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.

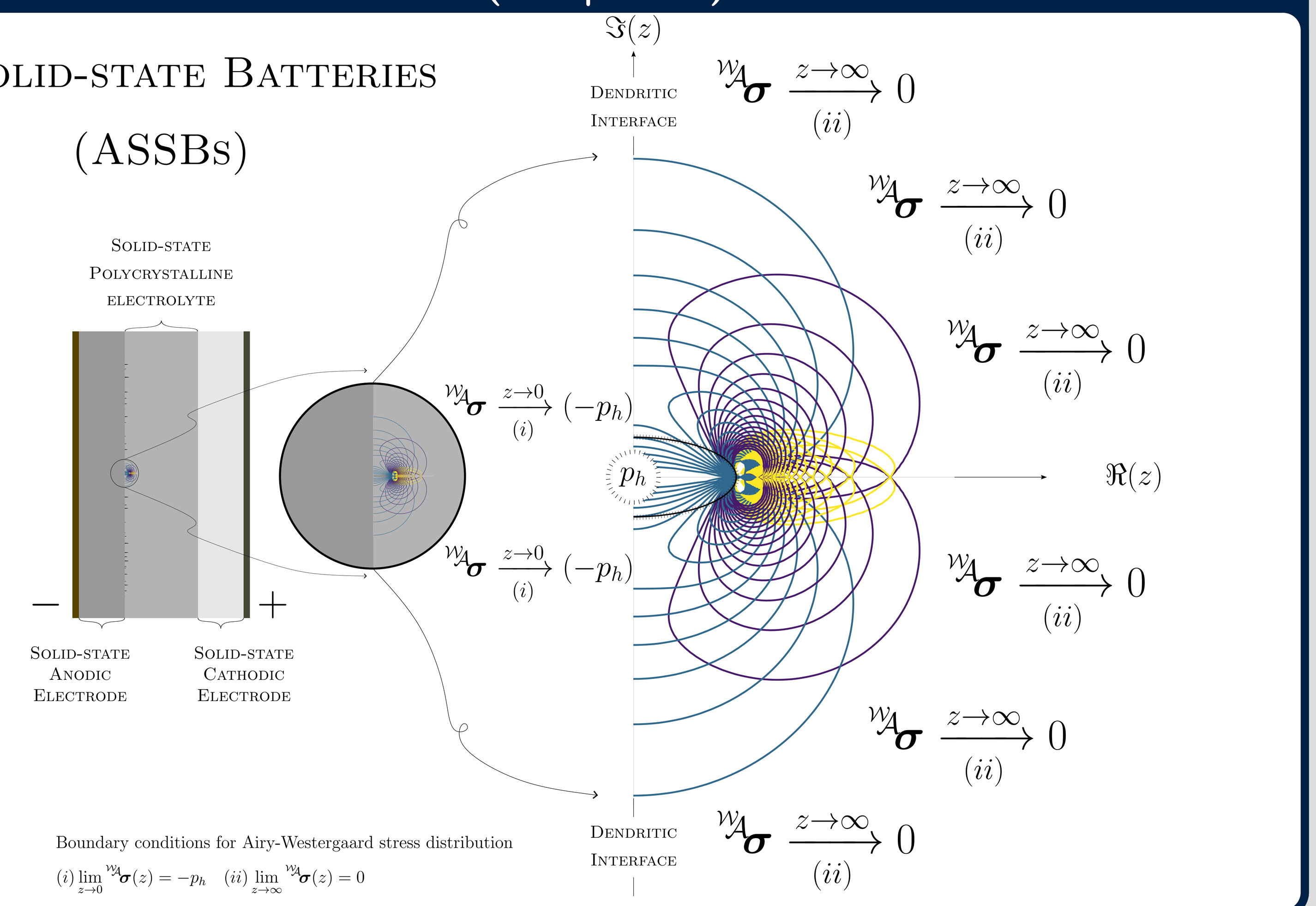
All-solid-state battery (ASSB) is one of promising candidates to overcome bottlenecks of c-LIBs. Thanks to solid-state electrolyte (SSE), ASSB is highly stable towards temperature and pressure. Nevertheless, Li-metal dendrite triggered at (SE|SSE)-interface [5] is the main drawback of ASSB since these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

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

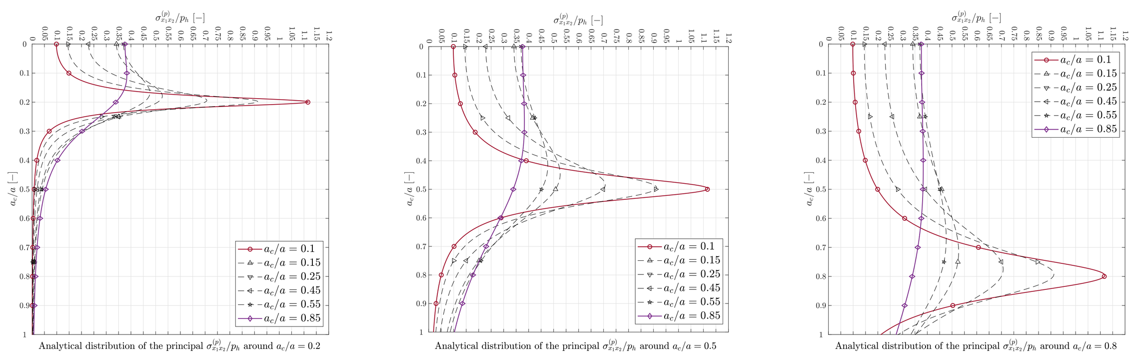
where $\boldsymbol{u}$ displacement field, θ temperature field, a crevice length, λ, μ Lamé constants, $\boldsymbol{d}^R \otimes \boldsymbol{d}^R$ embedded misorientation structural tensor, and γ cracking-surface energy density, can help to improve ASSB performance.

All-solid-state Batteries (ASSBs)



(SE|SSE)-Interface Analysis

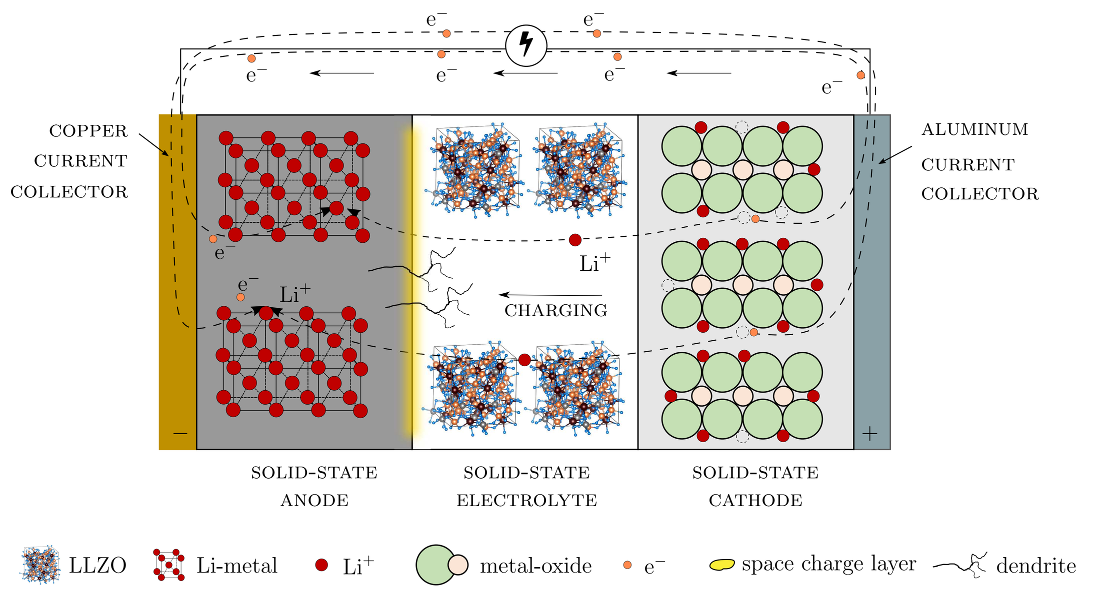
Interface between solid electrode and solid-state electrolyte (SE|SSE) taking place at space charge layer (SCL) [2] found in ASSBs critically exhibits mechanical and electrochemical instability [3]. This evidence points directly to the fact that the soft metallic li anode is erroneously prone to triggering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



Distribution: ana. max. shear stress ${}^{\mathcal{W}}\!\!\mathcal{A}\sigma^{\Pi}_{x_1x_2}$ around crack tip a_c.

Next-generation All-solid-state battery

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

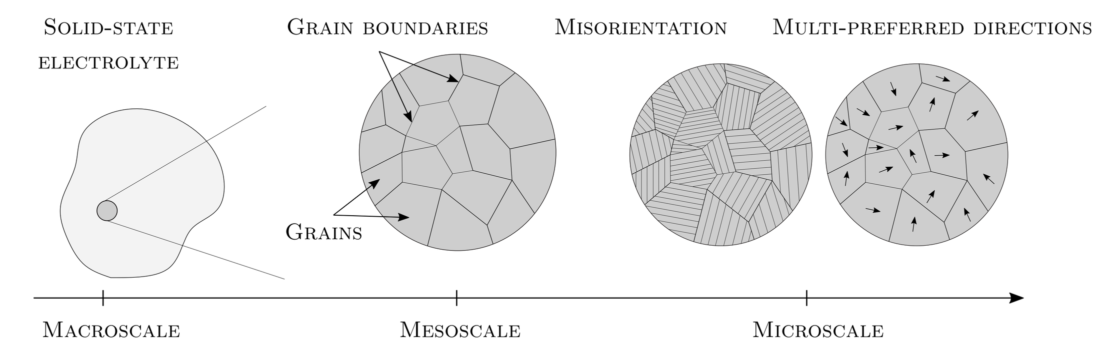


✓ **Thermodynamic consistency** is satisfied, followed by [2].
✓ **Closure** $\bar{\Omega}$ is fulfilled by 15 moments, followed by [4].

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.

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



Consequentially, 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 $\boldsymbol{u}$ and temperature field θ; structural tensor $\boldsymbol{M}$

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

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 $\rho(\boldsymbol{x}, t)$ 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. Then, the governing partial differential equation (PDE) of deformation takes the form

$$\partial_t \boldsymbol{u} + \nabla \cdot \left(\overset{4}{\mathbb{C}}{}^{f_{\text{alocation}}(\lambda,\mu,\boldsymbol{d}^R_{G_i,i=1,\dots,N},\boldsymbol{d}^E;\boldsymbol{x})} : \nabla \boldsymbol{u}^{(s)} \right) + \rho \boldsymbol{b} = -\rho \nabla V_e,$$

where $V_e : \mathbb{R}^3 \to \mathbb{R}$ 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

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

Surface energy is analysized 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

$$\partial_t \bar{\boldsymbol{u}} + \nabla \cdot \left(\overset{4}{\mathbb{C}}{}^{f_{\text{alocation}}(\lambda,\mu,\boldsymbol{d}^R_{G_i,i=1,\dots,N},\boldsymbol{d}^E;\boldsymbol{x})} : \nabla \boldsymbol{u}^{(s)} \right) + \rho \boldsymbol{b} = -\rho \nabla V_e, \tag{1}$$

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

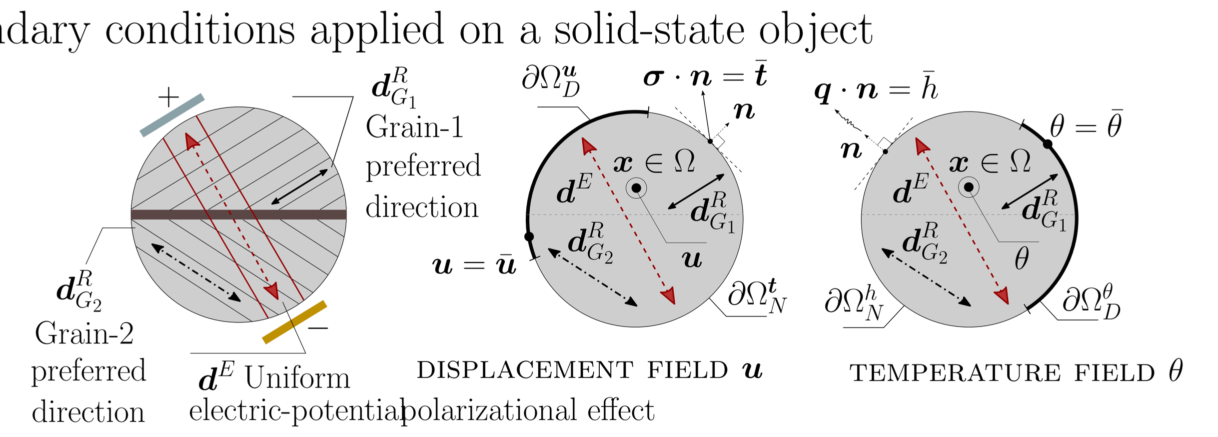
where deformation $\bar{\boldsymbol{u}}$ is (i) based on (1), and then (ii) for *Griffith*-analysis in (2).

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

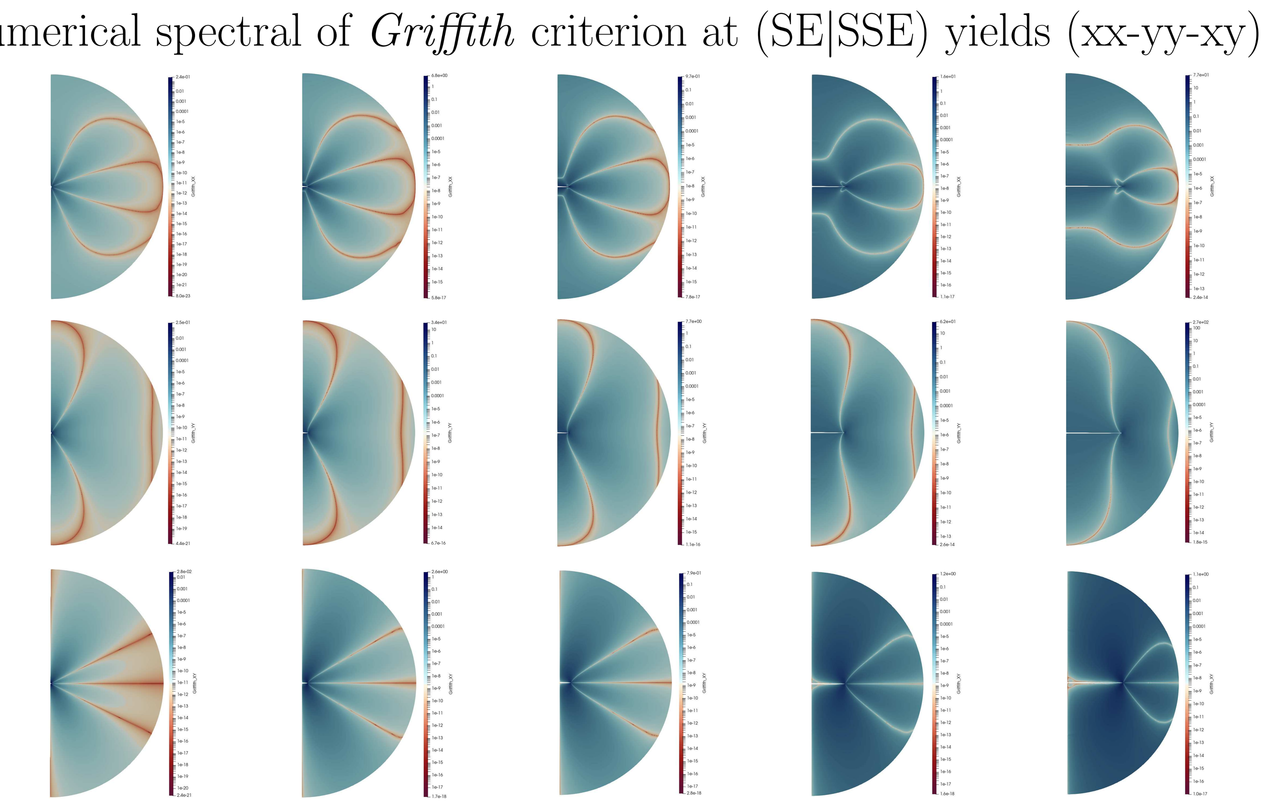
$$\mathcal{WA}: \begin{cases} \mathbb{C} \to \mathbb{C}, \\ z \mapsto \mathcal{WA}(z) := \Re(\oint\!\!\oint_\Gamma \mathcal{K}^{(*)}\, dz) + x_2 \Im(\oint_\Gamma \mathcal{K}^{(*)}\, dz), \end{cases} \quad \mathcal{K}^{(*)}: \begin{cases} \mathbb{C} \to \mathbb{C}, \\ z \mapsto \mathcal{K}^{(*)} := -p_h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

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)



(a) Case 1, $a_{\text{crevice}} = 0.01$; (b) Case 2, $a_{\text{crevice}} = 0.05$; (c) Case 3, $a_{\text{crevice}} = 0.1$; (d) Case 4, $a_{\text{crevice}} = 0.3$; (e) Case 5, $a_{\text{crevice}} = 0.5$

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

FEM: Strain energy density

Partial differential equation (PDE)

$$\nabla \cdot \left(\overset{4}{\mathbb{C}}{}^{D(\Omega)}_{(\lambda,\mu)} \nabla^{(s)} \boldsymbol{u} \right) + \rho \boldsymbol{b} = \boldsymbol{0}$$

Displacement vector field solution

$$u_i \leftarrow \boldsymbol{u} = \boldsymbol{K}^{-1} \boldsymbol{f}$$

Strain tensor

$$\varepsilon_{ij} = \tfrac{1}{2}(\partial_{x_j} u_i + \partial_{x_i} u_j)$$

Stress tensor

$$\sigma_{ij} = \textstyle\sum_{k,l} \overset{4}{\mathbb{C}}{}^{D(\Omega)}_{(\lambda,\mu)\,ijkl}\, \varepsilon_{kl}$$

Strain energy density

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

Strain solution takes the following form

$$\tfrac{1}{2}\textstyle\sum_{\alpha=1}^{N^{\text{P}}_{\text{node}}} \left(\sum_{L=1}^{N^{\text{node}}_{\text{dof}}} N^{\alpha}_{\xi_L, x_k} u^{\alpha}_l + \sum_{K=1}^{N^{\text{node}}_{\text{dof}}} N^{\alpha}_{\xi_K, x_l} u^{\alpha}_k \right)$$

Griffith-based critical stress

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

governs nucleation interface.

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