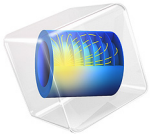

# Diffuse Double Layer with Charge Transfer

## *Introduction*

In the very vicinity of an electrode surface (in the range of up to a few nanometers), in the diffuse double layer, the assumption of electroneutrality is not valid due to charge separation. Typically the diffuse double layer may be of interest when modeling very thin layers of electrolyte, for instance in electrochemical capacitors and in atmospheric corrosion problems.

To model the behavior of the diffuse double layer, one needs to solve for the Nernst-Planck equations for all of the ions, in combination with the Poisson's equation for the potential. The combination of these equations is frequently referred to as the Poisson-Nernst-Planck (PNP) equations.

A problem that arises when modeling the PNP equations is that of how to handle the boundary condition for the potential equation. In this example an assumption of a Stern layer with a constant capacity is used to derive surface charge boundary conditions for Poisson's equation.

The model reproduces the results of Bazant and Chu (see Ref. 1 and Ref. 2).

See also the Diffuse Double Layer tutorial for an introduction to double layer modeling.

## *Model Definition*

The model geometry is in 1D (a single interval between 0 and L) and consists of one single domain, representing the electrolyte phase, including the diffuse double layer.

### 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 these are described by the Nernst-Planck equation

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

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) Faraday's constant, and $\phi$ (SI unit: V) the potential.

Assuming no homogeneous reactions in the electrolyte, the governing equations for the two species become:

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

For the potential, Poisson's equation states

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

where $\varepsilon$ is the permittivity (SI unit: F/m) and $\rho$ the charge density (SI unit: C/m$^3$), depending on the ion concentrations according to:

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

### BOUNDARY CONDITIONS

The boundaries reside in the reaction plane of the electrodes on each side. The same electrode reaction, in which the positive ion, $S^+$,participates, takes place on both electrodes.

$$S^+ + e^- \leftrightarrow S(s)$$

The reaction rate $r$ (SI unit: mol/(m$^2$·s)) is

$$r = K_a c_M \exp\left(\frac{\alpha_a F \phi_\Delta}{RT}\right) - K_c c_+ \exp\left(\frac{-\alpha_c F \phi_\Delta}{RT}\right)$$

where $K_a$ and $K_c$ (SI unit: m/s) are the anodic and cathodic rate constants, $c_M$ the metal species activity (SI unit: mol/m$^3$, constant) and $\alpha_a$ and $\alpha_c$ the anodic and cathodic transfer coefficients. $\phi_\Delta$ (SI unit: V) is the difference in potential between the metal phase, $\phi_M$ (SI unit: V), and the reaction plane:

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

The electrode reaction renders an inward flux for the positive ion according to

$$-\mathbf{n} \cdot \mathbf{J}_+ = r$$

on both boundaries. For the negative ion, a zero flux condition is used.

$$-\mathbf{n} \cdot \mathbf{J}_- = 0$$

Assuming the reaction plane to be placed at the boundary between the inner (compact) and diffuse double layer, and with the assumption of a Stern compact layer of a constant thickness, $\lambda_S$ (SI unit: m), one can derive the following Robin type of boundary condition for the potential:

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

This condition reduces to a Dirichlet voltage condition for $\lambda_S = 0$, that is, in the absence of a Stern layer. For the case of a nonzero stern layer thickness, the condition can be reformulated as a surface charge condition

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

### CELL POTENTIAL EQUATION

The problem formulated above can now be solved for given voltages of $\phi_M$ in the metal electrode phase for each side. Typically one grounds one electrode and specifies the cell voltage as $V$ so that

$$\phi_M\big|_{x=0} = 0$$
$$\phi_M\big|_{x=L} = V$$

However, to solve for a given cell current density, $i_{\text{cell}}$ (SI unit: $\text{A}/\text{m}^2$), with $V$ not known a priori, an additional global equation, solving for $V$, is used, fulfilling the condition:

$$i_{\text{cell}} = Fr\big|_{x=L}$$

### GLOBAL CONCENTRATION CONSTRAINT FOR THE NEGATIVE ION

When solving this system for a stationary solution, the negative ion concentration needs an additional "boot-strap" to render a stable, unique, solution. This is done by adding the following global constraint to the equation system:

$$c_0 L = \int_0^L c_- \, \mathrm{d}x$$

where $c_0$ is the initial ion concentration (SI unit: $\text{mol}/\text{m}^3$), equal for both ions.

The constraint assures that the total number of negative ions is preserved during the iterative solver process. (For time-dependent simulations the constraint can be omitted.)

### DIMENSIONLESS NUMBERS AND PARAMETER VALUES

A number of dimensionless numbers can be derived that govern the behavior of the cell. The problem is solved using a parametric study for a dimensionless parameter $\varepsilon_D = (0.001, 0.01, 0.1)$, defined as

$$\varepsilon_D = \lambda_D / L$$

$$\lambda_D = \sqrt{\frac{\varepsilon R T}{2 F^2 c_0}}$$

where $\lambda_D$ is the Debye length.

The current of the cell is defined via the dimensionless number $j$=0.9,

$$j = i_{\text{cell}} / i_D$$

$$i_D = 4 F D_+ c_0 / L$$

where $i_D$ is the Nernstian limiting current density.

The cathodic reaction rate constant is defined using the dimensionless number $k_c$ = 10,

$$k_c = \frac{K_c L}{4 D_+}$$

The rate of the anodic reaction term is governed by the dimensionless number $k_r$ = 10,

$$k_r = \frac{K_r L c_M}{4 D_+ c_0}$$

and the Stern layer thickness is set using the dimensionless number δ=0.1,

$$\delta = \frac{\lambda_S}{\lambda_D}$$

## *Results and Discussion*

The following dimensionless variables are used when presenting the results:

$$\tilde{x} = \frac{x}{L}$$

$$\tilde{c} = \frac{(c_+ + c_-)}{2 c_0}$$

$$\tilde{\rho} = \frac{(c_+ - c_-)}{2 c_0}$$

$$\tilde{\phi} = \frac{F \phi}{R T}$$

Figure 1 shows the dimensionless concentration, $\tilde{c}$ . The concentration gradients are steepest close to the electrodes.

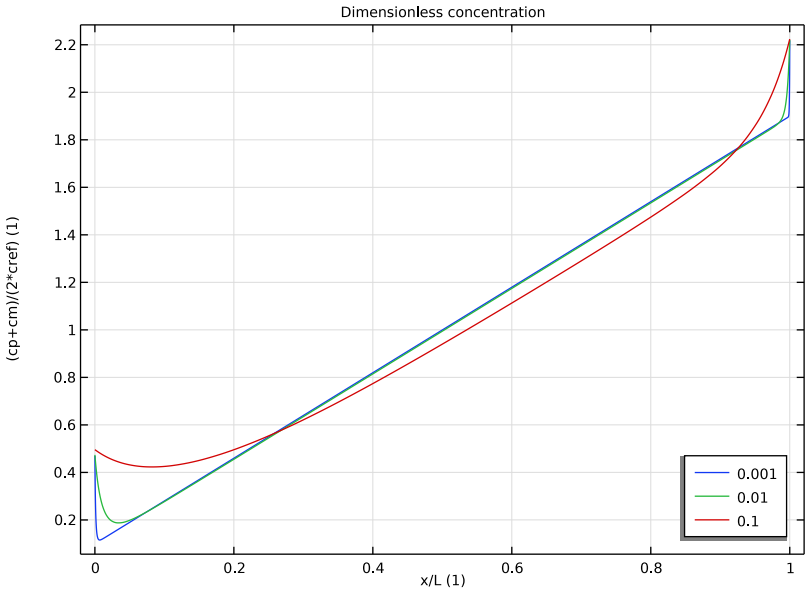


*Figure 1: Dimensionless concentration profile.*

Figure 2 shows the dimensionless charge density profile. Charge separation occurs close to the electrodes. For higher values of $\varepsilon_D$, the region of charge separation, the diffuse double layer, stretches further into the domain. This is expected since higher $\varepsilon_D$ values effectively mean a shorter domain length.

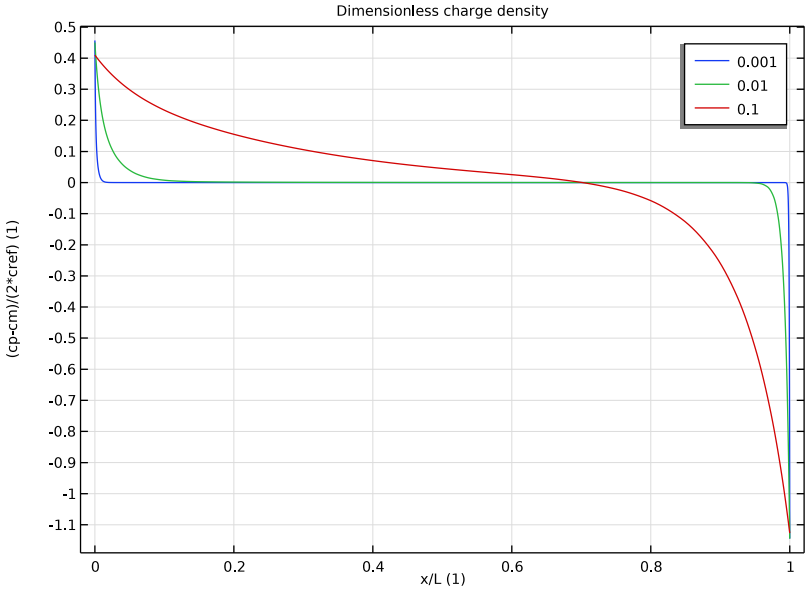


*Figure 2: Dimensionless charge density profile.*

Figure 3 shows the potential profile. For higher values of $\varepsilon_D$ the voltage over the cell decreases. This is an expected result since a shorter domain length shortens the potential losses due to ion transport.

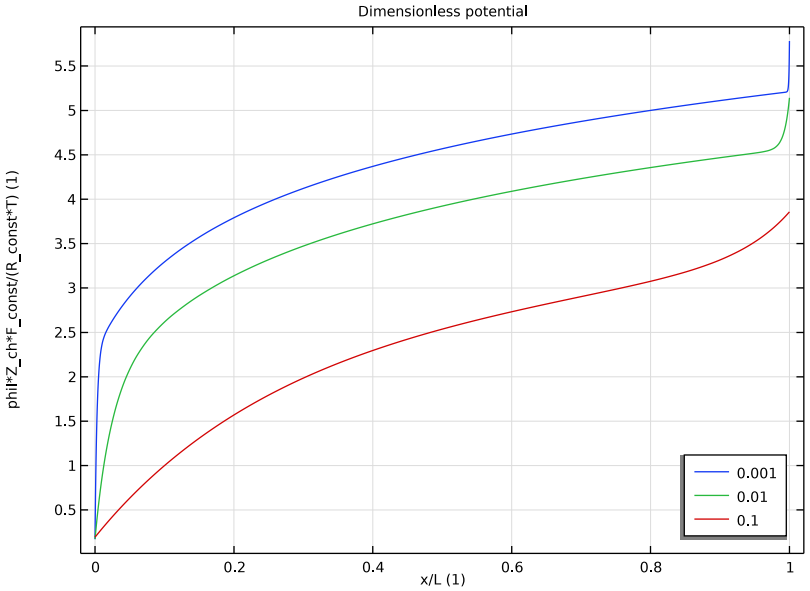


*Figure 3: Dimensionless potential profile.*

## *References*

1. M. Bazant, K. Chu, and B. Bayly, "Current-Voltage Relations for Electrochemical Thin Films," *SIAM Journal of Applied Math*, vol. 65, no. 5, pp. 1463–1484, 2005.

2. K. Chu and M. Bazant, "Electrochemical Thin Films at and Above the Classical Limiting Current," *SIAM Journal of Applied Math*, vol. 65, no. 5, pp. 1485–1505, 2005.

**Application Library path:** `Electrochemistry_Module/Tutorials/diffuse_double_layer_with_charge_transfer`

## *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 **Electrochemistry>Tertiary Current Distribution, Nernst-Planck>Tertiary, Electroneutrality (tcd)**.

3 Click **Add**.

4 Click **Study**.

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

6 Click **Done**.

### GLOBAL DEFINITIONS

*Parameters 1*

Start by loading some parameters from a text file.

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_with_charge_transfer_parameters.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 |

### DEFINITIONS

Proceed by adding some variable expressions. (Some of the expressions use variables that have not yet been defined and are hence marked in orange color. This is expected.)

*Variables 1*

1 In the **Model Builder** window, expand the **Component 1 (comp1)>Definitions** node.

2 Right-click **Definitions** and choose **Variables**.

3 In the **Settings** window for **Variables**, locate the **Variables** section.

4 Click **Load from File**.

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

### TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Now start setting up the physics. Begin with switching to the Poisson charge conservation model in the Tertiary Current Distribution, Nernst Planck.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Tertiary Current Distribution, Nernst-Planck (tcd)**.

2 In the **Settings** window for **Tertiary Current Distribution, Nernst-Planck**, locate the **Electrolyte Charge Conservation** section.

3 From the **Charge conservation model** list, choose **Poisson**.

4 Click to expand the **Dependent Variables** section. In the **Concentrations (mol/m³)** table, enter the following settings:

| |
|---|
| cp |
| cm |

*Species Charges 1*

1 In the **Model Builder** window, under **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd)** click **Species Charges 1**.

2 In the **Settings** window for **Species Charges**, locate the **Charge** section.

3 In the $z_{cp}$ text field, type `Z_ch`.

4 In the $z_{cm}$ text field, type `-Z_ch`.

*Electrolyte 1*

1 In the **Model Builder** window, click **Electrolyte 1**.

2 In the **Settings** window for **Electrolyte**, locate the **Diffusion** section.

3 In the $D_{cp}$ text field, type `Dp`.

4 In the $D_{cm}$ text field, type `Dm`.

*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 *cp* text field, type `cref`.

4 In the *cm* text field, type `cref`.

*Electrode Surface 1*

1 In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.

2 Select Boundary 1 only.

*Electrode Reaction 1*

1 In the **Model Builder** window, click **Electrode Reaction 1**.

2 In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the $\nu_{cp}$ text field, type `-1`.

4 Locate the **Equilibrium Potential** section. From the $E_{eq}$ list, choose **User defined**. Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Concentration dependent kinetics**.

5 In the $i_0$ text field, type `Ka*F_const*cM*Z_ch`.

6 In the $\alpha_a$ text field, type `alphaa*Z_ch`.

7 In the $\alpha_c$ text field, type `alphac*Z_ch`.

8 In the $C_O$ text field, type `Kc/Ka*cp/cM`.

*Electrode Surface 1*

In the **Model Builder** window, right-click **Electrode Surface 1** and choose **Duplicate**.

*Electrode Surface 2*

1 In the **Model Builder** window, click **Electrode Surface 2**.

2 In the **Settings** window for **Electrode Surface**, locate the **Boundary Selection** section.

3 Click **Clear Selection**.

4 Select Boundary 2 only.

5 Locate the **Electrode Phase Potential Condition** section. From the **Electrode phase potential condition** list, choose **Average current density**.

6 In the $i_{l,average}$ text field, type `icell`.

*Surface Charge Density 1*

1 In the **Physics** toolbar, click **Boundaries** and choose **Surface Charge Density**.

2 In the **Settings** window for **Surface Charge Density**, locate the **Boundary Selection** section.

3 From the **Selection** list, choose **All boundaries**.

4 Locate the **Surface Charge Density** section. In the $\rho_s$ text field, type `rho_s`.

5 Click the **Show More Options** button in the **Model Builder** toolbar.

6 In the **Show More Options** dialog box, in the tree, select the check box for the node **Physics>Equation-Based Contributions**.

7 Click **OK**.

## DEFINITIONS

*Integration 1 (intop1)*

1 In the **Definitions** toolbar, click **Nonlocal Couplings** and choose **Integration**.

2 Select Domain 1 only.

## TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Add a global constraint to boot-strap the average concentration of negative ions to the initial value.

*Global Constraint 1*

1 In the **Physics** toolbar, click **Global** and choose **Global Constraint**.

2 In the **Settings** window for **Global Constraint**, locate the **Global Constraint** section.

3 In the **Constraint expression** text field, type `intop1(cm)-(cref*L)`.

## 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 `T`.

## MESH 1

Edit the default meshing sequence. Make the mesh parameter dependent to make sure the mesh is always a well resolved at the boundaries. (The parametric sweep will change the size of the geometry during the solver process.)

### *Edge 1*

In the **Mesh** toolbar, click **Edge**.

### *Size 1*

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.
5. Select the **Maximum element size** check box. In the associated text field, type `L/20`.
6. Right-click **Size 1** and choose **Duplicate**.

### *Size 2*

1. In the **Model Builder** window, click **Size 2**.
2. In the **Settings** window for **Size**, locate the **Geometric Entity Selection** section.
3. From the **Geometric entity level** list, choose **Boundary**.
4. From the **Selection** list, choose **All boundaries**.
5. Locate the **Element Size Parameters** section. In the **Maximum element size** text field, type `lambdaD/10`.
6. Click **Build All**.

## STUDY 1

Solve the problem using a parametric sweep.

### *Parametric Sweep*

1. In the **Study** toolbar, click **Parametric Sweep**.
2. In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.
3. Click **Add**.
4. In the table, enter the following settings:

| Parameter name | Parameter value list | Parameter unit |
|---|---|---|
| epsilon (Dimensionless Debye length scale) | `0.001 0.01 0.1` | |

5 In the **Model Builder** window, click **Study 1**.

6 In the **Settings** window for **Study**, locate the **Study Settings** section.

7 Clear the **Generate default plots** check box.

8 In the **Study** toolbar, click **Compute**.

## RESULTS

Reproduce the figures from the Results and Discussion section in the following way:

### *1D Plot Group 1*

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

### *Line Graph 1*

1 Right-click **1D Plot Group 1** and choose **Line Graph**.

2 Select Domain 1 only.

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

4 In the **Expression** text field, type `(cp+cm)/(2*cref)`.

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

6 In the **Expression** text field, type `x/L`.

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

### *Dimensionless concentration*

1 In the **Model Builder** window, under **Results** click **1D Plot Group 1**.

2 In the **Settings** window for **1D Plot Group**, type `Dimensionless concentration` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/ Parametric Solutions 1 (sol2)**.

4 Click to expand the **Title** section. From the **Title type** list, choose **Label**.

5 Locate the **Legend** section. From the **Position** list, choose **Lower right**.

6 In the **Dimensionless concentration** toolbar, click **Plot**.

7 Right-click **Dimensionless concentration** and choose **Duplicate**.

### *Dimensionless charge density*

1 In the **Model Builder** window, under **Results** click **Dimensionless concentration 1**.

2 In the **Settings** window for **1D Plot Group**, type `Dimensionless charge density` in the **Label** text field.

3 Locate the **Legend** section. From the **Position** list, choose **Upper right**.

*Line Graph 1*

1. In the **Model Builder** window, expand the **Dimensionless charge density** node, then click **Line Graph 1**.
2. In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.
3. In the **Expression** text field, type `(cp-cm)/(2*cref)`.
4. In the **Dimensionless charge density** toolbar, click **Plot**.

*Dimensionless charge density*

In the **Model Builder** window, right-click **Dimensionless charge density** and choose **Duplicate**.

*Dimensionless potential*

1. In the **Model Builder** window, under **Results** click **Dimensionless charge density 1**.
2. In the **Settings** window for **1D Plot Group**, type `Dimensionless potential` in the **Label** text field.
3. Locate the **Legend** section. From the **Position** list, choose **Lower right**.

*Line Graph 1*

1. In the **Model Builder** window, expand the **Dimensionless potential** node, then click **Line Graph 1**.
2. In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.
3. In the **Expression** text field, type `phil*Z_ch*F_const/(R_const*T)`.
4. In the **Dimensionless potential** toolbar, click **Plot**.