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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 interfaces 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 Poisson's 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}:

$$x_{\mathrm{D}} = \sqrt{\frac{RT\varepsilon_{\mathrm{r}}\varepsilon_0}{2F^2 c_{\mathrm{bulk}}}} \qquad (1)$$

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:

$$C_{\mathrm{dl}} \approx \frac{\varepsilon_{\mathrm{r}}\varepsilon_0}{x_{\mathrm{D}} + x_{\mathrm{S}}} \tag{2}$$

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/m^3, i=+,-), of two ions of opposite charge (+1/-1) are solved for in the electrolyte phase. The fluxes ($\mathbf{J}_i$, SI unit: mol/(m^2·s)) of the ions are described by the Nernst–Planck equation

$$\mathbf{J}_i = -D_i\nabla c_i - u_{m,i}z_iFc_i\nabla\phi$$

with D_i (SI unit: m^2/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.

Assume that there are no homogeneous reactions of the ions in the solution. Then, conservation of mass requires that, for both species:

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

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

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

where ε is the permittivity (SI unit: F/m) and ρ the charge density (SI unit: C/m^3). 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, and $\mathbf{n}$ is the boundary normal vector, pointing outwards from the electrolyte domain.

For the case of a nonzero 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.

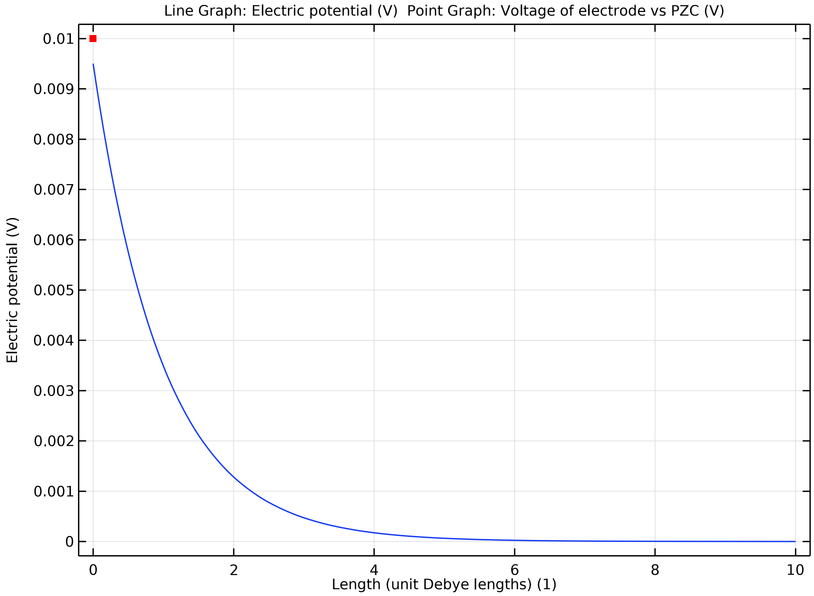

Figure 1: Electrolyte potential profile (blue line) and 10 mV applied electrode potential vs bulk solution (red dot).

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.

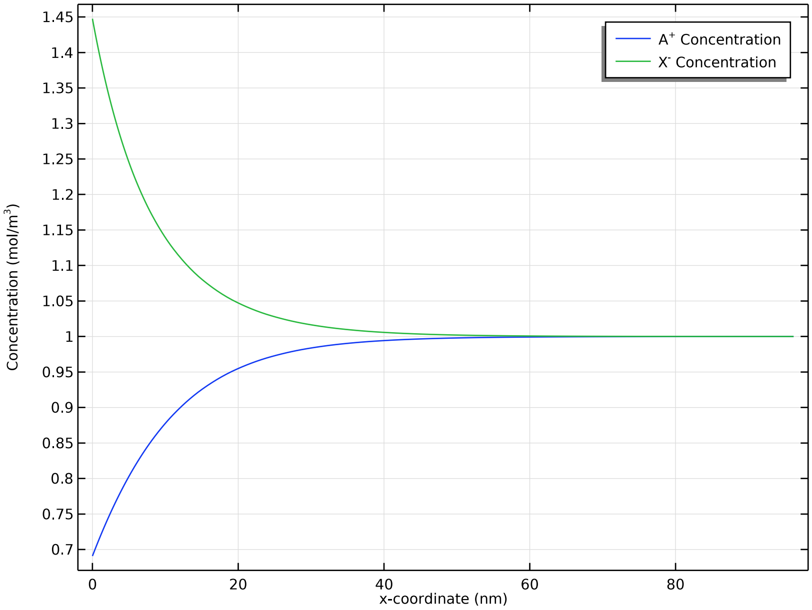

Figure 2: Concentration profile for the two ions, showing cation depletion (blue line) and anion accumulation (green line).

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.

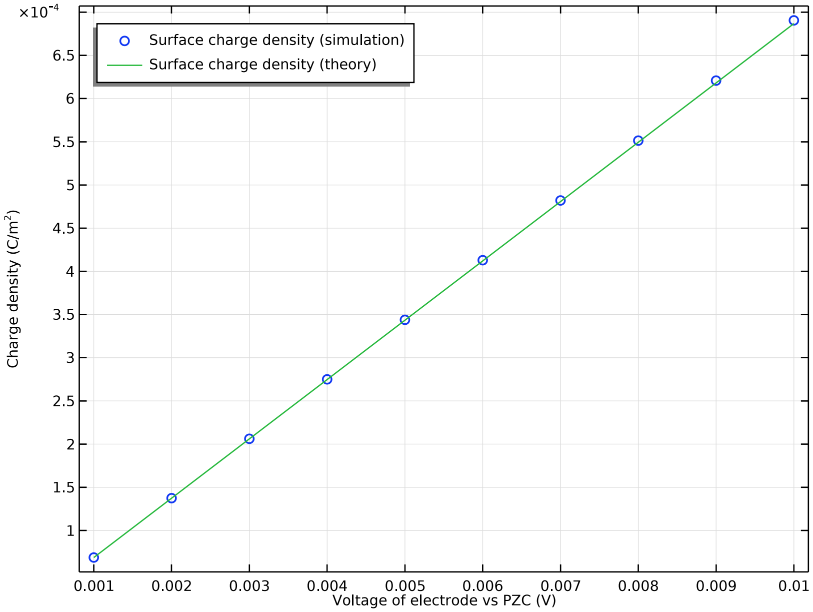

Figure 3: Surface charge density as a function of applied potential difference between the electrode and bulk solution, comparing simulation results with analytical theory derived in the limit of low applied potential.

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: `Electrodeposition_Module/Tutorials/diffuse_double_layer`

Modeling Instructions

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

NEW

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

MODEL WIZARD

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

2 In the **Select Physics** tree, select **Chemical Species Transport>Nernst-Planck-Poisson Equations**.

3 Click **Add**.

4 In the **Electric potential** text field, type `phi`.

5 In the **Added physics interfaces** tree, select **Transport of Diluted Species (tds)**.

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

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

`cA`
`cX`

8 Click **Study**.

9 In the **Select Study** tree, select **General Studies>Stationary**.

10 Click **Done**.

GLOBAL DEFINITIONS

Start by loading some parameters from a text file.

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

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

3 Click **Load from File**.

4 Browse to the model's Application Libraries 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 model's Application Libraries folder and double-click the file `diffuse_double_layer_variables.txt`.

GEOMETRY 1

Build the geometry as a single interval.

Interval 1 (i1)

1. In the **Model Builder** window, under **Component 1 (comp1)** right-click **Geometry 1** and choose **Interval**.
2. In the **Settings** window for **Interval**, locate the **Interval** section.
3. In the table, enter the following settings:

Coordinates (m)
`0`
`L_cell`

4. Click **Build All Objects**.

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 **Constitutive Relation D-E** section.
3. From the ε_r list, choose **User defined**. In the associated text field, type `eps_H2O`.

Surface Charge Density 1

1. In 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. In 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.

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 **Diffusion** section.
3. In the D_{cA} text field, type `DA`.
4. In the D_{cX} text field, type `DX`.
5. Locate the **Migration in Electric Field** section. In the z_{cA} text field, type `zA`.
6. In the z_{cX} text field, type `zX`.

Initial Values 1

1. In the **Model Builder** window, 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`.

Concentration 1

1. In 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`.

GLOBAL DEFINITIONS

Default Model Inputs

Set up the temperature value used in the entire model.

1. In the **Model Builder** window, under **Global Definitions** click **Default Model Inputs**.
2. In the **Settings** window for **Default Model Inputs**, locate the **Browse Model Inputs** section.
3. In the tree, select **General>Temperature (K) - minput.T**.
4. Find the **Expression for remaining selection** subsection. In the **Temperature** text field, type `T0`.

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 **Sequence Type** section.
3. From the list, choose **User-controlled mesh**.

Size 1

1. In the **Model Builder** window, 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 **Build All**.

STUDY 1

Step 1: Stationary

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

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

Parameter name	Parameter value list	Parameter unit
phiM (Voltage of electrode vs PZC)	`range(1,1,10)`	`mV`

6. In 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.

Line Graph 1

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

Point Graph 1

1. In the **Model Builder** window, right-click **Electric Potential (es)** and choose **Point Graph**.
2. Click the **Zoom Extents** button in the **Graphics** toolbar.
3. Select Boundary 1 only.

4. In the **Settings** window for **Point Graph**, locate the **y-Axis Data** section.
5. In the **Expression** text field, type `phiM`.
6. Locate the **x-Axis Data** section. 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. Click to expand the **Coloring and Style** section. Find the **Line style** subsection. From the **Line** list, choose **None**.
11. From the **Color** list, choose **Red**.
12. Find the **Line markers** subsection. From the **Marker** list, choose **Point**.
13. From the **Positioning** list, choose **In data points**.
14. In the **Electric Potential (es)** toolbar, click **Plot**.

Concentrations, All Species (tds)

1. In the **Model Builder** window, under **Results** click **Concentrations, All Species (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**.

Species A

1. In the **Model Builder** window, expand the **Concentrations, All Species (tds)** node, then click **Species A**.
2. In the **Settings** window for **Line Graph**, locate the **x-Axis Data** section.
3. From the **Unit** list, choose **nm**.
4. Click to expand the **Legends** section. From the **Legends** list, choose **Manual**.
5. In the table, enter the following settings:

Legends
`A<sup>+</sup> Concentration`

Species X

1. In the **Model Builder** window, click **Species X**.
2. In the **Settings** window for **Line Graph**, locate the **x-Axis Data** section.
3. From the **Unit** list, choose **nm**.
4. Locate the **Legends** section. From the **Legends** list, choose **Manual**.

5 In the table, enter the following settings:

Legends
`X<sup>-</sup> Concentration`

6 In the **Concentrations, All Species (tds)** toolbar, click **Plot**.

Surface Charge Density

1 In 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

1 Right-click **Surface Charge Density** and choose **Point Graph**.

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 `rho_surf`.

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

6 In the **Expression** text field, type `phiM`.

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

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

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

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
`Surface charge density (simulation)`

13 In the **Surface Charge Density** toolbar, click **Plot**.

Global 1

1 In the **Model Builder** window, right-click **Surface Charge Density** and choose **Global**.

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

3 In the table, enter the following settings:

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

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

5 In the **Expression** text field, type `phiM`.

6 Click to expand the **Coloring and Style** section. Click to expand the **Legends** section.

Surface Charge Density

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

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

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

4 In the associated text field, type `Charge density (C/m<sup>2</sup>)`.

5 Locate the **Legend** section. From the **Position** list, choose **Upper left**.

6 In the **Surface Charge Density** toolbar, click **Plot**.