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 $-d \le z \le d$.

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

$$\frac{\partial}{\partial t}n_\pm(\tilde{z},t) = -\frac{1}{d}\frac{\partial}{\partial \tilde{z}}j_\pm(\tilde{z},t) \tag{3}$$

and

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

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

The boundary conditions is given by:

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

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

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

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

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

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:

$$n_+(\tilde{z}, t) = \sum_{i=0}^{N} c_+^j(t) P_i(\tilde{z})$$

$$n_-(\tilde{z}, t) = \sum_{i=0}^{N} c_-^j(t) P_i(\tilde{z}) \tag{9}$$

$$V(\tilde{z}, t) = \sum_{i=0}^{N} c_v^j(t) P_i(\tilde{z})$$

Knowing that:

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

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

we can write:

$$\frac{\partial}{\partial z} V(\tilde{z}, t) = \sum_{i=0}^{N} \sum_{\substack{j=0 \\ i+j \text{ odd}}}^{i-1} (2j+1) c_v^i(t) P_j(\tilde{z}),$$

$$\frac{\partial^2}{\partial z^2} V = \sum_{i=0}^{N} \sum_{\substack{j=0 \\ j+i \text{ even}}}^{i-2} c_v^i(t) \left(j + \frac{1}{2} \right) (i(i+1) - j(j+1)) P_j(\tilde{z}) \tag{11}$$

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

$$R_\pm(\tilde{z}, t) = \frac{\partial}{\partial t} n_\pm(\tilde{z}, t) + \frac{1}{d} \frac{\partial}{\partial \tilde{z}} j_\pm(\tilde{z}, t)$$

$$R_V(\tilde{z}, t) = \frac{\partial^2}{\partial \tilde{z}^2} V(\tilde{z}, t) + \frac{q d^2}{\epsilon} (n_+(\tilde{z}, t) - n_-(\tilde{z}, t)). \tag{12}$$

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

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

$$\int_{\tilde{z}=-1}^{\tilde{z}=1} R_V(\tilde{z}, t) P_k(\tilde{z}) d\tilde{z} = 0 \tag{13}$$

Taking $i = 0, \ldots, N - 2$. Taking 2 extra equations for the boundary conditions, we will have $3N + 3$ equations for $3N + 3$ variables.

C. Manipulating Residuals equations:

1. Eletric potential equation.

Expanding the eletric potential equation(13):

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

Substituting (11) into (14):

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

$$(15)$$

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

The r.h.s can be simplified to:

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

$$= \frac{qd^2}{\epsilon}[c_+^k(t)-c_-^k(t)] \qquad (16)$$

The L.h.s:

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

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

Therefore we have:

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

The boundary conditions are:

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

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

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

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

$$(20)$$

2. Concentration equations:

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

$$R_\pm(\tilde{z},t) = \frac{\partial}{\partial t}n_\pm(\tilde{z},t) - \frac{\tilde{D}_\pm}{d}\frac{\partial}{\partial \tilde{z}}\left[\frac{\partial}{\partial \tilde{z}}n_\pm(\tilde{z},t) \pm \frac{q}{k_BT}n_\pm(\tilde{z},t)\frac{\partial}{\partial \tilde{z}}V(\tilde{z},t)\right]$$

$$= \frac{\partial}{\partial t}n_\pm(\tilde{z},t) - \frac{\tilde{D}_\pm}{d}\left\{\frac{\partial^2}{\partial \tilde{z}^2}n_\pm(\tilde{z},t) \pm \frac{q}{k_BT}\left[\frac{\partial}{\partial \tilde{z}}n_\pm(\tilde{z},t)\frac{\partial}{\partial \tilde{z}}V(\tilde{z},t) + n_\pm(\tilde{z},t)\frac{\partial^2}{\partial \tilde{z}^2}V(\tilde{z},t)\right]\right\} \qquad (21)$$

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

Going by parts:

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

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

$$= \sum_{i=0}^{N} \sum_{\substack{j=0 \\ i+j \text{ even}}}^{i-2} \frac{\tilde{D}_\pm}{d}\left(j+\frac{1}{2}\right)(i(i+1)-j(j+1)) c_\pm^i(t) \gamma_k \delta_{jk} \tag{23}$$

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

Yet another part:

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

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

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

And the final part:

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

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

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

Here goes the boundary conditions:

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

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

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

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

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

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

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:

$$\frac{\partial}{\partial t}\sigma_{\pm,1}(t)=\kappa_1\sum_{i=0}^{N}(-1)^i c_{\pm}^i(t)-\frac{1}{\tau_1}\sigma_{1,\pm}(t),$$

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