

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

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## Mathematical modelling for the next-generation All-solid-state batteries: Nucleation (SE|SSE)<sup>(\*)</sup>-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.

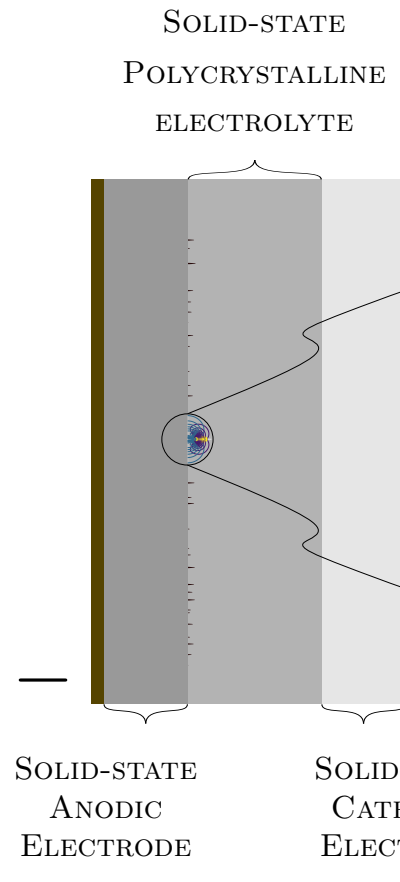
**All-solid-state battery** (ASSB) is one of promising candidates to overcome bottlenecks of c-LIBs. Thanks to **solid-state electrolyte** (SSE), ASSB is highly stable towards temperature and pressure. Nevertheless, Li-metal dendrite triggered at (SE|SSE)-interface [5] is the main drawback of ASSB since 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

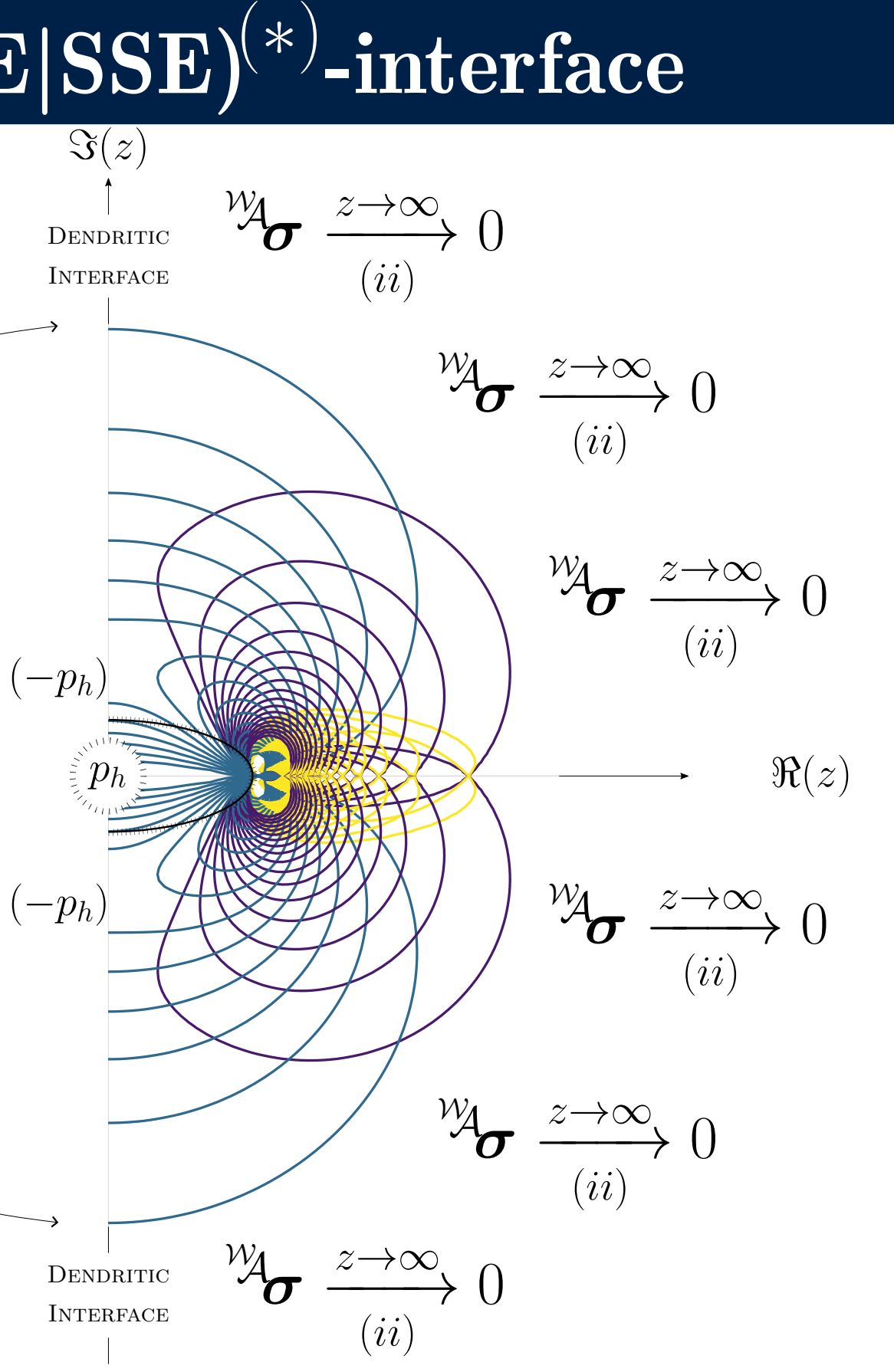
$$a_{\text{Griffith}} := a^* = \arg \min_{a \in \mathbb{R}} \left( \iint_{\Omega} f(a, \mathbf{u}, \theta; \lambda, \mu, \mathbf{d}^{(*)} \otimes \mathbf{d}^{(*)}) d\Omega - \iint_{\Gamma} f(a; \gamma) d\Gamma \right) \Big|_{\bar{\mathbf{u}}}$$

where  $\mathbf{u}$  displacement field,  $\theta$  temperature field,  $a$  crevice length,  $\lambda, \mu$  Lamé constants,  $\mathbf{d}^{(*)} \otimes \mathbf{d}^{(*)}$  embedded misorientation structural tensor, and  $\gamma$  cracking-surface energy density, can help to improve ASSB performance.

ALL-SOLID-STATE BATTERIES (ASSBs)

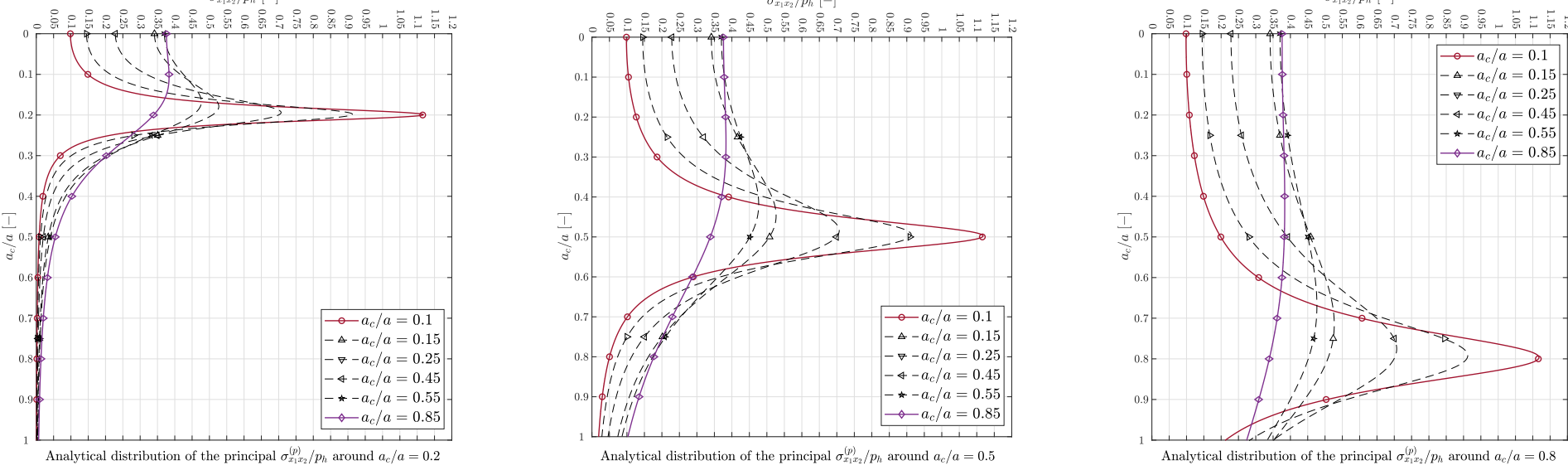


Boundary conditions for Airy-Westergaard stress distribution  
(i)  $\lim_{z \rightarrow 0} \mathcal{V}_A \sigma(z) = -p_h$  (ii)  $\lim_{z \rightarrow \infty} \mathcal{V}_A \sigma(z) = 0$



### (SE|SSE)-Interface Analysis

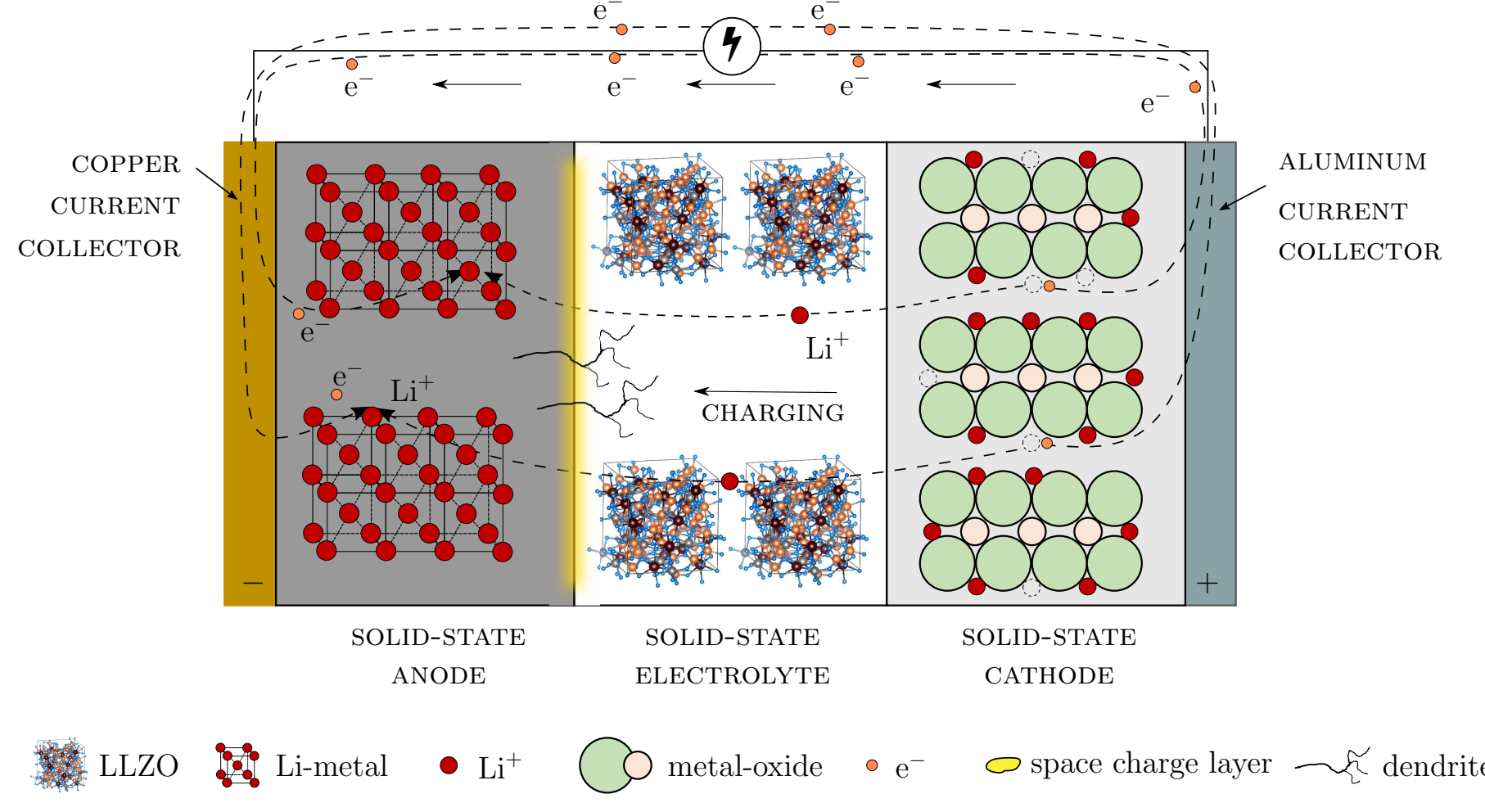
**Interface** between solid electrode and solid-state electrolyte (SE|SSE) taking place at space charge layer (SCL) [2] found in ASSBs critically exhibits mechanical and electrochemical instability [3]. This evidence points directly to the fact that the soft metallic Li anode is erroneously prone to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



Distribution: ana. max. shear stress  $\mathcal{V}_A \sigma_{x_1 x_2}$  around crack tip  $a_c$ .

### Next-generation All-solid-state battery

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

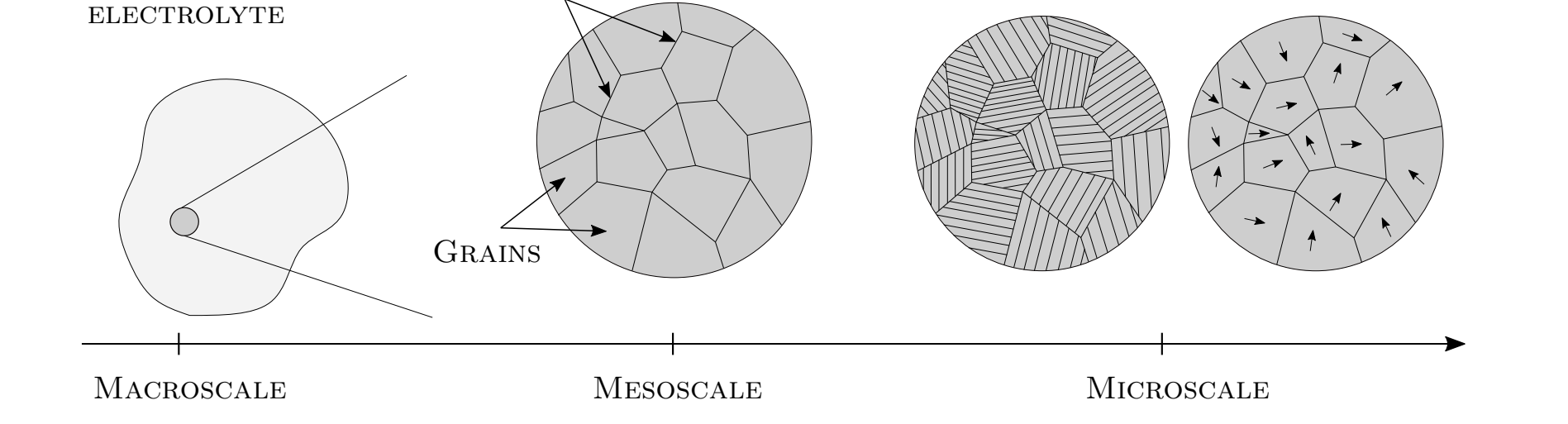


- ✓ **Thermodynamic consistency** is satisfied, followed by [2].
- ✓ **Closure**  $\bar{\Omega}$  is fulfilled by 15 moments, followed by [4].

### 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.

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



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  $\theta$ ; 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) for the thermodynamically consistent coupled problem with deformation field  $\mathbf{u}$  as its variable 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

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

**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

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

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

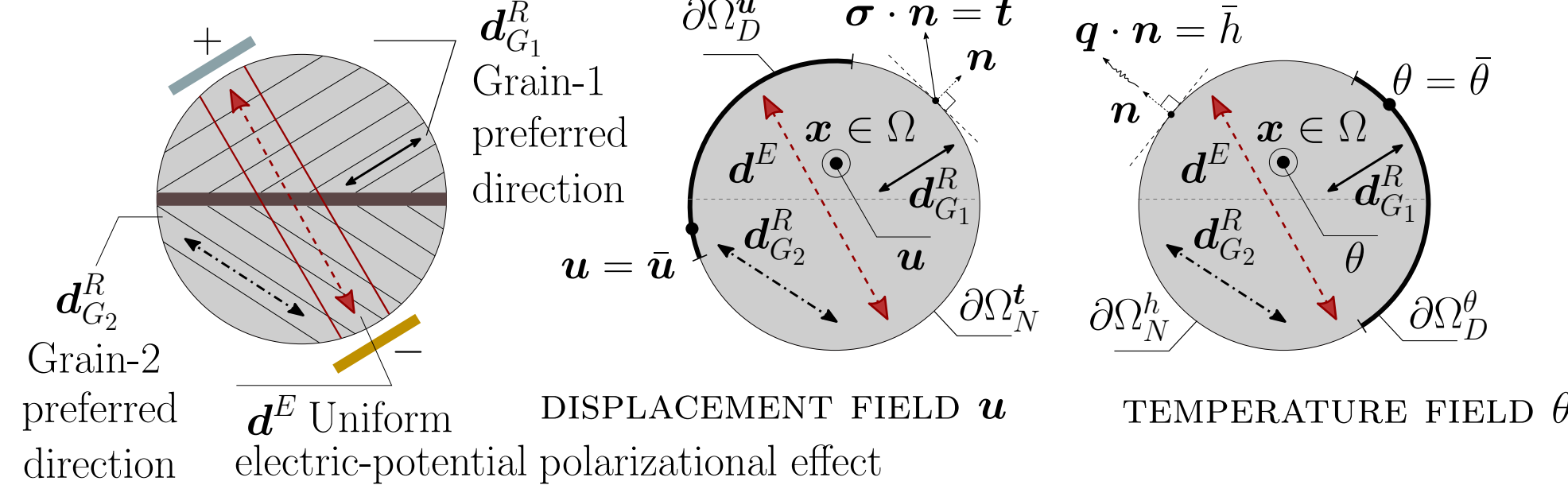
where deformation  $\bar{\mathbf{u}}$  is (i) based on (1), and then (ii) for *Griffith*-analysis in (2).

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

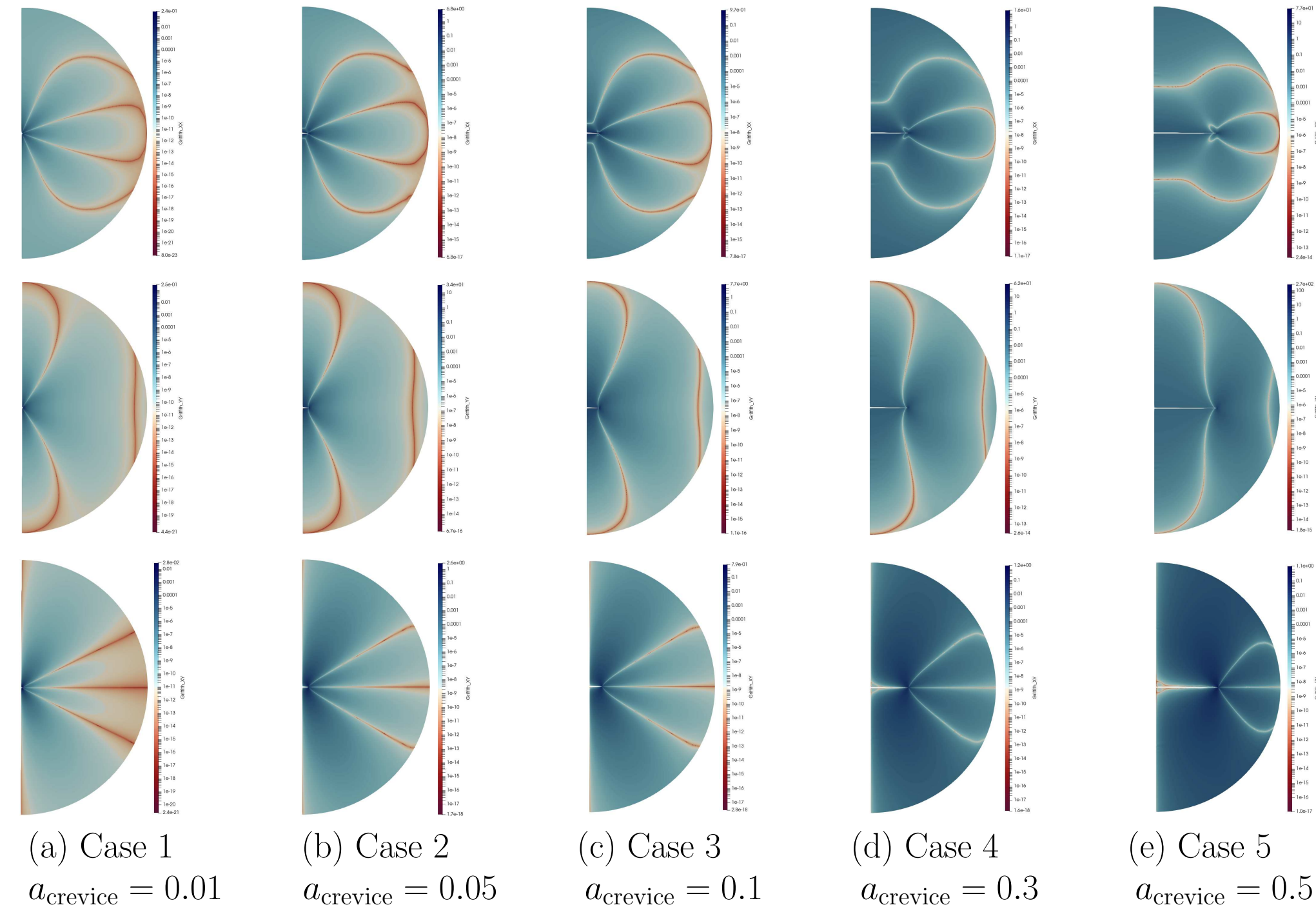
$$\mathcal{V}_A : \begin{cases} \mathbb{C} \rightarrow \mathbb{C}, \\ z \mapsto \mathcal{V}_A(z) := \Re \left( \oint_{\Gamma} \mathcal{K}^{(*)} dz \right) + x_2 \Im \left( \oint_{\Gamma} \mathcal{K}^{(*)} dz \right), \end{cases} \quad \mathcal{K}^{(*)} : \begin{cases} \mathbb{C} \rightarrow \mathbb{C},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

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

Boundary conditions applied on a solid-state object



Numerical spectral of *Griffith* criterion at (SE|SSE) yields (xx-yy-xy)



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

FEM: Strain energy density

Partial differential equation (PDE)

$$\nabla \cdot \left( \mathbb{C}^{\text{fallocation}}(\lambda, \mu, \mathbf{d}_{G_i}^R, i=1, \dots, N, \mathbf{d}^E; \mathbf{x}) : \nabla \mathbf{u}^{(s)} \right) + \rho \mathbf{b} = \mathbf{0}$$

Displacement vector field solution

$$\mathbf{u}_i \leftarrow \mathbf{u} = \mathbf{K}^{-1} \mathbf{f}$$

Strain tensor

$$\varepsilon_{ij} = \frac{1}{2} (\partial_x u_i + \partial_x u_j)$$

Stress tensor

$$\sigma_{ij} = \sum_{k,l} \mathbb{C}_{ijkl}^{(p(\Omega))} \varepsilon_{kl}$$

Strain energy density

$$\mathcal{E}_{\text{strain}} := \frac{1}{2} \sum_{i,j} \sigma_{ij} \varepsilon_{ij}$$

Strain solution takes the following form  
 $\frac{1}{2} \sum_{\alpha=1}^{N_{\text{node}}} \left( \sum_{L=1}^{N_{\text{node}}} \xi_L^{\text{dot}} N_{\alpha}^L u_k^L + \sum_{K=1}^{N_{\text{node}}} \xi_K^{\text{dot}} N_{\alpha}^K u_l^L \right)$   
where displacement field  $\mathbf{u}$  is known, numerically computed from the PDE above.

*Griffith*-based critical stress

$$\sigma_{\text{Griffith}} = \sqrt{\frac{2\gamma E}{\pi a_{\text{crevice}}}}$$

governs nucleation interface.

### Contact

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### References

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