

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.

This example shows how to couple the Nernst-Planck equations, solved using the Transport of Diluted Species interface, to the Poisson's equation, solved using the Electrostatics interface.

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).

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/m³, i=+,-), of two ions of opposite charge (+1/-1) are solved for in the electrolyte phase. The fluxes (\mathbf{J}_i , SI unit: mol/(m²·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: m²/s) being the diffusion coefficient, $u_{m,i}$ (SI unit: s·mol/kg) the mobility, F (SI unit: C/mol) Faraday's constant, and ϕ (SI unit: V) the potential.

Assuming no homogenous 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 ϵ is the permittivity (SI unit: F/m) and ρ the charge density (SI unit: C/m³), 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/(m²·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/m³, constant) and α_a and α_c the anodic and cathodic transfer coefficients. ϕ_{Δ} (SI unit: V) is the difference in potential between the metal phase, ϕ_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, λ_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 ϕ_M in the metal electrode phase for each side. Typically one grounds one electrode and specifies the cell voltage as V so that

$$\left. \begin{array}{l} \left. \phi_M \right|_{x = 0} = 0 \\ \left. \phi_M \right|_{x = L} = V \end{array} \right.$$

However, to solve for a given cell current density, i_{cell} (SI unit: A/m²), with V not known a priori, an additional global equation, solving for V, is used, fulfilling the condition:

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

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: mol/m³), 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

$$\varepsilon_D = \lambda_D / L$$
$$\lambda_D = \sqrt{\frac{\varepsilon RT}{2F^2 c_0}}$$

where λ_D is the Debye length.

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

$$j = i_{cell} / i_D$$
$$i_D = 4FD_+ c_0 / L$$

where i_D is the Nernstian limiting current density.

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

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

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

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

and the Stern layer thickness is set using the dimensionless number $\delta=0.1$,

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

Results and Discussion

The following dimensionless variables are used when presenting the results:

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

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

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

$$\tilde{\phi} = \frac{F\phi}{RT}$$

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 ε_D , the region of charge separation, the diffuse double layer, stretches further into the domain. This is expected since higher ε_D values effectively mean a shorter domain length.



Figure 2: Dimensionless charge density profile.

Figure 3 shows the potential profile. For higher values of ε_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.

Notes About the COMSOL Implementation

The element order is set to 2 for the Transport of Diluted Species to match the default element order 2 of the Electrostatics physics.

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

- I In the Model Wizard window, click ID.
- 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 **M** Done.

GLOBAL DEFINITIONS

Parameters 1

Start by loading some parameters from a text file.

- I In the Model Builder window, under Global Definitions click Parameters I.
- 2 In the Settings window for Parameters, locate the Parameters section.
- **3** Click **b** 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 I

Build the geometry as a single interval.

Interval I (i1)

- I In the Model Builder window, under Component I (compl) right-click Geometry I 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

- I In the Model Builder window, expand the Component I (compl)>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.

- I In the Model Builder window, under Component I (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** table, enter the following settings:

ср

cm

Electrolyte 1

- I In the Model Builder window, under Component I (compl)>Tertiary Current Distribution, Nernst-Planck (tcd) click Electrolyte I.
- 2 In the Settings window for Electrolyte, locate the Diffusion section.
- **3** In the D_{cp} text field, type Dp.

- **4** In the $D_{\rm cm}$ text field, type Dm.
- **5** Locate the **Migration in Electric Field** section. In the z_{cp} text field, type Z_ch.
- **6** In the $z_{\rm cm}$ text field, type -Z_ch.
- 7 Locate the Electrolyte Electric Field section. From the ϵ_r list, choose User defined.

Initial Values 1

- I In the Model Builder window, click Initial Values I.
- 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

- I In the Physics toolbar, click Boundaries and choose Electrode Surface.
- 2 Select Boundary 1 only.

Electrode Reaction I

- I In the Model Builder window, expand the Electrode Surface I node, then click Electrode Reaction I.
- **2** In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.
- **3** In the v_{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 α_a text field, type alphaa*Z_ch.
- 7 In the α_c text field, type alphac*Z_ch.
- **8** In the $C_{\rm O}$ text field, type Kc/Ka*cp/cM.

Electrode Surface 2

- In the Model Builder window, under Component I (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd) right-click Electrode Surface I and choose Duplicate.
- 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 $i_{1,average}$ text field, type icell.

Surface Charge Density I

- I 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 ρ_s text field, type rho_s.
- **5** Click the **5** 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)

- I 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 I

- I 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.

- I 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 I

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 I

In the Mesh toolbar, click 🛕 Edge.

Size 1

- I Right-click Edge I 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 L/20.

Size 2

- I Right-click Size I and choose Duplicate.
- 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 I

Solve the problem using a parametric sweep.

Parametric Sweep

- I 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	0.001 0.01 0.1	
length scale)		

- 5 In the Model Builder window, click Study I.
- 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:

I D Plot Group I

In the Home toolbar, click 🔎 Add Plot Group and choose ID Plot Group.

Line Graph 1

- I Right-click ID Plot Group I 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

- I In the Model Builder window, under Results click ID Plot Group I.
- 2 In the Settings window for ID Plot Group, type Dimensionless concentration in the Label text field.
- 3 Locate the Data section. From the Dataset list, choose Study I/ Parametric Solutions I (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 **O** Plot.

Dimensionless charge density

I Right-click Dimensionless concentration and choose Duplicate.

- 2 In the Settings window for ID 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

- I In the Model Builder window, expand the Dimensionless charge density node, then click Line Graph I.
- 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 **OD Plot**.

Dimensionless potential

- I In the Model Builder window, right-click Dimensionless charge density and choose Duplicate.
- 2 In the Settings window for ID Plot Group, type Dimensionless potential in the Label text field.
- 3 Locate the Legend section. From the Position list, choose Lower right.

Line Graph I

- I In the Model Builder window, expand the Dimensionless potential node, then click Line Graph I.
- 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 **I Plot**.