Species diffusion coupled to elasticity in lithium ion batteries

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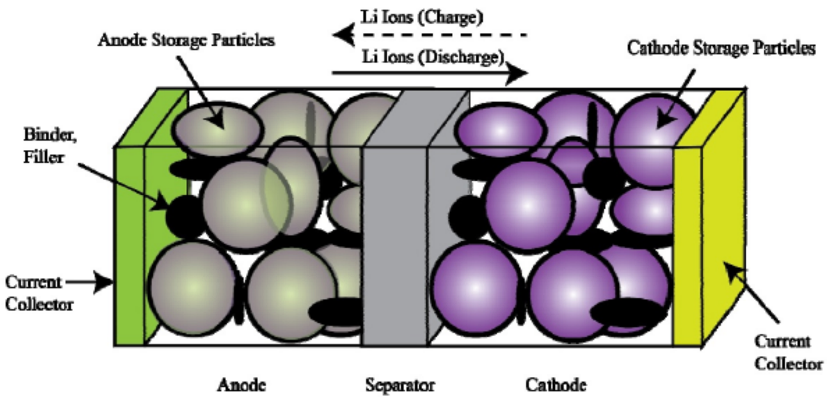
- Eshelby J.D., Elastic energy-momentum tensor, *J. Elasticity*, **5**, 321–335 (1975).
- Larché F., Cahn J.W., The interactions of composition and stress in crystalline solids, *J. of Research of the National Bureau of Standards*, **89**, 467–500 (1984).
- Wu C.H., The role of Eshelby stress in composition-generated and stress-assisted diffusion, *J.Mech.Phys.Solids*, **49**, 1771–1794 (2001).
- Meng Y.S. and Whittingham M.S., Introduction and foreword to focus issue on Intercalation Compounds for Rechargeable Batteries, *J. Electrochemical Society*, **160**, Y2–Y3 (2013).
- McMeeking R.M., Purkayastha R., The role of solid mechanics in electrochemical energy systems such as lithium-ion batteries, *Procedia IUTAM*, **10**, 294–306 (2014).
- Di Leo C.V., Rejovitzky E., Arnand L., A CahnHilliard-type phase-field theory for species diffusion coupled with large elastic deformations, *J.Mech.Phys.Solids*, **70**, 1–29 (2014)

Lithium ion battery



[from: McMeeking-Purkayastha, Procedia IUTAM (2014)]

Lithium ion battery

The main chemical reaction is the so-called *redox* reaction, which consists of a *reduction*

$$\mathrm{Li}^{+} + e^{-} \;\to\; \mathrm{Li}$$

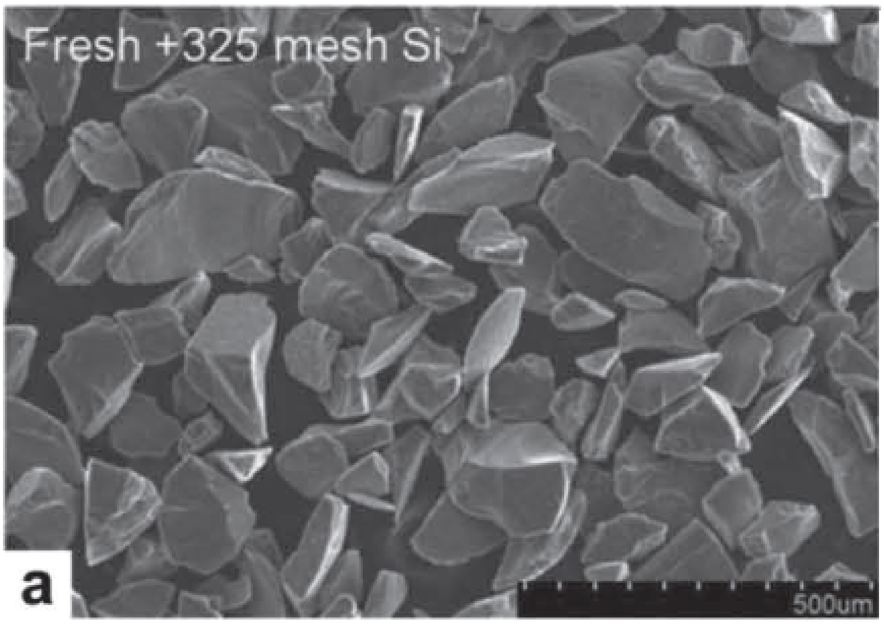
and an *oxidation*

$$\mathrm{Li} \;\to\; \mathrm{Li}^{+} + e^{-}$$

In the charging process there is a *reduction* in the *anode* followed by *intercalation*.

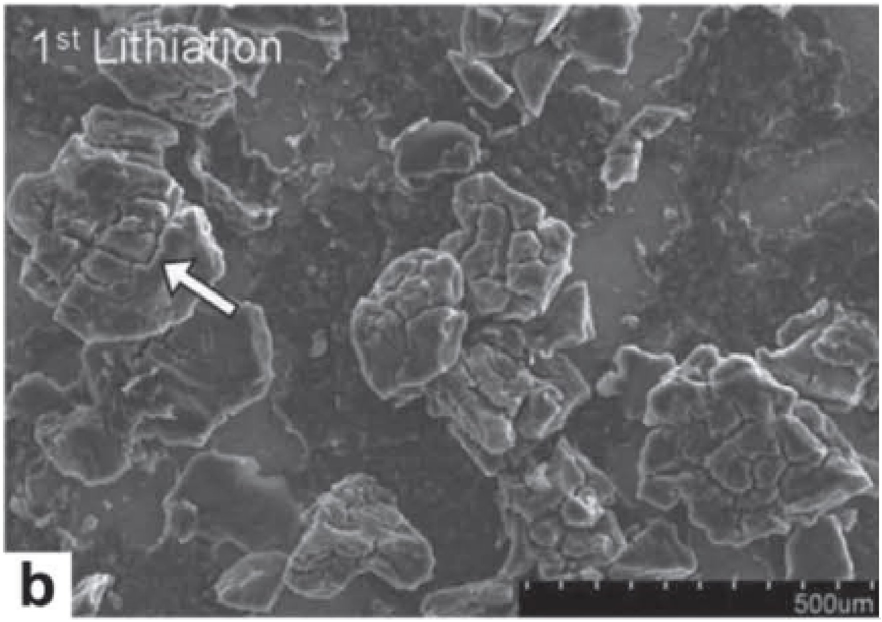
The *intercalation* process makes the host crystal lattice swell, with the molar volume increasing several times.

Anode Si particles



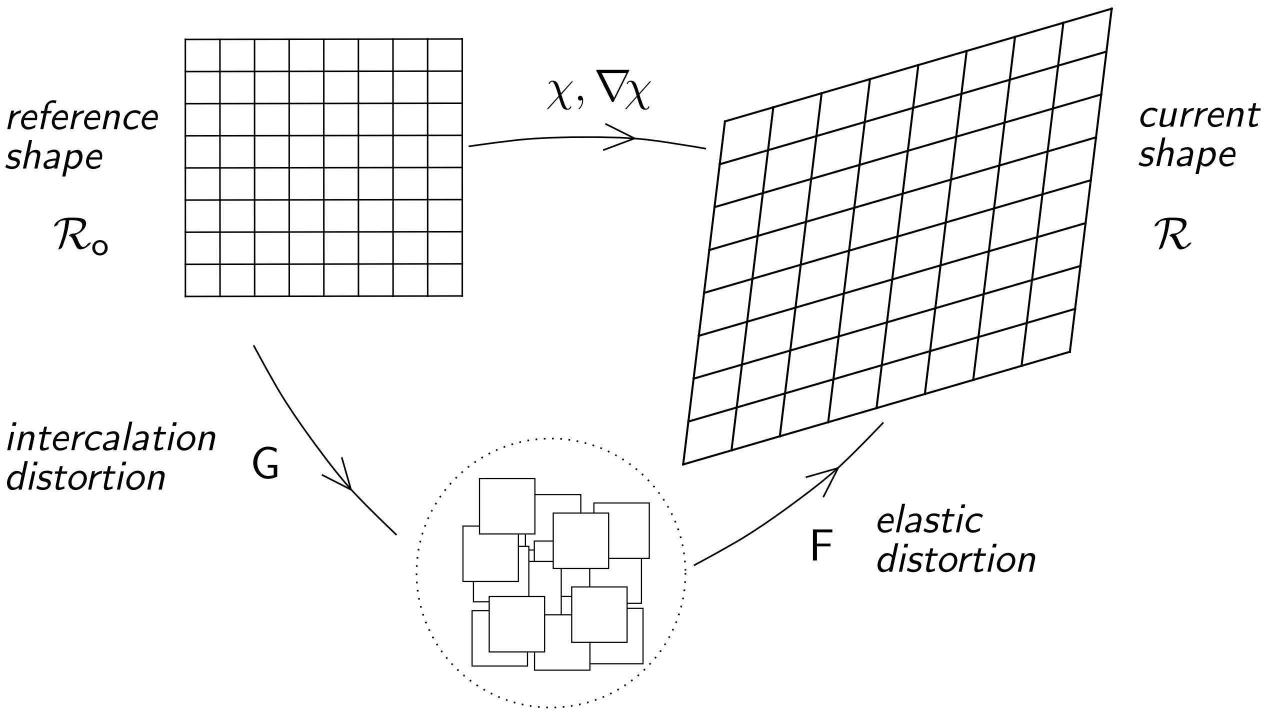
[from: McDowell-Lee-Nix-Cui, Adv.Mater. (2013)]

Anode Si particles



[from: McDowell-Lee-Nix-Cui, Adv.Mater. (2013)]

Decomposition of the deformation gradient $\nabla\chi$



$$\nabla\chi = \mathsf{F}\,\mathsf{G}$$

Kinematics and kinetics

Host material lattice deformation

$$\chi : \mathcal{R}_o \to \mathcal{R}$$

$$\nabla\chi = \mathsf{F}\,\mathsf{G}$$

Lithium concentration

$$c = \frac{\rho_{Li}}{\rho_o}$$

$$\mathsf{G} = \beta^{\frac{1}{3}}\,\mathsf{I}$$

$$\beta = 1 + \alpha\, c$$

$$\frac{\rho_{Li}}{\rho_o} = \frac{\text{molar density of Li atoms per unit reference volume}}{\text{molar density of lattice sites per unit reference volume}}$$

Molar conservation law for lattice sites

$$\frac{d}{dt}\int_{\mathcal{P}} \rho \, dV = \frac{d}{dt}\int_{\mathcal{P}_\circ} \rho_\circ \, dV = 0$$

$$\forall (\mathcal{P} \subset \mathcal{R} \, , \, \mathcal{P}_\circ \subset \mathcal{R}_\circ) \quad | \quad \chi : \mathcal{P}_\circ \to \mathcal{P}$$

ρ molar density of lattice sites per unit current volume

$$\Rightarrow \quad \dot{\rho} + \rho \, \mathrm{div} \, v = 0$$

$$\frac{d}{dt}\int_{\mathcal{P}} c \, \rho \, dV = \frac{d}{dt}\int_{\mathcal{P}_\circ} c \, \rho_\circ \, dV = \int_{\mathcal{P}_\circ} \dot{c} \, \rho_\circ \, dV = \int_{\mathcal{P}} \dot{c} \, \rho \, dV$$

$c \, \rho$ molar density of Li atoms per unit current volume

Species molar balance

$$\frac{d}{dt}\int_{\mathcal{P}} c \, \rho \, dV = -\int_{\partial\mathcal{P}} \mathrm{h} \cdot \mathrm{n} \, dA + \int_{\mathcal{P}} h \, dV$$

$$\int_{\mathcal{P}} \dot{c} \, \rho \, dV = -\int_{\partial\mathcal{P}} \mathrm{h} \cdot \mathrm{n} \, dA + \int_{\mathcal{P}} h \, dV$$

$$\dot{c} \, \rho = -\,\mathrm{div} \, \mathrm{h} + h$$

$$h = 0 \quad \Rightarrow \quad \dot{c} \, \rho = -\,\mathrm{div} \, \mathrm{h}$$

From molar balance to power balance

$$\dot{c}\,\rho = -\operatorname{div}\mathrm{h}$$

Introducing a scalar field μ (energy per mole of lithium) transforming the *molar balance* into a *power balance*

$$\int_{\mathcal{P}} \mu\,\dot{c}\,\rho\,dV = -\int_{\mathcal{P}} \mu\,\operatorname{div}\mathrm{h}\,dV \qquad \forall\mu$$

$$\operatorname{div}(\mu\,\mathrm{h}) = \mu\,\operatorname{div}\mathrm{h} + \nabla\mu\cdot\mathrm{h}$$

$$\int_{\mathcal{P}} \mu\,\dot{c}\,\rho\,dV = -\int_{\partial\mathcal{P}} \mu\,\mathrm{h}\cdot\mathrm{n}\,dA + \int_{\mathcal{P}} \mathrm{h}\cdot\nabla\mu\,dV \qquad \forall\mu$$

(μ is *the chemical potential*)

Species power balance

$$\int_{\mathcal{P}} \mu\,\dot{c}\,\rho\,dV = -\int_{\partial\mathcal{P}} \mu\,\mathrm{h}\cdot\mathrm{n}\,dA + \int_{\mathcal{P}} \mathrm{h}\cdot\nabla\mu\,dV \qquad \forall\mu$$

$$\int_{\mathcal{P}_\mathrm{o}} \mu_\mathrm{o}\,\dot{c}\,\rho_\mathrm{o}\,dV = -\int_{\partial\mathcal{P}_\mathrm{o}} \mu_\mathrm{o}\,\mathrm{h}_\mathrm{o}\cdot\mathrm{n}_\mathrm{o}\,dA + \int_{\mathcal{P}_\mathrm{o}} \mathrm{h}_\mathrm{o}\cdot\nabla\mu_\mathrm{o}\,dV \qquad \forall\mu_\mathrm{o}$$

$$\mathrm{h}_\mathrm{o} = (\det\mathrm{F}_\mathrm{o})\,\mathrm{F}_\mathrm{o}^{-1}\,\mathrm{h}$$

$$\mu_\mathrm{o}(\mathrm{x}) = \mu(\chi(\mathrm{x}))$$

Power balance

Species power balance

$$\int_{\mathcal{P}_o} \mu_o \, \dot{c}\, \rho_o \, dV = -\int_{\partial\mathcal{P}_o} \mu_o \, h_o \cdot n_o \, dA + \int_{\mathcal{P}_o} h_o \cdot \nabla \mu_o \, dV \qquad \forall \mu_o$$

Force power balance

$$\int_{\mathcal{P}_o} b_o \cdot v_o \, dV + \int_{\partial\mathcal{P}_o} t_o \cdot v_o \, dA = \int_{\mathcal{P}_o} S_o \cdot \nabla v_o \, dV \qquad \forall v_o$$

Free energy imbalance

Species power balance

$$\int_{\mathcal{P}_o} \mu_o \, \dot{c}\, \rho_o \, dV = \underbrace{-\int_{\partial\mathcal{P}_o} \mu_o \, h_o \cdot n_o \, dA}_{\textit{external power}} + \int_{\mathcal{P}_o} h_o \cdot \nabla \mu_o \, dV$$

Force power balance

$$\underbrace{\int_{\mathcal{P}_o} b_o \cdot v_o \, dV + \int_{\partial\mathcal{P}_o} t_o \cdot v_o \, dA}_{\textit{external power}} = \int_{\mathcal{P}_o} S_o \cdot \dot{F}_o \, dV$$

Free energy imbalance

$$S_o \cdot \dot{F}_o + \mu_o \, \dot{c}\, \rho_o - h_o \cdot \nabla \mu_o - \frac{d}{dt}\psi \geq 0$$

Free energy imbalance

$$\mathsf{S_o} \cdot \dot{\mathsf{F}}_o + \mu_o \, \dot{c} \, \rho_o - \mathsf{h_o} \cdot \nabla \mu_o - \frac{d}{dt}\psi \geq 0$$

$$\psi = \hat{\psi}(\mathsf{F_o}, c)$$

$$\frac{d}{dt}\psi = \mathsf{S_o} \cdot \dot{\mathsf{F}}_o + \mu_o \, \dot{c} \, \rho_o$$

$$-\mathsf{h_o} \cdot \nabla \mu_o \geq 0$$

$$\mathsf{h_o} = -M \, \nabla \mu_o \qquad \text{(Fick's law)}$$

Free energy expression

$$\hat{\psi}(\mathsf{F_o}, c) = \rho_o \, \varphi_c(c) + \det \mathsf{G} \, \varphi_e(\mathsf{F}, c)$$

$$\hat{\psi}(\mathsf{F_o}, c) = \det \mathsf{G} \, \varphi(\mathsf{F})$$

$$\frac{d}{dt}\varphi(\mathsf{F}) = \mathsf{S} \cdot \dot{\mathsf{F}}$$

$$\mathsf{F} = \mathsf{F_o} \, \mathsf{G}^{-1} \qquad \mathsf{G} = \beta^{\frac{1}{3}} \, \mathsf{I} \qquad \beta = 1 + \alpha \, c$$

$$\frac{d}{dt}\psi = \beta \, \mathsf{S} \cdot \dot{\mathsf{F}} + \alpha \, \varphi(\mathsf{F}) \, \dot{c}$$

Constitutive characterization

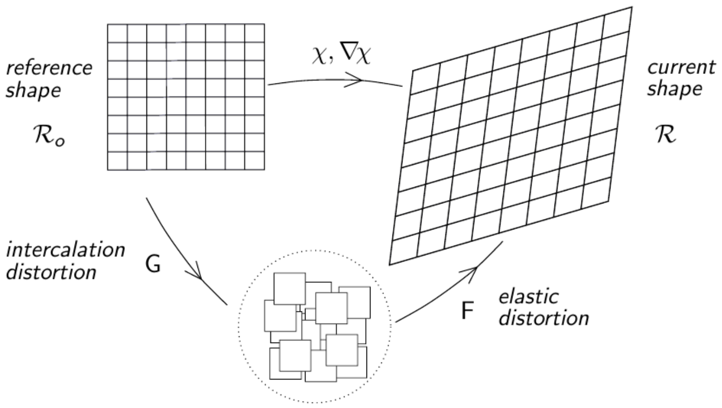
$$\mathsf{S}_\mathsf{o} \cdot \dot{\mathsf{F}}_\mathsf{o} + \mu_\mathsf{o}\, \dot{c}\, \rho_\mathsf{o} - \mathsf{h}_\mathsf{o} \cdot \nabla \mu_\mathsf{o} - \frac{d}{dt}\psi \geq 0$$

$$\frac{d}{dt}\psi = \beta\, \mathsf{S} \cdot \dot{\mathsf{F}} + \alpha\, \varphi(\mathsf{F})\, \dot{c}$$

$$\frac{d}{dt}\psi = \mathsf{S}_\mathsf{o} \cdot \dot{\mathsf{F}}_\mathsf{o} + \mu_\mathsf{o}\, \rho_\mathsf{o}\, \dot{c} = \beta\, \mathsf{S} \cdot \dot{\mathsf{F}} + \frac{1}{3}\alpha\, \mathsf{S} \cdot \mathsf{F}\, \dot{c} + \mu_\mathsf{o}\, \rho_\mathsf{o}\, \dot{c}$$

$$-\alpha\, \varphi(\mathsf{F}) + \frac{1}{3}\alpha\, \det \mathsf{F}\ \mathrm{tr}\, \mathsf{T} + \mu_\mathsf{o}\, \rho_\mathsf{o} = 0$$

Constitutive characterization



$$\mu_\mathsf{o} = \frac{\alpha}{\rho_\mathsf{o}}\left(\varphi(\mathsf{F}) - \frac{1}{3}\det \mathsf{F}\ \mathrm{tr}\, \mathsf{T}\right)$$

$$\mathsf{h}_\mathsf{o} = -M\ \nabla \mu_\mathsf{o}$$

$$\mathsf{S} \cdot \dot{\mathsf{F}} = \frac{d}{dt}\varphi(\mathsf{F})$$

Compressible neo-Hookean material

$$\varphi(\mathsf{F}) = k_I\,(\bar{\iota}_1 - 3) + k_V\,(J - 1)^2$$

$$\iota_1 = \operatorname{tr} \mathsf{F}^\mathsf{T}\mathsf{F}$$

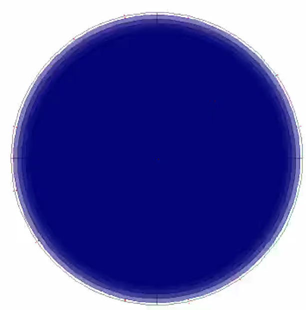
$$\bar{\iota}_1 = \iota_1\, J^{-\frac{2}{3}}$$

$$J = \det \mathsf{F}$$

$$\hat{\mathsf{S}}(\mathsf{F}) = 2\,k_I\,J^{-\frac{2}{3}}\,(\mathsf{F} - \frac{1}{3}\,\iota_1\,\mathsf{F}^{-\mathsf{T}}) + 2\,k_V\,(J-1)J\,\mathsf{F}^{-\mathsf{T}}$$

$$\hat{\mathsf{T}}(\mathsf{F}) = 2\,k_I\,J^{-\frac{5}{3}}\,(\mathsf{B} - \frac{1}{3}\,\iota_1\,\mathsf{I}) + 2\,k_V\,(J-1)\,\mathsf{I}$$

Constrained cylindrical particle



Constrained cylindrical particle

Let us consider deformations such that

$$G = \begin{pmatrix} \beta^{1/3} & 0 & 0 \\ 0 & \beta^{1/3} & 0 \\ 0 & 0 & \beta^{1/3} \end{pmatrix}$$

$$F_o = \begin{pmatrix} \lambda_r & 0 & 0 \\ 0 & \lambda_r & 0 \\ 0 & 0 & \lambda \end{pmatrix}$$

λ_r radial stretch
λ axial stretch

with the constraint

$$\lambda_r = 1$$

Constrained cylindrical particle

As a consequence

$$F = \begin{pmatrix} \beta^{-1/3} & 0 & 0 \\ 0 & \beta^{-1/3} & 0 \\ 0 & 0 & \lambda\,\beta^{-1/3} \end{pmatrix}$$

$$\varphi(F) = k_I \left(\frac{2+\lambda^2}{\lambda^{2/3}} - 3 \right) + k_V \left(\frac{\lambda}{\beta} - 1 \right)^2$$

Constrained cylindrical particle

$$\hat{\sigma}_a(\lambda, \beta) = \frac{4}{3}\, k_I\, \beta\, \frac{\lambda^2 - 1}{\lambda^{5/3}} + 2\, k_V \left(\frac{\lambda}{\beta} - 1\right)$$

$$\hat{\sigma}_r(\lambda, \beta) = -\frac{2}{3}\, k_I\, \beta\, \frac{\lambda^2 - 1}{\lambda^{5/3}} + 2\, k_V \left(\frac{\lambda}{\beta} - 1\right)$$

$$\hat{\mu}_o(\lambda, \beta) = \frac{\alpha}{\rho_o} \left(k_I \left(\frac{\lambda^2 + 2}{\lambda^{2/3}} - 3 \right) - k_V \left(\frac{\lambda}{\beta} - 1 \right) \right)$$

Constrained cylindrical particle

$$\hat{\sigma}_a(\lambda, \beta) = 0 \quad \Rightarrow \quad \lambda = \hat{\lambda}(\beta)$$

$$\operatorname{div} \mathrm{h}_o = -\dot{c}\, \rho_o$$

$$\mathrm{h}_o = -M\, \nabla \mu_o$$

$$\mu_o = \hat{\mu}_o(\lambda, \beta)$$

Constrained cylindrical particle

$$\hat{\sigma}_a(\lambda, \beta) = 0 \quad \Rightarrow \quad \lambda = \hat{\lambda}(\beta)$$

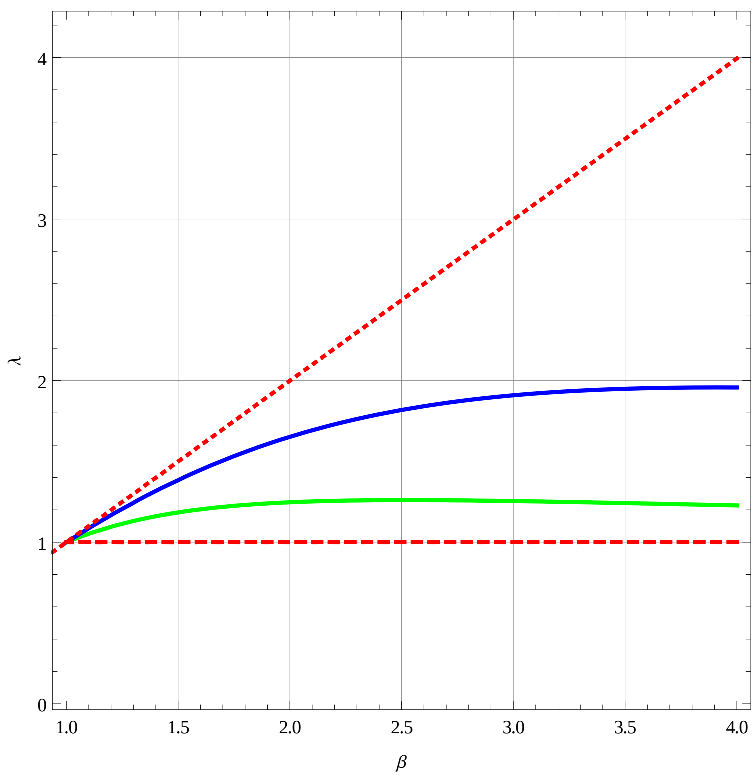
$$\mathrm{h}_\circ' = -\dot{c}\,\rho_\circ$$

$$\mathrm{h}_\circ = -d\,\mu_\circ'$$

$$\mu_\circ = \hat{\mu}_\circ(\lambda, \beta)$$

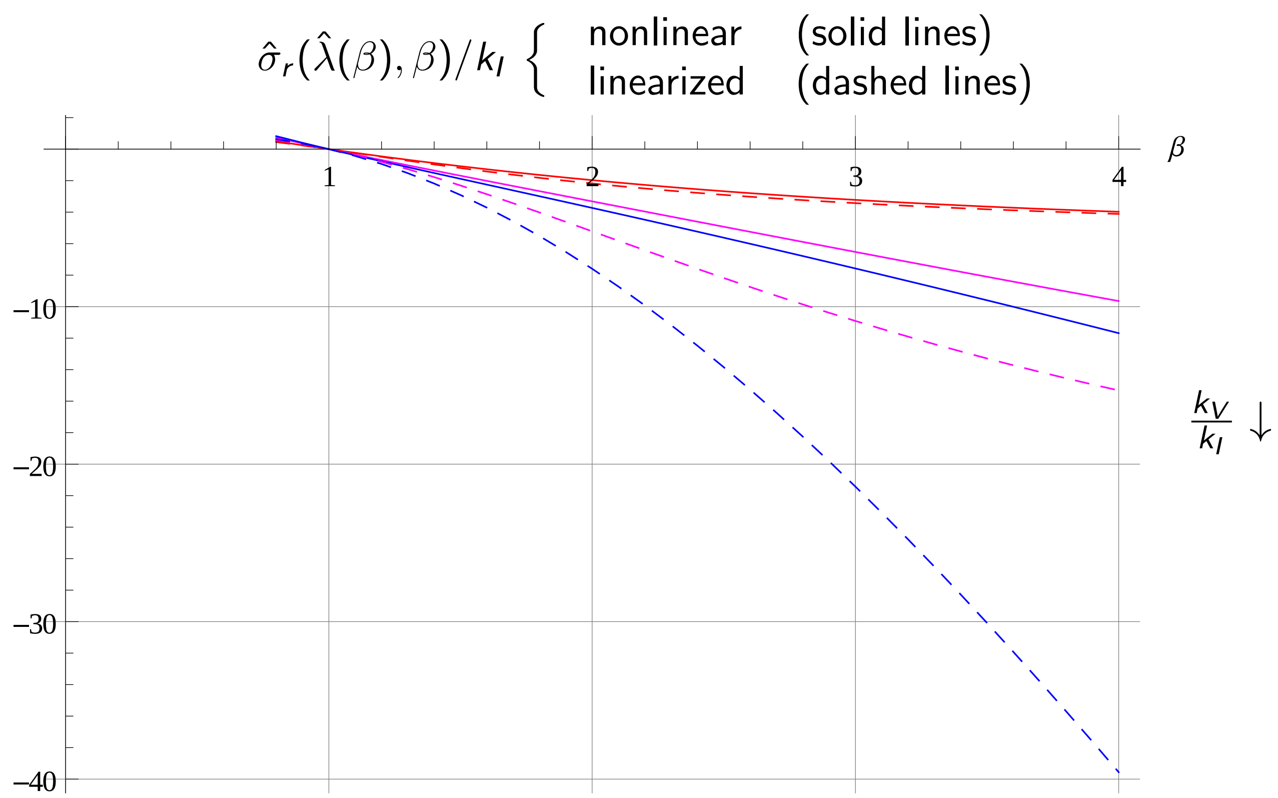
Constrained cylindrical particle

$\hat{\lambda}(\beta)$

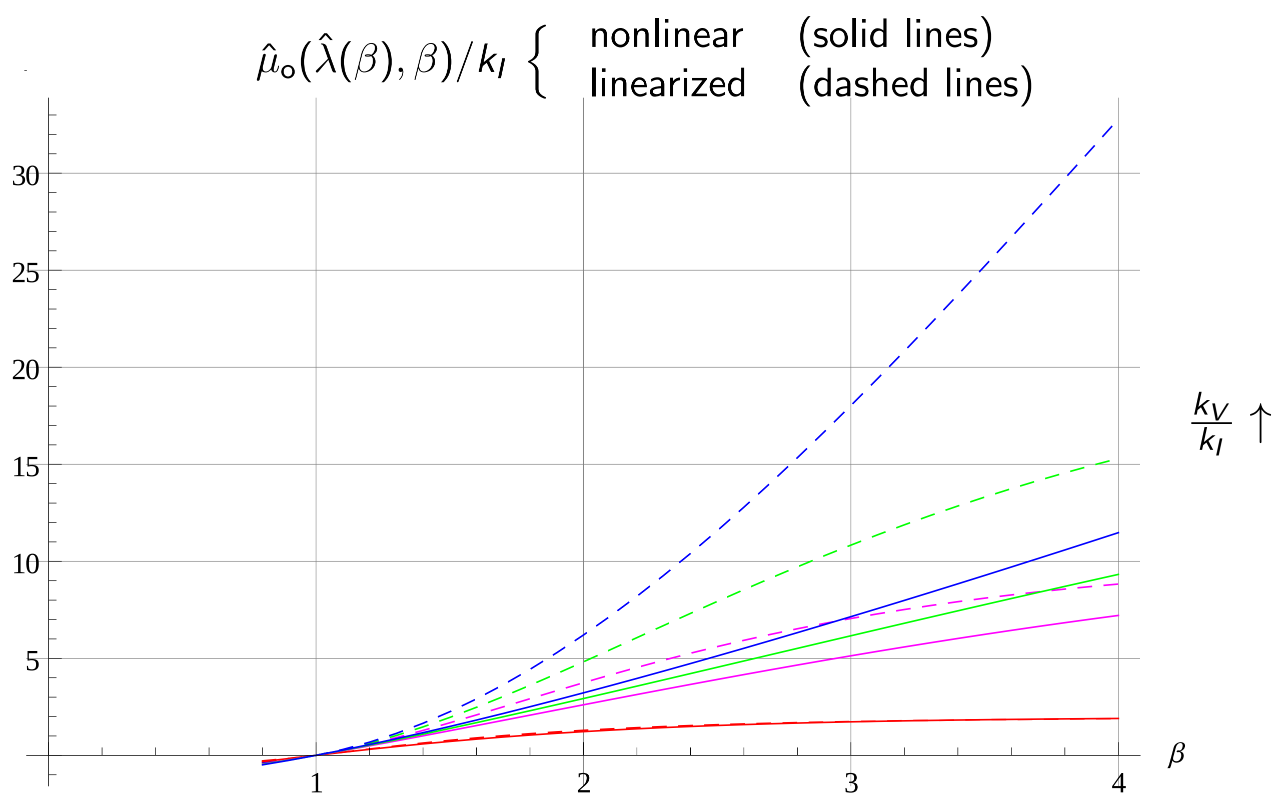


$\frac{k_V}{k_I} \downarrow$

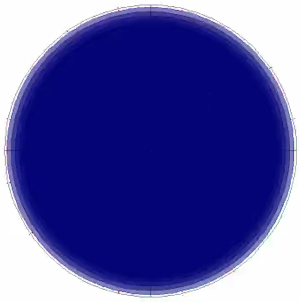
Constrained cylindrical particle



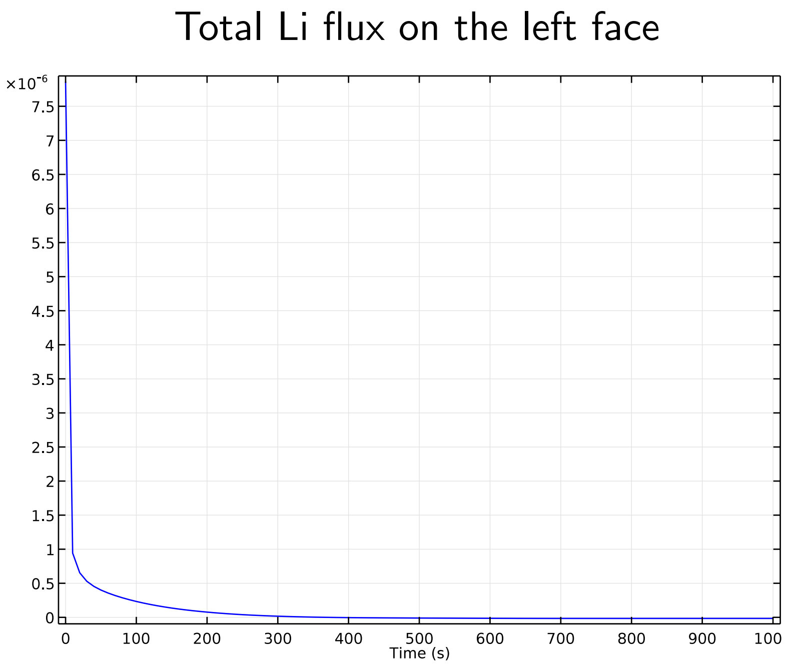
Constrained cylindrical particle



Particle surrounded by a constant lithium concentration



Cylindrical particle surrounded by a constant lithium concentration



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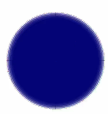
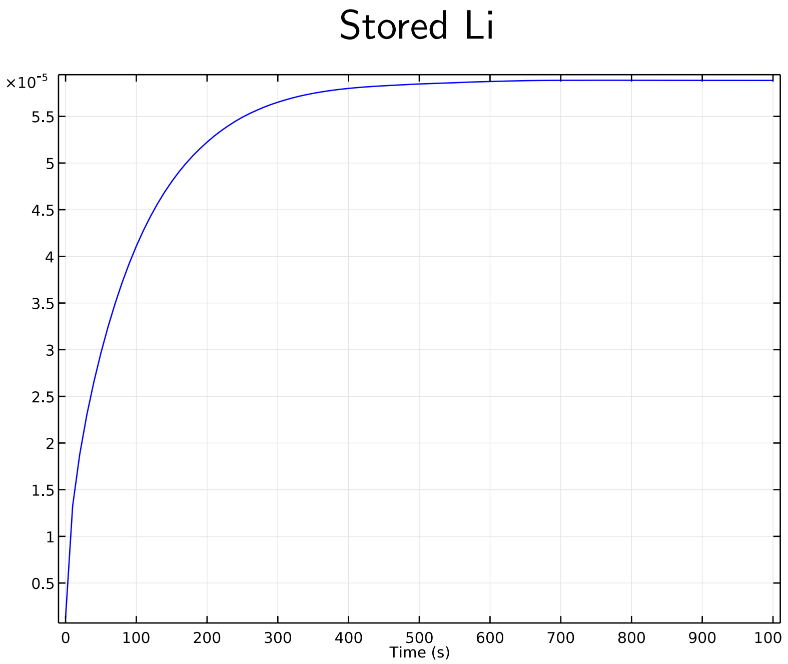


Cylindrical particle surrounded by a constant lithium concentration



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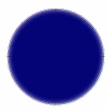
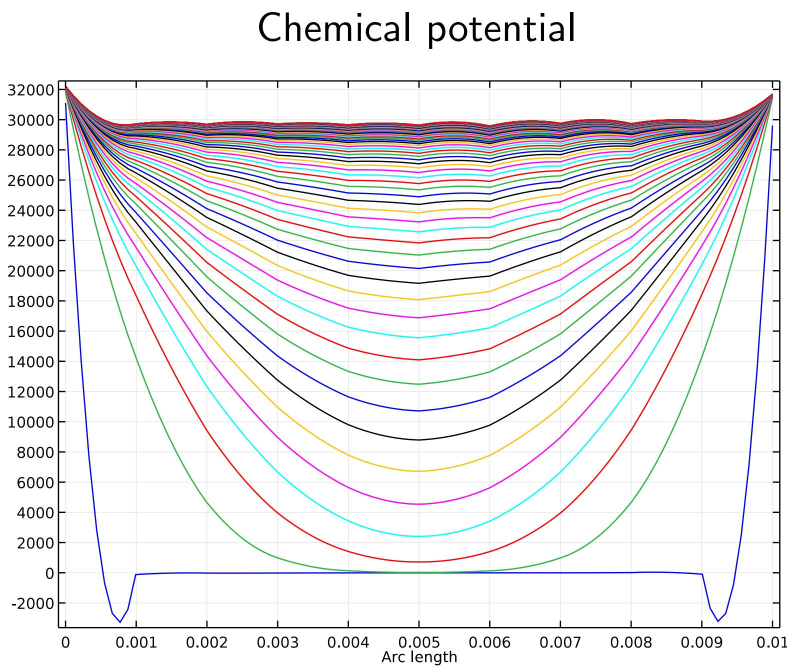


Cylindrical particle surrounded by a constant lithium concentration



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