

MATHEMATICAL MODELLING FOR ALL-SOLID-STATE BATTERY: (SE|SSE)-INTERFACE

Tuan Vo^{a,b,†}, Claas Hüter^b, Stefanie Braun^a, Manuel Torrilhon^a

^aDepartment of Mathematics, Applied and Computational Mathematics (ACoM), RWTH Aachen University, Schinkelstraße 02, 52062 Aachen, Germany

^bInstitute of Energy and Climate Research (IEK-2), Forschungszentrum Jülich, Wilhelm-Johnen-Straße, 52428 Jülich, Germany

Mathematical modelling for the next-generation All-solid-state batteries: Nucleation (SE|SSE)^(*)-interface

Rechargeable Lithium-ion battery (LIB) is at the heart of every electric vehicle (EV), portable electronic device, and energy storage system [1]. Nowadays, LIBs enable human life more efficient and help to solve global environment issues thanks to EVs' zero emission. However, conventional LIB (c-LIB) is sensible to temperature and pressure, hence, flammable and explosive, which is **undesirable**. This bottleneck is mainly due to **liquid-based electrolyte** found in c-LIBs.

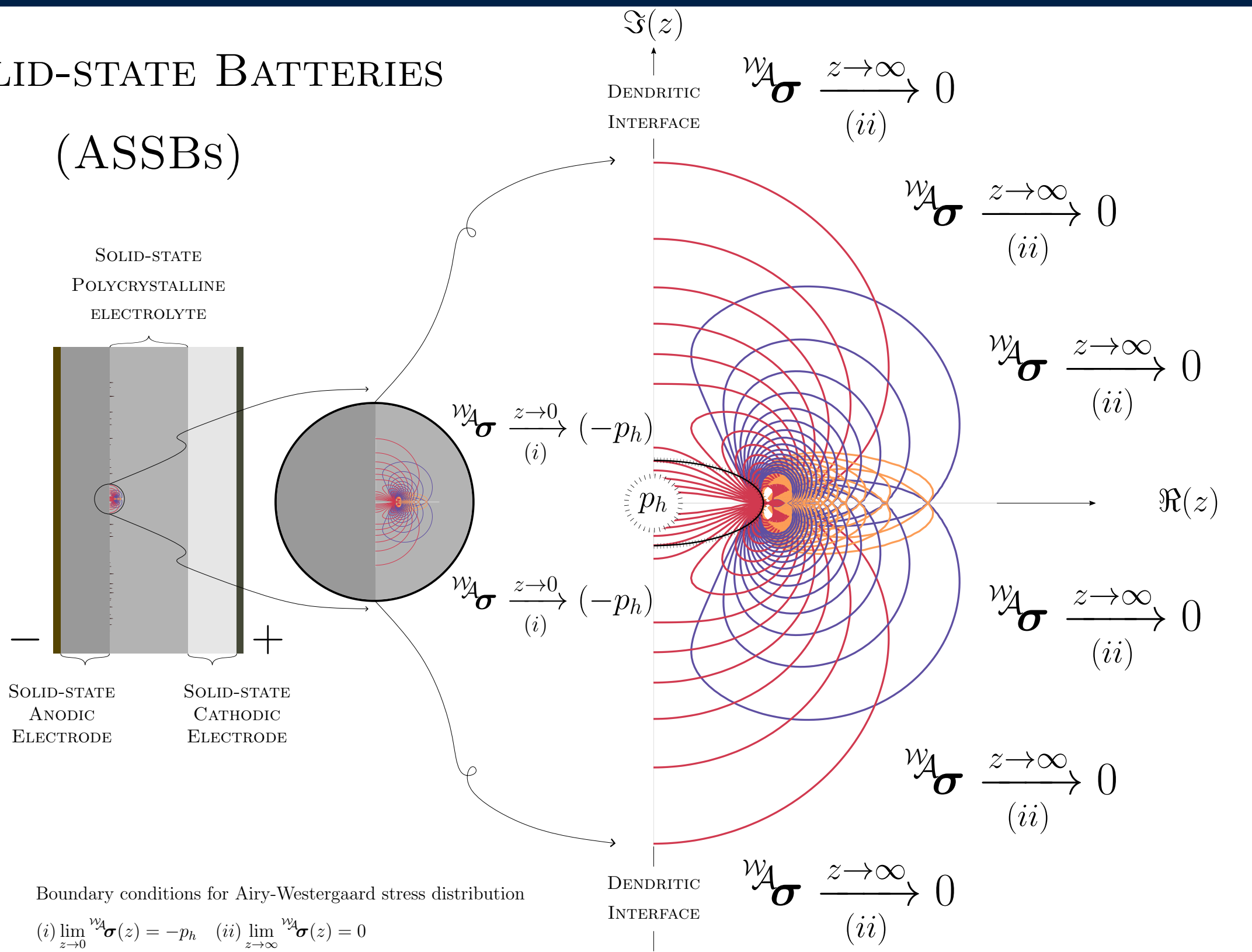
All-solid-state battery (ASSB) is one of promising candidates to overcome bottlenecks of c-LIBs. Thanks to **solid-state electrolyte** (SSE), ASSB is highly stable towards temperature and pressure. Nevertheless, Li-metal dendrite triggered at (SE|SSE)-interface [5] is the main drawback of ASSB since these dendritic threads extrapolate into SSE grain boundary network, causing crevice, degradation of ionic conductivity, and the probability of short-circuit, which is **unfavorable**.

Next-generation All-solid-state battery (ng-ASSB) with a consideration of **nucleation criterion** defined by

$$a_{\text{Griffith}} := a^* = \arg \min_{a \in \mathbb{R}} \iiint_{\Omega} f(a, \mathbf{u}, \theta; \lambda, \mu, \mathbf{d}^R \otimes \mathbf{d}^R) d\Omega - \iint_{\Gamma} f(a; \gamma) d\Gamma \Big|_{\mathbf{u}^{(s)}}$$

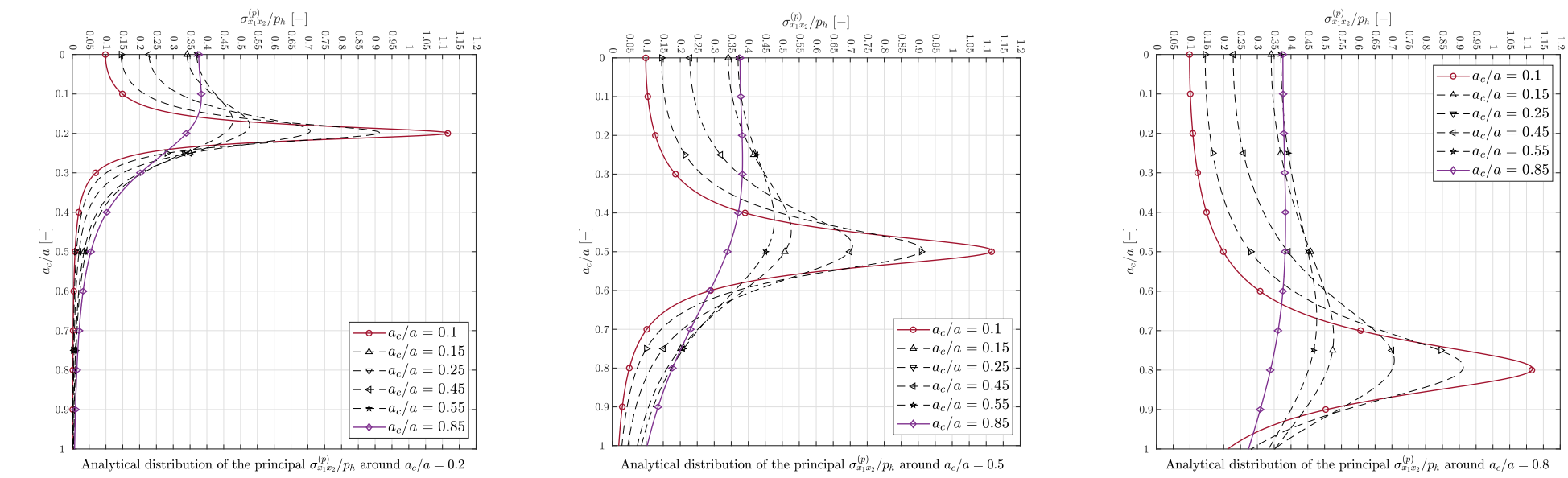
where \mathbf{u} displacement field, θ temperature field, a crevice length, λ, μ Lamé constants, $\mathbf{d}^R \otimes \mathbf{d}^R$ embedded misorientation structural tensor, and γ cracking-surface energy density, **can help** to improve ASSB performance.

ALL-SOLID-STATE BATTERIES (ASSBs)



(SE|SSE)-Interface Analysis

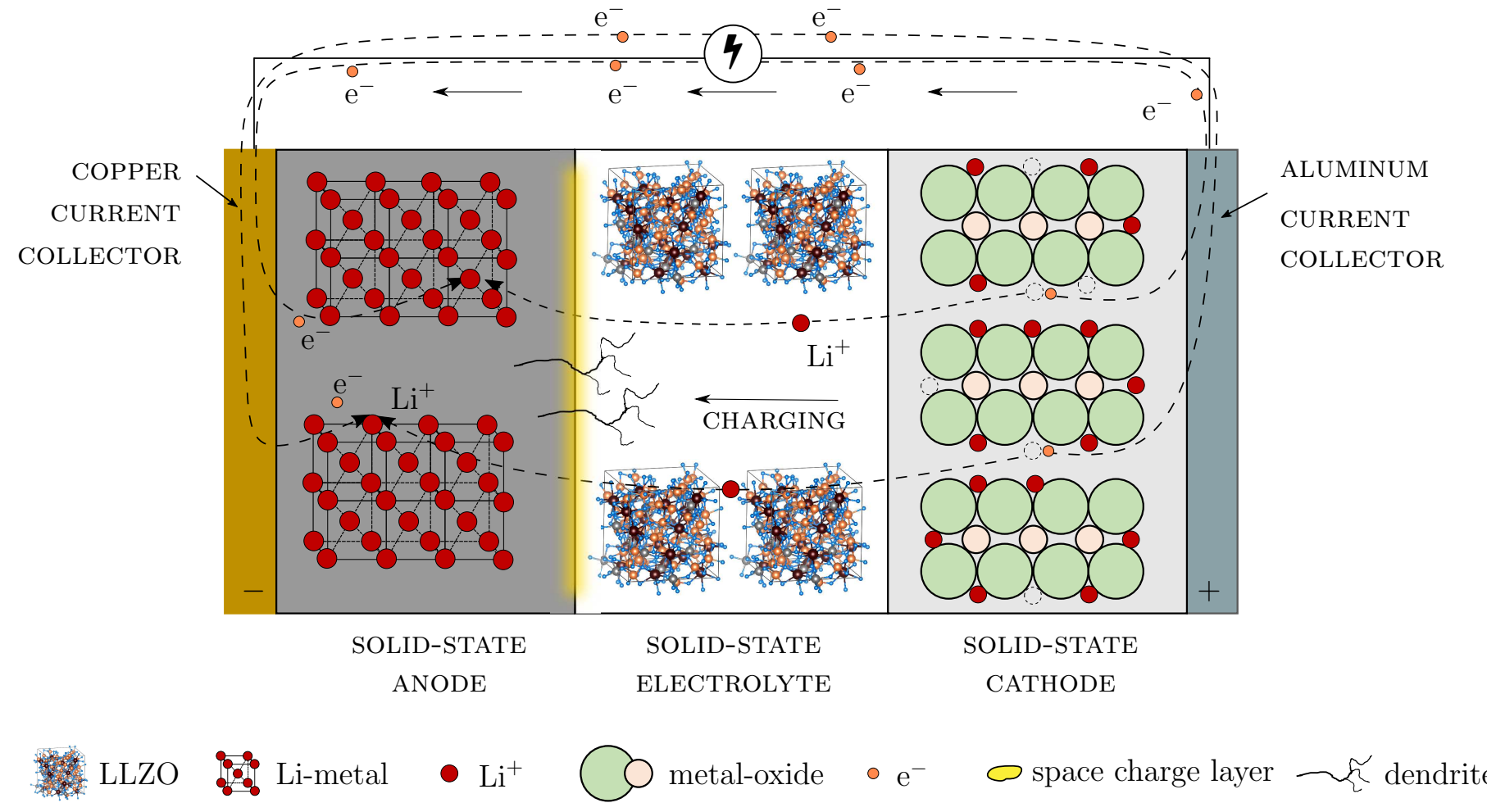
Interface between solid electrode and solid-state electrolyte (SE|SSE) taking place at space charge layer (SCL) [2] found in ASSBs critically exhibits mechanical and electrochemical instability [3]. This evidence points directly to the fact that the soft metallic Li anode is erroneously prone to triggering dendrites, under cycles of electric charge & discharge [5].



Distribution: ana. max. shear stress $w_A \sigma^{\text{II}}_{x_1 x_2}$ around crack tip a_c .

Next-generation All-solid-state battery

Nucleation criterion governs the instable (SE|SSE)-interface [3]

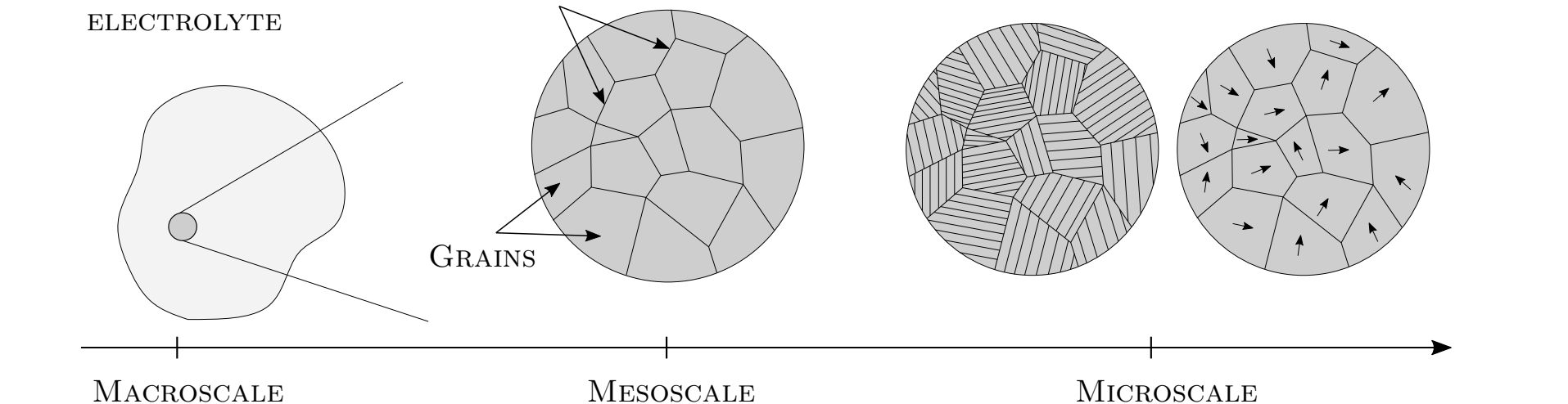


- ✓ **Thermodynamic consistency** is satisfied, followed by [2].
- ✓ **Closure** $\bar{\Omega}$ is fulfilled by 15 moments, followed by [4].

Embedded structural-tensor in SSE

Polycrystalline garnet-type SSE [5] such as LLZO exhibit grain boundary network, and grains with variation of {size, shape} under microscopic observation. Hence, this microstructure is potentially prone to nuances of destruction.

$$\mathbf{M} = \mathbf{d}_{G_1}^R \otimes \mathbf{d}_{G_2}^R \text{ given by } \mathbb{G} := \{\mathbf{Q}_{\parallel a}, \mathbf{Q}_{\perp a}\} \subset \mathcal{O}(3).$$



Consequently, dendrites contribute to degradation of ionic conductivity and tiny-cracks tracing along grain boundaries.

Nucleation interface: Taking place at the critically dendritic (SE|SSE)-interface

Coupled fields: Displacement field \mathbf{u} and temperature field θ ; structural tensor \mathbf{M}

$$\mathbf{u} : \begin{cases} \Omega \times \mathbb{R}_+ \rightarrow \mathbb{R}^3, \\ (\mathbf{x}, t) \mapsto \mathbf{u}(\mathbf{x}, t), \end{cases} \quad \theta : \begin{cases} \Omega \times \mathbb{R}_+ \rightarrow \mathbb{R}, \\ (\mathbf{x}, t) \mapsto \theta(\mathbf{x}, t), \end{cases} \quad \mathbf{M}_{i=1, \dots, N}^{\{RR, RE\}} : \begin{cases} \mathbf{d}_{\text{Grain } i}^R \otimes \mathbf{d}_{\text{Grain } i}^R \\ \mathbf{d}_{\text{Grain } i}^R \otimes \mathbf{d}^E \end{cases}$$

Governing conservation equations

$$\frac{d}{dt} \int_{\Omega} (\cdot) d\Omega = \int_{\Omega} (\cdot)^{\text{action}} d\Omega + \int_{\partial\Omega} (\cdot)^{\text{action}} d\partial\Omega + \int_{\Omega} (\cdot)^{\text{production (+/-)}} d\Omega$$

used to describe balance of mass, conservation of linear momentum, conservation of angular momentum, and conservation of energy with $\rho(\mathbf{x}, t)$ is mass density per unit volume (puv); $\mathbf{b}(\mathbf{x}, t)$ body force puv; $\mathbf{v}(\mathbf{x}, t)$ velocity; $e(\mathbf{x}, t)$ internal energy puv; $\mathbf{q}(\mathbf{x}, t)$ heat flux; $r(\mathbf{x}, t)$ heat source puv; $\boldsymbol{\sigma}$ Cauchy stress and $\boldsymbol{\varepsilon}$ infinitesimal strain. Then, the governing partial differential equation (PDE) of deformation takes the form

$$\partial_t \mathbf{u} + \nabla \cdot \left(\mathbb{C}^{\text{fallocation}}(\lambda, \mu, \mathbf{d}_{G_i}^R, i=1, \dots, N; \mathbf{d}^E; \mathbf{x}) : \nabla \mathbf{u}^{(s)} \right) + \rho \mathbf{b} = -\rho \nabla V_e,$$

where $V_e : \mathbb{R}^3 \rightarrow \mathbb{R}$ is the electric potential applied globally on ASSB. Due to nature setting of ASSB taking the form (SE|SSE|SE) the electric potential becomes uniform.

Strain energy is based on the deformation of SSE due to dendrite formation at (SE|SSE)-interface

$$\iiint_{\Omega} f(a, \mathbf{u}; \lambda, \mu, \mathbf{d} \otimes \mathbf{d}) d\Omega$$

Surface energy is analyzed based on the open crevice cracking at (SE|SSE)-interface affected by prescribed pressure

$$\iint_{\Gamma} f(a; \gamma) d\Gamma$$

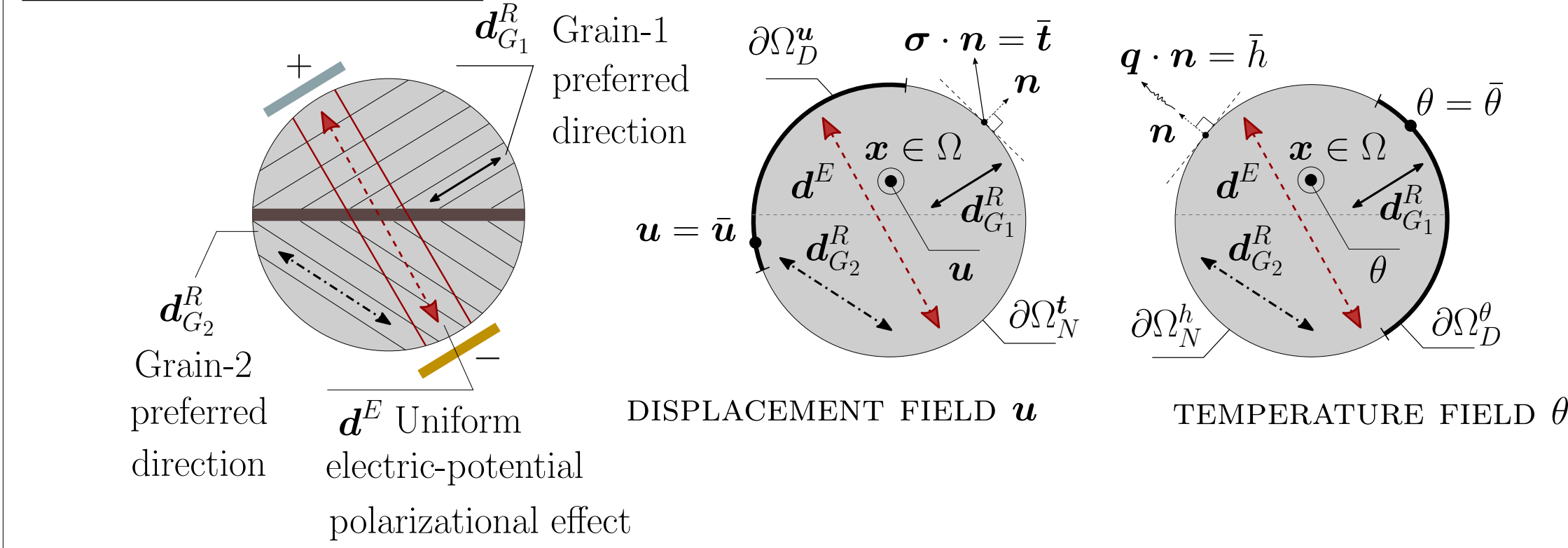
Therefore, the governing problem of dendritic nucleation at (SE|SSE) takes the form

$$\partial_t \bar{\mathbf{u}} + \nabla \cdot \left(\mathbb{C}^{\text{fallocation}}(\lambda, \mu, \mathbf{d}_{G_i}^R, i=1, \dots, N; \mathbf{d}^E; \mathbf{x}) : \nabla \mathbf{u}^{(s)} \right) + \rho \mathbf{b} = -\rho \nabla V_e, \quad (1)$$

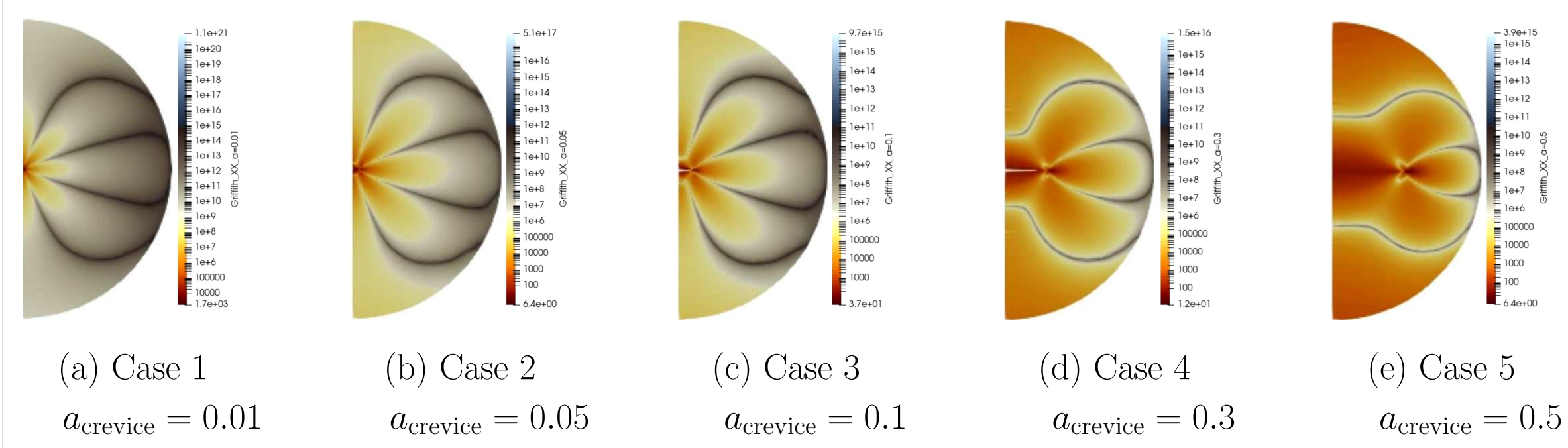
$$\text{s.t. } a_{\text{Griffith}} := a^* = \arg \min_{a \in \mathbb{R}} \iiint_{\Omega} f(a, \mathbf{u}, \theta; \lambda, \mu, \mathbf{d} \otimes \mathbf{d}) d\Omega - \iint_{\Gamma} f(a; \gamma) d\Gamma \Big|_{\bar{\mathbf{u}}} \quad (2)$$

where deformation $\bar{\mathbf{u}}$ is (i) based on (1), and then (ii) for *Griffith*-analysis in (2).

Boundary conditions



Numerical spectral of *Griffith* criterion in x -direction at (SE|SSE) yields



where a sample of 5 cases with various prescribed crevice length is studied.

Analysis: Airy-Westergaard function used for stress analysis: (i) max. shear stress and (ii) principal stresses

$$w_A : \begin{cases} \mathbb{C} \rightarrow \mathbb{C}, \\ z \mapsto w_A(z) := \Re \left(\oint_{\Gamma} \mathcal{K}^{(*)} dz \right) + x_2 \Im \left(\oint_{\Gamma} \mathcal{K}^{(*)} dz \right), \end{cases} \quad \mathcal{K}^{(*)} : \begin{cases} \mathbb{C} \rightarrow \mathbb{C}, \\ z \mapsto \mathcal{K}^{(*)} := -p_h + p_h / \sqrt{1 - a^2/z^2}, \end{cases}$$

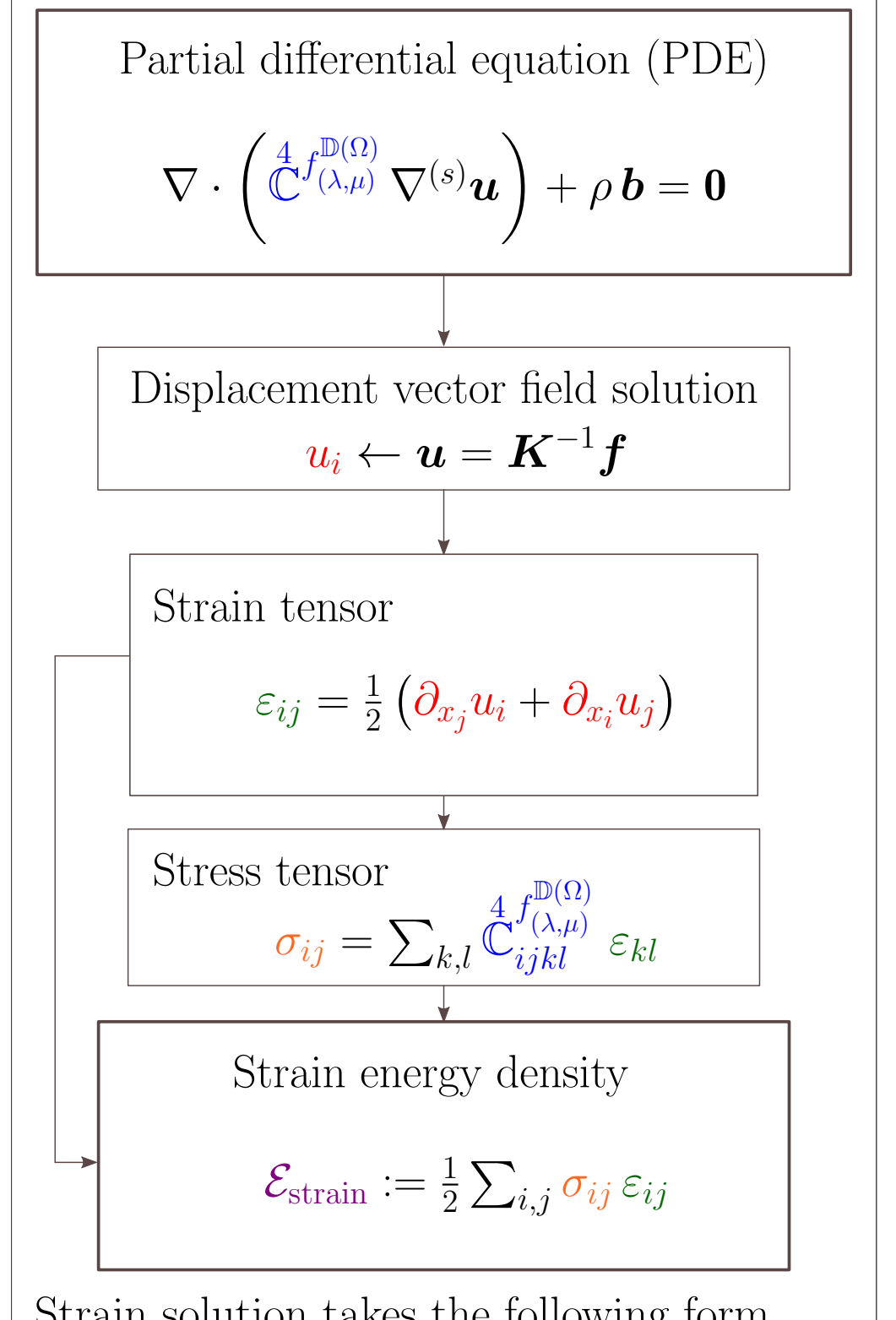
where a the crevice length, p_h pressure at the opening crevice on dendritic interface, and $\forall \{p_h, a\} \in \mathbb{R}_+$.

Numerics \rightarrow FEM: element matrix \mathbf{K}^e approx. by *Gauss quadrature*; indices imply $4 + 2 = 6$ for-loop:

$$\mathbf{K}_{ik}^{e\alpha\beta} = \int_{\Omega^\xi} \left(\mathcal{L}_1^\alpha \mathbb{C}_{i1k1}^{fGL}(\mathbf{x}) \mathcal{R}_1^\beta + \mathcal{L}_1^\alpha \mathbb{C}_{i1k2}^{fGL}(\mathbf{x}) \mathcal{R}_2^\beta + \mathcal{L}_2^\alpha \mathbb{C}_{i2k1}^{fGL}(\mathbf{x}) \mathcal{R}_1^\beta + \mathcal{L}_2^\alpha \mathbb{C}_{i2k2}^{fGL}(\mathbf{x}) \mathcal{R}_2^\beta \right) \det(\mathbf{J}) d\Omega^\xi$$

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

FEM: Strain energy density



Strain solution takes the following form

$$\frac{1}{2} \sum_{\alpha=1}^{N_{\text{node}}} \sum_{L=1}^{N_{\text{GL}}} \sum_{k=1}^{N_{\text{node}}} \mathcal{L}_{kL}^{\alpha} \mathcal{R}_k^{\beta} u_k^{\alpha} + \sum_{K=1}^{N_{\text{node}}} \mathcal{L}_{K1}^{\alpha} \mathcal{R}_K^{\beta} u_K^{\alpha}$$

Contact

Tuan Vo
vo@acom.rwth-aachen.de



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