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Mathematical Modeling All Solid State Batteries

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Introduction

Derivation of the 1-D model equations

- Model assumptions
- Transport equations
- Boundary conditions

Classification

Numerics

- Steady state solution
- Transient solution

Towards Optimization

- Weak formulation
- Performance citeria

Incorperating mechanical effects

- Cahn-Hilliard Approach
- Electrochemical interfacial kinetics

Introduction

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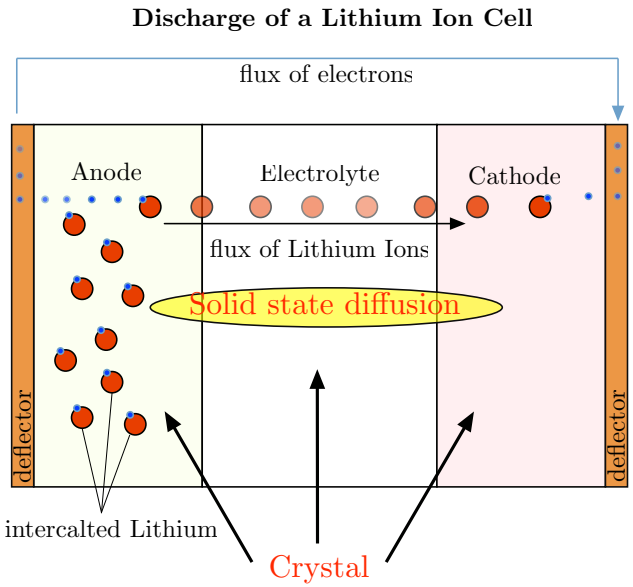
Bundesministerium für Bildung und Forschung

NETZWERKE GRUNDLAGENFORSCHUNG erneuerbare Energien und rationelle Energieanwendungen

Project LISA: Lithium insertation compounds for solar devices

- Part of the BMBF network: fundamental research on renewable energies
- Compound Project: Uni Kiel, TU Darmstadt, ZSW Ulm, Uni Ulm
- First example for considered material-configuration:

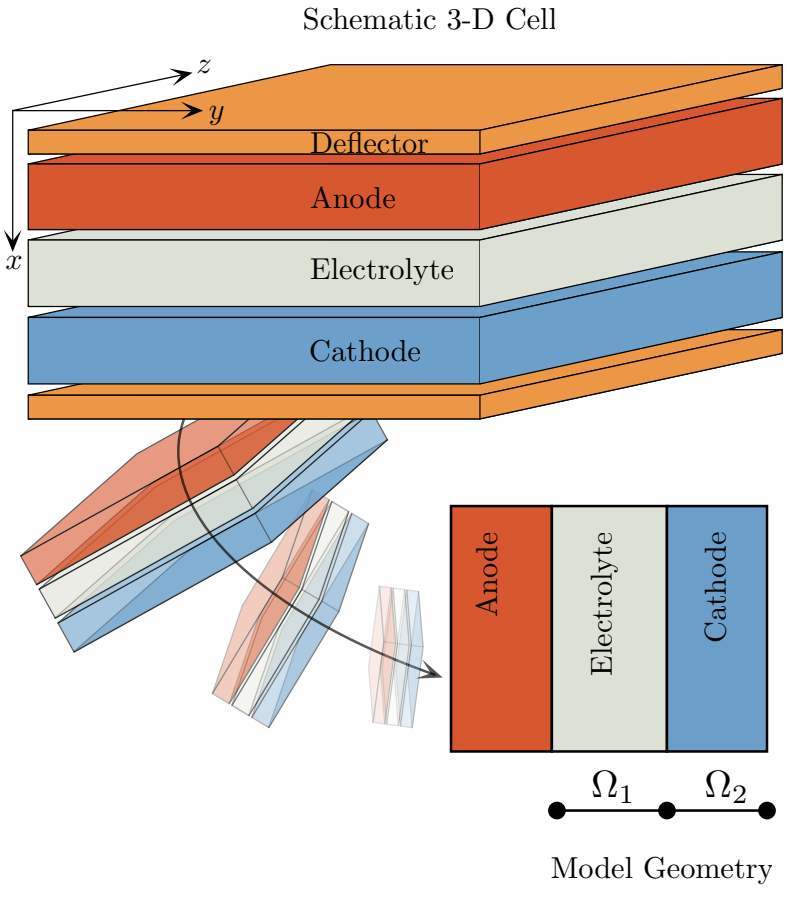
$$Li|Li_{5+x}BaLa_2Ta_2O_{11.5+0.5x}|TiO_2$$



Mathematical modeling and optimization of all solid state thin film lithium ion batteries

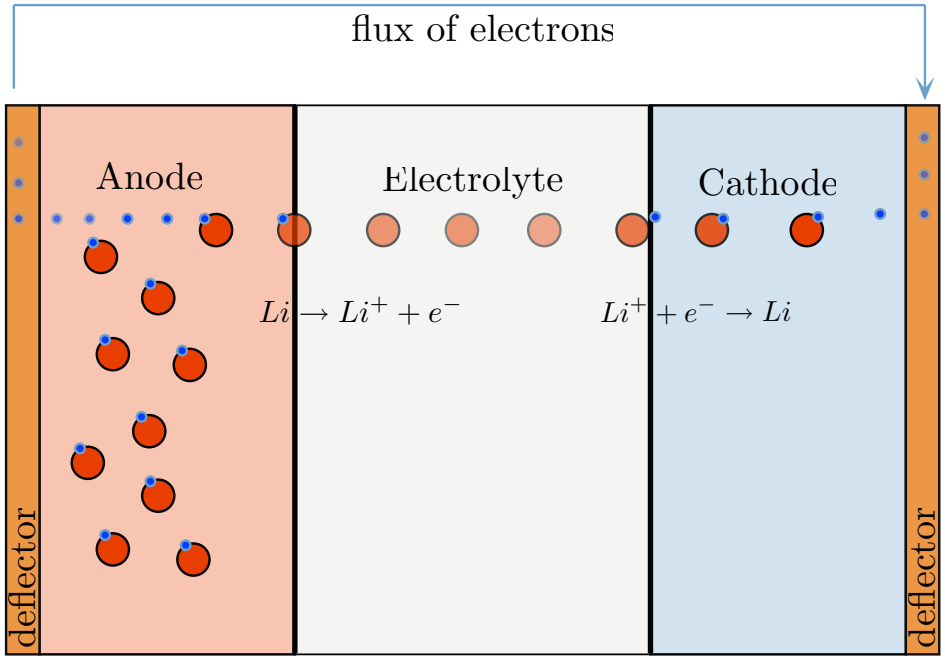
Part I: Derivation and Numerics of a model for all solid-state lithium ion batteries

Model assumptions



- Isotropic in y, z dimensions
- Perfect planar interfaces

Model assumptions



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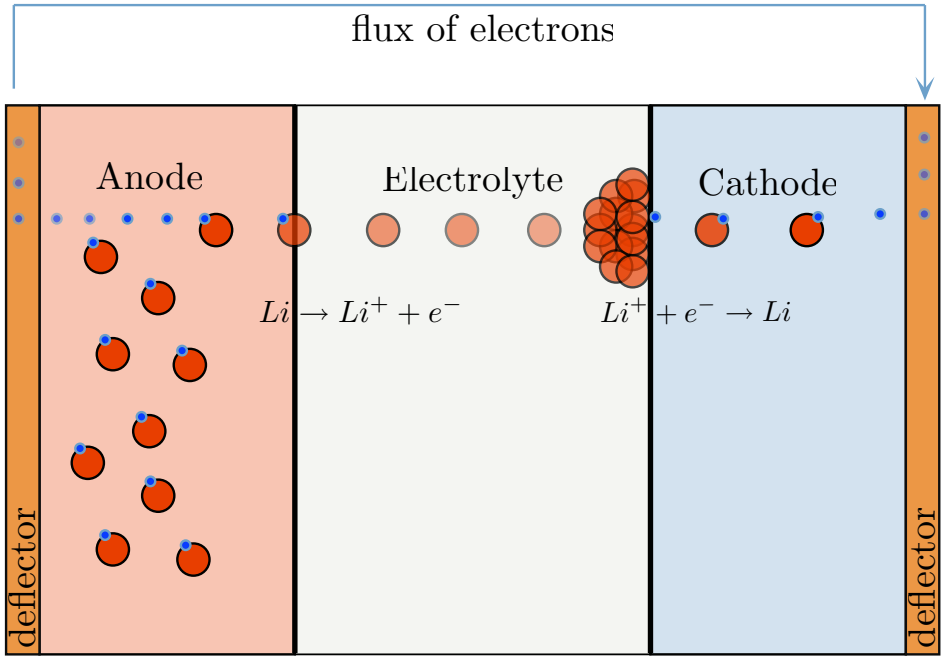

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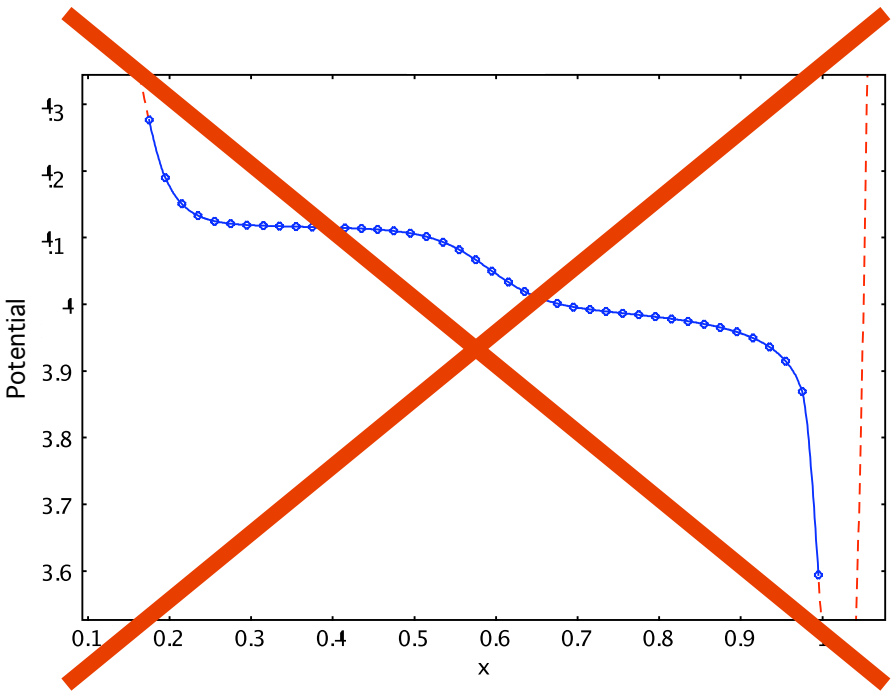

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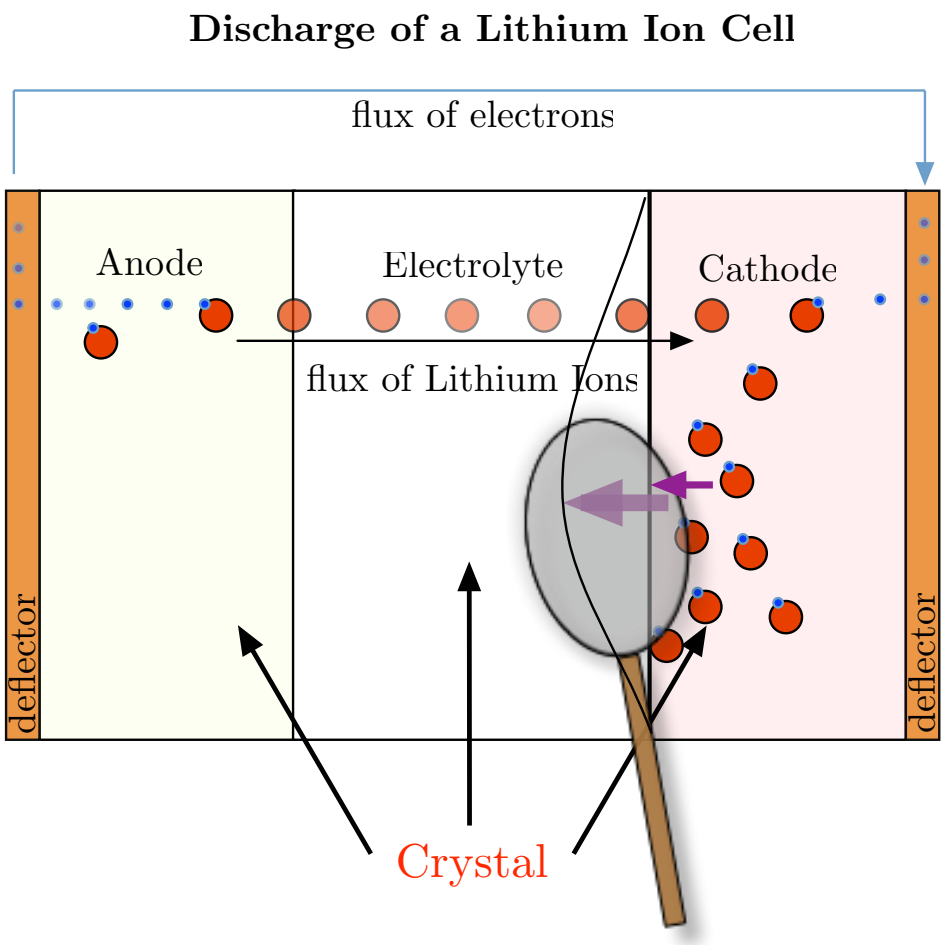

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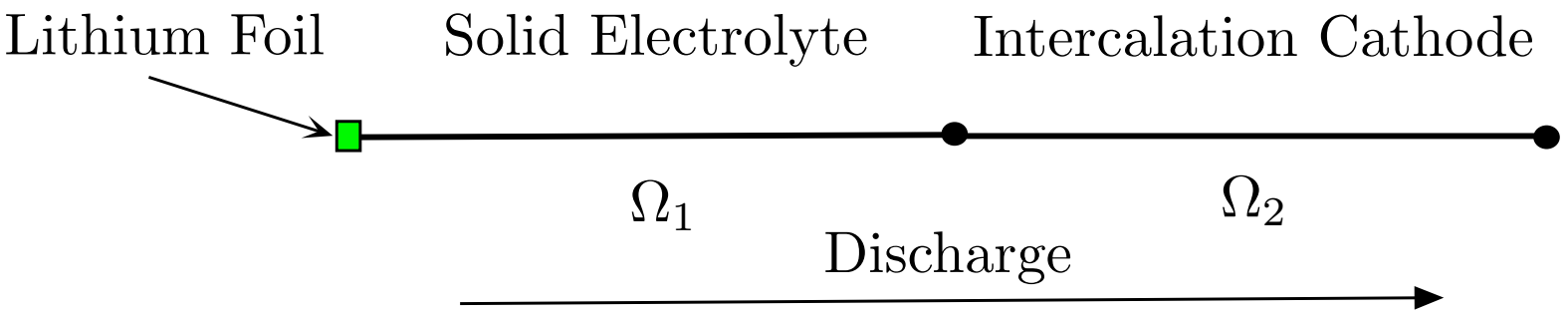
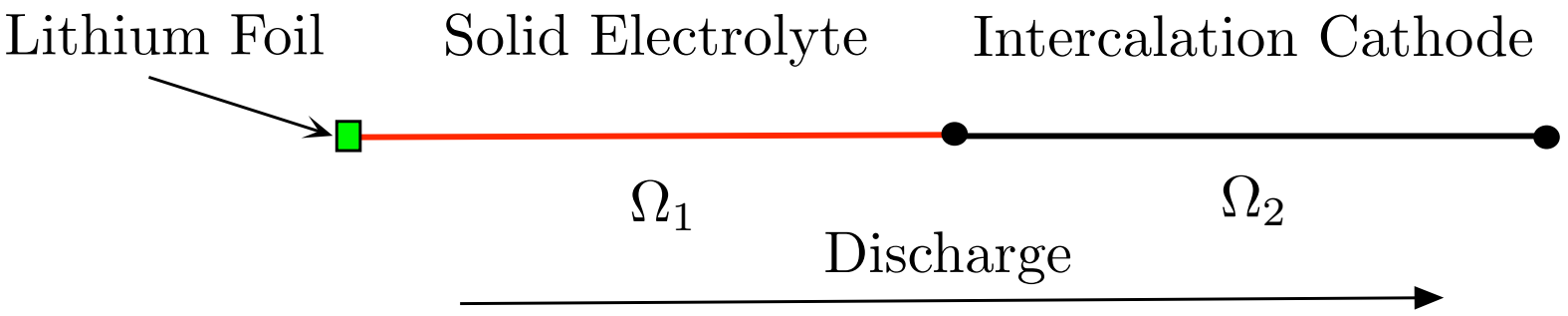
- Reactions only at the interfaces
- No repulsive ion-ion interaction $\Rightarrow D_{Li^+} = const.$
- Potentiostatic discharge
- No potential variation as function of status of charge (SOC) or intercalated lithium
- No mechanical effects of lithium intercalation

Overview


Lithium Foil
Solid Electrolyte
Intercalation Cathode
Ω_1
Ω_2
Discharge

Overview



- Ion diffusion
- Electric potential
- Variables:
  $C_{Li^+}(X,t), \Phi(X,t)$

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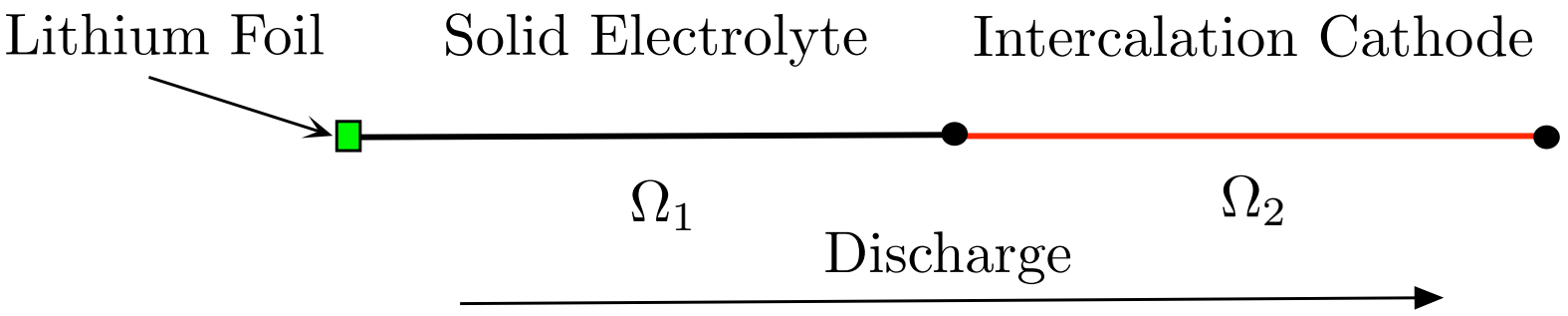

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- Variable: $C_{Li}(X,t)$

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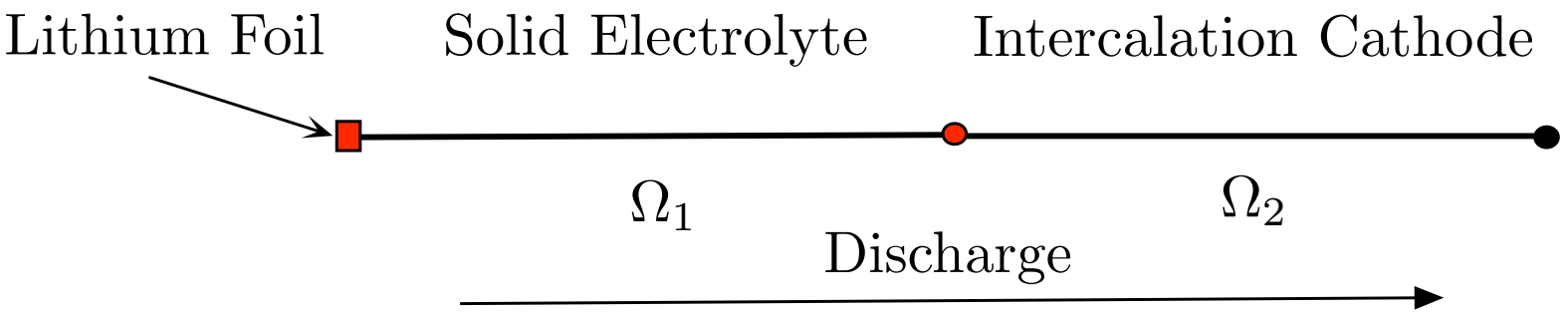

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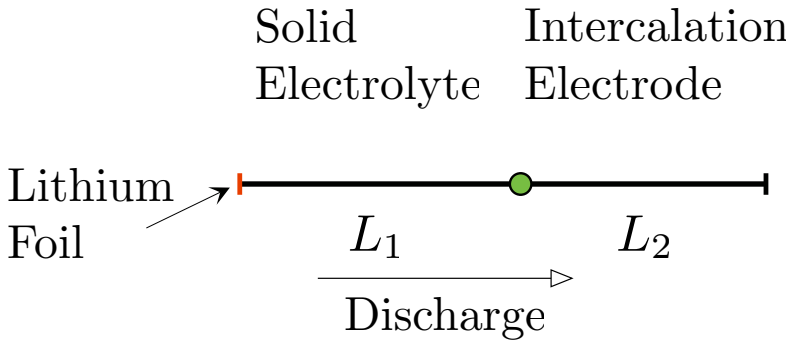
- Chemical reaction (deintercalation)
- Stern Layer potential drop

- Chemical reaction (intercalation)
- Stern Layer potential drop

Transport equations

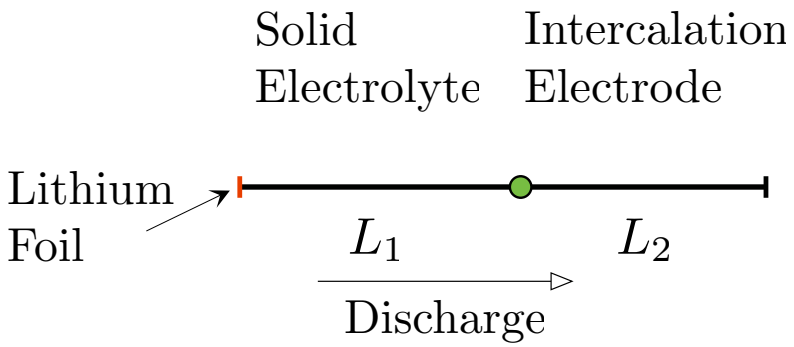


Continuity equation:

$$\frac{\partial C_i}{\partial t} = -\frac{\partial J_i}{\partial X}, \qquad i = Li^+, Li$$

- C_i - concentration of species i
- J_i - flux of species i in ....

Transport equations



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Solid electrolyte

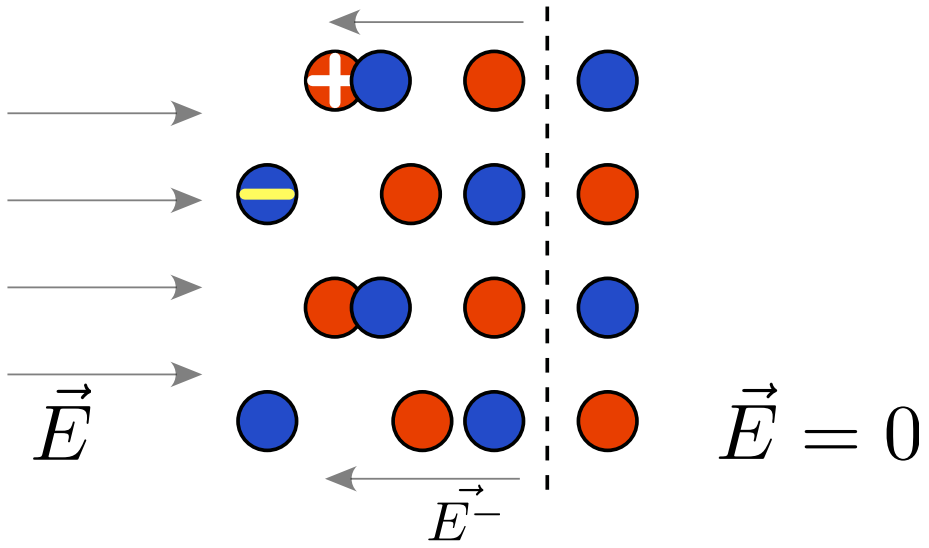
Nernst Planck flux: $$J_{Li^+} = -D_{Li^+}\frac{\partial C_{Li^+}}{\partial X} - B_{Li^+}C_{Li^+}\frac{\partial \Phi}{\partial X}$$

Poisson equation: $$-\frac{\partial}{\partial X}\left(\varepsilon_{E\ell}\frac{\partial \Phi}{\partial X}\right) = \rho_{E\ell}$$

Intercalation electrode

Fickian flux: $$J_{Li} = -D_{Li}\frac{\partial C_{Li}}{\partial X}$$

Electrostatic Field



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Poisson equation:
$$-\frac{\partial}{\partial X}\left(\varepsilon_{E\ell}\frac{\partial \Phi}{\partial X}\right) = \rho_{E\ell}$$
$$= F\left(C_{Li^+} - \underbrace{C_{Anions}}_{=fixed}\right)$$

Non-dimensional transport equations

Non-dimensional variables without subindices.

Solid electrolyte

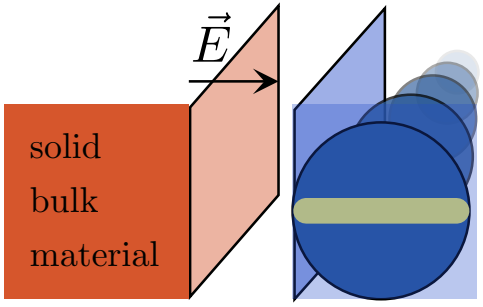
Nernst Planck equation: $\frac{\partial}{\partial \tau} c = \nabla \cdot (\boldsymbol{A}_1 \nabla c + \boldsymbol{A}_1 c \nabla \Phi)$ in $\mathcal{Q}_1 := \Omega_1 \times (0, \mathcal{T})$

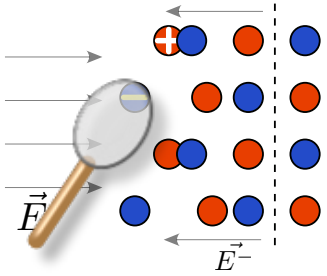
Poisson equation: $-\Delta \Phi = \frac{1}{2\varepsilon_{eff}^2}(c - c_{Anion})$ in $\mathcal{Q}_1 := \Omega_1 \times (0, \mathcal{T})$

Intercalation electrode

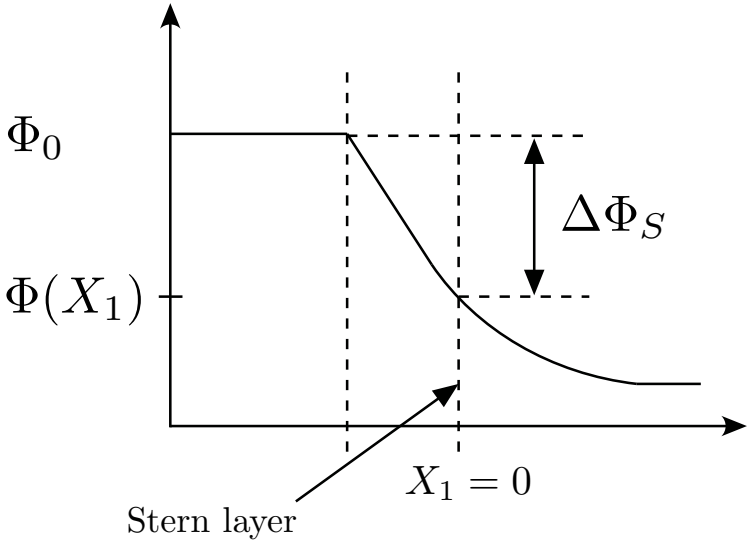
Diffusion equation: $\frac{\partial}{\partial \tau} \rho = \nabla \cdot (\boldsymbol{A}_2 \nabla \rho)$ in $\mathcal{Q}_2 := \Omega_2 \times (0, \mathcal{T})$

Derivation of Robin Boundary conditions for Φ





$$\Phi(X_1) = \Phi_0 - \Delta\Phi_S$$



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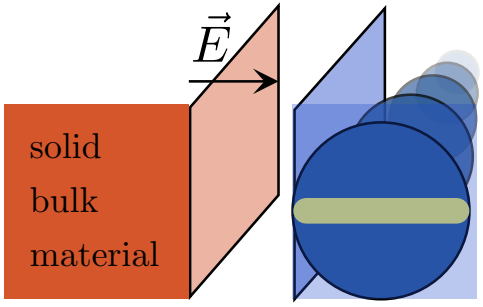

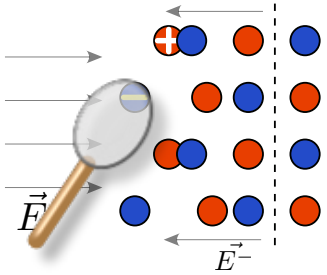

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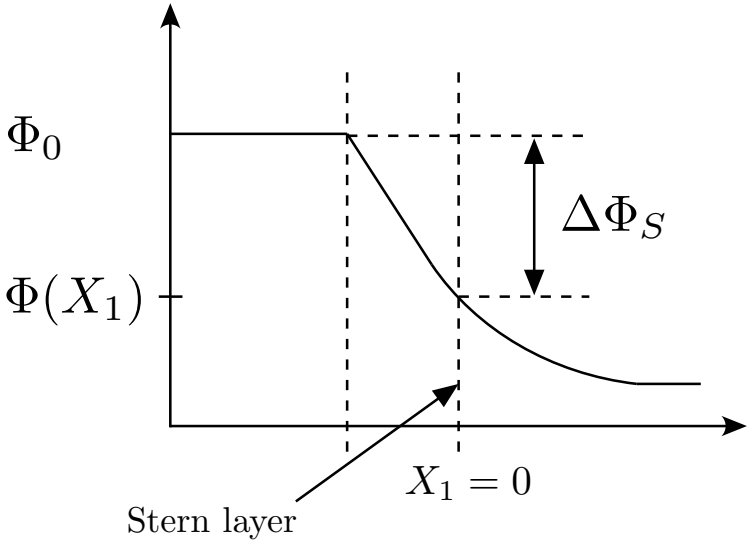
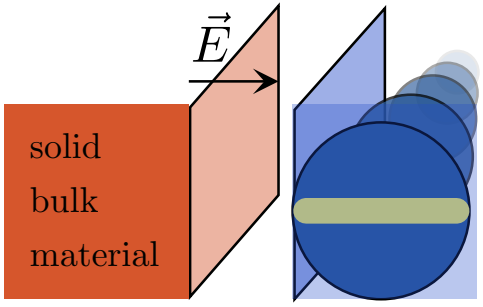


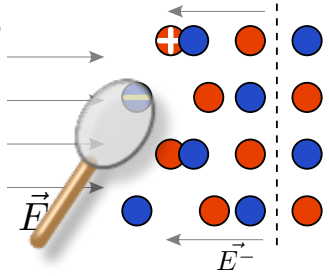
Treat the Stern Layer as (plate) capacitor

$$\hat{C}_S = \frac{Q}{\Delta\Phi_S} = \frac{1}{\Delta\Phi_S} A\varepsilon_0\varepsilon_r E$$

$$\Rightarrow \Delta\Phi_S = -\frac{1}{C_S}\varepsilon_0\varepsilon_r \frac{\partial\Phi}{\partial X_1}\Big|_{X_1=X_R}$$

Derivation of Robin Boundary conditions for Φ





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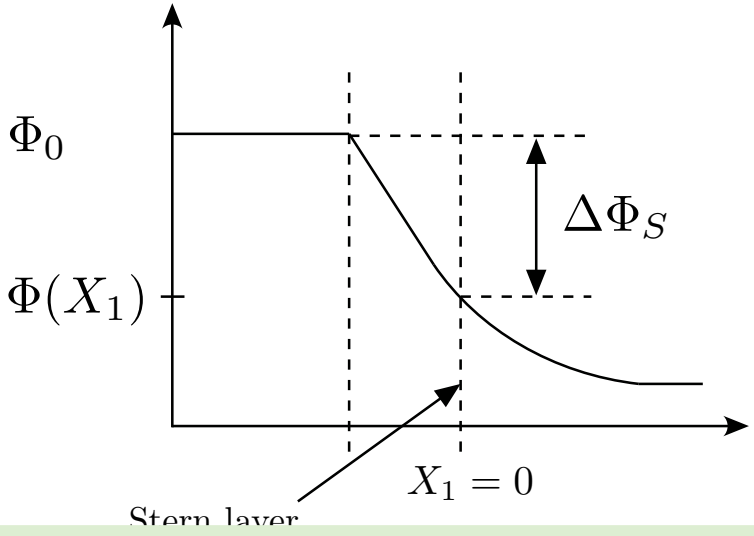

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Robin Boundary condition for Φ: (Bazant, Chu, Bayly, 2005)

$$\frac{\partial\Phi}{\partial n} + \frac{C_S}{\varepsilon_0\varepsilon_r}\Phi\Big|_{X_1=X_R} = \frac{C_S}{\varepsilon_0\varepsilon_r}\Phi_0$$

Mathematical description of chemical reactions

Basics:

Assume a fist order redox reaction $A \rightleftharpoons B$

$$\frac{\partial C_A}{\partial t} = \underbrace{-k_f\, C_A}_{A \to B} + \underbrace{k_b\, C_B}_{B \to A}$$

- C_A, C_B - concentrations of A, B,
- k_f, k_b - reaction rate coefficients.

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Transition state theory:

$$k_i = \frac{k_B\, T}{h} \exp\left(\frac{-G_i^{\ddagger 0}}{RT}\right)$$

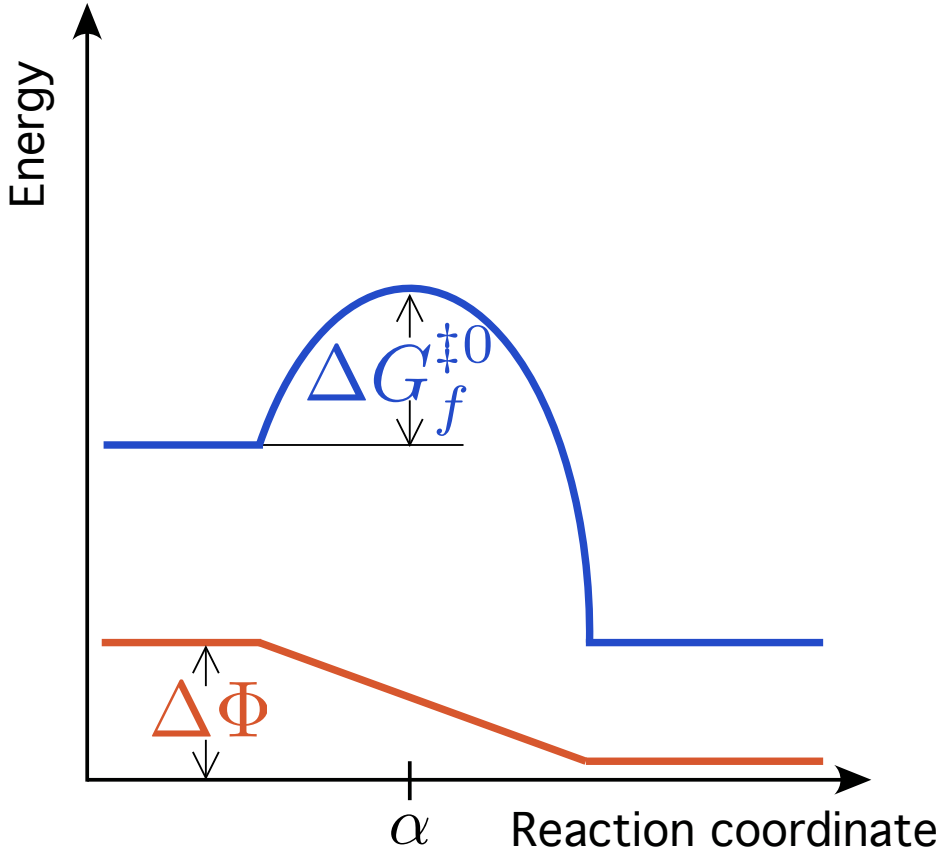
with

- $G_i^{\ddagger 0}$ - Gibbs free energy of activation,
- T - Temperature,
- k_B - Bolzmann constant,
- h - Planck constant.

Mathematical description of chemical reactions

Electrochemistry:

Chemical reactions are accelerated due to electric potential differences between reacting phases.



$$k_f = \frac{k_B\,T}{h}\exp\left(\frac{-G_f^{\ddagger 0}}{RT}\right)$$

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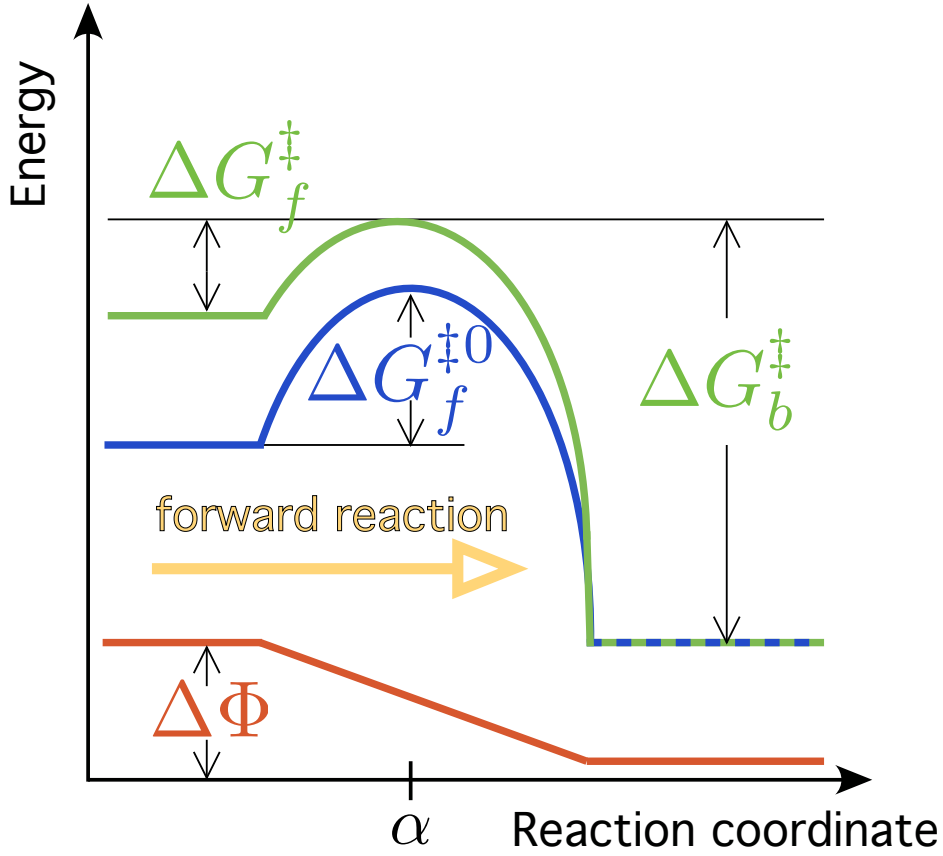

$$k_f = \frac{k_B\,T}{h}\exp\left(\frac{-(G_f^{\ddagger 0} - \alpha\Delta\Phi)}{RT}\right)$$

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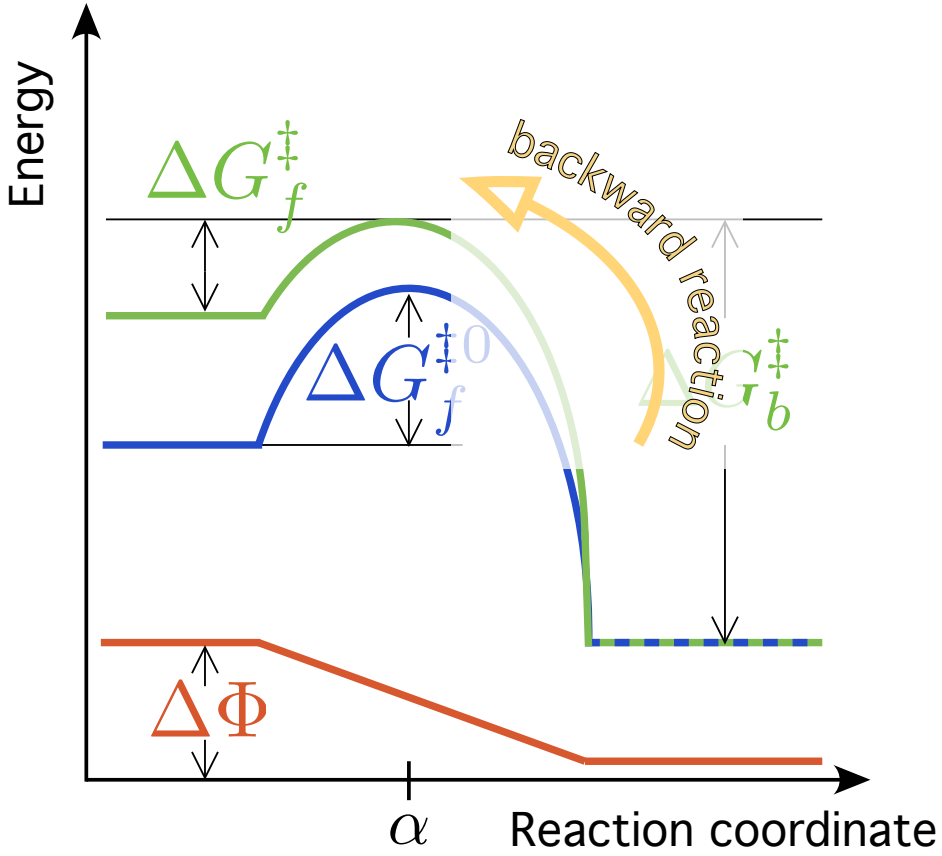

$$k_f = \hat{k}_f \exp\left(\frac{+\alpha\Delta\Phi}{RT}\right)$$

$$k_b = \frac{k_B\,T}{h} \exp\left(\frac{-(G_b^{\ddagger 0} + (1-\alpha)\Delta\Phi)}{RT}\right)$$

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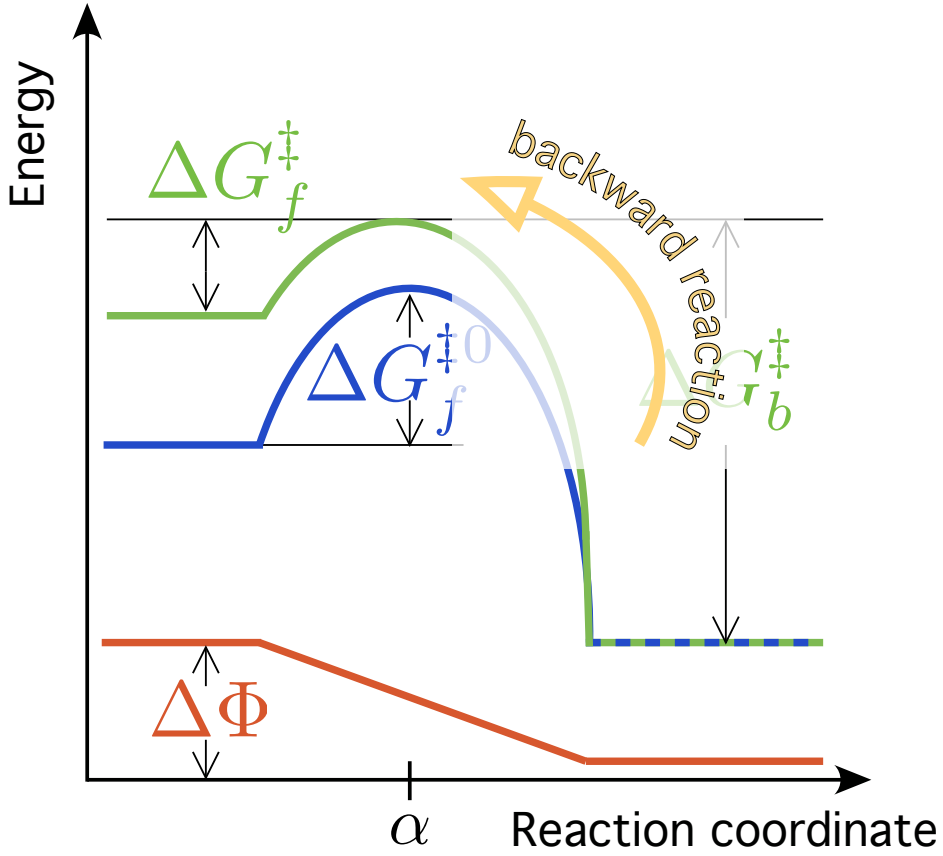

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Mathematical description of chemical reactions

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Frumkin-Butler-Volmer equation

$$\frac{\partial C_A}{\partial t} = -\hat{k}_f \cdot C_A \cdot \exp\left(\alpha \Delta\Phi\right) + \hat{k}_b \cdot C_B \cdot \exp\left(-(1-\alpha)\Delta\Phi\right)$$

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- $C_i(X,t)$ - concentration of species $i = A, B$

- With $\eta = \Delta\Phi - \Delta\Phi^{eq}$ the reaction rate is given by the classical Butler-Volmer equation (Doyle, Fuller, Newman, 1993)

Relate (surface) concentration to concentration flux

Definition: Surface concentration (in a continuum mechanical sense)

$$\tilde{C} := C(X)\big|_{X\in\Sigma_A} d_V \qquad \left[\frac{mol}{m^2}\right]$$

Surface reaction:

$$\frac{\partial \tilde{C}_A}{\partial t} = -k_f \tilde{C}_A + k_b \tilde{C}_B$$

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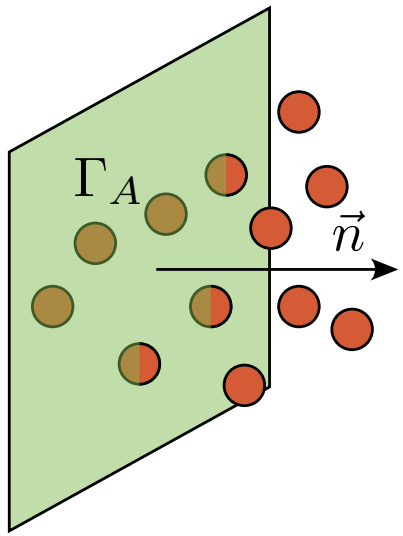

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Interpretation: Surface reaction as outward flux of C_A on $\Sigma_A := \Gamma_A \times (0, \mathcal{T})$.

$$nJ_A =$$

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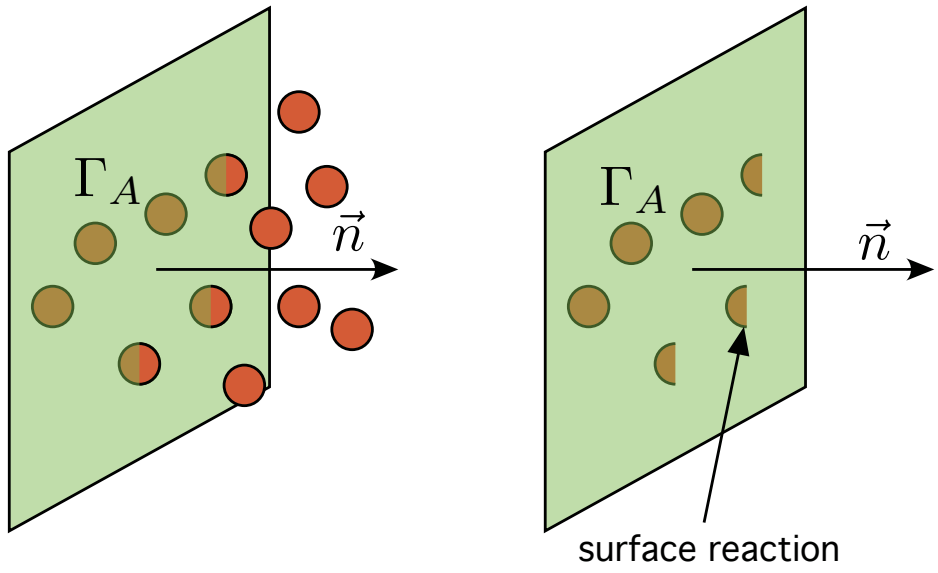

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$$nJ_A = -\frac{\partial \tilde{C}_A}{\partial t}$$

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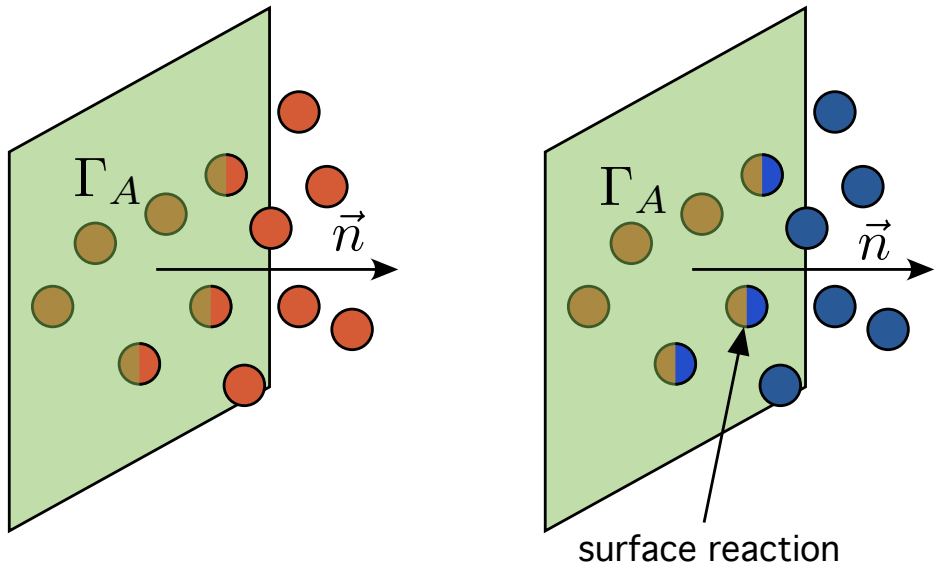

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Interpretation: Surface reaction as outward flux of C_A on $\Sigma_A := \Gamma_A \times (0, \mathcal{T})$.

$$nJ_A = -\frac{\partial \tilde{C}_A}{\partial t} = k_f\,\tilde{C}_A - k_b\,\tilde{C}_B = k_f\,d_V\,C_A\big|_{\Sigma_A} - k_b\,d_V\,C_B\big|_{\Sigma_A}$$

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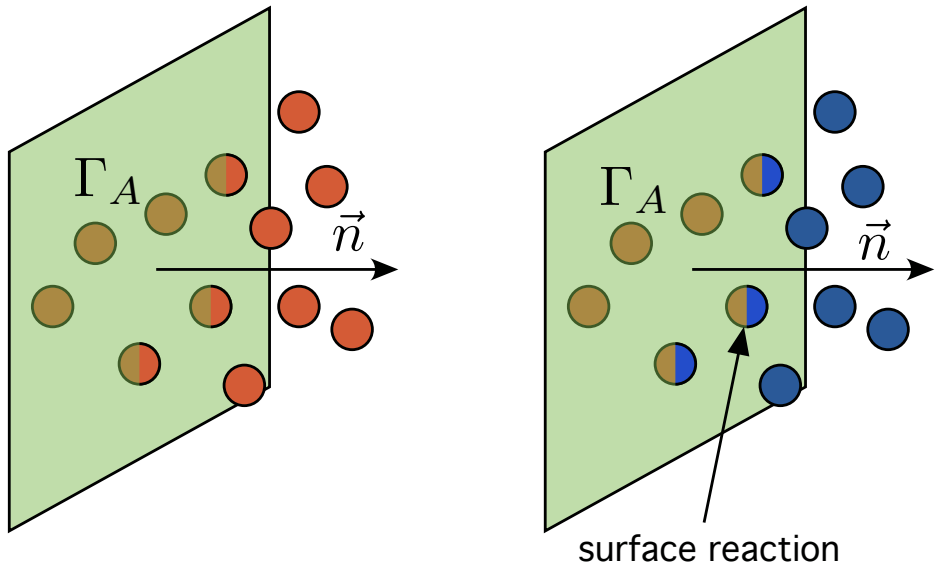

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Neumann Boundary Condition for C_A:

$$nJ_A = \hat{k}_f\, d_V \left[C_A \exp\left(\alpha(\Phi_0 - \Phi)\right)\right]\big|_{\Sigma_A} - \hat{k}_b\, d_V \left[C_B \exp\left(-(1-\alpha)(\Phi_0 - \Phi)\right)\right]\big|_{\Sigma_A}$$

Classification - In contrast to...

... Bazant or other Poisson-Nernst-Planck (PNP) systems for semiconductors

- Model for a complete time dependent battery discharge
- PNP system coupled with intercalation electrode
- Frumkin-Butler-Volmer equation as coupling boundary condition for intercalation

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... Newman

- Solid electrolyte with fixed anion structure
- Double layer potential drop:
  - ... diffuse: calculated with Poisson equation
  - ... Stern: calculated with Robin boundary conditions
- Frumkin-Butler-Volmer equation: reaction accelerated due to Stern layer potential drop
- Advantage/Disadvantage: based on non measurable paramerters

Known mathematical Results for the related models ...

...for nonstationary PNP systems:

- with homogeneous Neumann boundary conditions
  - Existence of a unique weak solution (Gajewsky, Gröger, 1986),
  - Asymptotic convergence to steady state (Biler, Hebisch, Nadzieja, 1994) with exponential rate (Arnold, Markowich, Toscani, 2000),
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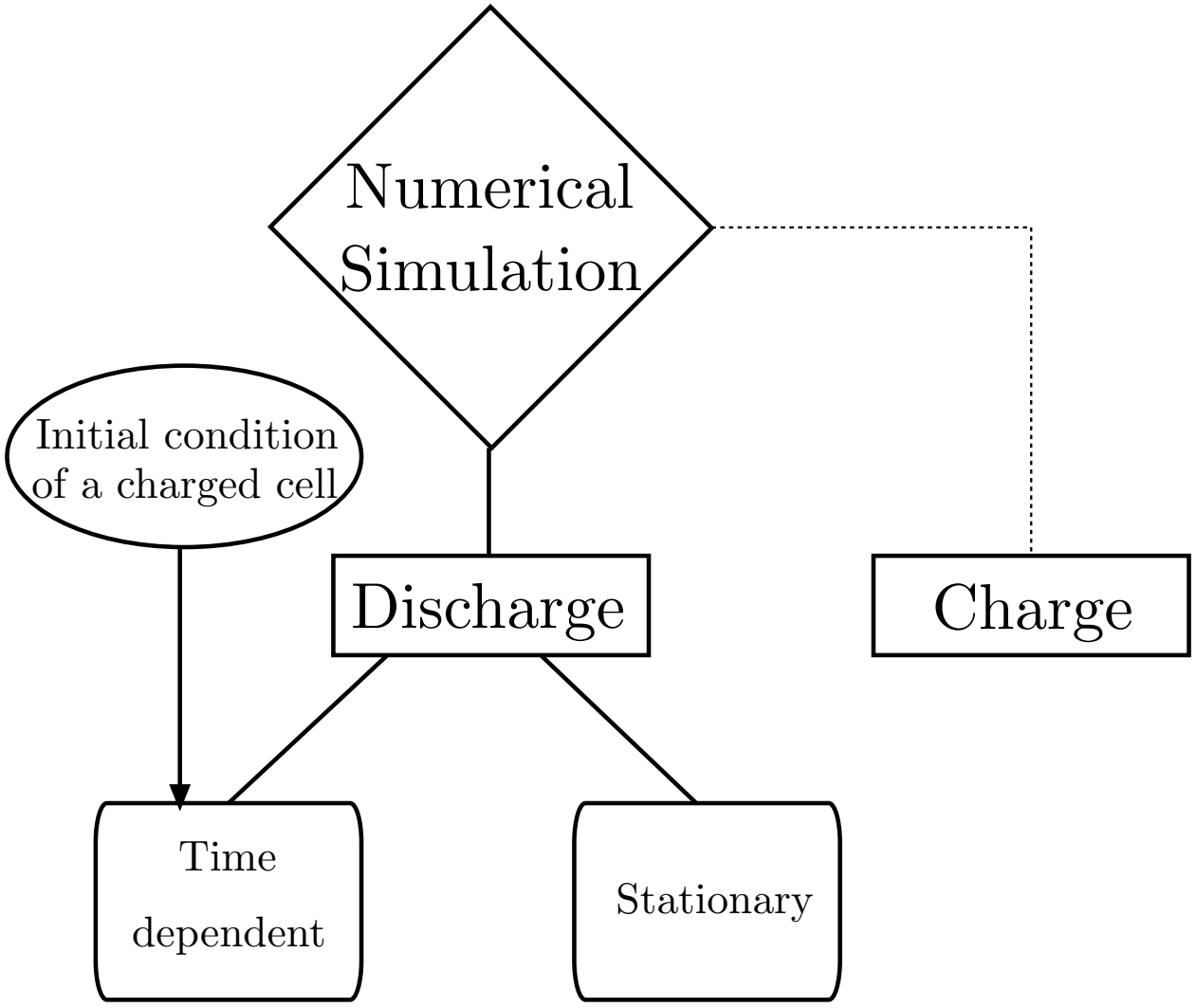
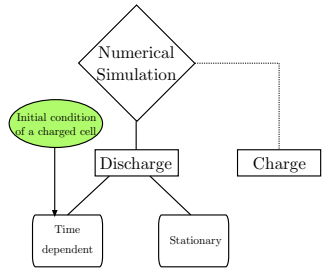
...for the macroscopic Newman system: (Wu, Xu, Zou, 2006)

- Local existence of a unique weak solution for the multidimensional case
- Global existence of a unique weak solution in the 1-D case

Numerical simulation - Overview



Initial Condition of a charged cell



Stationary system in the electrolyte ($\partial_\tau c = 0$):

$$0 = \frac{\partial^2}{\partial x_1} c(\cdot,\tau) + \frac{\partial}{\partial x_1}\left(c(\cdot,\tau)\frac{\partial}{\partial x_1}\varphi(\cdot,\tau)\right),$$

$$0 = \varepsilon^2 \frac{\partial^2}{\partial x_1}\varphi(\cdot,\tau) + \frac{1}{2}(c(\cdot,\tau) - c_A).$$

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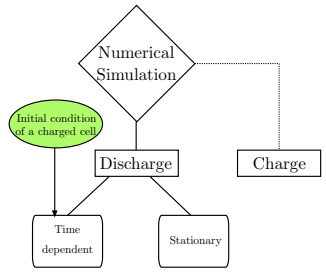

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Boundary conditions on $x_1 \in \{0,1\}$:

$$\frac{\partial}{\partial x_1} c(x_1,\tau) + c(x_1,\tau)\frac{\partial}{\partial x_1}\varphi(x_1,\tau) = 0,$$

$$\frac{\partial}{\partial x_1}\varphi(x_1,\tau) + \frac{1}{\gamma\varepsilon}\varphi(x_1,\tau) = \varphi_0,$$

with

- $\lambda_S := \varepsilon_0\varepsilon_r / C_S$,
- $\gamma := \lambda_S/\lambda_D$,
- $\lambda_D := \sqrt{\frac{\varepsilon_b RT}{2F^2 C^{bulk}_{Li^+}}}$.

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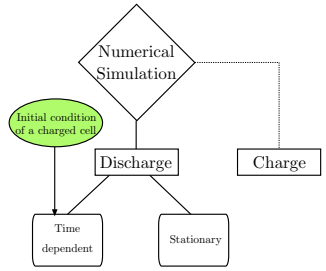

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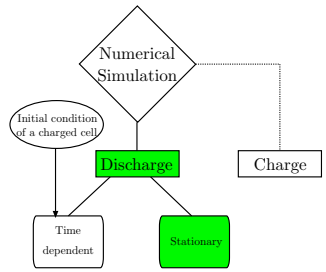
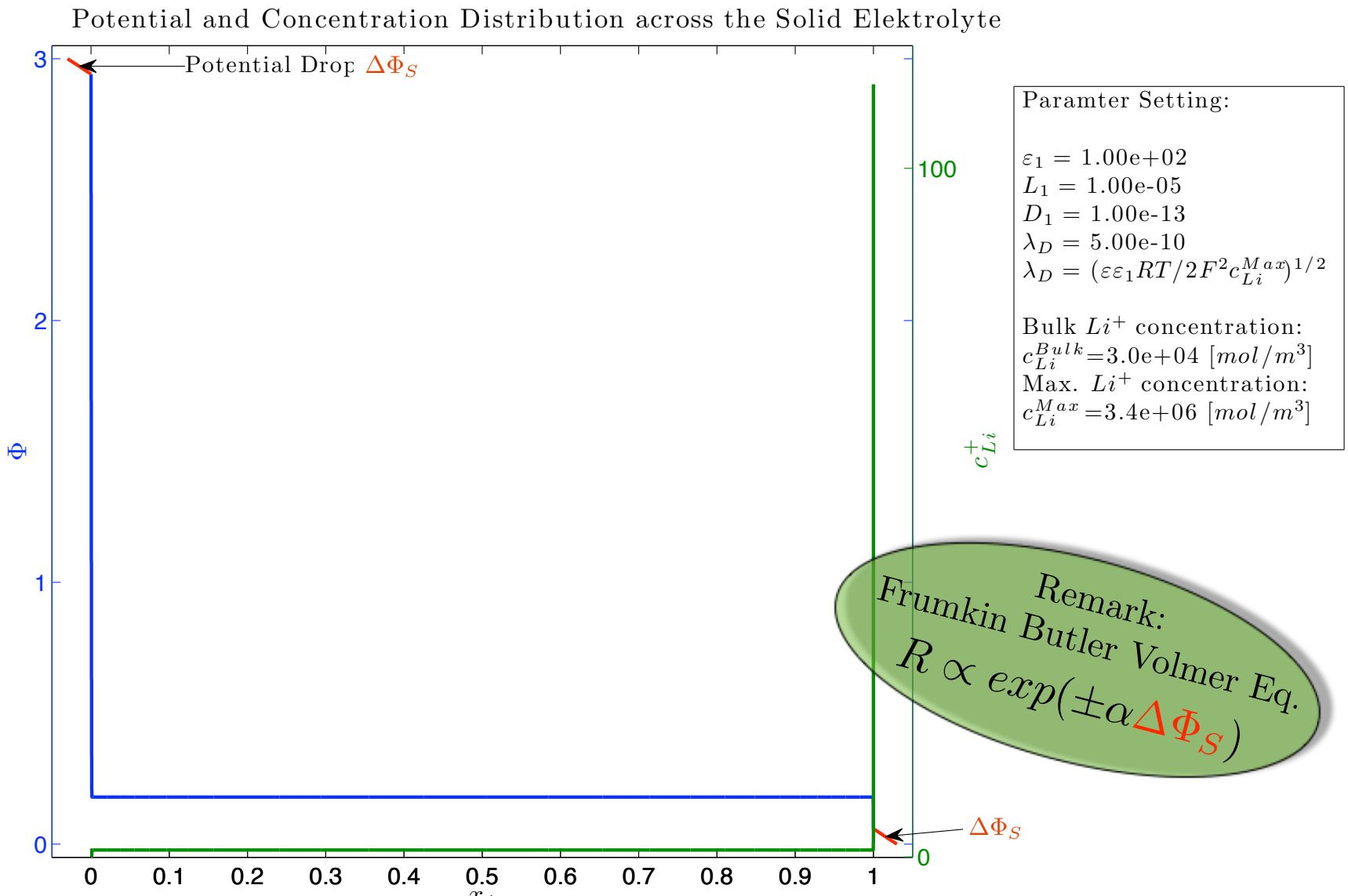
Additional weak constraint

$$\int_0^1 c(x_1)\, dx_1 = c_A.$$

Stationary solution with reaction - Variation of λ_D





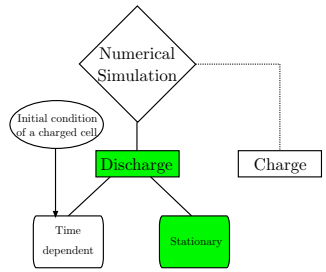
Paramter Setting:

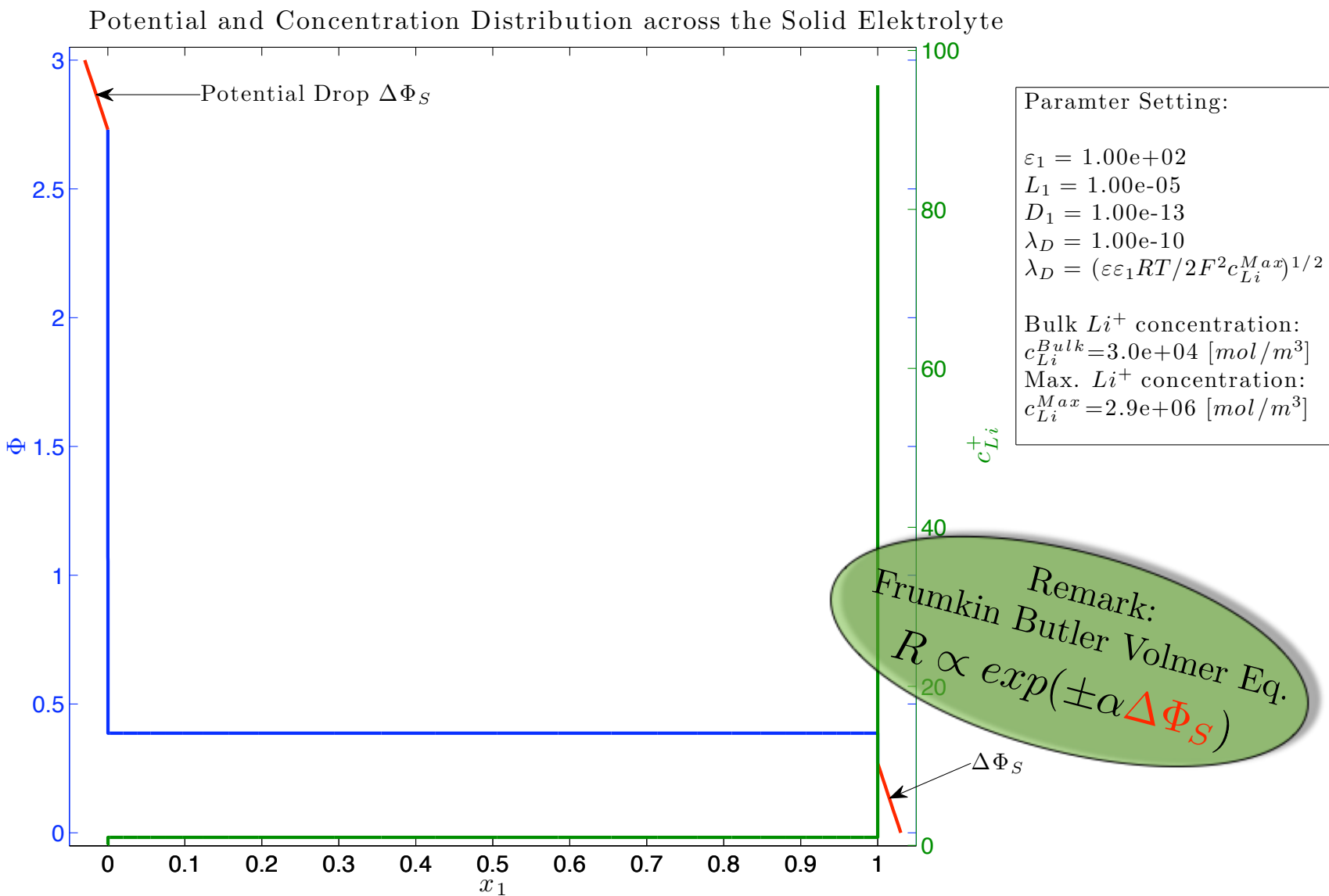
$\varepsilon_1 = 1.00\text{e+}02$
$L_1 = 1.00\text{e-}05$
$D_1 = 1.00\text{e-}13$
$\lambda_D = 5.00\text{e-}10$
$\lambda_D = (\varepsilon\varepsilon_1 RT/2F^2 c_{Li}^{Max})^{1/2}$

Bulk Li^+ concentration:
c_{Li}^{Bulk}=3.0e+04 $[mol/m^3]$
Max. Li^+ concentration:
c_{Li}^{Max}=3.4e+06 $[mol/m^3]$

Remark:
Frumkin Butler Volmer Eq.
$R \propto exp(\pm\alpha\Delta\Phi_S)$

Stationary solution with reaction - Variation of λ_D





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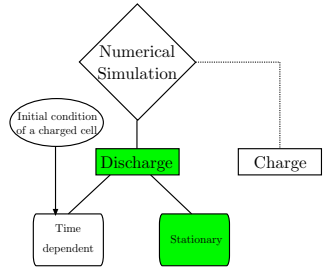

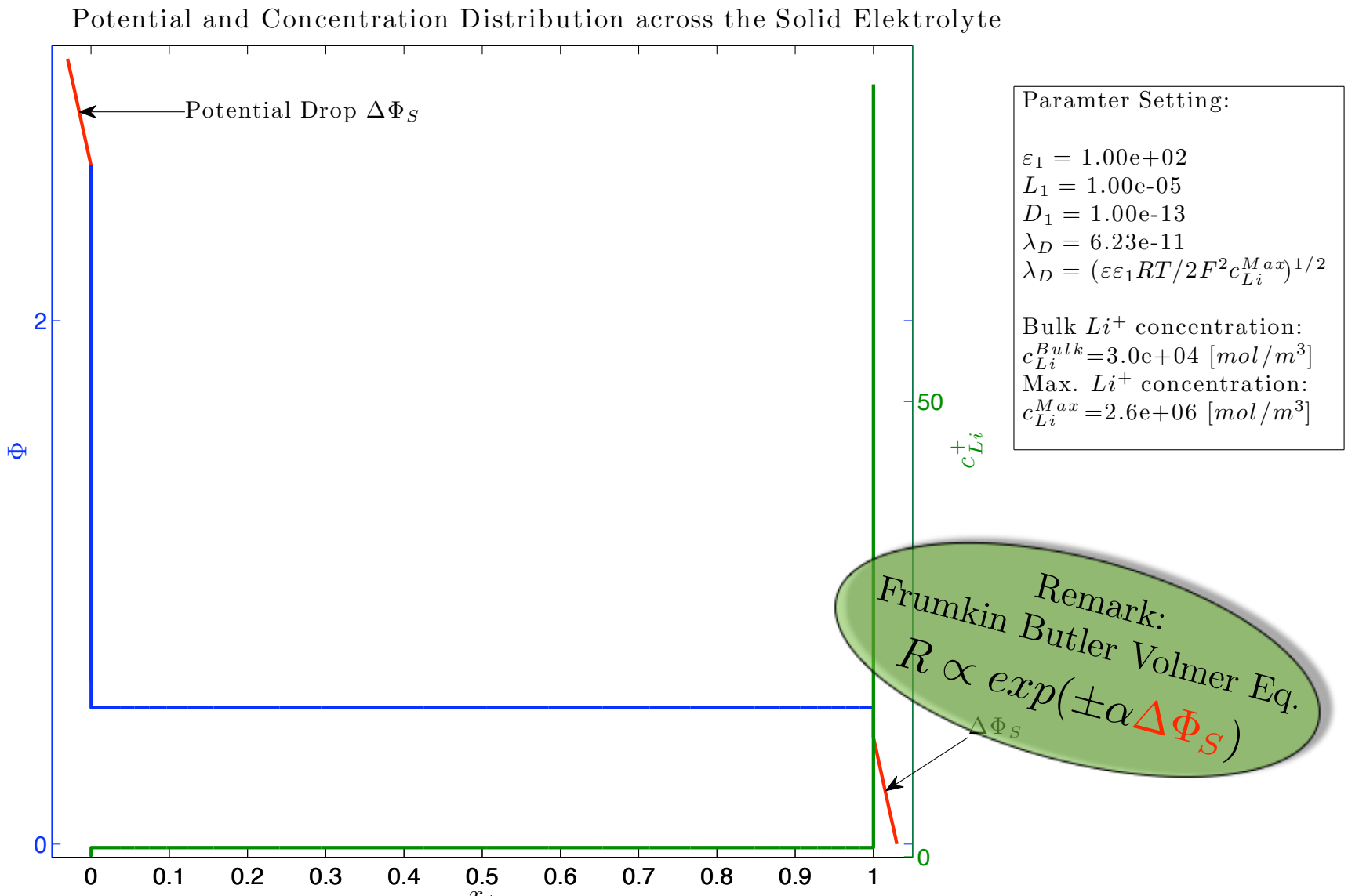

Model equations for discharge

d-dimensional equation system

$$\begin{aligned}
\frac{\partial}{\partial \tau} c &= \nabla \cdot \boldsymbol{A}_1(\nabla c + c \nabla \varphi) && \text{in } \mathcal{Q}_1, \\
0 &= \Delta \varphi + f(c) && \text{in } \mathcal{Q}_1, \\
\frac{\partial}{\partial \tau} \rho &= \nabla \cdot \boldsymbol{A}_2 \nabla \rho && \text{in } \mathcal{Q}_2,
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Boundary conditions

$$\begin{aligned}
n \cdot \boldsymbol{A}_1(\nabla c + c \nabla \varphi) &= R(c, \rho, \varphi) && \text{on } \Sigma_1, \\
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Initial values

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c(x, 0) &= c_0(x) && \text{in } \Omega_1, \\
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- $g := \begin{cases} \varphi_0, & \text{on } \Sigma_{1_1}, \\ 0, & \text{on } \Sigma_{1_2}, \end{cases}$
- $\alpha := 1/(\gamma\varepsilon)$. Additional isolation boundary conditions on all other boundaries

Differences to 1-D case

Model equations for discharge

d-dimensional equation system

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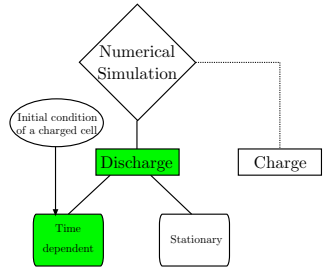
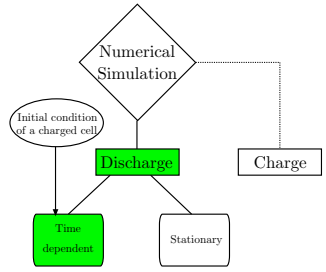
Nonlinearities

Time dependent discharge - $D_1 = 10^{-12}$



Time dependent discharge - $D_1 = 10^{-15}$



With suitable test functions $\tilde{c}, \tilde{\varphi}, \tilde{\rho}$ denote

$$\langle A_1(w,\varphi), \tilde{c}\rangle := \int_{\Omega_1} \boldsymbol{A}_1(\nabla w + w\nabla\varphi)\cdot\nabla\tilde{c}\,dx$$

$$\langle G_1(w,\varphi,u), \tilde{c}\rangle := \int_{\Gamma_1} R(w,\varphi,u)\tilde{c}\,dx$$

System of equations

$$c'(\tau) + A_1(c(\tau),\varphi(\tau)) = G_1(c(\tau),\varphi(\tau),\rho(\tau)),$$

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$$\langle A_2(u,\varphi), \tilde{\rho}\rangle := \int_{\Omega_2} \boldsymbol{A}_2\nabla u\cdot\nabla\tilde{\rho}\,dx$$

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$$\begin{aligned} c'(\tau) + A_1(c(\tau),\varphi(\tau)) &= G_1(c(\tau),\varphi(\tau),\rho(\tau)),\\ B\varphi(\tau) &= f(c(\tau)),\\ \rho'(\tau) + A_2(\rho(\tau)) &= G_2(c(\tau),\varphi(\tau),\rho(\tau)), \end{aligned}$$

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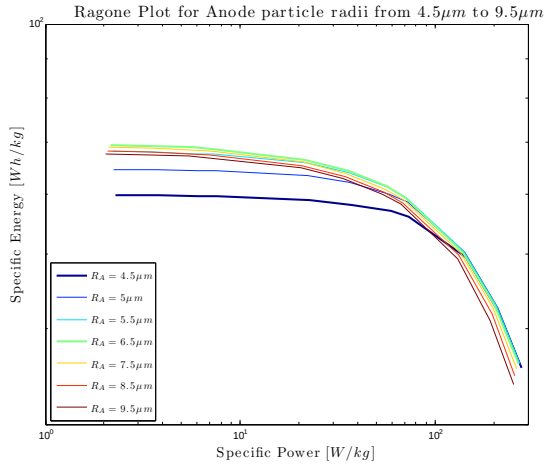
Specific energy

$$E = \frac{1}{M_A} \int_0^{\mathcal{T}} i\,V\,dt$$

Average specific power

$$P = \frac{1}{M_A \mathcal{T}} \int_0^{\mathcal{T}} i\,V\,dt$$



- $\mathcal{T}$ - discharge time,
- M_A - mass per unit area,
- V - cell potential,

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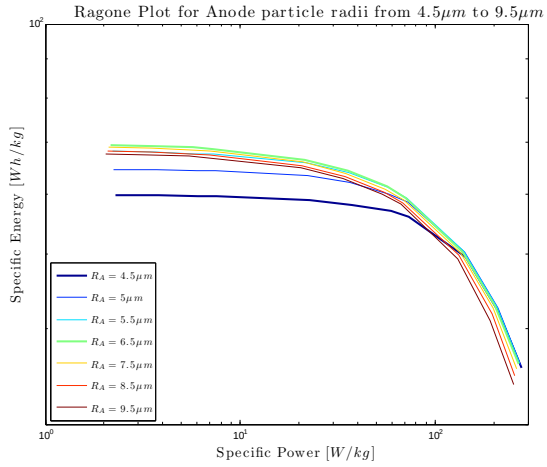
Average specific power

$$P = \frac{1}{M_A \mathcal{T}} \int_0^{\mathcal{T}} i\, V \, dt$$



- $\mathcal{T}$ - discharge time,
- M_A - mass per unit area,
- V - cell potential,

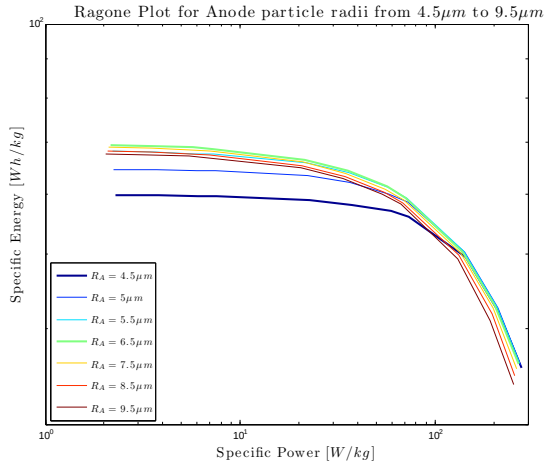
Total (discharge) current density: $i = i(t; V)$ (for galvanostatic discharge to a given applied voltage):

Specific energy

$$E(i;\,V) = \frac{1}{M_A}\int_0^{\mathcal{T}} i\,V\,dt$$

Average specific power

$$P(i;\,V) = \frac{1}{M_A\mathcal{T}}\int_0^{\mathcal{T}} i\,V\,dt$$



- $\mathcal{T}$ - discharge time,
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Total (discharge) current density: $i = i(t;\,V)$ (for galvanostatic discharge to a given applied voltage): sum of conduction and displacement current densities

$$i(t) = i_c(X,t) - \varepsilon_b \partial_t \partial_X \Phi(X,t)$$

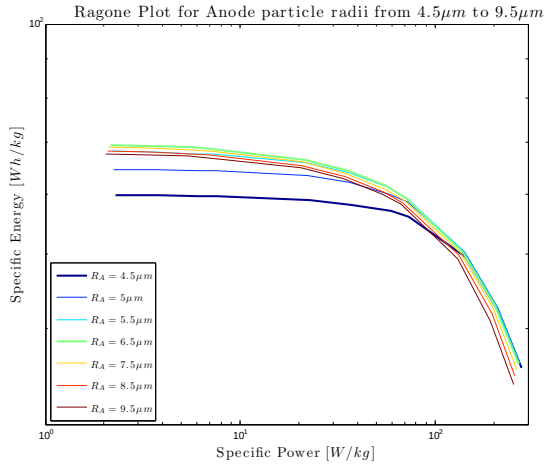
- $i_c = -F\left[D_{Li^+}\partial_X c(X,t) + B_{Li^+}\partial_X \Phi(X,t)\right]$,
- A electrode area,
- F Faraday constant.

Specific energy

$$E = \frac{1}{M_A} \int_0^{\mathcal{T}} i\, V\, dt$$

Average specific power

$$P = \frac{1}{M_A \mathcal{T}} \int_0^{\mathcal{T}} i\, V\, dt$$



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Denote $c(\tau) := c(\tau;\mu), \varphi(\tau) := \varphi(\tau;\mu), \rho(\tau) := \rho(\tau;\mu)$

$$\max \quad E(c,\varphi,\rho;\mu), \quad \max \quad P(c,\varphi,\rho;\mu) \quad \text{subject to}$$

$$\begin{aligned}
c'(\tau) + A_1(c(\tau),\varphi(\tau)) &= G_1(c(\tau),\varphi(\tau),\rho(\tau)), && \text{on } \mathcal{Q}_1,\\
B\varphi(\tau) &= f(c(\tau)), && \text{on } \mathcal{Q}_1,\\
\rho'(\tau) + A_2(\rho(\tau)) &= G_2(c(\tau),\varphi(\tau),\rho(\tau)), && \text{on } \mathcal{Q}_2,\\
c(x,0) &= c_0(x), && \text{on } \Omega_1,\\
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\end{aligned}$$

Denote $c(\tau) := c(\tau;\mu), \varphi(\tau) := \varphi(\tau;\mu), \rho(\tau) := \rho(\tau;\mu)$

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\end{aligned}$$

Question: Reasonable μ?

- Material parameters
  - Diffusion coefficients - D_{Li^+}, D_{Li}

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Question: Reasonable μ?

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  - Diffusion coefficients - D_{Li+}, D_{Li}
  - Permittivity of the electrolyte - ε

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Question: Reasonable μ?

- Material parameters
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  - Stiffness of the intercalation electrode

Denote $c(\tau) := c(\tau;\mu), \varphi(\tau) := \varphi(\tau;\mu), \rho(\tau) := \rho(\tau;\mu)$

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  - Permittivity of the electrolyte - ε
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- Geometric parameters
  - Component sizes: for 1-D length of electrolyte and electrode - L_1, L_2

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  - Component sizes: for 1-D length of electrolyte and electrode - L_1, L_2
  - Contact surface

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Question: Reasonable μ?

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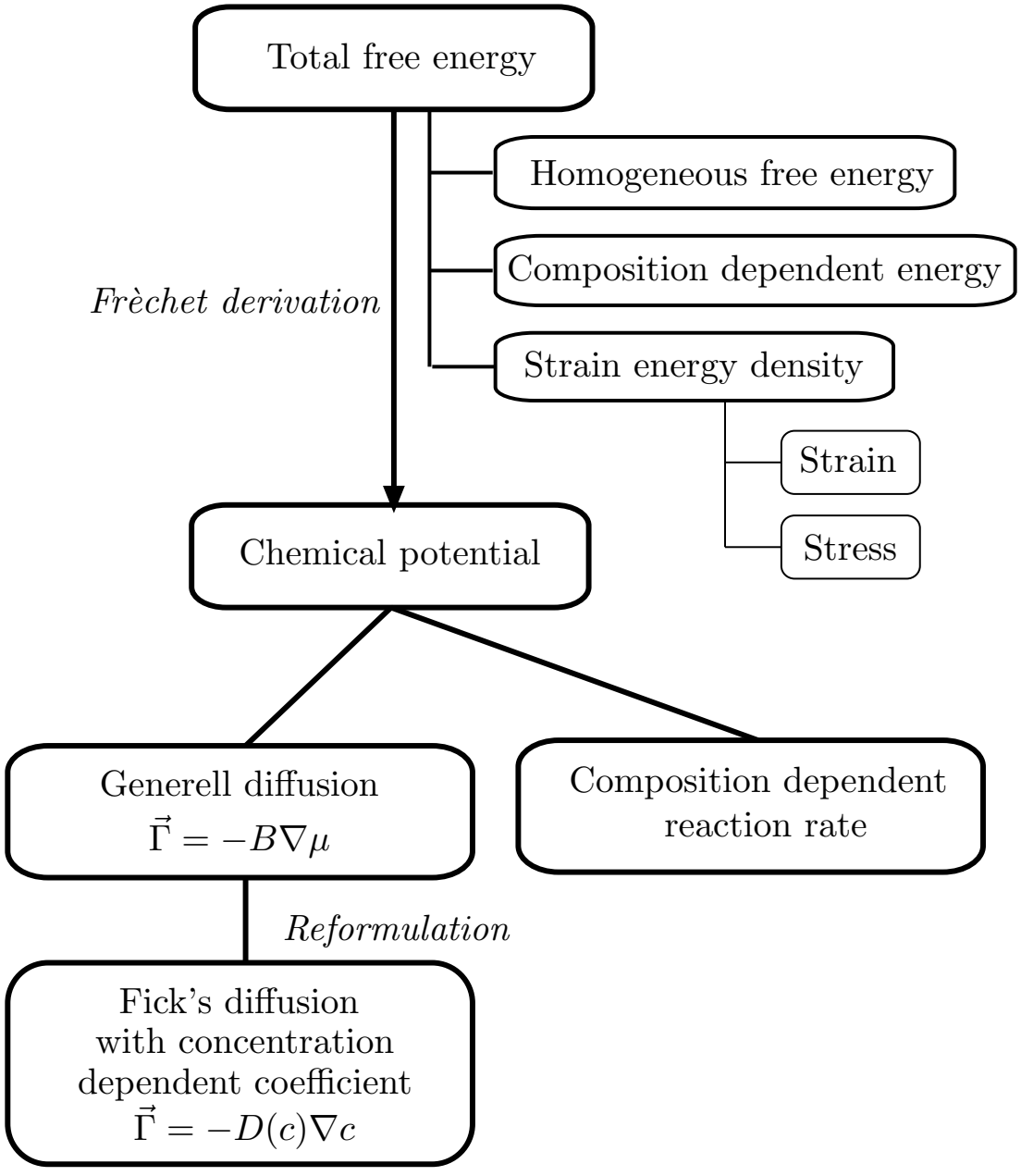
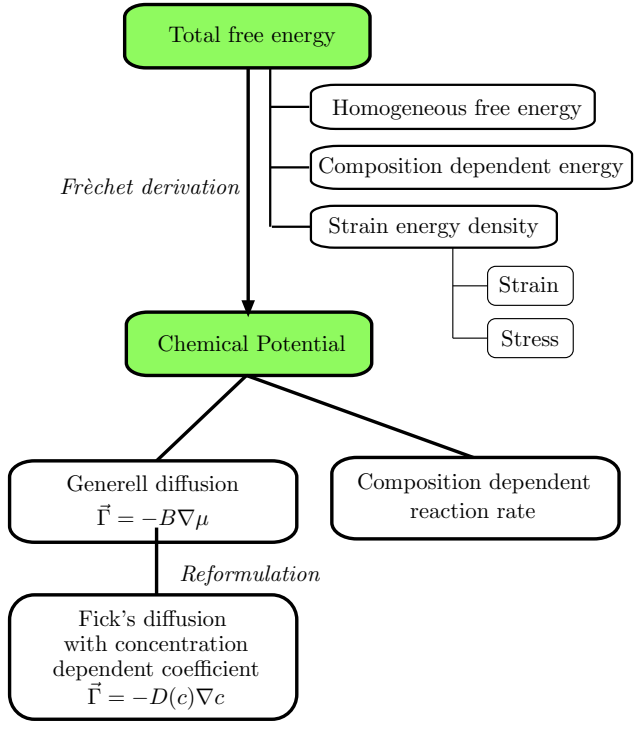
- Geometric parameters
  - Component sizes: for 1-D length of electrolyte and electrode - L_1, L_2
  - Contact surface
  - Composition of the electrode (not incorperated jet)

Part II: Incorperating mechanical effects

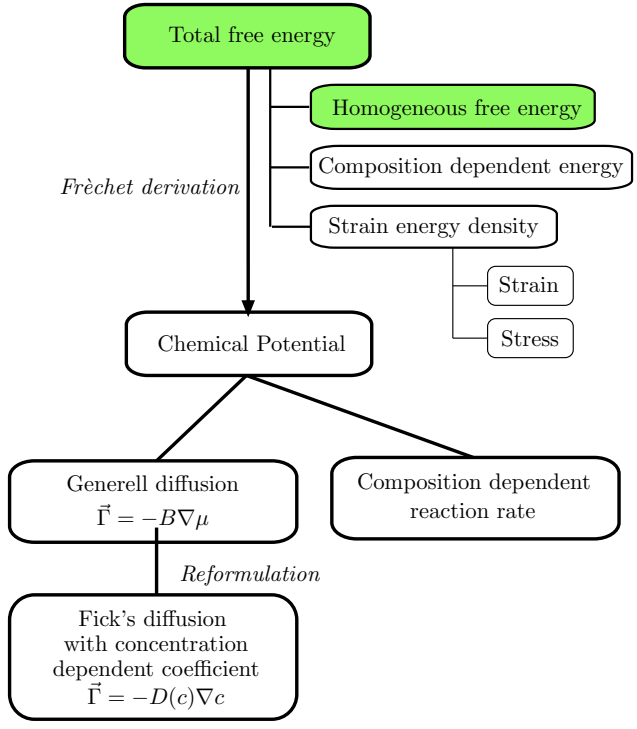

Total free energy
Homogeneous free energy
Composition dependent energy
Strain energy density
Strain
Stress
Frèchet derivation
Chemical potential
Generell diffusion
$\vec{\Gamma} = -B\nabla\mu$
Composition dependent reaction rate
Reformulation
Fick's diffusion with concentration dependent coefficient
$\vec{\Gamma} = -D(c)\nabla c$

Total free energy $$G[C_{Li}, \boldsymbol{e}] = \int_\Omega \Big[\underbrace{f^0(C_{Li}) + \frac{1}{2}\nabla C_{Li} \cdot \boldsymbol{K}\nabla C_{Li} + \mathcal{W}(C_{Li}, \boldsymbol{e})}_{=:F(C_{Li}(X), \nabla C_{Li}(X)),\ \text{def. } g:=\nabla C_{Li}} \Big] \, dx$$



Total free energy $$G[C_{Li}, \boldsymbol{e}] = \int_\Omega \Big[\underbrace{f^0(C_{Li}) + \frac{1}{2}\nabla C_{Li} \cdot \boldsymbol{K} \nabla C_{Li} + \mathcal{W}(C_{Li}, \boldsymbol{e})}_{=:F(C_{Li}(X), \nabla C_{Li}(X)),\ \text{def. } g := \nabla C_{Li}} \Big] \, dx$$

- Free energy (per molecule) of a homogeneous system



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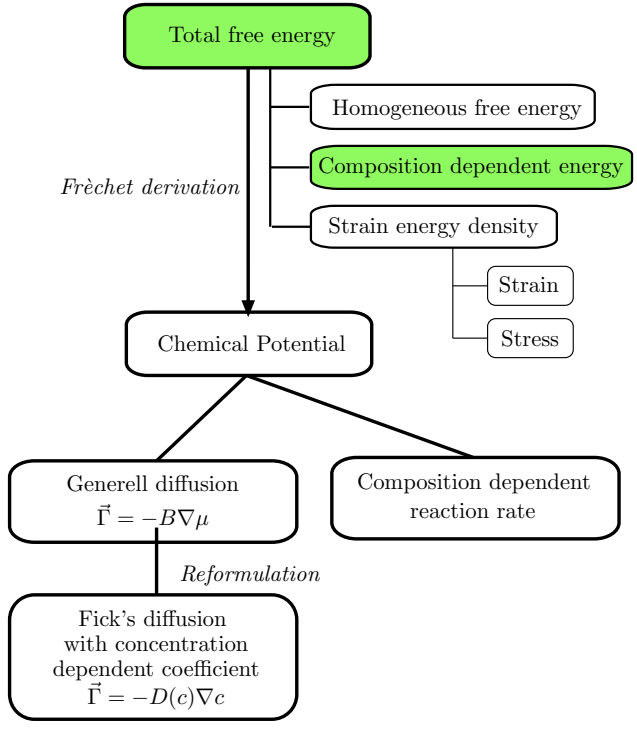
- Free energy (per molecule) of a homogeneous system
- Composition dependent energy



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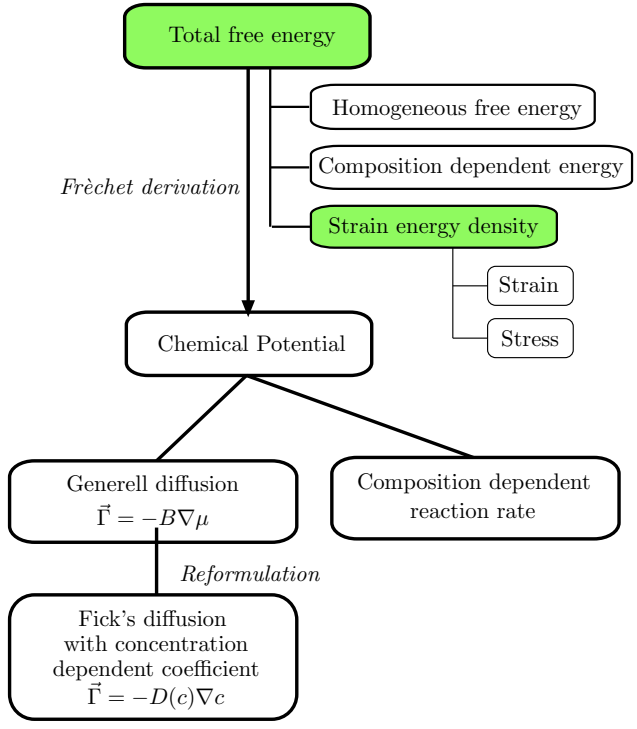
- Free energy (per molecule) of a homogeneous system
- Composition dependent energy
- Strain energy density (in a material point)



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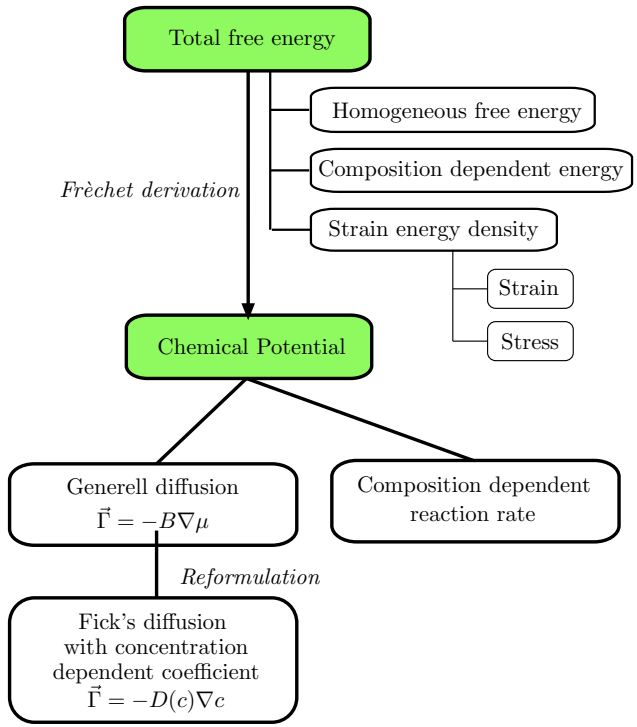

Chemical potential $$\mu_{Li} := \frac{\delta G[C_{Li}]}{\delta C_{Li}(X)}$$

Cahn-Hilliard equation

Instead of Fick's Diffusion ...

$$\partial_t C_{Li} = \nabla \cdot (\boldsymbol{D_{Li}} \nabla C_{Li})$$

Cahn-Hilliard equation

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$$\partial_t C_{Li} = \nabla \cdot (\boldsymbol{D_{Li}} \nabla C_{Li})$$

..diffusion in the chemical potential gradient

$$\begin{aligned} \partial_t C_{Li} &= \nabla \cdot (\boldsymbol{B_{Li}} \nabla \mu_{Li}) \\ &= \nabla \cdot \left(\boldsymbol{B_{Li}} \nabla \frac{\delta G[C_{Li}]}{\delta C_{Li}(X)} \right) \end{aligned}$$

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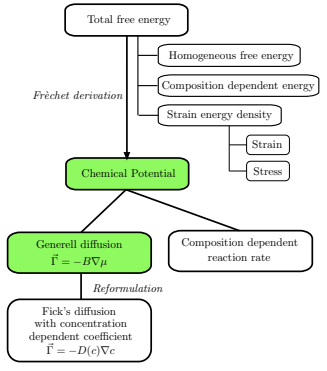


$$\implies \quad \partial_t C = \nabla \cdot \boldsymbol{B} \nabla \left(\frac{\partial f(C(X))}{\partial C} - \nabla \cdot \boldsymbol{K} \nabla C(X) + \frac{\partial \mathcal{W}(C(X), \boldsymbol{e}(X))}{\partial C} \right)$$

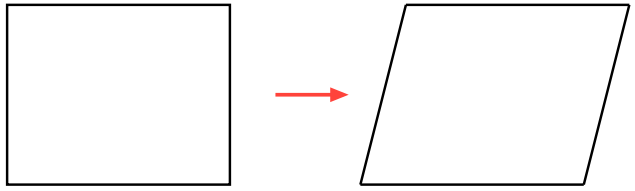
Problem: fourth oder PDE

Strain energy density

W.l.o.g. ...

- Linearised mechanical strain (relative to the referenz configuration)

$$\boldsymbol{e}(u(X)) = \frac{1}{2}\left(\nabla u(X) + \nabla u(X)^T\right)$$



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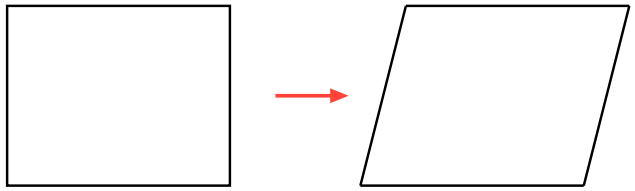
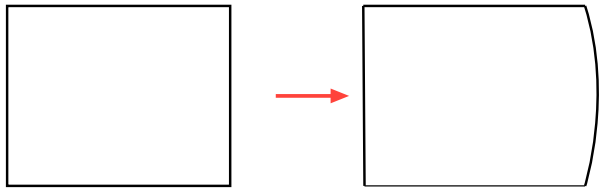


- Stress-free strain (dependent of local cristal structure and local composition)

$$\boldsymbol{e}^0(C_{Li}) = \boldsymbol{M}\, C_{Li}$$



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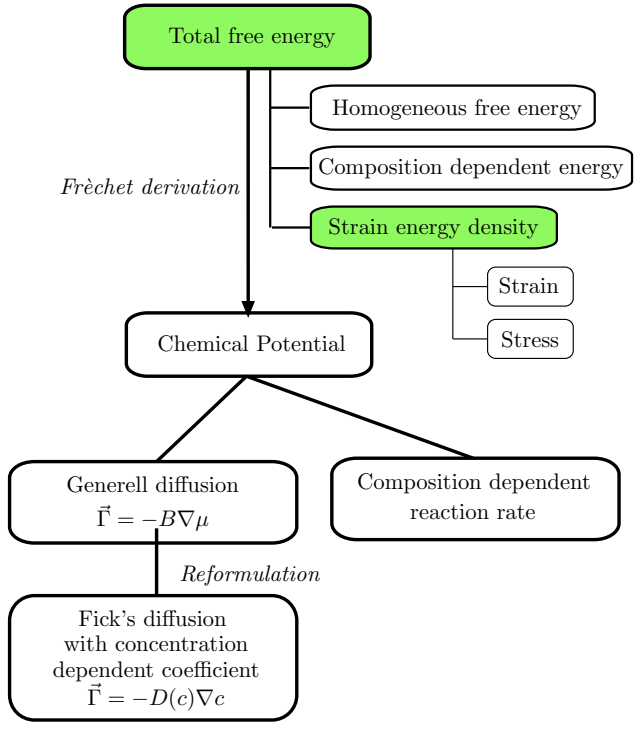

... with Hooks law of linear elasticity follows

$$\mathcal{W}(C_{Li}, \boldsymbol{e}) = \frac{1}{2}\underbrace{(\boldsymbol{e} - \boldsymbol{e}^0(C_{Li}))}_{=:\Delta\boldsymbol{e}(C_{Li})} : \underbrace{\boldsymbol{E}(C_{Li})\left(\boldsymbol{e} - \boldsymbol{e}^0(C_{Li})\right)}_{\boldsymbol{\sigma}(\Delta\boldsymbol{e}(C_{Li}))}$$

Equation System in the intercalation electrode

Generalized diffusion equation

$$\partial_t C_{Li} = \nabla \cdot \boldsymbol{B_{Li}} \nabla \mu_{Li}$$

$$\mu = \frac{\delta G[C_{Li}, u]}{\delta C_{Li}} = \frac{\partial f(C_{Li})}{\partial C_{Li}} - \nabla \cdot \boldsymbol{K} \nabla C_{Li} + \frac{\partial \mathcal{W}(C_{Li}, \nabla u)}{\partial C_{Li}}$$

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Quasi-static mechanic equilibrium (define $\boldsymbol{F} := \nabla u$)

$$-\nabla \cdot \boldsymbol{\sigma} = 0$$

$$\boldsymbol{\sigma} = \frac{\delta G[C_{Li}, u]}{\delta u} = -\frac{\partial \mathcal{W}(C_{Li}, \nabla u)}{\partial \boldsymbol{F}}$$

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^T$$

Hidden assumption: Mechanical equilibrium is attaint on a much faster time scale than diffusion takes place.

Equation System in the intercalation electrode

Ficks diffusion

$$\partial_t C_{Li} = \nabla \cdot \boldsymbol{D_{Li}} \nabla C_{Li}$$

Quasi-static mechanic equilibrium (define $\boldsymbol{F} := \nabla u$)

$$-\nabla \cdot \boldsymbol{\sigma} = 0$$

$$\boldsymbol{\sigma} = \frac{\delta G[C_{Li}, u]}{\delta u} = -\frac{\partial \mathcal{W}(C_{Li}, \nabla u)}{\partial \boldsymbol{F}}$$

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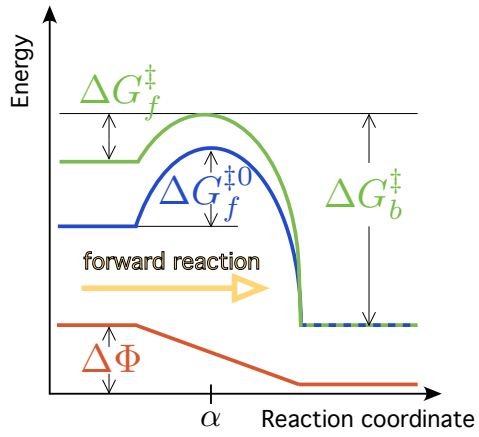
Electrochemical interfacial kinetics



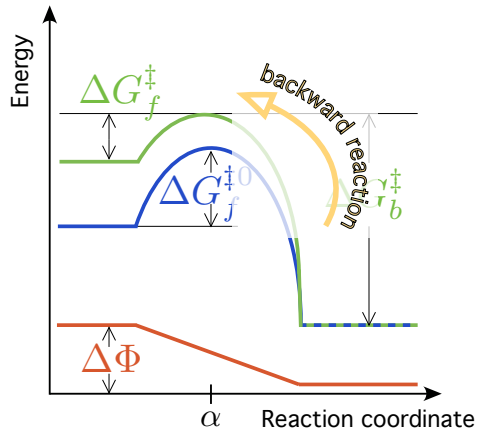
Frumkin-Butler-Volmer equation

(electrochemical driving force)

- So far, reaction rate depending on potential drop in the stern layer

$$R^{elec} = k_{f,i}\left[C_A\, e^{\alpha(\Delta\Phi_S)}\right] - k_{b,i}\left[C_B\, e^{-(1-\alpha)\Delta\Phi_S}\right]$$

Electrochemical interfacial kinetics



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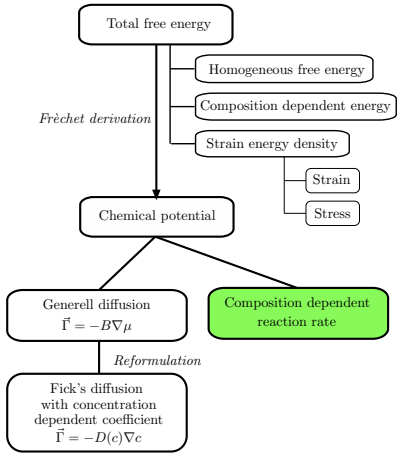

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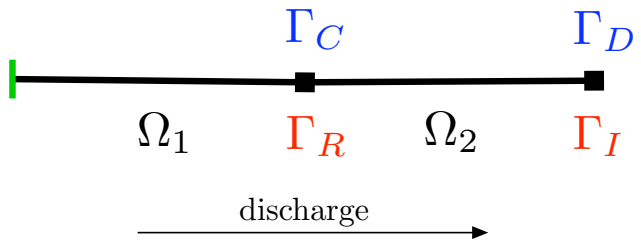
... incorperate **thermodynamic driving force**

- Reaction rate also depending on the composition

$$R^{chem} = k_{f,i}\left[C_A\, e^{\beta(\mu_A-\mu_B)}\, e^{\alpha(\Delta\Phi_S)}\right] - k_{b,i}\left[C_B\, e^{-\beta(\mu_A-\mu_B)}\, e^{-(1-\alpha)\Delta\Phi_S}\right]$$

Boundary conditions ...

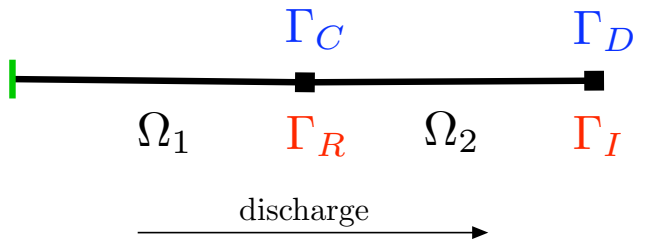


... for the diffusion equation

$$n \cdot \nabla(\boldsymbol{D}_{Li^+} \nabla C_{Li^+}) = -R^{chem}(C_{Li^+}, C_{Li}, \Phi, \Delta\mu) \qquad \text{on } \Gamma_R$$

$$n \cdot \nabla(\boldsymbol{D}_{Li^+} \nabla C_{Li^+}) = 0 \qquad \text{on } \Gamma_I$$

Boundary conditions ...



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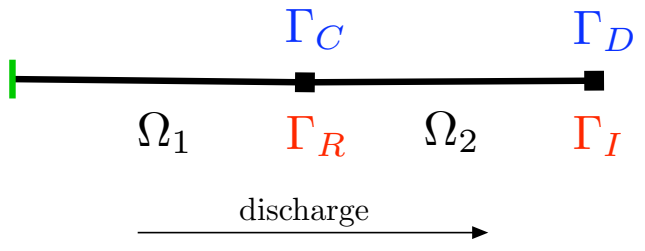
... for the mechanical equation

$$\boldsymbol{\sigma} n = 0 \quad \text{(surface forces in equilibrium)} \quad \text{on } \Gamma_F$$

Boundary conditions ...



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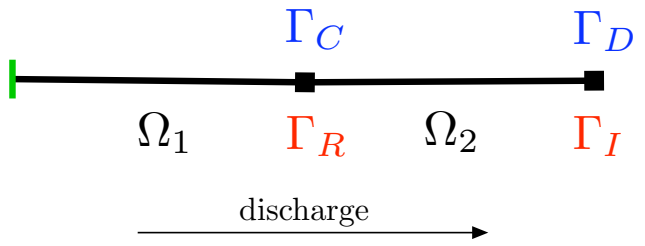
... or treat electrolyte as rigid body

$$u = 0 \quad \text{(fixed body)} \quad \text{on } \Gamma_D$$
$$n \cdot u \leq 0 \quad \text{(contact condition)} \quad \text{on } \Gamma_C$$

Boundary conditions ...



... for the diffusion equation

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$$n \cdot \nabla(\boldsymbol{D}_{Li^+} \nabla C_{Li^+}) = 0 \quad \text{on } \Gamma_I$$

... for the mechanical equation

$$\boldsymbol{\sigma} n = 0 \quad \text{(surface forces in equilibrium)} \quad \text{on } \Gamma_F$$

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$$u = 0 \quad \text{(fixed body)} \quad \text{on } \Gamma_D$$
$$n \cdot u \leq 0 \quad \text{(contact condition)} \quad \text{on } \Gamma_C$$

Question: Is there an attainable quasi-static mechanical equilibrium under these boundary conditions?

$\Longrightarrow$ Change to dynamic elasticity, moving boundaries

Questions and Discussion