Modeling the Diffuse Double Layer

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 physics interface, to the Poisson's equation, solved using the Electrostatics physics interface.

A problem that arises when modeling the PNP equations is 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 (mol/m^3, i=+,-), of two ions of opposite charge (+1/-1) are solved for in the electrolyte phase. The flux ($\mathbf{N}_i$, mol/(m^2·s)) of these are described by the Nernst-Planck equation

$$\mathbf{N}_i = -D_i \nabla c_i - u_{m,i} z_i F c_i \nabla \phi \tag{1}$$

with D_i (m^2/s) the diffusion coefficient, $u_{m,i}$ (s·mol/kg) the mobility, F (C/mol) Faraday's constant, and ϕ (V) the potential.

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

$$\nabla \cdot \mathbf{N}_i = 0 \tag{2}$$

For the potential, Poisson's equation states

$$\nabla \cdot (-\varepsilon \nabla \phi) = \rho \tag{3}$$

where ε is the permittivity (F/m) and ρ the charge density (C/m^3), depending on the ion concentrations according to:

$$\rho = F(c_+ - c_-) \tag{4}$$

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.

$$S^+ + e^- \leftrightarrow S(s) \tag{5}$$

The reaction rate r (mol/(m^2·s)) is

$$r = K_a c_M \exp\left(\frac{\alpha_a F \phi_\Delta}{RT}\right) - K_c c_+ \exp\left(\frac{-\alpha_c F \phi_\Delta}{RT}\right) \tag{6}$$

where K_a and K_c (m/s) are the anodic and cathodic rate constants, c_M the metal species activity (mol/m^3, constant) and α_a and α_c the anodic and cathodic transfer coefficients. ϕ_Δ (V) is the difference in potential between the metal phase, ϕ_M (V), and the reaction plane:

$$\phi_\Delta = \phi_M - \phi \tag{7}$$

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

$$-\mathbf{n} \cdot \mathbf{N}_+ = r \tag{8}$$

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

$$-\mathbf{n} \cdot \mathbf{N}_- = 0 \tag{9}$$

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

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of a constant thickness, λ_S (m), one can derive the following Robin type of boundary condition for the potential:

$$\phi + \lambda_S(\mathbf{n} \cdot \nabla\phi) = \phi_M \tag{10}$$

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 non-zero stern layer thickness, the condition can be reformulated as a surface charge condition

$$\mathbf{n} \cdot (-\varepsilon\nabla\phi) = -\frac{\varepsilon\phi_\Delta}{\lambda_S} \tag{11}$$

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

$$\begin{aligned} \phi_M\big|_{x=0} &= 0 \\ \phi_M\big|_{x=L} &= V \end{aligned} \tag{12}$$

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

$$i_{\text{cell}} = Fr\big|_{x=L} \tag{13}$$

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:

$$c_0 L = \int_0^L c_- \mathrm{d}x \tag{14}$$

where c_0 is the initial ion concentration (mol/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

$$\begin{aligned} \varepsilon_D &= \lambda_D / L \\ \lambda_D &= \sqrt{\frac{\varepsilon R T}{2 F^2 c_0}} \end{aligned} \tag{15}$$

where λ_D is the Debye length.

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

$$\begin{aligned} j &= i_{\text{cell}} / i_D \\ i_D &= 4 F D_+ c_0 / L \end{aligned} \tag{16}$$

where i_D is the Nernstian limiting current density.

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

$$k_c = \frac{K_c L}{4 D_+} \tag{17}$$

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

$$k_r = \frac{K_r L c_M}{4 D_+ c_0} \tag{18}$$

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

$$\delta = \frac{\lambda_S}{\lambda_D} \tag{19}$$

Results and Discussion

The following dimensionless variables are used when presenting the results:

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$$
\begin{aligned}
\tilde{x} &= \frac{x}{L} \\
\tilde{c} &= \frac{(c_+ + c_-)}{2c_0} \\
\tilde{\rho} &= \frac{(c_+ - c_-)}{2c_0} \\
\tilde{\phi} &= \frac{F\phi}{RT}
\end{aligned}
\tag{20}
$$

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

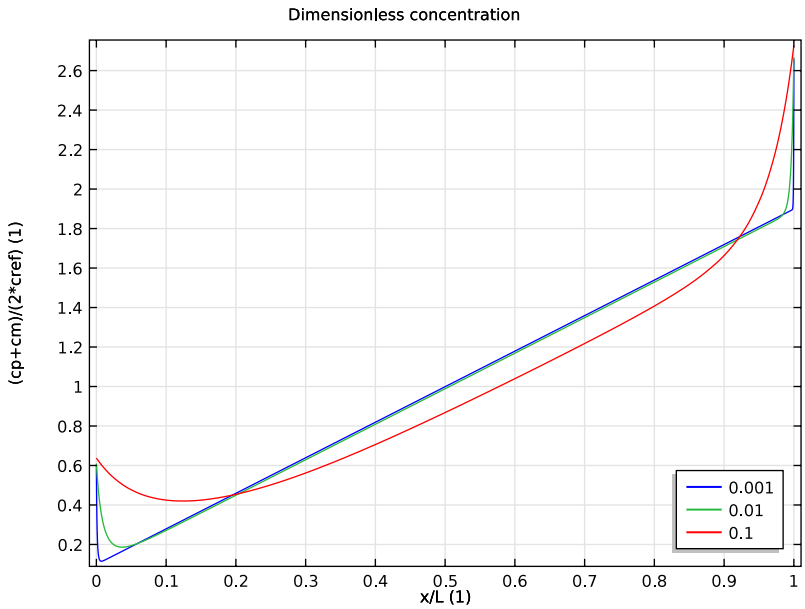

Figure 1: Dimensionless concentration profile.

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 means a shorter domain length.

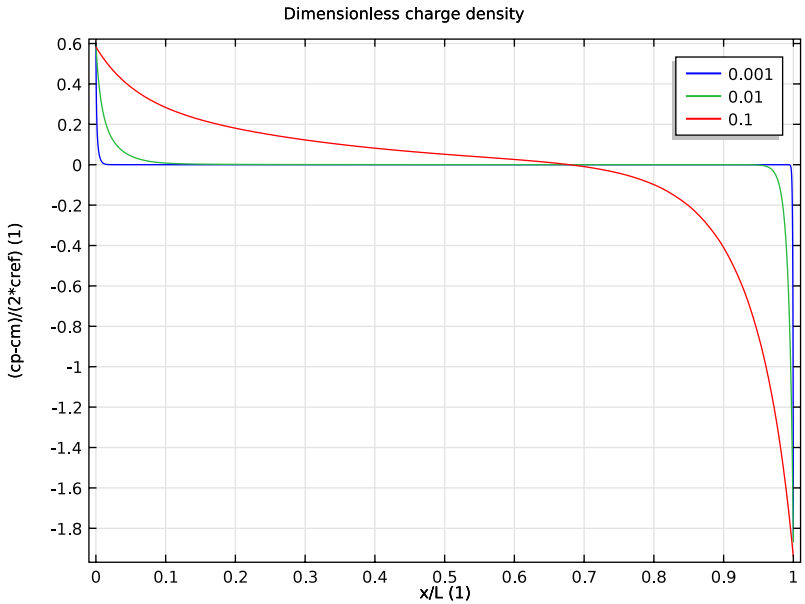

Figure 2: Dimensionless charge density profile.

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.

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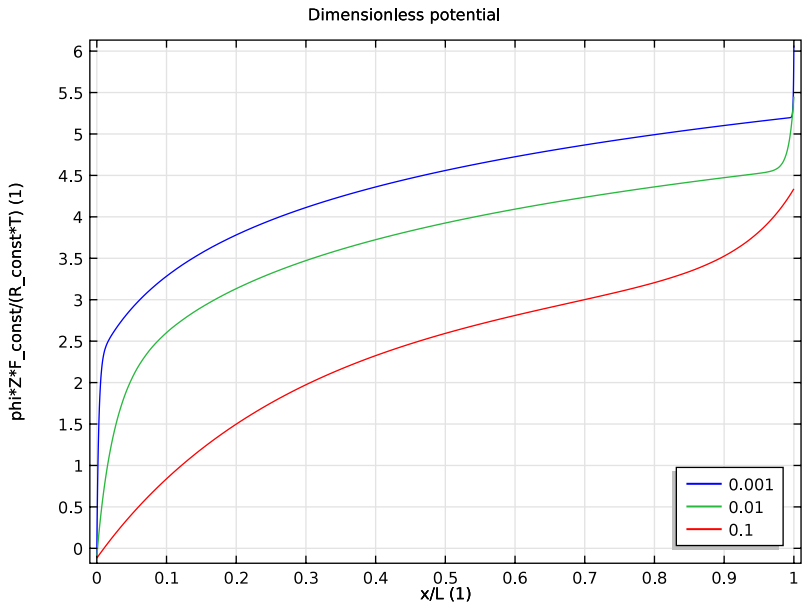

Figure 3: Dimensionless potential profile.

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 (2005), no. 5, pp. 1463–1484.

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

Model Library path: `Corrosion_Module/Verification_Models/diffuse_double_layer`

Modeling Instructions

MODEL WIZARD

1 Go to the **Model Wizard** window.

2 Click the **1D** button.

3 Click **Next**.

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

5 Click **Add Selected**.

6 Find the **Dependent variables** subsection. In the **Electric potential** edit field, type `phi`.

7 In the **Add physics** tree, select **Chemical Species Transport>Transport of Diluted Species (chds)**.

8 Click **Add Selected**.

9 Click **Add Concentration**.

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

cp
cm

11 In the **Add physics** tree, select **Mathematics>ODE and DAE Interfaces>Global ODEs and DAEs (ge)**.

12 Click **Add Selected**.

13 Click **Next**.

14 Find the **Studies** subsection. In the tree, select **Preset Studies for Selected Physics>Stationary**.

15 Click **Finish**.

GLOBAL DEFINITIONS

Start by loading some parameters from a text file.

Parameters

1 In the **Model Builder** window, right-click **Global Definitions** and choose **Parameters**.

2 In the **Parameters** settings window, locate the **Parameters** section.

3 Click **Load from File**.

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

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GEOMETRY 1

Build the geometry as a single interval.

Interval 1

1 In the **Model Builder** window, under **Model 1** right-click **Geometry 1** and choose **Interval**.

2 In the **Interval** settings window, locate the **Interval** section.

3 In the **Right endpoint** edit field, type `L`.

4 Click the **Build All** button.

5 Click the **Zoom Extents** button on the Graphics toolbar.

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, under **Model 1** right-click **Definitions** and choose **Variables**.

2 In the **Variables** settings window, locate the **Geometric Entity Selection** section.

3 From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundaries 1 and 2 only.

5 In the **Variables** settings window, locate the **Variables** section.

6 Click **Load from File**.

7 Browse to the model's Model Library folder and double-click the file `diffuse_double_layer_variables.txt`.

Variables 2

1 In the **Model Builder** window, right-click **Definitions** and choose **Variables**.

2 In the **Variables** settings window, locate the **Geometric Entity Selection** section.

3 From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 1 only.

5 Locate the **Variables** section. In the table, enter the following settings:

Name	Expression	Description
`phiM`	`0[V]`	`Metal phase potential (ground)`

Variables 3

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

2 In the **Variables** settings window, locate the **Geometric Entity Selection** section.

3 From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 2 only.

5 Locate the **Variables** section. In the table, enter the following settings:

Name	Expression	Description
phiM	V	Metal phase potential (cell voltage)

Integration 1

Add integration coupling operators to be used when setting up the global voltage equation and the global constraint.

1 Right-click **Definitions** and choose **Model Couplings>Integration**.

2 In the **Integration** settings window, locate the **Source Selection** section.

3 From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 2 only.

Integration 2

1 Right-click **Definitions** and choose **Model Couplings>Integration**.

2 Select Domain 1 only.

ELECTROSTATICS

Charge Conservation 1

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

1 In the **Model Builder** window, under **Model 1>Electrostatics** click **Charge Conservation 1**.

2 In the **Charge Conservation** settings window, locate the **Electric Field** section.

3 From the ε_r list, choose **User defined**.

Space Charge Density 1

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

2 Select Domain 1 only.

3 In the **Space Charge Density** settings window, locate the **Space Charge Density** section.

4 In the ρ_q edit field, type `F_const*Z*(cp-cm)`.

Surface Charge Density 1

1 Right-click **Electrostatics** and choose **Surface Charge Density**.

2 Select Boundaries 1 and 2 only.

3 In the **Surface Charge Density** settings window, locate the **Surface Charge Density** section.

4 In the ρ_s edit field, type `rho_s`.

TRANSPORT OF DILUTED SPECIES

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 **Model 1** click **Transport of Diluted Species**.

2 In the **Transport of Diluted Species** settings window, 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**.

Diffusion and Migration

1 In the **Model Builder** window, under **Model 1>Transport of Diluted Species** click **Diffusion and Migration**.

2 In the **Diffusion and Migration** settings window, locate the **Model Inputs** section.

3 In the V edit field, type `phi`.

4 In the T edit field, type `T`.

5 Locate the **Diffusion** section.

6 In the D_{cp} edit field, type `Dp`.

7 In the D_{cm} edit field, type `Dm`.

8 Locate the **Migration in Electric Field** section. In the z_{cp} edit field, type `Z`.

9 In the z_{cm} edit field, type `-Z`.

Flux 1

1 In the **Model Builder** window, right-click **Transport of Diluted Species** and choose **Flux**.

2 Select Boundaries 1 and 2 only.

3 In the **Flux** settings window, locate the **Inward Flux** section.

4 Select the **Species cp** check box.

5 In the $N_{0,\mathrm{cp}}$ edit field, type `r`.

Initial Values 1

1 In the **Model Builder** window, under **Model 1>Transport of Diluted Species** click **Initial Values 1**.

2 In the **Initial Values** settings window, locate the **Initial Values** section.

3 In the *cp* edit field, type `cref`.

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

5 In the **Model Builder** window's toolbar, click the **Show** button and select **Advanced Physics Options** in the menu.

Global Constraint 1

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

1 In the **Model Builder** window, right-click **Transport of Diluted Species** and choose **Global>Global Constraint**.

2 In the **Global Constraint** settings window, locate the **Global Constraint** section.

3 In the **Constraint expression** edit field, type `intop2(cm)-(cref*L)`.

GLOBAL ODES AND DAES

Global Equations 1

Finally, add the equation for the cell potential.

1 In the **Model Builder** window, under **Model 1>Global ODEs and DAEs** click **Global Equations 1**.

2 In the **Global Equations** settings window, locate the **Global Equations** section.

3 In the table, enter the following settings:

Name	f(u,ut,utt,t)	Description
V	`intop1(iloc)-icell`	Cell voltage

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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 **Model Builder** window, under **Model 1** right-click **Mesh 1** and choose **Edit Physics-Induced Sequence**.

Size 1

1 In the **Model Builder** window, under **Model 1>Mesh 1** right-click **Edge 1** and choose **Size**.
2 In the **Size** settings window, 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 edit field, type `L/20`.

Size 2

1 Right-click **Edge 1** and choose **Size**.
2 In the **Size** settings window, locate the **Geometric Entity Selection** section.
3 From the **Geometric entity level** list, choose **Boundary**.
4 Select Boundaries 1 and 2 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 edit field, type `lambdaD/10`.

Edge 1

Right-click **Edge 1** and choose **Build Selected**.

STUDY 1

Solve the problem using a parametric sweep.

Parametric Sweep

1 In the **Model Builder** window, right-click **Study 1** and choose **Parametric Sweep**.
2 In the **Parametric Sweep** settings window, locate the **Study Settings** section.
3 Click **Add**.

4 In the table, enter the following settings:

Parameter names	Parameter value list
epsilon	`0.001 0.01 0.1`

5 Right-click **Study 1** and choose **Compute**.

RESULTS

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

Dimensionless concentration 1

1 In the **Model Builder** window, expand the **Concentration (chds)** node, then click **Line Graph 1**.

2 In the **Line Graph** settings window, locate the **y-Axis Data** section.

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

4 Locate the **x-Axis Data** section. In the **Expression** edit field, type `x/L`.

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

6 In the **Model Builder** window, click **Concentration (chds)**.

7 In the **1D Plot Group** settings window, click to expand the **Title** section.

8 From the **Title type** list, choose **Manual**.

9 In the **Title** text area, type `Dimensionless concentration`.

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

11 Click the **Plot** button.

12 Right-click **Concentration (chds)** and choose **Rename**.

13 Go to the **Rename 1D Plot Group** dialog box and type `Dimensionless concentration` in the **New name** edit field.

14 Click **OK**.

Dimensionless charge density 1

1 Right-click **Concentration (chds)** and choose **Duplicate**.

2 In the **1D Plot Group** settings window, locate the **Title** section.

3 In the **Title** text area, type `Dimensionless charge density`.

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

5 In the **Model Builder** window, expand the **Dimensionless concentration 1** node, then click **Line Graph 1**.

6 In the **Line Graph** settings window, locate the **y-Axis Data** section.

7 In the **Expression** edit field, type `(cp-cm)/(2*cref)`.

8 Click the **Plot** button.

9 In the **Model Builder** window, right-click **Dimensionless concentration 1** and choose **Rename**.

10 Go to the **Rename 1D Plot Group** dialog box and type `Dimensionless charge density` in the **New name** edit field.

11 Click **OK**.

Dimensionless potential 1

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

2 In the **1D Plot Group** settings window, locate the **Title** section.

3 In the **Title** text area, type `Dimensionless potential`.

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

5 In the **Model Builder** window, expand the **Dimensionless charge density 1** node, then click **Line Graph 1**.

6 In the **Line Graph** settings window, locate the **y-Axis Data** section.

7 In the **Expression** edit field, type `phi*Z*F_const/(R_const*T)`.

8 Click the **Plot** button.

9 In the **Model Builder** window, right-click **Dimensionless charge density 1** and choose **Rename**.

10 Go to the **Rename 1D Plot Group** dialog box and type `Dimensionless potential` in the **New name** edit field.

11 Click **OK**.