Mathematical modeling for all-solid-state batteries

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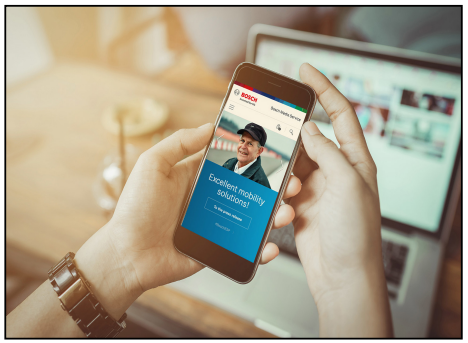
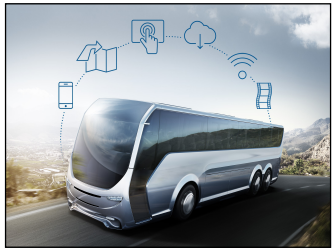
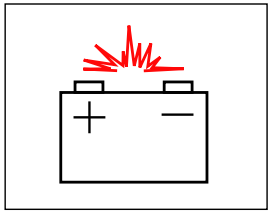
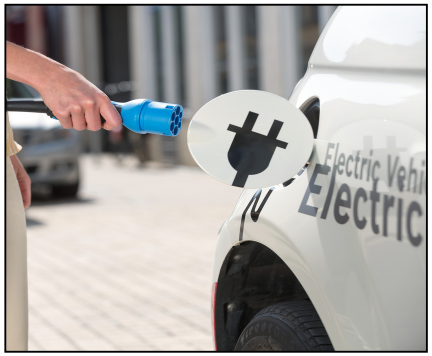
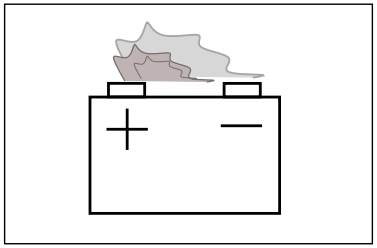
1. Motivation and overview

Applications and drawbacks of Lithium-ion batteries (LIBs)

LIBs have found many applications in every energy storage system such as:

- Smartphone and power tools use LIBs for their functionality.
- Electric vehicles nowadays become more popular due to their zero-emission by the application of LIBs.

Main drawbacks of non-solid electrolyte LIBs are named but a few:

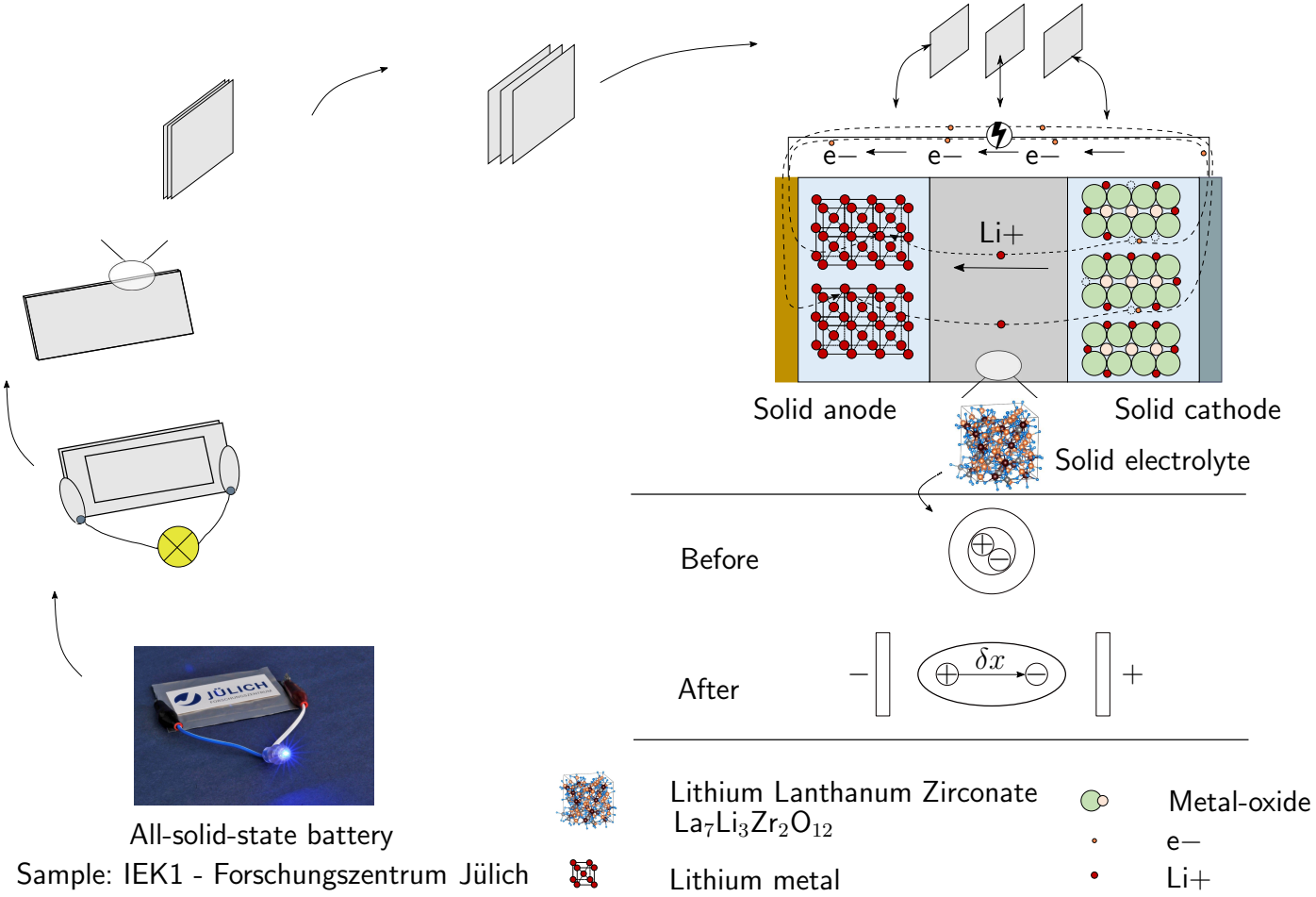
- Leakage of non-solid electrolyte could be observed under damage or after many cycles of charging/discharging.
- Non-solid electrolyte in LIBs may exhibit flammability or explosion due to its exposure to external media.

Why *all-solid-state* LIBs?

- *high energy density*
- *tiny memory effect*
- *low self-discharged*
- *non-flammable*
- *non-leakage*

1. Motivation and overview

Solid electrolyte is polarized under the applied electric potential.

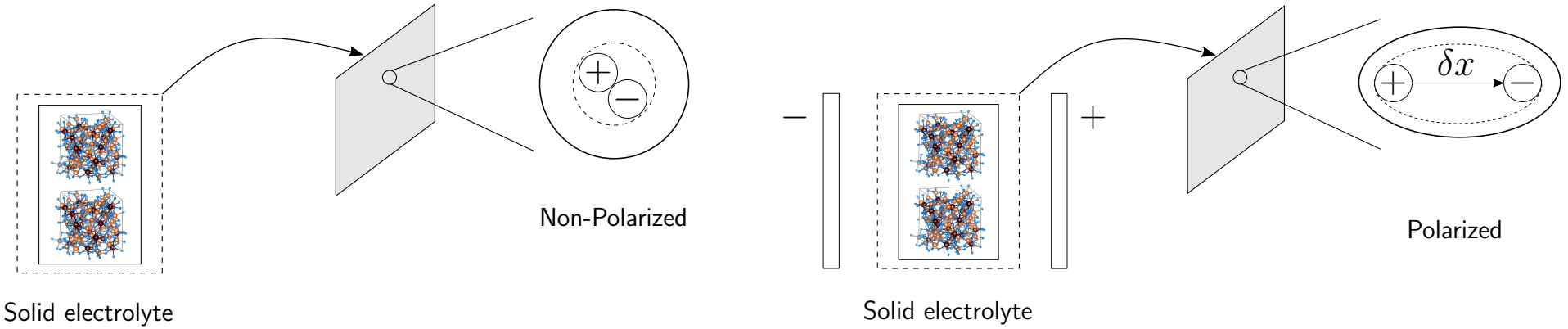


→ The polarized solid electrolyte exhibits **directional effect**.

→ The **polarized lattice** of solid electrolyte causes **overall deformation** in the bulk.

1. Motivation and overview

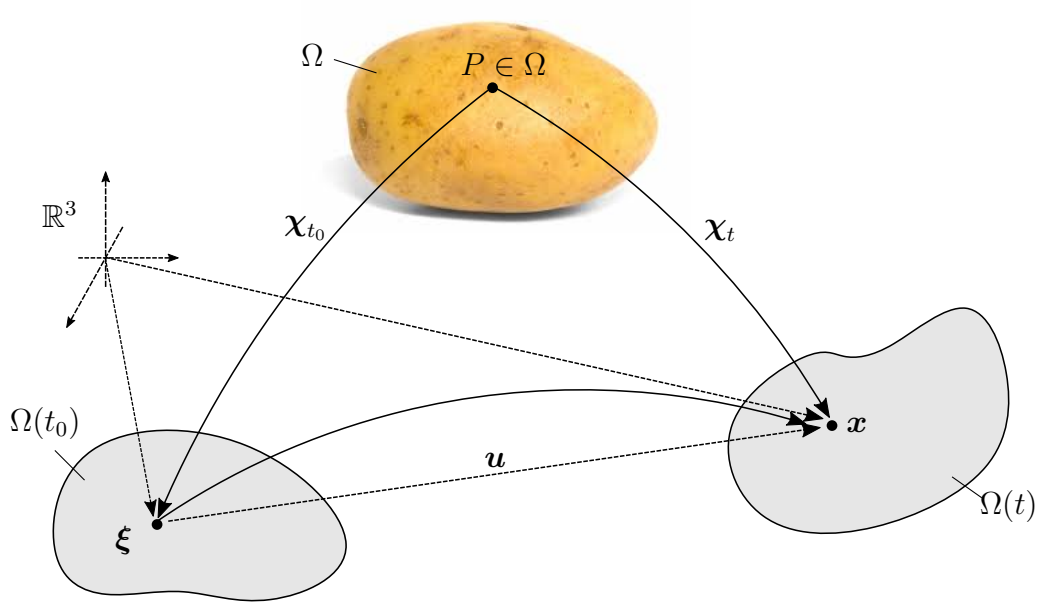
Polarization illustration



Goals:

- A **thermodynamically consistent** formulation for **constitutive relations**.
- Capture the **directional effect** due to polarization in the bulk of solid-electrolyte.
- **Numerical implementation** and illustrated **representative numerical results**.

Continuum physics kinematics



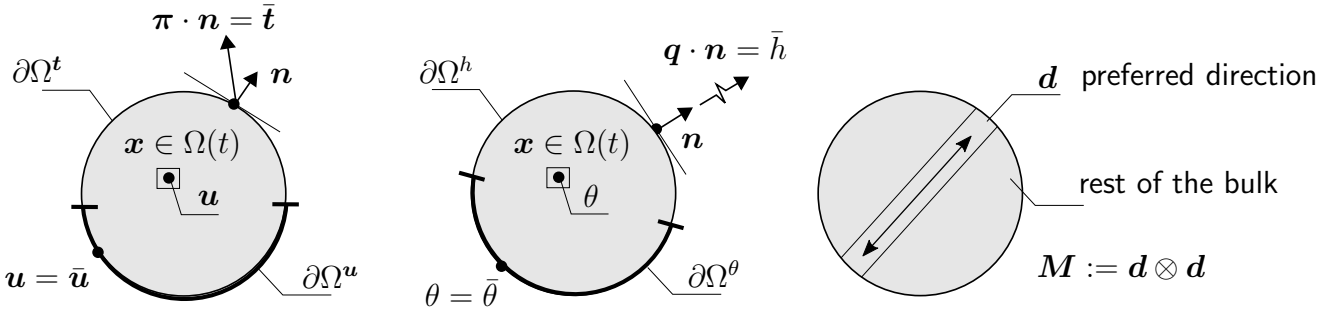
Reference/Lagrangian configuration Current/Eulerian configuration

Displacement vector: $\boldsymbol{u} = \boldsymbol{x} - \boldsymbol{\xi}$; Deformation gradient: $\boldsymbol{F} = \mathbf{1} + \partial \boldsymbol{u}/\partial \boldsymbol{\xi}$
Green-Lagrange strain tensor: $\boldsymbol{E} = 1/2(\boldsymbol{F}^\top \boldsymbol{F} - \mathbf{1})$
Infinitesimal strain required $\partial \boldsymbol{u}/\partial \boldsymbol{\xi} = \mathcal{O}(\varepsilon), \varepsilon \ll 1$ leads to

$$\boldsymbol{\varepsilon} := \frac{1}{2}\left[\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{\xi}} + \left(\frac{\partial \boldsymbol{u}}{\partial \boldsymbol{\xi}}\right)^\top\right]$$

$\rightarrow$ This kinematic relation is used for the current model of solid electrolyte.

Primary fields



DISPLACEMENT FIELD $\boldsymbol{u}$ TEMPERATURE FIELD θ STRUCTURE TENSOR $\boldsymbol{M}$

• Primary field variables and their gradients

Displacement field and temperature field

$$\boldsymbol{u}:\begin{cases}\Omega(t)\times\mathbb{R}_+\to\mathbb{R}^3,\\ (\boldsymbol{x},t)\mapsto\boldsymbol{u}(\boldsymbol{x},t),\end{cases}\qquad\text{and}\qquad\theta:\begin{cases}\Omega(t)\times\mathbb{R}_+\to\mathbb{R},\\ (\boldsymbol{x},t)\mapsto\theta(\boldsymbol{x},t),\end{cases}$$

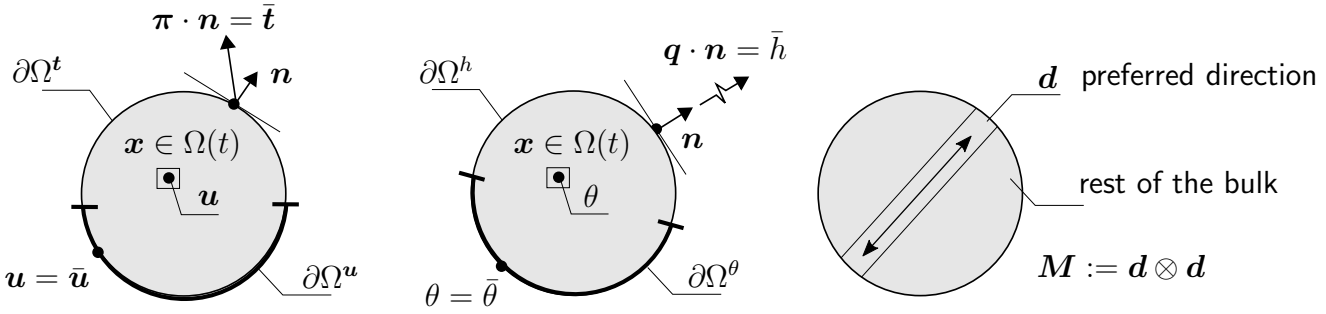
Gradient of displacement field $\boldsymbol{u}$ and temperature field θ

$$\boldsymbol{\varepsilon}=\nabla_s\boldsymbol{u}(\boldsymbol{x},t),\qquad\qquad\boldsymbol{g}:=\nabla\theta(\boldsymbol{x},t).$$

• Structure tensor $\boldsymbol{M}$

$$\boldsymbol{M}:=\boldsymbol{d}\otimes\boldsymbol{d}\qquad\text{where}\qquad\boldsymbol{d}:\begin{cases}[0,2\pi]\times[0,\pi]\to\mathbb{R}^3,\\ (\varphi,\theta)\mapsto(\sin\theta\cos\varphi,\ \sin\theta\sin\varphi,\ \cos\theta)\,.\end{cases}$$

Primary fields



DISPLACEMENT FIELD $\boldsymbol{u}$ TEMPERATURE FIELD θ STRUCTURE TENSOR $\boldsymbol{M}$

• Summary of local balance laws

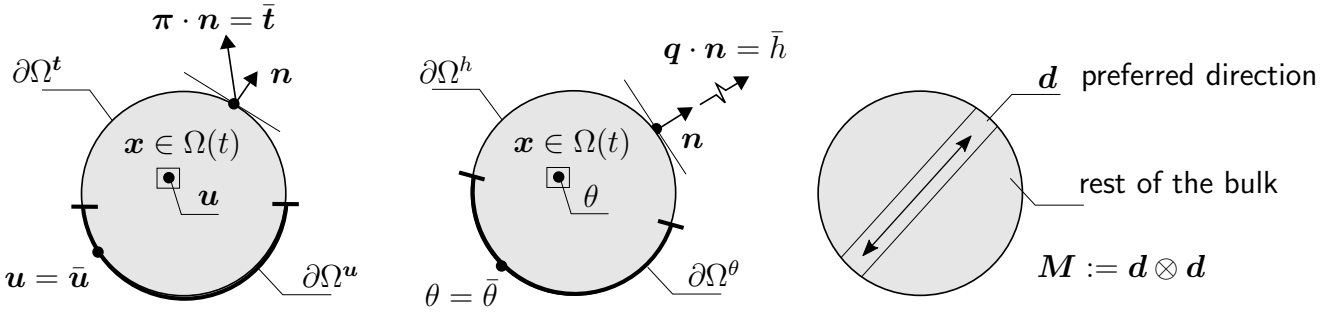
Local balance laws governing the infinitesimal elasticity

Balance of mass	$\dot{\rho}+\rho\,\mathrm{div}\,\boldsymbol{v}=0$
Balance of linear momentum	$\rho\dot{v}=\mathrm{div}\,\boldsymbol{\pi}+\rho\boldsymbol{b}$
Balance of angular momentum	$\boldsymbol{\pi}^{\top}=\boldsymbol{\pi}$
Balance of energy	$\rho\dot{e}=\boldsymbol{\pi}:\dot{\boldsymbol{\varepsilon}}+\rho r-\mathrm{div}\,\boldsymbol{q}$

where $\rho(\boldsymbol{x},t)$ is mass density per unit volume (puv); $\boldsymbol{b}(\boldsymbol{x},t)$ body force puv; $\boldsymbol{v}(\boldsymbol{x},t)$ velocity; $e(\boldsymbol{x},t)$ internal energy puv; $\boldsymbol{q}(\boldsymbol{x},t)$ heat flux; $r(\boldsymbol{x},t)$ heat source puv; $\boldsymbol{\pi}$ Cauchy stress and $\boldsymbol{\varepsilon}$ infinitesimal strain.

2. Mathematical modeling of coordinate-free structure-tensor-based material

Primary fields



DISPLACEMENT FIELD $\boldsymbol{u}$ TEMPERATURE FIELD θ STRUCTURE TENSOR $\boldsymbol{M}$

- **Entropy inequality**

Entropy Clausius-Planck inequality (CPI): $\boldsymbol{\pi} : \dot{\boldsymbol{\varepsilon}} - \rho\eta\dot{\theta} - \rho\dot{\Psi} - \frac{1}{\theta}\boldsymbol{q} \cdot \nabla\theta \geq 0$

- **Constitutive relations:** Consider the free energy function Ψ

Principle of material objectivity: $\Psi = \hat{\Psi}(\boldsymbol{\varepsilon}, \boldsymbol{M}, \theta, \nabla\theta) \rightarrow \dot{\Psi} = \partial_{\boldsymbol{\varepsilon}}\hat{\Psi}\dot{\boldsymbol{\varepsilon}} + \partial_{\boldsymbol{M}}\hat{\Psi}\dot{\boldsymbol{M}} + \partial_{\theta}\hat{\Psi}\dot{\theta} + \partial_{\nabla\theta}\hat{\Psi}\dot{\overline{\nabla\theta}}$

Insertion of $\dot{\Psi}$ to CPI yields: $\left[\boldsymbol{\pi} - \rho\partial_{\boldsymbol{\varepsilon}}\hat{\Psi}\right]\dot{\boldsymbol{\varepsilon}} - \rho\left[\eta + \partial_{\theta}\hat{\Psi}\right]\dot{\theta} - \left[\partial_{\nabla\theta}\hat{\Psi}\right]\dot{\overline{\nabla\theta}} \geq 0$

Constitutive relations: $\left[\boldsymbol{\pi} - \rho\partial_{\boldsymbol{\varepsilon}}\hat{\Psi}\right] = 0; \quad \left[\eta + \partial_{\theta}\hat{\Psi}\right] = 0; \quad \left[\partial_{\nabla\theta}\hat{\Psi}\right] = 0.$

$\rightarrow$ Thermodynamic consistency is satisfied.

2. Mathematical modeling of coordinate-free structure-tensor-based material

• Free energy function

$$\begin{aligned}\Psi(\boldsymbol{\varepsilon}, \boldsymbol{M}) &= \tilde{\Psi}(I_1, I_2, I_3, I_4, I_5; \lambda, \mu, \alpha, \beta) \\ &= \tilde{\Psi}_{\text{isotropic}}(I_1, I_2, I_3; \lambda, \mu) + \tilde{\Psi}_{\text{anisotropic}}(I_4, I_5; \alpha) + \tilde{\Psi}_{\text{coupling}}(I_1, I_2, I_3, I_4, I_5; \beta)\end{aligned}$$

where

$$I_1 = \text{tr}[\boldsymbol{\varepsilon}], \quad I_2 = \text{tr}[\boldsymbol{\varepsilon}^2], \quad I_3 = \text{tr}[\boldsymbol{\varepsilon}^3], \quad I_4 = \text{tr}[\boldsymbol{\varepsilon}\boldsymbol{M}], \quad I_5 = \text{tr}[\boldsymbol{\varepsilon}^2\boldsymbol{M}]$$

• Constitutive relations

Stress tensor

$$\begin{aligned}\boldsymbol{\pi} &= \partial_{\boldsymbol{\varepsilon}}\tilde{\Psi} \\ &= \partial_{\boldsymbol{\varepsilon}}\tilde{\Psi}_{\text{isotropic}} + \partial_{\boldsymbol{\varepsilon}}\tilde{\Psi}_{\text{anisotropic}} + \partial_{\boldsymbol{\varepsilon}}\tilde{\Psi}_{\text{coupling}}\end{aligned}$$

Tangent modulus

$$\begin{aligned}\mathbb{C} &= \partial_{\boldsymbol{\varepsilon}\boldsymbol{\varepsilon}}\tilde{\Psi} \\ &= \partial_{\boldsymbol{\varepsilon}}\boldsymbol{\pi} \\ &= \partial_{\boldsymbol{\varepsilon}\boldsymbol{\varepsilon}}\tilde{\Psi}_{\text{isotropic}} + \partial_{\boldsymbol{\varepsilon}\boldsymbol{\varepsilon}}\tilde{\Psi}_{\text{anisotropic}} + \partial_{\boldsymbol{\varepsilon}\boldsymbol{\varepsilon}}\tilde{\Psi}_{\text{coupling}}\end{aligned}$$

Problem to solve

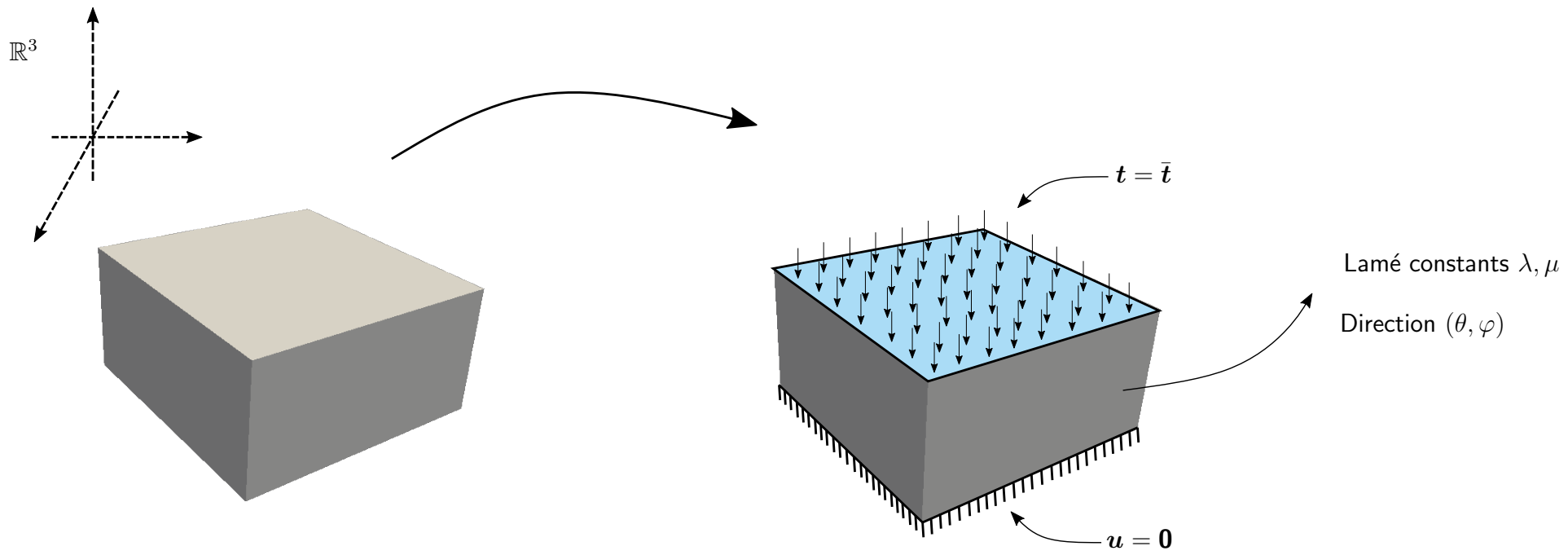
Find displacement $\boldsymbol{u}$ such that

PDE	$\pi_{ij,j} + \rho b_i = 0$
Constitutive relation	$\pi_{ij} = \mathbb{C}_{ijkl}\ \varepsilon_{kl}$
Kinematic relation	$\varepsilon_{kl} = \frac{1}{2}\left(\frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k}\right)$
Dirichlet BC	$u_i = \bar{u}_i$ on $\partial\Omega_{u_i}$
Neumann BC	$\pi_{ij} n_j = \bar{t}_i$ on $\partial\Omega_{t_i}$

where $\mathbb{C}_{ijkl} \mathrel{\widehat{=}} \hat{\mathbb{C}}(\lambda, \mu; \theta, \varphi; \alpha, \beta)$

3. Numerical implementation and representative numerical results

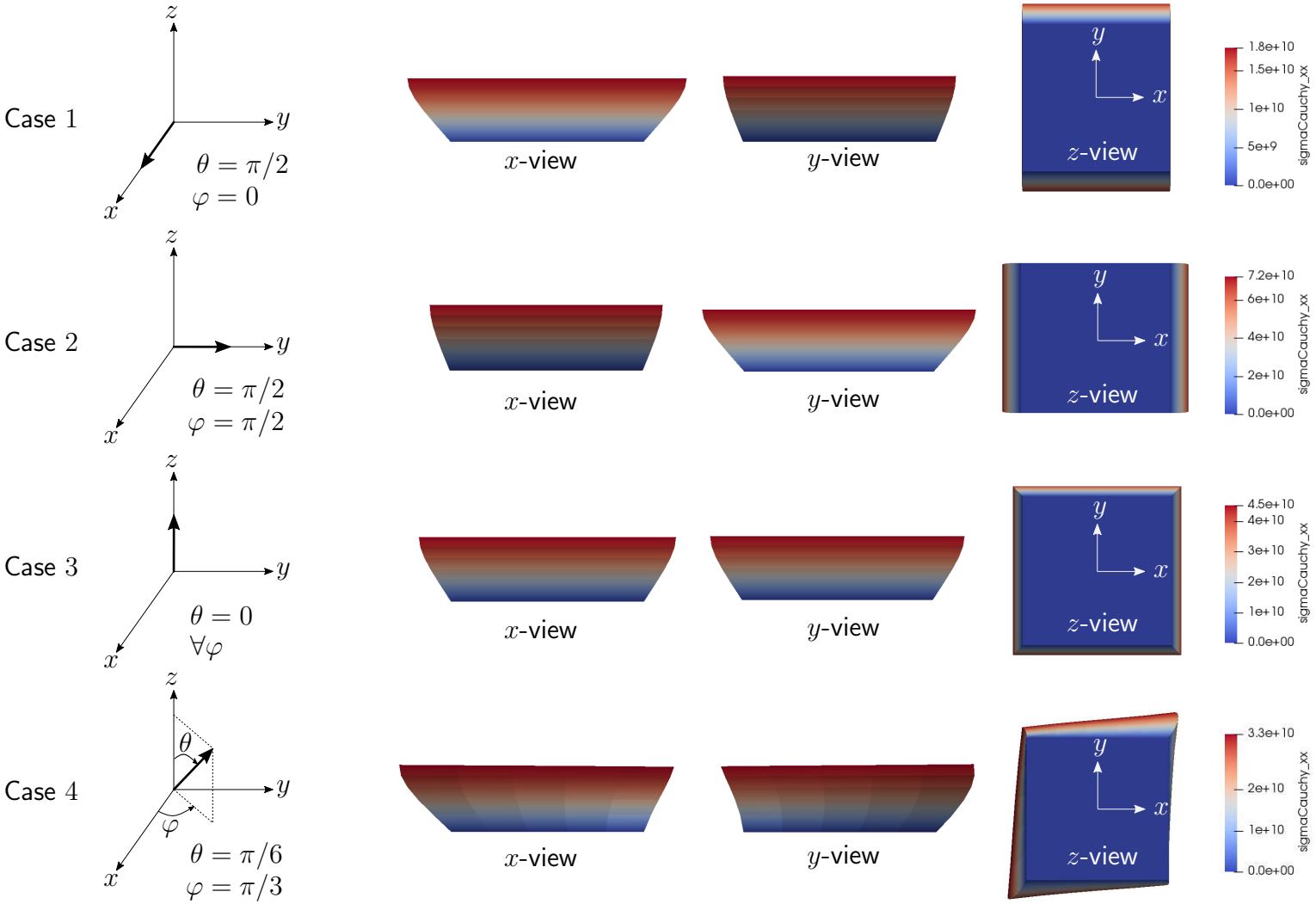
Setting up model



- Material parameters used in the bulk: Two Lamé constants λ and μ.
- Preferred direction is controlled by two angles (θ, φ).
- Bottom surface is fixed by Dirichlet boundary condition: $\boldsymbol{u} = \boldsymbol{0}$.
- Top surface is applied by Neumann boundary condition: $\boldsymbol{t} = \bar{\boldsymbol{t}}$.

3. Numerical implementation and representative numerical results

Preferred directions in different orientations

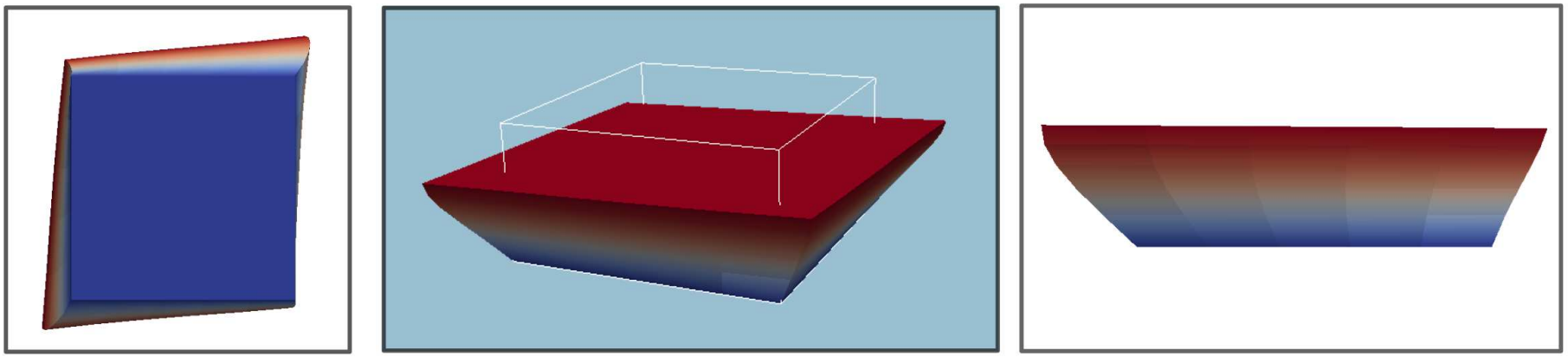


Observations

- Preferred direction in the bulk leads to "toughness" in that direction.

4. Summary and conclusions

Deformation of solid electrolyte due to preferred direction in 3-D is implemented and illustrated:



Results obtained

- A thermodynamically consistent formulation for constitutive relations has been considered and achieved.
- Directional effect due to polarization in the bulk of solid-electrolyte LIBs has been captured.
- Numerical implementation for 3-D model has been accomplished.
- Post-processing has been done for stress and strain.
- Illustration of the representative numerical results has been shown.

4. Summary and conclusions

Ongoing and future research directions

- Time-dependent implementation + Numerical analysis + Validations + Verification.
- Coupled electro-elastic problems could be taken into consideration.
- Bridging scale into quantum physics: Update information from quantum for continuum model.
- Dendrite formation: transport problem.