PiNeaple- Poisson-Nerst-Planck: spectral version.

R.F. de Souza

Nothing much abstract to to talk about.

I. INTRODUCTION:

II. TAU METHOD:

A. Equations:

$$\frac{\partial}{\partial t} n_{\pm}(z,t) = -\frac{\partial}{\partial z} j_{\pm}(z,t) \tag{1}$$

with

$$j_{\pm}(z,t) = -D_{\pm}\left[\frac{\partial}{\partial z} n_{\pm}(z,t) \pm \frac{q}{k_B T} n_{\pm}(z,t) \frac{\partial}{\partial z} V(z,t)\right] \tag{2}$$

and $-d \leq z \leq d$.

Substituting $\tilde{z} = z/d$:

$$\frac{\partial}{\partial t} n_{\pm}(\tilde{z},t) = -\frac{\partial}{\partial \tilde{z}} j_{\pm}(\tilde{z},t) \tag{3}$$

and

$$j_{\pm}(\tilde{z},t) = -\tilde{D}_{\pm}\left[\frac{\partial}{\partial \tilde{z}} n_{\pm}(\tilde{z},t) \pm \frac{q}{k_B T d^2} n_{\pm}(\tilde{z},t) \frac{\partial}{\partial \tilde{z}} V(\tilde{z},t)\right] \tag{4}$$

with $\tilde{D}_{\pm} = D_{\pm}/d^2$ and $-1 \leq z \leq 1$.

The boundary conditions is given by:

$$\begin{aligned} j_{\pm}(\tilde{z}=-1,t) &= -\kappa_1 n_{\pm}(\tilde{z}=-1,t) + \frac{1}{\tau_1}\sigma_{\pm,1}(t) \\ j_{\pm}(\tilde{z}=1,t) &= \kappa_2 n_{\pm}(\tilde{z}=1,t) - \frac{1}{\tau_2}\sigma_{\pm,2}(t) \end{aligned} \tag{5}$$

The $\sigma_{\pm,1}$ and $\sigma_{\pm,2}$ obeys:

$$\begin{aligned} \frac{\partial}{\partial t}\sigma_{\pm,1}(t) &= \kappa_1 n_{\pm}(\tilde{z}=-1,t) - \frac{1}{\tau_1}\sigma_{1,\pm}(t), \\ \frac{\partial}{\partial t}\sigma_{\pm,2}(t) &= \kappa_2 n_{\pm}(\tilde{z}=1,t) - \frac{1}{\tau_2}\sigma_{2,\pm}(t), \end{aligned} \tag{6}$$

The potential $V(\tilde{z},t)$ obeys the equation:

$$\frac{\partial^2}{\partial \tilde{z}^2} V(\tilde{z},t) = -\frac{q d^2}{\epsilon}\left(n_+(\tilde{z},t) - n_-(\tilde{z},t)\right) \tag{7}$$

with

$$V(\pm 1,t) = \pm\frac{V_0}{2}\exp(I\omega t) \tag{8}$$

B. Weighted residuals

We are going to develop the functions $n_+(\tilde{z},t)$, $n_-(\tilde{z},t)$ and $V(\tilde{z},t)$ in terms o Legendre polynomials as following:

$$\begin{aligned} n_+(\tilde{z},t) &= \sum_{i=0}^{N} c_+^j(t) P_i(\tilde{z}) \\ n_-(\tilde{z},t) &= \sum_{i=0}^{N} c_-^j(t) P_i(\tilde{z}) \\ V(\tilde{z},t) &= \sum_{i=0}^{N} c_v^j(t) P_i(\tilde{z}) \end{aligned} \tag{9}$$

Knowing that:

$$\begin{aligned} \frac{\partial}{\partial \tilde{z}} P_i(\tilde{z}) &= \sum_{\substack{j=0 \\ j+i \text{ odd}}}^{i-1} (2j+1) P_j(\tilde{z}), \quad \text{and} \\ \frac{\partial^2}{\partial \tilde{z}^2} P_i(\tilde{z}) &= \sum_{\substack{j=0 \\ i+j \text{ even}}}^{i-2} \left(j+\frac{1}{2}\right) \left(i(i+1) - j(j+1)\right) P_j(\tilde{z}), \end{aligned} \tag{10}$$

we can write:

$$\begin{aligned} \frac{\partial}{\partial z} V(\tilde{z},t) &= \sum_{i=0}^{N} \sum_{\substack{j=0 \\ i+j \text{ odd}}}^{i-1} (2j+1) {c^i}_v(t) P_j(\tilde{z}), \\ \frac{\partial^2}{\partial z^2} V &= \sum_{i=0}^{N} \sum_{\substack{j=0 \\ j+i \text{ even}}}^{i-2} {c^i}_v(t) \left(j+\frac{1}{2}\right) \left(i(i+1) - j(j+1)\right) P_j(\tilde{z}) \end{aligned} \tag{11}$$

Writing the equations (2) and (3) as a residual:

$$\begin{aligned} R_\pm(\tilde{z},t) &= \frac{\partial}{\partial t} n_\pm(\tilde{z},t) + \frac{\partial}{\partial \tilde{z}} j_\pm(\tilde{z},t) \\ R_V(\tilde{z},t) &= \frac{\partial^2}{\partial z^2} V(\tilde{z},t) + \frac{qd^2}{\epsilon}(n_+(\tilde{z},t) - n_-(\tilde{z},t)). \end{aligned} \tag{12}$$

We will multiply the residuals by $P_i(\tilde{z})$ and integrate from $\tilde{z}=-1$ to $\tilde{z}=1$:

$$\begin{aligned} \int_{\tilde{z}=-1}^{\tilde{z}=1} R_\pm(\tilde{z},t) P_k(\tilde{z}) d\tilde{z} &= 0 \\ \int_{\tilde{z}=-1}^{\tilde{z}=1} R_V(\tilde{z},t) P_k(\tilde{z}) d\tilde{z} &= 0 \end{aligned} \tag{13}$$

Taking $i = 0, \ldots, N$ give us $3N+3$ equations for $3N+3$ variables.

C. Manipulating Residuals equations:

1. *Eletric potential equation.*

Expanding the eletric potential equation(13):

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{\partial^2}{\partial z^2} V(\tilde{z},t) P_k(\tilde{z}) d\tilde{z} + \int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{qd^2}{\epsilon} \left[n_+(\tilde{z},t) - n_-(\tilde{z},t)\right] P_k(\tilde{z}) d\tilde{z} = 0 \quad \forall \quad i = 0, \cdots, N-2 \tag{14}$$

Substituting (11) into (14):

$$\int_{\tilde{z}=-1}^{\tilde{z}=1}\sum_{i=0}^{N}\sum_{\substack{j=0\\ j+i\text{ even}}}^{i-2}\left(j+\frac{1}{2}\right)(i(i+1)-j(j+1))\,c^i(t)P_j(\tilde{z})P_k(\tilde{z})d\tilde{z}+\int_{\tilde{z}=-1}^{\tilde{z}=1}\frac{qd^2}{\epsilon}\sum_{i=0}^{N}[c_+^j(t)-c_-^j(t)]P_k(\tilde{z})P_i(\tilde{z})d\tilde{z}=0 \tag{15}$$

for all $i=0,1,\cdots,N-2$.

The r.h.s can be simplified to:

$$\begin{aligned}\int_{\tilde{z}=-1}^{\tilde{z}=1}\frac{qd^2}{\epsilon}\sum_{i=0}^{N}[c_+^i(t)-c_-^i(t)]P_k(\tilde{z})P_i(\tilde{z})d\tilde{z}&=-\frac{qd^2}{\epsilon}\sum_{i=0}^{N}[c_+^i(t)-c_-^i(t)]\delta_{ik}\\&=\frac{qd^2}{\epsilon}[c_+^k(t)-c_-^k(t)]\end{aligned} \tag{16}$$

The L.h.s:

$$\begin{aligned}&\int_{\tilde{z}=-1}^{\tilde{z}=1}\sum_{i=0}^{N}\sum_{\substack{j=0\\ j+i\text{ even}}}^{i-2}\left(j+\frac{1}{2}\right)(i(i+1)-j(j+1))\,c^i(t)P_j(\tilde{z})P_k(\tilde{z})d\tilde{z}\\&=\sum_{i=0}^{N}\sum_{\substack{j=0\\ j+i\text{ even}}}^{i-2}\left(j+\frac{1}{2}\right)[i(i+1)-j(j+1)]\,c^i(t)\gamma_k\delta_{jk}\end{aligned}$$

Therefore we have:

$$\sum_{i=0}^{N}\sum_{\substack{j=0\\ j+i\text{ even}}}^{i-2}\left(j+\frac{1}{2}\right)[i(i+1)-j(j+1)]\,c^i(t)\gamma_k\delta_{jk}=-\frac{qd^2}{\epsilon}[c_+^k(t)-c_-^k(t)]\quad\forall\quad k=0,\cdots,N-2. \tag{17}$$

The boundary conditions are:

$$\sum_{i=0}^{N}c_v^i(t)P_i(\pm1)=\pm\frac{V_0}{2}\exp(I\omega t). \tag{18}$$

Knowing that $P_i(\pm1)=(\pm1)^i$, we can divide (18) into:

$$\sum_{i=0}^{N}c_v^i(t)=\frac{V_0}{2}\exp(I\omega t),$$

$$\sum_{i=0}^{N}(-1)^ic_v^i(t)=-\frac{V_0}{2}\exp(I\omega t). \tag{19}$$

$$\tag{20}$$

2. Concentration equations:

Writing the equations (2) and (3) as a residual:

$$\begin{aligned}R_\pm(\tilde{z},t)&=\frac{\partial}{\partial t}n_\pm(\tilde{z},t)-\tilde{D}_\pm\frac{\partial}{\partial\tilde{z}}\left[\frac{\partial}{\partial\tilde{z}}n_\pm(\tilde{z},t)\pm\frac{q}{k_BTd^2}n_\pm(\tilde{z},t)\frac{\partial}{\partial\tilde{z}}V(\tilde{z},t)\right]\\&=\frac{\partial}{\partial t}n_\pm(\tilde{z},t)-\tilde{D}_\pm\left\{\frac{\partial^2}{\partial\tilde{z}^2}n_\pm(\tilde{z},t)\pm\frac{q}{k_BTd^2}\left[\frac{\partial}{\partial\tilde{z}}n_\pm(\tilde{z},t)\frac{\partial}{\partial\tilde{z}}V(\tilde{z},t)+n_\pm(\tilde{z},t)\frac{\partial^2}{\partial\tilde{z}^2}V(\tilde{z},t)\right]\right\}\end{aligned} \tag{21}$$

$$\int_{\tilde{z}=-1}^{\tilde{z}=1}\frac{\partial}{\partial t}n_\pm(\tilde{z},t)P_i(\tilde{z})d\tilde{z}-\int_{\tilde{z}=-1}^{\tilde{z}=1}\tilde{D}_\pm\left\{\frac{\partial^2}{\partial\tilde{z}^2}n_\pm(\tilde{z},t)\pm\frac{q}{k_BTd^2}\left[\frac{\partial}{\partial\tilde{z}}n_\pm(\tilde{z},t)\frac{\partial}{\partial\tilde{z}}V(\tilde{z},t)+n_\pm(\tilde{z},t)\frac{\partial^2}{\partial\tilde{z}^2}V(\tilde{z},t)\right]\right\}P_i(\tilde{z})d\tilde{z}=0$$

Going by parts:

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{\partial}{\partial t} n_\pm(\tilde{z},t) P_k(\tilde{z}) d\tilde{z} d\tilde{z} = \frac{\partial}{\partial t} c^k_\pm(t)\gamma_k \tag{22}$$

$$\begin{aligned}
\int_{\tilde{z}=-1}^{\tilde{z}=1} \tilde{D}_\pm \frac{\partial^2}{\partial \tilde{z}^2} n_\pm(\tilde{z},t) P_k(\tilde{z}) d\tilde{z} &= \sum_{i=0}^{N} \sum_{\substack{j=0 \\ i+j \text{ even}}}^{i-2} \int_{\tilde{z}=-1}^{\tilde{z}=1} \left(j+\frac{1}{2}\right) \left(i(i+1) - j(j+1)\right) c^i{}_\pm(t) P_j(\tilde{z}) P_k(\tilde{z}) d\tilde{z}, \\
&= \sum_{i=0}^{N} \sum_{\substack{j=0 \\ i+j \text{ even}}}^{i-2} \left(j+\frac{1}{2}\right) \left(i(i+1) - j(j+1)\right) c^i{}_\pm(t) \gamma_k \delta_{jk}
\end{aligned} \tag{23}$$

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} P_k(\tilde{z}) P_j(\tilde{z}) P_i(\tilde{z}) d\tilde{z} = \frac{2}{2k+1} Cg(i,j,k,0,0,0)^2 \tag{24}$$

Yet another part:

$$\begin{aligned}
&\int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{q}{k_B T d^2} \frac{\partial}{\partial \tilde{z}} n_\pm(\tilde{z},t) \frac{\partial}{\partial \tilde{z}} V(\tilde{z},t) P_k(\tilde{z}) d\tilde{z} = \\
&= \frac{q}{k_B T d^2} \int_{\tilde{z}=-1}^{\tilde{z}=1} \sum_{i=0}^{N} \sum_{p=0}^{N} \sum_{\substack{j=0 \\ j+i \text{ odd}}}^{i-1} \sum_{\substack{q=0 \\ p+q \text{ odd}}}^{i-1} (2j+1)(2q+1) c^i_\pm(t) c^p_v(t) P_j(\tilde{z}) P_q(\tilde{z}) P_k(\tilde{z}) d\tilde{z} \qquad (25) \\
&= \frac{q}{k_B T d^2} \sum_{i=0}^{N} \sum_{p=0}^{N} \sum_{\substack{j=0 \\ j+i \text{ odd}}}^{i-1} \sum_{\substack{q=0 \\ p+q \text{ odd}}}^{i-1} 2(2j+1) c^i_\pm(t) c^p_v(t) Cg(j,k,q,0,0,0)^2 \qquad (26)
\end{aligned}$$

And the final part:

$$\begin{aligned}
&\int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{Dq}{k_B T d^2} n_\pm(\tilde{z},t) \frac{\partial^2}{\partial \tilde{z}^2} V(\tilde{z},t) d\tilde{z} = \\
&= \sum_{i=0}^{N} \sum_{p=0}^{N} \sum_{\substack{q=0 \\ p+q \text{ even}}}^{i-2} \int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{Dq}{k_B T d^2} c^i_\pm(t) c^p_v(t) \left(q+\frac{1}{2}\right) \left[p(p+1) - q(q+1)\right] P_i(\tilde{z}) P_q(\tilde{z}) P_k(\tilde{z}) d\tilde{z} \\
&= \sum_{i=0}^{N} \sum_{p=0}^{N} \sum_{\substack{q=0 \\ p+q \text{ even}}}^{i-2} \frac{Dq}{k_B T d^2} c^i_\pm(t) c^p_v(t) \frac{2\left(q+\frac{1}{2}\right)\left[p(p+1) - q(q+1)\right]}{2q+1} Cg(i,k,q,0,0,0)^2
\end{aligned} \tag{27}$$

Here goes the boundary conditions:

$$-\tilde{D}_\pm \left[\frac{\partial}{\partial \tilde{z}} n_\pm(\tilde{z},t) \pm \frac{q}{k_B T d^2} n_\pm(\tilde{z},t) \frac{\partial}{\partial \tilde{z}} V(\tilde{z},t)\right] + \kappa_1 n_\pm(\tilde{z}=1,t) - \frac{1}{\tau_1}\sigma_{\pm,1}(t) = 0 \tag{28}$$

$$-\tilde{D}_\pm \left[\frac{\partial}{\partial \tilde{z}} n_\pm(\tilde{z},t) \pm \frac{q}{k_B T d^2} n_\pm(\tilde{z},t) \frac{\partial}{\partial \tilde{z}} V(\tilde{z},t)\right] - \kappa_2 n_\pm(\tilde{z}=-1,t) + \frac{1}{\tau_2}\sigma_{\pm,2}(t) = 0 \tag{29}$$

Knowing that

$$P_i(\tilde{z}=\pm 1) = (\pm 1)^i \tag{30}$$

$$\frac{\partial}{\partial \tilde{z}} P_i(\tilde{z}=\pm 1) = \frac{1}{2}(\pm 1)^{(i-1)} i(i+1), \tag{31}$$

we have

$$\frac{\partial}{\partial \tilde{z}} V(\tilde{z}=\pm 1,t) = \sum_{i=0}^{N} \frac{1}{2}(\pm 1)^{i-1} i(i+1) c_v^i(t) \tag{32}$$

$$\sum_{i=0}^{N} \left[-\tilde{D}_{\pm} \frac{1}{2}(-1)^{(i-1)} i(i+1) + (-1)^i \left(\kappa_1 \mp \frac{q}{k_B T d^2} \frac{\partial}{\partial \tilde{z}} V(\tilde{z}=-1,t)\right)\right] c_{\pm}^i(t) - \frac{1}{\tau_1}\sigma_{1,\pm} = 0 \tag{33}$$

$$\sum_{i=0}^{N} \left[-\tilde{D}_{\pm} \frac{1}{2} i(i+1) \mp \frac{q}{k_B T d^2} \frac{\partial}{\partial \tilde{z}} V(\tilde{z}=-1,t) - \kappa_2 \right] c_{\pm}^i(t) + \frac{1}{\tau_2}\sigma_{2,\pm} = 0 \tag{34}$$

3. Sigma equations:

Knowing that:

$$\kappa_1 n_{\pm}(\tilde{z}=1,t) = \sum_{i=0}^{N} \kappa_1 c_{\pm}^i(t), \tag{35}$$

$$\kappa_2 n_{\pm}(\tilde{z}=-1,t) = \sum_{i=0}^{N} \kappa_2 (-1)^i c_{\pm}^i(t), \tag{36}$$

we have:

The $\sigma_{\pm,1}$ and $\sigma_{\pm,2}$ obeys:

$$\begin{aligned} \frac{\partial}{\partial t}\sigma_{\pm,1}(t) &= \kappa_1 \sum_{i=0}^{N} (-1)^i c_{\pm}^i(t) - \frac{1}{\tau_1}\sigma_{1,\pm}(t), \\ \frac{\partial}{\partial t}\sigma_{\pm,2}(t) &= \kappa_2 \sum_{i=0}^{N} c_{\pm}^i(t) - \frac{1}{\tau_1}\sigma_{2,\pm}(t), \end{aligned} \tag{37}$$