PiNeaple- Poisson-Nerst-Planck: spectral version.

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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:

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

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):

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

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:

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

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:

$$\sum_{i=0}^{N} c_v^i(t) P_i(\pm 1) = \pm \frac{V_0}{2} \exp(I\omega t). \tag{18}$$

Knowing that $P_i(\pm 1) = (\pm 1)^i$, we can divide (18) into:

$$\begin{aligned} \sum_{i=0}^{N} c_v^i(t) &= \frac{V_0}{2} \exp(I\omega t), \\ \sum_{i=0}^{N} (-1)^i c_v^i(t) &= -\frac{V_0}{2} \exp(I\omega t). \end{aligned} \tag{19}$$

$$\tag{20}$$

2. Concentration equations:

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

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

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

Going by parts:

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

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

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

Yet another part:

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{q}{k_B T d^2} \frac{\partial}{\partial \tilde{z}} n_{\pm}(\tilde{z},t) \frac{\partial}{\partial \tilde{z}} V(\tilde{z},t) P_k(\tilde{z}) d\tilde{z} =$$

$$= \frac{q}{k_B T d^2} \int_{\tilde{z}=-1}^{\tilde{z}=1} \sum_{i=0}^{N} \sum_{p=0}^{N} \sum_{\substack{j=0 \\ j+i \text{ odd}}}^{i-1} \sum_{\substack{q=0 \\ p+q \text{ odd}}}^{i-1} (2j+1)(2q+1) c_{\pm}^{i}(t) c_{v}^{p}(t) P_j(\tilde{z}) P_q(\tilde{z}) P_k(\tilde{z}) d\tilde{z} \tag{25}$$

$$= \frac{q}{k_B T d^2} \sum_{i=0}^{N} \sum_{p=0}^{N} \sum_{\substack{j=0 \\ j+i \text{ odd}}}^{i-1} \sum_{\substack{q=0 \\ p+q \text{ odd}}}^{i-1} (2j+1)(2q+1) c_{\pm}^{i}(t) c_{v}^{p}(t) \sqrt{\frac{(2j+1)(2k+1)}{(2q+1)}} Cg(j,k,q,0,0,0)^2 \tag{26}$$

And the final part:

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{Dq}{k_B T d^2} n_{\pm}(\tilde{z},t) \frac{\partial^2}{\partial \tilde{z}^2} V(\tilde{z},t) d\tilde{z} =$$

$$= \sum_{i=0}^{N} \sum_{p=0}^{N} \sum_{\substack{q=0 \\ p+q \text{ even}}}^{i-2} \int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{Dq}{k_B T d^2} c_{\pm}^{i}(t) c_{v}^{p}(t) \left(q+\frac{1}{2}\right) \left[p(p+1) - q(q+1)\right] P_i(\tilde{z}) P_q(\tilde{z}) P_k(\tilde{z}) d\tilde{z}$$

$$\sum_{i=0}^{N} \sum_{p=0}^{N} \sum_{\substack{q=0 \\ p+q \text{ even}}}^{i-2} \frac{Dq}{k_B T d^2} c_{\pm}^{i}(t) c_{v}^{p}(t) \left(q+\frac{1}{2}\right) \left[p(p+1) - q(q+1)\right] \sqrt{\frac{(2i+1)(2k+1)}{(2q+1)}} Cg(i,k,q,0,0,0)^2 \tag{27}$$

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

$$\frac{\partial}{\partial \tilde{z}} P_i(\tilde{z}=\pm 1) = \frac{1}{2} (\pm 1)^{(i-1)} i(i+1), \tag{30}$$

we have

$$\sum_{i=0}^{N} \left[-\tilde{D}_{\pm} \frac{1}{2} (-1)^{(i-1)} i(i+1) c_{\pm}^{i}(t) + (-1)^{i} \kappa_1 c_{\pm}^{i}(t)\right] - \frac{1}{\tau_1} \sigma_{1,\pm} = 0 \tag{31}$$

$$\sum_{i=0}^{N} \left[-\tilde{D}_{\pm} \frac{1}{2} i(i+1) c_{\pm}^{i}(t) - \kappa_2 c_{\pm}^{i}(t)\right] + \frac{1}{\tau_2} \sigma_{2,\pm} = 0 \tag{32}$$

3. Sigma equations:

Knowing that:

$$\kappa_1 n_\pm(\tilde{z}=1,t) = \sum_{i=0}^{N} \kappa_1 c_\pm^i(t), \tag{33}$$

$$\kappa_2 n_\pm(\tilde{z}=-1,t) = \sum_{i=0}^{N} \kappa_2 (-1)^i c_\pm^i(t), \tag{34}$$

we have:

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

$$\begin{aligned} \frac{\partial}{\partial t}\sigma_{\pm,1}(t) &= \kappa_1 \sum_{i=0}^{N} (-1)^i c_\pm^i(t) - \frac{1}{\tau_1}\sigma_{1,\pm}(t), \\ \frac{\partial}{\partial t}\sigma_{\pm,2}(t) &= \kappa_2 \sum_{i=0}^{N} c_\pm^i(t) - \frac{1}{\tau_1}\sigma_{2,\pm}(t), \end{aligned} \tag{35}$$