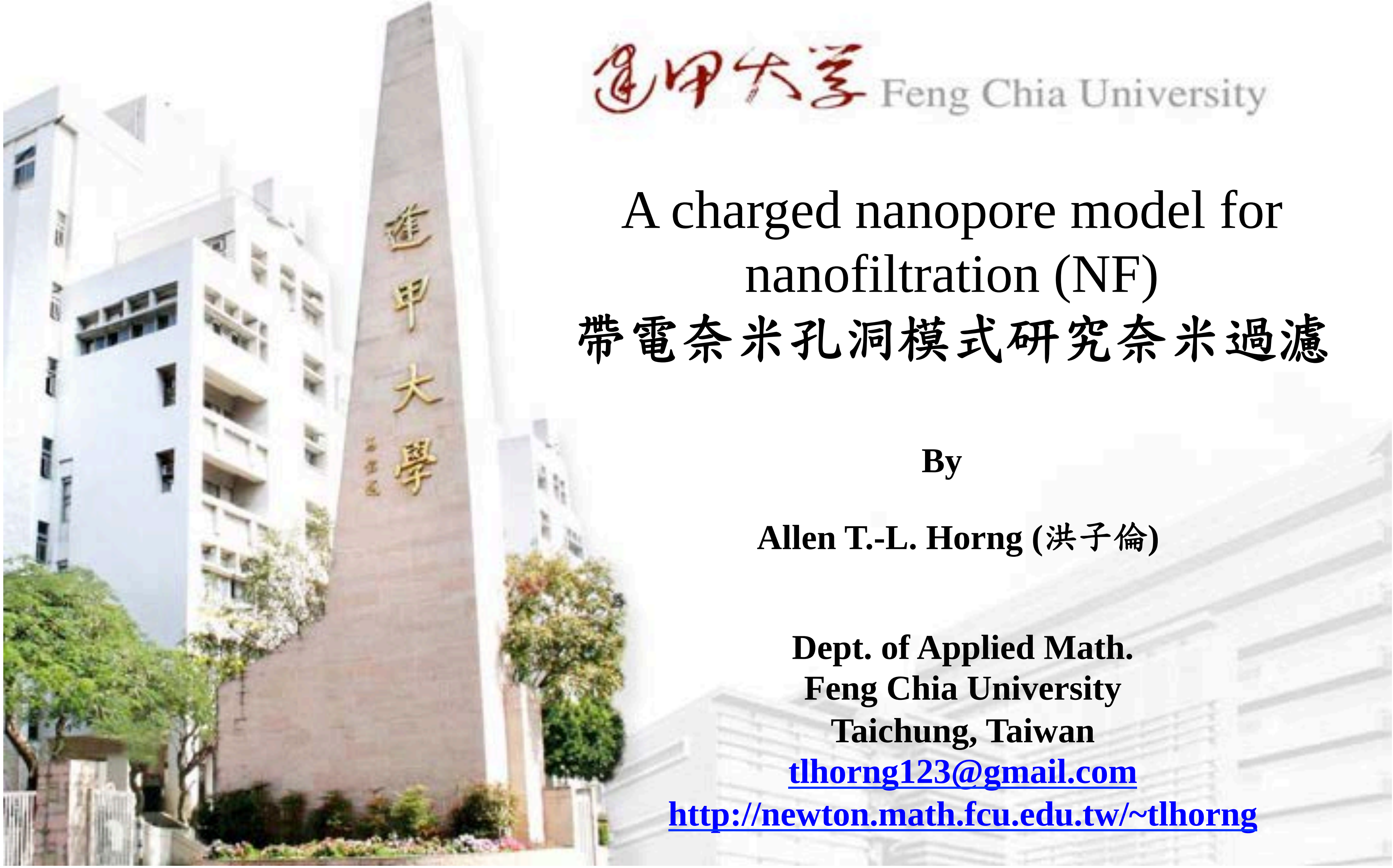


逢甲大學 Feng Chia University

A charged nanopore model for nanofiltration (NF)
帶電奈米孔洞模式研究奈米過濾

By

Allen T.-L. Horng (洪子倫)

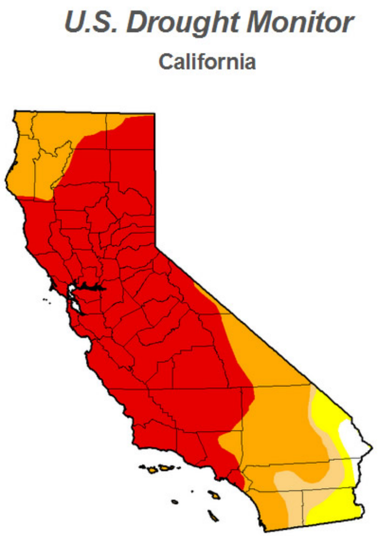
Dept. of Applied Math.
Feng Chia University
Taichung, Taiwan
tlhorng123@gmail.com
http://newton.math.fcu.edu.tw/~tlhorng

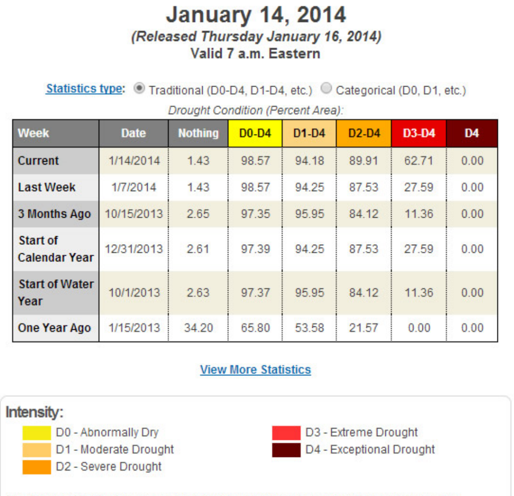
Abstract

Nanofiltration (NF) using membranes with numerous nanopores has gained its popularity in water treatment like desalination. Overlapped electric double layer (EDL) in charged nanopores makes the membrane to be ion selective and reach high rejection rate for salts when driving electrolyte through nanopores by pressure. It has its advantage over reverse osmosis (RO) with smaller pressure exerted and larger water throughput. Here a charged nanopore model under axisymmetric configuration is used to describe the physics and geometry of NF. Since the salt rejection process involves convection, diffusion and electro-migration of ions, joint of Poisson-Nernst-Planck (PNP) and Navier-Stokes (NS) equations, derived from first principle, is employed to study this problem. Steric effect would be significant inside nanopores, and a modified model of PNP with steric effect considered is actually used here. The computational results were compared with traditional 1D DSPM-DE model (Donnan Steric Pore Model-Dielectric Exclusion), and the agreement is quite satisfactory with the parameter describing steric effect being the only fitting parameter. From the results of our current model, both steric effect and dielectric exclusion contribute significantly to the salt rejection, and the detailed mechanism can be well observed and explained.

Keywords: Desalination, Nanofiltration, Electric Double Layer, Poisson-Nernst-Planck Equations, Navier-Stokes Equations, Steric effect

美國加州乾旱 (California mega-drought)…





January 14, 2014

(Released Thursday January 16, 2014)

Valid 7 a.m. Eastern

Statistics type: ● Traditional (D0-D4, D1-D4, etc.) ○ Categorical (D0, D1, etc.)

Drought Condition (Percent Area):

Week	Date	Nothing	D0-D4	D1-D4	D2-D4	D3-D4	D4
Current	1/14/2014	1.43	98.57	94.18	89.91	62.71	0.00
Last Week	1/7/2014	1.43	98.57	94.25	87.53	27.59	0.00
3 Months Ago	10/15/2013	2.65	97.35	95.95	84.12	11.36	0.00
Start of Calendar Year	12/31/2013	2.61	97.39	94.25	87.53	27.59	0.00
Start of Water Year	10/1/2013	2.63	97.37	95.95	84.12	11.36	0.00
One Year Ago	1/15/2013	34.20	65.80	53.58	21.57	0.00	0.00

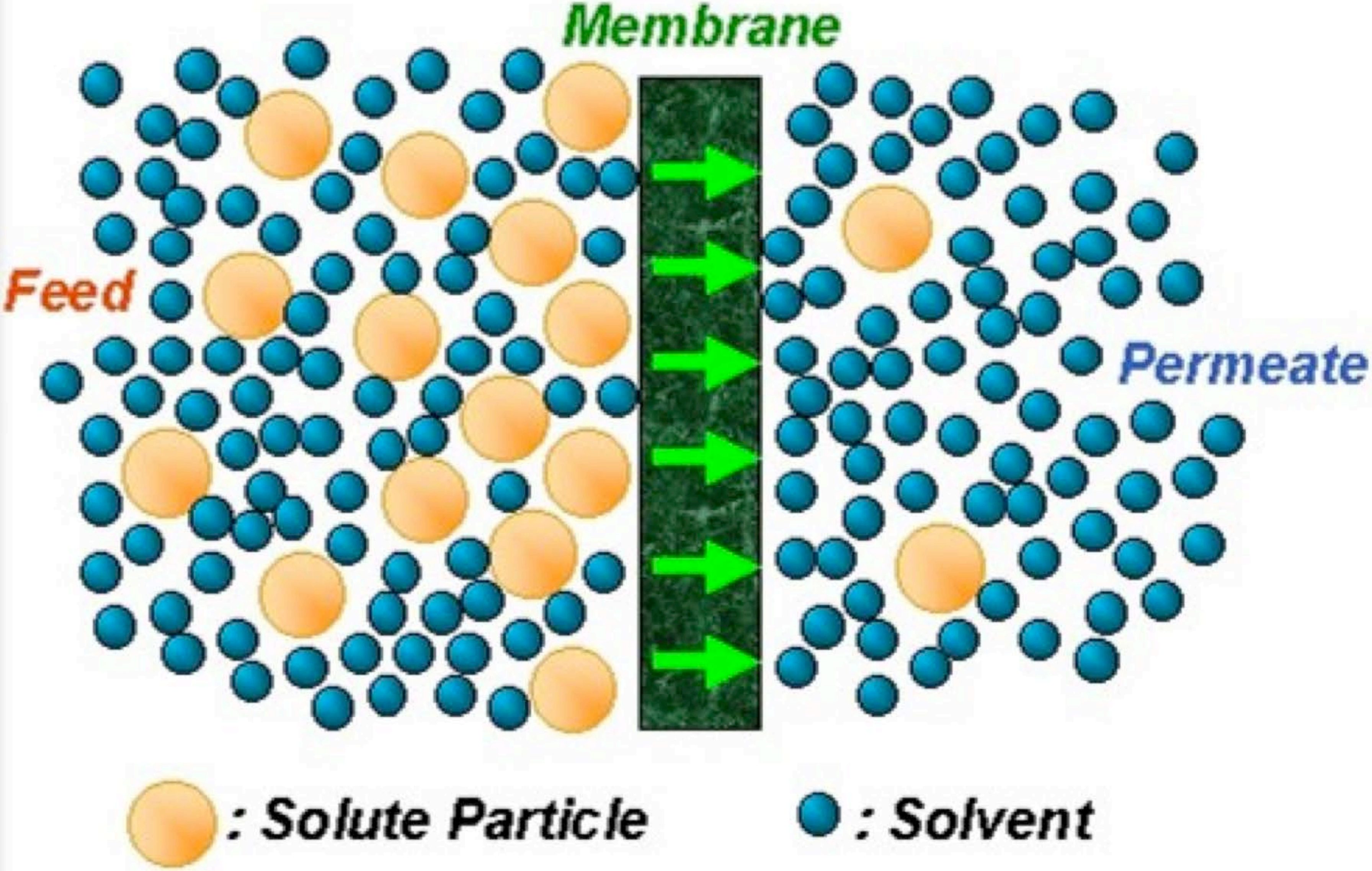
View More Statistics

Intensity:

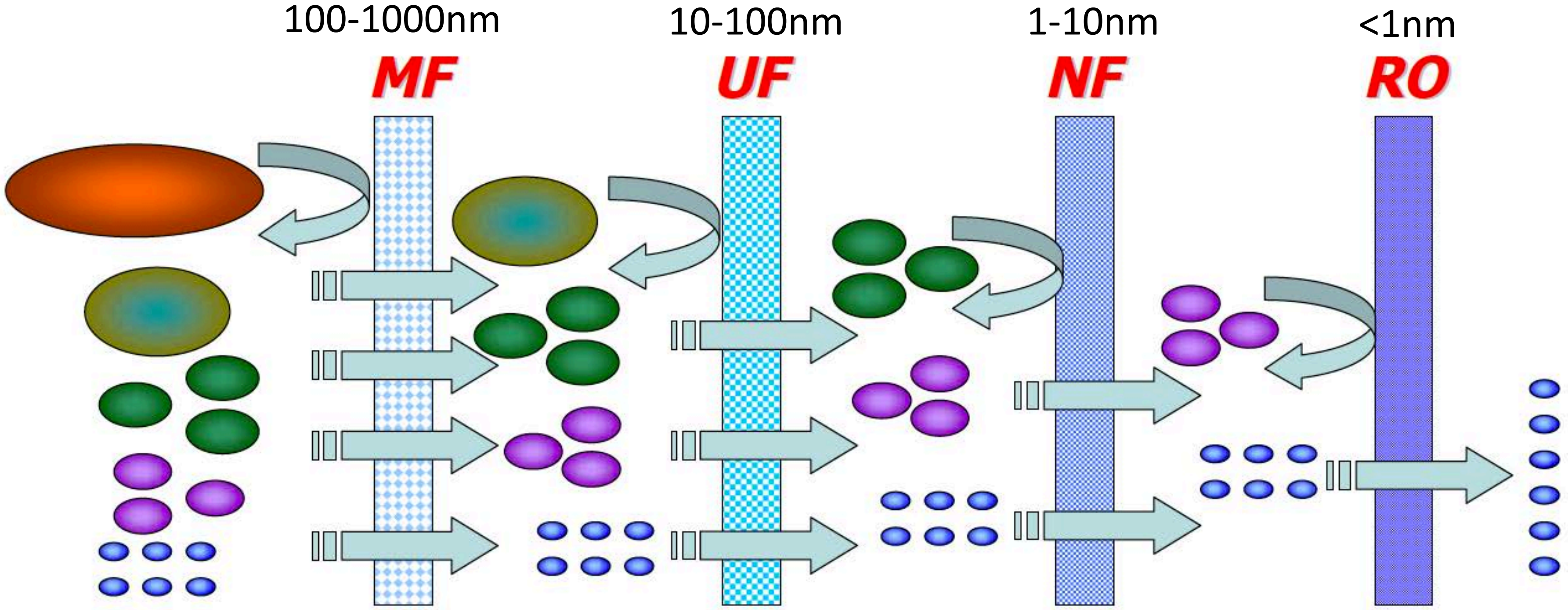
🟨 D0 - Abnormally Dry	🟥 D3 - Extreme Drought
🟧 D1 - Moderate Drought	🟥 D4 - Exceptional Drought
🟧 D2 - Severe Drought	

The Drought Monitor focuses on broad-scale conditions. Local conditions may vary. See accompanying text summary for forecast statements.

Membrane Separation

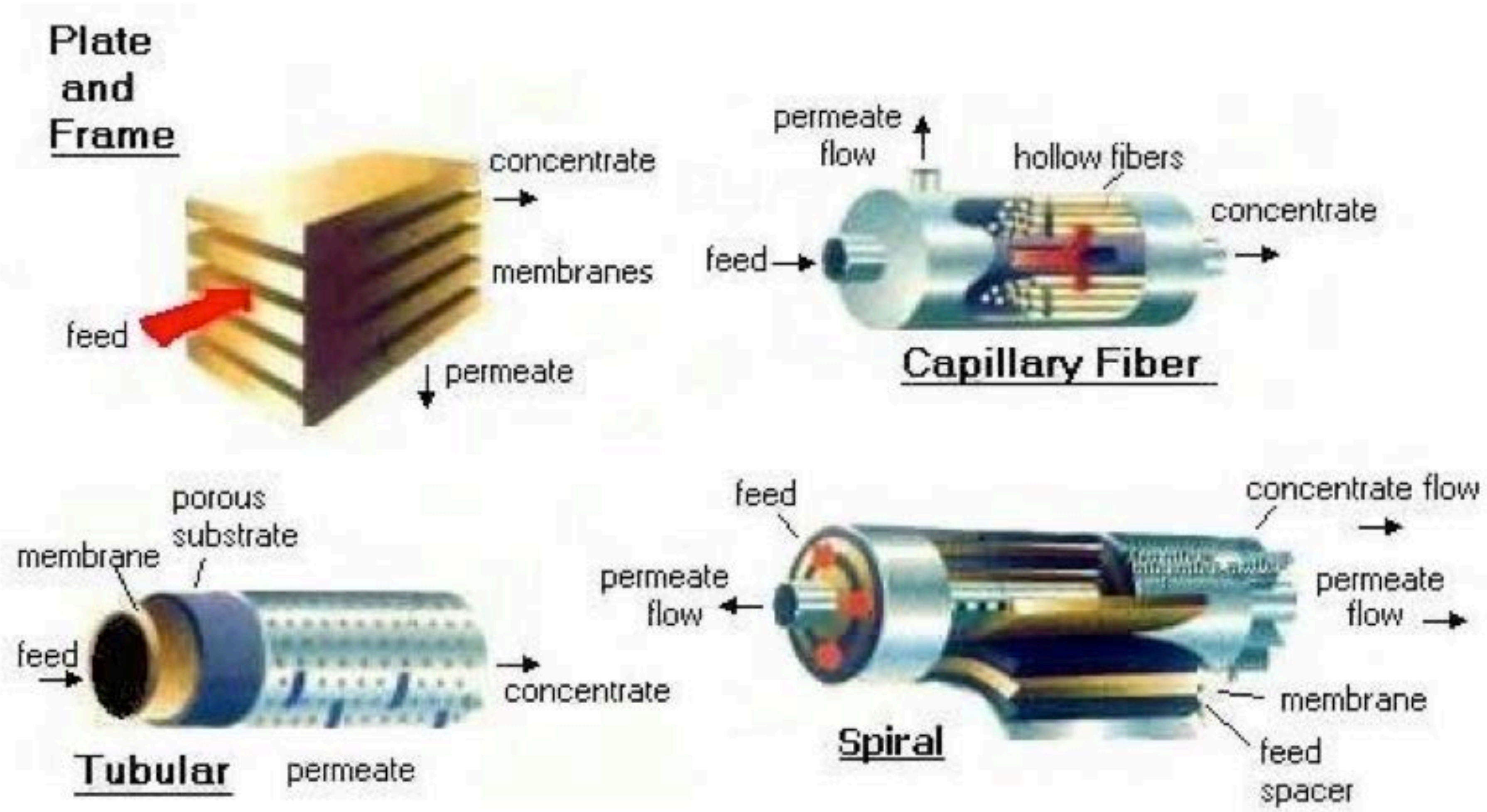


Pressure-Driven Membrane Processes

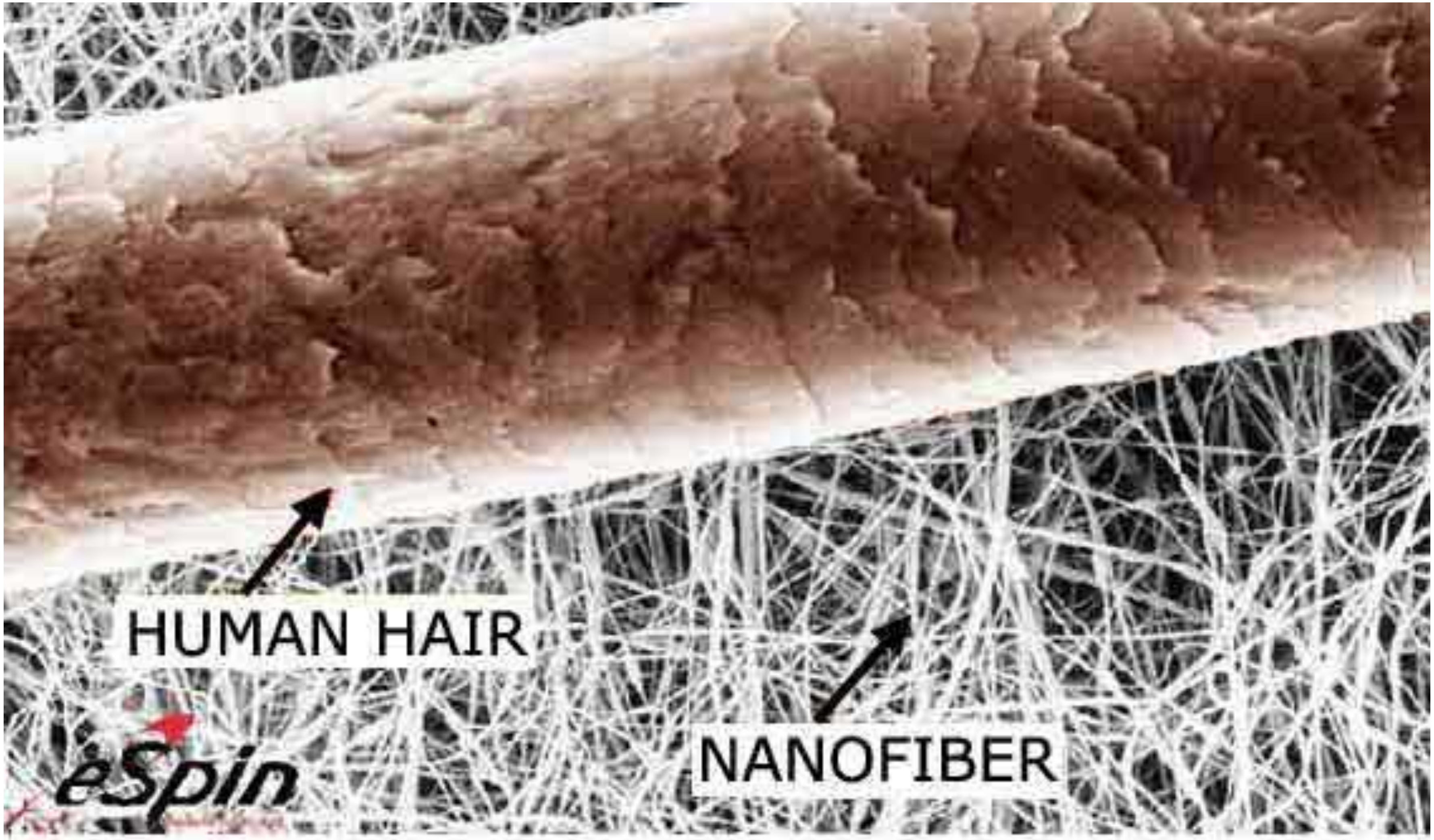


- ● *Suspended Solids (Particles)*
- ● *Macromolecules (Humics)*
- ● *Multivalent Ions (Hardness)*
- ● *Monovalent Ions (Na^+,Cl^-)*
- ●●● *Water Molecules*

Membrane Devices

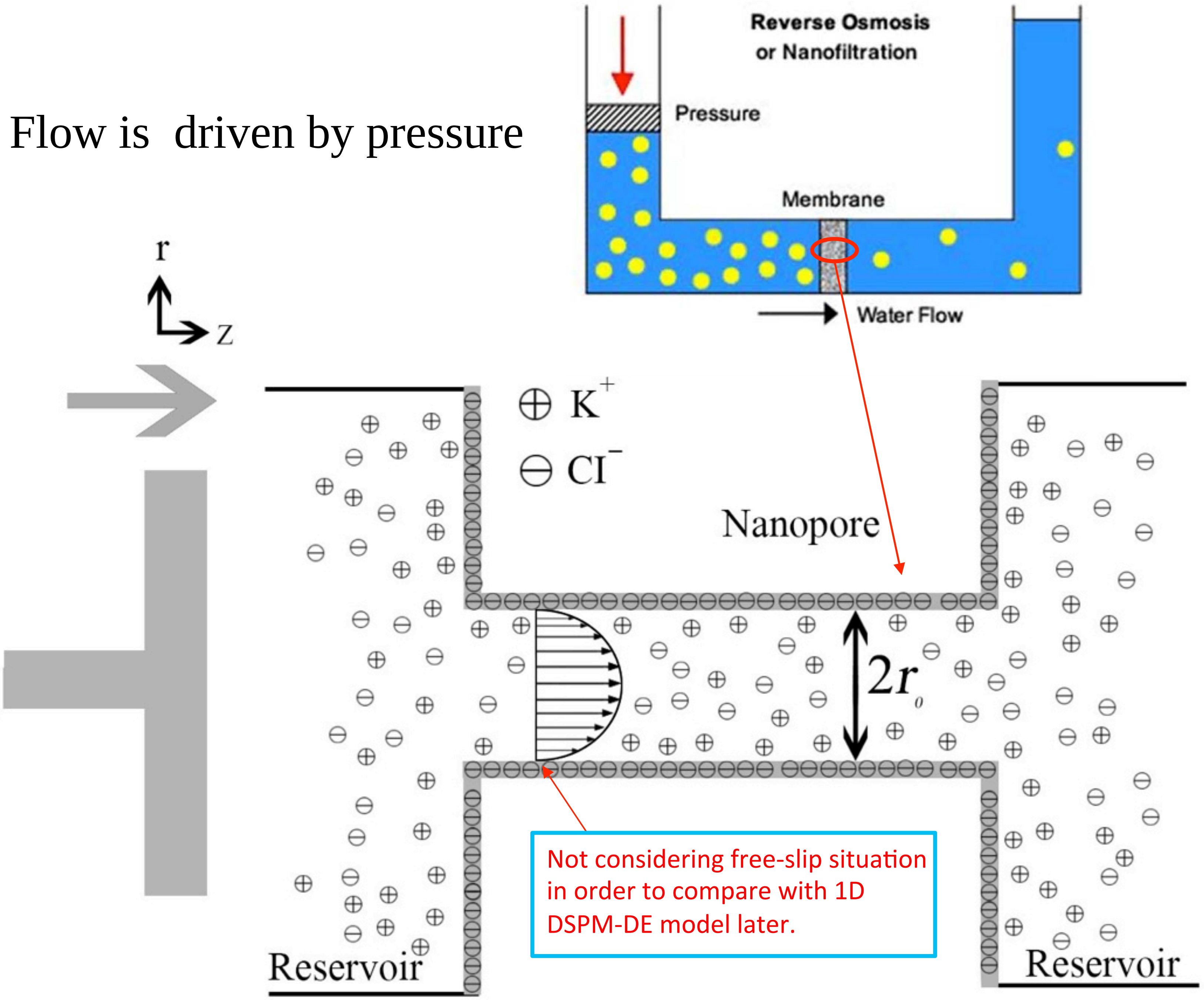


NF membrane



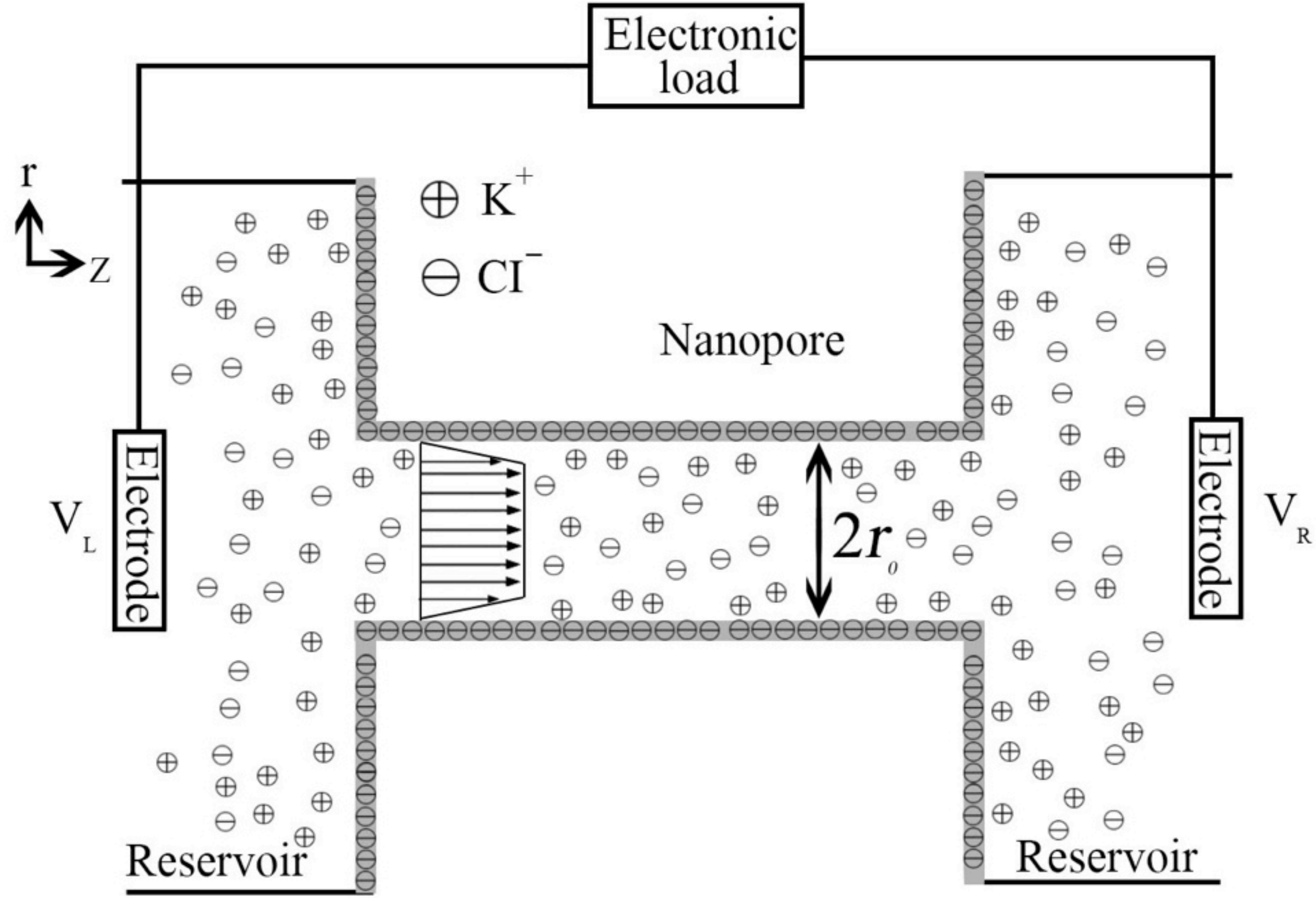
Courtesy of eSpin Technologies

Flow is driven by pressure



Not considering free-slip situation in order to compare with 1D DSPM-DE model later.

If driven by electric potential, will be electroosmotic flow (EOF.)



However, the sizes of ions are smaller than a nanopore. How does a nanopore sieve ions? The answer is by electrostatics (overlapping electric double layer).

Mathematical model: PNP-steric and Navier-Stokes equations in axisymmetric coordinate

Poisson-Nernst Planck equations with steric force terms (PNP-steric)

$$-\nabla\cdot(\varepsilon\nabla\phi) = \rho_0 e + \sum_{i=1}^{N} z_i e c_i,$$

$$\frac{\partial c_i}{\partial t} + \nabla\cdot\vec{J}_i = 0,$$

concentration-modulated cross diffusion

$$\vec{J}_i = \vec{u}c_i - D_i\nabla c_i - \frac{D_i c_i}{k_B T} z_i e\nabla\phi - \frac{D_i c_i}{k_B T}\sum_{j=1}^{N} g_{ij}\nabla c_j,\ \ i = 1,\cdots,N,$$

based on variation of free energy:

kinetic energy entropy electric energy steric energy

$$E_\delta = \int\left(\frac{\rho}{2}|\vec{u}|^2 + k_B T\sum_{i=1}^{N} c_i\log c_i + \tfrac{1}{2}\left(\rho_0 e + \sum_{i=1}^{N} z_i e c_i\right)\phi\right)d\vec{x} + \sum_{i,j=1}^{N} g_{ij}\int c_i(\vec{x})c_j(\vec{x})d\vec{x},$$

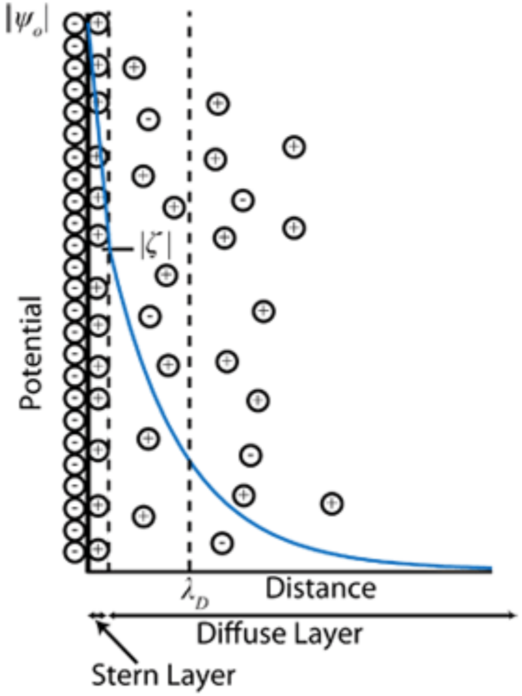
T.-L. Horng, T.-C. Lin, C. Liu and B. Eisenberg*, 2012, "PNP equations with steric effects: a model of ion flow through channels", Journal of Physical Chemistry B, 116: 11422-11441

Non-dimensionalization:

$$\tilde{c} = \frac{c_i}{c_0},\quad \tilde{\rho}_0 = \frac{\rho_0}{c_0},\quad \tilde{\phi} = \frac{\phi}{k_B T / e},\quad \tilde{s} = \frac{s}{L},\quad \tilde{t} = \frac{t}{L^2 / D_K},\quad \tilde{D}_i = \frac{D_i}{D_K},\quad \tilde{g}_{ij} = \frac{g_{ij}}{k_B T / c_0},$$

$$\tilde{\vec{J}}_i = \frac{\vec{J}_i}{c_0 D_K / L},\quad \tilde{I} = \frac{I}{c_0 D_K L},\quad \tilde{\vec{u}} = \frac{\vec{u}}{D_K / L}.$$

and obtain:



$$-\Gamma \nabla^2 \phi = \rho_0 + \sum_{i=1}^{N} z_i c_i,$$

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \vec{J}_i = 0,$$

$$\vec{J}_i = \vec{u} c_i - D_i \left(\nabla c_i - c_i z_i \nabla \phi - c_i \sum_{j=1}^{N} g_{ij} \nabla c_j \right),\ i = 1, \cdots, N,$$

where $\Gamma = \dfrac{\lambda_D^2}{L^2}$, and the Debye length $\lambda_D = \sqrt{\dfrac{\varepsilon k_B T}{c_0 e^2}}$.

Considering axisymmetric nanopore with binary electrolyte:

$$-\Gamma\left(\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial\phi}{\partial r}+\frac{\partial^2\phi}{\partial z^2}\right)=\rho_0+\sum_{i=1}^{N}z_i c_i,$$

$$\frac{\partial c_i}{\partial t}+\frac{1}{r}\frac{\partial\left(rJ_{i,r}\right)}{\partial r}+\frac{\partial J_{i,z}}{\partial z}=0,$$

$$J_{i,r}=u_r c_i-D_i\left(\frac{\partial c_i}{\partial r}+c_i z_i\frac{\partial\phi}{\partial r}+c_i\sum_{j=1}^{N}g_{ij}\frac{\partial c_j}{\partial r}\right),\qquad i=p,n,$$

$$J_{i,z}=u_z c_i-D_i\left(\frac{\partial c_i}{\partial z}+c_i z_i\frac{\partial\phi}{\partial z}+c_i\sum_{j=1}^{N}g_{ij}\frac{\partial c_j}{\partial z}\right),\qquad i=p,n.$$

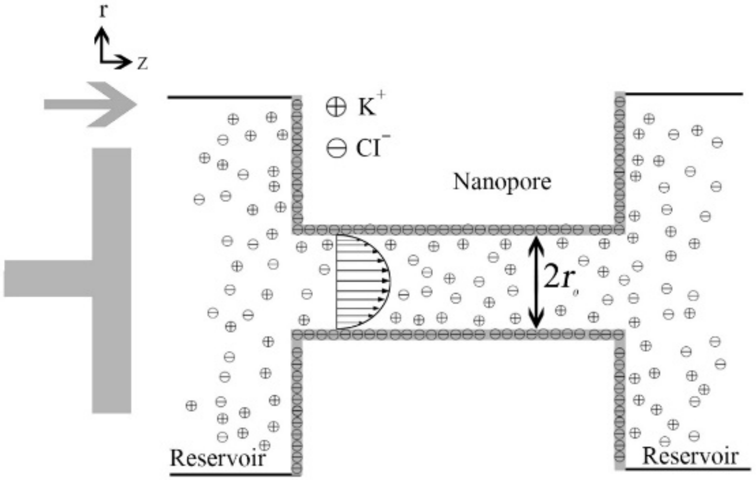
Upstream/downstream boundary conditions at reservoirs:

$$\phi = \phi_L, \ \text{ as } \ z \to -\infty; \quad \frac{\partial \phi}{\partial z} = 0, \ \text{ as } \ z \to \infty,$$

$$p = p_L, \ \text{ as } \ z \to -\infty; \quad \frac{\partial p}{\partial z} = 0, \ \text{ as } \ z \to \infty,$$

$$n = n_L, \ \text{ as } \ z \to -\infty; \quad \frac{\partial n}{\partial z} = 0, \ \text{ as } \ z \to \infty.$$

$$z_p p + z_n n = 0, \quad |z| \to \infty,$$



Boundary conditions at wall:

$$\Gamma \frac{\partial \phi}{\partial n} = \sigma, \qquad \vec{J}_p \cdot \vec{n} = \vec{J}_n \cdot \vec{n} = 0,$$

Symmetric boundary conditions at r=0 and $r_{\max}$:

$$\frac{\partial \phi}{\partial r} = \frac{\partial p}{\partial r} = \frac{\partial n}{\partial r} = 0.$$

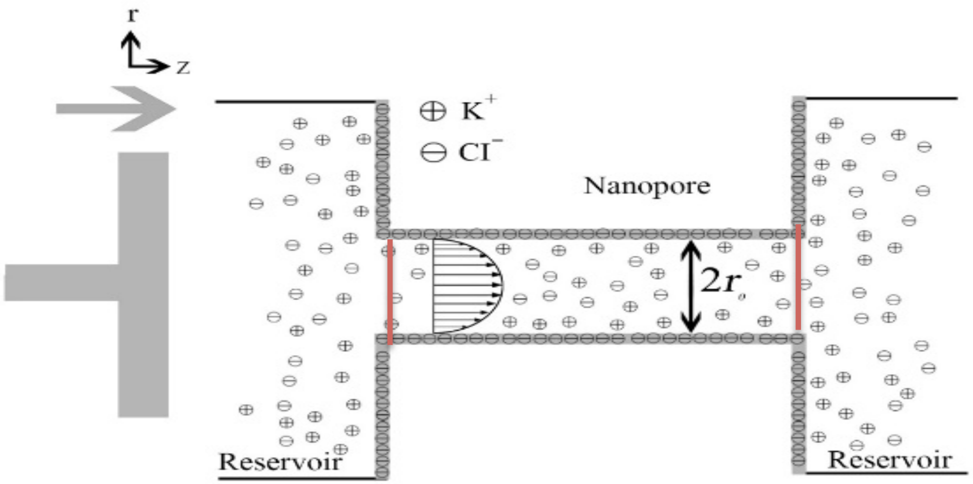
Interface (between pore and reservoirs denoted as red lines) conditions:

$$\phi_{bulk} = \phi_{pore}, \quad \left(\Gamma \frac{\partial \phi}{\partial z}\right)_{bulk} = \left(\Gamma \frac{\partial \phi}{\partial z}\right)_{pore},$$

a jump in concentration

$$\left(\vec{J}_i \cdot \vec{n}\right)_{bulk} = \left(\vec{J}_i \cdot \vec{n}\right)_{pore}, \quad \frac{c_{i,pore}}{c_{i,bulk}} = \exp\left(-\frac{\Delta E_{i,steric}}{k_B T}\right)\exp\left(-\frac{\Delta E_{i,solvation}}{k_B T}\right),$$

$$\frac{E_{i,steric}}{k_B T} = \sum_{j=1}^{N} g_{ij} c_i c_j, \quad \Delta E_{i,solvation} = \frac{z_i^2 e^2}{8\pi\varepsilon_o r_i}\left[\frac{1}{\varepsilon_{pore}} - \frac{1}{\varepsilon_{bulk}}\right] \quad \text{(Born model)}$$



$$J_i = -D_i \frac{\partial c_i}{\partial x} - \frac{D_i e}{k_B T} z_i c_i \frac{\partial \phi}{\partial x} - D_i \sum_j g_{ij} c_i \frac{\partial c_j}{\partial x} - \frac{D_i}{k_B T} c_i \frac{\partial E_{i,solvation}}{\partial x} + \frac{\partial \varphi}{\partial x} c_i,$$

where φ is velocity potential, $u = \frac{\partial \varphi}{\partial x}$.

$$\frac{J_i}{D_i c_i} = -\frac{1}{c_i}\frac{\partial c_i}{\partial x} - \frac{e z_i}{k_B T}\frac{\partial \phi}{\partial x} - \sum_j g_{ij} \frac{\partial c_j}{\partial x} - \frac{1}{k_B T}\frac{\partial E_{i,solvation}}{\partial x} + \frac{1}{D_i}\frac{\partial \varphi}{\partial x}$$

$$= -\frac{\partial}{\partial x}\left[\ln c_i + \frac{z_i \phi e}{k_B T} + \sum_j g_{ij} c_j + \frac{E_{i,solvation}}{k_B T} - \frac{\varphi}{D_i} \right] \qquad (1)$$

Assume interface is at $x = 0$. From continuity of flux, $J_i(0^-) = J_i(0^+)$.

Integrate (1) from -ε to ε, and let $\varepsilon \to 0$,

$$\text{LHS} = \lim_{\varepsilon\to 0}\int_{-\varepsilon}^{\varepsilon} \frac{J_i}{D_i c_i} dx \approx \lim_{\varepsilon\to 0}\left(\frac{J_i(0^+)\varepsilon}{D_i(0^+)c_i(0^+)} + \frac{J_i(0^-)\varepsilon}{D_i(0^-)c_i(0^-)} \right) = 0, \qquad (2)$$

$$\text{RHS} = -\left[\ln\frac{c_i(0^+)}{c_i(0^-)} + \sum_j \left[g_{ij}(0^+)c_j(0^+) - g_{ij}(0^-)c_j(0^-) \right] + \frac{\Delta E_{i,solvation}}{k_B T} - \left(\frac{\varphi(0^+)}{D_i(0^+)} - \frac{\varphi(0^-)}{D_i(0^-)} \right) \right], \qquad (3)$$

Without loss of generality, we can assume $\varphi(0^+) = \varphi(0^-) = \varphi(0) = 0,$ (2) and (3) become

$$\ln\frac{c_i(0^+)}{c_i(0^-)} = -\left[\sum_j \left[g_{ij}(0^+)c_j(0^+) - g_{ij}(0^-)c_j(0^-) \right] + \frac{\Delta E_{i,solvation}}{k_B T} \right] \quad \text{or}$$

$$\frac{c_i(0^+)}{c_i(0^-)} = \exp\left(-\sum_j \left[g_{ij}(0^+)c_j(0^+) - g_{ij}(0^-)c_j(0^-) \right] \right) \exp\left(-\frac{\Delta E_{i,solvation}}{k_B T} \right) = \exp\left(-\frac{\Delta E_{i,steric}}{k_B T} \right) \exp\left(-\frac{\Delta E_{solvation}}{k_B T} \right).$$

Navier-Stokes equations:

$$\vec{u} = u_r \vec{e}_r + u_z \vec{e}_z,$$

$$\frac{\partial u_z}{\partial z} + \frac{\partial u_r}{\partial r} + \frac{u_r}{r} = 0,$$

$$\frac{\partial u_z}{\partial t} + u_z \frac{\partial u_z}{\partial z} + u_r \frac{\partial u_z}{\partial r} = -\frac{1}{\rho}\frac{\partial p}{\partial z} + \nu\left(\frac{\partial^2 u_z}{\partial z^2} + \frac{\partial^2 u_z}{\partial r^2} + \frac{1}{r}\frac{\partial u_z}{\partial r}\right) + F_z,$$

$$\frac{\partial u_r}{\partial t} + u_z \frac{\partial u_r}{\partial z} + u_r \frac{\partial u_r}{\partial r} = -\frac{1}{\rho}\frac{\partial p}{\partial r} + \nu\left(\frac{\partial^2 u_r}{\partial z^2} + \frac{\partial^2 u_r}{\partial r^2} + \frac{1}{r}\frac{\partial u_r}{\partial r} - \frac{u_r}{r^2}\right) + F_r,$$

$$F_z = -\frac{\rho_e}{\rho}\frac{\partial \phi}{\partial z}, \quad F_r = -\frac{\rho_e}{\rho}\frac{\partial \phi}{\partial r},$$

$$\rho_e = \sum_i z_i c_i e$$

Non-dimensionalization:

$$\boxed{U_{ref} = \frac{D_K}{L}}, \quad \tilde{p} = \frac{p}{\rho U_{ref}^2}, \quad \tilde{u}_i = \frac{u_i}{U_{ref}}, \quad \tilde{r} = \frac{r}{L}, \quad \tilde{z} = \frac{z}{L}, \quad \tilde{t} = \frac{t}{\boxed{L^2 / D_K}}.$$

$$\frac{\partial u_z}{\partial z} + \frac{\partial u_r}{\partial r} + \frac{u_r}{r} = 0,$$

$$\frac{\partial u_z}{\partial t} + u_z \frac{\partial u_z}{\partial z} + u_r \frac{\partial u_z}{\partial r} = -\frac{\partial p}{\partial z} + Sc\left(\frac{\partial^2 u_z}{\partial z^2} + \frac{\partial^2 u_z}{\partial r^2} + \frac{1}{r}\frac{\partial u_z}{\partial r}\right) - G_x\left(\sum_i z_i c_i\right)\frac{\partial \phi}{\partial z},$$

$$\frac{\partial u_r}{\partial t} + u_z \frac{\partial u_r}{\partial z} + u_r \frac{\partial u_r}{\partial r} = -\frac{\partial p}{\partial r} + Sc\left(\frac{\partial^2 u_r}{\partial z^2} + \frac{\partial^2 u_r}{\partial r^2} + \frac{1}{r}\frac{\partial u_r}{\partial r} - \frac{u_r}{r^2}\right) - G_x\left(\sum_i z_i c_i\right)\frac{\partial \phi}{\partial r},$$

$$\boxed{Sc = \frac{\nu}{D_K} = 446,}$$

$$G_x = \frac{c_0 k_B T}{\rho U_{ref}^2},$$

Vorticity transport equation:

$$\vec{\omega} = \nabla \times \vec{u} = \vec{e}_\theta \left(\frac{\partial u_r}{\partial z} - \frac{\partial u_z}{\partial r} \right) = \vec{e}_\theta \omega,$$

$$\frac{\partial \omega}{\partial t} + u_z \frac{\partial \omega}{\partial z} + u_r \frac{\partial \omega}{\partial r} - \frac{u_r \omega}{r} = Sc \left(\frac{\partial^2 \omega}{\partial z^2} + \frac{\partial^2 \omega}{\partial r^2} + \frac{1}{r} \frac{\partial \omega}{\partial r} - \frac{\omega}{r^2} \right) - G_x \left(\sum_i z_i \frac{\partial c_i}{\partial z} \right) \frac{\partial \phi}{\partial r}$$

$$+ G_x \left(\sum_i z_i \frac{\partial c_i}{\partial r} \right) \frac{\partial \phi}{\partial z}.$$

Stokes stream function:

$$u_z = \frac{1}{r} \frac{\partial \Psi}{\partial r}, \; u_r = -\frac{1}{r} \frac{\partial \Psi}{\partial z},$$

$$\frac{\partial E^2 \Psi}{\partial t} + \frac{1}{r} \frac{\partial \Psi}{\partial z} \frac{\partial E^2 \Psi}{\partial r} - \frac{1}{r} \frac{\partial \Psi}{\partial r} \frac{\partial E^2 \Psi}{\partial z} + \frac{2}{r^2} \frac{\partial \Psi}{\partial z} E^2 \Psi = Sc E^4 \Psi$$

$$+ r G_x \left(\sum_i z_i \frac{\partial c_i}{\partial z} \right) \frac{\partial \phi}{\partial r} - r G_x \left(\sum_i z_i \frac{\partial c_i}{\partial r} \right) \frac{\partial \phi}{\partial z},$$

$$E^2 = \frac{\partial^2}{\partial r^2} - \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}, \qquad \omega = -\frac{1}{r} E^2 \Psi.$$

Boundary conditions:

$$u_z = U_0, \quad u_r = 0, \text{ as } |z| \to \infty,$$

$$u_z = u_r = 0, \text{ at wall,}$$

$$\frac{\partial u_z}{\partial r} = u_r = 0, \text{ at } r = 0, \; r_{\max}.$$

$$\Psi = \frac{1}{2}U_0 r^2, \quad \Psi_z = 0, \quad \text{as } |z| \to \infty,$$

$$\Psi = \frac{1}{2}U_0 r_{\max}^2, \quad \frac{\partial \Psi}{\partial n} = 0, \quad \text{at wall,}$$

$$\Psi = 0, \quad \frac{\partial \Psi}{\partial r} = 0, \quad \text{at } r = 0,$$

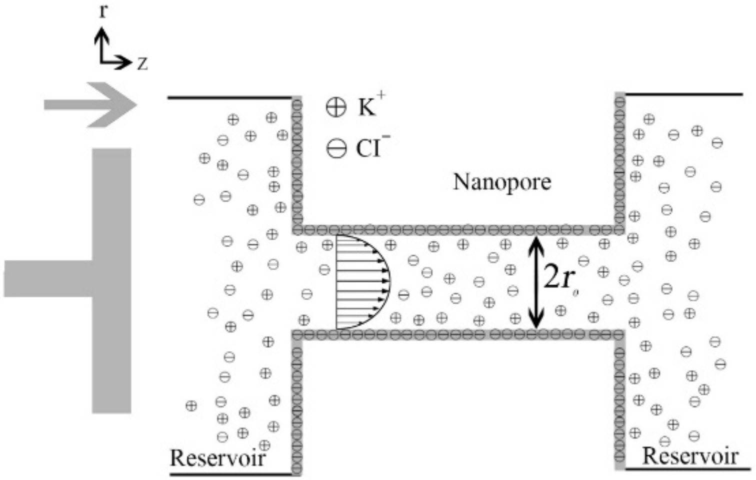
$$\Psi = \frac{1}{2}U_0 r_{\max}^2, \quad \frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial \Psi}{\partial r}\right) = 0, \quad \text{at } r = r_{\max}.$$

Decoupling of PNP-Steric and Navier-Stokes equations:

$$p = \bar{p} + \hat{p},$$

$$0 = -\frac{\partial \hat{p}}{\partial z} - G_x \left(\sum_i z_i c_i \right) \frac{\partial \phi}{\partial z},$$

$$0 = -\frac{\partial \hat{p}}{\partial r} - G_x \left(\sum_i z_i c_i \right) \frac{\partial \phi}{\partial r},$$



$$\frac{\partial u_z}{\partial t} + u_z \frac{\partial u_z}{\partial z} + u_r \frac{\partial u_z}{\partial r} = -\frac{\partial \bar{p}}{\partial z} + Sc \left(\frac{\partial^2 u_z}{\partial z^2} + \frac{\partial^2 u_z}{\partial r^2} + \frac{1}{r} \frac{\partial u_z}{\partial r} \right),$$

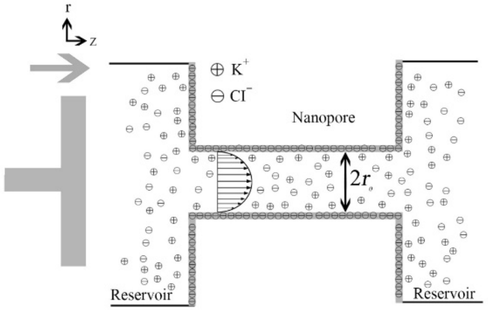
$$\frac{\partial u_r}{\partial t} + u_z \frac{\partial u_r}{\partial z} + u_r \frac{\partial u_r}{\partial r} = -\frac{\partial \bar{p}}{\partial r} + Sc \left(\frac{\partial^2 u_r}{\partial z^2} + \frac{\partial^2 u_r}{\partial r^2} + \frac{1}{r} \frac{\partial u_r}{\partial r} - \frac{u_r}{r^2} \right).$$

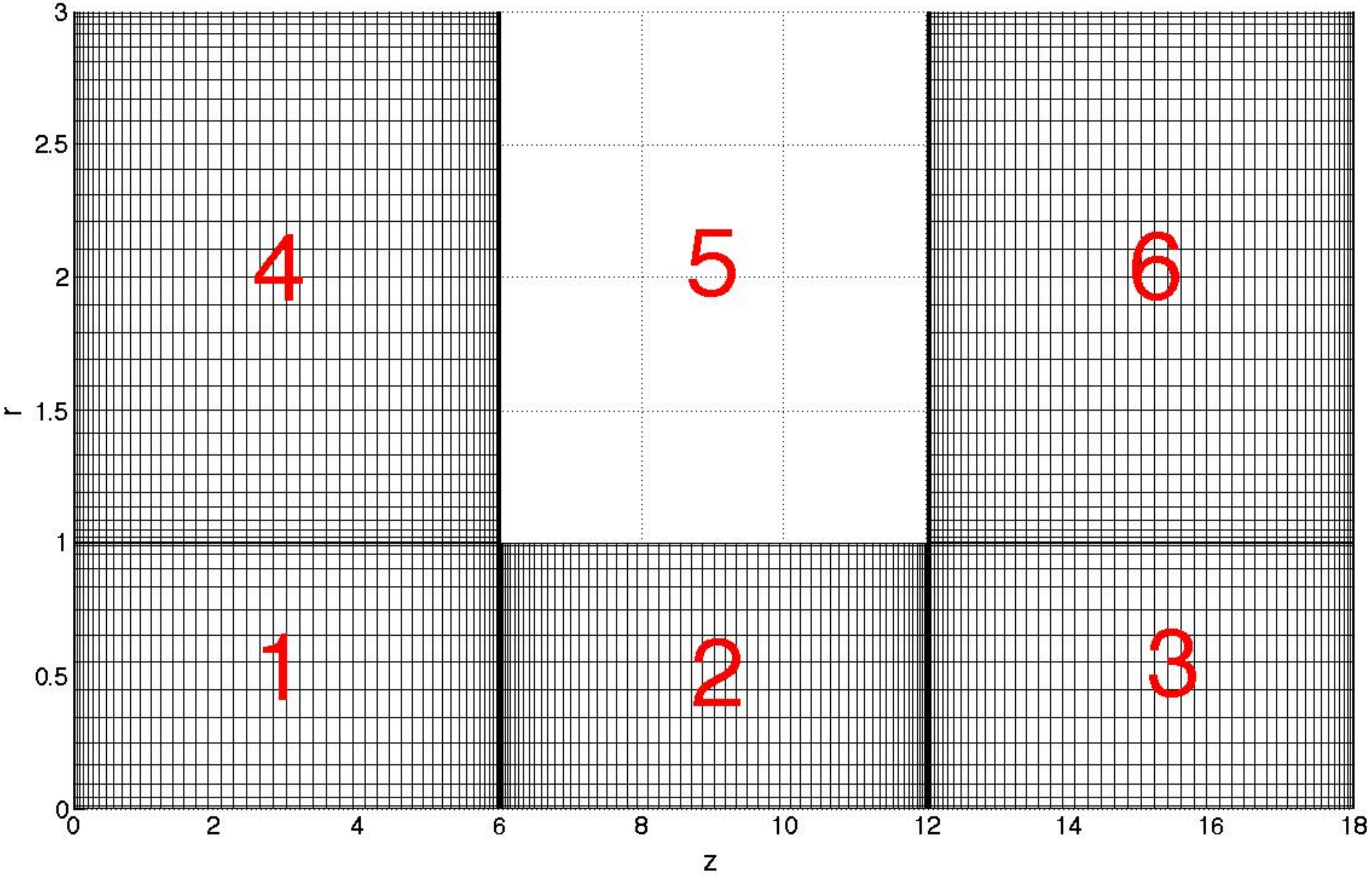
$$\frac{\partial E^2 \Psi}{\partial t} + \frac{1}{r} \frac{\partial \Psi}{\partial z} \frac{\partial E^2 \Psi}{\partial r} - \frac{1}{r} \frac{\partial \Psi}{\partial r} \frac{\partial E^2 \Psi}{\partial z} + \frac{2}{r^2} \frac{\partial \Psi}{\partial z} E^2 \Psi = Sc E^4 \Psi.$$

Numerical method

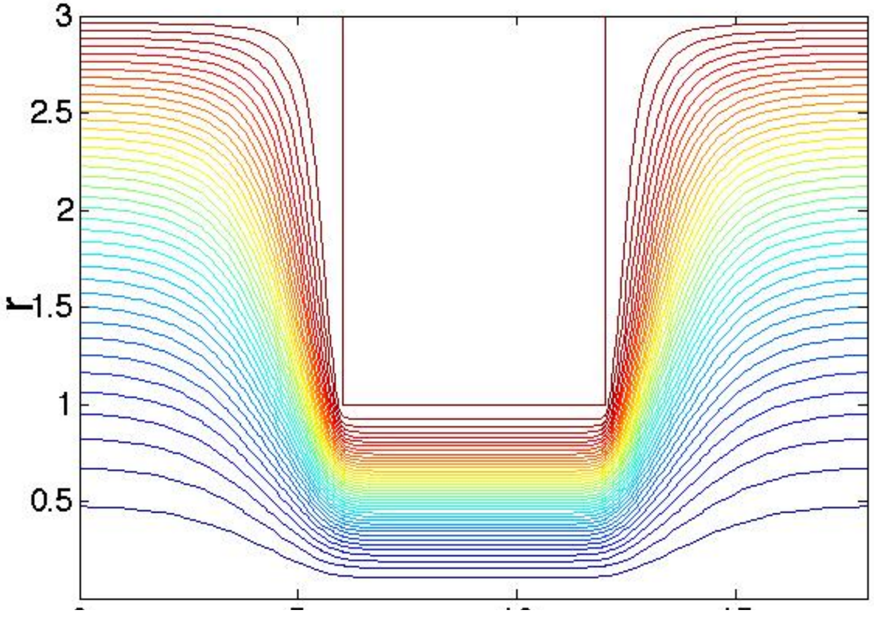
- Multi-block Chebyshev pseudopectral method together with the method of lines (MOL) to solve governing equations with the associated boundary/ interface conditions .
- Governing equations are first semi-discretized in space together with boundary conditions.
- The resulting equations are a set of coupled ordinary differential algebraic equations (ODAEs).
- The algebraic equations come from the Poisson equation and those boundary/interface conditions which are all time-independent.
- This ODAE system is index 1, which can be solved by many well-developed ODAE solvers. ode15s in MATLAB is a variable-order-variable-step index-1 ODAE solver, that can adjust the time-step to meet the specified error tolerance, and integrate with time efficiently. The numerical stability in time is automatically assured at the same time.
- The spatial discretization is performed by the highly-accurate Chebyshev pseudospectral method with Chebyshev Gauss-Lobatto grid and its associated collocation derivative matrix.

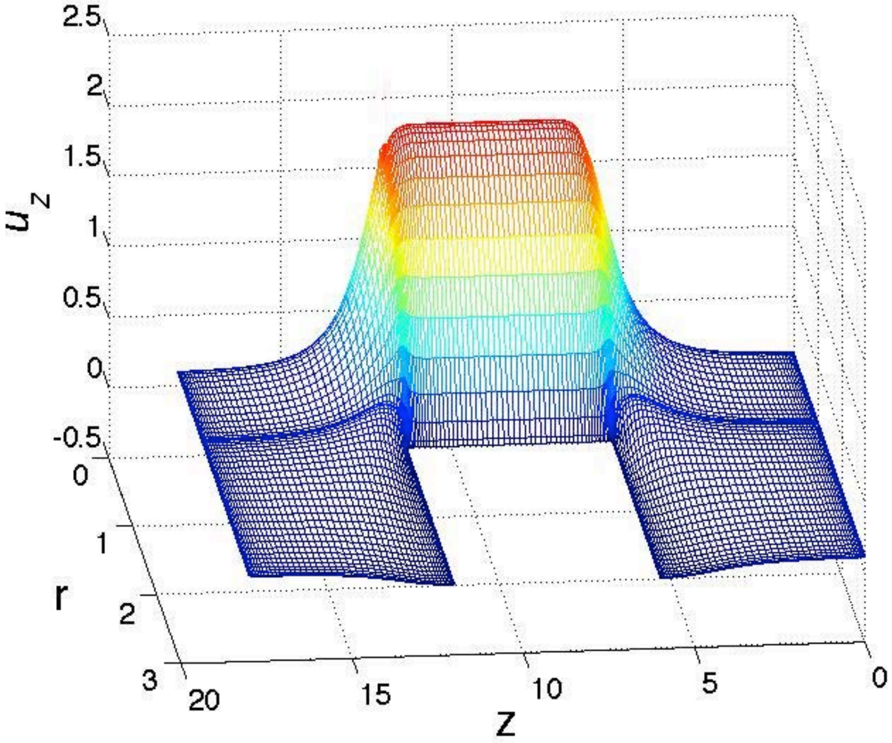
Domain decomposition

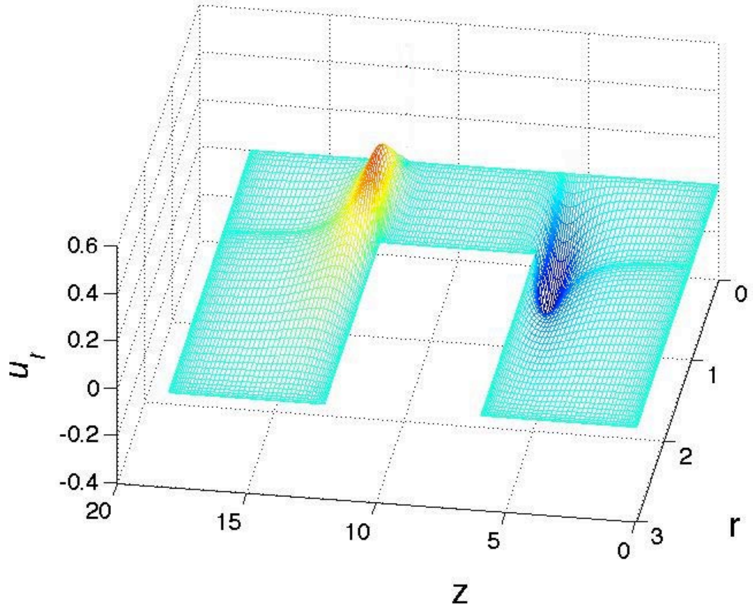


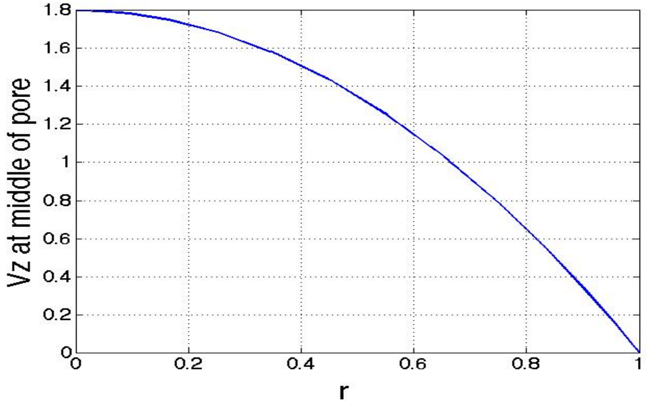


Streamlines and velocity profiles:









How good is our model? It will be compared with the most popular 1D NF model:
Donnan steric pore model with dielectric exclusion (DSPM-DE), which was developed by chemists.

Reference: A. A. Hussain, M. E. E. Abashar, and I. S. Al-Mutaz, Influence of ion size on the prediction of nanofiltration membrane systems, Desalination, 214 (2007) 150-166.

Only computing extended Nernst-Planck equation inside pore with interface conditions related to concentrations and electric potential at reservoirs.

Interface partition coefficient: $k_i = [\text{steric}] \times [\text{electrostatic (Donnan)}] \times [\text{solvation (Born)}] \times \ldots$

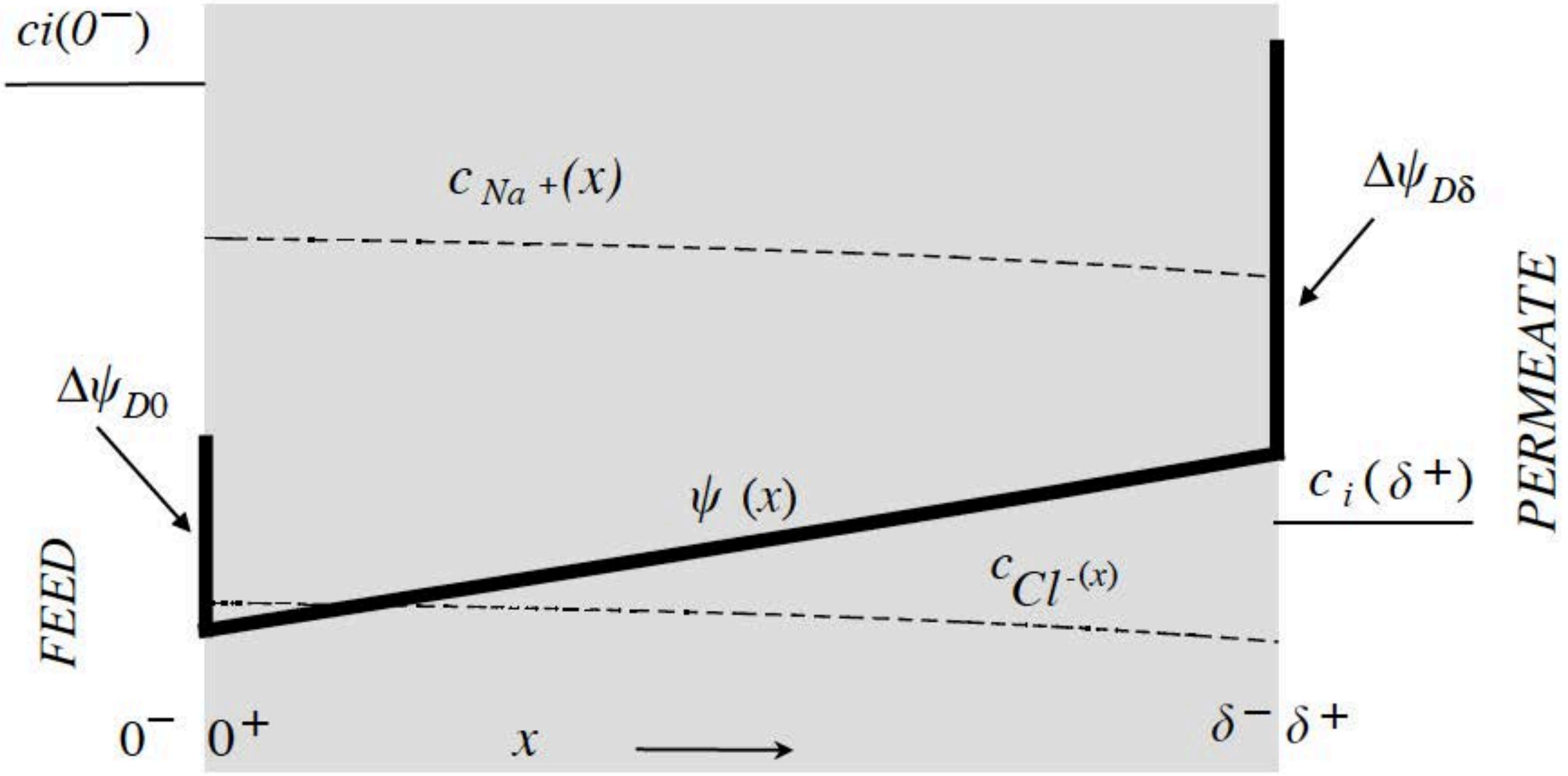


Fig. 1. Coordinates system for the NF model: electric potential and concentration profiles are reported with reference to NaCl–water solutions.

$$j_i = K_{ic} c_i u + \left(- \frac{c_i D_{ip}}{RT} \frac{d\mu_i}{dx} \right) \qquad (1)$$

(extended Nernst-Planck equation)

$$K_{ic} = (2 - \phi_i)(1.0 + 0.054\lambda_i - 0.988\lambda_i^2 + 0.441\lambda_i^3) \qquad (2)$$

$$\phi_i = (1 - \lambda_i)^2 \qquad (3)$$

(steric partition coefficient)

$$\lambda_i = \frac{r_i}{r_p} \qquad (4)$$

$$D_{ip} = K_{id} D_{i\infty} \frac{\eta_o}{\eta} \qquad (5)$$

(related to viscosity by Stokes-Einstein equation)

$$K_{id} = 1.0 - 2.304\lambda_i + 1.154\lambda_i^2 + 0.224\lambda_i^3 \qquad (6)$$

$$\frac{\eta}{\eta_o} = 1.0 + 18\left(\frac{d}{r_p}\right) - 9\left(\frac{d}{r_p}\right)^2 \qquad (7)$$

(d: thickness of the oriented swater layer, 0.28 nm)

$$\mu_i = RT\ln a_i + V_i P + z_i F\psi + \text{constant} \qquad (8)$$

$$a_i = \gamma_i c_i \qquad (9)$$

a_i: activity, γ_i: activity coefficient

0 (Debye-Huckel)

$$\begin{aligned} j_i = {} & K_{i,c} c_i(x) u - D_{ip} c_i(x) \partial_x \ln\gamma_i - D_{ip} \partial_x c_i(x) \\ & - \frac{1}{RT} V_i D_{ip} c_i(x) \partial_x P - \frac{F}{RT} z_i D_{ip} c_i(x) \partial_x \psi \end{aligned} \qquad (10)$$

((10) is from differentiating (8) and substituting into (1))

$$\partial_x P = \frac{\Delta P_e}{\Delta x} = \frac{8\eta u}{r_P^2} \qquad (11)$$

(Hagen-Poiseuille equation)

$$\Delta P_e = \Delta P - \Delta \pi \qquad (12)$$

(Van't Hoff $\Delta \pi = RT\sum_{i=1}^{n}\left(c_{i,w} - c_{i,p}\right)$)

$$j_i = \left[K_{ic} - \left(\frac{8\eta}{RTr_p^2} \right) D_{ip} V_i \right] c_i u - D_{ip} \frac{dc_i}{dx} - \frac{F}{RT} z_i D_{ip} c_i \frac{d\psi}{dx} \qquad (13)$$

((13) is from substituting (11) into (10), convection+diffusion+electro-migration)

$$j_i = C_i(\delta^+)u \qquad (14)$$

$$\frac{dc_i}{dx} = \left[\left[K_{ic} - \left(\frac{8\eta}{RTr_p^2} \right) D_{ip} V_i \right] c_i - C_i(\delta^+) \right] \frac{u}{D_{ip}} - \frac{F}{RT} z_i c_i \frac{d\psi}{dx} \qquad (15)$$

((15) is from
substituting (14)
into (13))

$$\sum_{i=1}^{n} z_i \frac{dc_i}{dx} = \sum_{i=1}^{n} \left[\left[K_{ic} - \left(\frac{8\eta}{RTr_p^2} \right) D_{ip} V \right] c_i - C_i(\delta^+) \right] \frac{z_i u}{D_{ip}} \qquad (16)$$

$$- \frac{F}{RT} \left(\sum_{i=1}^{n} z_i^2 c_i \right) \frac{d\psi}{dx}$$

Electro-neutrality at external solutions:

$$\sum_{i=1}^{n} z_i C_i(0^-) = 0, \quad \sum_{i=1}^{n} z_i C_i(\delta^+) = 0 \qquad (17)$$

Electro-neutrality inside the pore:

$$\sum_{i=1}^{n} z_i c_i(x) = -\chi_d, \quad 0 < x < \delta, \qquad (18)$$

$$\frac{d\psi}{dx} = \frac{\sum_{i=1}^{n}\left[\left[K_{ic} - \frac{8\eta}{RTr_p^2} D_{ip} V\right] c_i - C_i(\delta^+)\right]\frac{z_i u}{D_{ip}}}{\frac{F}{RT}\sum_{i=1}^{n} z_i^2 c_i} \qquad (19)$$

((19) is from differentiating (18) and substituting into (16))

$$k_i = [\text{steric}]\times[\text{electrostatic (Donnan)}]$$
$$\times[\text{solvation (Born)}]\times\ldots \qquad (20)$$

(partition coefficient)

$$k_i\Big|_0 = \frac{C_i(0^+)}{C_i(0^-)} = \phi_i \exp\left(-\frac{Fz_i}{RT}\Delta\psi_D(0)\right)$$
$$\exp\left(-\frac{\Delta W_i(0)}{kT}\right), \quad \sum_{i=1}^{n} z_i C_i(0^+) = \sum_{i=1}^{n} z_i C_i(0^-)\phi_i \qquad (21)$$
$$\exp\left(-\frac{Fz_i}{RT}\Delta\psi_D(0)\right)\exp\left(-\frac{\Delta W_i(0)}{kT}\right) = -\chi_d$$

(iterating on Donnan potential to satisfy electro-neutrality inside the pore)

$$k_i\Big|_\delta = \frac{C_i(\delta^-)}{C_i(\delta^+)} = \phi_i \exp\left(-\frac{Fz_i}{RT}\Delta\psi_D(\delta)\right)$$

$$\exp\left(-\frac{\Delta W_i(\delta)}{kT}\right), \quad \sum_{i=1}^{n} z_i C_i(\delta^-) = \sum_{i=1}^{n} z_i C_i(\delta^+)\phi_i \qquad (22)$$

$$\exp\left(-\frac{Fz_i}{RT}\Delta\psi_D(\delta)\right)\exp\left(-\frac{\Delta W_i(\delta)}{kT}\right) = -\chi_d$$

$$\Delta\psi_D(0) = \psi(0^+) - \psi(0^-) \quad \text{(feed)}$$

$$\Delta\psi_D(\delta) = \psi(\delta^-) - \psi(\delta^+) \quad \text{(permeate)} \qquad (23)$$

(a jump in electrical potential can be understood from EDL or Poisson equation)

$$\Delta W_i = \frac{z_i^2 e^2}{8\pi\varepsilon_o r_i}\left[\frac{1}{\varepsilon_p} - \frac{1}{\varepsilon_b}\right] \qquad (24)$$

(dehydration when ions entering pore, change of dielectric constant, solvation energy based on Born model)

$$\varepsilon_p = \frac{\int_0^{r_p-d} 2\pi r\varepsilon_b \, dr + \int_{r_p-d}^{r_p} 2\pi r\varepsilon^* \, dr}{\pi r_p^2} \qquad (25)$$

$$= \varepsilon_b - 2(\varepsilon_b - \varepsilon^*)\left(\frac{d}{r_p}\right) + (\varepsilon_b - \varepsilon^*)\left(\frac{d}{r_p}\right)^2$$

(the wall of pore covered by one layer of oriented water molecules of thickness *d* and dielectric constant *ε**)

$$R_i = 1 - \frac{C_i(\delta^+)}{C_i(0^-)} \qquad (26)$$

(rejection coefficient)

Results: a case of NF

Input Parameters:

- [KCl]=0.011982M, pore radius r_0=2nm, U_{ref}=0.97850m/s,
- 2 dielectric situations inside pore are considered:

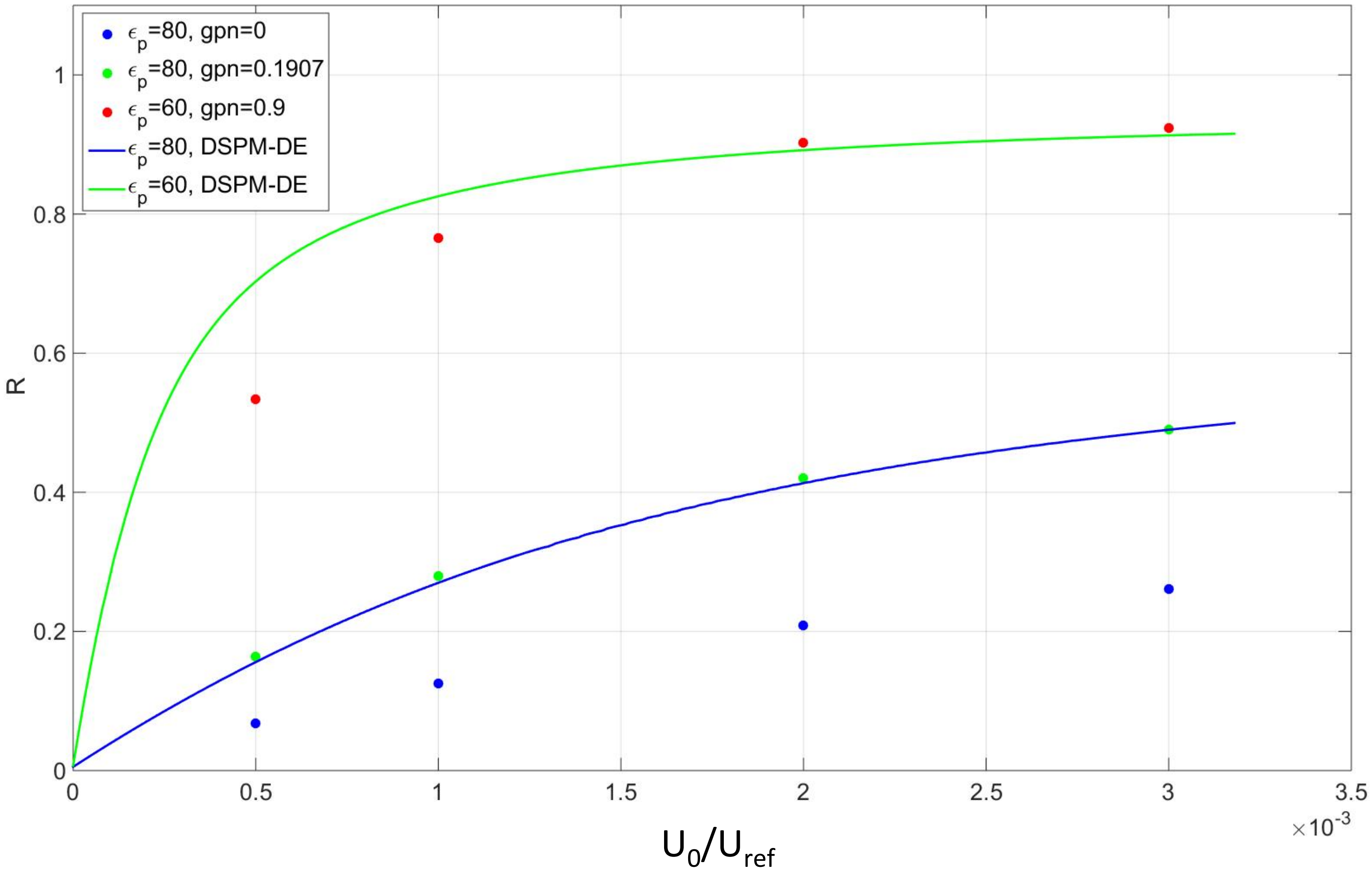
(1) ε_{pore}=80, λ_D=4nm, Γ_{p}=4,

(2) ε_{pore}=60, λ_D=3.4641nm, Γ_{p}=3,

- Dimensionless surface charge density σ=-2 (equivalent to ζ=-17.945mV), only distributed inside pore surface.
- $D_{pore}=0.25D_{bulk}$ (same input as in DSPM-DE).
- Input: a bunch of U_0/U_{ref} with various $g_{pn,pore}=g_{np,pore}$ ($g_{nn,pore}=g_{pp,pore}=0$, all $g_{ij,bulk}=0$).

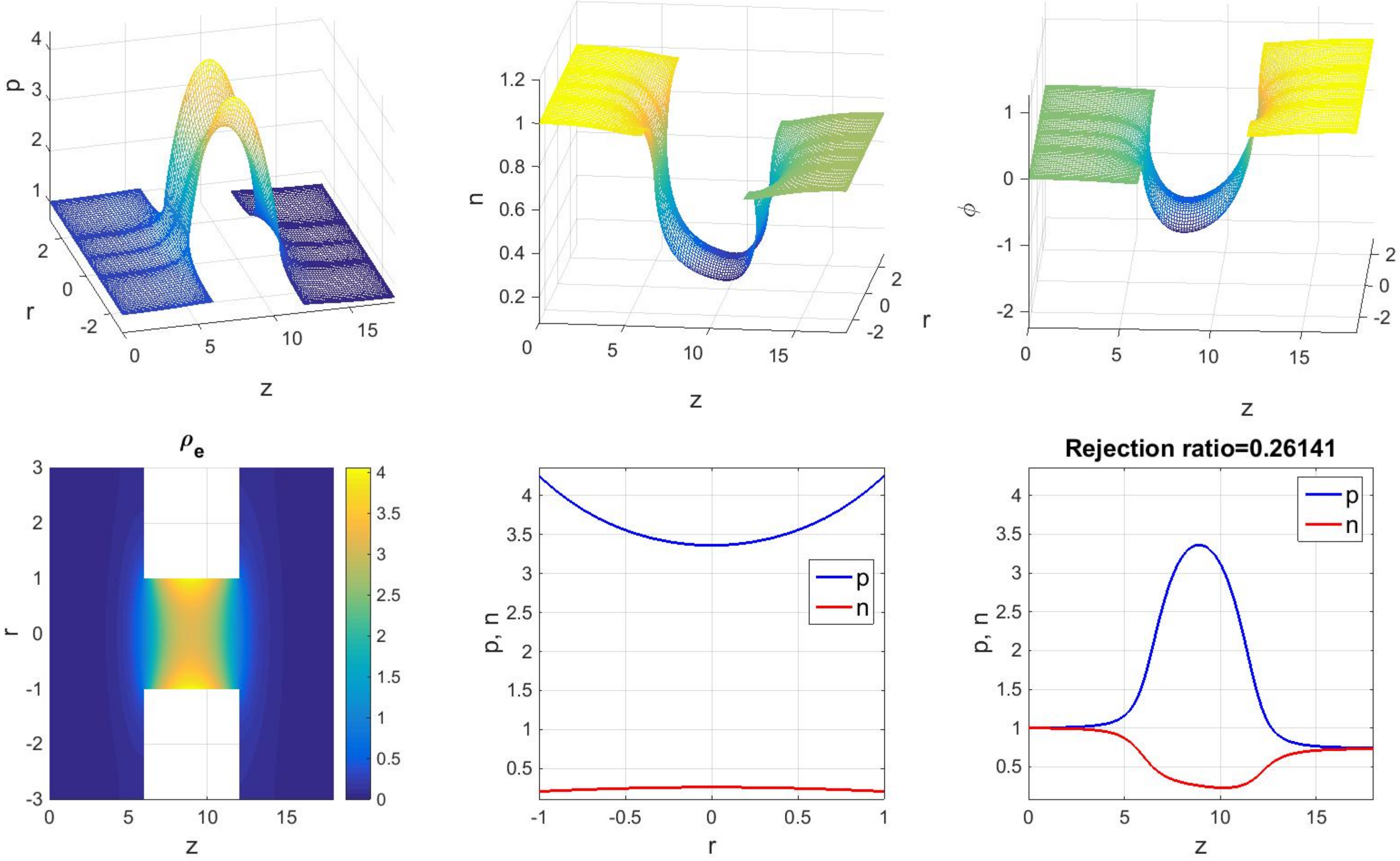
Output: salt rejection rate $R = \dfrac{c_i(-\infty)-c_i(\infty)}{c_i(-\infty)}$.

Comparison with DSPM-DE model



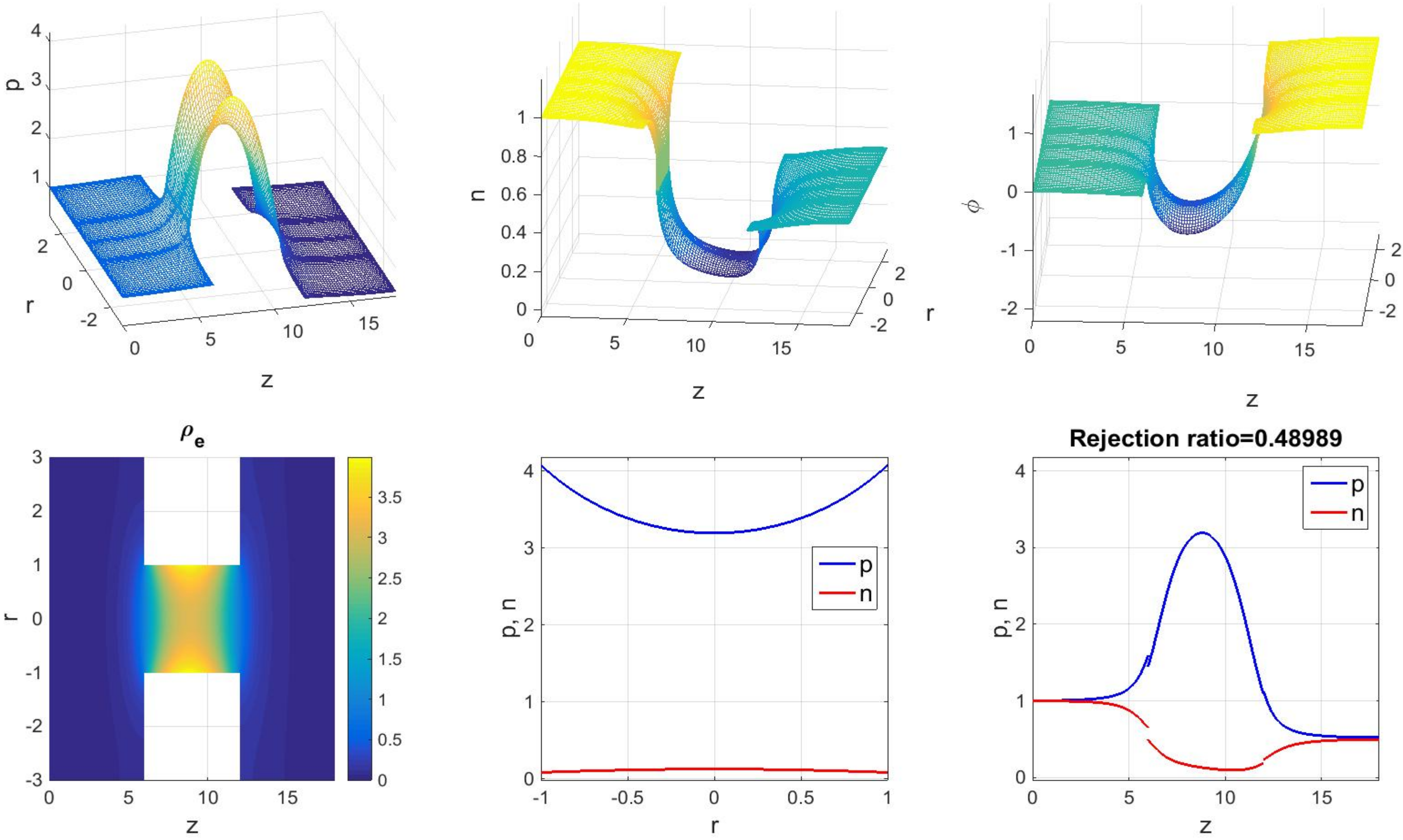
Generally, salt rejection increases with flow velocity (pressure).

ε_{pore}=80, U_0/U_{ref}=0.003, g_{pn}=0 (no steric effect).



Steady-state whole domain distributions of (a) p, (b) n, (c) ϕ, (d) ρ_e, (e) distributions of p, n versus r at z=9 (center location of pore) and (f) distribution of p and n along axis (r=0).

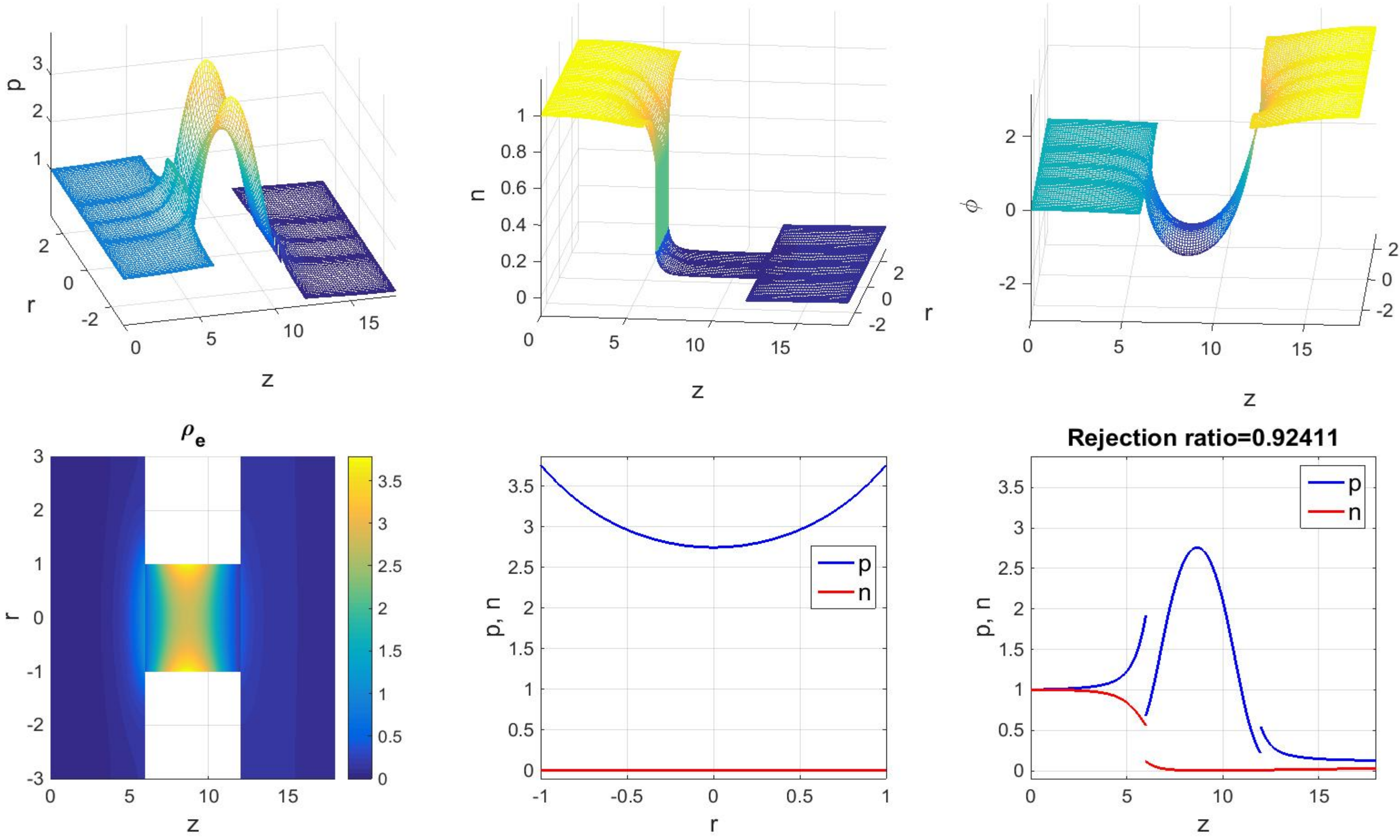
ε_{pore}=80, U_0/U_{ref}=0.003, g_{pn}=0.1907



weak
jump

Steady-state whole domain distributions of (a) p, (b) n, (c) ϕ, (d) ρ_e, (e) distributions of p, n versus r at z=9 (center location of pore) and (f) distribution of p and n along axis (r=0).

$E_{pore}=60$, $U_0/U_{ref}=0.003$, $g_{pn}=0.9$



strong jump: dielectric exclusion

Steady-state whole domain distributions of (a) p, (b) n, (c) ϕ, (d) ρ_e, (e) distributions of p, n versus r at z=9 (center location of pore) and (f) distribution of p and n along axis (r=0).

Conclusions

- Convection breaks symmetry and causes salt rejection when passing a charged nanopore.
- In NF, current NS-PNP-steric model agrees very well with DSPM-DE for ε_{pore}=80 (no dielectric exclusion), and OK at ε_{pore}=60 (having dielectric exclusion).
- Besides strong convection under overlapping double layers, high salt rejection is chiefly due to strong dielectric exclusion (large solvation energy difference between pore and reservoirs).
- With the difference of steric and solvation energies between reservoir and pore, jump condition on ionic concentrations at interface would happen, which can be derived from continuity of flux. The form turns out to be close to partition factors under Boltzmann distribution.


THANK YOU FOR YOUR ATTENTION
ANY QUESTIONS?
memegenerator.net

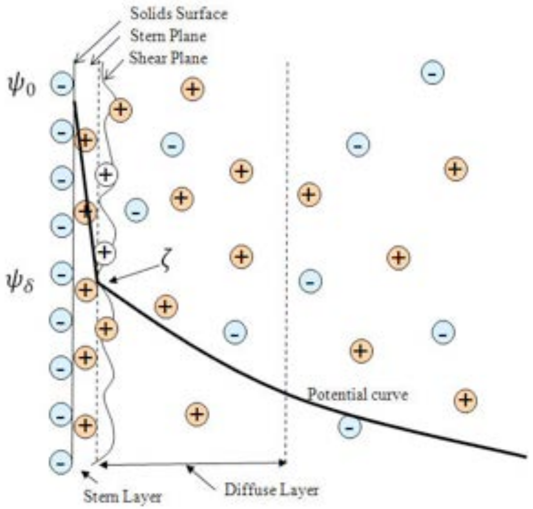

?
THANK YOU
FOR
YOUR
ATTENTION
NY QUESTION

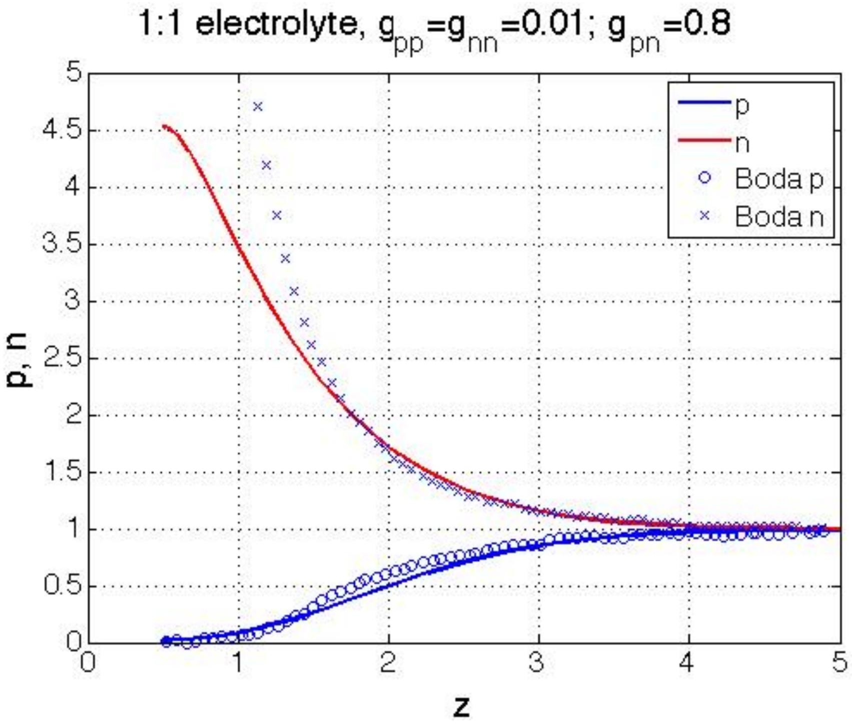

NOT SURE IF THANK YOU FOR YOUR ATTENTION
OR FOR NOT SLEEPING DURING MY PRESENTATION
memegenerator.net

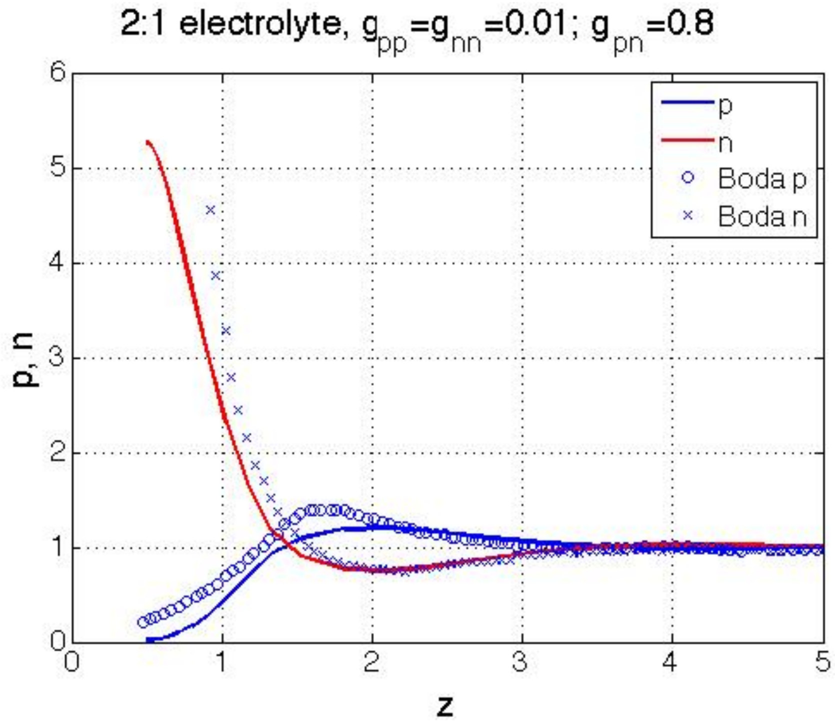
Conclusions and future works

- Convection breaks symmetry and causes salt rejection when passing a charged nanopore.
- In NF, NS-PNP-steric model agrees very well with DSPM-DE for $\varepsilon_p=80$ (no dielectric exclusion), and well at $\varepsilon_p=60$ (having dielectric exclusion).
- High salt rejection in DSPM-DE is chiefly due to strong dielectric exclusion (solvation energy barrier modeled by Born model here).
- With solvation energy, added into energy of present model, jump condition on ionic concentrations at interfaces happens and has been derived from continuity of flux.
- Large g_{pn} with bi-Laplacian diffusion (single-file diffusion) will be applied when the pore size is further reduced (more significant finite-size effect). [Q. Chen, J. D. Moore, Y.-C. Liu, T. J. Roussel, Q. Wang, T. Wu, and K. E. Gubbins, 2010, Transition from single-file to Fickian diffusion for binary mixture in single-walled carbon nanotubes, J. Chem. Phys., 113, 094501]

Importance of large g_{pn} with bi-Laplacian diffusion, eg. charged wall problem (EDL): result compared with Boda et al. (2002) (a MC simulation)




1:1 electrolyte, $g_{pp}=g_{nn}=0.01$; $g_{pn}=0.8$


2:1 electrolyte, $g_{pp}=g_{nn}=0.01$; $g_{pn}=0.8$

Over-screening will not happen in 2:1 electrolyte without large g_{pn} here.

How is the World's Water Distributed?

- Less than 3% of Earth's water is fresh water
- Most of it (97%) is undrinkable salt water in the oceans
- Of the fresh water, most is in ice caps and glaciers, and some is in ground water
- Less than 1% is in more easily accessible surface water (lakes, swamps, rivers, etc.)

No Single Cause for the Water Crisis

- Climate and geography
- Lack of water systems and infrastructure
- Depleting aquifers
- Inadequate sanitation and pollution
    - 2.6 billion people (40% of the world's population) lack access to sanitation systems that separate sewage from drinking water
    - Inadequate sanitation and no access to clean water have been highly correlated with disease
- Will worsen with increasing population, affluence

How Can We Address the Water Crisis?

- Use less water
  - More efficient irrigation, like drip irrigation; cover irrigation ditches
  - Low-flow shower and toilets; recycle gray water
  - Use native plants for crops and landscaping; no lawns in AZ
  - Eat less meat (especially beef)
  - Fix leaky distribution systems (Quabbin reservoir)
- Find new sources of clean water
  - Icebergs? Pump aquifers more and more? Use tankers?
- Treat the undrinkable water that we have
  - Use reverse osmosis to desalinize ***salt (ocean) water***
  - Clean ***polluted water*** using filters, chemicals, and UV light

Water Contaminants

Class	Typical Example
Suspended solids	Dirt, clay, colloidal materials
Dissolved organics	Trihalomethanes, synthetic organic chemicals, humic acids, fulvic acids
Dissolved ionics (salts)	Heavy metals, silica, arsenic, nitrate
Microorganisms	Bacteria, viruses, protozoan cysts, fungi, algae
Gases	Hydrogen sulfide, methane, radon

Portland ditches 140 million litres of drinking water after teenager caught urinating in reservoir

Updated Fri 18 Apr 2014, 5:33pm AEST

PHOTO: More than 140 million litres of water in a south-east Portland reservoir will be discarded. (Reuters: Steve Dipaola)

The Problem: Adequate Clean Water

Despite the apparent abundance of clean water in most of the US and the developed world, more than 20% of the Earth's population lacks clean, safe drinking water.

1D Mathematical model: Donnan steric pore model with dielectric exclusion (DSPM-DE)

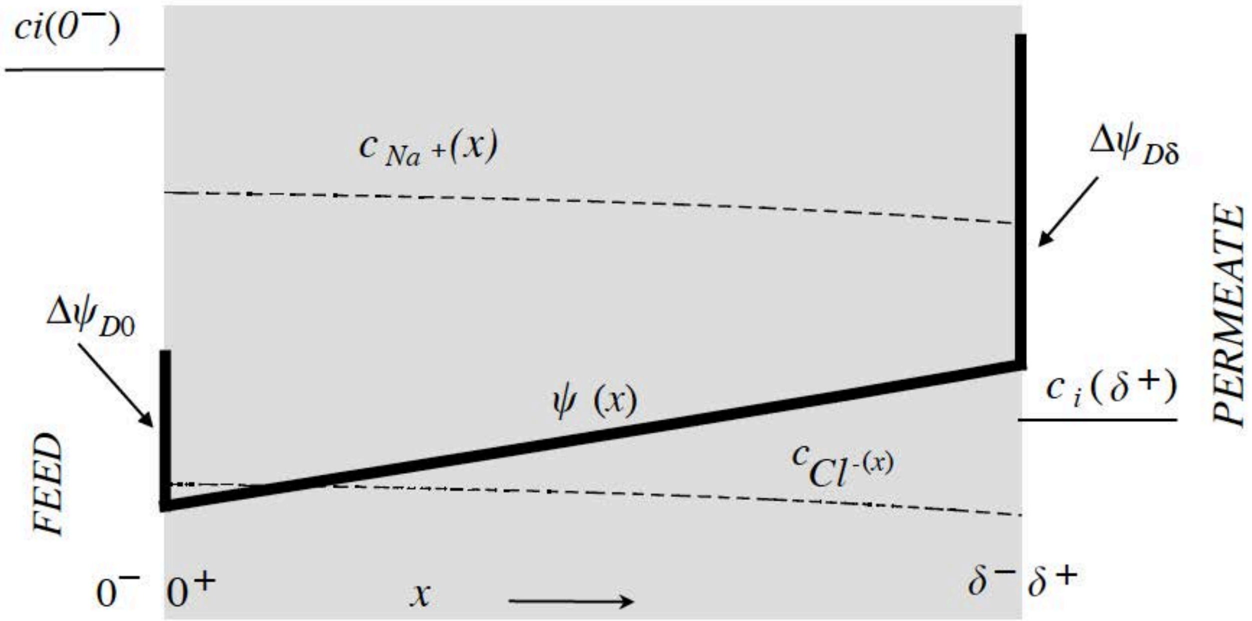


Fig. 1. Coordinates system for the NF model: electric potential and concentration profiles are reported with reference to NaCl–water solutions.

Approximation by Chebyshev polynomials

(1) Suppose that $u(x)$ is approximated by a truncated series of Chebyshev polynomials as

$$u(x) = \sum_{k=0}^{N} \hat{u}_k T_k(x),$$

where $T_k(x)$ denotes Chebyshev polynomial and $\hat{u}_k$ expansion coefficient.

(2) Choosing the Chebyshev Gauss-Lobatto collocations points:

$$x_j = \cos\frac{j\pi}{N}, \quad j = 0,1,\ldots,N,$$

(3) We can form the following discrete transform and inverse transform

$$\tilde{u}_k = \frac{2}{\bar{c}_k N} \sum_{j=0}^{N} \frac{1}{\bar{c}_j} u(x_j) T_k(x_j),$$

$$u(x_j) = \sum_{k=0}^{N} \tilde{u}_k T_k(x_j),$$

where $\bar{c}_j = \begin{cases} 2, & j = 0, N \\ 1, & \text{otherwise} \end{cases}$ and $\bar{c}_k = \begin{cases} 2, & k = 0, N \\ 1, & \text{otherwise} \end{cases}$.

(4) For pseudospectral method, interpolating $u(x)$ at the collocation points $x_j,\ j=0,1,\ldots,N$.

(5) Hence, $u(x)$ can be also expressed as

$$u(x)=\sum_{k=0}^{N} L_{N,k}(x)u(x_k),$$

where $L_{N,k}(x)$ is the Lagrange interpolating polynomial defined as

$$L_{N,k}(x)=\prod_{\substack{l=0\\ l\neq k}}^{N}\frac{x-x_l}{x_k-x_l}=\frac{(-1)^{N+k+1}(1-x)^2 T_N'(x)}{\overline{c}_k N^2(x-x_k)}.$$

(6) Then, the derivatives $\frac{du}{dx}(x_j)$ and $\frac{d^2u}{dx^2}(x_j)$ can be approximated as

$$\frac{du}{dx}(x_j)=\sum_{k=0}^{N}u(x_k)\frac{dL_{N,k}}{dx}(x_j)\ \text{ and }\ \frac{d^2u}{dx^2}(x_j)=\sum_{k=0}^{N}u(x_k)\frac{d^2L_{N,k}}{dx^2}(x_j),$$

where $\frac{dL_{N,k}}{dx}(x_j)$ is usually referred to the Chebyshev collocation derivative matrix.

Chebyshev Collocation Derivative Matrix

(1) The entries of first-order Chebyshev collocation derivative matrix with respect to x, based on Gauss-Lobatto collocation points, are given as below:

$$(D_x)_{00} = \frac{2N_x^2+1}{6}, \quad (D_x)_{N_x,N_x} = -\frac{2N_x^2+1}{6},$$

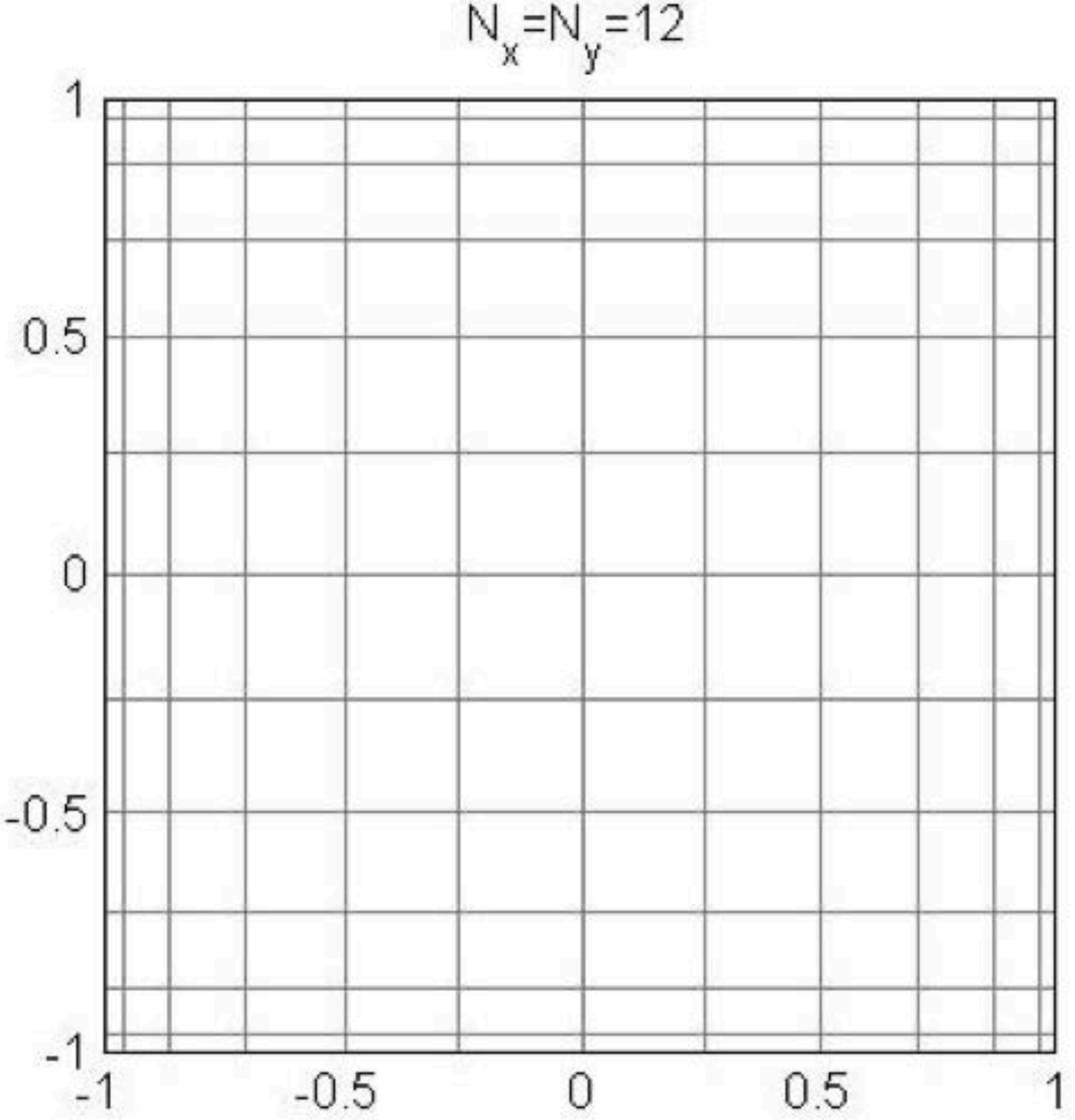
$$(D_x)_{jj} = \frac{-x_j}{2\left(1-x_j^2\right)}, \ j=1,2,\ldots,N_x-1, \qquad \text{where } c_i = \begin{Bmatrix} 2 & \text{for } i=0 \text{ or } N_x, \\ 1 & \text{otherwise} \end{Bmatrix}$$

$$(D_x)_{ij} = \frac{c_i(-1)^{i+j}}{c_j\left(x_i-x_j\right)}, \ i \neq j, \text{ and } i,j=0,1,2,\ldots,N_x,$$

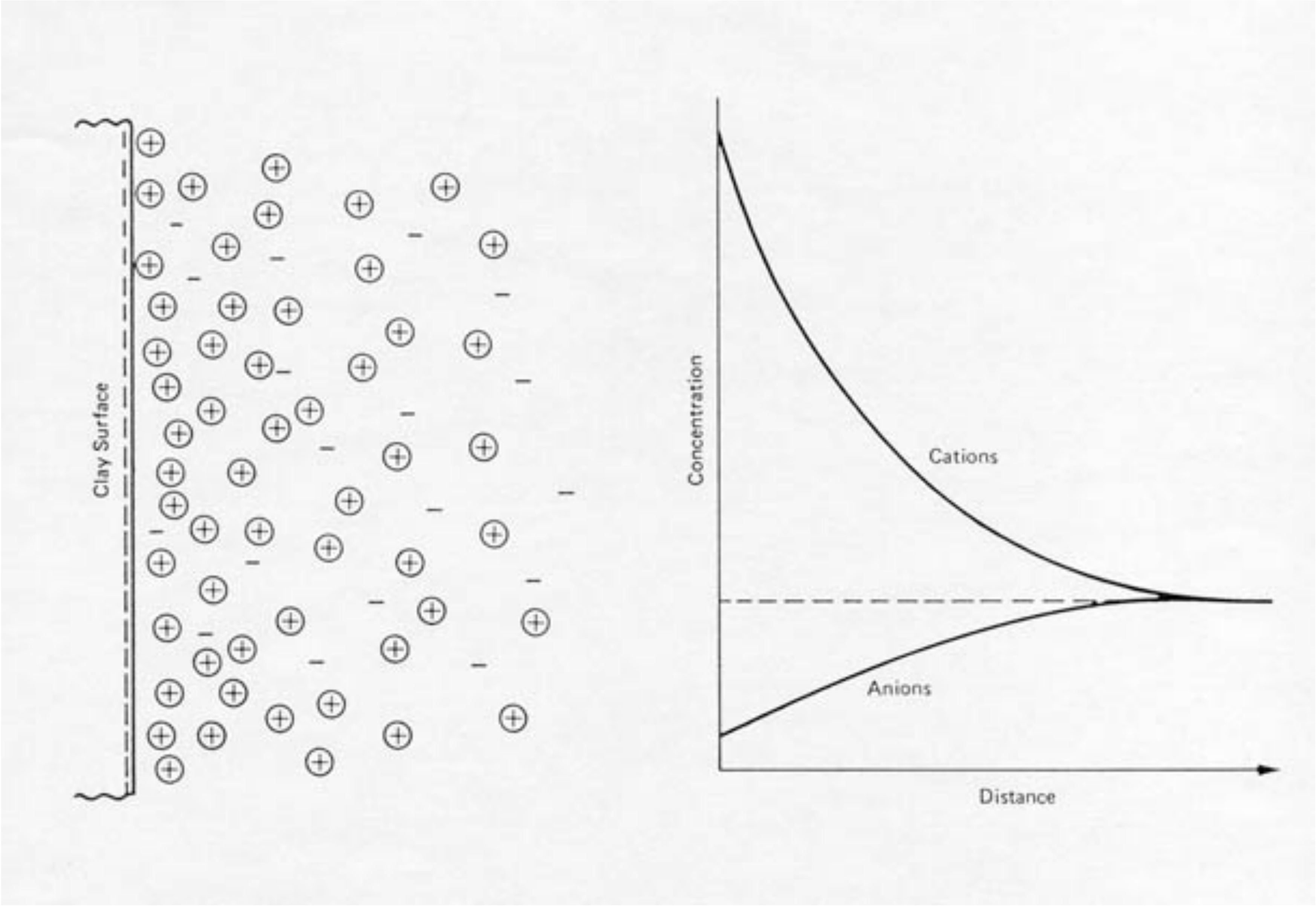
here $x_j = \cos\left(\frac{j\pi}{N_x}\right)$, $j=0,1,2,\ldots,N_x$ are Chebyshev Gauss-Lobatto collocation points. Also, there is a version for avoiding round-off error when N_x is large.
(W. Don and S. Solomonoff in SIAM J. Sci. Comp. Vol. 6, pp. 1253--1268 (1994))

(2) $D_{xx} = D_x^2$.

Chebyshev Gauss-Lobatto collocation mesh



Electric double layer (EDL)



Geometric configuration: a single nanopore

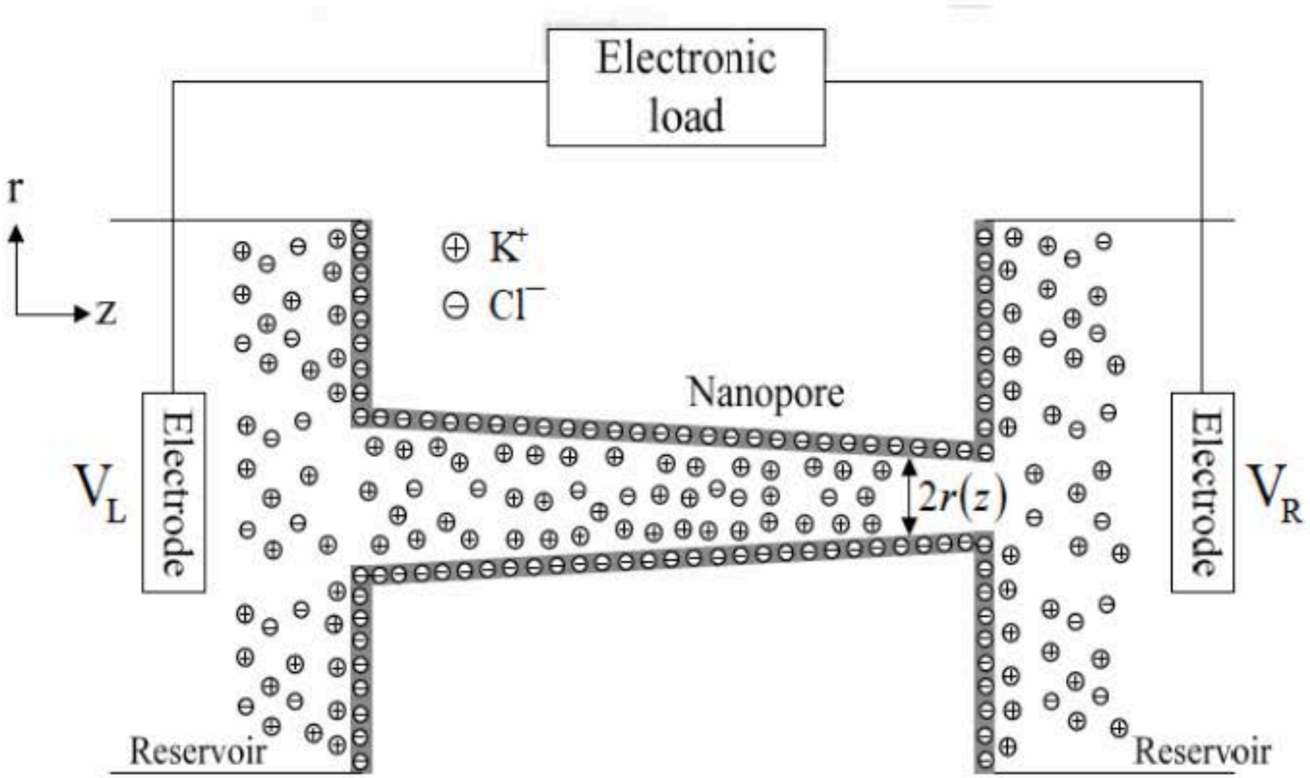
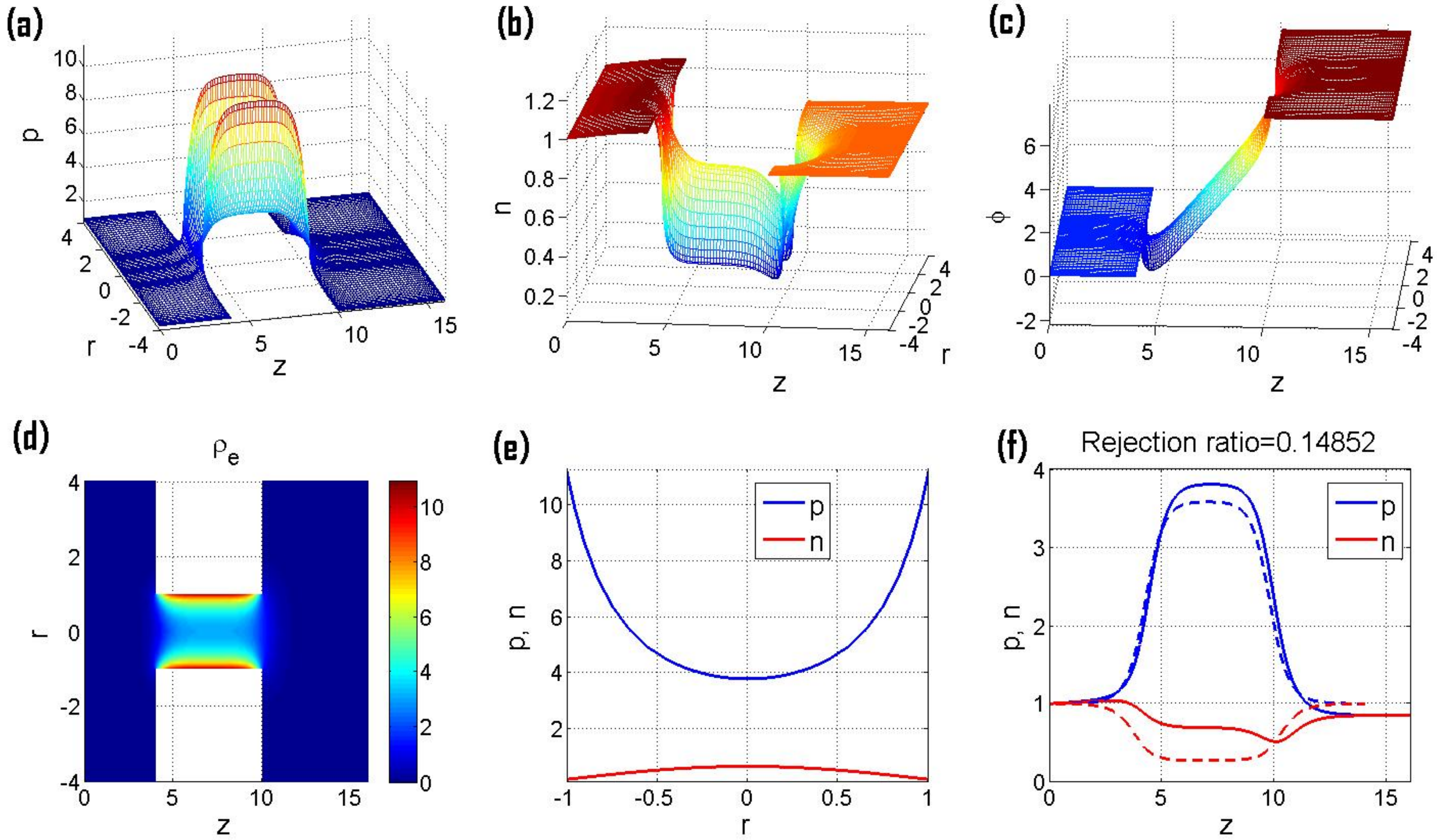
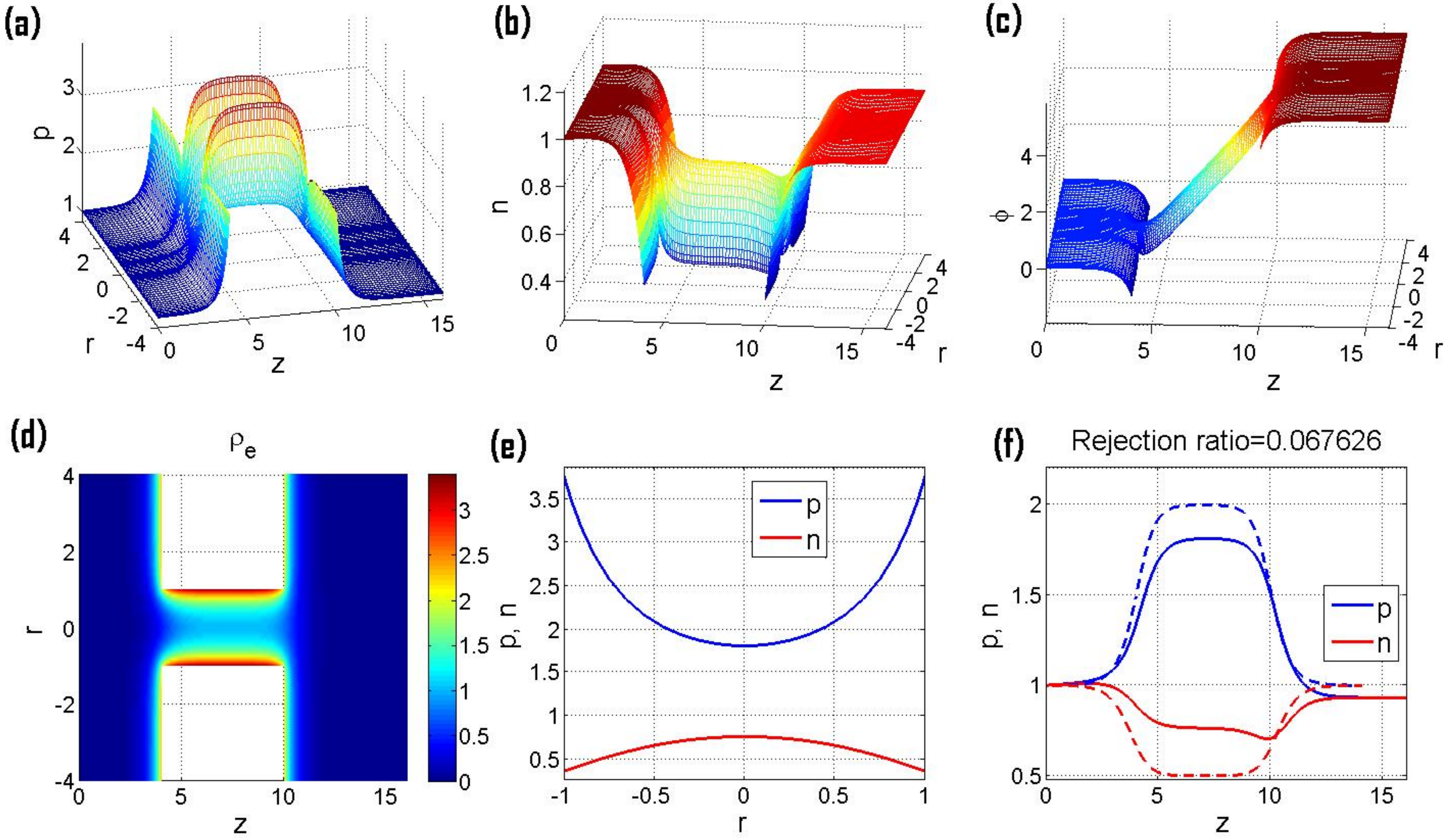


Figure 3: Schematic configuration of a nanopore connected to two reservoirs at both sides symbolizing a basic element of NF. The fluid flow can be driven either by pressure (RO) or electric potential (EOF).

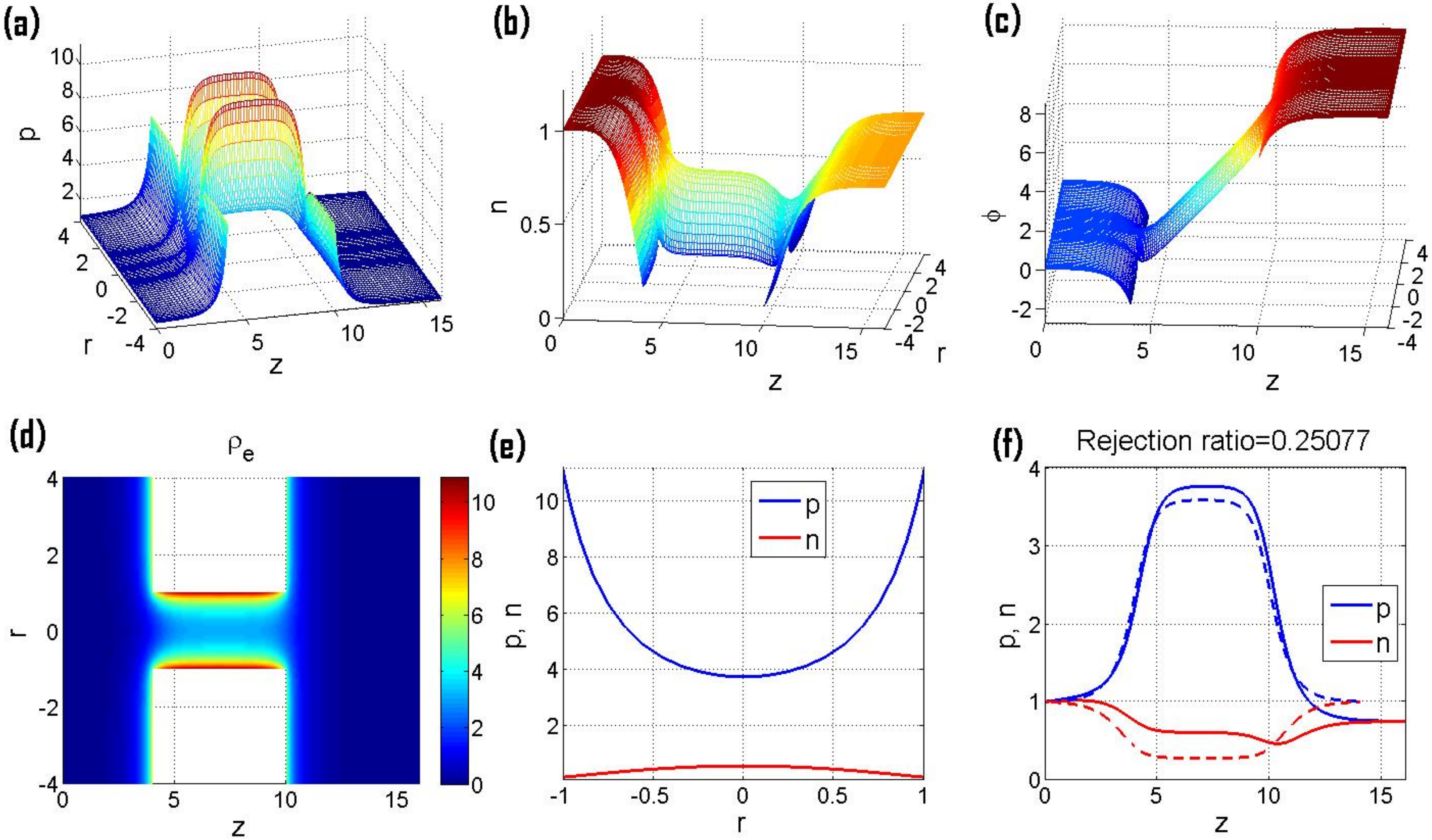
Parameters used: $Sc = 466, U_0 = 0.1, \sigma = 3, \Gamma = 1, \left(\frac{\partial \phi}{\partial n}\right)_p = 3, \left(\frac{\partial \phi}{\partial n}\right)_m = 0.$



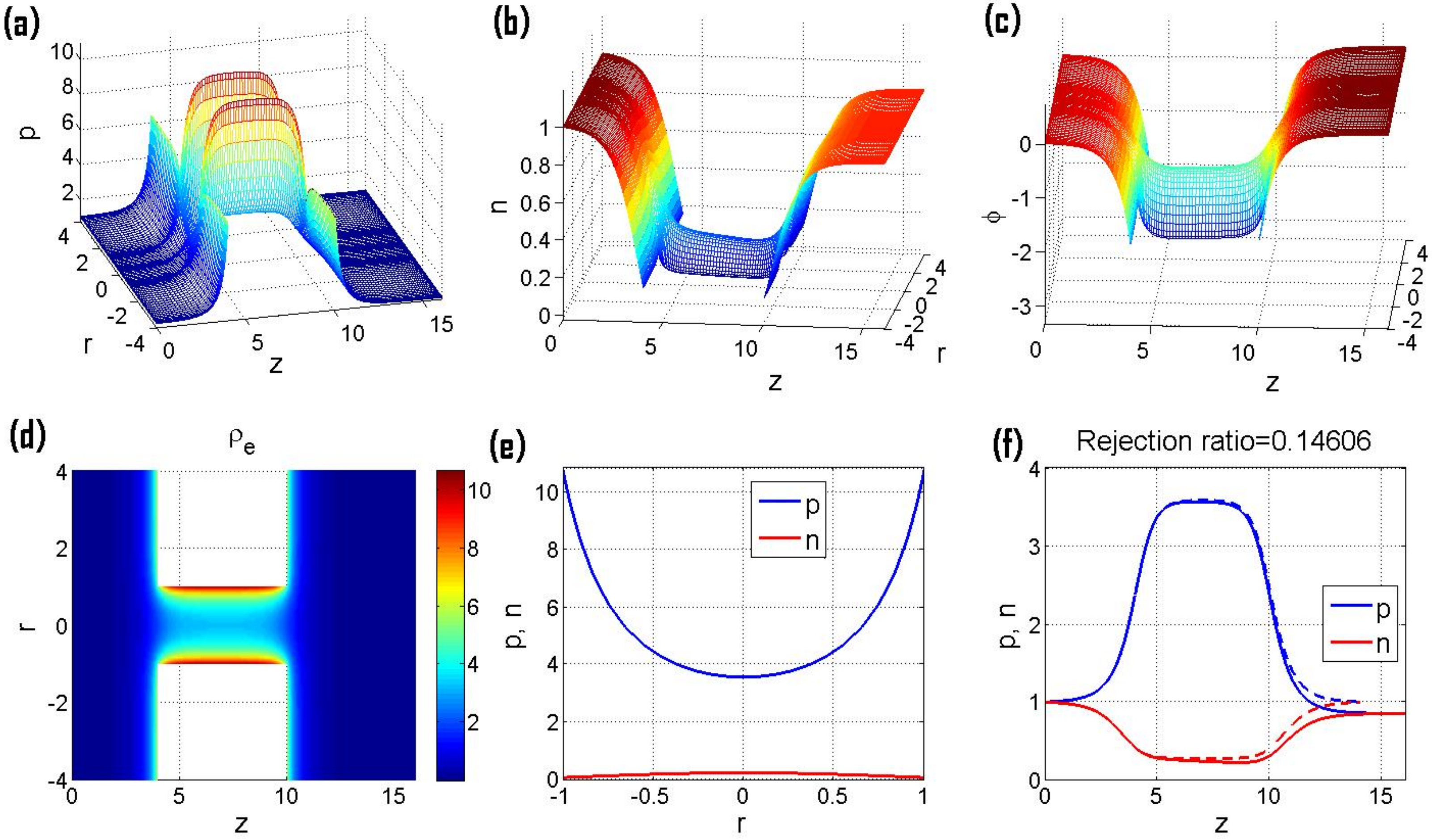
Parameters used: $Sc = 466, U_0 = 0.1, \sigma = 1, \Gamma = 0.5, \left(\frac{\partial \phi}{\partial n}\right)_p = 2, \left(\frac{\partial \phi}{\partial n}\right)_m = 2.$



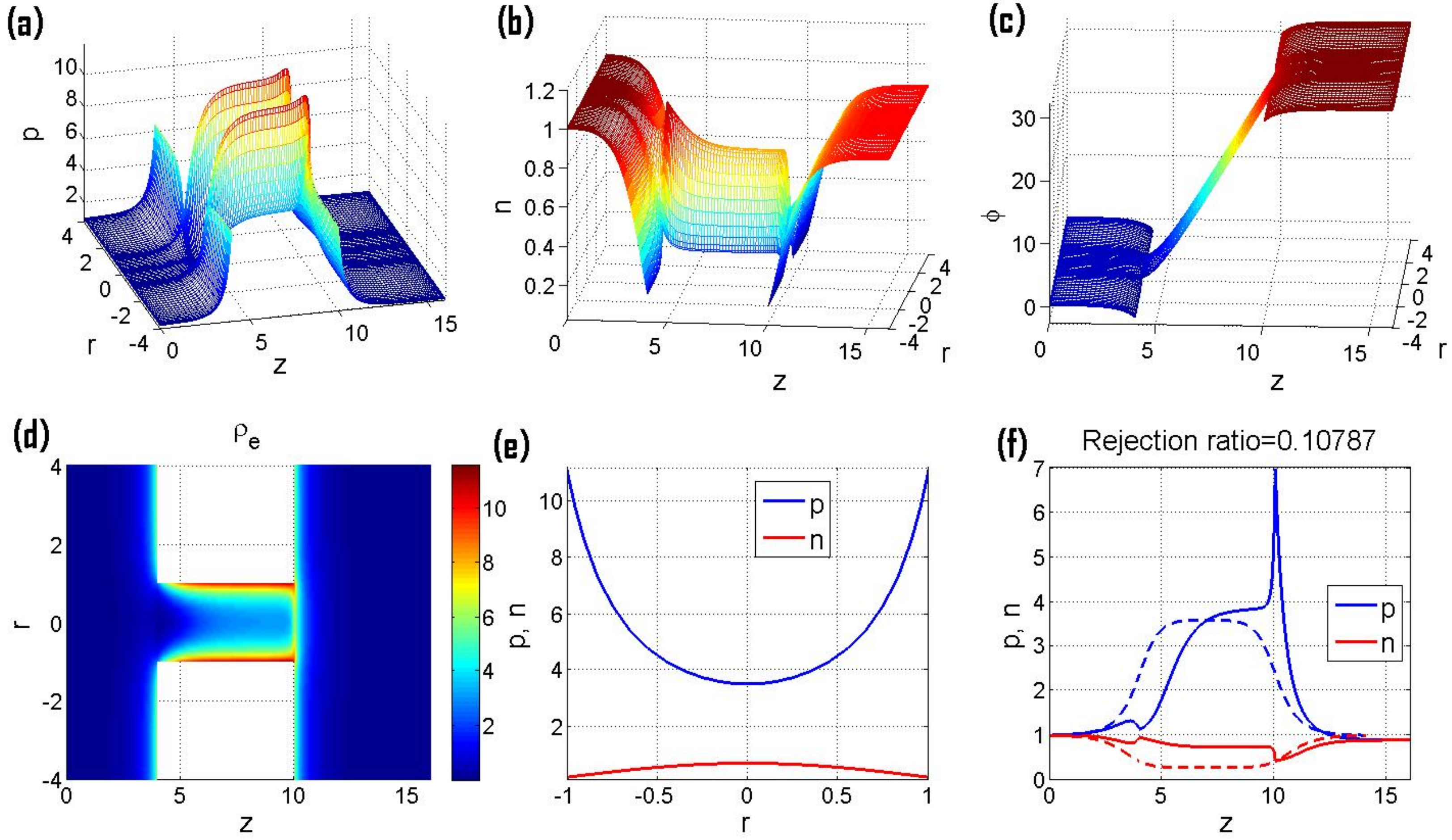
Parameters used: $Sc = 466, U_0 = 0.1, \sigma = 3, \Gamma = 1, \left(\frac{\partial \phi}{\partial n}\right)_p = 3, \left(\frac{\partial \phi}{\partial n}\right)_m = 3.$



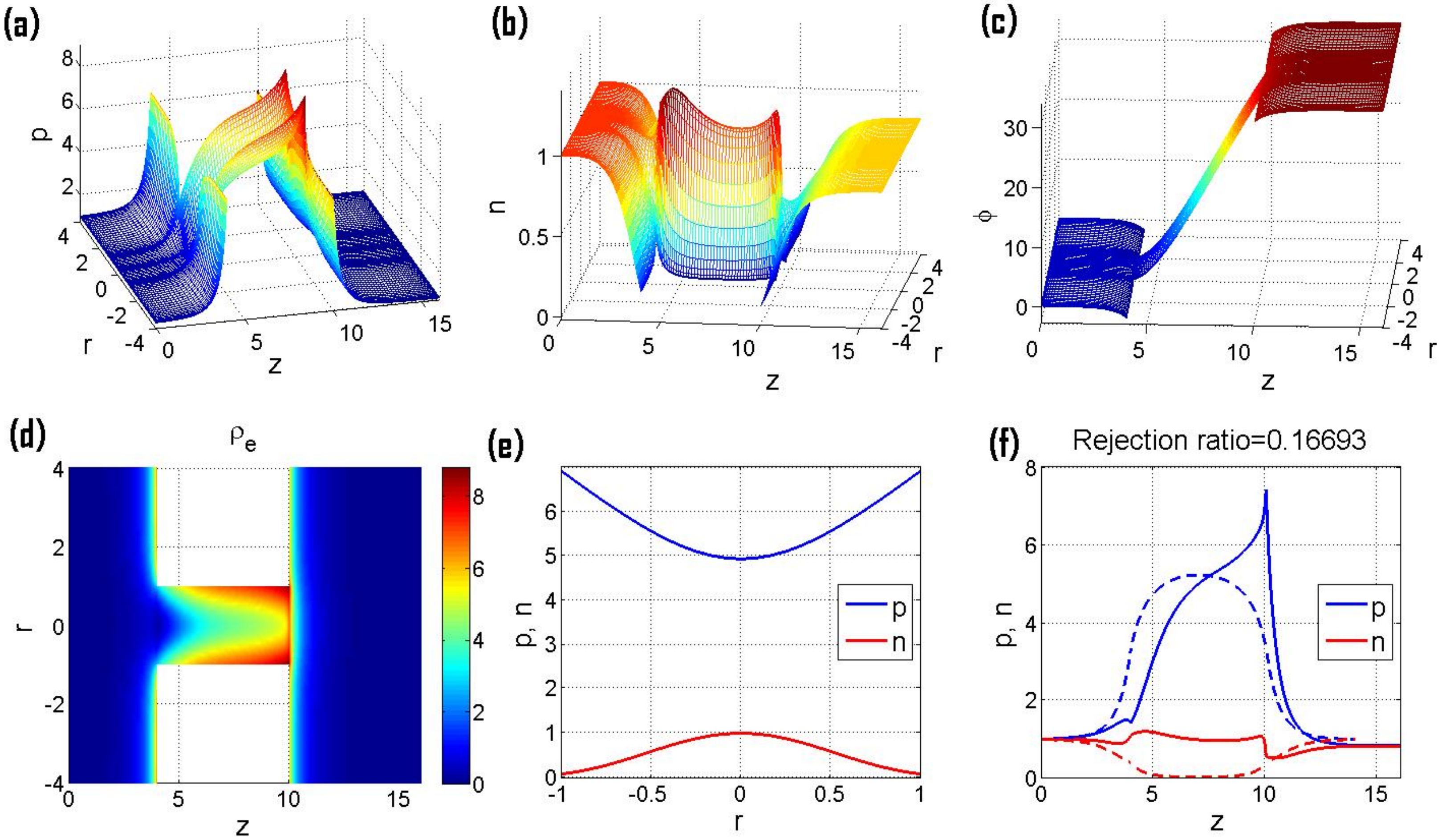
Parameters used: $Sc = 466, U_0 = 0.001, \sigma = 3, \Gamma = 1, \left(\frac{\partial \phi}{\partial n}\right)_p = 3, \left(\frac{\partial \phi}{\partial n}\right)_m = 3.$



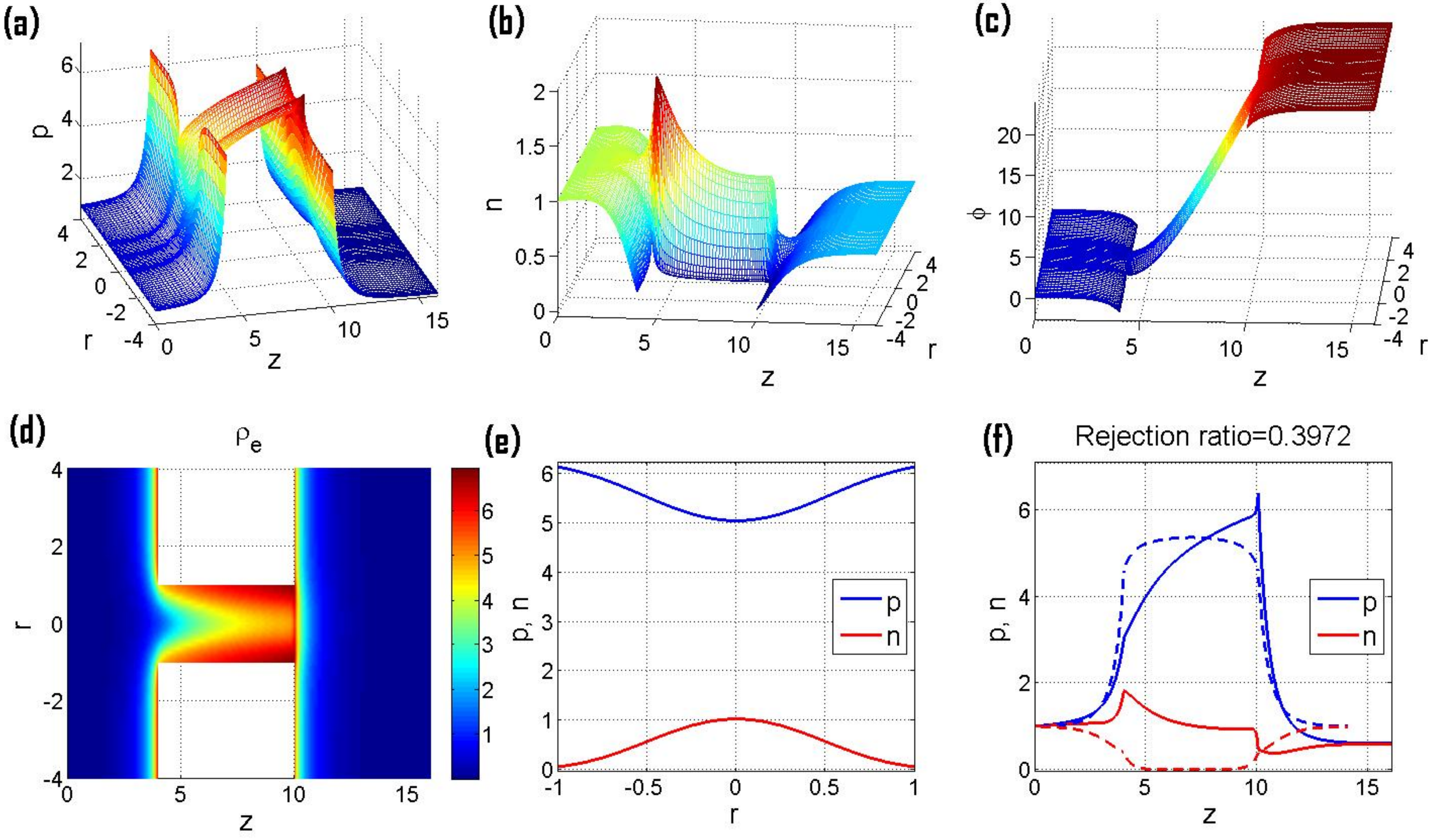
Parameters used: $Sc = 466, U_0 = 0.1, \sigma = 3, \Gamma = 1, \left(\frac{\partial \phi}{\partial n}\right)_p = 3, \left(\frac{\partial \phi}{\partial n}\right)_m = 3$. Ion diffusion coefficients inside nanopore are reduced to be 20% of bulk solution value.



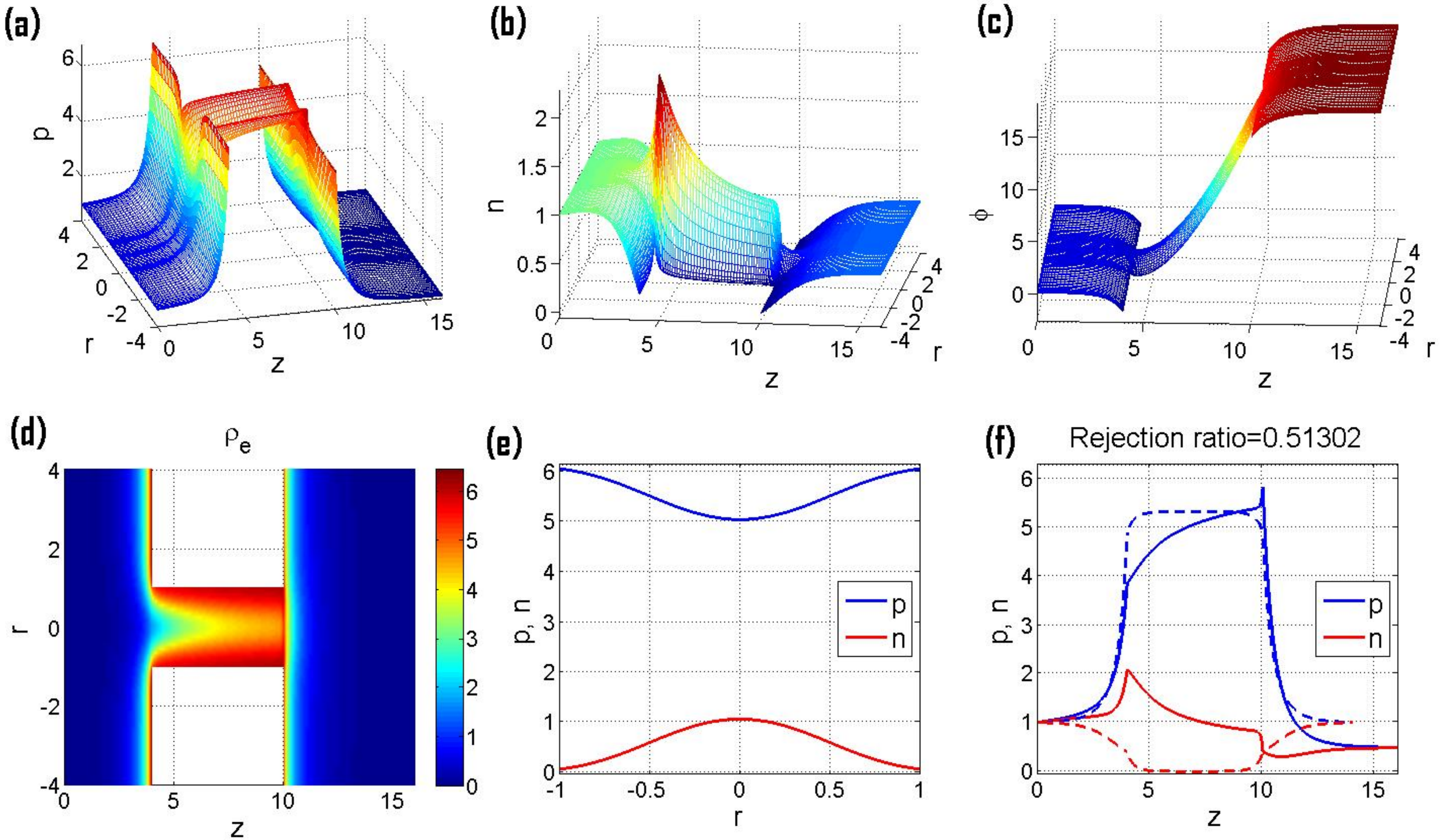
Parameters used: $Sc = 466, U_0 = 0.1, \sigma = 3, \Gamma = 1, \left(\frac{\partial \phi}{\partial n}\right)_p = 3, \left(\frac{\partial \phi}{\partial n}\right)_m = 3,$ $g_{ij} = 1, \ \forall i, j.$ Ion diffusion coefficients inside nanopore are reduced to be 20% of bulk solution value.



Parameters used: $Sc = 466, U_0 = 0.1, \sigma = 3, \Gamma = 1, \left(\frac{\partial \phi}{\partial n}\right)_p = 3, \left(\frac{\partial \phi}{\partial n}\right)_m = 3,$ $g_{ij} = 10,\ \forall i, j.$ Ion diffusion coefficients inside nanopore are reduced to be 20% of bulk solution value.

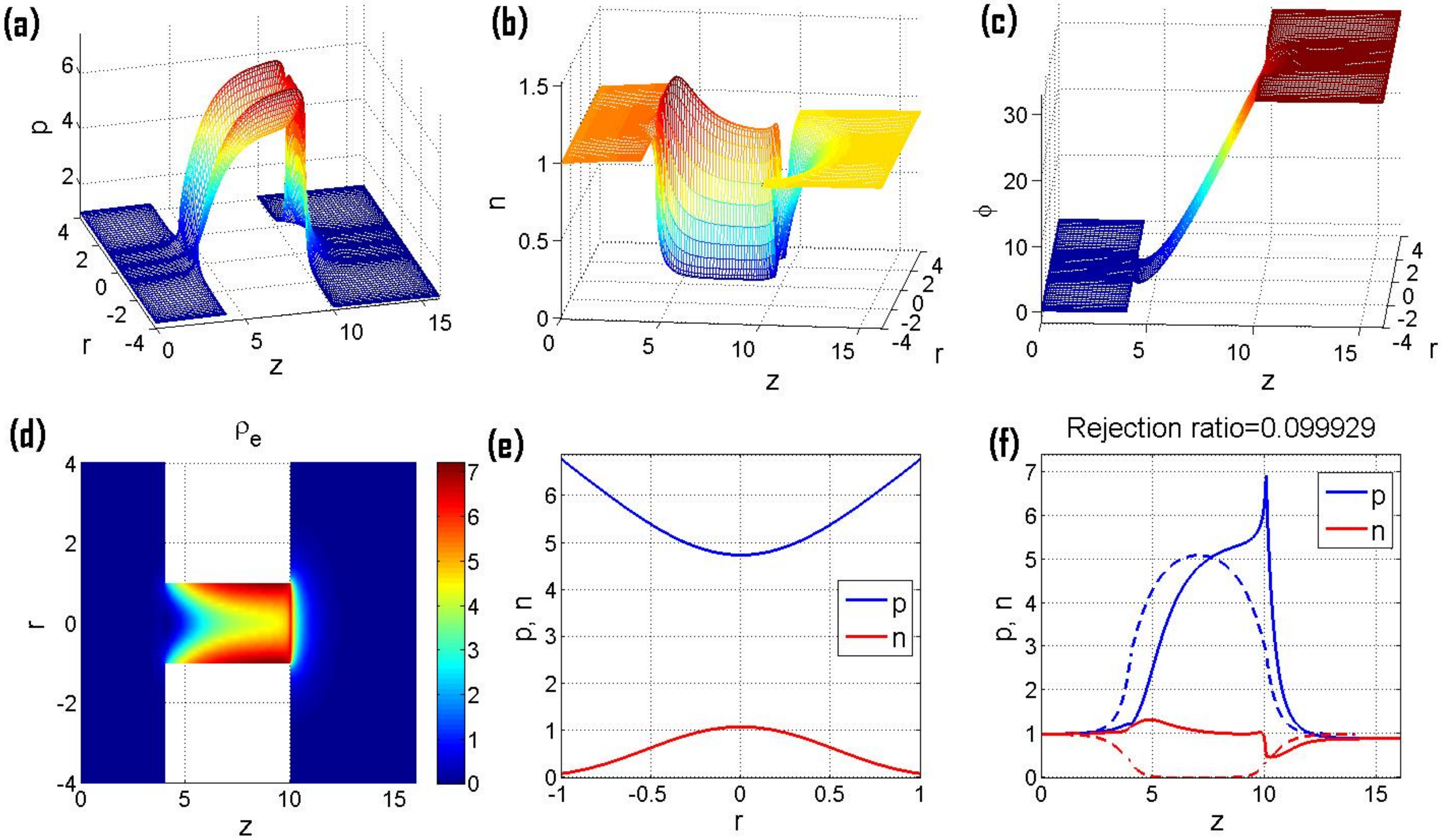


Parameters used: $Sc = 466, U_0 = 0.1, \sigma = 3, \Gamma = 1, \left(\frac{\partial \phi}{\partial n}\right)_p = 3, \left(\frac{\partial \phi}{\partial n}\right)_m = 3,$ $g_{ij} = 100,\ \forall i, j.$ Ion diffusion coefficients inside nanopore are reduced to be 20% of bulk solution value.



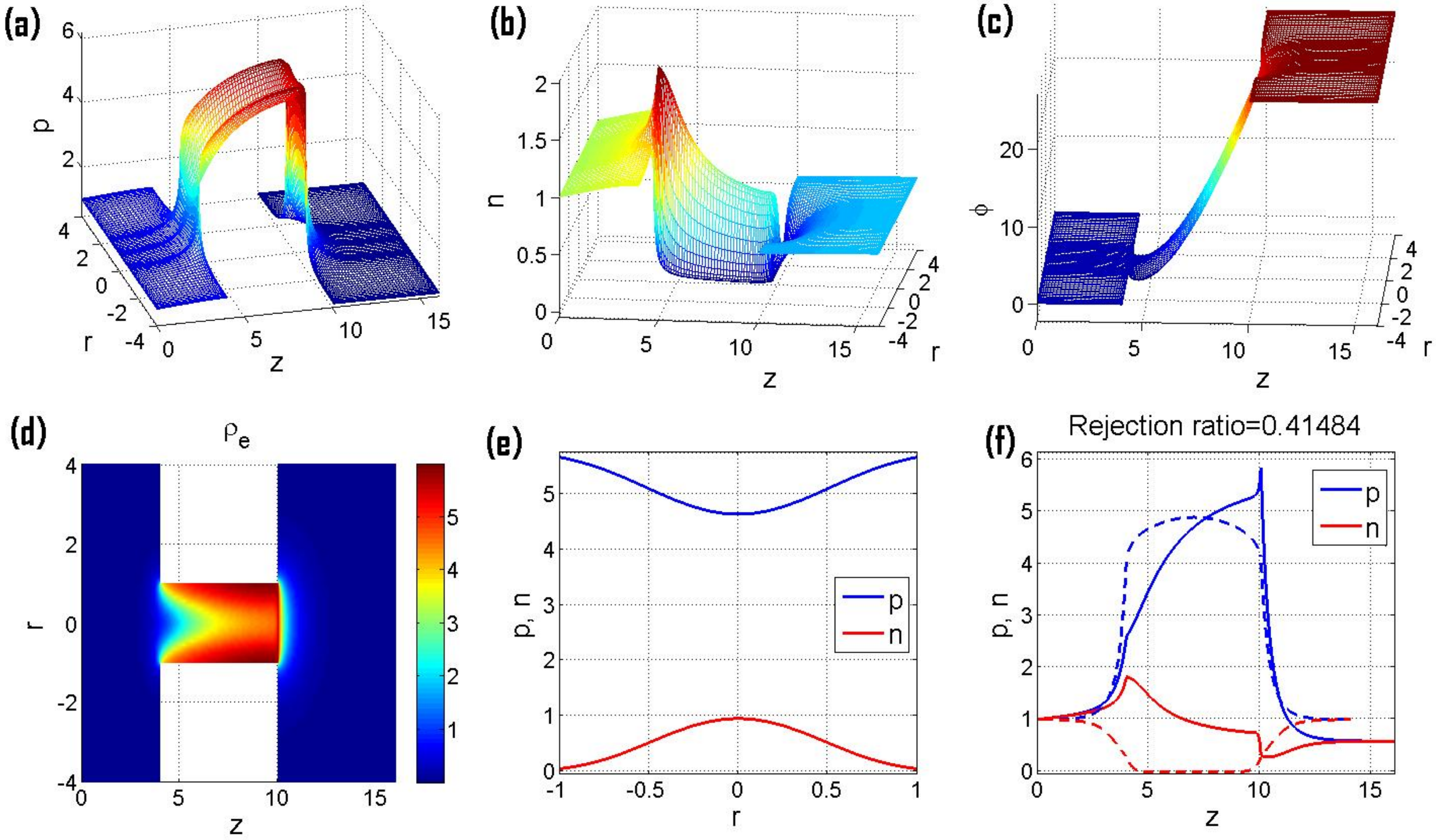
Parameters used: $Sc = 466, U_0 = 0.1, \sigma = 3, \Gamma = 1, \left(\frac{\partial \phi}{\partial n}\right)_p = 3, \left(\frac{\partial \phi}{\partial n}\right)_m = 0,$

$g_{ij} = 1, \ \forall i, j.$ Ion diffusion coefficients inside nanopore are reduced to be 20% of bulk solution value.



Parameters used: $Sc = 466, U_0 = 0.1, \sigma = 3, \Gamma = 1, \left(\frac{\partial \phi}{\partial n}\right)_p = 3, \left(\frac{\partial \phi}{\partial n}\right)_m = 0,$

$g_{ij} = 10,\ \forall i, j.$ Ion diffusion coefficients inside nanopore are reduced to be 20% of bulk solution value.



Parameters used: $Sc = 466, U_0 = 0.1, \sigma = 3, \Gamma = 1, \left(\frac{\partial \phi}{\partial n}\right)_p = 3, \left(\frac{\partial \phi}{\partial n}\right)_m = 0,$ $g_{ij} = 100,\ \forall i, j.$ Ion diffusion coefficients inside nanopore are reduced to be 20% of bulk solution value.

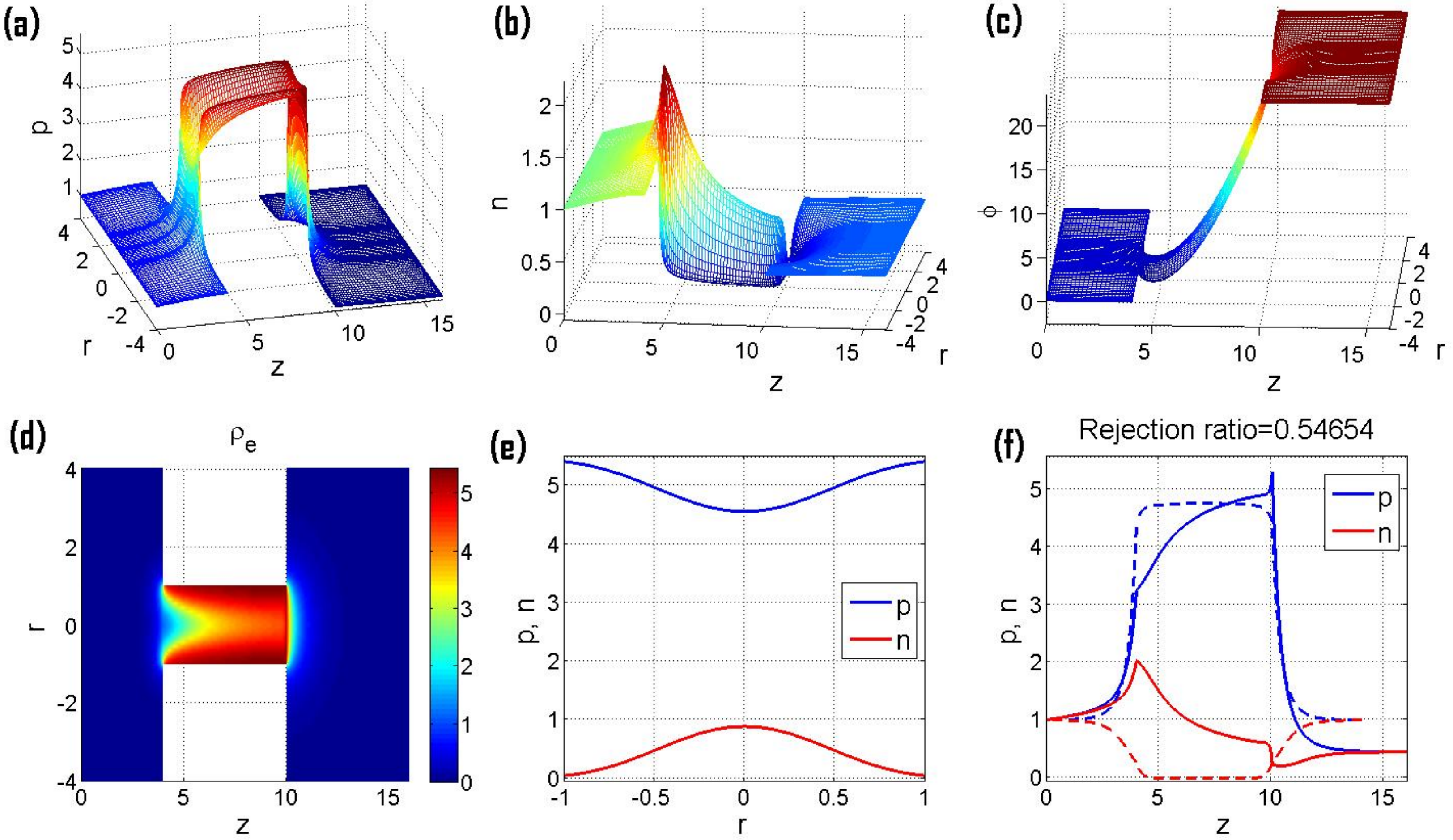


Table 1. Effect of Γ and $\left(\frac{\partial \phi}{\partial n}\right)_p = \left(\frac{\partial \phi}{\partial n}\right)_m$ on salt rejection rate under same σ

Γ and $\left(\frac{\partial \phi}{\partial n}\right)_p = \left(\frac{\partial \phi}{\partial n}\right)_m$	2 and 1.5	1 and 3	0.75 and 4	0.5 and 6
salt rejection ratio	0.2267	0.2508	0.2515	0.2439

Table 2. Effect of g_{ij} inside nanopore on salt rejection rate with σ=3 ($\Gamma = 1$, $\left(\frac{\partial \phi}{\partial n}\right)_p = \left(\frac{\partial \phi}{\partial n}\right)_m = 3$) and ion diffusion coefficient 80% discount inside pore

all g_{ij}	0	0.1	1	10	100
salt rejection ratio	0.1079	0.1120	0.1669	0.3972	0.5130

Table 3. Effect of g_{ij} inside nanopore on salt rejection rate with σ=3 ($\Gamma = 1$, $\left(\frac{\partial \phi}{\partial n}\right)_p = 3$, $\left(\frac{\partial \phi}{\partial n}\right)_m = 0$) and ion diffusion coefficient 80% discount inside pore

all g_{ij}	0	1	10	100
salt rejection ratio	0.0212	0.0999	0.4148	0.5456

日月潭九蛙現形 ...

後勁溪花37億除污 被日月光毀了…

Copyright. Chi Po-lin. Photographer. abovetaiwan@gmail.com

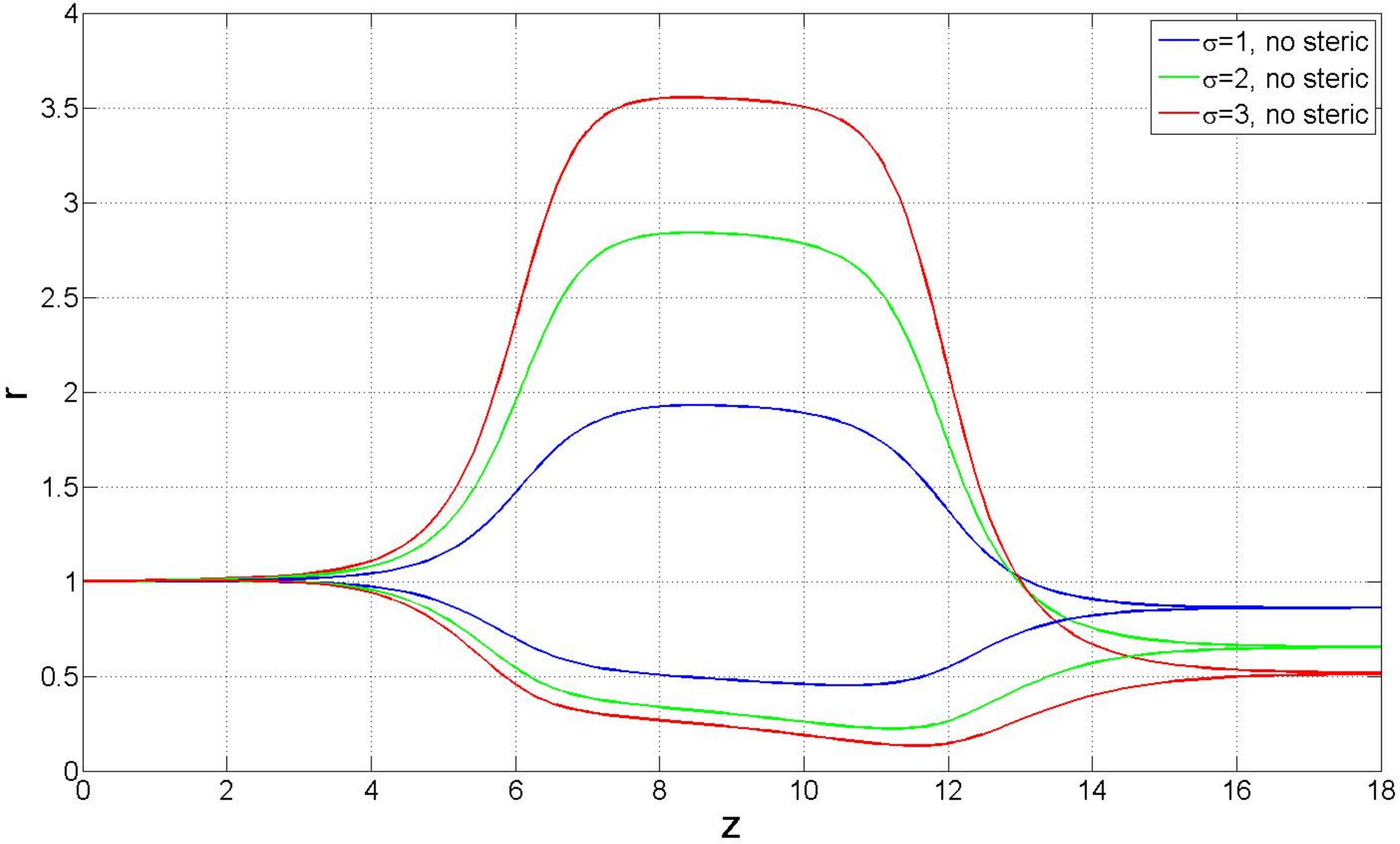
Results

KCl=0.749mM, λ_b=16nm, Γ=1, r_0=16nm, U_{ref}=0.1223m/s, σ=2 (ζ=34.07mV).
Diffusion coefficient in pore reduced to 0.75xbulk value.

Steady-state whole domain distributions of (a) p, (b) n, (c) ϕ, (d) ρ_e, (e) distributions of p, n versus r at z=7 (center location of pore) and (f) distribution of p and n along axis (r=0) with dash lines being the case being the case of U_0=0.001.

Salt rejection rate $R = \dfrac{c_i(-\infty) - c_i(\infty)}{c_i(-\infty)}$.

Effect of σ: distribution of *p* and *n* along axis (*r*=0)

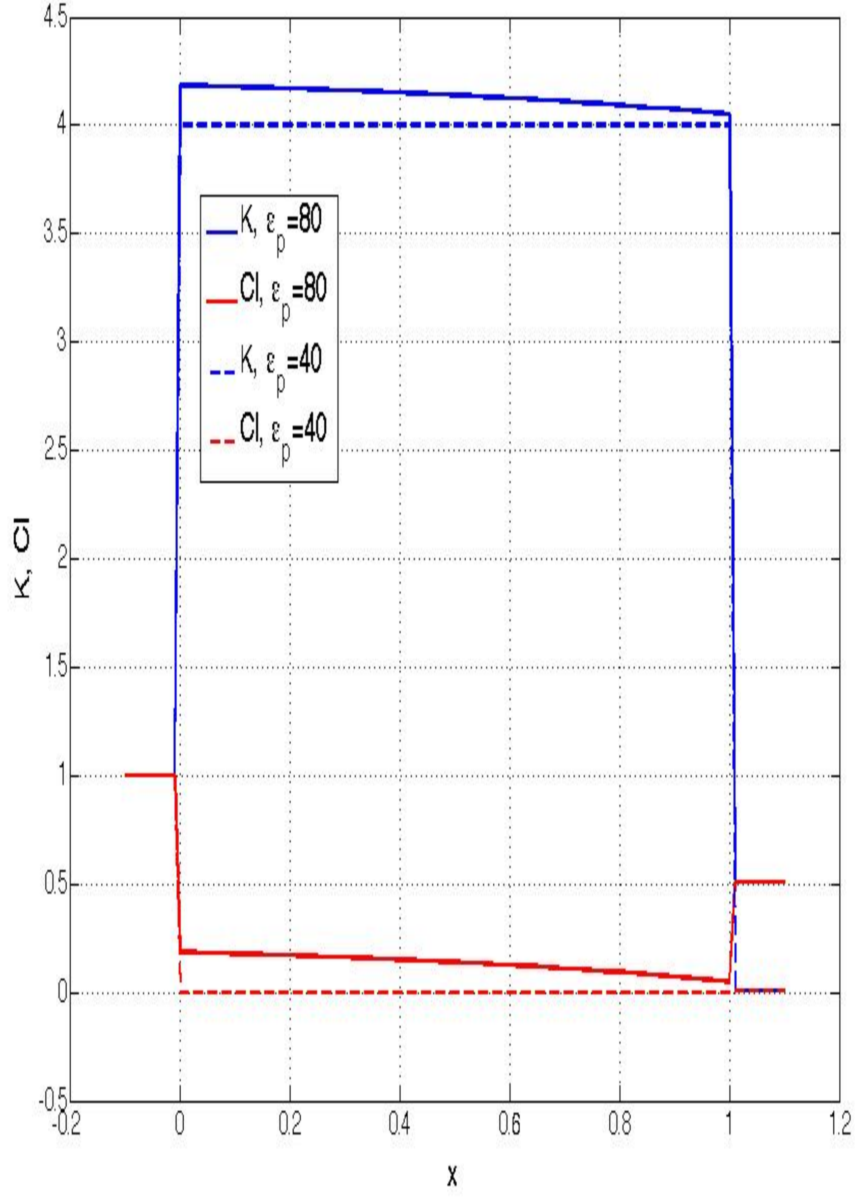


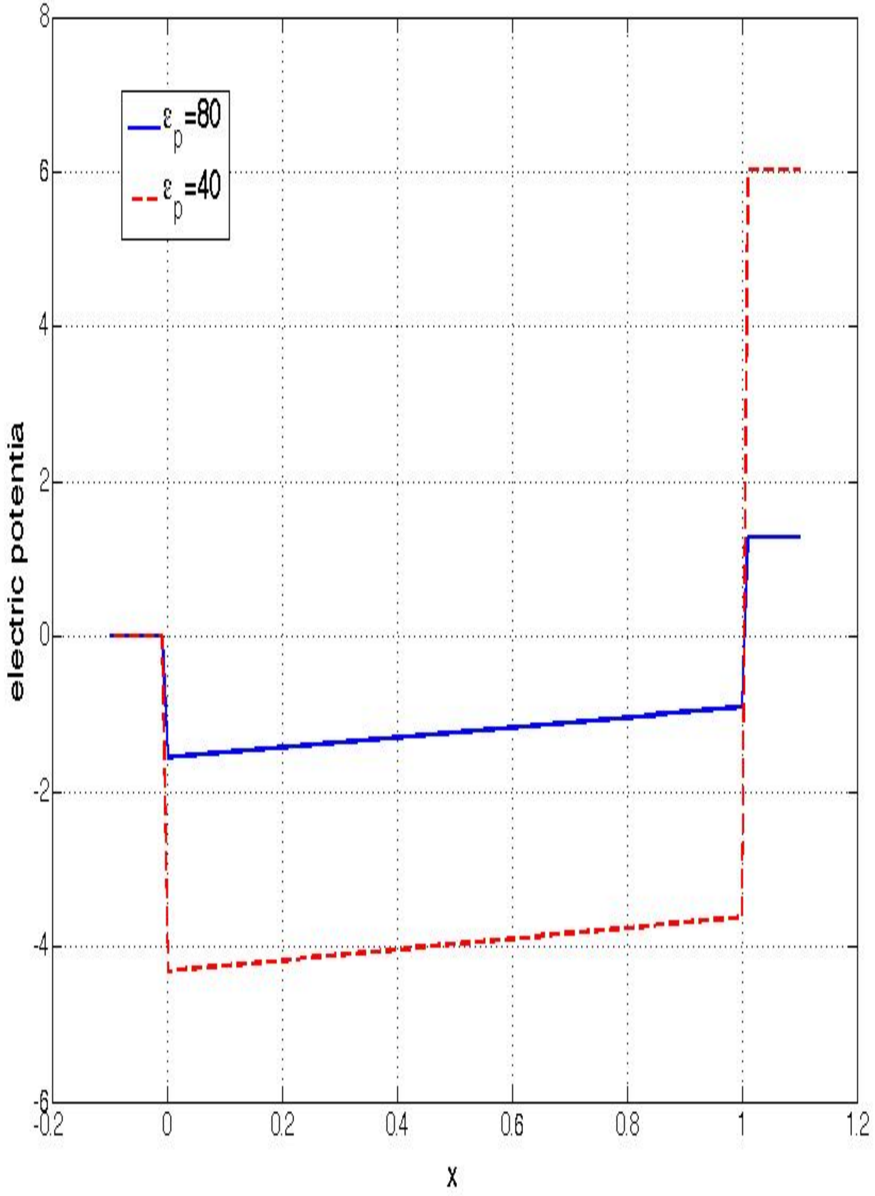
Abstract

Nanofiltration (NF) using membranes with numerous nanopores has gained its popularity in water treatment like desalination. Overlapped electric double layer (EDL) in charged nanopores makes the membrane to be ion selective and reach high rejection rate for salts when driving electrolyte through nanopores by pressure. It has its advantage over reverse osmosis (RO) with smaller pressure exerted and larger water throughput. Here a charged nanopore model is used to describe the physics and geometry of NF. Since the salt rejection process involves convection, diffusion and electro-migration of ions, joint of Poisson-Nernst-Planck (PNP) and Navier-Stokes (NS) equations is employed to study this problem. Steric effect would be significant inside nanopores, and a modified model of PNP with steric effect considered is actually used here. The computational results will be compared with traditional 1D model such as DSPM-DE (Donnan Steric Pore Model-Dielectric Exclusion), and the mechanism of salt rejection will be discussed. We hope we can gain as much physical insights as possible from such a model of simple geometry, and apply to much complicated charged nanopores like ion channel on cell membrane in the future.

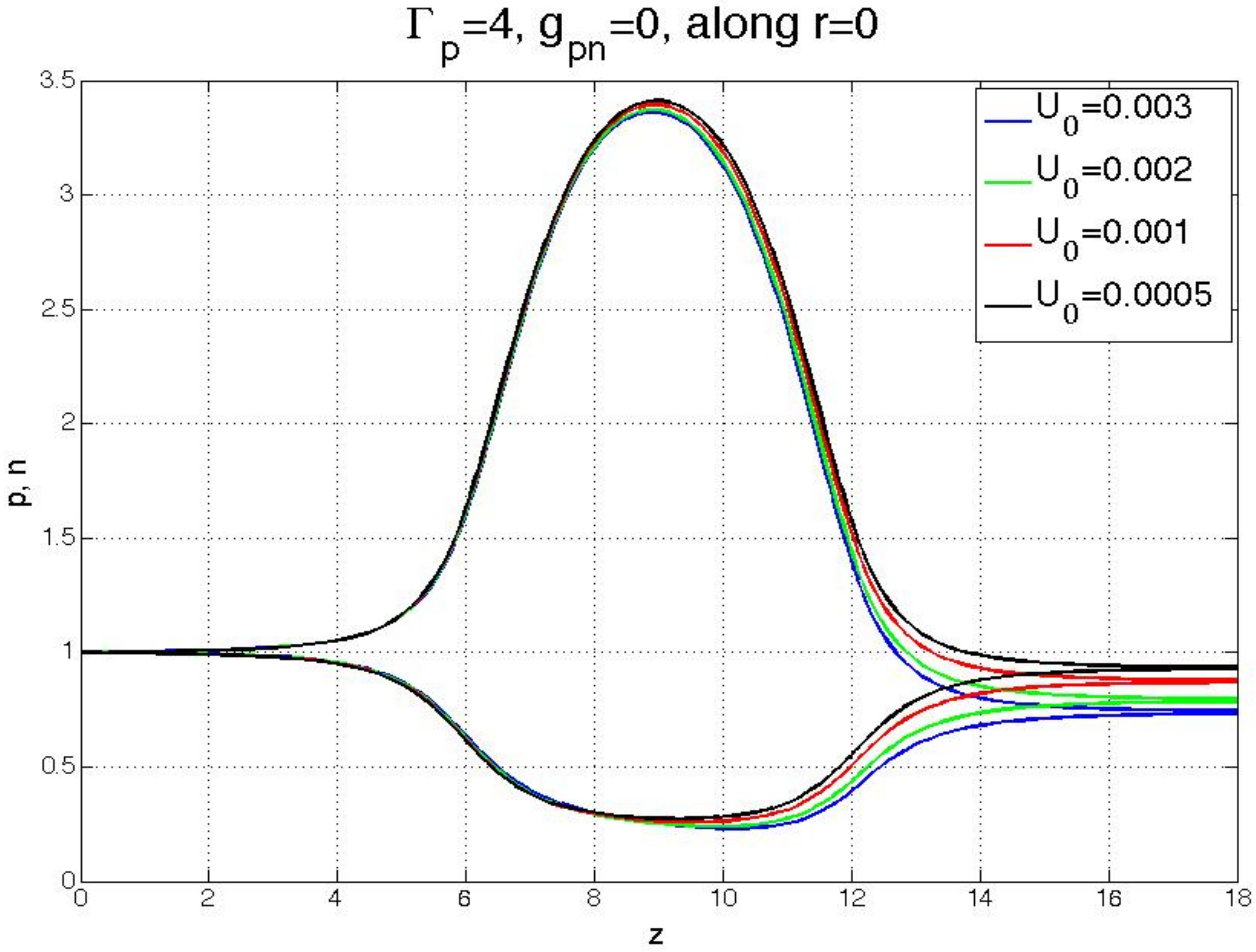
Keywords of the presentation: Desalination, nanofiltration, electric double layer, Poisson-Nernst-Planck equations, Navier-Stokes equations, steric effect.

DSPM-DE at U_0=0.003





Convection effect



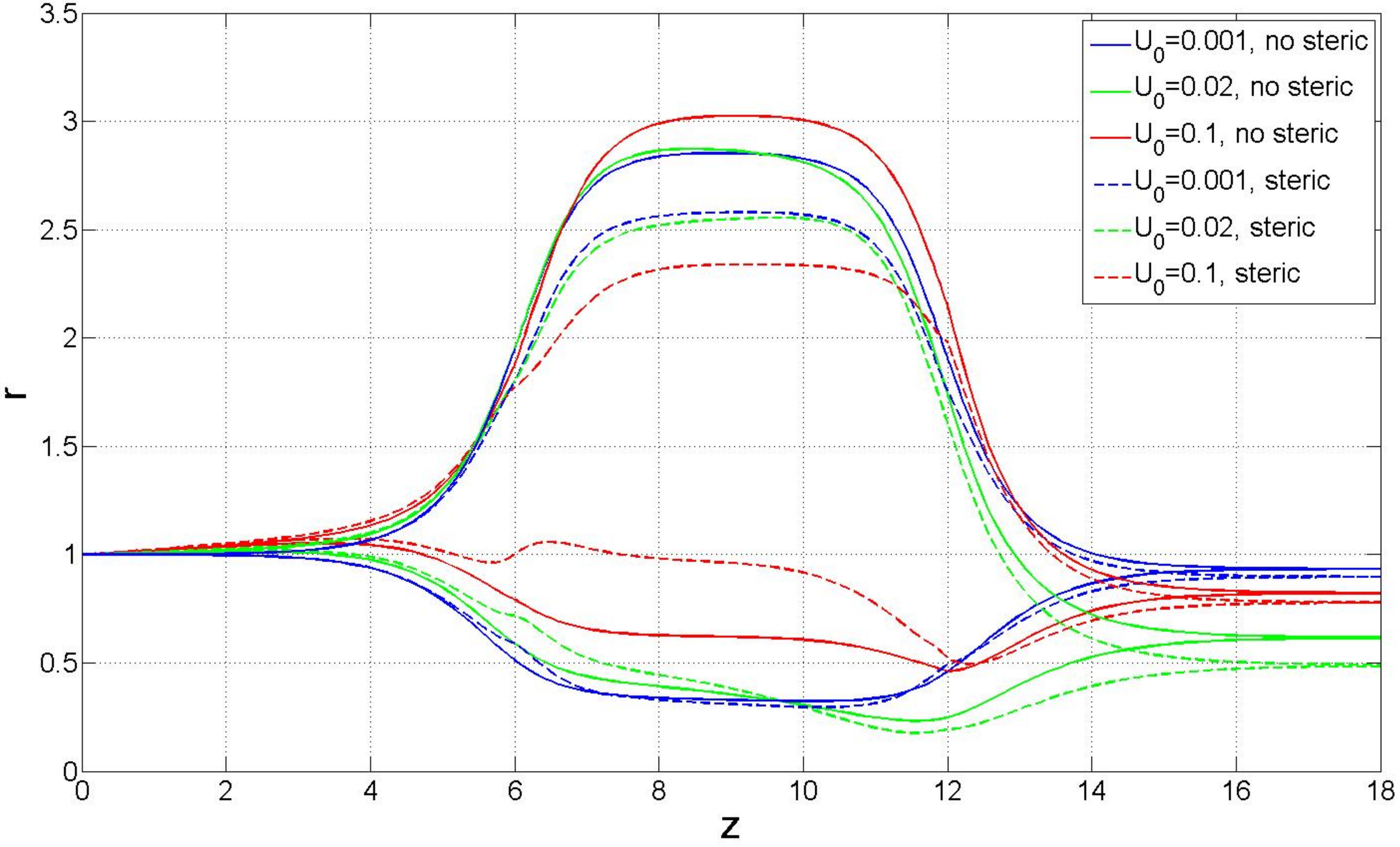
Results: a case of UF

Parameters:
[KCl]=7.4885e-4M, r_0=16nm, U_{ref}=0.12231m/s,
ε_p=80, λ_b=16nm, Γ_{p}=1.
Surface charge density σ=-2 (ζ=-34.069mV), distributed inside pore and membrane surface.
Diffusion coefficient in pore same as bulk value.

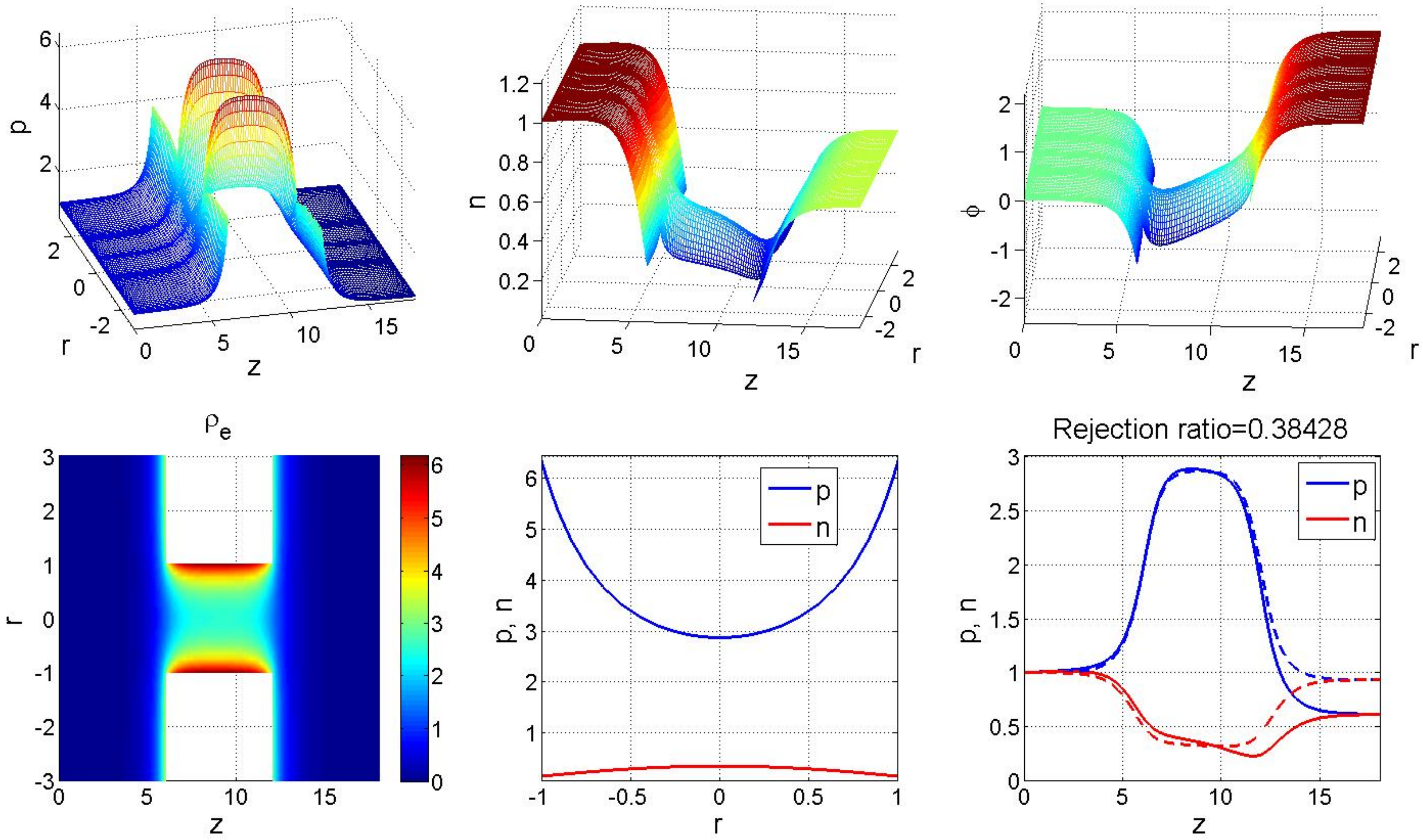
Input: a bunch of U_0's with various $g_{pn}=g_{np}$ ($g_{pn}=g_{np}=0$).

Output: salt rejection rate $R = \dfrac{c_i(-\infty) - c_i(\infty)}{c_i(-\infty)}$.

Distribution of p and n along axis (r=0), no steric: all g_{ij}=0; steric: g_{pp}=g_{nn}=0. g_{pn}=g_{np}=0.5

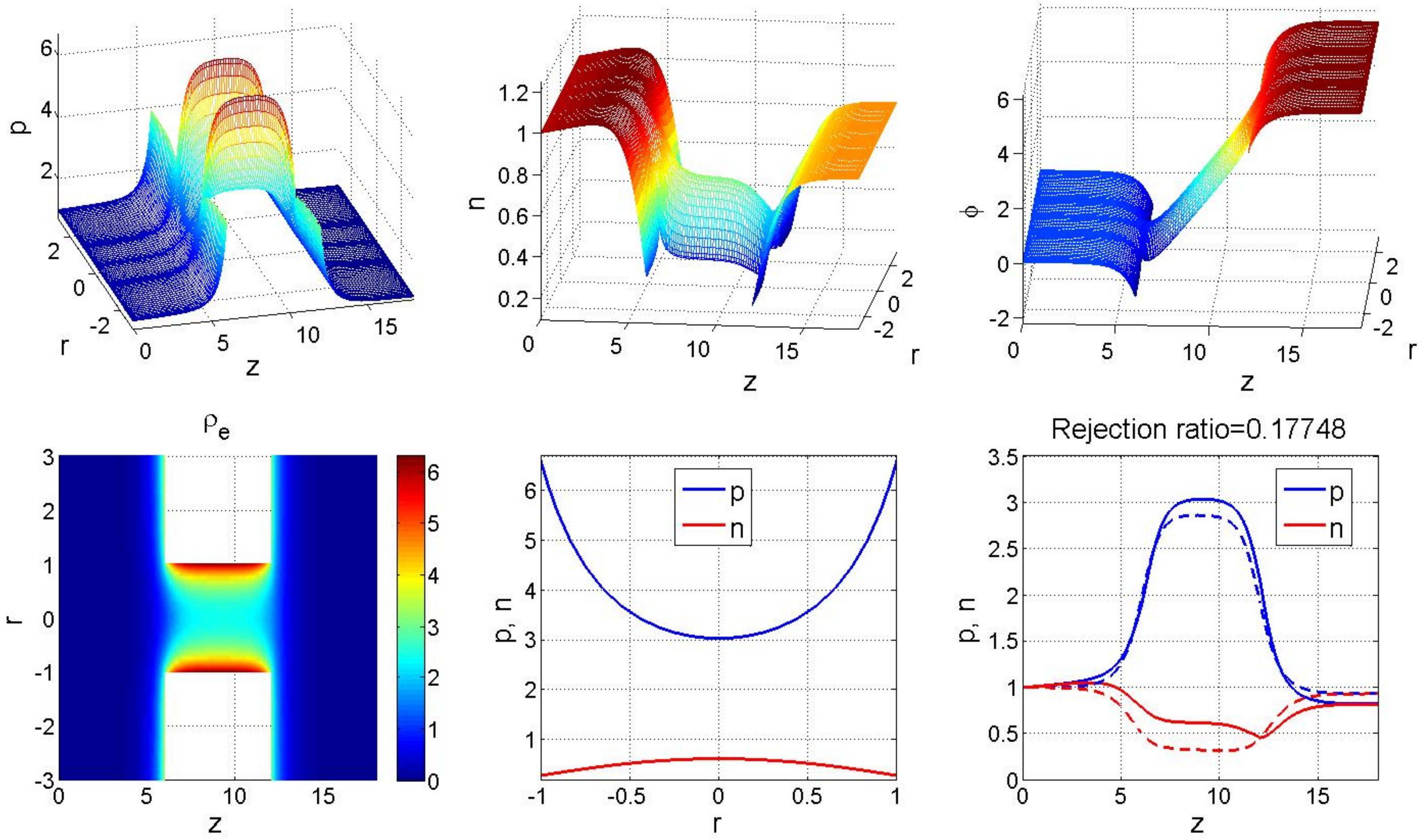


U_0=0.02, g_{pn}=0.



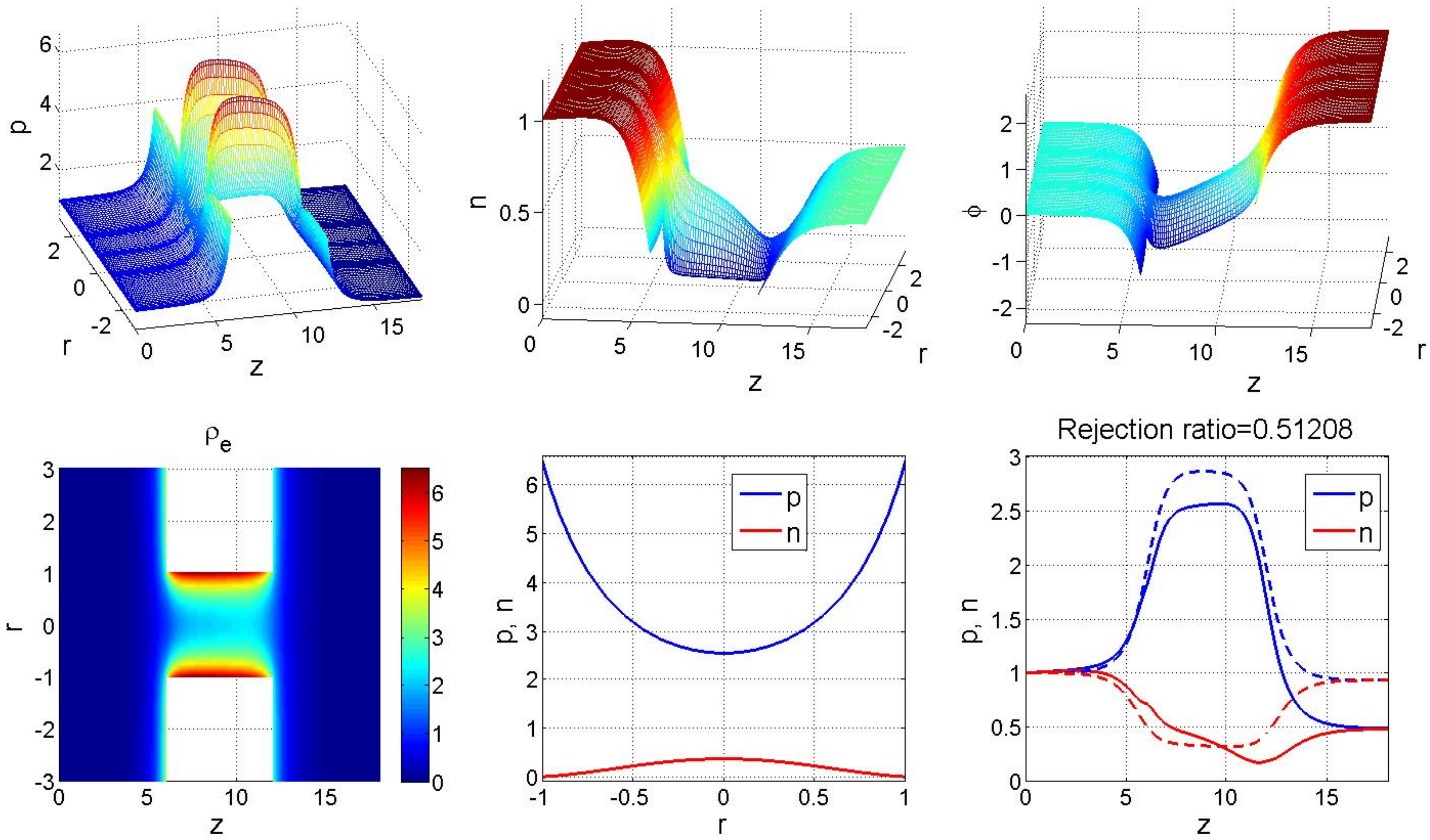
Steady-state whole domain distributions of (a) p, (b) n, (c) ϕ, (d) ρ_e, (e) distributions of p, n versus r at z=9 (center location of pore) and (f) distribution of p and n along axis (r=0) with dash lines being the case being the case of U_0=0.001.

U_0=0.1, g_{pn}=0.



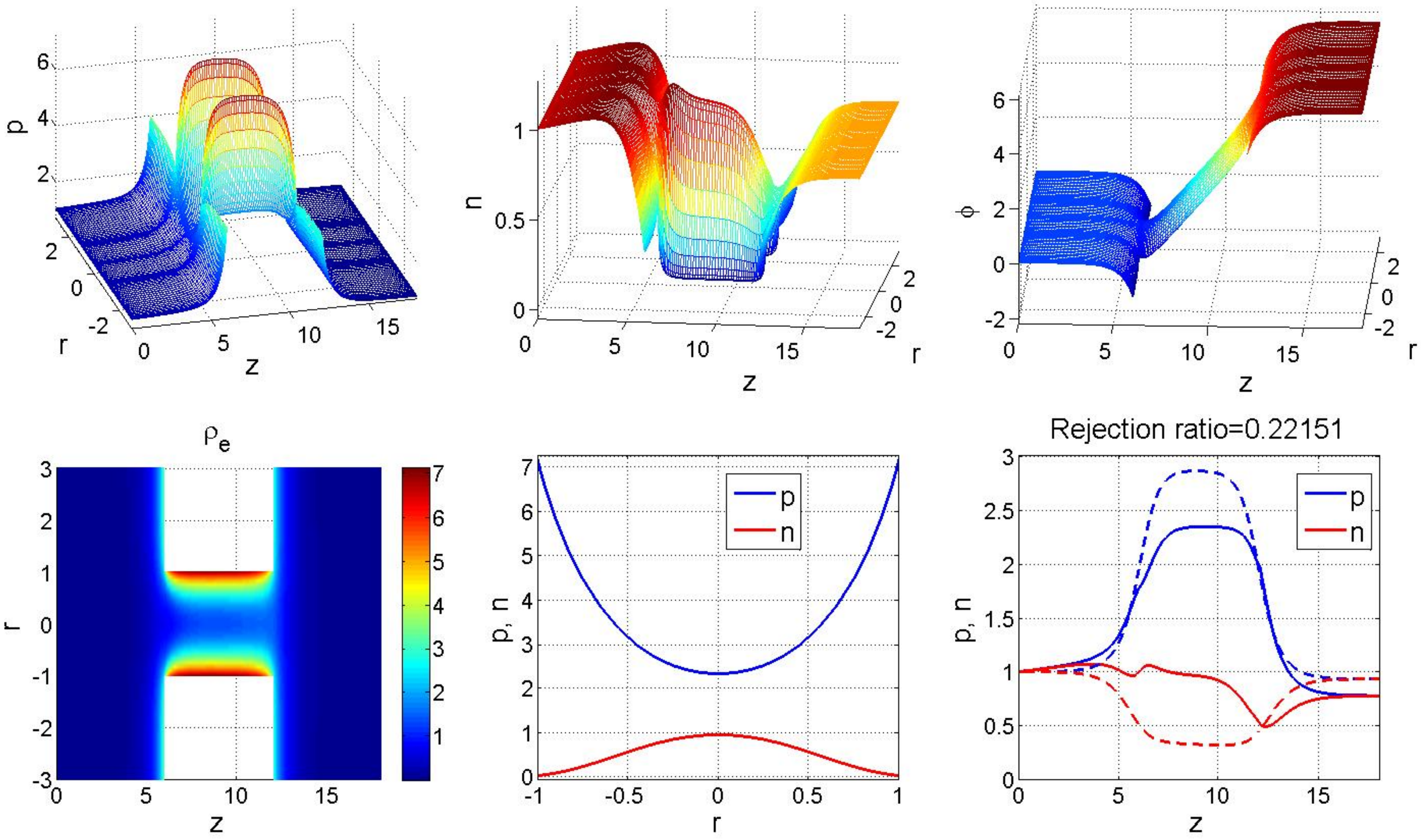
Steady-state whole domain distributions of (a) *p*, (b) *n*, (c) ϕ, (d) ρ_e, (e) distributions of *p*, *n* versus *r* at *z*=9 (center location of pore) and (f) distribution of *p* and *n* along axis (*r*=0) with dash lines being the case being the case of U_0=0.001.

U_0=0.02, g_{pn}=0.5



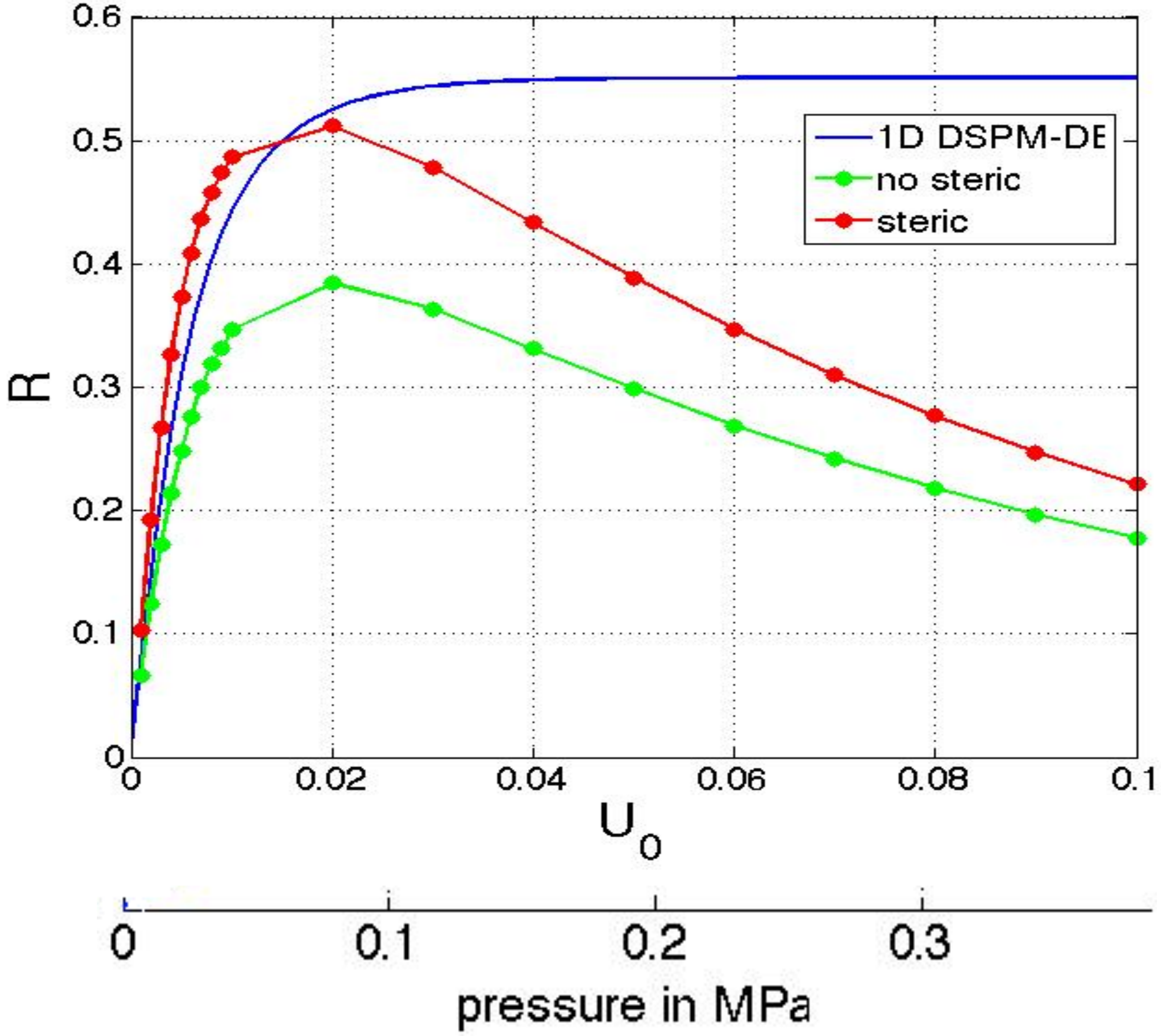
Steady-state whole domain distributions of (a) p, (b) n, (c) ϕ, (d) ρ_e, (e) distributions of p, n versus r at z=9 (center location of pore) and (f) distribution of p and n along axis (r=0) with dash lines being the case being the case of U_0=0.001.

U_0=0.1, g_{pn}=0.5

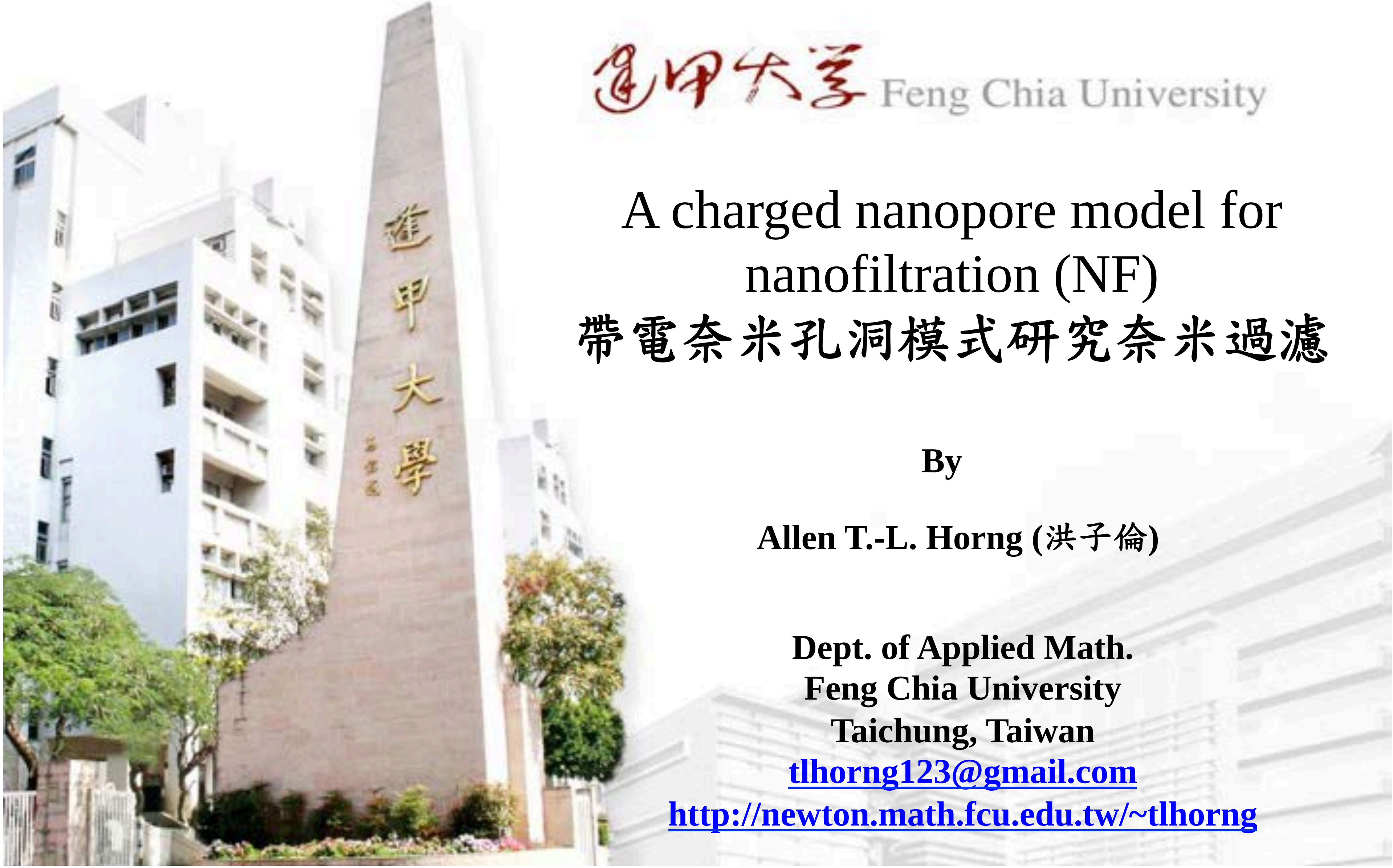


Steady-state whole domain distributions of (a) *p*, (b) *n*, (c) ϕ, (d) ρ_e, (e) distributions of *p*, *n* versus *r* at *z*=9 (center location of pore) and (f) distribution of *p* and *n* along axis (*r*=0) with dash lines being the case being the case of U_0=0.001.

UF case, no steric: all g_{ij}=0; steric: g_{pp}=g_{nn}=0, g_{pn}=g_{np}=0.5.



IMA Hot Topics Workshop **Mathematics of Biological Charge Transport: Molecules and Beyond, July 20-24, 2015**



逢甲大學 Feng Chia University

A charged nanopore model for nanofiltration (NF)
帶電奈米孔洞模式研究奈米過濾

By

Allen T.-L. Horng (洪子倫)

Dept. of Applied Math.
Feng Chia University
Taichung, Taiwan
tlhorng123@gmail.com
http://newton.math.fcu.edu.tw/~tlhorng

3rd International Workshop on Heat Transfer Advances for energy Conservation and Pollution Control (IWHT 2015), Taipei, Taiwan, 10/16-18, 2015.

逢甲大學 Feng Chia University

Mass transfer in a charged nanopore - a mathematical model for nanofiltration

By

Allen T.-L. Horng (洪子倫)*
Y.-H. Cheng (鄭憶湘)**

***Dept. of Applied Math.**
Feng Chia University
Taichung, Taiwan

****Dept. of Materials Integrity Research,**
Industrial Technology Research Institute,
Hsinchu, Taiwan

Results: a case of NF

Parameters:

[KCl]=0.011982M, r_0=2nm, U_{ref}=0.97850m/s,

4 dielectric situations inside pore are considered:

(1) $\varepsilon_p=80$, λ_b=4nm, $\Gamma_{\mathrm{p}}=4$,

(2) $\varepsilon_p=40$, λ_b=2.8284nm, $\Gamma_{\mathrm{p}}=2$,

(3) $\varepsilon_p=20$, λ_b=2nm, $\Gamma_{\mathrm{p}}=1$,

(4) $\varepsilon_p=10$, λ_b=1.4142nm, $\Gamma_{\mathrm{p}}=0.5$,

Surface charge density $\sigma=-2$ (ζ=-17.945mV), only distributed inside pore.

Diffusion coefficient in pore reduced to 0.25 bulk value (from DSPM-DE).

Input: a bunch of U_0's with various $g_{pn}=g_{np}$ ($g_{nn}=g_{pp}=0$).

Output: salt rejection rate $R= \dfrac{c_i(-\infty)-c_i(\infty)}{c_i(-\infty)}$.

- From the point of view of continuum model, ion channel is actually a charged nanopore immersed in electrolyte with complicated geometry (structure) and solvated environment.
- Model is also complicated (steric effect, solvation situation, …). Charge distribution is complicated. 3D Computation is difficult.
- Have we fully understood the physical mechanism of a simple charged nanopore? If not (at least for myself), let us study a simple cylindrical nanopore with uniform surface charge density first. Avoid complex geometry and charge distribution, and focus on effectiveness of model.
- Easier to conduct experiments to check model.
- Charged nanopore nowadays has important applications: desalination, supercapacitor (quick current for TESLA motor), DNA translocation, electro-kinetic battery …