Applications and Discretizations of the Poisson-Nernst-Planck Equations

Transport of Ionic Particles in Biological Environments

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Charge Carrier Transport

Charge carrier transport refers to phenomena where charged particles interact with one another through an electric field.

These systems are often encountered in biological and engineering settings, and simulation can help improve understanding the role of charged particles in cellular nanochannels, microfluidic chips, solar cells, etc.

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A brief history of time-dependent PNP

We are interested in charged particle transport in electrostatic systems when magnetic forces are negligible.

Nernst and Planck modeled these phenomena using a continuum model dating back to 1889, where the distribution of charged particles are distributed according to processes of drift and diffusion.

Connection to the Maxwell's equations

The PNP equations take root in the Maxwell equations:

$$\varepsilon_0 \nabla \cdot \vec{E} = \rho, \qquad \text{(Gauß's Law)}$$

$$\nabla \cdot \vec{B} = 0, \qquad \text{(Gauß's Law for Magnetism)}$$

$$\nabla \times \vec{E} = \frac{\partial \vec{B}}{\partial t}, \qquad \text{(Faraday's Law of Induction)}$$

$$\nabla \times \vec{B} = \mu_0 \left(\vec{j} + \varepsilon_0 \frac{\partial \vec{E}}{\partial t} \right). \qquad \text{(Ampère's Circuital Law)}$$

Connection to the Maxwell's equations

In simple cases:

- Magnetic field is absent: $\vec{B} = \vec{0}$

$$\nabla \times \vec{E} = \vec{0} \qquad \Longrightarrow \qquad \vec{E} = -\varepsilon_r \nabla \phi$$

- Ion flux driven by drift-diffusion

$$\vec{j_i} = -D_i \nabla \rho_i + \mu_i \rho_i \vec{E}$$

- Mass conservation

$$\frac{\partial \rho_i}{\partial t} = -\nabla \cdot \vec{j_i}$$

What modifications are permitted?

The PNP equations are used to model many devices that produce a wide variety of functionality

- generating electrical energy in a solar cell
- controlling fluid flow in microchannels
- gating ionic particles from proteins

What are permissible (consistent with Maxwell's equations) modifications that to generate this variety in functionality?

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Multi-Functionality

Material Parameters

A simple rescaling of the variables, in addition to the Einstein relation $(\kappa_B T)\mu_i = eD_i$, shows that all qualitative behavior of a simple PNP system can be reproduced by varying the electric permitivitty and ionic diffusivities.

$$\frac{\partial}{\partial t} p = \nabla \cdot [D_p(\nabla p + p\nabla\phi)],$$

$$\frac{\partial}{\partial t} n = \nabla \cdot [D_n(\nabla n - n\nabla\phi)],$$

$$-\nabla \cdot (\varepsilon \nabla\phi) = p - n.$$

A broad spectrum of qualitative behavior follows from relative scalings between coefficients and discontinuities of the coefficients, where we note $\varepsilon = \varepsilon(L, T, \rho_{\text{ref}})$.

Analyses should be flexible with the values of these parameters in order to be applicable to many devices.

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Analyses should be flexible with the values of these parameters in order to be applicable to many devices.

Multi-Functionality

Ionic Flux

While the Nernst-Planck equations describe ion diffusivity and electrostatic forces, additional physical forces can be taken into account in the ion flux

$$\vec{j} = -D\nabla\rho + \mu\rho\vec{E} + \vec{F}$$

These additional forces are often nonlinear expressions and may couple to other PDEs.

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Mass Conservation

In the context of devices, we typically deal with finite domains.

Mass conservation then requires a prescribed boundary and a set of boundary conditions, which indirectly influence the total ionic mass in a device.

Additionally, we may add terms to specify ion sources and sinks:

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \vec{j} + S$$

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Multi-Functionality

Thus, a broad spectrum of qualitative behavior follows from:

- scalings of coefficients and discontinuities of the coefficients
- modification to the ionic fluxes
- device-specific statement of mass conservation
- domain geometry and boundary conditions

Multi-Functionality

We are primarily interested modeling devices using that PNP equations.

The takeaway: chairs are held together by nails and glue, a book is held together by its binding, and devices in this talk are held together by PNP.

The PNP equations serve as a *platform* to connect a prescribed domain geometry, material parameters, and expressions for ion fluxes to create a device that subsequently yields some functionality, which depends on applied boundary conditions.

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Applications and Collaborations

This work focuses on applications, discretizations, and numerical solvers for PNP equations and is led by Prof. Jinchao Xu, with Xiaozhe Hu and M. M.

- Biology, Nanochannels (Profs Liu & Eisenberg, Penn State & Rush Medical)
- Electrokinetics (Department of Energy, Collaboratory on Mathematics for Mesoscopic Modeling of Materials)
- Solar Cell (Prof. Fonash, Penn State)
- LiPON Battery (Dr. G. Lin and Dr. B. Zheng, PNNL)
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Semi-conductors

A prominent application of PNP in engineering applications is to explore the efficiency and capability of various configurations of semi-conductor devices, such as transistors and diodes, numerically.

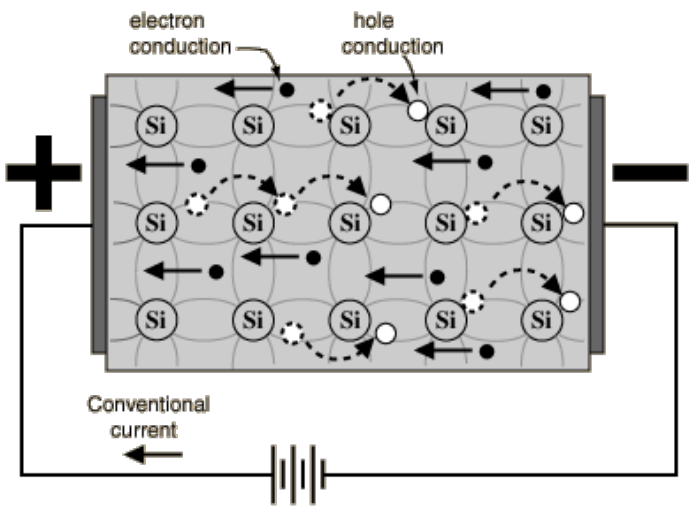

Figure: Semi-conductor

http://hyperphysics.phy-astr.gsu.edu/hbase/solids/intrin.html

Semi-conductors

By constructing a device using distinct semi-conductor materials, interactions between "electrons" and "holes" can modify current through the device.

We require:

- Discontinuous material parameters
- Modifications to ion fluxes
- Source terms added to mass conservation eqns

Semi-conductors

Doping

Combining several "doped" materials is modeled by using materials with distinct diffusivities and electric permittivity

$$\begin{aligned} \vec{j_p} &= -D_p(\nabla p + p\nabla\phi), \\ \vec{j_n} &= -D_n(\nabla n - n\nabla\phi), \\ -\nabla\cdot(\varepsilon_r\varepsilon_0\nabla\phi) &= p + p_f - (n + n_f), \end{aligned}$$

and *fixed* charges

$$\vec{j_{p_f}} = \vec{0} \qquad \text{and} \qquad \vec{j_{n_f}} = \vec{0}.$$

Semi-conductors

Recombination

Furthermore, since holes model the *lack* of an electron, holes and electrons are generated stochastically and can annihilate each other by recombination.

This is modeled by generation and recombination terms

$$\frac{\partial p}{\partial t} = -\nabla \cdot \vec{j_p} + G(p,n) - R(p,n)$$
$$\frac{\partial n}{\partial t} = -\nabla \cdot \vec{j_n} + G(p,n) - R(p,n)$$

Semi-conductors

Recombination

In photovoltaic semi-conductors (aka solar cells), electron/hole pairs are generated by an optical electric field

$$\nabla \times \nabla \times \vec{E}_{\text{opt}} + \kappa^2 \vec{E}_{\text{opt}} = \vec{F},$$

$$\frac{\partial p}{\partial t} = -\nabla \cdot \vec{j_p} + G(\vec{E}_{\text{opt}}) - R(p, n),$$

$$\frac{\partial n}{\partial t} = -\nabla \cdot \vec{j_n} + G(\vec{E}_{\text{opt}}) - R(p, n).$$

Semi-conductors

Materials, Geometry, and BCs

A specific device is modeled by

- material configuration
- shape of the device
- applied voltages

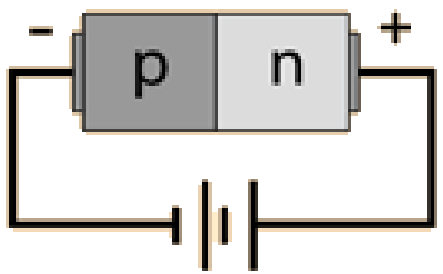

Figure: Diode

$$\frac{\partial p}{\partial t} = \nabla \cdot [D_p(\nabla p + p\nabla\phi)] - R(p,n),$$
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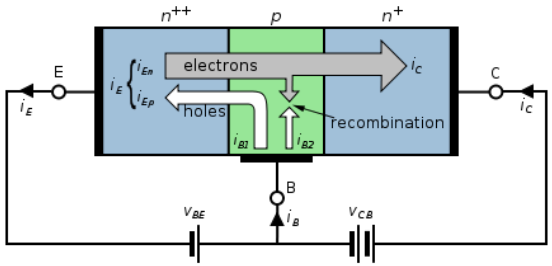

Figure: Bipolar Junction Transistor: forward and reverse current, saturation, cutoff

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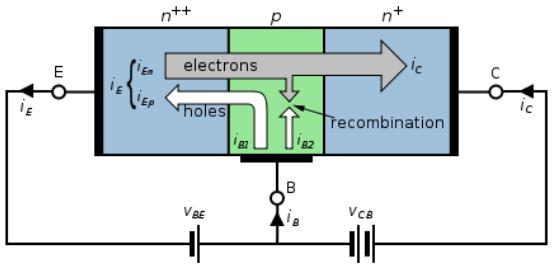

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Electrokinetics

We can enrich the functionality of a device by adding kinetic forces in the ionic flux:

$$\vec{j} = -D\nabla\rho - \mu\rho\nabla\phi + \rho\vec{u}.$$

This models electrokinetic systems where charged particles are suspended in an electrolyte.

Some phenomena modeled by this system are electroosmosis, electrophoresis, and streaming potentials/currents.

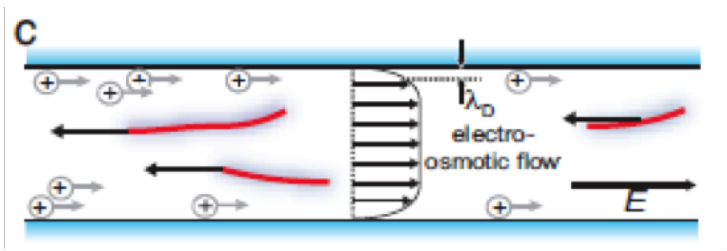


Figure: Electroosmosis in a capillary tube

Electrokinetics

Coupling the PNP equations with the incompressible Navier-Stokes equations expands the model to take into account the kinetic effects of charged particles suspended in an electrolyte.

$$
\begin{aligned}
p_t &= \nabla \cdot \left[D_p(\nabla p + p\nabla\phi) - p\vec{u} \right], \\
n_t &= \nabla \cdot \left[D_n(\nabla n - n\nabla\phi) - n\vec{u} \right], \\
-\nabla \cdot (\varepsilon \nabla\phi) &= p - n, \\
\vec{u}_t + (\vec{u}\cdot\nabla)\vec{u} &= \nu\nabla^2\vec{u} + \nabla\pi - (p-n)\nabla\phi, \\
\nabla \cdot \vec{u} &= 0.
\end{aligned}
$$

Electrokinetics

Electroosmosis

Electroosmosis refers to the phenomenon where a fluid is driven by electric forces.

This is an important model for engineering fluidic microchannels.

In these applications, controlling flows with small mechanical pumps and valves is difficult to design and fabricate without defects; electrokinetics can be used to remedy these issues.

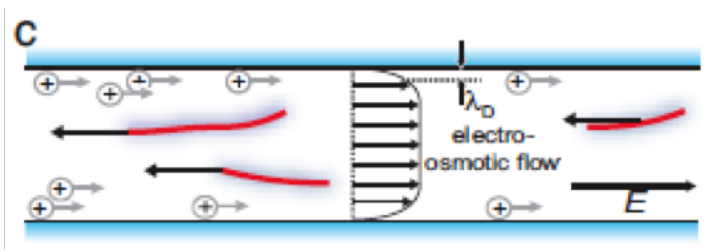


Figure: Electroosmosis in a capillary tube

Electrokinetics

Electroosmosis

For more complicated geometries, this can serve as a switch to control where the fluid flows.

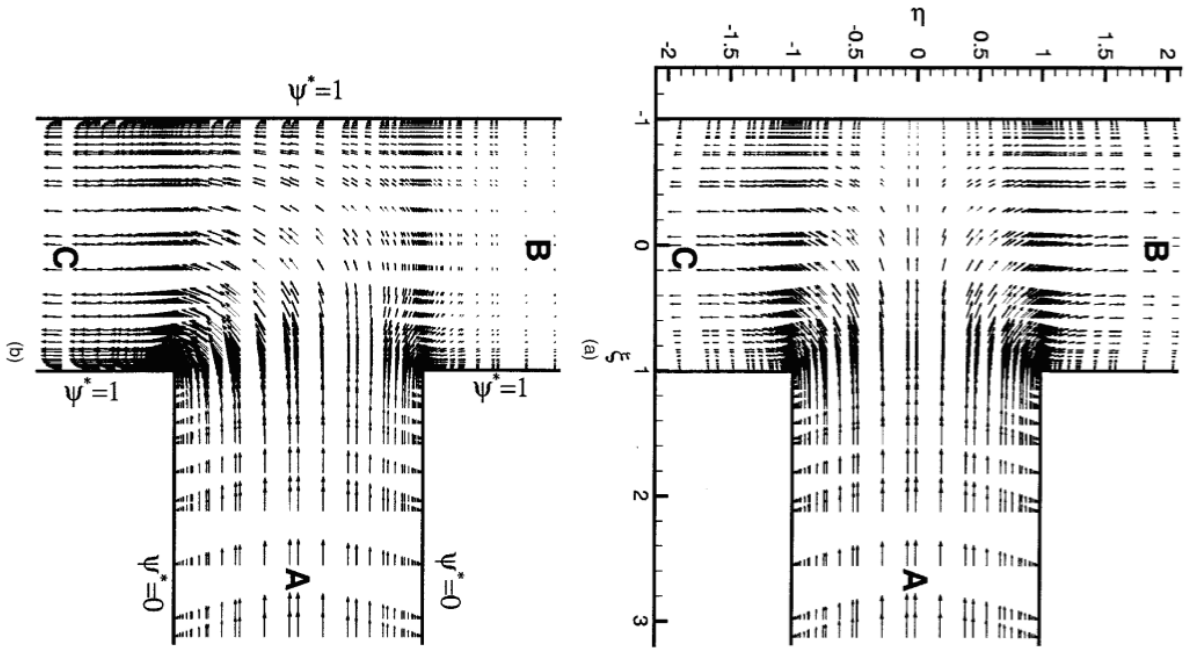


Figure: Controlled flow in T-juction

Dutta, Beskok, & Warburton, Num. Sim. of Mixed Electroosmotic/Pressure Driven Microflows (2002)

Electrokinetics

Microfluidic Diode and Transistors

Diodes and Bipolar Transistors can be built from a nanochannel connecting two salt baths.

Surface charges on a nannochannel can control the current in the channel.

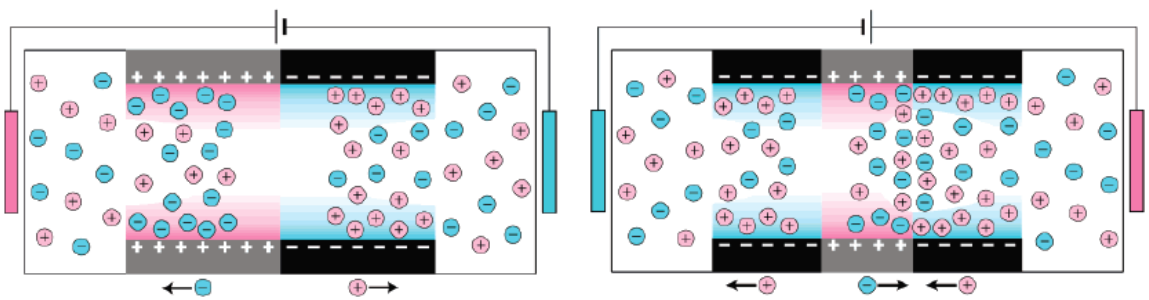


Figure: Nanofluidic Diode and Bipolar Transistor

Daiguji, Oka, & Shirono, Nanofluidic Diode and Bipolar Transistor

Electrokinetics

Electrophoresis

Another applications where the PNP equations are coupled with Navier-Stokes includes electrophoresis, where a solid charged particle is suspended in a charged fluid, and an applied electric field moves the solid.

In this application, the "boundary" moves as the charged particle is driven through the device.

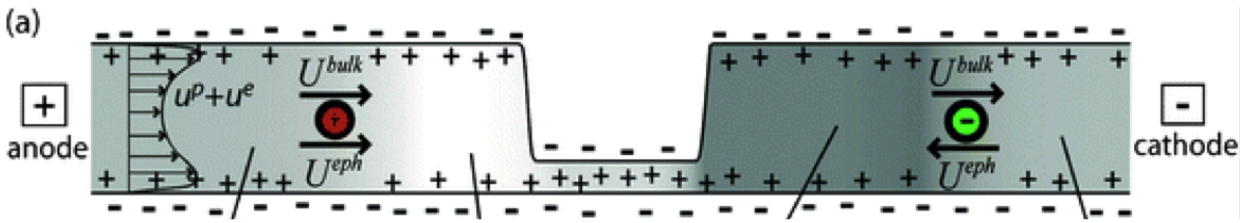


Figure: Electrophoresis

Zangle, Mani, & Santiago, Theory and experiments of concentration polarization and ion focusing at microchannel and nanochannel interfaces (2010)

Biological Applications

Passive transport through cell membrane

Modeling ions passing through the nanochannels of a cellular membrane is a well-studied example.

Passive transport through the nanochannel has been modeled using the PNP equations.

- Ion diffusivity and electric permittivity change from the bath to channel
- Complicated mesh geometries are needed to resolve proteins
- Fixed charges generate surface charges on protein
- Ionic fluxes must account for fixed charges and inter-ionic interactions

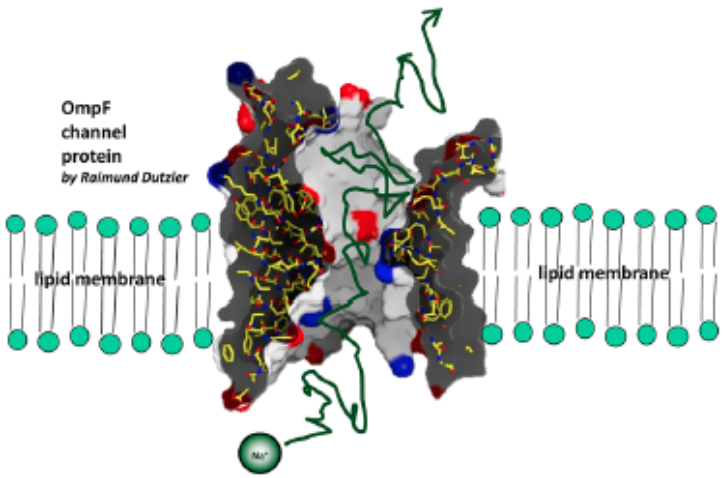


Figure: Passive Transport

Horng, Lin, Liu, & Eisenberg, PNP Equations with Steric Effects: A Model of Ion Flow through Channels (2012)

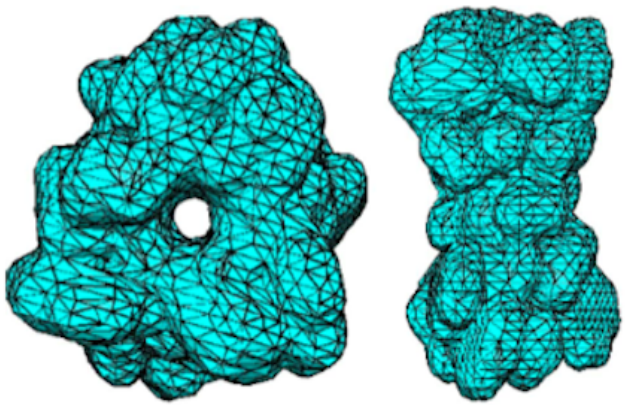
Biological Applications

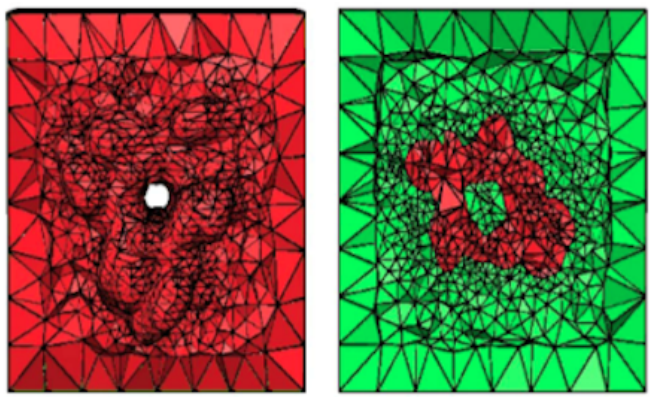
Passive transport: Geometry

The function of proteins are extremely sensitive to location of charges in proteins and protein shape.

Generating accurate, let alone adequate, protein meshes is a difficult task!

There exist software packages for mesh generation, such as **TMSmesh**, that are designed to produce high quality meshes for proteins.





Tu, Chen, Xie, Zhang, Eisenberg, & Lu, A Parallel Finite Element Simulator for Ion Transport through Three-Dimensional Ion Channel Systems (2013)

Biological Applications

Passive Transport: Permanent Charges

Within each protein, there are many permanent charges, which are modeled as point charges, to generate the surface charge on the protein.

The electric potential has a numerically stable decomposition into three components:

- Singular: $-\nabla \cdot (\varepsilon_p \nabla \phi_s(x)) = \sum_i \delta(|x - x_i|)$
  $\Longrightarrow \quad \phi_s = \sum \text{Coloumb potentials}\big|_{\Omega_p}$
- Harmonic: $-\nabla \cdot (\varepsilon_p \nabla \phi_h) = 0, \quad \phi_h\big|_{\partial\Omega_p} = -\phi_s\big|_{\partial\Omega_p}$
- Regular: $-\nabla \cdot (\varepsilon \nabla \phi_r) = p - n,$
  $\varepsilon_s \frac{\partial \phi_r}{\partial n} - \varepsilon_p \frac{\partial \phi_r}{\partial n} = \varepsilon_p \frac{\partial}{\partial n}(\phi_s + \phi_h)$ on $\partial\Omega_p$

$$\varepsilon = \begin{cases} \varepsilon_p, & \text{in protein} \\ \varepsilon_s, & \text{in solution} \end{cases}$$

Biological Applications

Passive Transport: Steric Effects

Due to the small scale of this process, the size of ions becomes increasingly important. This is especially true when studying channel selectivity.

Following Horng, Lin, Liu, Eisenberg, we can modify the ionic flux to account for repulsive size effects between ions:

$$\vec{j_p} = -D_p\big(\nabla p + p\nabla\phi + p(\varepsilon_{pp}\nabla p + \varepsilon_{pn}\nabla n)\big),$$
$$\vec{j_n} = -D_n\big(\nabla n - n\nabla\phi + n(\varepsilon_{np}\nabla p + \varepsilon_{nn}\nabla n)\big).$$

These modifications have recovered some selectivity behavior of ion nanochannels.

Further modifications employing relative drag have been analyzed to model ion crowding.

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PNP Models and their Differences

While it has been emphasized that there are some standard classes of modifications to the PNP system, the effects of these modifications should not be downplayed.

The resulting behavior of a given device can change drastically, as well as the analysis that is required to understand the model mathematically.

Our Goal

Our focus is on designing and analyzing numerical discretizations and solvers for the PNP equations.

We seek robust finite element discretizations for the PNP equations with solvers that have provable convergence and stability properties to work for a wide variety of applications.

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Formulating the PNP Equations

Primitive Variables

For a system with a single cation and anion, the formulation using **primitive** variables is

$$\frac{\partial}{\partial t} p = \nabla \cdot [D_p(\nabla p + p \nabla \phi)],$$
$$\frac{\partial}{\partial t} n = \nabla \cdot [D_n(\nabla n - n \nabla \phi)],$$
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plus suitable boundary conditions that depend on the device in question.

Formulation Selectivity

In proving results for the discrete system, we must choose the appropriate variables to discretize a priori, as this determines the restricted class of discrete test functions.

We would like to prove:

- An energy estimate for the discrete nonlinear solution
- Convergence to the discrete nonlinear solution
- Well-posedness of the linearized system

Energy Estimate for the Continuous Formulation

The solution of the simple PNP system satisfies the known energy law

$$\frac{d}{dt}\int_\Omega \frac{\varepsilon}{2}|\nabla\phi|^2 + p\log p + n\log n\,dx$$
$$= -\int_\Omega D_p p|\nabla(\log p + \phi)|^2 + D_n n|\nabla(\log n - \phi)|^2\,dx.$$

The energy norm used for this system is not typical of finite element discretizations where $p, n, \phi \in V_h = C_0 \cap \{\text{pw linear}\}$

Energy Estimate for the Continuous Formulation

The solution of the simple PNP system satisfies the known energy law

$$\frac{d}{dt}\int_\Omega \frac{\varepsilon}{2}|\nabla\phi|^2 + p\log p + n\log n\,dx$$
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The energy norm used for this system is not typical of finite element discretizations where $p, n, \phi \in V_h = \mathcal{C}_0 \cap \{\text{pw linear}\}$

Formulating the PNP Equations

Slotboom Variables

An alternate formulation to the primitive variables involves the **Slotboom** variables,

$$\bar{p} = e^{\phi} p, \qquad \bar{D}_p = D_p e^{-\phi},$$
$$\bar{n} = e^{-\phi} n, \qquad \bar{D}_n = D_n e^{\phi}.$$

Then,

$$\frac{\partial}{\partial t} e^{-\phi} \bar{p} = \nabla \cdot \left(\bar{D}_p \nabla \bar{p} \right),$$
$$\frac{\partial}{\partial t} e^{\phi} \bar{n} = \nabla \cdot \left(\bar{D}_n \nabla \bar{n} \right),$$
$$-\nabla \cdot (\varepsilon \nabla \phi) = e^{-\phi} \bar{p} - e^{\phi} \bar{n}.$$

Formulating the PNP Equations

Slotboom Variables

The Slotboom formulation is useful for proving analytical results such as a maximum principle, since the Nernst-Planck equations are symmetrized.

$$\frac{\partial}{\partial t} e^{-\phi} \bar{p} = \nabla \cdot \left(\bar{D}_p \nabla \bar{p} \right),$$

$$\frac{\partial}{\partial t} e^{\phi} \bar{n} = \nabla \cdot \left(\bar{D}_n \nabla \bar{n} \right).$$

Also, this formulation observes faster convergence numerically for nonlinear iterates.

One must be careful to account for the conditioning of the stiffness matrix, since the diffusion coefficient varies exponentially.

$$\bar{D}_p = D_p e^{-\phi}, \qquad \bar{D}_n = D_n e^{\phi}.$$

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$$\bar{D}_p = D_p e^{-\phi}, \qquad \bar{D}_n = D_n e^{\phi}.$$

Formulating the PNP Equations

Log-Density Variables

Using a log transformation, we define

$$\hat{p} = \log p, \qquad \hat{n} = \log n.$$

Then,

$$\begin{aligned} \frac{\partial}{\partial t} e^{\hat{p}} &= \nabla \cdot \left(D_p e^{\hat{p}} \nabla (\hat{p} + \phi) \right), \\ \frac{\partial}{\partial t} e^{\hat{n}} &= \nabla \cdot \left(D_n e^{\hat{n}} \nabla (\hat{n} - \phi) \right), \\ -\nabla \cdot (\varepsilon \nabla \phi) &= e^{\hat{p}} - e^{\hat{n}}. \end{aligned}$$

This formulation displays **nonlinear diffusion** and guarantees **positivity** of the ionic densities.

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Energy Estimate for Log-Density Weak Form

In order to prove the energy estimate, we assume a *closed* system and $\hat{p}, \hat{n} \in V_h \subset H^1$ and $\phi \in V_h' \subseteq V_h$.
Written in weak form:

$$\left(\frac{\partial}{\partial t} e^{\hat{p}}, \chi\right) + \left(D_p e^{\hat{p}} \nabla(\hat{p} + \phi), \nabla\chi\right) = 0,$$
$$\left(\frac{\partial}{\partial t} e^{\hat{n}}, \lambda\right) + \left(D_n e^{\hat{n}} \nabla(\hat{n} - \phi), \nabla\lambda\right) = 0,$$
$$\left(\varepsilon\nabla\phi, \nabla\psi\right) - \left(e^{\hat{p}} - e^{\hat{n}}, \psi\right) = 0.$$

Further, we assume the conservation of mass:

$$\frac{d}{dt}\int_\Omega e^{\hat{p}}\, dx = \frac{d}{dt}\int_\Omega e^{\hat{n}}\, dx = 0.$$

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$$\frac{d}{dt}\int_\Omega e^{\hat{p}}\, dx = \frac{d}{dt}\int_\Omega e^{\hat{n}}\, dx = 0.$$

Energy Estimate for Log-Density Weak Form

Choosing $\chi = \hat{p} + \phi$, $\lambda = \hat{n} - \phi$, and $\psi = \phi$ yields an energy estimate:

$$\left(\frac{\partial}{\partial t} e^{\hat{p}}, \hat{p}\right) + \left(\frac{\partial}{\partial t} e^{\hat{p}}, \phi\right) = -\left(D_p e^{\hat{p}} \nabla(\hat{p} + \phi), \nabla(\hat{p} + \phi)\right),$$

$$\left(\frac{\partial}{\partial t} e^{\hat{n}}, \hat{n}\right) - \left(\frac{\partial}{\partial t} e^{\hat{n}}, \phi\right) = -\left(D_n e^{\hat{n}} \nabla(\hat{n} - \phi), \nabla(\hat{n} - \phi)\right),$$

$$\left(\varepsilon \nabla\left(\frac{\partial}{\partial t}\phi\right), \nabla\phi\right) = \left(\frac{\partial}{\partial t} e^{\hat{p}}, \phi\right) - \left(\frac{\partial}{\partial t} e^{\hat{n}}, \phi\right),$$

Energy Estimate for Log-Density Weak Form

Adding the PNP equations gives

$$\left(\varepsilon\nabla(\frac{\partial}{\partial t}\phi),\nabla\phi\right)+\left(\frac{\partial}{\partial t}e^{\hat{p}},\hat{p}\right)+\left(\frac{\partial}{\partial t}e^{\hat{n}},\hat{n}\right)$$
$$=-\left(D_p e^{\hat{p}}\nabla(\hat{p}+\phi),\nabla(\hat{p}+\phi)\right)-\left(D_n e^{\hat{n}}\nabla(\hat{n}-\phi),\nabla(\hat{n}-\phi)\right)$$

and

$$\frac{d}{dt}\left(e^{\hat{p}},1\right)=\left(e^{\hat{p}},\frac{\partial}{\partial t}\hat{p}\right)=0,$$
$$\frac{d}{dt}\left(e^{\hat{n}},1\right)=\left(e^{\hat{n}},\frac{\partial}{\partial t}\hat{n}\right)=0.$$

Energy Estimate for Log-Density Weak Form

Combining these equations, we recover an energy estimate:

$$\left(\varepsilon\nabla\left(\frac{\partial}{\partial t}\phi\right),\nabla\phi\right)+\left(\frac{\partial}{\partial t}e^{\hat{p}},\hat{p}\right)+\left(\frac{\partial}{\partial t}e^{\hat{n}},\hat{n}\right)+\left(e^{\hat{p}},\frac{\partial}{\partial t}\hat{p}\right)+\left(e^{\hat{n}},\frac{\partial}{\partial t}\hat{n}\right)$$

$$=\frac{d}{dt}\int_{\Omega}\frac{\varepsilon}{2}|\nabla\phi|^2+\hat{p}e^{\hat{p}}+\hat{n}e^{\hat{n}}\,dx$$

$$=-\left(D_p e^{\hat{p}}\nabla(\hat{p}+\phi),\nabla(\hat{p}+\phi)\right)-\left(D_n e^{\hat{n}}\nabla(\hat{n}-\phi),\nabla(\hat{n}-\phi)\right).$$

Energy Estimate for Log-Density Weak Form

Combining these equations, we recover an energy estimate:

$$\left(\varepsilon\nabla(\frac{\partial}{\partial t}\phi),\nabla\phi\right)+\left(\frac{\partial}{\partial t}e^{\hat{p}},\hat{p}\right)+\left(\frac{\partial}{\partial t}e^{\hat{n}},\hat{n}\right)+\left(e^{\hat{p}},\frac{\partial}{\partial t}\hat{p}\right)+\left(e^{\hat{n}},\frac{\partial}{\partial t}\hat{n}\right)$$

$$= \frac{d}{dt}\int_\Omega \frac{\varepsilon}{2}|\nabla\phi|^2+\hat{p}e^{\hat{p}}+\hat{n}e^{\hat{n}}\,dx$$

$$= -\left(D_p e^{\hat{p}}\nabla(\hat{p}+\phi),\nabla(\hat{p}+\phi)\right)-\left(D_n e^{\hat{n}}\nabla(\hat{n}-\phi),\nabla(\hat{n}-\phi)\right).$$

Energy Estimate for Log-Density Weak Form

Written in terms of the primitive variables $p = e^{\hat{p}}, n = e^{\hat{n}}$, we have

$$\int_\Omega \frac{\varepsilon}{2}|\nabla\phi|^2 + \hat{p}e^{\hat{p}} + \hat{n}e^{\hat{n}}\,dx = \int_\Omega \frac{\varepsilon}{2}|\nabla\phi|^2 + p\log p + n\log n\,dx$$

and

$$-\Big(D_p e^{\hat{p}}\nabla(\hat{p}+\phi), \nabla(\hat{p}+\phi)\Big) - \Big(D_n e^{\hat{n}}\nabla(\hat{n}-\phi), \nabla(\hat{n}-\phi)\Big)$$
$$= -\int_\Omega D_p p|\nabla(\log p + \phi)|^2 + D_n n|\nabla(\log n - \phi)|^2\,dx.$$

Which shows that the solution for the semi-discrete system satisfies the same energy law as the continuous.

A Fully Discrete Energy Estimate

For the fully discrete system, we consider Backward Euler time-stepping:

$$\left(\frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}, \chi\right) + \left(D_p e^{\hat{p}_k} \nabla(\hat{p}_k + \phi_k), \nabla\chi\right) = 0,$$

$$\left(\frac{e^{\hat{n}_k} - e^{\hat{n}_{k-1}}}{\Delta t}, \lambda\right) + \left(D_n e^{\hat{n}_k} \nabla(\hat{n}_k + \phi_k), \nabla\lambda\right) = 0,$$

$$\left(\varepsilon\nabla\phi_k, \nabla\psi\right) - \left(e^{\hat{p}_k} - e^{\hat{n}_k}, \psi\right) = 0.$$

Subscripts denote the time-step.

A Fully Discrete Energy Estimate

For the fully discrete system, we consider Backward Euler time-stepping:

$$\left(\frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}, \chi\right) + \left(D_p e^{\hat{p}_k} \nabla(\hat{p}_k + \phi_k), \nabla\chi\right) = 0,$$
$$\left(\frac{e^{\hat{n}_k} - e^{\hat{n}_{k-1}}}{\Delta t}, \lambda\right) + \left(D_n e^{\hat{n}_k} \nabla(\hat{n}_k + \phi_k), \nabla\lambda\right) = 0,$$
$$\left(\varepsilon\nabla\phi_k, \nabla\psi\right) - \left(e^{\hat{p}_k} - e^{\hat{n}_k}, \psi\right) = 0.$$

Subscripts denote the time-step.

A Fully Discrete Energy Estimate

To maintain an analogous energy estimate, there are two alternative schemes for mass conservation:

$$\left(\frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}, 1\right) = 0 \quad \text{and} \quad \left(\frac{e^{\hat{n}_k} - e^{\hat{n}_{k-1}}}{\Delta t}, 1\right) = 0,$$

or

$$\left(e^{\hat{p}_{k-1}}, \frac{\hat{p}_k - \hat{p}_{k-1}}{\Delta t}\right) = 0 \quad \text{and} \quad \left(e^{\hat{n}_{k-1}}, \frac{\hat{n}_k - \hat{n}_{k-1}}{\Delta t}\right) = 0.$$

A Fully Discrete Energy Estimate

We first consider the conservation scheme

$$\left(\frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}, 1\right) = 0 \quad \text{and} \quad \left(\frac{e^{\hat{n}_k} - e^{\hat{n}_{k-1}}}{\Delta t}, 1\right) = 0.$$

For this discrete energy estimate, we must define an underlying finite element space.

A Fully Discrete Energy Estimate

Define $e^{\hat{p}(x,t)} = \sum_{k=1}^{m} b_k(t) e^{\hat{p}_k(x)}$: then for $t_{k-1} < t \leq t_k$,

$$\frac{\partial e^{\hat{p}(t)}}{\partial t} = \frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}$$

and

$$\frac{\partial \hat{p}(t)}{\partial t} = \frac{\partial}{\partial t} \log \left(\sum_{k=1}^{m} b_k(t) e^{\hat{p}_k(x)} \right)$$

$$= \frac{1}{\sum_{k=1}^{m} b_k(t) e^{\hat{p}_k(x)}} \frac{\partial}{\partial t} \sum_{k=1}^{m} b_k(t) e^{\hat{p}_k(x)} = \frac{1}{e^{\hat{p}(t)}} \frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}$$

A Fully Discrete Energy Estimate

Thus, the Nernst-Planck equation is

$$\left(\frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}, \hat{p}_k + \phi_k\right) = \left(\frac{\partial}{\partial t} e^{\hat{p}_k}, \hat{p}_k\right) + \left(\frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}, \phi_k\right)$$
$$= -\left(D_p e^{\hat{p}_k} \nabla(\hat{p}_k + \phi_k), \nabla(\hat{p}_k + \phi_k)\right)$$

and mass conservation is:

$$\left(\frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}, 1\right) = \left(e^{\hat{p}_k}, \frac{\partial \hat{p}_k}{\partial t}\right) = 0,$$

which combine into

$$\frac{\partial}{\partial t}\left(e^{\hat{p}_k}, \hat{p}_k\right) + \left(\frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}, \phi_k\right) = -\left(D_p e^{\hat{p}_k} \nabla(\hat{p}_k + \phi_k), \nabla(\hat{p}_k + \phi_k)\right).$$

A Fully Discrete Energy Estimate

We have

$$\frac{\partial}{\partial t}\left(e^{\hat{p}_k},\hat{p}_k\right)+\left(\frac{e^{\hat{p}_k}-e^{\hat{p}_{k-1}}}{\Delta t},\phi_k\right)=-\left(D_p e^{\hat{p}_k}\nabla(\hat{p}_k+\phi_k),\nabla(\hat{p}_k+\phi_k)\right)$$

$$\frac{\partial}{\partial t}\left(e^{\hat{n}_k},\hat{n}_k\right)-\left(\frac{e^{\hat{n}_k}-e^{\hat{n}_{k-1}}}{\Delta t},\phi_k\right)=-\left(D_n e^{\hat{n}_k}\nabla(\hat{n}_k-\phi_k),\nabla(\hat{n}_k-\phi_k)\right)$$

and

$$\left(\varepsilon\frac{\nabla\phi_k-\nabla\phi_{k-1}}{\Delta t},\nabla\phi_k\right)=\left(\frac{e^{\hat{p}_k}-e^{\hat{p}_{k-1}}}{\Delta t},\phi_k\right)-\left(\frac{e^{\hat{n}_k}-e^{\hat{n}_{k-1}}}{\Delta t},\phi_k\right).$$

A Fully Discrete Energy Estimate

We have

$$\frac{\partial}{\partial t}\left[\frac{\varepsilon}{2}(\nabla\phi_k,\nabla\phi_k)+\left(e^{\hat{p}_k},\hat{p}_k\right)+\left(e^{\hat{n}_k},\hat{n}_k\right)\right]$$
$$=-\left(D_p e^{\hat{p}_k}\nabla(\hat{p}_k+\phi_k),\nabla(\hat{p}_k+\phi_k)\right)$$
$$-\left(D_n e^{\hat{n}_k}\nabla(\hat{n}_k-\phi_k),\nabla(\hat{n}_k-\phi_k)\right)$$

It is important to bear in mind that this only holds at discrete time steps, t_k.

A Fully Discrete Energy Estimate

We have

$$\frac{\partial}{\partial t}\left[\frac{\varepsilon}{2}(\nabla\phi_k,\nabla\phi_k)+\left(e^{\hat{p}_k},\hat{p}_k\right)+\left(e^{\hat{n}_k},\hat{n}_k\right)\right]$$
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It is important to bear in mind that this only holds at discrete time steps, t_k.

A Fully Discrete Energy Estimate

This implies that mass is *exactly* conserved over time and

$$\begin{aligned}
\max_k \left\{ \frac{\varepsilon}{2} |\phi(t_k)|_1^2 + \left(e^{\hat{p}(t_k)}, \hat{p}(t_k) \right) + \left(e^{\hat{n}(t_k)}, \hat{n}(t_k) \right) \right\} \\
\leq \frac{\varepsilon}{2} |\phi(0)|_1^2 + \left(e^{\hat{p}(0)}, \hat{p}(0) \right) + \left(e^{\hat{n}(0)}, \hat{n}(0) \right) \\
- \sum_k \Delta t \Big[\left(D_p e^{\hat{p}_k} \nabla(\hat{p}_k + \phi_k), \nabla(\hat{p}_k + \phi_k) \right) \\
+ \left(D_n e^{\hat{n}_k} \nabla(\hat{n}_k - \phi_k), \nabla(\hat{n}_k - \phi_k) \right) \Big] \\
+ \text{quadrature error}
\end{aligned}$$

A Fully Discrete Energy Estimate

The alternate mass conservation scheme requires

$$\left(e^{\hat{p}}, \frac{\partial}{\partial t}\hat{p}\right) \approx \left(e^{\hat{p}_{k-1}}, \frac{\hat{p}_k - \hat{p}_{k-1}}{\Delta t}\right) = 0.$$

We note that this mass conservation constraints, together with a backward difference, yields an algebraic identity

$$\left(\frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}, \hat{p}_k\right) + \left(e^{\hat{p}_{k-1}}, \frac{\hat{p}_k - \hat{p}_{k-1}}{\Delta t}\right) = \left(\frac{\hat{p}_k e^{\hat{p}_k} - \hat{p}_{k-1} e^{\hat{p}_{k-1}}}{\Delta t}, 1\right).$$

A Fully Discrete Energy Estimate

The new identity along with same technique as the other (semi-)discrete energy estimates give

$$\frac{\varepsilon}{2}\frac{|\phi_k|_1^2 - |\phi_{k-1}|_1^2}{\Delta t} + \left(\frac{\hat{p}_k e^{\hat{p}_k} - \hat{p}_{k-1} e^{\hat{p}_{k-1}}}{\Delta t}, 1\right) + \left(\frac{\hat{n}_k e^{\hat{n}_k} - \hat{n}_{k-1} e^{\hat{n}_{k-1}}}{\Delta t}, 1\right)$$
$$\leq -\left(D_p e^{\hat{p}_k}\nabla(\hat{p}_k + \phi_k), \nabla(\hat{p}_k + \phi_k)\right)$$
$$-\left(D_n e^{\hat{n}_k}\nabla(\hat{n}_k - \phi_k), \nabla(\hat{n}_k - \phi_k)\right).$$

A Fully Discrete Energy Estimate

Summing over k gives

$$\begin{aligned}
&\max_k \left\{ \frac{\varepsilon}{2}|\phi_k|_1^2 + \left(\hat{p}_k e^{\hat{p}_k}, 1\right) + \left(\hat{n}_k e^{\hat{n}_k}, 1\right) \right\} \\
&\qquad \leq \frac{\varepsilon}{2}|\phi_0|_1^2 + \left(\hat{p}_0 e^{\hat{p}_0}, 1\right) + \left(\hat{n}_0 e^{\hat{n}_0}, 1\right) \\
&\qquad\quad - \sum_{k=1}^{m} \Delta t \Big[\left(D_p e^{\hat{p}_k} \nabla(\hat{p}_k + \phi_k), \nabla(\hat{p}_k + \phi_k)\right) \\
&\qquad\qquad + \left(D_n e^{\hat{n}_k} \nabla(\hat{n}_k - \phi_k), \nabla(\hat{n}_k - \phi_k)\right) \Big].
\end{aligned}$$

Comparing the Estimates

The first scheme: $\left(\frac{e^{\hat{p}_k} - e^{\hat{p}_{k-1}}}{\Delta t}, 1\right) = 0$ conserves mass exactly and obeys an energy law at each time step, though the final estimate has an additional quadrature error term.

The second scheme: $\left(e^{\hat{p}}, \frac{\partial}{\partial t}\hat{p}\right) \approx \left(e^{\hat{p}_{k-1}}, \frac{\hat{p}_k - \hat{p}_{k-1}}{\Delta t}\right) = 0$ has a favorable energy estimate, though the mass is only approximately conserved.

Software Packages

We leverage the FEniCS and FASP software packages.

FEniCS Software Package:

- Open source software, many collaborators
- Translates weak form into linear systems
- Interfaces with linear solvers

FASP Software Package:

- Developed at Penn State
- Fast solvers for linear systems

Robust Discretization

Nonlinear Problem

Our goal is to develop a software that can solve the PNP system for a wide variety range of parameters and applications with provable stability and well-posedness properties.

The nonlinearity of the system is believed to provide stability; a Newton solver is used since the energy is convex.

Convergence is presumed once the relative residual is below a predefined threshold.

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Robust Discretization

Nonlinear Problem

We take care to mention the case of modified ion fluxes or ion sources, as in the case of electrokinetics or ionic recombinations.

We take the Frechét derivative with respect to any additional terms along with the rest of the system to take a monolithic approach. So,

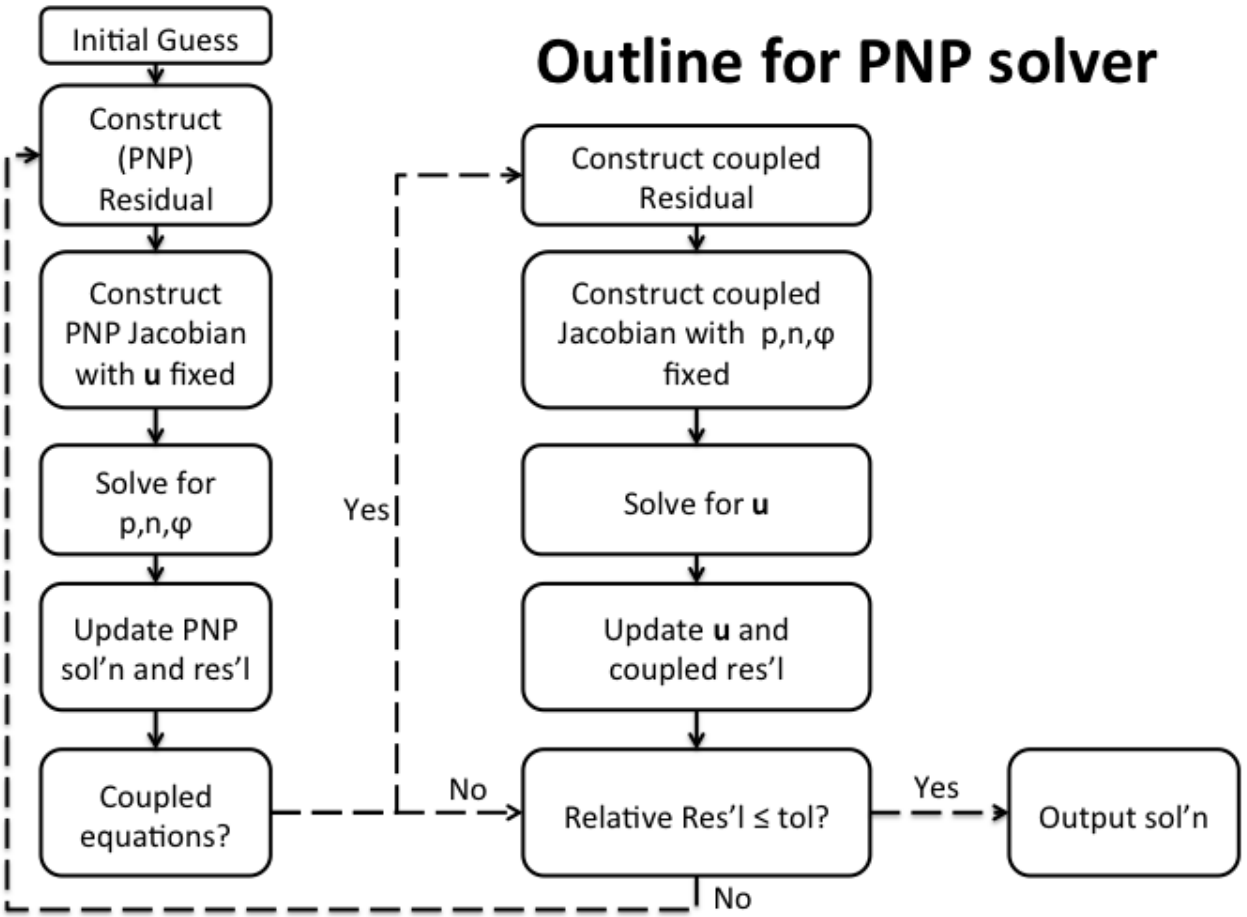
$$\vec{j_p} = -D_p\left(\nabla p + p\nabla\phi\right) + \vec{F}(p, n, \phi, u)$$

gives

$$\delta\vec{j_p} = -D_p\left(\nabla\delta p + \delta p\nabla\phi + p\nabla\delta\phi\right) + \left.\frac{\partial}{\partial\epsilon}\right|_{\epsilon=0} \vec{F}(p + \epsilon\delta p, n + \epsilon\delta n, \phi + \epsilon\delta\phi, u + \epsilon\delta u).$$

Robust Discretization

Nonlinear Problem



Robust Discretization

Linear Problem

Currently, we employ a block G-S solver with a preconditioner on the linearized system, which approximately solves PNP equations given additional forces, updates the solution, then solves any additional equations with $\hat{p}, \hat{n}, \phi$ fixed, updates the solution, and so cycles back and forth.

In this way, we can precondition the PNP system and the additional equations separately, while maintaining a monolithic approach.

Robust Discretization

Linear Problem

In both primitive and log-density variables, the Frechét derivative yields linear convection-dominated problems:

$$\frac{1}{\Delta t}\Big(p,\chi\Big) + \Big(\alpha_p \nabla p + \vec{\beta}_p p, \nabla\chi\Big) + \Big(\alpha_p \nabla\phi, \nabla\chi\Big) = (R_p,\chi),$$
$$\frac{1}{\Delta t}\Big(n,\lambda\Big) + \Big(\alpha_n \nabla n + \vec{\beta}_n n, \nabla\lambda\Big) + \Big(\alpha_n \nabla\phi, \nabla\lambda\Big) = (R_n,\lambda),$$
$$\Big(\varepsilon\nabla\phi, \nabla\psi\Big) - \Big(\gamma_p p - \gamma_n n, \psi\Big) = (R_\phi,\psi).$$

We use a quasi-Newton method, where an EAFE flux can be used to approximate the flux terms on an element-by-element basis:

$$\alpha_p \nabla p + \vec{\beta}_p p \approx J_p(p), \qquad \alpha_p \nabla p + \vec{\beta}_p p \approx J_n(n).$$

Robust Discretization

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$$\frac{1}{\Delta t}\Big(n,\lambda\Big) + \Big(\alpha_n \nabla n + \vec{\beta}_n n, \nabla\lambda\Big) + \Big(\alpha_n \nabla\phi, \nabla\lambda\Big) = (R_n,\lambda),$$
$$\Big(\varepsilon\nabla\phi, \nabla\psi\Big) - \Big(\gamma_p p - \gamma_n n, \psi\Big) = (R_\phi,\psi).$$

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Robust Discretization

Linear Problem

$$\begin{bmatrix} \varepsilon\text{-Poisson Stiffness Matrix} & -\left(\text{Mass Matrix}\right) & \text{Mass Matrix} \\ \text{Diffusion Stiffness Matrix} & \nabla\phi \text{ EAFE Stiffness Matrix} & 0 \\ -\left(\text{Diffusion Stiffness Matrix}\right) & 0 & -\nabla\phi \text{ EAFE Stiffness Matrix} \end{bmatrix}$$

Figure: The Jacobian matrix

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Linear Problem

Preconditioned Jacobi or Gauß-Seidel can be used to solve the linear system, though convergence depends on the conditioning of the full linear system.

In addition to the off-diagonal blocks, another difficulty can arise from the ε-Poisson block:

$$\Big(\varepsilon\nabla\phi, \nabla\psi\Big) - \Big(\gamma_p p - \gamma_n n, \psi\Big) = (f_\phi, \psi).$$

Often, this is singularly perturbed: $0 < \varepsilon \ll 1$.

A posteriori error estimators and mesh adaptivity can be used to resolve ϕ.

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Thank you for your attention