Direct pore-level multiphysical model for solar thermochemical fuel production reactor based on structured porous media

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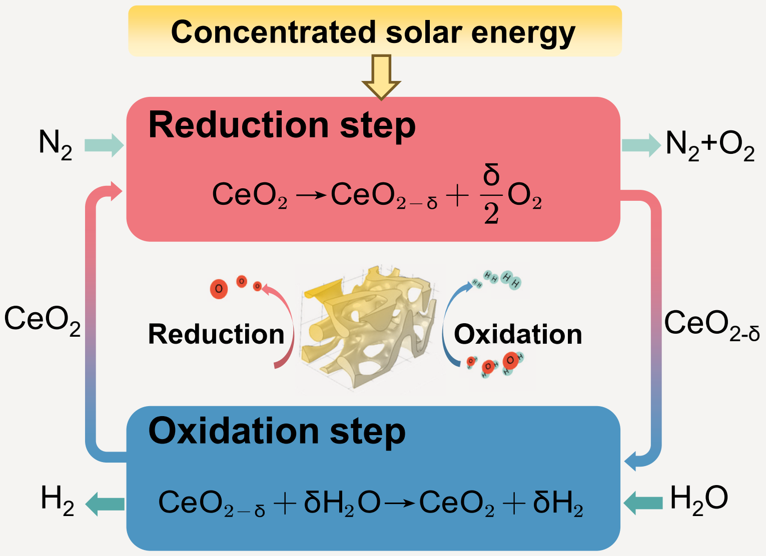
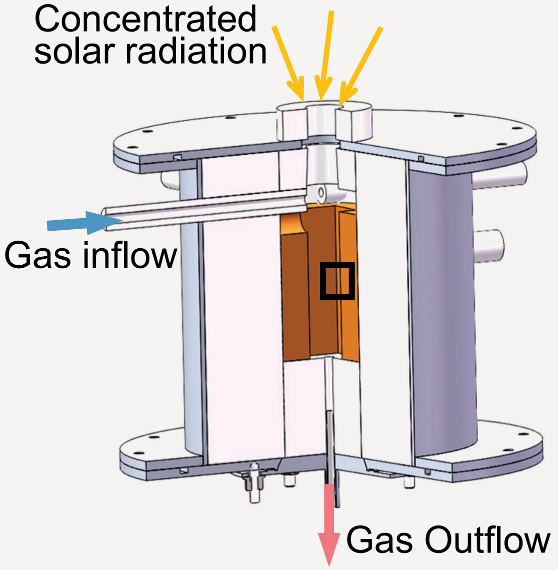
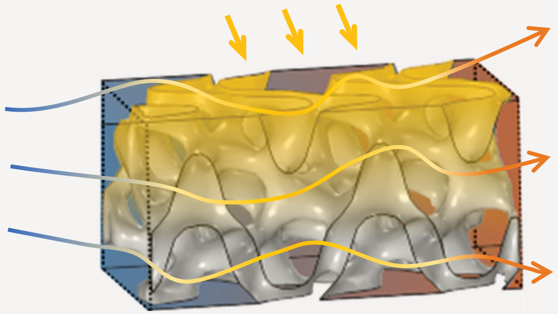
Motivation: Solar-driven Thermochemical Fuel Production



Reactor design



Pore-level scale



- **Functions of porous media**
  - Absorbing solar irradiation,
  - Facilitating mass transport,
  - Providing reaction sites.

- **Physical phenomenon involved**
  - Solar radiation absorbing,
  - Fluid flow and mass transfer,
  - Multi-mode heat transfer,
  - Bulk and surface chemical reactions.

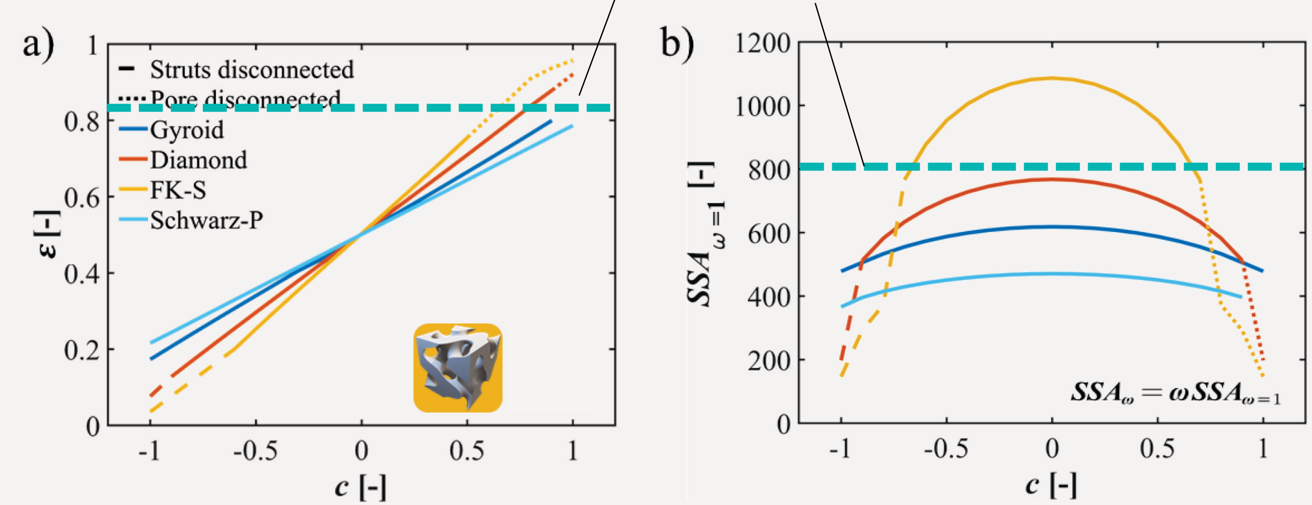
Triply Periodic Minimum Surface (TPMS) Structure

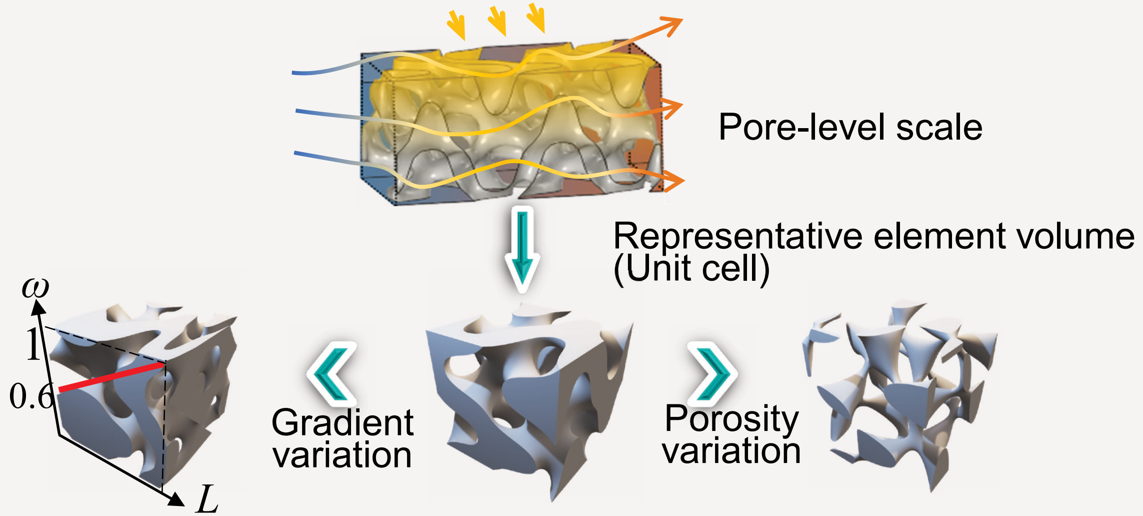
- **The FK-S structure**
  - Wide tunable porosity range,
  - High specific surface aera,
  - Mathematically controllable geometry.
    - Governing equation of FK-S structure

$$\cos(2\omega x)\sin(\omega y)\cos(\omega z) +$$
$$\cos(2\omega y)\sin(\omega z)\cos(\omega x) +$$
$$\cos(2\omega z)\sin(\omega x)\cos(\omega y) = c$$

    - ω controls cell length, larger ω → smaller cell length
    - c controls porosity, larger c → porosity

Typical value of 10 ppi reticulated porous ceria with pore-former[1]

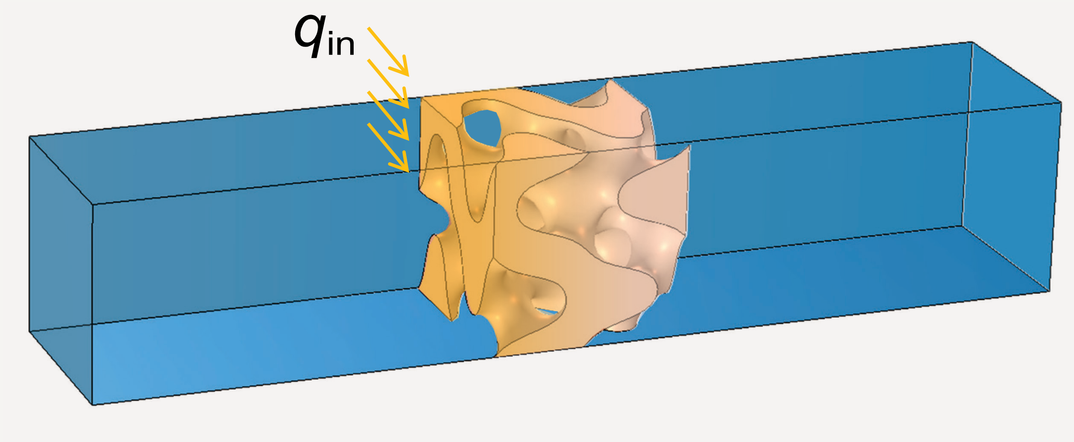




1. Ji, H. Il, Davenport, T. C., Ignatowich, M. J. & Haile, S. M. Gas-phase vs. material-kinetic limits on the redox response of nonstoichiometric oxides. *Phys. Chem. Chem. Phys.* **19**, 7420–7430 (2017).

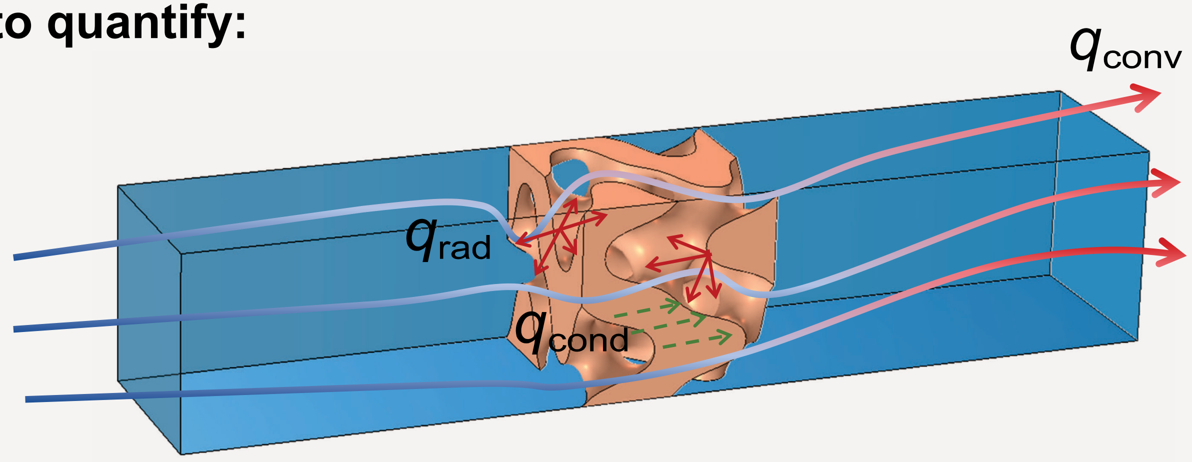
Objectives

- **To develop a multiphysical model, to quantify:**
  - Solar radiation absorption



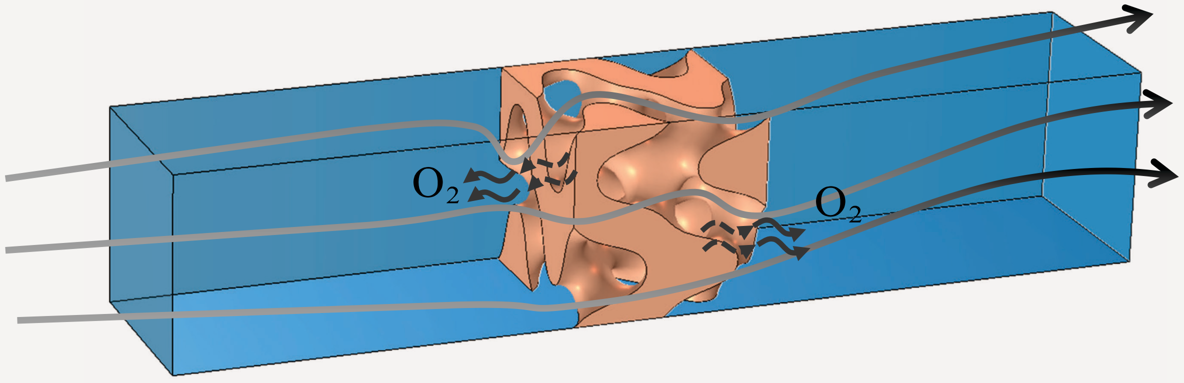
Objectives

- **To develop a fully coupled multiphysical model, to quantify:**
  - Solar radiation absorption
  - Fluid flow
  - Heat transfer (conduction, convection, radiation)



Objectives

- **To develop a fully coupled multiphysical model, to quantify:**
  - Solar radiation absorption
  - Fluid flow
  - Heat transfer
  - Species transport (Bulk diffusion and surface exchange kinetics)



→ **To improve performance of thermochemical fuel production by optimize the porous structure.**

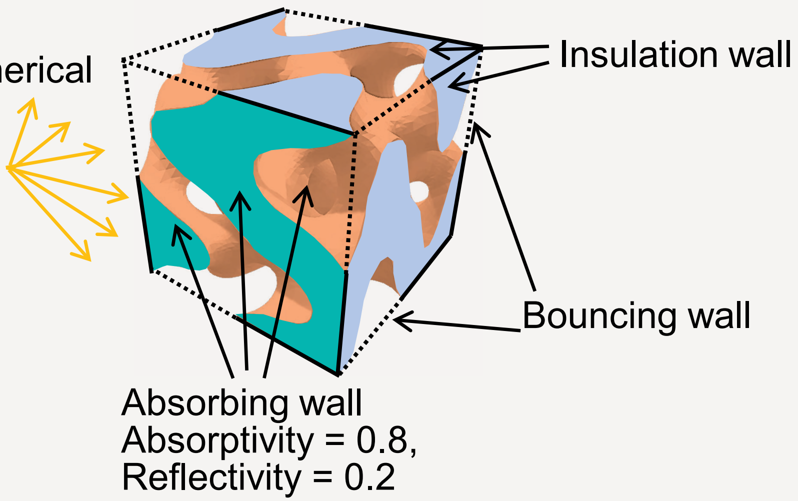
Model development: Fluid flow, optics, mass and heat transfer

- **Conservation equations**
  - Mass conservation $\frac{\partial \rho_f}{\partial t} + \nabla \cdot (\rho_f \mathbf{u}) = R_{O_2}$
    - $\nabla \cdot (\rho_f \mathbf{u})$ → Weakly compressible flow
    - R_{O_2} → Oxygen evolution from reduction reaction
  - Momentum conservation $\rho_f \frac{\partial u_f}{\partial t} + \rho_f (u_f \cdot \nabla) u_f = -\nabla p + \mu_f \nabla u_f$
  - Energy conservation
    - Solid phase $(\rho c_p)_s \frac{\partial T_s}{\partial t} = \nabla \cdot (k_s \nabla T_s) + \nabla q''_{rerad} + q'''_{red}$
      - $\nabla q''_{rerad}$ → Radiatively participating heat source
      - q'''_{red} → Reduction reaction
    - Fluid phase $(\rho c_p)_f \frac{\partial T_f}{\partial t} + \rho_f c_{p,f} \mathbf{u}_f \cdot \nabla T_f = \nabla \cdot (k_f \nabla T_f)$
  - Species conservation $\frac{\partial \rho \omega_{O_2}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \omega_{O_2}) + \nabla \cdot \mathbf{j}_{O_2} = R_{O_2}$

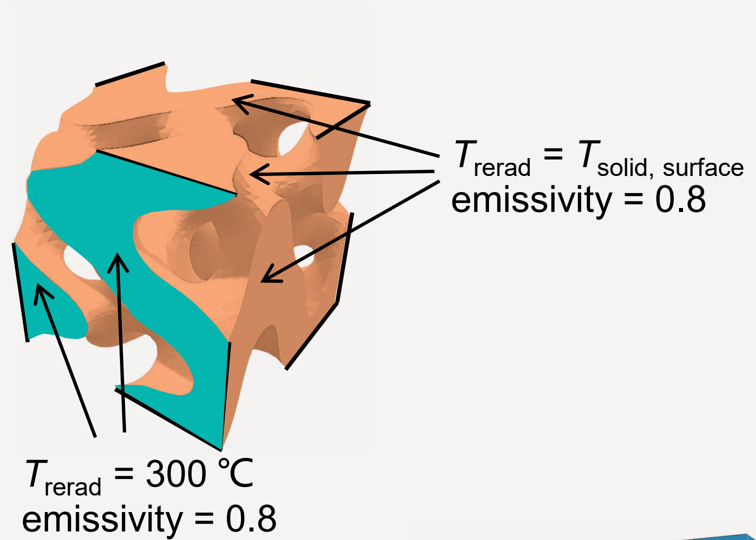
    Governed by oxygen species mass balance
    Diffusion model: mixture-averaged

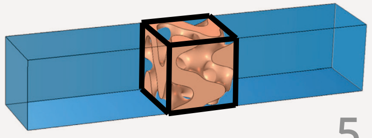
Model development: Fluid flow, optics, mass and heat transfer

- **Optics modeling**
  - **Monte Carlo method** to solve incident radiation absorbing distribution
  - Solid phase: opaque (no radiation propagation inside solid phase) and gray (all radiative properties are independent of wavelength)
  - Fluid phase: transparent (no ray extinction in fluid phase)

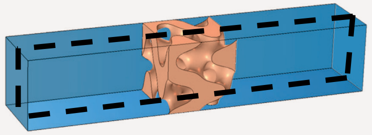


- **Reradiation modeling**
  - **Surface-to-surface radiation method**
  - Quantified between the solid phase surfaces
  - Re-radiation flux only depends on thermal radiation
  - Emission direction of surfaces are pointed into solid phase



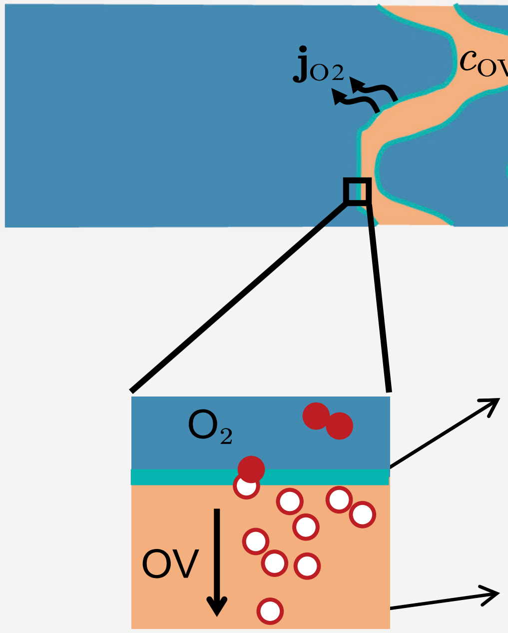


Model development: Mass transfer



Reduction reaction

$$CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2$$



Oxygen evolution[1]

$$k_{surf} = 10^{\left(0.84 * log10\left(\frac{p_{O_2}}{p_0}\right) - 0.99\right)} \ [cm/s]$$

Oxygen vacancy diffusion[2]

$$D_{bulk} = 1 * 10^{-4} \ [cm^2/s]$$

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Model development: Mass transfer

Equilibrium condition

- Thermochemical equilibrium

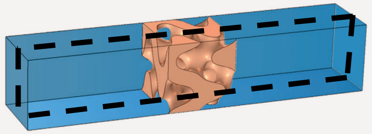
  $$\delta = f\left(T_s, \frac{p_{O_2}}{p_0}\right)$$

- Solid-fluid interface:
  - Oxygen surface exchange

    $$\mathbf{j}_{OV} = k_{surf}\left(c_{OV,surf} - c_{OV,eq}\right)$$

  - Energy consumption in reduction reaction

    $$Q''_{red} = \dot{n}''_{O2}\,\Delta H_{O2,surf}$$



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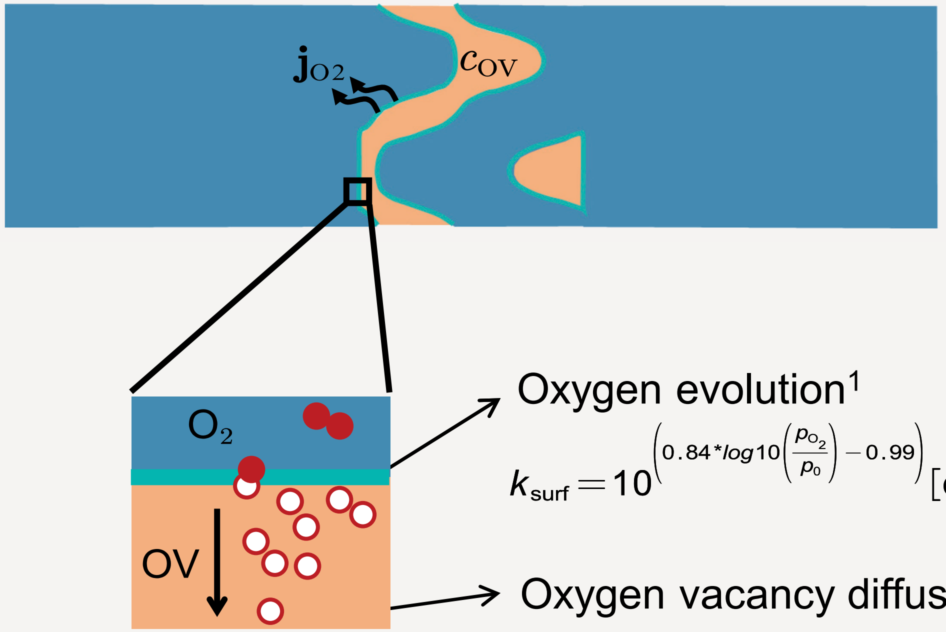

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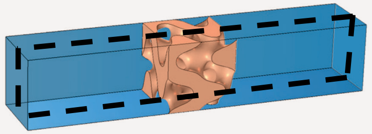

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Specie source

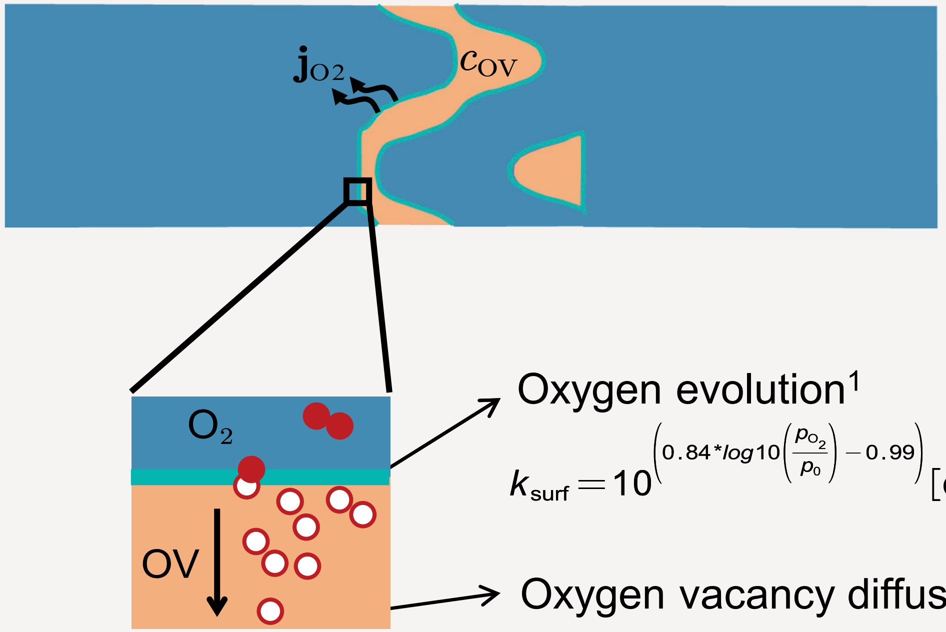
- Gas phase
  - Mass transport: Oxygen species mass balance

$$\frac{\partial \rho\,\omega_{O_2}}{\partial t} + \nabla\cdot(\rho\,\mathbf{u}\,\omega_{O_2}) + \nabla\cdot\mathbf{j}_{O_2} = R_{O_2}$$

Heat source & boundary mass flux

- Solid phase
  - Bulk diffusion: Ficker's law

$$\frac{\partial c_O}{\partial t} = D_b \nabla^2 c_O$$



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Model development: Mass transfer

Updated $\frac{p_{O_2}}{p_0}$

Updated T_s

- Thermochemical equilibrium

$$\delta = f\left(T_s, \frac{p_{O_2}}{p_0}\right)$$

- Solid-fluid interface:
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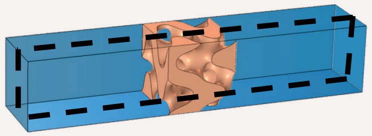

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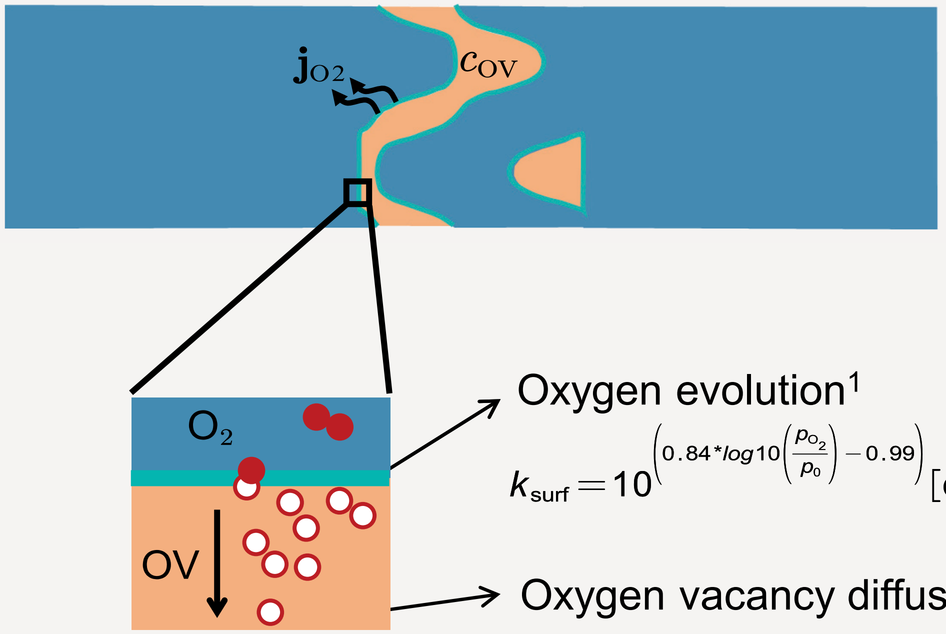

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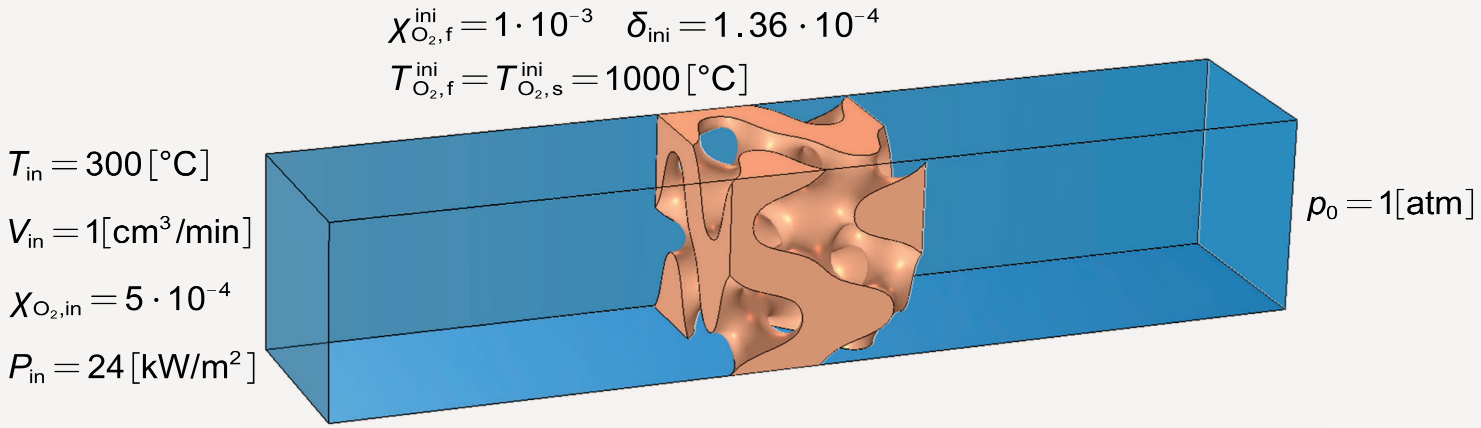
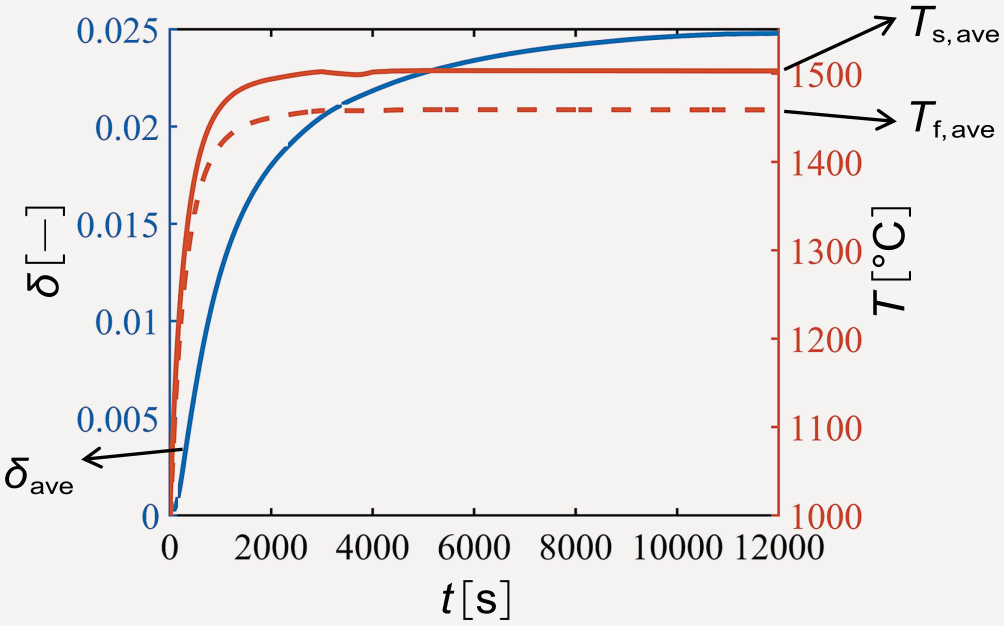
Results

- **Initial condition and boundary condition**



- **Temperature and oxygen non-stoichiometry**



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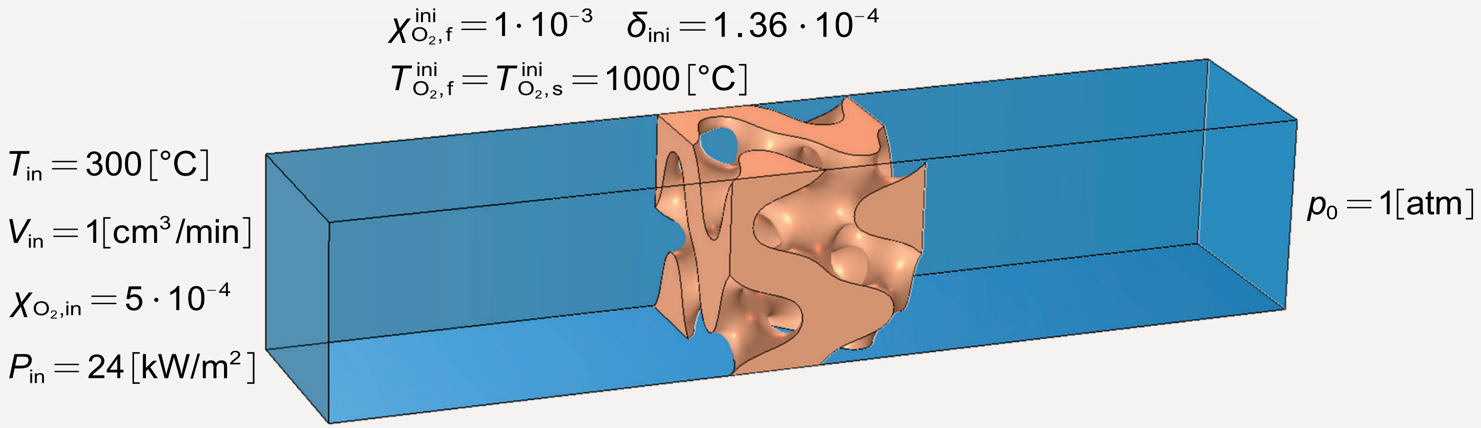

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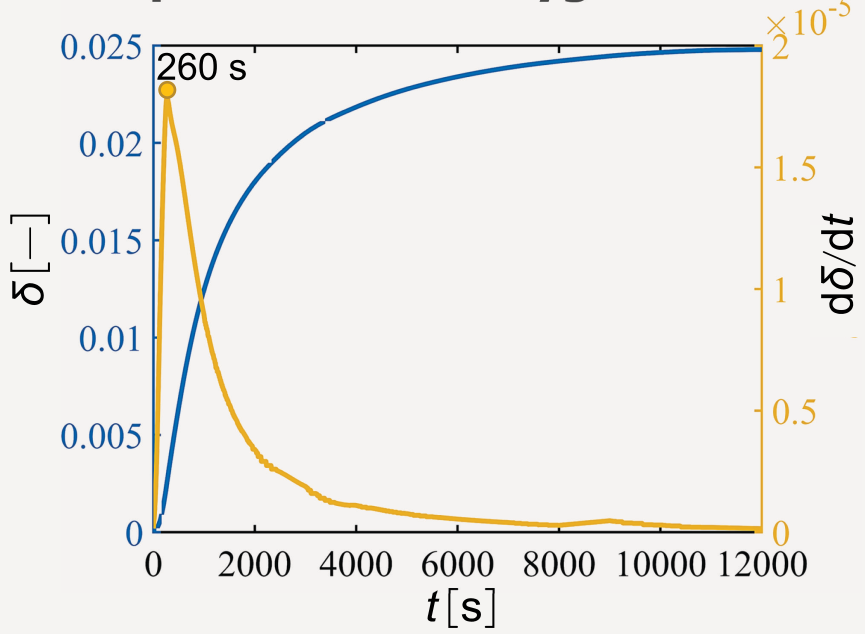
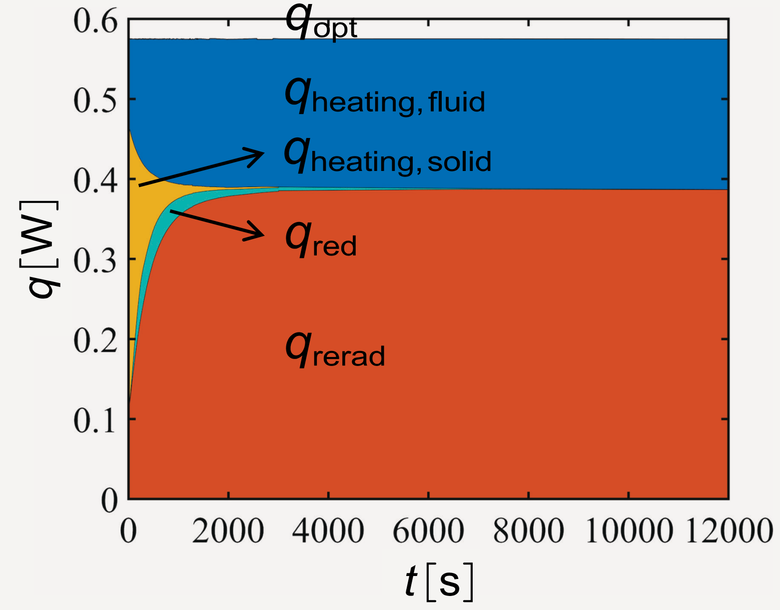
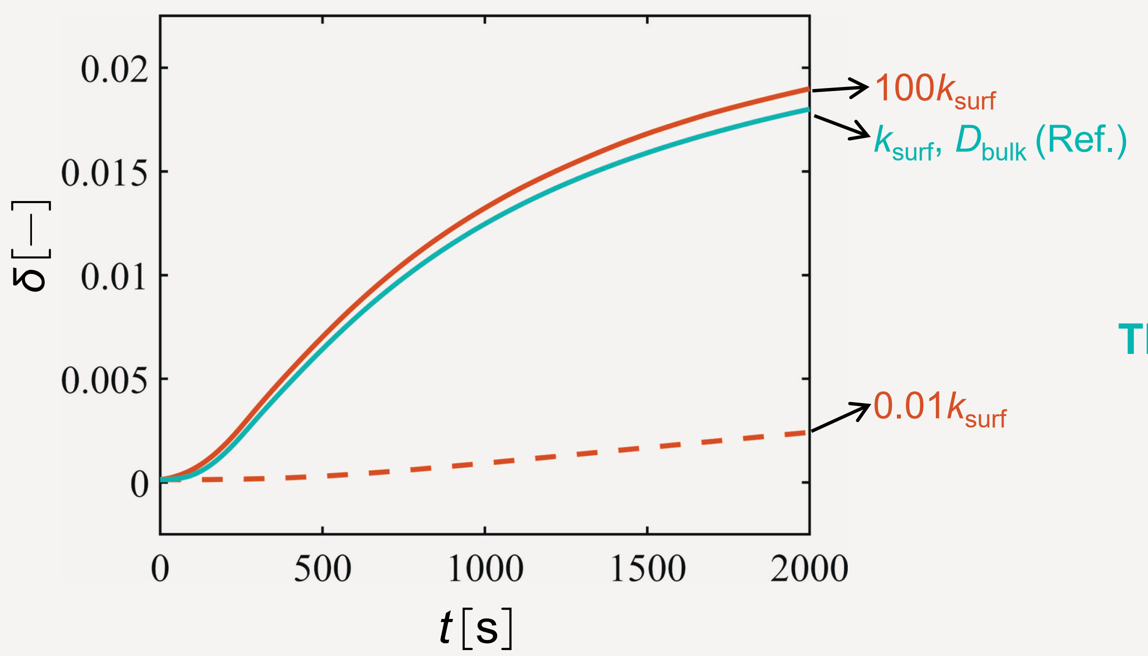


- **Energy balance**

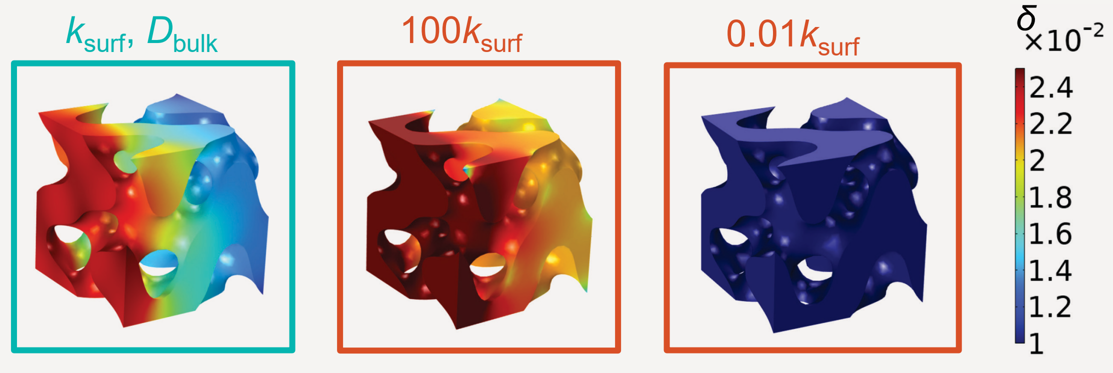


Results

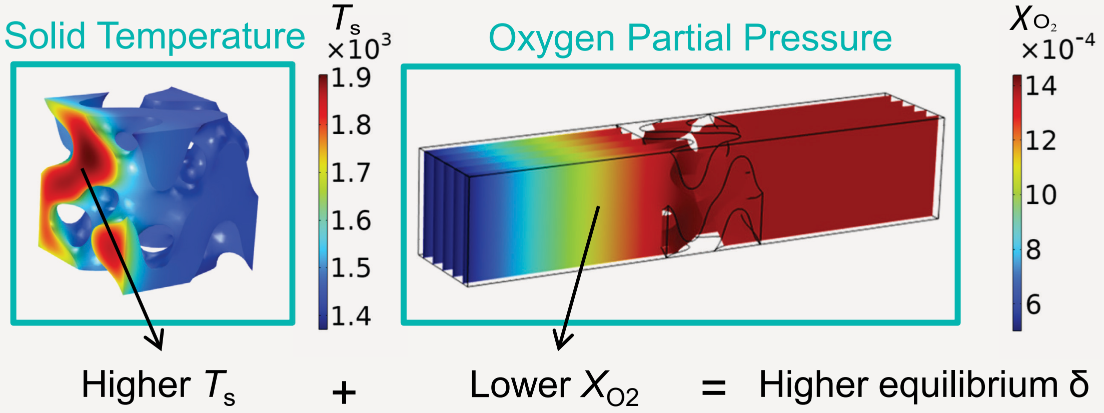
- **Impact of surface exchange coefficient k_{surf}**
  - Surface roughness can influence apparent k_{surf}.
  - The increasing of k_{surf} boosts reaction rate.
  - Low k_{surf} is a limiting factor.



The increasing of k_{surf} leads reduction extend accentuation.

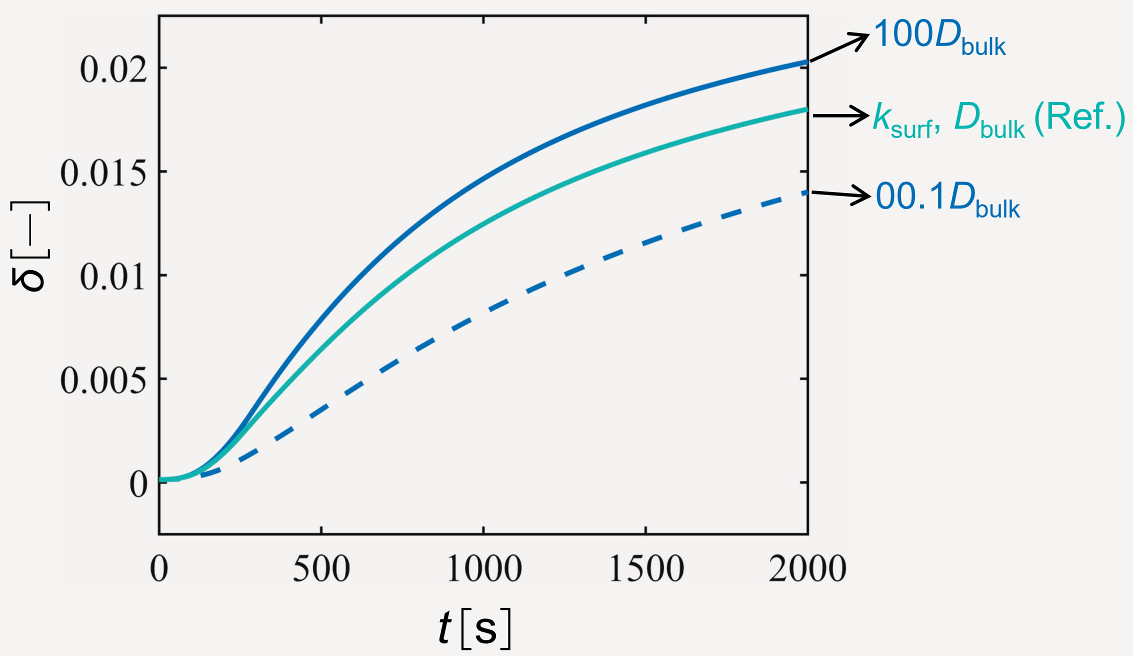


The gradient is caused by uneven temperature distribution.

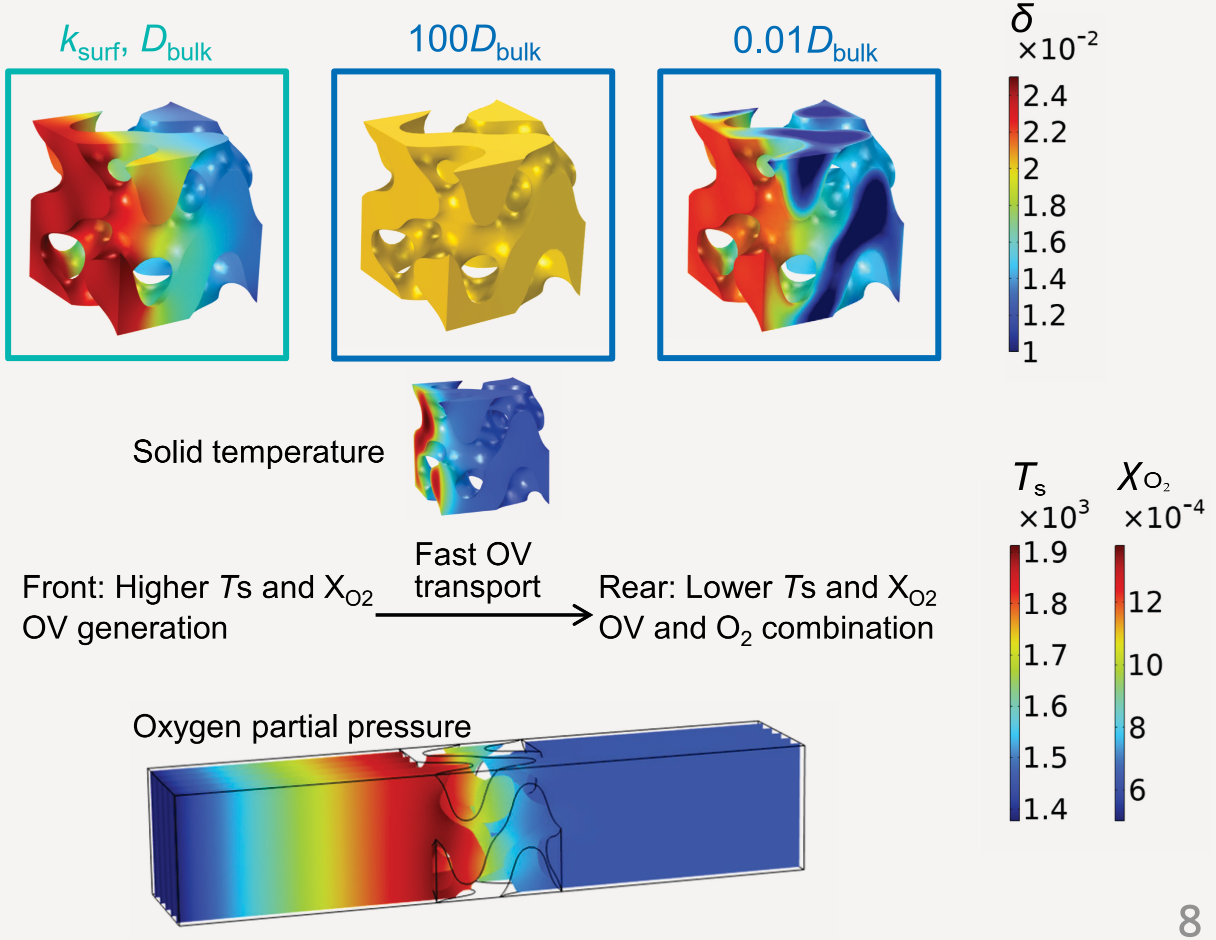


Results

- **Impact bulk diffusion coefficient D_{bulk}**
  - Large solid phase fraction can increase apparent D_{bulk}.
  - The increasing of D_{bulk} boosts reaction rate.
  - Low D_{bulk} is a limiting factor.

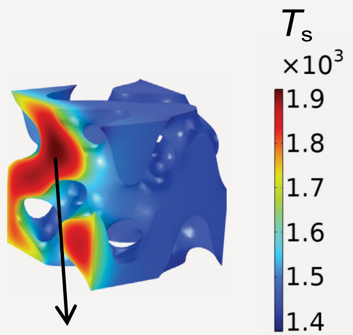


For low D_{bulk}, surface has higher reduction extend.



Outlook

- Direct pore-level multiphysical model
  - Input: Porous structure
  - Output: High fidelity physics field of solar-to-fuel performance
  - Application: gradient structure design



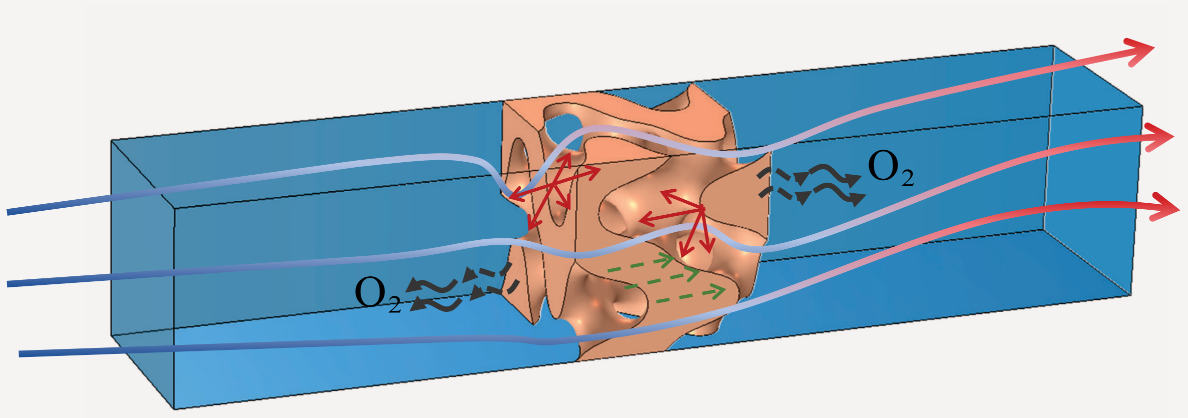
Location of the highest temperature spot

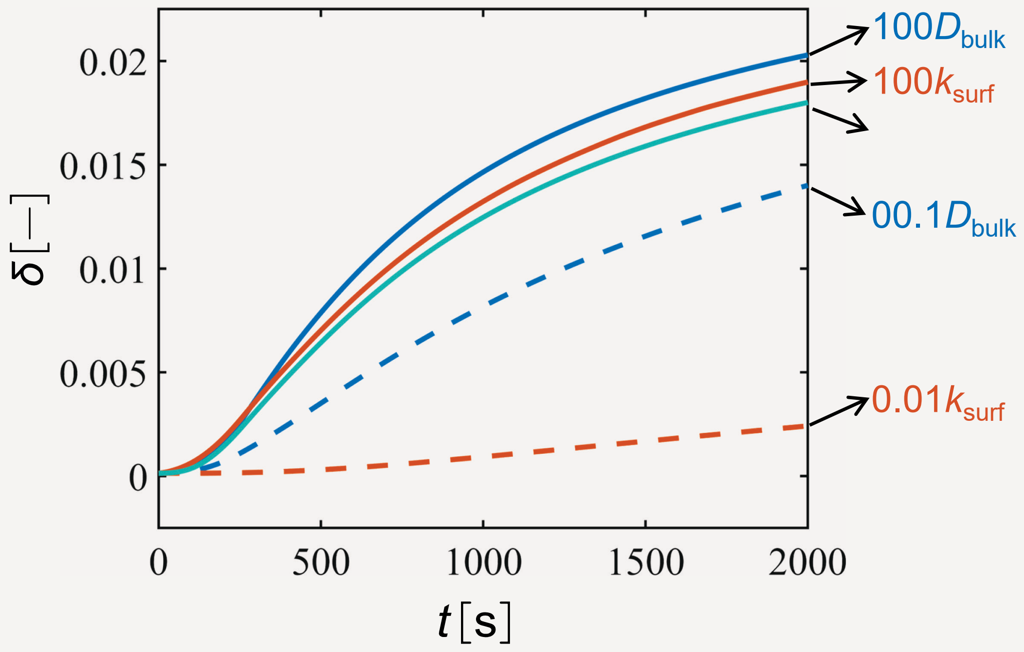
- For example： To minimize the temperature gradient
  - Management of incident radiation absorption
    - Smaller porosity at front surface to let more energy heat up rear part.
  - Increasing convective heat transfer
    - Tuning structure to achieve higher Nusselt number.

Summary

- **A comprehensive multi-physics model based on actual geometry of porous ceria has been developed including heat and mass transfer, species transport, solar absorption, as well as bulk vs. surface kinetics.**

- **The impacts of surface exchange coefficient and bulk diffusion coefficient on reduction reaction are compared.**





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