Manual and Theory – Electric Double Layer solver

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.
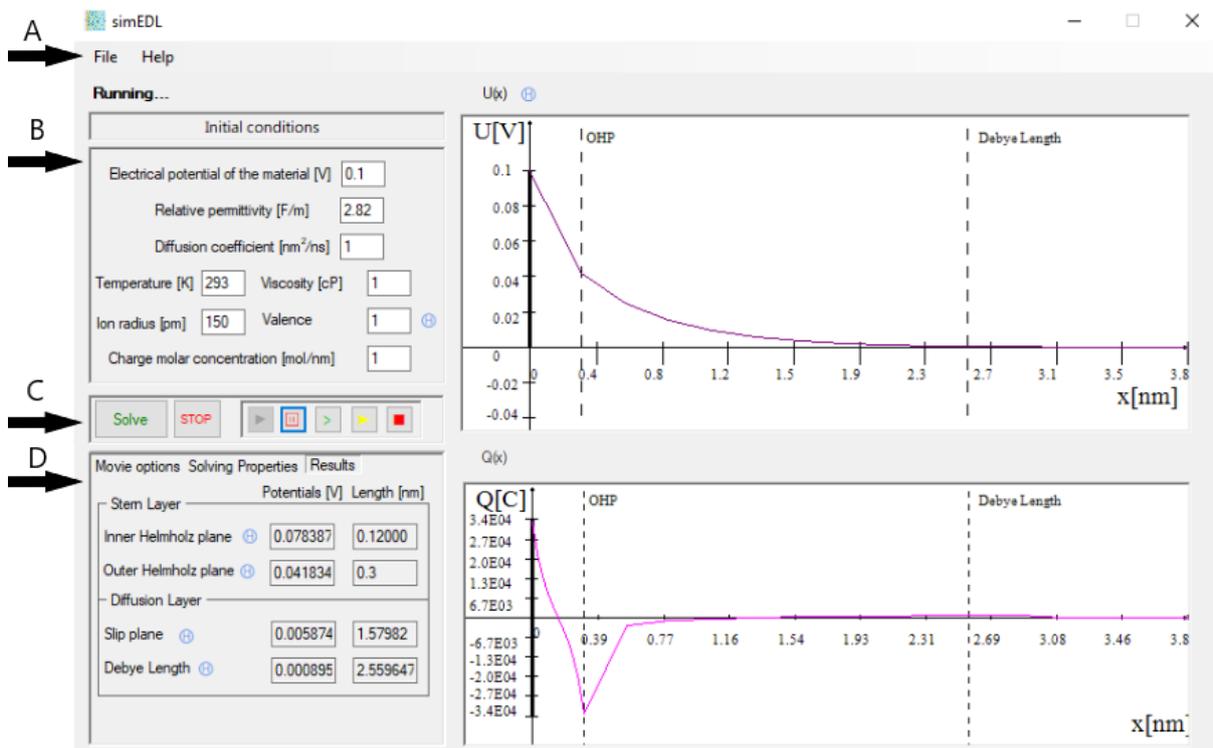

Fig. 1 simuEDL - Application layout

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:
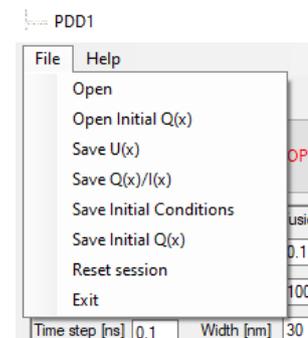   - .de3 - enables data reading as "1D Fields" in Quickwave

Fig. 2 Menu strip – File options

- o .csv – enables data reading as "Results" in Quickwave and in MS Excel
  - o .txt - neutral file format
- Save Initial Conditions -> Prompts the user to select a location for saving a file with the current initial conditions.
  - o 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.

Fig. 3 Save confirmation window

- Reset session - Restores the initial application settings
- Exit – Shuts down applications and creates a file with the currently used settings.
  - o Session file will also be created by turning off the application via the button etc.
  - o 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)
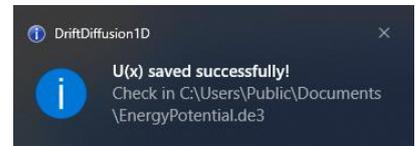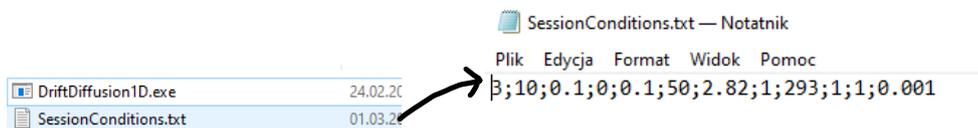

Fig. 4 The session file contains all the start conditions needed to restore the last work

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 – Initial Conditions

C. 1. Initial Conditions:

- *Electric potential of the material [V]* – voltage sustained on the electrode.
  - o Values from -100 to 100 can be selected (default 0).

- *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 [m^2/ns] –* describes the diffusion processes derived from the *Einstein relations*
  - Values above 0 can be selected (default 1).

- *Charge molar concentration [mol/m^3] –* molar concentration of positive Q+ and negative Q- ions
  - Values above 0 be selected (default 1).

- Valence – of an element is the measure of its combining capacity with other atoms when it forms chemical compounds or molecules (default 1).

- Viscosity – is a measure of its resistance to deformation at a given rate (default 1).

Section C – 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.

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".

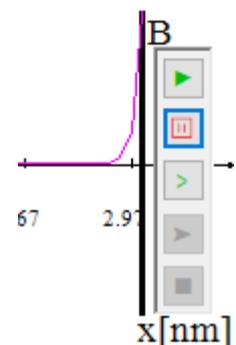- "Next step" button increases by 1 time / relaxation step.

Fig. 4 Movie control Panel

• "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".

Section D – Movie options & Solving properties & Results

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}

$$\left| \frac{U_{k+1,i,j} - U_{k,i,j}}{U_{k,i,j}} \right| \leqslant w_{zb} \qquad , \qquad (1)$$

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 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.
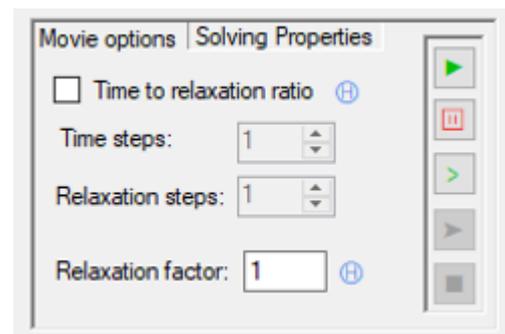

Fig. 5 Solving properties panel

$$U_{k+1,i,j} = (1 - r_c)U_{k,i,j} + r_c\left(\frac{U_{k,i+1,j} + U_{k,i-1,j}}{2} + \frac{Q^2\Delta x^2}{2\varepsilon_r\varepsilon_0}\right) \qquad (2)$$
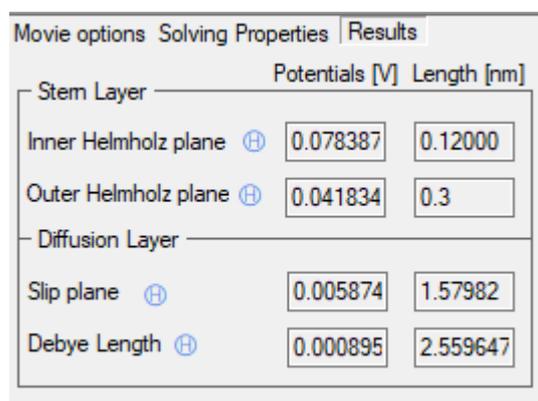
,

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],

- *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)

- *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).

D. 3 Results

The results calculated for the given initial values taking into account the distribution of electric potential and total charge distribution:

Fig. 6 Results properties panel

- Inner Helmholz plane is introduced as the plane formed by the centres of specifically adsorbed ions. In results is showed its position and value of calculated potential

- Outer Helmholtz plane passes through the centres of solvated ions at the distance of their closest approach to the electrode. Diffuse Layer is the region beyond the OHP. In results is showed its position and value of calculated potential

- Slip plane is the interface which separates mobile fluid form fluid that remains attached to the surface. In results is showed its position and value of calculated potential.

- Debye Length separate the zone where the electrode interacts with the electrolyte.

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

Performance of batteries is strongly influenced by the formation of an interfacial layer between the electrode and electrolyte, called solid electrolyte interface (SEI). A complete description of the physical-chemical phenomena occurring at SEI is very complex and its rigorous modelling would require an enormous amount of computing power. For the sake of simplification, various approaches are used, known more generally as the electric double layer (EDL). The most commonly used physical EDL models[14-16] are shown in the figure 7 below.
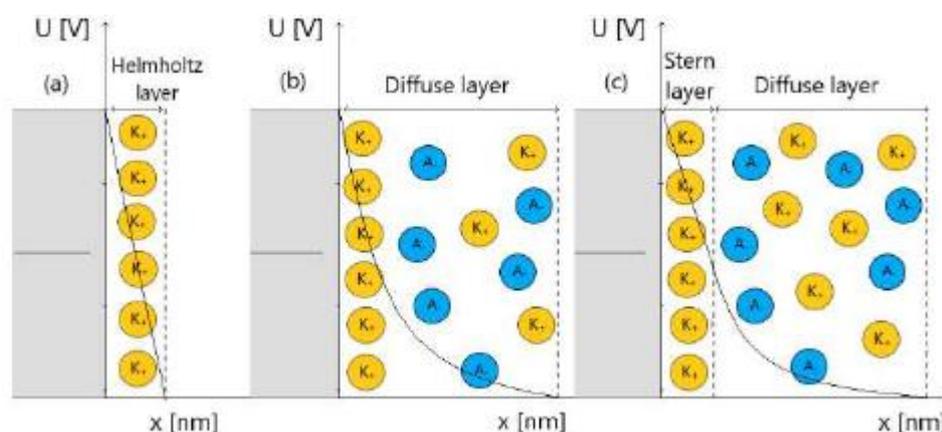

Fig. 7 Models characterizing the Electric Double Layer phenomenon

The Helmholtz (a) model assumes that in SEI an ionic layer is formed on the solid, which does not cause diffusion of the remaining ions in the electrolyte. The width of the formed layer of ions is equal to their diameter [17]. It is a small area compared to the width of the electric double layer. For this reason, its width can be omitted. It was also noticed that the ionic concentration of the electrolyte changes with the distance from the electrode satisfying the Maxwell‑ Boltzmann statistic. These

assumptions are included in the Gouy‑Chapman (b) model. The above two models have been combined and enhanced with additional features of this phenomenon. The next model (c) takes into account the adsorption of ions on the electrode surface, which causes the counter-ions to attract. This region is called the Stern layer. Along with the distance, the diffusion layer extends, in which the Coulomb interactions are taken into account. The newly developed software is based on this particular model. A half-cell system is considered in which the physical parameters of the electrolyte are known and the electric potential at the electrode is defined. It should be assumed that the Stern layer immediately appears next to the electrode, which is flat, uniformly charged and the ions adsorbed to it do not repel each other. In the diffusion part, the ions are treated as points and satisfy the Maxwell-Boltzmann equations. There is a continuous distribution of the dielectric constant er and temperature T along the entire system. Values such as electron mobility μ and diffusion coefficients Dc are discretized in relation to a given space. The electric potential U changes according to the molar concentration $n0$ change due to the movement of the ions. This directly affects to the charge density ρ .
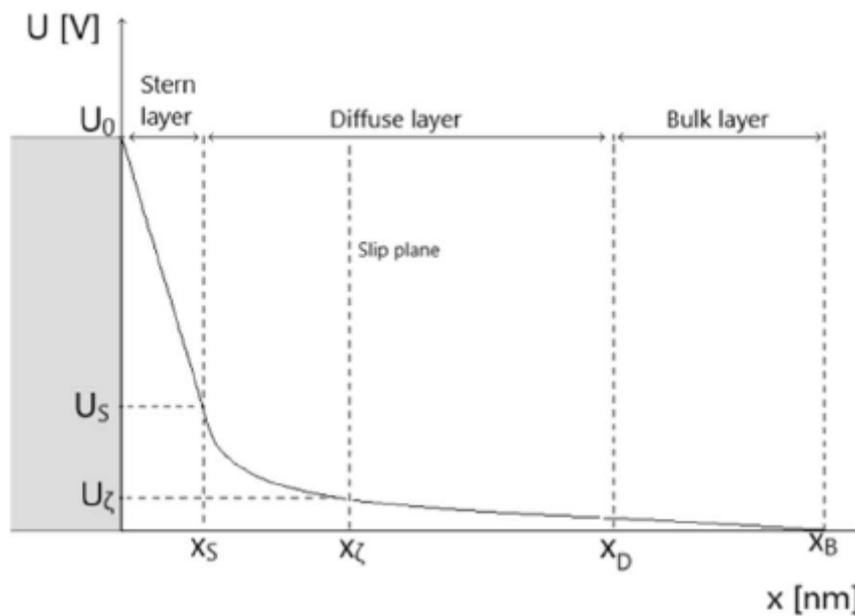

Fig. 8 Electric potential distribution in electric double layer EDL (Stern model)

For more information check: ”Open Platform tools to modelling electrochemical phenomena in solid electrolyte interphase” available on QWED website->Projects->NanoBat.
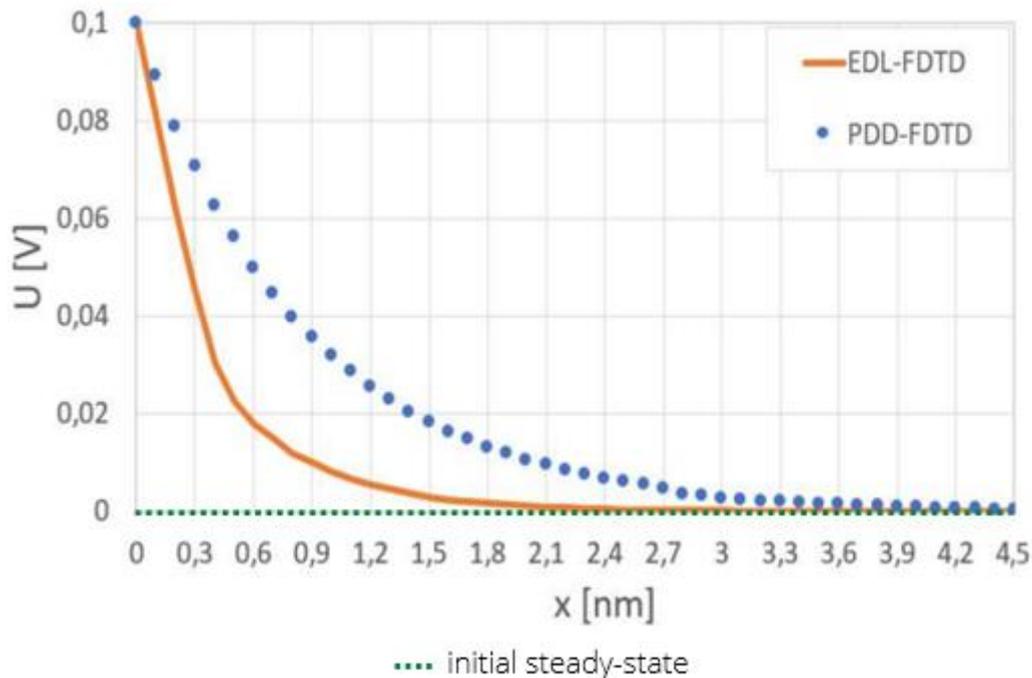
3. Examples

Fig. 9 Comparison of results form EDL – FDTD and PDD -FDTD (previous application available on

website)

The potential difference of the electrode with respect to the ground potential is equal to 0.1 V. There is a constant temperature T of 293 K and an relative permittivity er of 2.82 F/m along the entire system. The movement of ions is described by a diffusion coefficient Dc=10-9 m2/s. The mesh of 100 FDTD cells is set up and the time step is 0.1 ns. The simulation ends when the convergence condition for the equilibrium state of the system is satisfied. We now extend the simulation of the bulk electrolyte model to the model including interfacial effects. At the boundary of the system, there is an electrode/metal with a given potential of 0.1 V. The surrounding electrolyte is much larger than this electrode, so that its depth can be neglected. To implement the EDL model, it is necessary to define new initial conditions. An additional parameter of the electrolyte is the radius of its ions equal to 152 picometers and their valence equal to 1. Based on these values, the Stern potential US and the Debye length x_D are obtained analytically. With these boundary conditions, the FDTD algorithm is run. Concurrently solved equations for Stern and diffusion layers until currents cease in the system. In the Stern layer, the interpolated electric potential is linear and decreases strongly. Just near the adsorbed ions at the boundary of the Stern layer, the potential is equal to **42.7 mV**. From this point onwards the electric potential decreases until it reaches a value close to zero at a *Debye Length* point equal **2.58 nm**.

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

- Discretization = 100
- Electrical potential of the material [V] = 0.1 V
- Ion Radius [pm] – 152 pm
- Valence = 1
- Viscosity = 1
- Time step *[ns] = 0.1 ns*
- Time maximum *[ns] = 100 ns*
- Permittivity *[F/m] = 2.82 F/m*
- Diffusion coefficient *[m^2/ns] = 1 m^2/ns*
- Temperature *[K] = 298 K*
- Charge molar concentration *[mol/nm] = 1 mol/nm*
- Convergence condition = 0.001

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.)