Next-generation all-solid-state battery (#ASSB)

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

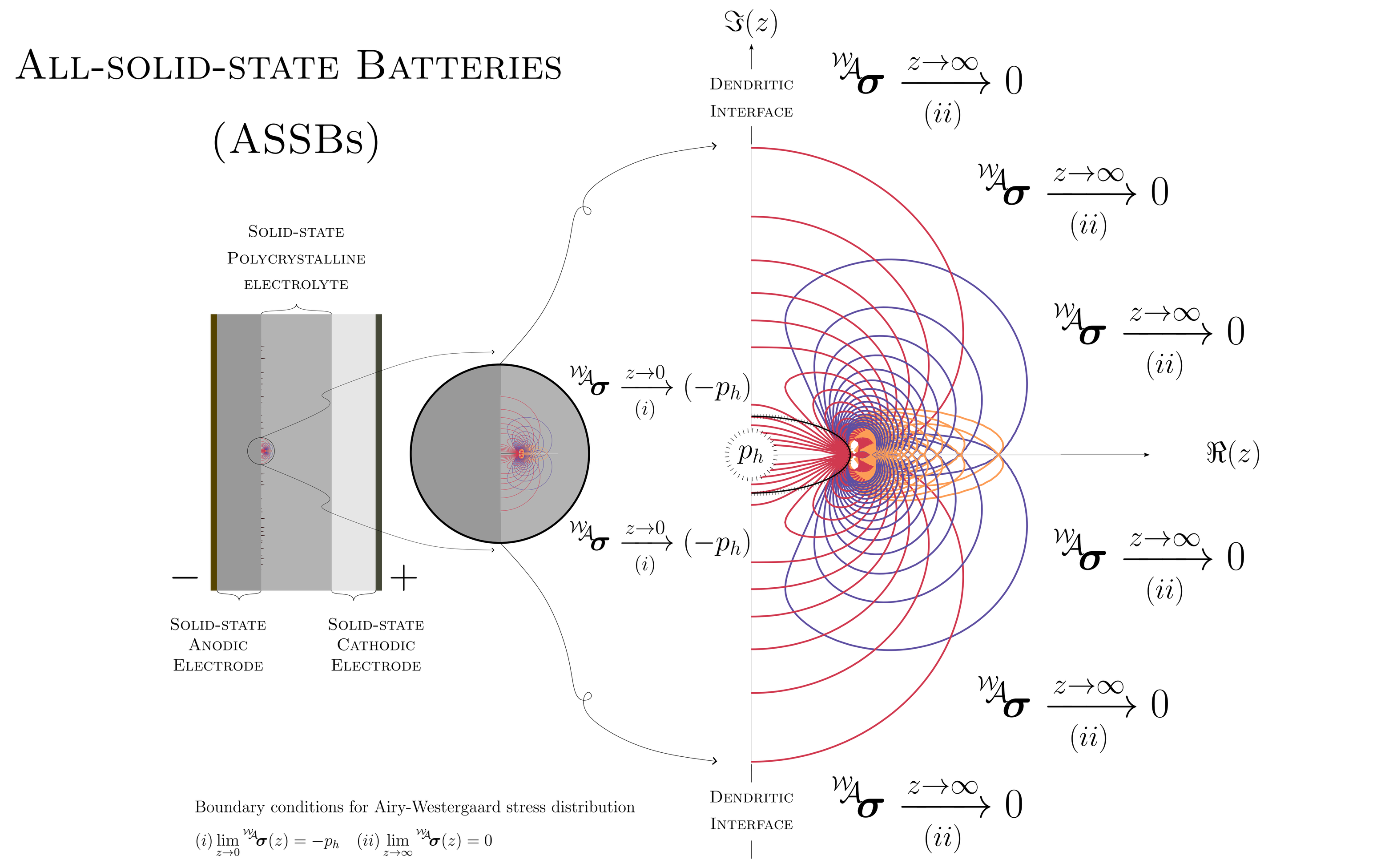
Rechargeable Lithium-ion battery (LIB) is at the heart of every electric vehicle (EV), portable electronic device, and energy storage system [1]. Nowadays, LIBs enable human life more efficient and help to solve global environment issues thanks to EVs' zero emission. However, conventional LIB (c-LIB) 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

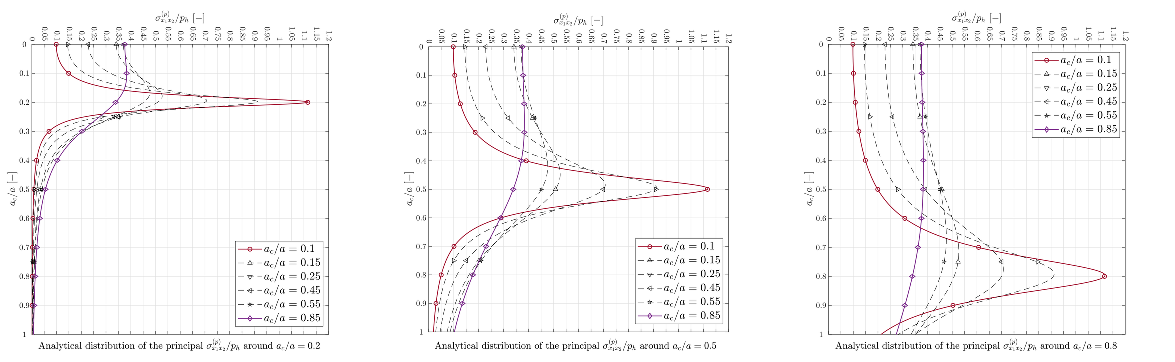
$$a_{\text{Griffith}} := a^* = \arg\min_{a\in\mathbb{R}} \iiint_\Omega f(a,\boldsymbol{u},\theta;\lambda,\mu,\boldsymbol{d}^R\otimes\boldsymbol{d}^R)\,d\Omega - \iint_\Gamma f(a;\gamma)\,d\Gamma\Big|_{\boldsymbol{u}^{(s)}}$$

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.



Interface Analysis

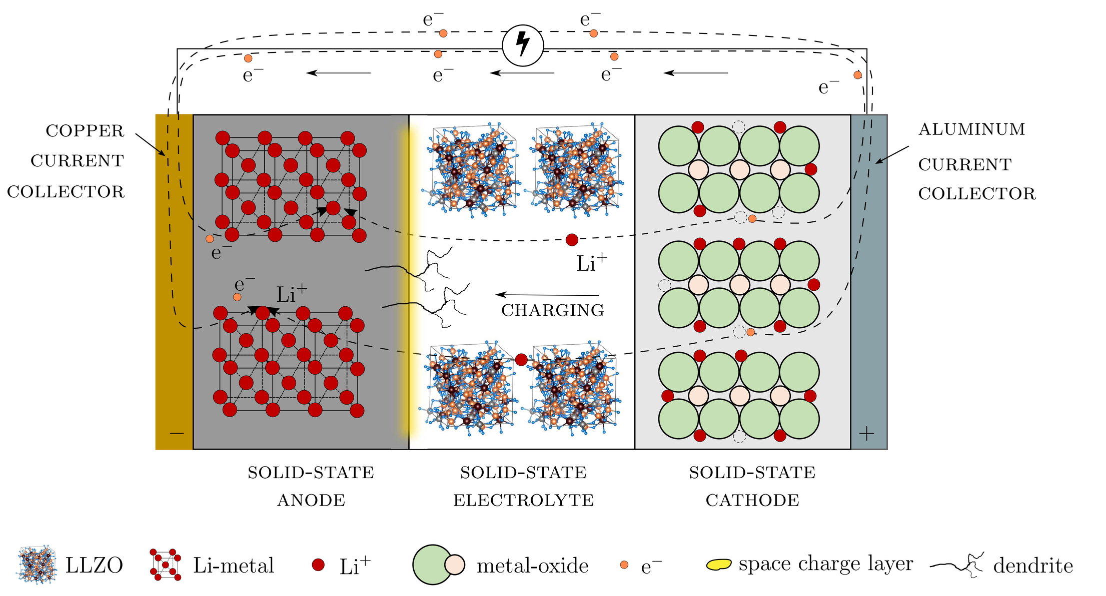
Interface between solid electrode and solid-state electrolyte (SE|SSE) taking place at space charge layer (SCL) [2] found in ASSBs critically exhibits mechanical and electrochemical instability [3]. This evidence points directly to the fact that the soft metallic li anode is erroneously prone to triggering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



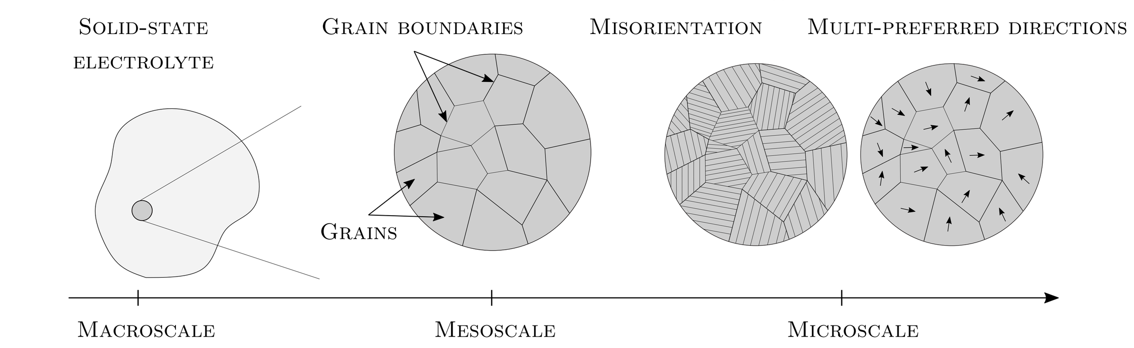
✓ **Thermodynamic consistency** is satisfied, followed by [2].

✓ **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 critical dendritic 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

$$\iint_\Gamma f(a;\gamma)\,d\Gamma$$

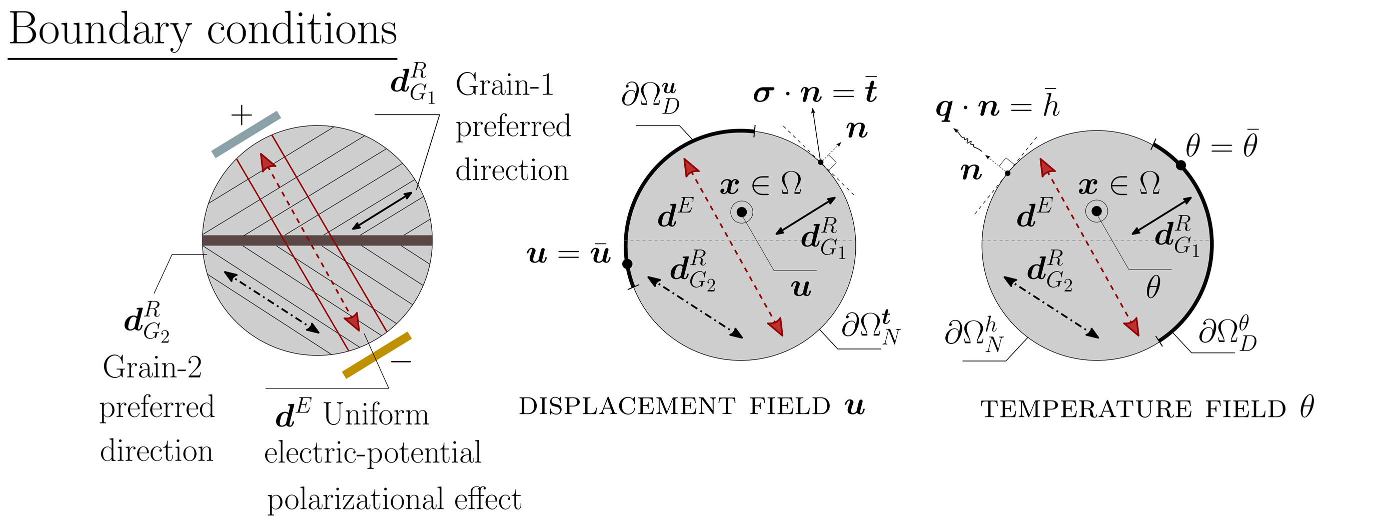
Therefore, the governing problem of dendritic nucleation at (SE|SSE) takes the form

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

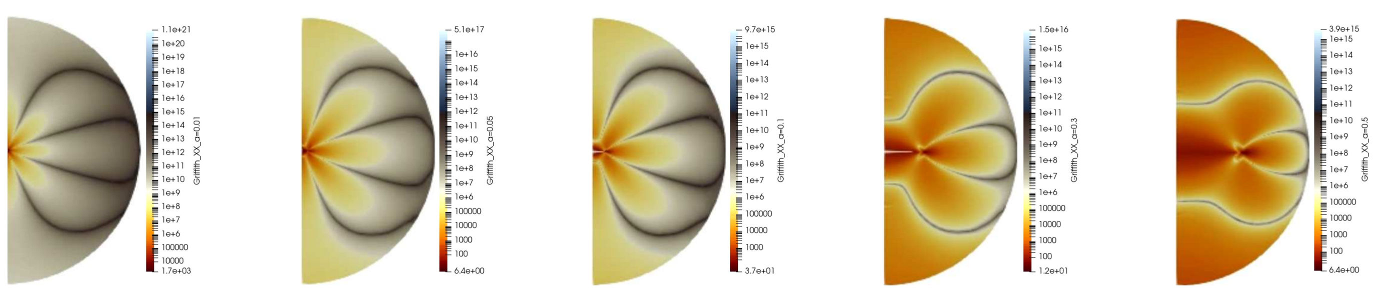
$$\text{s.t.}\quad a_{\text{Griffith}} := a^* = \arg\min_{a\in\mathbb{R}}\iiint_\Omega f(a,\boldsymbol{u},\theta;\lambda,\mu,\boldsymbol{d}\otimes\boldsymbol{d})\,d\Omega - \iint_\Gamma f(a;\gamma)\,d\Gamma\Big|_{\bar{\boldsymbol{u}}} \quad (2)$$

where deformation $\bar{\boldsymbol{u}}$ 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



(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)

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

Displacement vector field solution

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

Strain tensor

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

Stress tensor

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

Strain energy density

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

Strain solution takes the following form

$$\tfrac{1}{2}\textstyle\sum_{\alpha=1}^{\mathcal{N}^{\Omega^e}_{\text{node}}}\left(\sum_{L=1}^{\mathcal{N}^{\Omega\text{node}}_{\text{dof}}}N^\alpha_{,\xi_L}\xi_{L,x_k}u^\alpha_k + \sum_{K=1}^{\mathcal{N}^{\Omega\text{node}}_{\text{dof}}}N^\alpha_{,\xi_K}\xi_{K,x_l}u^\alpha_l\right)$$

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

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

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

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

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

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

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