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

$$\frac{\partial^2}{\partial \tilde{z}^2} V(\tilde{z},t) = -\frac{q d^2}{\epsilon}(n_+(\tilde{z},t) - n_-(\tilde{z},t)) \tag{5}$$

with

$$V(\pm 1, t) = \pm\frac{V_0}{2}\exp(I\omega t) \tag{6}$$

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:

$$\begin{aligned} n_+(\tilde{z},t) &= \sum_{i=0}^{N} c_+^j(t) P_i(\tilde{z}) \\ n_-(\tilde{z},t) &= \sum_{i=0}^{N} c_-^j(t) P_i(\tilde{z}) \\ V(\tilde{z},t) &= \sum_{i=0}^{N} c_v^j(t) P_i(\tilde{z}) \end{aligned} \tag{7}$$

Knowing that:

$$\frac{\partial}{\partial \tilde{z}} P_i(\tilde{z}) = \sum_{\substack{j=0 \\ j+i \text{ odd}}}^{i-1} (2j+1) P_j(\tilde{z}), \quad \text{and}$$
$$\frac{\partial^2}{\partial \tilde{z}^2} P_i(\tilde{z}) = \sum_{\substack{j=0 \\ i+j \text{ even}}}^{i-2} \left(j + \frac{1}{2}\right) \left(i(i+1) - j(j+1)\right) P_j(\tilde{z}), \tag{8}$$

we can write:

$$\frac{\partial}{\partial z} V(\tilde{z}, t) = \sum_{i=0}^{N} \sum_{\substack{j=0 \\ i+j \text{ odd}}}^{i-1} (2j+1) c^i{}_v(t) P_j(\tilde{z}),$$
$$\frac{\partial^2}{\partial z^2} V = \sum_{i=0}^{N} \sum_{\substack{j=0 \\ j+i \text{ even}}}^{i-2} c^i{}_v(t) \left(j + \frac{1}{2}\right) \left(i(i+1) - j(j+1)\right) P_j(\tilde{z}) \tag{9}$$

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

$$R_\pm(\tilde{z}, t) = \frac{\partial}{\partial t} n_\pm(\tilde{z}, t) + \frac{\partial}{\partial \tilde{z}} j_\pm(\tilde{z}, t)$$
$$R_V(\tilde{z}, t) = \frac{\partial^2}{\partial z^2} V(\tilde{z}, t) + \frac{qd^2}{\epsilon}(n_+(\tilde{z}, t) - n_-(\tilde{z}, t)). \tag{10}$$

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

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} R_\pm(\tilde{z}, t) P_k(\tilde{z}) d\tilde{z} = 0$$
$$\int_{\tilde{z}=-1}^{\tilde{z}=1} R_V(\tilde{z}, t) P_k(\tilde{z}) d\tilde{z} = 0 \tag{11}$$

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(11):

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{\partial^2}{\partial z^2} V(\tilde{z}, t) P_k(\tilde{z}) d\tilde{z} + \int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{qd^2}{\epsilon} \left[n_+(\tilde{z}, t) - n_-(\tilde{z}, t)\right] P_k(\tilde{z}) d\tilde{z} = 0 \quad \forall \quad i = 0, \cdots, N-2 \tag{12}$$

Substituting (9) into (12):

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} \sum_{i=0}^{N} \sum_{\substack{j=0 \\ j+i \text{ even}}}^{i-2} \left(j + \frac{1}{2}\right) \left(i(i+1) - j(j+1)\right) c^i(t) P_j(\tilde{z}) P_k(\tilde{z}) d\tilde{z} + \int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{qd^2}{\epsilon} \sum_{i=0}^{N} [c_+^j(t) - c_-^j(t)] P_k(\tilde{z}) P_i(\tilde{z}) d\tilde{z} = 0 \tag{13}$$

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

The r.h.s can be simplified to:

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{qd^2}{\epsilon} \sum_{i=0}^{N} [c_+^i(t) - c_-^i(t)] P_k(\tilde{z}) P_i(\tilde{z}) d\tilde{z} = -\frac{qd^2}{\epsilon} \sum_{i=0}^{N} [c_+^i(t) - c_-^i(t)] \delta_{ik}$$
$$= \frac{qd^2}{\epsilon} [c_+^k(t) - c_-^k(t)] \tag{14}$$

The L.h.s:

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

Therefore we have:

$$\sum_{i=0}^{N} \sum_{\substack{j=0 \\ j+i \text{ even}}}^{i-2} \left(j+\frac{1}{2}\right) \left[i(i+1) - j(j+1)\right] c^i(t) \gamma_k \delta_{jk} = -\frac{qd^2}{\epsilon} [c_+^k(t) - c_-^k(t)] \quad \forall \quad k = 0, \cdots, N-2. \tag{15}$$

The boundary conditions are:

$$\sum_{i=0}^{N} c_v^i(t) P_i(\pm 1) = \pm \frac{V_0}{2} \exp(I\omega t). \tag{16}$$

Knowing that $P_i(\pm 1) = (\pm 1)^i$, we can divide (16) into:

$$\sum_{i=0}^{N} c_v^i(t) = \frac{V_0}{2} \exp(I\omega t),$$
$$\sum_{i=0}^{N} (-1)^i c_v^i(t) = -\frac{V_0}{2} \exp(I\omega t). \tag{17}$$

(18)

2. Concentration equations:

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

$$R_\pm(\tilde{z},t) = \frac{\partial}{\partial t} n_\pm(\tilde{z},t) + \tilde{D}_\pm \frac{\partial}{\partial \tilde{z}} \left[\frac{\partial}{\partial \tilde{z}} n_\pm(\tilde{z},t) \pm \frac{q}{k_B T d^2} n_\pm(\tilde{z},t) \frac{\partial}{\partial \tilde{z}} V(\tilde{z},t) \right]$$
$$= \frac{\partial}{\partial t} n_\pm(\tilde{z},t) + \tilde{D}_\pm \left\{ \frac{\partial^2}{\partial \tilde{z}^2} n_\pm(\tilde{z},t) \pm \frac{q}{k_B T d^2} \left[\frac{\partial}{\partial \tilde{z}} n_\pm(\tilde{z},t) \frac{\partial}{\partial \tilde{z}} V(\tilde{z},t) + n_\pm(\tilde{z},t) \frac{\partial^2}{\partial \tilde{z}^2} V(\tilde{z},t) \right] \right\} \tag{19}$$

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

Going by parts:

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} \frac{\partial}{\partial t} n_\pm(\tilde{z},t) P_k(\tilde{z}) d\tilde{z} d\tilde{z} = \frac{\partial}{\partial t} c_\pm^k(t) \tag{20}$$

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} \tilde{D}_\pm \frac{\partial^2}{\partial \tilde{z}^2} n_\pm(\tilde{z},t) P_k(\tilde{z}) d\tilde{z} = \sum_{i=0}^{N} \sum_{\substack{j=0 \\ i+j \text{ even}}}^{i-2} \int_{\tilde{z}=-1}^{\tilde{z}=1} \left(j+\frac{1}{2}\right) \left(i(i+1) - j(j+1)\right) c^i{}_\pm(t) P_j(\tilde{z}) P_k(\tilde{z}) d\tilde{z},$$
$$= \sum_{i=0}^{N} \sum_{\substack{j=0 \\ i+j \text{ even}}}^{i-2} \left(j+\frac{1}{2}\right) \left(i(i+1) - j(j+1)\right) c^i{}_\pm(t) \gamma_k \delta_{jk} \tag{21}$$

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} P_j(\tilde{z})P_q(\tilde{z})P_k(\tilde{z})d\tilde{z} = \sqrt{\frac{(2j+1)(2k+1)}{(2q+1)}}Cg(j,k,q,0,0,0)^2 \tag{22}$$

Yet another part:

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

$$= \frac{q}{k_B T d^2}\int_{\tilde{z}=-1}^{\tilde{z}=1}\sum_{i=0}^{N}\sum_{p=0}^{N}\sum_{\substack{j=0\\ j+i \text{ odd}}}^{i-1}\sum_{\substack{q=0\\ p+q \text{ odd}}}^{i-1}(2j+1)(2q+1)c_\pm^i(t)c_v^p(t)P_j(\tilde{z})P_q(\tilde{z})P_k(\tilde{z})d\tilde{z} \tag{23}$$

$$= \frac{q}{k_B T d^2}\sum_{i=0}^{N}\sum_{p=0}^{N}\sum_{\substack{j=0\\ j+i \text{ odd}}}^{i-1}\sum_{\substack{q=0\\ p+q \text{ odd}}}^{i-1}(2j+1)(2q+1)c_\pm^i(t)c_v^p(t)\sqrt{\frac{(2j+1)(2k+1)}{(2q+1)}}Cg(j,k,q,0,0,0)^2 \tag{24}$$

And the final part:

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

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

$$\sum_{i=0}^{N}\sum_{p=0}^{N}\sum_{\substack{q=0\\ p+q \text{ even}}}^{i-2}\frac{Dq}{k_B T d^2}c_\pm^i(t)c_v^p(t)\left(q+\frac{1}{2}\right)\left[p(p+1)-q(q+1)\right]\sqrt{\frac{(2i+1)(2k+1)}{(2q+1)}}Cg(i,k,q,0,0,0)^2 \tag{25}$$