NOVEL CERAMICS AND COMPOSITES PROCESSING TECHNOLOGIES FOR ENERGY-INTENSIVE APPLICATIONS

27 SEPTEMBER, 2024

CEM-WAVE

The CEM-WAVE project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 958170 The content of this document reflects only its authors' view and the European Commission is not responsible for any use that might be made of the information it contains.

Why and **how**
Micro-Wave Chemical Vapor Infiltration
and other Thermal-Gradient Chemical Vapor Infiltration techniques
can achieve optimal Ceramic-Matrix Composites fabrication

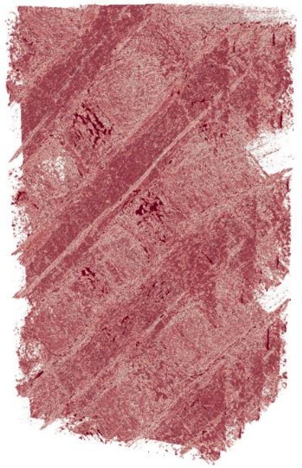
Pr. Gerard L. VIGNOLES

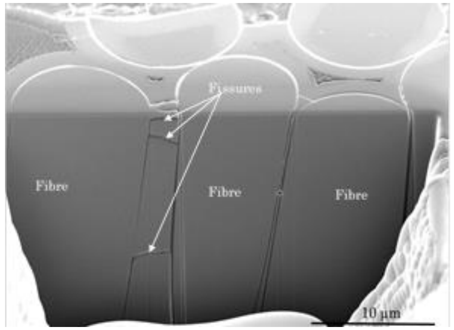
Lab. For ThermoStructural Composites

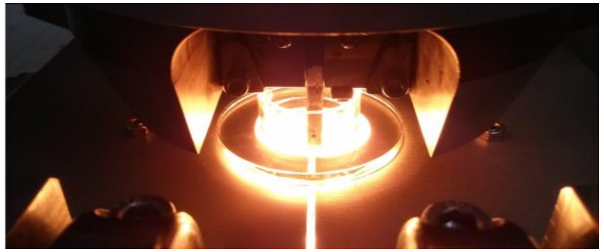
LABORATORY FOR THERMOSTRUCTURAL COMPOSITES

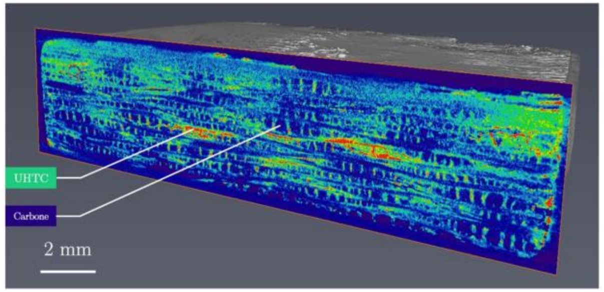
UMR 5801

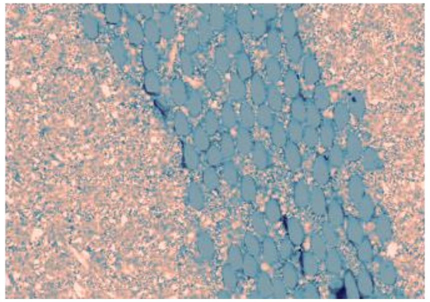
36 years of research & innovation on CMCs

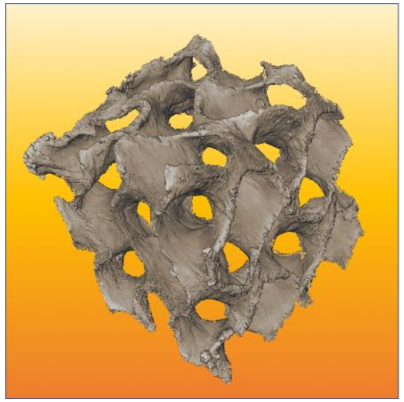








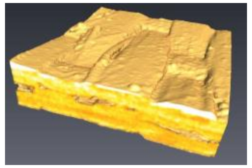
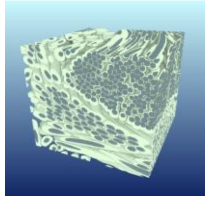
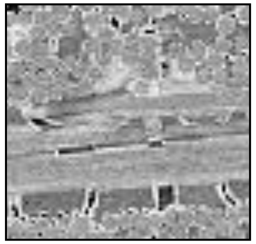
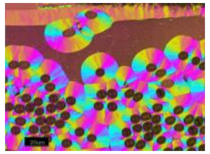
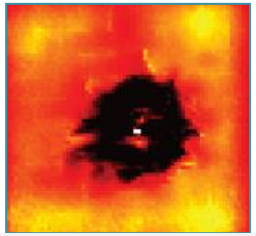
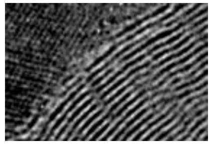
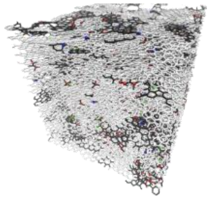
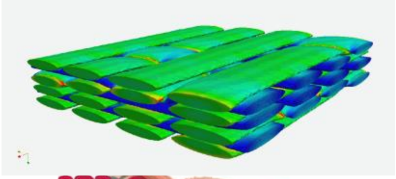
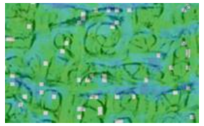
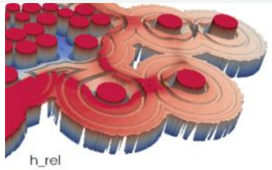




33 staff of which 16 publish, 8 non-academic
15 PhD candidates, 4 post-docs

Activities of LCTS on CMC: 4 axes

- Processing
  - Understanding mechanisms
  - New processes
- Structural/chemical characterisation
  - At all scales
- Behavior testing
  - Mechanical/thermal/chemical (corrosion/oxidation)
- Multi-scale modelling
  - Processes
  - Materials behavior

NATIONAL RESEARCH GROUP

CERAMIC MATRIX COMPOSITES : CHARACTERIZATION, MODELING, CONCEPTION

GDR 2065
Est. 2019

Director: G. L. VIGNOLES, vinhola@lcts.u-bordeaux.fr

COMPANIES

SAFRAN
Pyromeral Systems
MBDA MISSILE SYSTEMS
SAINT-GOBAIN
arianeGroup

Groupement de recherche
(CMC)²
Composites à Matrice Céramique
Conception, Modélisation, Caractérisation

+ 25 Universities & Engineering Schools

RESEARCH

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IRT SAINT EXUPÉRY

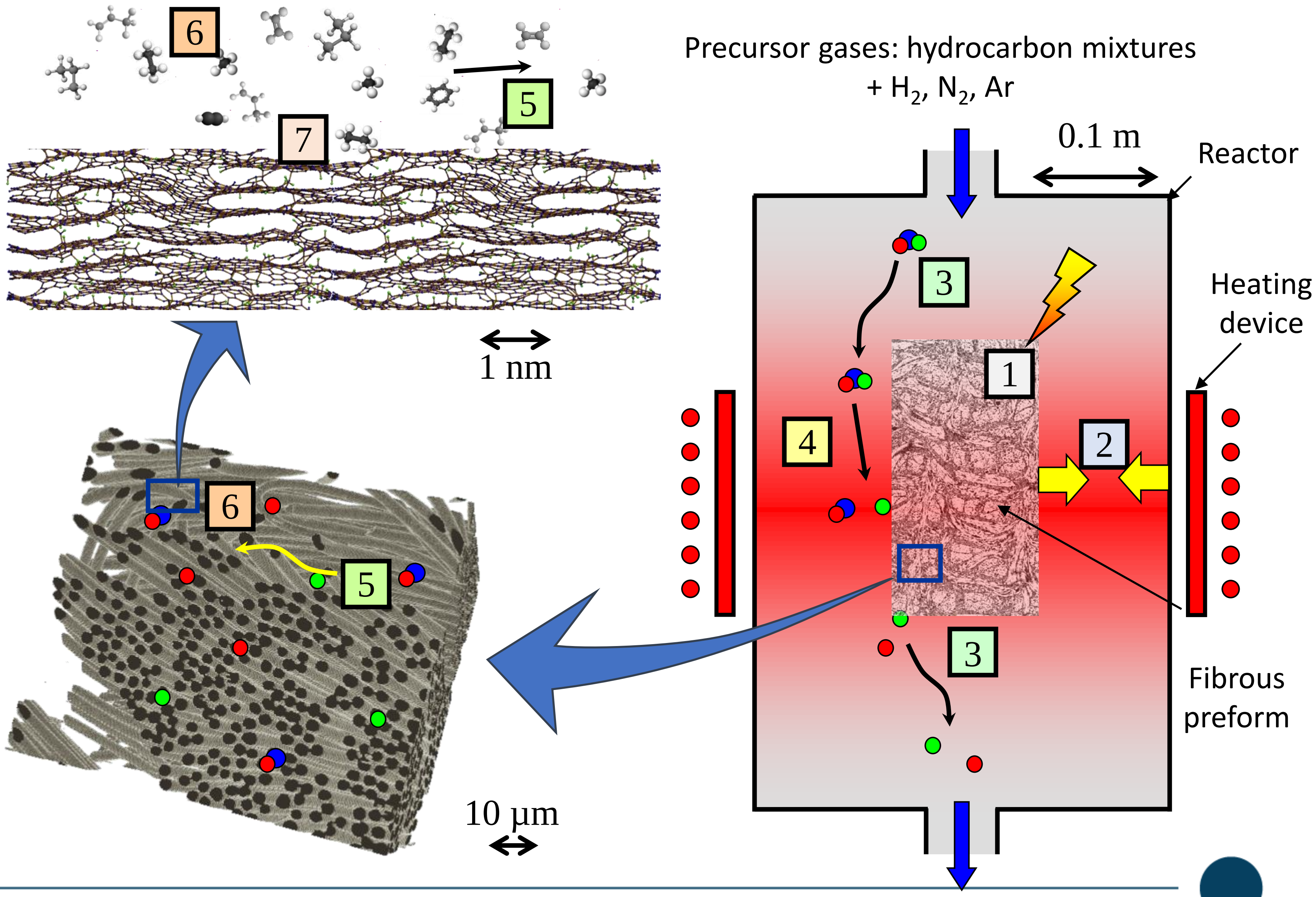
AGENCIES

ANDRA
DGA

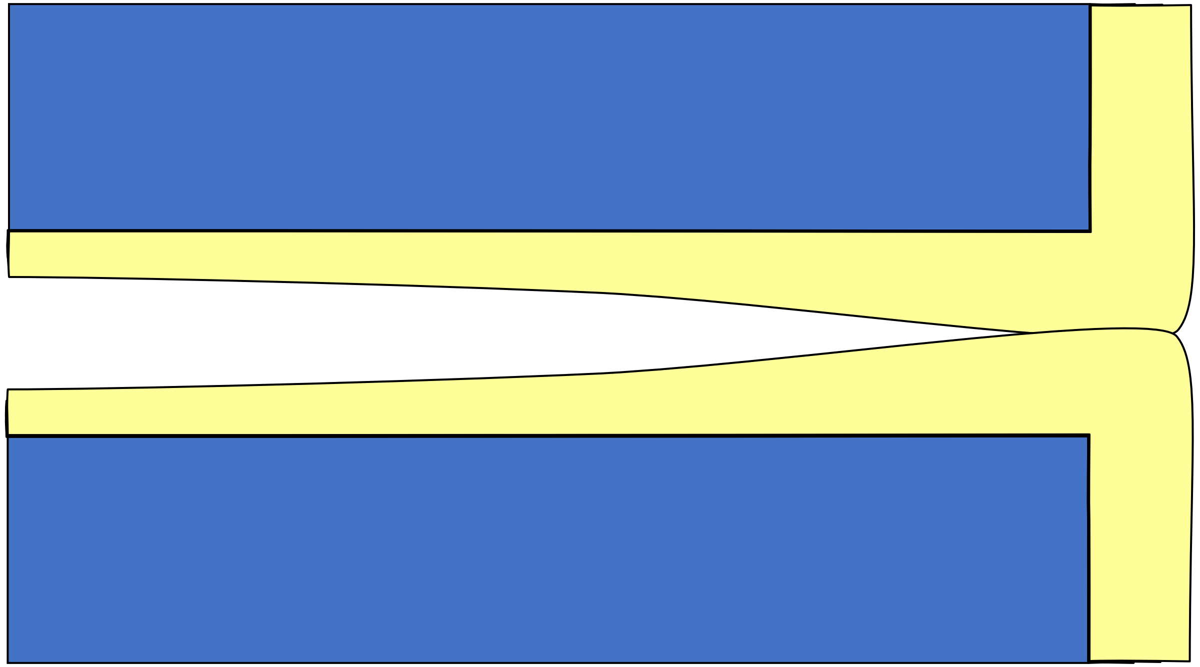
CMCs prepared by CVI

G. L. Vignoles, "Chemical Vapor Deposition/Infiltration Processes For Ceramic Composites", Ch. 8 of "*Advances in Composites Manufacturing and Process Design* ", P. Boisse Ed., Elsevier, pp. 147-176 (2016)

1 Heating
2 Cooling
3 Gas convection
4 Homog. reactions
5 Diffusion (+ Knudsen)
6 Homog. reactions
7 Heterog. reactions



The concept of Thermal-Gradient CVI



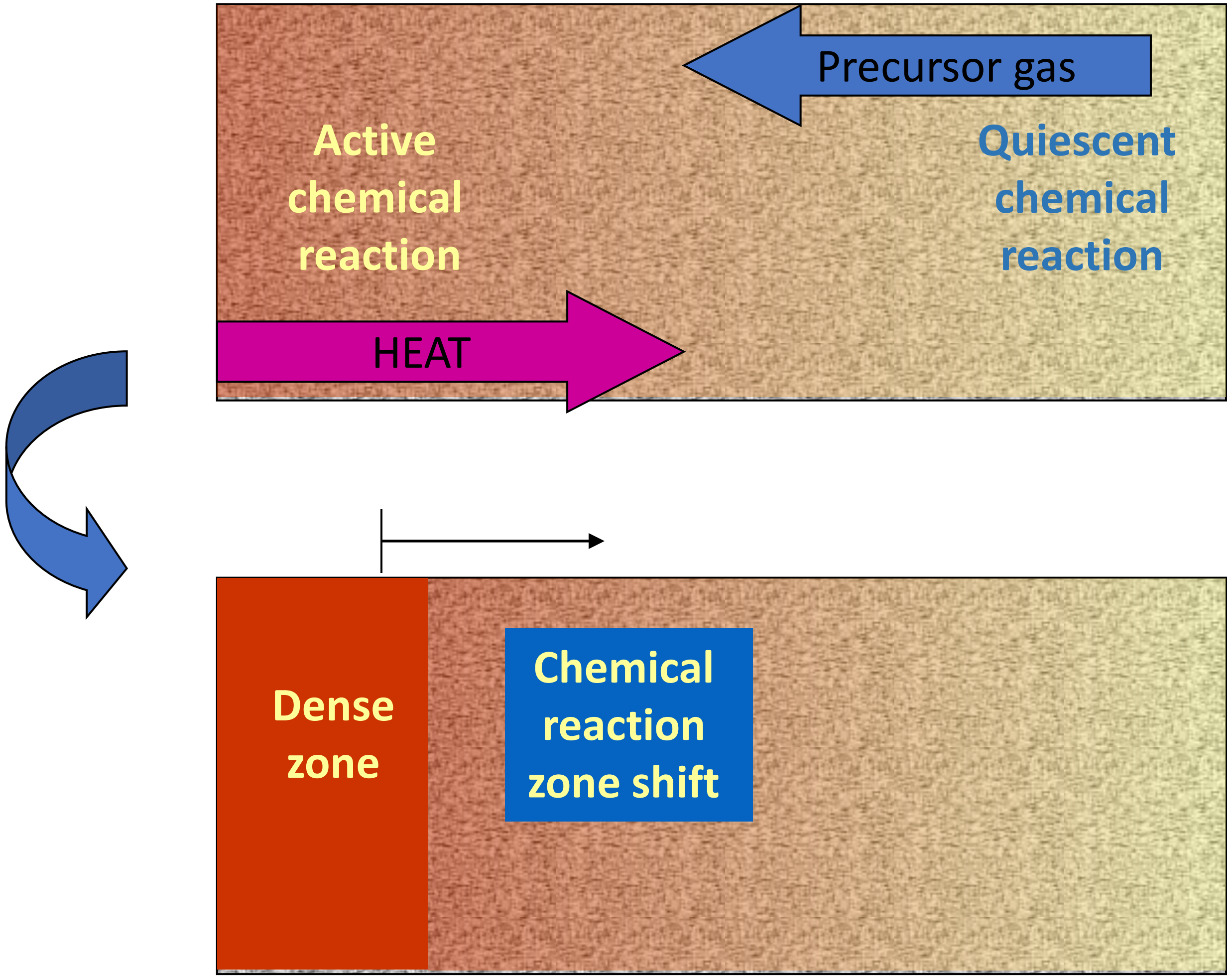
Isothermal infiltration

Premature pore plugging

Idea : chemical deposition should start from pore end !

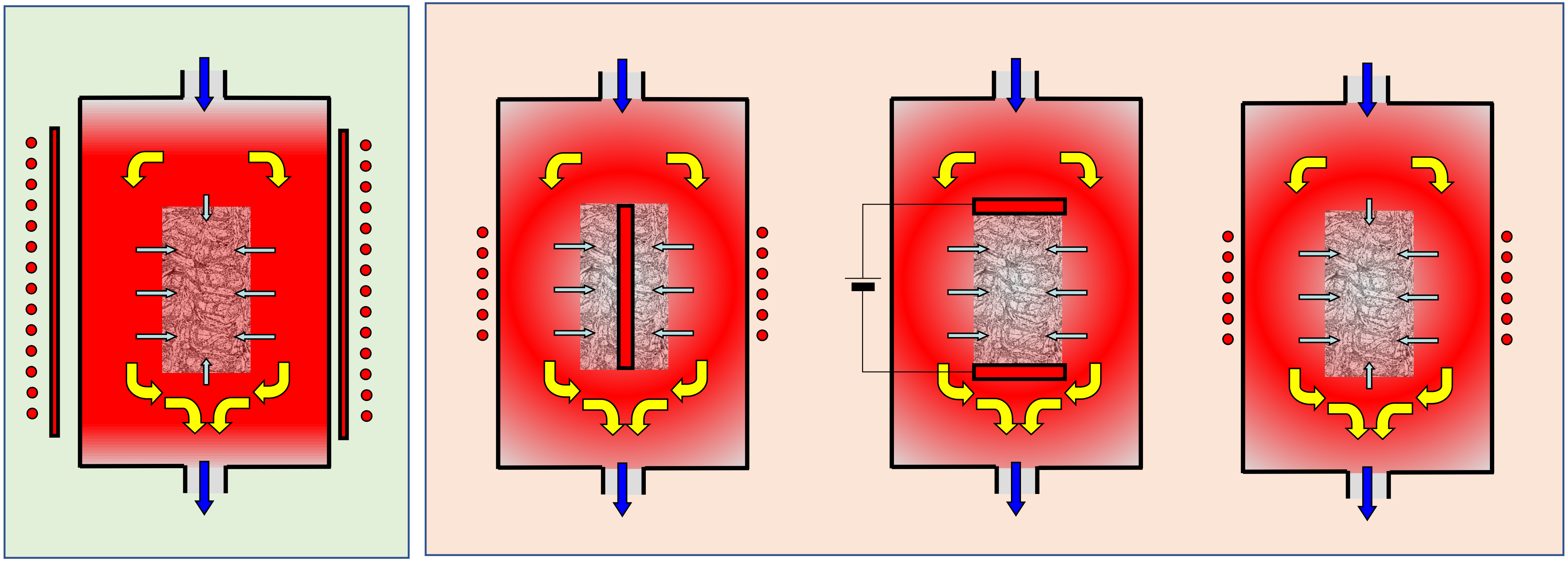
THERMAL GRADIENT (hot inside, cold outside)

TG-CVI : phenomena



Variations of CVI

G. L. Vignoles, "Chemical Vapor Deposition/Infiltration Processes For Ceramic Composites", Ch. 8 of "*Advances in Composites Manufacturing and Process Design* ", P. Boisse Ed., Elsevier, pp. 147-176 (2016)



Basic process :
I-CVI
Isothermal, isobaric

Thermal-gradient variations (TG-CVI)

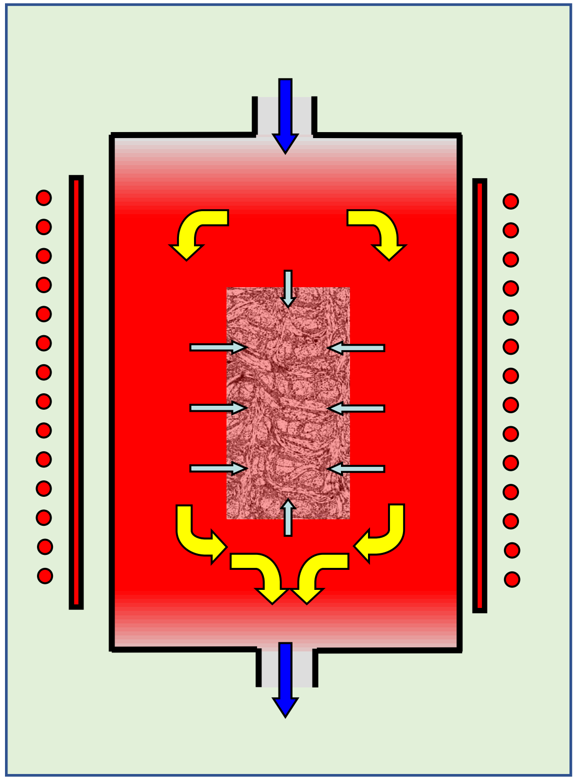
By contact
with hot susceptor
[Golecki *et al.*, 1994]

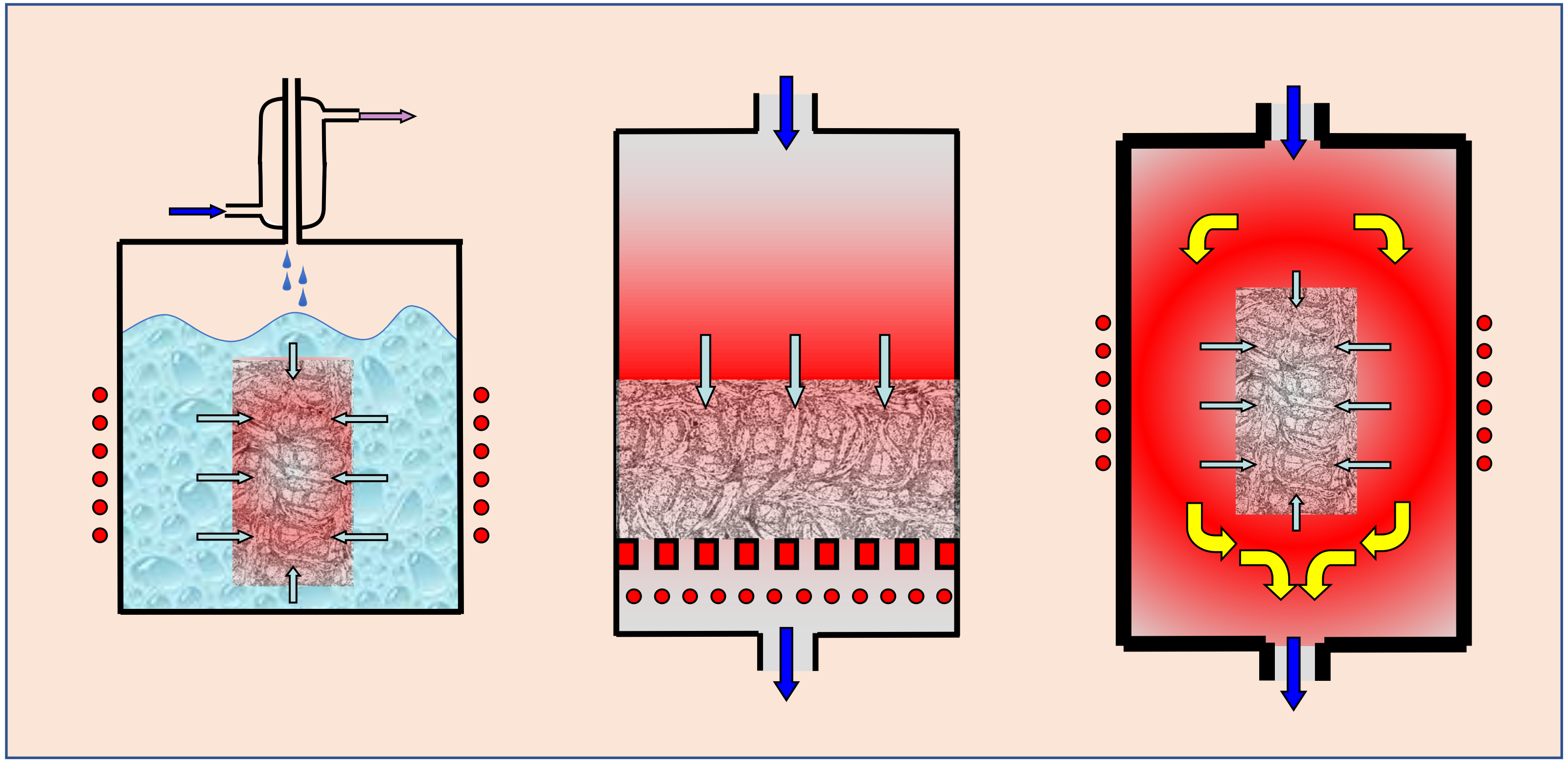
Electrical heating :
E-CVI
[Li *et al.*, 2008]

Direct coupling :
RF-CVI or MW-CVI
[Devlin *et al.*, 1992, 1996]

Variations of CVI

G. L. Vignoles, "Chemical Vapor Deposition/Infiltration Processes For Ceramic Composites", Ch. 8 of "*Advances in Composites Manufacturing and Process Design* ", P. Boisse Ed., Elsevier, pp. 147-176 (2016)





Basic process :
I-CVI
Isothermal, isobaric

Thermal-gradient variations (TG-CVI)

With boiling precursor:
« Film-boiling » or Kalamazoo
[Houdayer, 1984]

With pressure gradient:
P-CVI
[Besmann, 1991]

High-pressure (supercritical):
C-SCF-I
[Maillé, 2017]

CMC processed by *Micro-Wave CVI*

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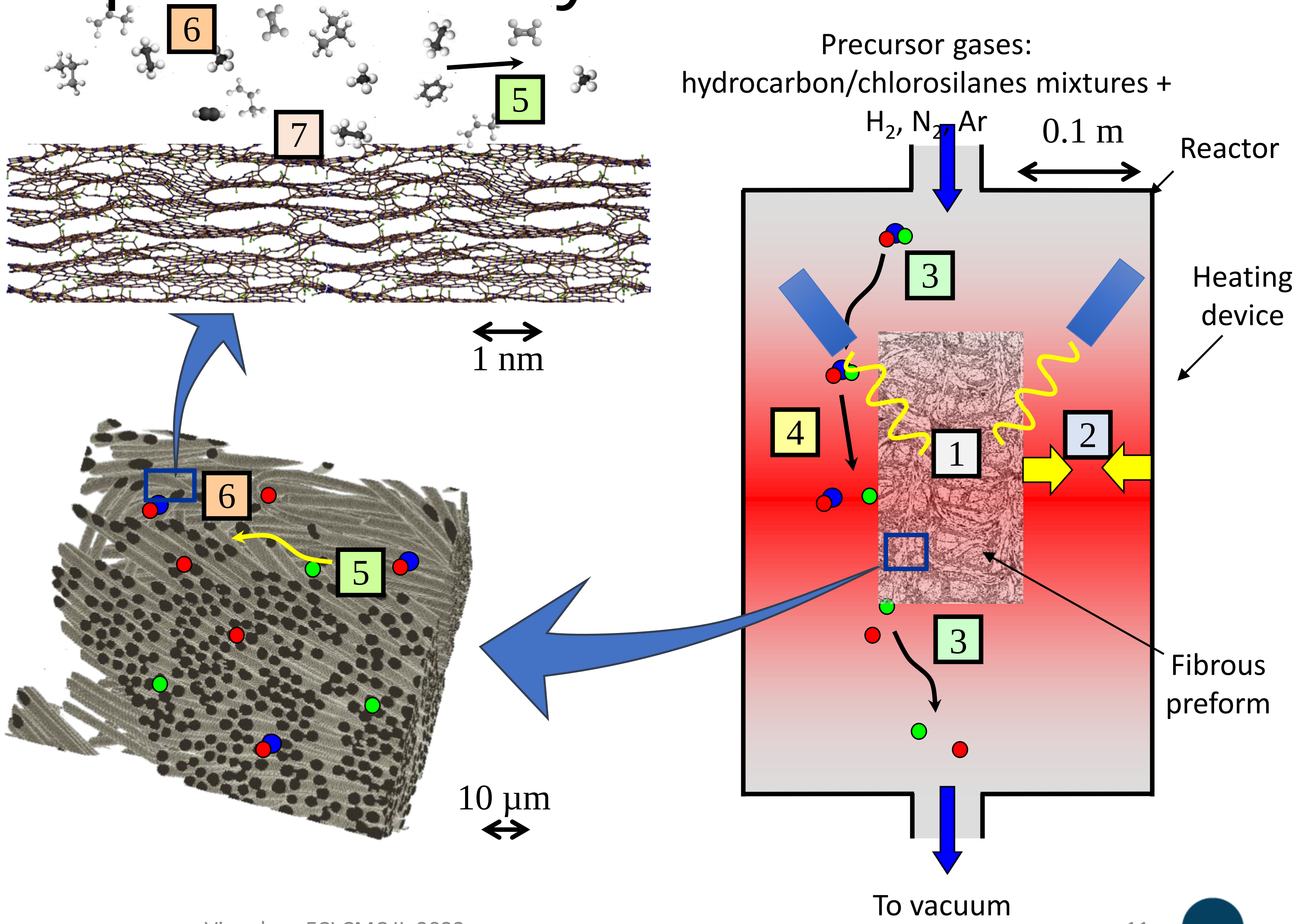


The starting point

The deposition reaction relies principally on three parameters :

$$R(x,t) = \sigma_v(\varepsilon)\, k(T)\, C^{\alpha}$$

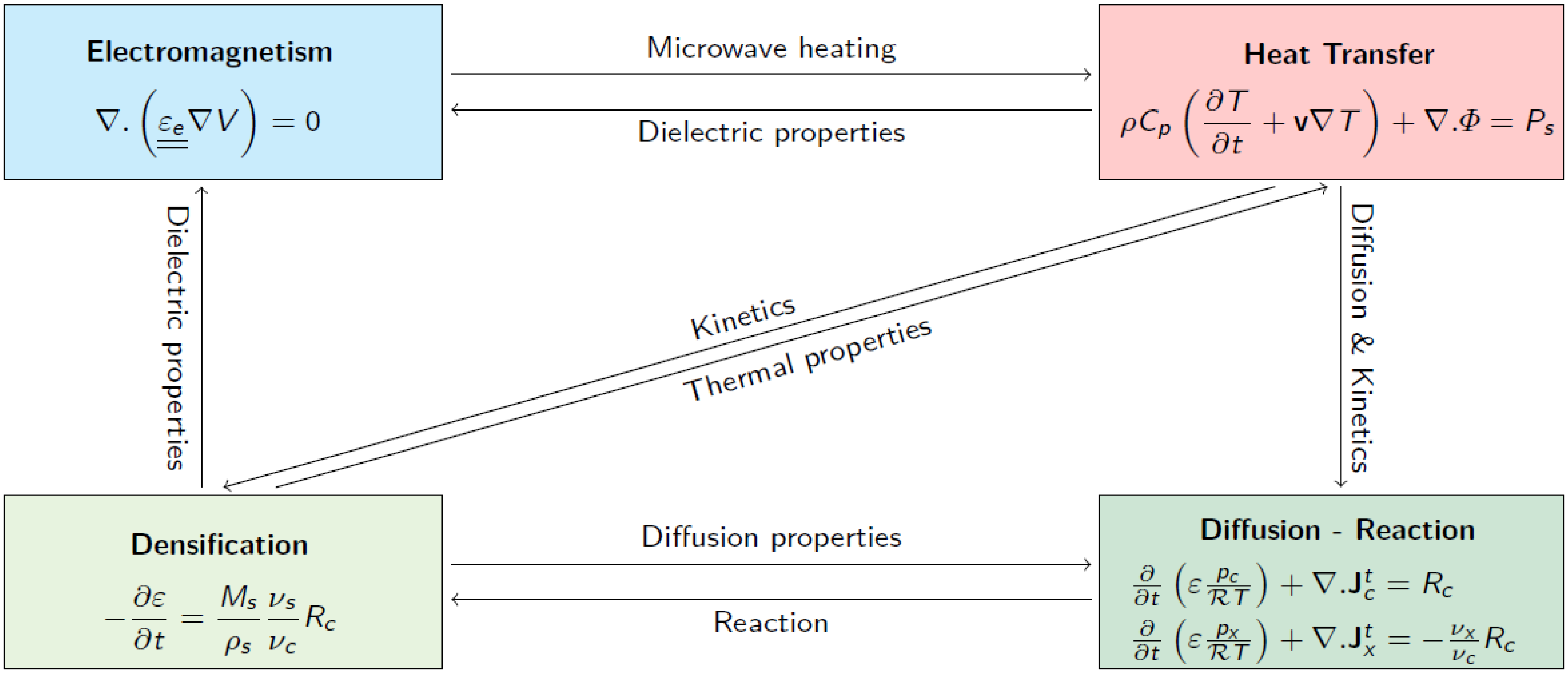
Internal surface area, depends on porosity ε

Temperature T through Arrhenius law

Gas precursor concentration, C

→ ***Three variables* (at least) are required to describe the reaction zone.**

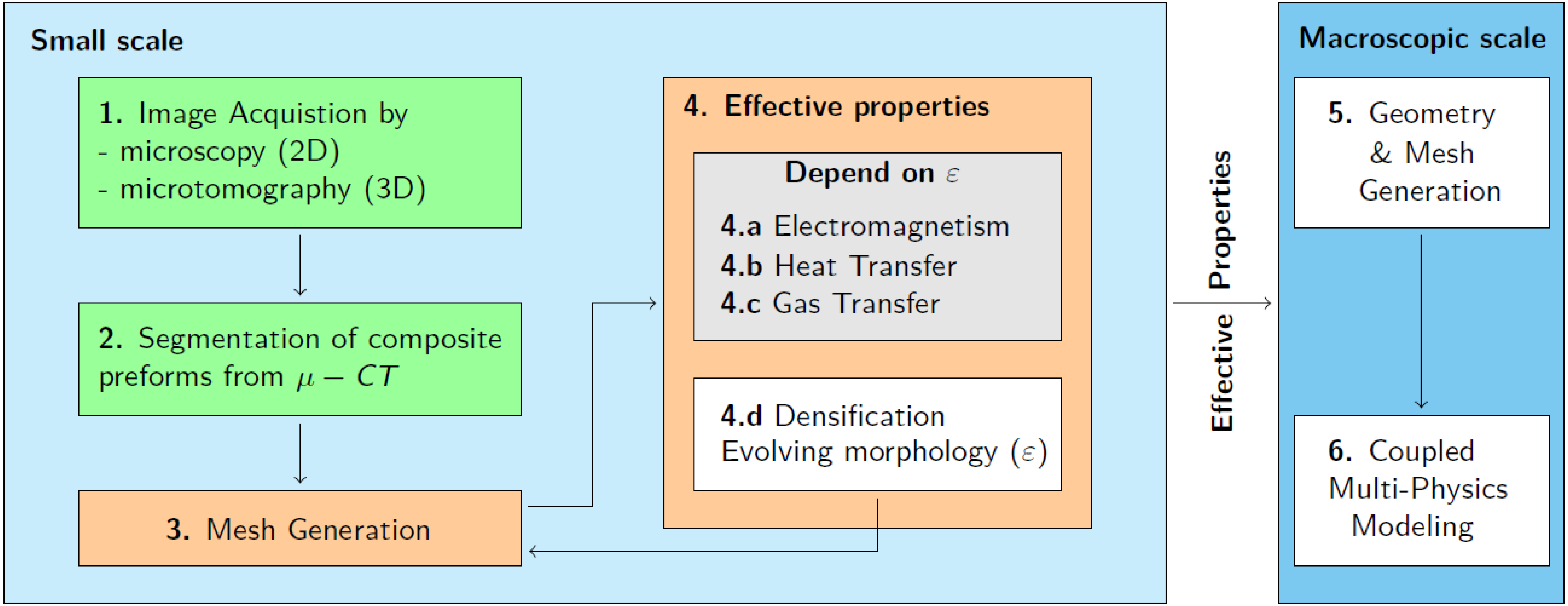
Multiphysics coupling



Effective properties to be computed

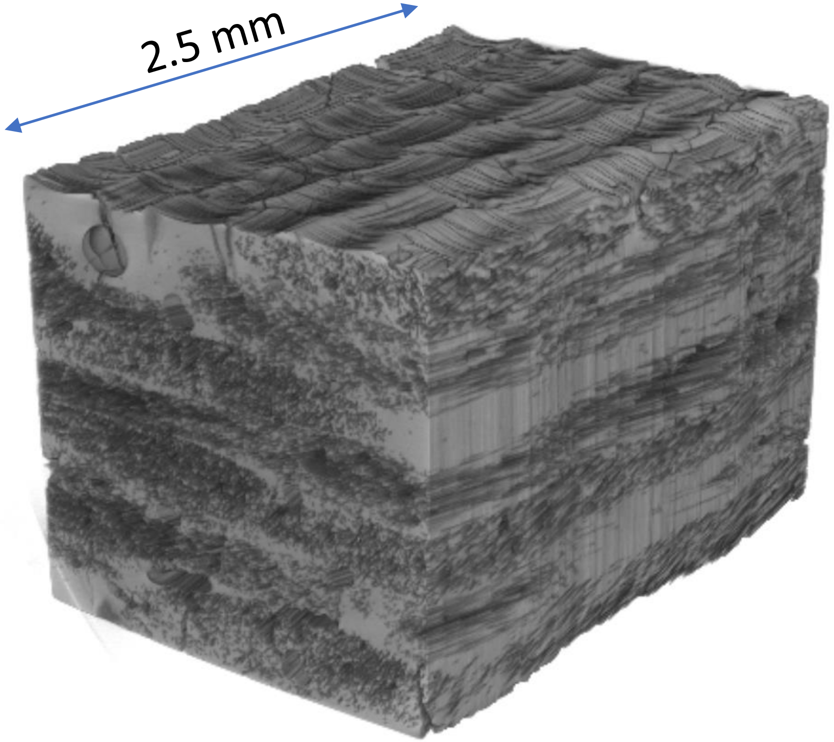
Physic	Effective propertie Computations	Numerical tools
Electromagnetism	Effective permittivity $\underline{\underline{\varepsilon}}$	FreeFEM++
Heat Transfer	Effective conductivity $\underline{\underline{k}}$	FreeFEM++
	Effective density ρ	Constitutive Law
	Effective heat capacity C_p	Constitutive Law
Gas Transfer	Effective diffusivity $\underline{\underline{D_g}}$	Random walks from Vignoles et al. (2011)

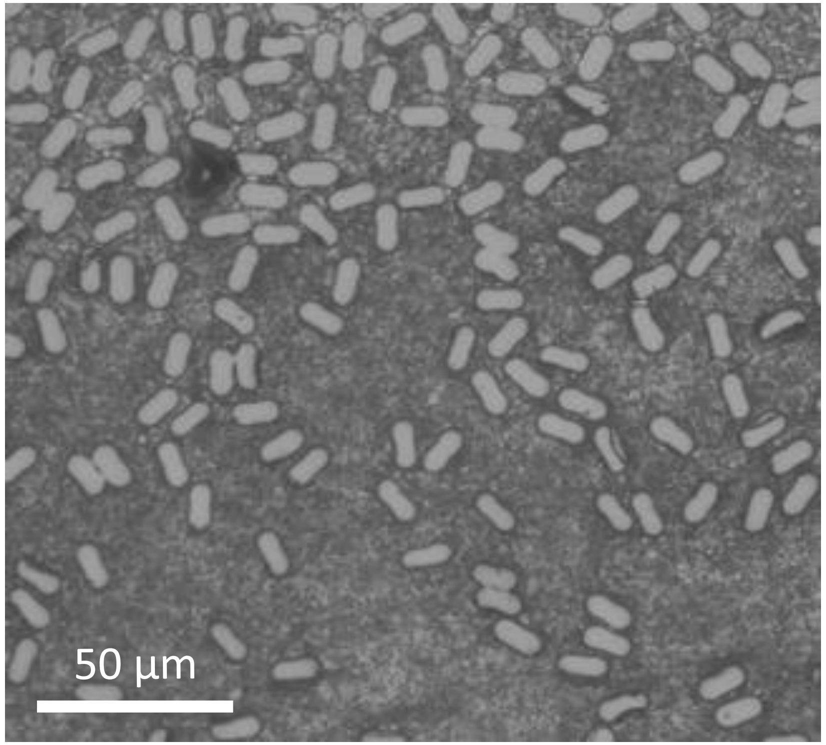
2-scale computational strategy



Multiscale in practice

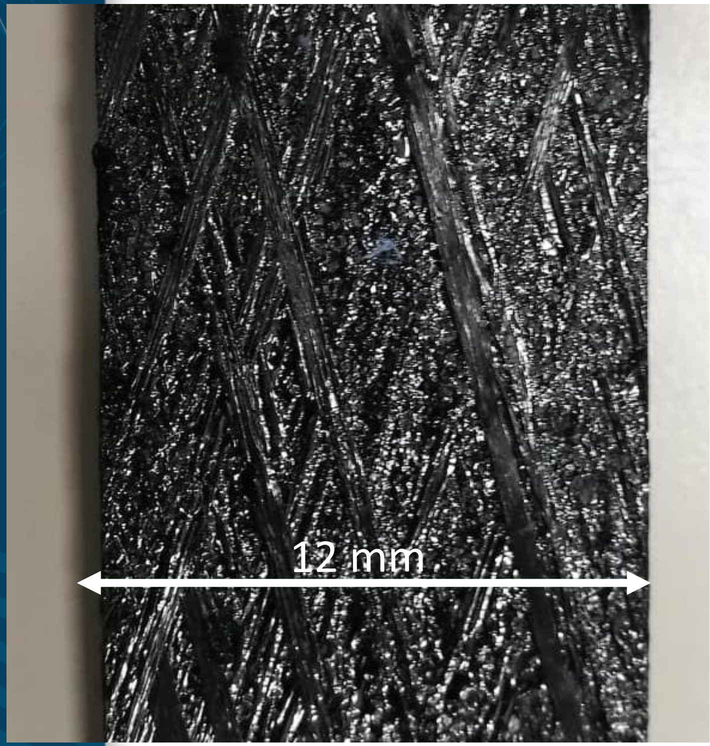
- CT and SEM / Ox-ox

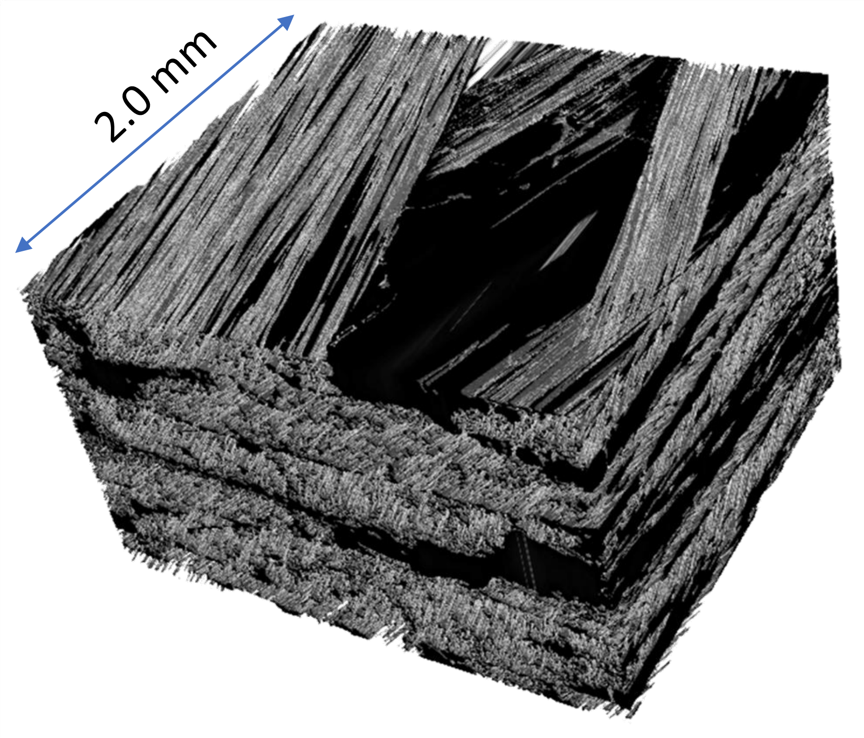




Multiscale in practice

- CT and SEM : SiC/(SiC) preform





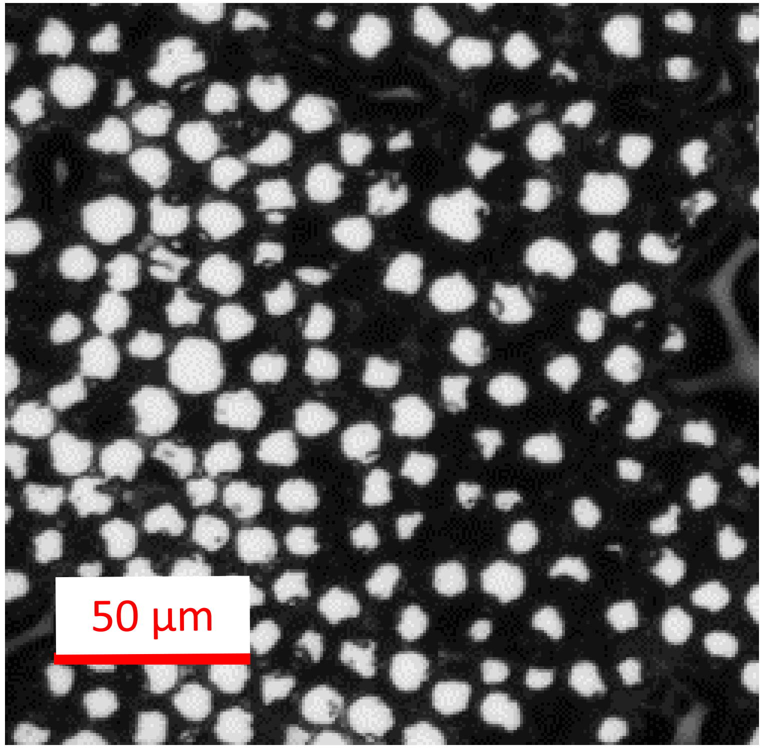
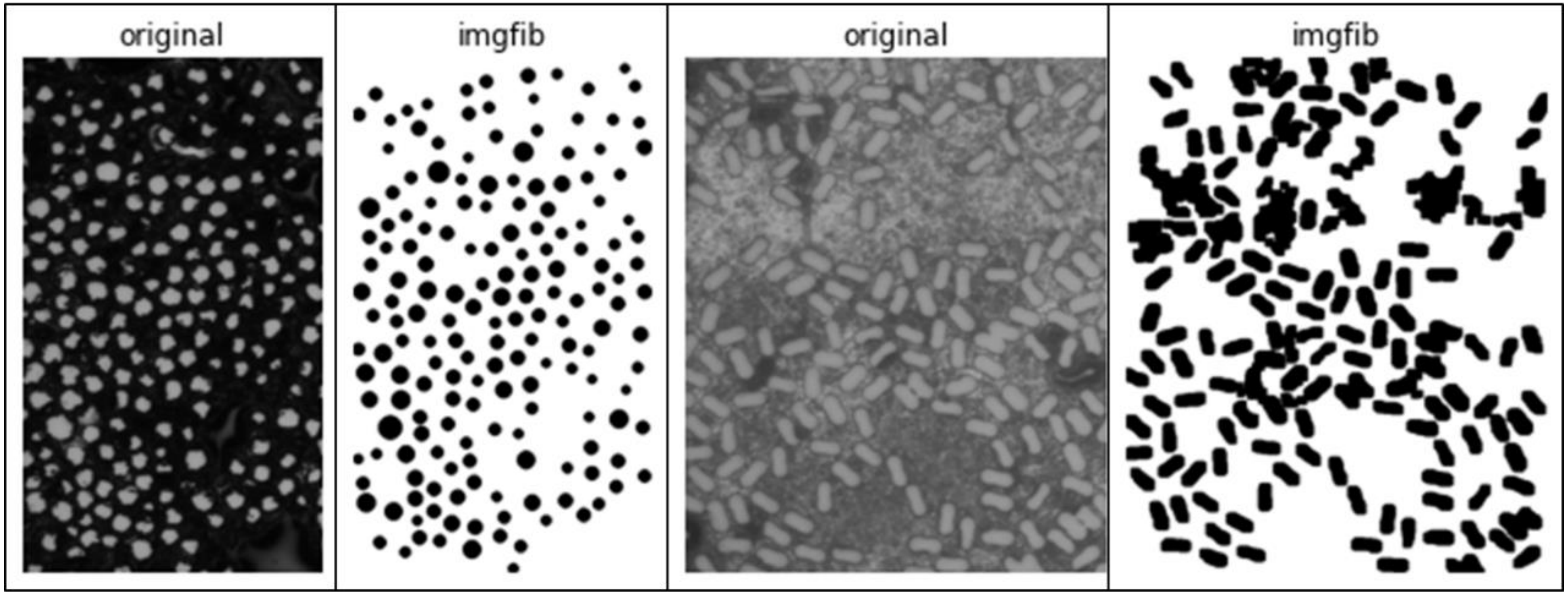


Image processing

- Application to the CEM-WAVE preforms

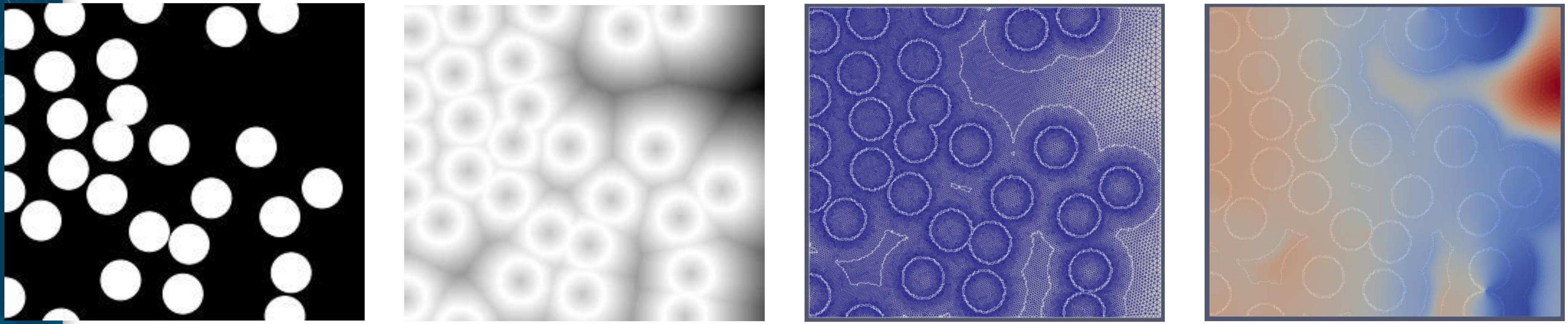
SiC fiber preform

Ox. fiber preform



Mesh procedure

- Using distance from the interphase to optimize the elements density



The effective property computation procedure

Instead of computing the actual temperature under a given applied gradient, we compute a « closure variable » b_i is the coefficient of proportionality of the temperature perturbation $T - \langle T \rangle$ with respect to the magnitude of the gradient applied in direction *i* $\|\langle \nabla T \rangle \cdot \boldsymbol{e_i}\|$:

$$b_i = \frac{T - \langle T \rangle}{\|\langle \nabla T \rangle \cdot \boldsymbol{e_i}\|}$$

$\langle * \rangle$ Is the space average operator

It allows obtaining the effective property tensor :

$$\langle \lambda \rangle_{ij} = \langle \lambda . \left(\delta_{ij} + \nabla_i b_j \right) \rangle$$

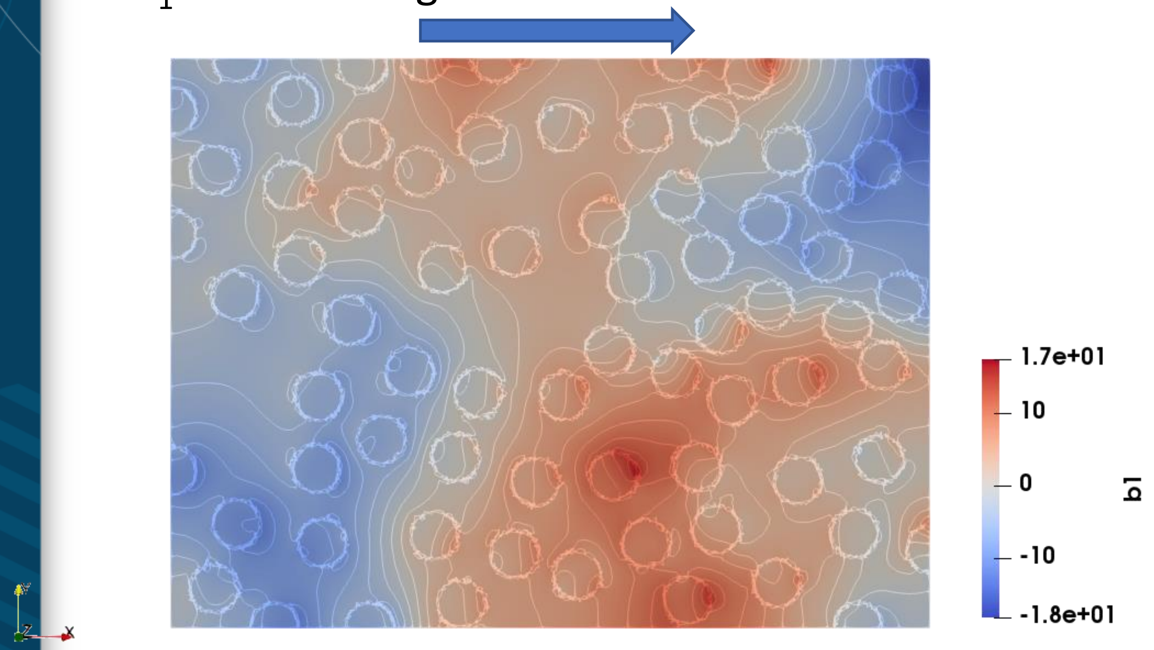
δ_{ij} is the Kronecker symbol :
1 if $i = j$, 0 else

$\boldsymbol{b}$-field for the thermal problem – computation of the effective thermal conductivity – Example

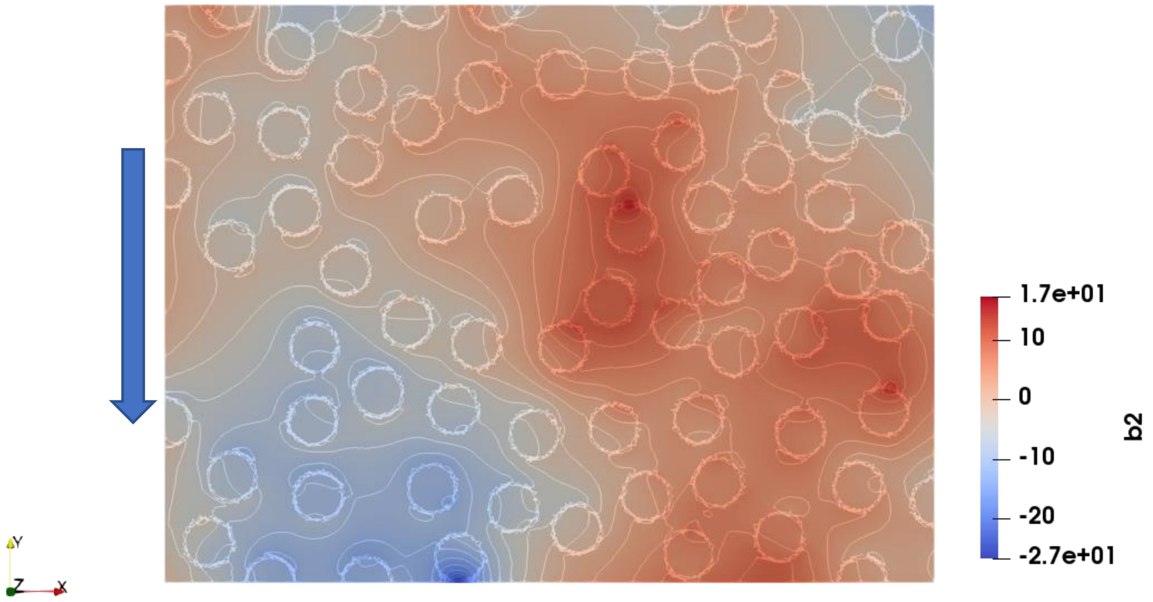
We solved the issue of handling non-periodic boundary conditions which are usually required for these computations.

- **Computation for a case that considers Matrix/Interphase/Fibers**

b_1 : horizontal gradient

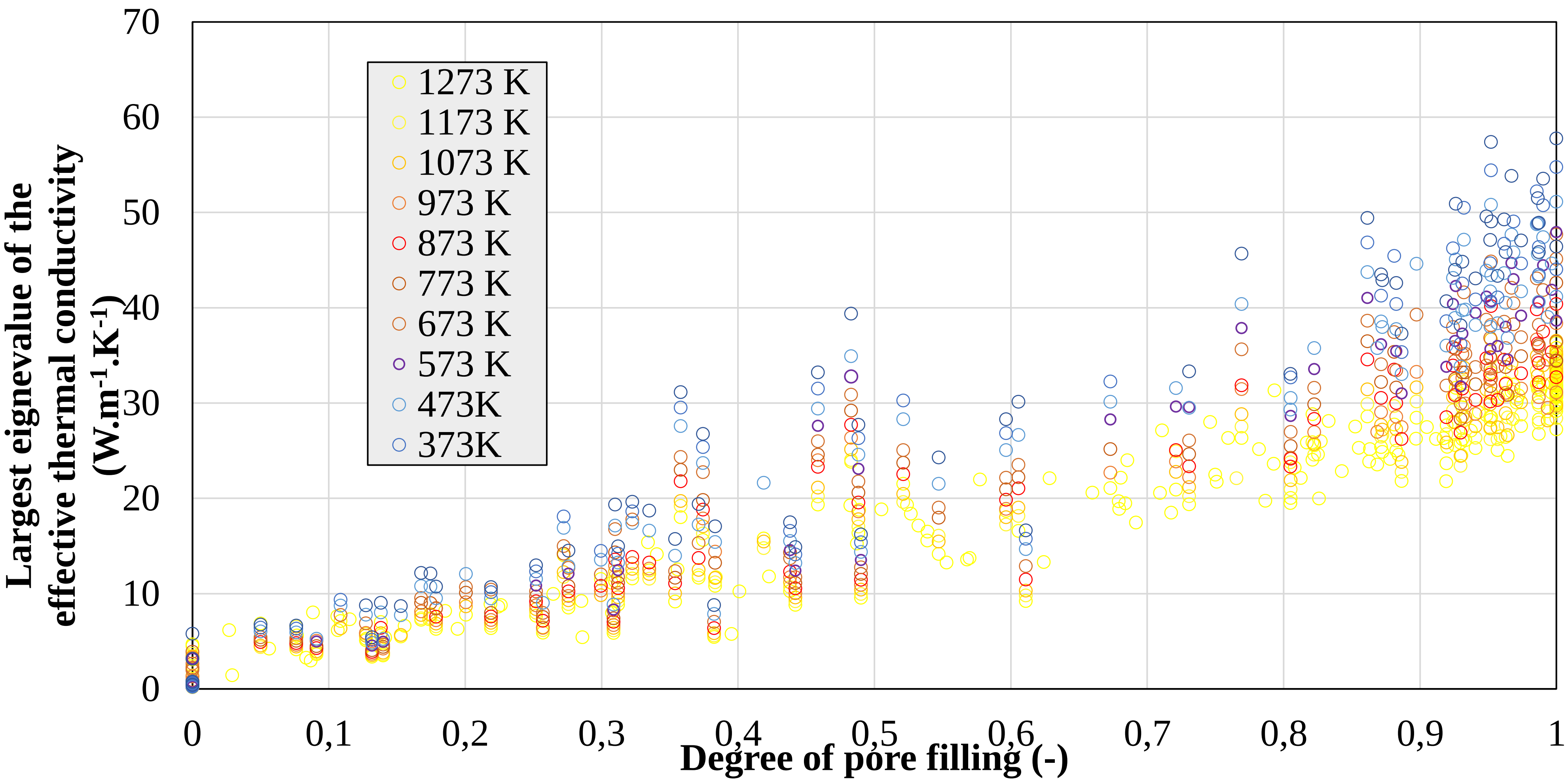


b_2 : vertical gradient



Homogenized properties

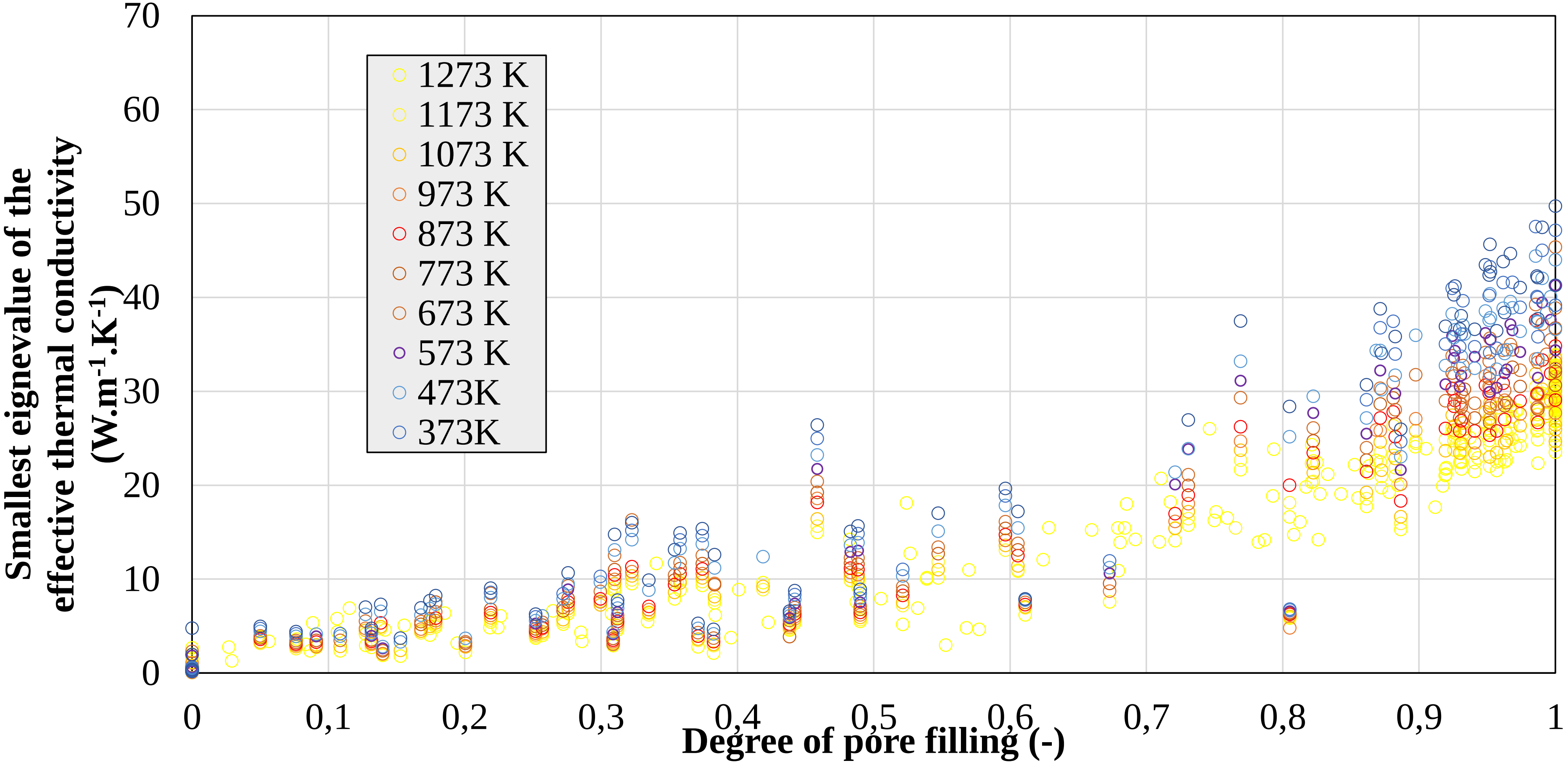
Heat conductivity : Highest eigenvalue



Properties also depend on the initial fiber volume fraction

Homogenized properties

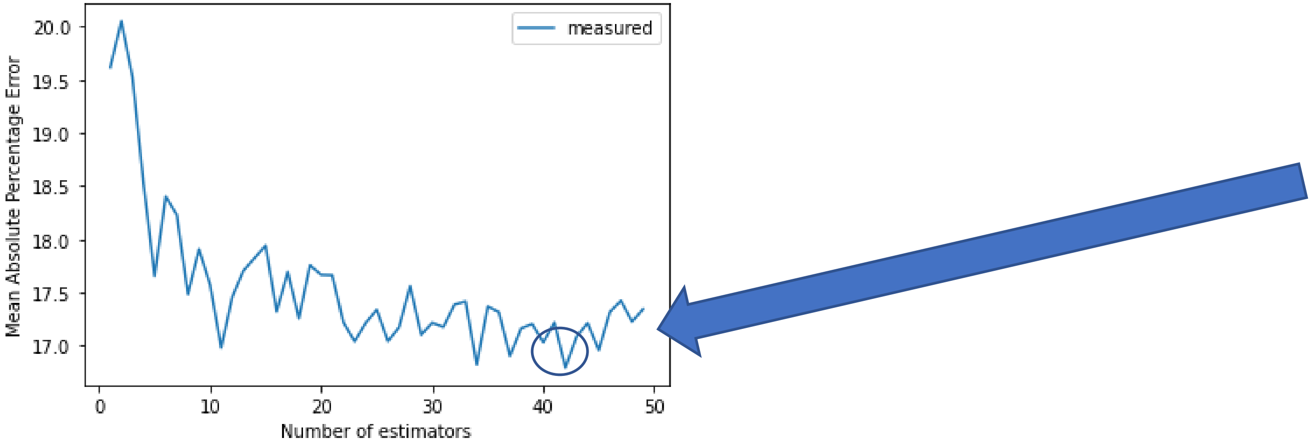
Heat conductivity : Lowest eigenvalue



Properties also depend on the initial fiber volume fraction

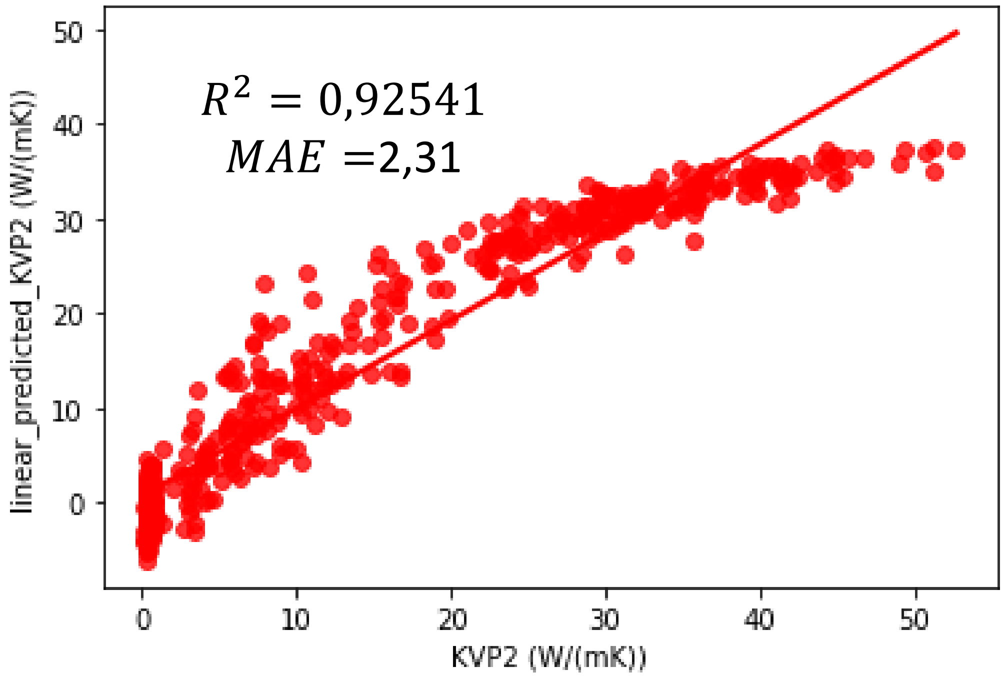
ML to correlate properties

- Obtained : thermal conductivity, dielectric permittivity, surface area
- Properties are correlated to : matrix vol. fraction (or DPF) and temperature, **but also to initial fiber vol. fraction**
- Obtaining an analytical function $\Psi = f(\phi_f, \phi_m, T)$ is hard work
- Instead, we can use a Random Forest Regression algorithm (`python/sklearn`)
- The number of estimators (« trees ») is optimized

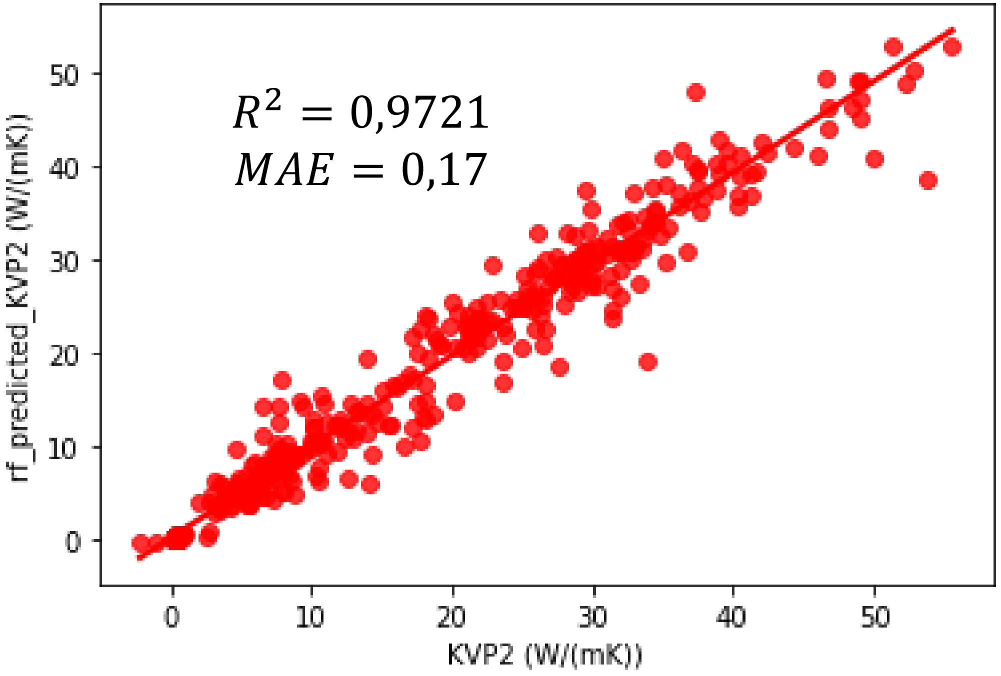


RFR vs. LR (Linear Regression)

The ML algorithm shows superior performances !



Linear Regression



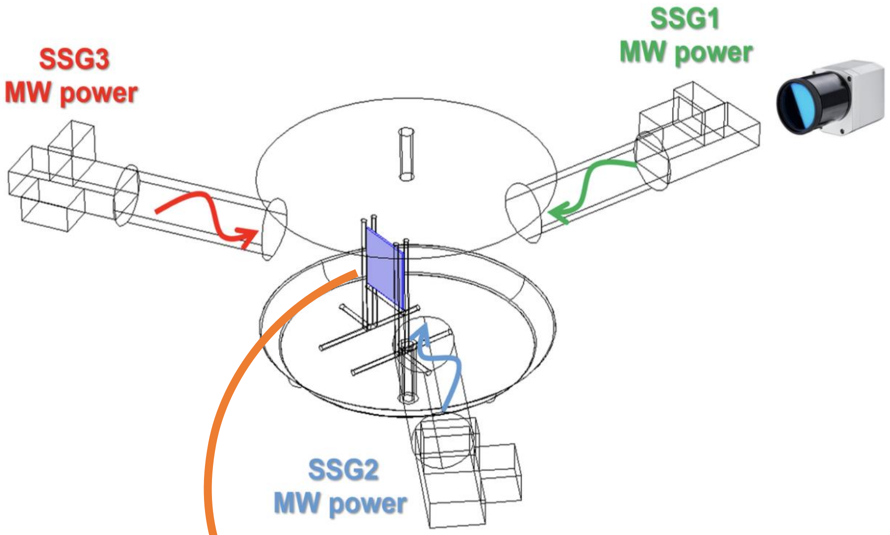
Random Forest , n_estimators=42

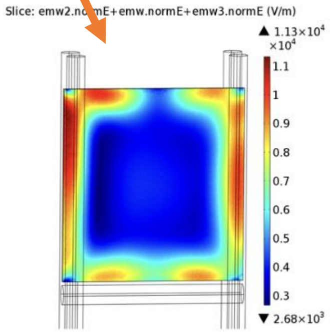
Large-scale modeling & validation

- An experimental case was modeled
  (data from IPCF-CNR : SiC/SiC MW-CVI in a test plate)
- A multiphysics model was run to reproduce the data
- An analytical study has been performed and compared
- Simple parameter variations were studied

Computations vs. experiments

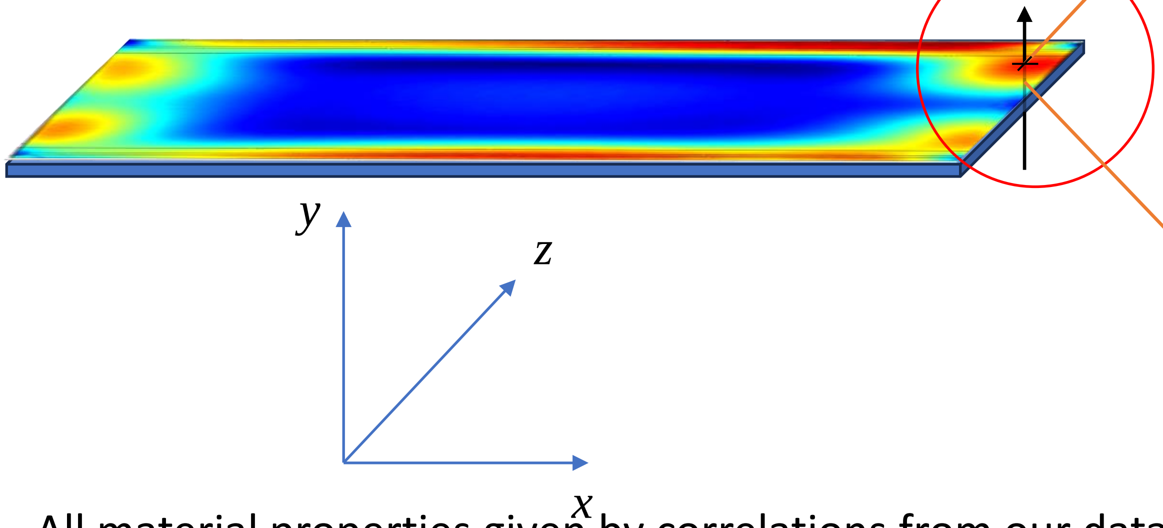
- Experiment :
  - IPCF-CNR experimental setup for SiC infiltration described in R. D'Ambrosio et al. , J. Eur. Ceram. Soc. (2020), 3019–3029 & Chem. Eng. J. 405 (2021), 126609.
  - Results detailed in a manuscript submitted to J. Eur. Ceram. Soc., under minor revision





Model setup

Pseudo-1D simulations through the thickness ;
location chosen at the hottest point
(as determined by previous Comsol simulations)



Upper surface ($y = h$) :

$$Re(H_z) = H_{z.0}(t)$$

$$-\lambda \nabla T.\mathbf{n} = e_{tot}\sigma_{SB}(T^4 - T_{ext}^4)$$

Interior :

$$\nabla^2 H_z - \omega^2 \mu \epsilon_0 \tilde{\epsilon} H_z = 0$$

$$\rho c_p \partial T/\partial t + \text{div.}(-\lambda \nabla T) = Q_{MW}\,(H_z.\ \tilde{\epsilon})$$

$$-\partial \varepsilon/\partial t = S_v\, k(T)\, C$$

Lower surface ($y = 0$) :

$$Re(H_z) = -H_{z.0}(t)$$

$$-\lambda \nabla T.\mathbf{n} = e_{tot}\sigma_{SB}(T^4 - T_{ext}^4)$$

All material properties given by correlations from our database :

$\lambda = f(T, \phi_f, \varepsilon)$

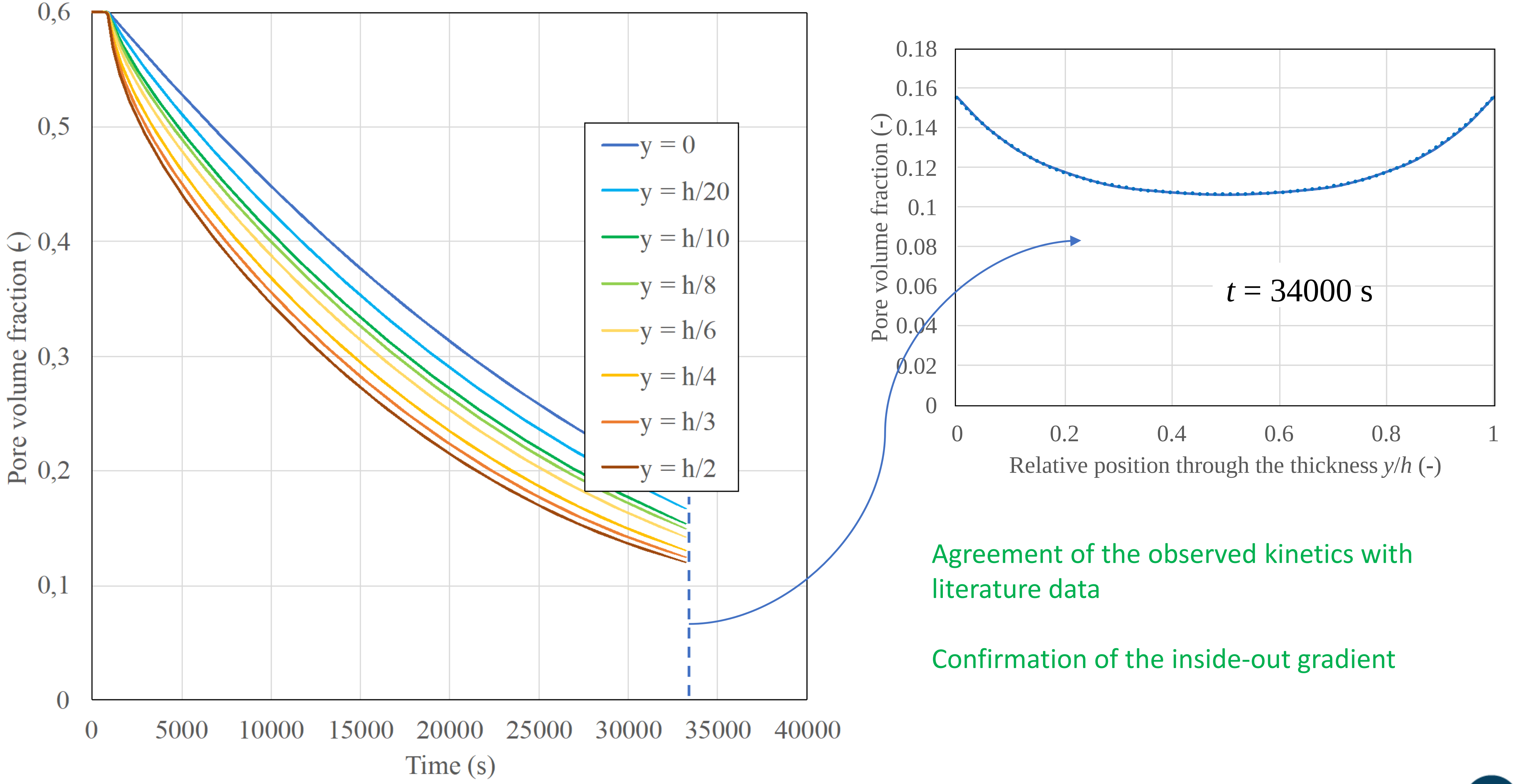
$\tilde{\epsilon} = f(T, \phi_f, \varepsilon)$

$\sigma_v = f(\phi_f, \varepsilon)$

+ Boundary field update equation to simulate a constant surface temperature equal to $T_{sp}(t)$:

$$\frac{dH_{z,0}}{dt} = -\frac{T(y=0) - T_{sp}(t)}{\tau}$$

Results



Agreement of the observed kinetics with literature data

Confirmation of the inside-out gradient

DISCUSSION

- Here, gas diffusion is never limiting ➔ the benefit of the inside-out thermal gradient is exploited.
- Let’s have a look at criteria based on dimensionless numbers …

The dimensionless numbers

- Φ is the Thiele modulus (associated to the hot side) : diffusion/reaction competition, responsible for possible depletion.

$$\Phi^2 = L^2 \frac{\sigma_v(\varepsilon_0) k(T_h)}{D}$$

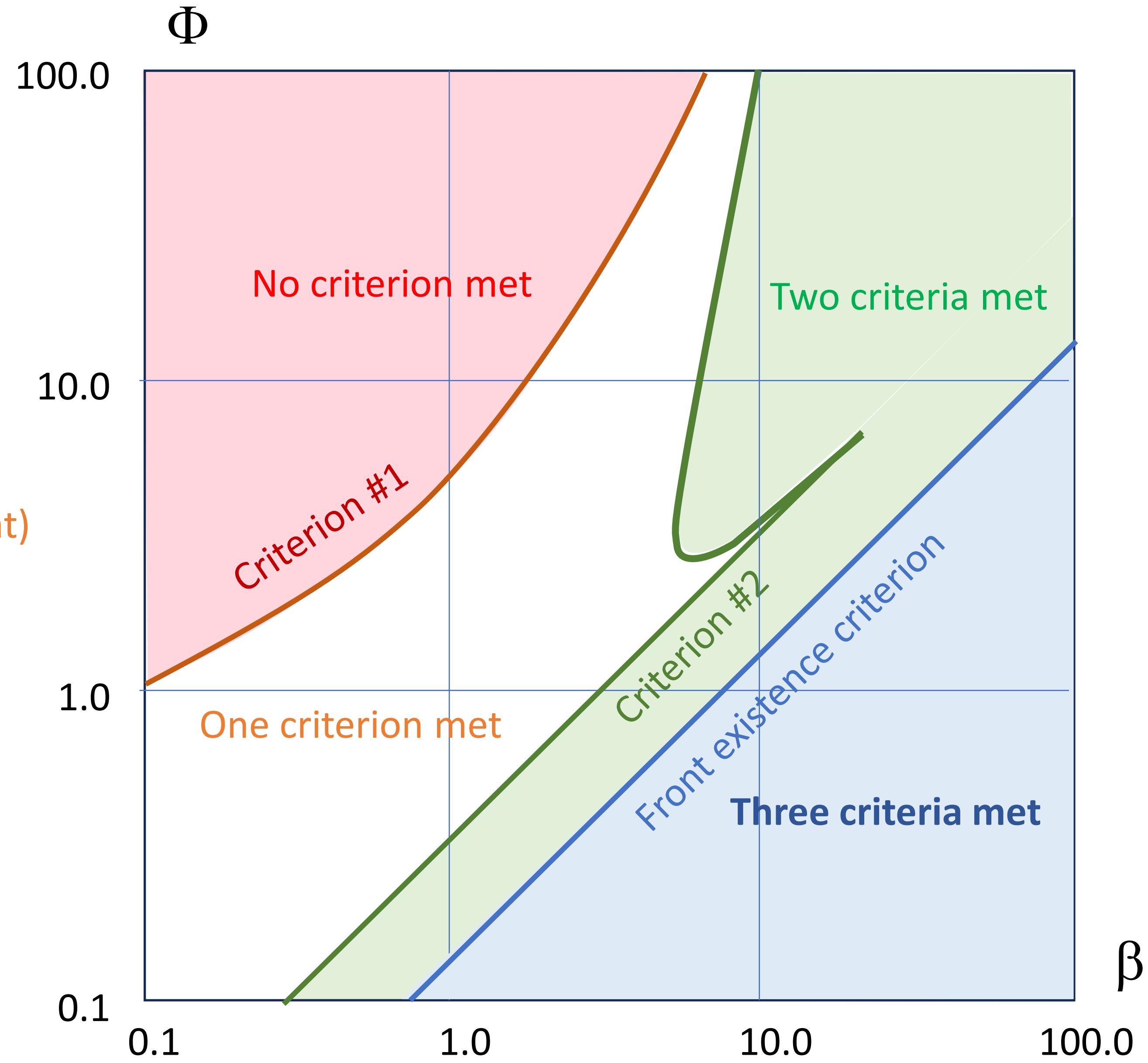
- β is the Zel'dovitch number : the relative thermal difference, amplified the activation energy.

$$\beta = \left(\frac{\Delta T}{T_h}\right)\left(\frac{E_a}{RT_h}\right)$$

Combining all three criteria

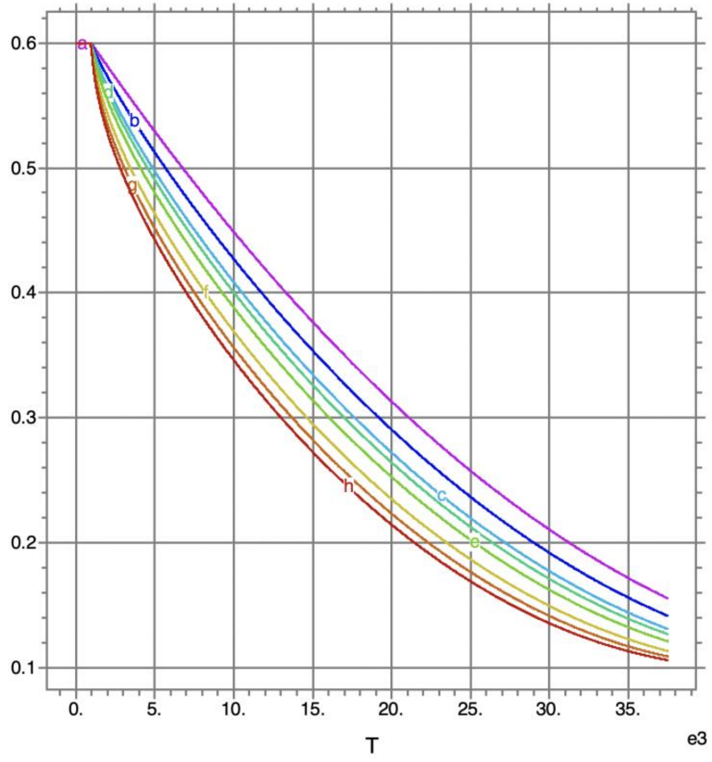
4 situations can occur :

- No criterion met : simple I-CVI
- One criterion met : faster inside, but crusting occurs already at start (trilby hat)
- Two criteria met : crusting eventually appears later (trilby hat)
- **Three criteria met : desired situation !**

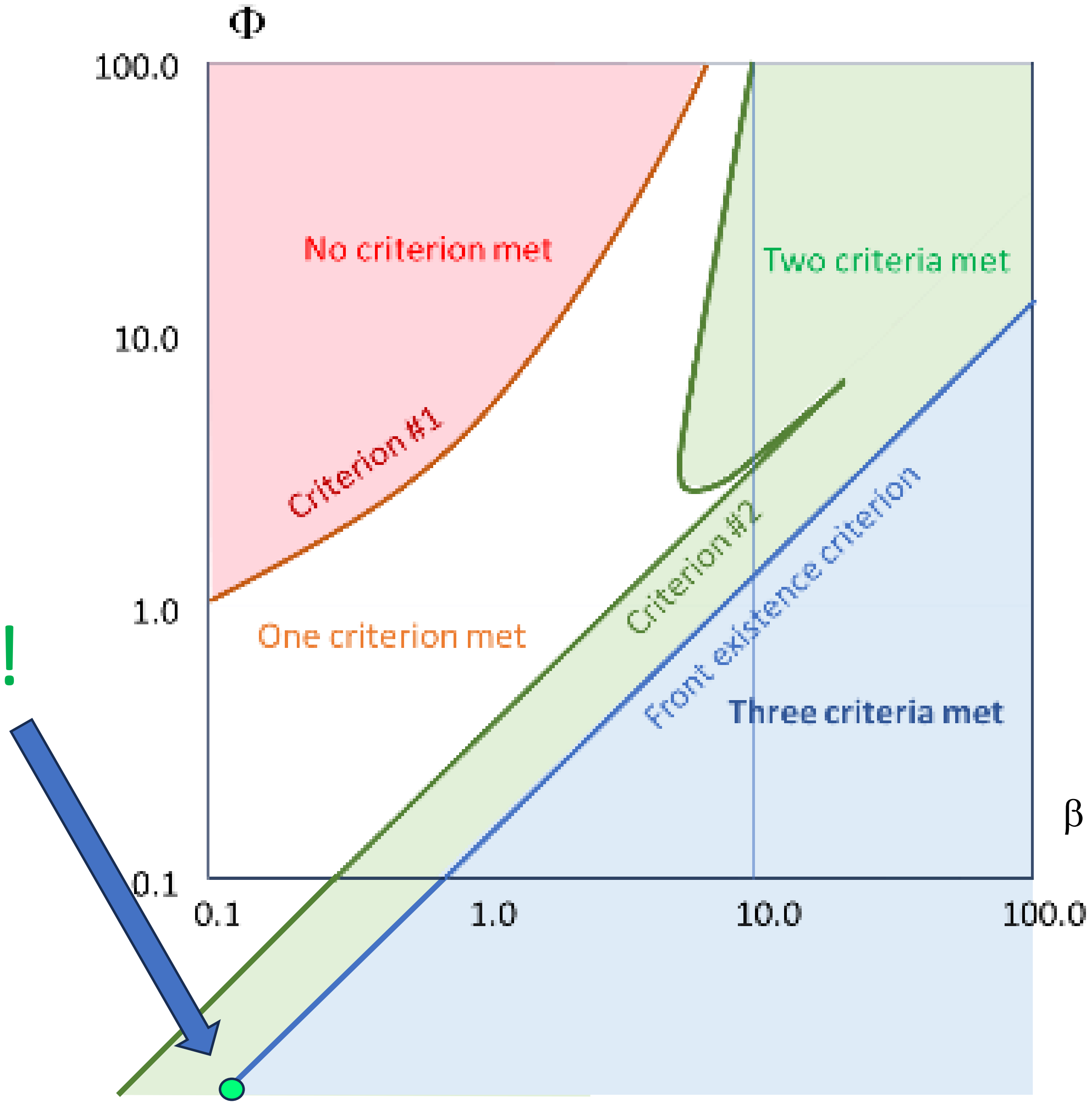


Dimensionless analysis

- Thiele modulus Φ : ~ 0.02
- Gradient parameter β : ~ 0.12

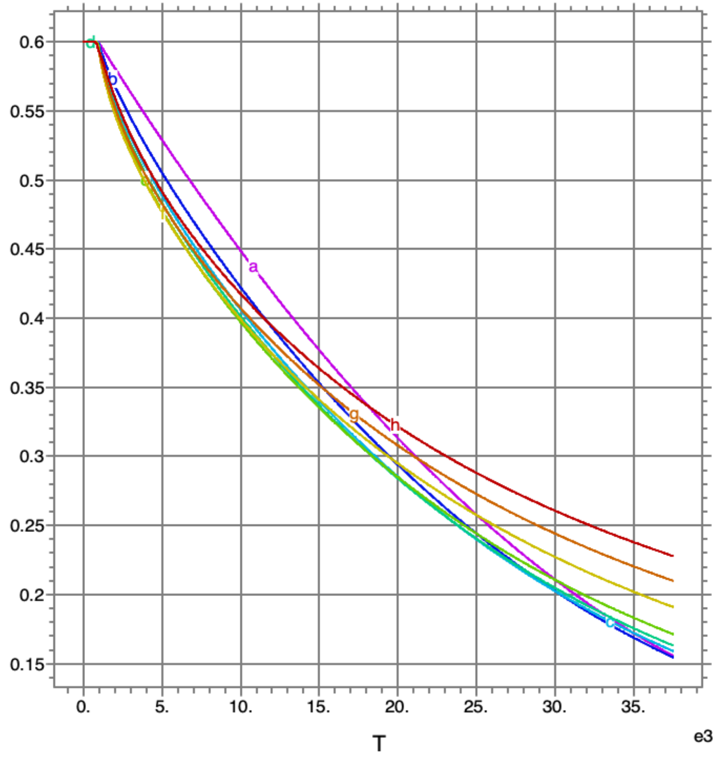


OK !

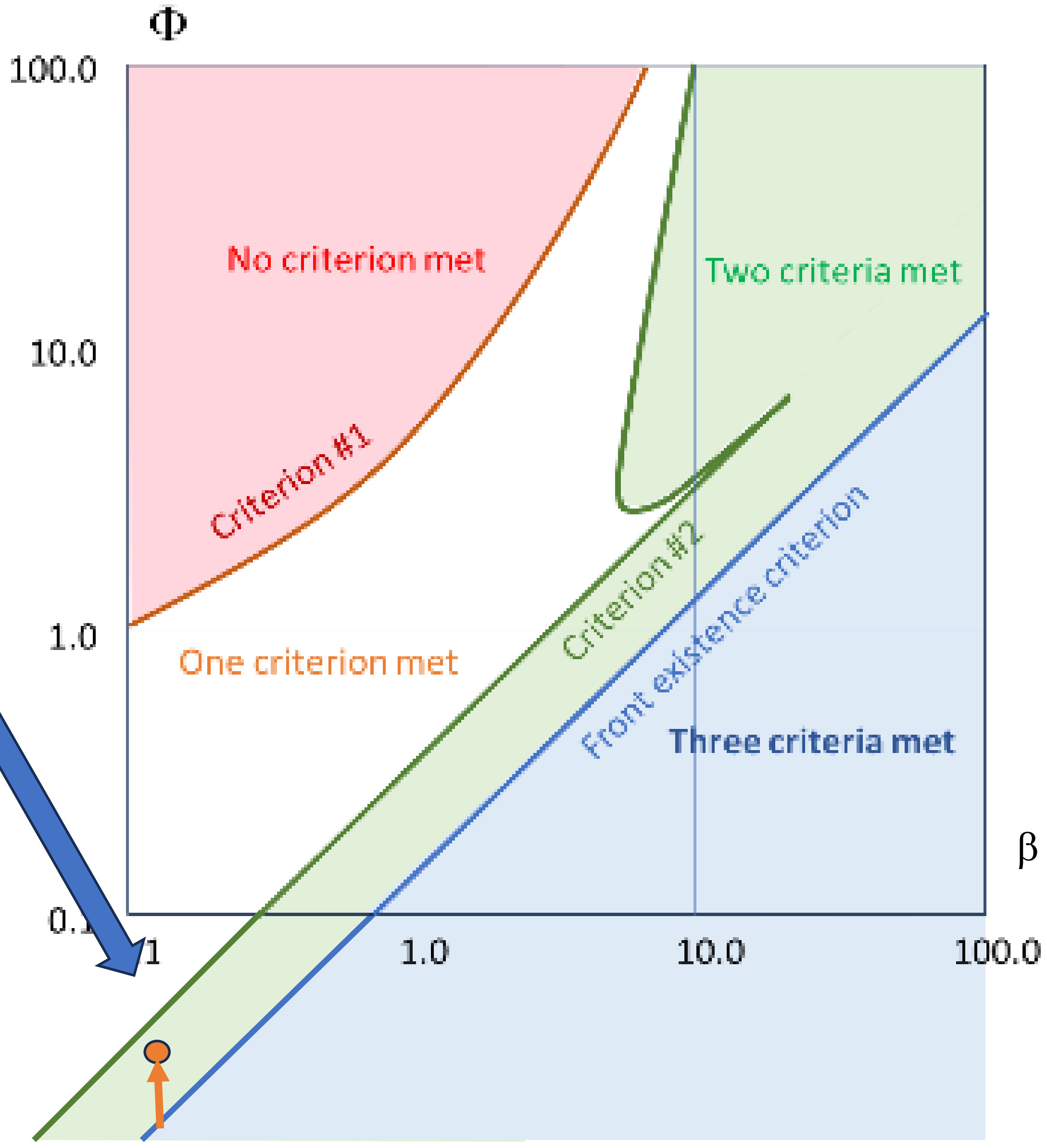


What if we increase thickness ?

- Doubling the thickness doubles the Thiele modulus

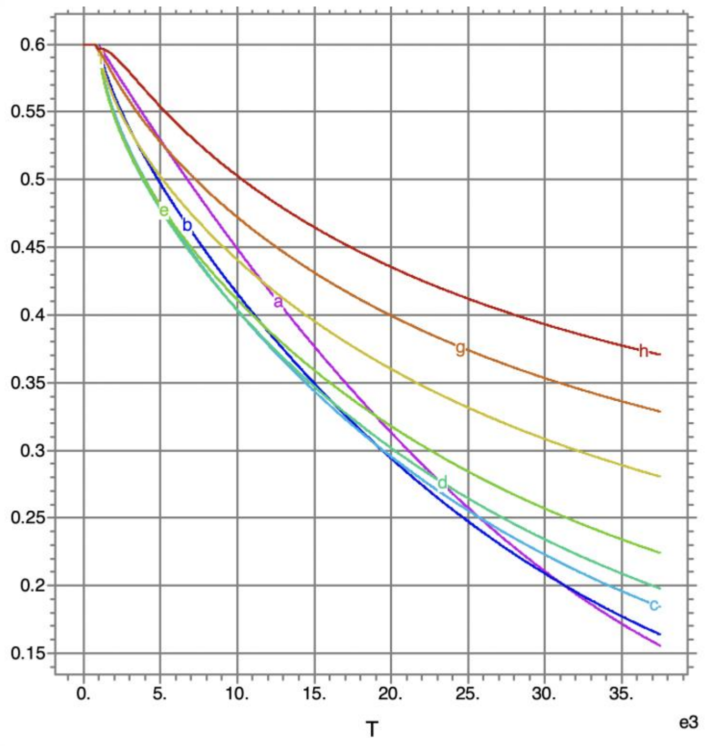


Danger ...

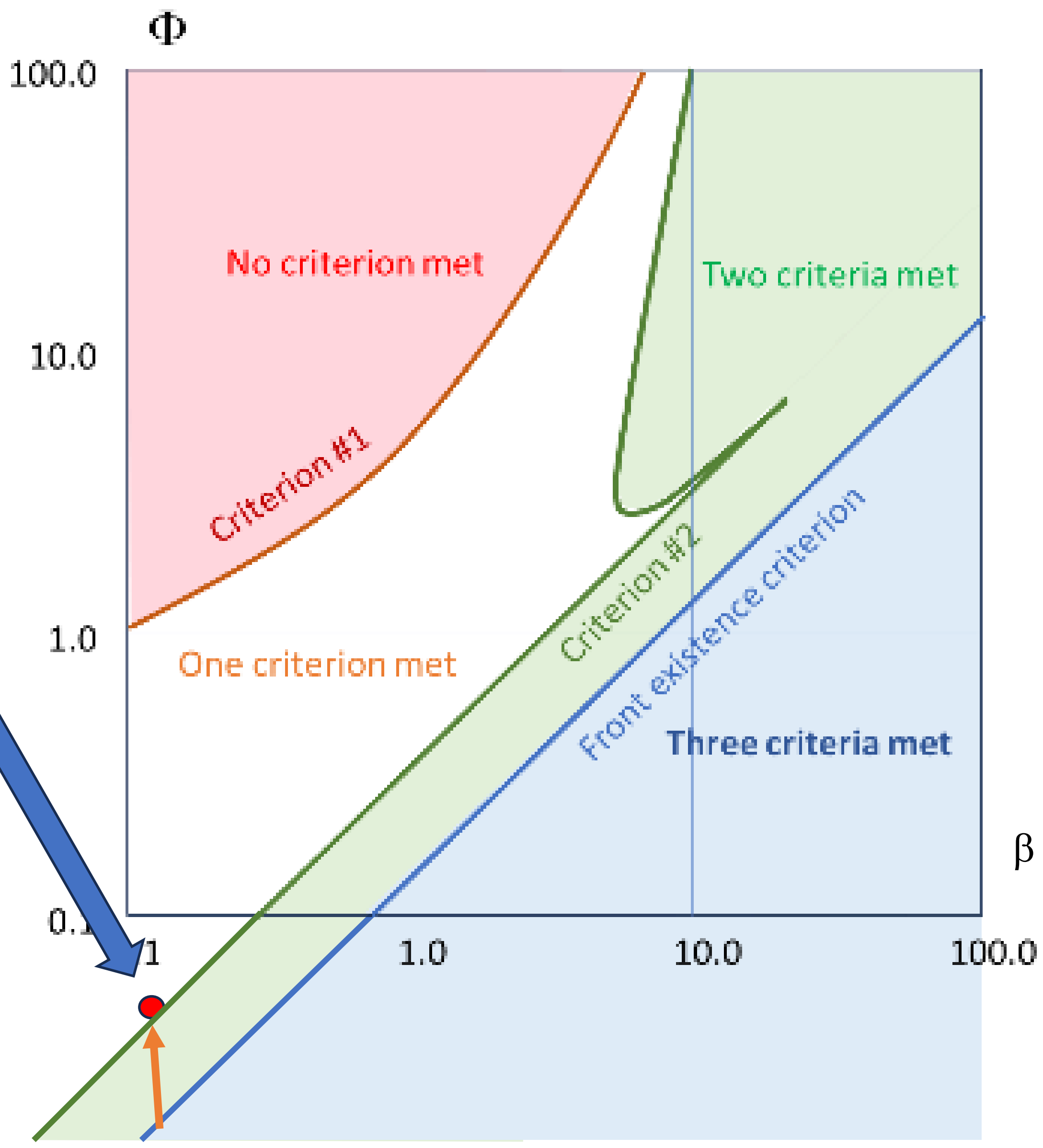


What if we increase thickness ?

- Tripling the thickness triples the Thiele modulus

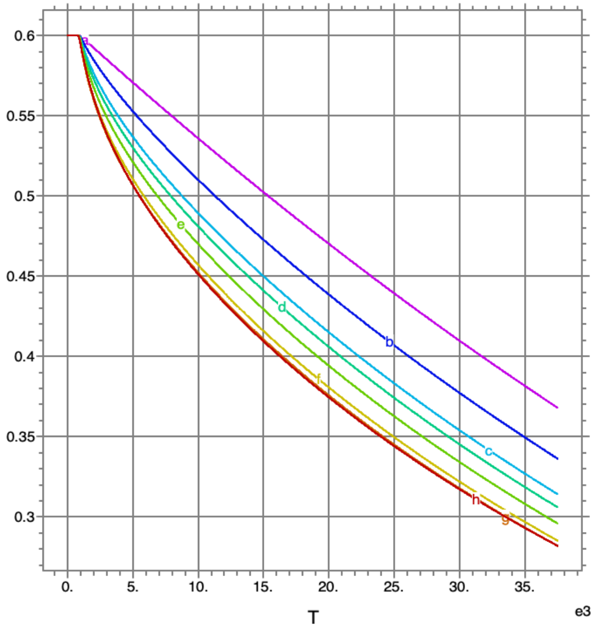


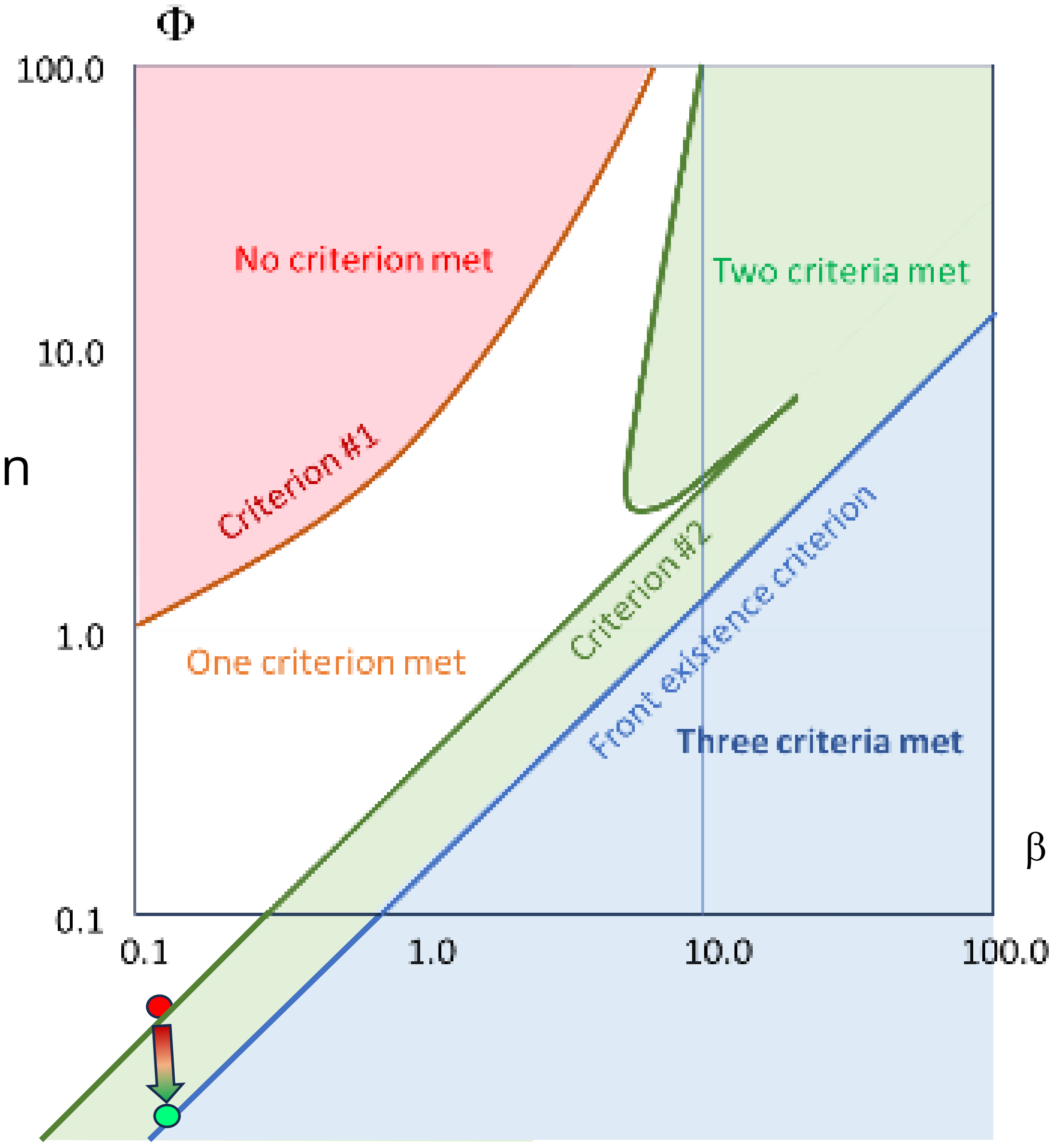
Danger …



What if we increase thickness ?

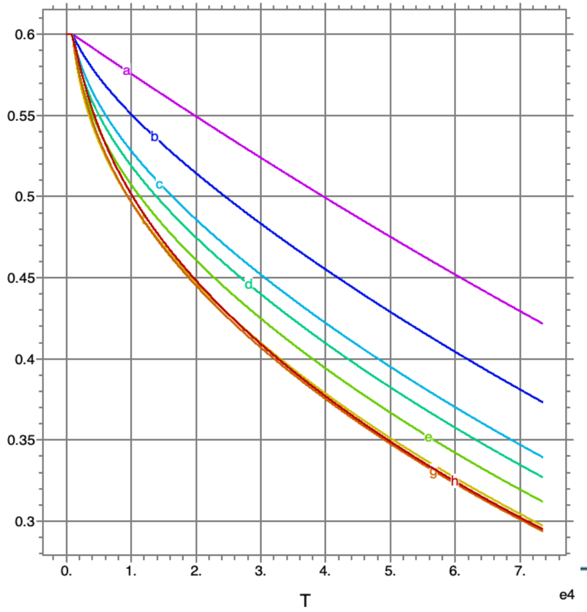
- Doubling the thickness doubles the Thiele modulus
- But **lowering the temperature** by **50K** can compensate

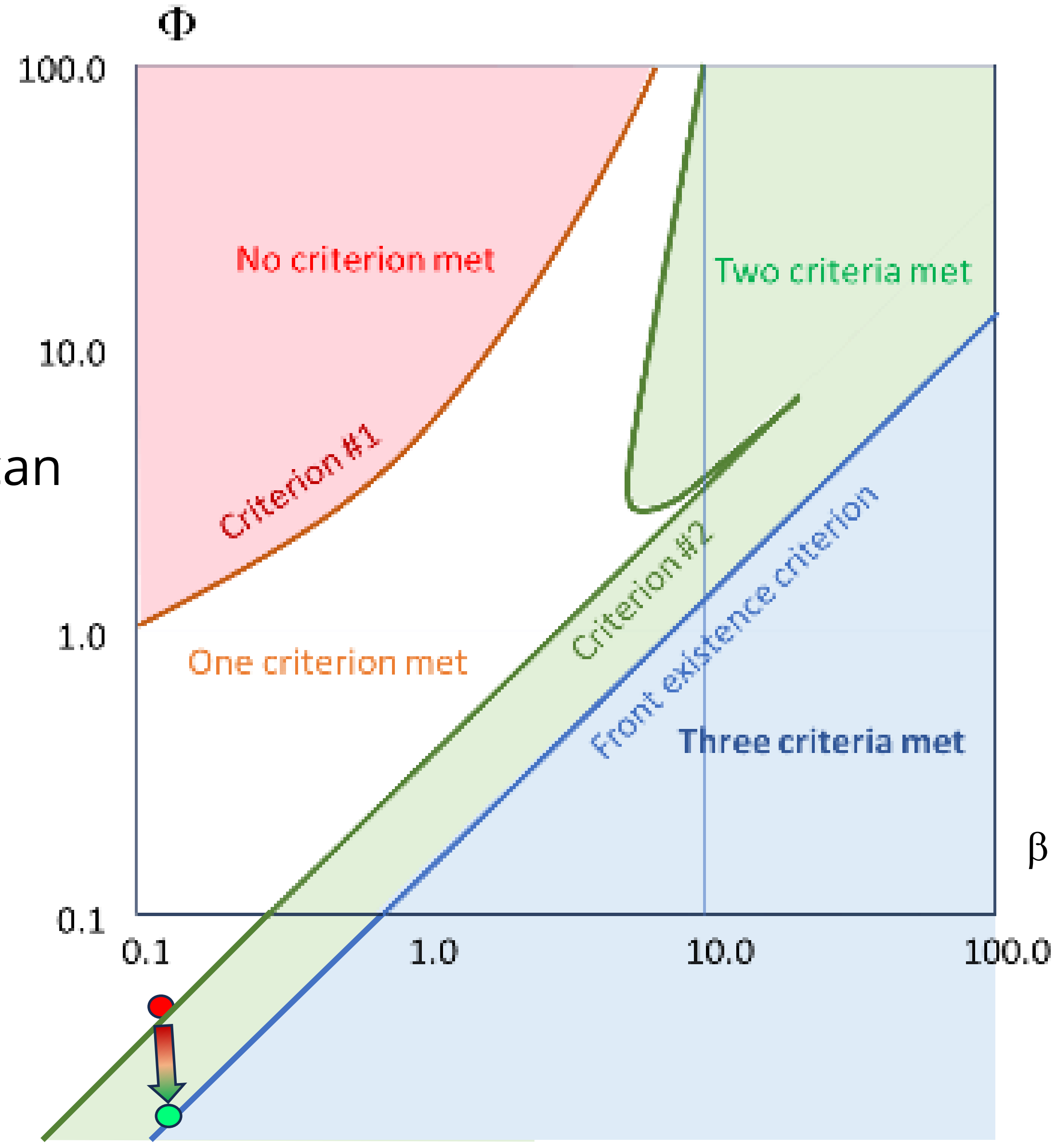




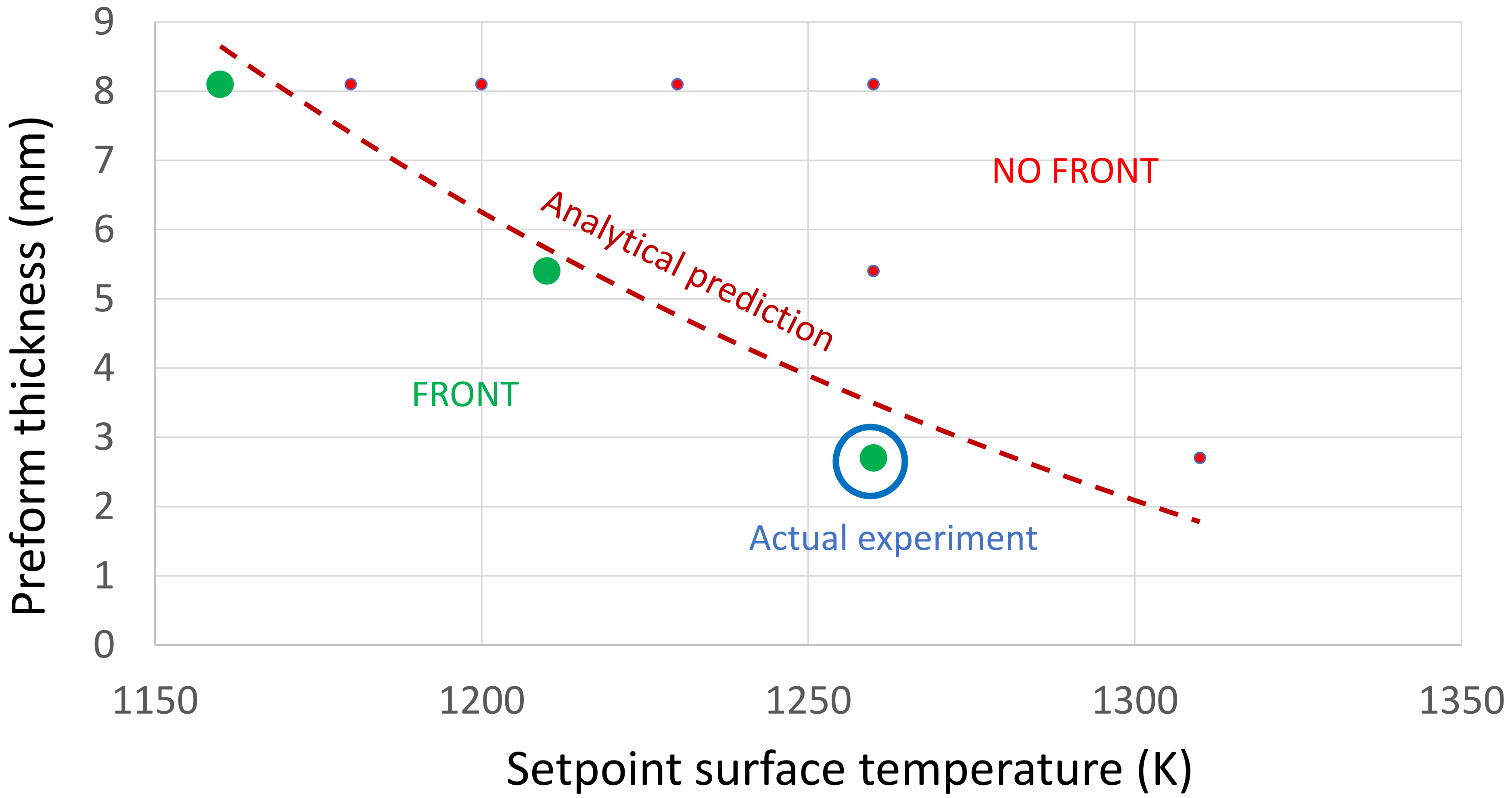
What if we increase thickness ?

- Tripling the thickness triples the Thiele modulus
- But **lowering the temperature** by **100K** can compensate





Temperature-thickness space



Main points

- Multiscale, multiphysics modeling developed to model MW-CVI

- Image-based modeling suite incorporates original techniques (adapted meshing, non-periodic BC)
- ML is useful to exploit the resulting correlations

- Multiphysics large-scale computations validated w.r.t. experiments
- Analytical study matches the detailed computations

- GUIDELINES FOR OPTIMAL MW-CVI ARE DELIVERED

NOVEL CERAMICS AND COMPOSITES PROCESSING TECHNOLOGIES FOR ENERGY-INTENSIVE APPLICATIONS

27 SEPTEMBER, 2024

THANK YOU

CEM-WAVE

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