Department of Energy
&
Department of Chemistry, Materials, and Chemical Engineering

POLITECNICO DI MILANO





Matteo Maestri & Alberto Cuoci

CatalyticFOAM

first principles multiscale modeling of heterogeneous catalytic reactors in OpenFOAM

HPC enabling of OpenFOAM for CFD applications

25 March 2015

Outline

- ✓ Introduction and motivation
- ✓ Development of the catalyticFOAM solver for the OpenFOAM® framework
  - ✓ Governing equations
  - ✓ Numerical methodology
- ✓ Validation and examples
  - ✓ CPO of CH_4 on platinum gauze (complex 3D geometry)
  - ✓ CPO of iso-octane (complex chemistry)
  - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
  - ✓ Packed bed reactors for industrial applications (complex 3D geometry)
- ✓ Extensions
  - ✓ KMC (Kinetic Monte Carlo)

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Chemical reactor engineering

Catalytic reactor design:

- ✓ **Important in chemical industry (~90% of industrial chemical processes are catalytic)**
- ✓ **Need for an accurate design to provide high yields (€)**
- ✓ **Need for a deep understanding for advanced design**

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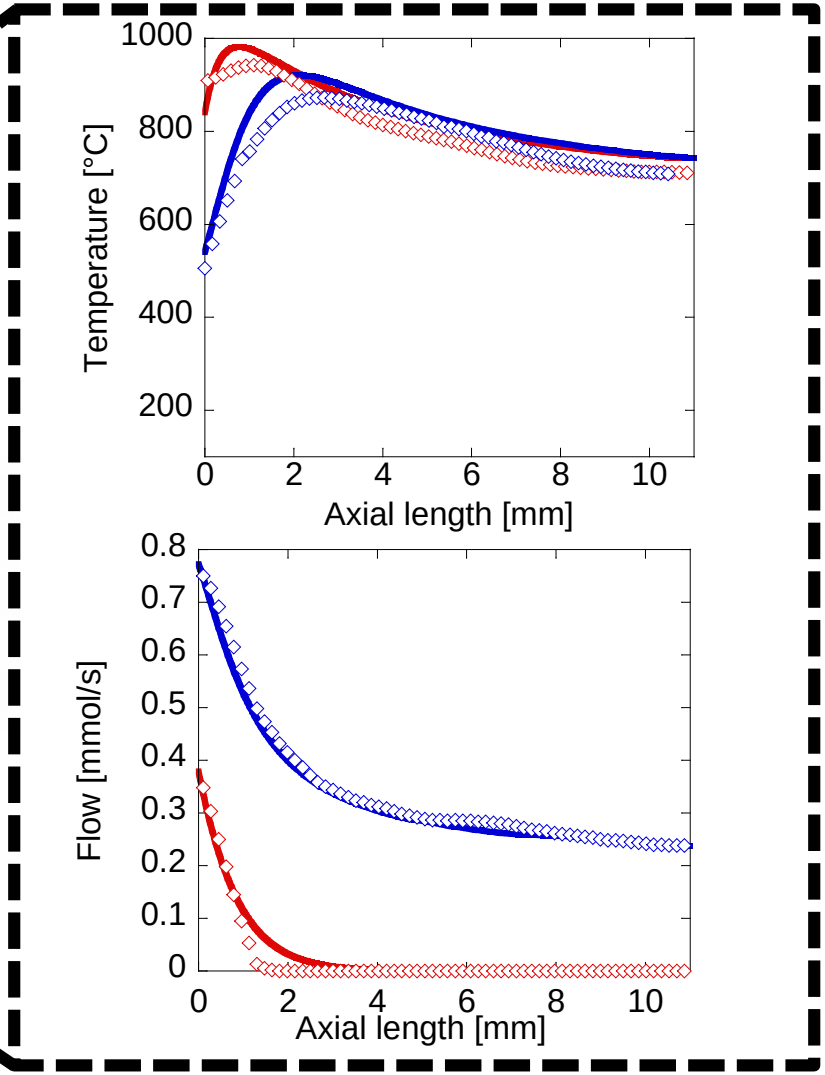
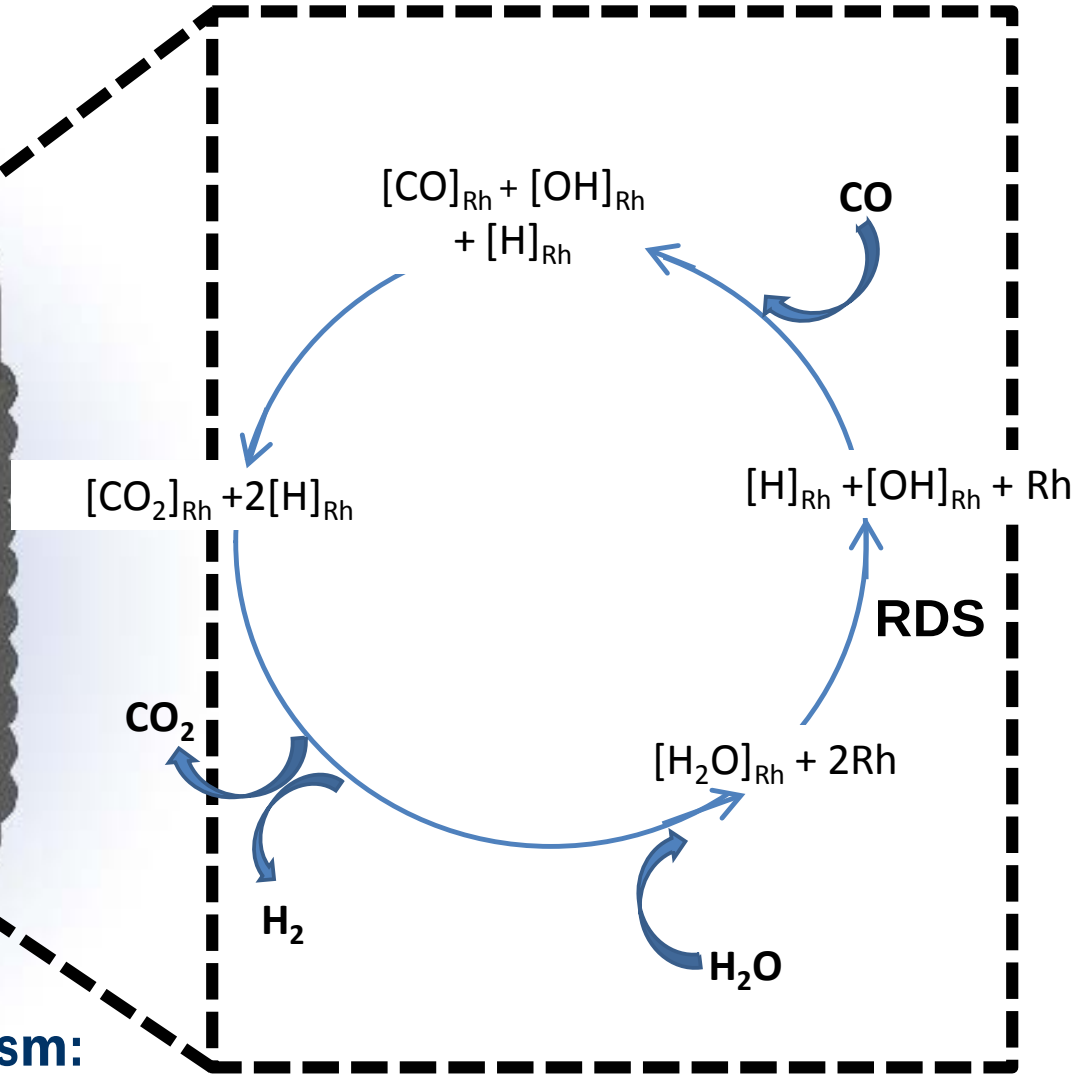
Chemical reactor design



Chemical reactor design



Dominant reaction mechanism: understanding & design

A multiscale phenomenon

Result of the interplay among phenomena at different scales

Microscale

$COOH^*+^* \rightarrow CO^*+OH^*$
$CO^*+OH^* \rightarrow COOH^*+^*$
$COOH^*+^* \rightarrow CO_2^*+H^*$
$CO_2^*+H^* \rightarrow COOH^*+^*$
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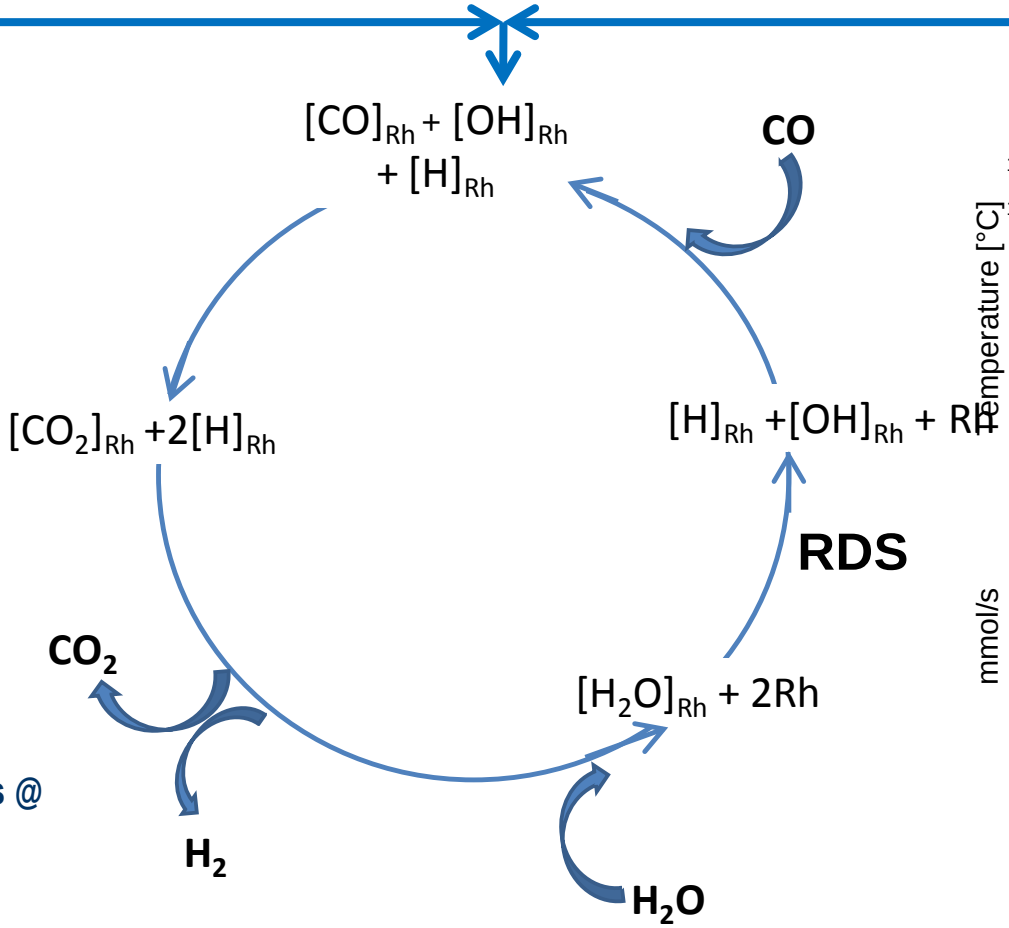
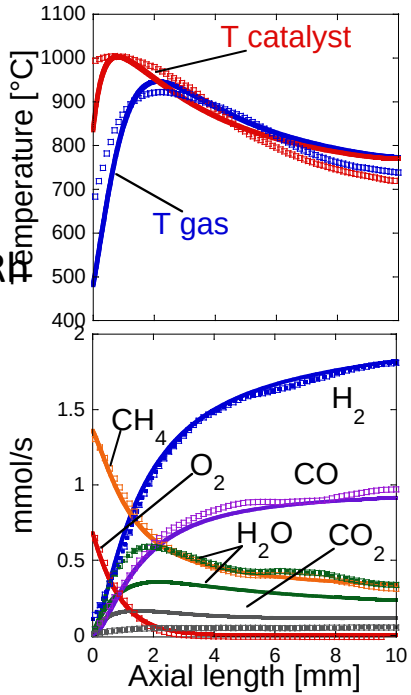
$CH^* + ^* \rightarrow C^* + H^*$
$C^* + H^* \rightarrow CH^* + ^*$
$CH_3^* + O^* \rightarrow CH_2^* + OH^*$
$CH_2^* + OH^* \rightarrow CH_3^* + O^*$
$CH^* + OH^* \rightarrow CH_2^* + O^*$
$CH_2^* + O^* \rightarrow CH^* + OH^*$
...

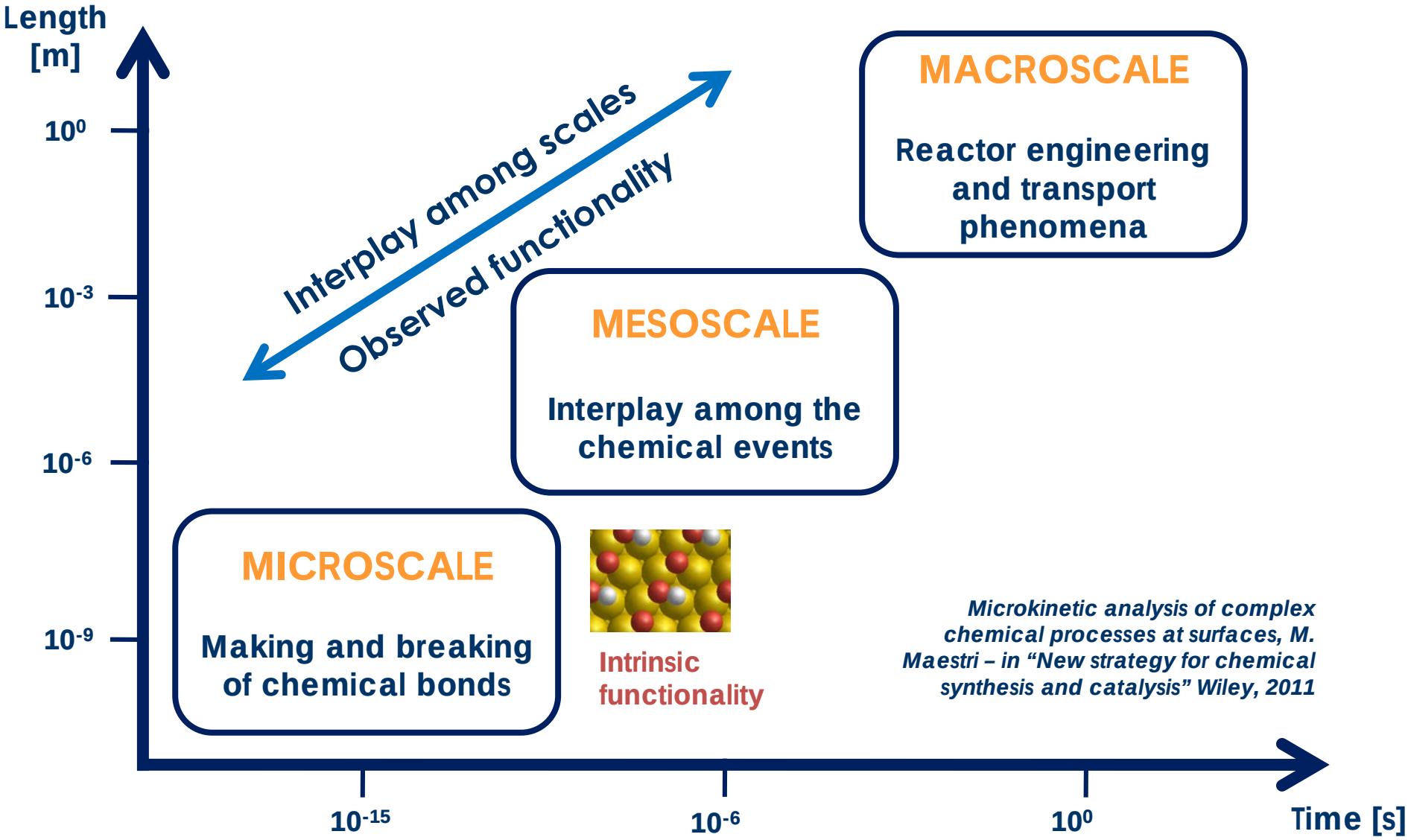
~ 10^2 potential steps @ different coverages



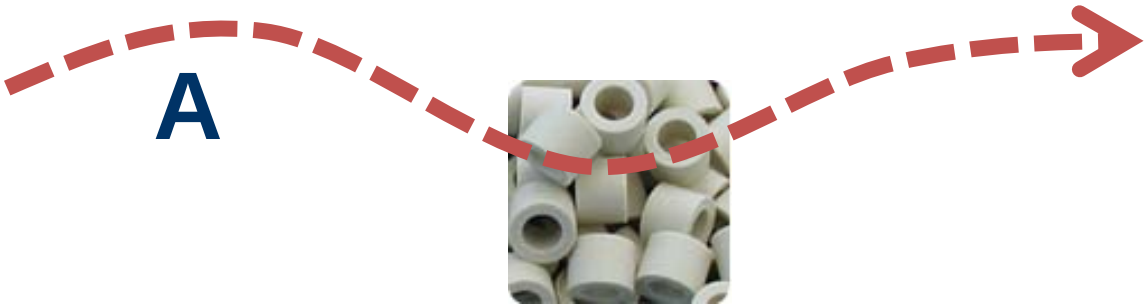
Macroscale



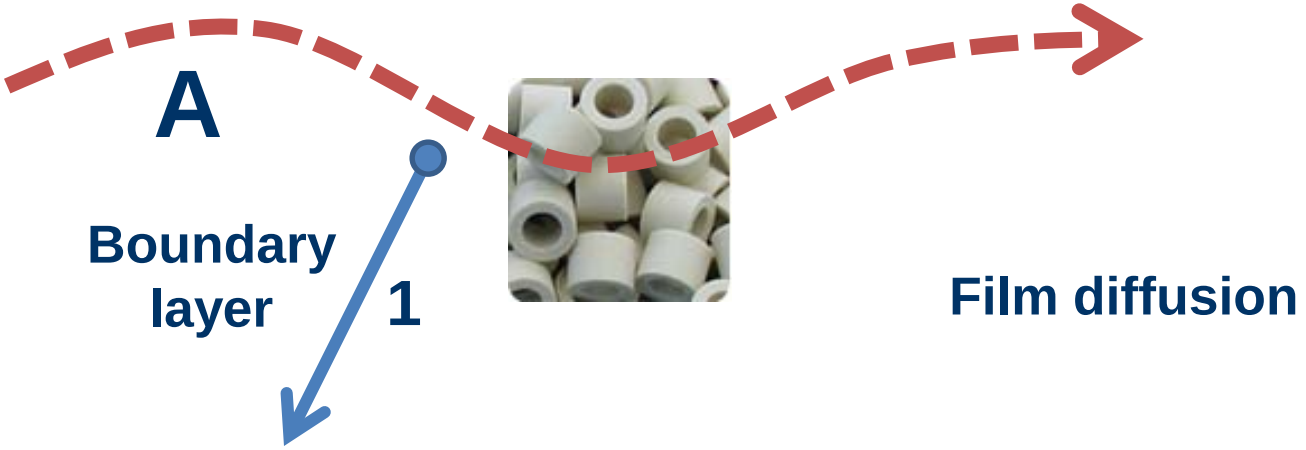
A multiscale phenomenon



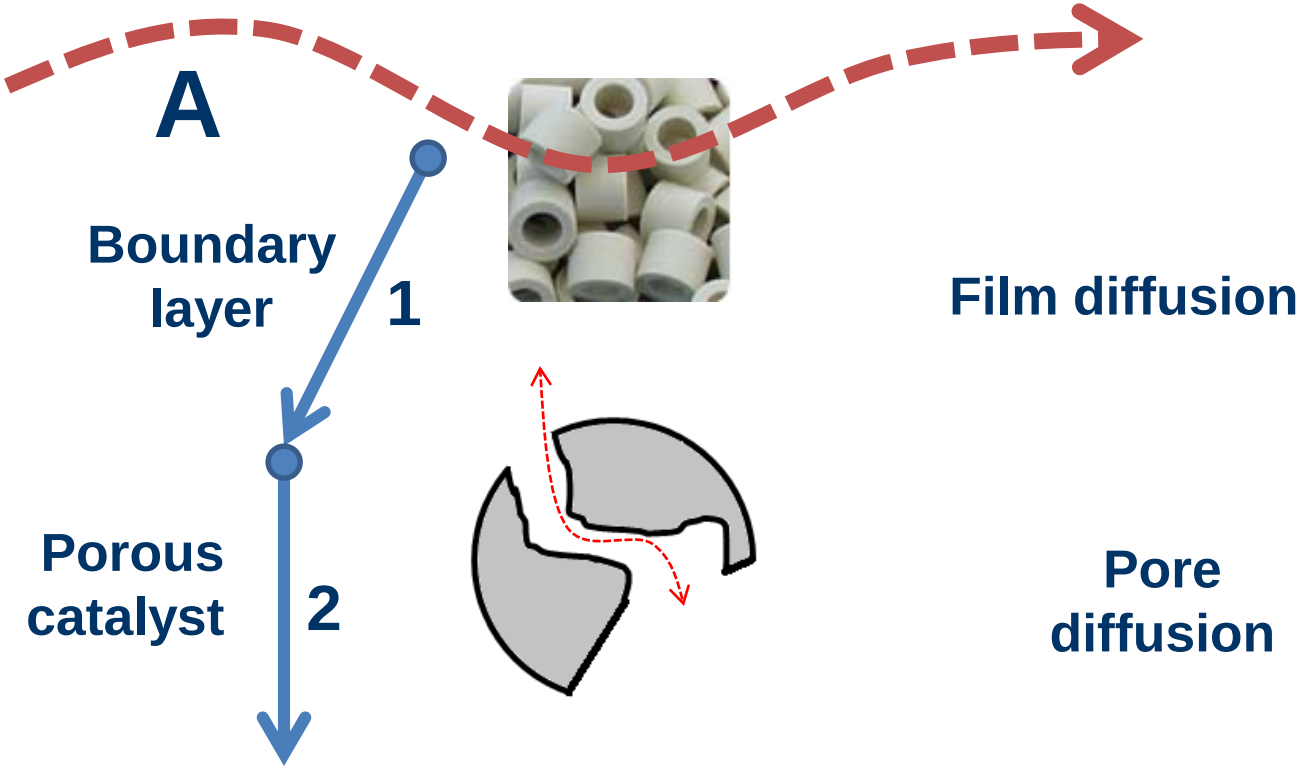
Catalysts at work (I)



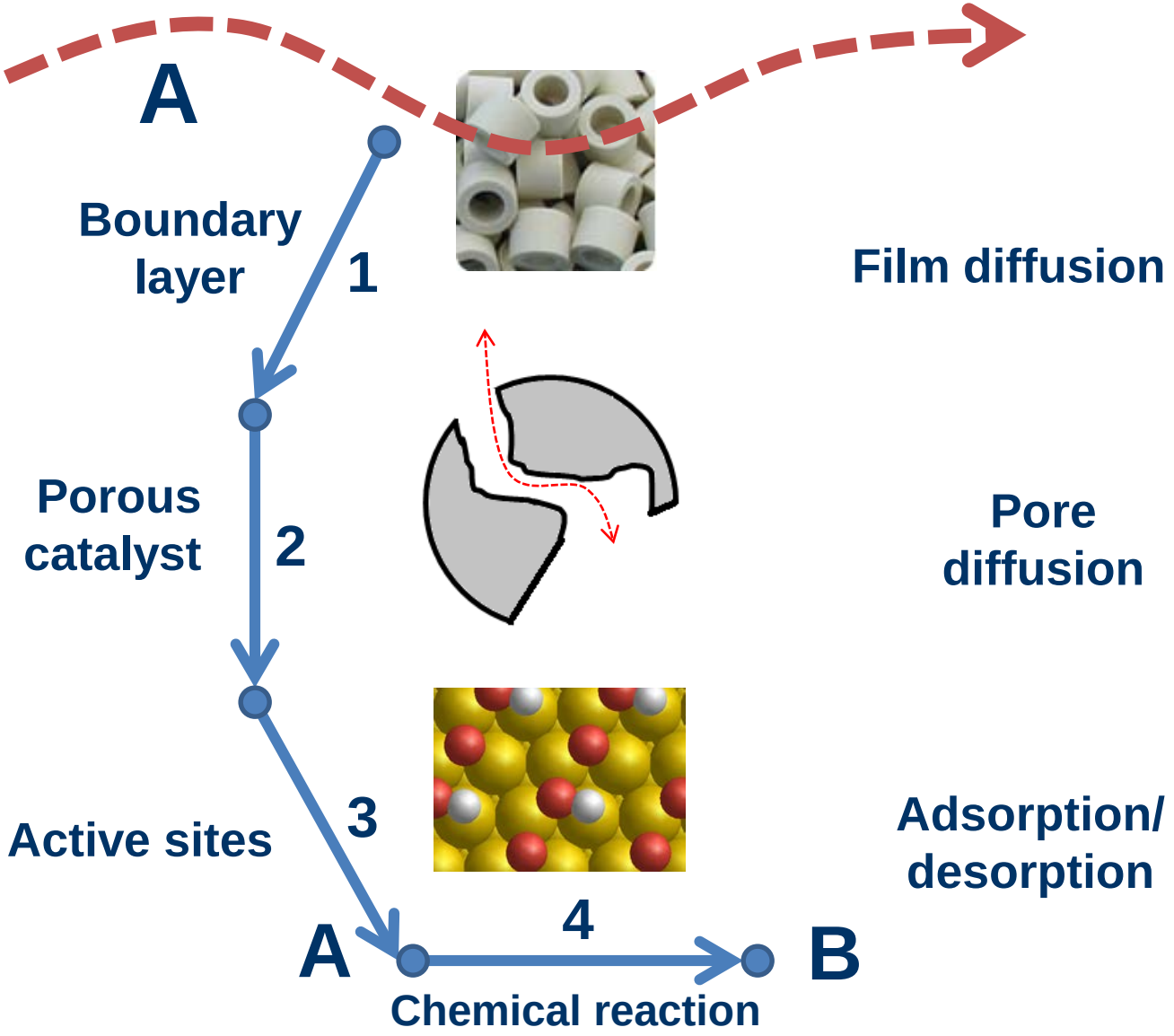
Catalysts at work (II)



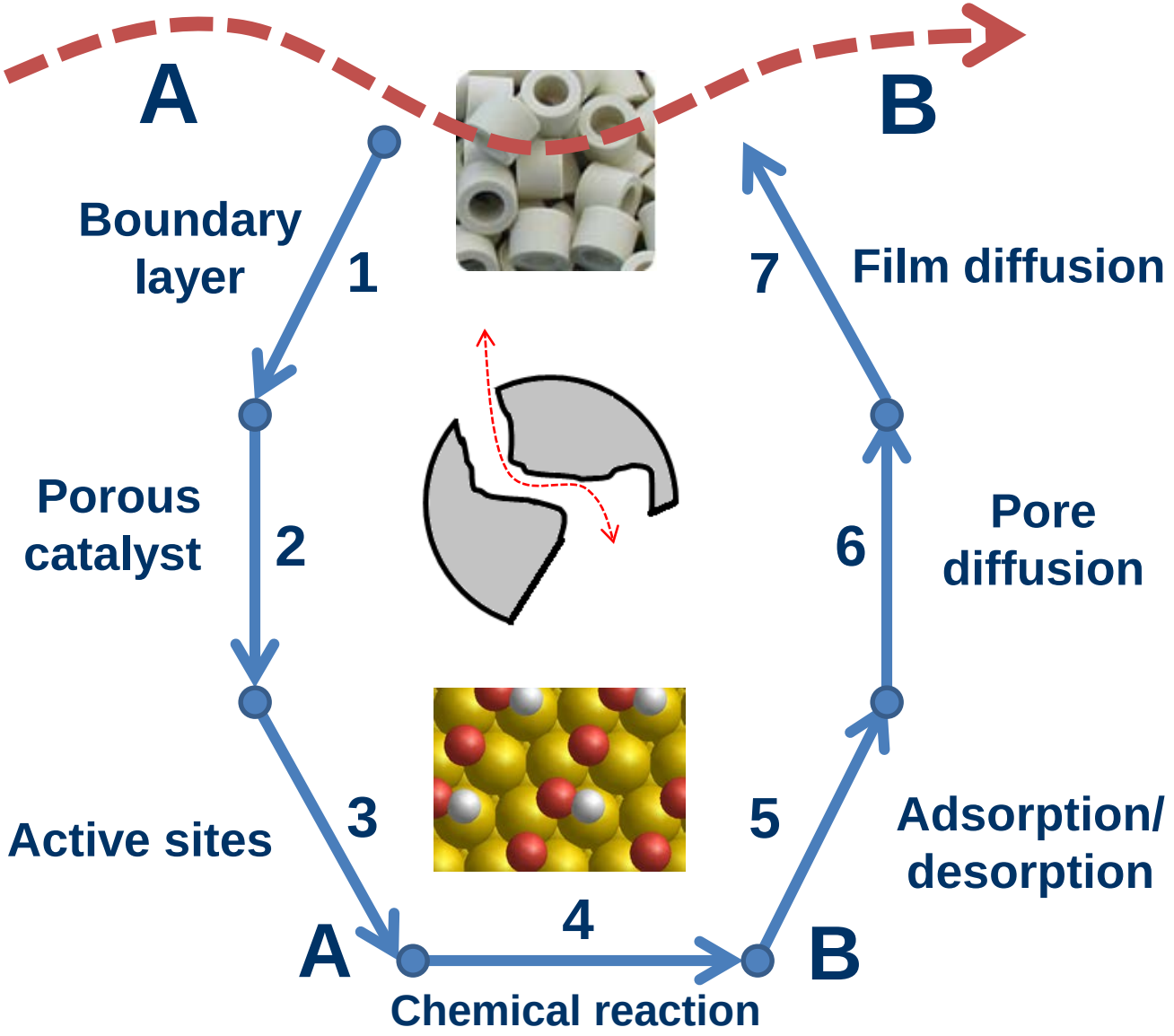
Catalysts at work (III)



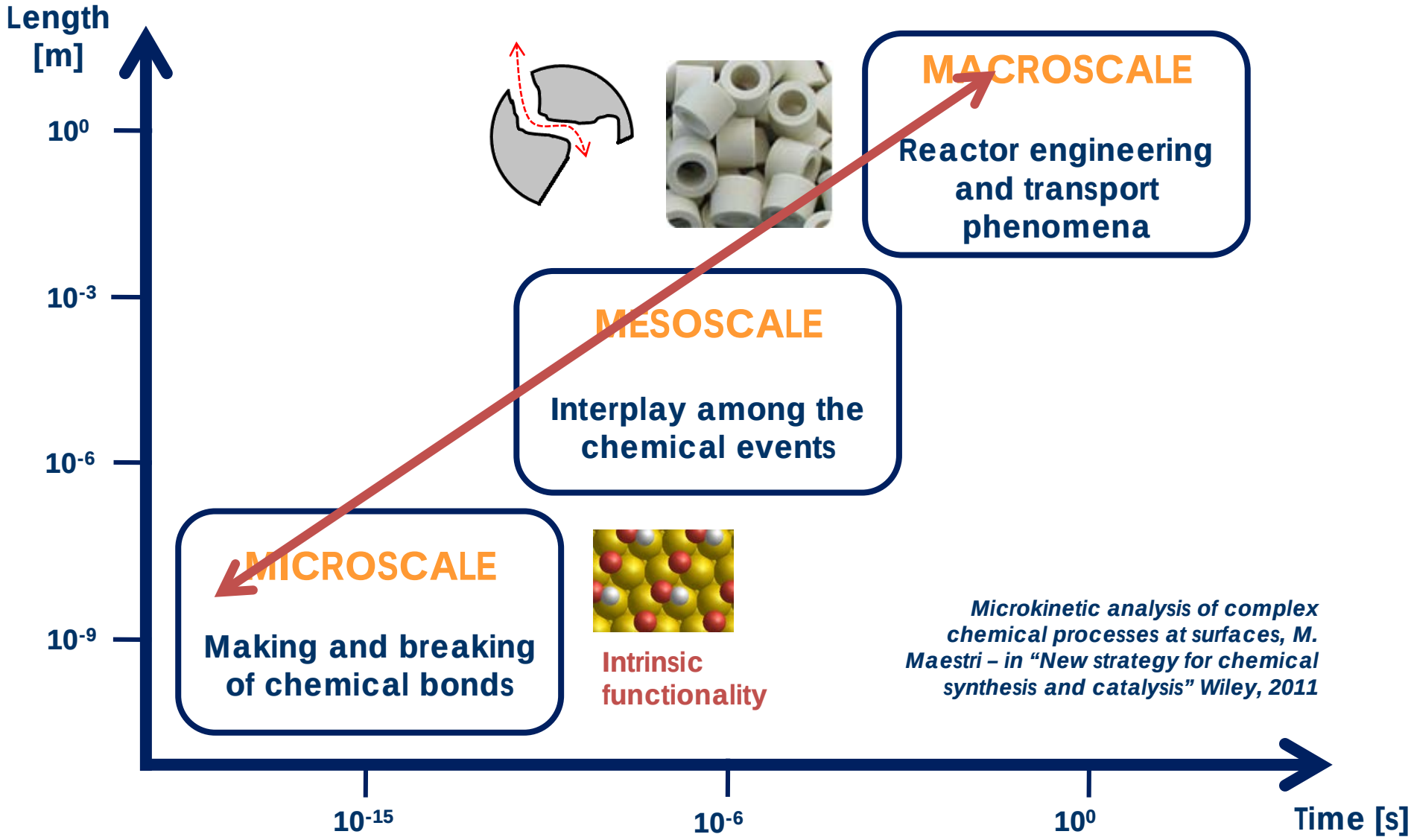
Catalysts at work (IV)



Catalysts at work (V)

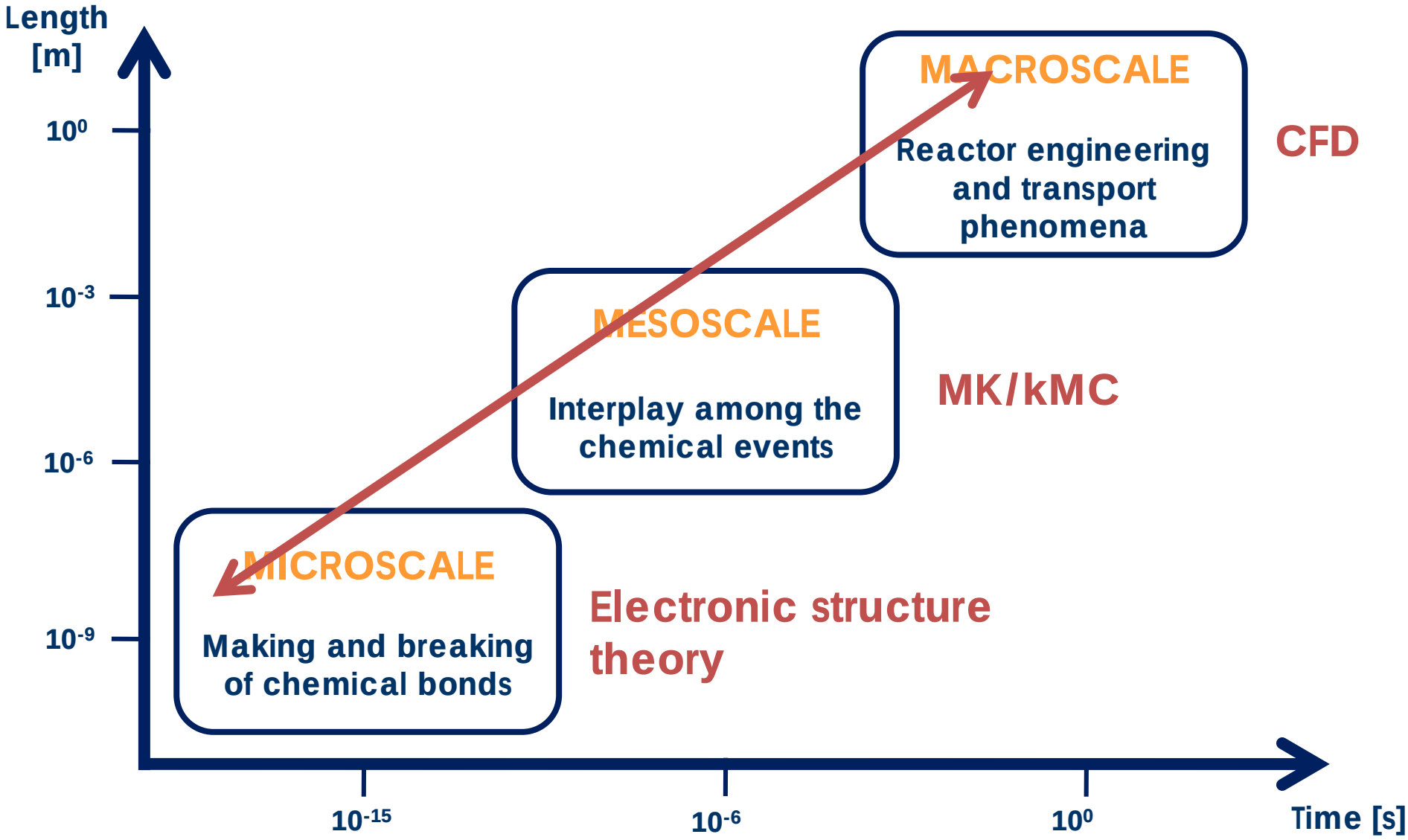


Need of bridging between the scales

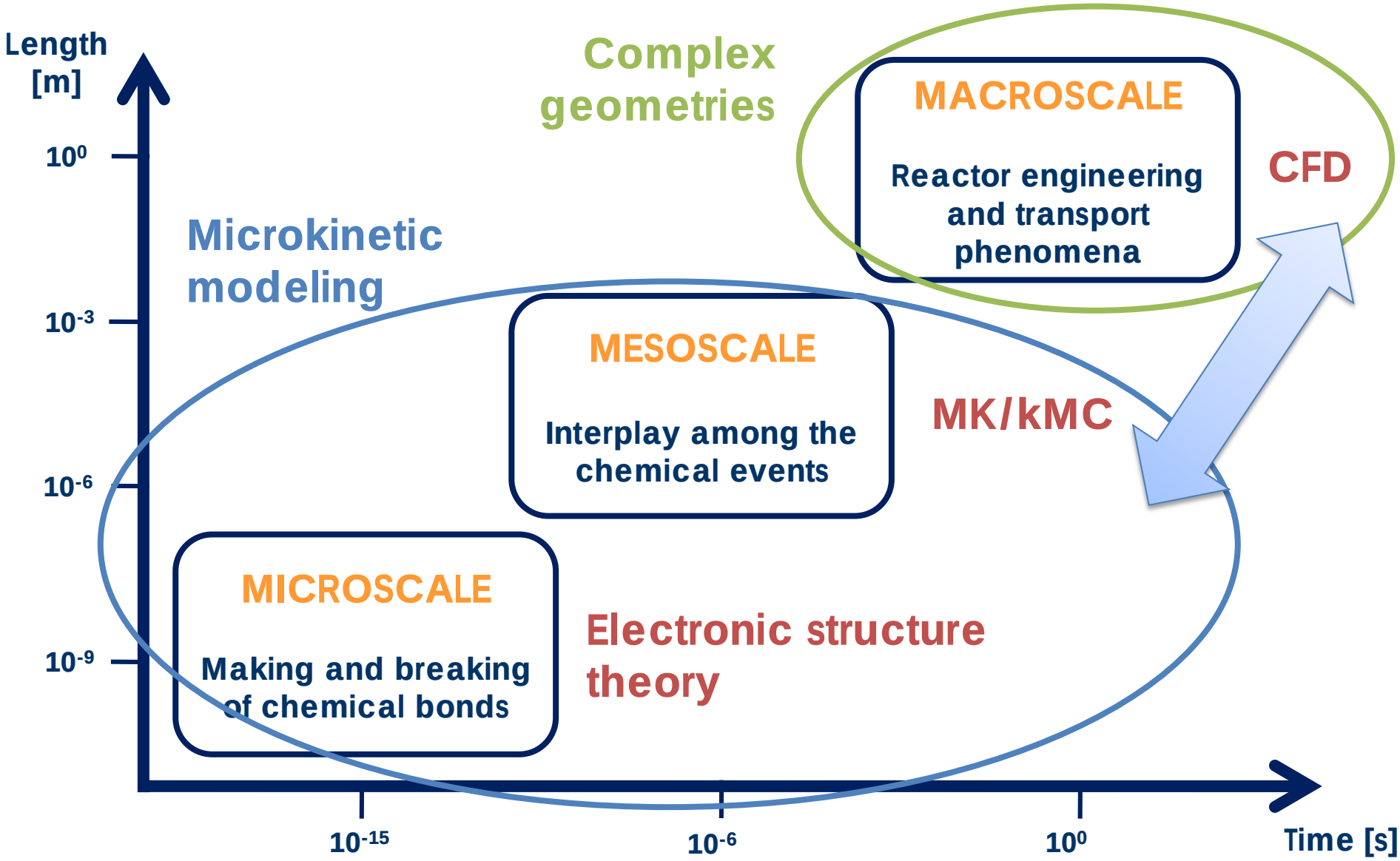


Microkinetic analysis of complex chemical processes at surfaces, M. Maestri – in "New strategy for chemical synthesis and catalysis" Wiley, 2011

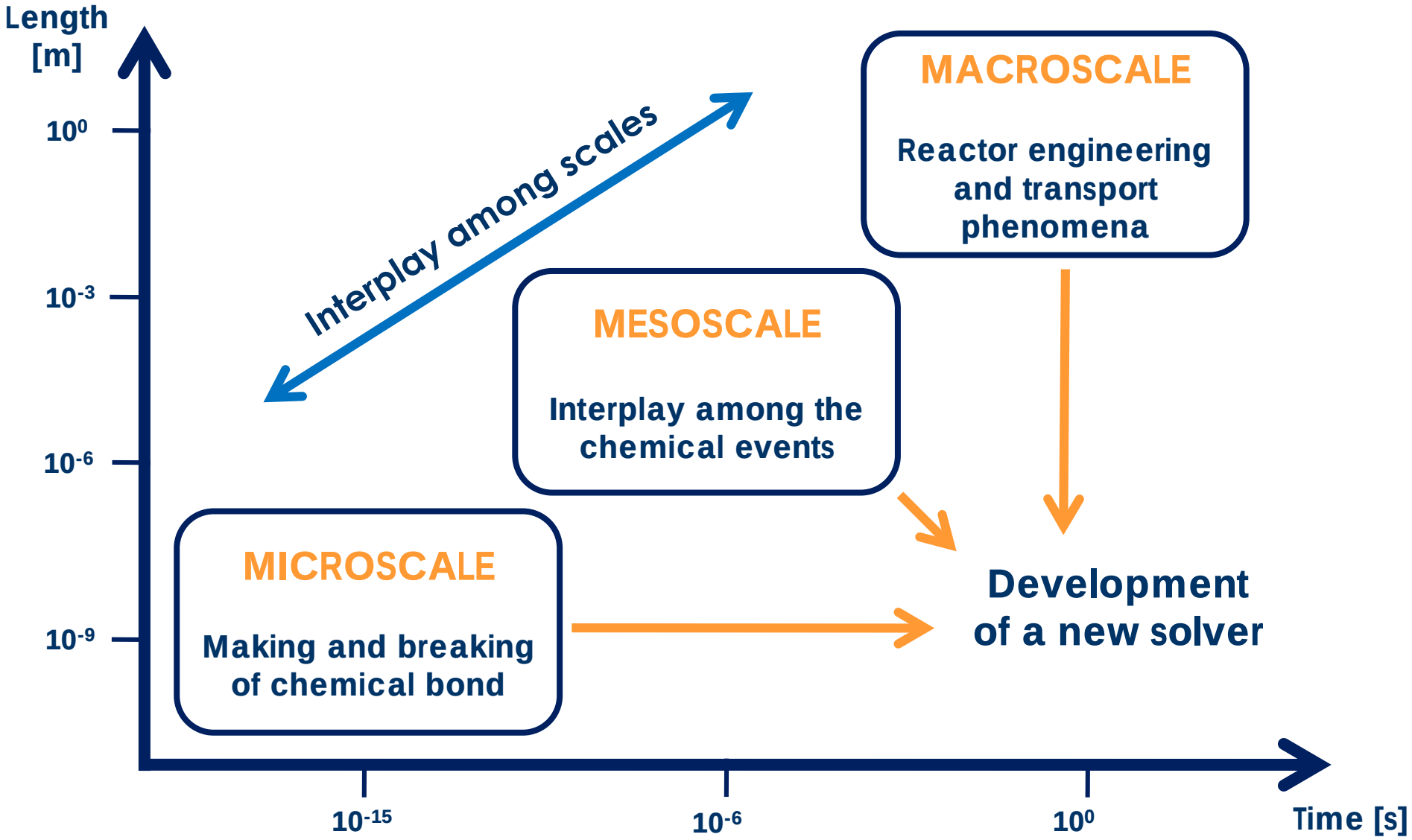
A *first-principles* approach to CRE



Microkinetic modeling and transport



Need of new numerical tools



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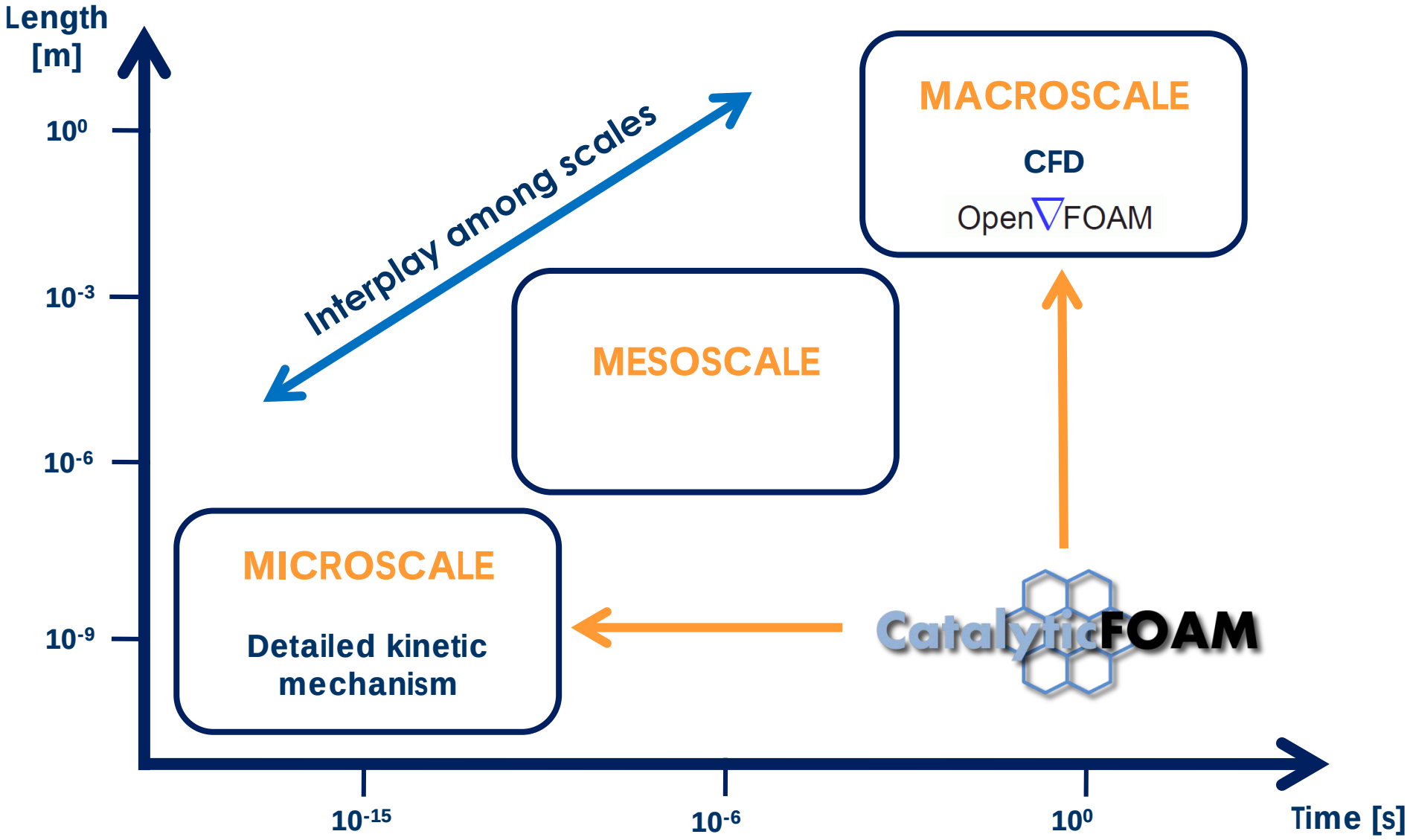

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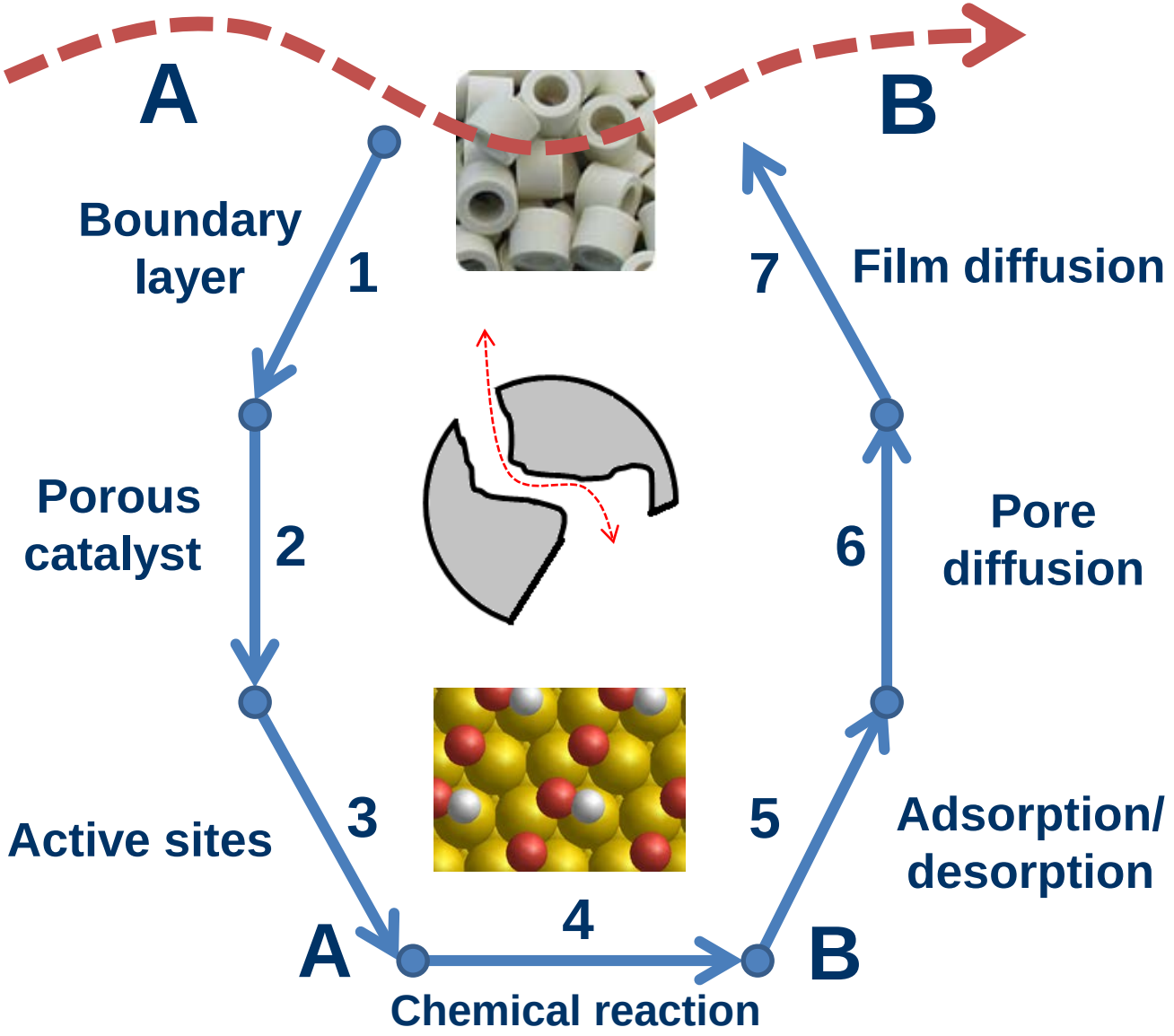
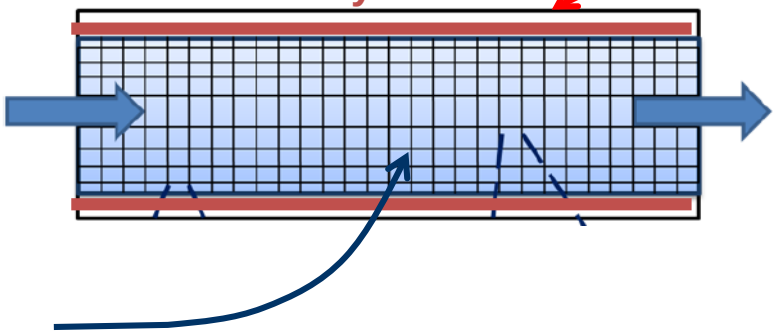
Catalysts at work



Governing equations



Catalytic walls

$$\sigma_{cat}\frac{\partial \theta_i}{\partial t} = \dot{\Omega}_i^{het} \qquad i = 1,\ldots,NS$$

Adsorbed (surface) species

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0$$ **continuity**

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v}\mathbf{v}) = -\nabla p + \nabla \cdot \left[\mu\left(\nabla \mathbf{v} + \nabla \mathbf{v}^T\right) - \frac{2}{3}\mu(\nabla \mathbf{v})\mathbf{I} \right] + \rho \mathbf{g}$$ **momentum**

$$\frac{\partial}{\partial t}(\rho \omega_k) + \nabla \cdot (\rho \omega_k \mathbf{v}) = -\nabla \cdot (\rho \omega_k \mathbf{V}_k) + \dot{\Omega}_k^{\text{hom}} \qquad k = 1,\ldots,NG$$ **gas-phase species**

$$\rho \hat{C}_P \frac{\partial T}{\partial t} + \rho \hat{C}_P \mathbf{v} \nabla T = \nabla \cdot (\lambda \nabla T) - \rho \sum_{k=1}^{NG} \hat{C}_{P,k} \omega_k \mathbf{V}_k - \sum_{k=1}^{NG} \hat{H}_k^{\text{hom}} \dot{\Omega}_k^{\text{hom}}$$ **gas-phase energy**

Boundary conditions

Non-catalytic walls

$$\nabla \omega_k \big|_{inert} = 0$$

$$T\big|_{inert} = f(t,T)$$

$$\nabla T\big|_{inert} = g(t,T)$$

Catalytic walls

$$\rho \Gamma_{k,mix} \left(\nabla \omega_k\right)\big|_{catalytic} = -\alpha_{cat}\, \dot{\Omega}_k^{het} \qquad k = 1,\ldots,NG$$

$$\lambda \left(\nabla T\right)\big|_{catalytic} = -\alpha_{cat} \sum_{j=1}^{NR} \Delta H_j^{het} \dot{r}_j^{het}$$

$$\sigma_{cat} \frac{\partial \theta_i}{\partial t} = \dot{\Omega}_i^{het} \qquad i = 1,\ldots,NS$$

Adsorbed (surface) species

Detailed microkinetic models

$COOH^* + * \rightarrow CO^* + OH^*$
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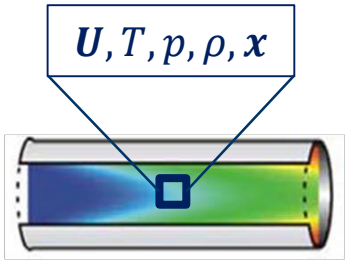
…

$$r_j = A_j \cdot T^{\beta_j} \cdot \exp\left(-\frac{E_{att,j}(\theta_i)}{RT}\right) \prod_{i=1}^{NC} (c_i)^{\nu_{ij}}$$

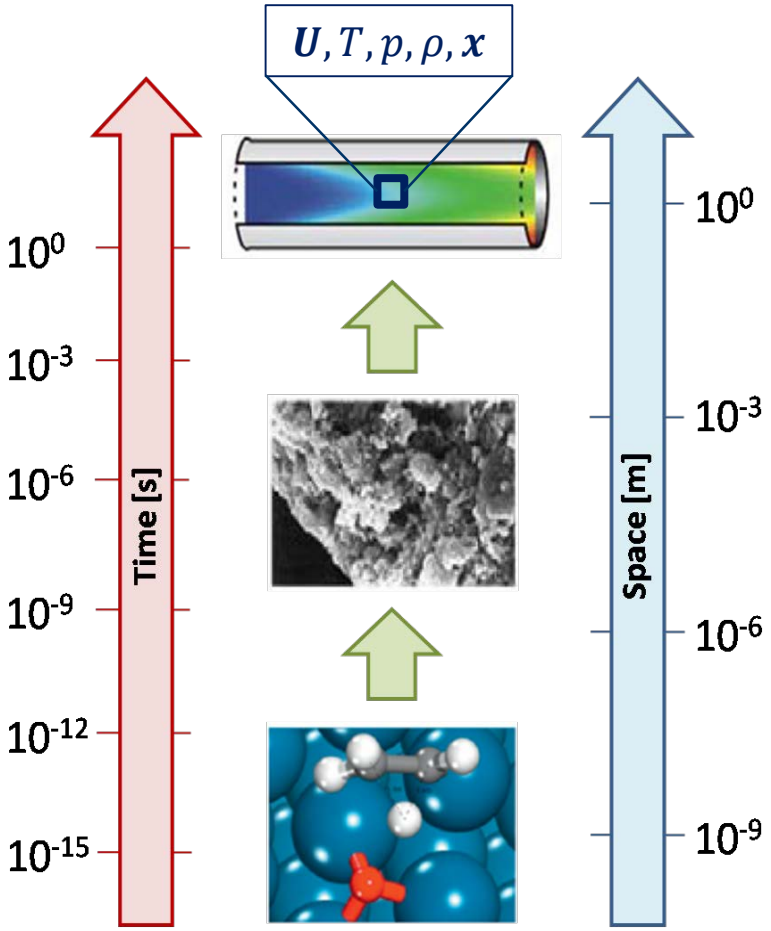
Numerical challenges (I)



- ✓ **Dimensions of the system**
  - **Proportional to the number of species**
  - **Proportional to the number of cells**

Numerical challenges (I)

- ✓ **Dimensions of the system**
  - Proportional to the number of species
  - Proportional to the number of cells
- ✓ **Stiffness**
  - Different temporal scales involved
  - Different spatial scales involved



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- ✓ **Dimensions of the system**
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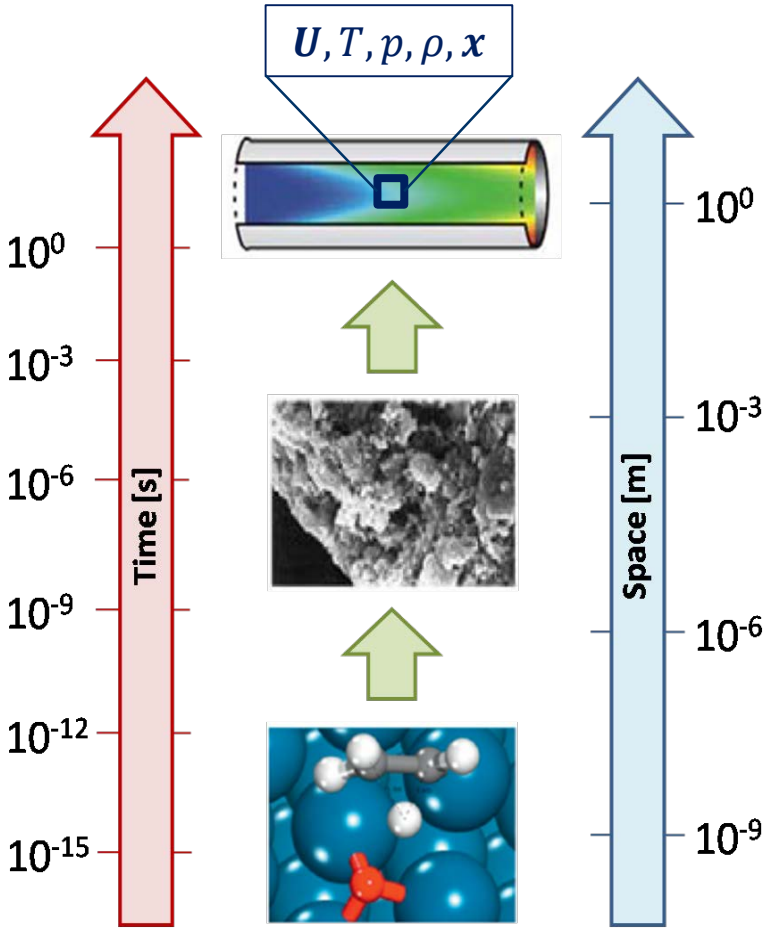
- ✓ **Non-linearity**
  - Source term non linear in concentrations and temperature
  - Coverage dependence of activation energy



$$r_j = A_j \cdot T^{\beta_j} \cdot \exp\left(-\frac{E_{att,j}(\theta_i)}{RT}\right) \prod_{i=1}^{NC} (c_i)^{\nu_{ij}}$$

Numerical challenges (II)

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} segregated approaches are not feasible

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Numerical solution

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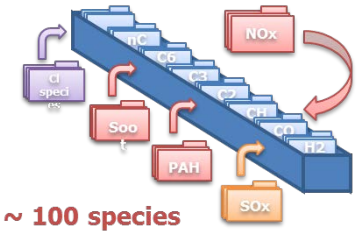
Fully segregated algorithms

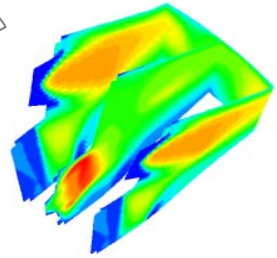
☺ easy to implement and computationally efficient
☹ unfeasible when large, stiff kinetic mechanisms are used

Detailed kinetic schemes



~ 100 species
~ 1000 reactions

Complex geometries



Strong non linearity of reaction terms
High stiffness

Fully coupled algorithms

☺ all the processes and their interactions are considered simultaneously
☺ natural way to treat problems with multiple stiff processes
☹ the resulting system of equations can be extremely large and the computational cost prohibitive

Operator-splitting methods

☺ usually avoid many costly matrix operations
☺ allow the best numerical method to be used for each type of term or process
☹ the resulting algorithms can be very complex and usually differ from term to term

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POLITECNICO DI MILANO

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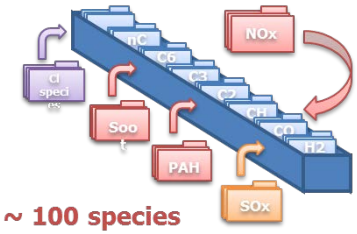

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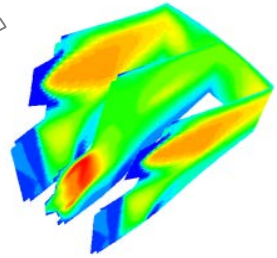

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catalyticFOAM

Operator-splitting algorithm

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Stiff reaction terms

PDE

$$\begin{cases} \dfrac{\partial}{\partial t}(\rho\omega_k) = -\nabla\cdot(\rho\omega_k\mathbf{v}) - \nabla\cdot(\rho\omega_k\mathbf{V}_k) + \dot{\Omega}_k^{hom} & k = 1,\ldots,NG \\ \rho\hat{C}_P\dfrac{\partial T}{\partial t} = -\rho\hat{C}_P\mathbf{v}\nabla T + \nabla\cdot(\lambda\nabla T) - \rho\sum_{k=1}^{NG}\hat{C}_{P,k}\omega_k\mathbf{V}_k - \sum_{k=1}^{NG}\hat{H}_k^{hom}\dot{\Omega}_k^{hom} \\ \sigma_{cat}\dfrac{\partial\theta_i}{\partial t} = \dot{\Omega}_i^{het} & i = 1,\ldots,NS \end{cases}$$

gas-phase species

gas-phase energy

adsorbed (surface) species

Finite volume discretization

After spatial discretization, the original PDE systems is transformed into an ODE system

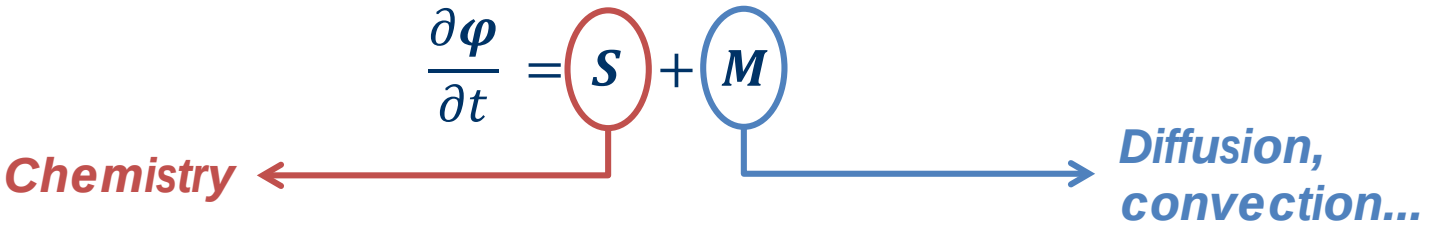
ODE

$$\begin{cases} \dfrac{\partial\omega_k}{\partial t} = M_k + S_k & k = 1,\ldots,NG \\ \dfrac{\partial T}{\partial t} = M^T + S^T \\ \dfrac{\partial\theta_i}{\partial t} = S_i^{het} & i = 1,\ldots,NS \end{cases}$$

S = terms associated to the stiff processes (homogeneous and heterogeneous reactions)

M = terms involving transport processes (convection and diffusion), non stiff and weakly non linear

Operator-splitting: an example (I)



Operator-splitting: an example (II)

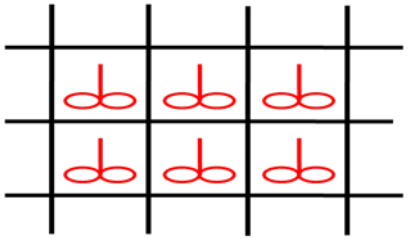
$$\frac{\partial \varphi}{\partial t} = S + M$$

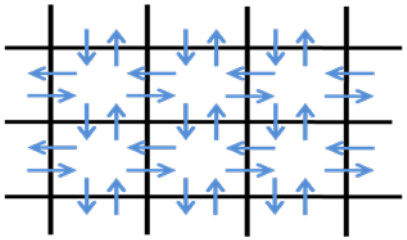
Chemistry ← S — M → **Diffusion, convection...**

Operator-splitting scheme

Chemical step

$$\frac{\partial \varphi}{\partial t} = S$$





$$\frac{\partial \varphi}{\partial t} = M$$

Transport step

Operator-splitting: an example (III)

$$\frac{\partial \varphi}{\partial t} = S + M$$

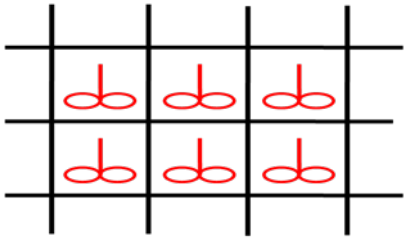
Chemistry

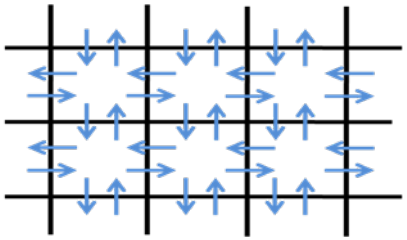
Diffusion, convection...

Operator-splitting scheme

Chemical step

$$\frac{\partial \varphi}{\partial t} = S$$





$$\frac{\partial \varphi}{\partial t} = M$$

Transport step

Operator-splitting: an example (IV)

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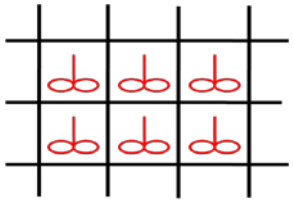
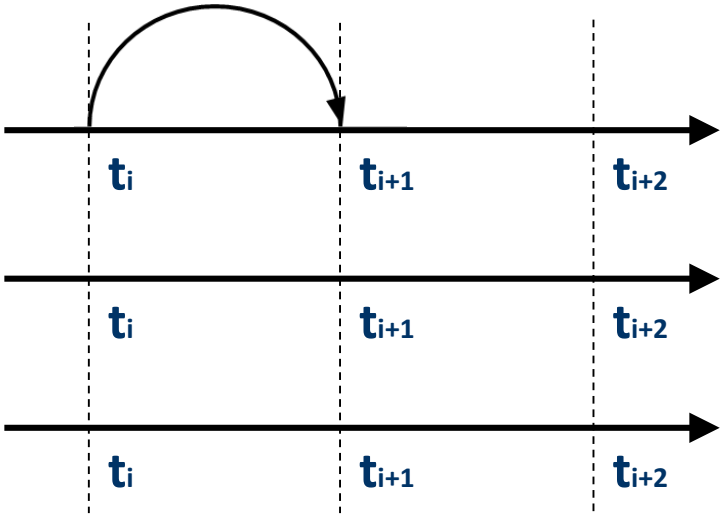
Chemistry ← S → **Diffusion, convection...**

Chemistry



$$\frac{\partial \varphi}{\partial t} = S$$

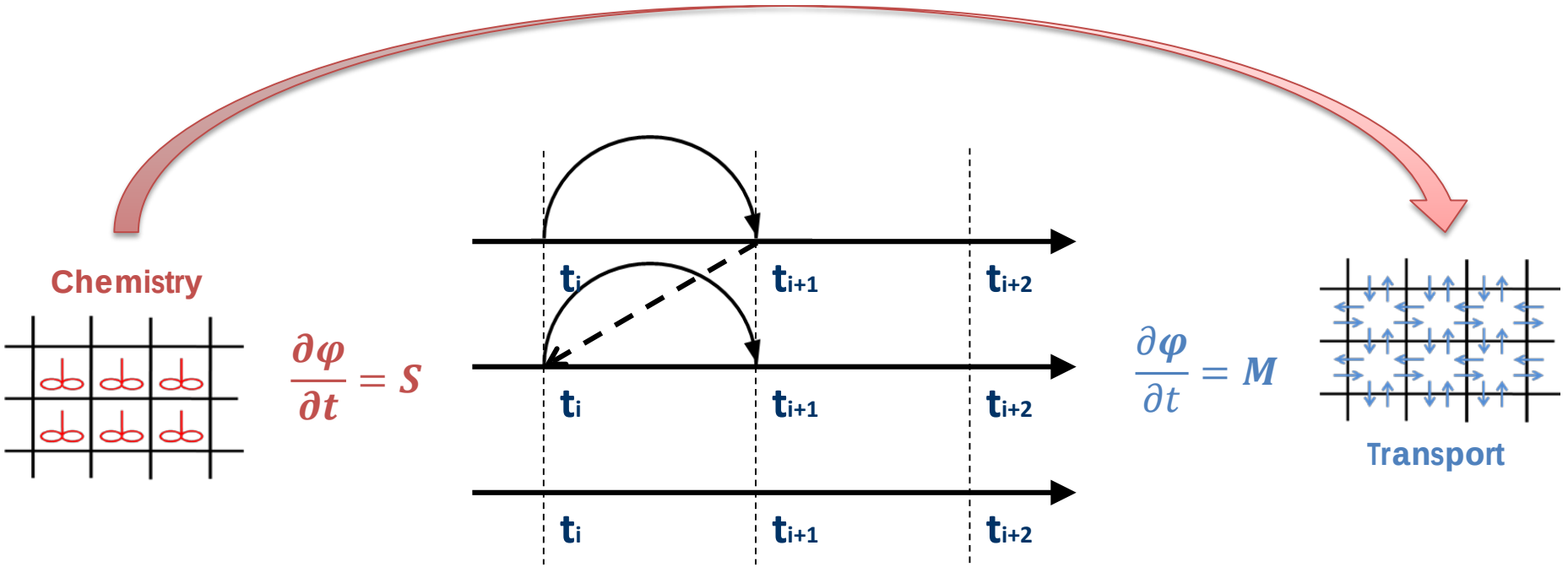


Operator-splitting: an example (V)

$$\frac{\partial \varphi}{\partial t} = S + M$$

Chemistry

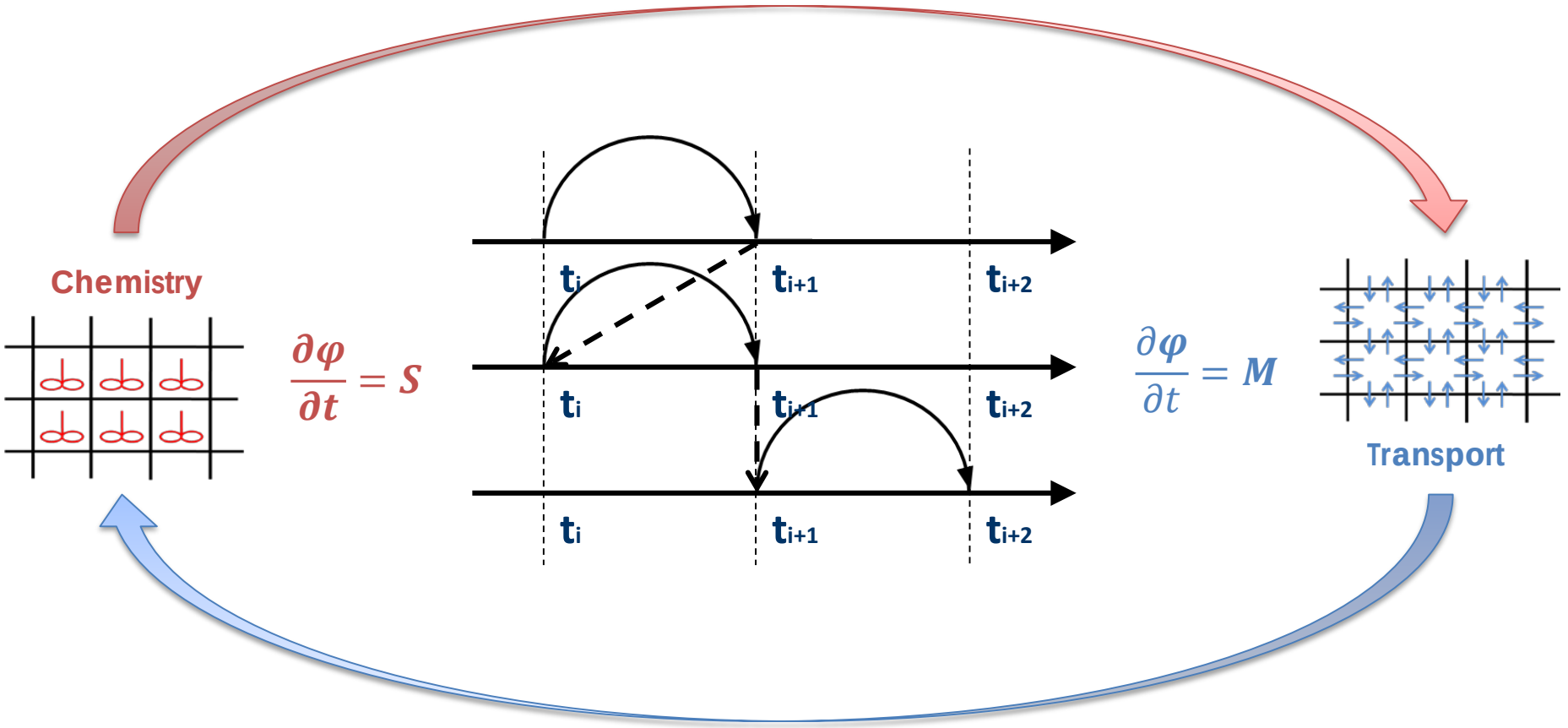
Diffusion, convection...



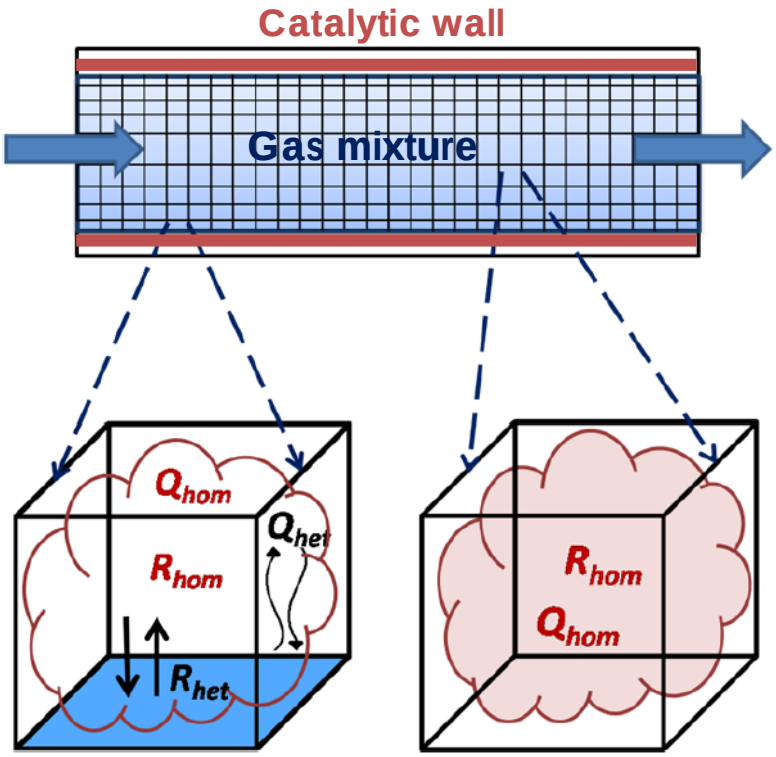
Operator-splitting: an example (VI)

$$\frac{\partial \varphi}{\partial t} = S + M$$

Chemistry ← S — M → **Diffusion, convection...**



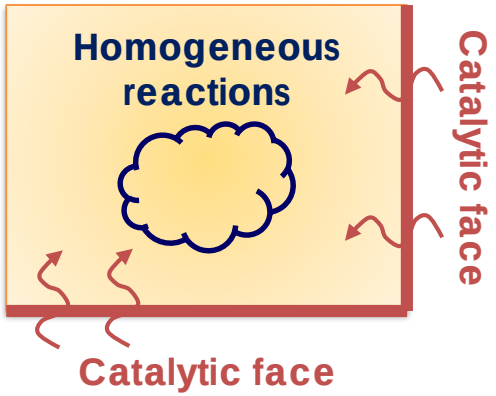
Operator-splitting in catalyticFOAM (I)



Each computational cell behaves as a chemical reactor in the splitting-operator algorithm (chemical step)

Each reactor is described by a set of stiff ODE, which must be integrated on the time step Δt

Operator-splitting in catalyticFOAM (II)



NF = number of catalytic faces

NG = number of gas-phase species

NS = number of adsorbed (surface) species

Equations: N = NG + 1 + NF· NS

Semi-batch reactor

$$\begin{cases} \rho \dfrac{d\omega_k}{dt} = \dot{\Omega}_k^{hom} + \dfrac{1}{V}\left\{ \sum_{j=1}^{NF} \alpha_j^{cat} A_j \dot{\Omega}_{k,j}^{het} - \omega_k \sum_{j=1}^{NF} \left[\alpha_j^{cat} A_j \sum_{k=1}^{NG} \dot{\Omega}_{k,j}^{het} \right] \right\} & k=1,\ldots,NG \\ \rho \hat{C}_P \dfrac{dT}{dt} = -\sum_{k=1}^{NG} \hat{H}_k^{hom} \dot{\Omega}_k^{hom} - \sum_{k=1}^{NS} \hat{H}_k^{het} \Omega_k^{het} & \\ \sigma_{cat} \dfrac{\partial \theta_{i,j}}{\partial t} = \dot{\Omega}_{i,j}^{het} & i=1,\ldots,NS \quad j=1,\ldots,NF \end{cases}$$

Gas-phase species

Gas-phase temperature

Adsorbed species

Operator-splitting in catalyticFOAM (III)

Homogeneous reactions

~~NF = number of catalytic faces~~

NG = number of gas-phase species

~~NS = number of adsorbed (surface) species~~

Unknowns N = NG + 1 + ~~NF· NS~~

Batch reactor

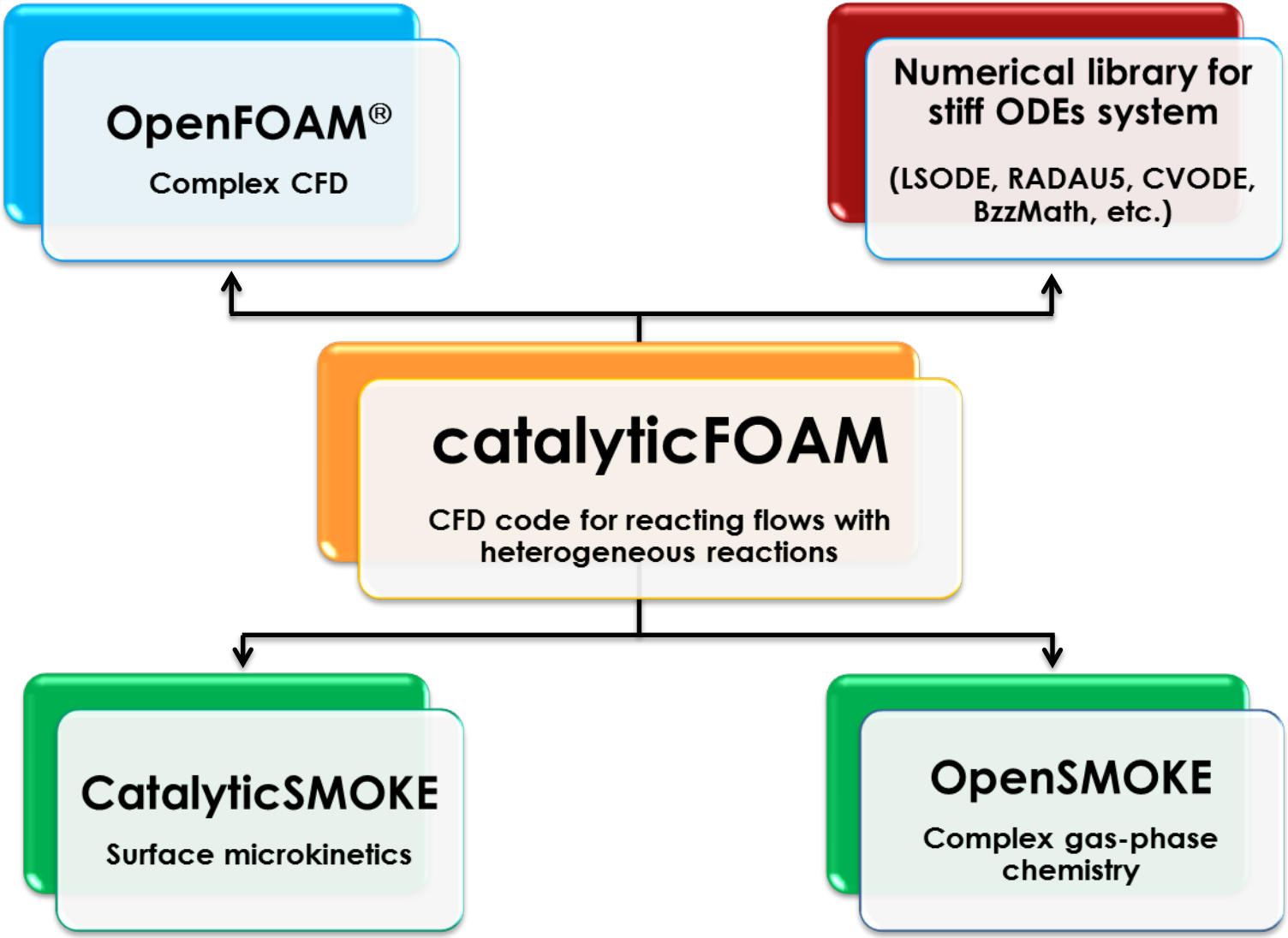
$$\begin{cases} \rho \dfrac{d\omega_k}{dt} = \dot{\Omega}_k^{hom} + \dfrac{1}{V}\left\{ \sum_{j=1}^{NF} \alpha_j^{cat} A_j \dot{\Omega}_{k,j}^{het} - \omega_k \sum_{j=1}^{NF} \left[\alpha_j^{cat} A_j \sum_{k=1}^{NG} \dot{\Omega}_{k,j}^{het} \right] \right\} & k=1,\dots,NG \\ \rho \hat{C}_P \dfrac{dT}{dt} = -\sum_{k=1}^{NG} \hat{H}_k^{hom} \dot{\Omega}_k^{hom} - \sum_{k=1}^{NS} \hat{H}_k^{het} \Omega_k^{het} & \\ \sigma_{cat} \dfrac{\partial \theta_{i,j}}{\partial t} = \dot{\Omega}_{i,j}^{het} & i=1,\dots,NS \quad j=1,\dots,NF \end{cases}$$

Gas-phase species

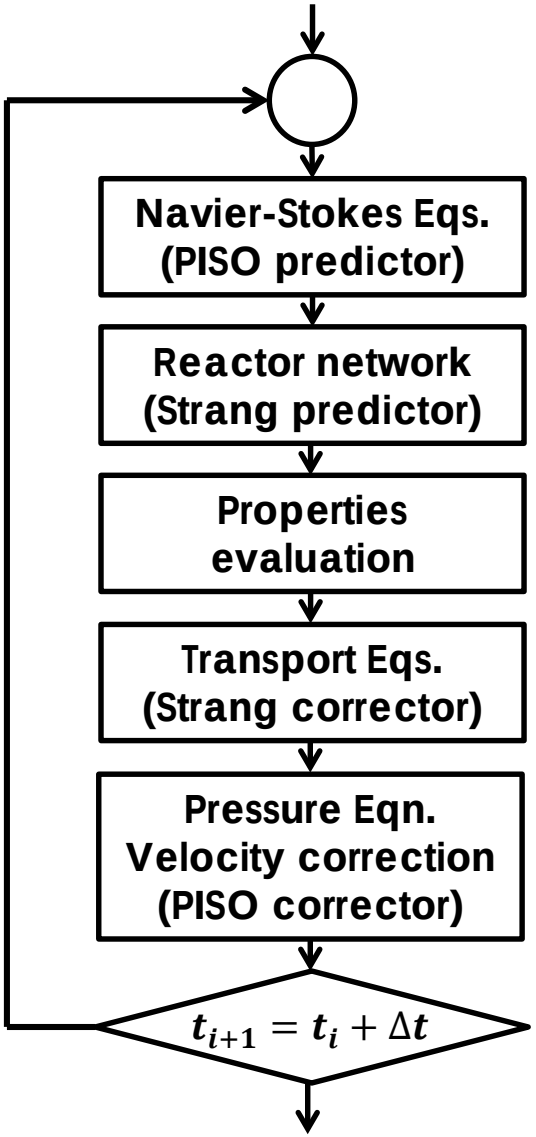
Gas-phase temperature

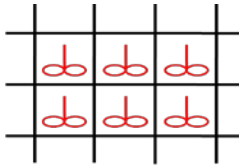
Adsorbed species

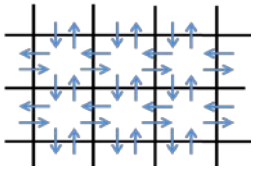
catalyticFOAM structure



Solution procedure







Main features:

- ✓ Solution of the Navier-Stokes equations (laminar and turbulent regime)
- ✓ No limit to the number of species and reactions
- ✓ Isothermal and adiabatic conditions

catalyticFoam.C

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```
while (runTime.run())  loop
{
        #include "readTimeControls.H"
        #include "readPISOControls.H"
        #include "compressibleCourantNo.H"
        #include "setDeltaT.H"

        runTime++;

        #include "rhoEqn.H"    Continuity equation

        for (label ocorr=1; ocorr <= nOuterCorr; ocorr++)
        {
                #include "UEqn.H"              Momentum equations
                #include "chemistry.H"         Chemical step
                #include "properties.H"
                #include "YEqn.H"
                #include "TEqn.H"              Transport step

                for (int corr=1; corr<=nCorr; corr++)    PISO loop
                {
                        #include "pEqn.H"
                }
        }

        #include "write.H"     Post-processing
}
```

Chemical step

```
Loop over all the reactors
{
        if reactor is catalytic
        {
                assembling ODE initial values
                (gas-phase species, temperature, adsorbed species)

                solving the ODE system

                moving the solution to OpenFOAM
        }

        else
        {
                assembling ODE initial values
                (gas-phase species and temperature)

                solving the ODE system

                moving the solution to OpenFOAM
        }
}
```

Numerical library for stiff ODE systems

(OpenSMOKE++, CVODE, LSODE, etc.)

Stiff ODE solvers in catalyticFOAM (I)

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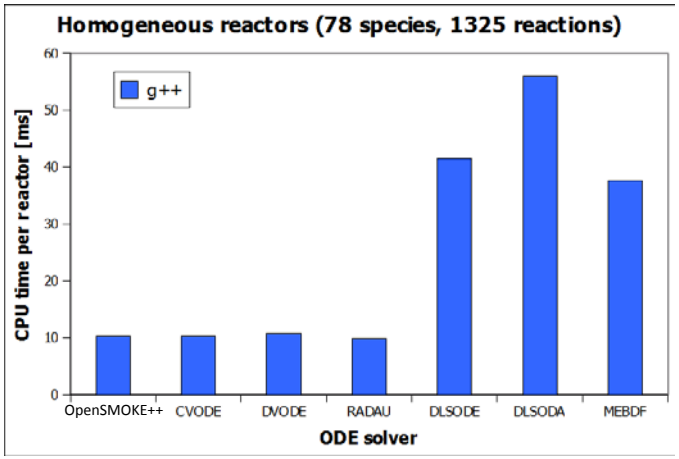
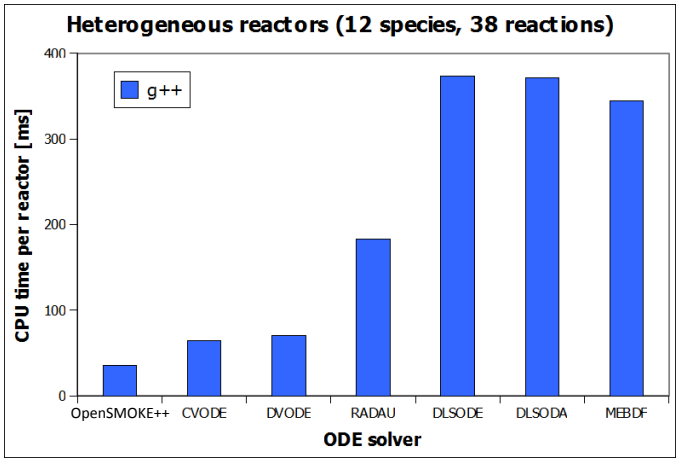
	Language	Linear system solution	Parallel	Code available	License
OpenSMOKE++	C++	Direct	No	Yes	Free
DVODE	FORTRAN	Direct	No	Yes	Free
CVODE	C	Direct/Iterative	Yes	Yes	Free
DLSODE	FORTRAN	Direct	No	Yes	Free
DLSODA	FORTRAN	Direct	No	Yes	Free
RADAU5	FORTRAN	Direct	No	Yes	Free
LIMEX4	FORTRAN	Direct	No	Yes	Free only for academic use
MEBDF	FORTRAN	Direct	No	Yes	Free

Most of the CPU Time (80-90%) is spent for the numerical integration of the ODE systems corresponding to the homogeneous and heterogeneous reactors

The best performances are obtained using the following solvers: OpenSMOKE++, CVODE, DVODE

Performances of stiff ODE solvers: CPU time





Details about the C++ implementation

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For each solver a common C++ interface was created

Creation of ODE System objects

```
ODESystem_BatchReactor_Homogeneous_DVODE *odeSystemObject_Homogeneous;
odeSystemObject_Homogeneous =
        ODESystem_BatchReactor_Homogeneous_DVODE::GetInstance();
```

Creation of ODE System Solver

```
OpenSMOKE::OpenSMOKE_DVODE<ODESystem_BatchReactor_Homogeneous_DVODE>
ode_Homogeneous(odeSystemObject_Homogeneous);
```

Loop on every computational cell

```
ode_Homogeneous.SetMaximumNumberOfSteps(100000);
ode_Homogeneous.SetAnalyticalJacobian(false);
ode_Homogeneous.SetAbsoluteTolerance(aTol);
ode_Homogeneous.SetRelativeTolerance(rTol);
ode_Homogeneous.SetInitialValues(t0,Y0);
ode_Homogeneous.Solve(tf);
ode_Homogeneous.Solution(yF);
```

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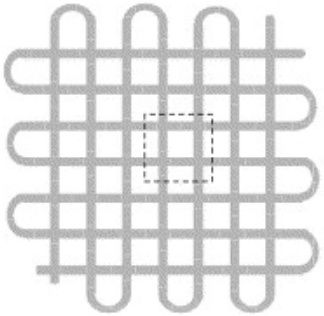
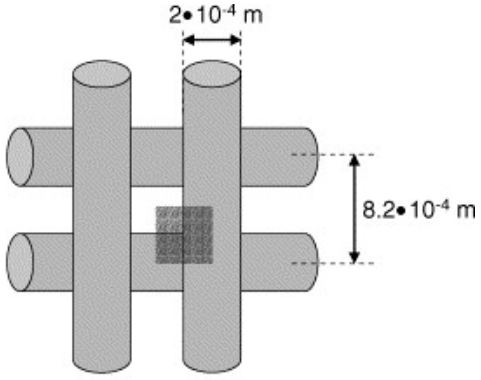
  - ✓ **CPO of CH_4 on platinum gauze (complex 3D geometry)**
  - ✓ CPO of iso-octane (complex chemistry)
  - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
  - ✓ Packed bed reactors for industrial applications (complex 3D geometry)
- ✓ Extensions
  - ✓ KMC (Kinetic Monte Carlo)

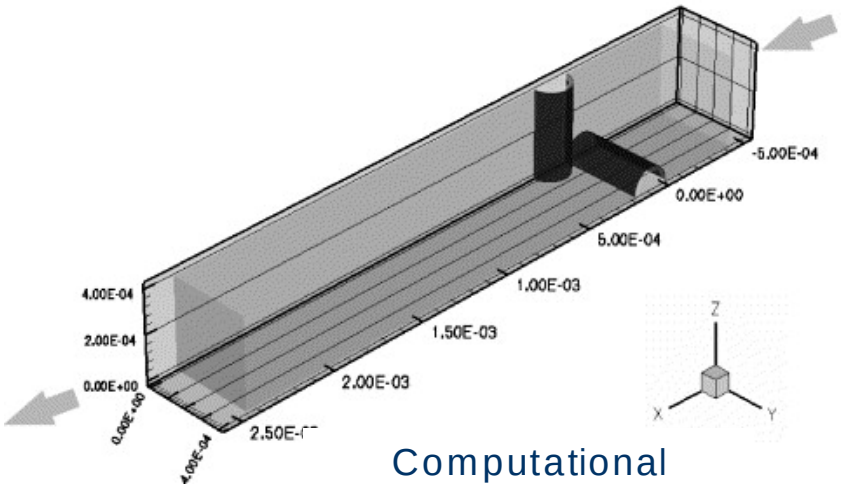
CPO of methane over platinum gauze (I)



Original gauze structure



Detail of wire intersections

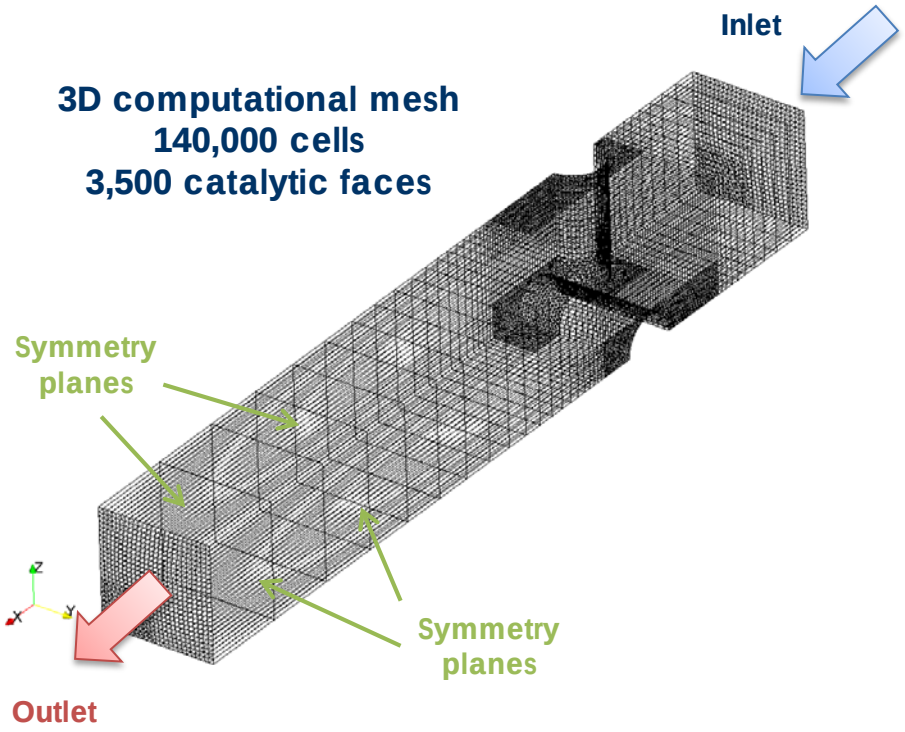


Computational domain

Operating conditions	
Inlet temperature	600 K
Inlet velocity	10 m/s
Gauze temperature	1000-1200 K
CH_4 mole fraction	0.143 (-)
O_2 mole fraction	0.057 (-)
He mole fraction	0.80 (-)
Pressure	1.3 bar
Pt site density	$2.72\ 10^{-9}$ mol/cm^2
Catalytic surf.	5 cm^{-1}

R. Quiceno, J. Perez-Ramirez, J. Warnatz, O. Deutschmann, *Modeling the high-temperature catalytic partial oxidation of methane over platinum gauze: detailed gas-phase and surface chemistries coupled with 3D flow simulations, Applied Catalysis A: General 303 (2006) 166-176*

CPO of methane over platinum gauze (II)



- Centered (2nd order) spatial discretization
- Implicit Euler time integration
- Max Courant number 0.05

Heterogeneous kinetics

- 11 Surface Species
- 36 Surface Reactions

www.detchem.com/mechanisms

R. Quiceno, et al., *Applied Catalysis A: General 303 (2006) 166-176*

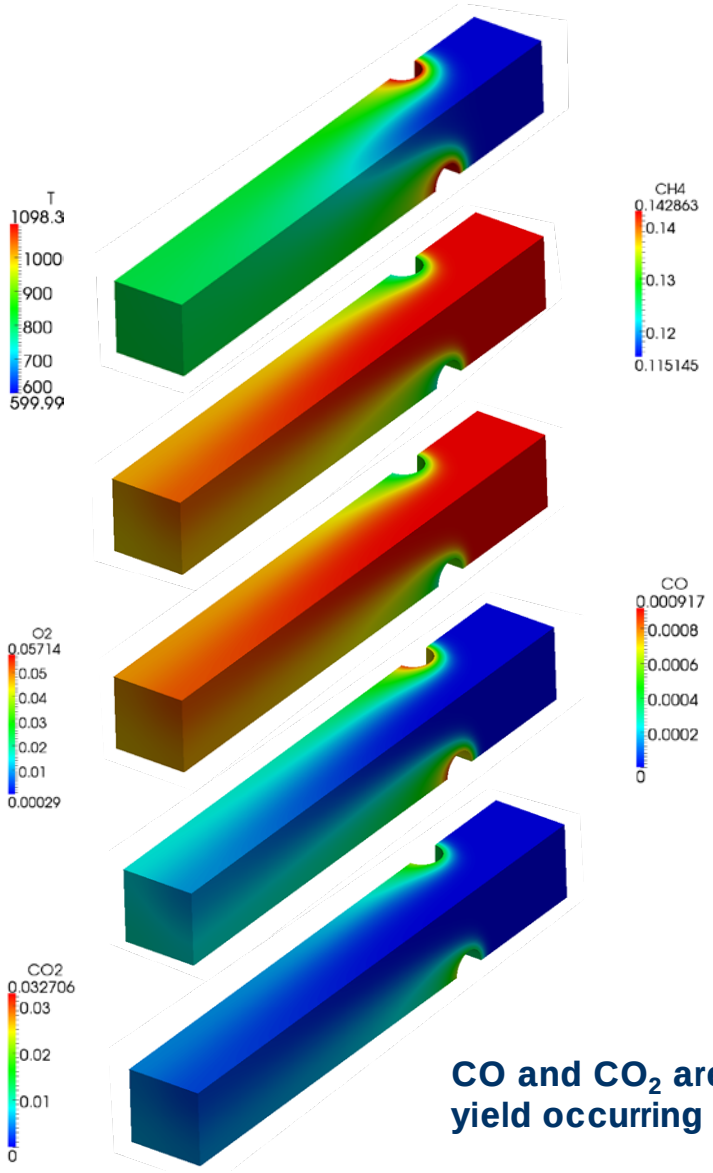
Homogeneous kinetics

- 25 Species
- 300 Reactions

http://creckmodeling.chem.polimi.it/

E. Ranzi, et al., *Progress in Energy Combustion Science, 38 (2012) 468-501*

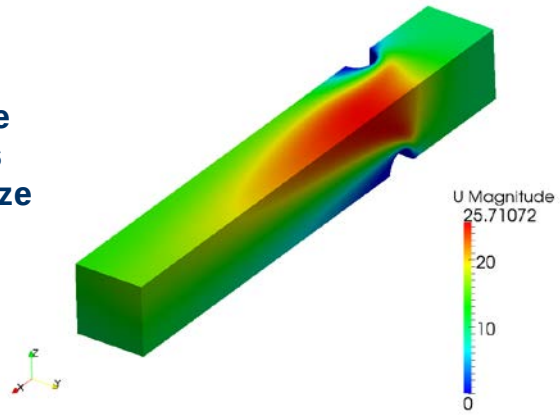
CPO of methane over platinum gauze (III)



T_{inlet} = 600K
T_{gauze} = 1000K

The temperature of the mixture becomes uniform at 2-3 wires diameters downstream the gauze

2 days of calculation on 12 cores



- ✓ Under the conditions used in these tests the homogeneous reactions are not relevant
- ✓ Simulations performed with and without the gas-phase reactions exhibit very similar results
- ✓ The concentration of radical species in the gas phase is negligible

CO and CO_2 are produced on the surface of the catalytic wires, with their maximal yield occurring at the crossing of the wires

CPO of methane over platinum gauze (IV)

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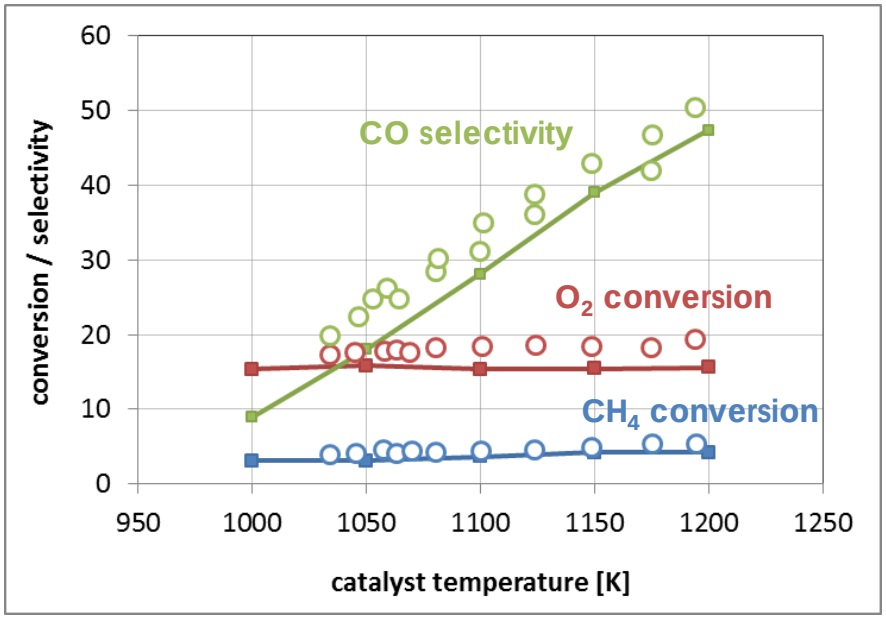
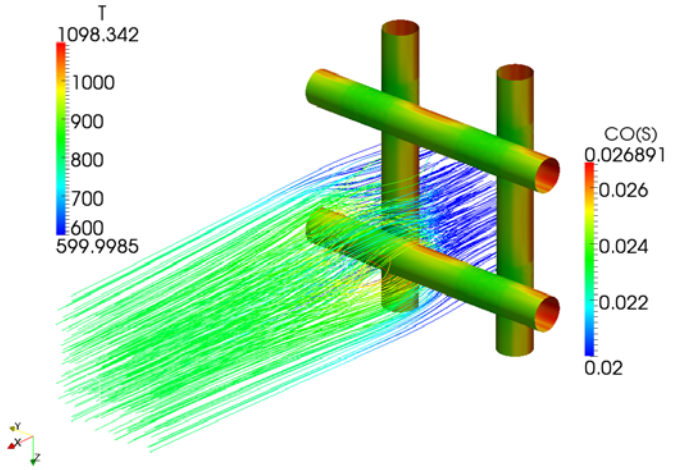
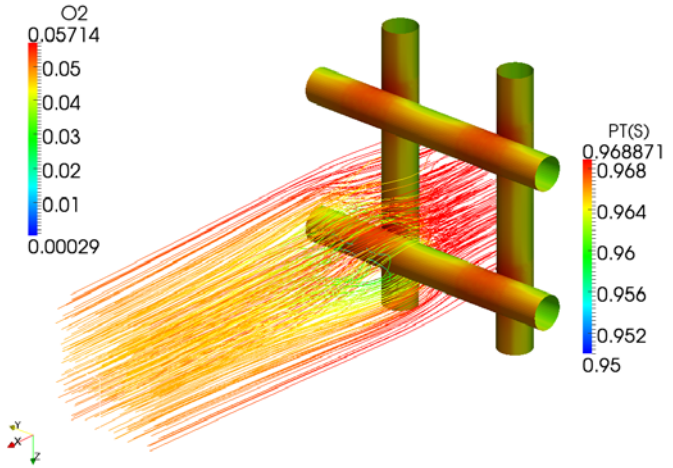
Comparison with experimental data



- ✓ CH4 and O2 conversions are not temperature dependent
- ✓ The CO selectivity is strongly influenced by the gauze temperature





- ✓ Mass fraction of main adsorbed species (CO(s), OH(s), etc.) is maximum downstream, where the inlet mixture meet the catalyst wires

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CPO of iso-octane over rhodium catalyst (I)

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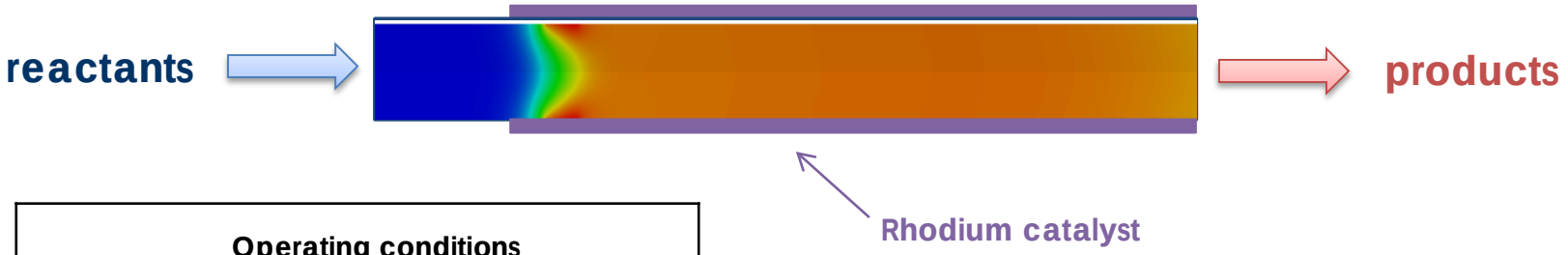
Sketch of a single channel (circular section)



Operating conditions	
Inlet temperature	1076 K
Inlet velocity	0.90 m/s
Wall temperature	1076 K
iC_8H_{18} mole fraction	0.143 (-)
O_2 mole fraction	0.057 (-)
N_2 mole fraction	0.80 (-)
Pressure	1 atm
Rh site density	$2.49\ 10^{-9}$ mol/cm^2
Catalytic surf.	5 cm^{-1}

Heterogeneous kinetics
- 17 Surface Species
- 56 Surface Reactions

www.detchem.com/mechanisms

Homogeneous kinetics
- 168 Species
- 5,400 Reactions

http://creckmodeling.chem.polimi.it/

M. Hartmann, L. Maier, H.D.Minh, O. Deutschmann, *Catalytic partial oxidation of iso-octane over rhodium catalyst: an experimental, modeling and simulation study, Combustion and Flame 157 (2010) 1771-1782*

CPO of iso-octane over rhodium catalyst (II)

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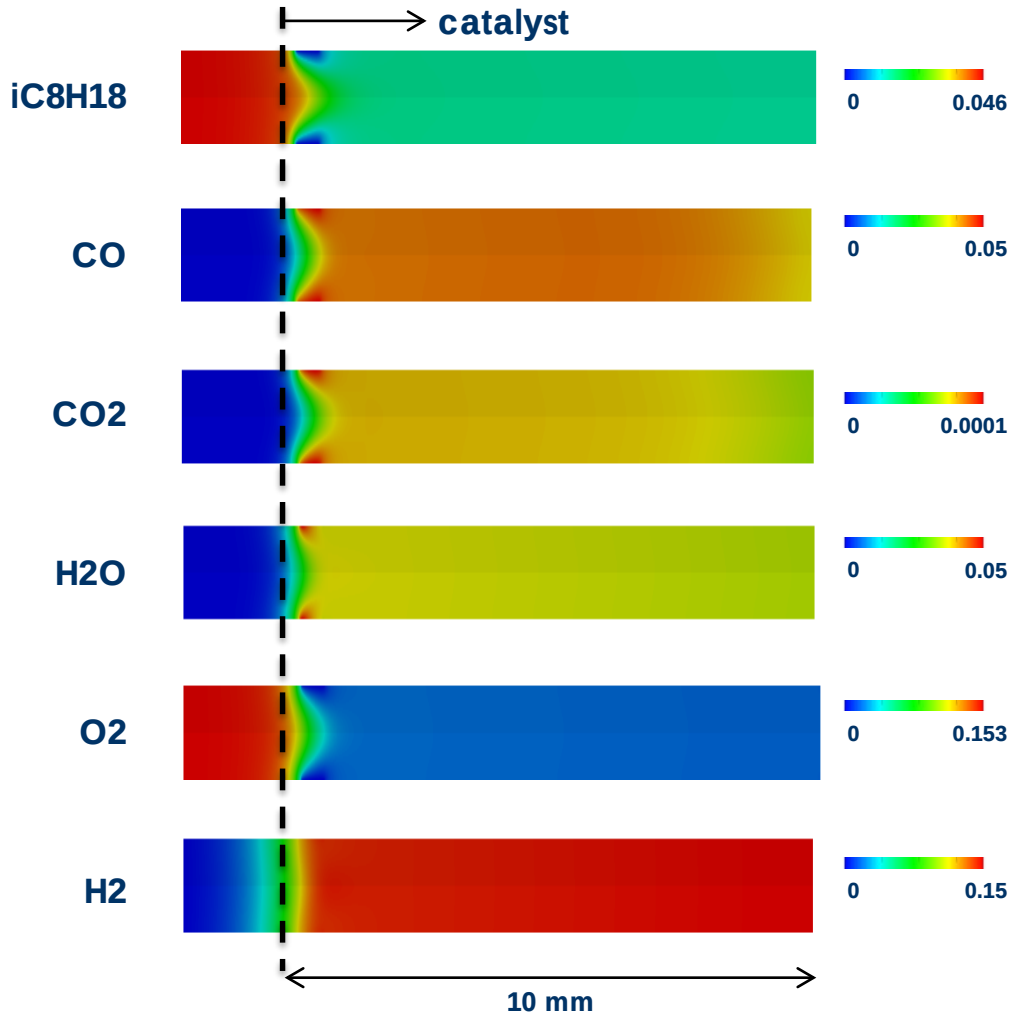
Gas-phase main species
2D mesh (4,000 cells)



4 days of calculation on 12 cores

The catalytic surface reaction is very fast in the entrance (first 1 mm)

Strong back-diffusion of H2: importance of diffusion coefficients

Strong radial gradient are present in the first mm of the reactor

The concentration of iC8H18 and O2 on the surface is practically zero, which means that catalytic reactions are mass-transfer limited

CPO of iso-octane over rhodium catalyst (III)

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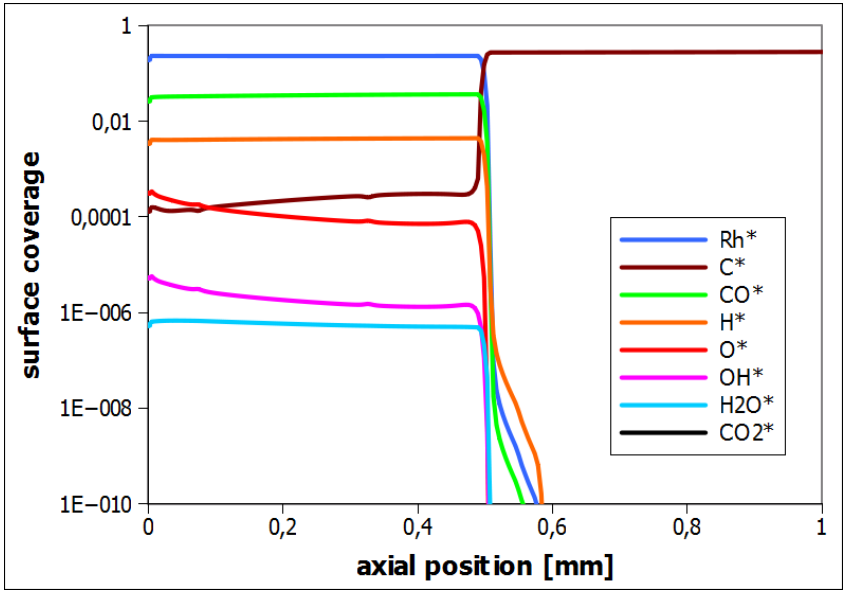
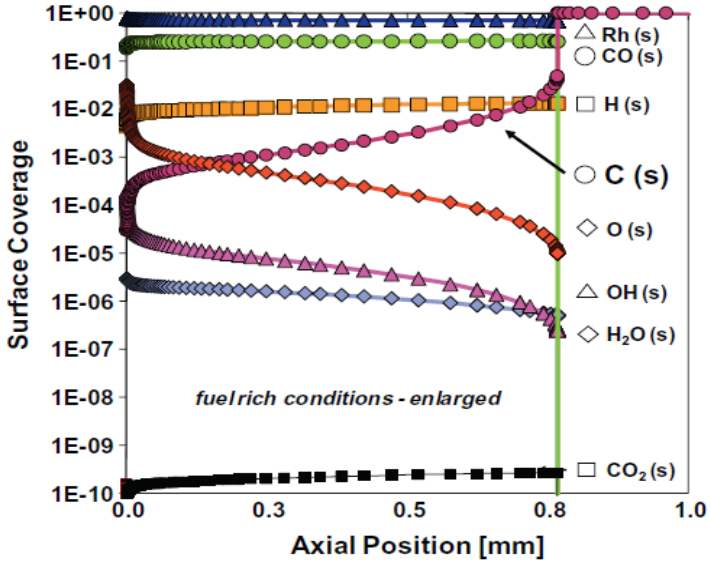
CatalyticFOAM
2D mesh (5,000 cells)

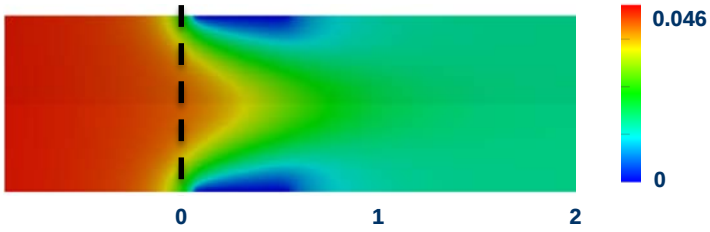


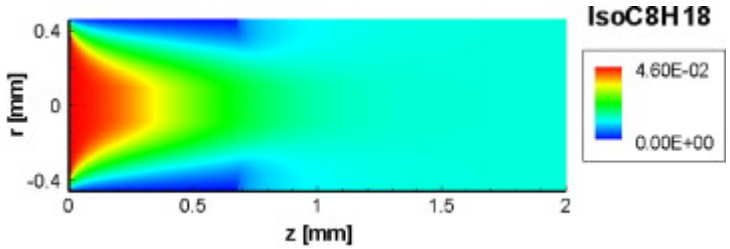
DETCHEM^{CHANNEL}
www.detchem.com



M. Hartmann, et al., *Combustion and Flame 157 (2010) 1771-1782*

iC8H18





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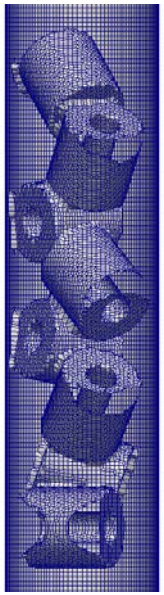
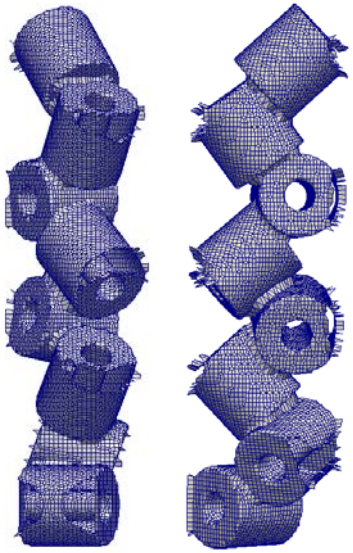
Tubular reactor with Raschig rings (I)

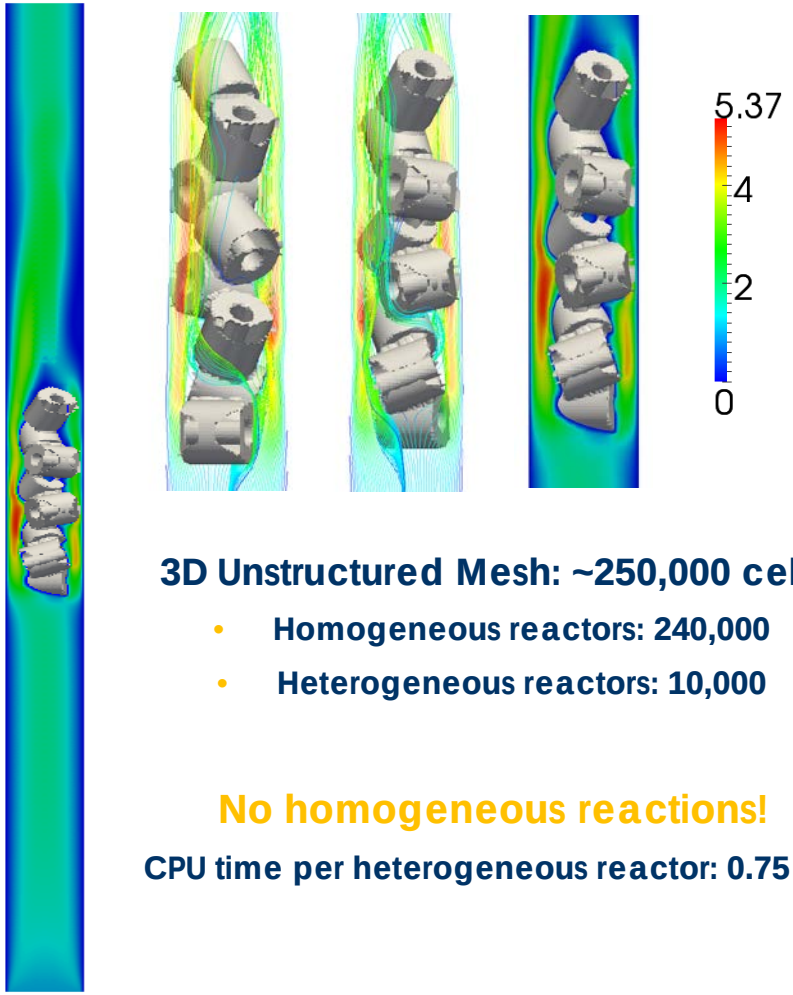




Inlet mixture

Operating conditions	
Internal diameter	1 cm
Total length	15 cm
CH_4 mole fraction	0.100 (-)
O_2 mole fraction	0.056 (-)
N_2 mole fraction	0.844 (-)
Temperature	873.15 K
Residence time	0.15 s

Velocity Field [m/s]



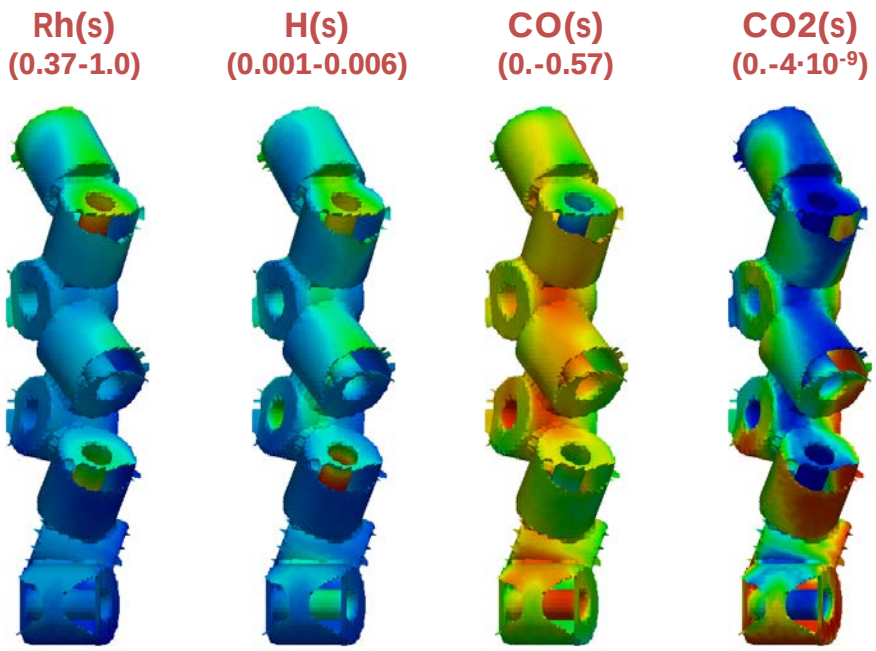
3D Unstructured Mesh: ~250,000 cells

- **Homogeneous reactors: 240,000**
- **Heterogeneous reactors: 10,000**

No homogeneous reactions!

CPU time per heterogeneous reactor: 0.75 ms

Tubular reactor with Raschig rings (II)



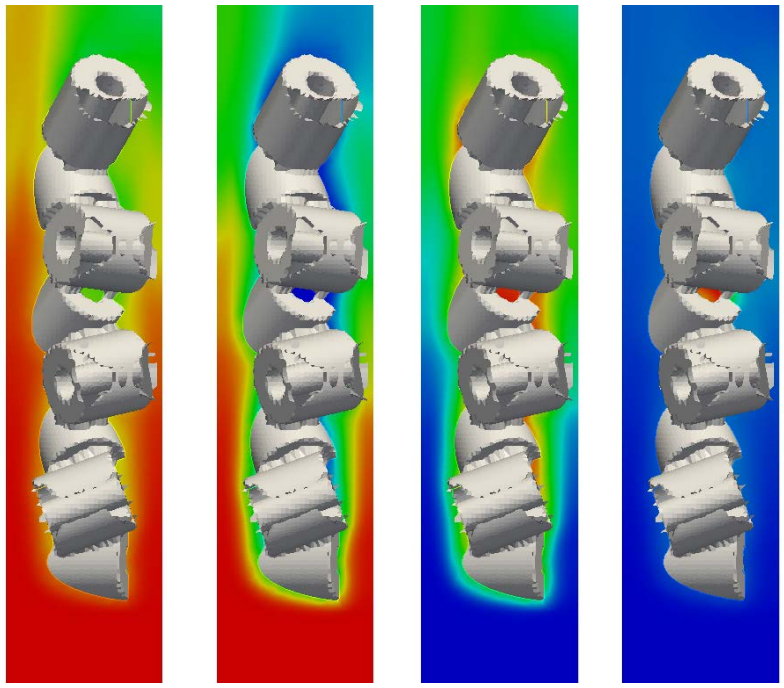
Adsorbed species (mass fractions)

C1 microkinetic model on Rh

82 reaction steps
13 adsorbed species
UBI-QEP and DFT refinement

M. Maestri et al., AIChE J., 2009

Gas-phase species (mole fractions)



Tubular reactor with Raschig rings (III)

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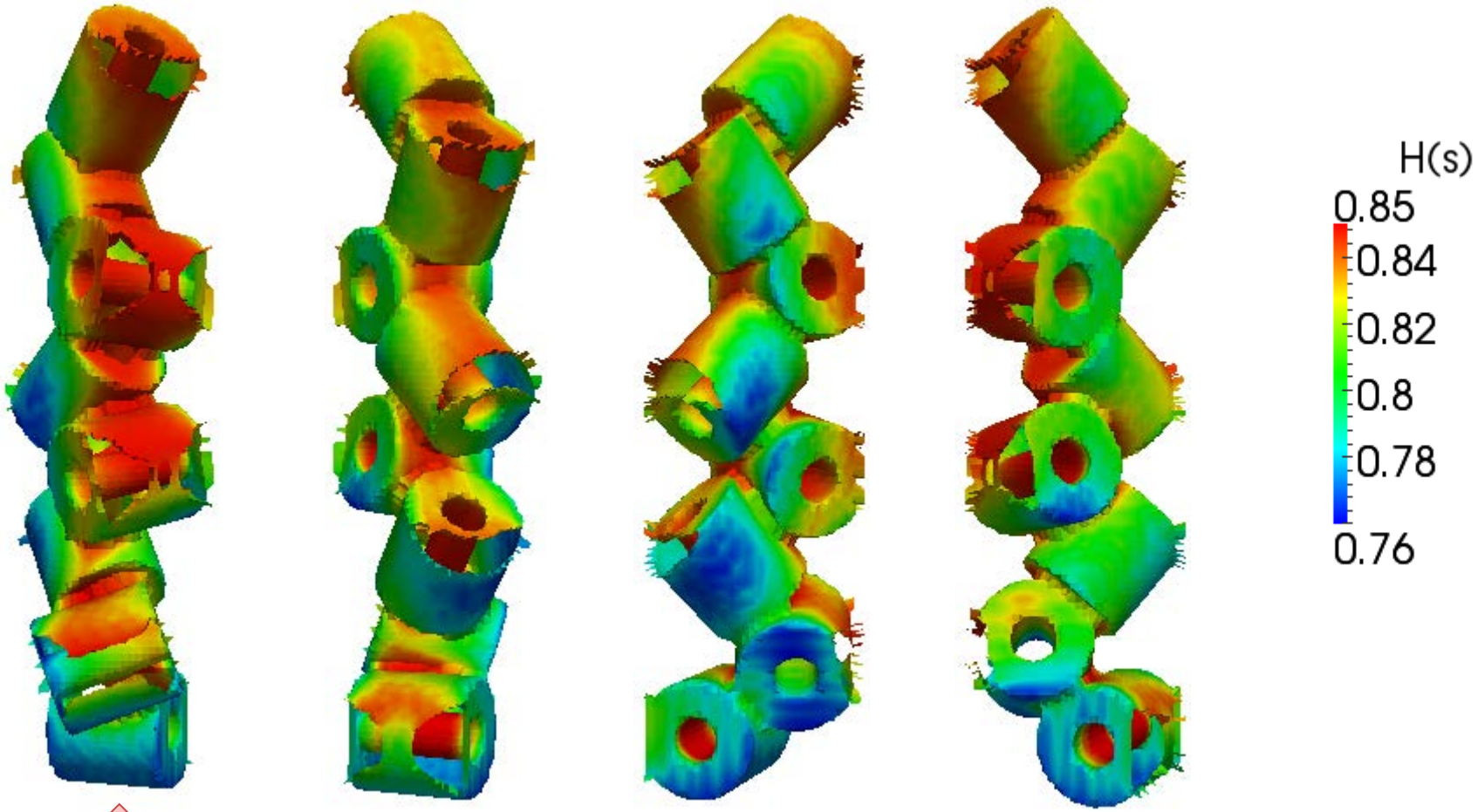
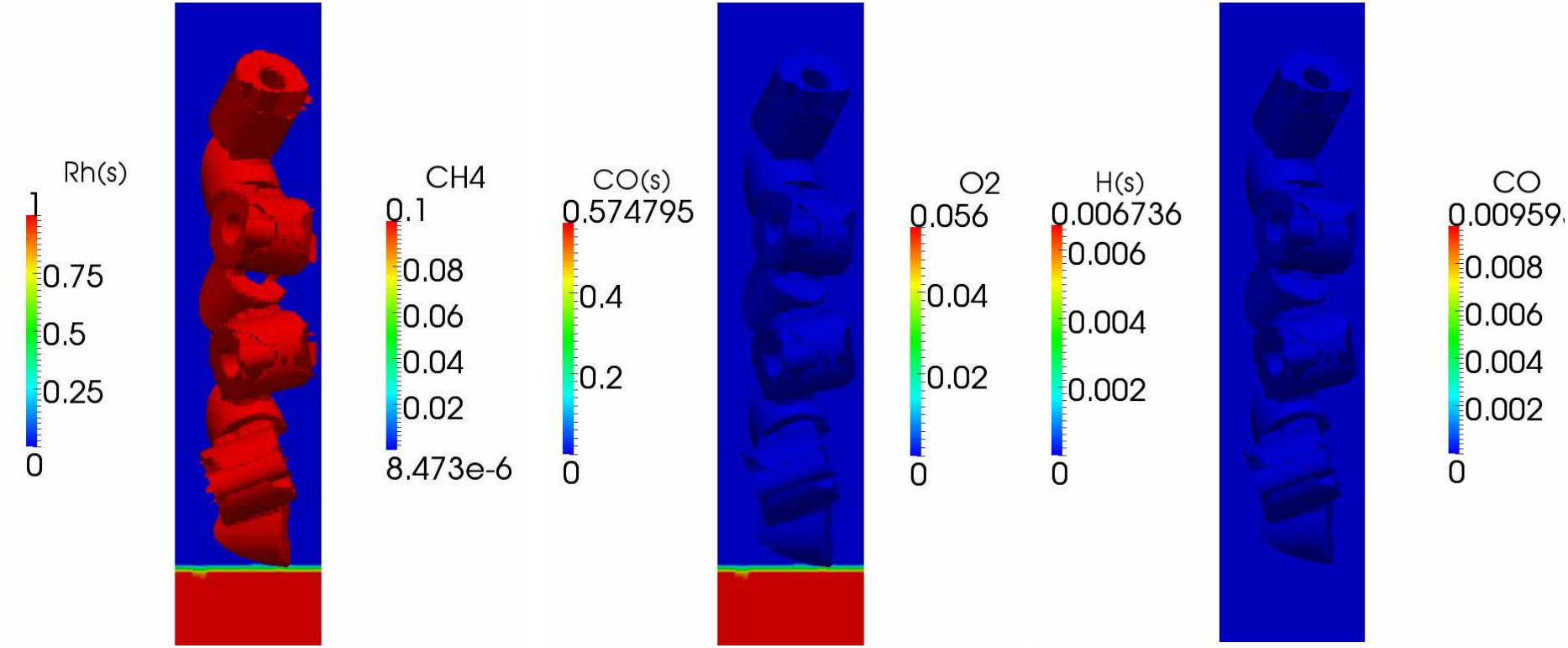
Adsorbed species at the catalyst surface



Tubular reactor with Raschig rings (IV)

Dynamics of the system



Outline

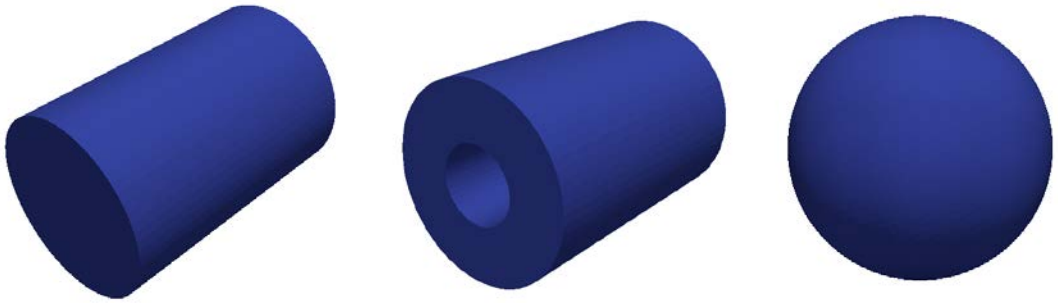
- ✓ Introduction and motivation
- ✓ Development of the catalyticFOAM solver for the OpenFOAM® framework
  - ✓ Governing equations
  - ✓ Numerical methodology
- ✓ **Validation and examples**
  - ✓ CPO of CH_4 on platinum gauze (complex 3D geometry)
  - ✓ CPO of iso-octane (complex chemistry)
  - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
  - ✓ **Packed bed reactors for industrial applications (complex 3D geometry)**
- ✓ Extensions
  - ✓ KMC (Kinetic Monte Carlo)

Analysis of performances

POLITECNICO DI MILANO

Investigated structures

- Cylinders
- Rings
- Spheres

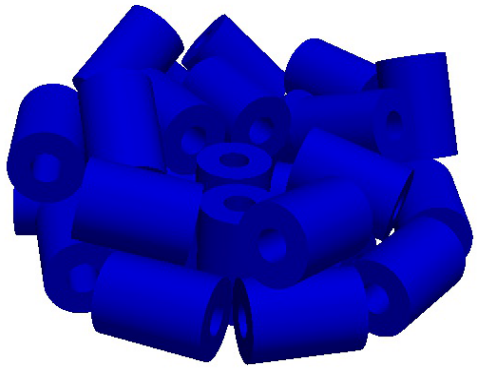


Same catalytic area

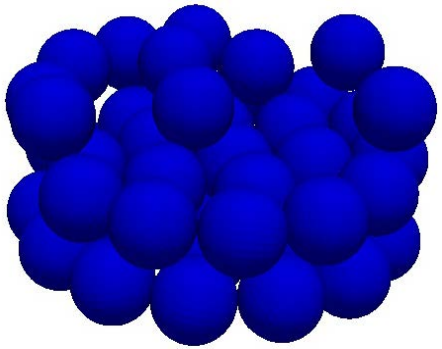
	$A_{single\ element}$ [m²]	N
Sphere	1.13×10^{-4}	50
Ring	1.88×10^{-4}	30
Cylinder	1.57×10^{-4}	36

36 cylinders

30 rings



50 spheres



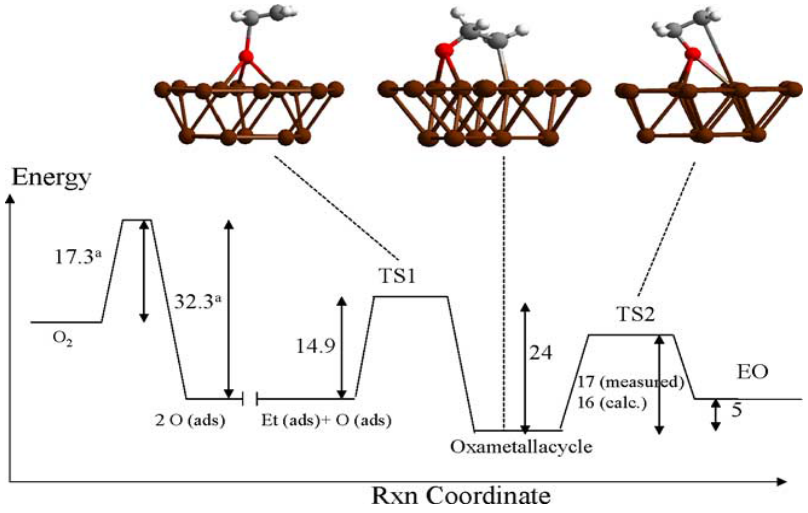
Global kinetic scheme

Micro-kinetic model

$$step\ 1 \quad O_2 + 2^* \leftrightarrow 2O^*$$
$$step\ 2 \quad C_2H_4 + * \leftrightarrow C_2H_4^*$$
$$step\ 3 \quad O^* + C_2H_4^* \leftrightarrow C_2H_4O^* + *$$
$$step\ 4 \quad C_2H_4O^* \leftrightarrow C_2H_4O + *$$

Global kinetic scheme

KINETIC MODEL PARAMETERS	
A	9.85E5 1/(atm m^3 s)
Eatt	15 Kcal/mol
m	0.65
n	0.71



Suljo Linic and Mark A. Barteau, Construction of a reaction coordinate and a microkinetic model for ethylene epoxidation on silver from DFT calculations and surface science experiments, November 2002, Journal of catalyst, pag 200-213

$$r = k_{overall}(P_{O_2})^n (P_{C_2H_4})^m$$

$$k_{overall} = Ae^{-\frac{E_{att}}{RT}}$$

Operating conditions

OPERATING CONDITIONS	
C_2H_4 Molar Fraction	35.0 %
O_2 Molar Fraction	5.0 %
CH_4 Molar Fraction	60.0 %
Pressure	15 atm
Temperature	432 – 550 K
Inlet Velocity	1 m/s

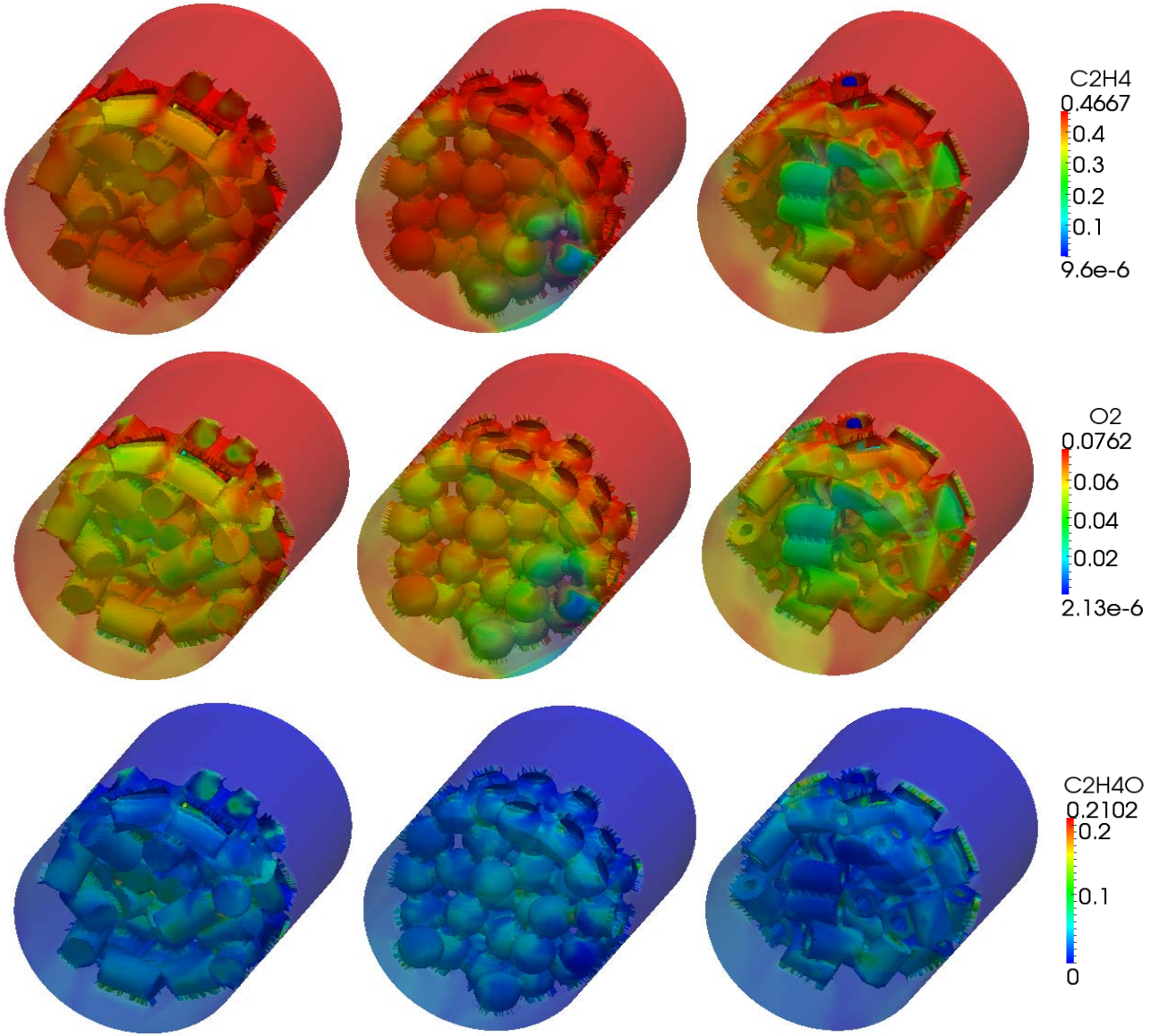
- ✓ Oxygen based process
- ✓ Methane as inert component
- ✓ Isothermal simulations at 432 K, 490 and 550 K
- ✓ Adiabatic simulations at 432 K
- ✓ Multiregion simulations at 490 K

Isothermal simulations: 432 K

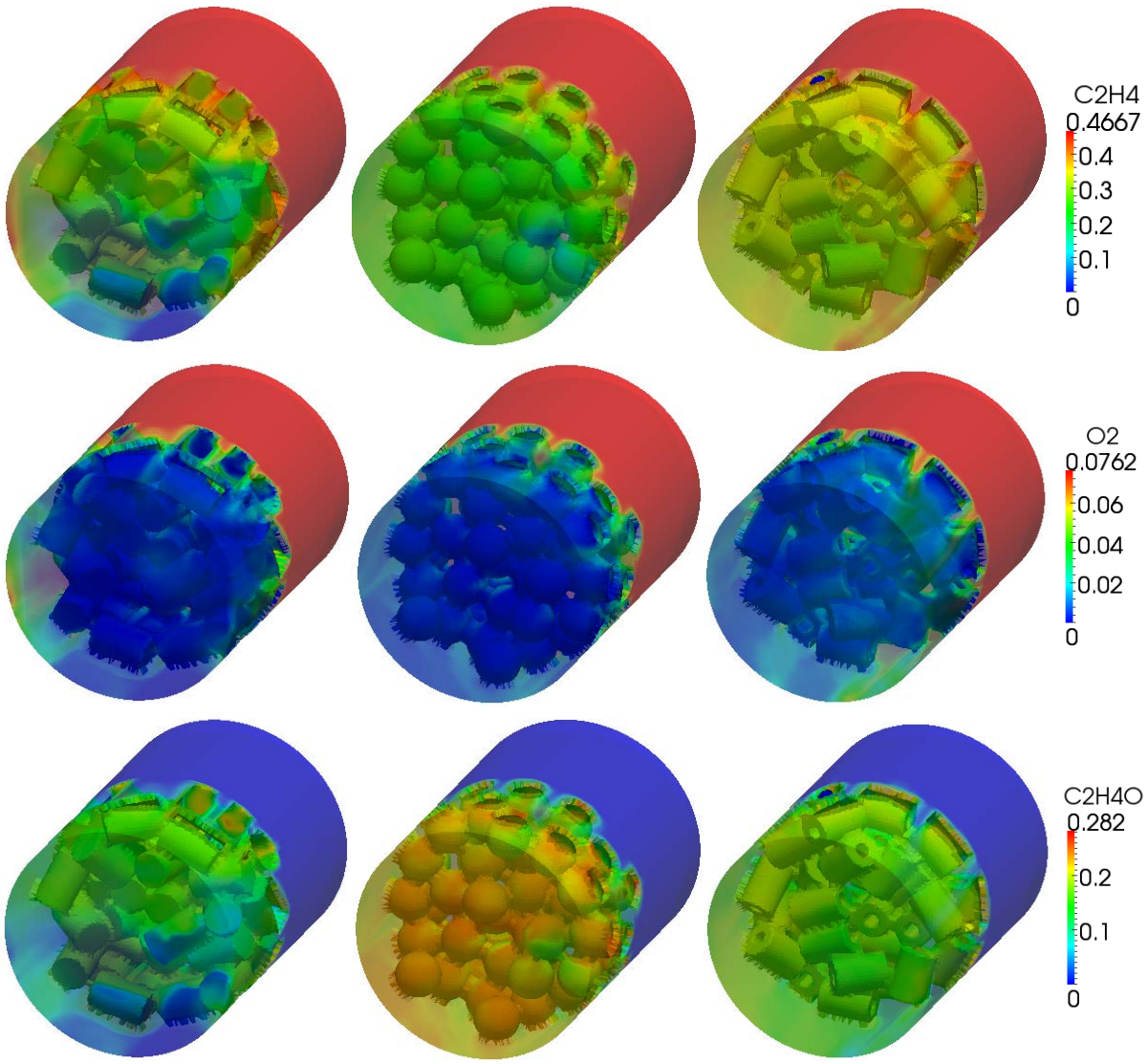
POLITECNICO DI MILANO

The behaviour of the three packed beds is almost the same

3 days on 8 cores



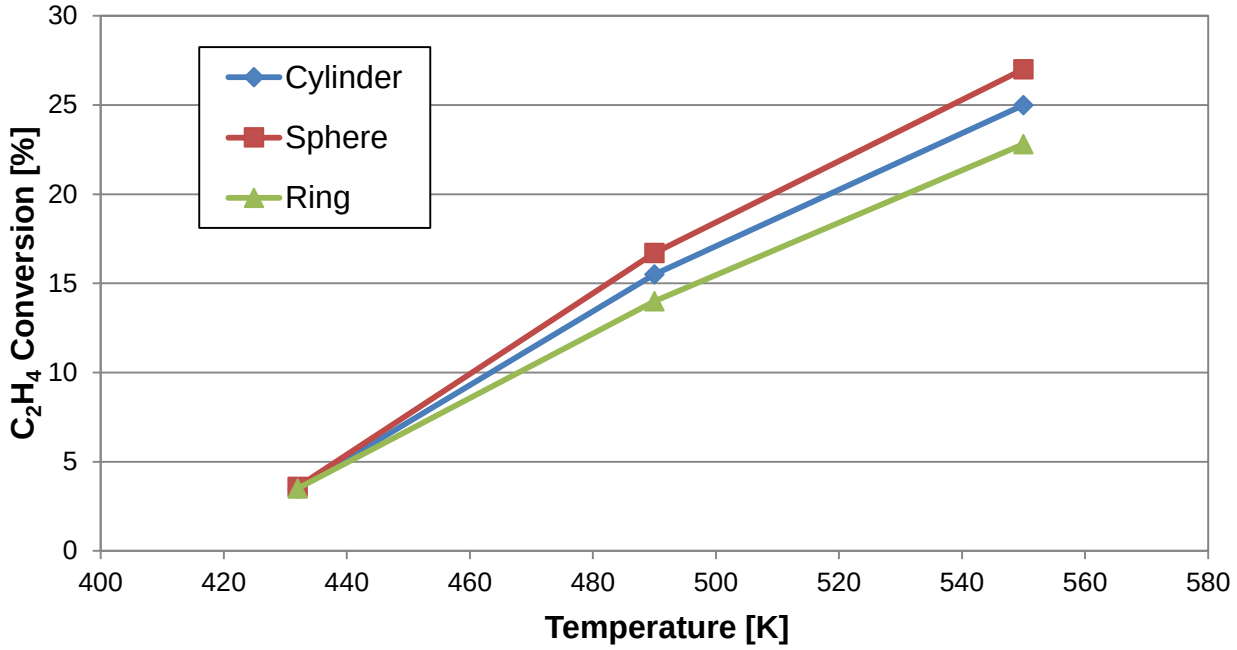
Isothermal simulations: 550 K



Spheres at high temperature can guarantee the higher conversion

Isothermal simulations

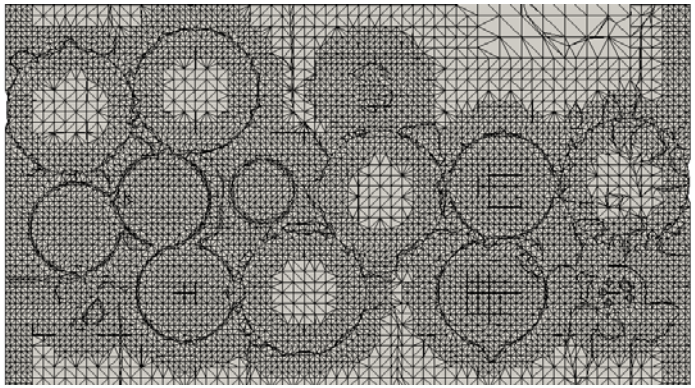
C_2H_4 Conversion vs Temperature

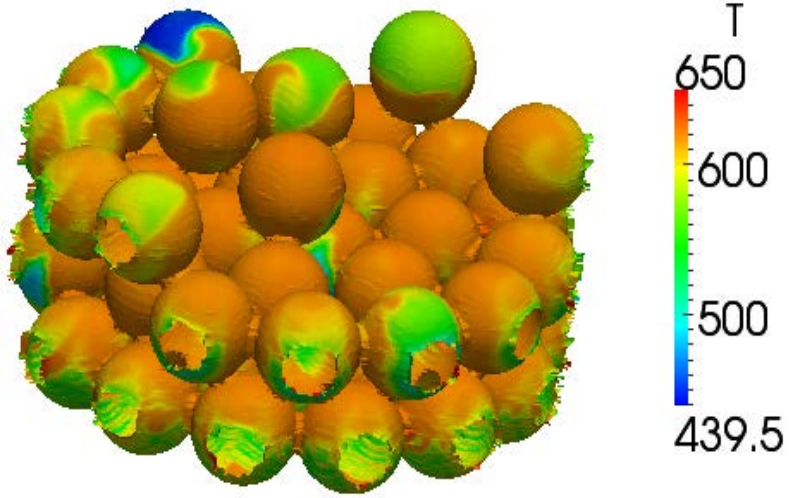


	432 K	490 K	550 K
Cylinders	3.5 %	15. 5%	25.0 %
Spheres	3.6 %	16.7 %	27.0 %
Rings	3.5 %	14.1 %	22.8 %

Extension to multiregion

Multiregion Mesh: the spheres have been meshed with the same level of refinement of the bulk phase - conformal mesh





Adiabatic simulations
Need to have very fine meshes close to the reactor wall

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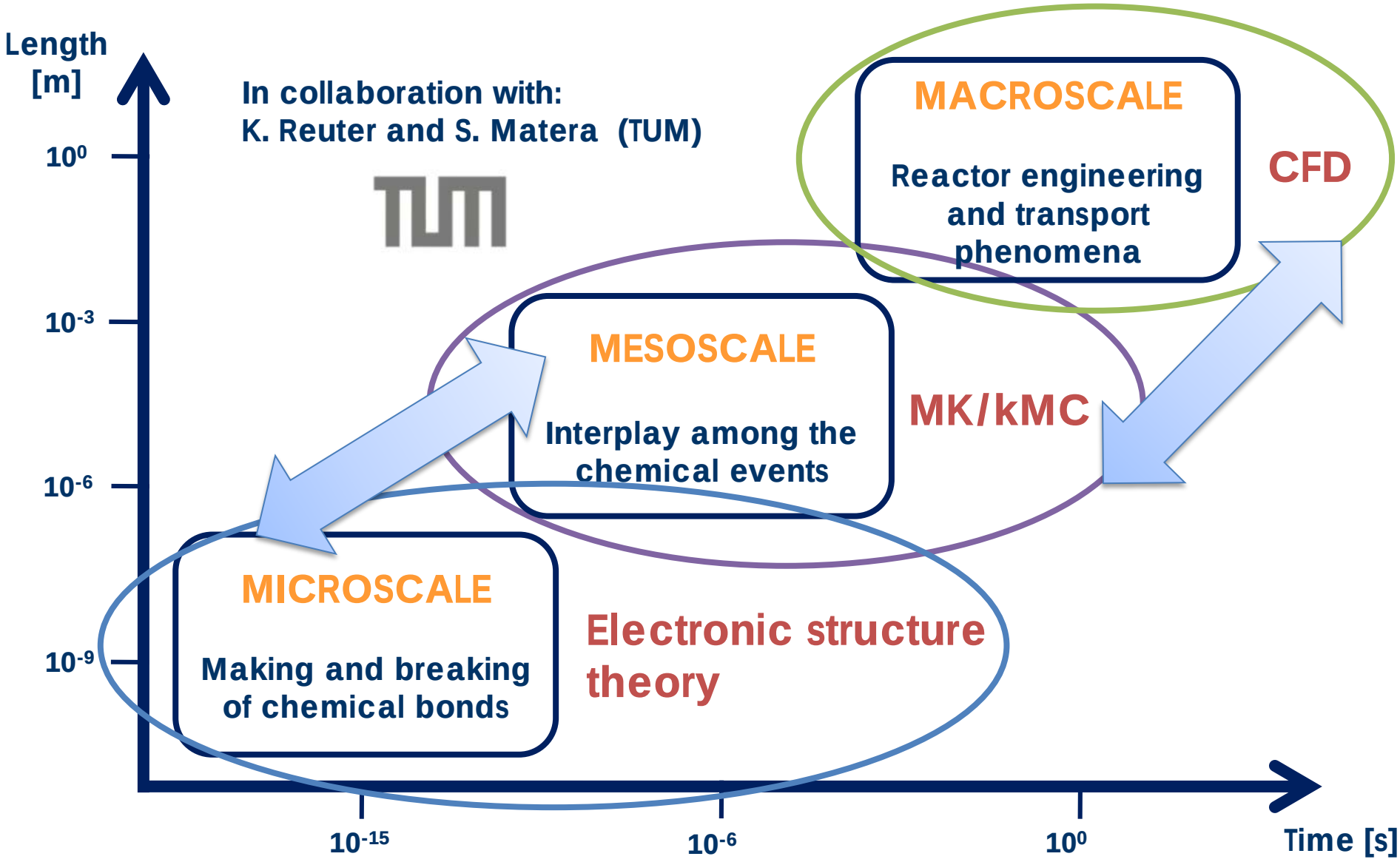
  - ✓ CPO of iso-octane (complex chemistry)
  - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
  - ✓ Packed bed reactors for industrial applications (complex 3D geometry)
- ✓ **Extensions**
  - ✓ **KMC (Kinetic Monte Carlo)**

Extension to kinetic Monte Carlo

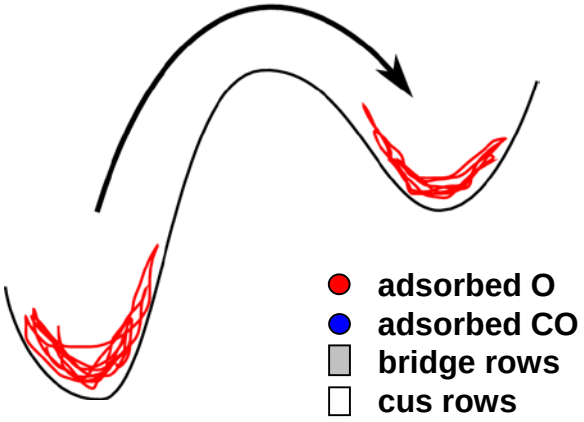


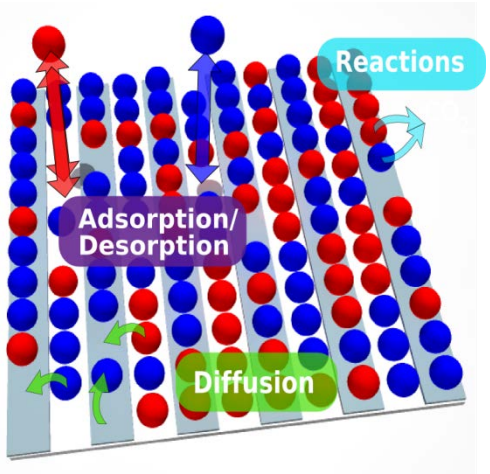
First-principles kinetic Monte Carlo

- ✓ Evaluate the statistical interplay of large number of elementary processes
- ✓ open non-equilibrium system → need to explicitely follow the time evolution
- ✓ rare event dynamics → Molecular Dynamics simulations unsuitable. Map on a lattice model→ Markov jump process description

$$\frac{d}{dt}P(\boldsymbol{x},t)=\sum_{y}k(\boldsymbol{x},\boldsymbol{y})P(\boldsymbol{y},t)-\sum_{y}k(\boldsymbol{y},\boldsymbol{x})P(\boldsymbol{x},t)$$

- ✓ Each site *a* has own entry in *x* denoting its adsorbate state x_a
- ✓ Simulate trajectories *x*(*t*) (**kinetic Monte Carlo**)





K. Reuter and M. Scheffler, *Phys. Rev. B* 73, 045433 (2006)

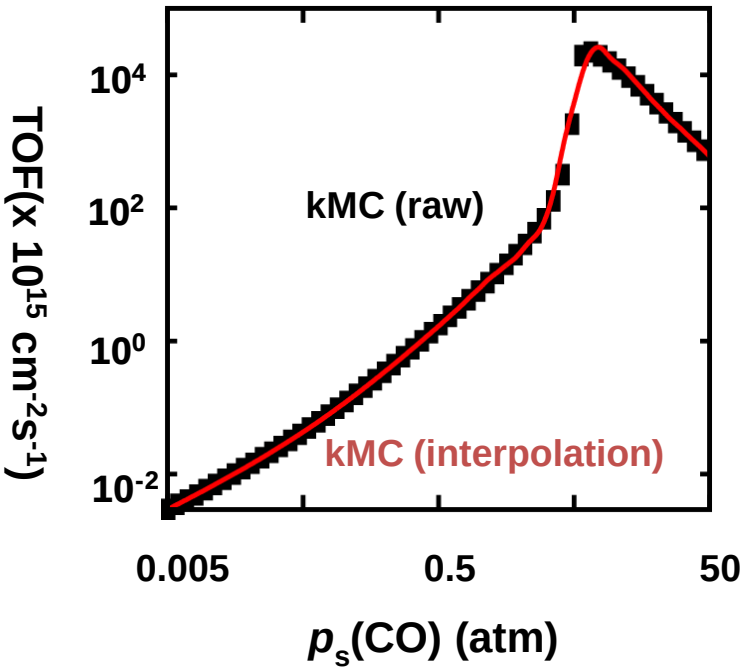
“Effective” bridging between the scales

- ✓ Continuum equations need boundary conditions for the mass fluxes j^{α} at the surface:

$$j_n^{\alpha} = \nu^{\alpha} M^{\alpha} \mathbf{TOF}$$

- ✓ **Coupled problem**: to determine the TOF with 1p-kMC the pressures at the surface are needed, but the pressure field depends on the TOF
- ✓ **kMC too expensive** for direct coupling to the flow solver
- ✓ Run kMC beforehand and interpolate (Modified Shepard)
- ✓ Very efficient
- ✓ Easily extendable to more complex geometries

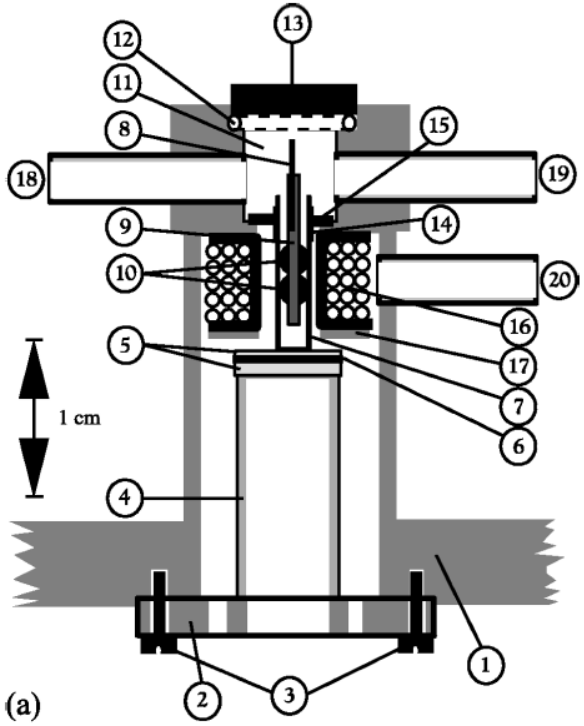
T_s = 600K, $p_s(O_2)$= 1atm



S. Matera and K. Reuter, *Catal. Lett.* 133, 156-159 (2009); *Phys. Rev. B* 82, 085446 (2010)

An example: The reactor STM (I)

The Reactor STM



Rasmussen, Hendriksen, Zeijlemaker, Ficke, Frenken, *The Reactor STM: A scanning tunneling microscope for investigation of catalytic surfaces at semi-industrial reaction conditions*, Review of Scientific Instruments, 69(11), (1998)

CO oxidation on Ru_2O

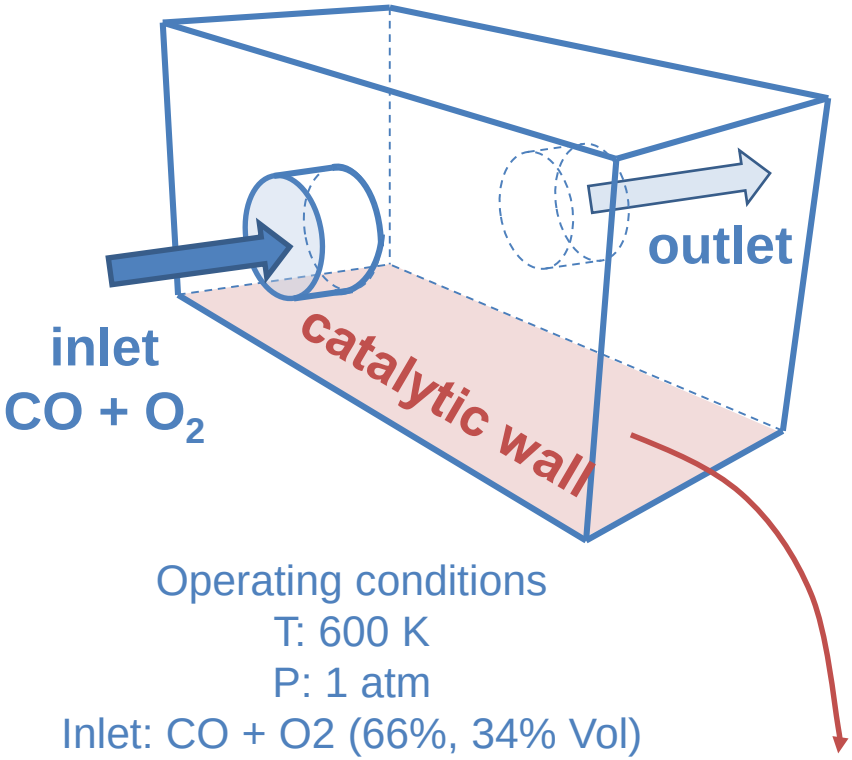
Rate constants $k(x,y)$ from DFT and harmonic Transition State Theory

Model system

- ✓ CO oxidation on $RuO_2(110)$
- ✓ 2 types of sites, bridge and cus

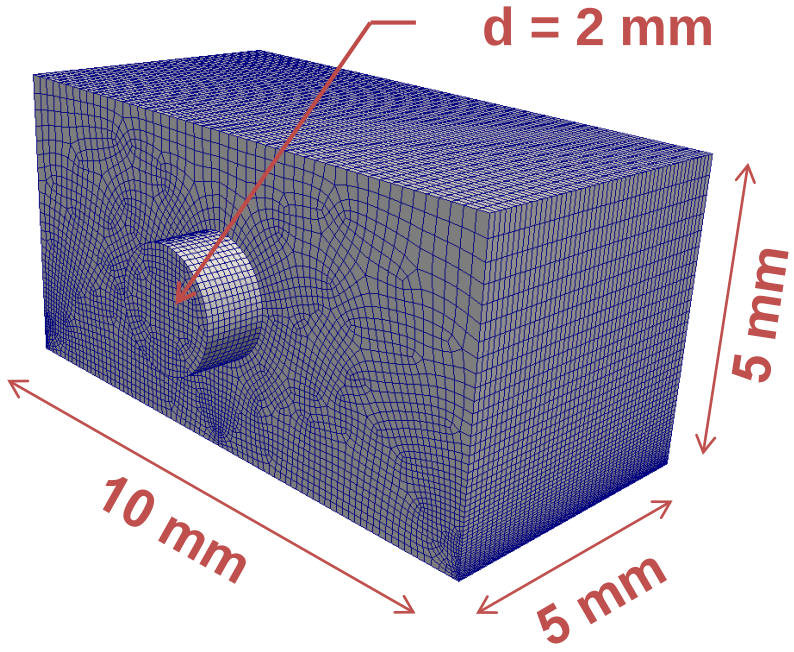
K. Reuter and M. Scheffler, *Phys. Rev. B* 73, 045433 (2006)

An example: The reactor STM (II)



Operating conditions
T: 600 K
P: 1 atm
Inlet: CO + O2 (66%, 34% Vol)
Inlet velocity: 5 cm/s

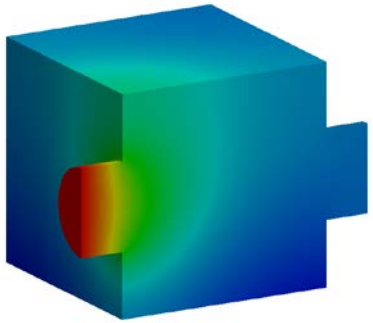
Catalytic Wall
Catalyst: Ru_2O

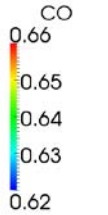


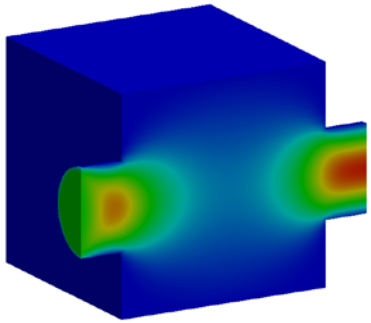
Computational details
Mesh: unstructured, ~90,000 cells
Discretization: 2nd order, centered
Max time step: 10^{-4} s
CPU time: ~2 s per time step

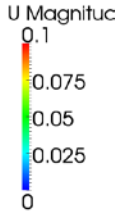
An example: The reactor STM (III)

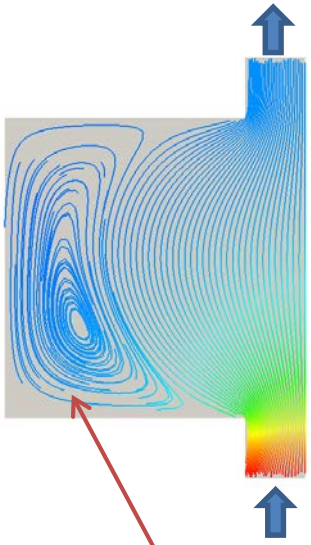
Steady-state results

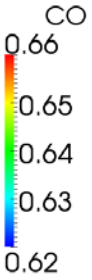


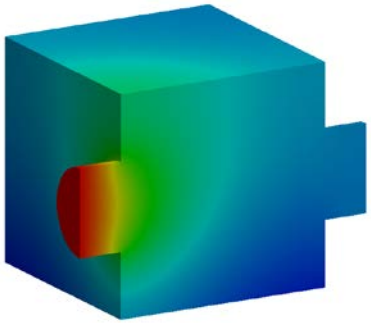


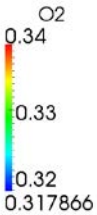


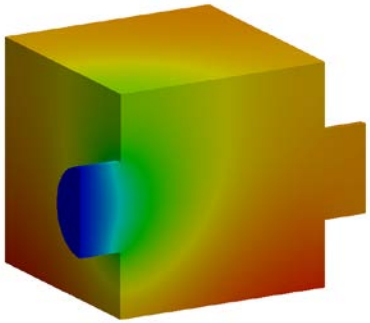












Strong recirculations

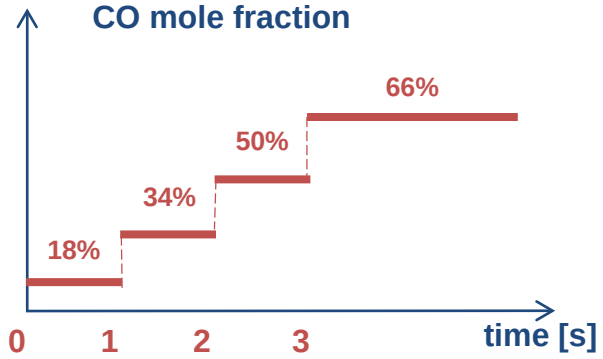
An example: The reactor STM (IV)

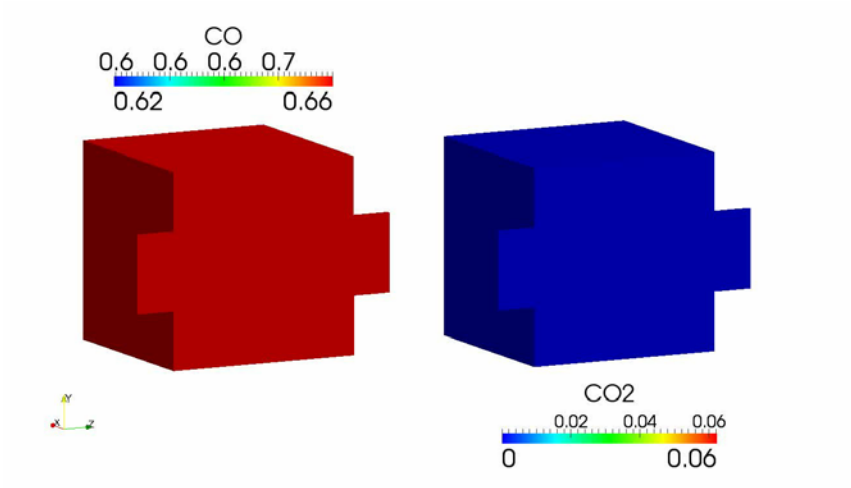
Dynamic results

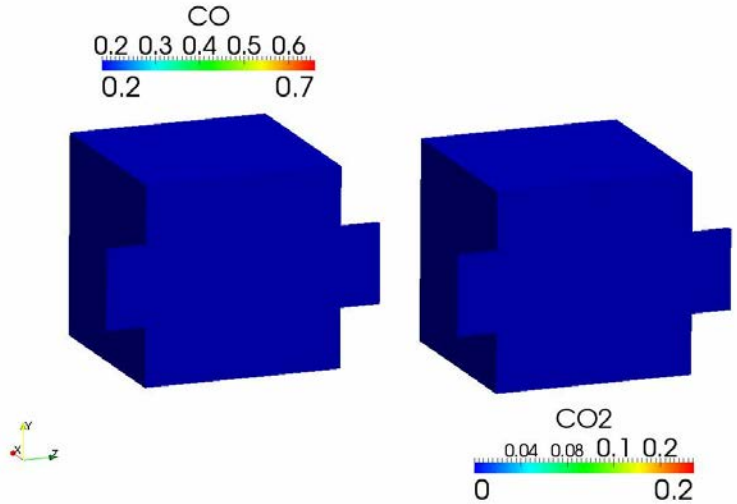
Operating conditions
T: 600 K
P: 1 atm
Inlet: CO + O2 (66%, 34% Vol)
Inlet velocity: 5 cm/s

Initial conditions:
CO + O2 (66%, 34% Vol)

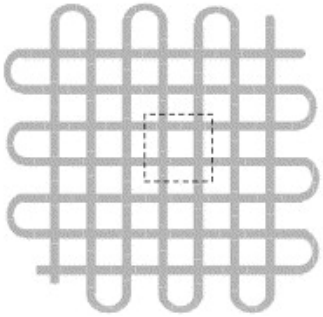
The CO mole fraction in the inlet stream increases during the time



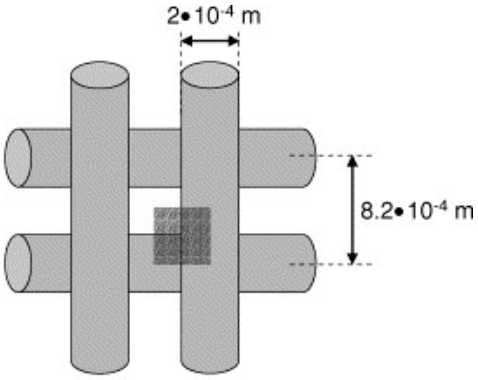




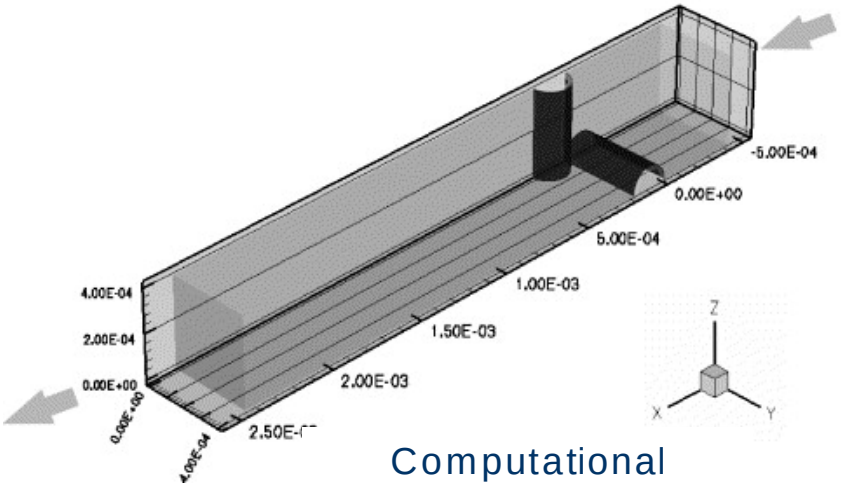
An example: the catalytic gauze (I)



Original gauze structure

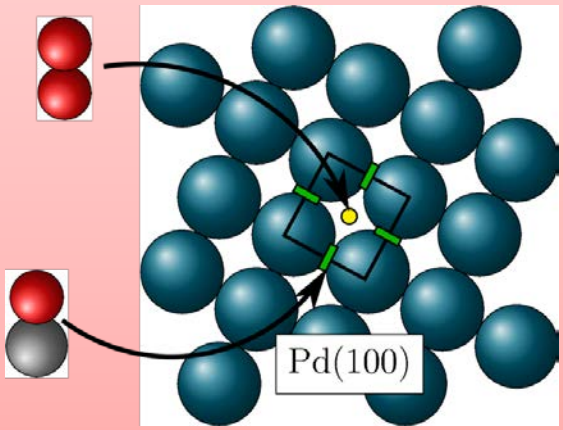


Detail of wire intersections

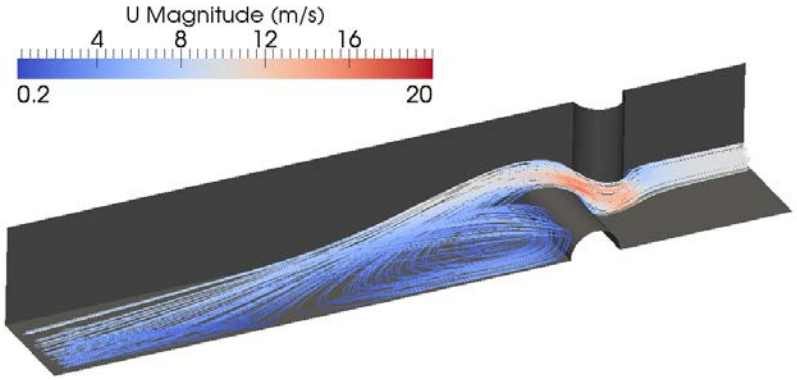


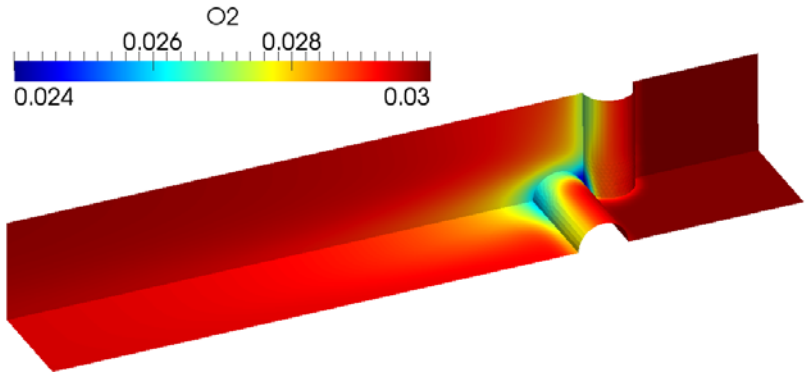
Computational domain

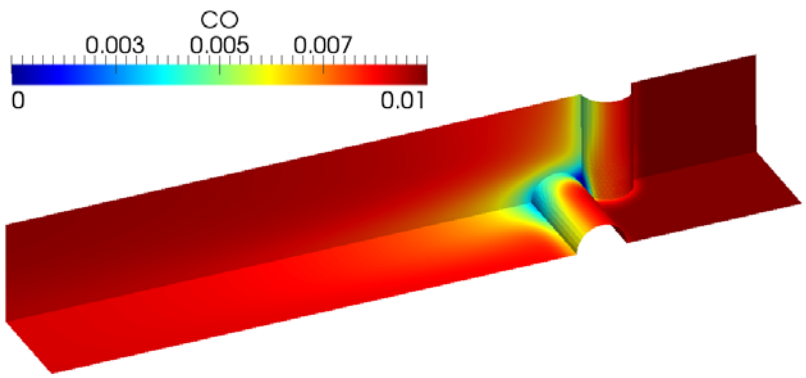
- Rate constants $k(x,y)$ from DFT and harmonic Transition State Theory
- Model system: CO oxidation on Pd(100):

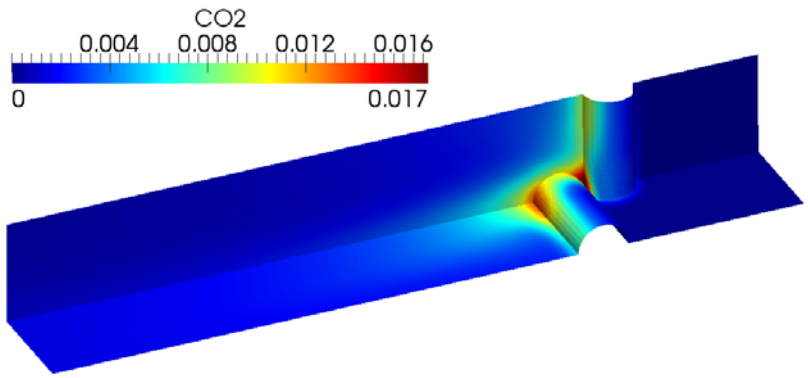


An example: the catalytic gauze (II)

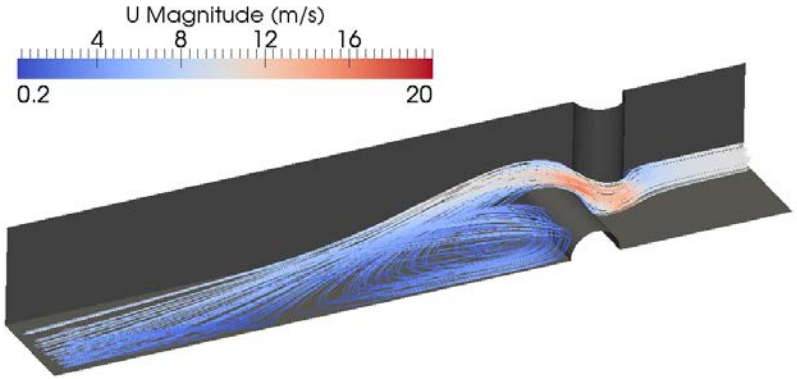


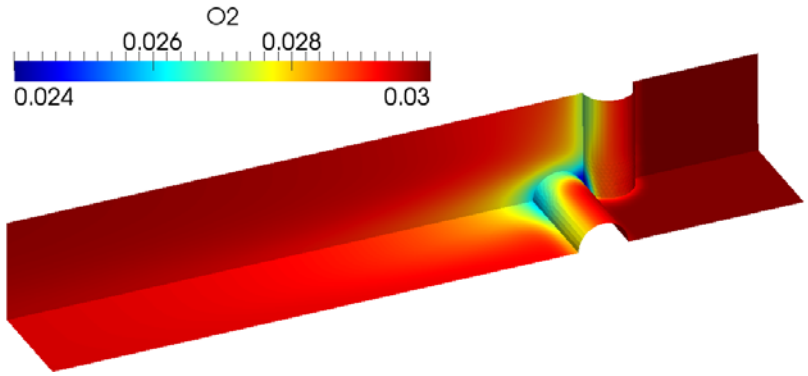


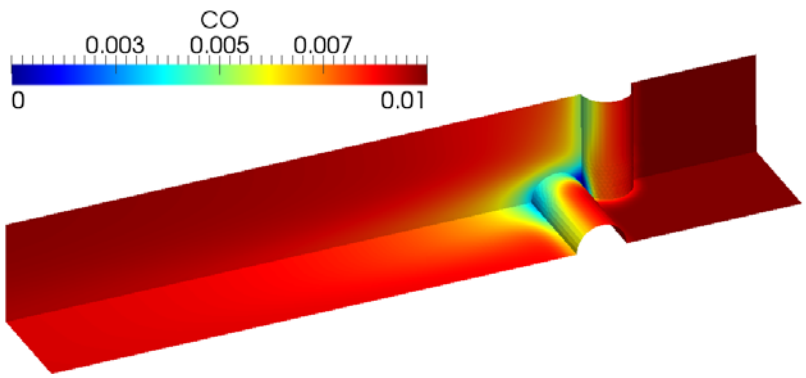


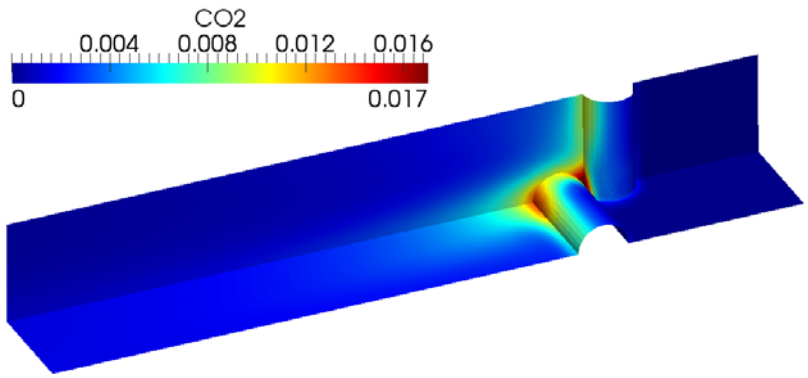


An example: the catalytic gauze (III)









DFT → **kMC** → **CFD**

The catalyticFOAM Group

POLITECNICO DI MILANO

The catalyticFOAM Group

Matteo Maestri
heterogeneous catalysis, multiscale modeling, microkinetic modeling

Alberto Cuoci
CFD, numerical methods

Stefano Rebughini (PhD Student)
Hierarchical analysis of complex reacting systems

Mauro Bracconi (PhD student)
ISAT, complex geometries

Former Students

Sandro Goisis and Alessandra Osio
Development of numerical methodology

Tiziano Maffei
Improvement of multi-region solver

Giancarlo Gentile and Filippo Manelli
Development of multi-region solver

The catalyticFOAM web-site

The catalyticFOAM code can be freely downloaded from our web site:

http://www.catalyticfoam.polimi.it/

Statistics since April 2013

Unique visitors: 2,500

Visits: 4,200 (~6 per day)

Visits from 76 different countries

About 200 registered users

Release - Policy

The catalyticFOAM software is fully compatible with OpenFOAM version 2.3.x.

Nevertheless, it is not approved or endorsed by ESI/OpenCFD, the producer of the OpenFOAM software and owner of the OPENFOAM® and OpenCFD® trade marks.

Software is released under the L-GPL license through an independent webiste: www.catalyticfoam.polimi.it

Publications

Publications on international journals

M.Maestri, A.Cuoci, *Coupling CFD with detailed microkinetic modeling in heterogeneous catalysis,* Chemical Engineering Science 96(7), pp. 106-117 (2013) DOI: 10.1016/j.ces.2013.03.048

Matera, S., Maestri, M., Cuoci, A., Reuter, K. , *Predictive-quality surface reaction chemistry in real reactor models: Integrating first-principles kinetic monte carlo simulations into computational fluid dynamics,* ACS Catalysis 4(11), pp. 4081-4092 (2014) DOI: 10.1021/cs501154e

Maffei, T., Rebughini, S., Gentile, G., Lipp, S., Cuoci, A., Maestri, M., *Handling Contact Points in Reactive CFD Simulations of Heterogeneous Catalytic Fixed Bed Reactors,* Submitted to Industrial & Engineering Chemistry Research (2015)

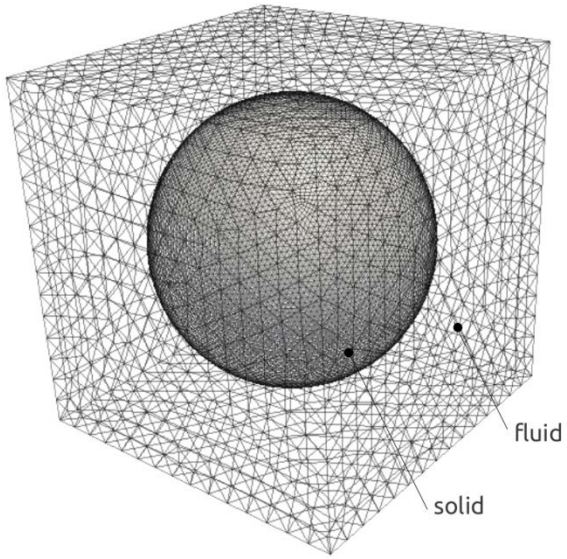
T. Maffei, G. Gentile, F. Manelli, S. Lipp, M.Maestri, A.Cuoci, *Multi-region approach in modeling gas-solid catalytic reactors,* In preparation

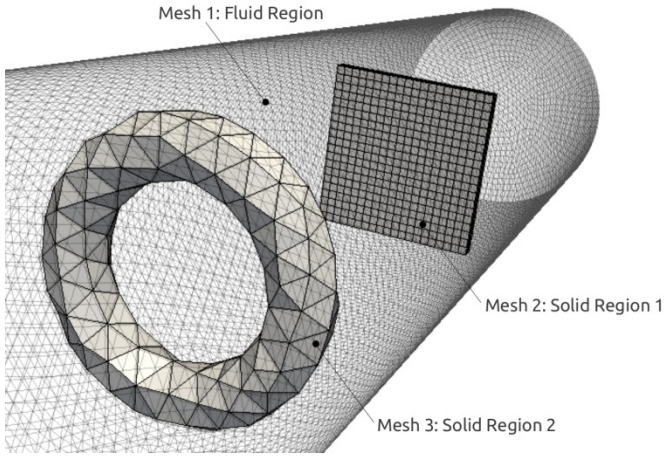
Additional slides

Outline

- ✓ Introduction and motivation
- ✓ **Development of the catalyticFOAM solver for the OpenFOAM® framework**
  - ✓ Governing equations
  - ✓ Numerical methodology
  - ✓ **Extension to the multi-region modeling**
- ✓ Validation and examples
  - ✓ Annular reactor (simple chemistry)
  - ✓ CPO of CH_4 on platinum gauze (complex 3D geometry)
  - ✓ CPO of iso-octane (complex chemistry)
  - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
  - ✓ Packed bed reactors for industrial applications (complex 3D geometry)
  - ✓ Micro-channel reactors (Hierarchical analysis)
- ✓ Extensions
  - ✓ KMC (Kinetic Monte Carlo)
- ✓ Conclusions and future works

Motivation



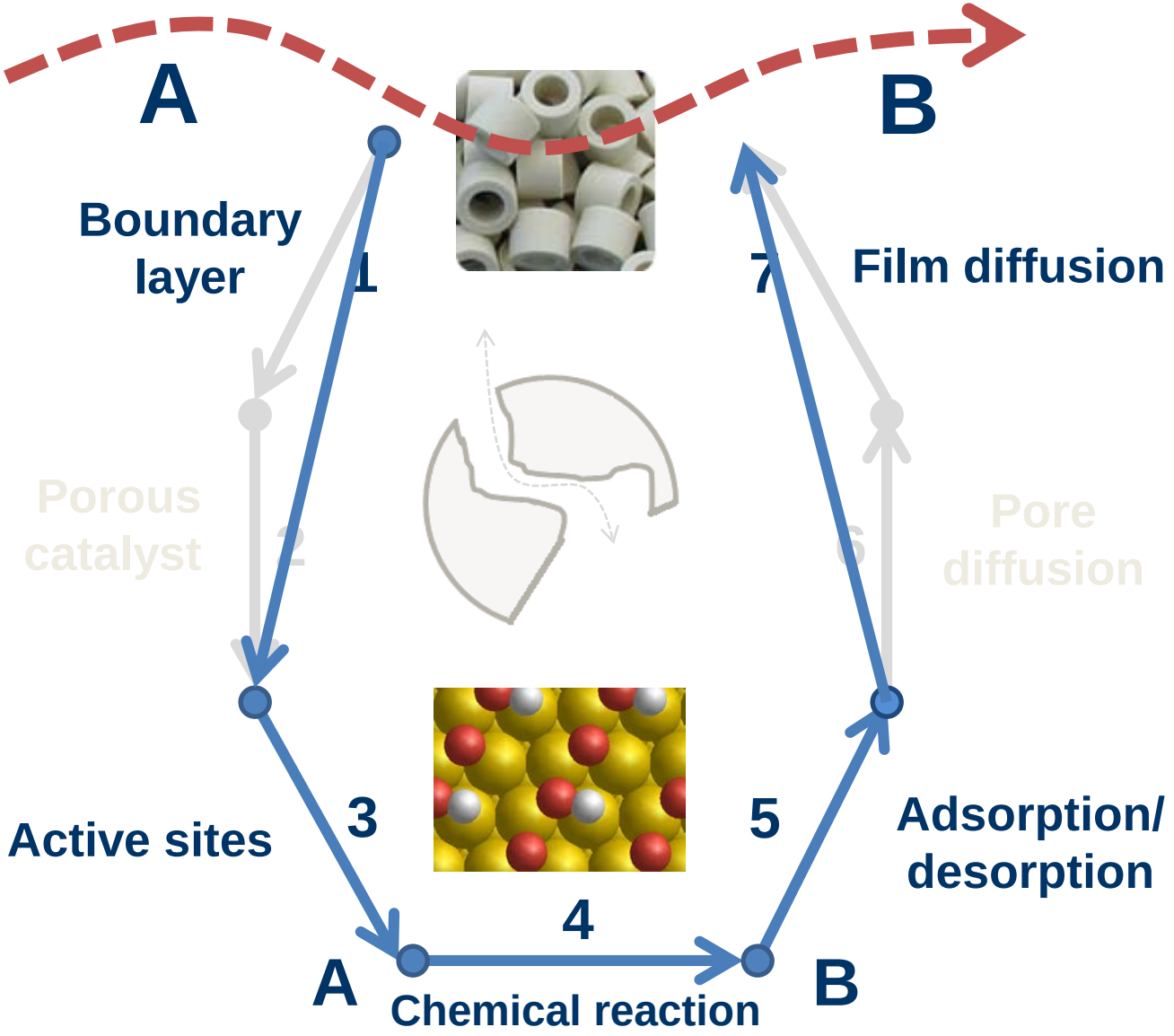


- ✓ In the original version of catalyticFOAM the catalyst morphology is not detailed
- ✓ the presence of the catalyst was accounted for by as boundary condition imposing continuity between the reactive flux and the diffusive flux to and from the catalytic surface.

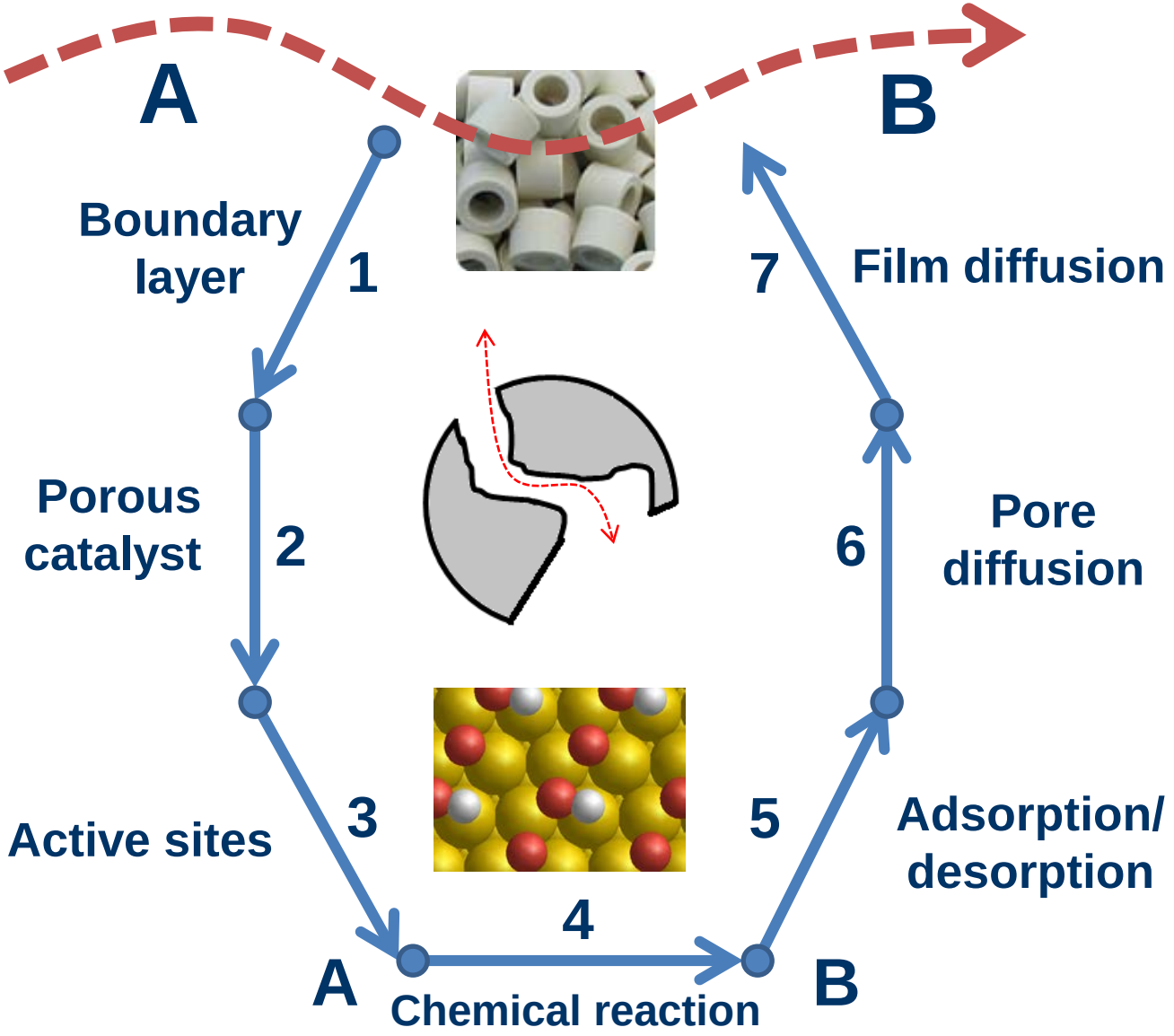
This approach does not account for diffusive limitations in the solid phase or in general for the intra-solid transport phenomena

Need of a Multi-Region Solver (gas phase + solid phases)

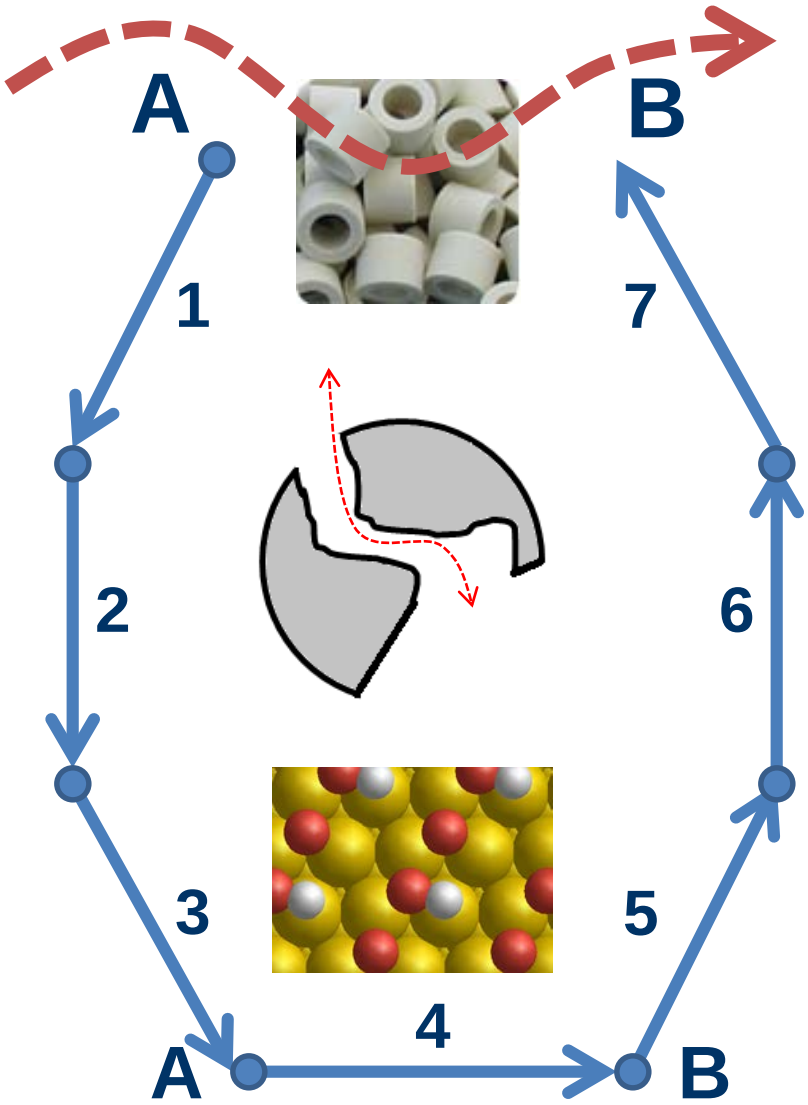
Microkinetic modeling and CFD



Internal transport phenomena



Internal transport phenomena



Gas Phase

$$\begin{cases} \dfrac{\partial(\rho\omega_i)}{\partial t} + \nabla(\rho \boldsymbol{U}\omega_i) = \nabla(\rho D_i \nabla\omega_i) + \sum_j R_j \nu_{ij} MW_i \\ c_p \dfrac{\partial(\rho T)}{\partial t} + c_p \nabla(\rho \boldsymbol{U} T) = \nabla(\mathrm{k}\nabla \mathrm{T}) + \sum_j R_j \Delta H_j \\ \dfrac{\partial(\rho \boldsymbol{U})}{\partial t} + \nabla(\rho \boldsymbol{U}\boldsymbol{U}) = -\nabla p + \nabla(\mu \nabla \boldsymbol{U}) + \rho \boldsymbol{g} \\ \dfrac{\partial \rho}{\partial t} + \nabla(\rho \boldsymbol{U}) = 0 \end{cases}$$

Solid Phase

$$\begin{cases} \dfrac{\partial(\rho^{mix}\omega_i)}{\partial t} = \nabla\left(\rho^{mix} D_{eff,i} \nabla\omega_i\right) + \left(\sum_j R_{het,j} \nu_{ij} MW_i\right) \cdot a_{cat} \\ c_{p,sol} \dfrac{\partial(\rho_{sol} T)}{\partial t} = \nabla\left(\mathrm{k}_{eff} \nabla \mathrm{T}\right) + \sum_j R_{het,j} \Delta H_j \cdot a_{cat} \\ \Gamma_{site} \dfrac{\partial \vartheta_i}{\partial t} = R_{i,surf} \end{cases}$$

Multiple meshes for multiple regions

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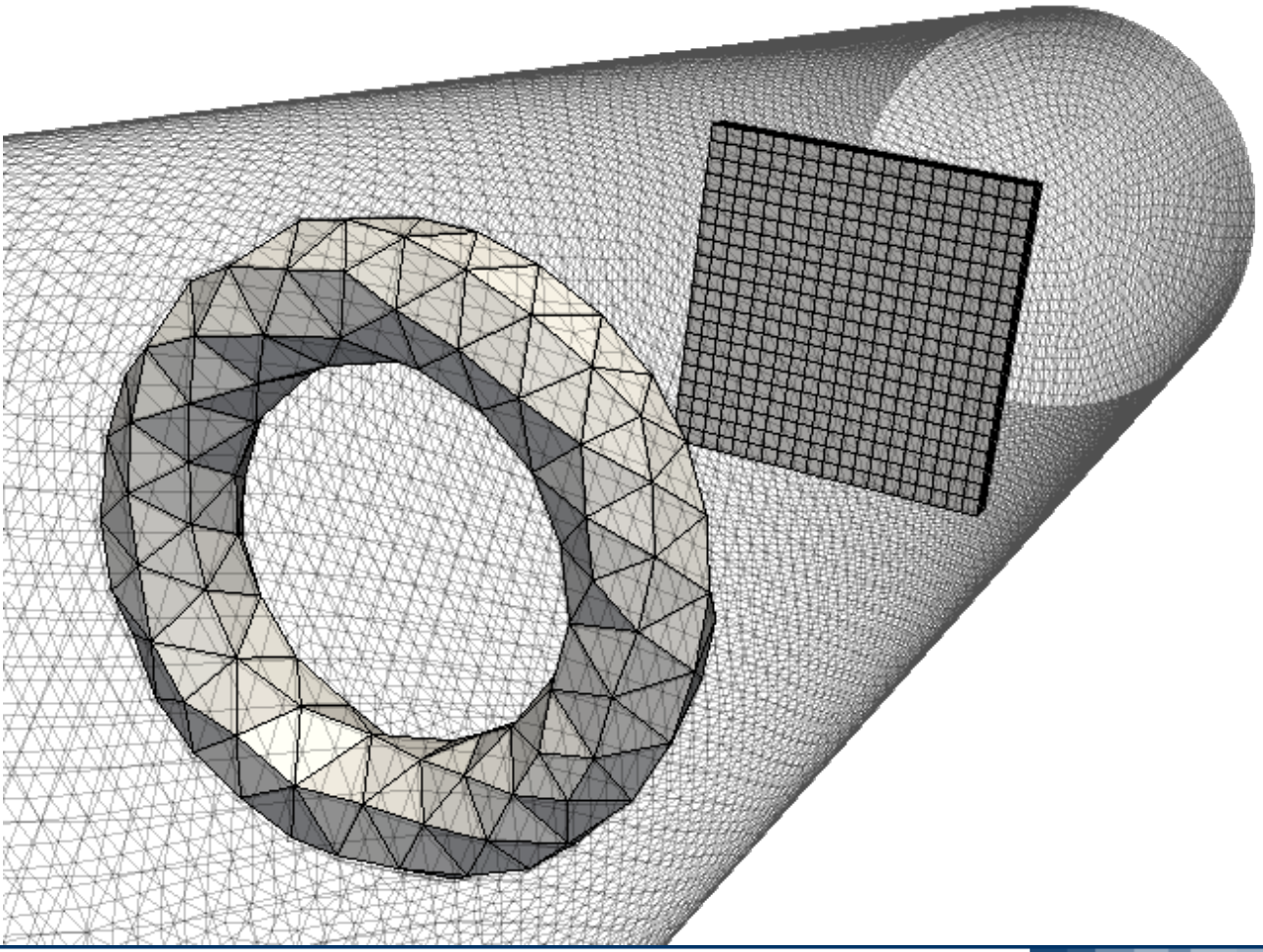
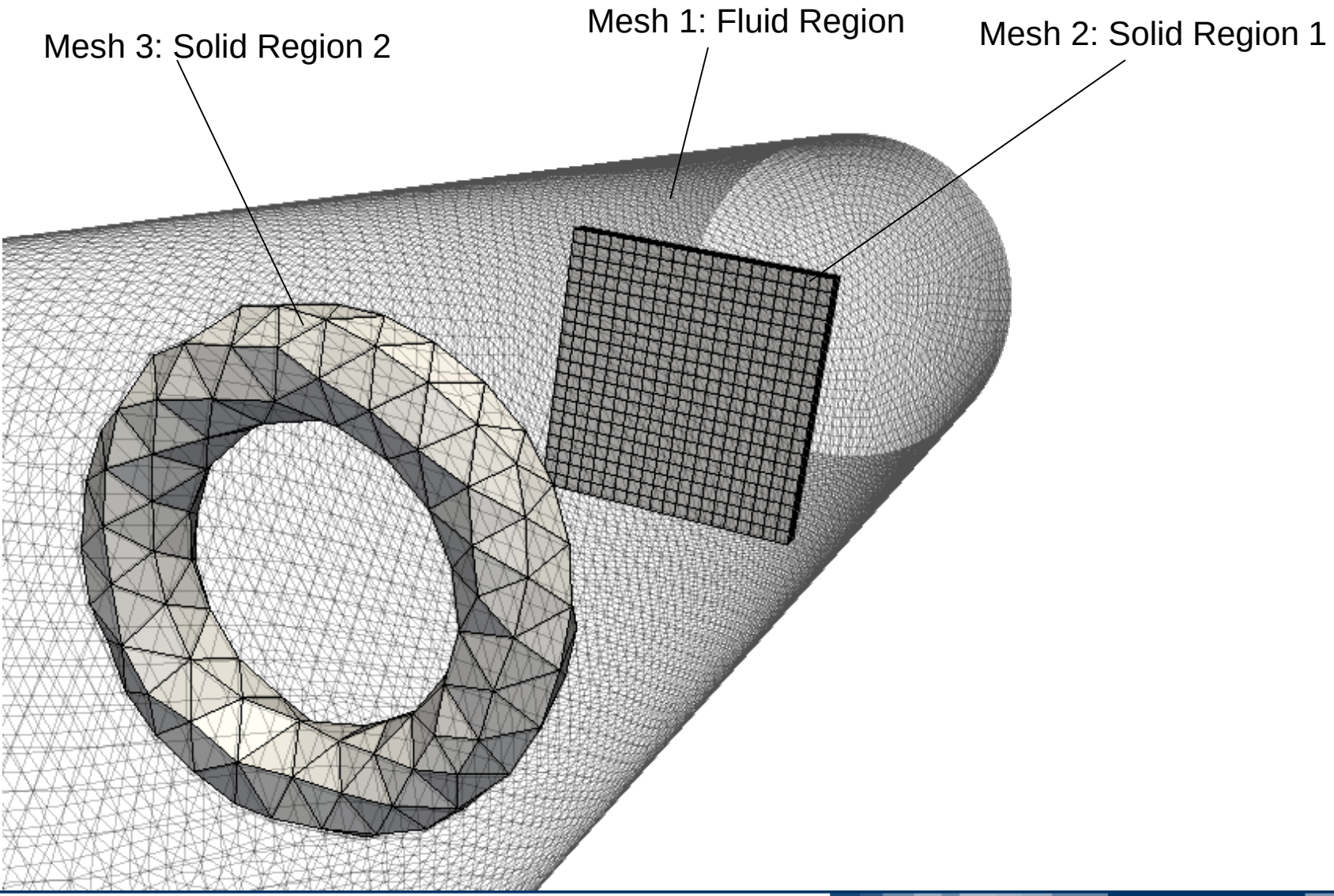
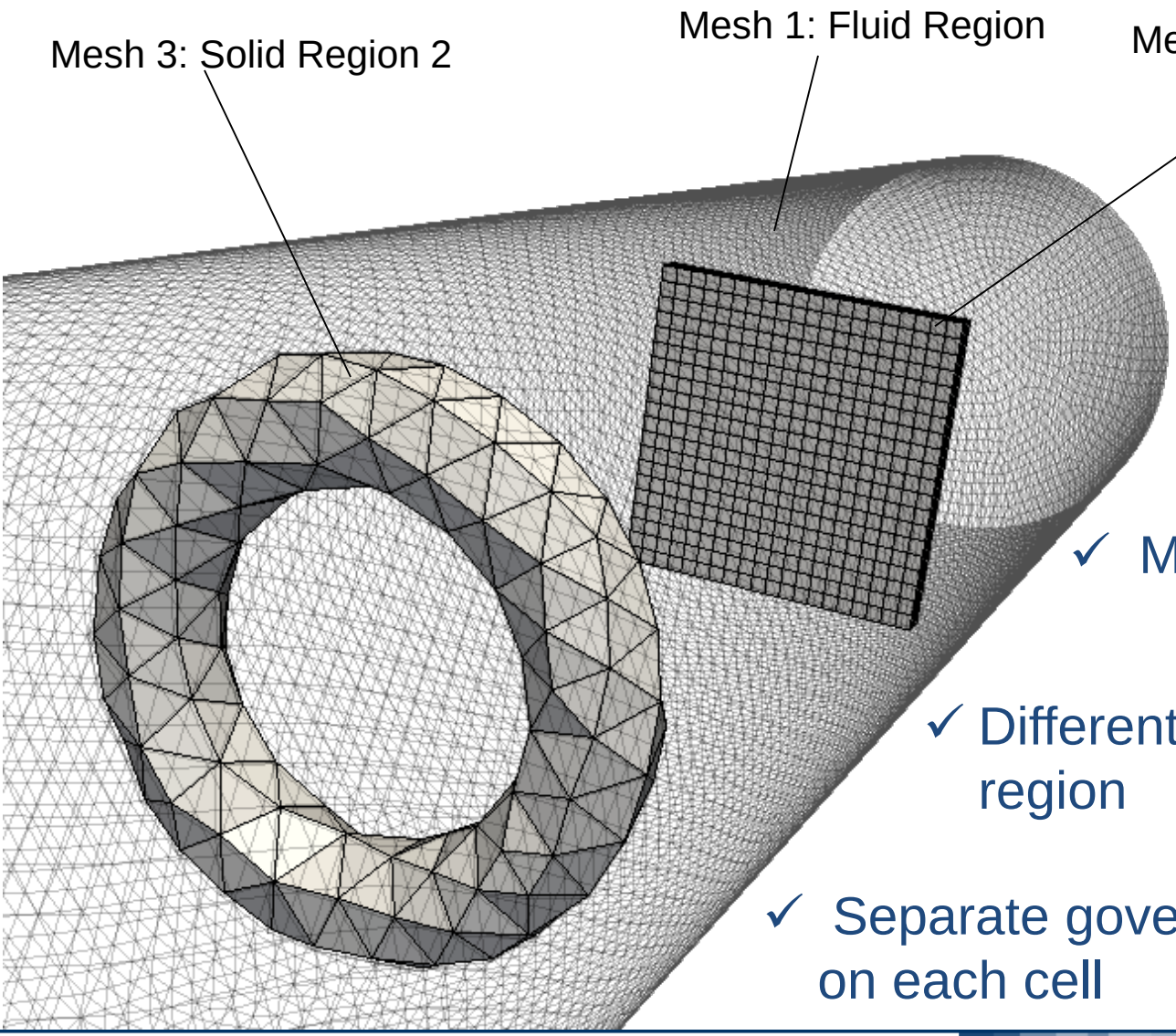


Multiple meshes for multiple regions



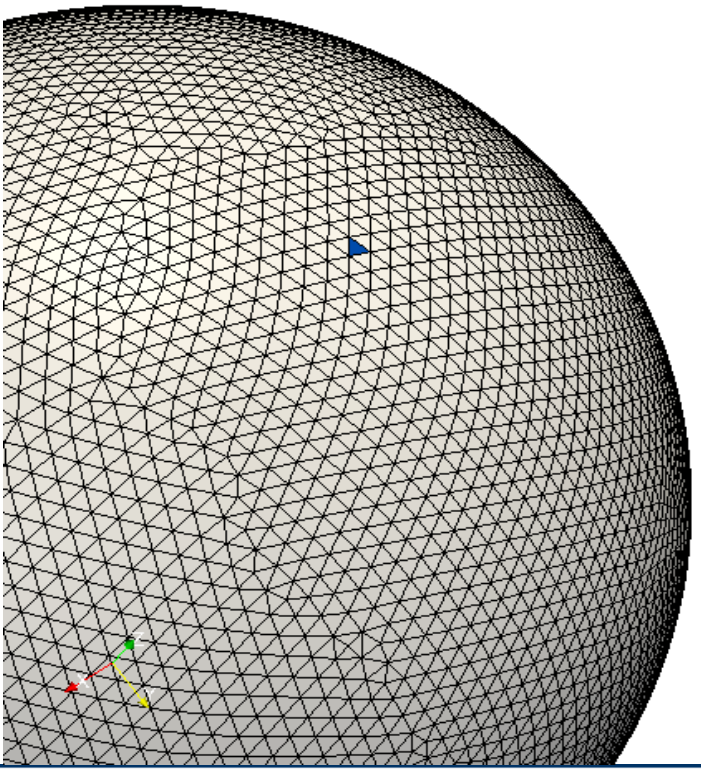
Multiple meshes for multiple regions



- ✓ Multiple meshes
- ✓ Different properties for each region
- ✓ Separate governing equations on each cell

Linking the regions

How to couple at the interface?

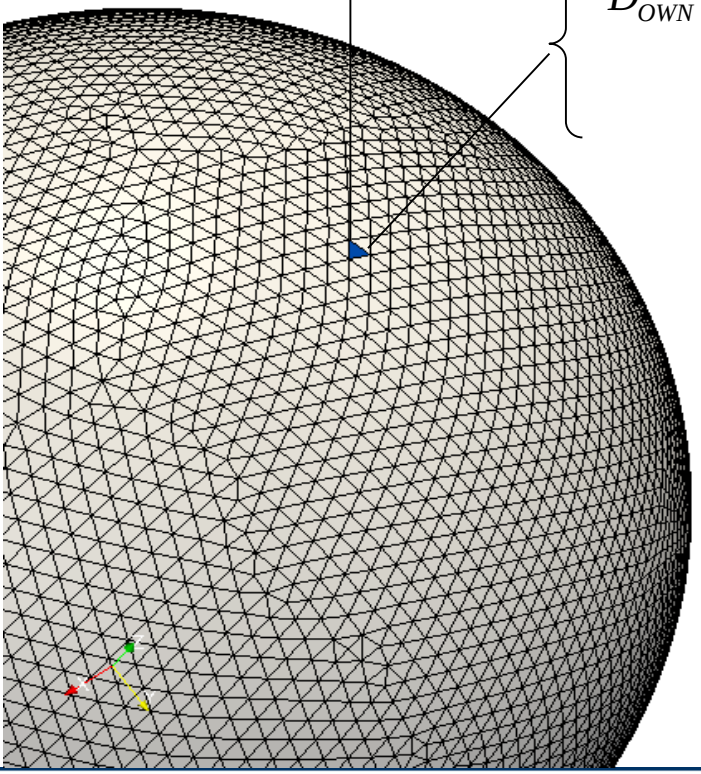


Linking the regions

$$\begin{cases} k_{\mathrm{OWN,I}} \nabla T_{OWN(I)} = k_{\mathrm{NBR,I}} \nabla T_{NBR(I)} \\ T_{\mathrm{OWN,I}} = T_{\mathrm{NBR,I}} \end{cases}$$

How to couple at the interface?

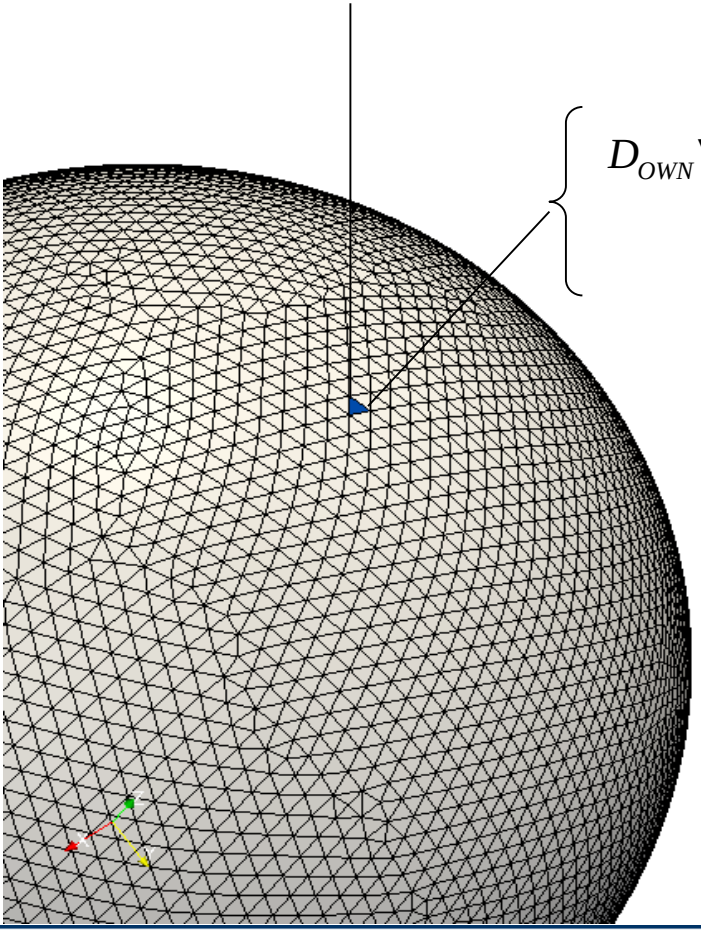
$$\begin{cases} D_{OWN} \nabla C_{OWN(I)} = D_{NBR} \nabla C_{NBR(I)} \\ C_{\mathrm{OWN,I}} = C_{\mathrm{NBR,I}} \end{cases}$$



Linking the regions

$$\begin{cases} k_{\mathrm{OWN,I}} \nabla T_{OWN(I)} = k_{\mathrm{NBR,I}} \nabla T_{NBR(I)} \\ T_{\mathrm{OWN,I}} = T_{\mathrm{NBR,I}} \end{cases} \Rightarrow T_{I.OWN} = \frac{\frac{k_{OWN} \cdot T_{OWN}}{\Delta_{OWN}} + \frac{k_{NBR} \cdot T_{NBR}}{\Delta_{NBR}}}{\frac{k_{OWN}}{\Delta_{OWN}} + \frac{k_{NBR}}{\Delta_{NBR}}}$$

Mixed boundary conditions at the interface



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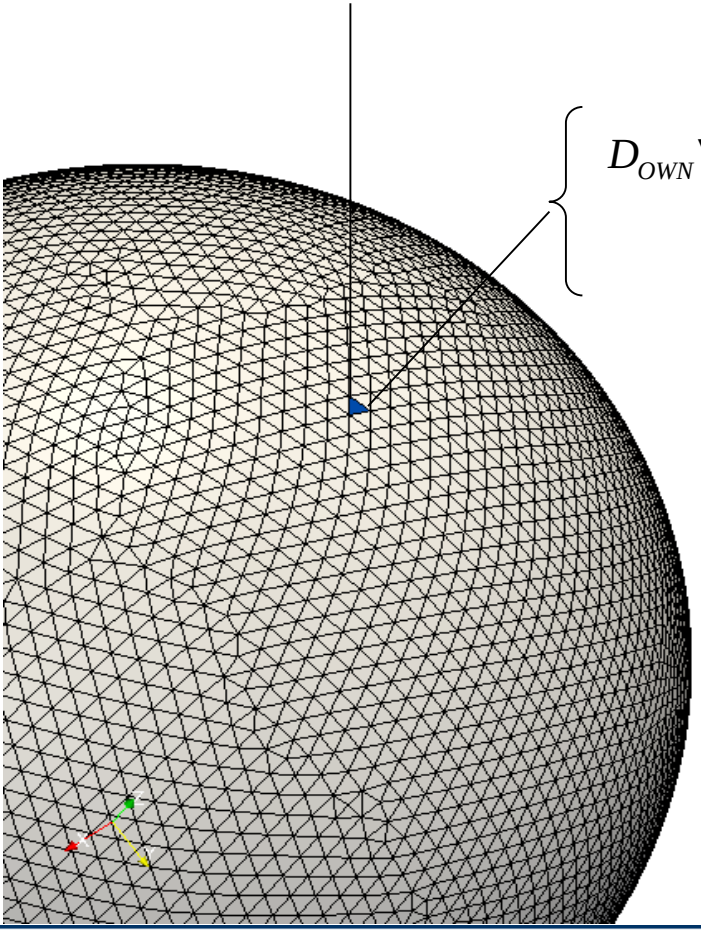

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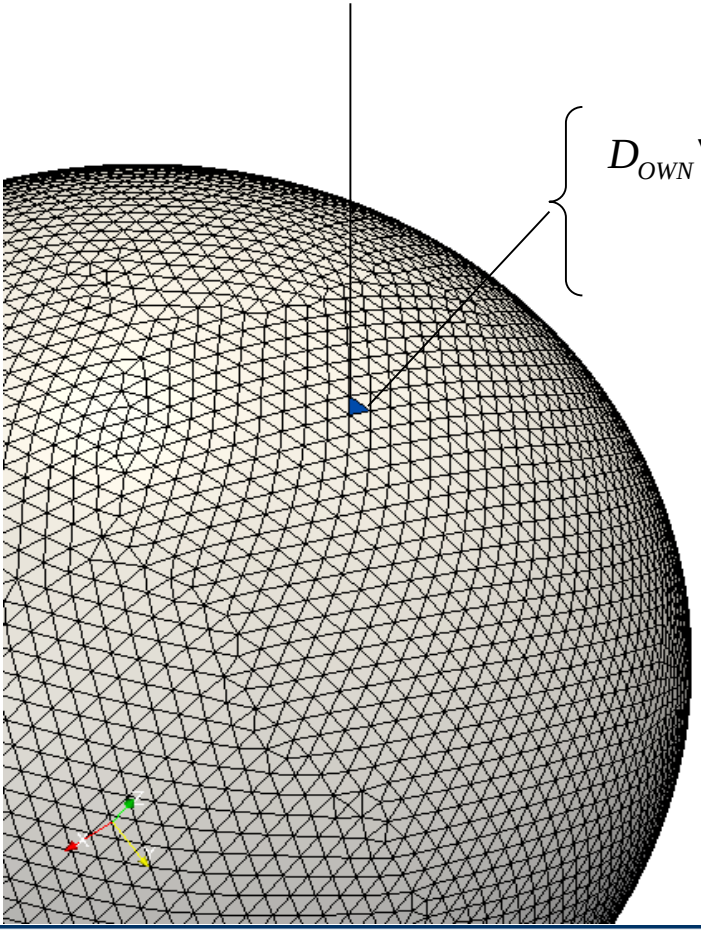
Partitioned Approach

1) Solve in each zone with mixed BCs

Linking the regions

$$\begin{cases} k_{\mathrm{OWN,I}} \nabla T_{OWN(I)} = k_{\mathrm{NBR,I}} \nabla T_{NBR(I)} \\ T_{\mathrm{OWN,I}} = T_{\mathrm{NBR,I}} \end{cases} \Rightarrow T_{I.OWN} = \frac{\frac{k_{OWN} \cdot T_{OWN}}{\Delta_{OWN}} + \frac{k_{NBR} \cdot T_{NBR}}{\Delta_{NBR}}}{\frac{k_{OWN}}{\Delta_{OWN}} + \frac{k_{NBR}}{\Delta_{NBR}}}$$

Mixed boundary conditions at the interface



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Partitioned Approach

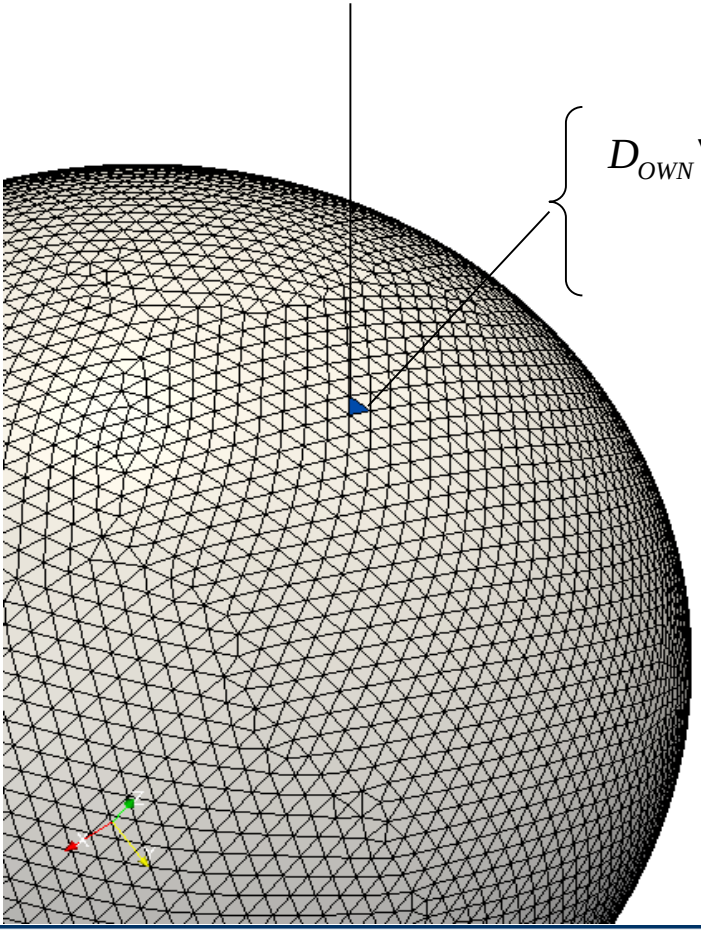
1) Solve in each zone with mixed BCs

2) Update interface values and solve in the neighboring region

Linking the regions

$$\begin{cases} k_{\mathrm{OWN,I}} \nabla T_{OWN(I)} = k_{\mathrm{NBR,I}} \nabla T_{NBR(I)} \\ T_{\mathrm{OWN,I}} = T_{\mathrm{NBR,I}} \end{cases} \Rightarrow T_{I.OWN} = \frac{\frac{k_{OWN} \cdot T_{OWN}}{\Delta_{OWN}} + \frac{k_{NBR} \cdot T_{NBR}}{\Delta_{NBR}}}{\frac{k_{OWN}}{\Delta_{OWN}} + \frac{k_{NBR}}{\Delta_{NBR}}}$$

Mixed boundary conditions at the interface



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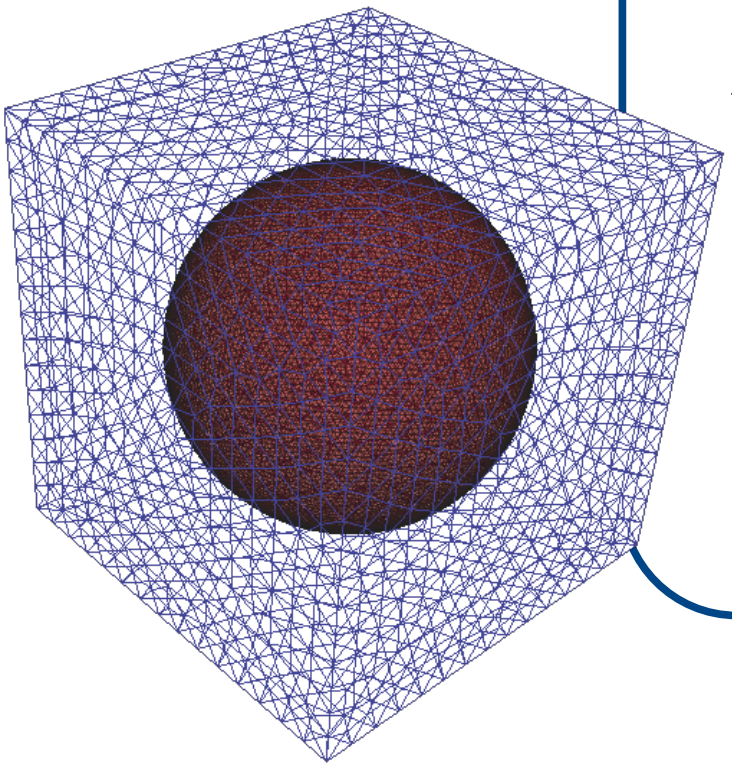
Partitioned Approach

1) Solve in each zone with mixed BCs
2) Update interface values and solve in the neighboring region
3) Iterate till convergence is reached

Coupling structure



Fluid Region

$$\frac{d\left(\rho_{mix} Y_i\right)}{dt} = \nabla\left(\rho_{mix} D_{\mathrm{mix,i}} \nabla\left(Y_i\right)\right) - \nabla\left(\Phi Y_i\right)$$

$$\frac{d\left(\rho_{mat} c_p T\right)}{dt} = \nabla\left(k \nabla\left(T\right)\right) - C_p^{mix} \nabla\left(\Phi T\right)$$

with the mixed BCs on the interface:

$$T_{\mathrm{I,FLU}} = \frac{\frac{k_{FLU} \cdot T_{FLU}}{\Delta_{FLU}} + \frac{k_{SOL} \cdot T_{SOL}}{\Delta_{SOL}}}{\frac{k_{FLU}}{\Delta_{FLU}} + \frac{k_{SOL}}{\Delta_{SOL}}}$$

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Coupling structure

Solid Region

$$\begin{cases} \dfrac{d(\rho_{mix} Y_i)}{dt} = \nabla\left(\rho_{mix} D_{\mathrm{mix,i}} \nabla(Y_i)\right) \\ \dfrac{d(\rho_{mat} c_p T)}{dt} = \nabla(k \nabla(T)) \end{cases}$$

with the mixed BCs on the interface:

$$T_{\mathrm{I,SOL}} = \frac{\dfrac{k_{SOL} \cdot T_{SOL}}{\Delta_{SOL}} + \dfrac{k_{FLU} \cdot T_{FLU}}{\Delta_{FLU}}}{\dfrac{k_{SOL}}{\Delta_{SOL}} + \dfrac{k_{FLU}}{\Delta_{FLU}}}$$

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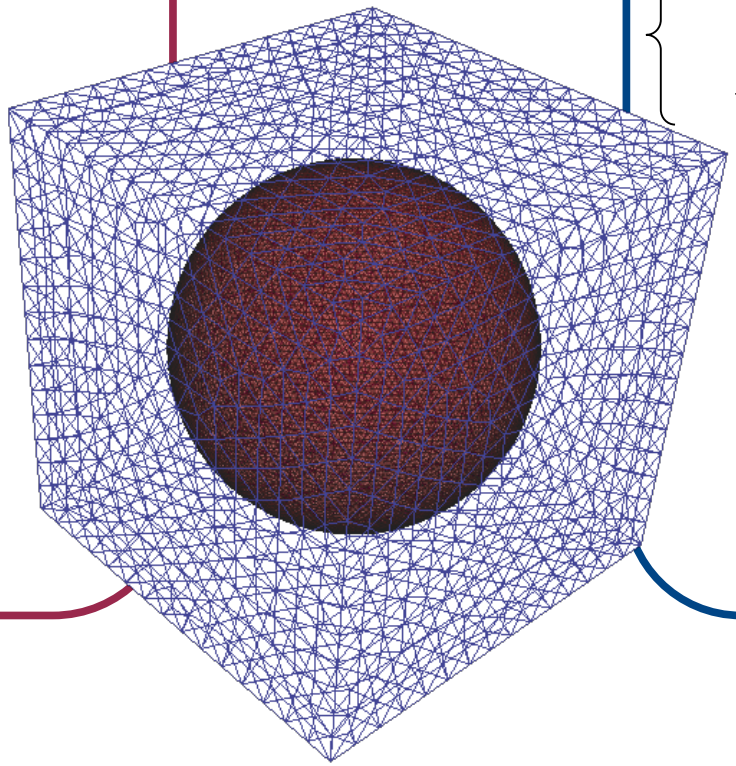

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Coupling structure

Solid Region

$$\begin{cases} \dfrac{d(\rho_{mix} Y_i)}{dt} = \nabla\left(\rho_{mix} D_{\mathrm{mix,i}} \nabla(Y_i)\right) \\ \dfrac{d(\rho_{mat} c_p T)}{dt} = \nabla(k \nabla(T)) \end{cases}$$

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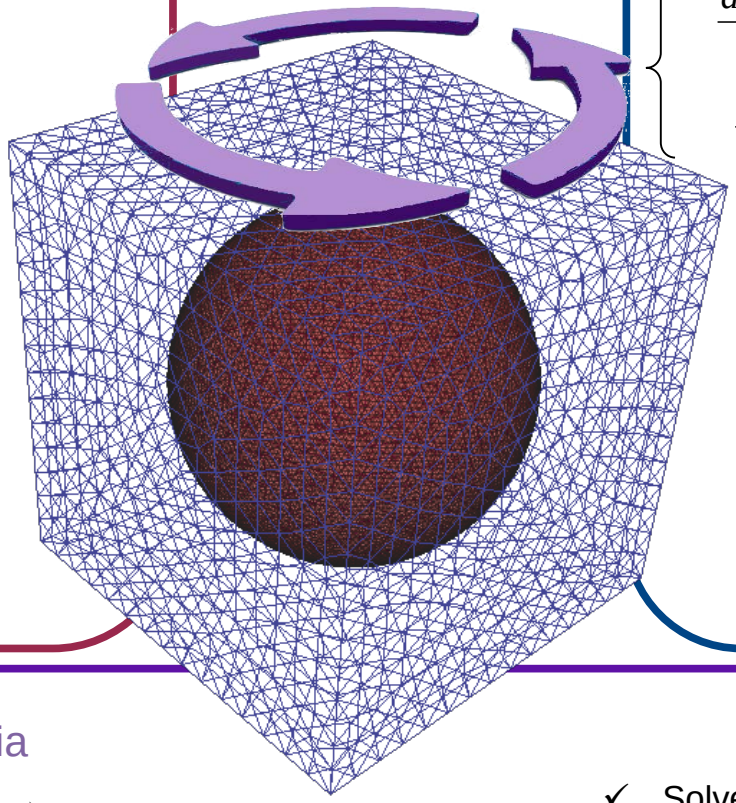

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Convergence Criteria

$$\left|T^{(k)} - T^{(k-1)}\right| \le absTol_T \quad \left|T^{(k)} - T^{(k-1)}\right| \div T^{(k-1)} \le relTol_T$$

$$\left|Y_i^{(k)} - Y_i^{(k-1)}\right| \le absTol_Y \quad \left|Y_i^{(k)} - Y_i^{(k-1)}\right| \div Y_i^{(k-1)} \le relTol_Y$$

Coupling Loop

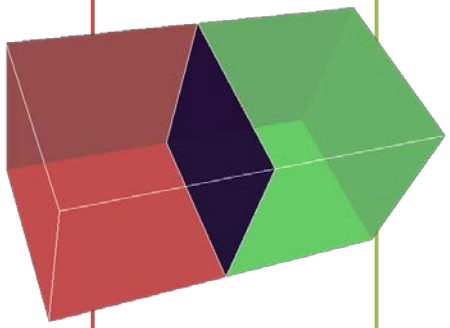
Coupling Method

- ✓ Solve alternatively for every cell of the 2 coupled regions
- ✓ Check for convergence: if reached, proceed to next time step

Multi-region solver architecture

for each time step...

Solve Solid



Solve Fluid

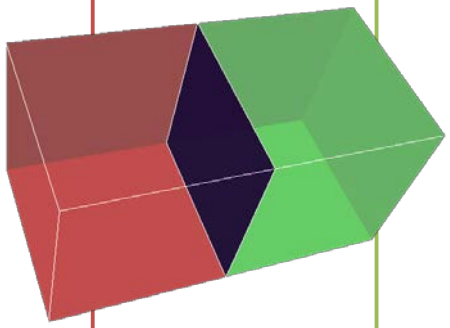
↓

Multi-region solver architecture

for each time step...

Solve Solid

Solve Fluid



Continuity Equation

Navier-stokes Equations

Pressure Corrector

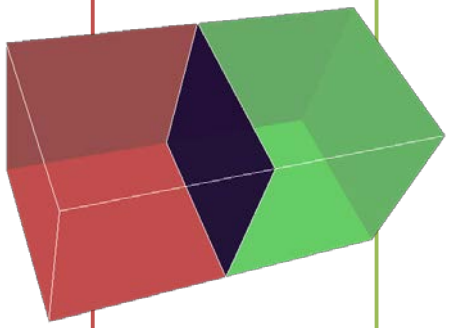
PISO predictor-corrector loop

Multi-region solver architecture

for each time step...

Solve Solid

Solve Fluid



- Continuity Equation
- Mass Transfer Equation
- Heat Transfer Equation
- Fluid Chemistry
  - Homogeneous reactions
- Update Fluid Properties
- Navier-stokes Equations
- Pressure Corrector

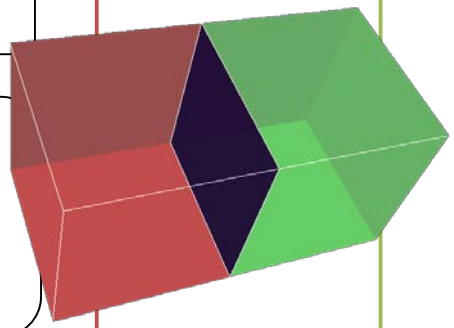
PISO predictor-corrector loop

Multi-region solver architecture

for each time step...

Solve Solid

- Mass Transfer Equation
- Heat Transfer Equation
- Solid Chemistry
  - Homogeneous and heterogeneous reactions
  - Site species conservation
- Update Solid Properties



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PISO predictor-corrector loop

Multi-region solver architecture

for each time step...

Solve Solid

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- Heat Transfer Equation
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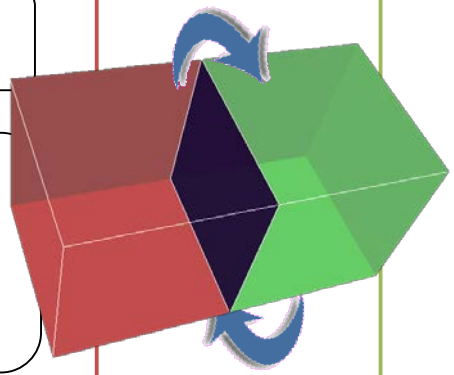
  - Homogeneous and heterogeneous reactions
  - Site species conservation
- Update Solid Properties

Coupling loop convergence check

Coupling Loop



Coupling Loop

Solve Fluid

- Continuity Equation
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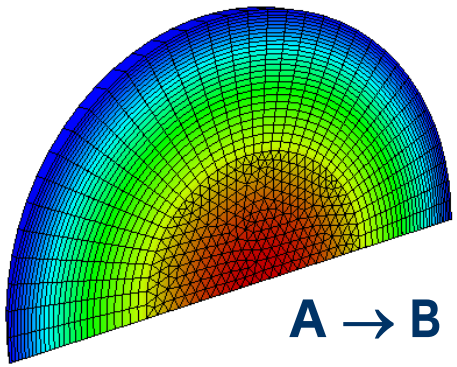
- Pressure Corrector

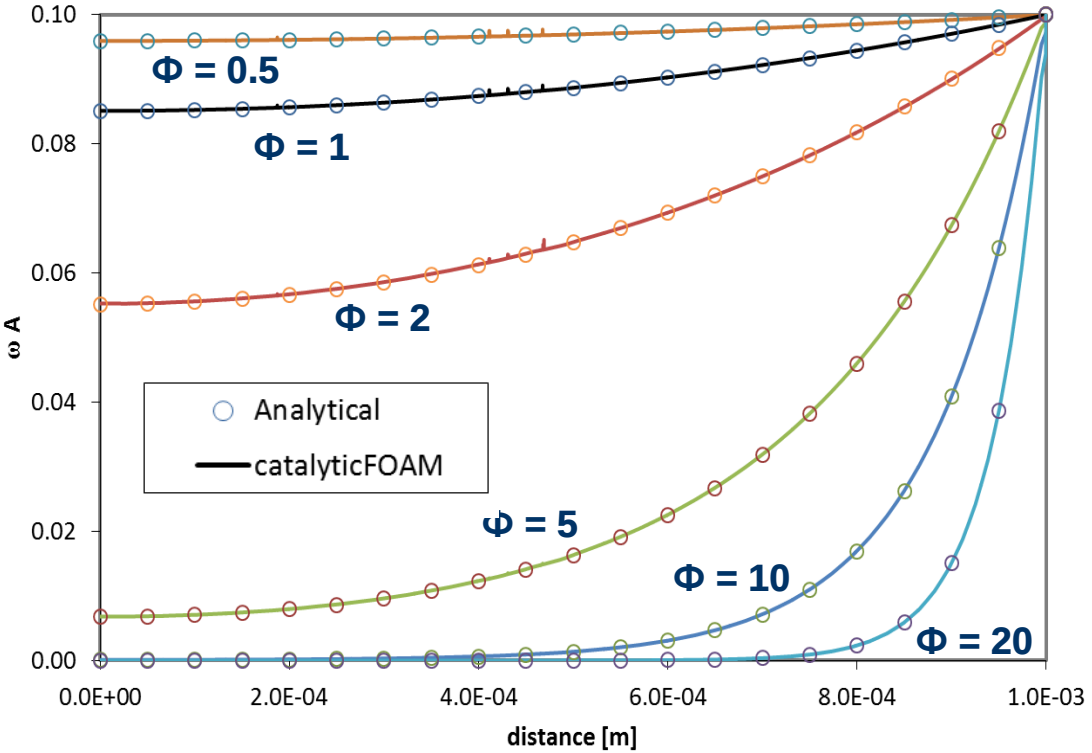
PISO predictor-corrector loop

CatalyticFOAM multiRegion

Validation with analytical solution

$$\wp_{A,eff}\,\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dC_A}{dr}\right)=k_r C_A \quad\Longrightarrow\quad C_A = C_{A,s}\,\frac{\sinh\left(\phi\dfrac{r}{R}\right)}{\dfrac{r}{R}\sinh(\phi)}$$





Outline

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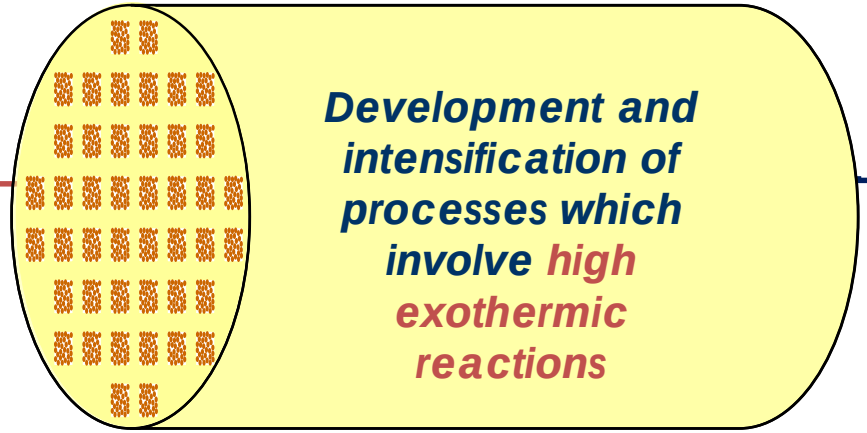
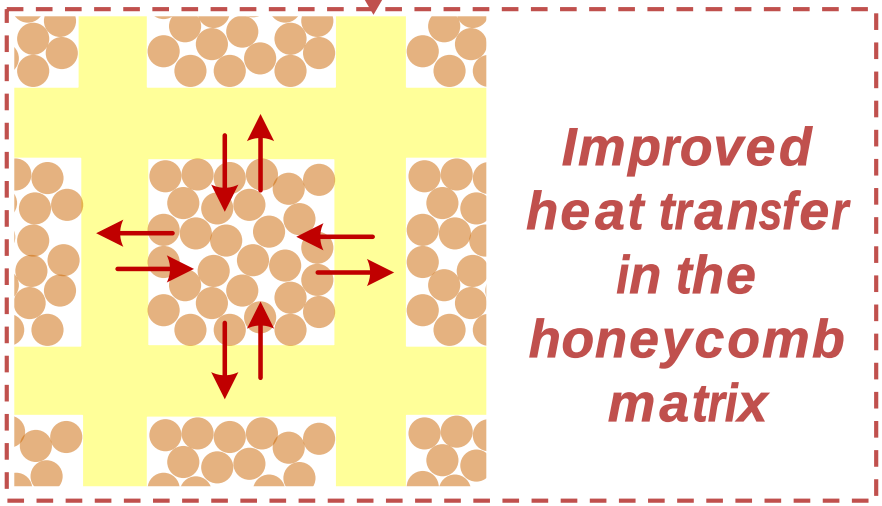
  - ✓ CPO of iso-octane (complex chemistry)
  - ✓ Tubular reactor with Raschig rings (complex 3D geometry)
  - ✓ Packed bed reactors for industrial applications (complex 3D geometry)
  - ✓ **Micro-channel reactors (Hierarchical analysis)**
- ✓ Extensions
  - ✓ KMC (Kinetic Monte Carlo)
- ✓ Conclusions and future works

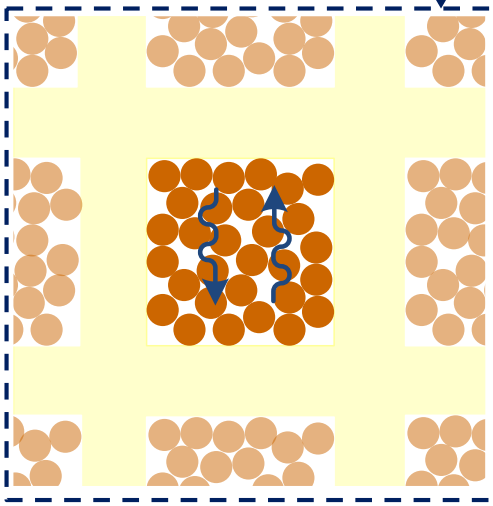
Micro-channel technology (I)



Development and intensification of processes which involve high exothermic reactions



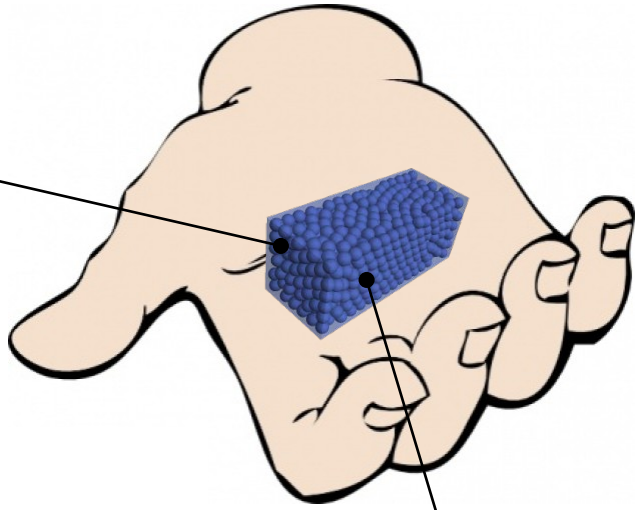
Improved heat transfer in the honeycomb matrix



Improved mass transfer in the packed bed channel

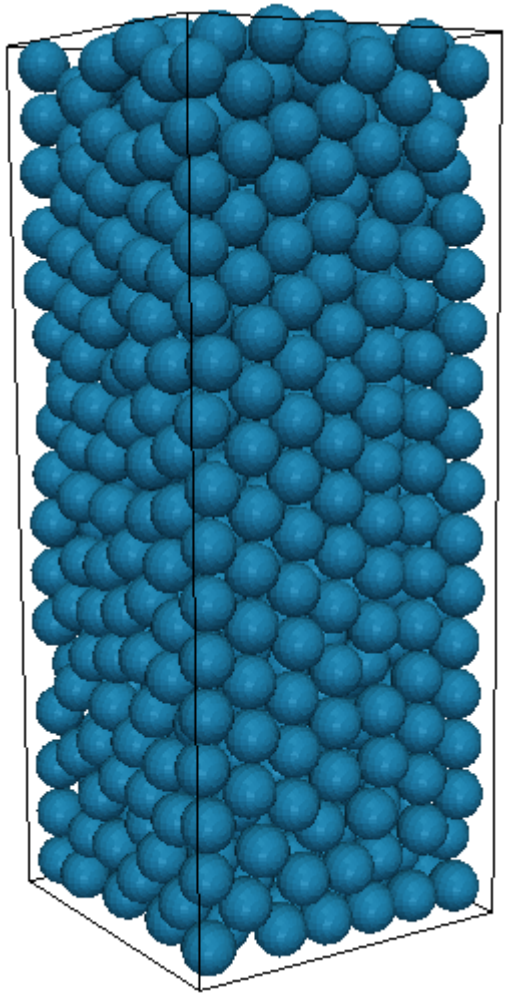
Micro-channel technology (II)

How "unconventional" geometry influences the mass transfer in micro-channel reactors?



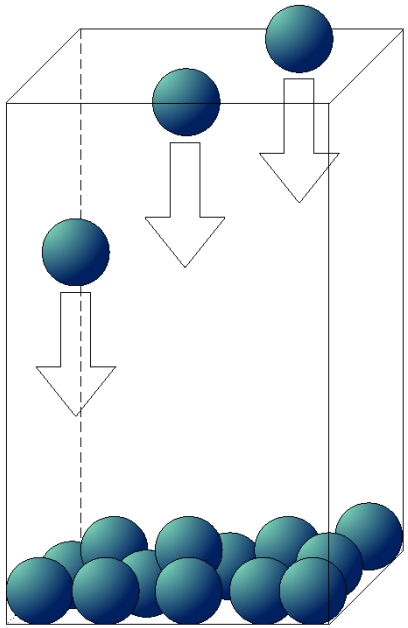
Can literature correlations (developed for industrial reactors) describe mass transfer phenomena in micro-channel reactors?

Micro-channel reactor generation



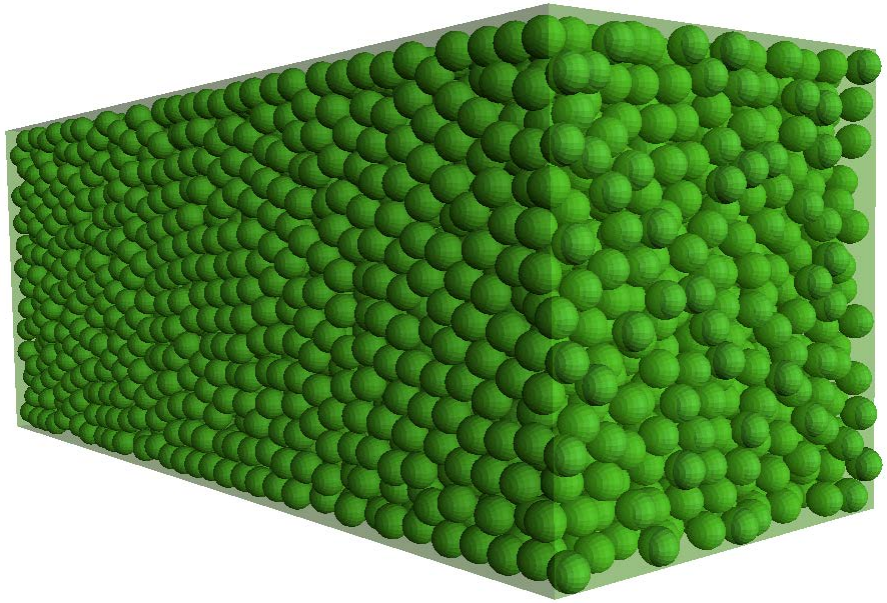
Two-step Monte Carlo process based on the algorithm of Soppe[1]

H. J. Freund, Erlangen Universität, DE

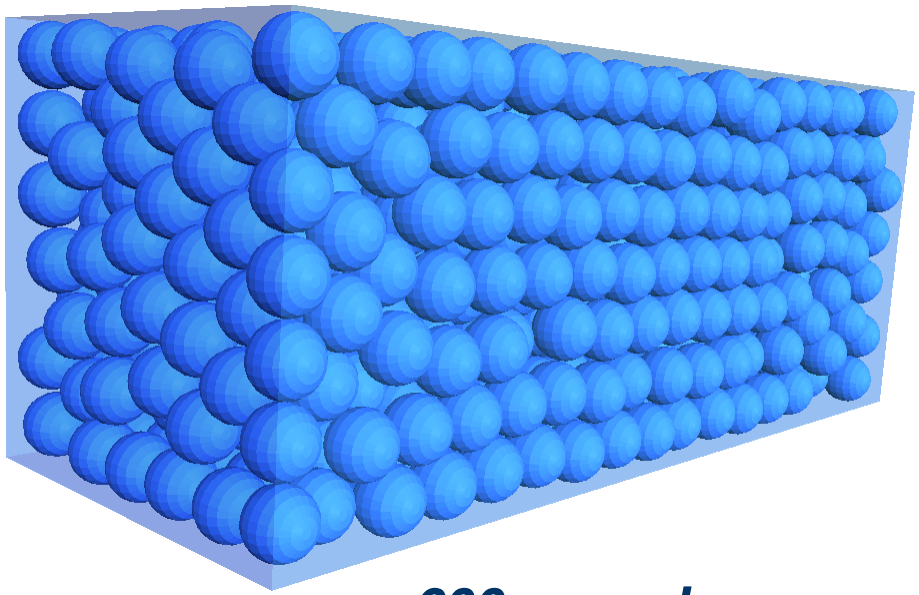


Soppe, W., *Computer simulation of random packing of hard spheres.* Powerd Techol., 1990. 62: p. 189-196.

Investigated micro-channel reactors



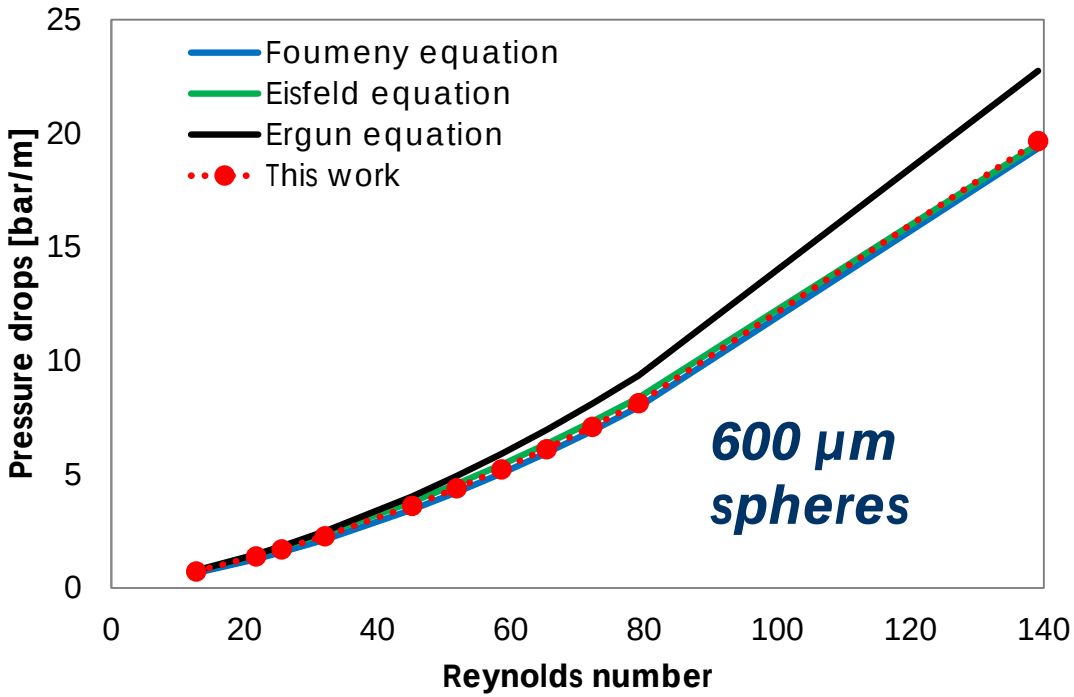
300 µm spheres



600 µm spheres

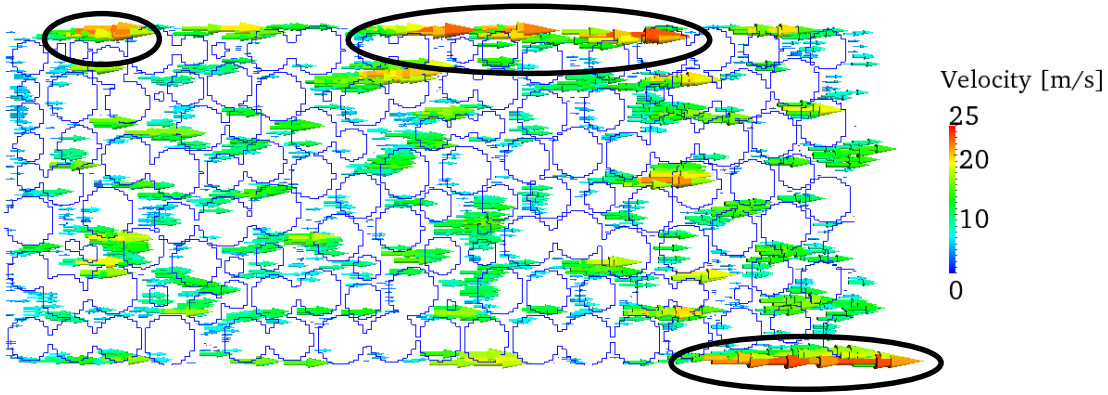
	Green channel	Blue channel
Particle diameter [m]	300×10^{-6}	600×10^{-6}
Reactor length [m]	12.5×10^{-3}	12.5×10^{-3}
Tube diameter [m]	4×10^{-3}	4×10^{-3}

Pressure drops: 600 *μm (blue channel)*



Particle Reynolds number

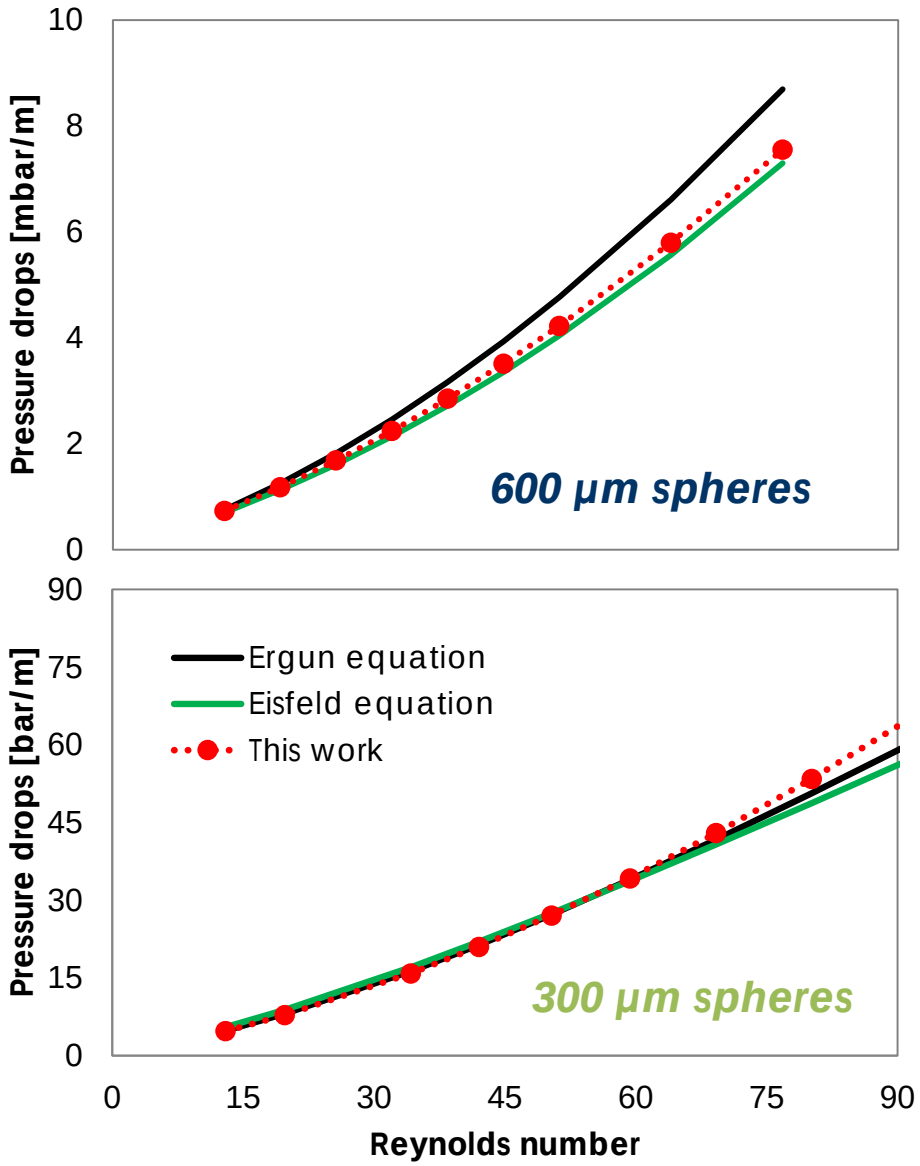
$$\mathrm{Re} = \frac{\rho v D_{Particle}}{\mu}$$



$$N = \frac{D_{Tube}}{D_{Particle}}$$

Tube-to-particle diameter ratio* describes *wall effects

Pressure drops: a comparison



Pressure drops in the reactor with 600 µm sphere diameter are controlled by wall effects

Pay attention: same tube-to-particle diameter ratio of the previous micro-channel reactor studied

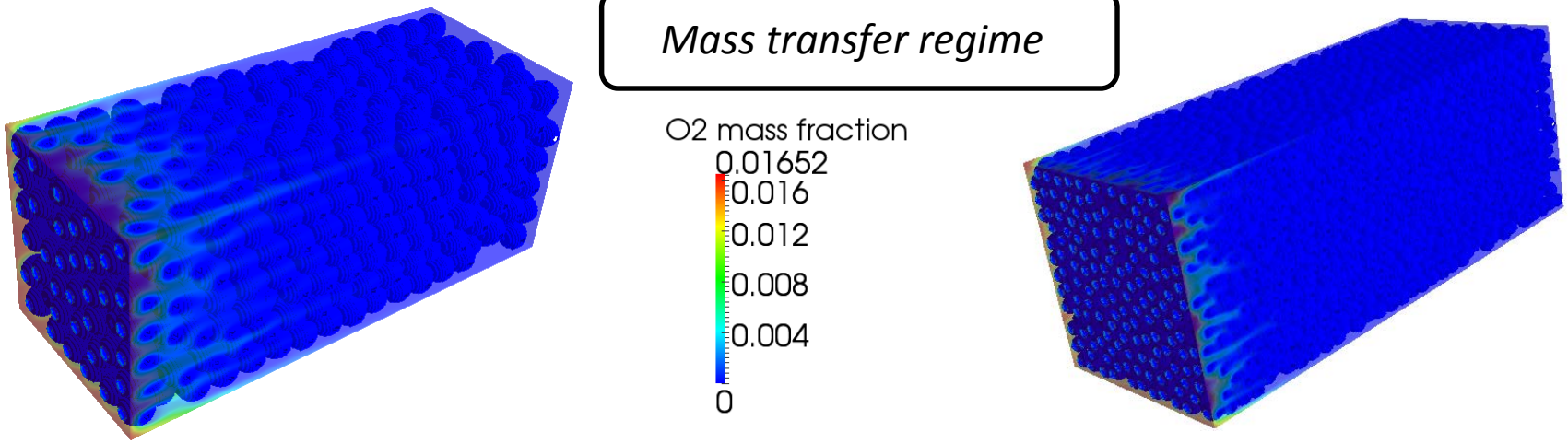
Pressure drops in micro-channel reactor with 300 µm sphere diameter are high and wall effects are negligible

Mass transfer coefficient (I)

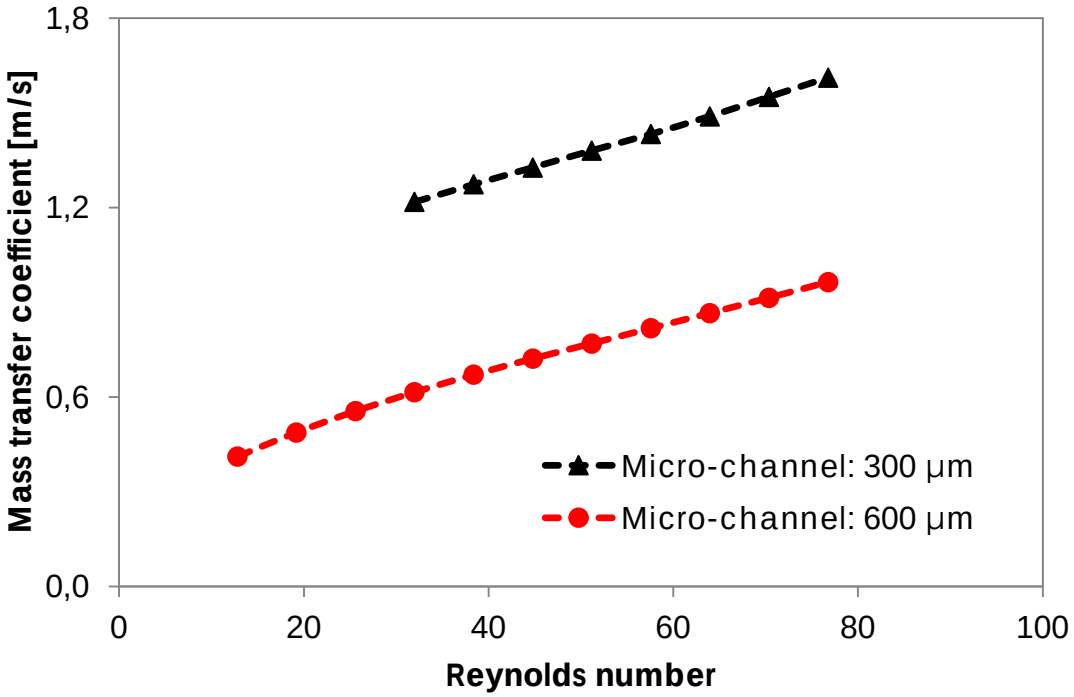
	Value	Unit dimension
Temperature	653	K
Out let pressure	101325	Pa
Inlet molar fraction		
Nitrogen (N_2)	0.95	
Oxygen (O_2)	0.014	
Hydrogen (H_2)	0.036	

- ✓ Irreversible first-order kinetics model at the catalytic wall *(Da ≈ 100)*
- ✓ Identical condition within each channel
- ✓ Isothermal condition
- ✓ Laminar flow *(10 < Re < 90)*
- ✓ Characteristic length: $D_{Particle}$

Mass transfer regime



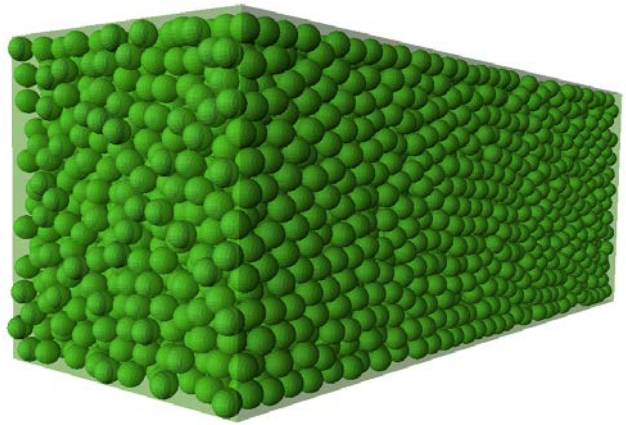
Mass transfer coefficient (II)



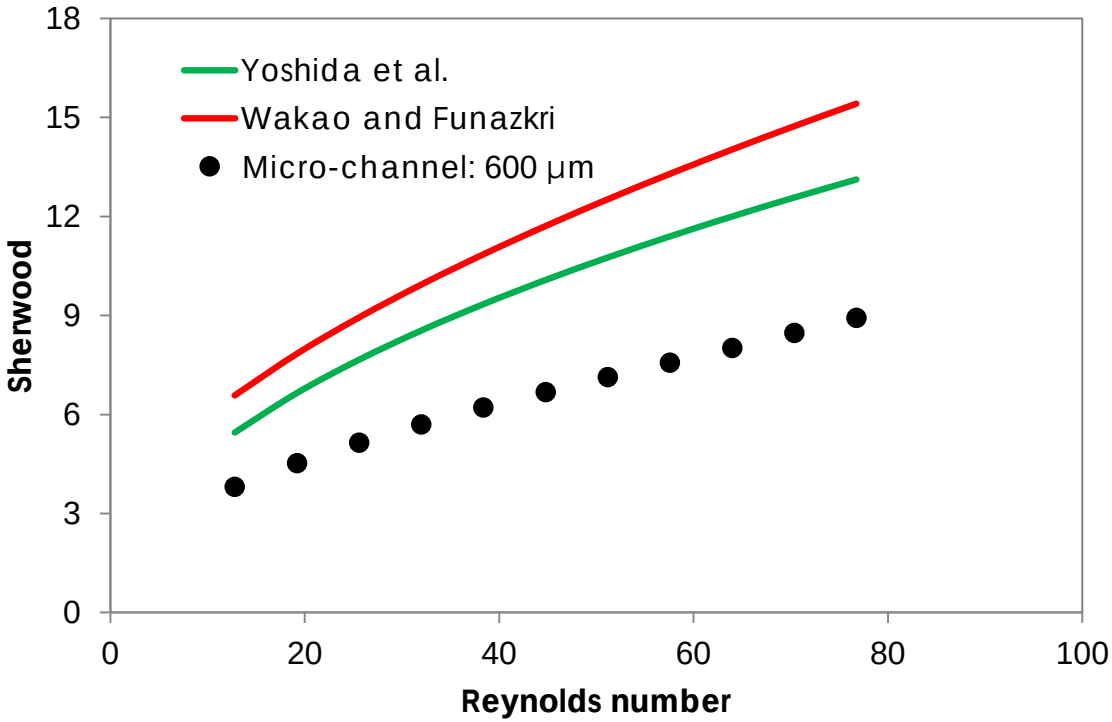
Mass transfer coefficient estimated with Integral Mass Balance (IMB) method:

$$K_{mat,i} = \frac{-u_{in}\ln(1-\chi)}{a_v L}$$

The ***mass transfer coefficient is higher for the micro-channel reactor with the sphere diameter of 300 µm***



Sherwood number: *600 µm*



***Yoshida et al.*[2]**

$$J_m = \frac{0.91}{\mathrm{Re}^{0.51}}\psi$$

***Wakao and Funazkri*[1]**

$$Sh = 2 + 1.1\mathrm{Re}^{0.6}\, Sc^{1/3}$$

Schmidt number:

$$Sc = \frac{\mu}{\rho \mathfrak{D}_i}$$

Particle Reynolds number:

$$\mathrm{Re} = \frac{\rho v D_{Particle}}{\mu}$$

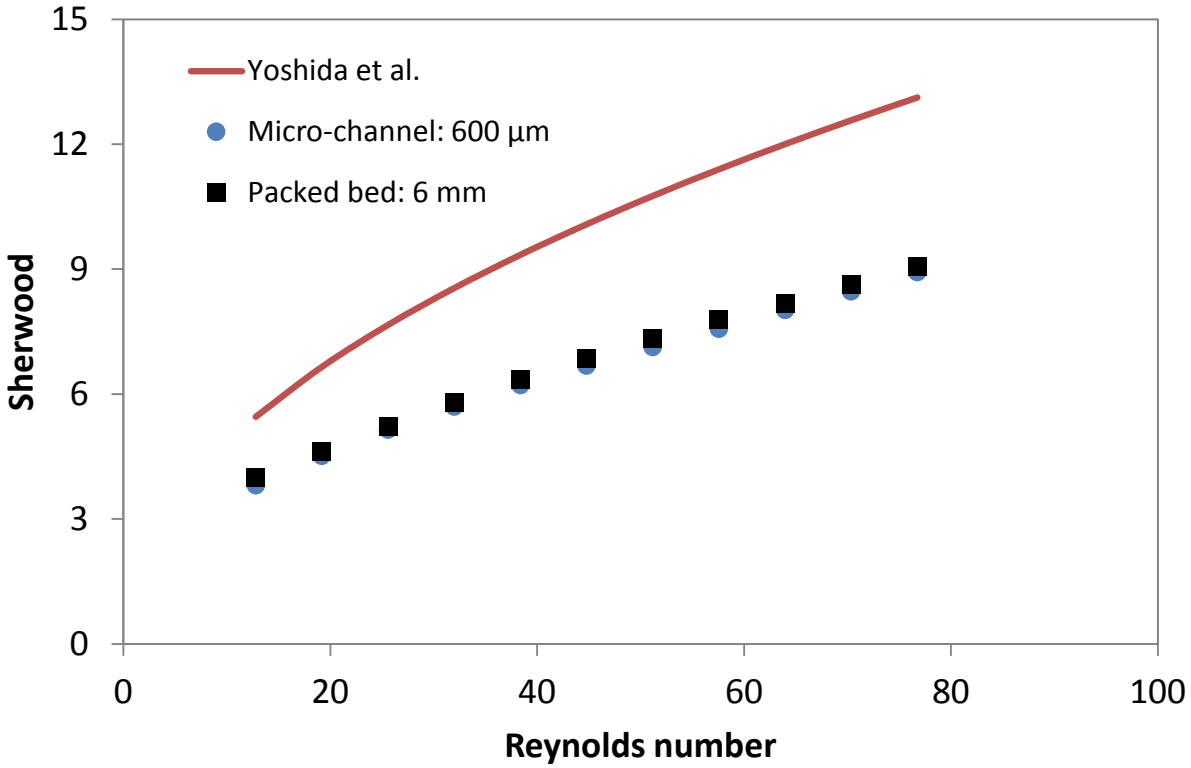
Yoshida Reynolds number:

$$\mathrm{Re} = \frac{\rho v D_{Particle}}{6\mu(1-\varepsilon)}$$

Wakao, N. and T. Funazkri, *Effect of fluid dispersion coefficients on particle-to-fluid mass transfer coefficients in packed beds: Correlation of sherwood numbers.* Chemical Engineering Science, 1978. 33(10): p. 1375-1384.

Yoshida, F., D. Ramaswami, and O.A. Hougen, *Temperatures and partial pressures at the surfaces of catalyst particles.* AIChE Journal, 1962. 8(1): p. 5-11.

Why the difference?



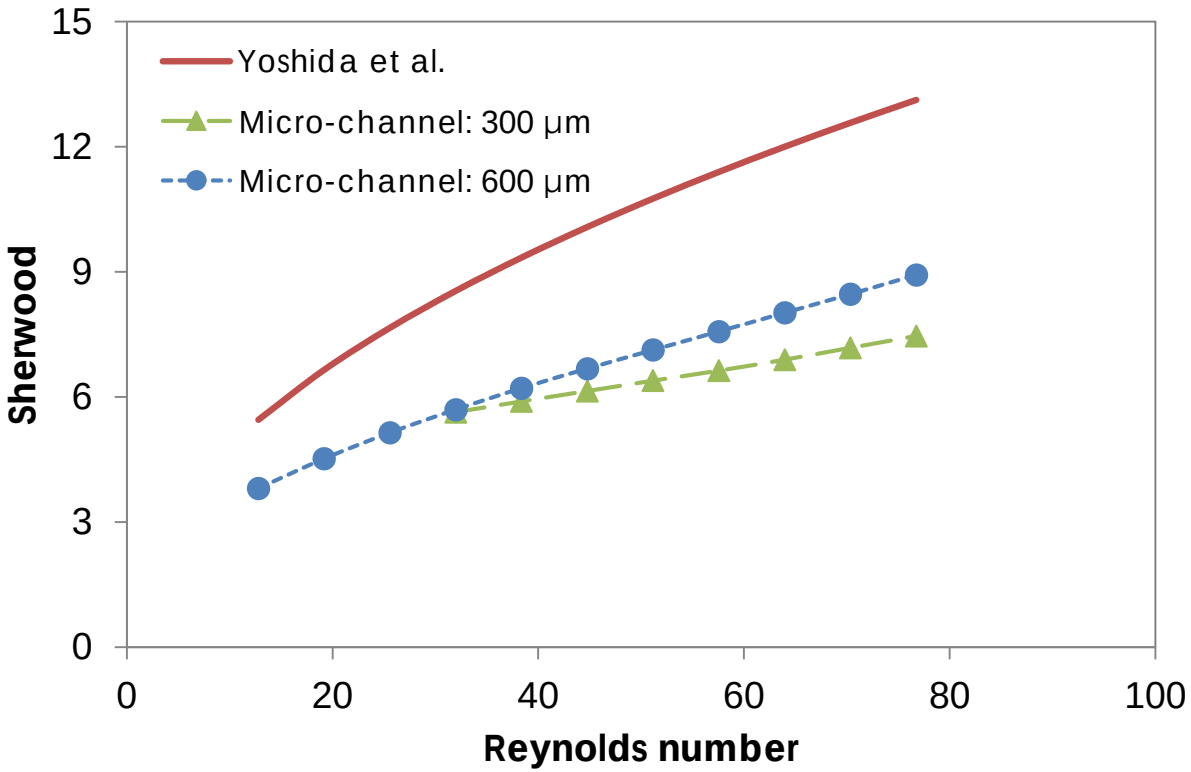
This comparisons shows that the different Sherwood number depends on the tube-to-particle diameter ratio

$$N = \frac{D_{Tube}}{D_{Particle}}$$

and NOT on micro-dimensions

	Particle diameter [m]	Tube diameter [m]	Tube-to-particle diameter ratio
Micro-channel	600×10^{-6}	4×10^{-3}	6.7
Conventional packed bed	6×10^{-3}	40×10^{-3}	6.7

Why the difference?

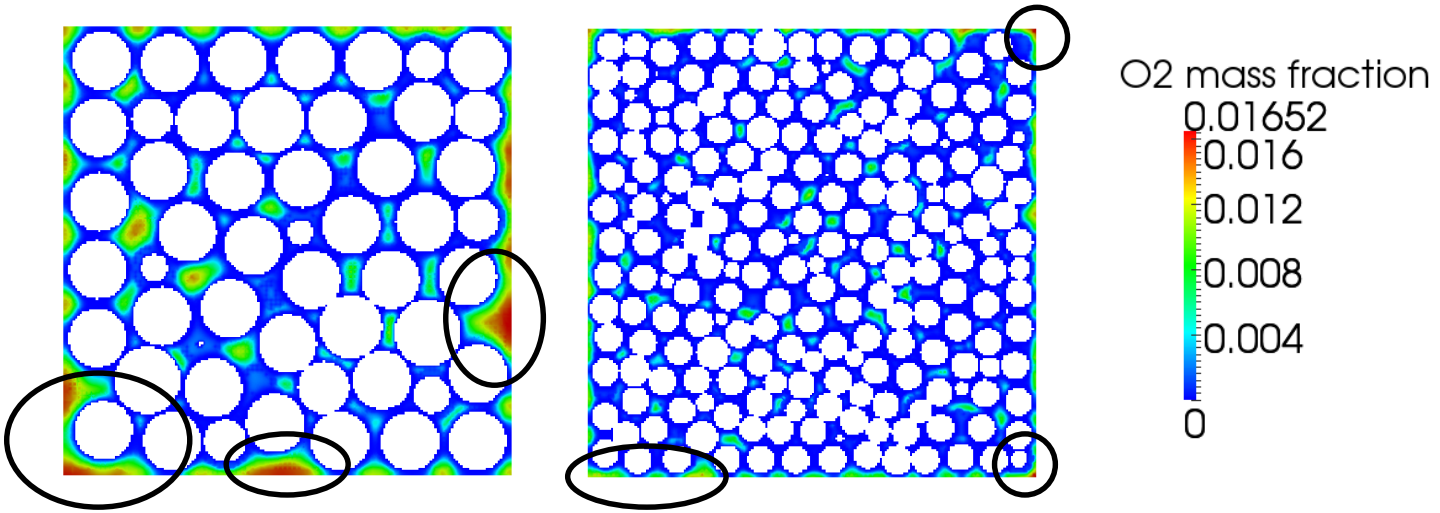


The Sherwood number depends on the tube-to-particle diameter ratio

$$N = \frac{D_{Tube}}{D_{Particle}}$$

	Particle diameter [m]	Tube diameter [m]	Tube-to-particle diameter ratio
Micro-channel	600×10^{-6}	4×10^{-3}	6.7
Micro-channel	300×10^{-6}	4×10^{-3}	13.3

Wall effects



600 µm sphere diameter

300 µm sphere diameter

The higher mass transfer coefficient for micro-channel with 300 µm depends on the lower influence of the wall effects

The mass transfer coefficient is reduced by wall effects also in the micro-channel with 300 µm