Modification of PNP-steric model with additional bi-Laplacian diffusion

Tzyy-Leng Horng (洪子倫)
Department of Applied Mathematics
Feng Chia University
Taichung, Taiwan
E-mail: tlhorng123@gmail.com
http://newton.math.fcu.edu.tw/~tlhorng

Collaborators: B. Eisenberg, T. C. Lin, C. Liu and etc.

PNP steric model

THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

pubs.acs.org/JPCB

PNP Equations with Steric Effects: A Model of Ion Flow through Channels

Tzyy-Leng Horng

Department of Applied Mathematics, Feng Chia University, 100 Wen-Hwa Road, Taichung, Taiwan 40724

Tai-Chia Lin

Department of Mathematics, Taida Institute for Mathematical Sciences (TIMS), No. 1, Sec. 4, National Taiwan University, Roosevelt Road, Taipei 106, Taiwan

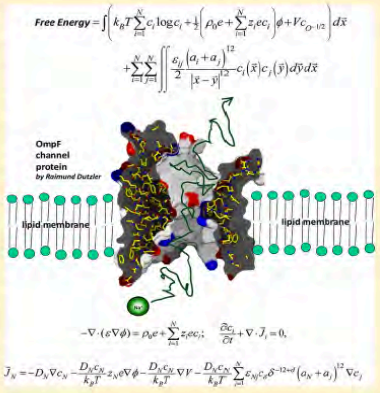
Chun Liu

Department of Mathematics, Pennsylvania State University University Park, Pennsylvania 16802, United States

Bob Eisenberg*

Department of Molecular Biophysics and Physiology, Rush University, 1653 West Congress Parkway, Chicago, Illinois 60612, United States

ABSTRACT: The flow of current through an ionic channel is studied using the energetic variational approach of Liu applied to the primitive (implicit solvent) model of ionic solutions. This approach allows the derivation of self-consistent (Euler−Lagrange) equations to describe the flow of spheres through channels. The partial differential equations derived involve the global interactions of the spheres and are replaced here with a local approximation that we call steric PNP (Poisson−Nernst−Planck) (Lin, T. C.; Eisenberg, B. To be submitted for publication, 2012). Kong combining rules are used and a range of values of steric interaction parameters are studied. These parameters change the energetics of steric interaction but have no effect on diffusion coefficients in models and simulations. Calculations are made for the calcium (EEEE, EEEA) and sodium channels (DEKA) previously studied in Monte Carlo simulations with comparable results. The biological function is quite sensitive to the steric interaction parameters, and we speculate that a wide range of the function of channels and transporters, even enzymes, might depend on such terms. We point out that classical theories of channels, transporters, and enzymes depend on ideal representations of ionic solutions in which nothing interacts with nothing, even in the enormous concentrations found near and in these proteins or near electrodes in electrochemical cells for



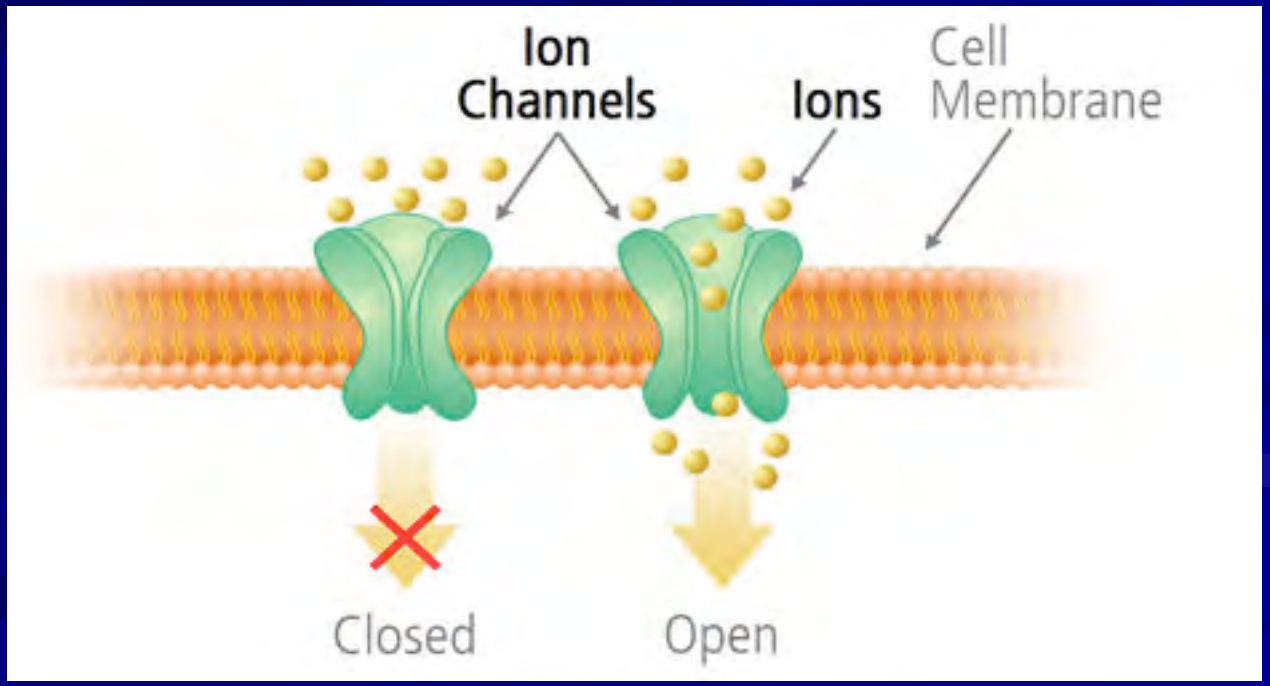
T.-L. Horng, T.-C. Lin, C. Liu and B. Eisenberg*, 2012, "PNP equations with steric effects: a model of ion flow through channels", Journal of Physical Chemistry B, 116: 11422-11441

Motivation

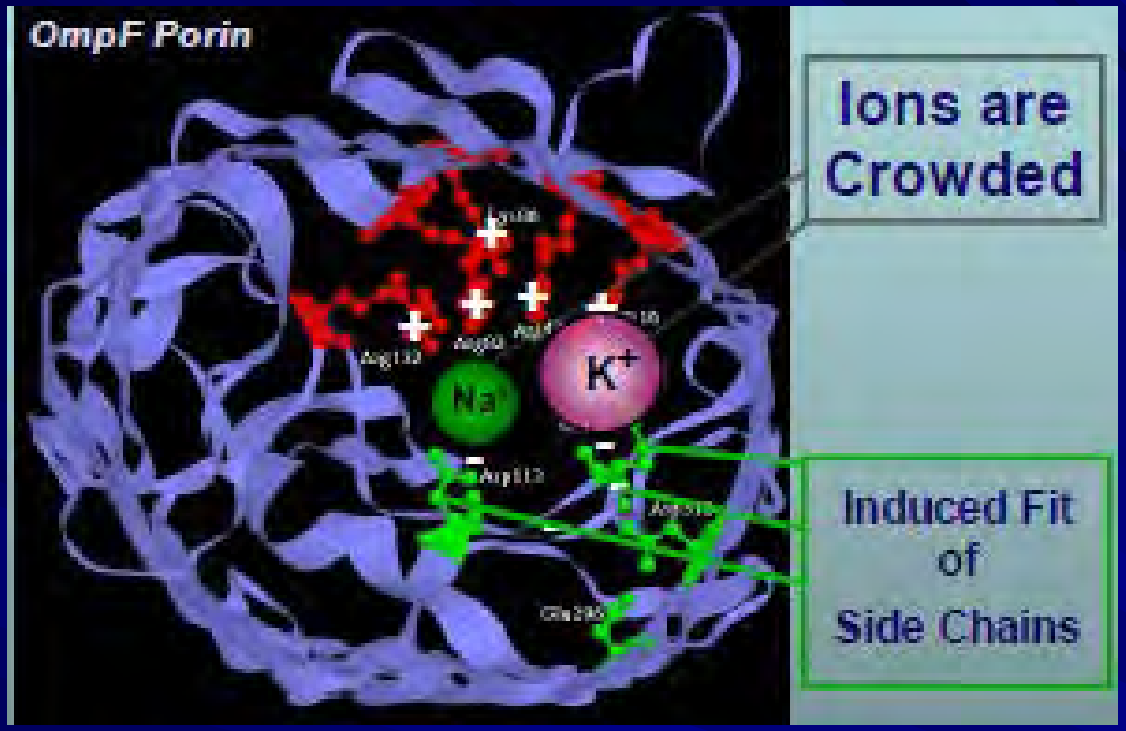
- Ion transport is crucial in the study of many physical and biological problems, such as
- electro-kinetic fluids like fuel cell, EOF, electrophoresis, nano-filtration, and etc. (PNP + Navier-Stokes eqs. + etc.)
- ion channels in cell membranes

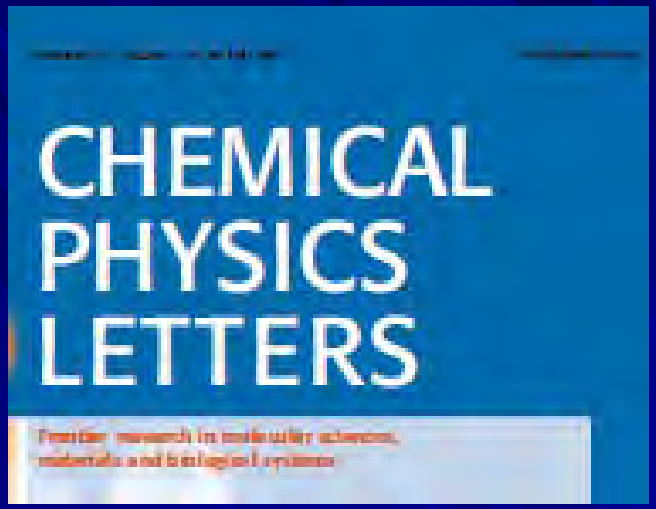
Ion Channels of Membrane

Ion channels are pores in cell membranes and the gatekeepers for cells to control the movement of anions and cations across cell membranes.



3 major issues: gating, permeation and selectivity (focused here).





B. Eisenberg 2011

Everything Interacts with Everything Else

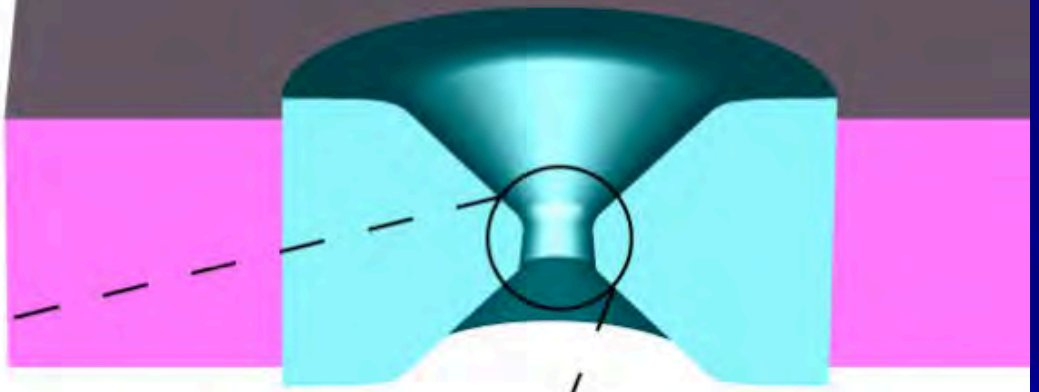
in crowded active sites

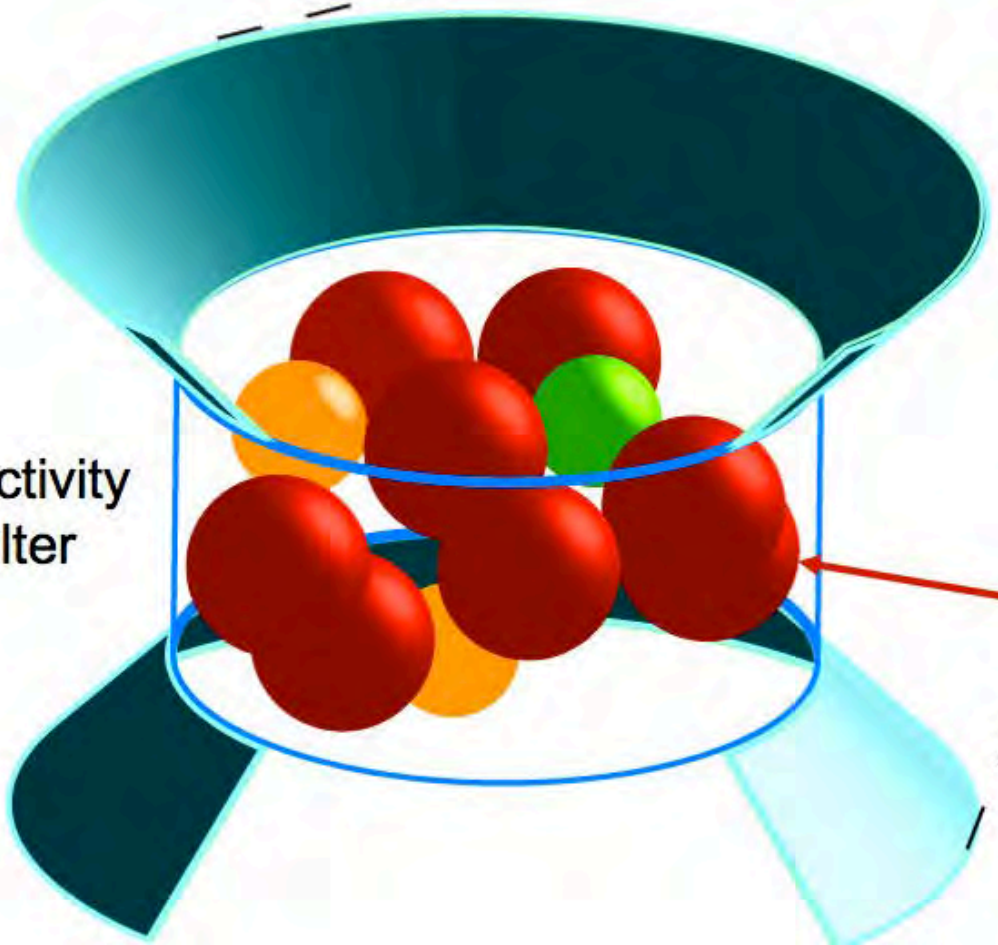
reduced geometry, X-ray structure unavailable.

Selectivity Filter

Crowded with Charge

L type Ca Channel





Selectivity Filter

Na^{+}

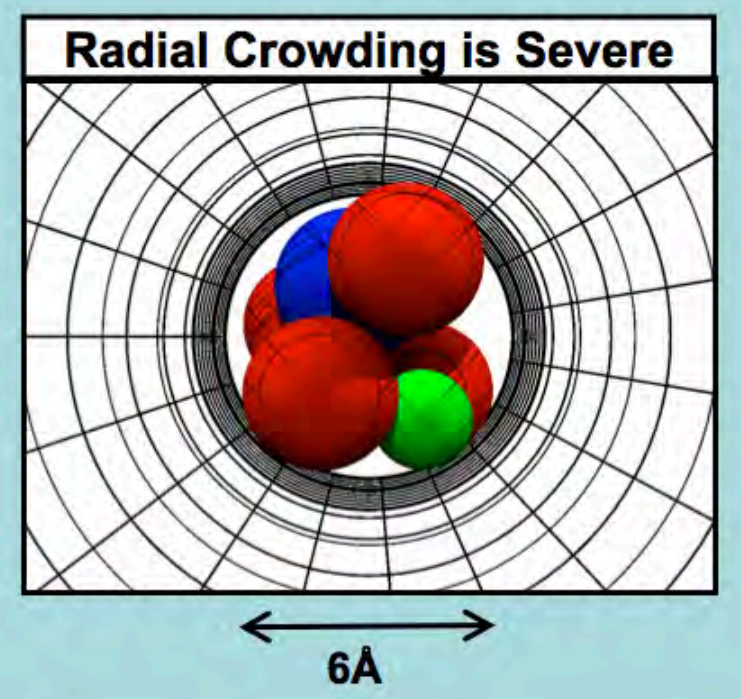
Ca^{++}

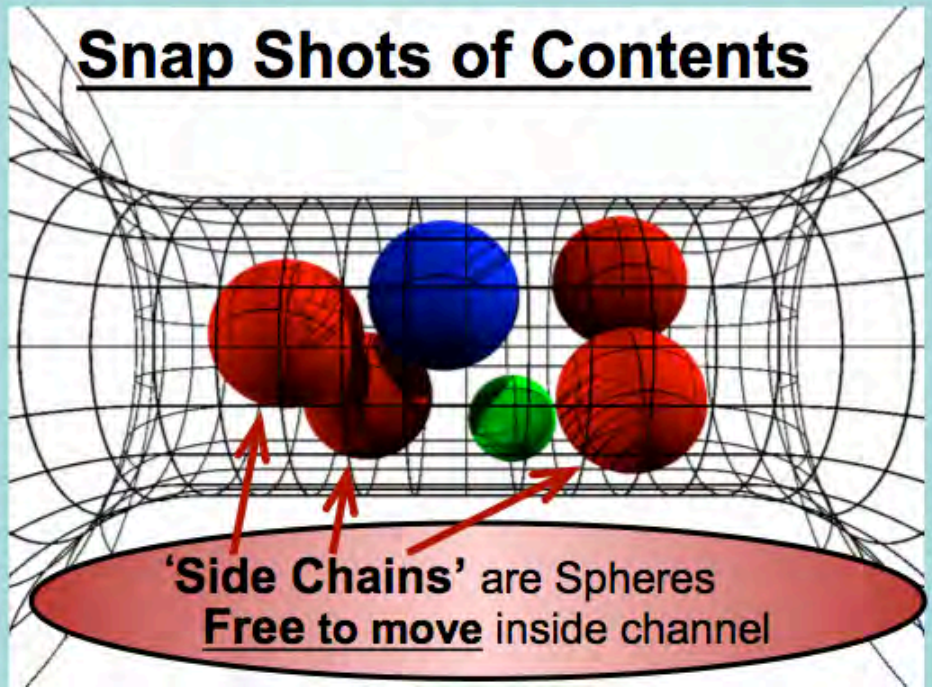
$O^{-1/2}$

"Side Chains"

Wolfgang Nonner

Crowded Ions





Ion Diameters *'Pauling' Diameters*	
Ca^{++}	1.98 Å
Na^{+}	2.00 Å
K^{+}	2.66 Å
'Side Chain' Diameter	
Lysine K	3.00 Å
D or E	2.80 Å
Channel Diameter 6 Å	

Parameters are Fixed in all calculations in all solutions for all mutants

Experiments and Calculations done at pH 8

Boda, Nonner, Valisko, Henderson, Eisenberg & Gillespie

Methods

- Monte Carlo (energy minimization)
- Molecular Dynamics (Large ODE systems)
- Brownian Dynamics (Langevin eq. similar to MD but treating water implicitly. 1e5 speed-up than MD.)
- PDE models (PNP, PB types)

PNP (Poisson-Nernst-Planck)

$$\frac{\partial c_n}{\partial t} = \nabla \cdot \left\{ D_n \left(\nabla c_n - \frac{e}{k_B T} c_n \nabla \phi \right) \right\},$$

$$\frac{\partial c_p}{\partial t} = \nabla \cdot \left\{ D_p \left(\nabla c_p + \frac{e}{k_B T} c_p \nabla \phi \right) \right\},$$

$$\varepsilon \nabla^2 \phi = -e c_n + e c_p,$$

- A standard n transport being crucia many physical and biologic
- Mathematical results: existence, uniqueness and long time dynamics (Arnold et al,'99 and Biler et al, '00)
- Beautiful math theorems but can not show the selectivity of ion channels.

Finite Size Effect

- When ions concentrate into narrow regions, each ion has its own size with strong repulsion to the other ions because two ions can not occupy at the same place.

But the PNP equations presume ions as point particles without size

The PNP system has to be modified

Modified PNP

- PNP + exclusion terms (size effects)

Density functional theory

Gillespie, Nonner and Eisenberg 2002

Liquid-state theory (same size ions)

Kilic, Bazant, and Ajdari 2007 (modified Andelman's model to get MPNP)

Lennard-Jones potential (different size ions)

Eisenberg, Hyon and Liu 2010

Model of Borukhov, Andelman and Orland (1997)

$$F = U - TS,$$

$$U = \int d\mathbf{r}\left(-\frac{\varepsilon}{2}|\nabla\psi|^2 + zec_+\psi - zec_-\psi\right)$$

$$-TS = \frac{kT}{a^3}\int d\mathbf{r}\{c_+a^3\ln(c_+a^3) + c_-a^3\ln(c_-a^3) + (1 - c_+a^3 - c_-a^3)\ln(1 - c_+a^3 - c_-a^3)\}.$$

Free energy

$$\nabla^2\psi = \frac{zec_0}{\varepsilon}\frac{2\sinh\left(\frac{ze\psi}{kT}\right)}{1 + 2\nu\sinh^2\left(\frac{ze\psi}{2kT}\right)}$$

MPB and MPNP (from Bazant)

$$\frac{\partial c_\pm}{\partial\tau} = D\nabla^2 c_\pm \pm \frac{D}{k_BT}ze\nabla\cdot(c_\pm\nabla\psi) + a^3D\nabla\cdot\left(\frac{c_\pm\nabla(c_+ + c_-)}{1 - c_+a^3 - c_-a^3}\right)$$

The Lennard-Jones (LJ) potential

- a well-known mathematical model for the interaction between a pair of ions (Van der Waals force)
- has tremendous applications in biology, chemistry and physics

$$\Psi(x) = \frac{C_1}{r^{12}} - \frac{C_2}{r^6} \quad \text{for} \quad r = |x| > 0, \quad x \in \mathbb{R}^d,$$

Energy functional in Eisenberg, Hyon and Liu (2010)

$$E = \int \left(k_B T \sum_{i=1}^{N} c_i \log c_i + \frac{1}{2}(\rho_0 e + \sum_{i=1}^{N} z_i e c_i)\phi + V c_O^{-1/2} \right) d\vec{x}$$

$$+ \sum_{i=1}^{N} \sum_{j=1}^{N} \int\int \frac{\varepsilon_{ij}}{2} \frac{(a_i + a_j)^{12}}{|\vec{x} - \vec{y}|^{12}} c_i(\vec{x})\, c_j(\vec{y})\, d\vec{y}\, d\vec{x}$$

Everything interacts with everything else' in ionic solutions through the non-local term characterizing hard sphere repulsion

MPNP Model of Eisenberg, Hyon and Liu (2010)

diffusion

electro-migration

steric effect: hard sphere repulsion expressed by LJ

restraining potential for side chain $O^{-1/2}$ to remain within filter

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \left[D_i \left\{ \nabla c_i + \frac{c_i}{k_B T} \left(z_i e \nabla \phi + \sum_{j=1}^{N} \nabla \int \frac{c_0 \varepsilon_{i,j} (a_i + a_j)^{12}}{|\vec{x} - \vec{y}|^{12}} c_j(\vec{y})\, d\vec{y} \right) + M_i c_i \nabla \psi \right\} \right]$$

$$-\nabla \cdot (\varepsilon \nabla \phi) = \rho_0 + \sum_{i=1}^{N} z_i e c_i, \qquad \text{for } i, j = 1, \cdots, N, \tag{1.3}$$

$$\frac{\partial \psi}{\partial t} = 0.$$

where

$$\psi = \begin{cases} 0, & \text{for the inside of channel,} \\ 1, & \text{for the outside of channel,} \end{cases} \quad c_0 = \begin{cases} 1, & i = j, \\ \frac{1}{2}, & i \neq j, \end{cases} \quad M_i = \begin{cases} 5 & \text{for } O^{-1/2} \text{ ion} \\ 0 & \text{otherwise,} \end{cases}$$

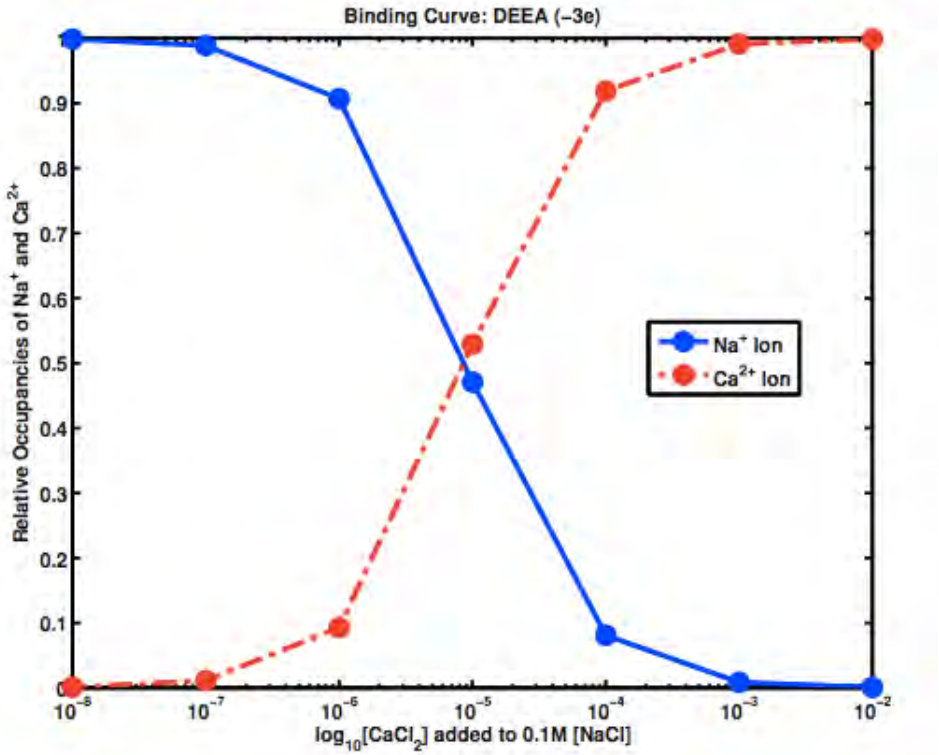
and ρ_0 is the permanent charge in the system.

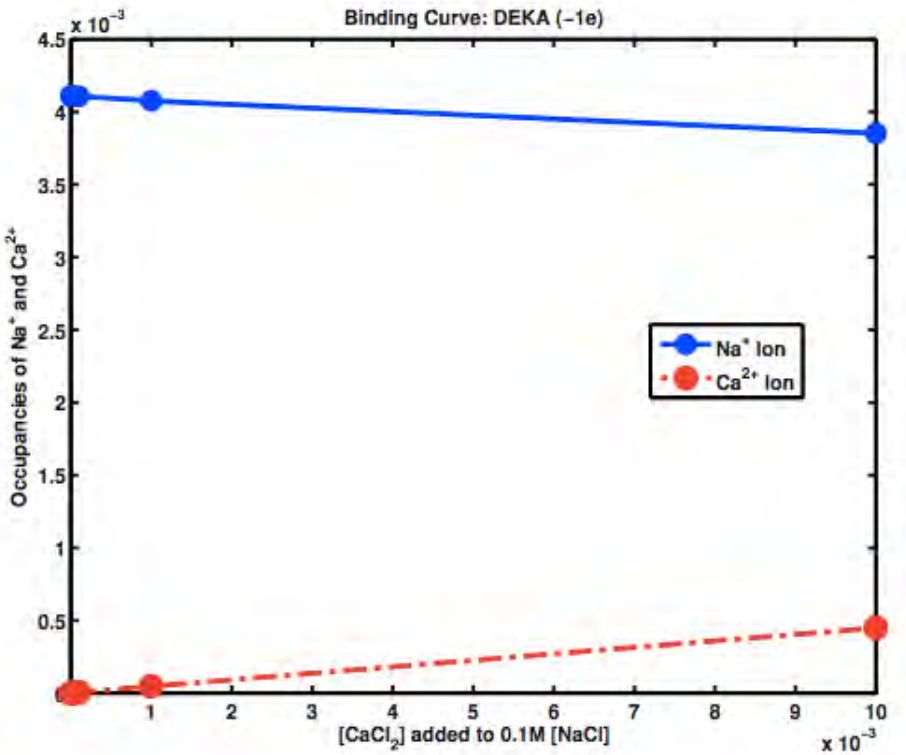
1D Results of Eisenberg, Hyon and Liu (2010) model to study Ca and Na channel selectivity with binding curves as follows:

DEKA Sodium Channel 6 Å

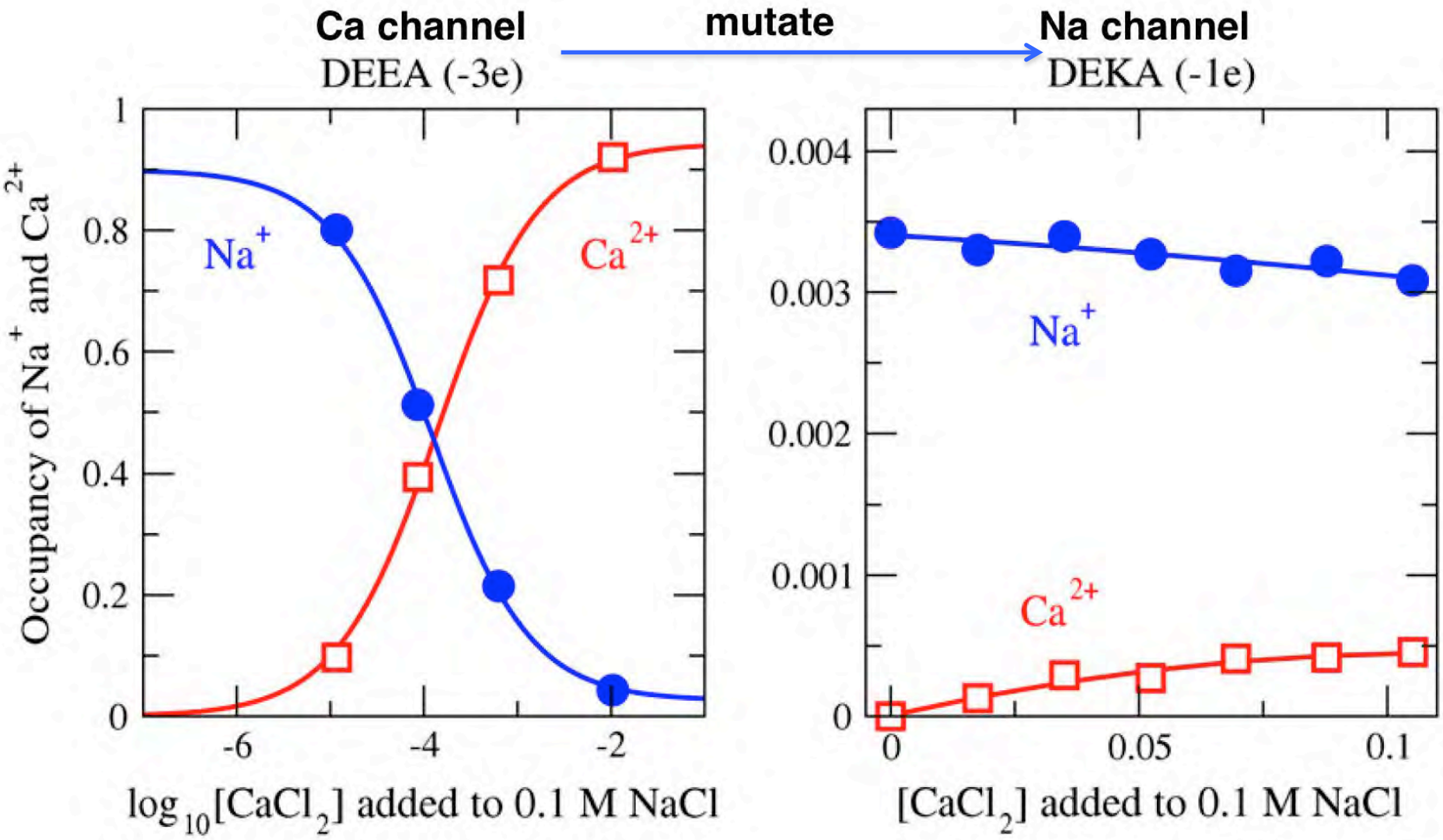
Aspartate	D	Acid	Negative
Glutamate	E	Acid	Negative
Lysine	K	Basic	Positive
Alanine	A	Aliphatic	Neutral

$$\text{binding ratio} = (\text{number of } Ca^{2+} \text{ ions inside the filter}) / (\text{number of } Na^{+} \text{ ions inside the filter} + \text{number of } Ca^{2+} \text{ ions inside the filter})$$





Good agreement with Boda et al. (2007) Monte Carlo simulation



Main difficulty of Eisenberg, Hyon and Liu (2010) model

- The LJ potential integral is extremely singular. Need to use flat-top cut-off length based on center-to-center distance among spherical particles.
- Hard to compute the LJ integral by convolution (domain problem, boundary problem).
- Restraining potential ψ alone is not enough to keep $O^{-1/2}$ inside filter.

New approach to the LJ potential

- Use band-limited functions to approximate the LJ potential.
- Find the approximate energy functional without singular integrals.
- Derive the PNP-steric model which is much simpler than the model of Eisenberg, Hyon and Liu (2010).
- Details in Eisenberg and Lin (2013).

Horng, Lin, Liu, and Eisenberg (2012)

$$E_\delta = \int (k_B T \sum_{i=1}^{N} c_i \log c_i + \frac{1}{2}(\rho_0 e + \sum_{i=1}^{N} z_i e c_i)\phi + V c_O^{-1/2})\, d\vec{x}$$

$$+ \sum_{i,j=1}^{N} \frac{g_{ij}}{2} \int c_i(\vec{x})\, c_j(\vec{x})\, d\vec{x}$$

which gives eqs 2, 3, 6, and 7, where $g_{ij} = \varepsilon_{ij}(a_i+a_j)^{12} S_\delta$ for $i = 1,\cdots, N-1$ and $g_{Nj} = \varepsilon_{Nj}(a_i + a_j)^{12} c_\delta S_\delta$.

ε_{ij}'s are coupling constants in steric effect. ε_{ii}'s are mostly determined by LJ parameter C_1 (in water solution), and ε_{ij}'s ($i \neq j$) by combining rule such as Kong rule or Lorenz-Berthelot rule.

PNP-steric model in Horng, Lin, Liu, and Eisenberg (2012)

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

$$\frac{\partial c_i}{\partial t} + \nabla \cdot J_i = 0,$$

Integral replaced by derivative (non-local becoming local) since hard sphere repulsion, unlike Columbic force, characterized by LJ is actually rather short-distance.

$$J_i = -D_i \nabla c_i - \frac{D_i c_i}{k_B T} z_i e \nabla \phi - \frac{D_i c_i}{k_B T} \sum_{j=1}^{N} g_{ij} \nabla c_j + M_i c_{O^{-1/2}} \nabla V,$$

$M_i = 1$, if $i = O^{-1/2}$; $M_i = 0$, otherwise.

Steric effect modify self-diffusion and cause cross-diffusion with effective self-diffusion coefficient:

$$\widetilde{D}_i = D_i \left(1 + \frac{g_{ii} c_i}{k_B T}\right).$$

1D PNP steric model considering variable cross-sectional area

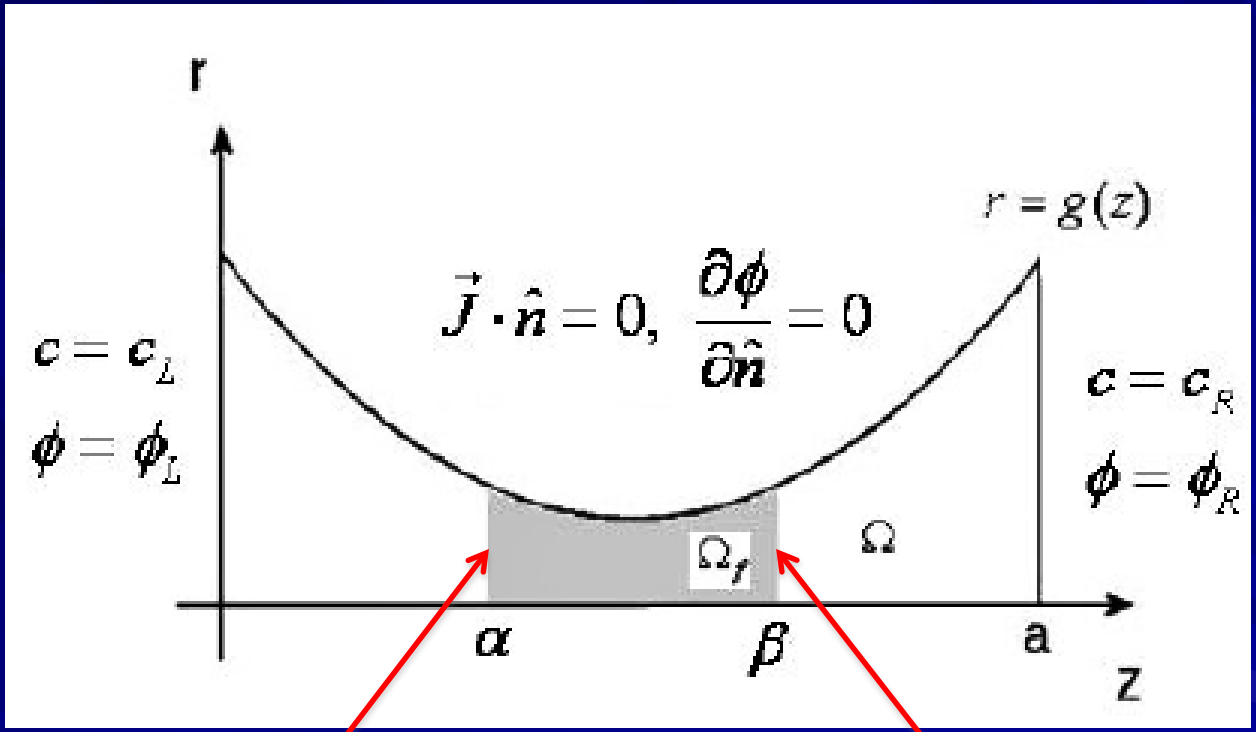
$$-\frac{1}{A}\frac{\partial}{\partial z}\left(\varepsilon A\frac{\partial \phi}{\partial z}\right)=\rho_0+\sum_{i=1}^{N} z_i e c_i,$$

$$\frac{\partial c_i}{\partial t}+\frac{1}{A}\frac{d}{dz}(AJ_i)=0,$$

$$J_i=-D_i\frac{\partial c_i}{\partial z}-\frac{D_i c_i}{k_B T}z_i e\frac{\partial \phi}{\partial z}-\frac{D_i c_i}{k_B T}\sum_{j=1}^{N} g_{ij}\frac{\partial c_j}{\partial z}-M_i c_i\frac{\partial V}{\partial z},$$

$$M_i=1,\ \text{if}\ \ i=O^{-1/2};\ M_i=0,\ \text{otherwise.}$$

Boundary and interface conditions



$J_{O^{-\frac{1}{2}}}(\alpha) = J_{O^{-\frac{1}{2}}}(\beta) = 0.$

no-flux boundary conditions for $O^{-1/2}$,

side-chain $O^{-1/2}$ needs to stay in the channel filter.

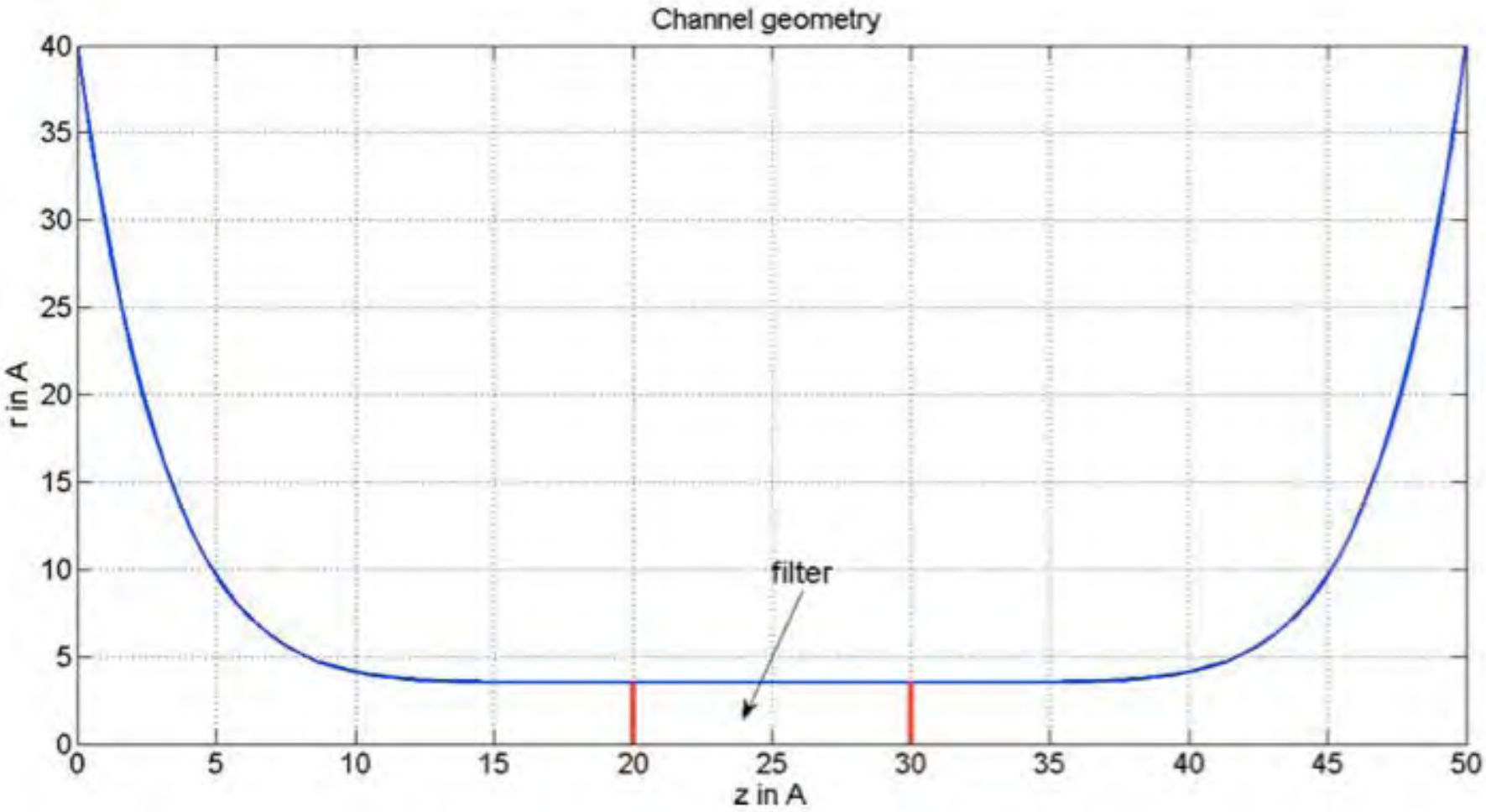


Figure 3. Channel geometry. A precise specification of the geometry of our model.

Determining g_{ij}

$$\varepsilon_{Na,Na}/\varepsilon_{Cl,Cl}/\varepsilon_{Ca,Ca}/\varepsilon_{O,O}/\varepsilon_{Na,Cl}/\varepsilon_{Na,Ca}/\varepsilon_{Na,O}/\varepsilon_{Cl,Ca}/\varepsilon_{Cl,O}/\varepsilon_{Ca,O}$$

$$= 1:1:1:1.56:0.955:1.00:1.28:0.961:1.21:1.28$$

$$g_{Na,Na}/g_{Cl,Cl}/g_{Ca,Ca}/g_{O,O}/g_{Na,Cl}/g_{Na,Ca}/g_{Na,O}/g_{Cl,Ca}/g_{Cl,O}/g_{Ca,O}$$

$$= 1:2280:1.64:164:42.2:0.642:8.20:50.4:327:10.0$$

Table 1. Effect of Increasing ε_{global} on the Ca Binding Ratio with $[Ca^{2+}]_L = [Ca^{2+}]_R = 1$ mM $[Na^+]_L = [Na^+]_R = 100$ mM, $\phi_L = \phi_R = 100$ mM, and $V_{max} = 200$

$g_{Na,Na}$	0	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1
$g_{Na,Cl}$	0	0	0	0	0	0
$g_{Cl,Cl}$	0	0	0	0	0	0
$g_{Na,Ca}$	0	6.41×10^{-5}	6.41×10^{-4}	6.41×10^{-3}	6.42×10^{-2}	6.42×10^{-1}
$g_{Cl,Ca}$	0	0	0	0	0	0
$g_{Ca,Ca}$	0	1.64×10^{-4}	1.64×10^{-3}	1.64×10^{-2}	1.64×10^{-1}	1.64
$g_{Na,O^{-1/2}}$	0	8.19×10^{-4}	8.19×10^{-3}	8.19×10^{-2}	8.20×10^{-1}	8.20
$g_{Cl,O^{-1/2}}$	0	0	0	0	0	0
$g_{Ca,O^{-1/2}}$	0	1.00×10^{-3}	1.00×10^{-2}	1.00×10^{-1}	1.0034	1.00×10^{1}
$g_{O^{-1/2},O^{-1/2}}$	0	1.63×10^{-2}	1.64×10^{-1}	1.64	1.65×10	1.64×10^{2}
Ca binding ratio	0.602	0.594	0.754	0.861	0.825	0.72

Ca^{+2} pushing away Na^{+} (EEEE: Ca channel)

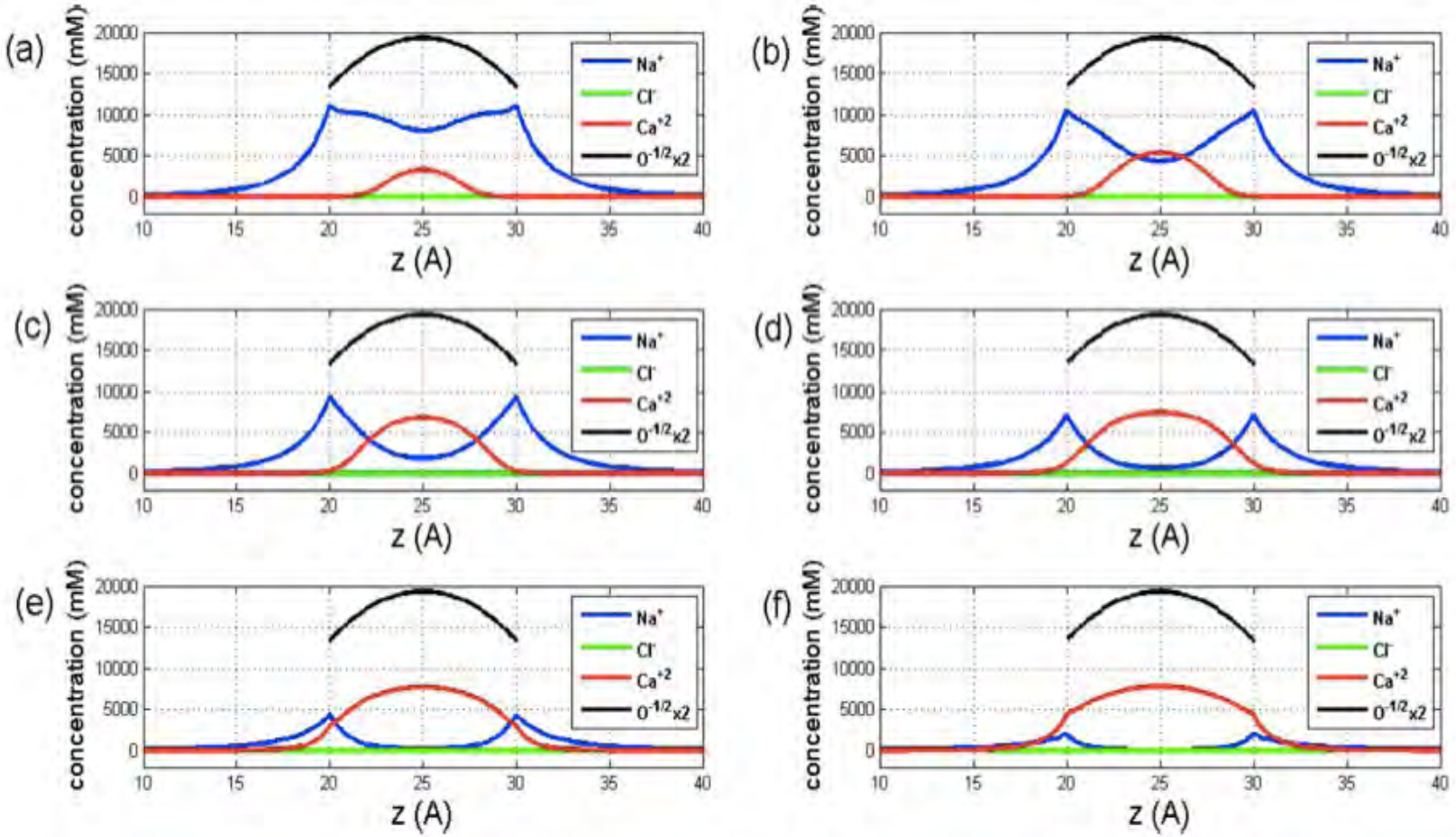


Figure 7. Species concentration distributions under various $[Ca^{2+}]_L = [Ca^{2+}]_R$ with $g_{Na,Na} = 0.01$ (with finite-size effect). V_{max} 200, $\phi_L = \phi_R = 100$ mV, and $[Na^+]_L = [Na^+]_R = 100$ mM: (a) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-7}$ M, (b) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-6}$ M, (c) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-5}$ M, (d) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-4}$ M, (e) $[Ca^{2+}]_L = [Ca^{2+}]_R = 1$ mM, (f) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10$ mM. Note the 2-fold scaling of the $O^{-1/2}$ concentration.

Ca^{+2} failing to push away Na^{+} (DEKA: Na channel)

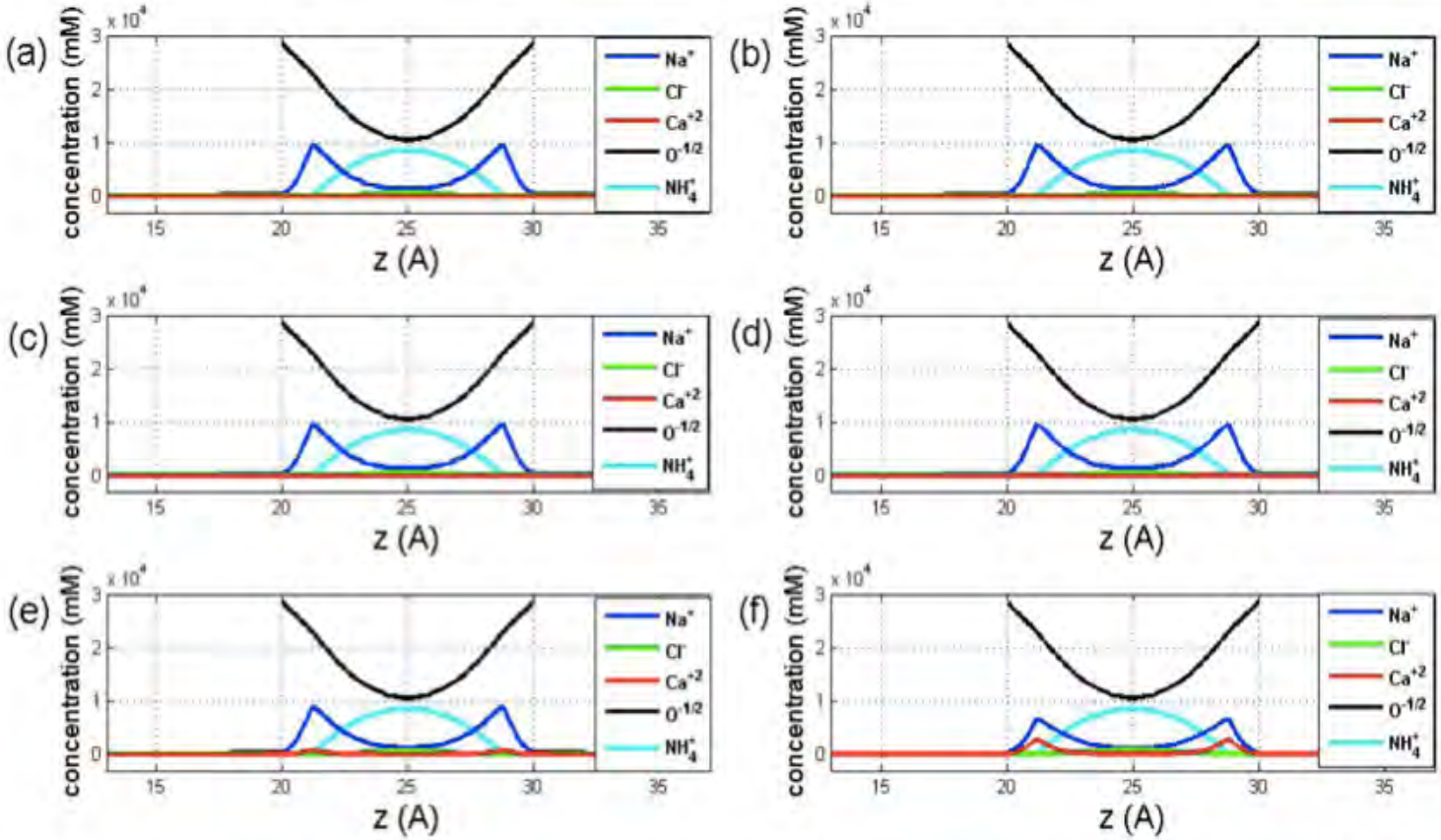


Figure 10. Species concentration distributions under various $[Ca^{+2}]_L = [Ca^{+2}]_R$ with $g_{Na,Na} = 0.01$ (having a finite-size effect). $V_{max} = -200$ for glutamate side chain, $V_{max} = 200$ for lysine side chain, $\phi_L = \phi_R = 100$ mV, and $[Na^+]_L = [Na^+]_R = 100$ mN: (a) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-7}$ M, (b) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-6}$ M, (c) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-5}$ M, (d) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-4}$ M, (e) $[Ca^{2+}]_L = [Ca^{2+}]_R = 1$ mM, and (f) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10$ mM. Note that the scaling of $[O^{-1/2}]$ is the same as the scaling of other concentrations in this figure, unlike that in Figures 4, 6, and 7.

Binding curves from PNP-steric model

DEKA Sodium Channel 6 Å

Aspartate	D	Acid	Negative
Glutamate	E	Acid	Negative
Lysine	K	Basic	Positive
Alanine	A	Aliphatic	Neutral

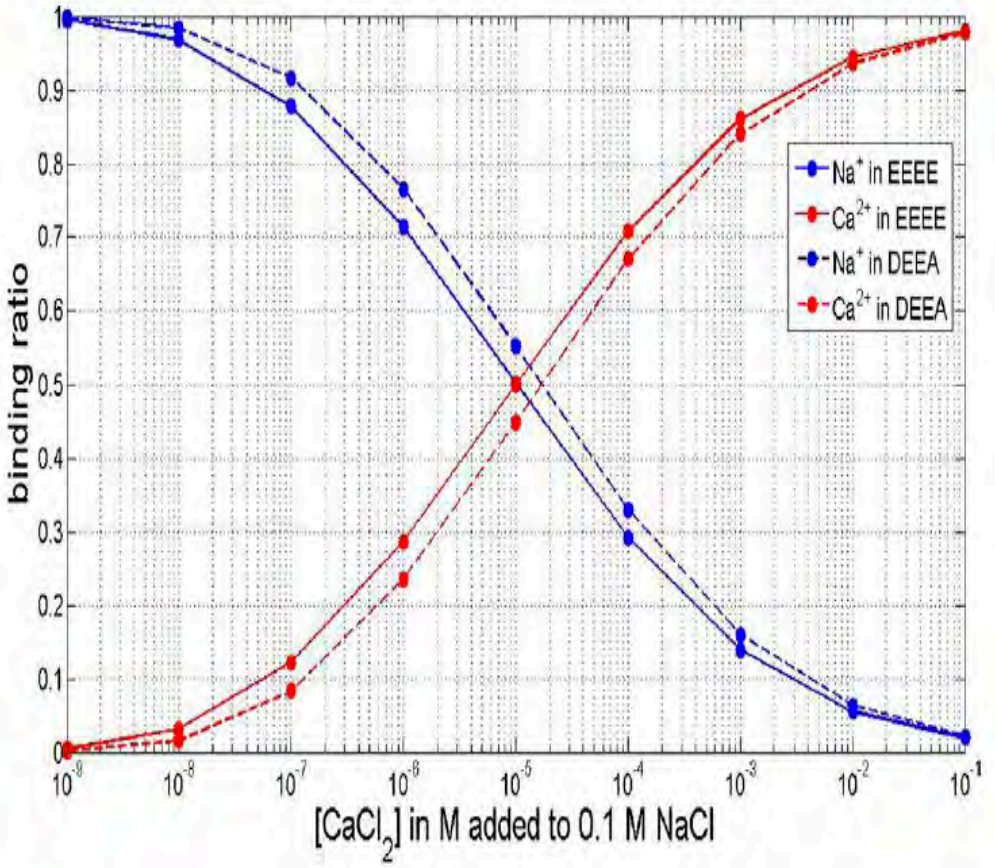


Figure 8. Binding curves of EEEE (−4e) and DEEA (−3e).

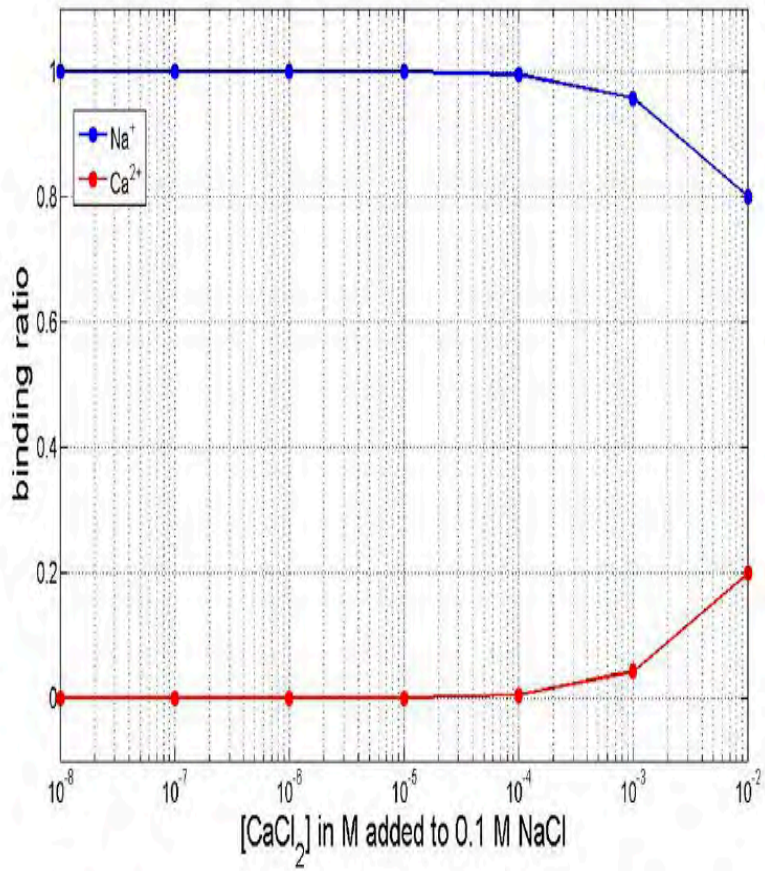


Figure 9. Binding curves of DEKA (−1e).

Ca+2 still pushing away Na+ even in pure PNP (EEEE: Ca channel)

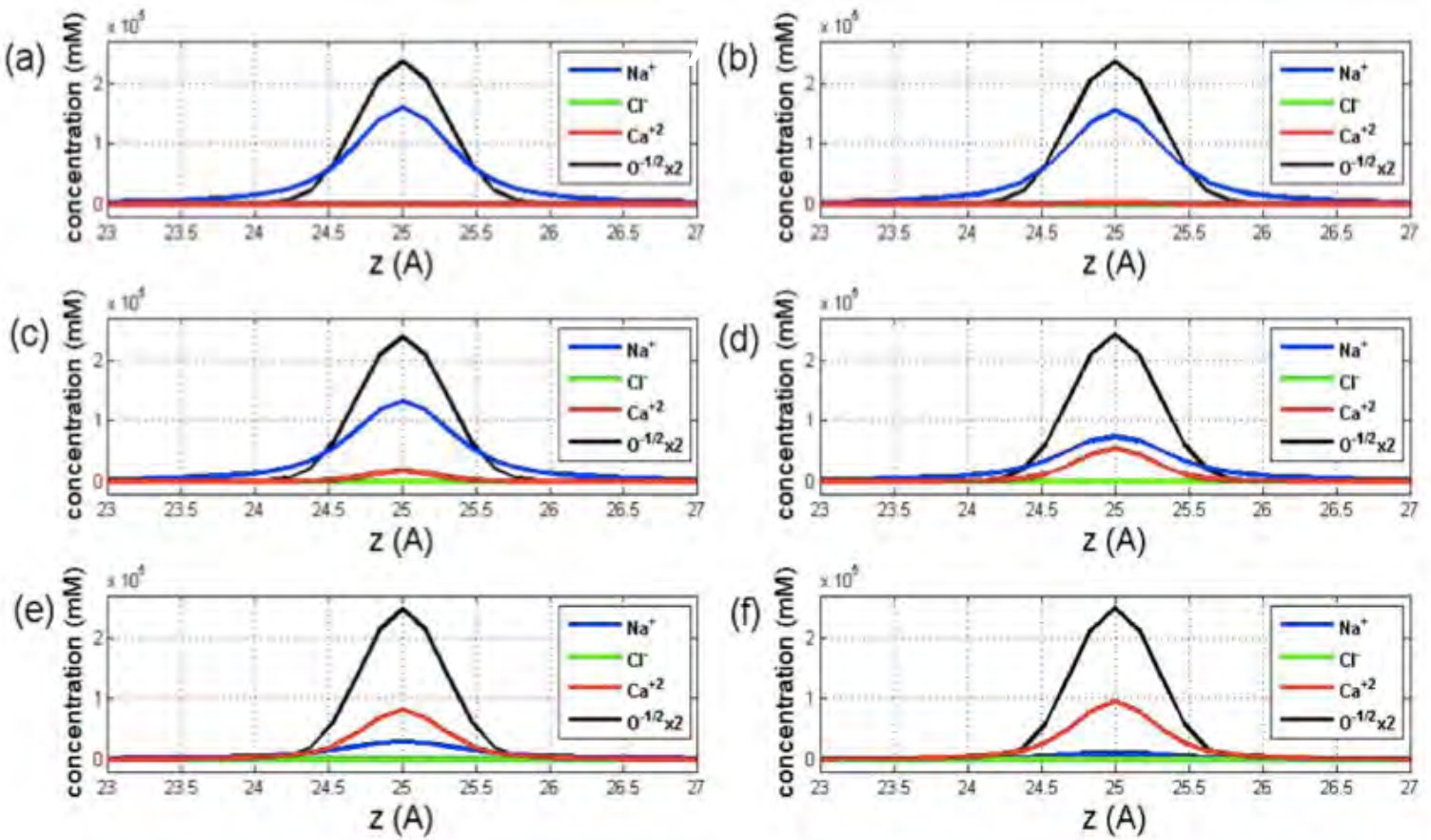


Figure 6. Species concentration distributions under various $[Ca^{2+}]_L = [Ca^{2+}]_R$ with $g_{Na,Na} = 0$ (no finite-size effect). $V_{max} = 200$, $\phi_L = \phi_R = 100$ mV, and $[Na^+]_L = [Na^+]_R = 100$ mM: (a) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-7}$ M; (b) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-6}$ M; (c) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-5}$ M; (d) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10^{-4}$ M; (e) $[Ca^{2+}]_L = [Ca^{2+}]_R = 1$ mM; (f) $[Ca^{2+}]_L = [Ca^{2+}]_R = 10$ mM. Note the 2-fold scaling of the $O^{-1/2}$ concentration.

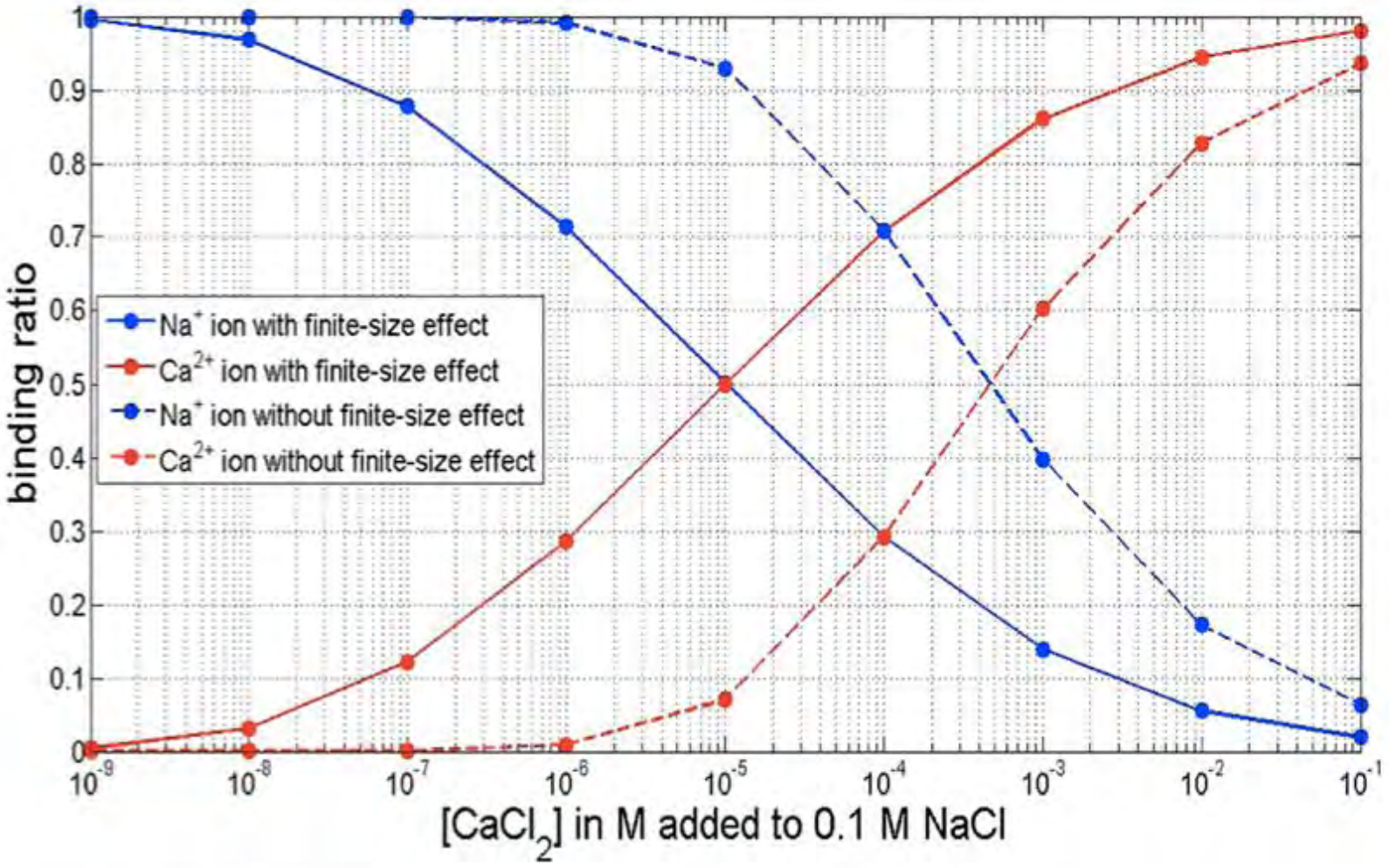


Figure 5. Binding curves corresponding to Table 2.

Ca^{2+} would still push away Na^{+} in DEKA channel when using pure PNP!

Short summary

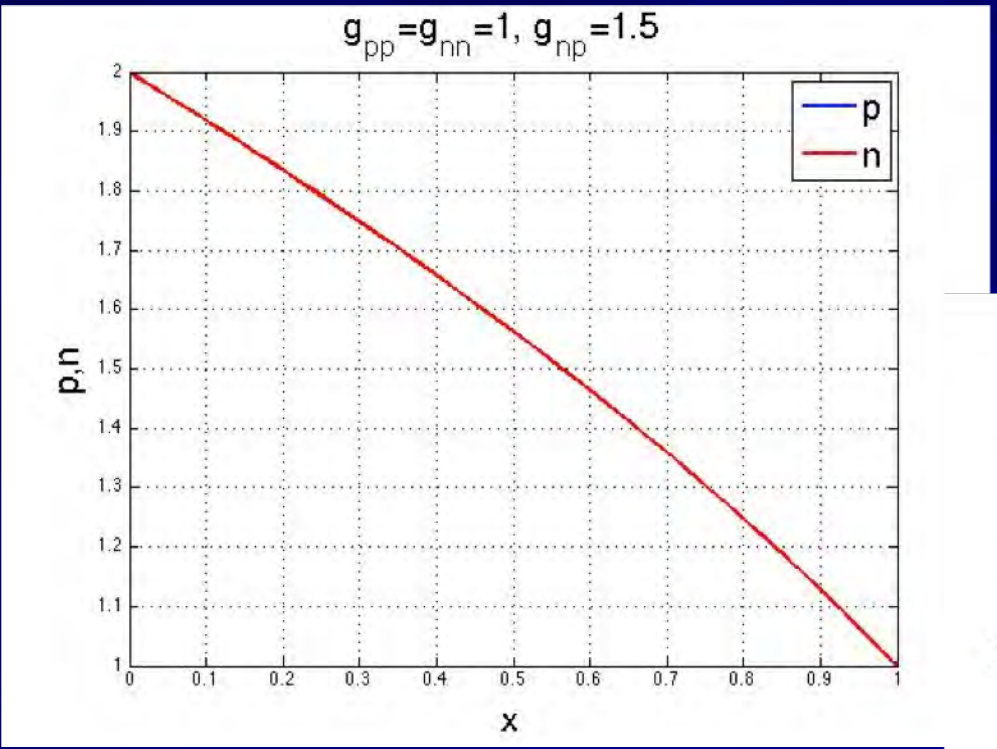
- Selectivity chiefly comes from electrostatic interaction, which is further enhanced by steric effect.
- Strong permanent charges from side chain in EEEE (-4e) and DEEA (-3e) favor the affinity with Ca^{2+}, but no so in DEKA (-1e) due to weak permanent charge.
- In DEKA, steric effect would dominate then.

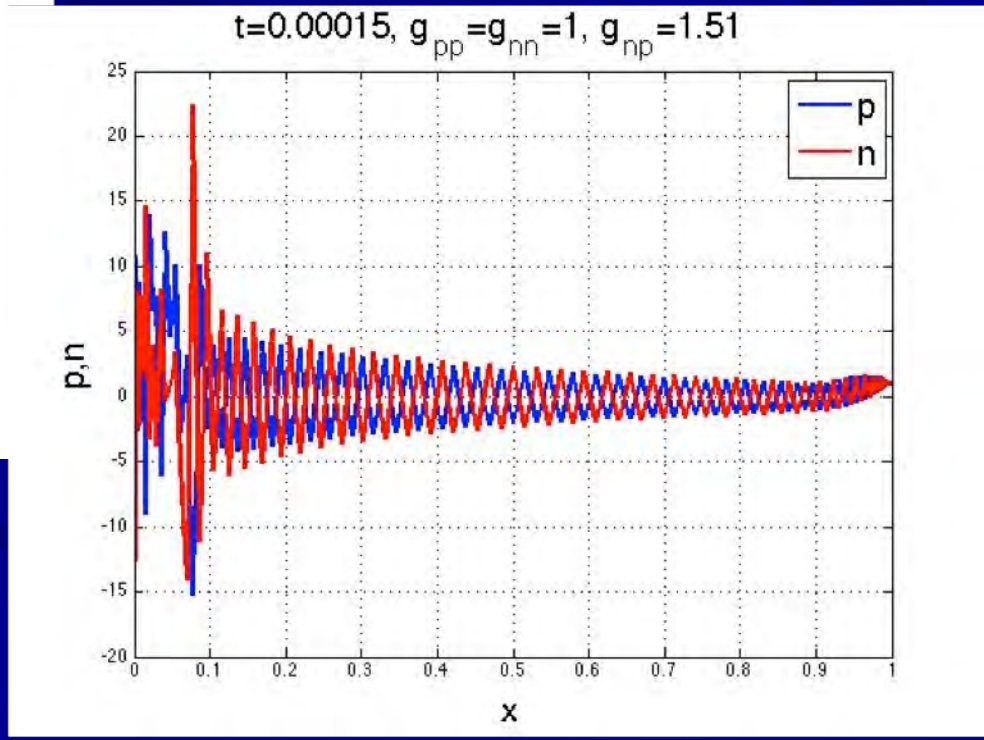
PNP steric model still needs modifications

- Intrinsic high-mode instability when $g_{ij}^2 > c g_{ii} g_{jj}$.
- Empirical ionic diffusion coefficient (1/20 bulk value) and dielectric constant (30) in filter were used.
- Not considering de-hydration/re-solvation energy like Born model for each ion.

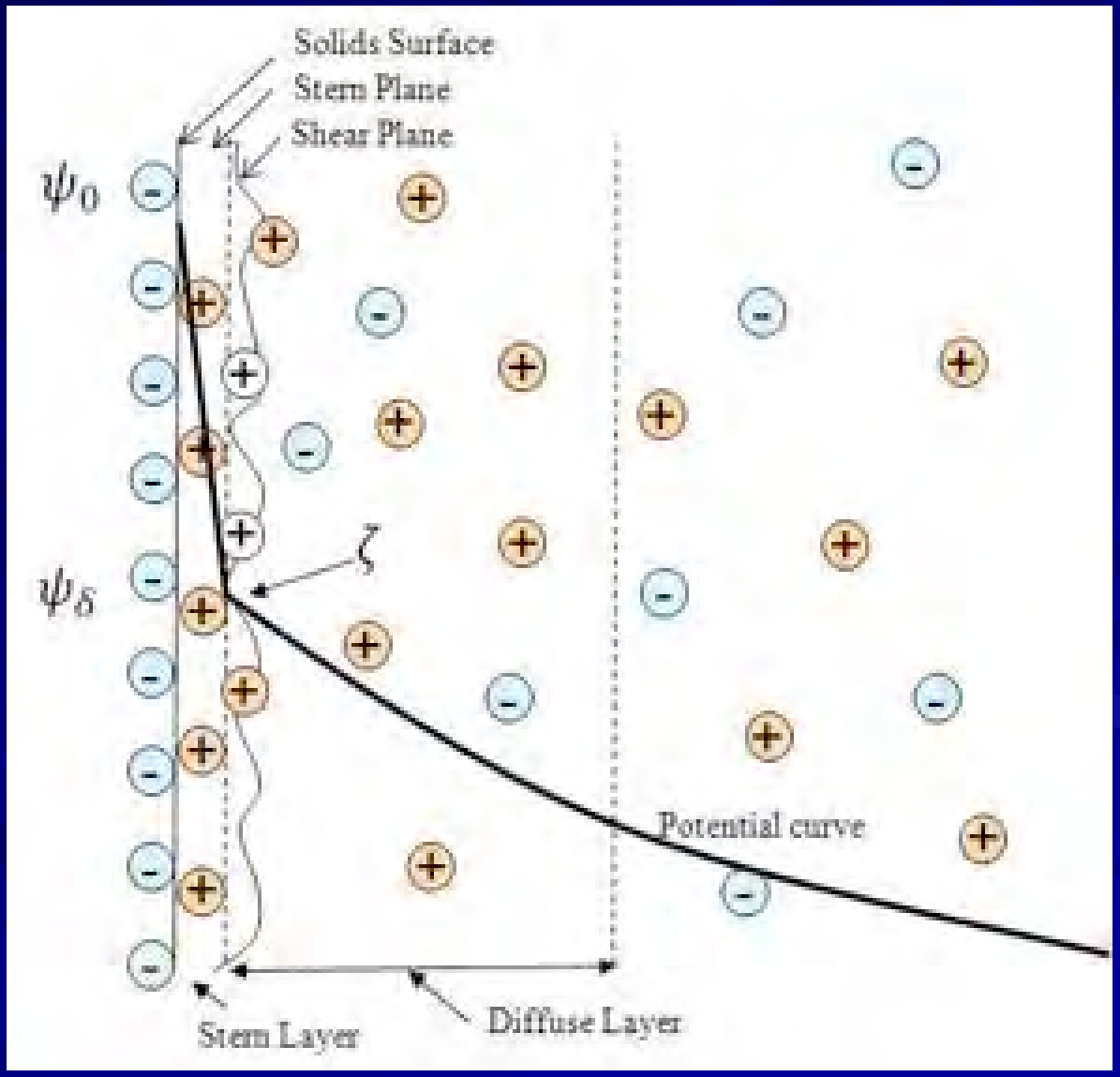
$$\Delta W_i = \frac{z_i^2 e^2}{8\pi\varepsilon_0 a_i}\left(\frac{1}{\varepsilon_{\Omega_f}} - \frac{1}{\varepsilon_\Omega}\right)$$

High-mode instability

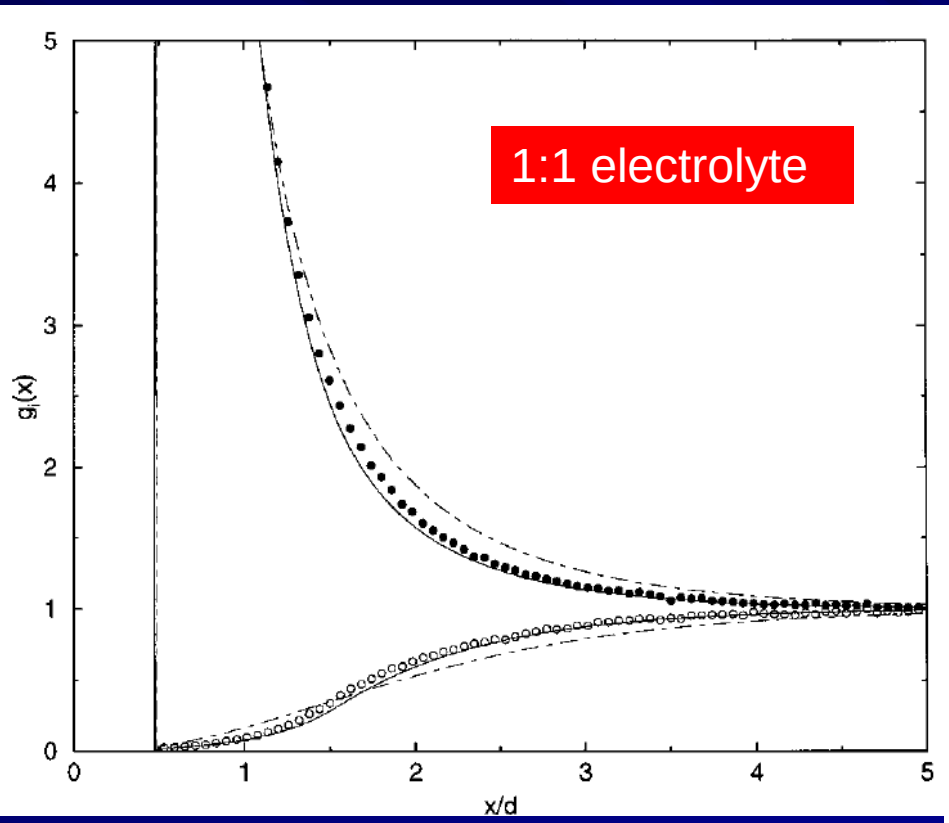


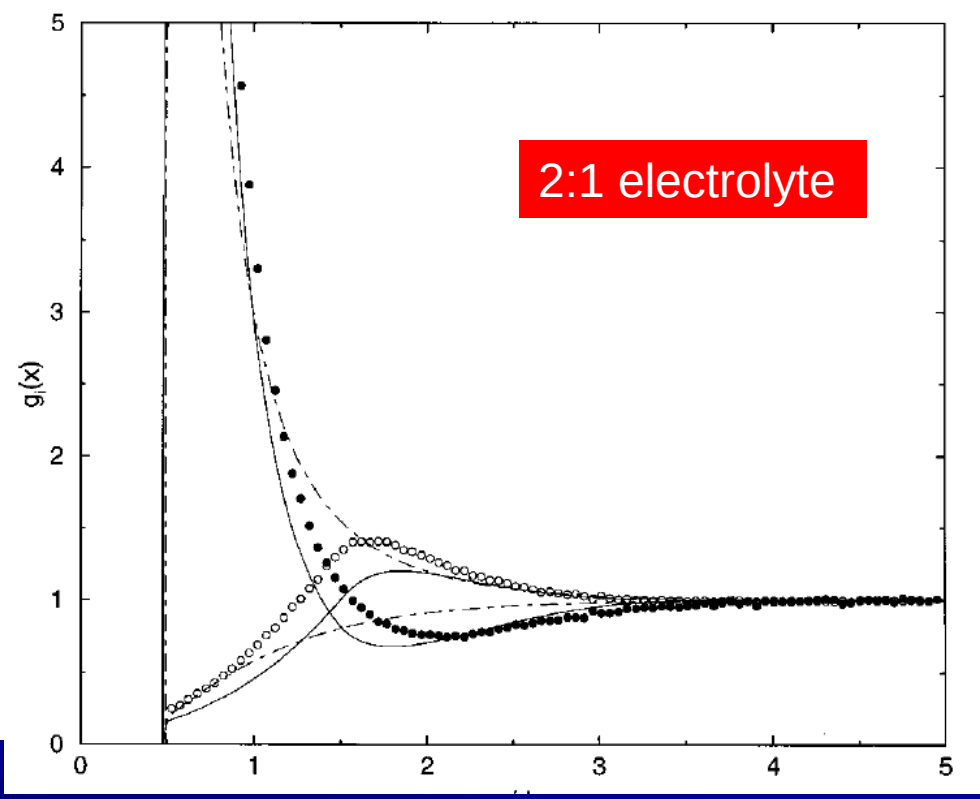


Charged wall problem (EDL)



Overscreening in 2:1 electrolyte





Boda et al. (2002)

PNP-steric + bi-Laplacian diffusion for charged wall problem

$$-\frac{\partial}{\partial z}\left(\varepsilon\frac{\partial \phi}{\partial z}\right) = z_p e c_p + z_n e c_n,$$

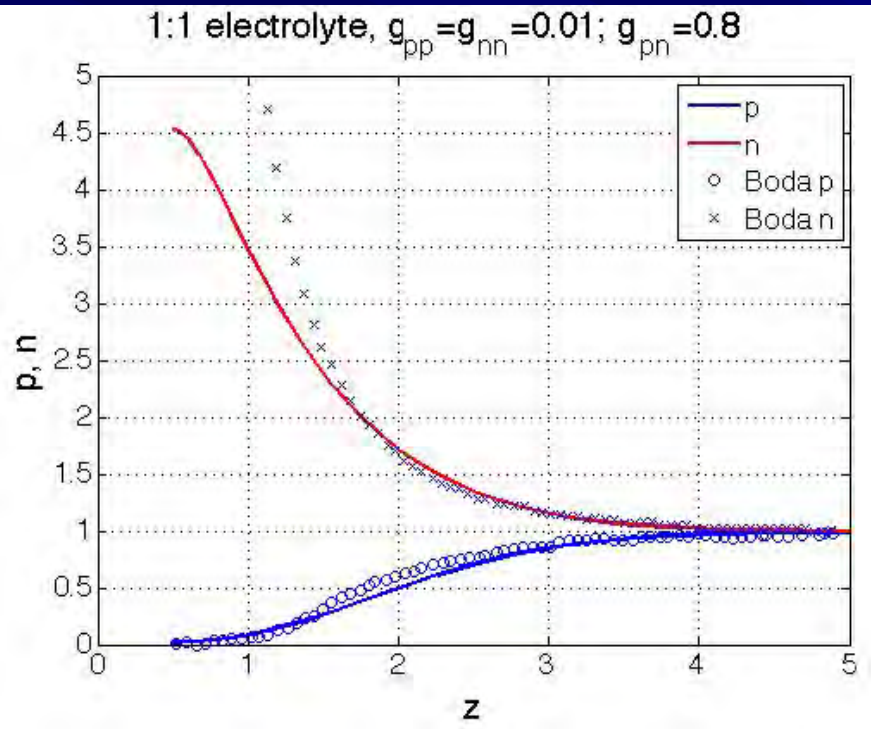
$$\frac{\partial c_i}{\partial t} + \frac{d}{dz}(J_i) = 0, \qquad i = p, n.$$

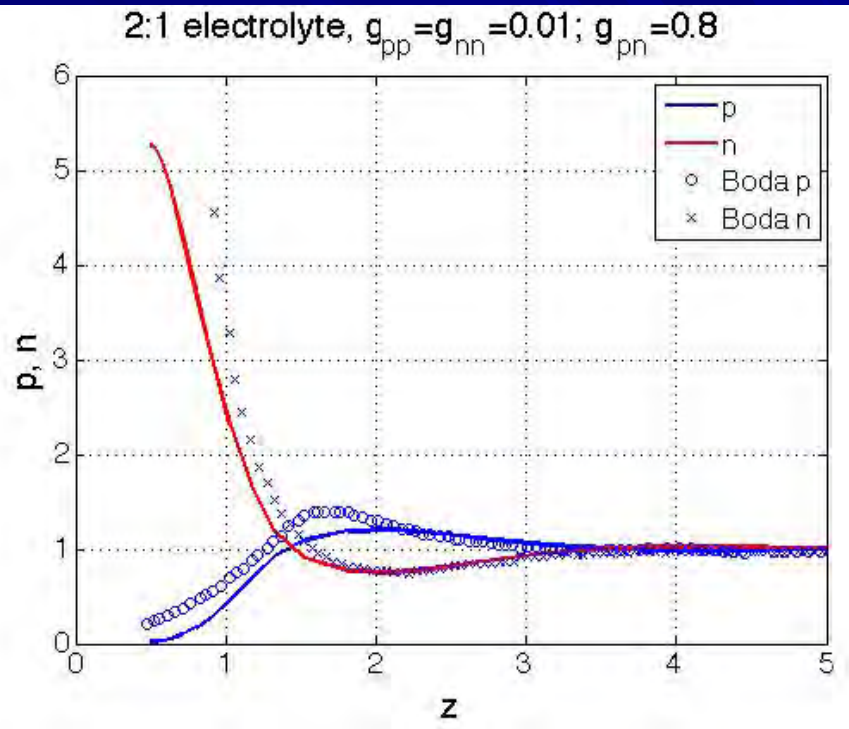
bi-Laplacian diffusion used to suppress high-mode instability

$$J_i = -D_i\frac{\partial c_i}{\partial z} - \frac{D_i c_i}{k_B T} z_i e \frac{\partial \phi}{\partial z} - \frac{D_i c_i}{k_B T}\sum_j g_{ij}\frac{\partial c_j}{\partial z} + \alpha\frac{\partial^3 c_i}{\partial z^3},$$

$$J_i(0,t) = 0, \quad \phi(0,t) = \phi_0, \text{ or } \phi_z(0,t) = \sigma, \quad c_i(\infty,t) = c_{\infty,i}, \quad \phi(\infty,t) = 0,$$

Result compared with Boda et al. (2002)





Overscreening will not happen in 2:1 electrolyte without large g_{pn} here. Combining rule fails here.

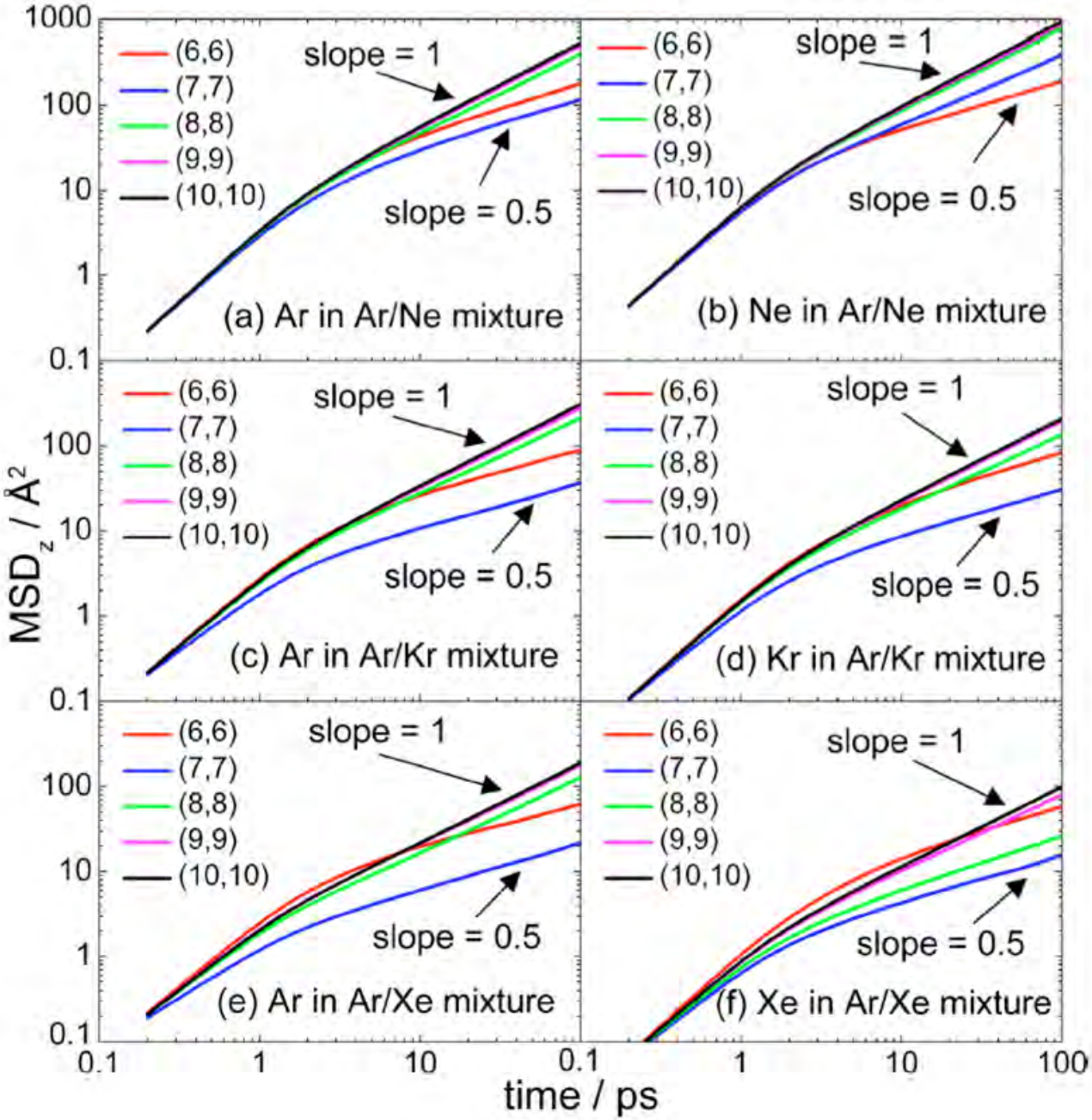
Justification of bi-Laplacian diffusion

- 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.
- Above is a MD simulation, and the major results are:

When tube radius is large, $\lim_{t\to\infty}\left\langle\left[z(t)-z(0)\right]^2\right\rangle = 2Dt \Rightarrow u_t = Du_{xx}$ (Fickian diffusion),

When tube radius is small, $\lim_{t\to\infty}\left\langle\left[z(t)-z(0)\right]^2\right\rangle = 2\alpha\sqrt{t} \Rightarrow u_t = -\alpha u_{xxxx}$ (single-file diffusion).

- From the MD results in next slide, single-file diffusion looks like traveling wave.
- Can we realize this MD experiment by a continuum model?



Chen et al. (2010)

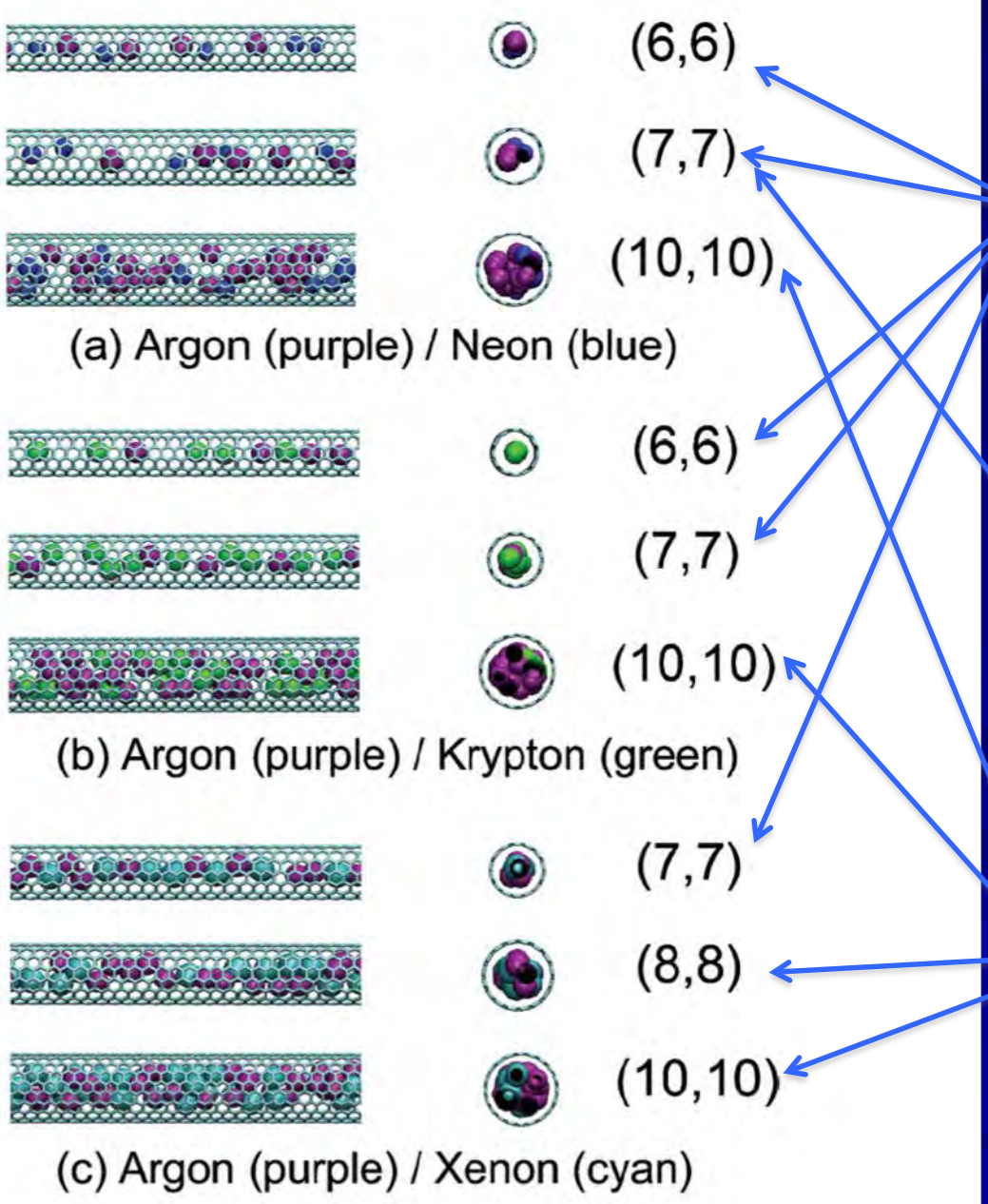


FIG. 1. Simulation snapshots in carbon nanotubes consisting of equimolar mixtures of (a) Ar/Ne, (b) Ar/Kr, and (c) Ar/Xe.

(single-file diffusion)

like traveling wave

(in between)

(Fickian diffusion)

Chen et al. (2010)

Continuum model to mimic MD

- *p*: concentration of Ar, *n*: concentration of Ne.
- These inert gases are not ions, no electrostatic force here.
- No self-diffusion, since Ar and Ne are not solute in solvent (like water). Ar and Ne are not colliding with water molecules generating Brownian motion.
- Diffusion coefficient is a macroscopic property.

$$J_p = -g_{pp} p p_x - g_{np} p n_x + \alpha_p p_{xxx},$$

$$J_n = -g_{nn} n n_x - g_{np} n p_x + \alpha_n n_{xxx},$$

$$p_t + \left(J_p\right)_x = 0, \quad n_t + \left(J_n\right)_x = 0.$$

$$\text{IC: } p(x,0) = p_L + \left(p_R - p_L\right)x + 0.05 * \sin(10\pi x),$$

$$n(x,0) = n_L + \left(n_R - n_L\right)x - 0.05 * \sin(10\pi x),$$

$$\text{BC: } p\left(0,t\right) = p_L,\ p\left(1,t\right) = p_R,$$

$$n\left(0,t\right) = n_L,\ n\left(1,t\right) = n_R,$$

$$p_x\left(0,t\right) = p_x\left(1,t\right) = n_x\left(0,t\right) = n_x\left(1,t\right) = 0.$$

Results

- $\alpha_p=\alpha_n$=3e-6, $p_L=n_L$=1.01, $p_R=n_R$=1.
- g_{np}=1.01, $g_{nn}=g_{pp}$=1.0090, evolving to traveling wave, animation.
- g_{np}=1.01, $g_{nn}=g_{pp}$=1.0092, evolving to steady state, animation.

The current model is by no means perfect. It requests further continuous modifications.

Future work with Peikun Yang:

Governing equations for 1D charged wall problem with water being an explicit species:

$$-\frac{d}{dz}\left(\varepsilon_{\infty}\frac{c_o}{c_o(\infty)}\frac{d\phi}{dz}\right)=z_o e c_o(z)-z_o e c_o(z+d)+\sum_{i=1}^{N} z_i e c_i, \tag{1a}$$

$$P=z_o d, \tag{1b}$$

$$P=-\varepsilon_0 \chi^e c_o \frac{d\phi}{dz}, \tag{1c}$$

effective dielectric constant $\varepsilon=\varepsilon_{\infty}\dfrac{c_o}{c_o(\infty)}$,

$$\frac{\partial c_i}{\partial t}+\frac{d}{dz}J_i=0, \qquad \frac{\partial c_o}{\partial t}+\frac{d}{dz}J_o=0, \tag{2}$$

$$J_i=-D_{i,\infty}\frac{dc_i}{dz}-\frac{D_{i,\infty}c_i}{k_B T}z_i e\frac{d\phi}{dz}-c_i\sum_{j=1}^{N} g_{i,j}\frac{dc_j}{dz}-c_i g_{i,o}\frac{dc_o}{dz}, \tag{3}$$

effective self-diffusion coefficient $D_i=D_{i,\infty}+g_{i,i}c_i$,

$$J_o=-\mu_o c_o z_o e\frac{d\phi}{dz}-c_o\sum_{j=1}^{N} g_{o,j}\frac{dc_j}{dz}, \tag{4}$$

with boundary conditions

$$\phi(0,t)=\phi_0, \qquad \phi(\infty,t)=0, \tag{5}$$

$$J_i(0,t)=J_o(0,t)=0, \qquad c_i(\infty,t)=c_{i,\infty}, \qquad c_o(\infty,t)=c_{o,\infty}. \tag{6}$$

Thank you for your attentions.
Questions?