Electrochemistry: Advanced Modeling and Simulations, AGH, Kraków.
Notes for the Project, part 1 (description of NPP model and numerical aspects)
Department of Solid State Chemistry

Introduction

The goal of this project is to understand physicochemical model and develop the numerical simulations of electrodiffusion problems in one dimensional geometry. This model can be used in particular to predict the membrane potential and consequently be applied to more fundamental modeling of ion selective membrane electrodes (ISEs) than is offered by classical steady state, semi-empirical descriptions based on the Nikolskii-Eisenman equation. Such membranes are basic part of chemical sensors use in ***analytical chemistry***. After learning how to simulate concentration profiles and electric potential time evolution students will proceed to the second part of the project which is to present the impedance spectra derived from basic electrodiffusion equations. In this model, electrodiffusion (diffusion and migration under the electrical field) is governed by the Nernst-Planck flux formula (*constitutive equation*), and the electric interaction of species is described by the Poisson equation.[1]

This is the first part of the assignment which contains a theoretical description of the mathematical model with short introduction to the C++ implementation issues. The second part contains details on what students are required to carry out.

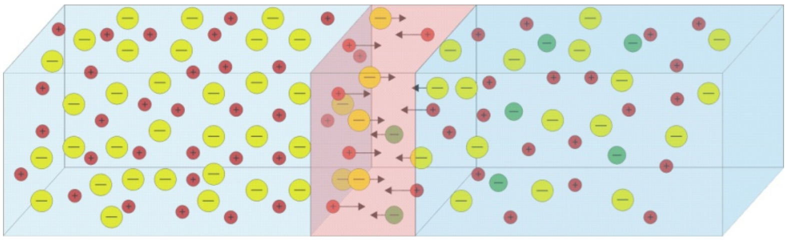

Fig. 1. A three-dimensional view of a flat shaped membrane surrounded by electroneutral electrolyte solutions. The membrane itself is not electroneutral and due to the charge separation a potential difference is developed across it.

Electro-diffusion in a membrane

A schematic view of the membrane with diffusing species is presented in Fig. 1. The membrane is of course a three-dimensional object but if we can assume its homogeneity in y and z axis a description may be reduced to one-dimensional model in which the membrane is represented simply as an interval $[0,\, d]$ on the real axis $\mathbb{R}$. This is illustrated in Fig. 3.

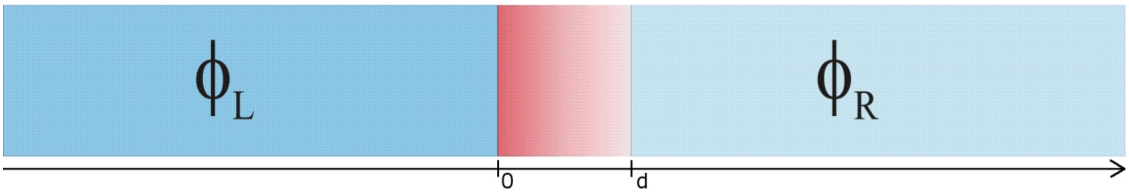

Fig. 2. One-dimensional representation of the membrane.

The ion flux in space is described the Nernst-Planck formula

[1] In fact the basic law which will be used here is Gauss law, $\operatorname{div} E = \frac{1}{\varepsilon\varepsilon_0}\rho$, not the Poisson equation $\Delta\varphi = -\frac{1}{\varepsilon\varepsilon_0}\rho$, where φ is the electric potential. Even more, the Gauss law will not be used in the stated form, but instead we will make use of the so called displacement current equation which can be derived from Gauss law.

$$J_i(x,t) = -D_i \frac{\partial c_i}{\partial x}(x,t) + D_i \frac{F}{RT} z_i c_i(x,t) E(x,t), \quad (i = 1,\dots,r) \tag{0.1}$$

where:

r – the number of components (species),
c_i – the concentration of the *i*-th species,
D_i – the diffusion coefficient of the *i*-th species,
z_i – the charge number (valence) of the *i*-th species (for non-ionic component $z_i = 0$),
E – the electric field,
R, F, T – the gas constant, Faraday constant, and absolute temperature.

The law of mass conservation (also referred to as the continuity equation) in a differential form reads as

$$\frac{\partial c_i}{\partial t} = -\frac{\partial J_i}{\partial x}, \quad (i = 1,\dots,r). \tag{0.2}$$

This is however not enough as we have $r+1$ unknown functions $c_1,\dots,c_r,E$ and the mass conservation (for each component) in (0.2) provides r equations. To relate electric field with concentration we can use the Gauss law which in one dimension has the form

$$\frac{\partial E}{\partial x} = \frac{1}{\varepsilon_r \varepsilon_0} \rho, \tag{0.3}$$

where ε_0 – the permittivity of free space (electric constant), ε_r – the relative permittivity of the material, ρ – the space charge density. If the concentrations are expressed in [mol/m^3], then the charge density is

$$\rho(x,t) = F \sum_{i=1}^{r} z_i c_i(x,t). \tag{0.4}$$

Combining (0.3) and (0.4) gives

$$\frac{\partial E}{\partial x}(x,t) = \frac{F}{\varepsilon} \sum_{i=1}^{r} z_i c_i(x,t), \tag{0.5}$$

where for short we used $\varepsilon = \varepsilon_r \varepsilon_0$. But we will not use it in this form. If we are to base the numerics on the method of line it is more convenient to have expression for $\frac{\partial E}{\partial t}$ rather than $\frac{\partial E}{\partial x}$. From (0.5) and (0.2) we infer the following

$$\frac{\partial}{\partial t}\frac{\partial E}{\partial x} = \frac{F}{\varepsilon}\frac{\partial}{\partial t}\sum_{i=1}^{r} z_i c_i = \frac{F}{\varepsilon}\sum_{i=1}^{r} z_i \frac{\partial c_i}{\partial t} = -\frac{F}{\varepsilon}\sum_{i=1}^{r} z_i \frac{\partial J_i}{\partial x},$$

and making use of $\frac{\partial}{\partial t}\frac{\partial E}{\partial x} = \frac{\partial^2 E}{\partial t \partial x} = \frac{\partial}{\partial x}\frac{\partial E}{\partial t}$ (this symmetry is true provided that $E = E(x,t)$ is smooth enough) the above equality can be rearranged as

$$\frac{\partial}{\partial x}\left(\frac{\partial E}{\partial t} + \frac{F}{\varepsilon}\sum_{i=1}^{r} z_i J_i\right) = 0 \qquad \text{for } x \in [0,\, d].$$

This equation in turn says that the expression in the bracket does not depend on the space variable $x \in [0,\, t]$. In other words

$$\frac{\partial E}{\partial t} + \frac{F}{\varepsilon}\sum_{i=1}^{r} z_i J_i = \frac{1}{\varepsilon} I(t), \tag{0.6}$$

or

$$\frac{\partial E}{\partial t} = \frac{1}{\varepsilon} I(t) - \frac{F}{\varepsilon}\sum_{i=1}^{r} z_i J_i. \tag{0.7}$$

In this form of Gauss equation called the displacement current equation the term $I(t)$ is interpreted as the total current density flowing through the membrane.

To summarize we have the following set of partial differential equations (PDEs) describing the electro-migration movement of species in the membrane

$$\begin{cases} \dfrac{\partial c_i}{\partial t} = -\dfrac{\partial J_i}{\partial x}, \quad (i = 1, \dots, r), \\ \dfrac{\partial E}{\partial t} = \dfrac{1}{\varepsilon} I(t) - \dfrac{F}{\varepsilon}\displaystyle\sum_{i=1}^{r} z_i J_i, \end{cases} \tag{0.8}$$

where $J_i = -D_i\left(\dfrac{\partial c_i}{\partial x} - \dfrac{F}{RT} z_i c_i E\right)$.

The NPP system (0.8) must be completed with the boundary conditions. The simplest ones would be the Dirichlet boundary conditions at both end of the membrane

$$\begin{cases} c_i(0,t) = c_{i,L}, \;\; c_i(d,t) = c_{i,L}, \\ i = 1, \dots, r, \end{cases} \tag{0.9}$$

where $c_{i,L}$ and $c_{i,R}$ denote the concentrations in the left and right bathing solutions respectively. In particular the conditions (0.9) mean that there is no jump of concentrations at the interface. More general conditions that we are going to adopt here are the so called Chang-Jaffé boundary conditions which prescribe the fluxes at the membrane boundaries. They relate the interfacial fluxes to heterogeneous rate constants and concentrations at the surfaces inside and outside the interfaces as following

$$\begin{cases} J_i(0,t) = k_{i,Lf} c_{i,L} - k_{i,Lb} c_i(0,t), \\ J_i(d,t) = -k_{i,Rf} c_{i,R} + k_{i,Rb} c_i(d,t), \\ i = 1,\dots,r, \end{cases} \tag{0.10}$$

where $k_{i,Lf}, k_{i,Lb}, k_{i,Rf}, k_{i,Rb}$ are forward and backward heterogeneous rate constants at the left and right interface for *i*-th species. Let us note that if, for example $k_{i,Lb} = k_{i,Lf} = 0,$ then the left interface is impermeable to the component *i*-th (it is blocked). On the outer hand vary large $k_{i,Lf}$ means that the interface dos not hinder passage of the component form the bulk into the membrane. If both are very large, $k_{i,Lf} = k_{i,Lb} \to \infty,$ passage in both direction at that boundary is free. In practice "very large" means here values of the order $100\ [m/s]$.

The final information needed to describe completely this membrane system in time evolution way are the initial conditions. They prescribe the values of concentrations and electric field in the membrane at time $t = 0.$ Thus we have

$$\begin{cases} c_i(x,0) = c_{0,i}(x), \qquad (i = 1,\dots,r), \\ E(x,0) = E_0(x), \end{cases} \tag{0.11}$$

where functions $c_{0,i}(x),\ E_0(x)$ for $x \in [0,\ d]$ are given.

The use of the initial conditions differ a bit depending on whether we perform the simulations for standard potentiometric or for electrochemical impedance spectra (EIS) applications.

For the potentiometric response modeling the usual starting point for simulations are initial conditions that satisfy electroneutrality thus

$$\begin{cases} c_i(x,0) = c_{0,i}(x), \qquad (i = 1,\dots,r), \\ E(x,0) = 0, \end{cases} \tag{0.12}$$

and initial concentrations hold $\sum_{i=1}^{r} z_i c_{0,i}(x) = 0.$ In most cases here the functions $c_{0,i}(x)$ are piece-wise constant.

For impedance spectra (EIS) simulations we have to compute the potential response of the steady state system which was slightly perturbed. To obtain the steady state (bear in mind the conditions (0.12) are not steady state values in general) we start with usual initial conditions of the type (0.12) and carry out computations until the steady state is reached. At this stage the values of c_i and E do not change further in time and the describe our membrane at steady state. Now, we take these profiles as the initial conditions (0.11) and add a perturbation by way of a small current I in (0.8). The resulting potential evolution is transformed by way of suitably chosen transform (based on the *Fourier transform*) which finally produces the sought for impedance spectra.

Dimensionless NPP system of equations

The NPP system embodied in equations (0.8) and conditions (0.10), (0.11) can now be numerically treated. However, it is profitable to introduce a set of dimensionless quantities of length, time, concentrations and electric field. From a pure mathematical perspective such change of variables gives fully equivalent system, but may be helpful for numerical computations. Firstly, the number of parameter appearing in equations will be decreased. Secondly, the numerical accuracy may be substantially improved.

The equations may be converted into a set of dimensionless (rescaled) equations with the following transformations (overbar denotes a dimensionless quantity: $\overline{q}$ – dimensionless, q – with units)

$$\begin{aligned}
&x = x_s\overline{x},\ \ t = t_s\overline{t},\ \ c = c_s\overline{c},\ \ E = E_s\overline{E},\\
&\lambda = \frac{c_s\cdot(F\cdot x_s)^2}{RT\varepsilon_r\varepsilon_0},\ \ \frac{F}{RT}E_s x_s = 1,\ \ k_s = \frac{x_s}{t_s},\\
&\overline{D}_i = D_i\cdot t_s / x_s^2,\ \ \overline{k}_i = k_i / k_s.
\end{aligned} \tag{0.13}$$

where x_s, t_s, c_s, E_s are suitable scaling factors for distance, time, concentration and electric field. After calculations we arrive at the following rescaled form of NPP system for $\overline{x}\in[0,\ \overline{d}\,]$

$$\begin{cases}
\dfrac{\partial\overline{c}_i}{\partial\overline{t}} = -\dfrac{\partial\overline{J}_i}{\partial\overline{x}}, \qquad i = 1,\ldots,r,\\[2ex]
\dfrac{\partial\overline{E}}{\partial\overline{t}} = -\lambda\displaystyle\sum_{i=1}^{r} z_i\overline{J}_i,
\end{cases} \tag{0.14}$$

where the flux is given by

$$\overline{J}_i = -\overline{D}_i\frac{\partial\overline{c}_i}{\partial\overline{x}} + \overline{D}_i z_i\overline{c}_i\overline{E}. \tag{0.15}$$

The Chang-Jaffé boundary conditions

$$\begin{cases}
\overline{J}_i(0,\overline{t}) = \overline{k}_{i,Lf}\overline{c}_{i,L} - \overline{k}_{i,Lb}\overline{c}_i(0,\overline{t}),\\
\overline{J}_i(\overline{d},\overline{t}) = -\overline{k}_{i,Rf}\overline{c}_{i,R} + \overline{k}_{i,Rb}\overline{c}_i(\overline{d},\overline{t}),
\end{cases} \tag{0.16}$$

where $\overline{k}_{i,Lf}$, $\overline{k}_{i,Lb}$, $\overline{k}_{i,Rf}$, $\overline{k}_{i,Lb}$ are rescaled (dimesionless) heterogeneous rate constants for the left and right membrane boundary.

To ease the burden of notation we drop the overbars in all quantities hereafter.

Space discretization

The schematic view of the space grid together with the location of concentrations, fluxes and electric field points are presented in the Fig. 3.

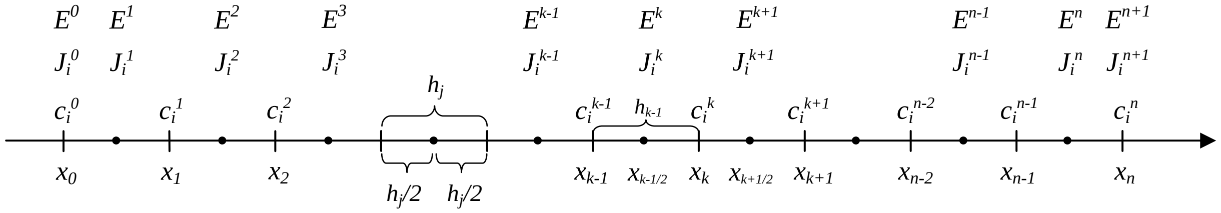
E^0 E^1 E^2 E^3 E^{k-1} E^k E^{k+1} E^{n-1} E^n E^{n+1}
J_i^0 J_i^1 J_i^2 J_i^3 J_i^{k-1} J_i^k J_i^{k+1} J_i^{n-1} J_i^n J_i^{n+1}
c_i^0 c_i^1 c_i^2 h_j c_i^{k-1} h_{k-1} c_i^k c_i^{k+1} c_i^{n-2} c_i^{n-1} c_i^n
x_0 x_1 x_2 $h_j/2$ $h_j/2$ x_{k-1} $x_{k-1/2}$ x_k $x_{k+1/2}$ x_{k+1} x_{n-2} x_{n-1} x_n

Fig. 3. Space grid and discretized functions $c_i(x,t)$ and $E(x,t)$.

$$\begin{aligned}
&\frac{dc_i^0}{dt}(t)=\frac{\partial c_i}{\partial t}(x_0,t)=-\frac{\partial J_i}{\partial x}(x_0,t)\approx-\frac{J_i^1-J_i^0}{(\frac{1}{2}h_0)}, && k=0,\\
&\frac{dc_i^k}{dt}(t)=\frac{\partial c_i}{\partial t}(x_k,t)=-\frac{\partial J_i}{\partial x}(x_k,t)\approx-\frac{J_i^{k+1}-J_i^k}{h_k}, && k=1,\ldots,n-1,\\
&\frac{dc_i^n}{dt}(t)=\frac{\partial c_i}{\partial t}(x_n,t)=-\frac{\partial J_i}{\partial x}(x_n,t)\approx-\frac{J_i^{n+1}-J_i^n}{(\frac{1}{2}h_{n-1})}, && k=n.
\end{aligned} \tag{0.17}$$

The flux is approximated at internal nodes by the following finite differences

$$J_i^k=-D_i\left(\frac{c_i^k-c_i^{k-1}}{h_{k-1}}-z_i\frac{c_i^k+c_i^{k-1}}{2}E^k\right), \quad k=1,\ldots,n-1. \tag{0.18}$$

Thus combining (0.17) and (0.18) we obtain (for internal nodes)

$$\frac{dc_i^k}{dt}=\frac{2D_i}{h_{k-1}+h_k}\left[\frac{c_i^{k+1}-c_i^k}{h_k}-\frac{c_i^k-c_i^{k-1}}{h_{k-1}}+\frac{1}{2}z_i\left((c_i^k+c_i^{k-1})E^k-(c_i^{k+1}+c_i^k)E^{k+1}\right)\right], \tag{0.19}$$
$$k=1,\ldots,n-1.$$

Space discretization for the electric field at the internal nodes gives

$$\frac{dE^k}{dt}(t)=\frac{\partial E}{\partial t}(x_{k-1/2},t)=-\lambda\sum_{i=1}^{r}z_iJ_i^k,$$

what after taking account of (0.18) can be written as

$$\frac{dE^k}{dt}=\lambda\sum_{i=1}^{r}z_iD_i\left(\frac{c_i^k-c_i^{k-1}}{h_{k-1}}-z_i\frac{c_i^k+c_i^{k-1}}{2}E^k\right), \quad k=1,\ldots,n. \tag{0.20}$$

On the boundaries (that is $x=x_0$ and $x=x_n$) we have to use expressions (0.16) for fluxes which have the following form in the discrete notation

$$\begin{cases} J_i^0=k_{i,Lf}c_{i,L}-k_{i,Lb}c_i^0, \\ J_i^{n+1}=-k_{i,Rf}c_{i,R}+k_{i,Rb}c_i^n. \end{cases} \tag{0.21}$$

Hence on the boundaries we have for concentrations

$$\begin{aligned}
\frac{dc_i^0}{dt}(t) &= -\frac{J_i^1 - J_i^0}{(\frac{1}{2}h_0)} = \frac{2}{h_0}\left(D_i\left(\frac{c_i^1 - c_i^0}{h_0} - z_i\frac{c_i^1 + c_i^0}{2}E^1 \right) + k_{i,Lf}c_{i,L} - k_{i,Lb}c_i^0 \right),\\
\frac{dc_i^n}{dt}(t) &= -\frac{J_i^{n+1} - J_i^n}{(\frac{1}{2}h_{n-1})} = \frac{2}{h_{n-1}}\left(k_{i,Rf}c_{i,R} - k_{i,Rb}c_i^n - D_i\left(\frac{c_i^n - c_i^{n-1}}{h_{n-1}} - z_i\frac{c_i^n + c_i^{n-1}}{2}E^n \right)\right),
\end{aligned}\tag{0.22}$$

an for electric field

$$\begin{aligned}
\frac{dE^0}{dt} &= \lambda\sum_{i=1}^{r} z_i(-k_{i,Lf}c_{i,L} + k_{i,Lb}c_i^0),\\
\frac{dE^{n+1}}{dt} &= \lambda\sum_{i=1}^{r} z_i(k_{i,Rf}c_{i,R} - k_{i,Rb}c_i^n).
\end{aligned}\tag{0.23}$$

The system consisting of (0.19), (0.20), (0.22), and (0.23) is in fact a system of ordinary differential equations (ODEs) which can be numerically integrated. For convenience we repeat it here in one compact form

$$\begin{aligned}
\frac{dc_i^0}{dt} &= \frac{2}{h_0}\left(D_i\left(\frac{c_i^1 - c_i^0}{h_0} - z_i\frac{c_i^1 + c_i^0}{2}E^1 \right) + k_{i,Lf}c_{i,L} - k_{i,Lb}c_i^0 \right), && k = 0,\\
\frac{dc_i^k}{dt} &= \frac{2D_i}{h_{k-1} + h_k}\left[\frac{c_i^{k+1} - c_i^k}{h_k} - \frac{c_i^k - c_i^{k-1}}{h_{k-1}} + \frac{1}{2}z_i\left((c_i^k + c_i^{k-1})E^k - (c_i^{k+1} + c_i^k)E^{k+1} \right) \right], && 1 \le k \le n-1,\\
\frac{dc_i^n}{dt} &= \frac{2}{h_{n-1}}\left(k_{i,Rf}c_{i,R} - k_{i,Rb}c_i^n - D_i\left(\frac{c_i^n - c_i^{n-1}}{h_{n-1}} - z_i\frac{c_i^n + c_i^{n-1}}{2}E^n \right)\right), && k = n,\\
\frac{dE^0}{dt} &= \lambda\sum_{i=1}^{r} z_i(-k_{i,Lf}c_{i,L} + k_{i,Lb}c_i^0), && k = 0,\\
\frac{dE^k}{dt} &= \lambda\sum_{i=1}^{r} z_i D_i\left(\frac{c_i^k - c_i^{k-1}}{h_{k-1}} - z_i\frac{c_i^k + c_i^{k-1}}{2}E^k \right), && 1 \le k \le n,\\
\frac{dE^{n+1}}{dt} &= \lambda\sum_{i=1}^{r} z_i(k_{i,Rf}c_{i,R} - k_{i,Rb}c_i^n), && k = n+1.
\end{aligned}\tag{0.24}$$

The unknown function are: $c_i^k :[k = 0,\ldots,n,\ i = 1,\ldots,r];\ E^k : [k = 0,\ldots,n+1]$ thus the number of differential equations in this system is $(r+1)(n+1)+1$. But if we want now to apply some numerical procedure to integrate the system of ODEs (0.24) we have to resolve one problem. Namely, most procedures implemented in C/C++ language require the input function (right-hand side) defined through one-dimensional table. For example the integrator that will be used here, RADAU5, has the main routine called `StiffIntegratorT` that must be provided with ODEs system based on the following form (N = number of equations)

$$\begin{cases} y_0' = f_0(t, y_0, \ldots, y_{N-1}), \\ y_0' = f_1(t, y_0, \ldots, y_{N-1}), \\ \vdots \\ y_{N-1}' = f_{N-1}(t, y_0, \ldots, y_{N-1}), \end{cases} \tag{0.25}$$

in which all equations are referenced by a single index $j = 0, \ldots, N-1$. Technically this information is provided in the form of a C++ function that has the following prototype (x here stands for time, t)

```
void Function(double x, double *y, double *f)
```

and it directly fits into the form (0.25) as now we can define Function by straightforward substitution

```
void Function(double x, double *y, double *f) {
  f[0] = f₀(x, y[0],...,y[N-1];
  f[1] = f₁(x, y[0],...,y[N-1];
...
}
```

However, our discretized NPP system (0.24) is not expressed in the form (0.25) because we have used there a double index notation c_i^k where i stands for a component and k for a node. We have to devise some way of converting c_i^k into y_ℓ. The simplest solution seems to be the following translation

$$\ell(i,k) = (n+1)\cdot(i-1)+k. \tag{0.26}$$

In this scheme: $i = 1, \ldots, r,\ k = 0, \ldots, n$ (for concentrations) and $i = r+1,\ k = 0, \ldots, n+1$ (for electric field). To present it in more clear way we work out in details two species (components).

One index notation for – the two component case $(r = 2)$

Transformation $(i,k) \mapsto j$, is displayed below

$$\begin{array}{l} c_1^0, c_1^1, c_1^2, \ldots,\ c_1^{n-2},\ c_1^{n-1},\ c_1^n,\ c_2^0,\ \ c_2^1,\ c_2^2,\ \ldots,\ \ c_2^{n-2}, c_2^{n-1}, c_2^n,\ \ E^0,\ \ E^1,\ \ E^2\ ,\ldots,\ E^{n-1}, E^n,\ E^{n+1} \\ y_0, y_1, y_2, \ldots, y_{n-2}, y_{n-1}, y_n,\ y_{n+1}, y_{n+2}, y_{n+3}, \ldots, y_{2n-1}, y_{2n}, y_{2n+1}, y_{2n+2}, y_{2n+3}, y_{2n+4}, \ldots, y_{3n+1},\ y_{3n+2}, y_{3n+3} \end{array} \tag{0.27}$$

The high-hand side of the ODEs system $y_j' = f_j(y_0, \ldots, y_{3n+3})$ in $\mathbb{R}^{3n+4}$, $(j = 0, \ldots, 3n+3)$, described by (0.24) takes now the following form

$$f_0 = \frac{2}{h_0}\left(D_1\left(\frac{y_1 - y_0}{h_0} - z_1 \frac{y_1 + y_0}{2} y_{2n+3} \right) + k_{1,Lf} c_{1,L} - k_{1,Lb} y_0 \right), \qquad j = 0,$$

$$f_j = \frac{2D_1}{h_{j-1} + h_j}\left[\frac{y_{j+1} - y_j}{h_j} - \frac{y_j - y_{j-1}}{h_{j-1}} - z_1\left(\frac{y_{j+1} + y_j}{2} y_{2n+2+j+1} - \frac{y_j + y_{j-1}}{2} y_{2n+2+j} \right) \right], \quad j = 1, \ldots, n-1,$$

$$f_n = \frac{2}{h_{n-1}}\left(k_{1,Rf} c_{1,R} - k_{1,Rb} y_n - D_1\left(\frac{y_n - y_{n-1}}{h_{n-1}} - z_1 \frac{y_n + y_{n-1}}{2} y_{3n+2} \right) \right), \qquad j = n,$$

$$f_{n+1} = \frac{2}{h_0}\left(D_2\left(\frac{y_{n+2} - y_{n+1}}{h} - z_2 \frac{y_{n+2} + y_{n+1}}{2} y_{2n+3} \right) + k_{2,Lf} c_{2,L} - k_{2,Lb} y_{n+1} \right), \qquad j = n+1,$$

$$f_j = \frac{2D_2}{h}\left[\frac{y_{j+1} - y_j}{h_{j-n-1}} - \frac{y_j - y_{j-1}}{h_{j-n-2}} - z_2\left(\frac{y_{j+1} + y_j}{2} y_{n+1+j+1} - \frac{y_j + y_{j-1}}{2} y_{n+1+j} \right)\right], \qquad j = n+2,\ldots,2n,$$

$$f_{2n+1} = \frac{2}{h_{n-1}}\left(k_{2,Rf} c_{2,R} - k_{2,Rb} y_{2n+1} - D_2\left(\frac{y_{2n+1} - y_{2n}}{h} - z_2 \frac{y_{2n+1} + y_{2n}}{2} y_{3n+2} \right)\right), \qquad j = 2n+1,$$

$$f_{2n+2} = \lambda\left(z_1(-k_{1,Lf} c_{1,L} + k_{1,Lb} y_0) + z_2(-k_{2,Lf} c_{2,L} + k_{2,Lb} y_{n+1}) \right), \quad j = 2n+2,$$

$$f_j = \lambda\left(z_1 D_1\left(\frac{y_{j-2n-2} - y_{j-2n-3}}{h_{j-2n-3}} - z_1 \frac{y_{j-2n-2} + y_{j-2n-3}}{2} y_j \right) + z_2 D_2\left(\frac{y_{j-n-1} - y_{j-n-2}}{h_{j-2n-3}} - z_2 \frac{y_{j-n-1} + y_{j-n-2}}{2} y_j \right)\right),$$

$$j = 2n+3,\ldots,3n+2,$$

$$f_{3n+3} = \lambda\left(z_1(k_{1,Rf} c_{1,R} - k_{1,Rb} y_n) + z_2(k_{2,Rf} c_{2,R} - k_{2,Rb} y_{2n+1}) \right), \qquad j = 3n+3.$$

One index notation for any number of species

In a general case of any r it is convenient to use auxiliary function for translation from two indices (i,k) to one. A natural choice is (0.26) although in the actual code a slight modification was applied and the function really is

$$\ell(i,k) = (n+1)\cdot i + k, \tag{0.28}$$

due to the fact that tables in C++ are normally indexed from 0, thus it is more convenient to number components by index i that runs from 0 up to $r-1$. Hence $0 \le i \le r-1$ refers to concentrations and $i = r$ refers to electric field. Using this device the coding is straightforward implementation of formulas from (0.24). For example the part corresponding to internal nodes for concentrations (the second equation in (0.24)) is codes as follows

```
for (i=0; i <= r-1; i++)
  for (k=1; k <= n-1; k++) {
    tmp = (y[l(i,k+1)]-y[l(i,k)])/h[k]-0.5*z[i]*(y[l(i,k+1)]+y[l(i,k)])*y[l(r,k+1)];
    tmp += -(y[l(i,k)]-y[l(i,k-1)])/h[k-1]+0.5*z[i]*(y[l(i,k)]+y[l(i,k-1)])*y[l(r,k)];
    f[l(i,k)] = 2*D[i]*tmp/(h[k-1]+h[k]);
  }
```

The total membrane potential

At any time the total membrane potential $\Phi_{Tot}(t)$ can be computed by integrating the electric field across the membrane of thickness d:

$$\Phi_{Tot}(t) = -\int_0^d E(x,\,t)dx. \tag{0.29}$$

In the numerical solution to NPP system we employed the space grid shown in Fig. 3 so the values of electric $\{E^k\}_{k=0}^{n+1}$ field are known at points $x_0,\ x_{k-1/2}(1 \le k \le n),\ x_n$. The integral (0.29) is numerically approximated by the trapezoidal rule over each sub interval

$$[x_0, x_{1/2}], \ldots, [x_{k-1/2}, x_{k+1/2}], \ldots, [x_{n-1/2}, x_n],$$

hence

$$\begin{aligned}
&\Phi_{Tot}(t) = -\int_0^d E(x,\, t)dx \approx \\
&\frac{h_0}{2}\frac{E^0+E^1}{2} + \frac{h_0+h_1}{2}\frac{E^1+E^2}{2} + \cdots + \frac{h_{n-2}+h_{n-1}}{2}\frac{E^{n-1}+E^n}{2} + \frac{h_{n-1}}{2}\frac{E^n+E^{n+1}}{2} = \\
&\frac{1}{4}\left(h_0(E^0+E^1) + h_{n-1}(E^n+E^{n+1}) + \sum_{k=1}^{n-1}(h_{k-1}+h_k)(E^k+E^{k+1}) \right).
\end{aligned}$$