Lecture 2

Basic concepts of electrochemical processes, the stages of electrode reaction. Modelling of diffuse double layer

Goal of the Lecture

The goal of this lecture is to develop students' understanding of the physical and mathematical foundations of the diffuse double layer (DDL) and its role in electrochemical systems. The lecture aims to link electrochemical theory-specifically the Nernst-Planck-Poisson formulation and Gouy-Chapman-Stern (GCS) theory-to their computational implementation in COMSOL Multiphysics, preparing students for modeling charge distribution and potential profiles at electrode-electrolyte interfaces.

Lecture Objectives

By the end of this lecture, students will be able to:

1. **Explain** the physical origin of the double-layer structure and its dependence on electrode potential and ionic composition.
2. **Derive and interpret** the Nernst–Planck–Poisson (NPP) equations describing charge and mass distribution in dilute electrolytes.
3. **Compare** the Gouy–Chapman and Stern models of the electrical double layer and discuss their assumptions and limitations.
4. **Set up and solve** a basic electrostatic–mass transport coupled model for a diffuse double layer in COMSOL Multiphysics.
5. **Analyze** the influence of applied potential and ionic strength on double-layer thickness and surface charge density.

When a polarizable electrode is held at a certain voltage compared to a reference, it will have a corresponding net surface charge density. This charge attracts or repels ions in the neighboring solution, depending on their charge.

At equilibrium, there is a layer of space charge density adjacent to the electrode due to unequal amounts of different types of ions.

The charge in solution is equal and opposite to the charge on the electrode: "double layer" (**Figure 1**).

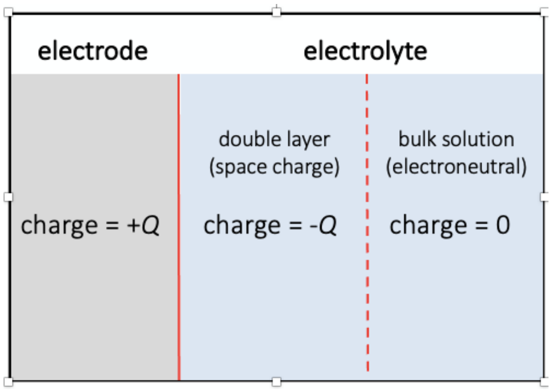


Figure 1. Simplified scheme of the double "layer".

Electrostatics

The electric field obeys **Gauss's law**.

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_{\text{soln}} \varepsilon_0}$$

– assume that solvent permittivity is unaffected by ion density (dilute solution).

– assume that only dissolved ions contribute to the space charge density in solution.

$$\rho = F \sum_i z_i c_i$$

E = electric field (V/m); ρ = space charge density (C/m^3); $\varepsilon_{\text{soln}}$ = solvent dielectric constant; ε_0 = vacuum permittivity; F = Faraday constant; z_i = charge number of ion i; c_i = concentration of ion i (mol/m^3).

Mass transport of diluted species

Dilute species (at low concentration) obey the Nernst-Planck equations for mass transport.

– flux includes diffusion and migration terms

– assume no reactions in solution (no source term)

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = 0$$

$$\mathbf{N}_i = -D_i \nabla c_i + z_i c_i u_i \mathbf{E}$$

$$u_i = \frac{F}{RT} D_i$$

N$_i$ = molar flux of ion i (mol/(m^2*s)); D_i = diffusion coefficient of ion i (m^2/s); u_i = electrical mobility of ion i (m^2/s/V); R = gas constant; T = temperature (K).

Nernst-Planck-Poisson equations

Combine the equations at steady-state.

Nernst-Planck-Poisson (or Poisson-Nernst-Planck) equations describes charge and mass distribution in dilute electrolyte.

- for ***n*** ions, gives (***n+1***) equations in (***n+1***) unknowns:
- ***n*** ion concentrations
- electric potential (***φ***)

$$\nabla \cdot \left(D_i \nabla c_i + z_i \frac{F}{RT} D_i c_i \nabla \phi \right) = 0$$

$$\nabla^2 \phi + \frac{F}{\varepsilon_{\text{soln}} \varepsilon_0} \sum_i z_i c_i = 0$$

Gouy-Chapman theory

- Solve Nernst-Planck-Poisson equations at steady-state to find double layer structure.
- Specify a charge density or fixed potential at the electrode surface.
- Set electroneutral bulk concentrations and zero electrical potential at large distance.

Key prediction of Gouy-Chapman theory:

- Extent of the double layer (region of space charge density) is of the order of the Debye length x_D.

$$x_{\text{D}} = \sqrt{\frac{RT \varepsilon_{\text{soln}} \varepsilon_0}{2F^2 I_{\text{ion}}}}$$

$$I_{\text{ion}} = \frac{1}{2} \sum_i z_i^2 c_{i,\text{bulk}}$$

Stern modification (GCS theory)

Account for potential drop across the region from the metal surface to the centre line of the closest approach of an ion.

- This line is called the outer Helmholtz plane (OHP).
- Region outside the OHP is the “diffuse double layer” where there is space charge due to ion excess / depletion.

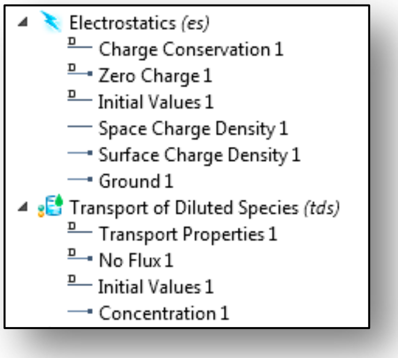
- Region inside the OHP is the “compact double layer” or “Stern layer” where the electric field is near-constant.

Treat the solvent inside the OHP as a classical rectilinear dielectric of fixed length (x_S), usually < 1 nm.

$$\phi_{\mathrm{OHP}} = \phi_{\mathrm{M}} - x_{\mathrm{S}} \frac{\rho_{\mathrm{surf}}}{\varepsilon_{\mathrm{soln}}\varepsilon_0}$$

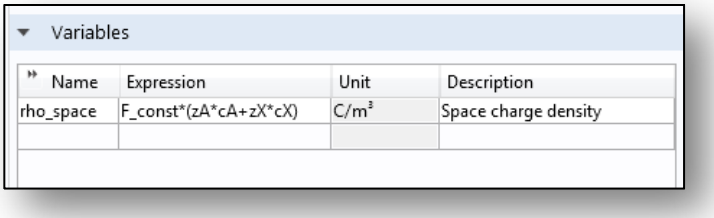
Setup interfaces and domains in COMSOL Multiphysics

- Couple **Electrostatics** with **Transport of Diluted Species**.
- Solve for as many concentrations as there are ions.



- Electrostatics *(es)*
  - Charge Conservation 1
  - Zero Charge 1
  - Initial Values 1
  - Space Charge Density 1
  - Surface Charge Density 1
  - Ground 1
- Transport of Diluted Species *(tds)*
  - Transport Properties 1
  - No Flux 1
  - Initial Values 1
  - Concentration 1

- Add a **Space Charge Density** to electrostatics according to the ion concentrations.



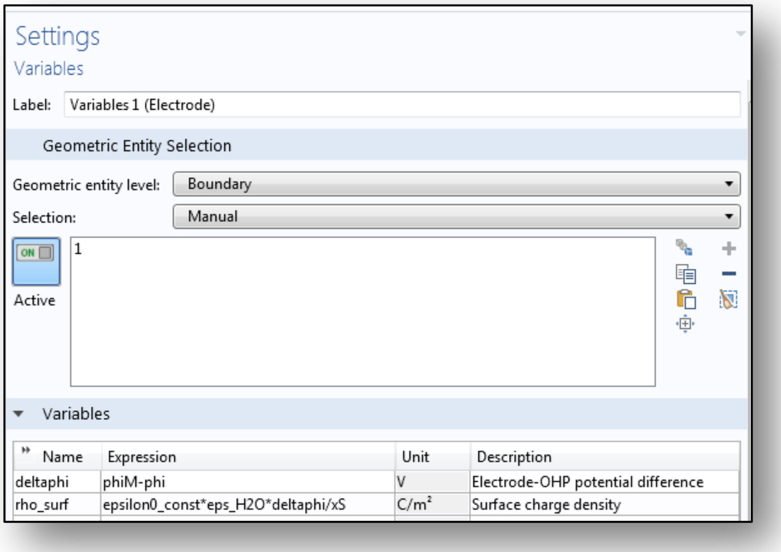
Variables

Name	Expression	Unit	Description
rho_space	F_const*(zA*cA+zX*cX)	C/m^3	Space charge density

Setup (electrode boundary)

Electrode:

- Set a **Surface Charge Density** in **Electrostatics**.
- The surface charge density is a function of the applied voltage and the local electric potential according to the Stern expression.
- Set **No Flux** of ions (no electrode reaction).



Label: Variables 1 (Electrode)

Geometric Entity Selection

Geometric entity level: Boundary

Selection: Manual

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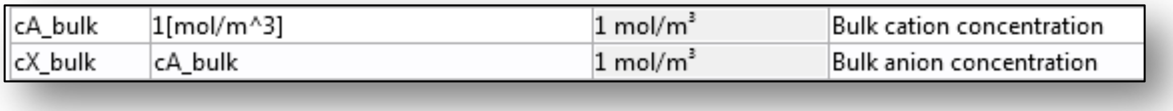
Variables

Name	Expression	Unit	Description
deltaphi	phiM-phi	V	Electrode-OHP potential difference
rho_surf	epsilon0_const*eps_H2O*deltaphi/xS	C/m²	Surface charge density

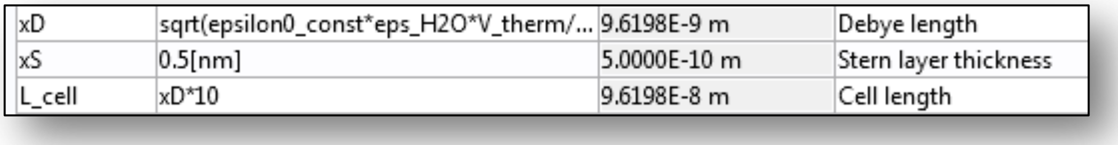
Setup (bulk boundary)

Bulk:

- Set **Ground** in **Electrostatics**.
- Bulk boundary must be several Debye lengths from the surface in order that the electric field tends to zero here.
- Set **Concentration** condition to define bulk ion concentrations.
- Bulk ion concentrations must be defined to give a neutral solution.



cA_bulk	1[mol/m^3]	1 mol/m³	Bulk cation concentration
cX_bulk	cA_bulk	1 mol/m³	Bulk anion concentration



xD	sqrt(epsilon0_const*eps_H2O*V_therm/…	9.6198E-9 m	Debye length
xS	0.5[nm]	5.0000E-10 m	Stern layer thickness
L_cell	xD*10	9.6198E-8 m	Cell length

Results

- Parametric sweep on voltage vs potential of zero charge (PZC) of the working electrode, from ***1*** to ***10 mV***.
- ***Potential*** and ***concentration*** profiles for the double layer.
- Output "*rho_surf*" to find surface charge.

Questions for Self-Examination

1. What is the physical meaning of the electrical double layer and how is it formed at the electrode–electrolyte interface?
2. Write the general form of the Nernst–Planck equation. What physical processes do the diffusion and migration terms represent?
3. What additional equation must be coupled to the Nernst–Planck equations to describe the electric potential in the electrolyte?
4. What assumptions are made in the Gouy–Chapman theory for the diffuse double layer?
5. How does the Debye length depend on the ionic concentration and dielectric constant of the solvent?
6. What modification does the Stern model introduce compared to the Gouy–Chapman theory?
7. Why is it important to place the bulk boundary several Debye lengths away in COMSOL simulations?
8. How does an increase in electrode potential influence the shape of the potential and concentration profiles in the DDL?

Assignment Title: *Simulation of the Diffuse Double Layer Using the Poisson–Nernst–Planck Approach in COMSOL Multiphysics*

Objective:
To simulate and visualize the potential and ionic concentration profiles across the diffuse double layer using COMSOL Multiphysics, applying the coupled **Electrostatics** and **Transport of Diluted Species** interfaces.

Tasks:

1. **Model setup:**
    - Open the COMSOL model **“Diffuse Double Layer”** (available in the Application Library or via COMSOL Model Gallery).
    - Create a **1D geometry** representing an electrolyte region extending several Debye lengths from an electrode.
    - Define two ionic species (e.g., Na^+ and Cl^-) with equal bulk concentration (e.g., 0.01 M).
2. **Physics coupling:**
    - Add **Electrostatics (es)** and **Transport of Diluted Species (tds)** interfaces.
    - In *Electrostatics*, include **Space Charge Density** using ion concentrations from *tds*.
    - In *tds*, include **Migration in Electric Field** and disable convection.

3. **Boundary conditions:**
    - At the electrode surface: specify a **Surface Charge Density** as a function of applied potential.
    - At the bulk boundary: set **Ground** (ϕ = 0 V) and fixed bulk concentrations for ions.
    - Ensure the computational domain extends ≥ 10× the expected Debye length.
4. **Simulation:**
    - Perform a **parametric sweep** of electrode potential from –10 mV to +10 mV relative to the potential of zero charge (PZC).
    - Plot the resulting **electric potential** and **ionic concentration** profiles as a function of distance from the electrode.
    - Extract **surface charge density (ρ_surf)** and **Debye length (λ_D)** from results.
5. **Report:**
    - Include COMSOL screenshots of:
      a. Potential profile (ϕ vs. x)
      b. Cation and anion concentration profiles (c_i vs. x)
    - Write a 2-page report discussing:
        - The physical meaning of the potential and charge profiles.
        - The effect of applied potential and electrolyte concentration.
        - How the simulation reflects Gouy–Chapman–Stern theory predictions.

Learning Outcomes

Learning Outcome (LO)	Indicator of Achievement (ID)	Description
LO 1: Explain the principles of modelling electrochemical systems and appraise the use of modelling in electrochemical research.	ID 1.2: Explain the principles of charge transfer and mass transfer stages of electrode reaction.	Students will demonstrate the ability to describe and model the charge and mass transfer processes governing the formation of the electrical double layer using theoretical and computational approaches.

References:

1. https://www.comsol.com/model/diffuse-double-layer-21981
2. Chapter 13: "Double-Layer Structure and Adsorption" in *Electrochemical Methods: Fundamentals and Applications, 2nd ed.*, 2001, Wiley.
3. Franco, A. A., Doublet, M. L., Bessler, W. G. (Eds.). Physical Multiscale Modeling and Numerical Simulation of Electrochemical Devices, Springer, 2015.