Nerst-Plank Equation

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D\nabla c - c\mathbf{v} + \frac{Dze}{k_{\mathrm{B}}T} c \left(\nabla\phi + \frac{\partial \mathbf{A}}{\partial t} \right) \right]$$

***v* = 0**

φ* = *constant
A* = *constant

$$\frac{\partial c}{\partial t} = \nabla \cdot D\nabla c$$

D = constant

$$\frac{\partial c}{\partial t} = D\nabla \cdot \nabla c = \nabla^2 c$$

In 1D:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

https://www.dam.brown.edu/people/alcyew/handouts/numdiff.pdf

$O(\Delta x^2)$ centered difference approximations:
$f'(x): \quad \{f(x+\Delta x) - f(x-\Delta x)\}/(2\Delta x)$
$f''(x): \quad \{f(x+\Delta x) - 2f(x) + f(x-\Delta x)\}/\Delta x^2$

$O(\Delta x^2)$ forward difference approximations:
$f'(x): \quad \{-3f(x) + 4f(x+\Delta x) - f(x+2\Delta x)\}/(2\Delta x)$
$f''(x): \quad \{2f(x) - 5f(x+\Delta x) + 4f(x+2\Delta x) - f(x+3\Delta x)\}/\Delta x^3$

$O(\Delta x^2)$ backward difference approximations:
$f'(x): \quad \{3f(x) - 4f(x-\Delta x) + f(x-2\Delta x)\}/(2\Delta x)$
$f''(x): \quad \{2f(x) - 5f(x-\Delta x) + 4f(x-2\Delta x) - f(x-3\Delta x)\}/\Delta x^3$

$O(\Delta x^4)$ centered difference approximations:
$f'(x): \quad \{-f(x+2\Delta x) + 8f(x+\Delta x) - 8f(x-\Delta x) + f(x-2\Delta x)\}/(12\Delta x)$
$f''(x): \quad \{-f(x+2\Delta x) + 16f(x+\Delta x) - 30f(t) + 16f(x-\Delta x) - f(x-2\Delta x)\}/(12\Delta x^2)$

In interior:

$$c_{x,t+dt} = \left(c_{x,t} + D\left[\frac{c_{x+dx,t} - 2c_{x,t} + c_{x-dx,t}}{dx^2}\right]\right) dt$$

On left boundary:

$$c_{x,t+dt} = \left(c_{x,t} + D\left[\frac{2c_{x,t} - 5c_{x+dx,t} + 4c_{x+2dx,t} - c_{x+3dx,t}}{dx^2}\right]\right) dt$$

NOT NEEDED

On right boundary:

$$c_{x,t+dt} = \left(c_{x,t} + D\left[\frac{2c_{x,t} - 5c_{x-dx,t} + 4c_{x+2dx,t} - c_{x+3dx,t}}{dx^2}\right]\right) dt$$

Boundary conditions:

$$\left.\frac{dc}{dx}\right|_L = 0 \implies \frac{c_1 - c_0}{dx} = 0 \implies c_1 = c_0$$

$$\left.\frac{dc}{dx}\right|_R = 0 \implies \frac{c_N - c_{N-1}}{dx} = 0 \implies c_N = c_{N-1}$$

$$\frac{\partial c}{\partial t} = \nabla \cdot \left[D\nabla c - c\mathbf{v} + \frac{Dze}{k_{\mathrm{B}}T} c \left(\nabla\phi + \frac{\partial \mathbf{A}}{\partial t} \right) \right]$$

D = constant, v = 0, dA/dt = 0

$$\implies \frac{\partial c}{\partial t} = \nabla \cdot \left[D\nabla c + \frac{Dze}{k_B T} c\nabla\phi \right] \implies \frac{\partial c}{\partial t} = D\nabla^2 c + \nabla \cdot \left[\frac{Dze}{k_B T} c\nabla\phi \right]$$

$$\implies \frac{\partial c}{\partial t} = D\nabla^2 c + \frac{DZe}{k_B T} \nabla \cdot [c\nabla\phi]$$

Vector identity: $\nabla \cdot (c\vec{A}) = c\nabla \cdot \vec{A} + (\nabla c) \cdot \vec{A}$

$$\implies \frac{\partial c}{\partial t} = D\nabla^2 c + \frac{DZe}{k_B T} \left[c\nabla \cdot \nabla\phi + \nabla c \cdot \nabla\phi \right]$$

$$\implies \frac{\partial c}{\partial t} = D\nabla^2 c + \frac{DZe}{k_B T} c\nabla^2\phi + \frac{DZe}{k_B T} \nabla c \cdot \nabla\phi$$

In 1D:

$$\implies \frac{\partial c}{\partial t} = D\frac{d^2 c}{dx^2} + \frac{DZe}{k_B T} c\frac{d^2\phi}{dx^2} + \frac{DZe}{k_B T} \frac{dc}{dx} \frac{d\phi}{dx}$$

Finite difference expansion:

For interior points (i.e. not $c_{t,x=0}$ or $c_{t,x=N}$)

$$\frac{c_{t+1} - c_t}{\delta t} = D\frac{c_{x+1} - 2c_x + c_{x-1}}{\delta x^2} + \eta c_x \frac{\phi_{x+1} - 2\phi_x + \phi_{x-1}}{\delta x^2} + \eta \left[\frac{c_{x+1} - c_{x-1}}{2\delta x} \right] \left[\frac{\phi_{x+1} - \phi_{x-1}}{2\delta x} \right]$$

$$let\text{:}\ A = \frac{\phi_{x+1} - 2\phi_x + \phi_{x-1}}{\delta x^2}, \quad B = \frac{\phi_{x+1} - \phi_{x-1}}{2\delta x}$$

$$\implies c_{t+1,x} = c_{t,x} + \frac{D}{\delta x^2} [c_{t,x+1} - 2c_{t,x} + c_{t,x-1}]\ \delta t + \eta A B c_{t,x}\ \delta t + \frac{\eta B}{2\delta x} [c_{t,x+1} - c_{t,x-1}]\ \delta t$$

$$\Longrightarrow c_{t+1,x} = c_{t,x-1}\left[\frac{D\delta t}{\delta x^2} - \frac{\eta B\delta t}{2\delta x}\right] + c_{t,x}\left[1 - \frac{2D\delta t}{\delta x^2} + \eta AB\delta t\right] + c_{t,x+1}\left[\frac{D\delta t}{\delta x^2} + \frac{\eta B\delta t}{2\delta x}\right]$$

Finite Difference expansion for exterior (boundary) points:

NOT NEEDED

$$\frac{\partial c}{\partial t} = D\frac{d^2c}{dx^2} + \frac{DZe}{k_BT}c\frac{d^2\phi}{dx^2} + \frac{DZe}{k_BT}\frac{dc}{dx}\frac{d\phi}{dx}$$

$$let:\ A = \frac{\phi_{x+1} - 2\phi_x + \phi_{x-1}}{\delta x^2}, \quad B = \frac{\phi_{x+1} - \phi_{x-1}}{2\delta x}$$

$$\frac{d^2f}{dx^2} \approx \frac{f(x+2\delta x) - 2f(x+\delta x) + f(x)}{\delta x^2}$$

$$\frac{d^2f}{dx^2} \approx \frac{f(x) - 2f(x-\delta x) + f(x-2\delta x)}{\delta x^2}$$

Boundary conditions:

$$\left.\frac{dc}{dx}\right|_L = 0 \Longrightarrow \frac{c_1 - c_0}{dx} = 0 \Longrightarrow c_1 = c_0$$

$$\left.\frac{dc}{dx}\right|_R = 0 \Longrightarrow \frac{c_N - c_{N-1}}{dx} = 0 \Longrightarrow c_N = c_{N-1}$$

On left/right boundary:

$$\Longrightarrow \frac{\partial c}{\partial t} = D\frac{d^2c}{dx^2} + \frac{DZe}{k_BT}c\frac{d^2\phi}{dx^2} + \cancelto{0}{\frac{DZe}{k_BT}\frac{dc}{dx}\frac{d\phi}{dx}}$$

$$let:\ A = \frac{\phi_{x+1} - 2\phi_x + \phi_{x-1}}{\delta x^2}, \quad B = \frac{\phi_{x+1} - \phi_{x-1}}{2\delta x}$$

$$\Longrightarrow c_{t+1,x} = c_{t,x} + D\left[\frac{c_{t,x+1} - 2c_{t,x} + c_{t,x-1}}{\delta x^2}\right]\delta t + \frac{ADZe}{k_BT}c_{t,x}\,\delta t$$