Ablation of PICA-like Materials
Surface or Volume phenomenon?

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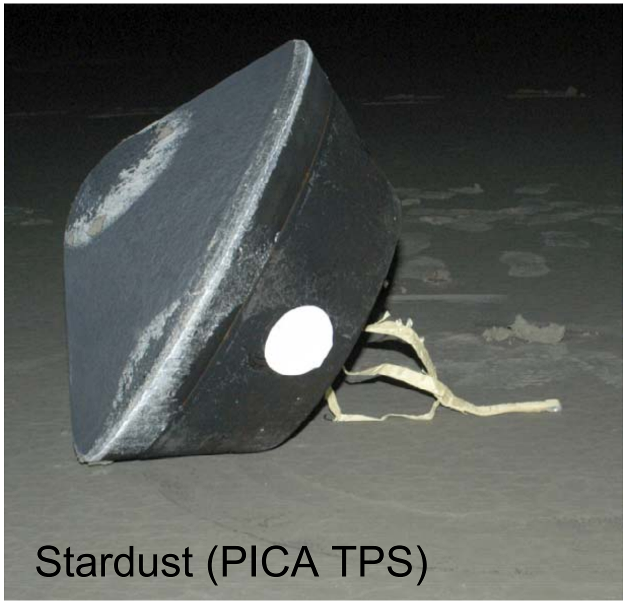

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. Introduction and Objective

"The time to study and fully understand the limits of PICA is NOW"
B. Laub and E. Venkatapathy, IPPW5, 2007.

- **Introduction :**
  - The ablation of the char layer in ablative material is usually described in term of recession velocity. This "surface" description is valid for dense materials.
  - However, the recession of the average surface in porous materials may not recede uniformly but matrix and fibers may progressively vanish in depth inside the structure : "volume ablation".
  - PICA-like materials are porous and may undergo volume ablation with two important consequences :
    - The material weakens in volume and is possibly subject to mechanical erosion (Spallation)
    - The ablation enthalpy distributed in volume modifies the thermal response

- **Objectives of this presentation:**
  - Model and understand ablation using a porous medium model
  - Estimate whether volume ablation is an important phenomenon or not
  - Decide if an elaborated model taking into account a volume ablation fully coupled with pyrolysis have to be developed (many years of development). If it is the case, a first model will be presented.

. OUTLINE

1. **Modeling of the structure of PICA-like materials**

2. **Modeling of the Ablation of porous materials**
   - Microscopic model
   - Numerical Simulation at microscopic scale
   - Homogenization → macroscopic behavior

3. **Application to Stardust Reentry Conditions**
   - Macroscopic model including blowing effects
   - Volume or Surface Ablation?

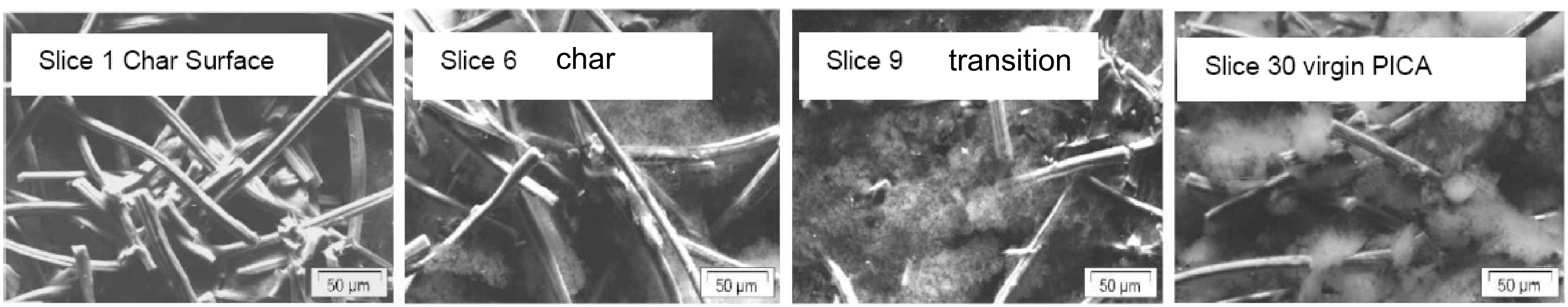
4. **Possible ablation model for a volumetric coupling with Pyrolysis**

5. **Conclusion & Next steps**

1. Modeling of the structure of PICA-like materials

Structure of “PICA-like” materials

- **Preform :**
  - Random arrangement of carbon fibers
  - High porosity
- **Matrix :**
  - Phenolic resin
  - Low mass fraction
- **Material type :**
  - Ablator
  - Low density

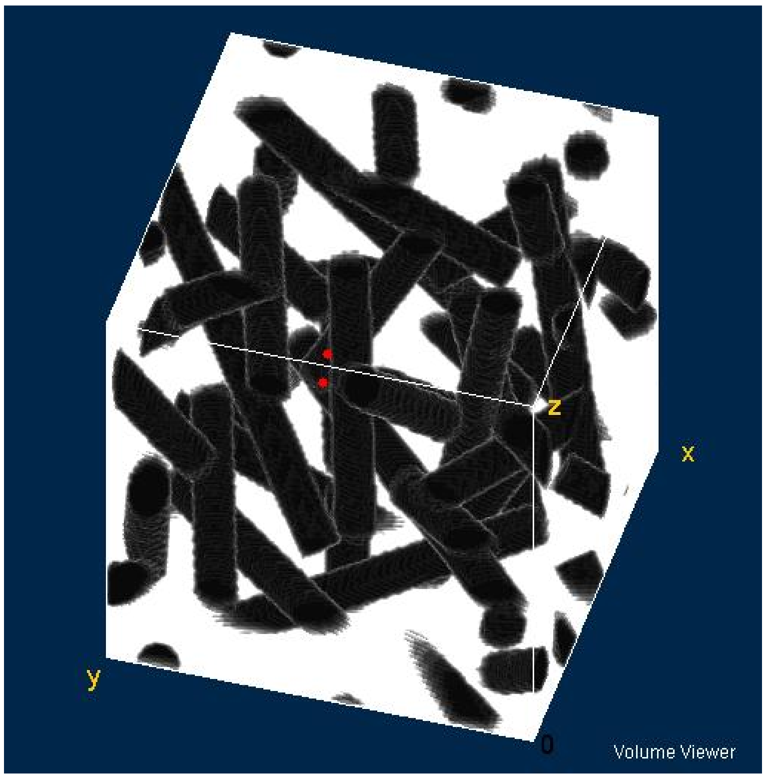


M. Stackpoole et al., AIAA 2008-1202 (Reno 2008)

1. Modeling of the structure of PICA-like materials

Fibrous preform : fiber size / orientation / porosity (statistical)

- **Random drawing of non-overlapping cylinders** (Monte-Carlo algorithm)
- **Cylinders more or less parallel to the surface** (Bias on azimuthal angle)
- **Choice of a Length/Radius ratio** (around 50 for PICA-like materials)

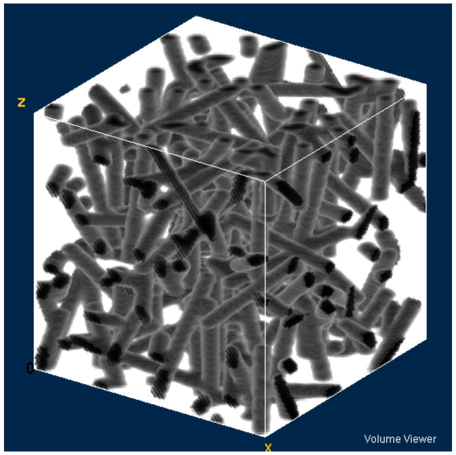


Totally Random

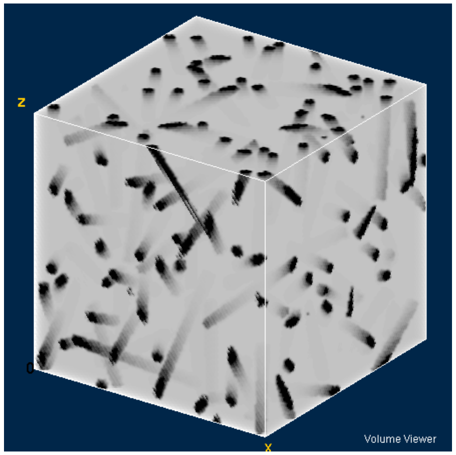
Complementary Azimutal angle : +/- 15°

Interesting result : limit porosity = 0.85 for totally random structures / 0.9 for parallel

- **Before pyrolysis : different possibilities**
  - Thin layer of matrix surrounding the fibers
  - “Fluffy” matrix occupying the pores of the fibrous structure
- **After pyrolysis : matrix structure is modified**
  - Due to an important mass loss during pyrolysis
  - Resulting structure varies with experimental conditions
- **Models :**



Thin matrix layer around the fibers



Virgin fluffy matrix homogeneous at fiber scale

2. Ablation model for porous media

Objective and assumptions

- **Objective :**
  - Estimate whether volume ablation is an important phenomenon or not using a simple model
  - ➢ In order to decide if an elaborated model taking into account a volume ablation fully coupled with pyrolysis have to be developed

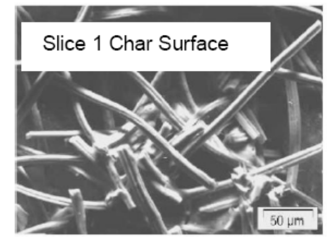
- **Main Hypothesis :**
  - If volume ablation occurs, it occurs mainly in the char layer
  - ➢ Ablation model loosely coupled with pyrolysis

- **Approach :**
  - Multiscale modeling: microscopic scale (fibers) → macroscopic scale (composite)
  - Numerical models to provide guidelines and accurate results
  - Simplified analytical models to provide understanding
  - Application of the models to flight conditions (includes a loosely coupling with pyrolysis)

2. Ablation model for porous media

Reaction/Transport & Recession model in a carbon felt

- **Idea :** Use a simplified model to try and understand the Ablation of porous media
- **Hypotheses :**
  - Simplified structure : carbon fibers randomly oriented
  - Simple chemistry (C_s oxidized by 0_2 or sublimated)
- **<u>Starting point :</u>** differential recession of a heterogeneous surface ***S*** by gasification

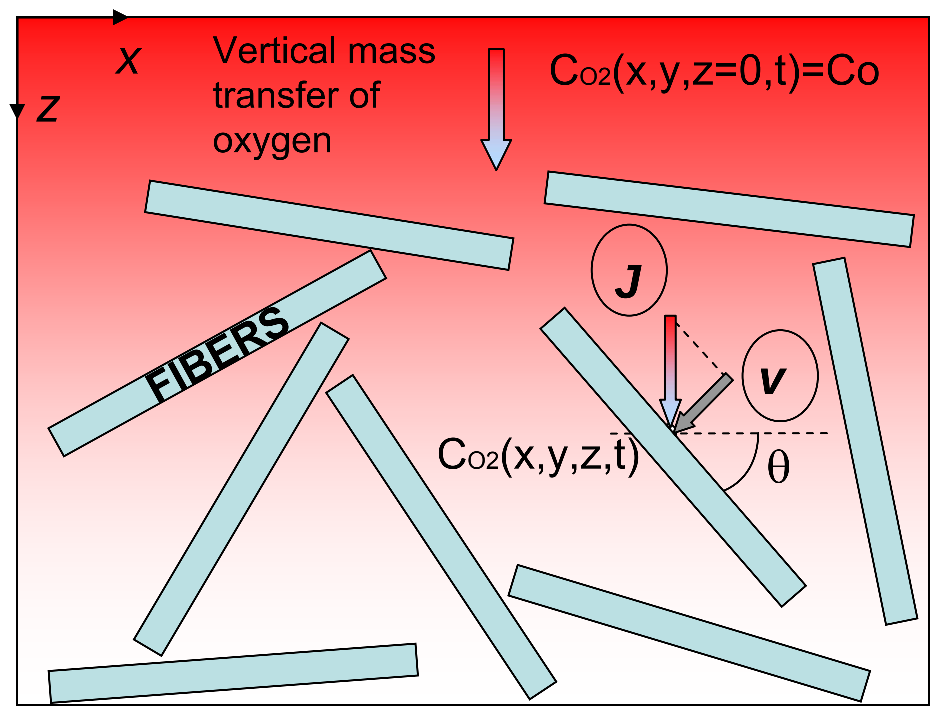


$$\frac{\partial S}{\partial t} + \mathbf{v}.\nabla S = 0$$

$$\mathbf{v} = \Omega \cdot J \cdot \mathbf{n}$$

$$J = k_f C$$

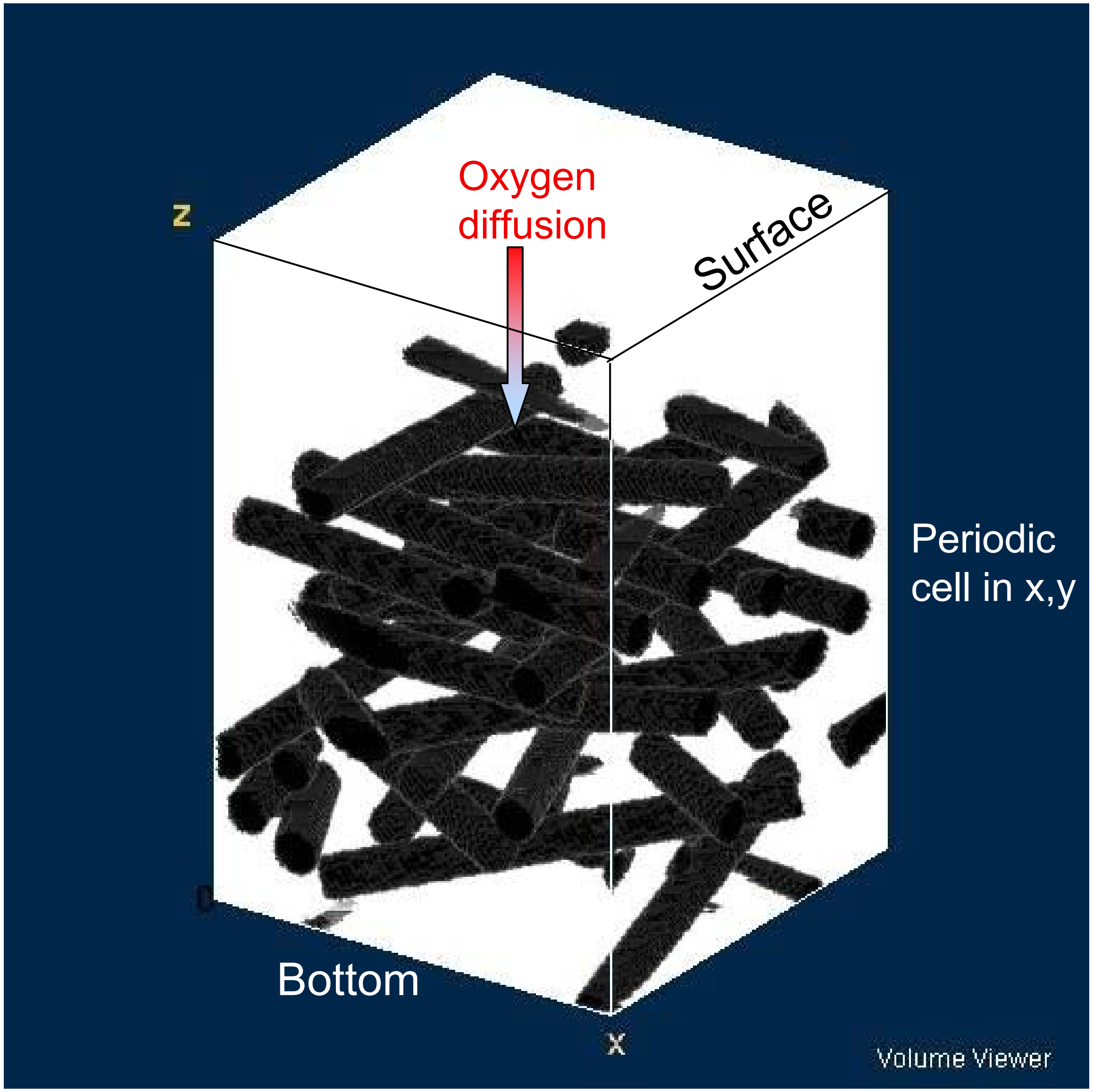
$$\frac{\partial C}{\partial t} + \nabla \cdot (-D \nabla C) + \vec{v}_g \cdot \nabla C = 0$$



<u>N.B.</u> : oxidation notations BUT sublimation is mathematically equivalent

2. Ablation model for porous media

Reaction/Diffusion : Simulation (1/2) : diffusion << reaction ($D/L \ll k_f$)

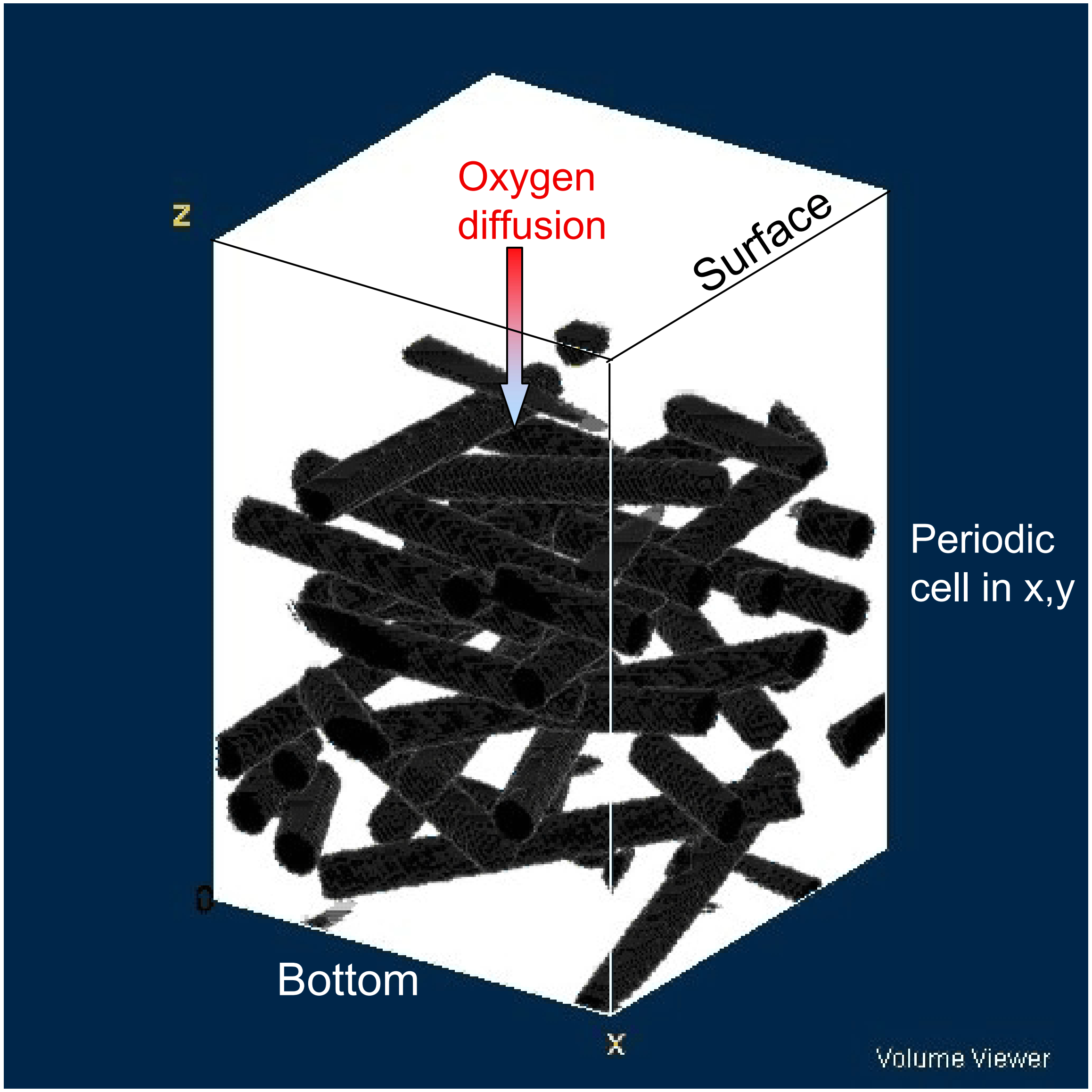


Hypotheses:
-Isothermal
-No pyrolysis gas

Simulation tool

2. Ablation model for porous media

Reaction/Diffusion : Simulation (2/2) : diffusion >> reaction (D/L >> k_f)

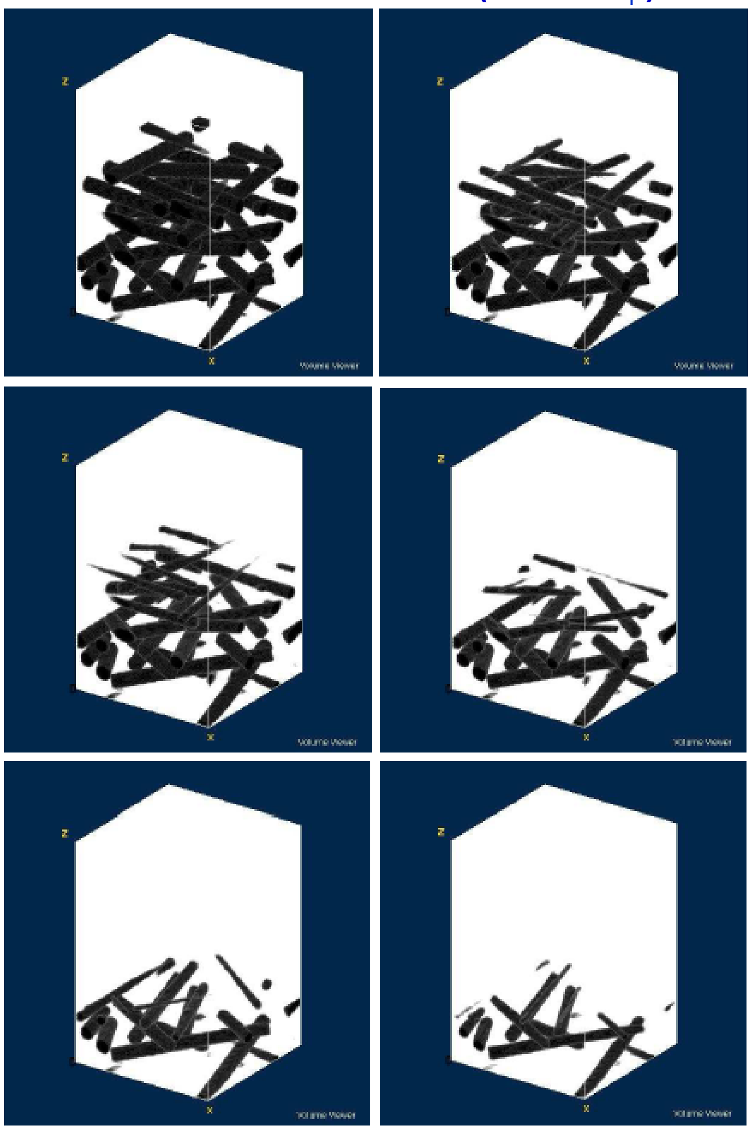


Hypotheses:
-Isothermal
-No pyrolysis gas

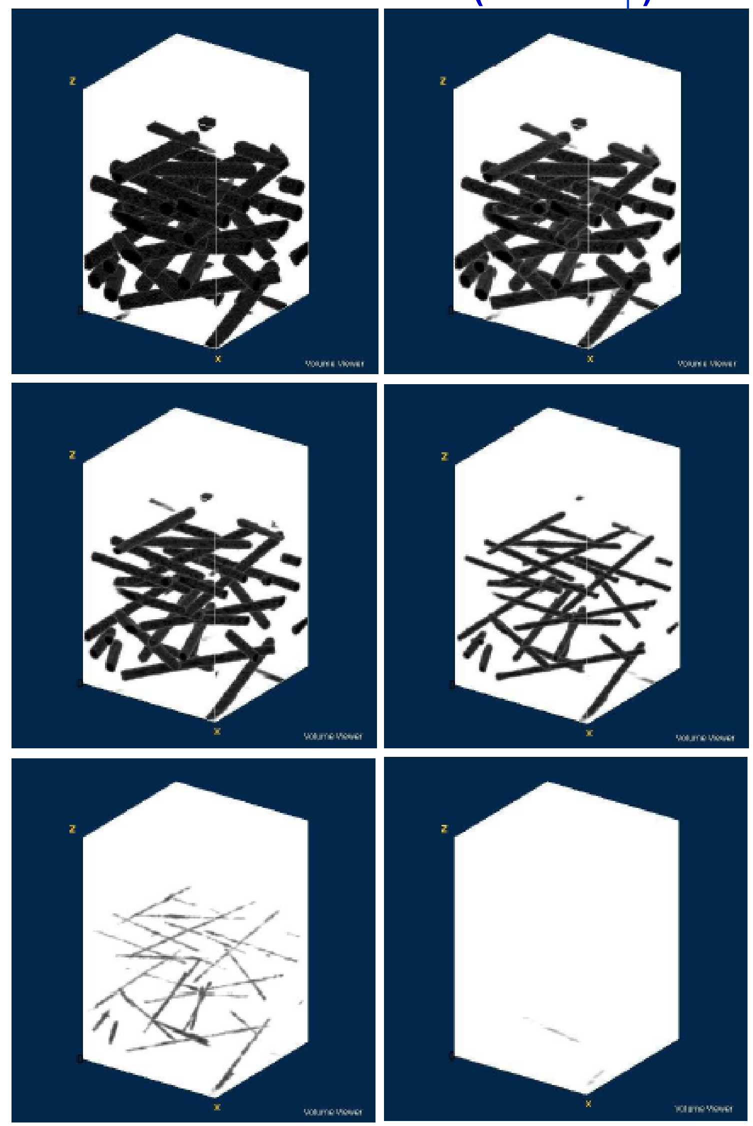
2. Ablation model for porous media

Surface or Volume ? → depends on experimental conditions

Surface Ablation ($D/L \ll k_f$)



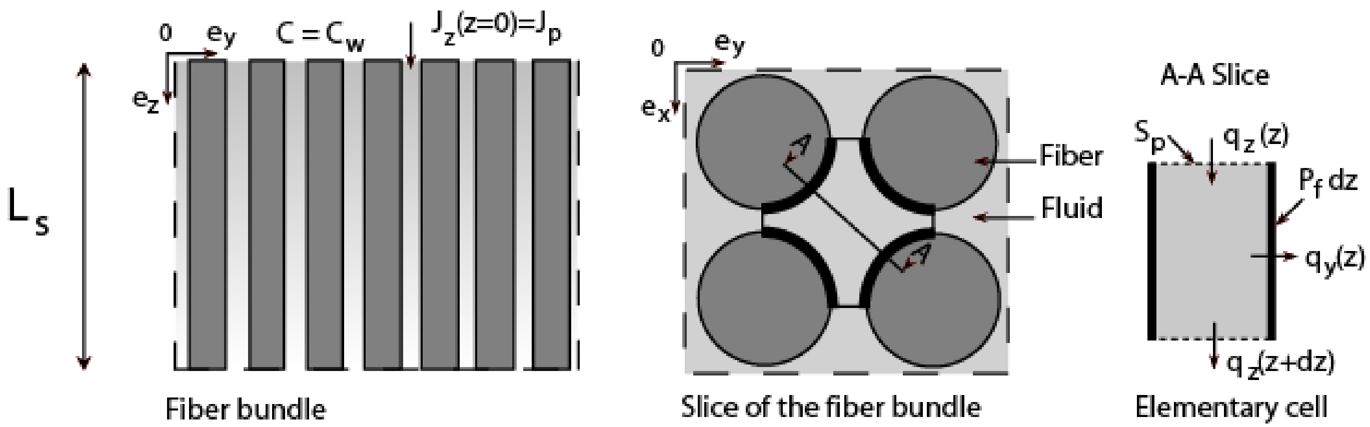
Volume Ablation ($D/L \gg k_f$)



2. Ablation model for porous media

Homogenization and Analytical solution (hyp. : no recession)

- **Volume or surface? →Key information : C, oxidant concentration**
- 1D model to obtain an analytical solution : C (z) = f (experimental conditions)



Mass balance in steady state :

$$q_z(z) - q_z(z+dz) = q_y(z)$$

$$-D\nabla(C(z) - C(z+dz))S_p = k_f C(z) P_f dz$$

$$S_p/P_f = \varepsilon/s$$

s (m²/m³) : specific surface

$$\boxed{C(z) = C_0 \frac{\cosh[\Phi(z/L_s - 1)]}{\cosh \Phi}}$$

$$\boxed{\text{Thiele number} : \Phi = \frac{L_s}{\sqrt{\frac{D_{eff}}{s k_f}}}}$$

Hyp., bulk diffusion between perpendicular fibers: $D_{eff} = \varepsilon D$

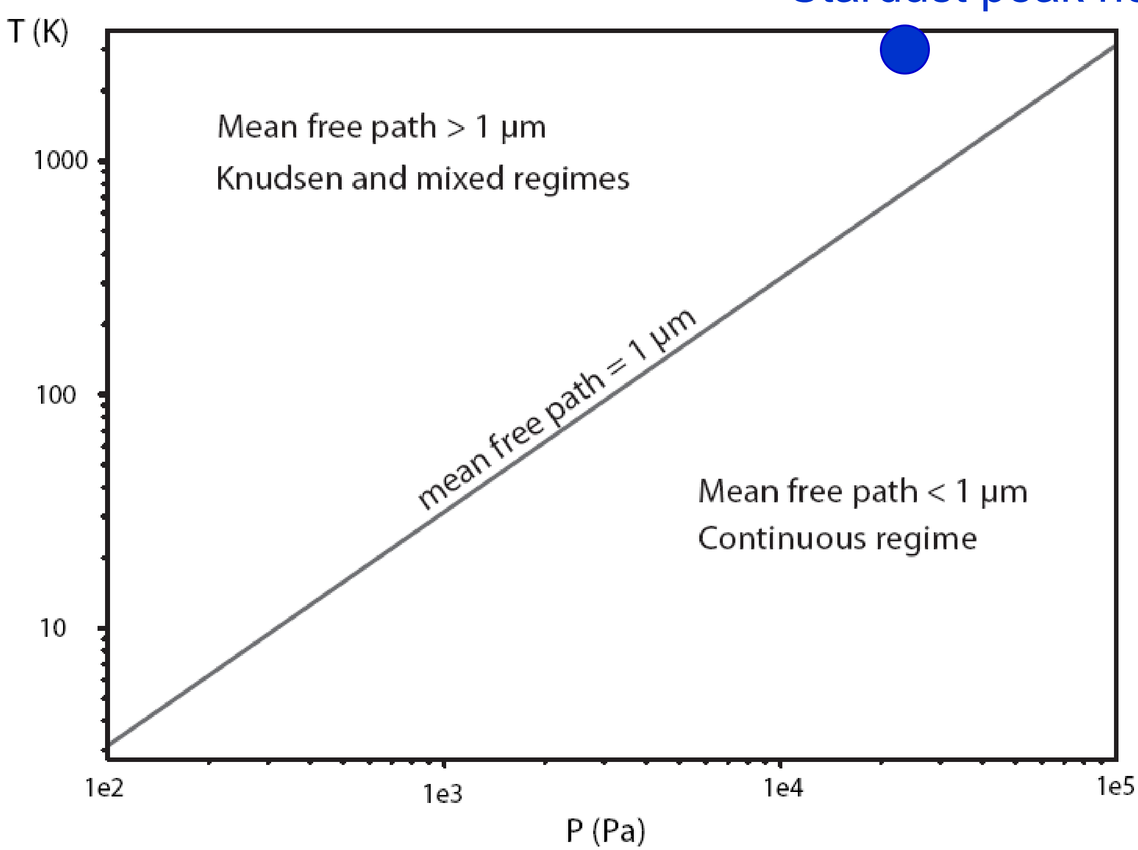
BUT…

2. Volume Ablation model

Validity domain of the continuous regime hypothesis

- **Knudsen number :** $Kn = \bar{\lambda} / d_p$ (continuous regime for *Kn < 0.02*)
- **Pore size around 50µm → Knudsen regime for mean free path < 1µm**
- **Air :** $\bar{\lambda} = 95 \cdot 10^{-9} \cdot \dfrac{10^5 \cdot T}{298 \cdot P}$

Stardust peak heating *(Kn=0.08)*



Reentry conditions : Knudsen regime inside the porous medium

↓

Model still correct in Knudsen regime?

2. Ablation model for porous media

Model still correct in *Kn* regime but with a modified diffusion coefficient

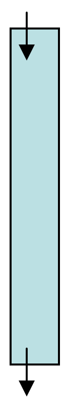
- **Knudsen effects : Diffusion coefficient in a capillary (Bosanquet model)**

$$\frac{1}{D_{ref}} = \frac{1}{D_B} + \frac{1}{D_K} = \frac{1}{\frac{1}{3}\bar{v}\bar{\lambda}} + \frac{1}{\frac{1}{3}\bar{v}d_p}$$ (harmonic average)

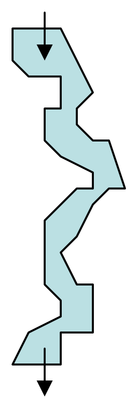
- **Fibers randomly oriented :** tortuosity effects non negligible in *Kn* regime

$$D_{eff} = \frac{\varepsilon}{\eta} D_{ref}$$

Tortuosity has to be obtained by Monte Carlo simulation inside the porous media (not available yet in the literature for non-overlapping fibers)



$\eta \approx 1$



$\eta > 1$

$\eta > 1$

2. Ablation model for porous media

Determination of the effective diffusion coefficient D_{eff}

- **Monte Carlo Simulation :**
  - Random Walk rules :
    - (T,P) fixed = ($\overline{\lambda}$,D) fixed
    - λ : Maxwell-Boltzmann distribution
    - constant velocity norm

    (D = 1/3 $\overline{v}$ $\overline{\lambda}$) with 3D random direction drawing

1) Displacement ξ of 10000 walkers followed during τ (chosen for convergence)

2) Einstein relation on diffusion process :

$$D_{e\,j} = \frac{\left\langle \xi_j^2 \right\rangle}{2\tau}$$

- **Tortuosity as a function of *Kn* for the fibrous material of this study**

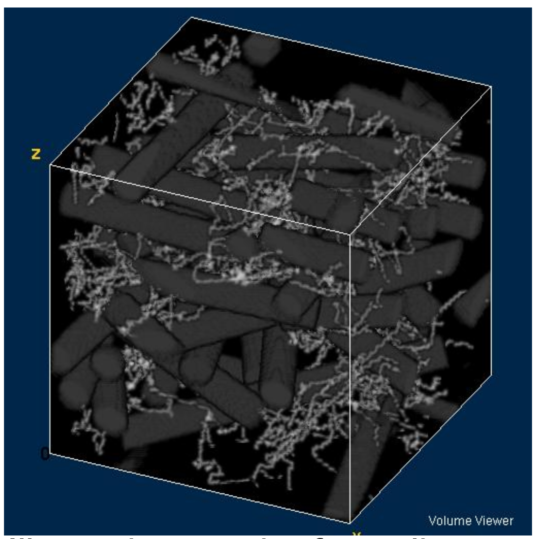
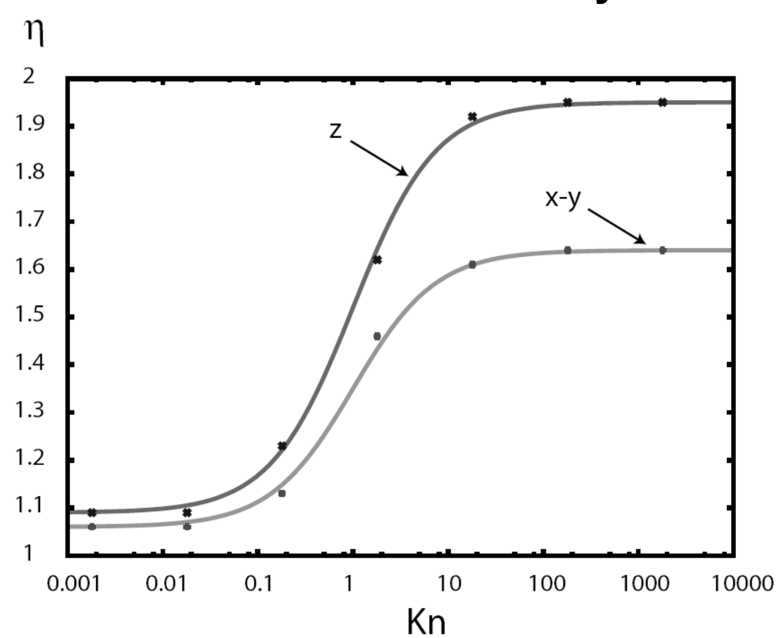


Illustration : path of a walker in a periodic cell



2. Ablation model for porous media

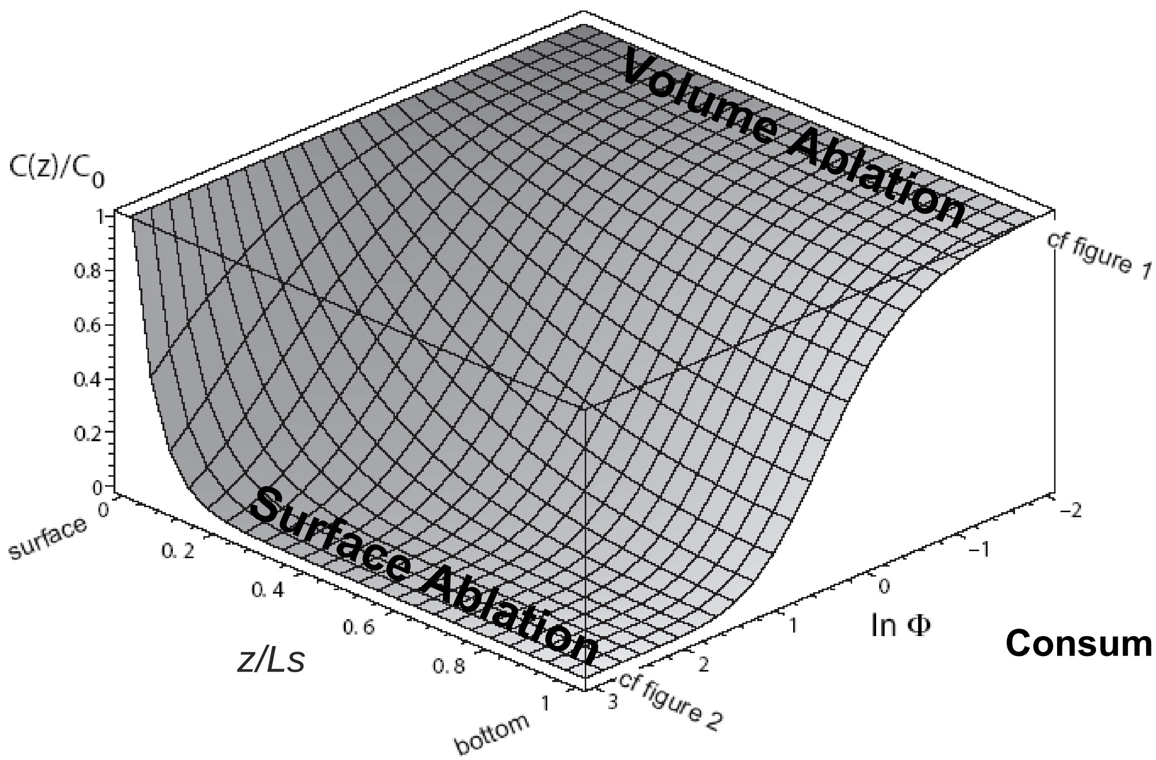
Parametrical analysis

- **Concentration gradient (1D model) as a function of Thiele number**

$$C(z) = C_0 \frac{\cosh\left[\Phi(z/L_s - 1)\right]}{\cosh\Phi}$$

Thiele number

$$\Phi = \frac{L_s}{\sqrt{\dfrac{D_{eff}}{sk_f}}}$$



L_s: material depth (m)
D_{eff}: effective diffusivity (m²/s)
k_f: fiber reactivity (m/s)
s : specific surface (m^2/m^3)

Consumption / diffusion velocities for porous media

3. Application to Stardust Reentry Conditions

Model must include blowing effect (pyrolysis gas)

- **Steady state equation including the convective term (continuous regime)**

$$\frac{\partial^2 C}{\partial z^2} + \frac{1}{L_C}\frac{\partial C}{\partial z} + \frac{1}{L_R^{\ 2}} C = 0 \quad \text{with} \quad L_C = \frac{D}{v_g} \quad \text{and} \quad L_R = \sqrt{\frac{D_{eff}}{sk_f}}$$

- **Solution (of the quadratic ODE with one Dirichlet B.C. : C(z=0)=C_0)**

$$C(z) = C_0 \exp\left[-\frac{z}{L_C}\left(1 + \sqrt{1/4 + \left(\frac{L_C}{L_R}\right)^2}\right)\right]$$

$L_C > 10 L_R \longrightarrow$ Blowing effect negligible (on concentration gradient)

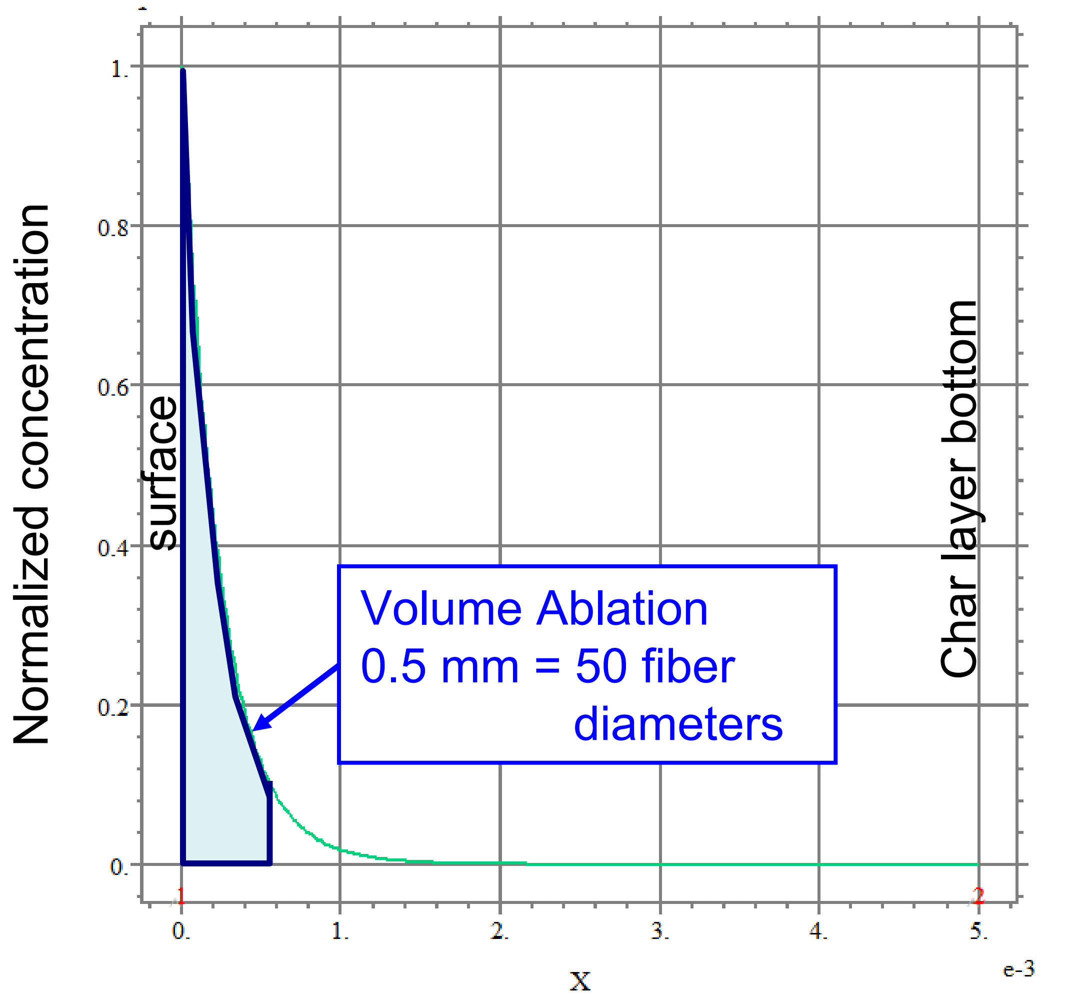
Example : Stardust peak heating

$L_C / L_R = 0.145 \longrightarrow$ Blowing effect almost negligible

3. Application to Stardust Reentry Conditions

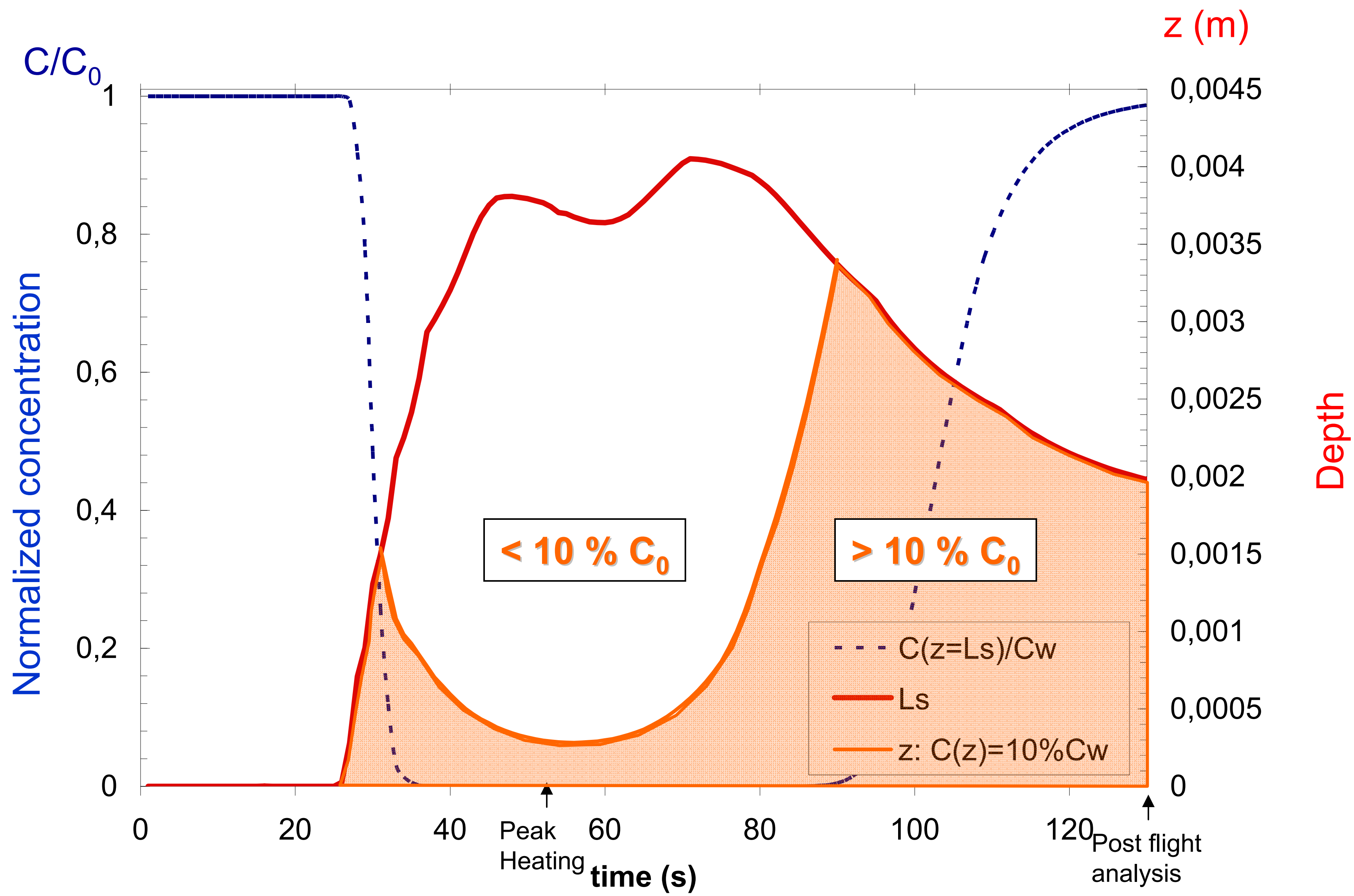
Stardust Peak Heating (stagnation point)

- **model including blowing effects + thermal gradients** (data from FIAT simulations) : Concentration in the char layer (FE solution: FlexPDE code)



3. Application to Stardust Reentry Conditions

Stardust trajectory (stagnation point)



4. Volume coupling of Pyrolysis & Ablation

Integration of ablation in the pyrolysis model : first ideas

Mass balance

$$\frac{\partial \varepsilon \rho_g}{\partial t} + \nabla \cdot (\varepsilon \rho_g \vec{v}_g) = -\frac{\partial \varepsilon_m \rho_m}{\partial t} - \frac{\partial \varepsilon_f \rho_f}{\partial t} \qquad \varepsilon + \varepsilon_m + \varepsilon_f = 0$$

Momentum balance

$$\varepsilon \vec{v}_g = -\frac{\overline{\overline{K}}}{\mu} \cdot \nabla p$$

Energy balance

$$(\varepsilon \rho_g c_g + \varepsilon_f \rho_f c_f + \varepsilon_m \rho_m c_m)\frac{\partial T}{\partial t} = \nabla \cdot (\overline{\overline{k}} \cdot \nabla T) - \varepsilon \rho_g c_g \vec{v}_g \cdot \nabla T + \delta h_p \frac{\partial \varepsilon_m \rho_m}{\partial t} + \delta h_{abl} \frac{\partial \varepsilon_f \rho_f}{\partial t}$$

Pyrolysis law

$$\rho_m = \rho_v - \sum_{i=1}^{n\_laws} (\rho_{v,i} - \rho_{p,i})\xi_i \quad with \quad \frac{\partial \xi_i}{\partial t} = (1 - \xi_i)^{n_i} A_i \exp\left(-\frac{E_{A_i}}{RT}\right)$$

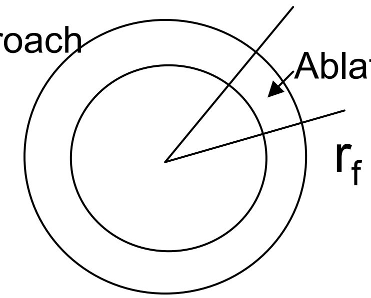
Ablation law (fibers)

$$\rho_f = const. \qquad \frac{\partial \varepsilon_f}{\partial t} = ?$$

4. Volume coupling of Pyrolysis & Ablation

Multiscale modeling of the ablation of the carbon felt

- Ablation : surface phenomenon at microscopic scale, but volumetric at macroscopic scale



  - **Mean fiber diameter evolution**

$$\frac{\partial d_f(z,t)}{\partial t} = -\Omega_s 2k_f(T)C(z,t)$$

  - **Homogenization : fiber diameter → mean porosity**

$$\varepsilon(z,t) = 1-(1-\varepsilon_0)\left(\frac{d_f(z,t)}{d_{f\_0}}\right)^2$$

  - **Convenient variable for ablation modeling : ε**

$$\frac{\partial \varepsilon C(z,t)}{\partial t} - div(D_{eff}(T,P)grad(C(z,t))) = \frac{4\ k_f\ (T)\ C(z,t)}{d_{f\_0}}\left[(1\text{-}\varepsilon(z,t))(1\text{-}\varepsilon_0)\right]^{0.5}$$

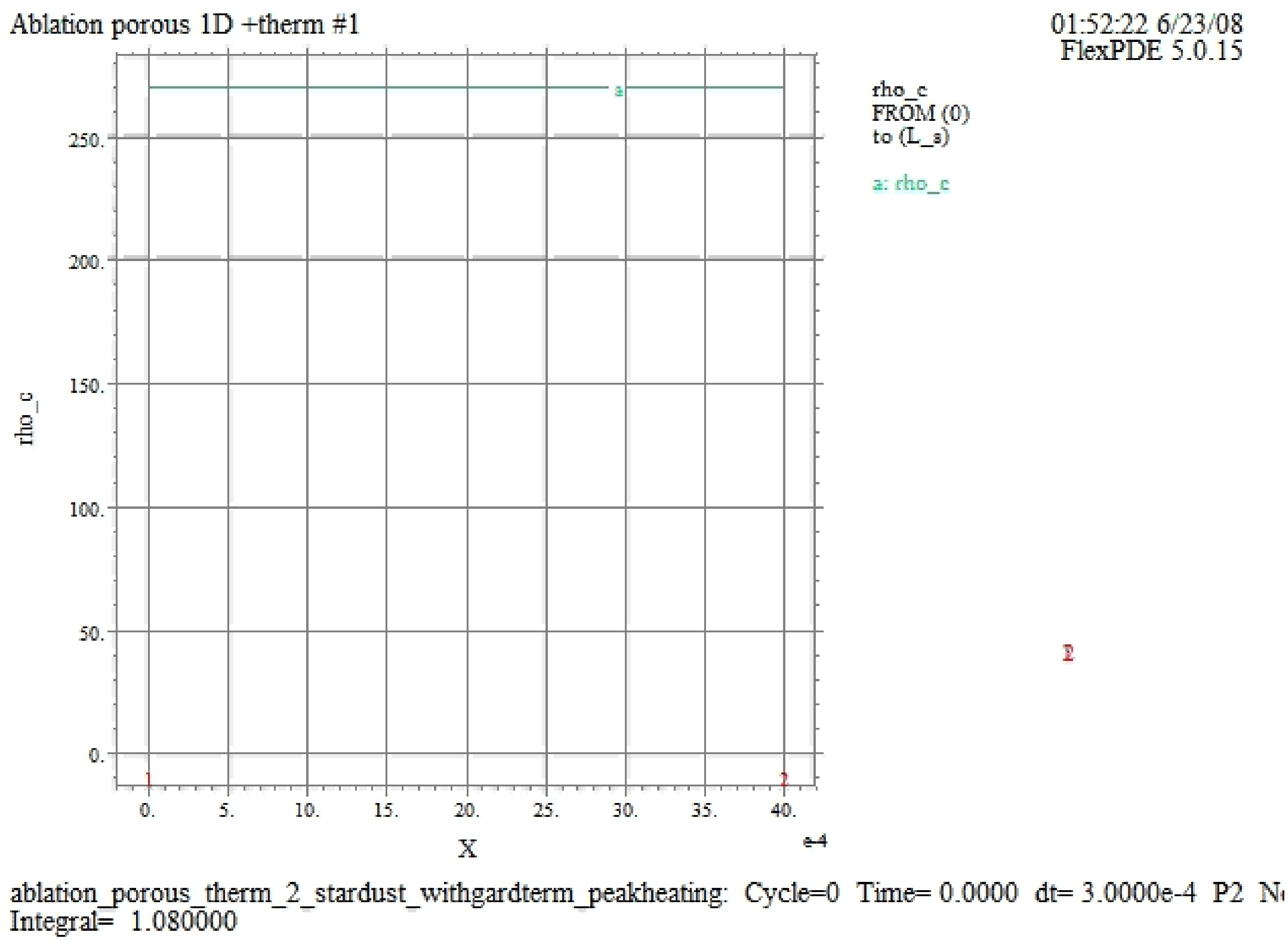
  - **Density :**

$$\rho_{material} = (1-\varepsilon)\rho_f$$

4. Volume coupling of Pyrolysis & Ablation

Illustration of the proposed Ablation law for Stardust Peak Heating thermal conditions

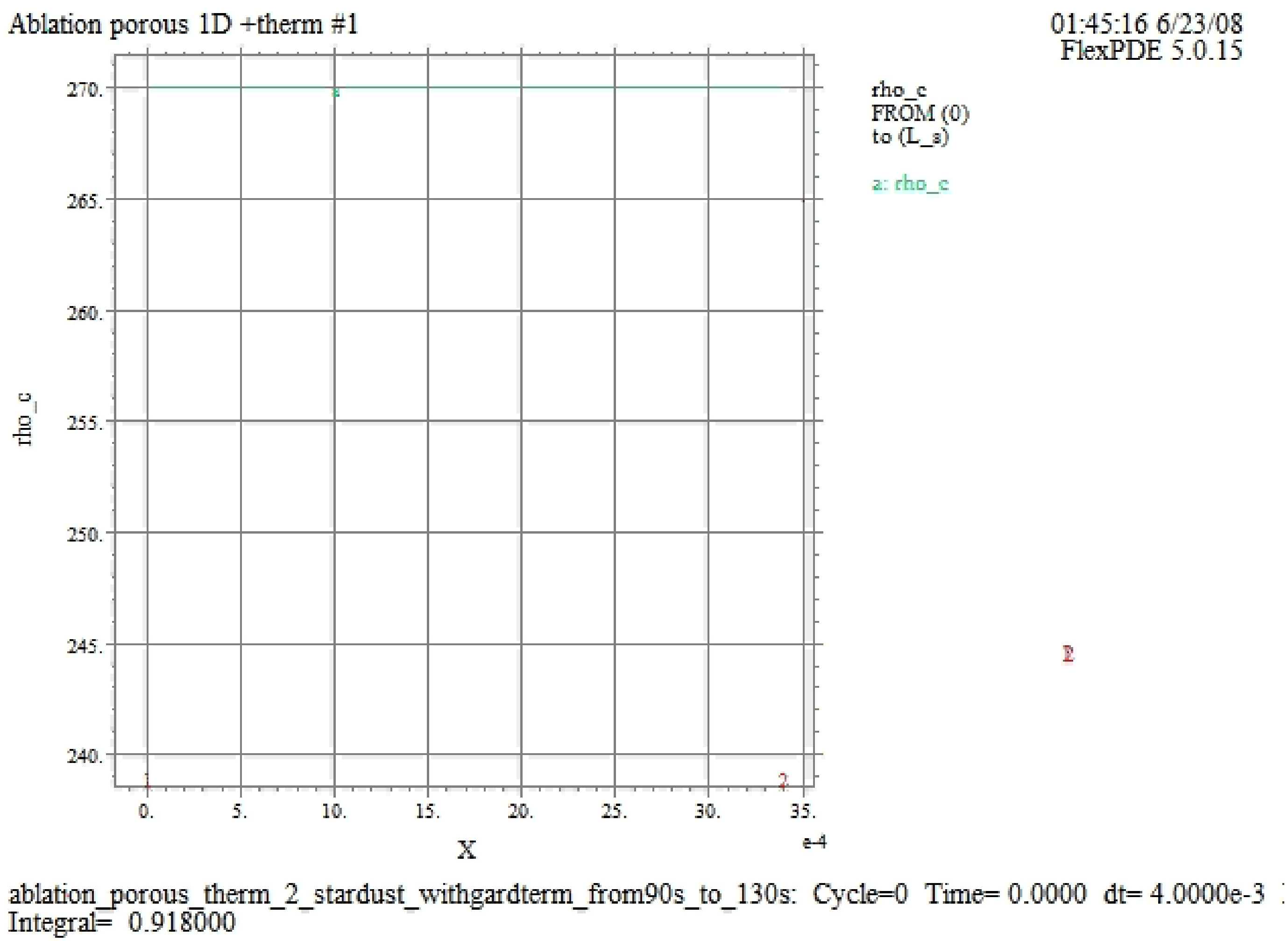
- Simulation of the “oxidation part” of ablation (loosely coupled with pyrolysis) in the carbon felt



4. Volume coupling of Pyrolysis & Ablation

Stardust conditions : pure oxidation from 90s ($T<T_{sublim}$) to 130s ($T>T_{oxi}$)

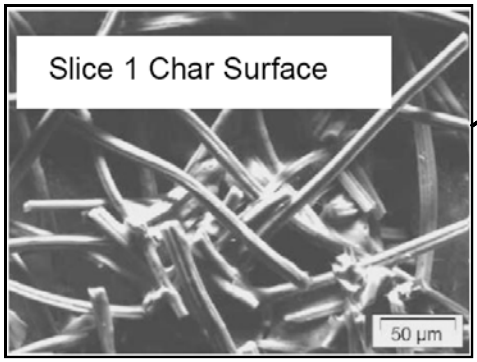
- **Simulated in the carbon felt**

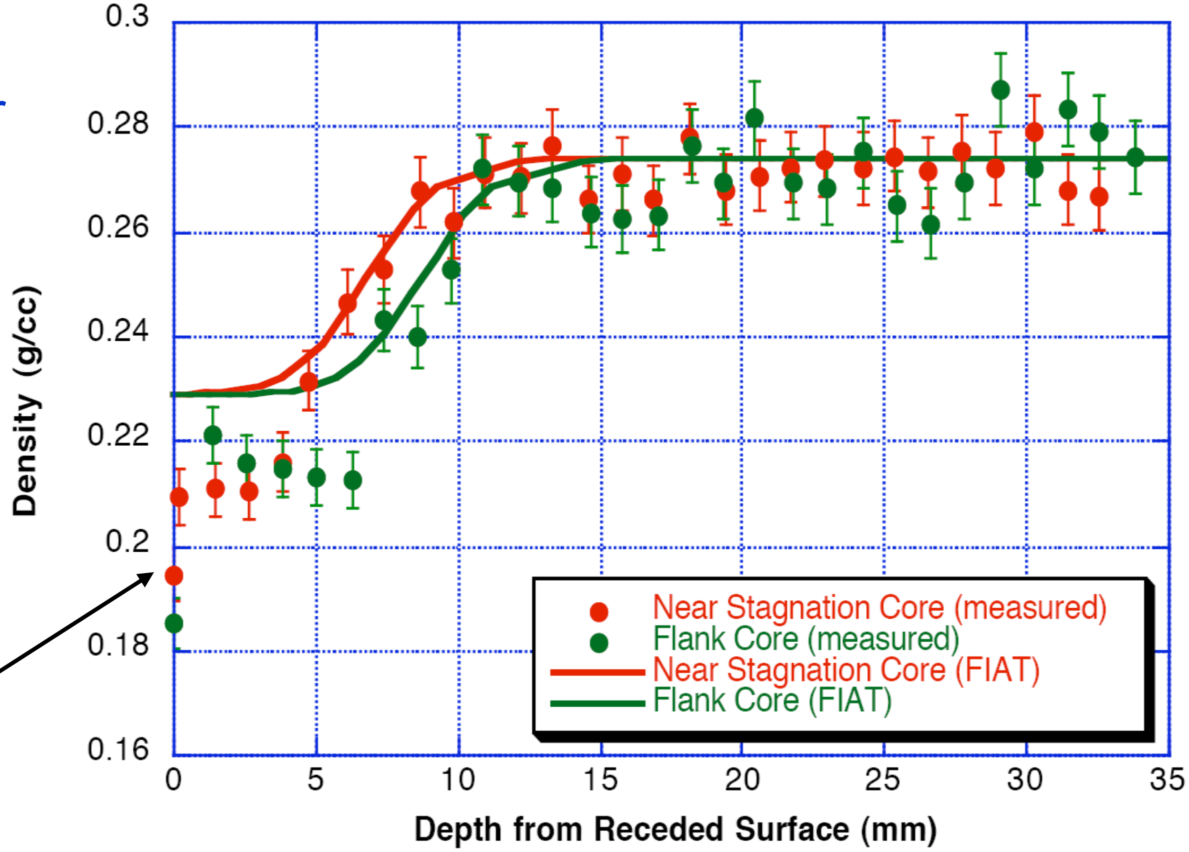


Material Behavior Analysis (cont.)

Literature : Stardust Post-flight Analysis

- **Overall behavior well predicted by current models (FIAT simulation presented below)**
- **BUT : char zone density overestimated**
  - ➢ Volume ablation could be the cause of the lower density observed
  - ➢ The fluffy matrix of PICA is likely to play an important role into volume ablation prevention





M. Stackpoole et al., AIAA 2008-1202 (Reno 2008)

. Conclusion / Next steps

- Porous media model for the ablation of fibrous materials
  - Importance of Thiele Number (diffusion/reaction competition in porous media)
  - Knudsen regime inside the porous media
  - Volume / Surface phenomenon? → depends on experimental conditions
  - Stardust conditions:
    - Low effect of blowing on mass transfer inside the porous media
    - ablation by oxidation in volume for a carbon felt
  - Idea for volume coupling of pyrolysis and ablation at macroscopic scale

- Next steps :
  - Modeling
    - Improve material structure description
    - Sublimation
    - In depth equilibrium chemistry
    - Spallation model (more basic : density threshold)
    - Same approach for heat transfer in porous media (conduction, convection, radiation)

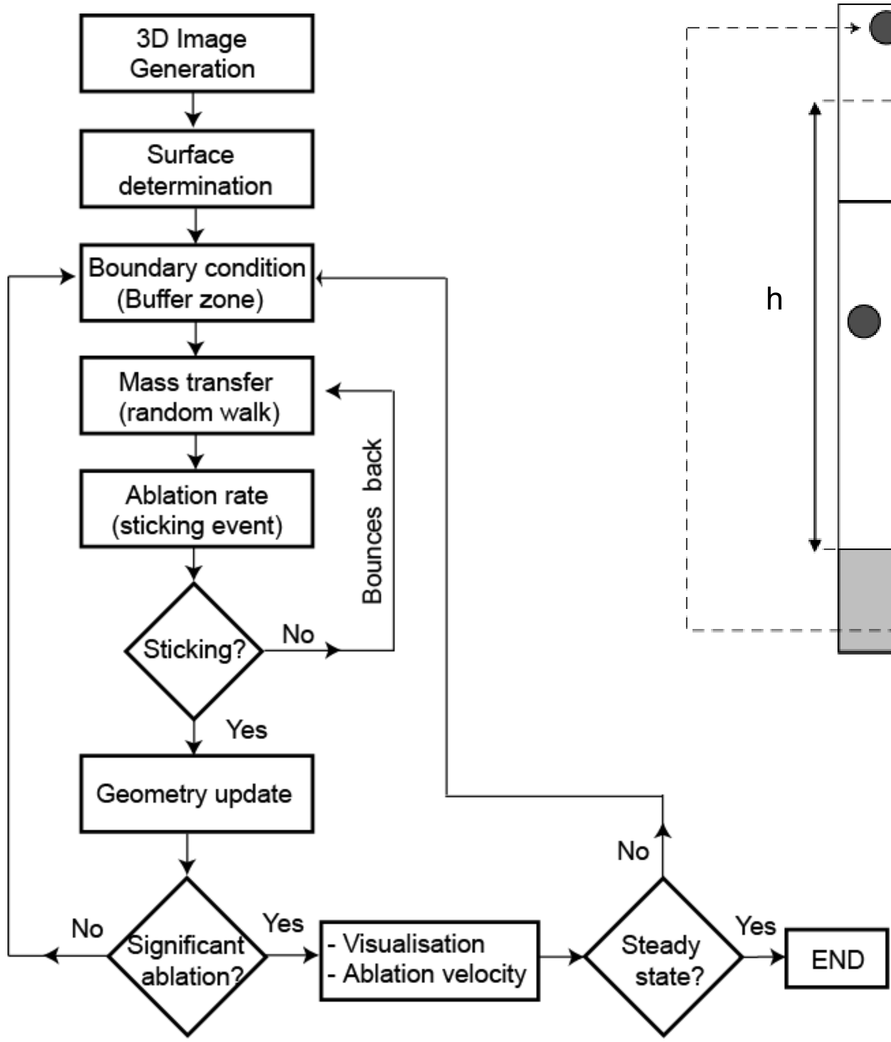
  - Specific experiments to validate the porous media model and the future pyrolysis-ablation coupled model

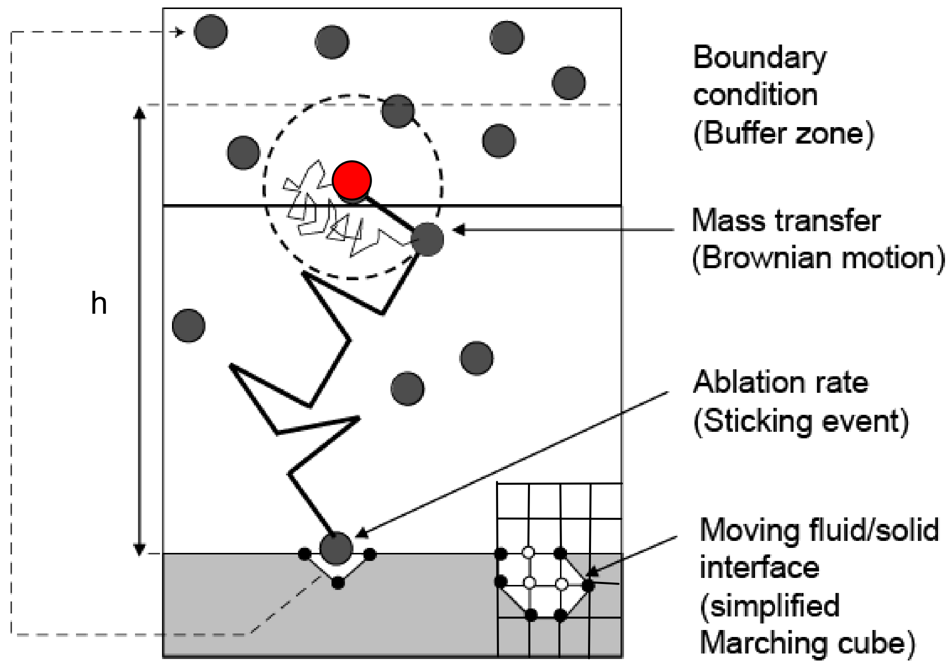
ANNEXES

. Simulation tool : AMA

Brownian Motion simulation technique / Marching Cube front tracking

- Efficient, Robust, No matrix inversion





Original features:

- Sensory Brownian Motion : automatic refinement close to the wall (cf. mesh refinement for Eulerian methods)
- Sticking probability adapted to Brownian Motion (to simulate first order heterogeneous reactions)

3 kinds of Experiments

Improvement & Validation of the models

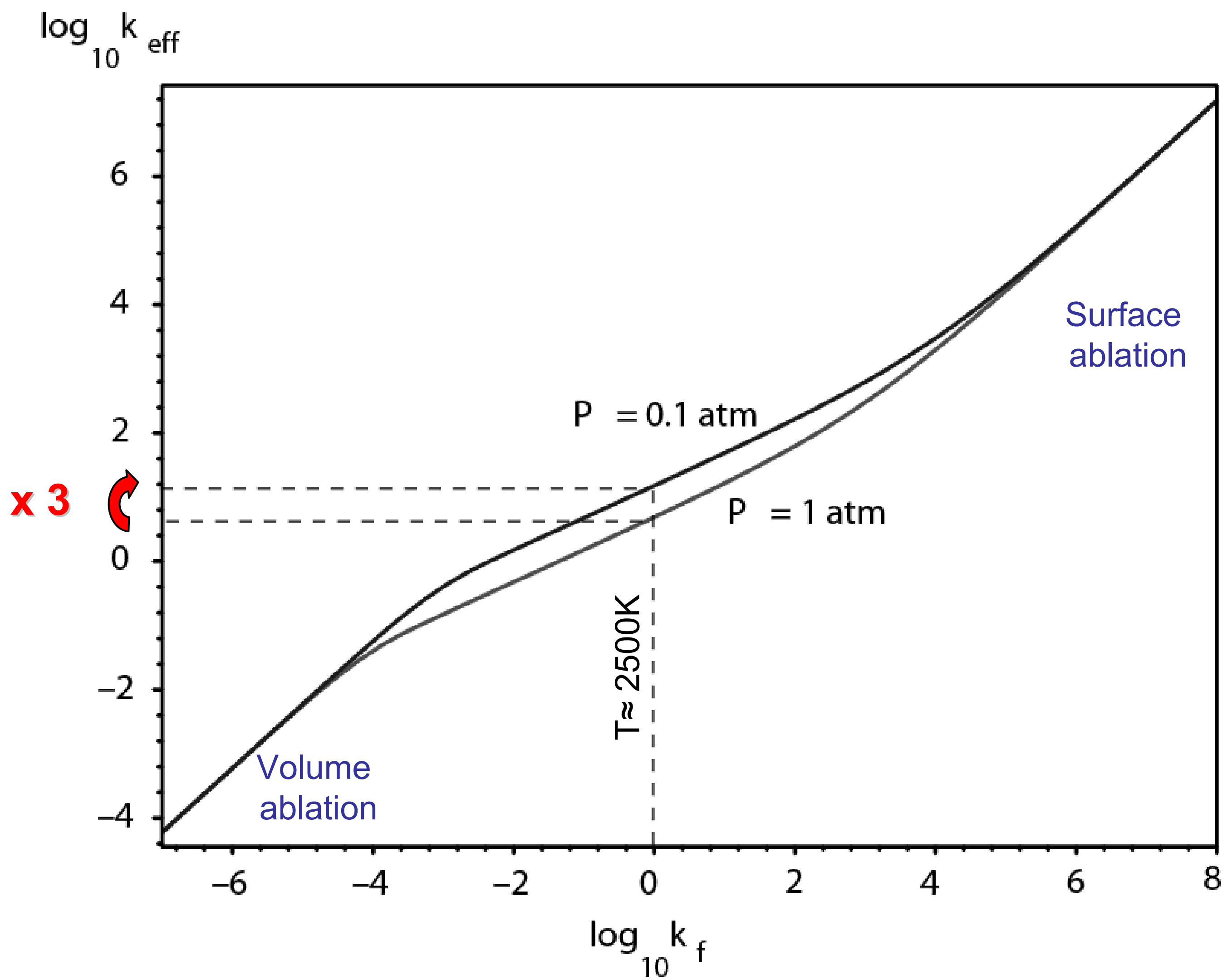
	Device	Measured data	Dimension & scale	Time scale	Difficulty	Interest	Other comments
Microstructure	**SEM*** (Scanning Electron Microscopy)	**Architecture** (intuitive) resolution: 100 nm	2D surface micro to macro	1 month	Image analysis	Help into architecture modeling at all scales	Relatively low cost for fast preliminary results
	TOMO** (X-ray scanning micro-tomography)	**Architecture** (accurate) resolution : 1µm	3D micro	1+ year	- prepare samples - image segmentation	Enable an accurate direct numerical simulation	Key results -> master or PhD student in Bordeaux? +10kEuros
Physico-chemistry	**TGA**** (Thermo Gravimetric Analysis) + mass spectrometer	**Chemistry** Pyrolysis gas analysis Carbon fibers reactivity to these gas	1D micro	1+ year	- data analysis	Understanding of heterogeneous and homogeneous chemistry	- No rush - Data from 1970 - Useful again for porous TPS
	Short ramp IR tests* 0-2500K	**Effective conductivity** k=f(T)	3D macro	6 month	-thermocouple position -data analysis	Useful for radiation analysis	Needed ASAP
Validation	**Long steady state IR tests**** (+ tangential blowing)	**Thermal gradient** **Density profile** **Recession**	3D micro 2D ortho macro	1-2 years	-thermocouple position -quantify spallation= f(shear stress)	Ablation/pyrolysis coupling Spallation Model validation	Parametrical study on blowing and grad(T)
	Plasma tests**	**idem**	3D micro 2D ortho macro	2-3 years	-test conditions -data analysis	Global validation fluid + mater	Parametrical study on P, T, v

* : to be done in priority with available funding / ** : to plan now and begin in 1 year

ANNEXE. Ablation model for porous media

The effective reactivity of the porous media is not intrinsic

Effective reactivity = reactivity of a flat and homogeneous material (cf graphite) that would lead to the same ablation rate under similar entry conditions



(D~1/P)