Mathematical modeling for all-solid-state batteries

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Contents

- Motivation and overview
- Mathematical modeling for thermodynamic-consistent electrolyte solid
- Numerical implementation, representative results and applications
- Summary and conclusions

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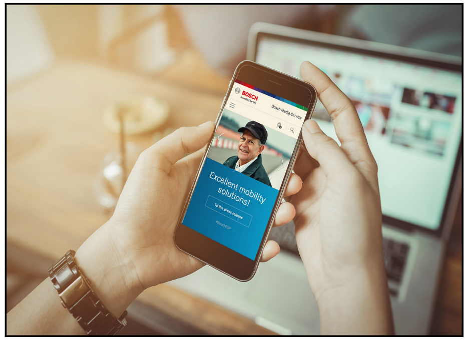
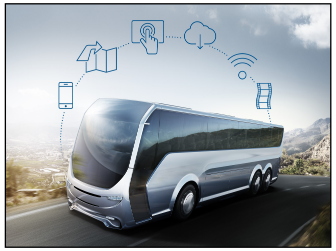
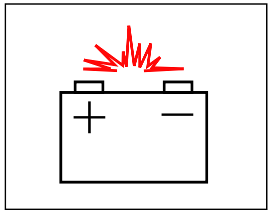
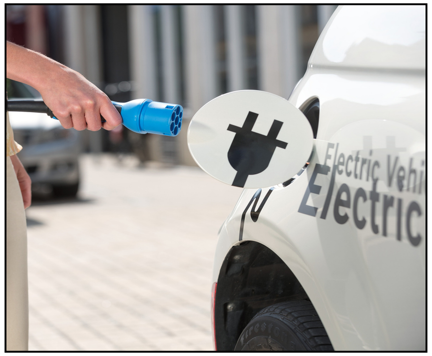
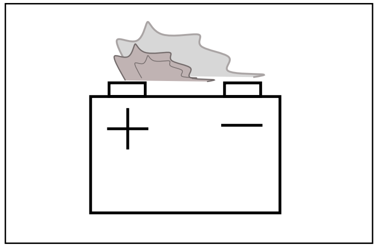
1. Motivation and overview

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:

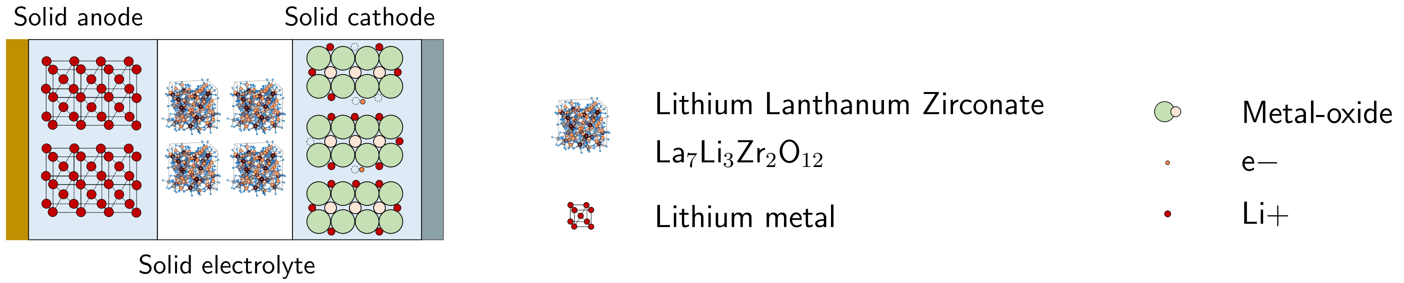
- Leakage of non-solid electrolyte could be observed under damage or after many cycles of charging/discharging.
- Non-solid electrolyte in LIBs may exhibit flammability or explosion due to its exposure to external media.

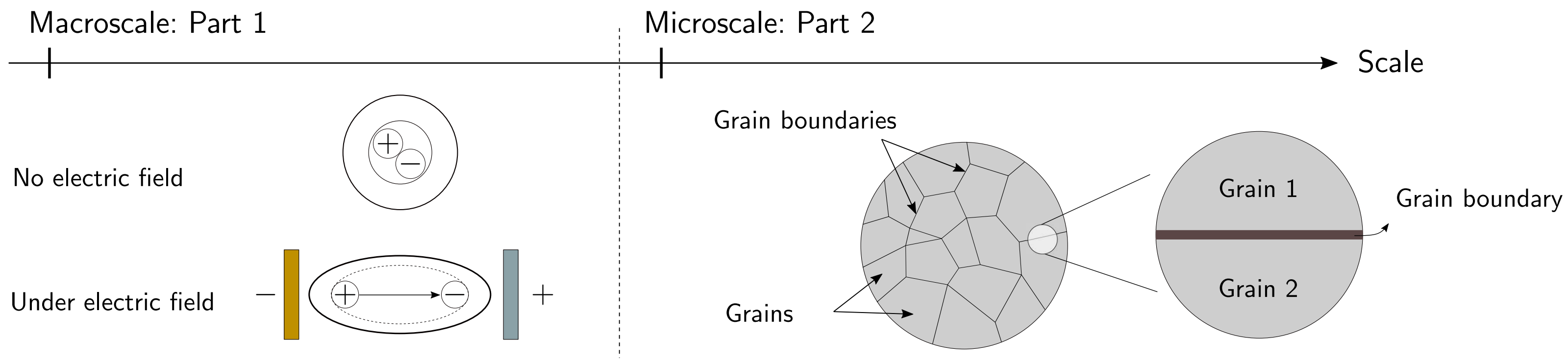
Why *all-solid-state* LIBs?

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

1. Motivation and overview

All-solid-state battery means material made of anode, cathode and electrolyte are all of solid.



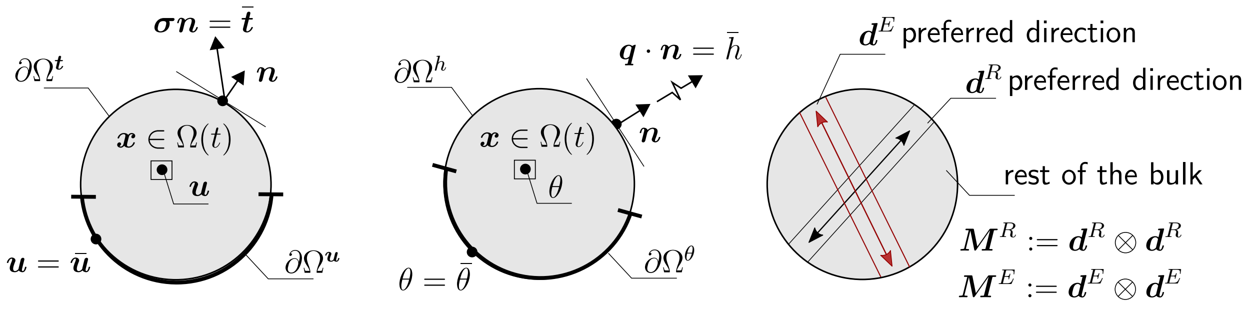


Goals:

- A mathematical model holds **thermodynamical consistency**.
- Part 1: Capture the **directional effect** due to polarization in the bulk of solid-electrolyte.
- Part 2: Describe the **distinctive behavior** of solid-electrolyte **across** grains and grain boundaries.
- **Numerical implementation** and illustrated **representative numerical results**.

2. Mathematical modeling for thermodynamic-consistent electrolyte solid

Primary fields



DISPLACEMENT FIELD $\boldsymbol{u}$ TEMPERATURE FIELD θ STRUCTURE TENSOR $\boldsymbol{M}^R \circ \boldsymbol{M}^E$

- **Primary field variables and their gradients**

Displacement field and temperature field

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

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

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

- **Kinematic relation:** Infinitesimal strain $\boldsymbol{\varepsilon}$

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

→ This kinematic relation is used for the current model of solid electrolyte.

2. Mathematical modeling for thermodynamic-consistent electrolyte solid

- **Summary of local balance laws:** Local balance laws governing the infinitesimal elasticity

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

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; $\boldsymbol{\sigma}$ Cauchy stress and $\boldsymbol{\varepsilon}$ infinitesimal strain.

- **Entropy inequality**

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

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

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

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

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

$\rightarrow$ Thermodynamic consistency is satisfied.

2. Mathematical modeling for thermodynamic-consistent electrolyte solid

• Free energy function

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

where

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

• Constitutive relations

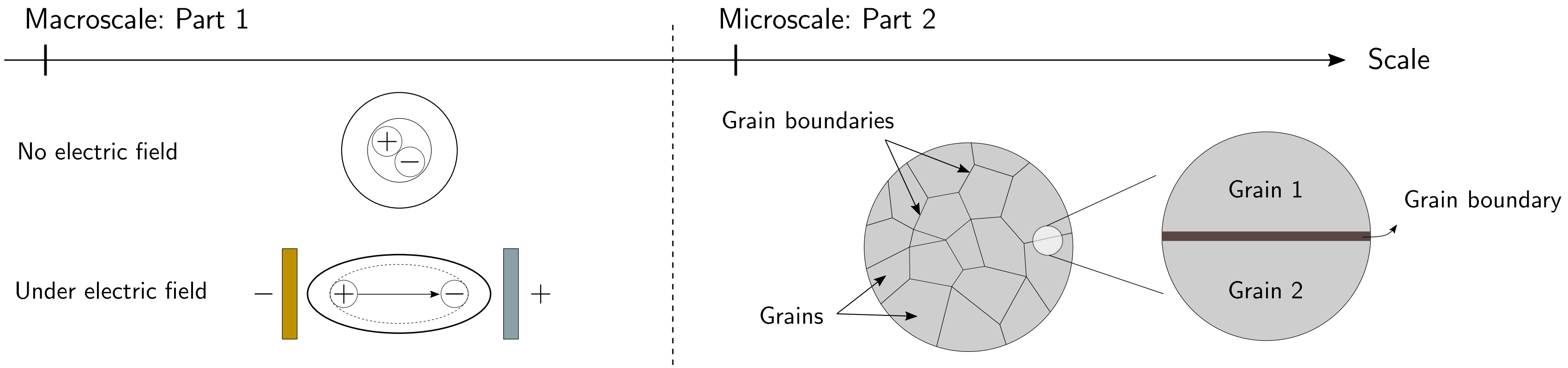
Stress tensor

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

Tangent modulus

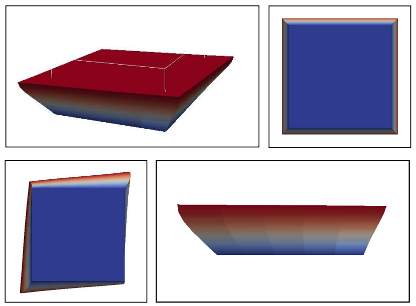
$$\boxed{\begin{aligned}\mathbb{C} &= \partial_{\varepsilon\varepsilon}\tilde{\Psi} \\ &= \partial_{\varepsilon}\boldsymbol{\sigma} \\ &= \partial_{\varepsilon\varepsilon}\tilde{\Psi}_{\text{isotropic}} + \partial_{\varepsilon\varepsilon}\tilde{\Psi}_{\text{anisotropic}} + \partial_{\varepsilon\varepsilon}\tilde{\Psi}_{\text{coupling}}\end{aligned}}$$

Overview of problems across length scale



Summary of part 1:

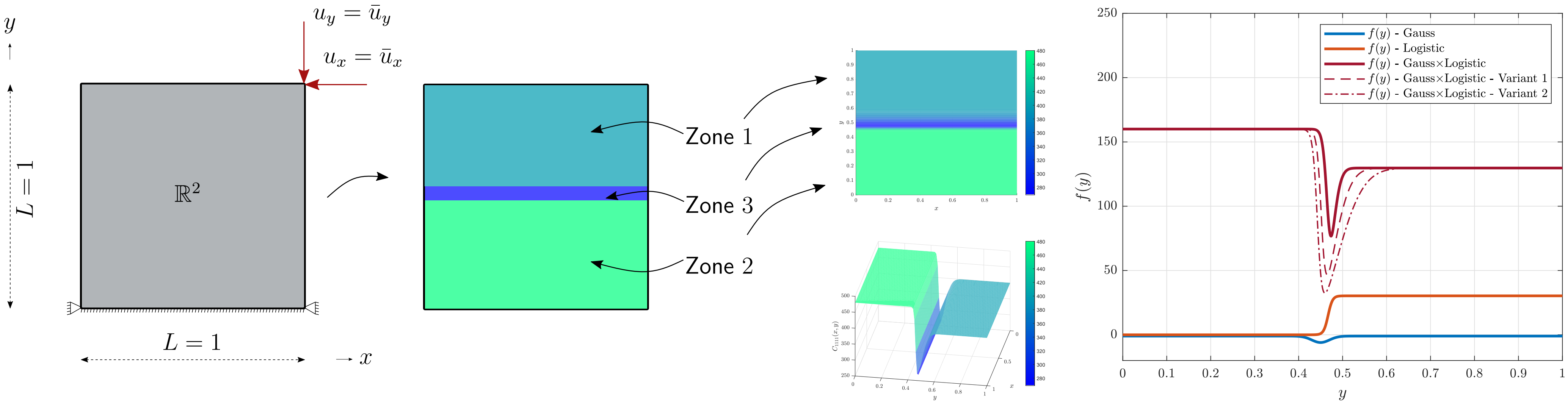
- Presented at SSD Workshop, Aachen
- Directional effect in macroscale
- Structure tensor $\boldsymbol{M} = \boldsymbol{d} \otimes \boldsymbol{d}$
- Numerical implementation in 3D



To discuss part 2 in the next slides:

- Microscale consideration
- Grain 1 behaves differently from Grain 2
- Mobility function for material properties f^{GL}
- Spatial dependence of tangent modulus $\mathbb{C}_{ijkl}$
- Connection of grain boundary and Griffith criterion

Setting up model: Definition of boundary conditions and Gauss-Logistic function f^{GL}



Boundary conditions | Distribution of material property | Plot of material properties | Gauss-Logistic function f^{GL}

- Dirichlet BC $\partial\Omega_{\boldsymbol{u}}$ is fixed at $\boldsymbol{u}_{\text{lower line}} = \boldsymbol{0}$ and $\boldsymbol{u}_{\text{top-right corner}} = \bar{\boldsymbol{u}}$; the rest is applied by Neumann BC: $\boldsymbol{t} = \bar{\boldsymbol{t}}$.
- Physical domain Ω includes 3 zones: Zone 1 and 2 aimed for *grains*; Zone 3 for *grain boundary*.
- The two Lamé functions $f_\lambda^{GL}(y)$ and $f_\mu^{GL}(y)$ depend on space and govern material properties of the bulk.
- Gauss-Logistic function $f^{GL}(y; \alpha, \beta, \gamma, \nu, \tau, \zeta)$ defines the two Lamé functions:

$$f^{GL}(y) = -\underbrace{\left(\alpha \exp\left(-\frac{(y-\beta)^2}{2 \times \tau^2}\right) + 1\right)}_{=f^G(y)} \times \underbrace{\left(\frac{1}{\zeta + \exp\left(-\gamma \times (y - \beta)\right)}\right)}_{=f^L(y)} + \nu$$

3. Numerical implementation, representative results and applications (Part 2)

Problem to solve: Find displacement u_i such that

- **Strong form**: Governing PDE for vector-unknown displacement $\boldsymbol{u}$ with sufficient boundary conditions given

$$\nabla \cdot \mathbb{C}^{f^{GL}}(y) \nabla_s \boldsymbol{u} + \rho \boldsymbol{b} = \boldsymbol{0}$$

which is a system of interlocking unknowns u_i and written in index notation as follows

PDE	$\sigma_{ij,j} + \rho b_i = 0$
Constitutive relation	$\sigma_{ij} = \mathbb{C}^{f^{GL}}_{ijkl}(y)\ \varepsilon_{kl}$
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	$\sigma_{ij} n_j = \bar{t}_i$ on $\partial\Omega_{t_i}$

where $\mathbb{C}^{f^{GL}}_{ijkl}(y) \mathrel{\widehat{=}} \hat{\mathbb{C}}(f^{GL}_{\lambda}(y), f^{GL}_{\mu}(y))$

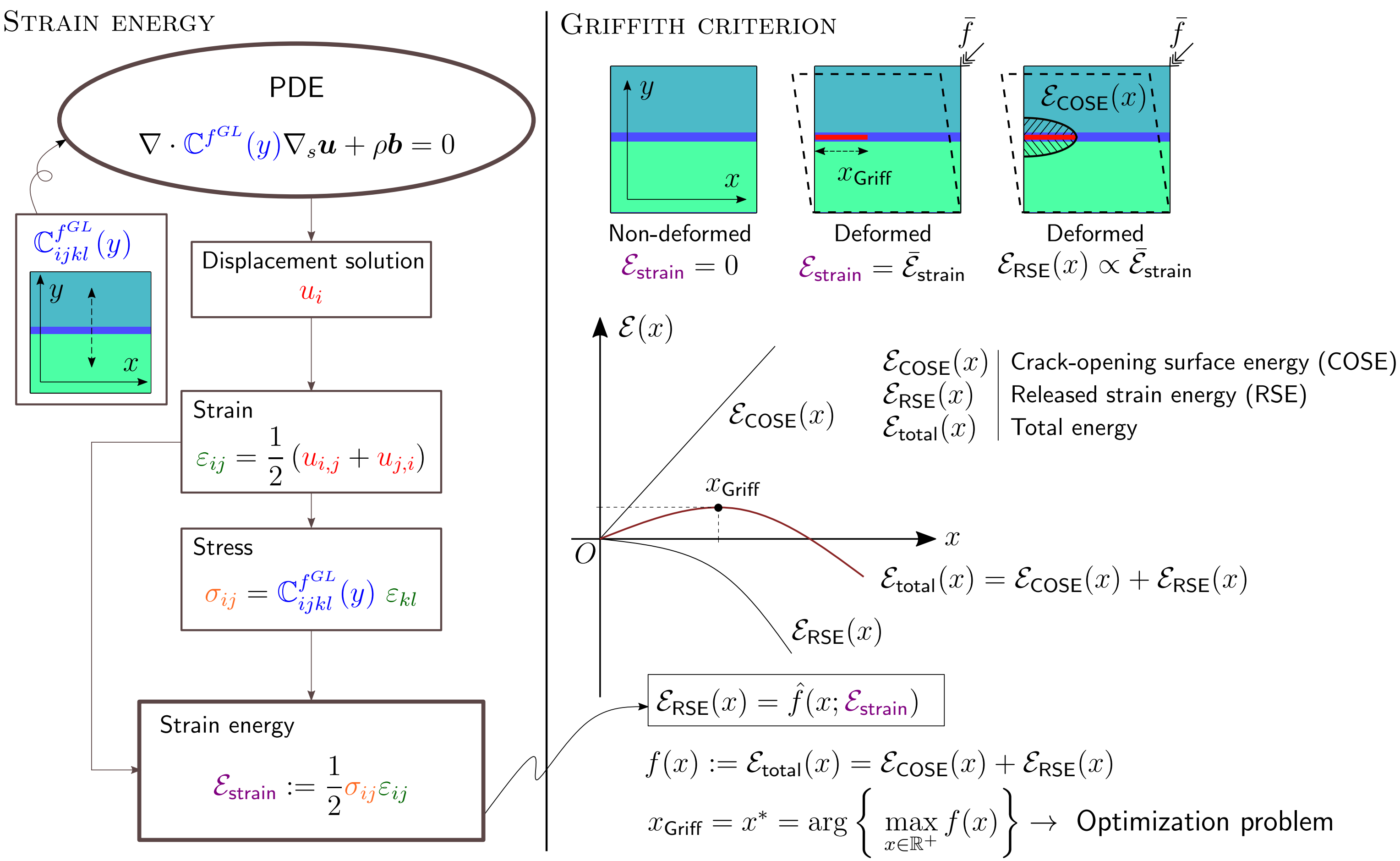
- **Weak form**: Seeking solutions numerically

$$\int_{\Omega^e} \delta u^h_{i,j}\ \mathbb{C}^{f^{GL}}_{ijkl}(y)\ u^h_{k,l}\ d\Omega^e = \int_{\Omega^e} \delta u^h_i\ \rho b_i\ d\Omega^e + \int_{\partial\Omega^e_{t_i}} \delta u^h_i\ \bar{t}_i\ d\partial\Omega^e$$

$\rightarrow$ The tangent modulus $\mathbb{C}^{f^{GL}}_{ijkl}(y)$ is a 4th order tensor and its entries are **spatially dependent** in y-direction.

3. Numerical implementation, representative results and applications (Part 2)

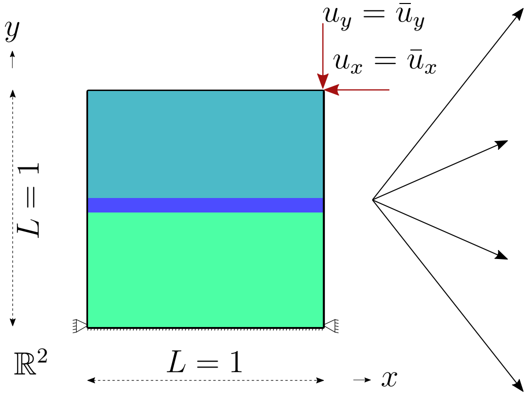
Applications: Strain energy $\mathcal{E}_{\text{strain}}$ and Griffith criterion x_{Griff}



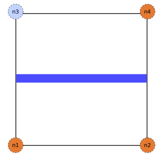
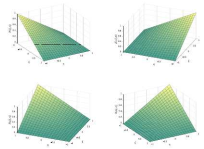
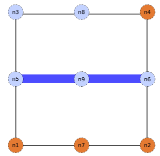
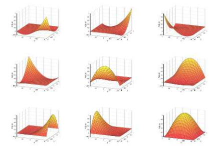
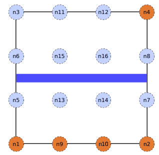
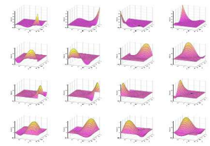
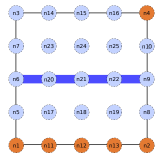
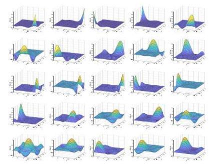
→ Strain energy $\mathcal{E}_{\text{strain}}$ offers essential information for Griffith criterion x_{Griff} analysis.

→ Griffith criterion x_{Griff} is the **critical virtual crack length**, which is a useful measure for solid material failure.

Numerical approach: Discretization



Boundary conditions

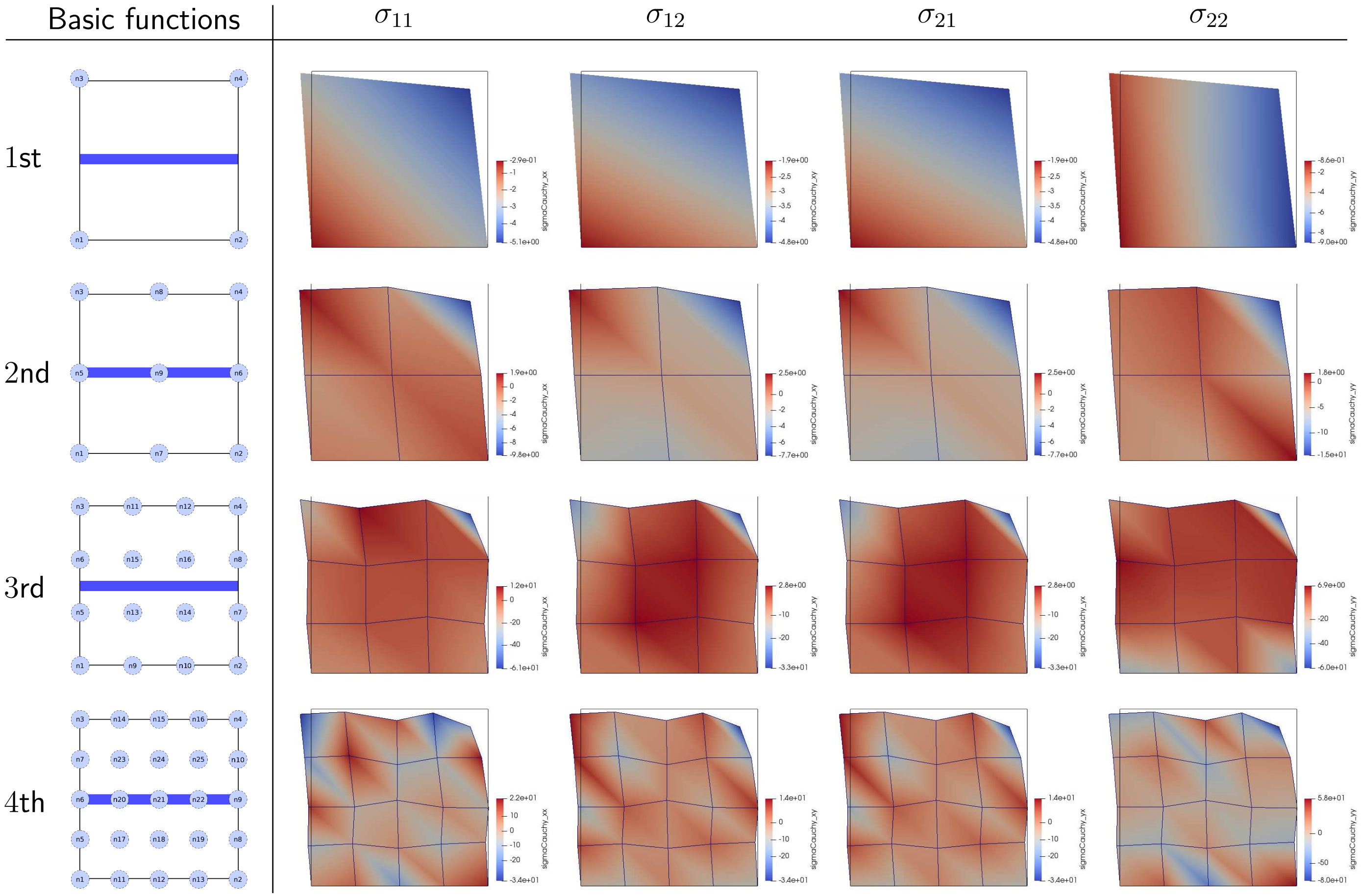
Order of basis functions		$\mathcal{N}^{\Omega^e}_{\text{DOFs}}$	$\left(K^{\alpha\beta}_{\mathrm{e}\,ik}\right)_{\text{size}}$	$\mathcal{N}_{\text{integrals}}$	$\left(\mathcal{N}_{\text{integrals}}\right)^{\text{Matlab}}_{\text{time}}$	Plot of basis functions
Linear		8	$K_{8\times 8}$	64	$\sim$ 20 mins	
Quadratic		18	$K_{18\times 18}$	324	$\sim$ 40 mins	
Cubic		32	$K_{32\times 32}$	1024	$\sim$ 3 hours	
Quartic		50	$K_{50\times 50}$	2500	$\sim$ 6 hours	

- Derivation of weak form leads to a system of linear algebraic equations: $\boldsymbol{K}^e \boldsymbol{u}^e = \boldsymbol{f}^e \rightarrow$ Solve for $\boldsymbol{u}^e$.
- Element stiffness matrix $\boldsymbol{K}^e$: known; approximated by Gauss quadrature rule; index notation implies $4+2$ *for*-loop:

$$K^{\alpha\beta}_{\mathrm{e}\,ik} = \int_{\Omega^\xi} \left(\mathcal{L}^\alpha_1 \, \mathbb{C}^{fGL}_{i1k1}(y) \, \mathcal{R}^\beta_1 + \mathcal{L}^\alpha_1 \, \mathbb{C}^{fGL}_{i1k2}(y) \, \mathcal{R}^\beta_2 + \mathcal{L}^\alpha_2 \, \mathbb{C}^{fGL}_{i2k1}(y) \, \mathcal{R}^\beta_1 + \mathcal{L}^\alpha_2 \, \mathbb{C}^{fGL}_{i2k2}(y) \, \mathcal{R}^\beta_2 \right) \det(\boldsymbol{J}) \, d\Omega^\xi$$

where $\mathcal{L}^\alpha_j$ and $\mathcal{R}^\beta_l$ are gradients of basis functions at node α^{th} and β^{th}, respectively.

Stress solution: $\sigma_{ij} = \mathbb{C}^{f^{GL}}_{ijkl}(y)\ \varepsilon_{kl} = \mathbb{C}^{f^{GL}}_{ijkl}(y)\ \frac{1}{2}\sum_{\alpha=1}^{\mathcal{N}^{\Omega^e}_{\text{node}}} \left(\sum_{L=1}^{\mathcal{N}^{\Omega_{\text{node}}}_{\text{dof}}} N^{\alpha}_{,\xi_L}\xi_{L,x_k}u^{\alpha}_k + \sum_{K=1}^{\mathcal{N}^{\Omega_{\text{node}}}_{\text{dof}}} N^{\alpha}_{,\xi_K}\xi_{K,x_l}u^{\alpha}_l\right)$



Observations
- Stress solution σ_{ij} is of interest as it links to Gauss-Logistic-based tangent modulus $\mathbb{C}^{f^{GL}}_{ijkl}(y)$.
- Color gradient illustrates solution of stress distributed over physical domain Ω.

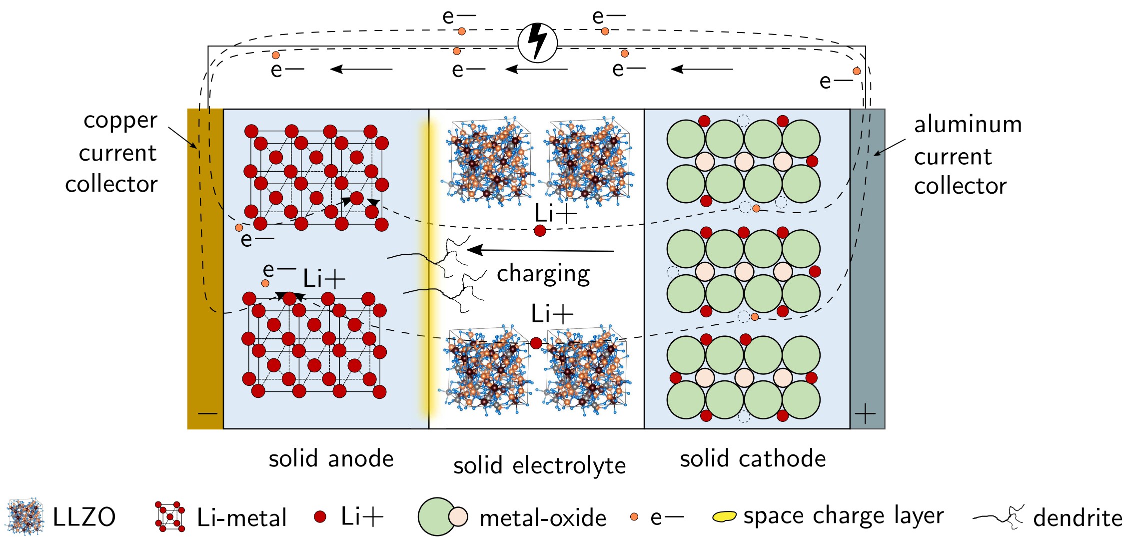
4. Summary and conclusions

Results obtained

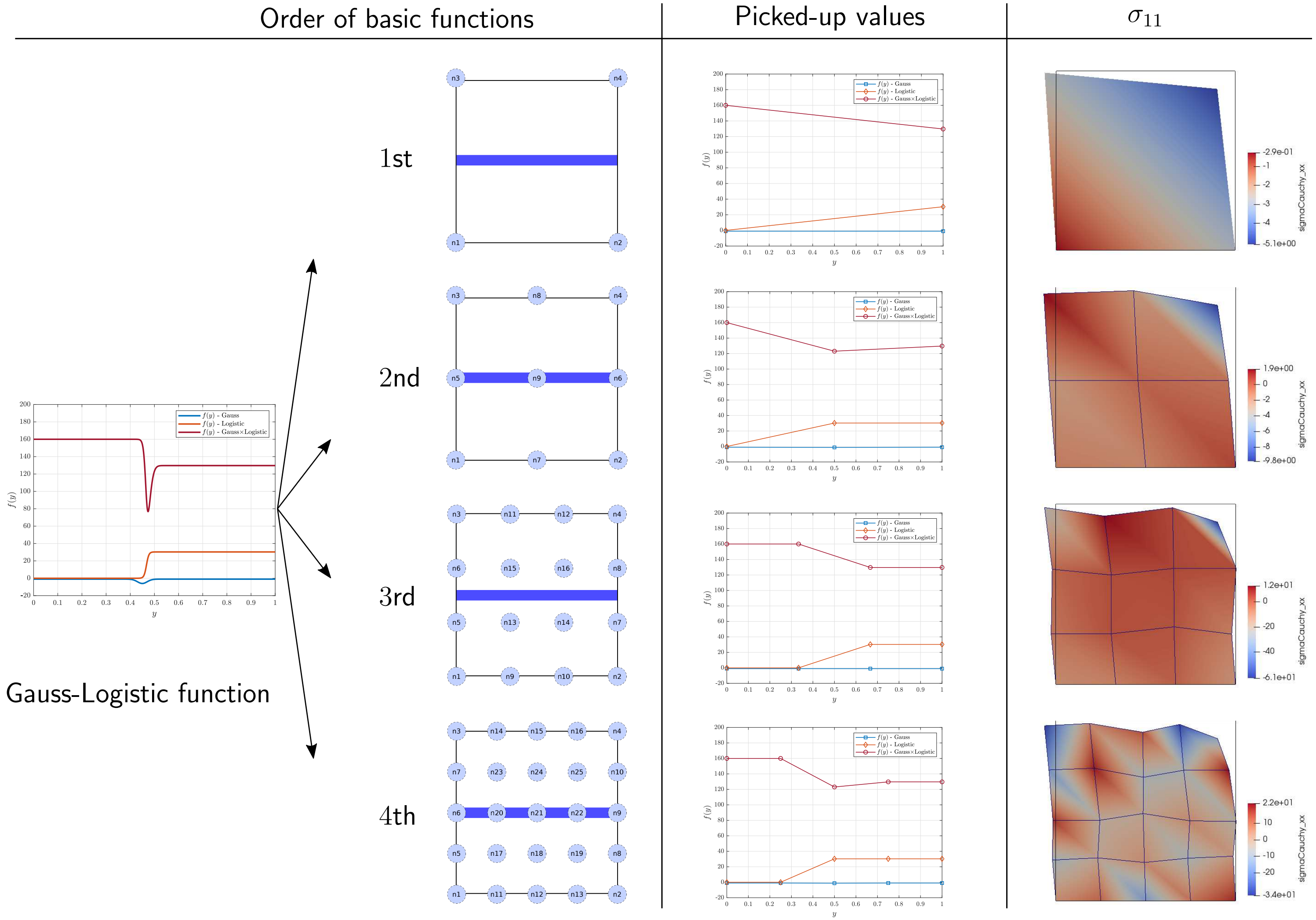
- Directional effect has been modeled (Part 1) and spatial dependence problem has been described (Part 2).
- Post-processing done for stress, strain and strain energy, which is essential for Griffith criterion analysis.

Ongoing and future research directions

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



Backup: Stress solution explanation (Part 2)



Possibilities

- Increase the order of basis functions.
- Distribute more nodes at and surrounding *areas of much-more-deformation*.