

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)^(*)-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.

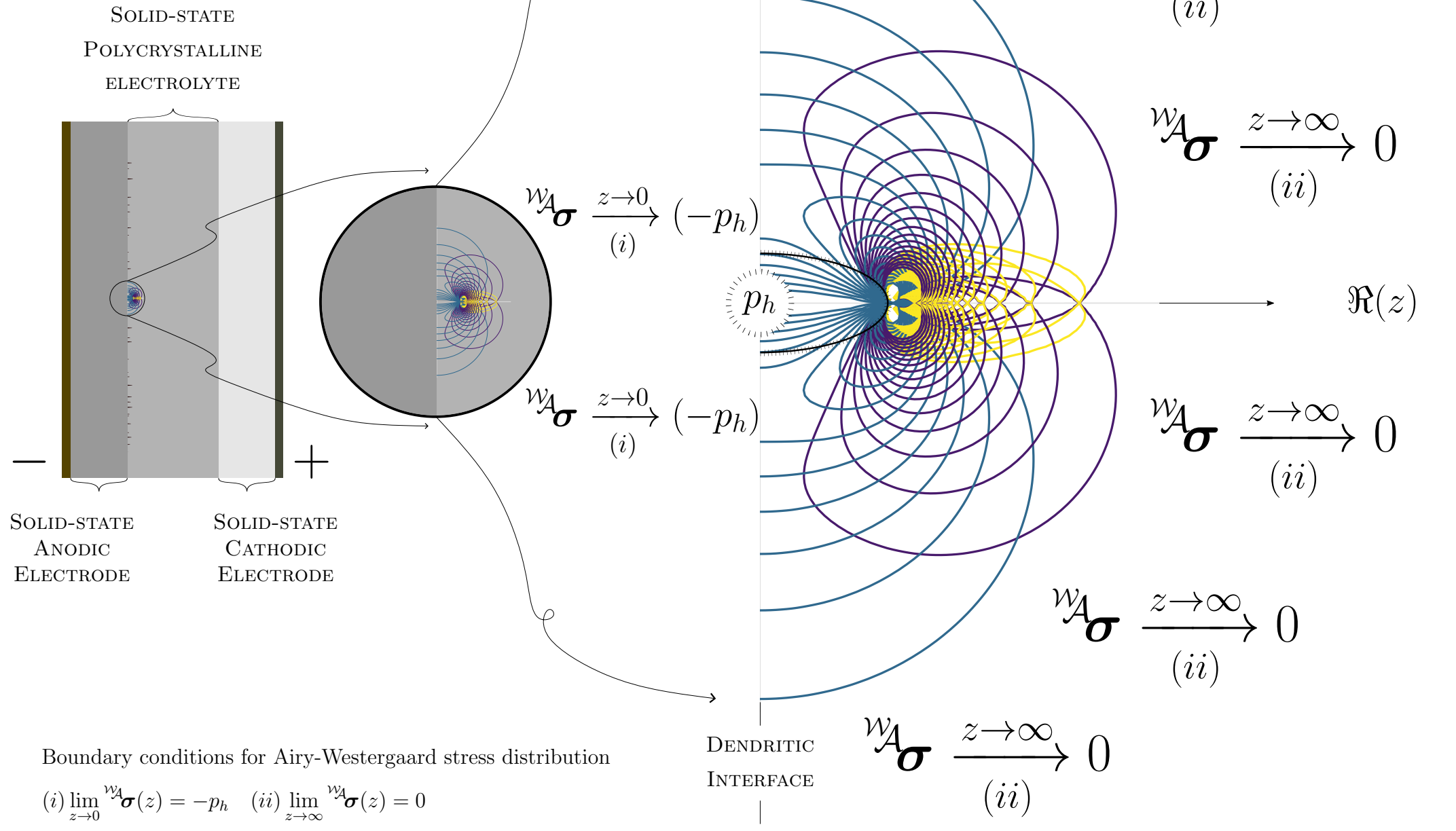
All-solid-state battery (ASSB) is one of promising candidates to overcome bottlenecks of c-LIBs. Thanks to **solid-state electrolyte** (SSE), ASSB is highly stable towards temperature and pressure. Nevertheless, Li-metal dendrite triggered at (SE|SSE)-interface [5] is the main drawback of ASSB since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

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

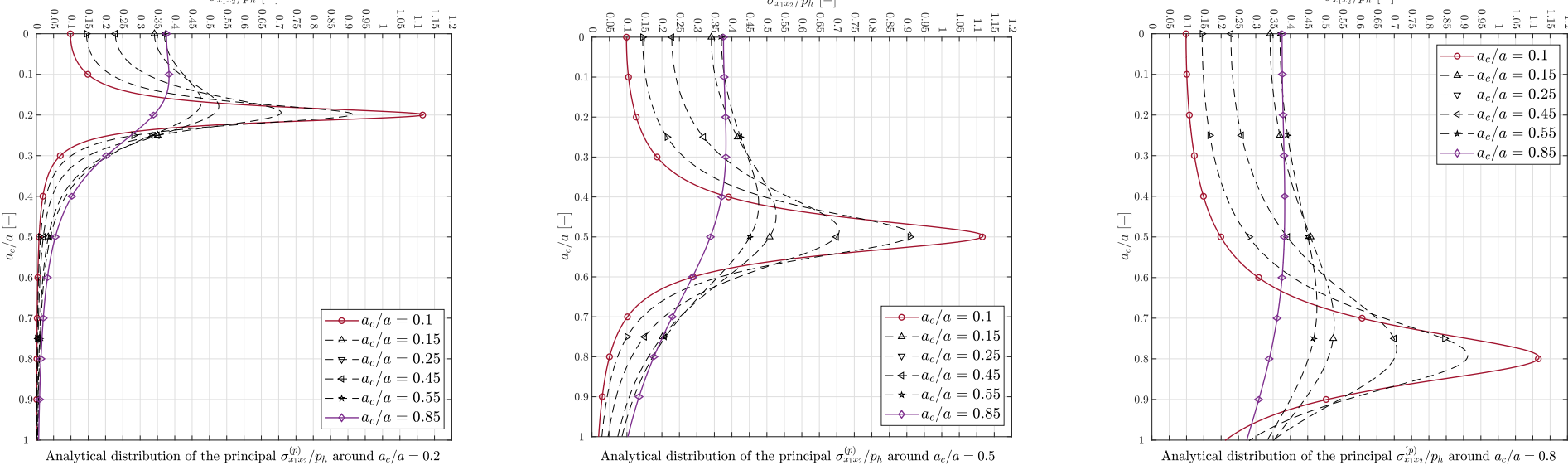
where \mathbf{u} displacement field, θ temperature field, a crevice length, λ, μ Lamé constants, $\mathbf{d}^{(*)} \otimes \mathbf{d}^{(*)}$ embedded misorientation structural tensor, and γ cracking-surface energy density, can help to improve ASSB performance.

ALL-SOLID-STATE BATTERIES (ASSBs)



(SE|SSE)-Interface Analysis

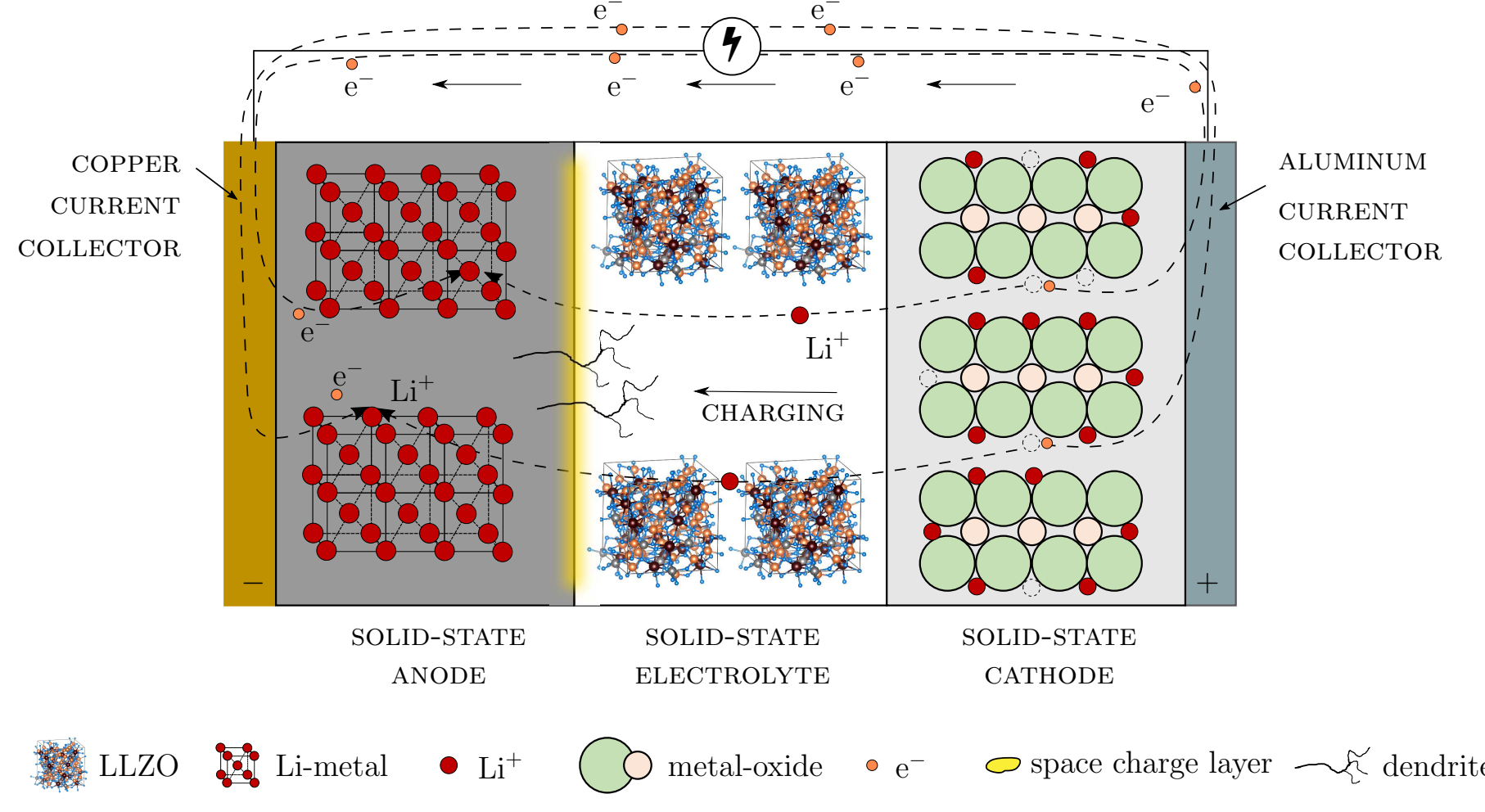
Interface between solid electrode and solid-state electrolyte (SE|SSE) taking place at space charge layer (SCL) [2] found in ASSBs critically exhibits mechanical and electrochemical instability [3]. This evidence points directly to the fact that the soft metallic Li anode is erroneously prone to triggering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



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

Next-generation All-solid-state battery

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

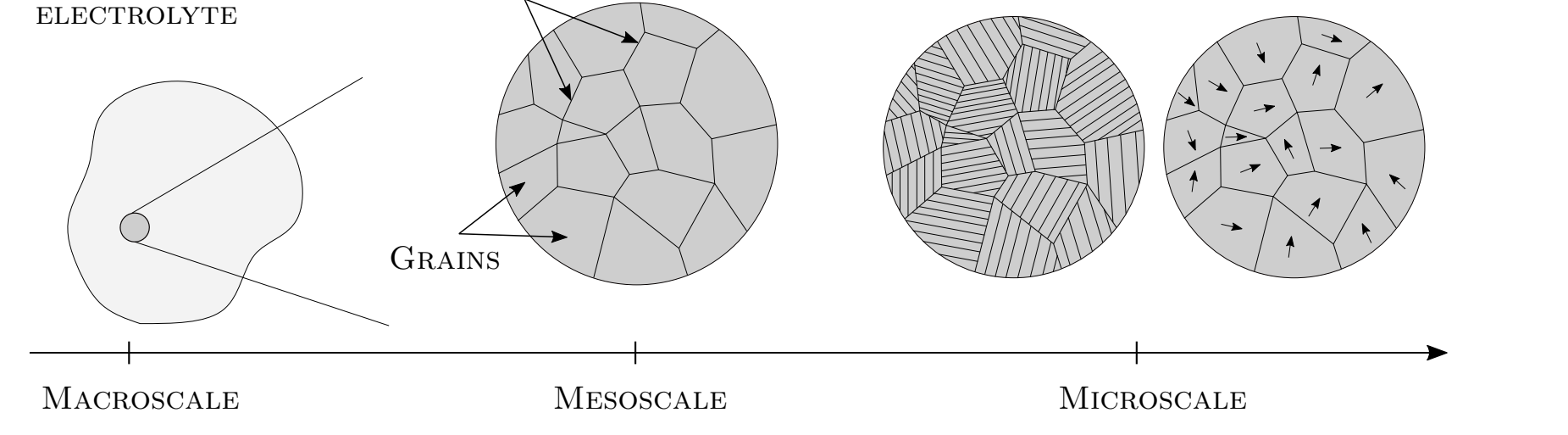


- ✓ **Thermodynamic consistency** is satisfied, followed by [2].
- ✓ **Closure** $\bar{\Omega}$ is fulfilled by 15 moments, followed by [4].

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 θ ; structural tensor \mathbf{M}

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

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

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

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

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

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

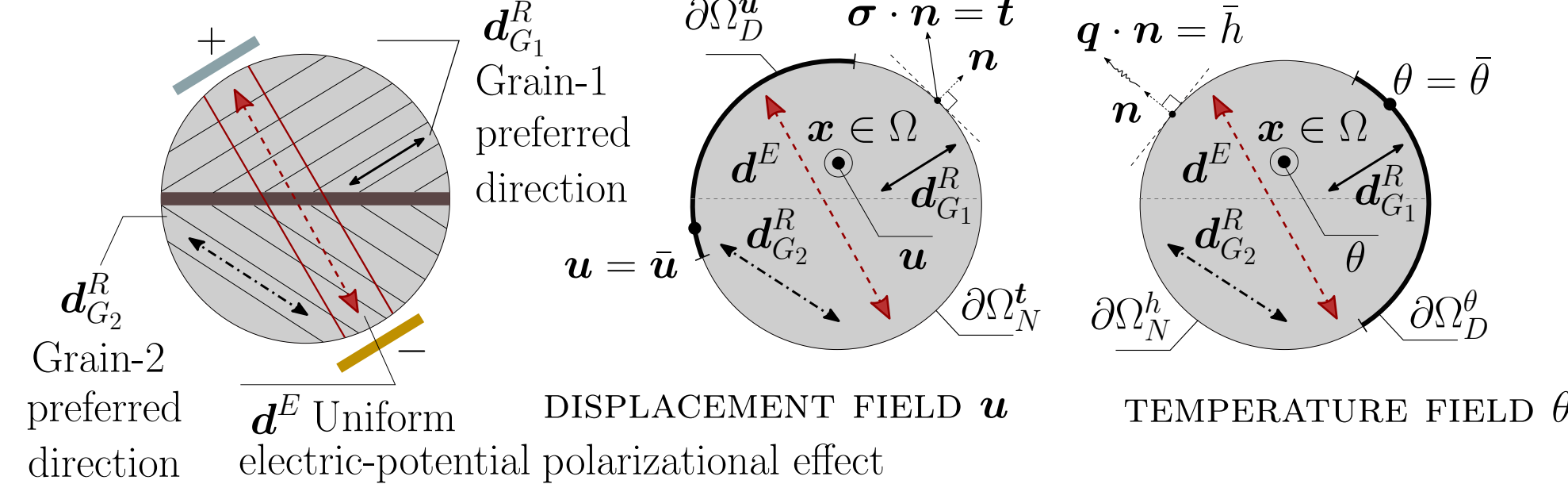
where deformation $\bar{\mathbf{u}}$ is (i) based on (1), and then (ii) for *Griffith*-analysis in (2).

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

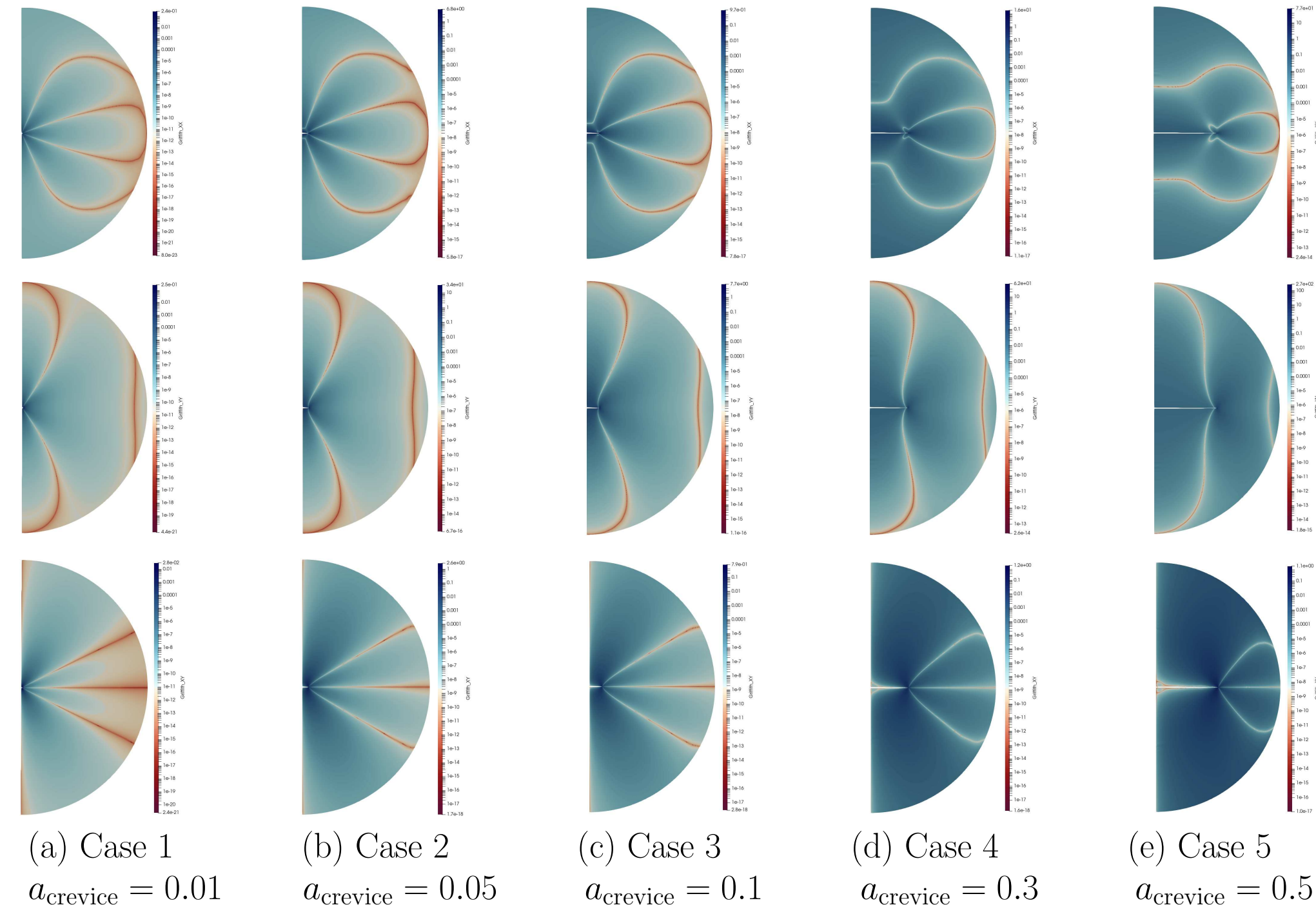
$$w_A : \left\{ \begin{array}{l} \mathbb{C} \rightarrow \mathbb{C}, \\ z \mapsto w_A(z) := \Re \left(\oint_{\Gamma} \mathcal{K}^{(*)} dz \right) + x_2 \Im \left(\oint_{\Gamma} \mathcal{K}^{(*)} dz \right), \end{array} \right. \quad \mathcal{K}^{(*)} : \left\{ \begin{array}{l} \mathbb{C} \rightarrow \mathbb{C},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

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)

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

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

$$\sigma_{ij} = \sum_{k,l} \mathbb{C}_{ijkl}^{f_{\text{allocation}}}(\lambda, \mu, \mathbf{d}_{G_i, i=1, \dots, N}^R; \mathbf{d}^E; \mathbf{x}) \varepsilon_{kl}$$

Strain energy density

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

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

Griffith-based critical stress

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

governs nucleation interface.

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References

- [1] **T.Vo**, *Modeling the swelling phenomena of li-ion batt. cells based on a numerical chemo-mech. coupled approach*. MA, Robert Bosch Battery Systems GmbH, **2018**.
- [2] **S.Braun**, C.Yada, and A.Latz, *Thermodynamically consistent model for Space-Charge-Layer formation in a solid electrolyte*. Jr.Phys. Chem., 119, 22281-22288, **2015**.
- [3] **C.Hüter**, S.Fu, M.Finsterbusch, E.Figgemeier, L.Wells, and R.Spatschek, *Electrode-electrolyte interface stability in solid state electrolyte system: influence of coating thickness under varying residual stresses*. AIMS Materials Science, 4(4):867-877, **2017**.
- [4] **M.Torrilhon**. *Modeling nonequilibrium gas flow based on moment equations*. Annual Review of Fluid Mechanics, 48(1):429-458, **2016**.
- [5] **S.Kim**, J.S.Kim, L.Miara, Y.Wang, S.K.Jung, S.Y.Park, Z.Song, H.King, M.Badding, J.M.Chang, V.Roev, G.Yoon, R.Kim, J.H.Kim, K.Yoon, D.Im, and K.Kang, *High-energy and durable li metal batt. using garnet-type solid electrolytes with tailored li-metal compatibility*. Nature Communications, 13(1):1883, **2022**.