# Classical Models of the Interface between an Electrode and an Electrolyte

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**Abstract:** An electrical double layer (EDL) plays a major role in understanding the interface between a charged surface (e.g. an implant) and ionic liquids (e.g. body fluids). The three classical models of the EDL (Helmholtz, Gouy – Chapman and Stern Model) are numerically solved for a flat surface electrode in the 3D Electrostatics mode of Comsol Multiphysics® 3.5a Software. The values of the electric potential drop near the electrode's surface are compared and it is shown their area of validity. The double layer capacitance is computed analytically, numerically and measured by Electrochemical Impedance Spectroscopy (EIS) and it has been shown that the classical models do not agree with the experimental measurements.

**Keywords:** Electrical double layer, capacitance, FEM, simulation

## 1. Introduction

The clinical success of an implant depends on the profound knowledge of the interaction between the biomaterial and the cells. The contact between the implant and the body fluids results into formation of an EDL. This double layer consists of a layer of electrons (if the non-electrolytic phase is a metal or electronic conductor), a layer of adsorbed ions, and a diffuse double layer with an ionic atmosphere, where ions with a sign opposite to the electrode surface are found to be present in excess compared to the bulk. The EDL is formed simultaneously after the contact of the electrode with the electrolyte and results into a fall of the electric potential, assisting proteins adhesion and the resulting cell spreading. Therefore, EDL has a huge impact on the analysis and simulation of electrical interactions of implants with the bio-system.

## 2. Electrical Double Layer

The present paper is concerned with the comparison of the classical models of the EDL, which consider the electrolyte as a continuum dielectric solvent and dilute ionic solution. The electrode is perfectly polarized and any chemical reactions on it are neglected. A circular plate condensator with electrode radius R=10 nm and potentials of ±50 mV, filled with Sodium Chloride (NaCl) electrolyte with concentration of 0.1 and 0.01 M is regarded here.

### 2.1 Helmholtz Model

The first and simplest double layer model, created in 1879 by Helmholtz [4], considered the concept of the charge separation at the interface between a metallic electrode and an electrolyte solution.
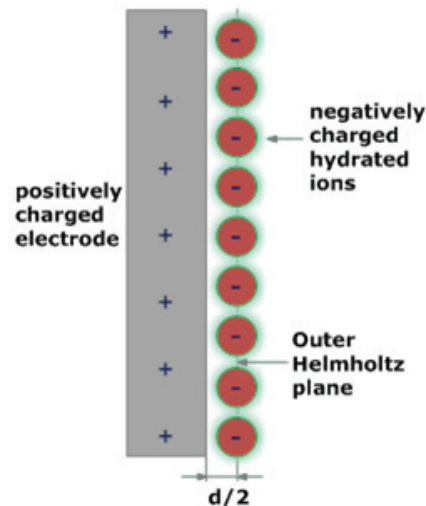


**Figure 1**. Helmholtz Model

The electrode holds a charge density ($\sigma_M$) arising from either an excess ($-\sigma_M$) or deficiency ($+\sigma_M$) of electrons at the electrode surface. The charge on the electrode is balanced by redistribution of the ions in the solution by an equal but

oppositely charged amount of ions. The result is two layers of opposite charge separated by some distance l=d/2 limited to the radius d/2 of the attracted ions and a single layer of solvation around each ion (fig.1).

The line drawn through the centre of such ions marks the boundary known as the 'Outer Helmholtz Plane' (OHP) and the region within it the electrical double layer.

The potential in the Helmholtz layer is described by the Poisson's equation in 1D, which relates the potential with the charge distribution

$$\frac{\partial^2 \varphi}{\partial x^2} = -\frac{\rho(x)}{\varepsilon_r \varepsilon_0}, \qquad (1)$$

where $\varphi$ is the electric potential, $\rho$ is the charge density, x is the distance from the electrode, $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon_r$ is the relative permittivity of the medium.

The approach treats the ions as point charges and this allows us to rewrite Eq-n (1) between the two layers to

$$\frac{\partial^2 \varphi}{\partial x^2} = 0. \qquad (2)$$

This behaviour is comparable to the classical problem of a parallel-plate capacitor i.e. EDL is capable of storing electric charge. Therefore, the double layer capacitance per unit area is given as:

$$C_H = \frac{\varepsilon_0 \varepsilon_r}{l}, \qquad (3)$$

where $l$ is the thickness of the double layer.

For $\varepsilon_0 = 8.854 \times 10^{-12} \ F/m$, $\varepsilon_r = 78.5$ and $l = 0.3 \times 10^{-9} m$, we get

$$C_H = 231.41 \mu F / cm^2. \qquad (4)$$

The model does not account for the dependence of the measured capacity on potential or electrolyte concentration. Another drawback is the neglect of interactions that occur away from the OHP.

### 2.2 Gouy-Chapman Model

Gouy and Chapman [2, 3] were the first to consider the thermal motion of ions near a charged surface. They pictured a diffuse double layer (DDL) consisting of counterions (i.e. ions of opposite charge to the surface), which are attracted to the surface and co-ions repelled by it embedded in a dielectric continuum described by the Poisson - Boltzmann (PB) differential equation.
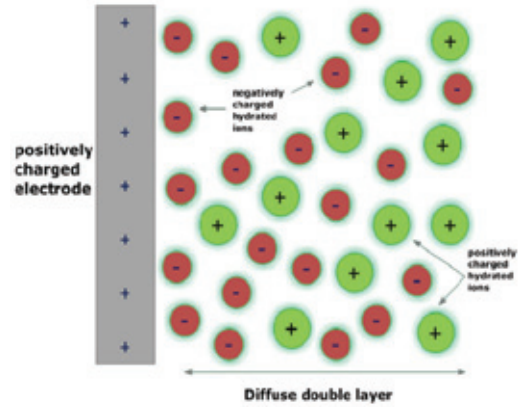


**Figure 2**. Gouy-Chapman Model

The distribution of ions is described by the Boltzmann distribution:

$$n_i = n_i^0 \exp\left(\frac{-z_i e \varphi}{kT}\right), \qquad (5)$$

where $n_i^0$ is the concentration of ion $i$ in the bulk, e is the unit charge, $z_i$ - charge on the ion $i$, k – Boltzmann constant, T – absolute temperature.

The total charge density per unit volume for all ionic species is the sum over all ions:

$$\rho(x) = \sum_i n_i z_i e = \sum_i n_i^0 z_i e \exp\left(\frac{-z_i e \varphi}{kT}\right). (6)$$

Combining Eq. (1) and Eq. (6) leads to the Poisson-Boltzmann equation:

$$\frac{\partial^2 \varphi}{\partial x^2} = -\frac{e}{\varepsilon_r \varepsilon_0} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e \varphi}{kT}\right). \qquad (7)$$

By using the property of derivatives,

$$\frac{\partial^2 \varphi}{\partial x^2} = \frac{1}{2} \frac{\partial}{\partial \varphi}\left(\frac{\partial \varphi}{\partial x}\right)^2 \qquad (8)$$

PB equation can be solved as

$$d\left(\frac{\partial\varphi}{\partial x}\right)^2 = -\frac{2e}{\varepsilon_r\varepsilon_0}\sum_i n_i^0 z_i \exp\left(\frac{-z_i e\varphi}{kT}\right)d\varphi . \quad (9)$$

For the following boundary conditions,

$$
\begin{aligned}
x = 0 & \qquad \varphi = \varphi_0 \\
x = \infty & \qquad \varphi \rightarrow 0 \quad \left(\frac{\partial\varphi}{\partial x}\right) = 0
\end{aligned}
\qquad (10)
$$

where $\varphi_0$ is the potential at the electrode, the integration yields to

$$\left(\frac{\partial\varphi}{\partial x}\right)^2 = \frac{2kT}{\varepsilon_r\varepsilon_0}\sum_i n_i^0\left[\exp\left(\frac{-z_i e\varphi}{kT}\right) - 1\right]. \quad (11)$$

For a symmetrical (z:z) electrolyte, Eq. (11) has the form

$$\frac{\partial\varphi}{\partial x} = \left(\frac{8kTn^0}{\varepsilon_r\varepsilon_0}\right)^{1/2}\sinh\left(\frac{ze\varphi}{2kT}\right). \quad (12)$$

The characteristic distance for the diffuse layer thickness is given as

$$\kappa^{-1} = \left(\frac{\varepsilon_r\varepsilon_0 k_B T}{2n_i^0 z^2 e^2}\right)^{1/2}. \quad (13)$$

The charge density of the diffuse layer is used as

$$
\begin{aligned}
\sigma_M &= \varepsilon_r\varepsilon_0\left(\frac{\partial\varphi}{\partial x}\right)_{x=0} \\
&= \left(8kTn_i^0\varepsilon_r\varepsilon_0\right)^{1/2}\sinh\left(\frac{ze\varphi_0}{2kT}\right)
\end{aligned}
\qquad (14)
$$

By differentiating, the differential capacitance is obtained as

$$
\begin{aligned}
C_{GC} &= \frac{d\sigma_M}{d\varphi_0} \\
&= \left(\frac{2z^2 e^2 n_i^0 \varepsilon_r\varepsilon_0}{kT}\right)^{1/2}\cosh\left(\frac{ze\varphi_0}{2kT}\right)
\end{aligned}
\qquad (15)
$$

In order to assess the validity of the model, the following parameters $\varphi_0 = 50$ mV, z=1, $c_\infty = 0.1$ M are chosen and the differential capacitance is determined as

$$C_{GC} = 77.16\,\mu F/cm^2. \quad (16)$$

The Gouy-Chapman Model is a continuum meanfield-like approach assuming point-like ions in thermodynamic equilibrium and neglecting statistical correlations. For low concentration electrolytes, this theory has been successful in predicting ionic profiles close to planar and weakly curved surfaces and the resulting forces. However, it is known to overestimate strongly ionic concentrations close to charged surfaces. In particular, this shortcoming of the PB theory is pronounced for highly charged surfaces and multivalent ions.

### 2.3 Stern Model

In 1924 Stern [6] simply developed the double-layer theory by suggesting a more realistic way of describing the physical situation at the interface. He combined the two previous models by adapting the compact layer of ions used by Helmholtz and next to the diffuse layer of Gouy-Chapman extending into the bulk solution. He took into account the fact that ions have finite size, and consequently the closest approach of OHP to the electrode will vary with the ionic radius.
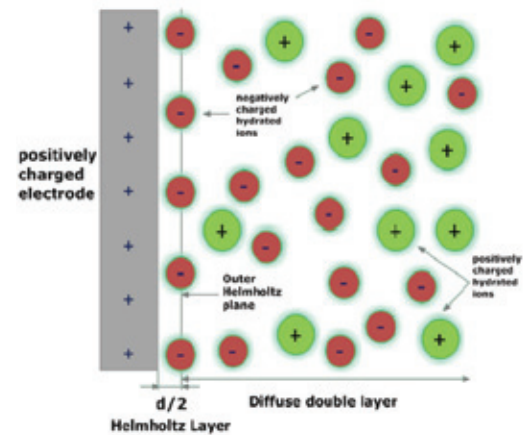


**Figure 3**. Stern Model

In mathematical terms the differential capacitance of the double layer $C_s$ is equivalent to two capacitors in series or

$$\frac{1}{C_s} = \frac{1}{C_H} + \frac{1}{C_{GC}} , \qquad (17)$$

where $C_H$ is the capacitance of the charges held inside the OHP and $C_{GC}$ is the capacitance of the diffuse layer.

By substituting the already received values, we obtain

$$C_s = 57.92 \mu F / cm^2 . \qquad (18)$$

## 3. Numerical Simulations with COMSOL Multiphysics

### 3.1 Geometry and Subdomain Parameters

The 3D Electrostatic mode of the AC/DC module is used to simulate the three classical models of the EDL as an ideal parallel-plate capacitor. In correspondence with the experimental setup, the capacitor has a cylindrical form with a diameter and length of 20 nm. Additional plates in a distance of 0.3 nm corresponding to the radius of a hydrated ion are included.
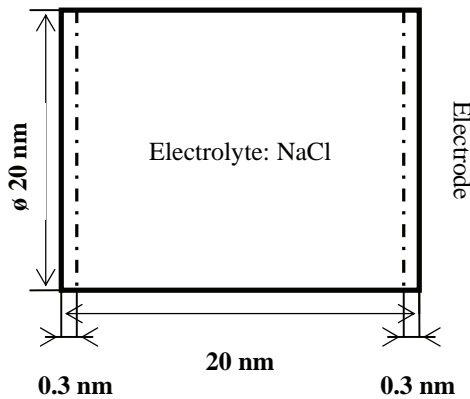


**Figure 4**. The model geometry

In the 3D Electrostatics Mode, the following equation is solved

$$-\nabla \cdot \left( \varepsilon_0 \varepsilon_r \nabla \varphi \right) = \rho \qquad (19)$$

and respectively for the above described models we implement the r.h.s. of Eq-ns (1), (12) and a combination of them in the Stern Model.
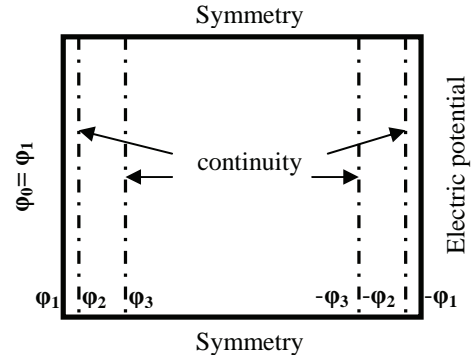
### 3.2 Boundary Conditions



**Figure 5**. Boundary conditions

The boundary conditions for the Helmholtz Model was chosen so that the electric potential of the electrode $\varphi_0 = \varphi_1$ and of the OHP at a distance of 0.3 nm to be set to continuity meaning that the normal component of the electric displacement is continuous across the interior boundary. Similarly, the Gouy-Chapman Model was implemented, but its inner plate was placed in a $\kappa^{-1}$ distance. Stern model is simply a combination of the latter ones. The outer boundaries are chosen in the way that the normal component of the electric displacement to be zero.
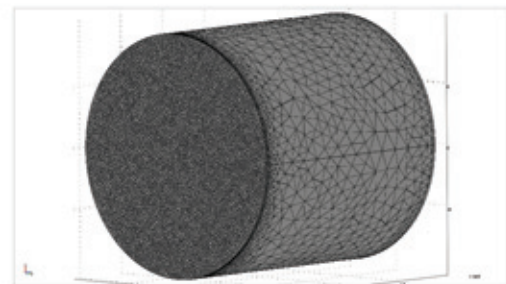
### 3.3 Mesh Generation



**Figure 6**. Mesh generation for the used geometry

For the models, a triangular mesh (Fig. 6) was used with a finer mesh between the electrode and the OHP and a coarser one between the two opposite electrodes. The number of degrees of freedom solved for all models is around 200 000 and the solution time nearly 40 s.

### 3.4 Postprocessing

The capacitance for all models is calculated by finding the charge Q obtained by integrating over area A the electric displacement multiplied by the normal vector (normD_emes)

$$Q = \oint_{\Gamma_i} D_0 \cdot n dA \tag{20}$$

$$C = \frac{Q}{\Delta \varphi} \tag{21}$$

For the Helmholtz Model, the parameters are obtained as

$$\varphi_1 = 0.05V$$
$$\varphi_2 = 0.0485V$$
$$Q_H = 1.09178 \times 10^{-18} C$$

and the differential capacitance $C_H$ is

$$C_H = \frac{Q_H}{\varphi_1 - \varphi_2} = 231.69 \mu F / cm^2 . \tag{22}$$

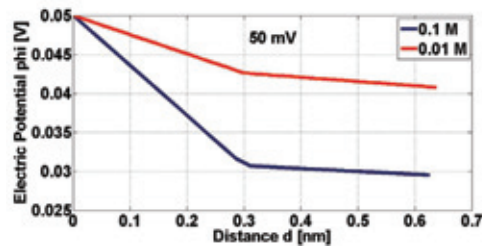This value coincides absolutely to the analytical result as obtained in Eq. (4).



**Figure 7**. Electric potential distribution for Helmholtz Model with $\varphi_0$ =50 mV and NaCl concentration of 0.1 and 0.01 M.

The electric potential in the Helmholtz Model (Fig.7) has a linear fall between the electrode's surface and the OHP and the numerical simulation confirms this result.

The electric potential drop in the Gouy-Chapman Model has an exponential form (Fig. 8), which was validated by varying the NaCl concentration between 0.1 and 0.01 M.
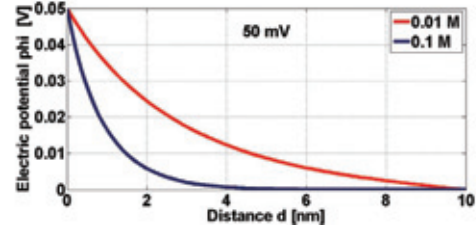


**Figure 8**. Electric potential distribution for Gouy-Chapman Model with $\varphi_0$ =50 mV and NaCl concentration of 0.1 and 0.01 M.

The parameters used here are

$$\varphi_1 = 0.05V$$
$$\varphi_3 = 0.02537V$$
$$Q_{GC} = 5.70365 \times 10^{-18} C$$

thus

$$C_{GC} = \frac{Q_{GC}}{\varphi_1 - \varphi_3} = 73.74 \mu F / cm^2 . \tag{23}$$

As the analytical value takes into account the whole electrolyte, we need to add the effect of the rest charge further away from the Debye length $\kappa^{-1}$ as

$$\varphi_3 = 0.02537V$$
$$\varphi_4 = -\varphi_3$$
$$Q_{electrolyte} = 5.242254 \times 10^{-19} C$$

$$C_{electrolyte} = \frac{Q_{electrolyte}}{\varphi_3 - \varphi_4} = 3.29 \mu F / cm^2 . \tag{24}$$

Summing up Eq. (23) and Eq. (24) gives

$$C_{GC} = 77.03 \mu F / cm^2 . \tag{25}$$

As we have seen that approximation is reasonable and provides a consistent result with the theory and Eq. (16).

In Stern Model, the electric potential has a linear fall within the OHP and an exponential one in the diffuse layer (Fig. 9).
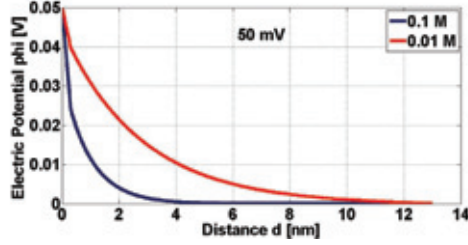


**Figure 9**. Electric potential distribution for Stern Model with $\varphi_0$ =50 mV and NaCl concentration of 0.1 and 0.01 M.

The parameters for the Stern Model are as follows:

$$\varphi_1 = 0.05V$$

$$\varphi_2 = 0.040212V$$

$$\varphi_3 = 0.019118V$$

$$\varphi_4 = -\varphi_3$$

$$Q_H = 7.124756 \times 10^{-18} C$$

$$Q_{GC} = 4.564242 \times 10^{-18} C$$

$$Q_{electrolyte} = 5.429012 \times 10^{-19} C$$

yielding to

$$C_H = \frac{Q_H}{\varphi_1 - \varphi_2} = 231.7 \mu F / cm^2 \qquad (26)$$

$$C_{GC} = \frac{Q_{GC}}{\varphi_2 - \varphi_3} = 68.88 \mu F / cm^2 \qquad (27)$$

$$C_{electrolyte} = \frac{Q_{electrolyte}}{\varphi_3 - \varphi_4} = 4.52 \mu F / cm^2 \qquad (28)$$

Finally, the differential capacitance in Stern Model is equal to

$$C_s = \frac{1}{C_H} + \frac{1}{C_{GC}} = 53.0957 \mu F / cm^2 \qquad (29)$$

and taking into account the capacitance in the rest of the electrolyte by summing up Eq. (28) and (29), the $C_s$ is obtained as

$$C_s = 57.6157 \mu F / cm^2 \qquad (30)$$

which is a good approximation of Eq. (18).
The comparison between the models (Fig.10) shows that for low concentration electrolytes like 0.01 M NaCl, the Stern Model has similar behavoiur to Gouy-Chapman Model.
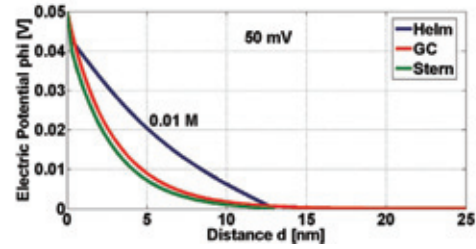


**Figure 10**. Comparison of the Helmholtz, Gouy-Chapman and Stern Model for NaCl concentration of 0.01 M

## 4. Experimental Measurements

The electrochemical experiments [5] were performed by a three-electrode technique in a glass containing 80 cm$^3$ of a phosphate-buffered saline PBS (pH 7.2) electrolyte solution. A Ti specimen served as working electrode and as reference system a saturated calomel electrode KE-10 (Sensortechnik Meinsberg, Germany). The counter electrode consisted of a platinium sheet placed in a 30-mm distance planar to the working electrode. All measurements were performed at room temperature (22+-1 $^0$C).
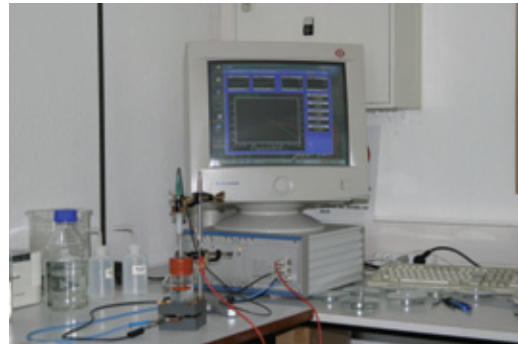


**Figure 11**. Experimental setup for EIS

Electrochemical impedance spectroscopy (EIS) [1] was performed with the electrochemical measuring system IM6e (ZAHNER, Germany). We measured in the frequency range of 1mHz to 10 kHz in the single sine mode with an ac amplitude of 10 mV with respect to open-circuit potential (OCP). The EIS data were analysed using THALES software from ZAHNER.

Voltammetric experiments were also performed with the Zahner system to get a quasi-stationary current-potential curve. The potential scans were carried out from -0.5 V (SCE) to 0 V (SCE) in anodic direction with a scan rate 0.5 mV/s. Values for OCP, corrosion current ($i_{corr}$), corrosion resistance ($R_{corr}$) and cathodic Tafel slope were obtained by classical Tafel analysis of the cathodic branch.

A chronoamperometric experiment was used to determine the amount of charge required for reloading of the double layer capacity for a 20 mV potential jump. The resulting current transients were recorded for 10 s with a resolution of 10 ms and integrated.

The capacitance obtained for a polished Ti is around $6 \mu F / cm^2$.

## 5. Discussion

The Helmholtz Model of the double layer seems to be appropriate for polarisable electrodes in sufficiently high concentrations of electrolyte (>1 M). At lower electrolyte concentrations (< 0.1 M), new features appear in the measurement of the double layer capacitance as a function of potential which cannot be explained by the Helmholtz Model. The Gouy-Chapman Model is a continuum meanfield-like approach assuming point-like ions in thermodynamic equilibrium and overestimates strongly ionic concentrations close to the charged surface.

**Table 1:** Differential capacitance values of the EDL

|  | Helm-holtz Model | Gouy-Chapman Model | Stern Model | Experi-ment |
|---|---|---|---|---|
| $C_{dl}$ [$\mu F/cm^2$] analytical | 231.41 | 77.16 | 57.92 | 6 |
| $C_{dl}$ [$\mu F/cm^2$] numerical | 231.69 | 77.03 | 57.61 | 6 |

Even though Stern made a key improvement of the model, the capacitance value received by measurement is much smaller than that obtained analytically and numerically (Table 1).

## 6. Conclusion

Generally, the classical models describe the fundamental behaviour of the ions near the electrode's surface forming the double layer. However, they ignore key factors as ion-ion correlations, electrostatic image interactions, steric effects, overlapping of ions leading to inconsistency with the experimental results. Therefore, as the aim of our future work is the implementation of an EDL model on non-planar electrodes with well-predefined geometrical structures, we need another approach, which will incorporate all these factors.

## 7. References

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## 8. Acknowledgements