

Manual and Theory

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1. Application layout

Software simulates a nanometer 1D space filled with an electrolyte and bounded by two electrodes. In such a system there is a physical phenomenon of the flow of ions. In simulation separate currents are taken into account for positive and negative ions. They combine the influence of the existing electric field on the charges with the diffusion process due to charge distribution. Electric potential at the two electrodes is defined by the user and it is constant during the simulation, thus satisfying the Dirichlet boundary condition. After the user enters the rest of the initial conditions, the calculations of the current (I), charges (Q) and electric potential (U) begin using the FDTD algorithm.

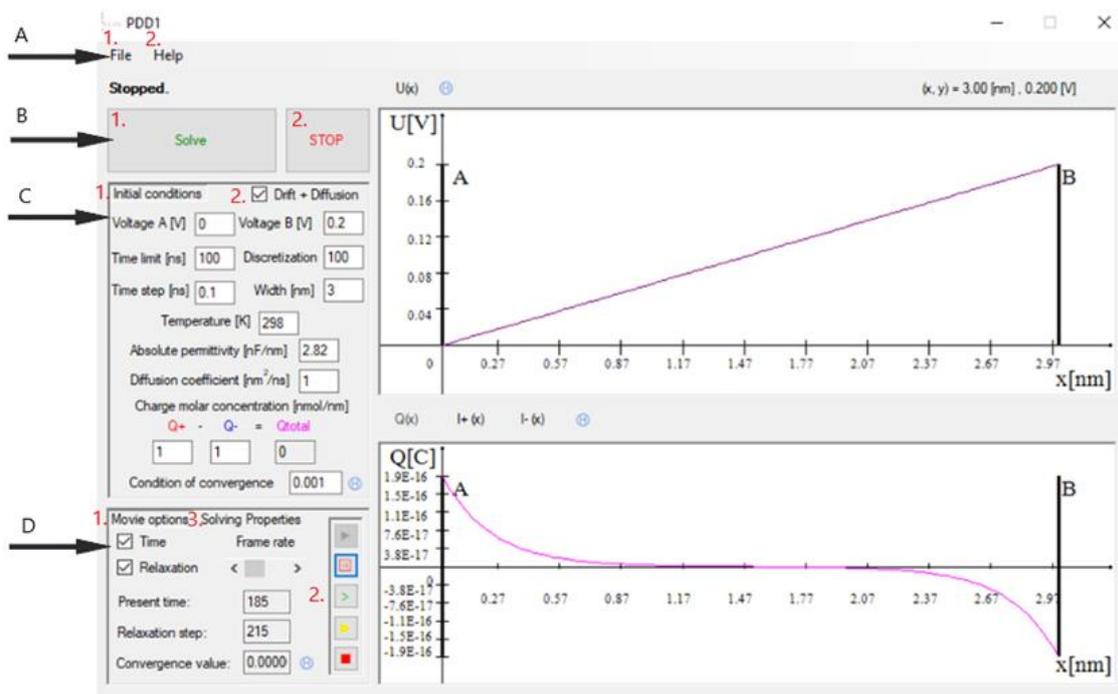


Fig. 1 PDD1 - Application layout

Section A – Menu strip

A.1. File

The list of possible I / O data operations is expanded in this menu selection.

- Open -> Displays a standard dialog box that prompts the user to open a file with initial conditions.
- Open Initial Q(x) -> as above, it allows to open a saved initial charge distribution.
- Save U(x) and Save Q(x)/I(x) -> Prompts the user to select a location for saving a file with data from charts. There are 3 file format selections:
 - .de3 - enables data reading as “1D Fields” in Quickwave
 - .csv – enables data reading as “Results” in Quickwave and in MS Excel
 - .txt - neutral file format

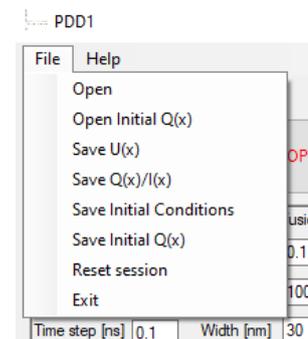


Fig. 2 Menu strip – File options

- Save Initial Conditions -> Prompts the user to select a location for saving a file with the current initial conditions.
 - A confirmation window will appear once the save has been successfully completed (Fig. 3)
- Save Initial Q(x) - as above, it allows to save calculated charge distribution for future loading.
- Reset session - Restores the initial application settings
- Exit – Shuts down applications and creates a file with the currently used settings.
 - Session file will also be created by turning off the application via the button etc.
 - These settings are loaded the next time the application is started. The file should be created in the same folder as the executable .exe file (If unsuccessful, check public documents)

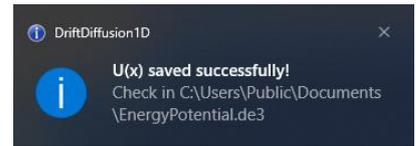


Fig. 3 Save confirmation window



Fig. 4 The session file contains all the start conditions needed to restore the last work

A.2. Help

Displays a window with information about editing files with initial conditions.

In Fig. 4 the numbers from the left are:

- Width [nm]
- Discretization
- Voltage on the left electrode A [V]
- Voltage on the right electrode B [V]
- Time step [ns]
- Time maximum [ns]
- Permittivity [F/m]
- Diffusion coefficient [m²/ns]
- Temperature [K]
- Positive charge molar concentration [mol/m]
- Negative charge molar concentration [mol/m]
- Convergence condition

Some objects have an icon . After pressing it, information about this object will appear.

Section B – Instant Solver

B. 1. Pressing a “Solve” button will calculate the electric potential $U(x)$, charge distribution $Q(x)$ and obtained currents $I(x)$. The condition for completing the calculations is to obtain convergence by relaxation (*Condition of convergence*) and the “Time limit” parameter. For more information check next page - Section C.

B. 2 If the calculations cannot reach convergence then the “STOP” button should be selected to force the algorithm to stop.

Section C – Initial Conditions

C. 1. Initial Conditions:

- *Voltage A [V]* – voltage sustained on the left electrode.
 - Values from -100 to 100 can be selected (default 0).
- *Voltage B [V]* – voltage sustained on the right electrode.
 - Values from -100 to 100 can be selected (default 0.1).
- *Time limit [ns]* - for drift and diffusion equations, a parameter that will stop the algorithm from solving further. In *Section D* the number of relaxation steps performed to the time steps taken will appear.
 - Values above 0 and more than *Time step* can be selected (default 10).
- *Discretization* - divides the space into a given number of sections
 - • Values from 2 to 501 can be selected (default 100)
- *Time step [ns]* – used to calculate the current (Δt)
 - • Values above 0 and below *Time limit* can be selected (default 0.1).
- *Width [nm]* - the distance between parallel electrodes
 - Values from 0 to 1000 can be selected (default 3).
- *Temperature [K]* - thermodynamic parameter
 - Values above 0 can be selected (default 293).
- *Absolute permittivity [F/m]* - electrical properties of the environment, depending on the filling material
 - Values from 0 to 1000 can be selected (default 2.82).
- *Diffusion coefficient [m²/ns]* – describes the diffusion processes derived from the *Einstein relations*
 - Values above 0 can be selected (default 1).
- *Charge molar concentration [mol/m³]* – molar concentration of positive Q+ and negative Q- ions
 - Values above 0 be selected (default 1).
- *Condition of convergence* – A comparison criterion between the values of the calculated electric potential U [V] to the given value. The smaller the convergence condition, the more accurate the final result should be.
 - Values from 0 to 1 can be selected (default 0.001).

C. 2. Drift + Diffusion check box

Enables on / off solving of drift and diffusion equations during algorithm operation.

When it is on, the currents for each time step are calculated. Based on the new current values, the electric charges are calculated. The relaxation technique is then used to obtain new electrical potentials. When off, only the Poisson equation is computed.

Section D – Movie options & Solving properties

D. 1. Pressing the tabs will change the view between “Movie options” and “Solving properties”.

- *Time and relaxation* checkboxes - by default, both are selected, which means that the charts will display both changes caused by the next time step and the relaxation step. They can be displayed separately.
- *Present time* – displays the current time value for the simulation
- *Relaxation step* - displays the current relaxation step for the simulation
- *Convergence Value* - Value that is compared to the convergence condition ω_{zb}

$$\left| \frac{U_{k+1,i,j} - U_{k,i,j}}{U_{k,i,j}} \right| \leq \omega_{zb} \quad , \quad (1)$$

U – energy potential [V], ω_{zb} – convergence value and notation; k –relaxation steps, i – width steps, j – time steps

- *Frame rate* – a scroll bar to speed up or slow down the browsing of the solution

D. 2. Movie control panel

The panel has an additional option to change its position by holding the left mouse button on it (Fig. 4) .

-  • “Play” button starts the simulation from the current time / relaxation step. The movie continues until the maximum time or convergence is reached.
-  • “Pause” button stops the simulations at the current time / relaxation step. To resume simulation press “Play” button or “Continue”.
-  • “Next step” button increases by 1 time / relaxation step.
-  • “Continue” button is only available when the time limit has been reached. It allows the simulation to continue.
-  • “Stop” button scrolls to the beginning of the entire simulation to its beginning. Enables the “Play” button and disables “Continue”.

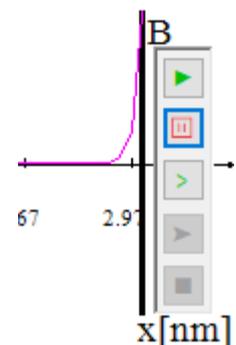


Fig. 4 Movie control Panel

D. 3 Solving properties

By selecting the "Solving properties" tab, two new options will be displayed modifying the calculation method:

- *Time to relaxation ratio* - It allows to control the number of time steps to relaxation steps performed. The condition of convergence ceases to have an effect on relaxation.
- *Relaxation factor* - enables the use of the sub-relaxation (value from 0 to 1) and over-relaxation (value from 1 to 2) methods to solve the Poisson equation.

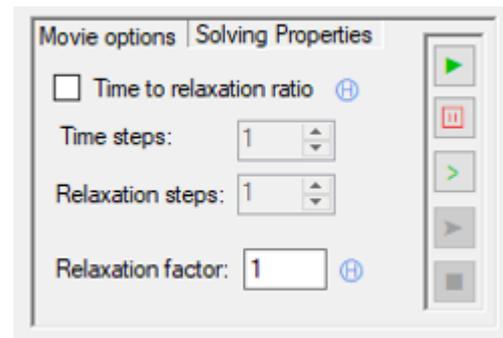


Fig. 5 Solving properties panel

$$U_{k+1,i,j} = (1 - r_c)U_{k,i,j} + r_c \left(\frac{U_{k,i+1,j} + U_{k,i-1,j}}{2} + \frac{Q^2 \Delta x^2}{2\epsilon_r \epsilon_0} \right) \quad (2)$$

where r_c – relaxation factor, Q – total charge [C/m³], Δx - spatial step, ϵ_r – absolute permittivity [F/m], ϵ_0 – vacuum permittivity [F/m],

2. Theory

Applying the charge conservation principle to an isolated algebraic system the sum of the charges of all bodies does not change. It is worth noting that the problem of electrostatics itself assumes that the charges in the considered systems are at rest or move very slowly. This makes it possible to ignore the effect of this phenomenon on the system. Influence between such charges is described by Coulomb's law. Charges placed in space create a property called a field electrical power, which acts on every other endowed body within it by exerting an electrical force on it. In the presence of the action of conservative forces, which are electrostatic forces, it makes sense to introduce the concept of potential energy. Assuming that the charges moves at a constant rate velocity, changes in kinetic energy may be neglected. The potential energy divided by the electric charge gives us the value of the electric potential. Changes of this electric potential along some space gives the value of the electric field. A semiconductor or electrolytes when connected to a voltage and current source can act as a path along which charges flow. If at the ends of such materials the potential difference is sustained, then a non-zero electric field is created in it inside (non-stationary state). The amount of charge flowing through such material to unit of time is called the amperage. The electric field propagating in such a medium affects the electrons causing their thermal motion to overlap a certain average drift velocity. The diffusion problem described by Fick's law, which allows for prediction of concentration change as a function of time. Diffusion coefficient and the electron mobility for a semiconductor or electrolyte are related by relation Einstein.

2.1 Physical model

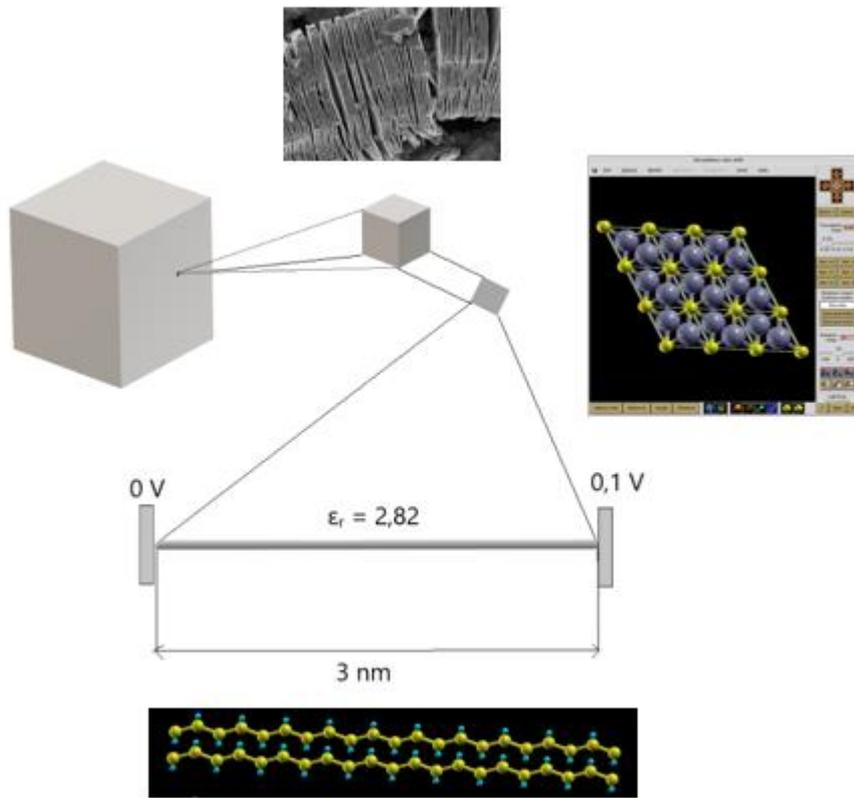


Fig. 6 Schematic drawing of the considered space of this 1D problem

A one-dimensional space system bounded by two electrodes to which a constant voltage can be applied is considered. The space between them is filled with electrolyte with a given permittivity, diffusion coefficients and temperature. There are positively or negatively charged ions in a specific molar concentration in the electrolyte.

The average size of the atom is equal to 1 Å (Angstrom). Atomic bonds are formed between them. In the case of electrolytes, these are the ionic bonds that hold these atoms a certain distance apart. One of the crystal structures in Figure 6 is a functionalized carbon chain. This is a good representation of the nanometer space, which is filled with only a few atoms with a countable number of electrons.

2.2 Solving scheme

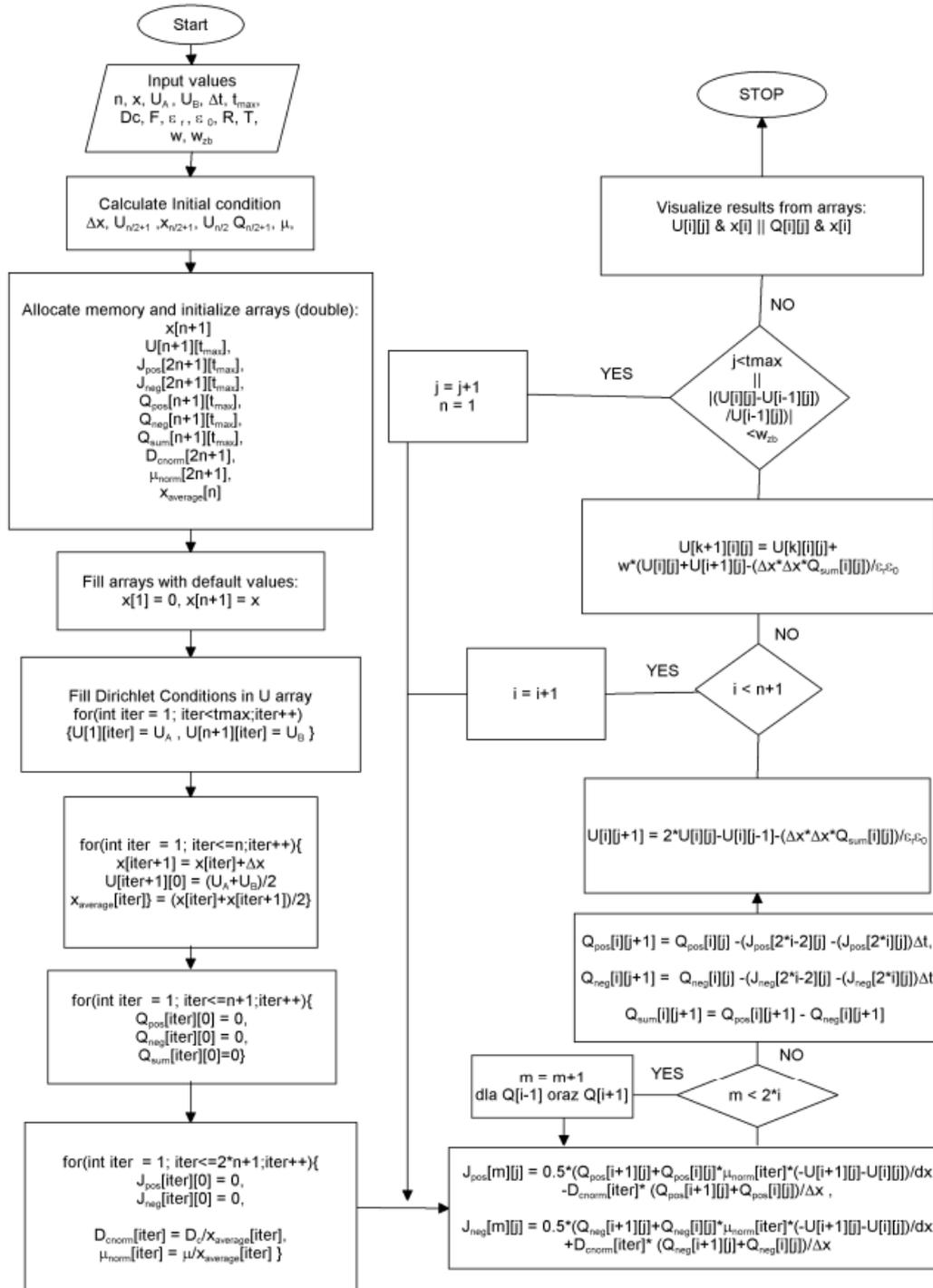


Fig. 7 Block diagram of solving the FDTD algorithm for conjugated Poisson and drift-diffusion equations

1. Begin Algorithm
2. User input values from file/textboxes and code initialized constants, where:

- n - discretization
- x - width [nm]
- U_A, U_B – voltage [V]
- T – temperature [K]
- D_c – diffusion coefficient [m^2/ns]
- ϵ_r – przenikalność elektryczna ośrodka [F/m]
- Δt – time step [ns]
- t_{max} – time maximum [ns]
- F – Faraday constant = 96485,3[C/mol]
- ϵ_0 – vacuum permittivity = $8,85 * 10^{-12}$ [F/m]
- R – gas constant = 8,314 [J/mol*K]
- w_{zb} – convergence condition

3. Calculate initial values:

- Δx – width value between charges q_i and q_{i+1} . Spatial points b and a where is the voltage applied U_A and U_B ;

$$\Delta x = \frac{b - a}{n} \quad (3)$$

- $U_{n/2}$ – average of the applied electric potential

$$U_{n/2} = \frac{U_B - U_A}{2} \quad (4)$$

- $Q_{n/2+1}$ – elementary charge located in the center of the system, calculated from Gauss's law.

$$\vec{D} = \epsilon_0 \epsilon_r \vec{E} \quad (5)$$

$$\nabla \cdot \vec{D} = \epsilon \nabla \cdot \vec{E} = \rho$$

- μ - mobility of charges [$m^2/V*s$]

$$\mu = \frac{FD_c}{k_B T} = \frac{nFD_c}{RT}, \quad k_B = \frac{R}{N_A} \quad (6)$$

4. Creating arrays and filling them with initial data

- For an array of X spaces, enter 0 as the first element and the last user-entered value for the space width.
- For the electric potential U table, enter the time-invariant U_A and U_B values according to the Dirichlet condition for the table boundary elements.
- For tables of electric potential U according to the formula (4), width X and means of width $X_{average}$ corresponding to the points for current enter according to the diagram.

$$x_{i+1} = x_i + \Delta x$$

(7)

$$\Delta x_{average} = \frac{\Delta x_i + \Delta x_{i+1}}{2}$$

- For tables of positive and negative charges and their sums, enter the initial values, for charges equal to 0, the Laplace solution will be obtained, if the charge inserted there will be consistent with the formulas (5), the Poisson solution will be obtained.
- For the current tables, assume 0 in the entire space. In the next step it will be calculated on the basis of the arrangement of charges in the space. With the same iteration of filling the tables, the normalized values of the diffusion coefficient should be calculated D_{cnorm} and μ_{norm} :

$$\mu_{norm_i} = \frac{\mu_i}{\Delta x_{average_i}}$$

(8)

$$D_{cnorm_i} = \frac{D_{c_i}}{\Delta x_{average_i}}$$

5. Algorithm

5.1 First, the values of currents at points between the charges q_i for the compatible iteration J_i and the preceding iteration J_{i-1} should be calculated. Considering the above equations:

$$J_{+i,j} = 0.5 \cdot (Q_{+i+1,j} + Q_{+i,j}) \cdot \mu_{norm_i} \cdot \left(-\frac{U_{i+1,j} - U_{i,j}}{\Delta x} \right) - D_{c_{norm_i}} \left(\frac{Q_{+i+1,j} + Q_{+i,j}}{\Delta x} \right)$$

$$J_{-i,j} = 0.5 \cdot (Q_{-i+1,j} + Q_{-i,j}) \cdot \mu_{norm_i} \cdot \left(-\frac{U_{i+1,j} - U_{i,j}}{\Delta x} \right) + D_{c_{norm_i}} \left(\frac{Q_{-i+1,j} + Q_{-i,j}}{\Delta x} \right)$$
(9)

5.2 Having information about the currents occurring between the charge q_i at point x_i , it is possible to calculate the change in the value of the charge through the sum of the opposite charges:

$$Q_{+i,j+1} = Q_{+i,j} - (J_{+i,j} - J_{+i-1,j})\Delta t$$

$$Q_{-i,j+1} = Q_{-i,j} - (J_{-i,j} - J_{-i-1,j})\Delta t$$

$$Q_{sum_{i,j+1}} = Q_{+i,j+1} - Q_{-i,j+1}$$
(10)

5.3 Calculations from 5.1 and 5.2 shall be performed until the tables i and j are filled with results. Count while $i \leq n, j < t_{max}$.

5.4 After filling the tables of q_i charges, calculate the new values of the electric potentials U_i at points x_i by solving the Poisson equation. The k notation was introduced to define the degree of system relaxation.

$$U_{k+1,i,j} = 0.5 \cdot (U_{k,i+1,j} - U_{k,i-1,j}) - \frac{\Delta x^2 Q_{sum_{i,j}}}{\epsilon_0 \epsilon_r}$$
(11)

5.5 Check whether the calculations are converged through the equation (1).

5.6 If the condition is not met, go back to point 5.1 until it the condition of convergence is obtained. Then stop algorithm.

3. Examples

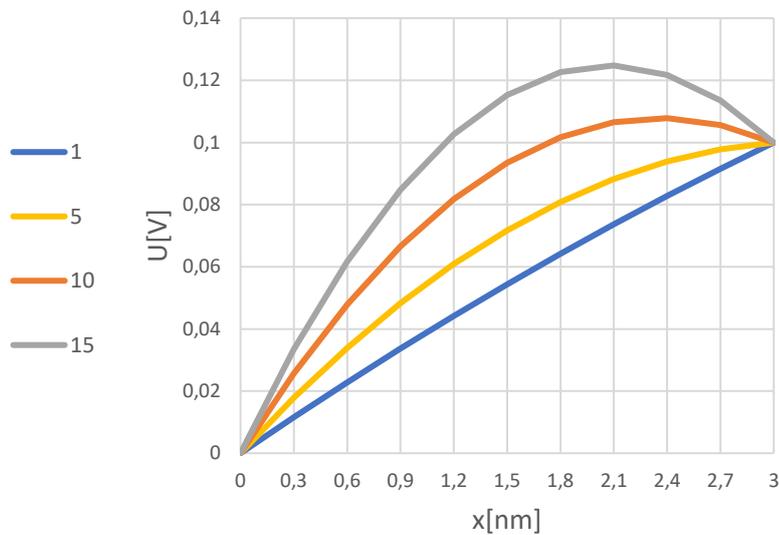


Fig. 8 Electric potential (U) distribution limited by electrodes of 0.1 V potential difference with positive charges of molar concentration from 1 – 15 mol/m³

To receive these results, uncheck the checkbox “Drift + Diffusion” and select the following initial conditions:

- Width [nm] = 3
- Discretization = 10
- Voltage on the left electrode A [V] = 0
- Voltage on the right electrode B [V] = 0.1
- Time step [ns] = ----
- Time maximum [ns] = -----
- Permittivity [F/m] = 2.82
- Diffusion coefficient [m²/ns] = 1
- Temperature [K] = 298
- Positive charge molar concentration [mol/nm] = 1/5/10/15
- Negative charge molar concentration [mol/nm] = 0
- Convergence condition = 0.001

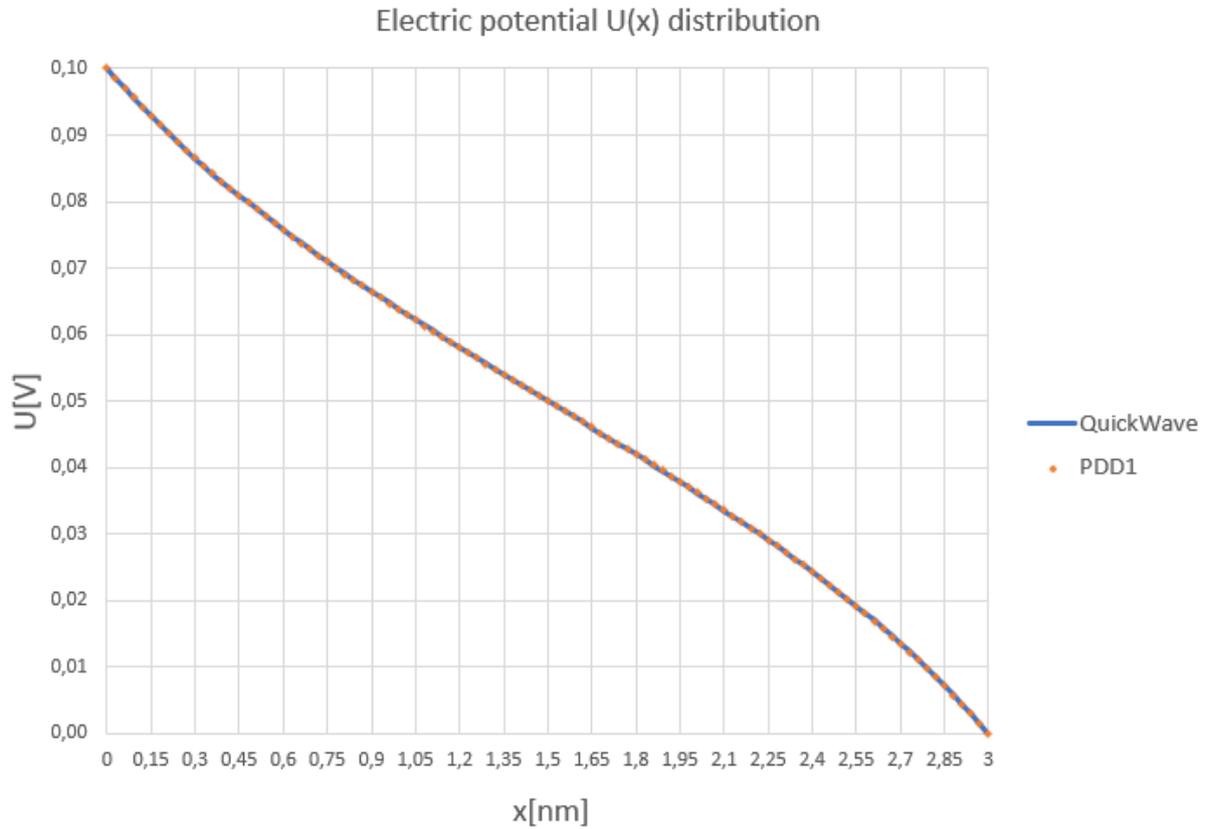


Fig 3. Electric potential $U(x)$ distribution in 3 nm space limited by electrodes of 0.1 V and 0 V potential with initial uniform concentration of positive and negative ions of 1 mol/m^3

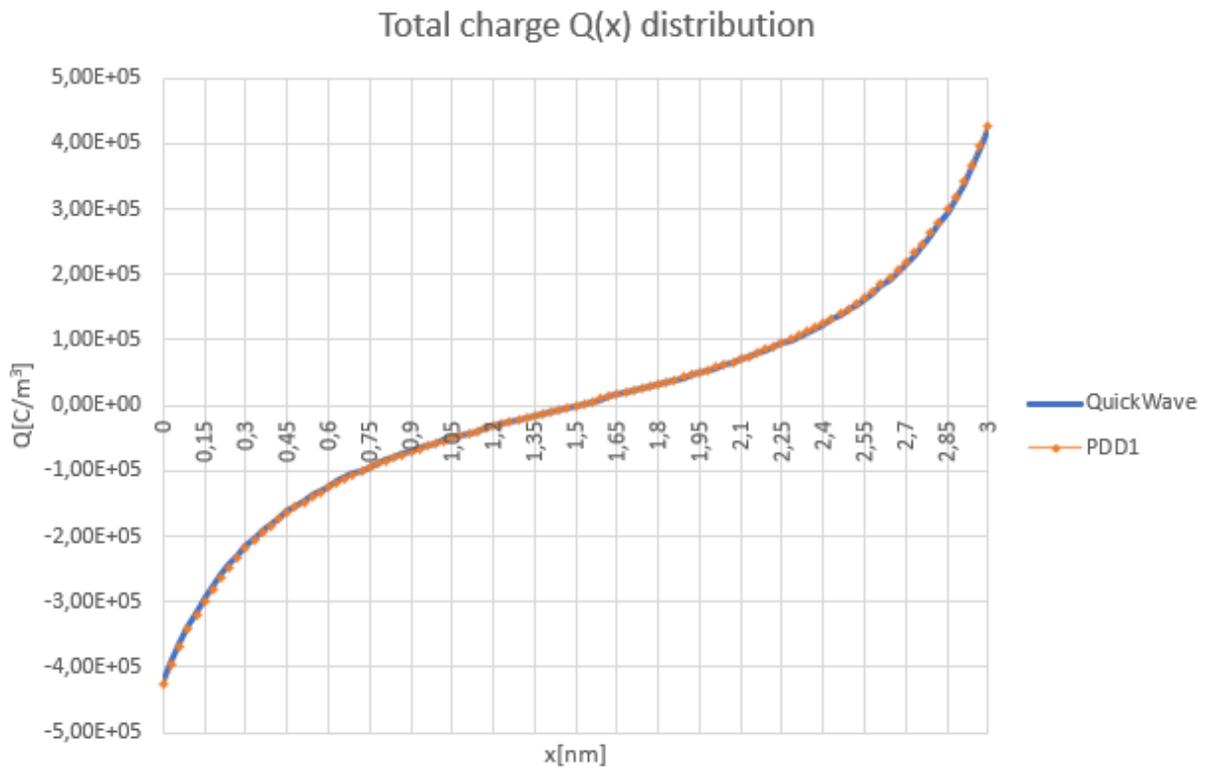


Fig 4. Total charge $Q(x)$ distribution in 3 nm space limited by electrodes of 0 V and 0.1 V potential with initial uniform concentration of positive and negative ions of 1 mol/m^3 .

To receive these results, check the checkbox “Drift + Diffusion” and select the following initial conditions:

- Width [nm] = 3
- Discretization = 100
- Voltage on the left electrode A [V] = 0.1
- Voltage on the right electrode B [V] = 0
- Time step [ns] = 0.1
- Time maximum [ns] = 1000
- Permittivity [F/m] = 2.82
- Diffusion coefficient [m²/ns] = 1
- Temperature [K] = 298
- Positive charge molar concentration [mol/nm] = 1
- Negative charge molar concentration [mol/nm] = 1
- Convergence condition = 0.001

Use “Play”  button.

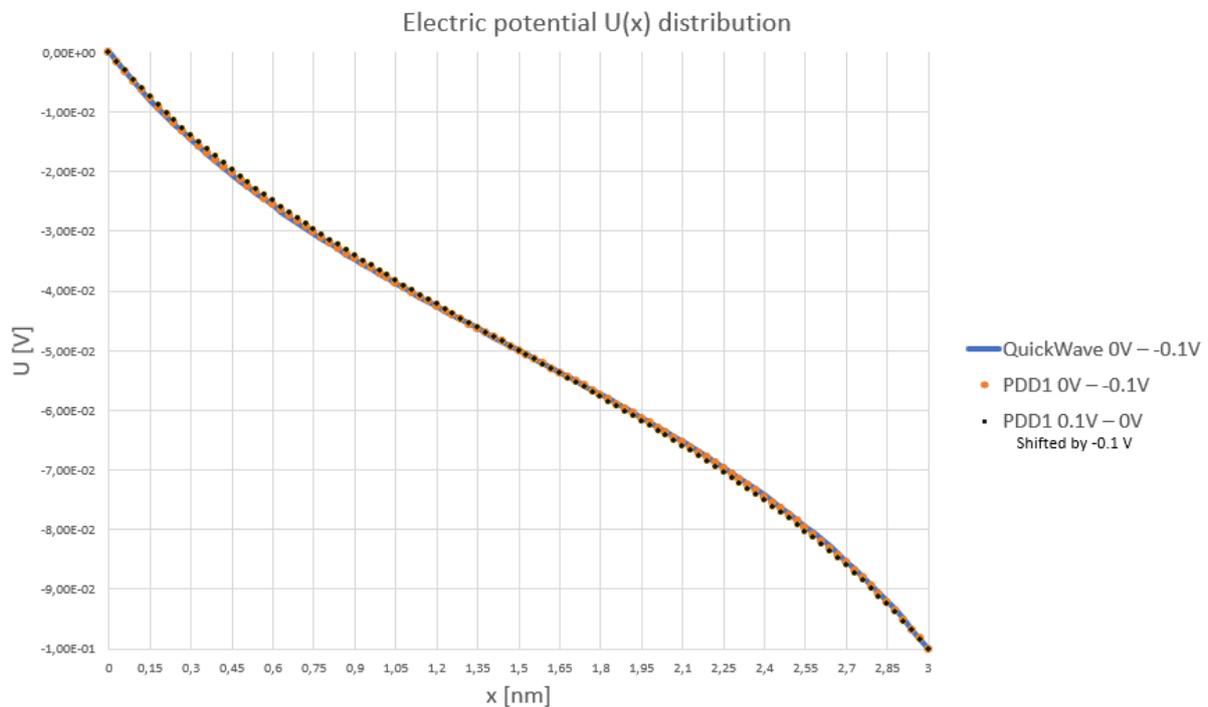


Fig 5. Electric potential $U(x)$ distribution in 3 nm space limited by electrodes of 0 V and -0.1 V potential and shifted by -0.1V electric potential $U(x)$ distribution limited by electrodes of 0.1V – 0 V.

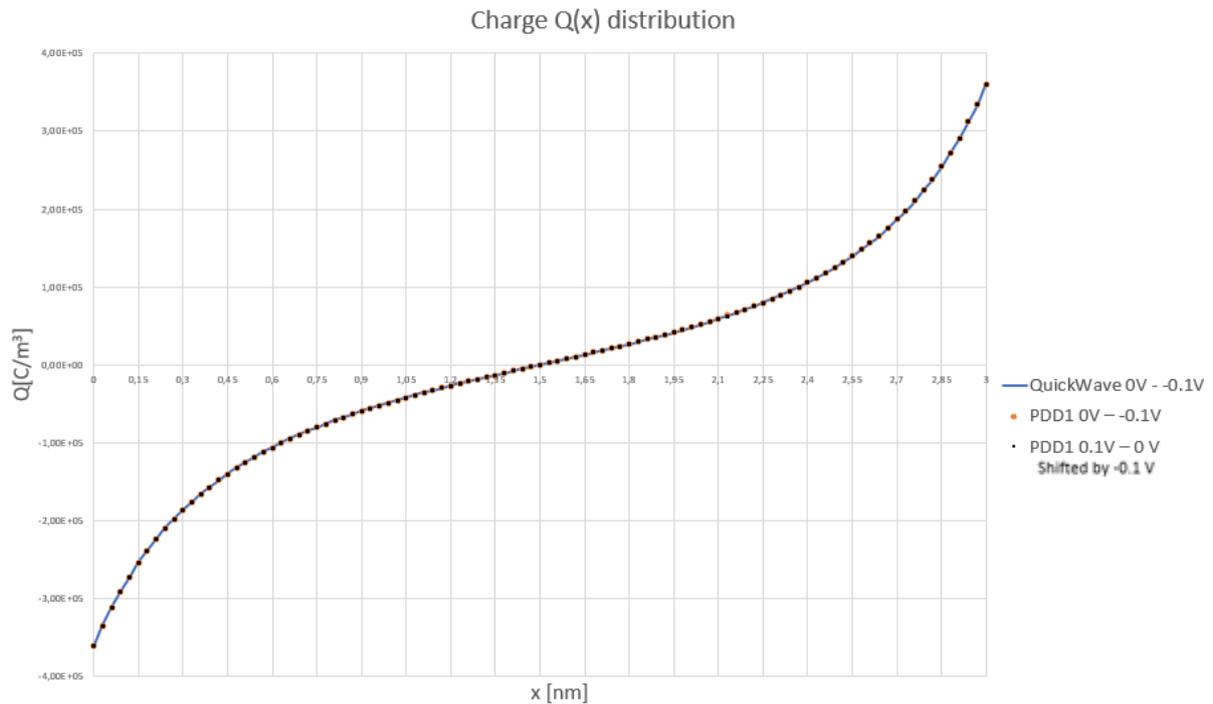


Fig 6. Charge $Q(x)$ distribution in 3 nm space limited by electrodes of 0 V and -0.1 V potential and shifted by -0.1V charge $Q(x)$ distribution limited by electrodes of 0.1V – 0 V.

To receive these results, check the checkbox “Drift + Diffusion” and select the following initial conditions:

- Width [nm] = 3
- Discretization = 100
- Voltage on the left electrode A [V] = 0
- Voltage on the right electrode B [V] = -0.1
- Time step [ns] = 0.1
- Time maximum [ns] = 1000
- Permittivity [F/m] = 2.82
- Diffusion coefficient [m^2/ns] = 1
- Temperature [K] = 298
- Positive charge molar concentration [mol/nm] = 1
- Negative charge molar concentration [mol/nm] = 1
- Convergence condition = 0.001

Use “Play”  button.

Electric potential $U(x)$ distribution

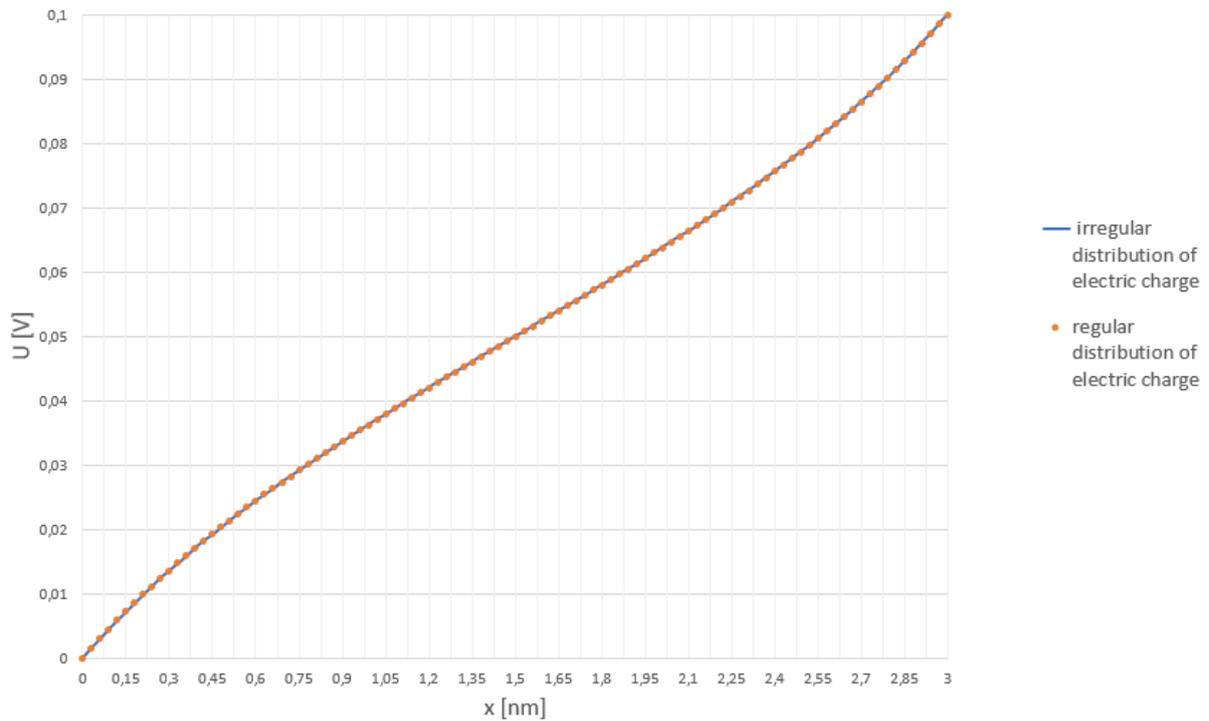


Fig 7. Electric potential $U(x)$ distribution in 3 nm space limited by electrodes of 0 V and 0.1 V potential with an initial regular/irregular charge $Q(x)$ distribution

Charge $Q(x)$ distribution

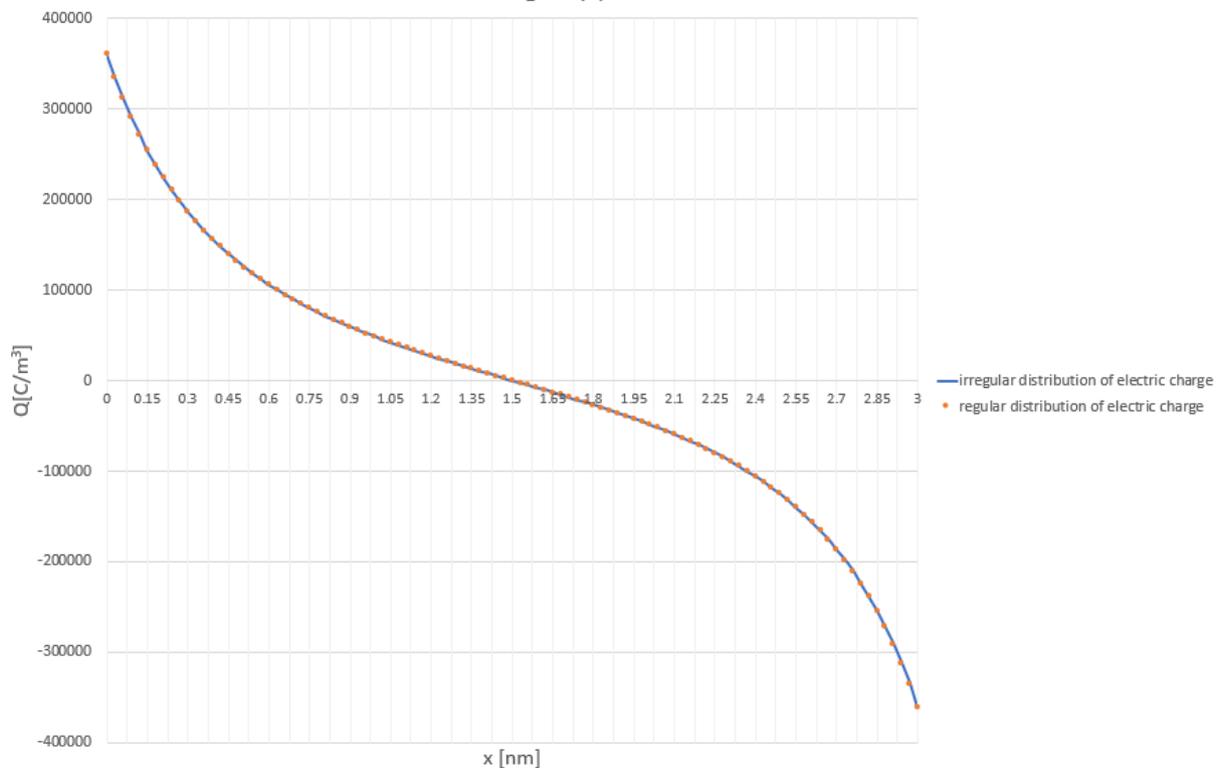


Fig 7. Charge $Q(x)$ distribution in 3 nm space limited by electrodes of 0 V and 0.1 V potential with an initial regular/irregular charge $Q(x)$ distribution

To receive these results, first some distribution of the charge needs to be saved (check 1. A Menu Strip – File), then restart algorithm by press Stop  button. After that load the saved electric charge distribution from file, uncheck “Drift + Diffusion” checkbox and run the algorithm via the play  button. Use initials from below:

- Width [nm] = 3
- Discretization = 100
- Voltage on the left electrode A [V] = 0
- Voltage on the right electrode B [V] = 0.1
- Time step [ns] = 0.1
- Time maximum [ns] = 1000
- Permittivity [F/m] = 2.82
- Diffusion coefficient [m²/ns] = 1
- Temperature [K] = 298
- Positive charge molar concentration [mol/nm] = 1
- Negative charge molar concentration [mol/nm] = 1
- Convergence condition = 0.001

Solve with “Play” button.

3. System requirements

Minimum system requirements:

- 1 GHz x86/x86-64 (32-bit/64-bit) or higher processor
- 1 GB (32-bit) / 2 GB (64-bit) RAM
- Graphics: DirectX 9.0, WDDM 1.0 or better
- 128 MB VRAM
- 400kB hard disk space
- Mouse or other pointing device
- Microsoft Windows 7 x64 operating system
- .NET Framework 3.5 (**Windows 7 (all editions)** and above includes the **.NET Framework 3.5** as an Operating System component.)