

# Manual and Theory

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# 1. Application layout

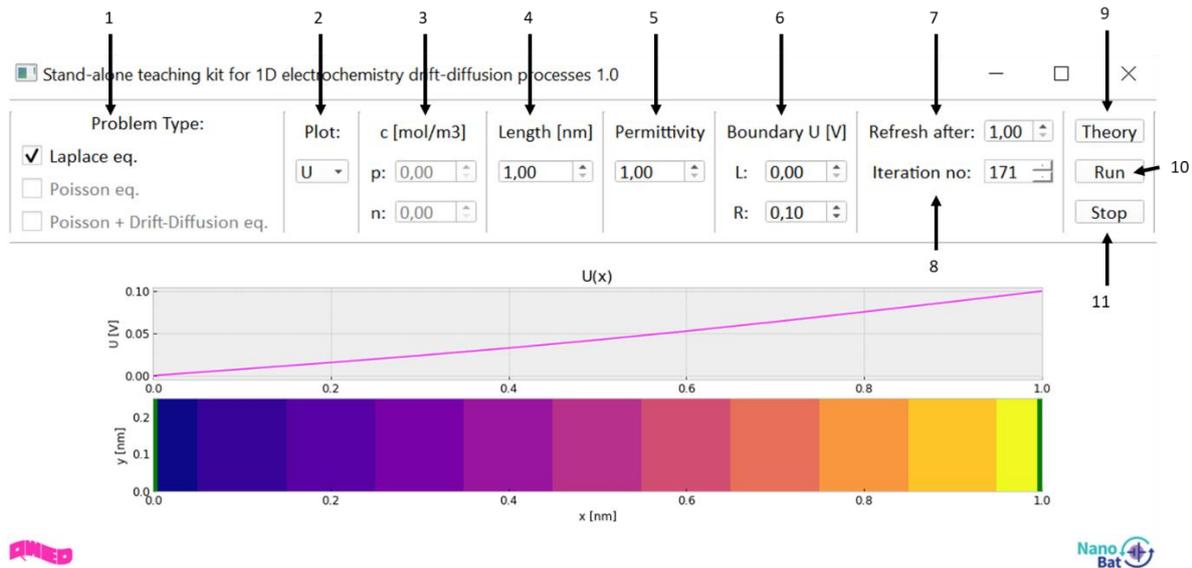


Fig. 1.1 Application layout

1. *Problem type* – allows for a definition of a problem type. There are three options to choose from:

- Laplace equation,
- Poisson equation,
- Poisson + Drift-Diffusion equation.

2. *Plot* – allows one to select a variable to be displayed. There are different variables available for display depending on the *Problem type*:

- Laplace equation (Electric potential (U), Electric fields (Ex, Ey)),
- Poisson equation (Electric potential (U), Electric fields (Ex, Ey), total charge (q\_tot), positive charge (q\_p), negative charge (q\_n)),
- Poisson + Drift-Diffusion equation (Electric potential (U), Electric fields (Ex, Ey), total charge (q\_tot), positive charge (q\_p), negative charge (q\_n)).

3. *c* – molar concentration of positive (p) and negative (n) ions. This option is not available for Laplace eq. *Problem type* (default value equal 0 is used) and for Poisson eq. *Problem type* only the amount of positive ions can be changed (default value of negative ions concentration equal 0 is used).

4. *Length* – the distance between parallel electrodes (indicated by green color in Fig. 1.2)

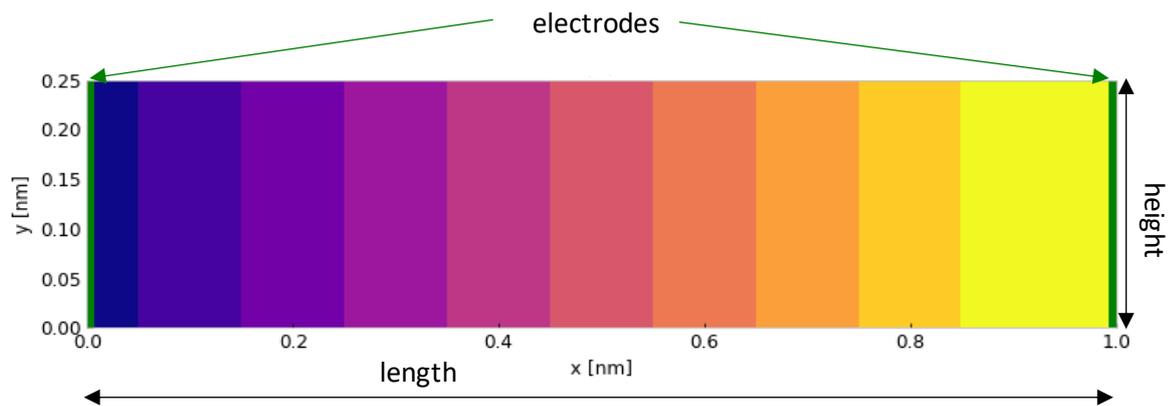


Fig. 1.2. System geometry

5. *Permittivity* – allows changing the value of electrolyte permittivity
6. *Boundary U* – allows specifying the value of electric potential on the left (L) and right (R) electrode
7. *Refresh after* – allows specifying the number of iterations after which the displayed plot will be refreshed
8. *Iteration no* – shows the iteration number for which the results are currently shown in the graph
9. *Theory* – this button opens a new window with a “Manual and Theory” file
10. *Run* – this button starts the visualization of simulation results
11. *Stop* – this button stops the visualization of simulation results

## 2. Theory and Examples

Computational electromagnetics (CEM) is a powerful tool used in electrical engineering as well as a very promising tool for use in other industries that require the simultaneous solution of Maxwell's equations with equations describing other physical processes.

Nowadays, more and more attention is paid to the area of energy materials, such as batteries or photovoltaics. Electromagnetic testing of such materials is gaining popularity but requires that charge transport mechanisms be taken into account in order to properly interpret the testing results. For example, a physical model of the ion transport process in the electrolyte must be considered in Li-ion batteries, which are one of the most popular electrical energy storage devices in various applications. Coupled electrochemical models are therefore necessary in battery research.

The presented application enables modeling of coupled electrochemical phenomena occurring at electrolyte/electrode interfaces. The application can be used to visualize three different models of increasing complexity. The problems are solved using coupled Laplace / Poisson and drift-diffusion equations, which create a basic model of ion transport process in the electrolyte, as in e.g. in popular Li-ion batteries.

### 2.1. Physical model

A region filled with an electrolyte and polarized by fixed-potential electrodes is considered. The following physical quantities are available for display:

- electric potential (U) distribution,
- E-field distribution,
- charge distribution (total, positive and negative),

all in time and space.

#### 2.2.1. Electrostatics

The first part of the model, consisting of (1), (2) and (3), is used for obtaining the electrical potential distribution in our space. Using the definition of electric potential the electric field distribution in space is obtained:

$$\mathbf{E} = -\nabla U \quad (1)$$

The electric charge density in space is checked using Gauss law:

$$\nabla \cdot \mathbf{D} = \rho_g \quad (2)$$

$$\oint_S \mathbf{D} \cdot d\mathbf{S} = q_g \quad (3)$$

Finally, the electric potential is updated using Poisson's equation (in the case when there is no initial charge in the system Laplace's equation (4) is used):

$$\Delta U = -\frac{\rho_t}{\epsilon_r \epsilon_0} \quad (4)$$



$$\Delta U = 0 \quad (4)$$

### 2.2.2. Drift-diffusion model

In the second part of the model the process of flow of ions (positive and negative) is taken into account. The separate currents for positive ( $\mathbf{j}_p$ ) and negative ( $\mathbf{j}_m$ ) ions are calculated using drift-diffusion equation. It combines the influence of existing electric field on the charges with diffusion process ( $D_c$  – diffusion coefficient,  $\mu$  – mobility):

$$\mathbf{j}_p = q_p \mu \mathbf{E} - D_c \nabla q_p \quad (5)$$

$$\mathbf{j}_m = q_m \mu \mathbf{E} + D_c \nabla q_m \quad (6)$$

The resulting currents cause a change in the position of ions in the modeled space in time and using the continuity equation we obtain the distribution of ions for each moment in time.

$$\oint_S \mathbf{j}_p \cdot d\mathbf{S} = -\frac{dq_p}{dt} \quad (7)$$

$$\oint_S \mathbf{j}_m \cdot d\mathbf{S} = \frac{dq_m}{dt} \quad (8)$$

### 2.2.3. Discretization

The solutions are found using discretized forms of equations listed in two previous sections and some other modifications that are explained below.

$$E_{x_{ij}} = -\frac{(U_{i+1,j} - U_{ij})}{\Delta x_{ij}} \quad (9)$$

$$E_{y_{ij}} = -\frac{(U_{i,j+1} - U_{ij})}{\Delta y_{ij}} \quad (10)$$

Equation (1) in discretized form is (9) and (10), additionally a  $d$  quantity is introduced and given by:

$$d_x = D_x * \Delta y_{avg} \Delta z_{avg} \quad (11)$$

$$d_y = D_y * \Delta x_{avg} \Delta z_{avg} \quad (12)$$

Where  $\Delta z_{avg} = 1$  and:

$$\Delta x_{avg} = \frac{\Delta x_i + \Delta x_{i-1}}{2} \quad (13)$$

$$\Delta y_{avg} = \frac{\Delta y_j + \Delta y_{j-1}}{2} \quad (14)$$

The  $d_x$  and  $d_y$  values are used in discretized form of Gauss law:

$$q_{g_{ij}} = d_{x_{ij}} - d_{x_{i-1,j}} + d_{y_{ij}} - d_{y_{i,j-1}} \quad (15)$$



In section A, electric potential is updated using Poisson's equation (4). However, in this case, a relaxation technique is used:

$$U_{ij} = U_{ij} - r^* / \epsilon_0 (q_{gij} - q_{ij}) \quad (16)$$

$r^*$  is a relaxation coefficient expressed as:

$$r^* = \frac{r}{\Delta z_{avg}} \quad (17)$$

and  $(q_{gij} - q_{ij})$  is a difference between total charge obtained from Gauss law and total charge given as a initial condition.

Drift-diffusion equations are discretized to form:

$$j_{pxij} = q_{pxavgij} \mu^* E_x - D_c^* \frac{q_{p_{i+1,j}} - q_{p_{ij}}}{\Delta x} \quad (18)$$

$$j_{mxij} = q_{mxavgij} \mu^* E_x + D_c^* \frac{q_{m_{i+1,j}} - q_{m_{ij}}}{\Delta x} \quad (19)$$

where:

$$q_{xavgij} = \frac{q_{i+1,j} + q_{ij}}{2} \quad (20)$$

and  $\mu^*$ ,  $D_c^*$  are normalized  $\mu$  and  $D_c$  parameters:

$$\mu^* = \frac{\mu}{\Delta x_{avg} \Delta x} \quad (21)$$

$$D_c^* = \frac{D_c}{\Delta x_{avg}} \quad (22)$$

The discretized forms of continuity equations (7), (8) are presented below:

$$q_{p_{ij}}(t) = q_{p_{ij}}(t-1) - (j_{px_{i,j}} - j_{px_{i-1,j}}) \Delta t - (j_{py_{i,j}} - j_{py_{i,j-1}}) \Delta t \quad (23)$$

$$q_{m_{ij}}(t) = q_{m_{ij}}(t-1) + (j_{mx_{i,j}} - j_{mx_{i-1,j}}) \Delta t + (j_{my_{i,j}} - j_{my_{i,j-1}}) \Delta t \quad (24)$$

The total charge is expressed as the difference between positive and negative charges:

$$q_{total} = q_p - q_m \quad (25)$$

## 2.2. Examples

There are three *Problem Types* available for simulation and in all three cases, a region with length specified in Length option is terminated by two planar electrodes with electric potential (U) specified in Boundary U option. Such settings as well as the applied material parameters are representative of the so-called half-cell setup for the testing of battery materials.



### 2.2.1. Laplace equation.

The first example concerns electrostatics in a region without charges. This corresponds to the computation of the Laplace equation and finding the electrostatic potential distribution. Check the checkbox with Laplace eq. in the *Problem Type* section and run the simulation with the default settings. After 70 iterations, you will see the same  $U$  distribution as in Fig. 2.1.

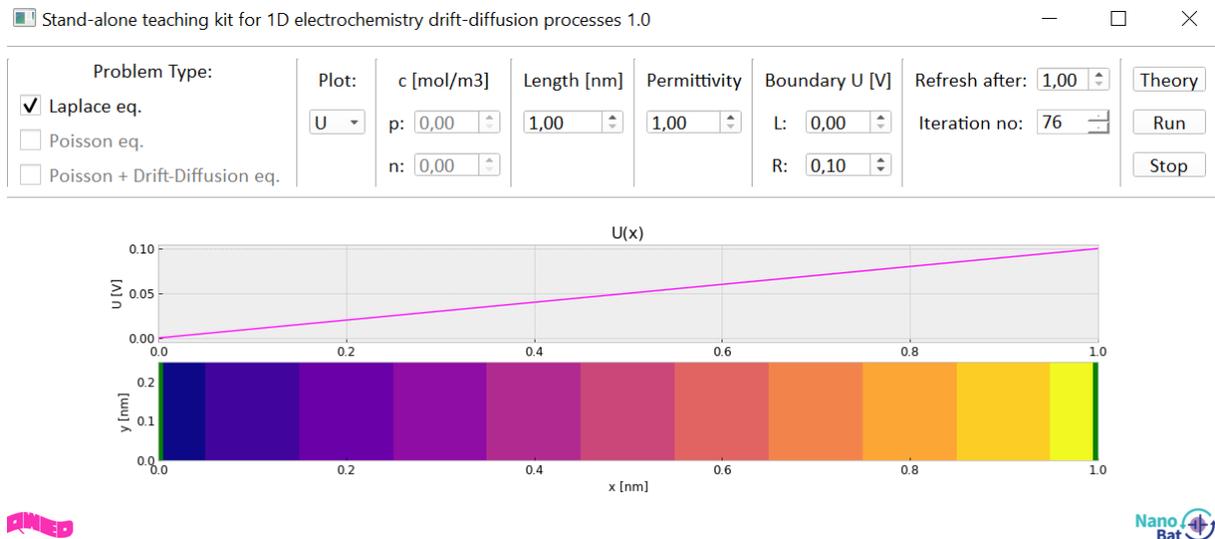


Fig. 2.3  $U$  distribution for Laplace eq. Problem Type

### 2.2.2. Poisson equation.

In the second problem, ions are uniformly distributed as the initial condition. The ions are assumed to be static, which has the physical sense of zero diffusivity and mobility. Due to the charges, instead of the Laplace equation, the Poisson equation is now computed to find the electrostatic potential distribution. If densities of negative and positive charges are equal, the net charge is zero and the solution is the same as for the Laplace equation. Any net charge will, however, cause a deformation of the linear  $U(x)$  solution by a parabolic component. In Poisson eq. *Problem Type* only positive charges are considered nonzero in the modeled space. For the increasing molar densities of positive charges, the parabolic component of the potential distribution becomes increasingly significant and a local maximum of the potential shifts towards the grounded (lower potential) electrode, as shown in Fig. 2.3., Fig. 2.4. and Fig. 2.5.

The results obtained with our algorithm (based on the Finite-Difference Time-Domain (FDTD) method) were compared with the results obtained from the analytical solution. The comparison is shown in Fig. 2.2.

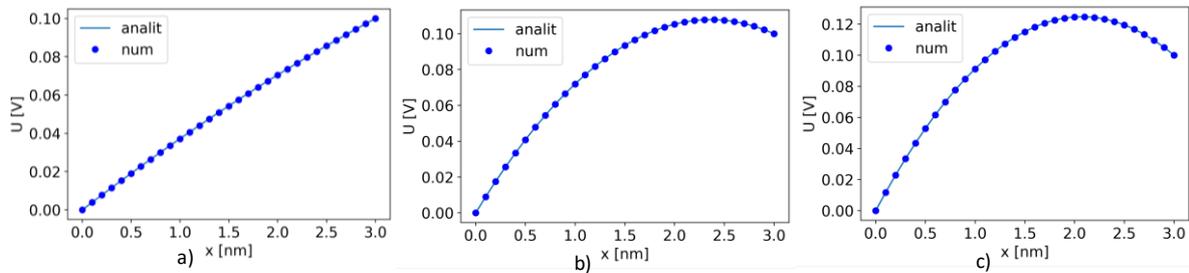


Fig. 2.2. Electric potential ( $U$ ) distribution in 3 nm space limited by electrodes of 0.1 V potential difference, filled with electrolyte of  $\epsilon_r = 2.82$  and static positive charges of molar concentration: (a) 1 mol/m<sup>3</sup>, (b) 10 mol/m<sup>3</sup>, and (c) 15 mol/m<sup>3</sup>.

In order to obtain the same results as presented in Fig. 2.3., Fig. 2.4. and Fig. 2.5. check the checkbox with Poisson eq. in the *Problem Type* section and run the first simulation with *Length* changed to 2 nm. After 150 iterations, you will see the same  $U$  distribution as in Fig. 2.2.

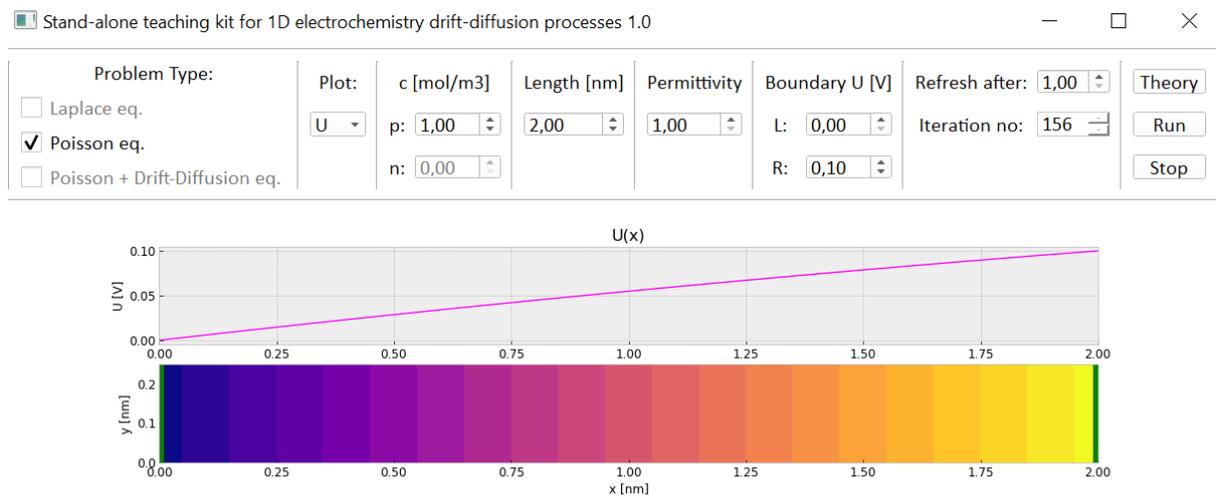


Fig. 2.3.  $U$  distribution for Poisson eq. *Problem Type* and  $c=1$  mol/m<sup>3</sup>

Next, stop the simulation, increase positive ions molar concentration ( $c$ ) to 5 and run a new simulation.

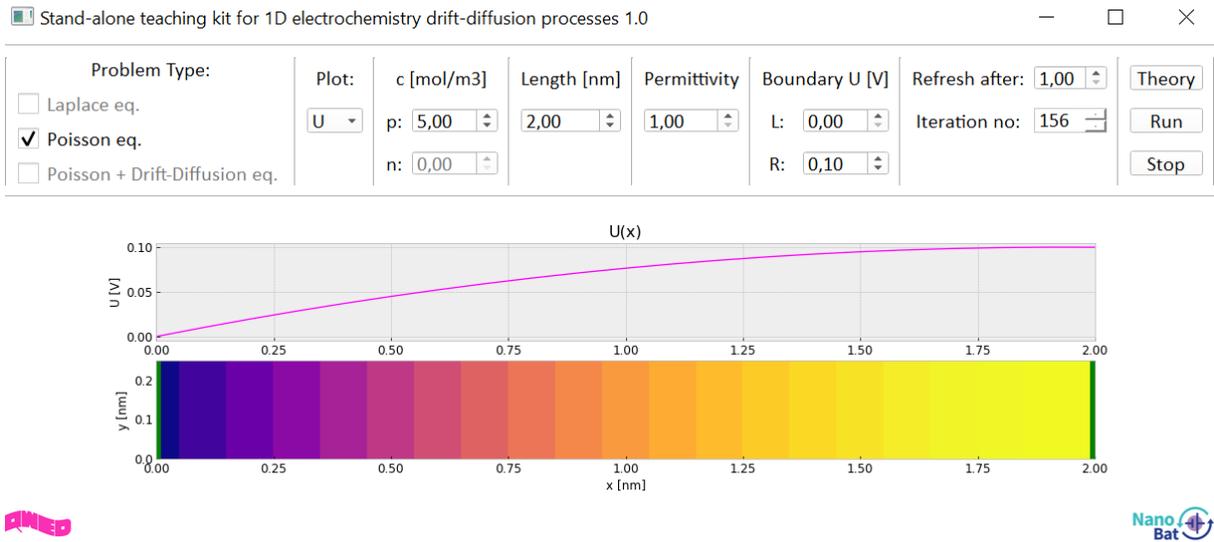


Fig. 2.4. U distribution for Poisson eq. Problem Type and  $c=5 \text{ mol/m}^3$

Then stop the simulation, increase positive ions molar concentration ( $c$ ) to 15 and again run a new simulation.

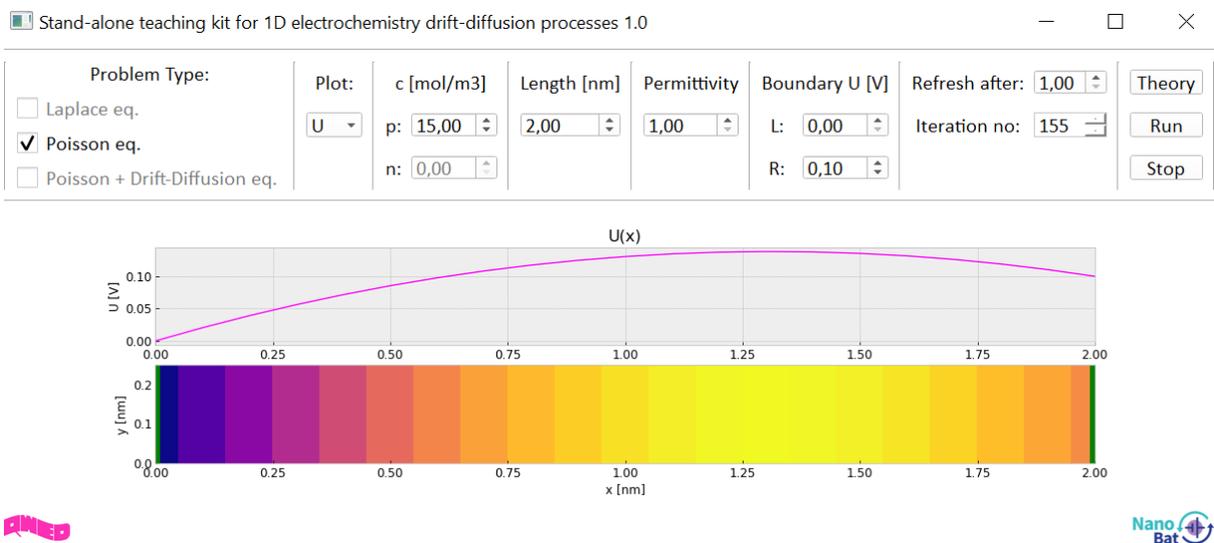


Fig. 2.6.. U distribution for Poisson eq. Problem Type and  $c=10 \text{ mol/m}^3$

### 2.2.3. Poisson + Drift-Diffusion equations.

In the third problem, the Poisson equation is coupled with the drift-diffusion equations. The initial condition is imposed by uniformly distributed positive and negative ions, but now the ions have finite diffusivity ( $10^{-9} \text{ m}^2/\text{s}$ ) and mobility ( $4.036 \cdot 10^{-13}$ ). The evolution of the distribution of charges is found by the time-stepping of eqs. (23), (24); at each time step, a new potential distribution is obtained by relaxation (9)-(16) leading to new current distributions given by (18)(19).

In this case, an analytical solution is not easily available, so for comparison, a FEM solution is obtained using commercial COMSOL software [1]. A perfect agreement between our FDTD solution and FEM solutions is demonstrated in Fig. 2.7.

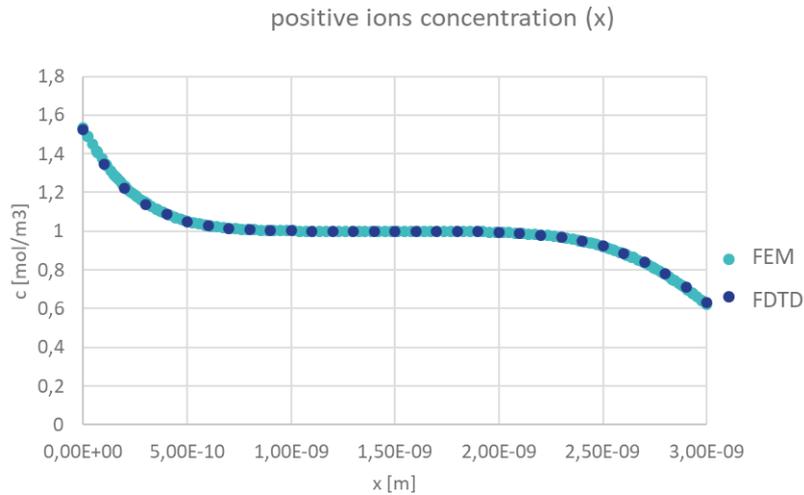


Fig. 2.7. Positive charge concentration distribution in space limited by electrodes of 0.1 V potential difference, filled with electrolyte of  $\epsilon_r = 2.82$ , with initial uniform concentration of positive and negative ions of  $1 \text{ mol/m}^3$  and  $D_c = 10^{-9} \text{ m}^2/\text{s}$ .

In order to obtain the same results as presented in Fig. 2.8. check the checkbox with Poisson + Drift-Diffusion eq. in the *Problem Type* section, change variable in *Plot* to  $q_t$  (total charge) and change *Length* to 2 nm. Then run the simulation and after 200 iterations, you will see the same  $q_t$  distribution as in Fig. 2.8.

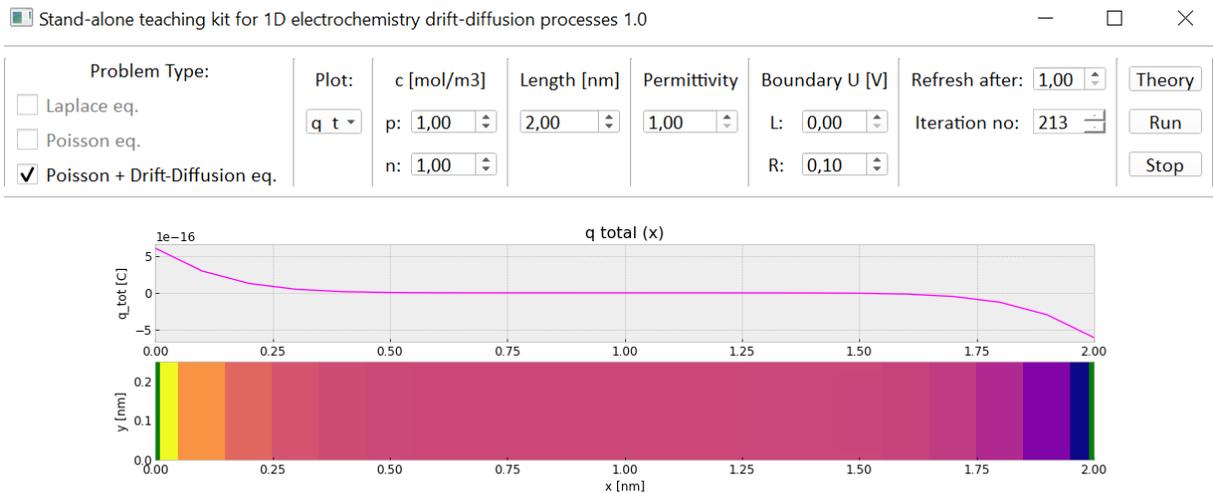


Fig. 2.8. Total charge distribution for Poisson + Drift-Diffusion eq. Problem Type

### 3. Version 1.0 limitations

The values of spatial steps and time steps are fixed for all types of simulations and equal to 0.1 nm and  $10^{-13} \text{ s}$  respectively. For this reason, for some values of parameters (e.g.  $c$ , *Boundary U*) the simulation will not converge. These application limitations will be alleviated in a future release.

[1] COMSOL software: <https://www.comsol.com/products>

