

PiNeaple- Poisson-Nerst-Planck: spectral version.

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Nothing much abstract to to talk about.

I. INTRODUCTION:

II. TAU METHOD:

A. Equations:

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

with

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

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

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

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

and

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

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

The boundary conditions is given by:

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

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

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

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

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

with

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

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 of Legendre polynomials as following:

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

Knowing that:

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

we can write:

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

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

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

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

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

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

C. Manipulating Residuals equations:

1. Electric potential equation.

Expanding the electric potential equation(13):

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

Substituting (11) into (14):

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

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

The r.h.s can be simplified to:

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

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:

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

The boundary conditions are:

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

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

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

$$(20)$$

2. Concentration equations:

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

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

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

Going by parts:

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

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

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

Yet another part:

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

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

And the final part:

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

Here goes the boundary conditions:

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

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

Knowing that

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

we have

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

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

3. *Sigma equations:*

Knowing that:

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

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

we have:

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

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