinh[2\theta]}{2} \right] \, d\theta \]

\[ \frac{d\theta}{d\chi} = \frac{-\sinh[\theta]}{\sinh[\theta]} \]

If the potential applied to the metal surface is small we can assume a linear approximation and

\[ \sinh[\theta_0] \geq \theta_0 \]

Debye Length

\[ \sigma_D = -\frac{4zec^z}{k} \theta_0 \]

\[ = \frac{4zec^z}{k} \left( \frac{ze\phi_0}{2k_\beta T} \right) \]

\[ = \frac{2z^2e^z c^z}{k k_\beta T} \phi_0 = -e\phi_0 \]

Note that the sign of \( \sigma_D \) is opposite to that of \( \theta_0 \). Hence a positive \( \theta_0 \) implies that negative ions are attracted to interface and vice versa.

Diffuse Layer capacitance \( C_D \)

We define the differential capacitance of the diffuse layer as

\[ C_D = -\frac{d\sigma_D}{d\phi_0} = \frac{d\sigma_M}{d\phi_0} = -\frac{ze}{2k_\beta T} \frac{d\sigma_D}{d\theta_0} \]

Charge density within diffuse layer is

\[ \sigma_D = -\frac{4zec^z}{k} \sinh[\theta_0] \]

We recall that Debye Length (diffuse layer thickness is

\[ L_D = \frac{1}{k} = \frac{1}{ze} \left( \frac{ek_\beta T}{2c^z} \right) \]

\[ = \frac{2z^2e^z c^z}{k k_\beta T} = ek \]

\[ C_D = \varepsilon k \cosh[\theta_0] \]

\[ = \frac{2z^2e^z c^z}{k k_\beta T} \sinh[\theta_0] \]

\[ = \frac{2z^2e^z c^z}{k k_\beta T} \cosh \left[ \frac{ze\phi_0}{2k_\beta T} \right] \]

\[ = \varepsilon \kappa \cosh \left[ \frac{ze\phi_0}{2k_\beta T} \right] \]

\[ C_D = \varepsilon \kappa \cosh[\theta_0] \]

\( C_D \) depends on potential. It is not constant.
Variation of diffuse layer capacitance with potential.

\[ C_d = \left( \frac{\partial \sigma_M}{\partial \Delta_{\text{HP}}^0} \phi \right) = \sqrt{\frac{2\varepsilon_0^2 \varepsilon \varepsilon_i c_0}{kT \cosh\left(\frac{e\Delta_{\text{HP}}^0 \phi}{2kT}\right)}} \]

How good is the diffuse layer Theory in practice?

Diffuse layer model also applies for colloidal particle/solution interface. Double layer modelling still being performed at research level to various degrees of sophistication.

Potential dependence of the differential capacitance at the Hg/KF interface:
- a: 1.000 M
- b: 0.100 M
- c: 0.010 M
- d: 0.001 M

Dashed lines are obtained from eq. 6.5 for concentrations of 0.01 and 0.001 M.
Electroneutrality breakdown in diffuse layer region:

Planar surface.

\[
\frac{c_i}{c^*} = \tanh\left(\frac{1}{2} (\chi + f(\theta_0)) \right)
\]

\[
\frac{c}{c^*} = \coth\left(\frac{1}{2} (\chi + f(\theta_0)) \right)
\]

\[
\theta_0 > 0 \quad f(\theta_0) = -\ln\left(\tanh\left(\frac{\theta_0}{2}\right)\right)
\]

\[
\theta_0 < 0 \quad f(\theta_0) = -\ln\left(\tanh\left(-\frac{\theta_0}{2}\right)\right)
\]

Counterion concentration increases close to charged solid surface and co-ion concentration decreases close to charged surface.

Typical variation of \( C_{DL} \) with applied potential.

Hg/aqueous KCl interface.

Modern models incorporating specific adsorption of ions in the inner compact layer, allied with a model for the water structure in the inner layer explain the capacitance maximum.
One currently accepted model is the BDM model. It represents the situation on the solution side of the interface in terms of a triple layer. An inner Helmholtz plane (IHP) is introduced and is regarded as the locus of the electrical centers of specifically adsorbed ions. These anions are strongly adsorbed onto the electrode surface and are partially desolvated. This fact causes a reversal of electrostatic potential in the region between the IHP and the OHP. A primary and secondary water layer is introduced with differing dielectric properties. The primary water layer ($\varepsilon_r = 5$) is located immediately adjacent to the metal electrode surface. The secondary water layer ($\varepsilon_r = 36$) is located as a hydration sphere around a solvated cation and anion.
Polarizable and non-polarizable interfaces.

Electrode/solution interface
Electrical equivalent circuit

Ideally Polarizable Interface: \( R_{CT} \to \infty \)

Ideally non-polarizable Interface: \( R_{CT} \to 0 \)

Charge transfer occurs across M/S interface

Simple equivalent circuit representation of electrode/solution interface region.

\( i = i_C + i_F \)

Double layer charging current always present in addition to Faradaic current in electrochemical measurements.

Evaluation of \( C_{DL} \) (and hence \( i_c \)) always necessary when making kinetic measurements at short timescales.
Experimental interrogation of electrode/solution interfaces.

- **Conventional electrochemical techniques.**
  - Based on measurement of current, potential and charge.
  - CV, RDV, RRDV, PSCA, CIS etc.
  - Applied both to macrosized and microelectrodes.
  - Theory, instrumentation, and practice well developed.
  - No direct information on microscopic structure of electrode/solution interface.

- **Spectroscopic techniques.**
  - Provides useful chemical information about species at interfaces.
  - FTIR, Raman, UV/VIS, XPS, EXAFS, Ellipsometry, EC/NMR (new technique, very specialised, limited application at present).

- **Scanning probe microscopy.**
  - High resolution topographical imaging of electrode surfaces with atomic resolution. Surface reactivity also probed with high spatial resolution.
  - STM, AFM, SECM.