Nonlinear Poisson-Nernst Planck Equations for Ion Flux

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Credits

this talk is based on joint work with

- Martin Burger (WWU Münster)
- Marie-Therese Wolfram (Vienna)
Motivation

Analysis for stationary nonlinear PNP

Numerical Simulations
Motivation

aim: modelling of transport and diffusion with size exclusion

application:
- ion channels/nanopores
- human crowds
- swarming
- chemotaxis
Ion Channels so far

PNP system in three dimensions for ion densities $c_i$:

\[- \lambda^2 \Delta V = \sum z_i c_i + f\]  Poisson equation

\[\partial_t c_i = \nabla \cdot (D_i (\nabla c_i + c_i z_i \nabla V))\]  Nernst-Planck equation

- $\lambda^2$ permittivity
- $z_i$ valence
- $f(x)$ protein charge
- $D_i$ Diffusion coefficients

problem: size effects in small channels
Jump Exclusion Process

lattice based modelling:

- jump probability to neighbouring lattice sites given by diffusion, external and interaction fields
- modified by exclusion principle, only jumps to free sites
- closure relation: probability of finding empty site instead of exact exclusion in the ensemble average
Model with Size-Exclusion

rescaling of lattice
limit of lattice site distance to zero
Taylor expansion of master equation

resulting model:
\[ \partial_t c_i = \partial_x (D_i ((1 - \rho) \partial_x c_i + c_i \partial_x \rho + z_i c_i (1 - \rho) \partial_x V)) \]

total volume density \( \rho(x, t) = \sum c_j(x, t) \)

1D \( \Rightarrow \) single file movement
Nonlinear PNP

multidimensional model:

\[ \partial_t c_i = \nabla \cdot (D_i((1 - \rho)\nabla c_i + c_i \nabla \rho + z_i c_i (1 - \rho) \nabla \mathbf{V})) \]

- movement is driven by diffusion and interactions among particles and externally applied field
- mean field approach
- model describes average densities of particles
Boundary Conditions for Ion Channels

concentration: \( c_i(x, t) = \gamma_i(x) \quad x \in \Gamma_D \)

no flux: \( J_i(x, t) \cdot n = 0 \quad x \in \Gamma_N \)

charge neutrality: \( \sum z_j \gamma_j(x) = 0 \) in bathes

electrical potential: \( V(x, t) = V_0^D(x) + UV_1^D(x) \quad x \in \Gamma_D \)

no flux: \( \nabla V(x, t) \cdot n = 0 \quad x \in \Gamma_N \)
Entropy

entropy for this process:

\[ E = \int_{\Omega} \sum (c_i \log c_i + (1 - \rho) \log(1 - \rho) + z_i c_i V) \, dx \]

entropy dissipation:

\[ \frac{d}{dt} E = - \int_{\Omega} \sum c_j (1 - \rho) |\nabla u_j|^2 \, dx \]

⇒ decreasing

in equilibrium, entropy is minimal at fixed total mass.
Equilibria

stationary solutions are minimizers of the entropy

\[ 0 = J_{i\infty} = -D_i ((1 - \rho_{\infty}) \nabla c_{i\infty} + c_{i\infty} \nabla \rho_{\infty} + z_i c_{i\infty} (1 - \rho_{\infty}) \nabla V_{i\infty}) \]

generalized Boltzmann distributions:

\[ c_{i\infty} = \frac{k_i \exp(-z_i V_{i\infty})}{1 + \sum k_j \exp(-z_j V_{j\infty})} \quad k_i \geq 0 \]

modified Poisson-Boltzmann equation:

\[ -\epsilon \Delta V_{i\infty} = \frac{\sum z_j k_j \exp(-z_j V_{\infty})}{1 + \sum k_j \exp(-z_j V_{\infty})} + f \]
Analysis for stationary system

system of equations:

\[-\lambda^2 \Delta V = \sum z_j \cdot c_j + f,\]

\[0 = \nabla \cdot \left( D_i ((1 - \rho) \nabla c_i + c_i \nabla \rho + z_i c_i (1 - \rho) \nabla V) \right)\]

entropy variables \( u_i = \log c_i - \log (1 - \rho) + z_i V \)

system in entropy variables:

\[-\lambda^2 \Delta V - \sum \frac{z_k \exp(u_k - z_k V)}{1 + \sum \exp(u_j - z_j V)} = f\]

\[\nabla \cdot \left( D_i \frac{\exp(u_i - z_i V)}{(1 + \sum \exp(u_j - z_j V))^2} \nabla u_i \right) = 0\]
Global Existence

We can show that there exists a weak solution of

\[-\lambda^2 \Delta V = \sum z_j c_j + f\]

\[0 = \nabla \cdot (D_i((1 - \rho)\nabla c_i + c_i \nabla \rho + z_i c_i (1 - \rho) \nabla V)),\]

such that

\[0 \leq c_i \leq 1, \quad \rho \leq 1 \quad \text{a.e. in } \Omega.\]
Uniqueness

*uniqueness in general case cannot be expected!*

but we can find uniqueness in simpler situations. We can show:

- uniqueness around small potential
- uniqueness around small boundary values
Reduction to One Dimension

- cross section of filter much smaller than longitudinal extension
  \(\Rightarrow\) nearly one dimensional process
- approximate three dimensional model by one dimensional one

rescale: \(x, \ y^\epsilon = \epsilon y, \ z^\epsilon = \epsilon z,\)

Assume \(a(x) = \int \int dy \ dz\) denotes shape/area function of channel

reduced one dimensional system

\[-\lambda^2 \partial_x (a \partial_x V) = a \left( \sum c_j + f \right)\]

\[D_i \partial_x \left( a \frac{\exp(u_i - z_i V)}{1 + \sum \exp(u_j - z_j V))^2} \partial_x u_i \right) = 0\]
L-type Calcium Channel

- $Na^+$, $Ca^{2+}$ and $Cl^-$ in bathes
- $8 O^{-1/2}$ are fixed charge in channel

radius channel: 0.4nm  length channel: 1nm
radius bath: 2.4nm  length bath: 2nm
\[- \lambda^2 \nabla \cdot (a \nabla V) = a \left( \sum_k \frac{z_k \exp(u_k - z_k V)(1 - c_O)}{1 + \sum_j \exp(u_j - z_j V)} + f \right) \] (1)

\[0 = \nabla \cdot \left( a D_i \frac{\exp(u_i - z_i V)(1 - c_O)^2}{\left(1 + \sum_j \exp(u_j - z_j V)\right)^2} \nabla u_i \right) \] (2)

\[i = Na^+, Ca^{2+}, Cl^-\]. Solve iterative:
\[V^0\] initial datum for \[V\], \[u^0_i\] for \[u_i\]:

1. Given \[V^j\] solve (2) for \[u^j_i, i = Ca^{2+}, Na^+, Cl^-\].

2. Given \[u^j_i\] solve the nonlinear Poisson equation (1) for \[V^{j+1}\] using Newton’s method.

3. Go to 1) until convergence.
Conductance for L-type Calcium selective Channel

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Motivation Analysis for stationary nonlinear PNP Numerical Simulations

Nonlinear Poisson-Nernst Planck Equations for Ion Flux

Universität Münster
Parameters for Computation

<table>
<thead>
<tr>
<th>Meaning</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boltzmann constant $k_B$</td>
<td>$1.3806504 \times 10^{-23}$</td>
<td>J/K</td>
</tr>
<tr>
<td>Temperature $T$</td>
<td>300</td>
<td>K</td>
</tr>
<tr>
<td>Avogadros constant $N_A$</td>
<td>$6.02214179 \times 10^{23}$</td>
<td>N/mol</td>
</tr>
<tr>
<td>Vacuum permittivity $\epsilon_0$</td>
<td>$8.854187817 \times 10^{-12}$</td>
<td>F/m</td>
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<tr>
<td>Relative permittivity $\epsilon_r$</td>
<td>78.4</td>
<td></td>
</tr>
<tr>
<td>Elementary charge $e$</td>
<td>$1.602176 \times 10^{-19}$</td>
<td>C</td>
</tr>
<tr>
<td>Particle radius</td>
<td>0.15</td>
<td>nm</td>
</tr>
<tr>
<td>Typical length $\tilde{L}$</td>
<td>5</td>
<td>nm</td>
</tr>
<tr>
<td>Typical concentration $\tilde{c}$</td>
<td>$3.7037 \times 10^{25}$</td>
<td>N/l</td>
</tr>
<tr>
<td>Typical voltage $\tilde{V}$</td>
<td>100</td>
<td>mV</td>
</tr>
<tr>
<td>Diffusion coefficient $Ca^{2+}$</td>
<td>$7.9 \times 10^{-10}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>Diffusion coefficient $Na^{+}$</td>
<td>$1.33 \times 10^{-9}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>Diffusion coefficient $Cl^{-}$</td>
<td>$2.03 \times 10^{-9}$</td>
<td>m$^2$/s</td>
</tr>
</tbody>
</table>
effective parameters:

\[ \lambda^2 = \frac{\epsilon_0 \epsilon_r \tilde{V}}{e \tilde{L}^2 \tilde{c}} = 4.68 \times 10^{-4} \]

\[ \eta = \frac{e \tilde{V}}{k_B T} = 3.87 \]
Motivation Analysis for stationary nonlinear PNP Numerical Simulations

**Stationary Profile for PNP**

0.1 mol/l NaCl in both baths
5 × 10^{-3} mol/l CaCl₂ left, 0.1 mol/l CaCl₂ in right bath
Stationary Profile for nonlinear PNP

0.1 mol/l NaCl in both bathes
$5 \times 10^{-3}$ mol/l CaCl$_2$ left, 0.1 mol/l CaCl$_2$ in right bath
Current

$V_L = 50\text{mV}, \quad V_R = 0\text{mV}, \quad 0.1\text{mol/l NaCl in both baths,}$

$5 \times 10^{-3}\text{mol/l CaCl}_2 \text{ right, } \text{CaCl}_2 \text{ added to left bath,}$
I/V curve

0.1 mol/l NaCl in both baths
5 \times 10^{-3} \text{mol/l CaCl}_2 \text{ left, 0.1 mol/l CaCl}_2 \text{ in right bath}
Current for a changing Charge Profile

\[ f(x) = \begin{cases} 
0 & x < 0.5 - 0.1\epsilon \\
c_O/\epsilon & 0.5 - 0.1\epsilon \leq x \leq 0.5 + 0.1\epsilon \\
0 & x > 0.5 + 0.1\epsilon 
\end{cases} \]
Mole Fraction

total concentration of mixture: 0.1mol/l
AMFE

symmetric bathes, 0.1mol/l NaCl
$V_L=0\text{mV}$, $V_R=-20\text{mV}$
thank you for your attention!