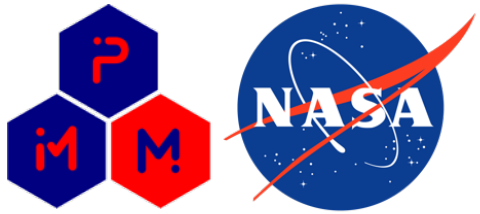



# PuMA and Multiscale Modeling

Presenters: Federico Semeraro

Krishnan S. Gopalan

Project contributors: Joseph C. Ferguson, Marcos Acin, Arnaud Borner, John Thornton Francesco Panerai, Nagi N. Mansour

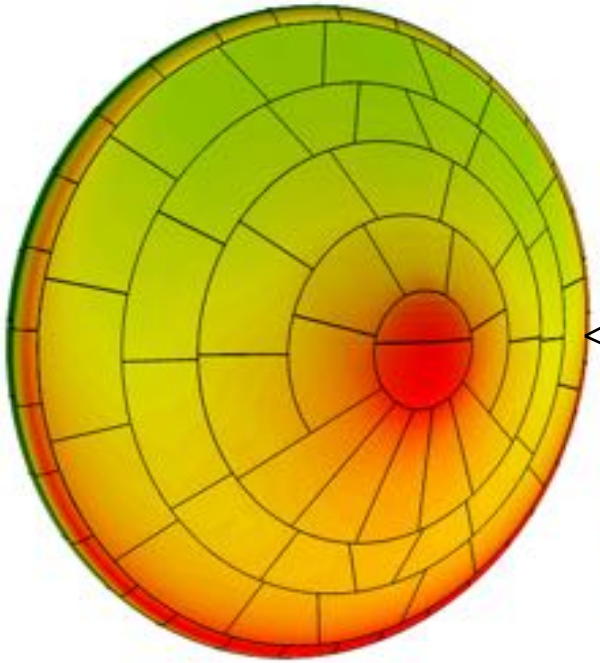
# Content

- Motivation
- Overview of PuMA
- Effective properties for fibrous media
  - ❖ Fiber orientation
  - ❖ Thermal conductivity
  - ❖ Elasticity
- Surface chemistry
  - ❖ Molecular beam
  - ❖ Oxidation model

# Modeling Thermal Protection Systems

## Macroscale Modeling

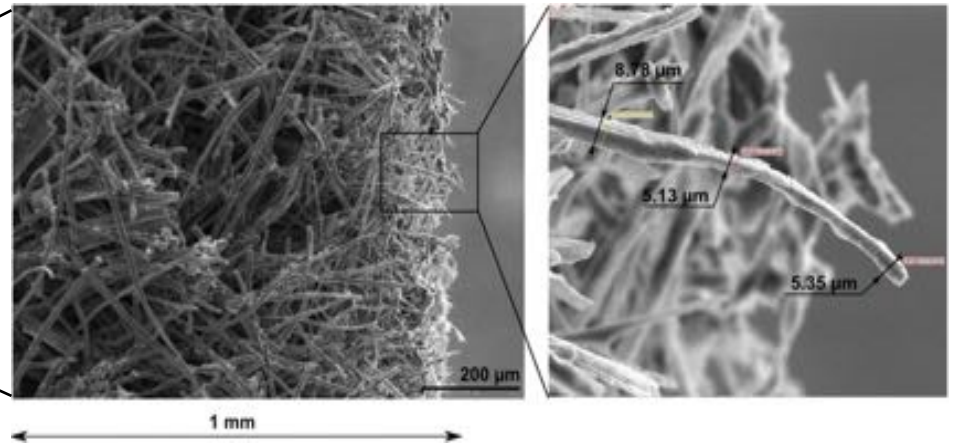
Full scale material response solvers, using volume-averaged techniques to solve conservation equations for ablation



Simulation of surface temperature for MSL heatshield

## Microscale Modeling

Used to inform material properties and material response parameters used in macro-scale modeling




Lachaud and Mansour, *JTHT* 2013

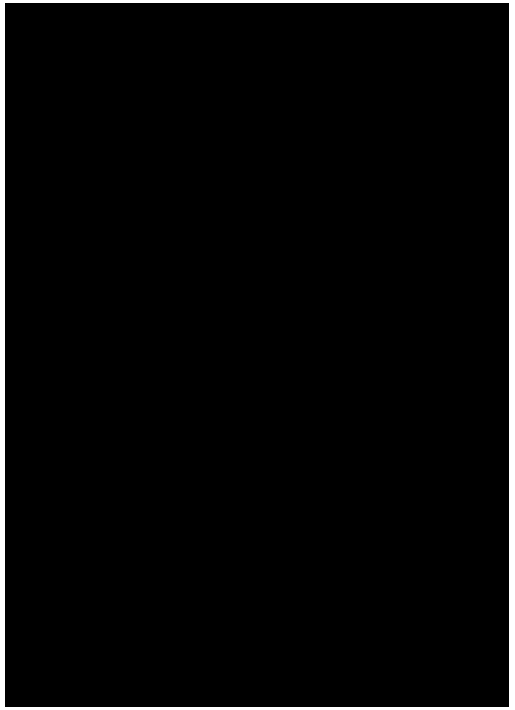
# X-Ray Microtomography

Collect X-ray images of the sample as you rotate it through 180°


Penetrating power

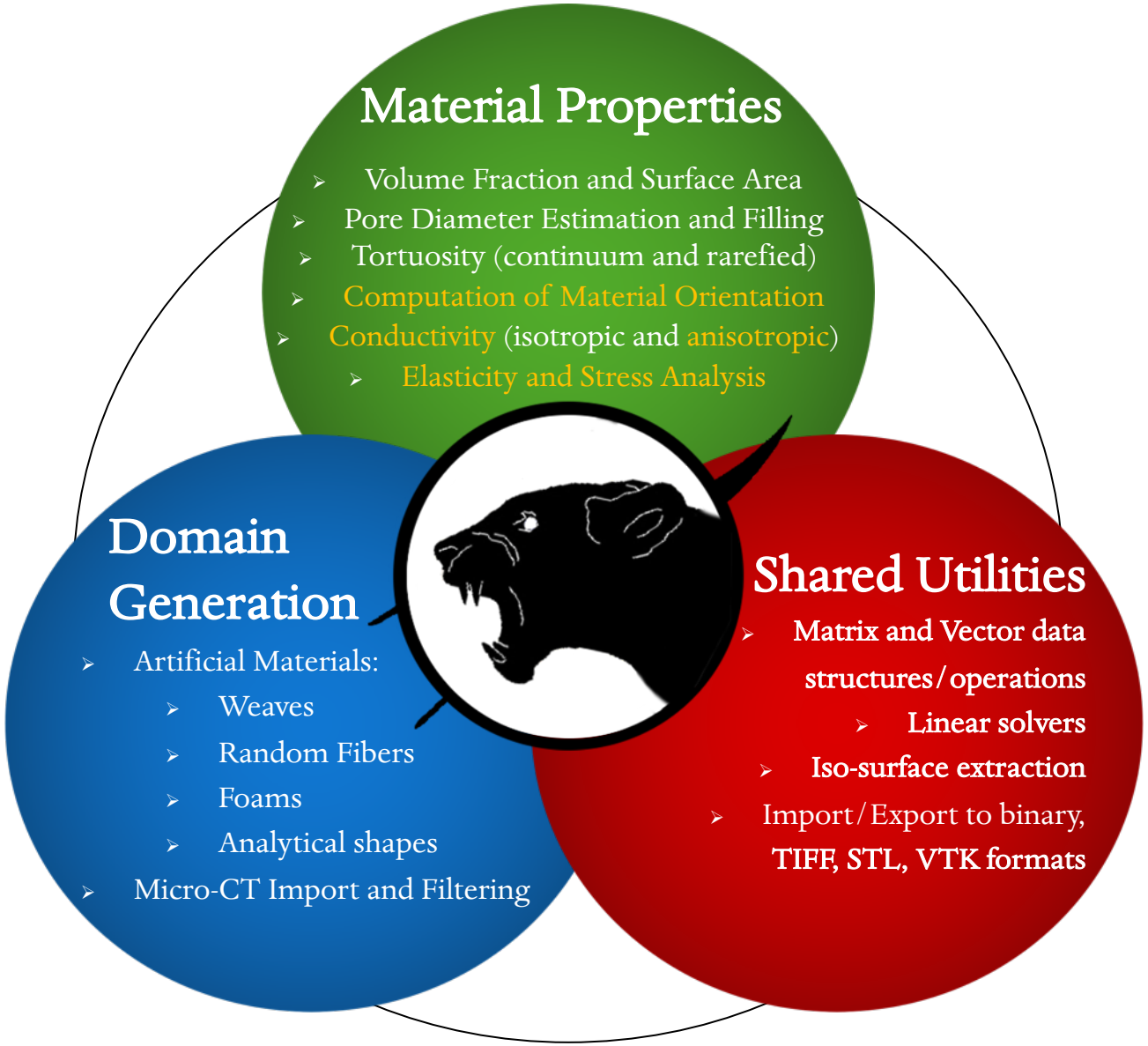
Multiple angles

Use this series of images to reconstruct the 3D object



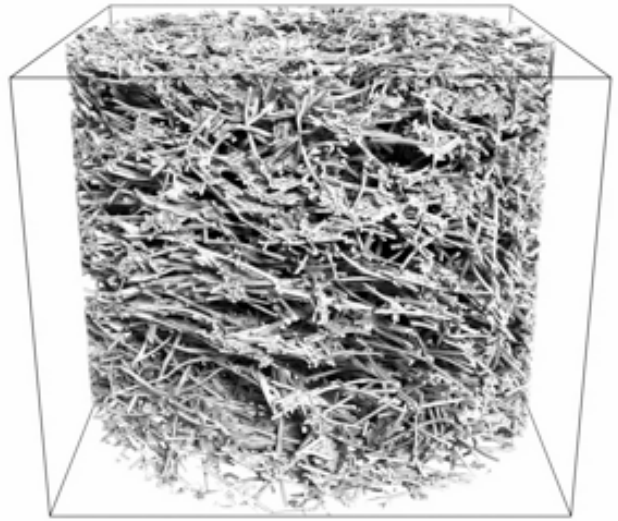
Courtesy of D. Parkinson (ALS)

# Porous Microstructure Analysis (PuMA)



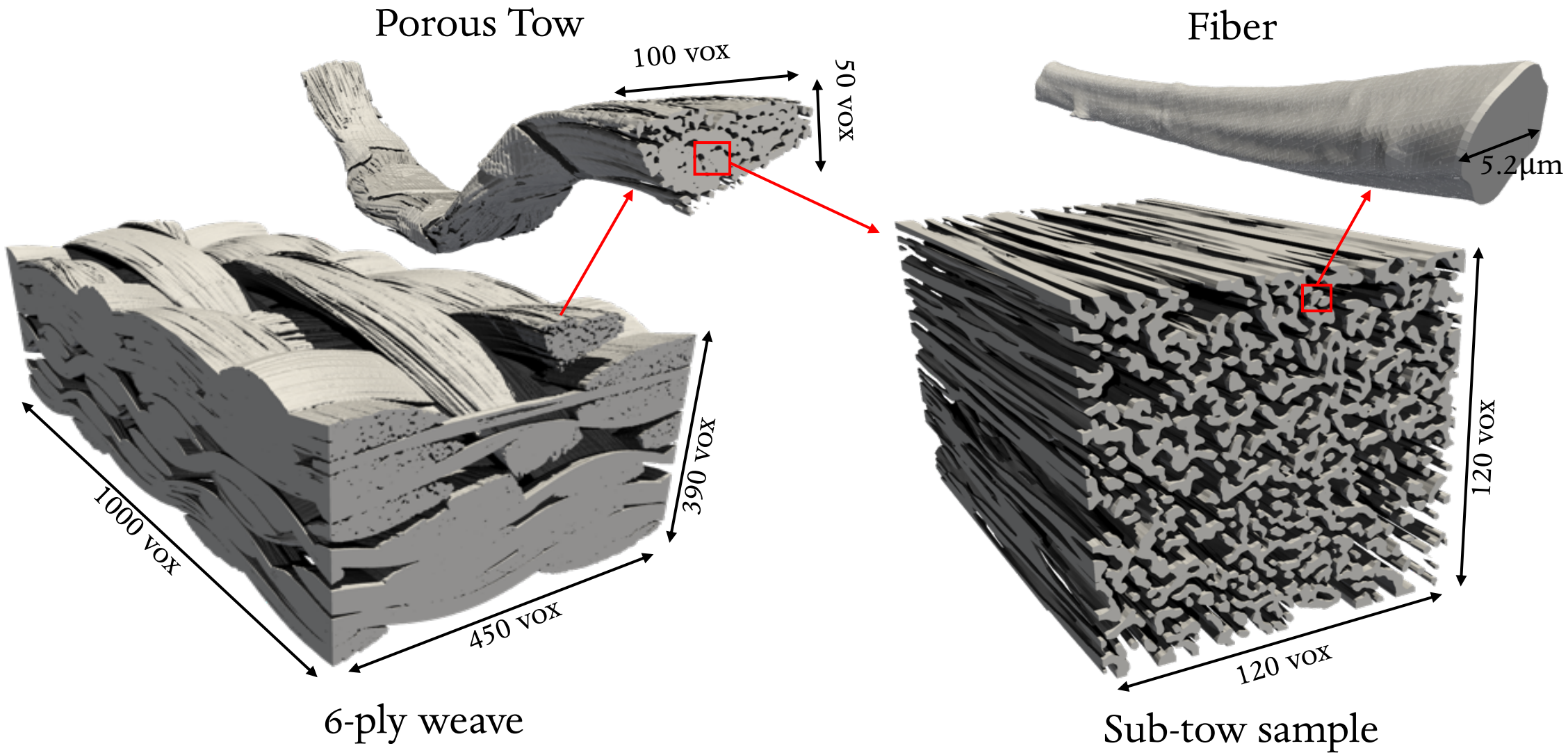

New features in Version 3:

- Modular C++ library
- Redesigned GUI
- Wrapped as Python module
- Linux and Mac compatibility



CT Reconstruction of FiberForm

# A Multiscale Problem

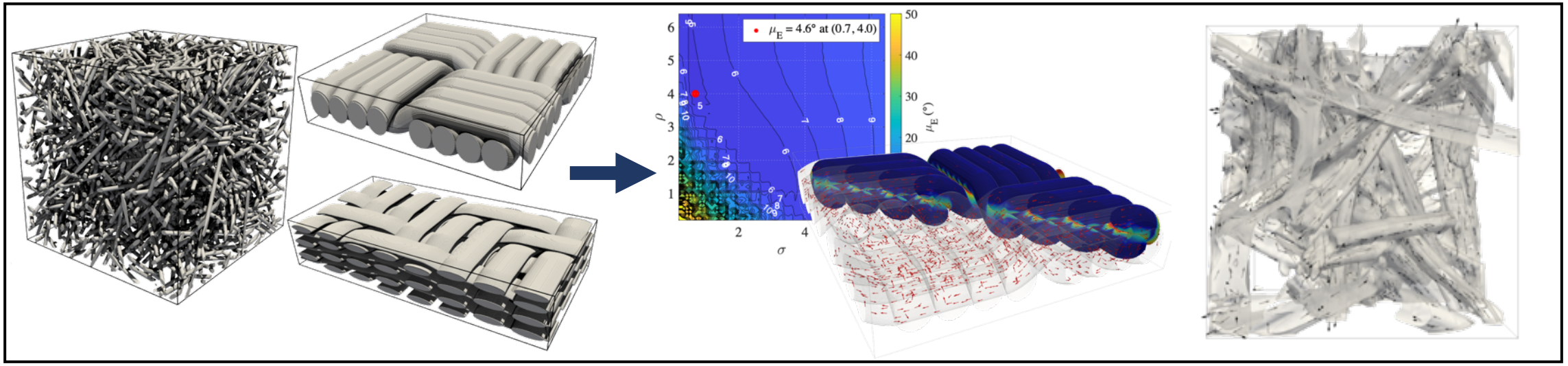



6-ply weave

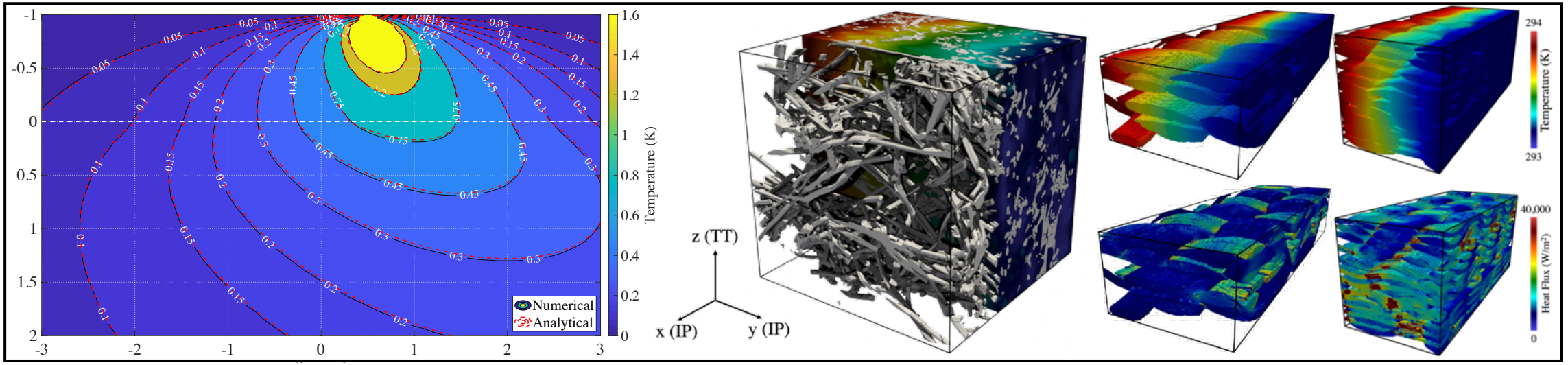
Sub-tow sample

# Effective properties for fibrous media

Semeraro, F., Ferguson, J.C., Panerai, F., King, R.J. and Mansour, N.N., Anisotropic analysis of fibrous and woven materials **part 1: Estimation of local orientation**. *Computational Materials Science*, 178, p.109631. (2020)

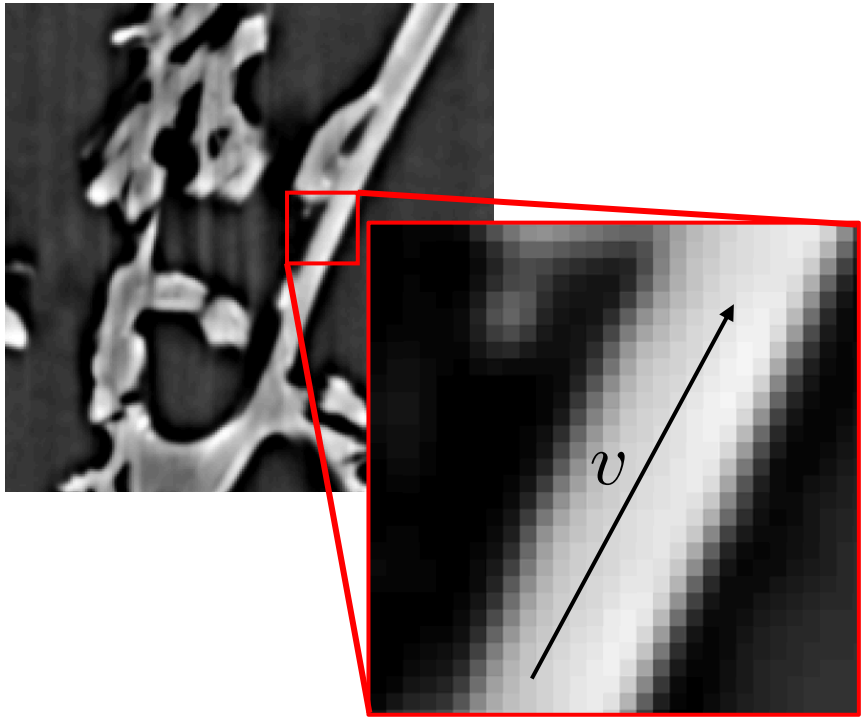



Semeraro, F., Ferguson , J.C, Acin, M., Panerai, F. and Mansour, N.N., Anisotropic analysis of fibrous and woven materials **part 2: Computation of effective conductivity**. *Computational Materials Science*, 186, p.109956. (2021)

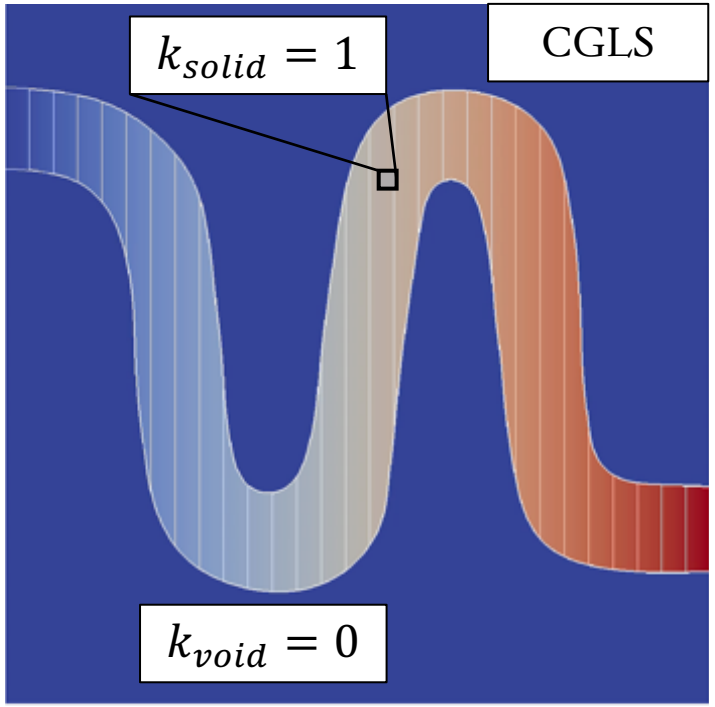


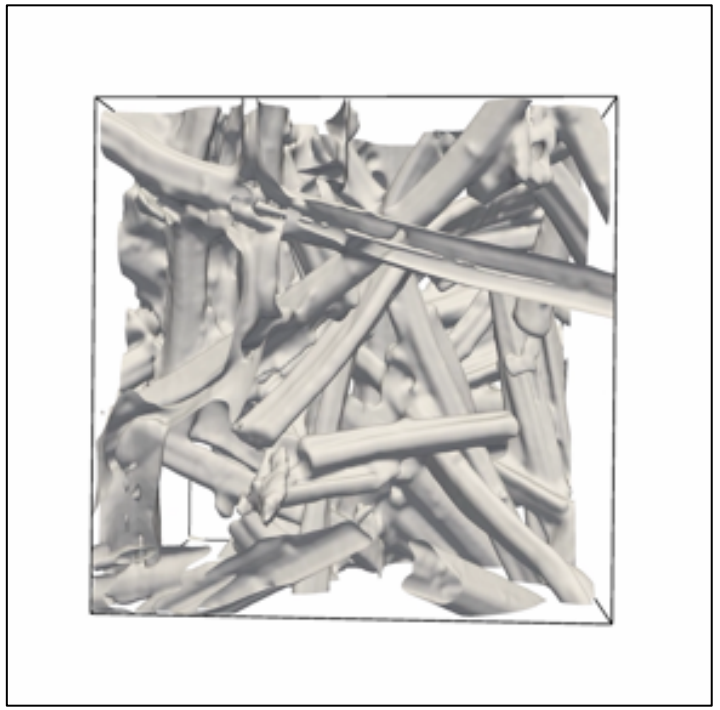
# Fiber Orientation Methods

| Structure Tensor | Artificial Flux | Ray Casting |
| --- | --- | --- |



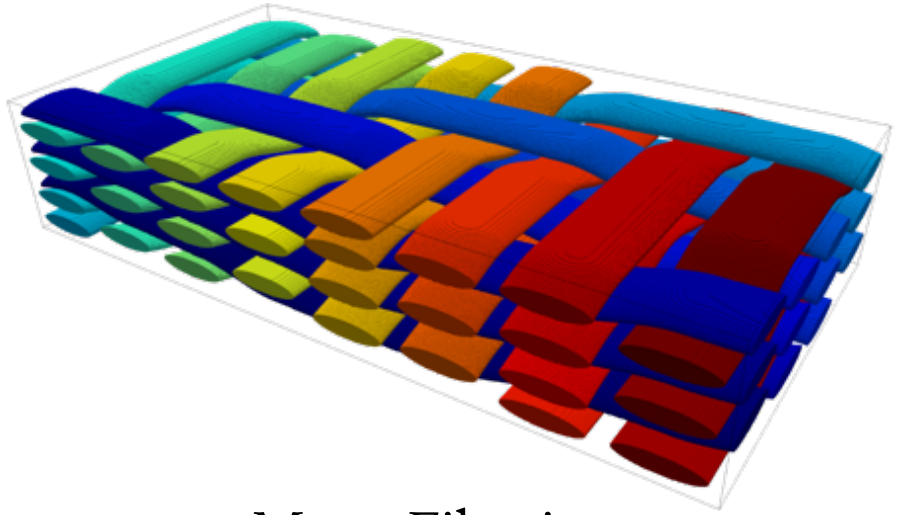

$$(I(x+v) - I(x))^2 \approx 0$$



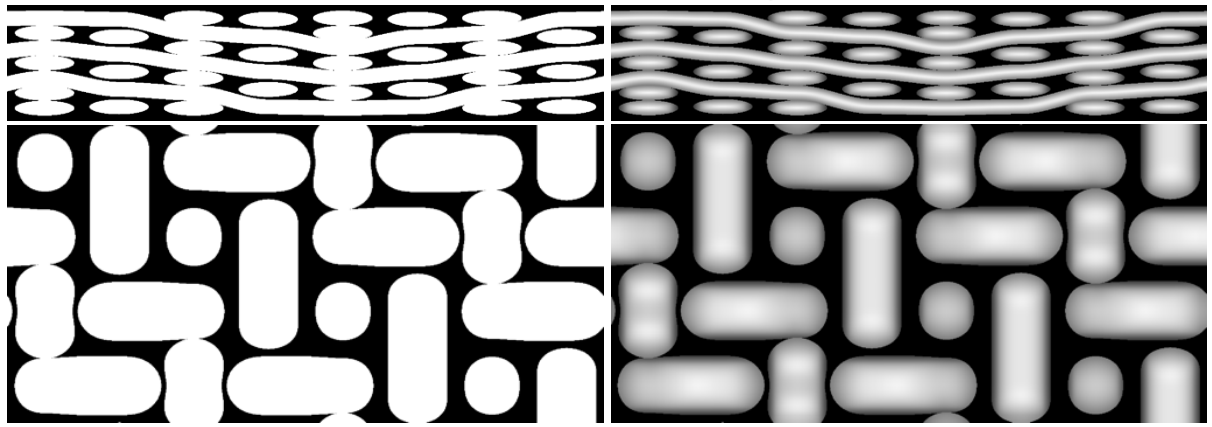



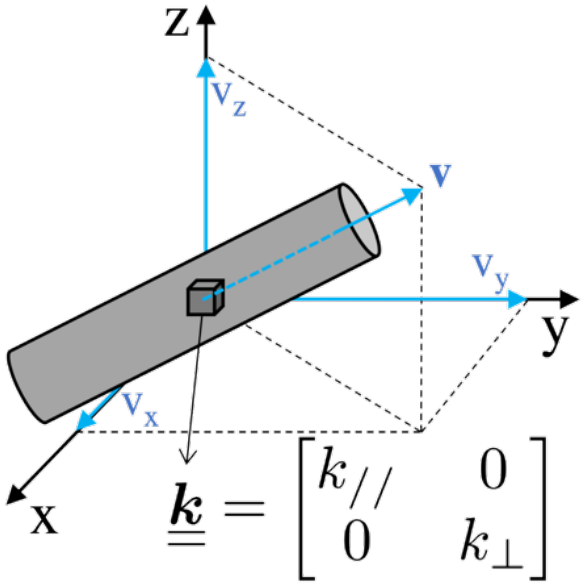
# Workflow for Weave Orientation

Individual tow segmentation

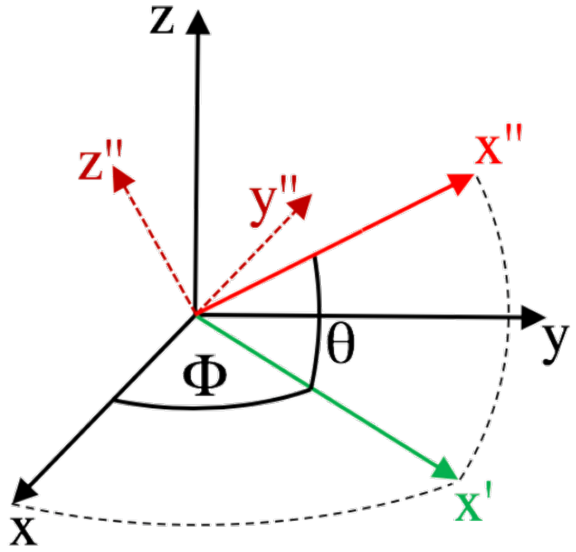


Mean Filtering





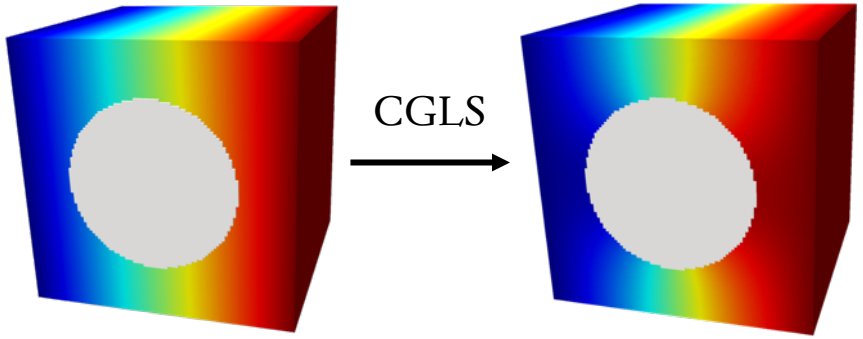

$$\underline{\underline{k}} = \begin{bmatrix} k_{//} & 0 \\ 0 & k_{\perp} \end{bmatrix}$$




$$\boldsymbol{q} = \underbrace{\left[\boldsymbol{R}^{-1}\boldsymbol{k}''\boldsymbol{R}\right]}_{\boldsymbol{k}} \nabla T$$

$$\boldsymbol{R} = \begin{bmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{bmatrix} \begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

# Effective Thermal Conductivity



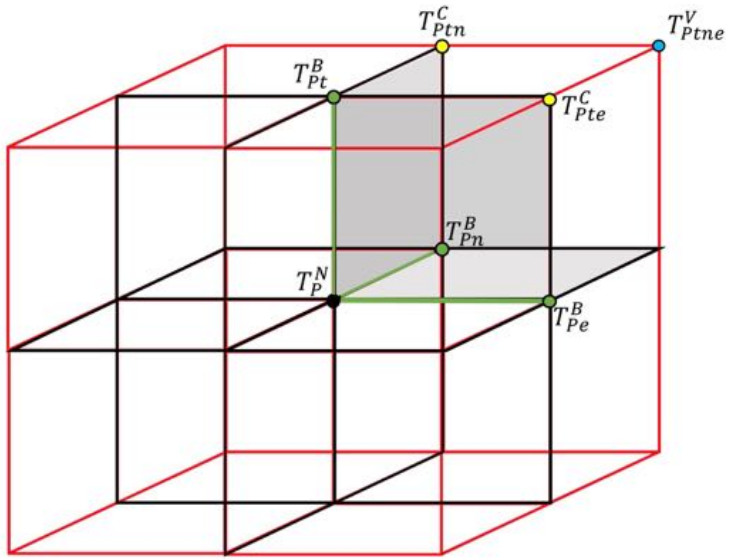
CGLS

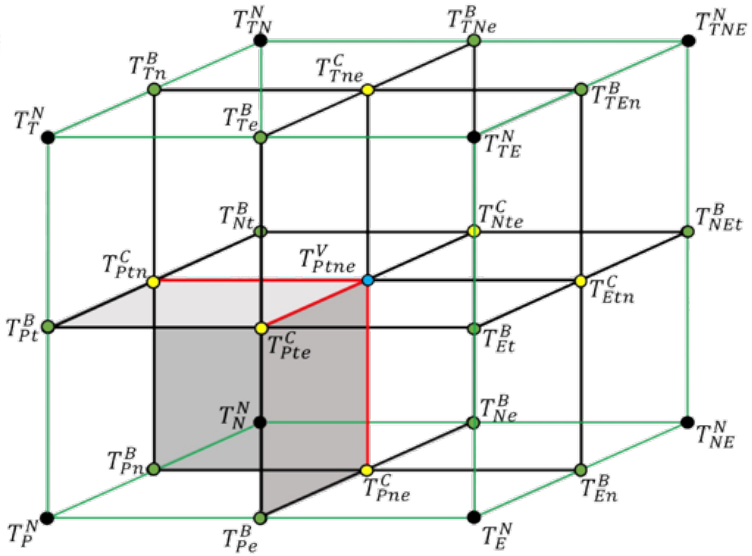


$$\longrightarrow \boldsymbol{k}_{eff} = q^x \cdot L_x$$

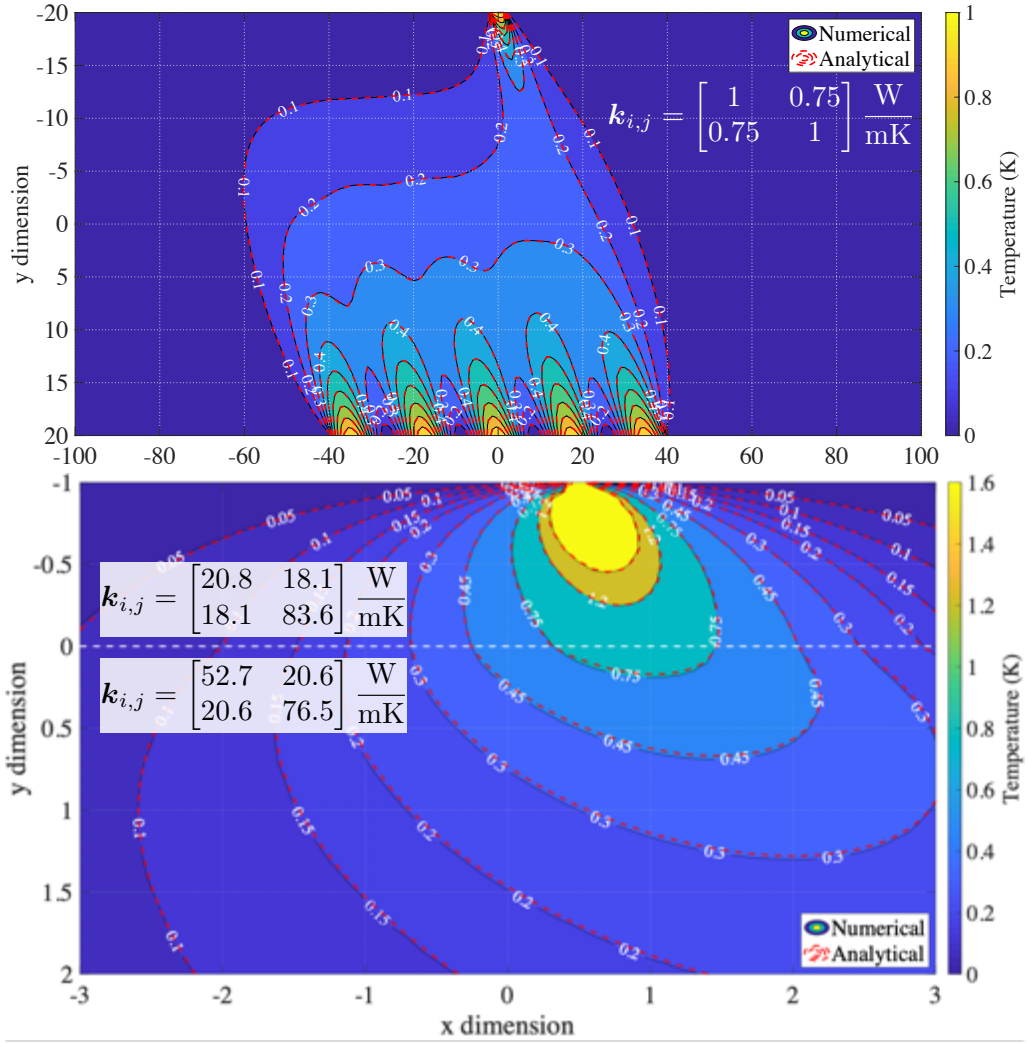
$$\nabla \cdot \boldsymbol{q} = 0 \longrightarrow \boldsymbol{q}(x,t) = \boldsymbol{E}(x)\,\boldsymbol{T}^N(x,t)$$

Multi-Point Flux Approximation (MPFA):

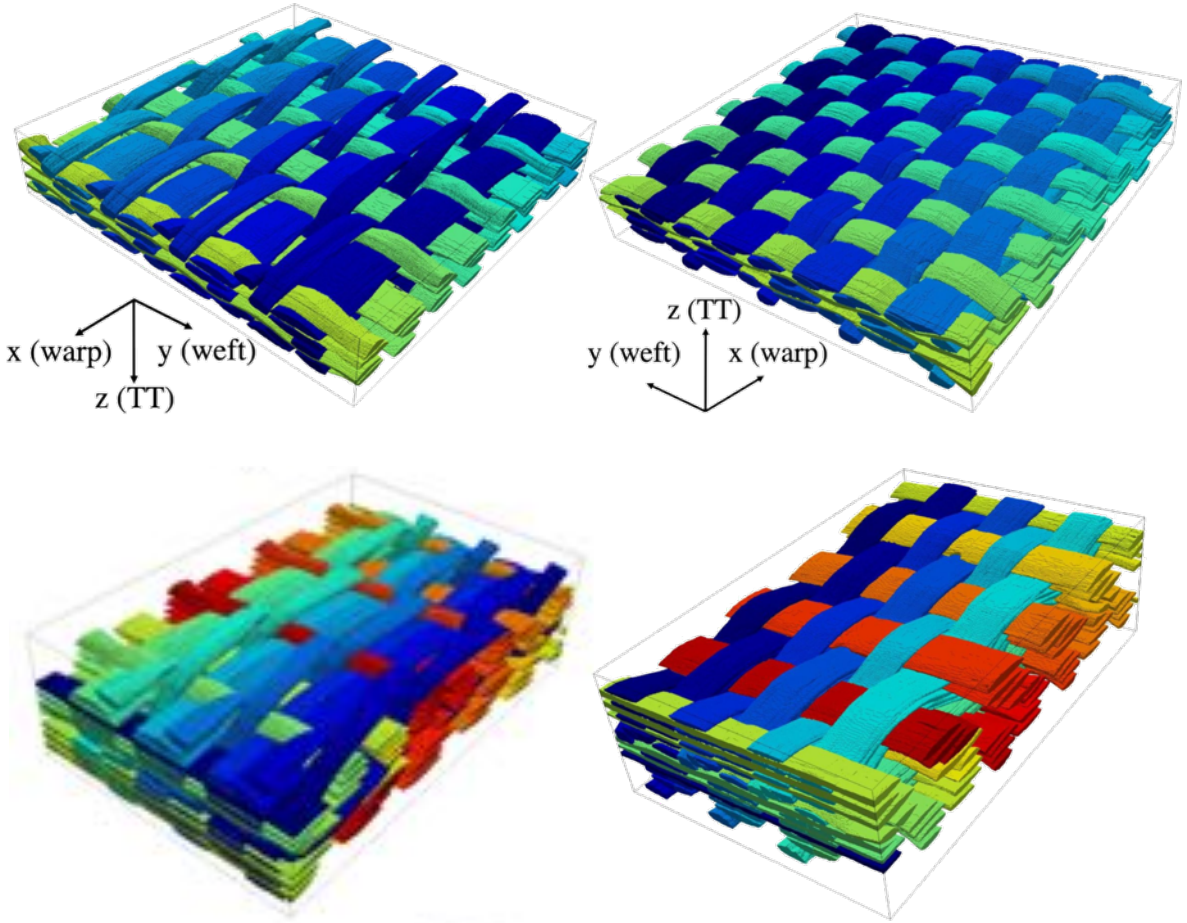


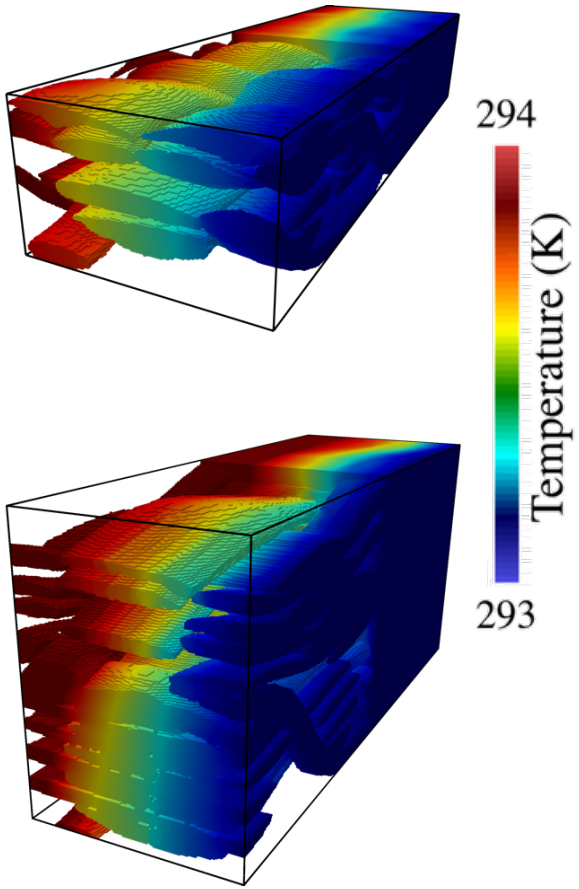



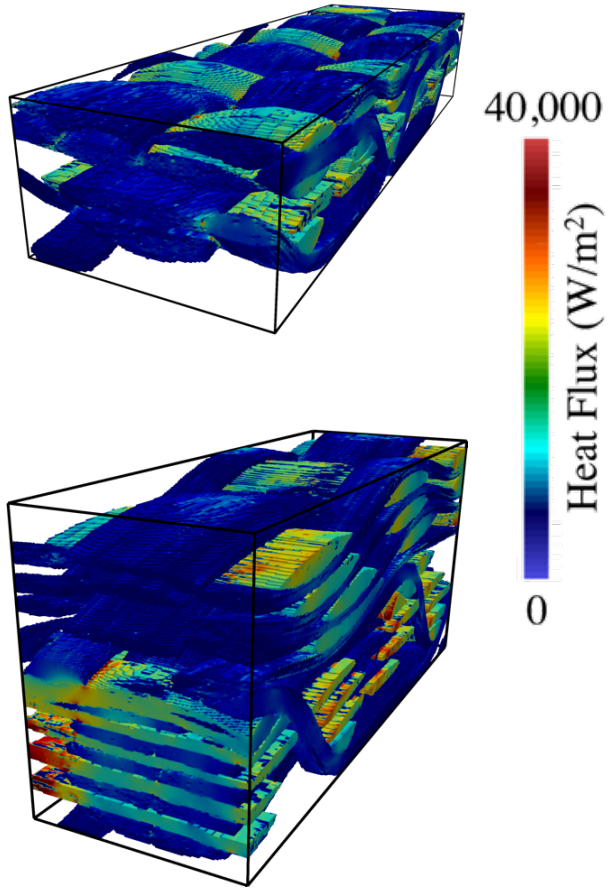

Verification against analytical solutions



# ADEPT Validation



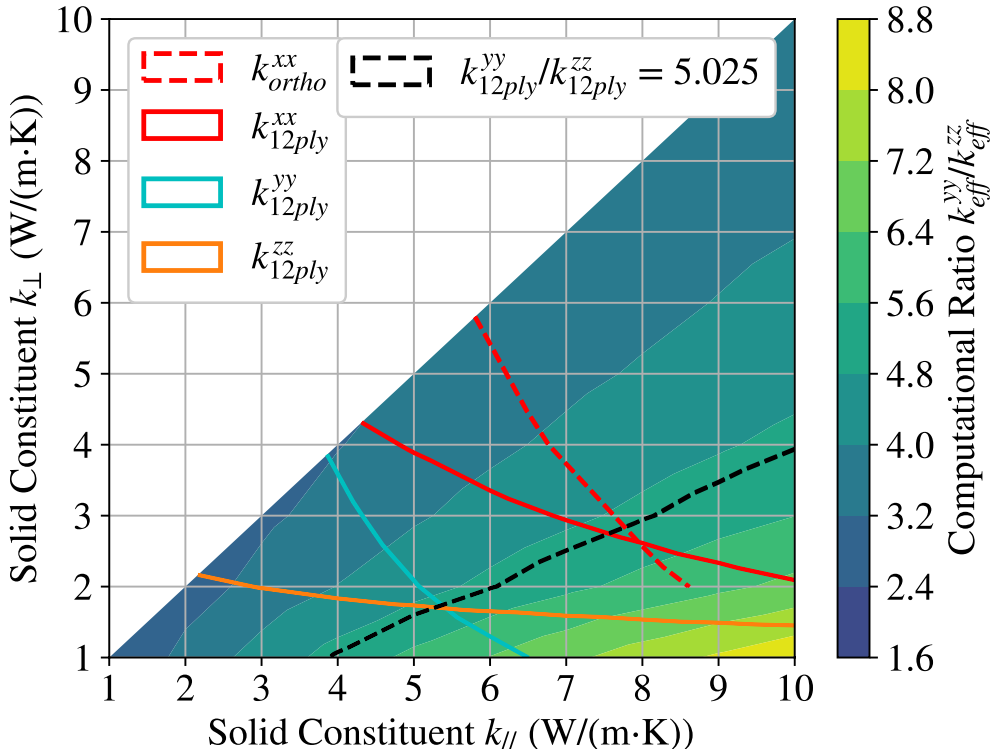



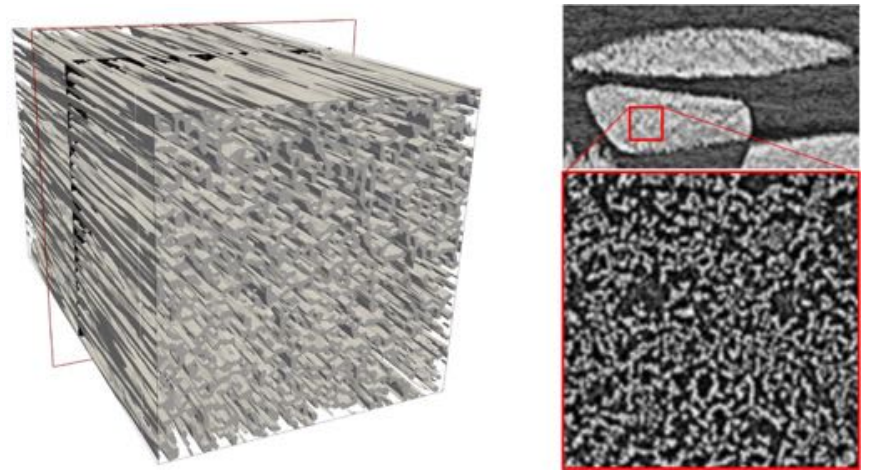
# Single Fiber Conductivity Estimation

Two experimental values at Room Temperature:

$$\boldsymbol{k}_{eff}^{ortho} = \begin{bmatrix} 2.342 & - & - \\ - & 1.766 & - \\ - & - & 0.305 \end{bmatrix} \quad \boldsymbol{k}_{eff}^{12ply} = \begin{bmatrix} 2.184 & - & - \\ - & 1.980 & - \\ - & - & 0.394 \end{bmatrix}$$




$$[k_{//}^{weft}, k_{\perp}^{weft}] = [5.4, 1.8] \quad \text{and} \quad [k_{//}^{warp}, k_{\perp}^{warp}] = [7.7, 2.7] \frac{\text{W}}{\text{mK}}$$



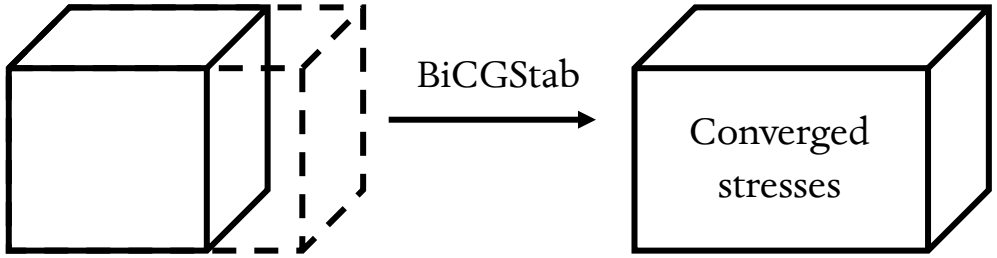
$$[k_{//}, k_{\perp}] = [9.7, 5.5] \frac{\text{W}}{\text{mK}}$$

$$\boldsymbol{k}_{eff}^{4ply} = \begin{bmatrix} 1.750 & -0.032 & -0.024 \\ -0.093 & 1.490 & 0.002 \\ 0.039 & 0.001 & 0.193 \end{bmatrix} \quad \boldsymbol{k}_{eff}^{6ply} = \begin{bmatrix} 1.740 & -0.141 & -0.020 \\ -0.105 & 1.710 & -0.005 \\ 0.091 & -0.023 & 0.200 \end{bmatrix}$$

$$\boldsymbol{k}_{eff}^{8ply} = \begin{bmatrix} 1.830 & -0.244 & 0.016 \\ -0.192 & 1.510 & 0.005 \\ 0.039 & 0.000 & 0.231 \end{bmatrix} \quad \boldsymbol{k}_{eff}^{12ply} = \begin{bmatrix} 2.310 & -0.414 & 0.000 \\ -0.524 & 2.030 & 0.071 \\ 0.007 & 0.005 & 0.504 \end{bmatrix}$$

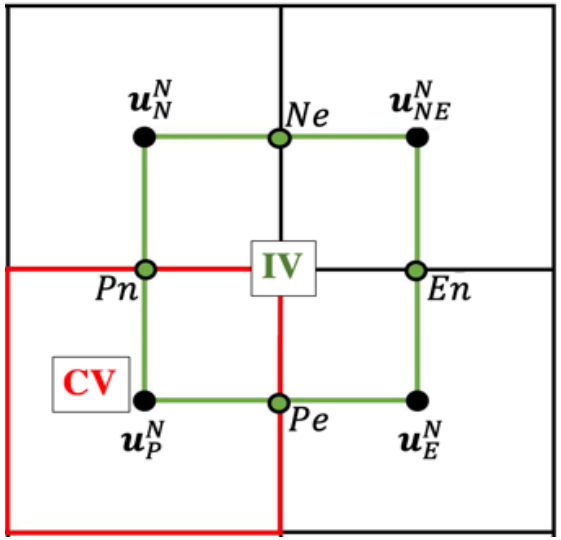
# Effective Elasticity

Semeraro, F., Acin, M., Panerai, and Mansour, N.N., Anisotropic analysis of fibrous and woven materials
**part 3: Computation of effective elasticity**. *Computational Materials Science*, (work in progress)



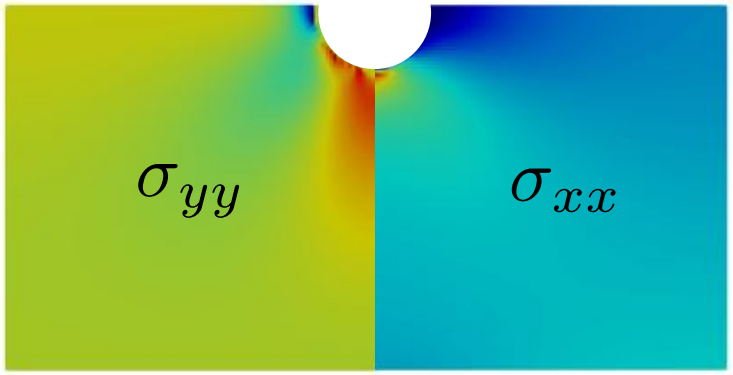

Multi-Point Stress Approximation (MPSA)

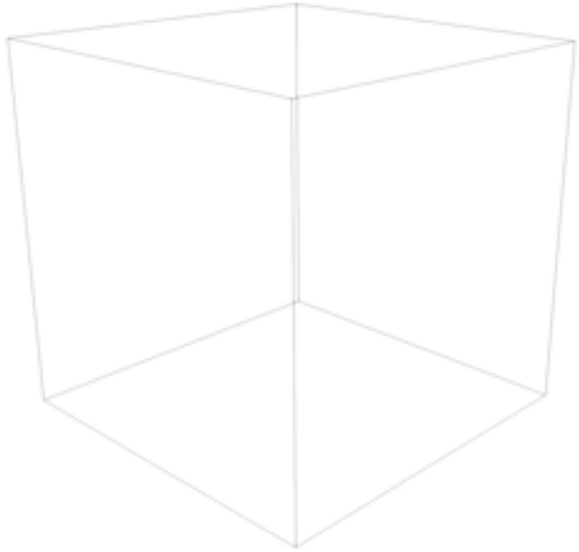
$$C_{eff} = \boldsymbol{\sigma}^x \cdot L_x$$






Verification against analytical solution

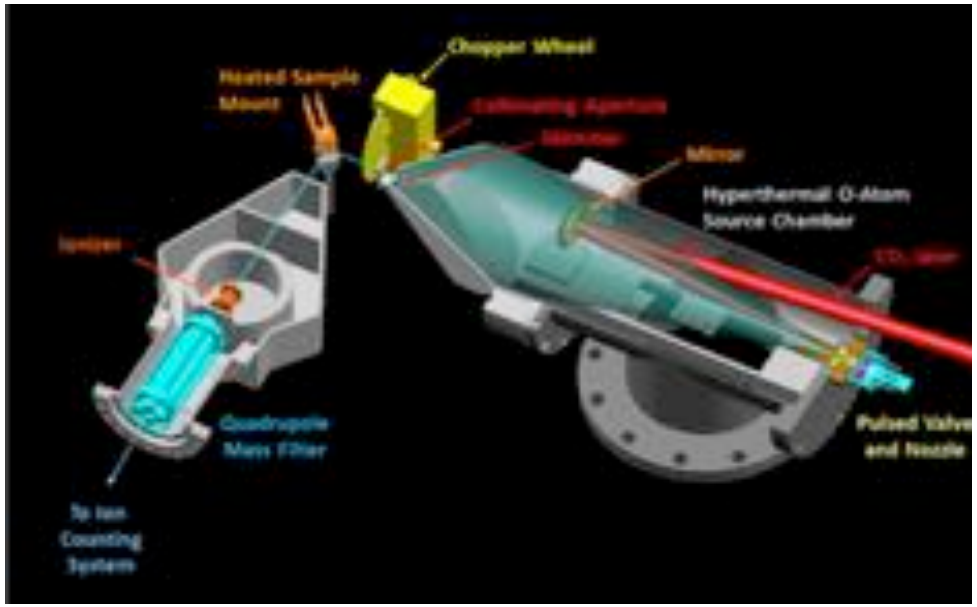


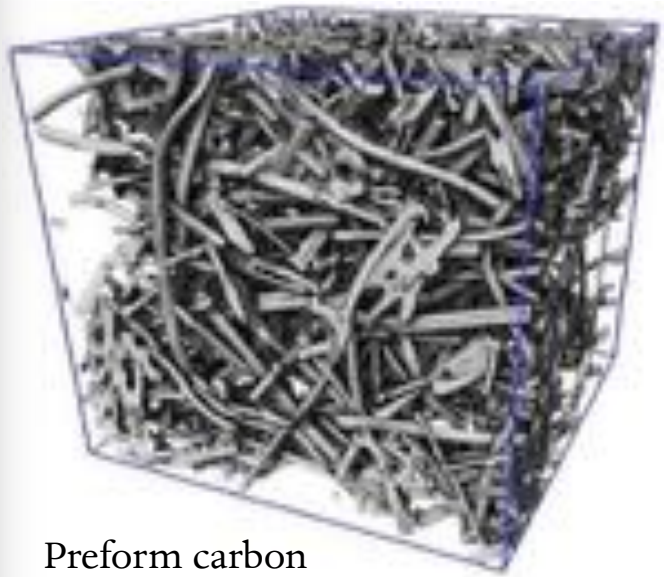
# Application motivation

**Objectives:**

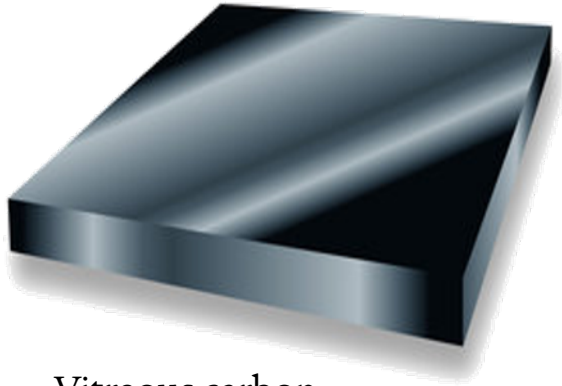
- **Characterize recession/ablation of carbon surface coated with NuSil due to oxidation**
- Develop a predictive model for use in microscopic (DSMC, PuMA) and macroscopic (CFD, MRC) solvers




Murray *et al*



Preform carbon



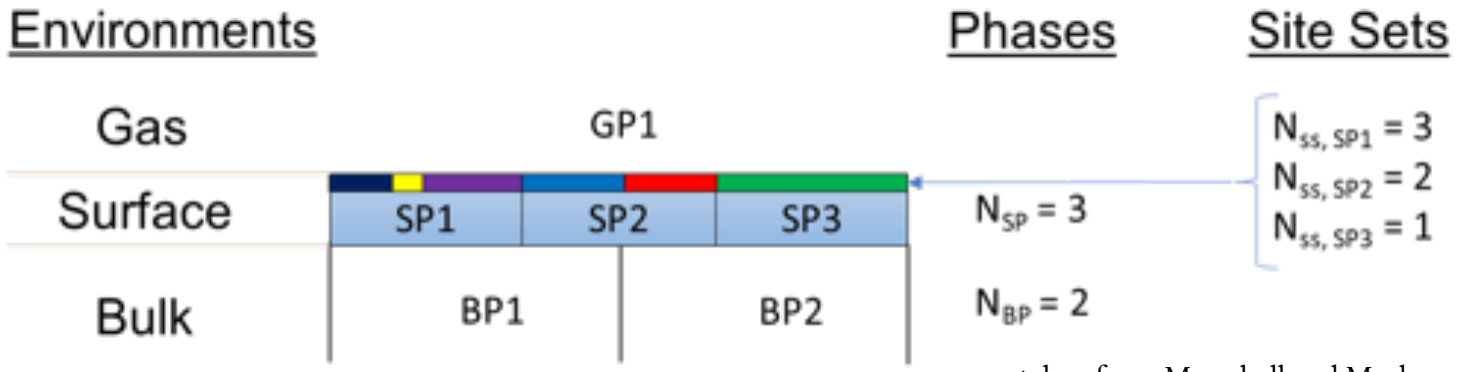
Vitreous carbon

Image courtesy: Prof. Panerai

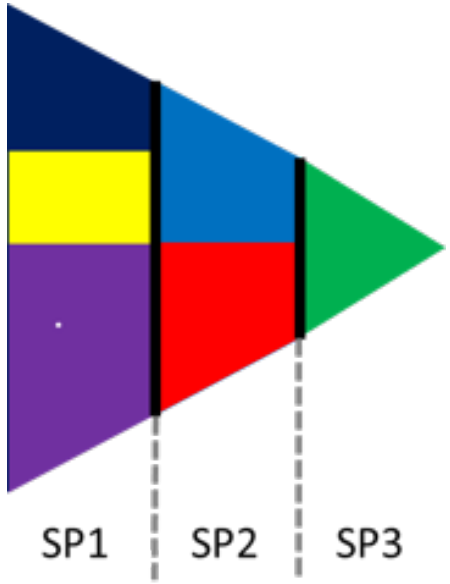
SPI Supplies

# Surface chemistry framework

- Methodology to represent surface sites similar to Marschall, Maclean and Driver [4] for CFD.
- Particles adsorbed (deleted) and desorbed (created), surface element stores adsorbed particle concentration.
- Surface reactions based on concentration within surface element.
- Multiple triangulated elements (like cells) on surfaces
- Langmuir model for surface sites.



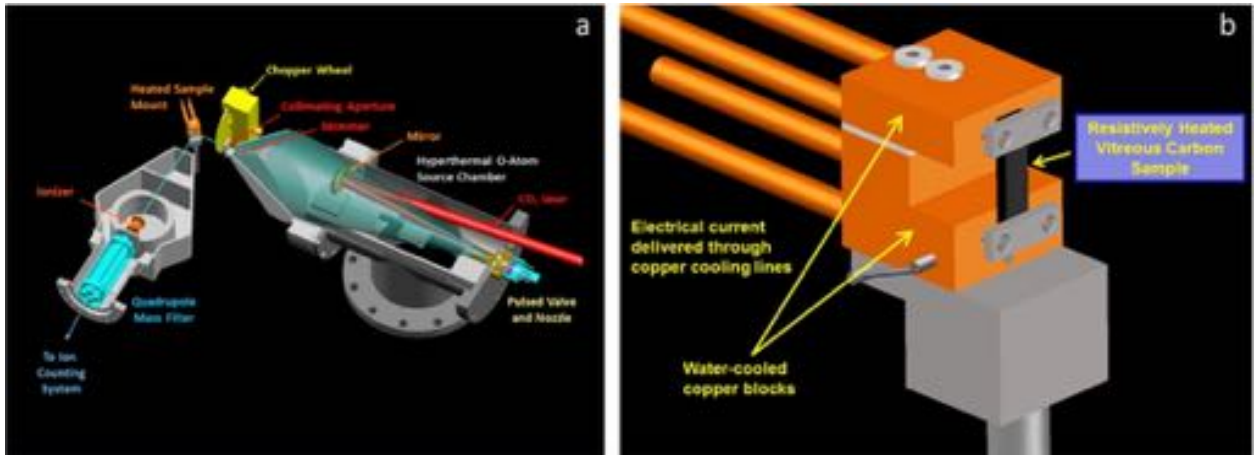

taken from Marschall and Maclean.



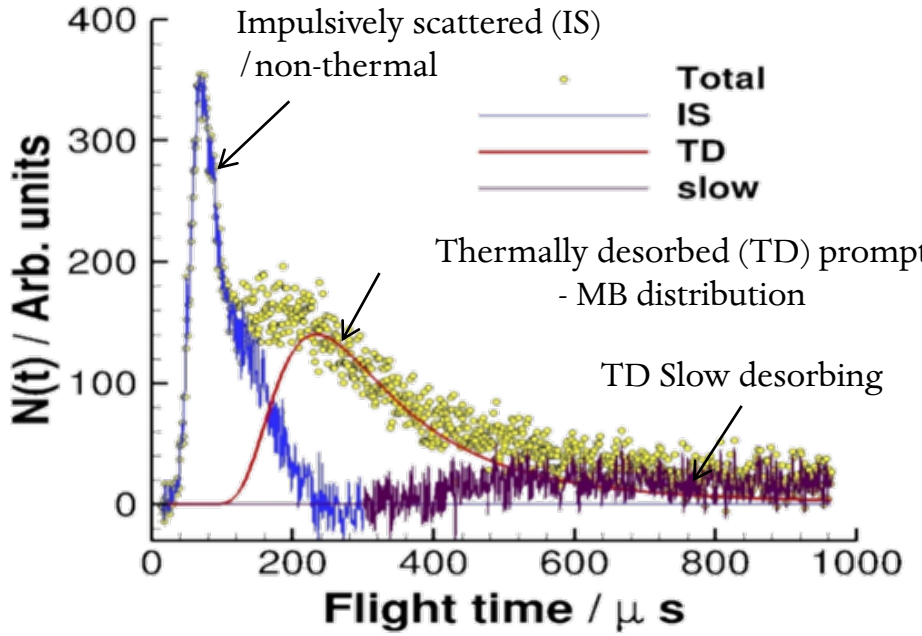

Marschall, J., & MacLean, M. (2011). Finite-rate surface chemistry model, I: Formulation and reaction system examples. AIAA Paper, 3783, 2011.

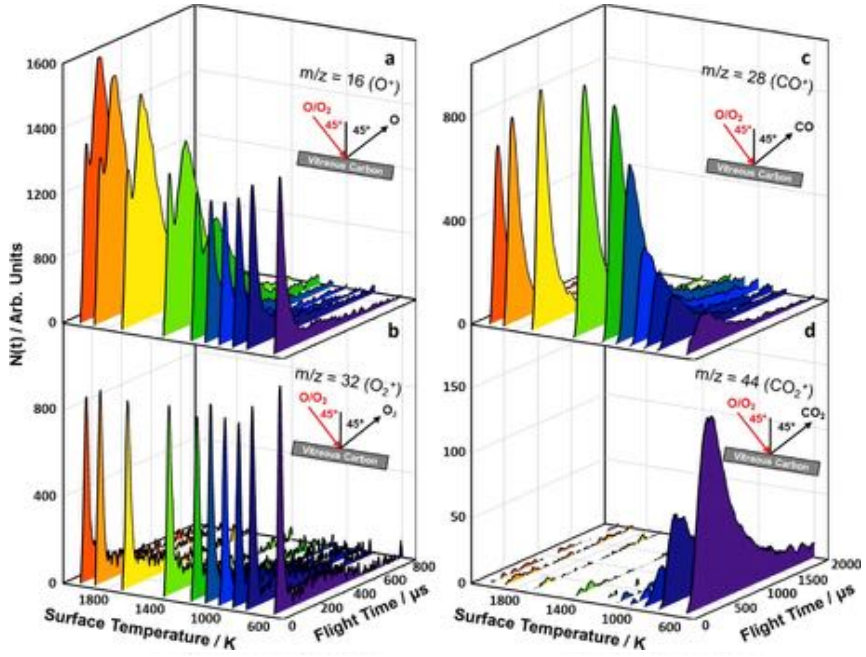
# PuMA simulation

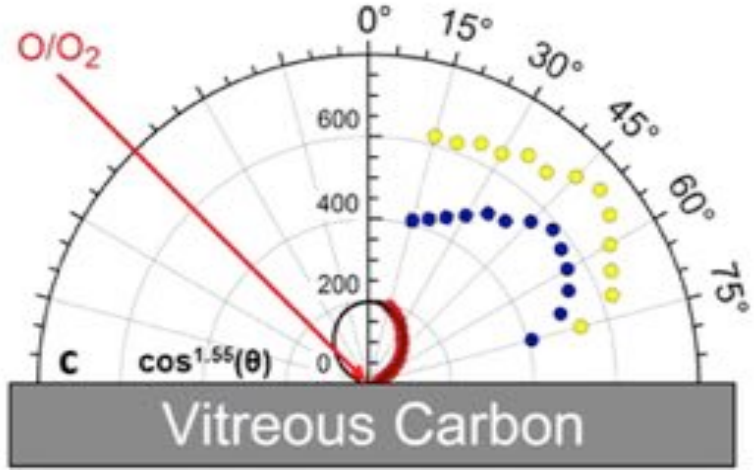
# Molecular Beam Experimental Setup




Murray *et al*




Murray, V J., et al. *The Journal of Physical Chemistry C* 119.26 (2015): 14780-14796.

# Carbon Oxidation Model

| Type | Mechanisms | Reaction |
|---|---|---|
| Adsorption | Adsorption | $O(g) + (s) \longrightarrow O(ads)$ |
| Adsorption-mediated GS reactions | LH1 O formation | $O(ads) \longrightarrow O(TD)(g) + (s)$ |
| | LH1 CO formation | $O(ads) + C(b) + O'(ads) \longrightarrow CO(g) + (s) + O'(ads)$ |
| | LH1 $CO_2$ formation | $O(ads)+O(s)+C(b)+4O'(ads) \longrightarrow CO_2(g)+2(s)+4O'(ads)$ |
| | LH3 O{a} formation | $O(ads) \longrightarrow O\{a\}(s)$ |
| | LH3 CO{a} formation | $O(ads) + C(b) + O'(ads) \longrightarrow CO\{a\}(s) + O'(ads)$ |
| | LH3 CO{b} formation | $O(ads) + C(b) + O'(ads) \longrightarrow CO\{b\}(s) + O'(ads)$ |
| PS reactions | LH3 O{a} desorption | $O\{a\}(s) \longrightarrow O(g) + (s)$ |
| | LH3 CO{a} desorption | $CO\{a\}(s) \longrightarrow CO(g) + (s)$ |
| | LH3 CO{b} desorption | $CO\{b\}(s) \longrightarrow CO(g) + (s)$ |

Fast TD reactions

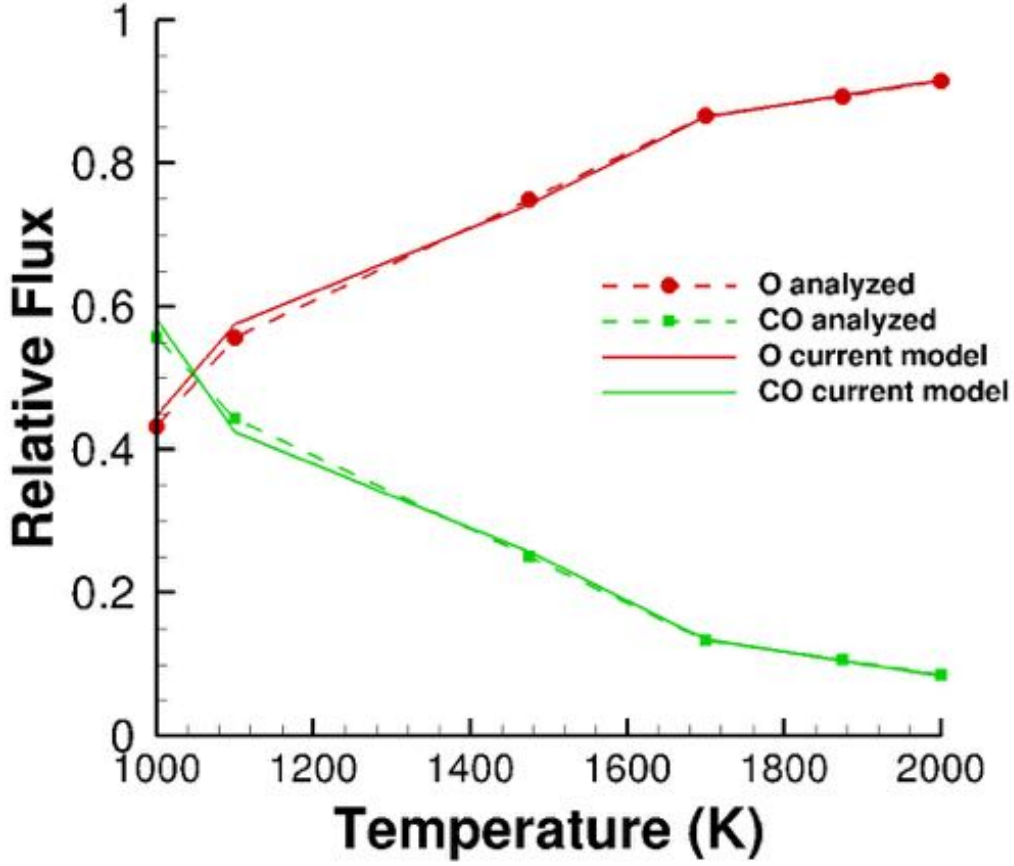
Slow formation reactions

Desorption reactions

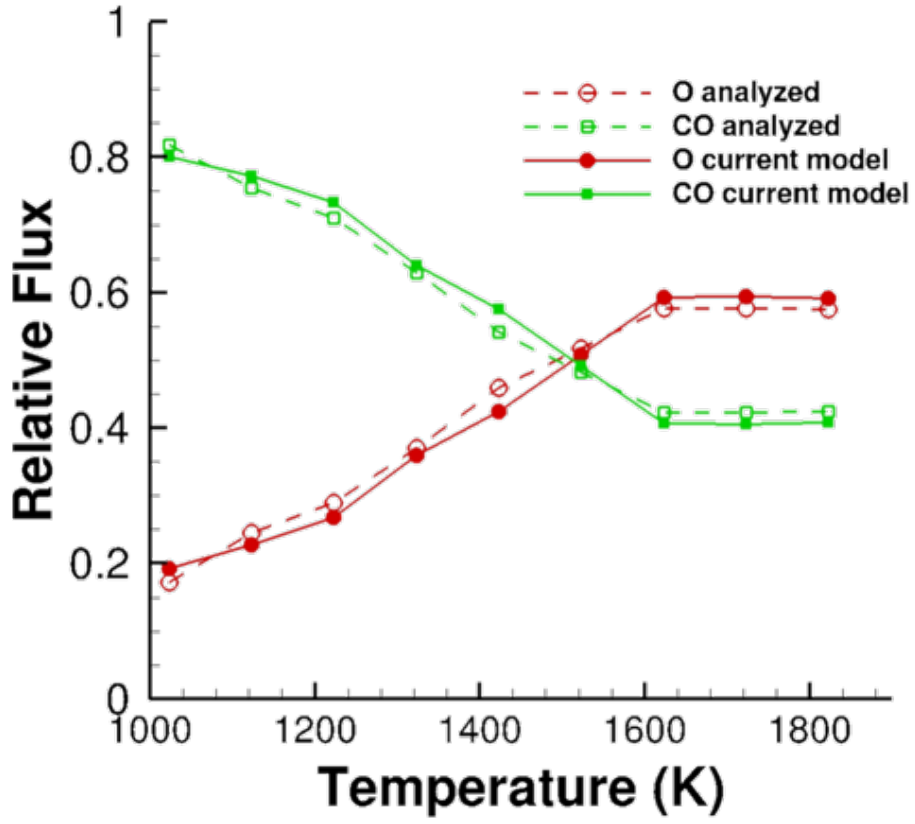
K. Swaminathan-Gopalan *et al.*, "***Development and validation of a finite-rate model for carbon oxidation by atomic oxygen.***" Carbon 137 (2018): 313-332.

# Vitreous and Preform Carbon model

Vitreous carbon model




Preform carbon model



# Effective model for macroscopic solvers

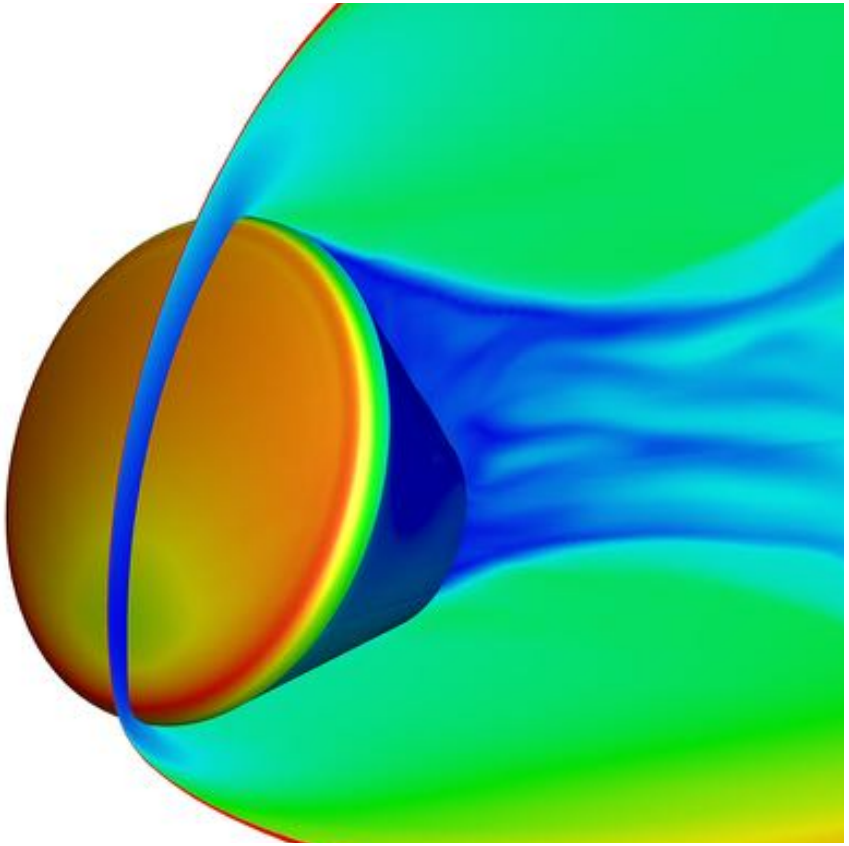
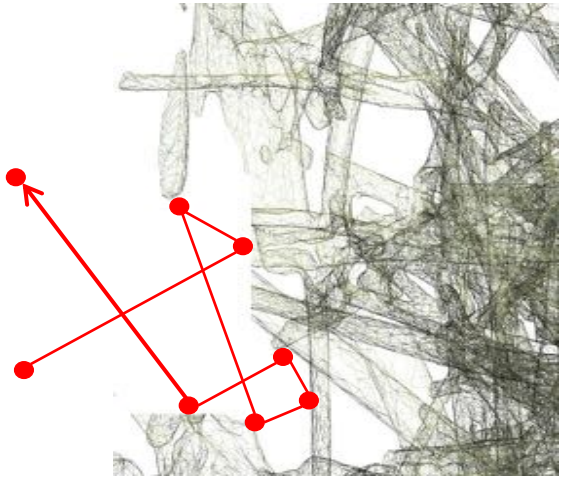
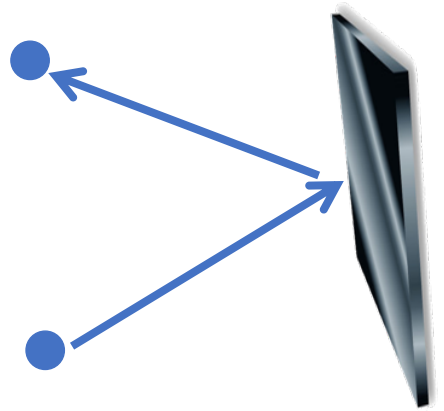


Image credit: NASA

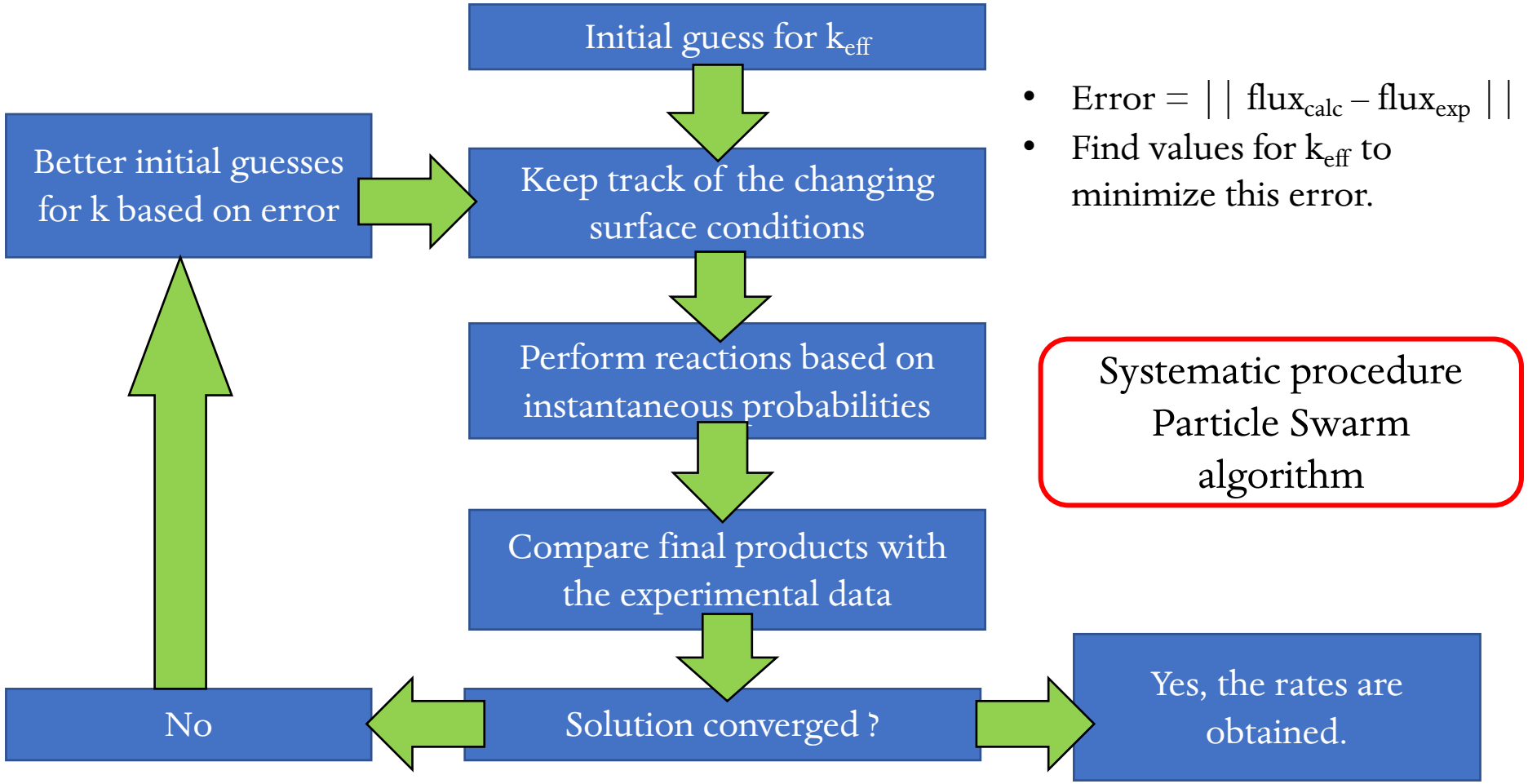


Real model
Rates → k



Effective model
Rates → $k_{eff}$

# Reaction Rate Constants Fitting Method

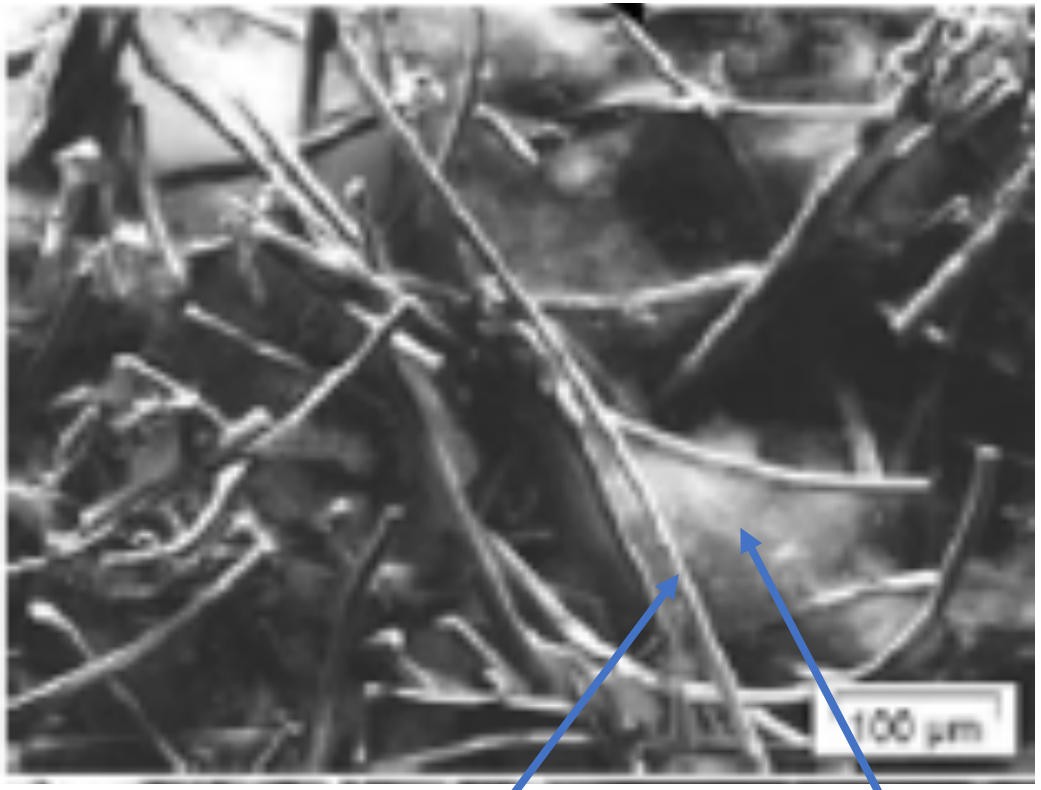



- Error = $|| flux_{calc} - flux_{exp} ||$
- Find values for $k_{eff}$ to minimize this error.

Systematic procedure Particle Swarm algorithm

K. Swaminathan Gopalan and K. A. Stephani. In *47th AIAA Thermophysics Conference*, p. 4347. 2017.

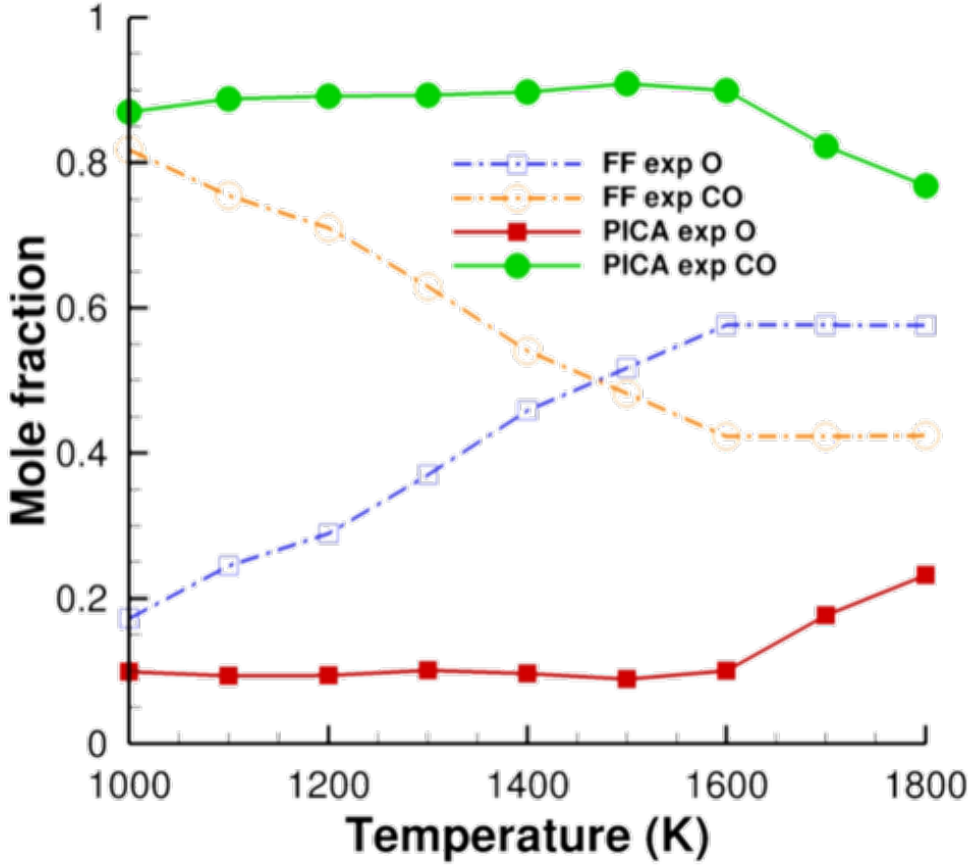
# PICA oxidation model




Preform carbon

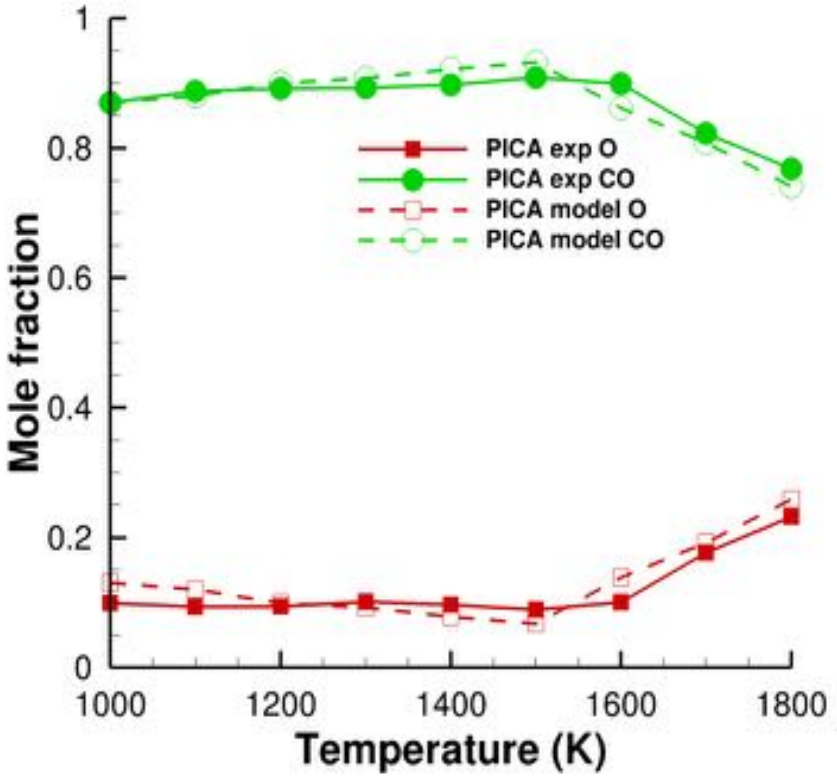
PICA CHAR

2 phase model




- PICA and FF trends are qualitatively and quantitatively different.
  - Difference in reactivity.
  - Difference in porosity.

# PICA oxidation model

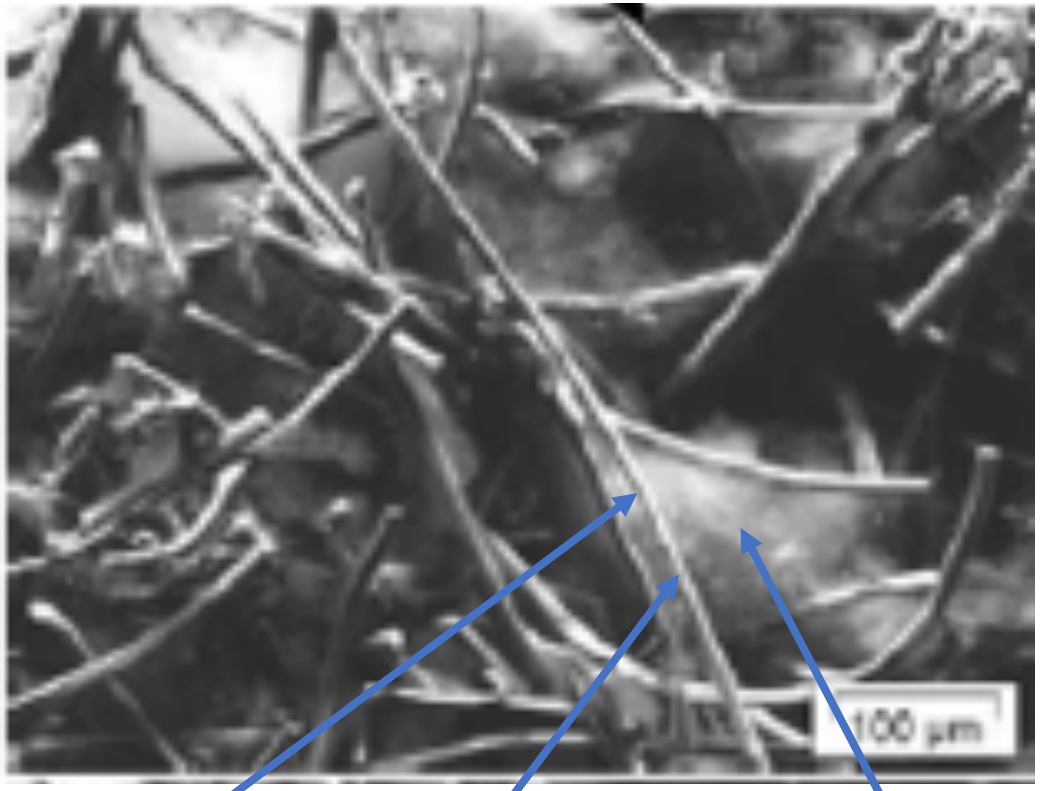



| Mechanisms | Reaction | Rate constant (k) |
|---|---|---|
| Adsorption | $O(g) + (s) \longrightarrow O(ads)$ | $\frac{1}{\Phi} * \frac{1}{4}\sqrt{\frac{8k_bT_s}{\pi m}} * 1$ |
| TD O formation | $O(ads) \longrightarrow O(TD)(g) + (s)$ | $0.946\ exp(-\frac{4686.98}{T_s})$ |
| TD CO formation | $O(ads) + C(b) + O'(ads) \longrightarrow CO(g) + (s) + O'(ads)$ | $\frac{1}{\Phi} * 4262.96\ exp(-\frac{7669.43}{T_s})$ |
| LH O{a} formation | $O(ads) \longrightarrow O\{a\}(s)$ | 1 |
| LH CO{a} formation | $O(ads) + C(b) + O'(ads) \longrightarrow CO\{a\}(s) + O'(ads)$ | $\frac{1}{\Phi} * 1226.66\ exp(-\frac{5992.25}{T_s})$ |
| LH CO{b} formation | $O(ads) + C(b) + O'(ads) \longrightarrow CO\{b\}(s) + O'(ads)$ | $\frac{1}{\Phi} * 388.87\ exp(-\frac{2174.87}{T_s})$ |
| LH O{a} desorption | $O\{a\}(s) \longrightarrow O(g) + (s)$ | $0.05\ T^2\ exp\left(-\frac{3177.2}{T_s}\right)$ |
| LH CO{a} desorption | $CO\{a\}(s) \longrightarrow CO(g) + (s)$ | $4485.5\ exp\left(-\frac{1581.4}{T_s}\right)$ |
| LH CO{b} desorption | $CO\{b\}(s) \longrightarrow CO(g) + (s)$ | $1.20\ exp\left(-\frac{2251.60}{T_s}\right)$ |

- New 2 phase model for PICA
  - Phase 1: FiberForm – same rates as preform carbon model.
  - Phase 2: PICA char – new rates for same reactions.

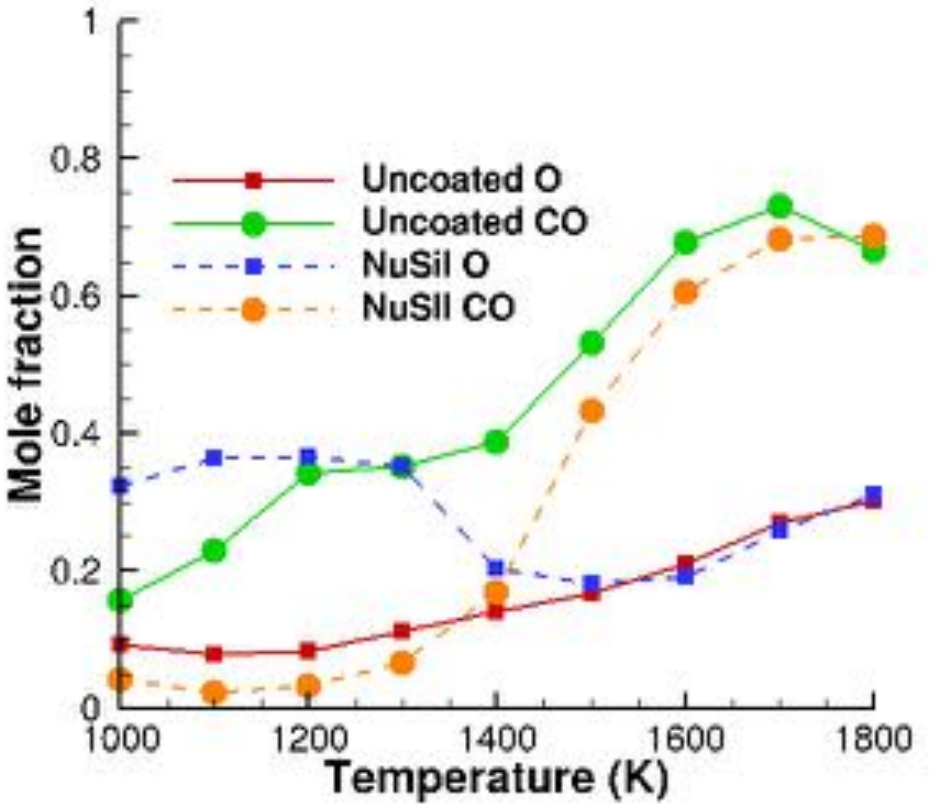
- Newly developed PICA model agrees well with the experiments.

# PICA-NuSil oxidation model




NuSil Preform carbon PICA CHAR

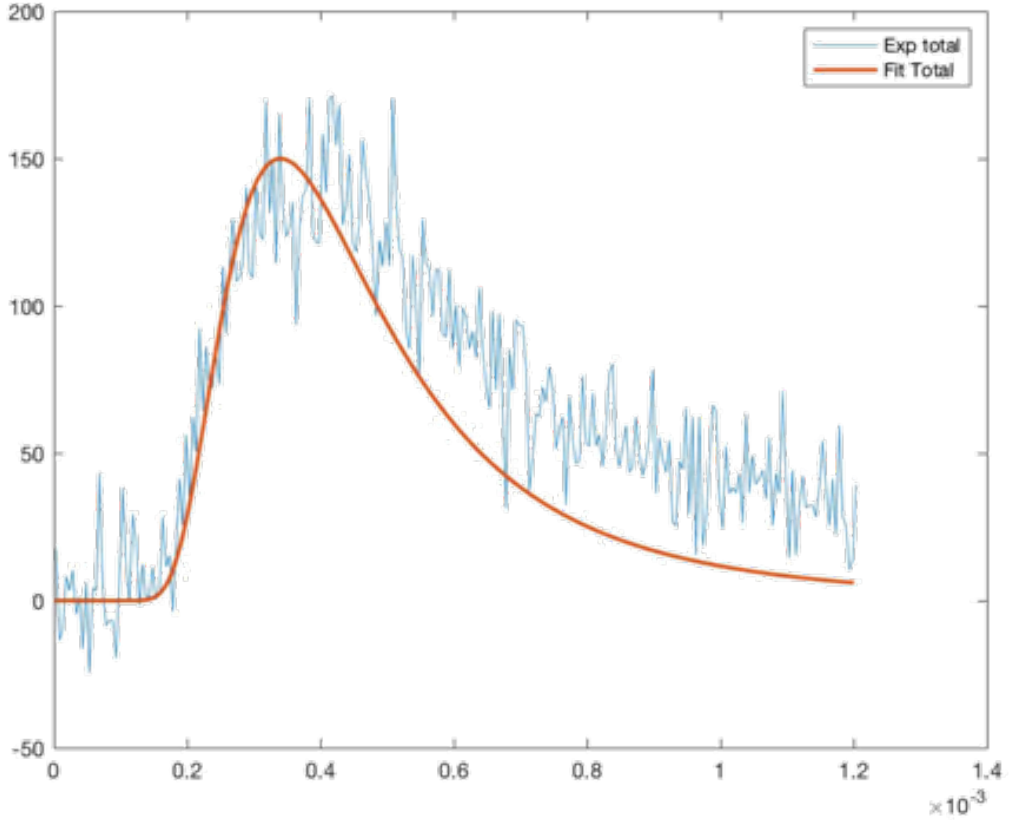
3 phase model




- PICA and FF trends are qualitatively and quantitatively different.
  - Difference in reactivity.
  - Difference in porosity.

# SiO reactions

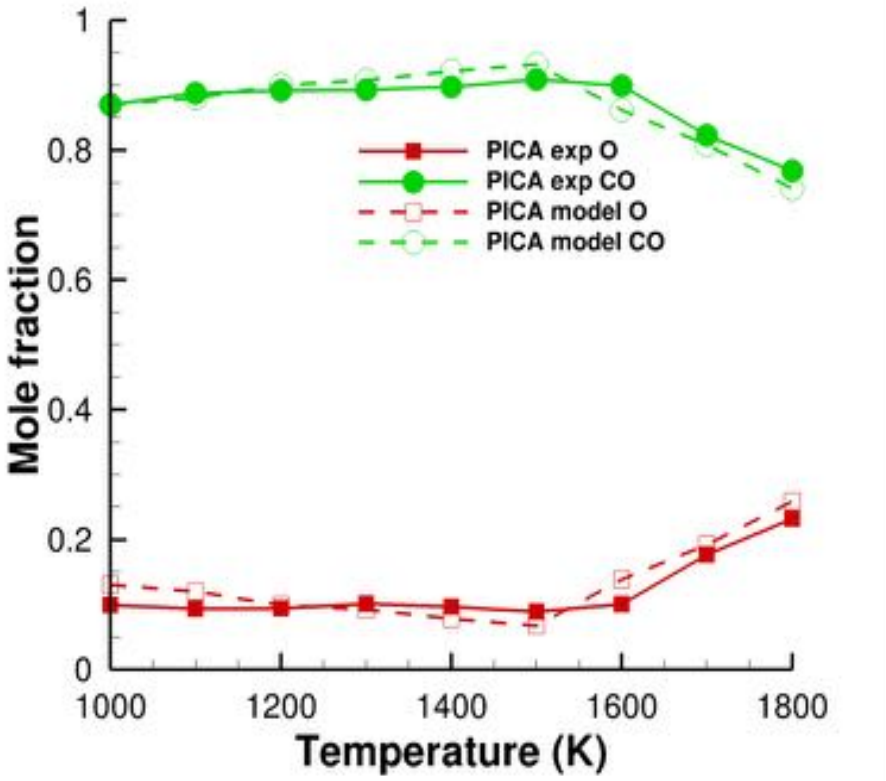
PICA-NuSil T = 1800K SiO TOF




| Mechanisms | Reaction |
|---|---|
| Scattering | $O(g) + Si(s) \longrightarrow O(g) + Si(s)$ |
| TD SiO formation | $O(g) + Si(s) \longrightarrow SiO(g) + (s)$ |
| LH SiO formation | $O(g) + Si(s) \longrightarrow SiO(g) + (s)$ |

- SiO TOF has a fast TD and slow desorption component.

# PICA-NuSil oxidation model




| Mechanisms | Reaction |
|---|---|
| Scattering | $O(g) + Si(s) \longrightarrow O(g) + Si(s)$ |
| TD SiO formation | $O(g) + Si(s) \longrightarrow SiO(g) + (s)$ |
| LH SiO formation | $O(g) + Si(s) \longrightarrow SiO(g) + (s)$ |

- New 3 phase model for PICA-NuSil
  - Phase 1: FiberForm – same rates as preform carbon model.
  - Phase 2: PICA char – same rates as PICA 2 phase model.
  - Phase 3: NuSil – new rates for same reactions.

- Newly developed PICA-NuSil model agrees well with the experiments.