

Diffuse Double Layer

Introduction

Close to an electrode surface, ions in the electrolyte are attracted and repelled by unscreened excess charge on the electrode. This region is called the *diffuse double layer*. Its size is normally a few nanometers away from the electrode surface. The electrical interactions here mean that charge separation can occur, and the assumption of local electroneutrality is not valid. The study of the diffuse double layer is important to applications that consider very thin layers of electrolyte, such as electrochemical capacitors, atmospheric corrosion problems, ion-selective field effect transistors (ISFETs), and nanoelectrochemistry.

This example shows how to define a double layer model by combining the **Transport of Diluted Species** and **Electrostatics** physics to account for mass transfer and charge transfer respectively. The model contains one charged electrode adjacent to bulk solution.

One of the simplest physical models of the double layer is the Gouy-Chapman-Stern (GCS) model. In Gouy-Chapman theory (Ref. 1, Ref. 2), the diffuse double layer is treated as a multiphysics coupling of the Nernst-Planck equations for mass transport of all of the ions, with the Poisson equation (Gauss's law) for the charge density and electric field. The combination of these equations is frequently referred to as the Poisson-Nernst-Planck (PNP) equations or Nernst-Planck-Poisson (NPP) equations.

Gouy-Chapman theory predicts the spatial extent of the diffuse double layer to be of the same order as the Debye length for the solution, defined for a monovalent binary electrolyte with concentration c_{bulk} and solvent relative permittivity ϵ_r :

$$x_D = \sqrt{\frac{RT\epsilon_r\epsilon_0}{2F^2 c_{\text{bulk}}}} \quad (1)$$

The Stern modification (Ref. 3) to the Gouy-Chapman theory additionally considers the electric field inside a plane called the *outer Helmholtz plane* (OHP). This is the plane of closest approach to the electrode for dissolved ions in solution, due to the finite size of the ions and surrounding solvent molecules. In the distance of a fraction of a nanometer between this plane and the electrode surface, Stern's theory describes the electrolyte as a dielectric of constant permittivity. This uncharged region of the double layer is sometimes called the *compact double layer*.

When there is a low applied potential ($< RT/F \sim 25$ mV), the Gouy-Chapman-Stern theory has an analytical solution. The capacitance is predicted to be the same as for a parallel plate capacitor whose electrode separation is equal to the sum of the Stern layer size and the Debye length:

$$C_{\text{dl}} \approx \frac{\epsilon_r \epsilon_0}{x_D + x_S} \quad (2)$$

Model Definition

The model geometry is in 1D (a single interval between 0 and L) and consists of a single domain, representing the electrolyte phase from the electrode through the diffuse double layer, as far as the electroneutral bulk solution. The compact component of the double layer is handled using a boundary condition set at $x = 0$.

DOMAIN EQUATIONS

The concentrations, c_i (SI unit: mol/m³, $i=+, -$), of two ions of opposite charge (+1/-1) are solved for in the electrolyte phase. The fluxes (\mathbf{N}_i , SI unit: mol/(m²·s)) of the ions are described by the Nernst-Planck equation

$$\mathbf{N}_i = -D_i \nabla c_i - u_{m,i} z_i F c_i \nabla \phi$$

with D_i (SI unit: m²/s) being the diffusion coefficient, $u_{m,i}$ (SI unit: s·mol/kg) the mobility, F (SI unit: C/mol) the Faraday constant, and ϕ (SI unit: V) the electric potential in the electrolyte phase.

We assume no homogeneous reactions of the ions in solution. Then, conservation of mass requires that, for both species:

$$\nabla \cdot \mathbf{N}_i = 0$$

For the potential, the Poisson equation (Gauss's law) states

$$\nabla \cdot (-\epsilon \nabla \phi) = \rho$$

where ϵ is the permittivity (SI unit: F/m) and ρ the charge density (SI unit: C/m³). The charge density depends on the ion concentrations according to:

$$\rho = F(c_+ - c_-)$$

BOUNDARY CONDITIONS

We choose the bulk solution as the ground condition for the electrolyte potential:

$$\phi = 0$$

which is set at the outer boundary.

The ion concentrations are set to their bulk values at the outer boundary. Because bulk solution is electroneutral, the positive and negative ions have equal concentrations here.

From Gauss's law, the electric field inside the compact double layer is constant because this layer is uncharged and has a uniform permittivity. Hence, according to the Stern theory for a compact double layer of a constant thickness, λ_S (SI unit: m), the following Robin-type boundary condition applies for the electrolyte potential:

$$\phi + \lambda_S(\mathbf{n} \cdot \nabla\phi) = \phi_M$$

where ϕ_M (SI unit: V) is the applied potential of the electrode, as measured against bulk solution.

For the case of a non-zero Stern layer thickness, the condition can be reformulated as a surface charge condition that depends on the potential difference, ϕ_Δ (SI unit: V), between the electrode potential and the electrolyte potential at the outer Helmholtz plane ($x = 0$):

$$\mathbf{n} \cdot (-\varepsilon\nabla\phi) = -\frac{\varepsilon\phi_\Delta}{\lambda_S}$$

where

$$\phi_\Delta = \phi_M - \phi$$

The **Surface Charge Density** condition in **Electrostatics** is used to define the above condition. The problem is solved for a sweep of values of ϕ_M from 1 mV to 10 mV.

If the electrode is inert to electrolysis of the ions at the electrolyte-electrode interface, no flux of the ions into the electrode surface can occur. Hence, **No Flux** conditions are used for both ion concentrations at the electrode boundary.

Results and Discussion

Figure 1 shows the potential profile in the electrolyte as a line graph and the potential at the electrode as a point.

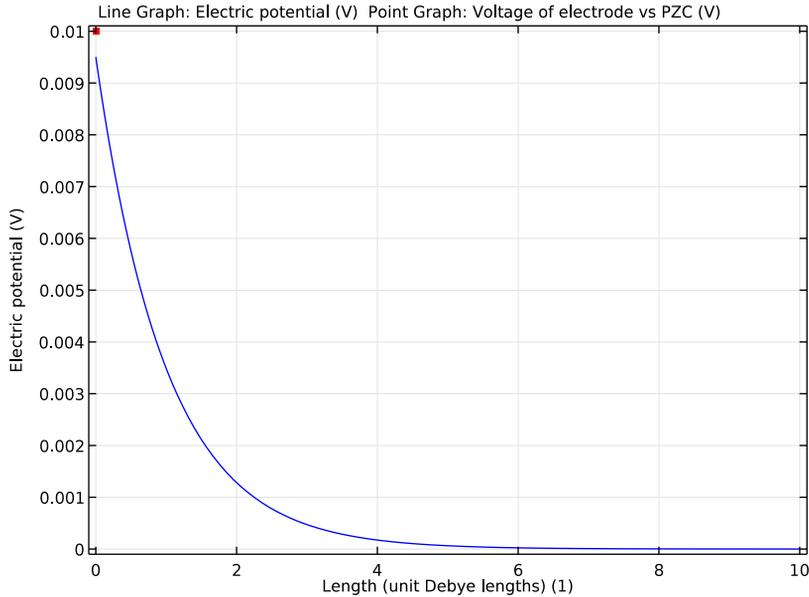


Figure 1: Electrolyte potential profile (blue line) and 10 mV applied electrode potential vs bulk solution (red dot).

The potential difference between the red dot (electrode surface) and the value of the blue line at $x = 0$ represents the potential difference over the compact double layer. The electrolyte potential falls off exponentially on the Debye length scale (Equation 1), as predicted by Gouy-Chapman theory.

Figure 2 shows the concentrations of the two ionic species. Because the electrode is polarized positively against bulk solution, it is positively charged and attracts anions while repelling cations. The concentration profiles confirm that the anion in the electrolyte is accumulated at the surface, while the cation is depleted.

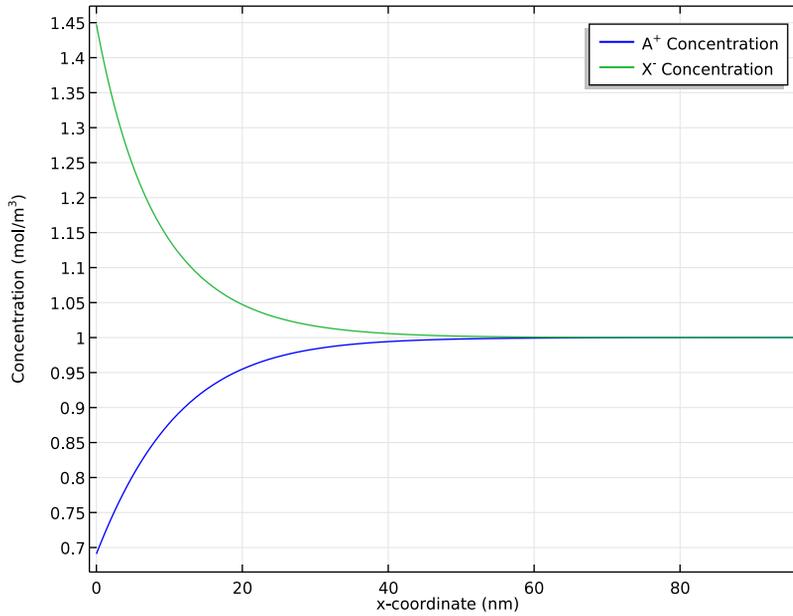


Figure 2: Concentration profile for the two ions, showing cation depletion (blue line) and anion accumulation (green line).

Figure 3 shows the surface charge dependence on the applied potential. This agrees precisely with the low potential analytical expression (Equation 2) for the smaller potentials. At 10 mV applied potential, a small deviation is observed as the low potential approximation becomes less precise.

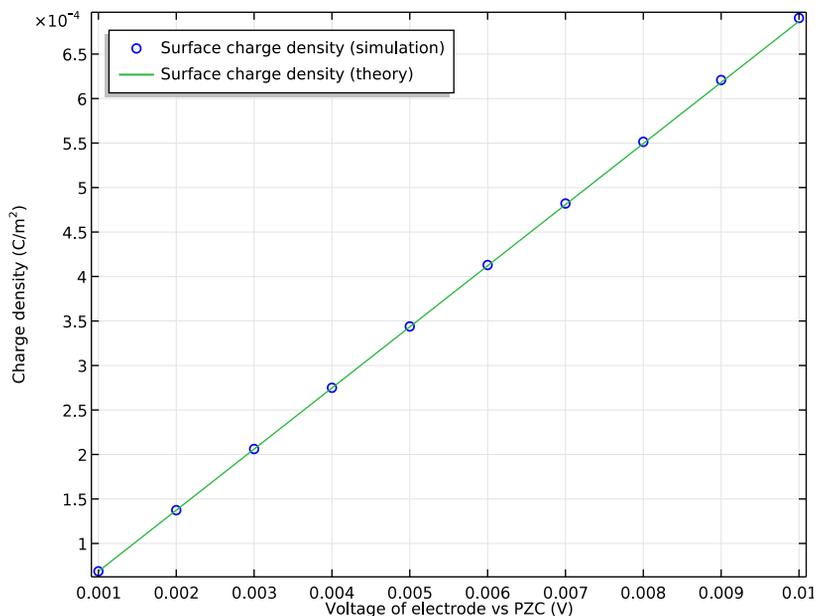


Figure 3: Surface charge density as a function of applied potential difference between the electrode and bulk solution, comparing simulation results with analytical theory derived in the limit of low applied potential.

References

1. L.G. Gouy, *Comptes Rendues Hebdomadaires des Séances de l'Académie des Sciences*, vol. 149, pp. 654-657, 1909.
2. D.L. Chapman, *Philosophical Magazine*, vol. 25, pp. 475-481, 1913.
3. O. Stern, *Zeitschrift für Elektrochemie*, vol. 30, pp. 508-516, 1924.
4. A.J. Bard and L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Hoboken, 2001.

Application Library path: Batteries_and_Fuel_Cells_Module/
General_Electrochemistry/diffuse_double_layer

Modeling Instructions

From the **File** menu, choose **New**.

NEW

1 In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click **ID**.

2 In the **Select physics** tree, select **AC/DC>Electrostatics (es)**.

3 Click **Add**.

4 In the **Electric potential** text field, type ϕ .

5 In the **Select physics** tree, select **Chemical Species Transport>Transport of Diluted Species (tds)**.

6 Click **Add**.

7 In the **Number of species** text field, type 2.

8 In the **Concentrations** table, enter the following settings:

cA

cX

9 Click **Study**.

10 In the **Select study** tree, select **Preset Studies for Selected Physics Interfaces>Stationary**.

11 Click **Done**.

GLOBAL DEFINITIONS

Start by loading some parameters from a text file.

Parameters

1 On the **Home** toolbar, click **Parameters**.

2 In the **Settings** window for Parameters, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the application's Application Library folder and double-click the file `diffuse_double_layer_parameters.txt`.

DEFINITIONS

Proceed by adding some variable expressions from a text file.

Variables 1

- 1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Definitions** and choose **Variables**.
- 2 In the **Settings** window for Variables, locate the **Variables** section.
- 3 Click **Load from File**.
- 4 Browse to the application's Application Library folder and double-click the file `diffuse_double_layer_variables.txt`.

GEOMETRY 1

Build the geometry as a single interval.

Interval 1 (i1)

- 1 On the **Geometry** toolbar, click **Interval**.
- 2 In the **Settings** window for Interval, locate the **Interval** section.
- 3 In the **Right endpoint** text field, type `L_cell`.
- 4 Click the **Build All Objects** button.

ELECTROSTATICS (ES)*Charge Conservation 1*

Now start setting up the physics, begin with the Electrostatics physics (Poisson's equation).

- 1 In the **Model Builder** window, under **Component 1 (comp1)**>**Electrostatics (es)** click **Charge Conservation 1**.
- 2 In the **Settings** window for Charge Conservation, locate the **Electric Field** section.
- 3 From the ϵ_r list, choose **User defined**. In the associated text field, type `eps_H2O`.

Space Charge Density 1

- 1 On the **Physics** toolbar, click **Domains** and choose **Space Charge Density**.
- 2 In the **Settings** window for Space Charge Density, locate the **Domain Selection** section.
- 3 From the **Selection** list, choose **All domains**.
- 4 Locate the **Space Charge Density** section. In the ρ_v text field, type `rho_space`.

Surface Charge Density 1

- 1 On the **Physics** toolbar, click **Boundaries** and choose **Surface Charge Density**.
- 2 Select Boundary 1 only.

- 3 In the **Settings** window for Surface Charge Density, locate the **Surface Charge Density** section.
- 4 In the ρ_s text field, type rho_surf.

Ground 1

- 1 On the **Physics** toolbar, click **Boundaries** and choose **Ground**.
- 2 Select Boundary 2 only.

TRANSPORT OF DILUTED SPECIES (TDS)

Now set up the model for the transport of the ions. Enable migration and change the element order to 2 to match the default element order of the Electrostatics physics.

- 1 In the **Model Builder** window, under **Component 1 (comp1)** click **Transport of Diluted Species (tds)**.
- 2 In the **Settings** window for Transport of Diluted Species, locate the **Transport Mechanisms** section.
- 3 Clear the **Convection** check box.
- 4 Select the **Migration in electric field** check box.
- 5 In the **Model Builder** window's toolbar, click the **Show** button and select **Discretization** in the menu.
- 6 Click to expand the **Discretization** section. From the **Concentration** list, choose **Quadratic**.

Transport Properties 1

- 1 In the **Model Builder** window, under **Component 1 (comp1)>Transport of Diluted Species (tds)** click **Transport Properties 1**.
- 2 In the **Settings** window for Transport Properties, locate the **Model Inputs** section.
- 3 In the V text field, type phi.
- 4 In the T text field, type T0.
- 5 Locate the **Diffusion** section. In the D_{cA} text field, type DA.
- 6 In the D_{cX} text field, type DX.
- 7 Locate the **Migration in Electric Field** section. In the z_{cA} text field, type zA.
- 8 In the z_{cX} text field, type zX.

Initial Values 1

- 1 In the **Model Builder** window, under **Component 1 (comp1)>Transport of Diluted Species (tds)** click **Initial Values 1**.

- 2 In the **Settings** window for Initial Values, locate the **Initial Values** section.
- 3 In the cA text field, type cA_bulk .
- 4 In the cX text field, type cX_bulk .
- 5 In the **Model Builder** window, click **Transport of Diluted Species (tds)**.

Concentration 1

- 1 On the **Physics** toolbar, click **Boundaries** and choose **Concentration**.
- 2 Select Boundary 2 only.
- 3 In the **Settings** window for Concentration, locate the **Concentration** section.
- 4 Select the **Species cA** check box.
- 5 In the $c_{0,cA}$ text field, type cA_bulk .
- 6 Select the **Species cX** check box.
- 7 In the $c_{0,cX}$ text field, type cX_bulk .

MESH 1

Edit the default meshing sequence, the mesh parameters are dependent of the Debye length to make sure the mesh is always a well resolved.

- 1 In the **Model Builder** window, under **Component 1 (comp1)** click **Mesh 1**.
- 2 In the **Settings** window for Mesh, locate the **Mesh Settings** section.
- 3 From the **Sequence type** list, choose **User-controlled mesh**.

Size 1

- 1 In the **Model Builder** window, under **Component 1 (comp1)>Mesh 1** right-click **Edge 1** and choose **Size**.
- 2 In the **Settings** window for Size, locate the **Element Size** section.
- 3 Click the **Custom** button.
- 4 Locate the **Element Size Parameters** section. Select the **Maximum element size** check box.
- 5 In the associated text field, type h_max .

Size 2

- 1 Right-click **Edge 1** and choose **Size**.
- 2 In the **Settings** window for Size, locate the **Geometric Entity Selection** section.
- 3 From the **Geometric entity level** list, choose **Boundary**.
- 4 Select Boundary 1 only.

- 5 Locate the **Element Size** section. Click the **Custom** button.
- 6 Locate the **Element Size Parameters** section. Select the **Maximum element size** check box.
- 7 In the associated text field, type `h_max_surf`.
- 8 Click the **Build All** button.

STUDY I

Step 1: Stationary

Solve the problem using an Auxiliary sweep for a range of potentials.

- 1 In the **Model Builder** window, under **Study I** click **Step 1: Stationary**.
- 2 In the **Settings** window for Stationary, click to expand the **Study extensions** section.
- 3 Locate the **Study Extensions** section. Select the **Auxiliary sweep** check box.
- 4 Click **Add**.
- 5 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
<code>phiM</code>	<code>range(1, 1, 10)</code>	mV

- 6 On the **Home** toolbar, click **Compute**.

RESULTS

Electric Potential (es)

Reproduce the figures from the [Results and Discussion](#) section as follows:

- 1 In the **Settings** window for 1D Plot Group, locate the **Data** section.
- 2 From the **Parameter selection (phiM)** list, choose **Last**.
- 3 Locate the **Plot Settings** section. Select the **y-axis label** check box.
- 4 In the **Model Builder** window, expand the **Electric Potential (es)** node, then click **Line Graph 1**.
- 5 In the **Settings** window for Line Graph, locate the **x-Axis Data** section.
- 6 From the **Parameter** list, choose **Expression**.
- 7 In the **Expression** text field, type `x/xD`.
- 8 Select the **Description** check box.
- 9 In the associated text field, type `Length (unit Debye lengths)`.

10 In the **Model Builder** window, click **Electric Potential (es)**.

Point Graph 1

On the **Electric Potential (es)** toolbar, click **Point Graph**.

Electric Potential (es)

- 1** Click the **Zoom Extents** button on the **Graphics** toolbar.
- 2** Select Boundary 1 only.
- 3** In the **Settings** window for Point Graph, locate the **y-Axis Data** section.
- 4** In the **Expression** text field, type ϕ_M .
- 5** Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.
- 6** In the **Expression** text field, type x/x_D .
- 7** Select the **Description** check box.
- 8** In the associated text field, type Length (unit Debye lengths).
- 9** Click to expand the **Coloring and style** section. Locate the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **None**.
- 10** From the **Color** list, choose **Red**.
- 11** Find the **Line markers** subsection. From the **Marker** list, choose **Point**.
- 12** From the **Positioning** list, choose **In data points**.
- 13** On the **Electric Potential (es)** toolbar, click **Plot**.

Concentration (tds)

- 1** In the **Model Builder** window, under **Results** click **Concentration (tds)**.
- 2** In the **Settings** window for 1D Plot Group, locate the **Data** section.
- 3** From the **Parameter selection (phiM)** list, choose **Last**.
- 4** Click to expand the **Title** section. From the **Title type** list, choose **None**.
- 5** In the **Model Builder** window, expand the **Concentration (tds)** node, then click **Line Graph 1**.
- 6** In the **Settings** window for Line Graph, locate the **x-Axis Data** section.
- 7** From the **Parameter** list, choose **Expression**.
- 8** In the **Expression** text field, type x .
- 9** From the **Unit** list, choose **nm**.
- 10** Click to expand the **Legends** section. Select the **Show legends** check box.
- 11** From the **Legends** list, choose **Manual**.

12 In the table, enter the following settings:

Legends
A^{+} Concentration

13 Right-click **Results>Concentration (tds)>Line Graph 1** and choose **Duplicate**.

14 In the **Settings** window for Line Graph, locate the **y-Axis Data** section.

15 In the **Expression** text field, type cX .

16 Locate the **Legends** section. In the table, enter the following settings:

Legends
X^{-} Concentration

17 On the **Concentration (tds)** toolbar, click **Plot**.

1D Plot Group 3

1 On the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.

2 In the **Settings** window for 1D Plot Group, type Surface Charge Density in the **Label** text field.

3 Locate the **Title** section. From the **Title type** list, choose **None**.

Point Graph 1

On the **Surface Charge Density** toolbar, click **Point Graph**.

Surface Charge Density

1 Select Boundary 1 only.

2 In the **Settings** window for Point Graph, locate the **y-Axis Data** section.

3 In the **Expression** text field, type ρ_{surf} .

4 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

5 In the **Expression** text field, type ϕ_M .

6 Locate the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **None**.

7 Find the **Line markers** subsection. From the **Marker** list, choose **Circle**.

8 From the **Positioning** list, choose **In data points**.

9 Click to expand the **Legends** section. Select the **Show legends** check box.

10 From the **Legends** list, choose **Manual**.

11 In the table, enter the following settings:

Legends

Surface charge density (simulation)

12 On the **Surface Charge Density** toolbar, click **Plot**.

13 In the **Model Builder** window, click **Surface Charge Density**.

Global 1

On the **Surface Charge Density** toolbar, click **Global**.

Surface Charge Density

1 In the **Settings** window for Global, locate the **y-Axis Data** section.

2 In the table, enter the following settings:

Expression	Unit	Description
Cd_GCS*phiM	C/m ²	Surface charge density (theory)

3 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

4 In the **Expression** text field, type phiM.

5 Click to expand the **Coloring and style** section. Click to expand the **Legends** section. In the **Model Builder** window, click **Surface Charge Density**.

6 In the **Settings** window for 1D Plot Group, locate the **Plot Settings** section.

7 Select the **y-axis label** check box.

8 In the associated text field, type Charge density (C/m²).

9 Click to expand the **Legend** section. From the **Position** list, choose **Upper left**.

10 On the **Surface Charge Density** toolbar, click **Plot**.