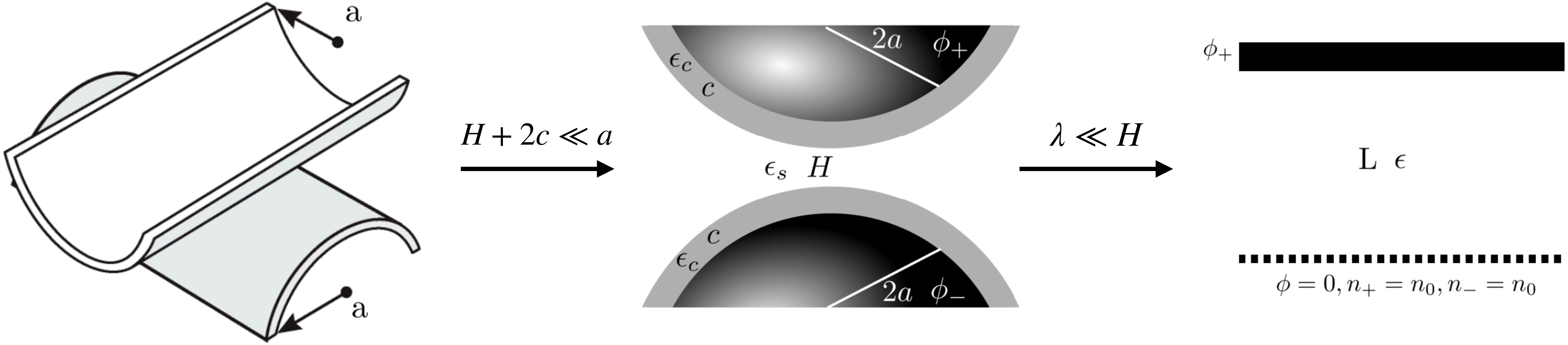
Ions in an AC Electric Field

Chen Huang 2022.1.14


a
a
$H + 2c \ll a$
ϵ_c
c
$2a$
ϕ_+
ϵ_s H
c
ϵ_c
$2a$
ϕ_-
$\lambda \ll H$
ϕ_+
L ϵ
$\phi = 0, n_+ = n_0, n_- = n_0$

Poisson-Nernst-Planck equation ($\sigma = \pm$)

$$\frac{\partial n_\sigma}{\partial t} = \nabla \cdot D_\sigma \left(\nabla n_\sigma + \sigma \frac{e z_\sigma}{k_B T} n_\sigma \nabla \phi \right)$$

$$\Delta \phi = -\frac{e}{\epsilon} \left(z_+ n_+ - z_- n_- \right)$$

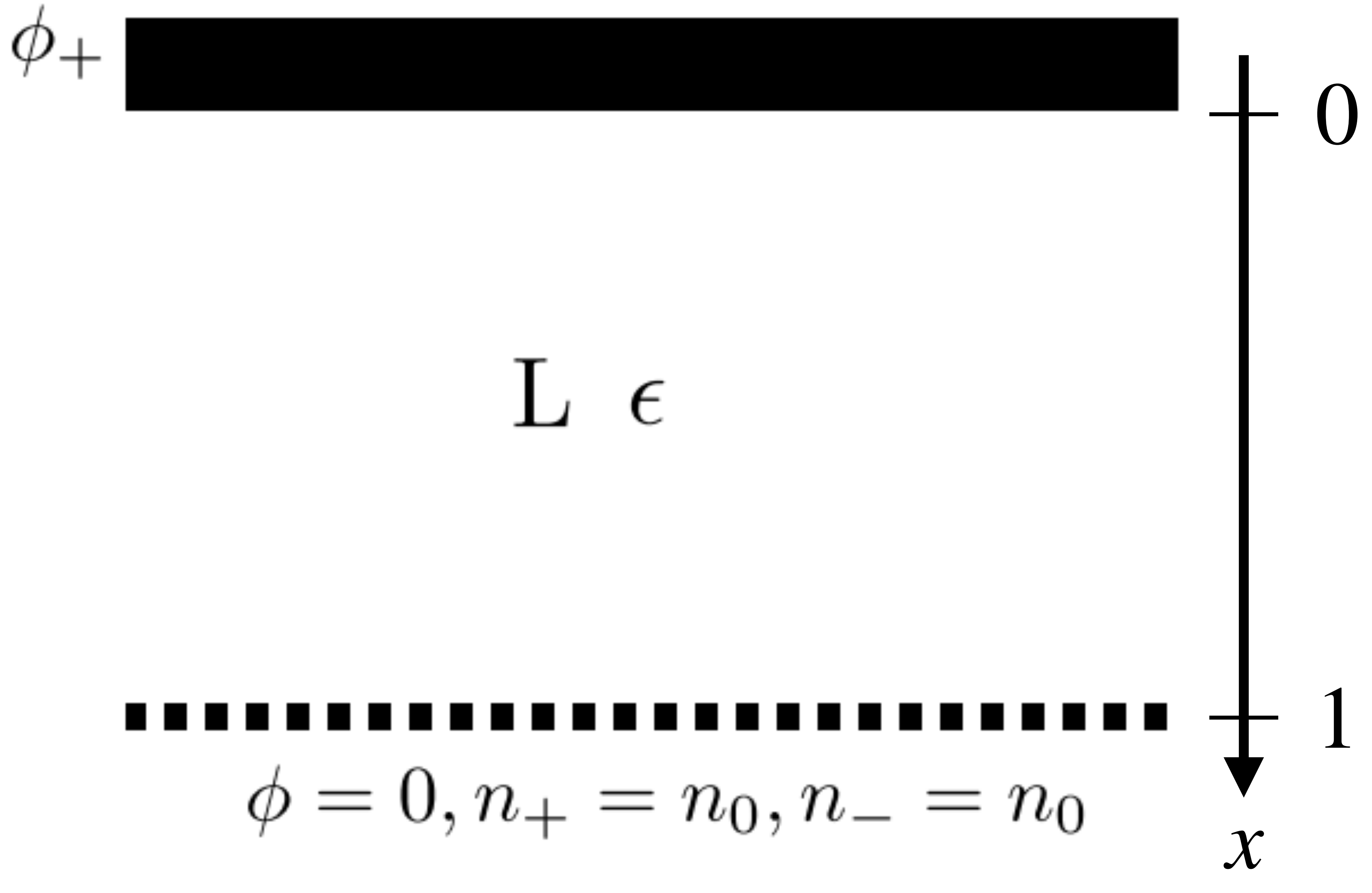
Boundary condition

$$\mathbf{n} \cdot \mathbf{j}_\sigma = -D_\sigma \left(\mathbf{n} \cdot \nabla n_\sigma + \sigma \frac{z_\sigma e}{k_B T} n_\sigma \mathbf{n} \cdot \nabla \phi \right) = 0,$$

$$z_+ n_+^b = z_- n_-^b \quad \rightarrow \quad n_-^b = n_0 \frac{z_+}{z_-} = \frac{n_0}{\kappa}$$

Poisson-Nernst-Planck方程描述导电物质中离子浓度与电压之间的关系
Nernst-Planck方程是用来描述在离子浓度梯度(Δn)及电场梯度(ΔV)共同存在的情况下,穿过渗透膜的离子流大小(Φ)的方程

1D model



$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{1}{\delta^2}\left(n_+ - n_-\right)$$

$$\frac{\partial n_+}{\partial t} = \delta^2 \left(\frac{\partial^2 n_+}{\partial x^2} + z_+ \frac{\partial}{\partial x} \left(n_+ \frac{\partial \phi}{\partial x} \right) \right)$$

$$\frac{\partial n_-}{\partial t} = \delta^2 \chi \left(\frac{\partial^2 n_-}{\partial x^2} - z_+ \kappa \frac{\partial}{\partial x} \left(n_- \frac{\partial \phi}{\partial x} \right) \right)$$

Boundary condition

① $x = 0$ no flux (solid wall)

$$\frac{\partial n_+}{\partial x} + z_+ n_+ \frac{\partial \phi}{\partial x} = 0,$$

$$\frac{\partial n_-}{\partial x} - z_+ \kappa n'_- \frac{\partial \phi}{\partial x} = 0$$

② $x = 1$ contact with a reservoir

$$n_+(1,t) = 1, \quad n_-(1,t) = 1$$

③ Assumption

$$\phi(0,t) = -V_0 \sin(\omega t), \quad \phi(1,t) = 0$$

Separation of variables

$$f(x,t) = \sum_k f(x) e^{ki\omega t}$$

$$\begin{aligned}\phi(x,t) = V_0 &\left(\phi_1^{(1)} e^{i\omega t} + \phi_{-1}^{(1)} e^{-i\omega t}\right) \\ &+V_0^2 \left(\phi_{-2}^{(2)} e^{2i\omega t} + \phi_0^{(2)} + \phi_{-2}^{(2)} e^{-2i\omega t}\right) \\ &+O(V_0^3),\end{aligned}$$

$$\begin{aligned}n_\pm(x,t) = V_0 &\left(n_{\pm,1}^{(1)} e^{i\omega t} + n_{\pm,-1}^{(1)} e^{-i\omega t}\right) \\ &+V_0^2 \left(n_{\pm,-2}^{(2)} e^{2i\omega t} + n_{\pm,0}^{(2)} + n_{\pm,-2}^{(2)} e^{-2i\omega t}\right) \\ &+O(V_0^3),\end{aligned}$$

First order

$$\frac{\mathrm{d}^2\phi_1^{(1)}}{\mathrm{d}x^2} = -\frac{1}{\delta^2}\left(n_{+,1}^{(1)} - n_{-,1}^{(1)}\right)$$

$$\frac{\mathrm{d}^2 n_{+,1}^{(1)}}{\mathrm{d}x^2} = \frac{i\omega}{\delta^2} n_{+,1}^{(1)} - z_+ n_{+,0}\frac{\mathrm{d}^2\phi_1^{(1)}}{\mathrm{d}x^2}$$

$$\frac{\mathrm{d}^2 n_{-,1}^{(1)}}{\mathrm{d}x^2} = \frac{i\omega}{\delta^2\chi} n_{-,1}^{(1)} + z_+\kappa n_{-,0}\frac{\mathrm{d}^2\phi_1^{(1)}}{\mathrm{d}x^2}$$

$\downarrow$ Decouple

$$\frac{\mathrm{d}^2 n_{+,1}^{(1)}}{\mathrm{d}x^2} = \left(\frac{i\omega}{\delta^2} + \frac{z_+}{\delta^2}\right) n_{+,1}^{(1)} - \frac{z_+}{\delta^2} n_{-,1}^{(1)},$$

$$\frac{\mathrm{d}^2 n_{-,1}^{(1)}}{\mathrm{d}x^2} = -\frac{z_+\kappa}{\delta^2} n_{+,1}^{(1)} + \left(\frac{i\omega}{\delta^2\chi} + \frac{z_+\kappa}{\delta^2}\right) n_{-,1}^{(1)}.$$

① $x = 0$ no flux boundary

$$\left.\frac{\mathrm{d}n_{+,1}^{(1)}}{\mathrm{d}x} + z_+ n_{+,0}\frac{\mathrm{d}\phi_1^{(1)}}{\mathrm{d}x}\right|_0 = 0,$$

$$\left.\frac{\mathrm{d}n_{-,1}^{(1)}}{\mathrm{d}x} - z_+\kappa m_{-,0}\frac{\mathrm{d}\phi_1^{(1)}}{\mathrm{d}x}\right|_0 = 0$$

② $x = 1$ free flux boundary

$$n_{+,1}^{(1)}(1) = 0, \quad n_{-,1}^{(1)}(1) = 0,$$

③ Potential

$$\phi_1^{(1)}(0) = -\frac{1}{2i}, \quad \phi_1^{(1)}(1) = 0.$$

$$\phi_1^{(1)} = \int\left[\int \frac{-1}{\delta^2}\left(n_{+,1}^{(1)} - n_{-,1}^{(1)}\right)\mathrm{d}x + c_5\right]\mathrm{d}x + c_6$$

Second Order

$$\frac{\mathrm{d}^2\phi_0^{(2)}}{\mathrm{d}x^2} = -\frac{1}{\delta^2}\left(n_{+,0}^{(2)} - n_{-,0}^{(2)}\right)$$

$$\frac{\mathrm{d}^2 n_{+,0}^{(2)}}{\mathrm{d}x^2} = -z_+ n_{+,0}\frac{\mathrm{d}^2\phi_0^{(2)}}{\mathrm{d}x^2} - z_+\boxed{\frac{\mathrm{d}F_{+,0}^{(2)}}{\mathrm{d}x}}$$

$$\frac{\mathrm{d}^2 n_{-,0}^{(2)}}{\mathrm{d}x^2} = z_+\kappa n_{-,0}\frac{\mathrm{d}^2\phi_0^{(2)}}{\mathrm{d}x^2} + z_+\kappa\boxed{\frac{\mathrm{d}F_{-,0}^{(2)}}{\mathrm{d}x}}$$

$$\frac{\mathrm{d}n_{+,0}^{(2)}}{\mathrm{d}x} + z_+\left(n_{+,0}\frac{\mathrm{d}\phi_0^{(2)}}{\mathrm{d}x} + \boxed{F_{+,0}^{(2)}}\right)\Bigg|_0 = 0,$$

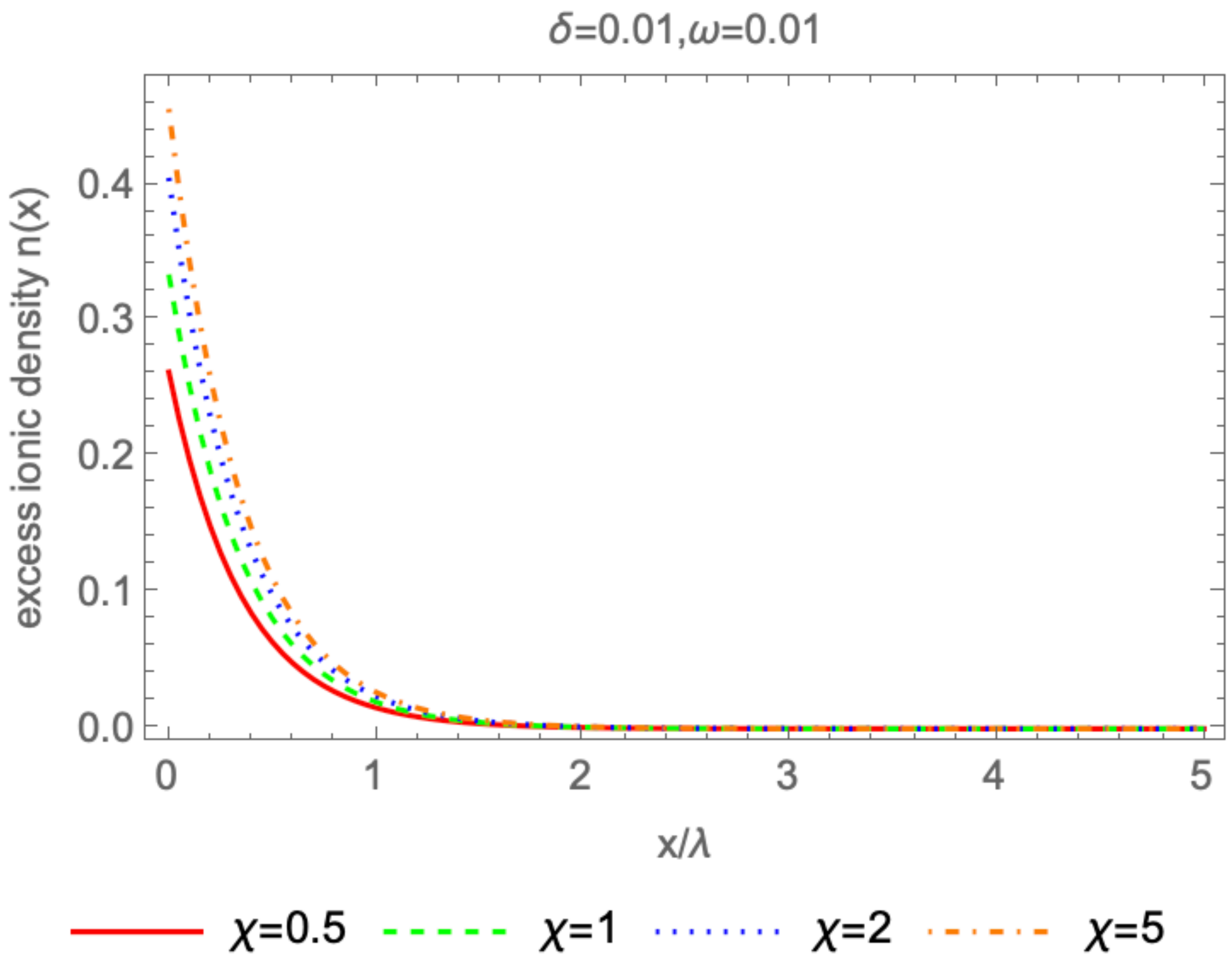
$$\frac{\mathrm{d}n_{-,0}^{(2)}}{\mathrm{d}x} - z_+\kappa\left(n_{-,0}\frac{\mathrm{d}\phi_0^{(2)}}{\mathrm{d}x} + \boxed{F_{-,0}^{(2)}}\right)\Bigg|_0 = 0,$$

$$n_{+,0}^{(2)}(1) = 0, \quad n_{-,0}^{(2)}(1) = 0$$

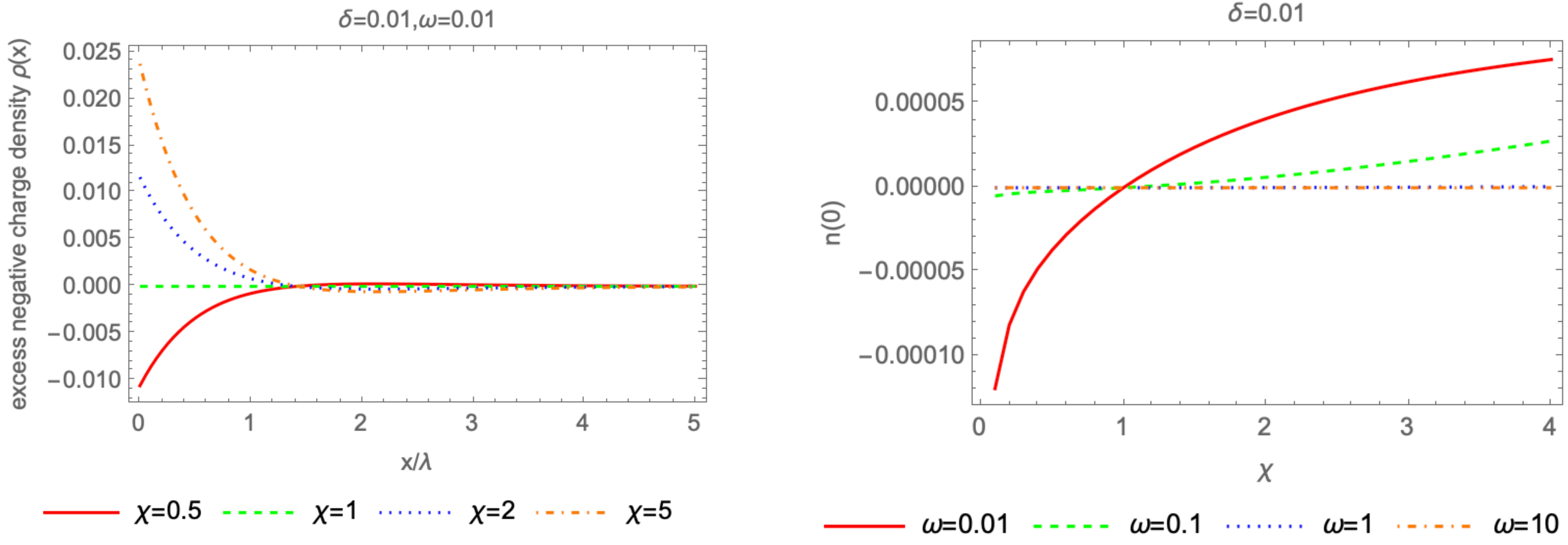
$$\phi_0^{(2)}(0) = 0, \quad \phi_0^{(2)}(1) = 0$$

$$F_{+,0}^{(2)} = n_{+,1}^{(1)}\frac{\mathrm{d}\phi_{-1}^{(1)}}{\mathrm{d}x} + n_{+,-1}^{(1)}\frac{\mathrm{d}\phi_1^{(1)}}{\mathrm{d}x}$$

$$F_{-,0}^{(2)} = n_{-,1}^{(1)}\frac{\mathrm{d}\phi_{-1}^{(1)}}{\mathrm{d}x} + n_{-,-1}^{(1)}\frac{\mathrm{d}\phi_1^{(1)}}{\mathrm{d}x}$$



$\chi = \frac{D_-}{D_+}$ D_σ diffusion constant $n = n^{(2)}_{+,0} + n^{(2)}_{-,0}$



$$\chi = \frac{D_-}{D_+} \qquad \rho = n^{(2)}_{+,0} - n^{(2)}_{-,0} \qquad n = n^{(2)}_{+,0} + n^{(2)}_{-,0}$$

Origin of the force

Stress tensor

$$\mathbf{T} = \mathbf{T}^e + \mathbf{T}^s + \mathbf{T}^m$$

$\mathbf{T}^e$ from the electrostatic field $\quad \mathbf{T}^e = \epsilon \mathbf{E}\mathbf{E} - \frac{\epsilon}{2}\left(1 - \frac{\rho}{\epsilon}\frac{\partial \epsilon}{\partial \rho}\bigg|_T\right) E^2 \mathbf{I}$

$\mathbf{T}^s$ from the presence of the solute particles in the fluid $\quad \mathbf{T}^s = -k_B T n \mathbf{I}$

$\mathbf{T}^m$ from the mechanical pressure and viscous stress $\quad \mathbf{T}^m = -p\mathbf{I}$

In the dielectric liquid the electrostatic part of the stress tensor has the form of the Maxwell stress tensor

$$\mathbf{T}^e = \epsilon \mathbf{E}\mathbf{E} - \frac{\epsilon}{2}\left(1 - \frac{\rho}{\epsilon}\left.\frac{\partial \epsilon}{\partial \rho}\right|_T\right) E^2 \mathbf{I}$$

$\Downarrow$

Assumptions:

1. The fluid flow is incompressible (ρ = const)
2. There is no gradient of the dielectric properties in the system

$$\mathbf{T}^e = \epsilon \mathbf{E}\mathbf{E} - \frac{\epsilon}{2} E^2 \mathbf{I}$$

$\Downarrow$ $\nabla \times \mathbf{E} = 0$

$$\mathbf{f}^e = \rho_e \mathbf{E}$$

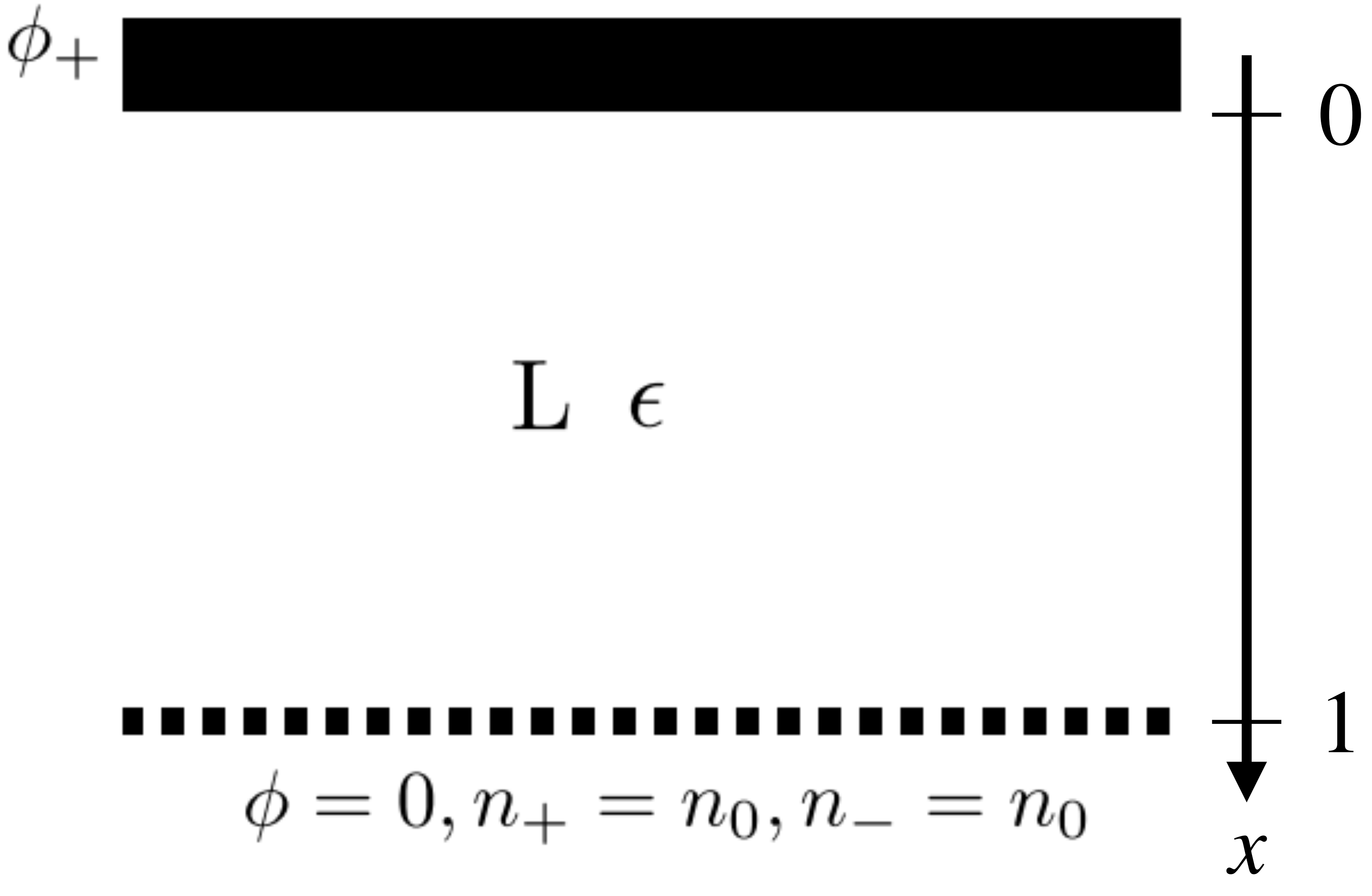
Force balance equation

$$0 = \nabla \cdot (\mathbf{T}^m + \mathbf{T}^e + \mathbf{T}^s) \Longrightarrow 0 = -\nabla p + \rho_e \mathbf{E} - k_B T \nabla n$$

$\Downarrow$ Integral

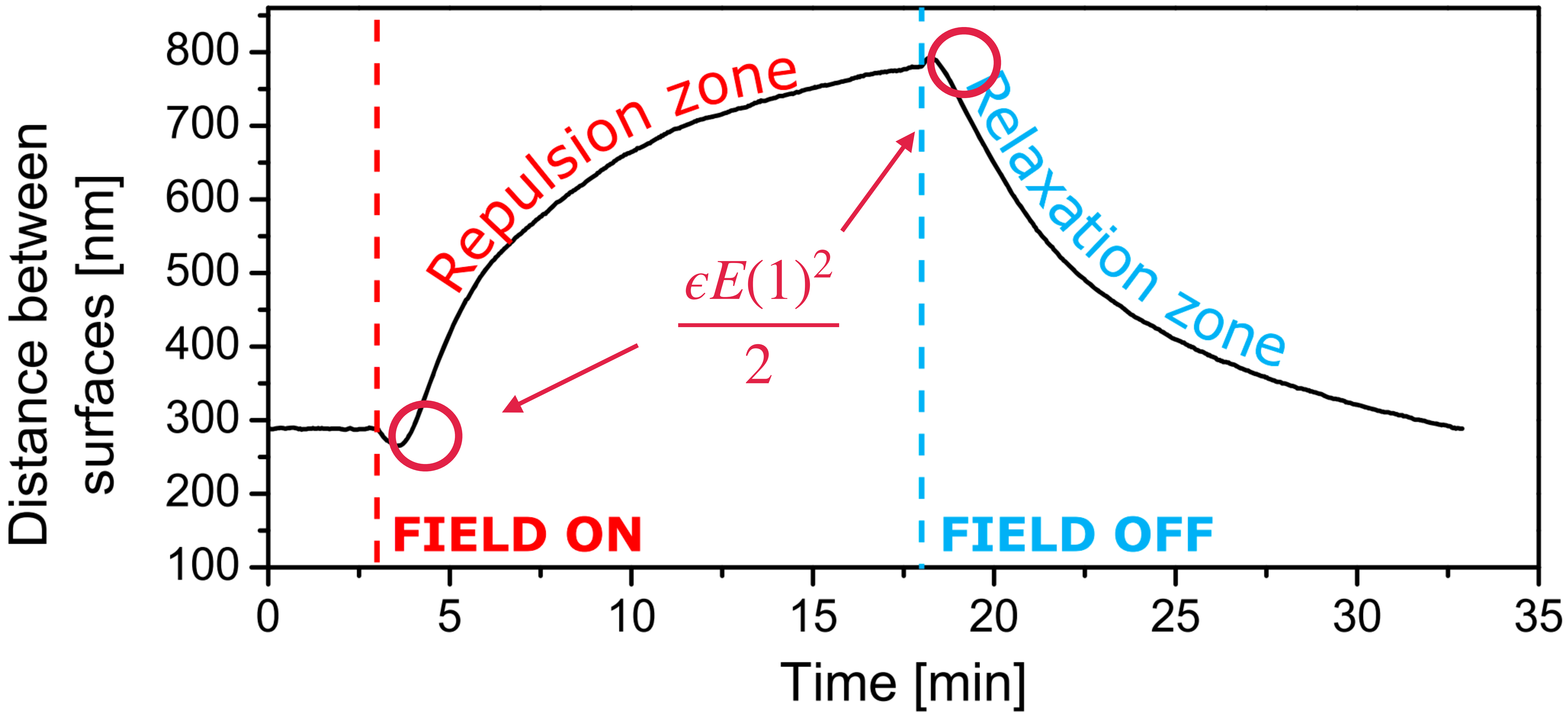
In one dimension

$$p(x_1) - p(x_2) = \left(\frac{\epsilon E(x_1)^2}{2} - k_B T n(x_1) \right) - \left(\frac{\epsilon E(x_2)^2}{2} - k_B T n(x_2) \right)$$



The force acting on the wall

$$\begin{aligned} f &= -\frac{\epsilon E^2(0)}{2} + k_b T n(0) + p(0) \\ &= -\frac{\epsilon E^2(1)}{2} + k_b T n(1) + p(1) \\ &\overset{p(1)=0}{=\!=} -\frac{\epsilon E^2(1)}{2} + k_b T n(1) \end{aligned}$$



$$E^2 = V_0^2 \frac{\mathrm{d}\phi_{+,1}^{(1)}}{\mathrm{d}x} \frac{\mathrm{d}\phi_{-,1}^{(1)}}{\mathrm{d}x} = V_0^2 \left| \frac{\mathrm{d}\phi_{+,1}^{(1)}}{\mathrm{d}x} \right|^2$$

$$n = V_0^2 \left(n_{+,0}^{(2)} + n_{-,0}^{(2)} \right)$$

$$f = -\frac{\epsilon E^2(1)}{2} + k_b T n(1) \propto V_0^2$$

$$\lambda = \sqrt{\frac{\epsilon k_B T}{e^2 z_+^2 n_0}}$$

$$\chi = \frac{D_-}{D_+}$$

$$\delta = \frac{\lambda}{L}$$