CECAM International Summer School

Hot topic 4

First-principles based catalytic reaction engineering

Matteo Maestri

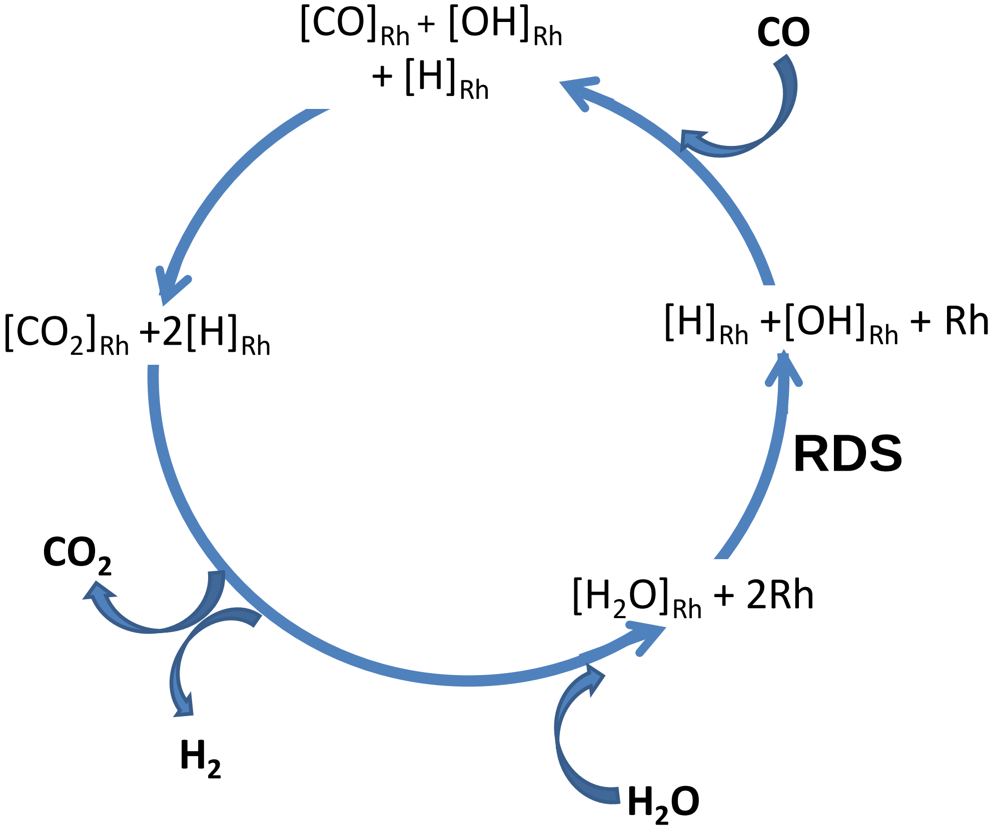
POLITECNICO MILANO

July 23, 2013

Conversationshaus - Norderney, Germany

Catalytic cycle

Consists of the elementary steps through which the reactants convert to the products



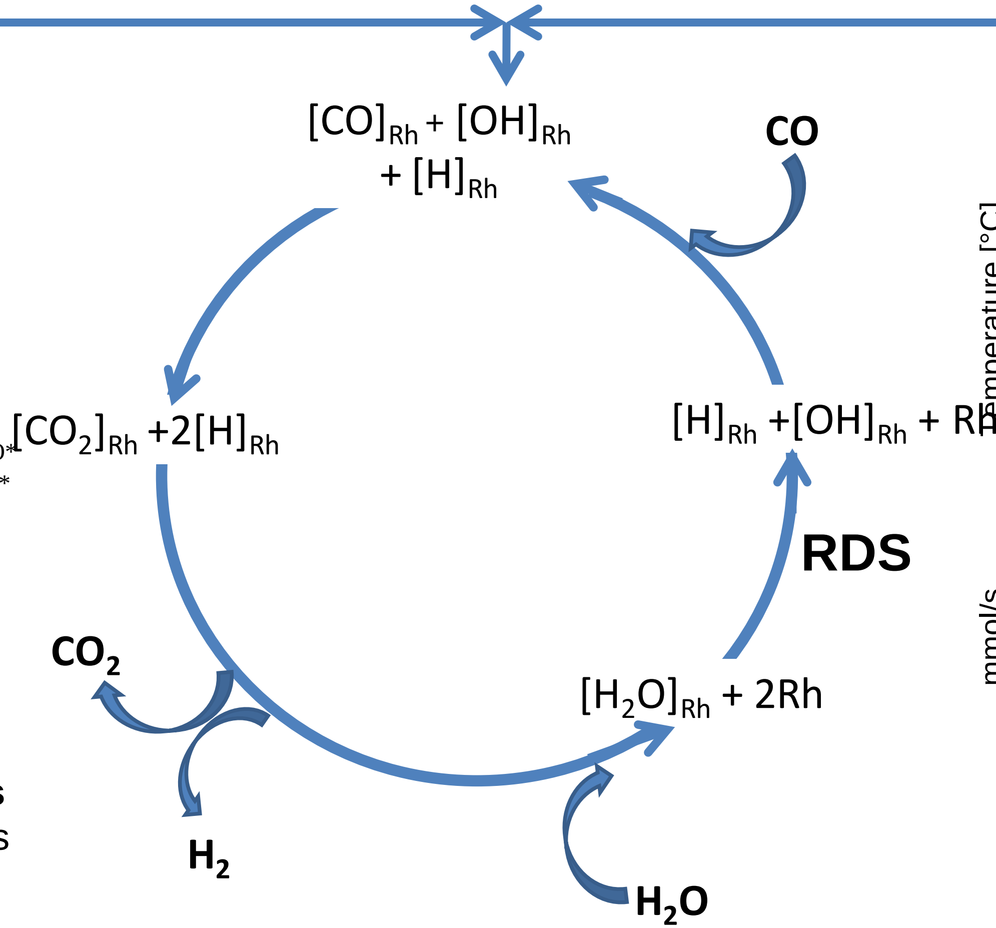
"*E pluribus unum*"

Result of the interplay among phenomena at different scales

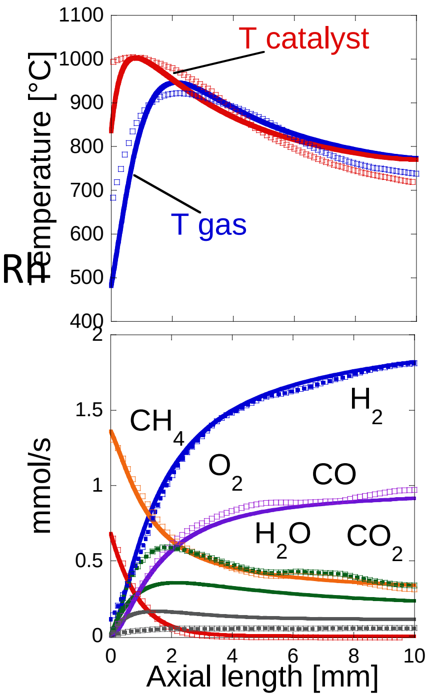
Microscale

$COOH^{*}+{}^{*} \rightarrow CO^{*}+OH^{*}$
$CO^{*}+OH^{*} \rightarrow COOH^{*}+{}^{*}$
$COOH^{*}+{}^{*} \rightarrow CO_2^{*}+H^{*}$
$CO_2^{*}+H^{*} \rightarrow COOH^{*}+{}^{*}$
$CO_2^{*} + H_2O^{*} \rightarrow COOH^{*} + OH^{*}$
$COOH^{*} + OH^{*} \rightarrow CO_2^{*} + H_2O^{*}$
$CO_2^{*}+H^{*} \rightarrow HCOO^{**}$
$HCOO^{**} \rightarrow CO_2^{*}+H^{*}$
$CO_2^{*} + OH^{*} + {}^{*} \rightarrow HCOO^{**} + O^{*}$
$HCOO^{**} + OH^{*} \rightarrow CO_2^{*} + H_2O^{*}$
$CH^{*} + H^{*} \rightarrow CH_2^{*} + {}^{*}$
$CH^{*} + {}^{*} \rightarrow C^{*} + H^{*}$
$C^{*} + H^{*} \rightarrow CH^{*} + {}^{*}$
$CH_3^{*} + O^{*} \rightarrow CH_2^{*} + OH^{*}$
$CH_2^{*} + OH^{*} \rightarrow CH_3^{*} + O^{*}$
$CH^{*} + OH^{*} \rightarrow CH_2^{*} + O^{*}$
$CH_2^{*} + O^{*} \rightarrow CH^{*} + OH^{*}$
…

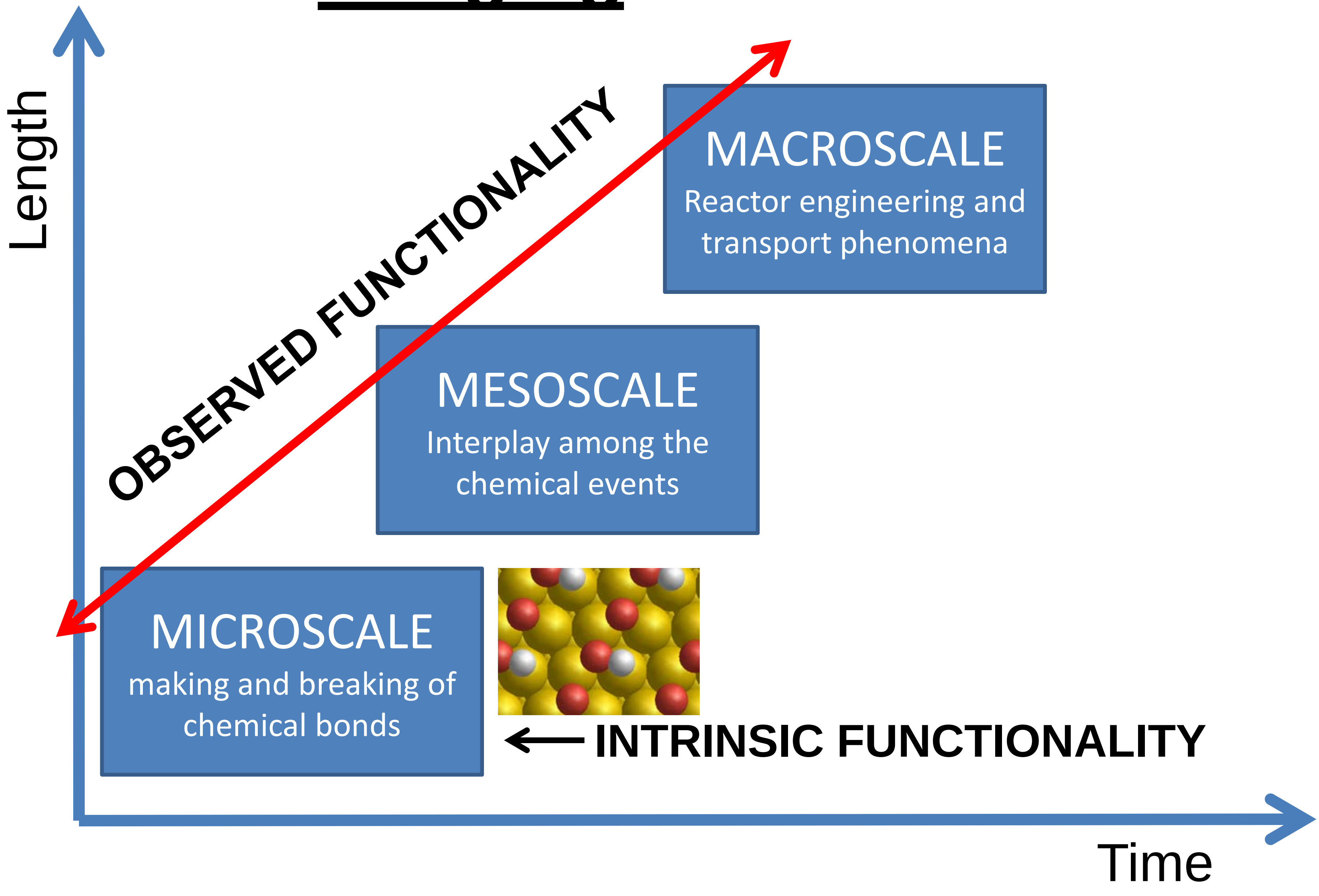
~ 10^2 potential steps
@ different coverages



Macroscale



Need of **bridging** between the scales



Science

AAAS

Frontiers in Reactor Engineering
Milorad P. Dudukovic
Science **325**, 698 (2009);
DOI: 10.1126/science.1174274

PERSPECTIVE

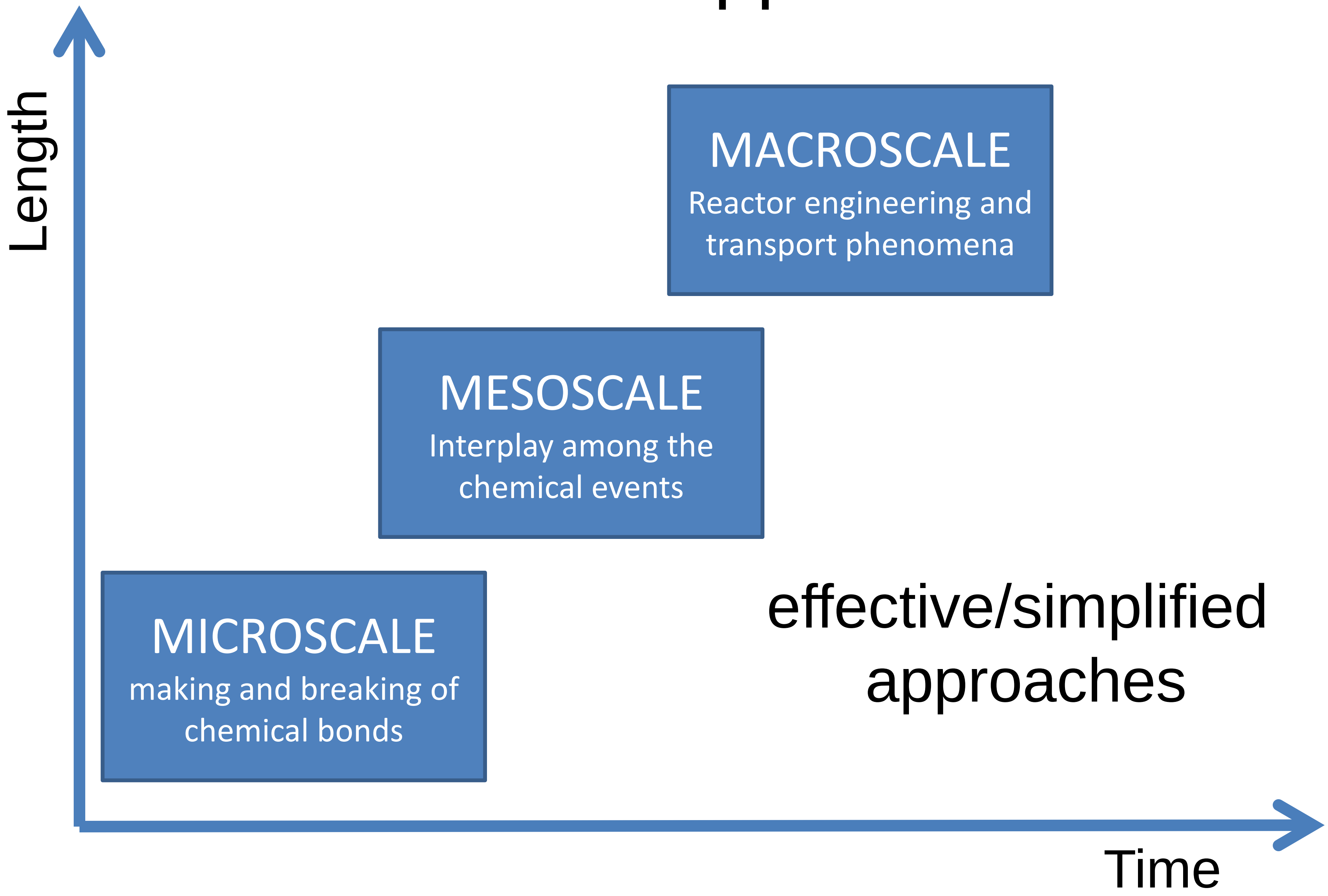
Frontiers in Reactor Engineering

Milorad P. Dudukovic

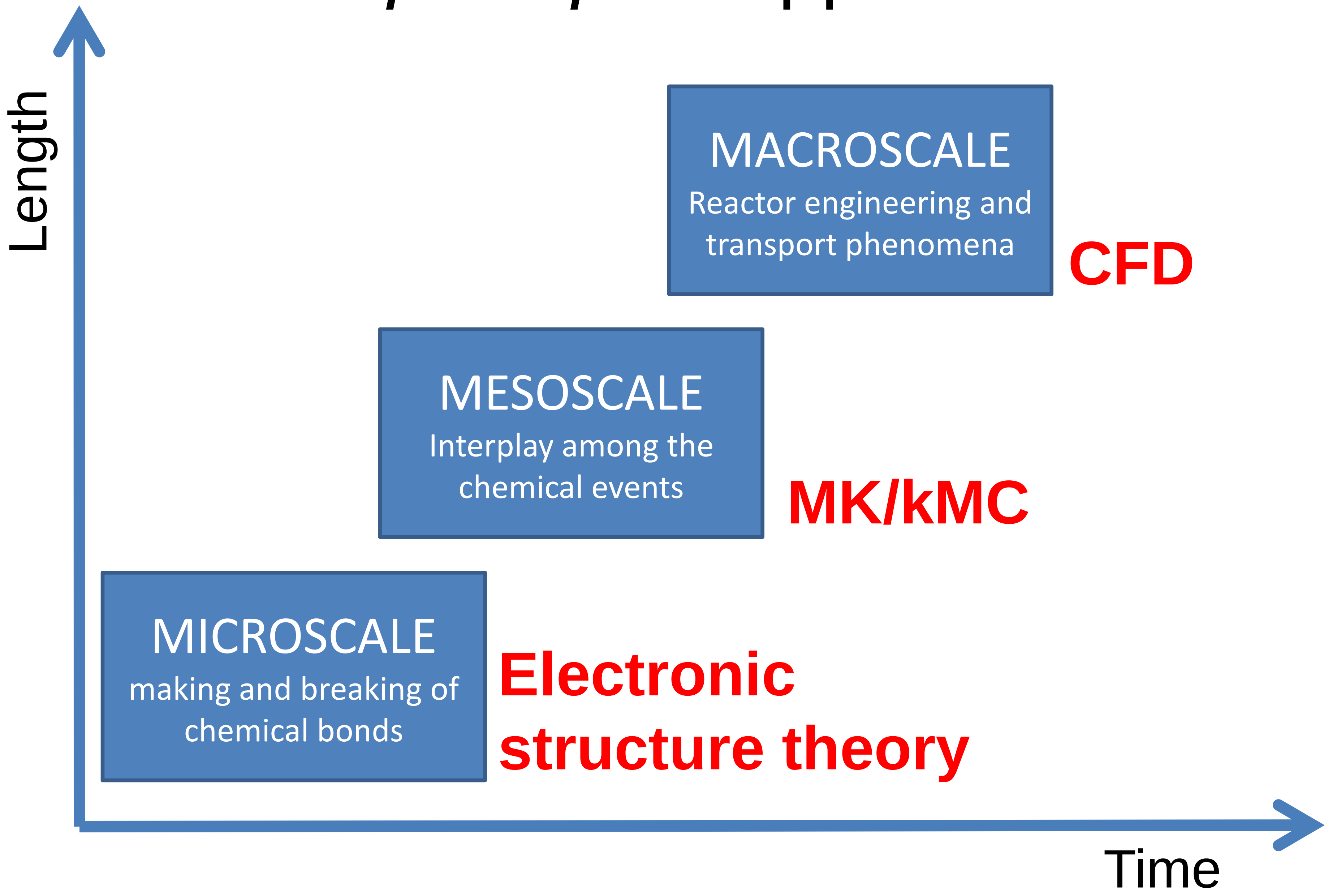
The key challenge for reactor engineering is to establish the scientifically based sustainable technologies necessary for meeting the future energy, environmental, and materials needs of the world. This goal requires advancing our scientific understanding of multiscale kinetic transport interactions to enable better reactor choice and to ensure higher reactor and process efficiencies.

Our current increased awareness of the finiteness of our resources raises the bar for future reactor technology. Instead of continuing the application of principles at the rudimentary level, the main task now is to provide an improved scientific basis for conducting chemical transformations in an environmentally acceptable, energy-efficient, and sustainable manner.

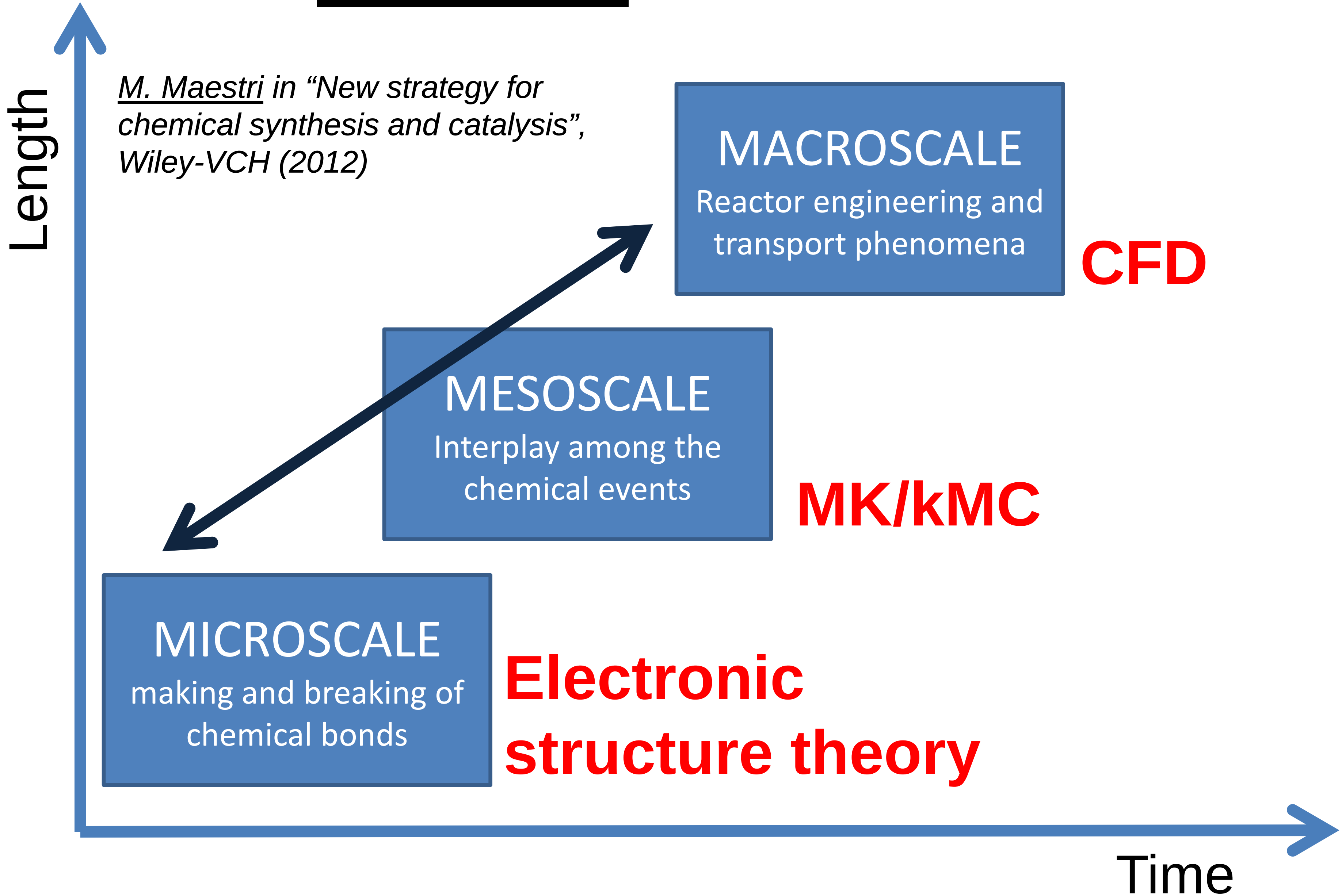
From a “traditional” approach to CRE…



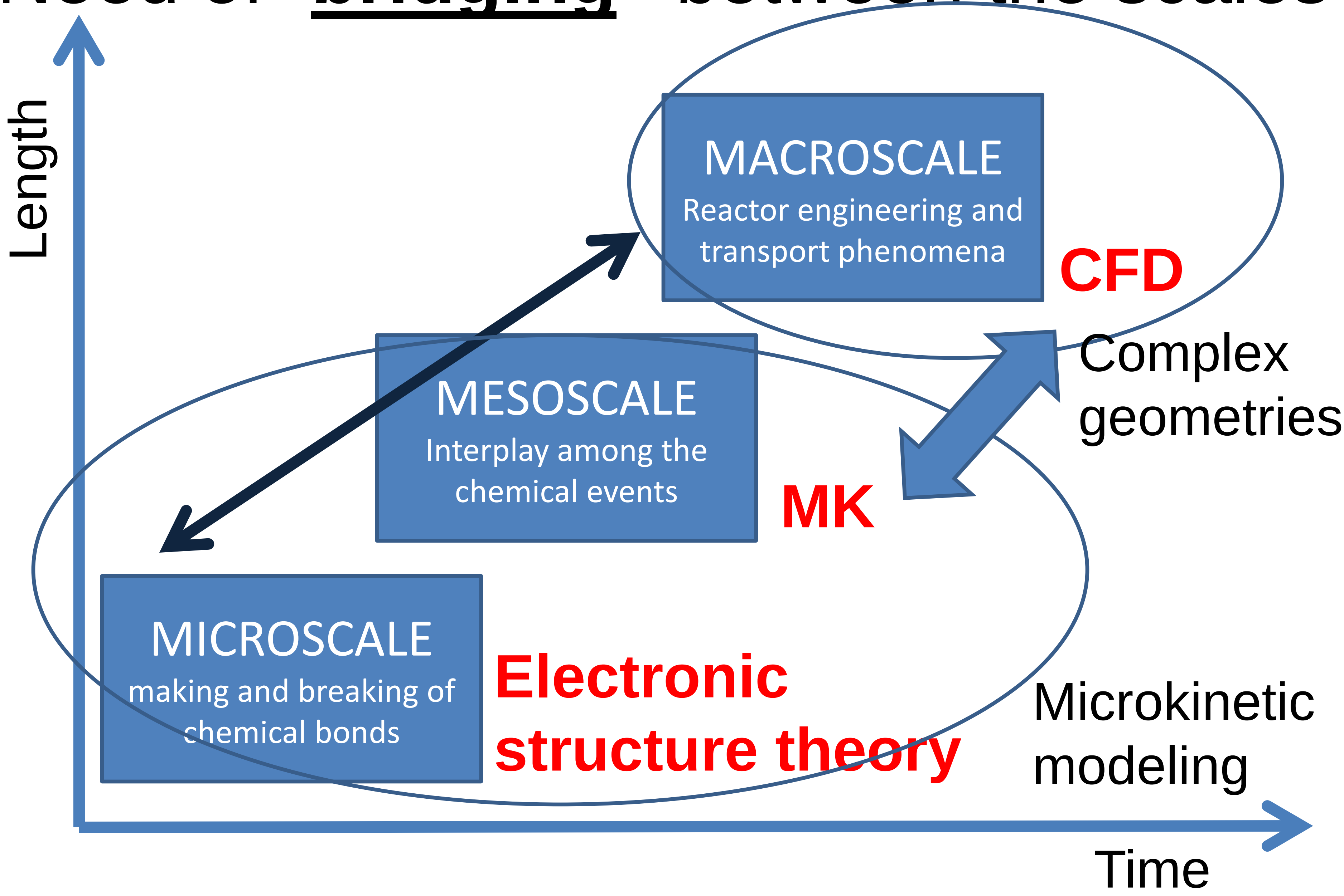
…to a *first-principles* approach to CRE



Need of “**bridging**” between the scales



Need of “**bridging**” between the scales



Outline

Length

- ✓ Methodology
- ✓ Show-cases

MACROSCALE
Reactor engineering and transport phenomena

MESOSCALE
Interplay among the chemical events

MICROSCALE
making and breaking of chemical bonds

Time

M. Maestri & A. Cuoci
www.catalyticfoam.polimi.it

Outline

Length

- ✓ Methodology
- ✓ Show-cases

MACROSCALE
Reactor engineering and transport phenomena

MESOSCALE
Interplay among the chemical events

MICROSCALE
making and breaking of chemical bonds

Scholar examples this afternoon in the tutorial

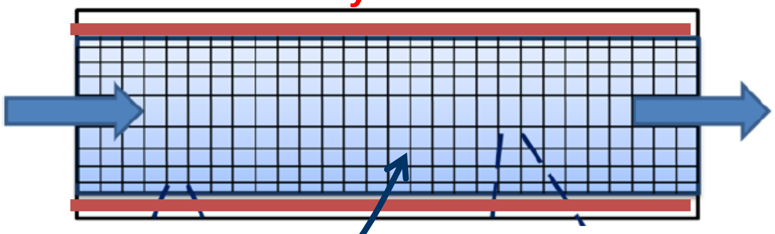
CatalyticFOAM

POLITECNICO MILANO

M. Maestri & A. Cuoci
www.catalyticfoam.polimi.it

Time

Governing equations



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

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

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

Governing equations

Non-catalytic walls

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

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

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

Catalytic walls

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

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

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

Adsorbed (surface) species

Detailed microkinetic models

COOH*+* → CO*+OH*
CO*+OH* → COOH*+*
COOH*+* → CO_2*+H*
CO_2*+H* → COOH*+*
CO_2* + H_2O* → COOH* + OH*
COOH* + OH* → CO_2* + H_2O*
CO_2*+H* → HCOO**
HCOO** → CO_2*+H*
CO_2* + OH* + *→ HCOO** + O*
HCOO** + OH* → CO_2* + H_2O*
CH* + H* → CH_2* + *
CH* + * → C* + H*
C* + H* → CH* + *
CH_3* + O* → CH_2* + OH*
CH_2* + OH* → CH_3* + O*
CH* + OH* → CH_2* + O*
CH_2* + O* → CH* + OH*
…

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

<u>M. Maestri</u>, Microkinetic analysis of complex chemical processes at surface, in "New strategy for chemical synthesis and catalysis", Wiley-VCH (2012)

Numerical challenges

✓ **Dimensions of the system**

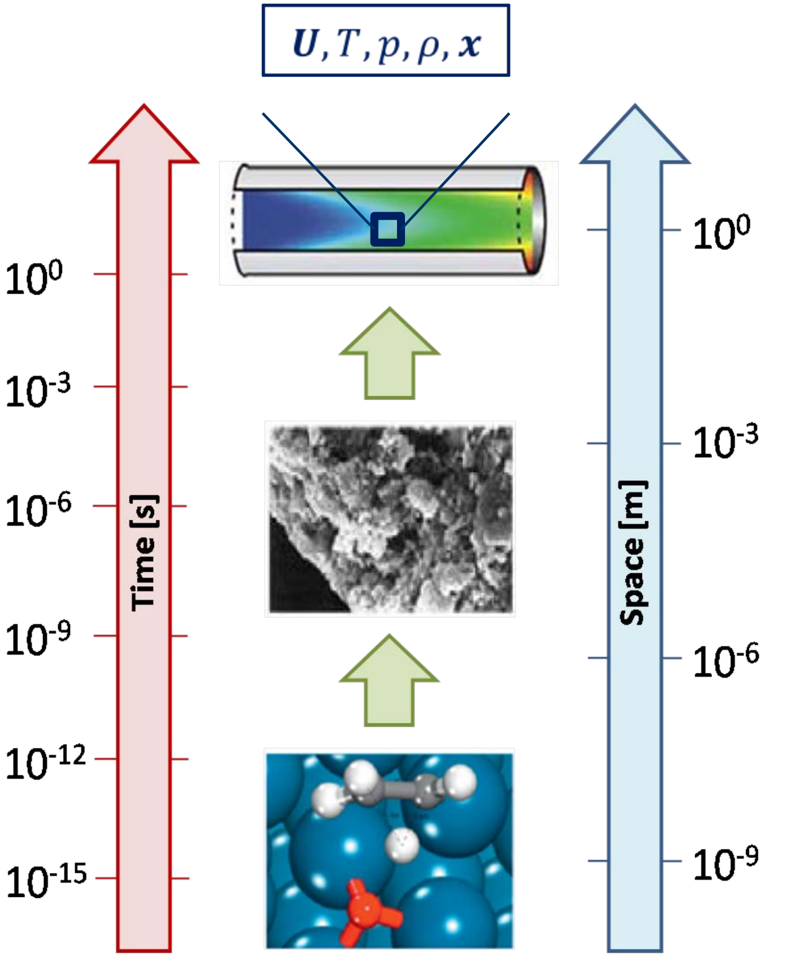
- Proportional to the number of species
- Proportional to the number of cells

✓ **Stiffness**

- Different temporal scales involved
- Different spatial scales involved

✓ **Non-linearity**

- Source term non linear in concentrations and temperature
- Coverage dependence of activation energy



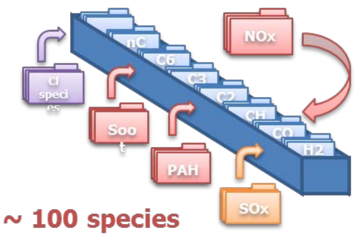
$$r_j = A_j \cdot T^{\beta_j} \cdot \exp\left(-\frac{E_{att,j}(\theta_i)}{RT}\right) \prod_{i=1}^{NC} (c_i)^{\nu_{ij}}$$

Numerical solution

Fully segregated algorithms

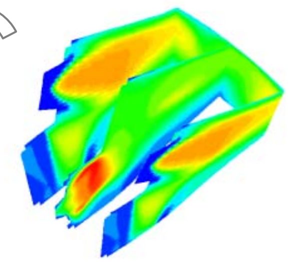
☺ easy to implement and computationally efficient
☹ unfeasible when large, stiff kinetic mechanisms are used

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

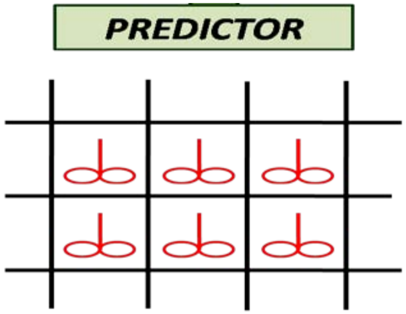
Operator-splitting algorithm

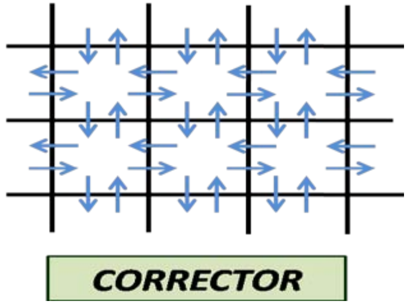
$$\frac{\partial \varphi}{\partial t} = S + M$$

Reaction ← S | M → *Diffusion, convection...*

Strang splitting scheme

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



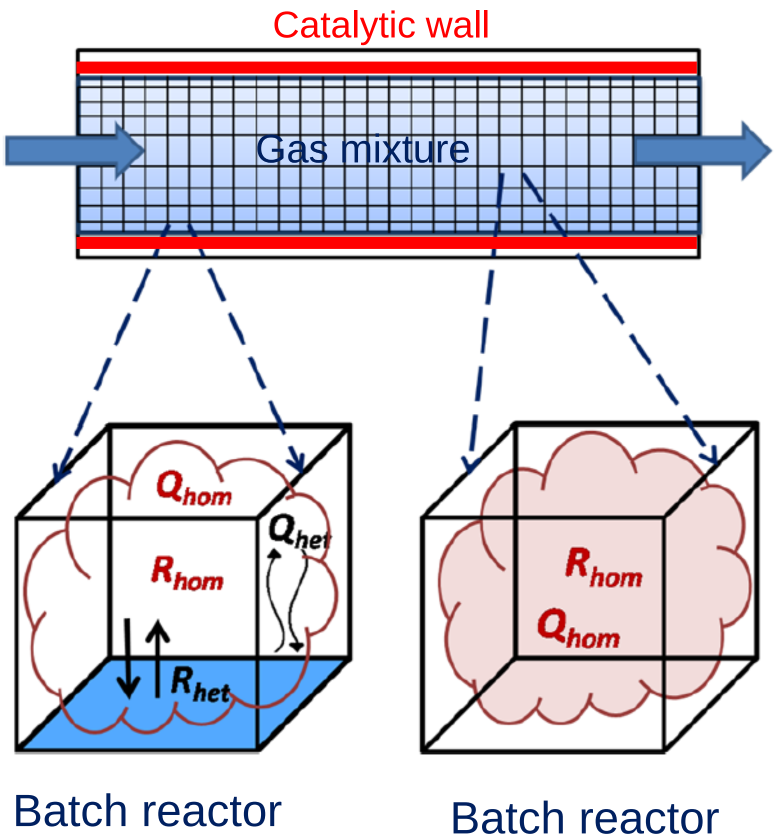


$$\frac{\partial \varphi}{\partial t} = M$$

Z. Ren, S. B. Pope, Journal of Computational Physics, 2008

M. Maestri, A. Cuoci, Chemical Engineering Science, 96 (2013) 106-117

Reactor network

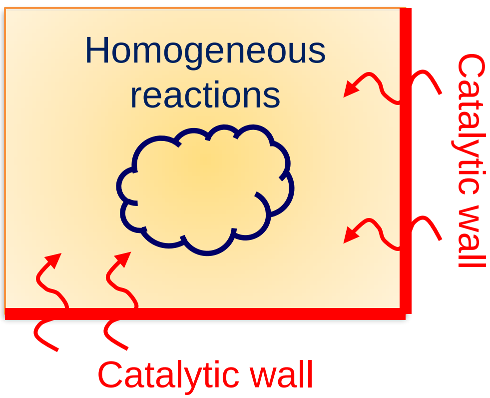


Each computational cell behaves as a chemical reactor in the splitting-operator algorithm (chemical step)

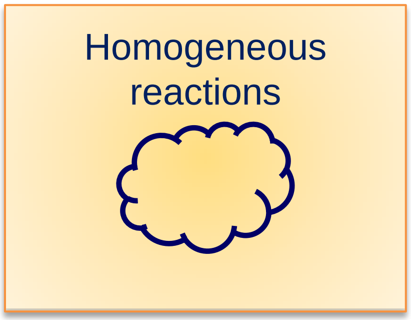
Each reactor is described by a set of stiff ODE, which must be integrated on the time step Δt

M. Maestri, A. Cuoci, Chemical Engineering Science, 96 (2013) 106-117

Reactor network

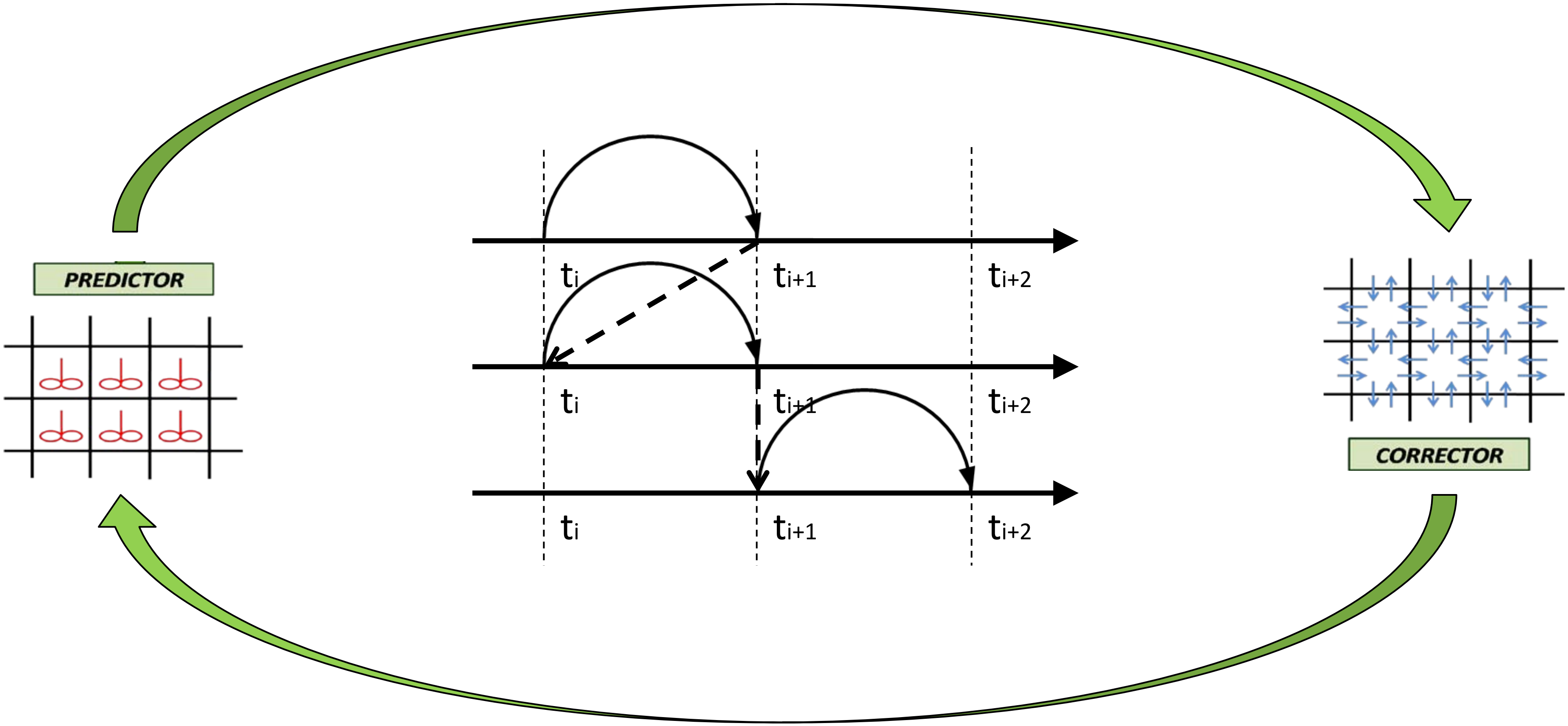


$$\begin{cases} \rho \dfrac{d\omega_k}{dt} = \dot{\Omega}_k^{hom} + \dfrac{1}{V}\left\{ \sum_{j=1}^{NF} \alpha_j^{cat} A_j \dot{\Omega}_{k,j}^{het} - \omega_k \sum_{j=1}^{NF} \left[\alpha_j^{cat} A_j \sum_{k=1}^{NG} \dot{\Omega}_{k,j}^{het} \right] \right\} & \text{k=1,NG} \\ \rho \hat{C}_P \dfrac{dT}{dt}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



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

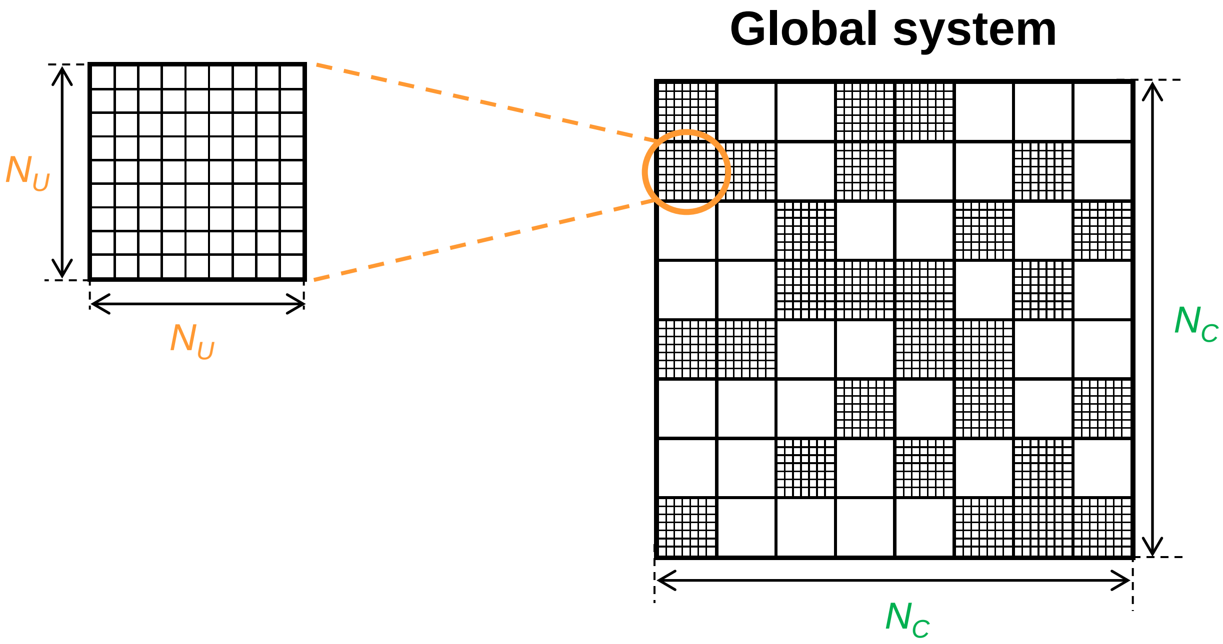
Operator-splitting algorithm



The procedure is iterated on the next time step

M. Maestri, A. Cuoci, Chemical Engineering Science, 96 (2013) 106-117

Jacobian matrix



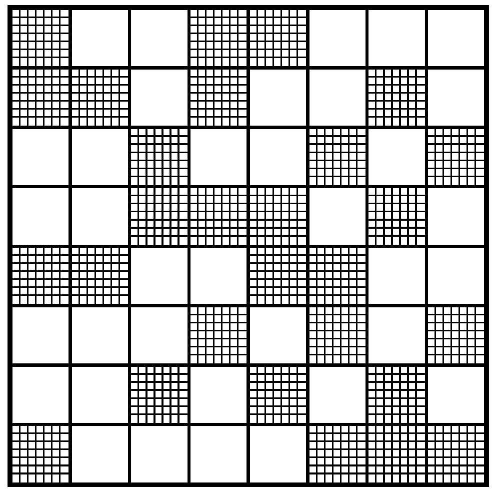
$$\frac{\partial \varphi}{\partial t} = M + S$$

Jacobian matrix:

- ✓ **Sparse**
- ✓ **Unstructured**
- ✓ **Blocks**

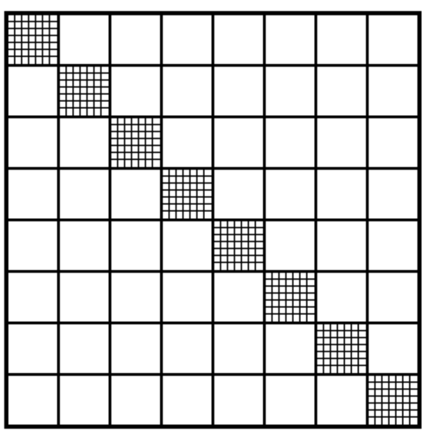
Source term

Global system



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

Source term



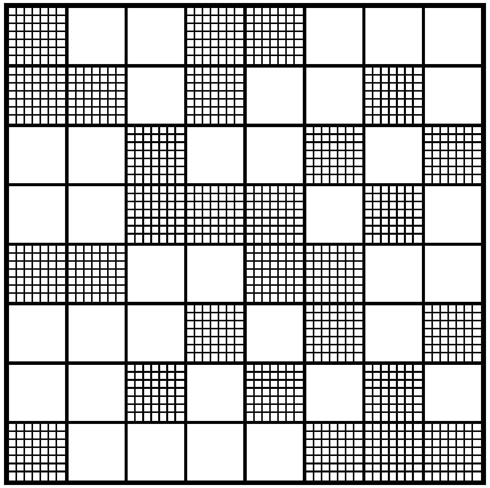
$$\frac{\partial \varphi}{\partial t} = S$$

Jacobian matrix:

- ✓ **Sparse**
- ✓ **Diagonal**

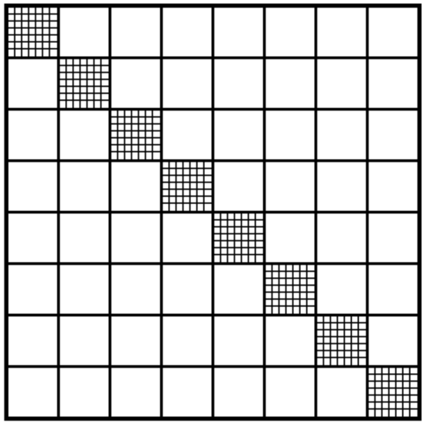
Transport term

Global system



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

Source term

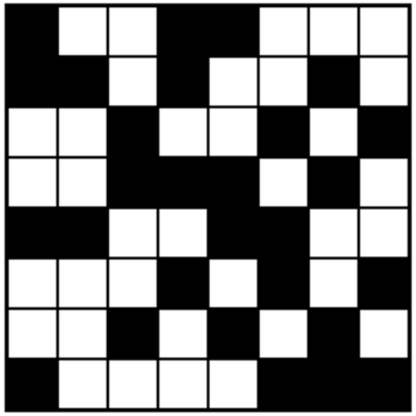


$$\frac{\partial \varphi}{\partial t} = S$$

Jacobian matrix:

- ✓ Sparse
- ✓ Unstructured

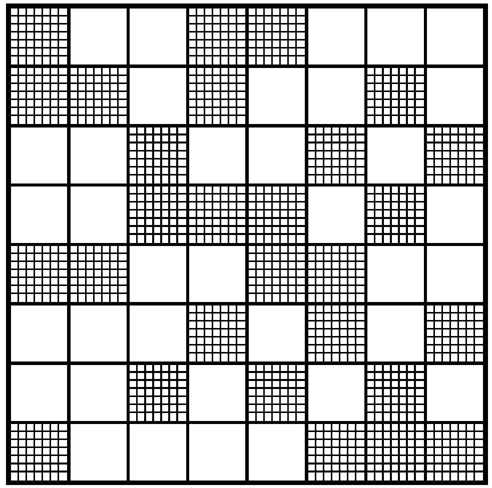
Transport term



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

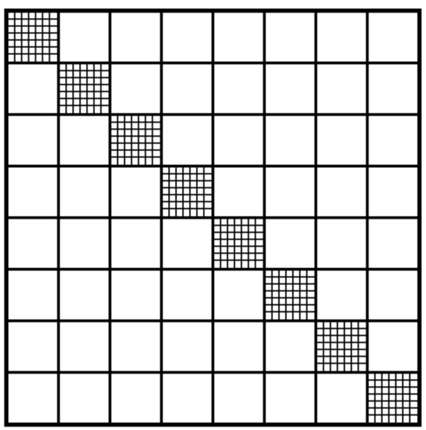
Operator-splitting algorithm

Global system



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

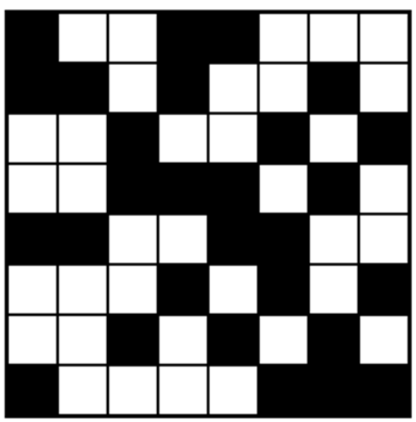
Source term



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

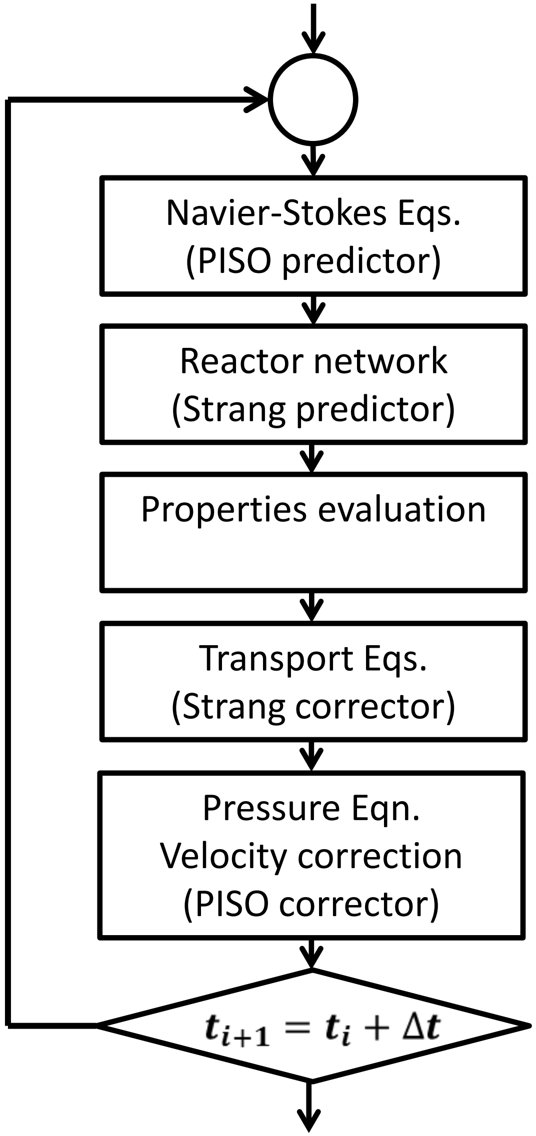
Use of a suitable algorithm for each sub-problem

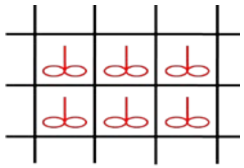
Transport term

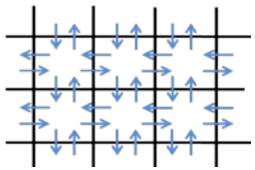


$$\frac{\partial \varphi}{\partial t} = M$$

Solution procedure





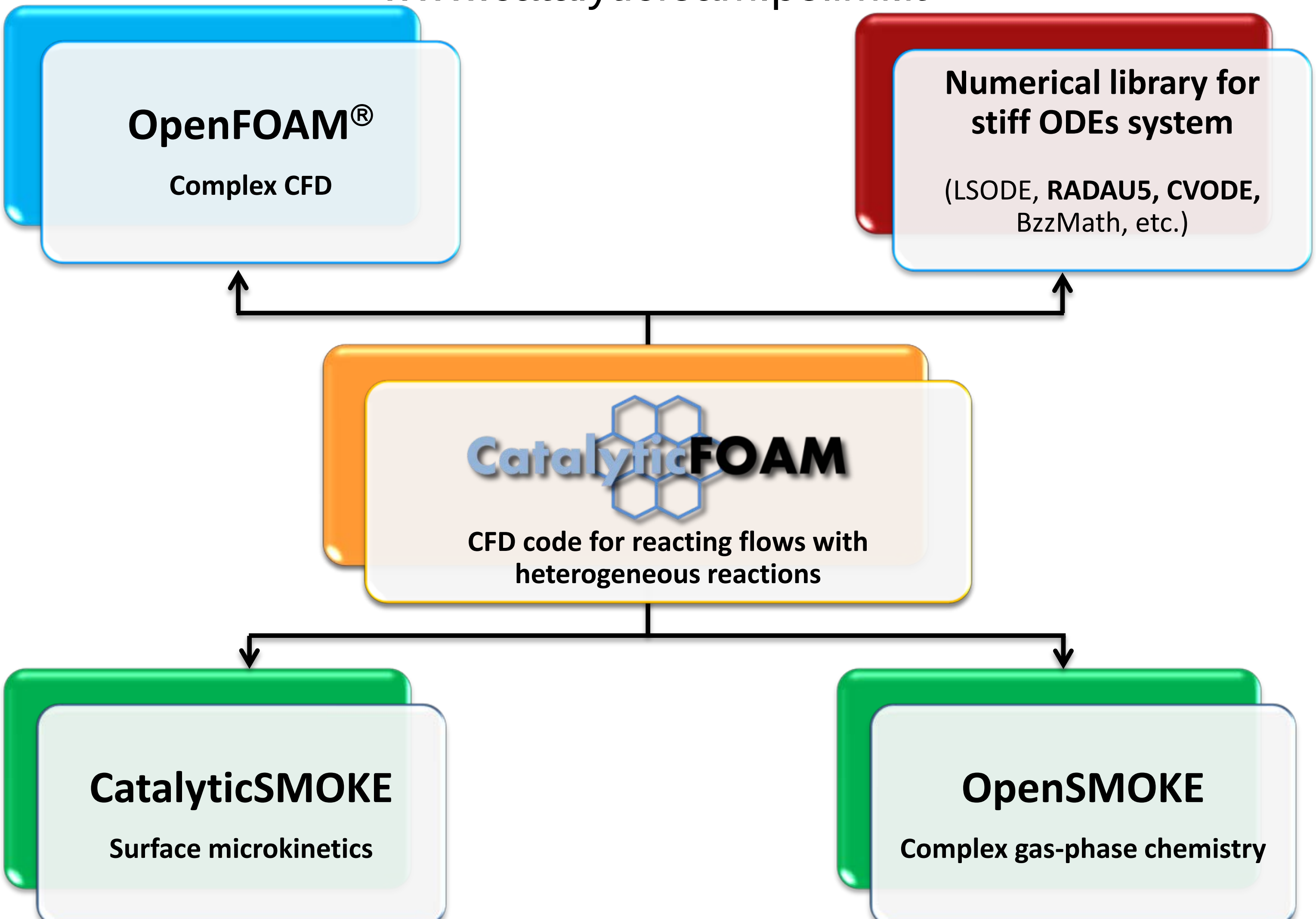


Main features:

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

catalyticFOAM structure

www.catalyticfoam.polimi.it



M. Maestri, A. Cuoci, Chemical Engineering Science, 96 (2013) 106-117

Outline

✓ Methodology

✓ Show-cases

Length

MACROSCALE
Reactor engineering and transport phenomena

MESOSCALE
Interplay among the chemical events

MICROSCALE
making and breaking of chemical bonds

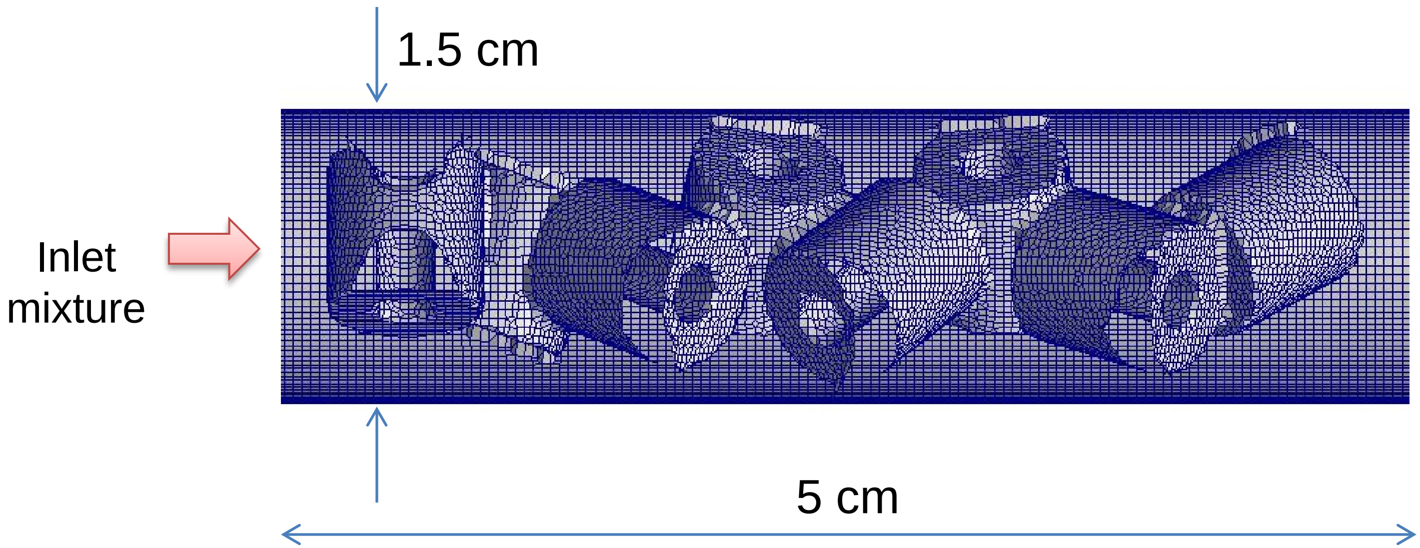
Time

CatalyticFOAM

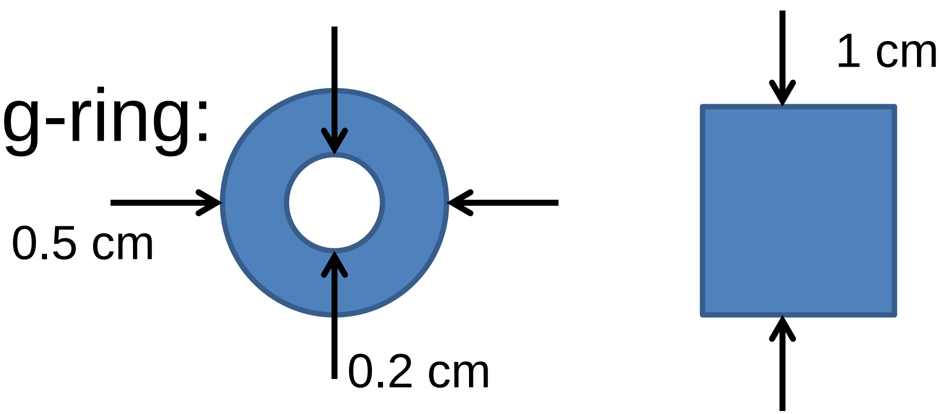
M. Maestri & A. Cuoci

www.catalyticfoam.polimi.it

Show-case I: Rashig-ring bed



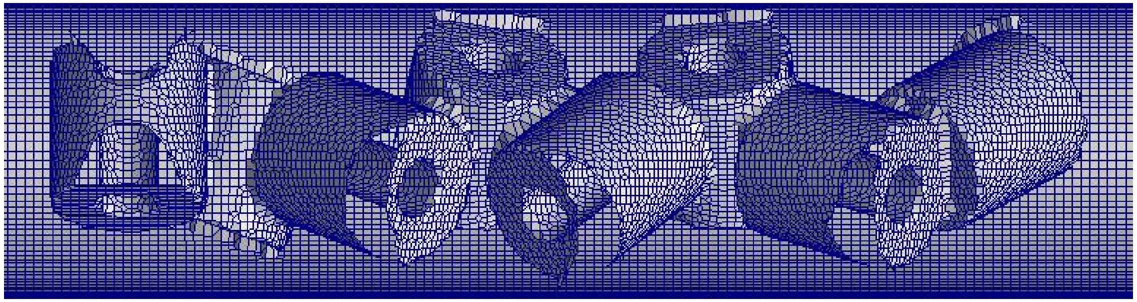
Rashig-ring:



Mesh generation in collaboration with Dr. S. Lipp – BASF SE, DE

Show-case I: Rashig-ring bed

Laminar flow (Re = 50)



Inlet mixture

Operating conditions	
Internal diameter	**1.5 cm**
Total length	**5 cm**
H_2 mole fraction	**0.04 (-)**
O_2 mole fraction	**0.01 (-)**
N_2 mole fraction	**0.95 (-)**
Temperature	**473.15 K**
Inlet velocity	**0.2 m/s**

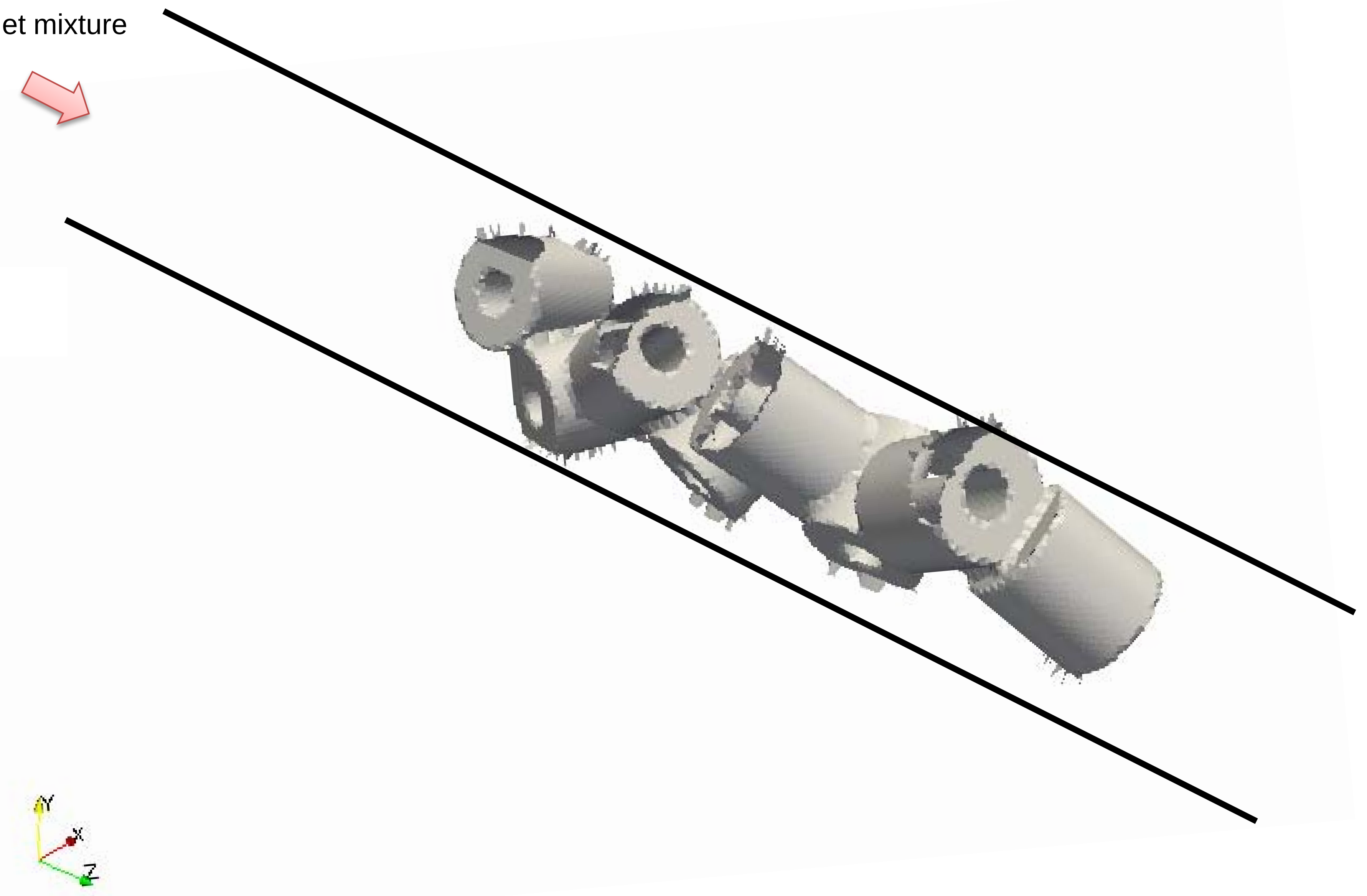
C1 microkinetic model on Rh:

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

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

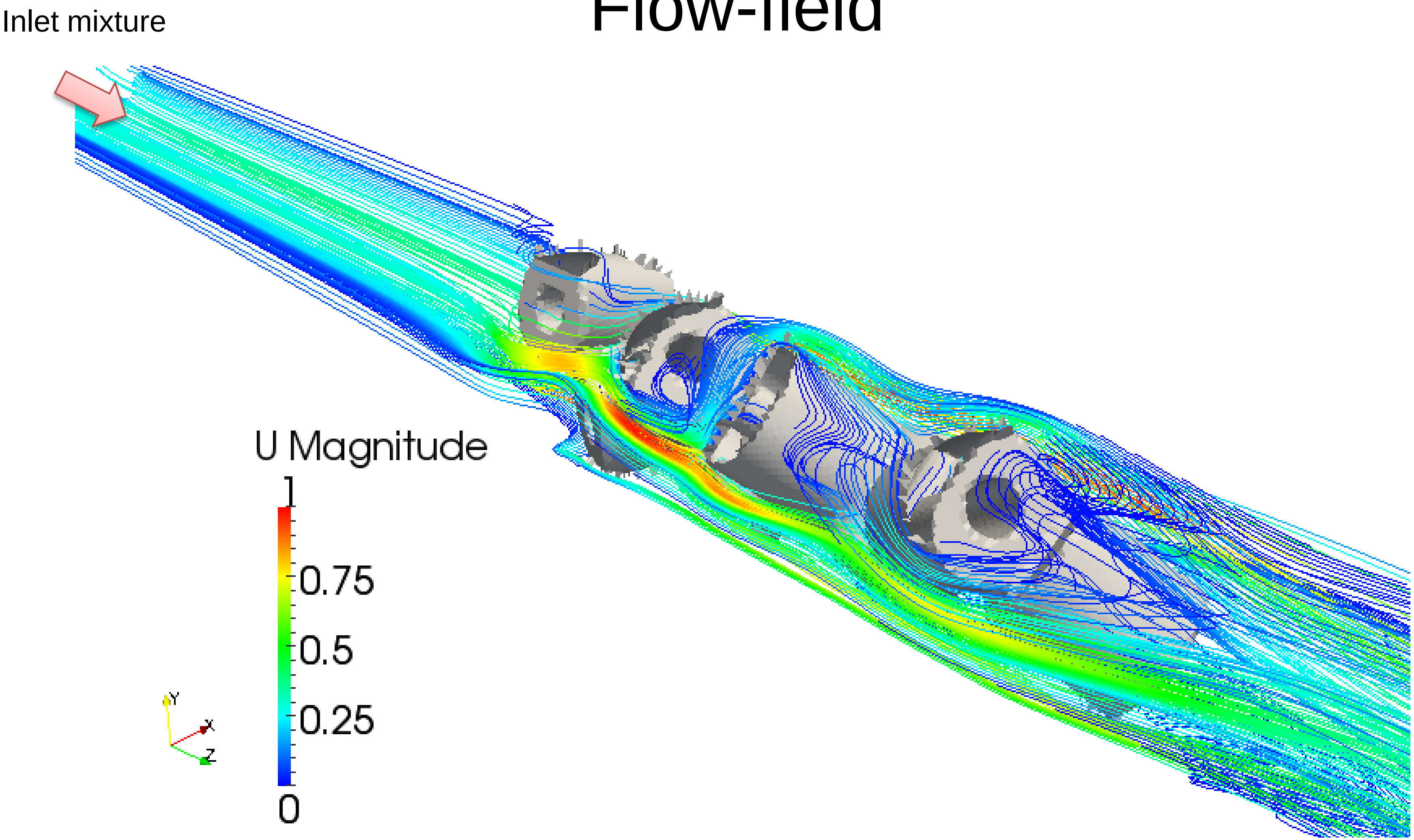
Show-case I: Rashig-ring bed

Inlet mixture



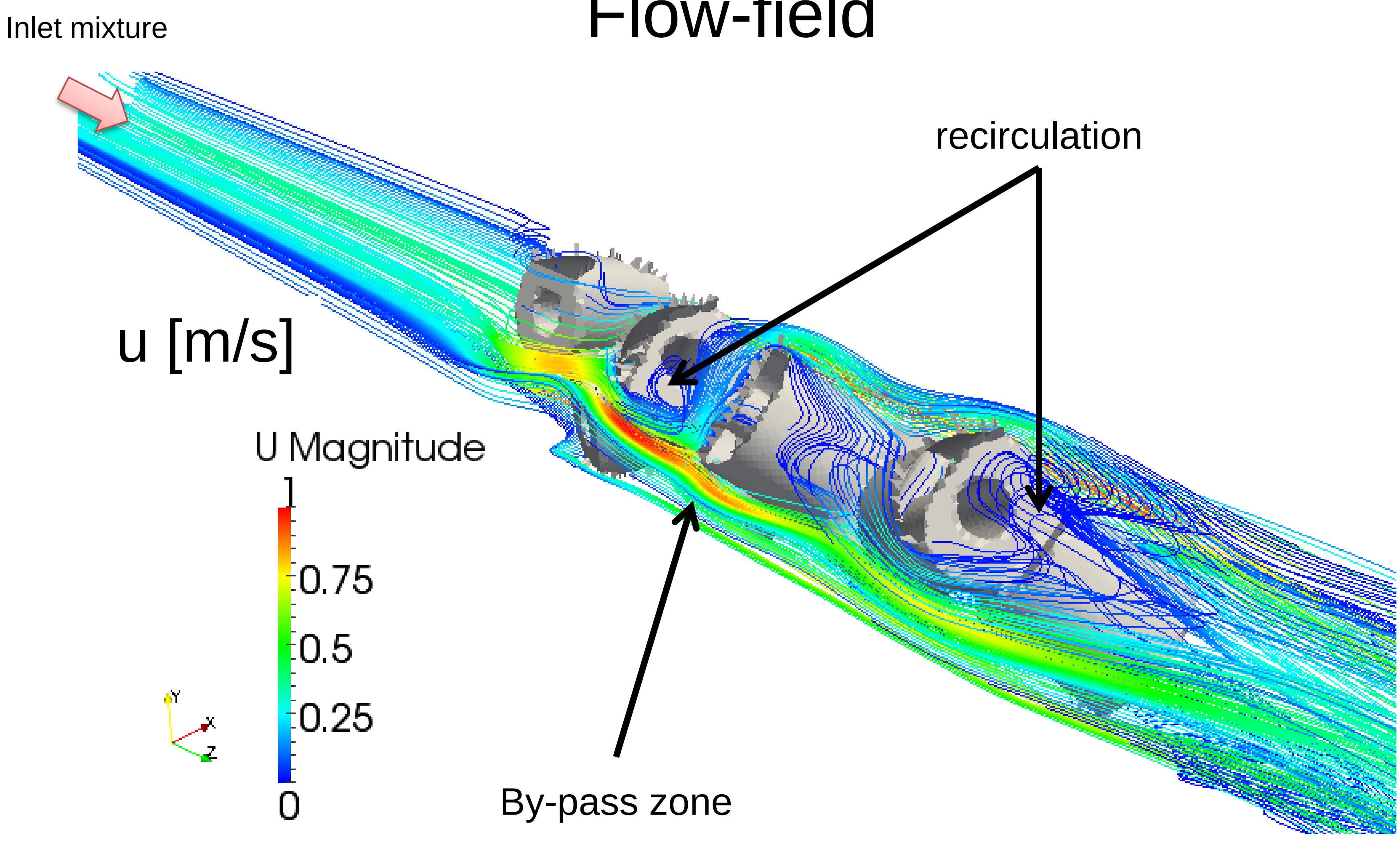
Show-case I: Rashig-ring bed

Flow-field



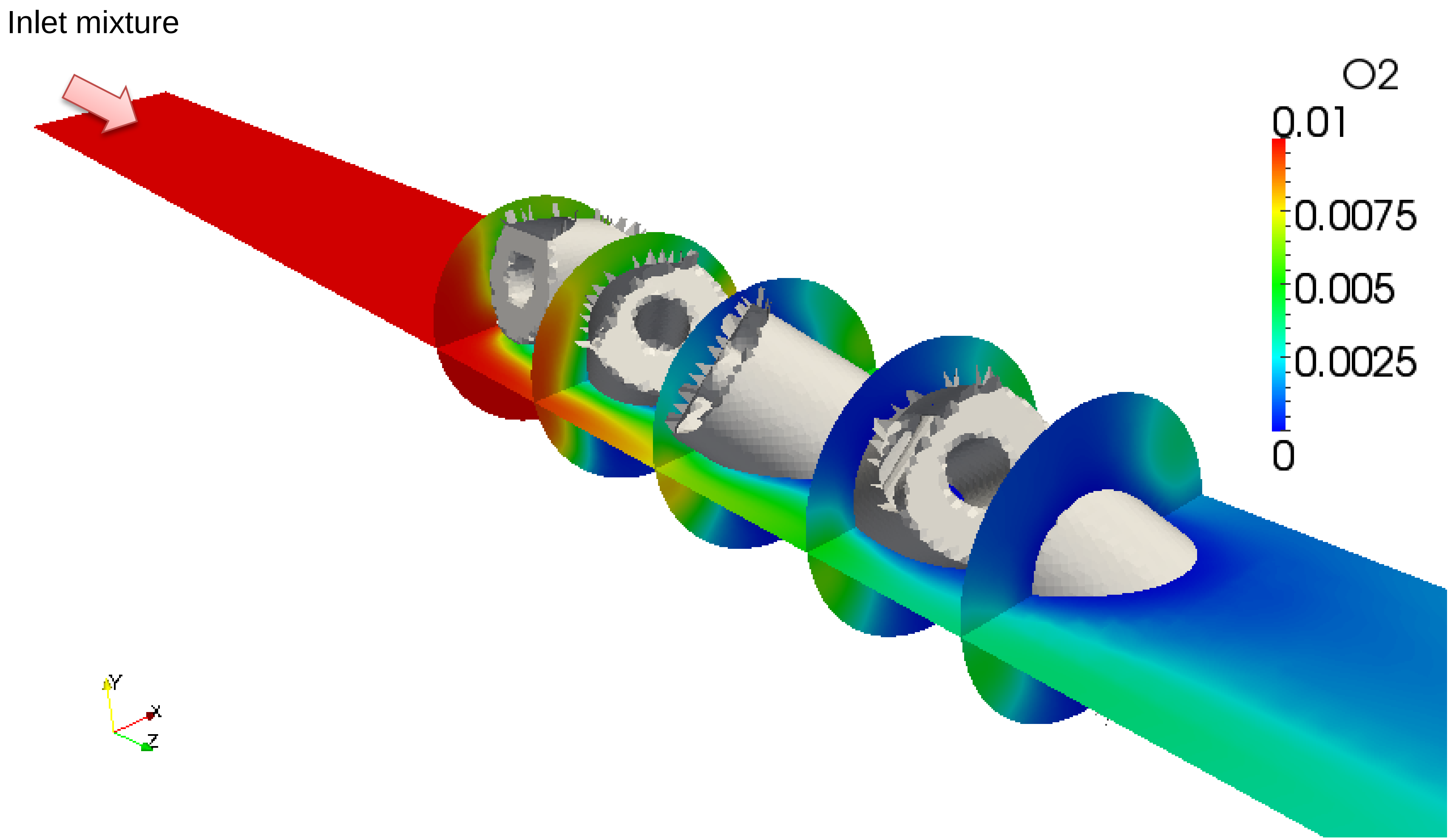
Show-case I: Rashig-ring bed

Flow-field



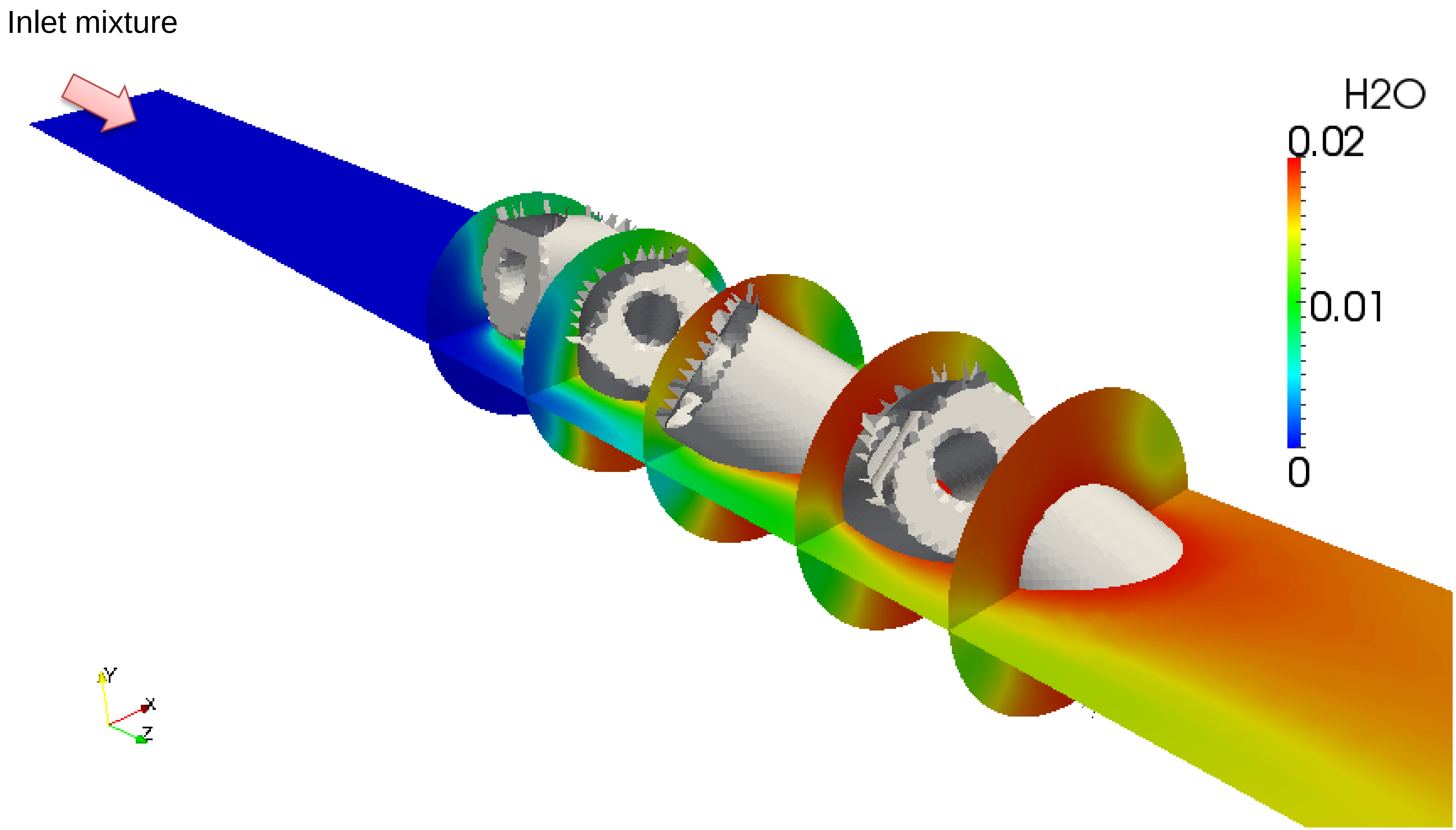
Show-case I: Rashig-ring bed

Gas-phase species



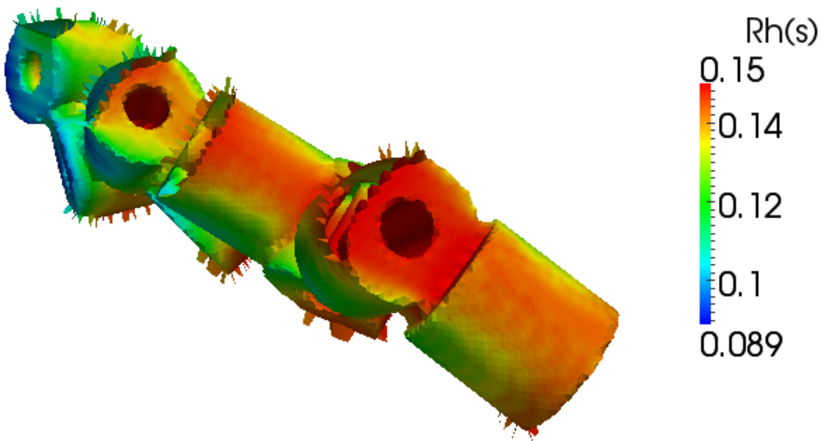
Show-case I: Rashig-ring bed

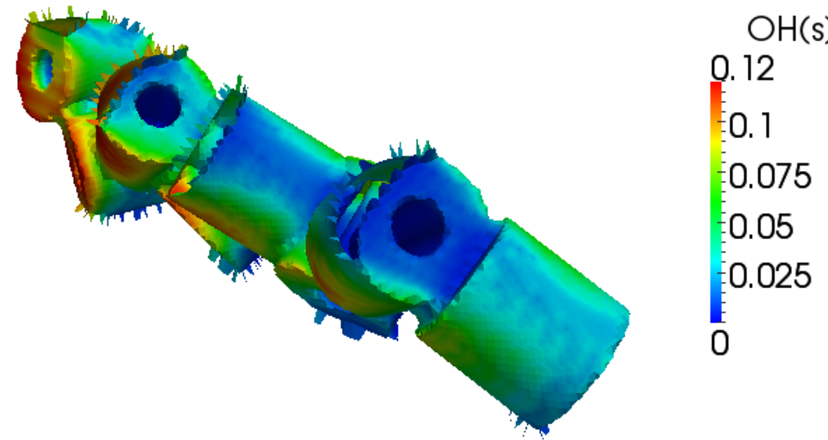
Gas-phase species

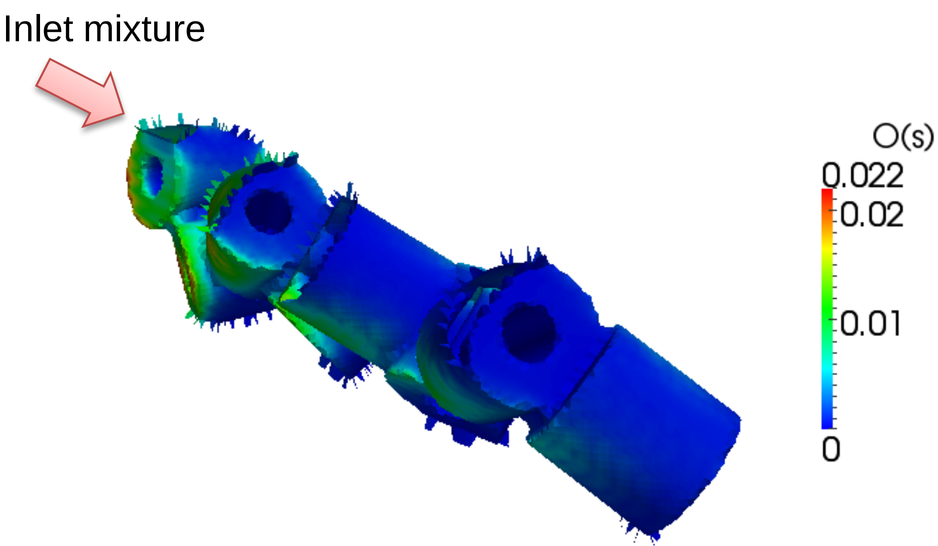


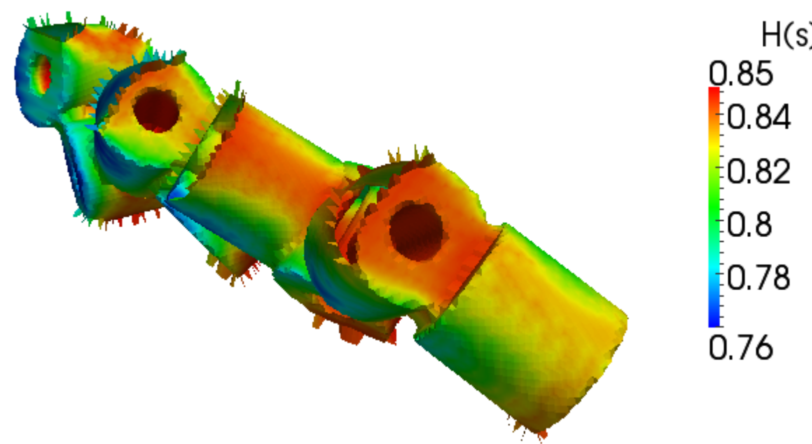
Show-case I: Rashig-ring bed

Adsorbed species at the catalyst surface



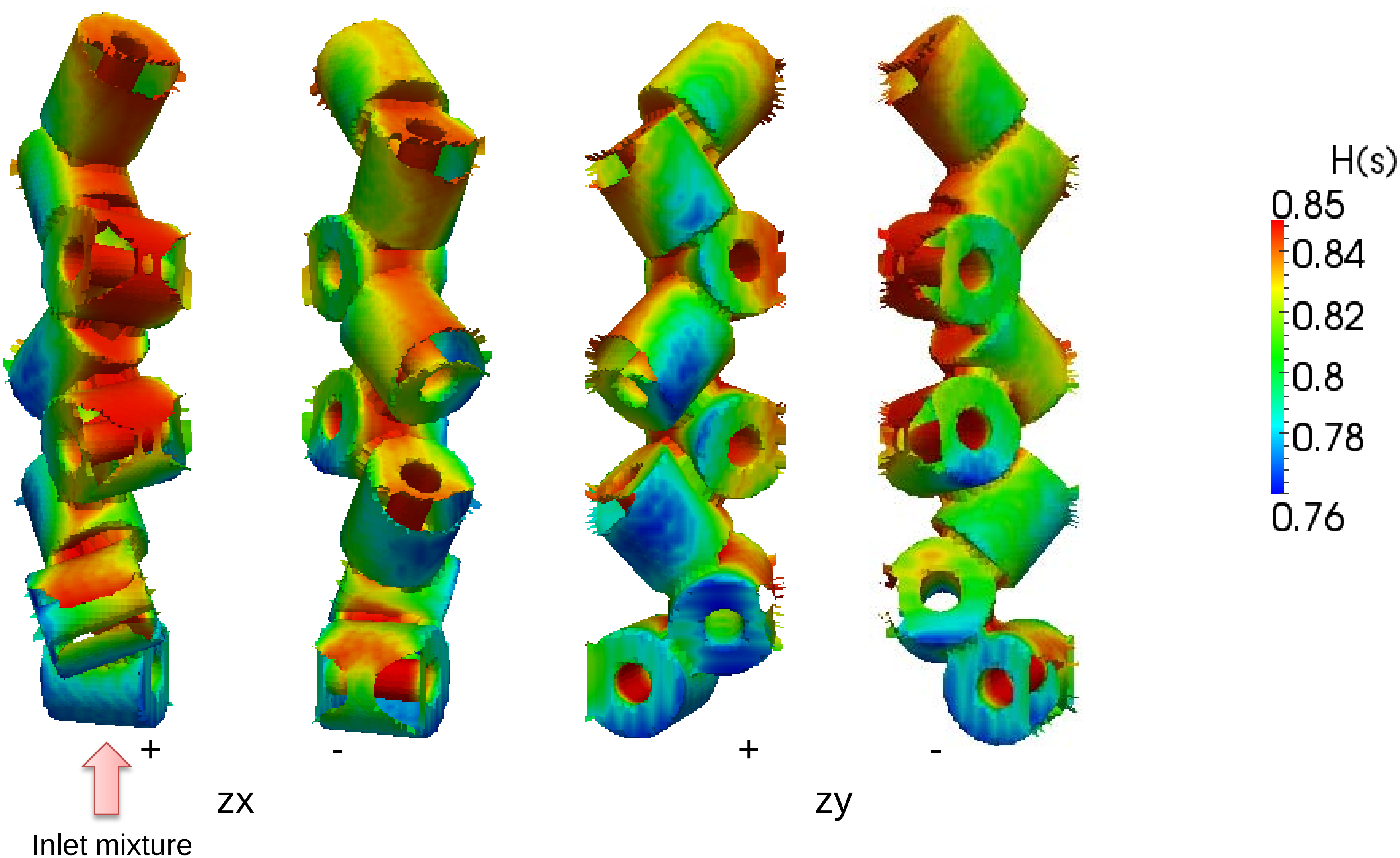






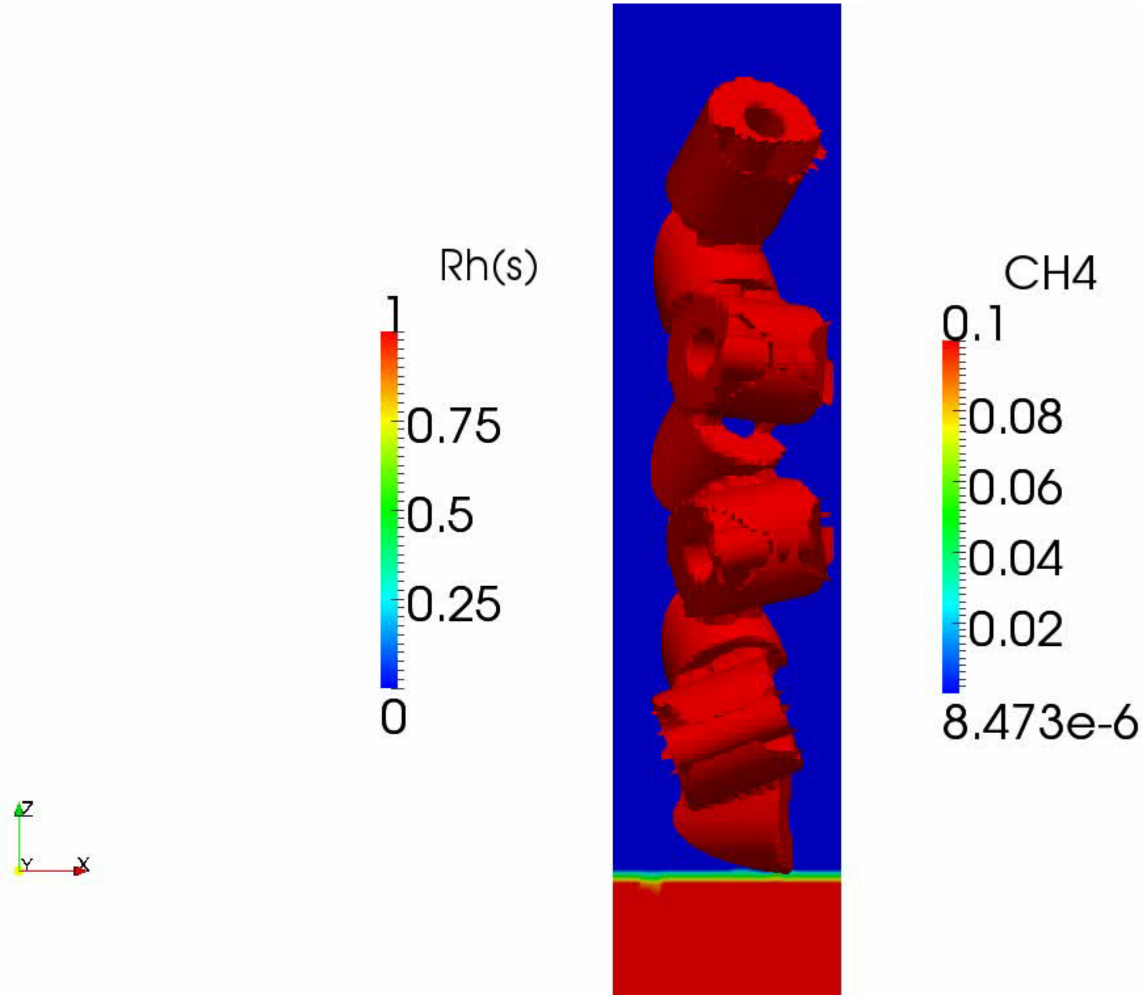
Show-case I: Rashig-ring bed

Adsorbed species at the catalyst surface



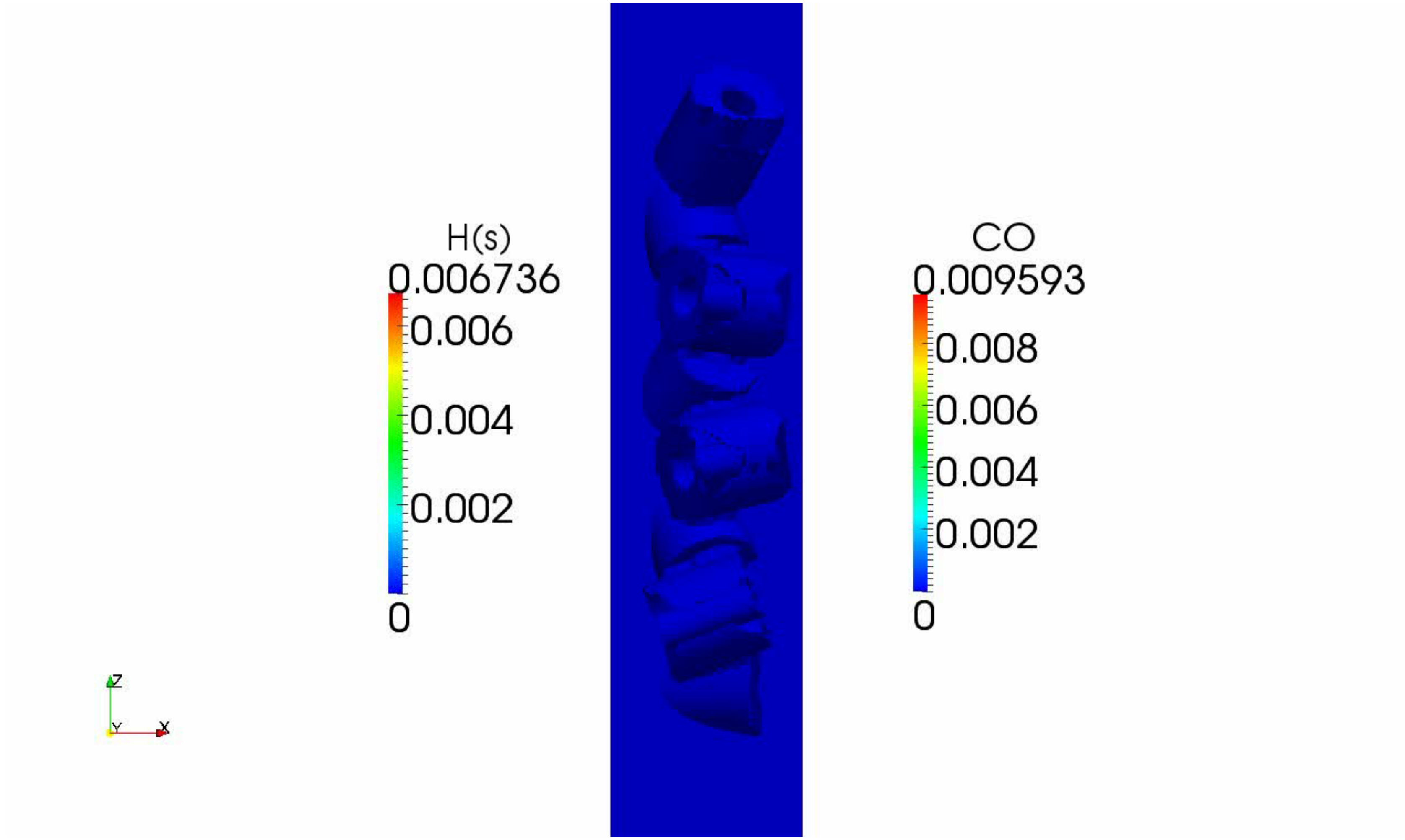
Show-case I: Rashig-ring bed

Dynamics of the system

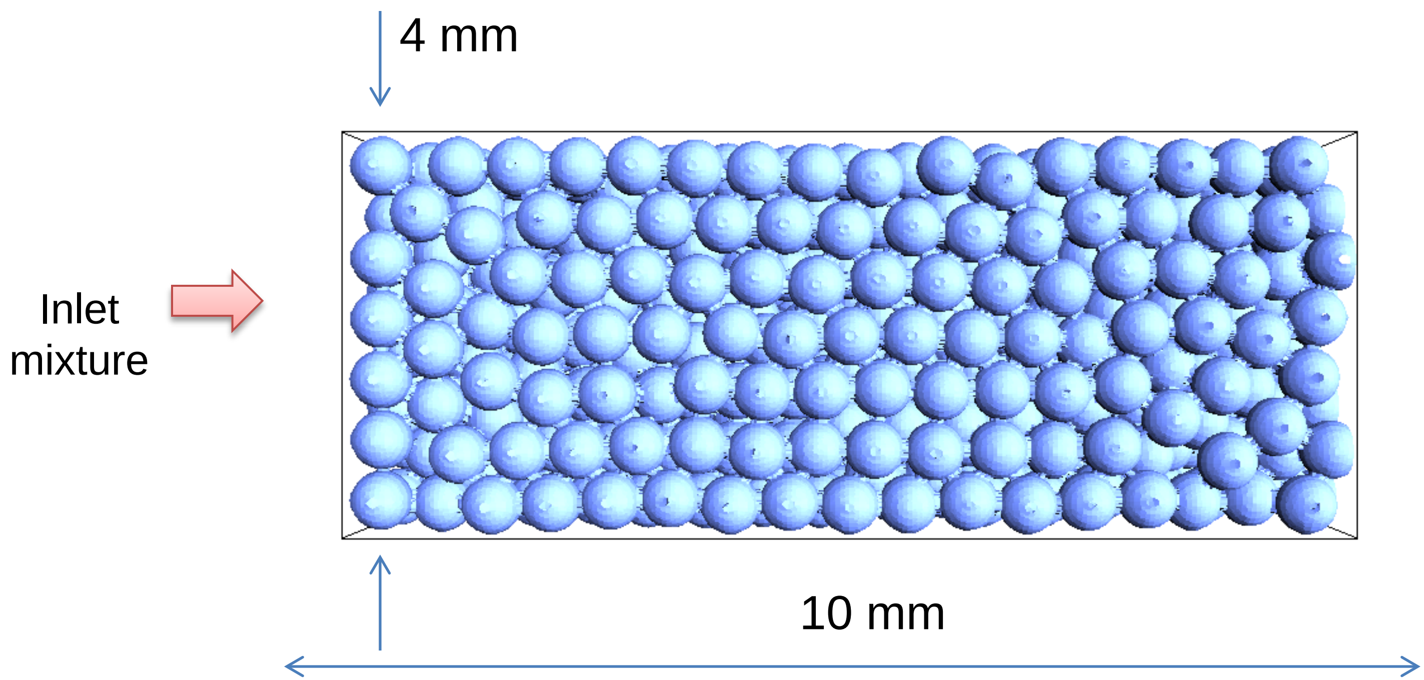


Show-case I: Rashig-ring bed

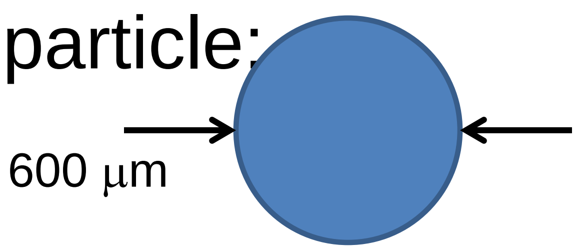
Dynamics of the system



Show-case II: packed bed of spheres

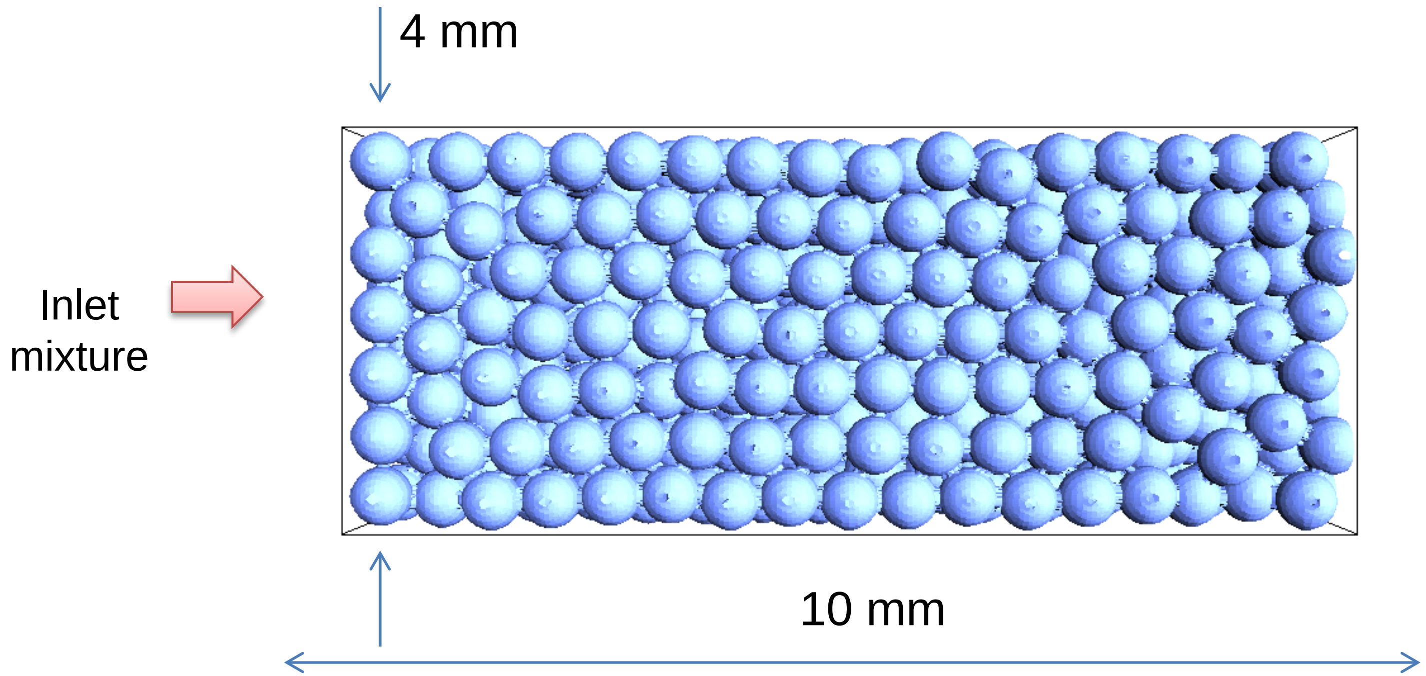


Catalytic particle:



Mesh generation in collaboration with Prof. Freund – Erlangen University, DE

Show-case II: packed bed of spheres



3D Unstructured Mesh: ~2,000,000 cells

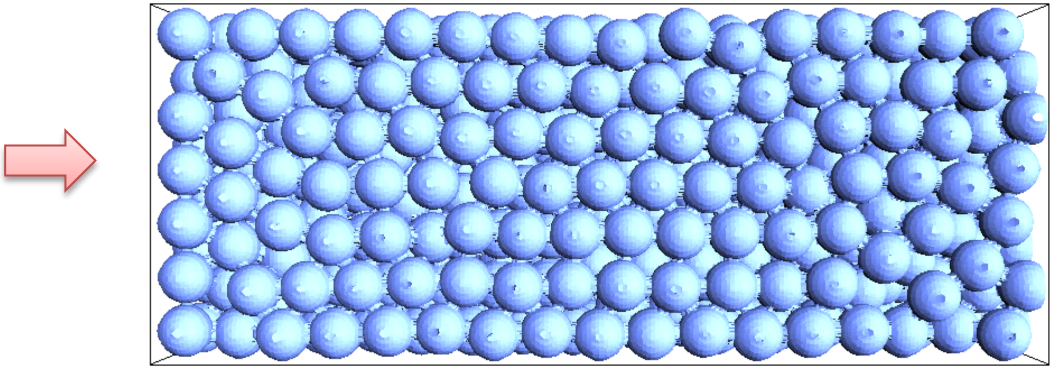
✓Homogeneous reactors: ~1,000,000

✓Heterogeneous reactors: ~1,000,000

Show-case II: packed bed of spheres

Laminar flow (Re = 20)

Inlet mixture



Operating conditions	
Inlet diameter	**4 mm**
Total length	**10 mm**
H_2 mole fraction	**0.036(-)**
O_2 mole fraction	**0.014(-)**
N_2 mole fraction	**0.95 (-)**
Temperature	**573 K**
Inlet velocity	**1.7 m/s**

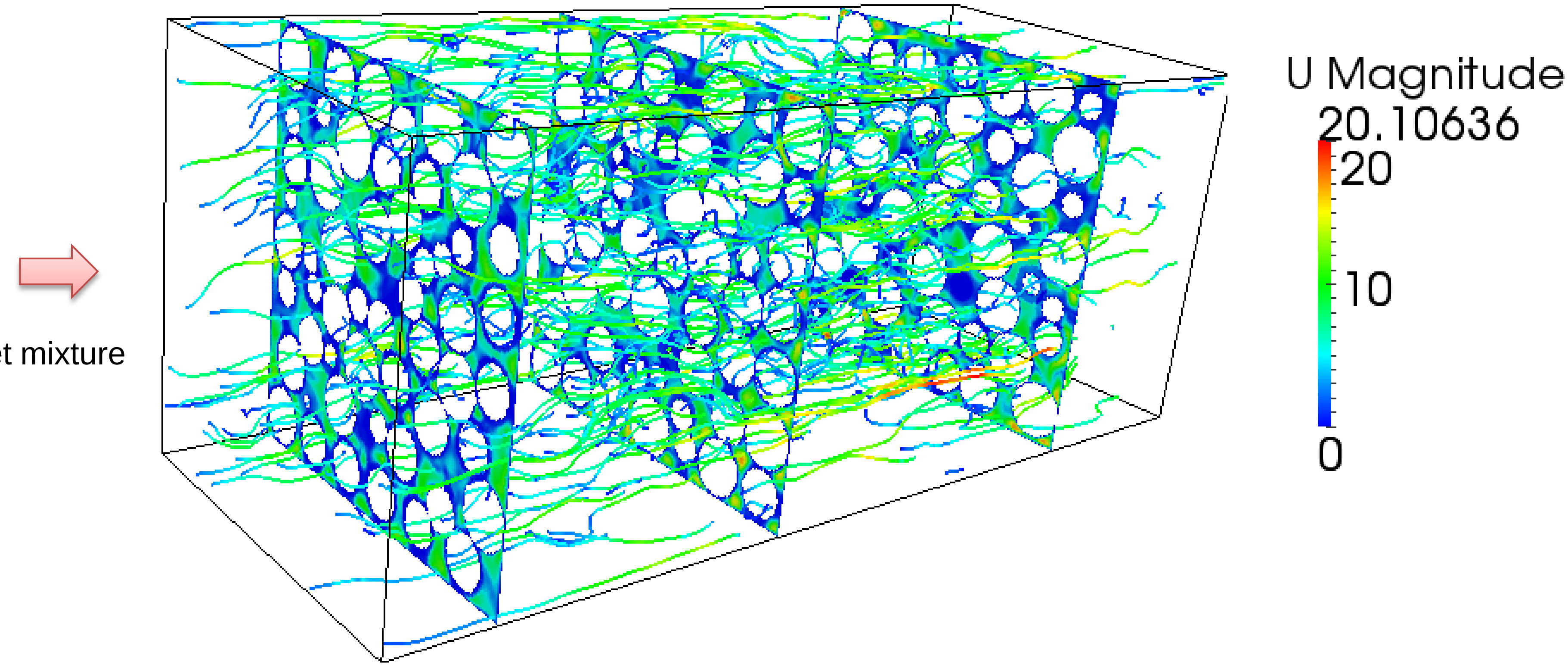
C1 microkinetic model on Rh:

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

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

Show-case II: packed bed of spheres

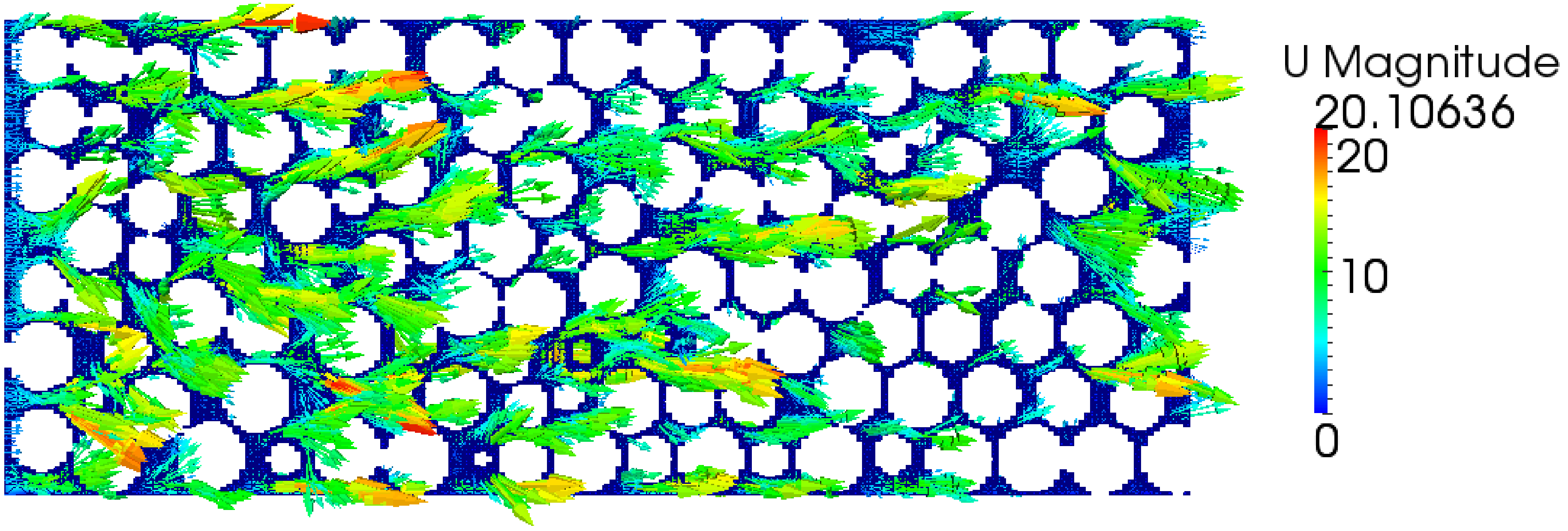
Flow-field



Inlet mixture

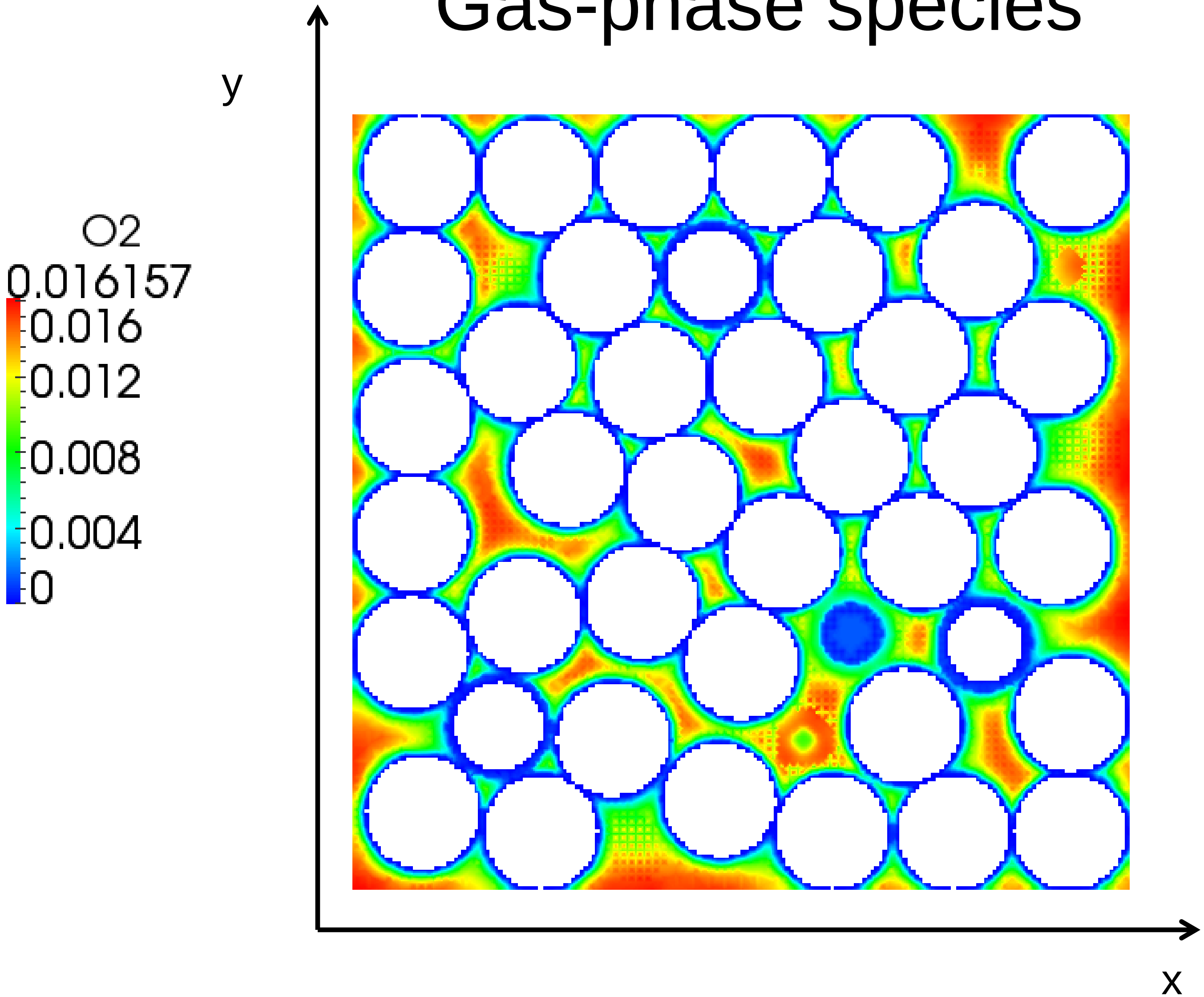
Show-case II: packed bed of spheres

Flow-field



Show-case II: packed bed of spheres

Gas-phase species



A "*first-principles*" approach to CRE

Length

CatalyticFOAM

MACROSCALE

Reactor engineering and transport phenomena

CFD

MESOSCALE

Interplay among the chemical events

kMC

In collaboration with:
K. Reuter and S. Matera (TUM)

TECHNISCHE UNIVERSITÄT MÜNCHEN

MICROSCALE

making and breaking of chemical bonds

MK

M. Maestri & A. Cuoci

www.catalyticfoam.polimi.it

Time

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

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

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

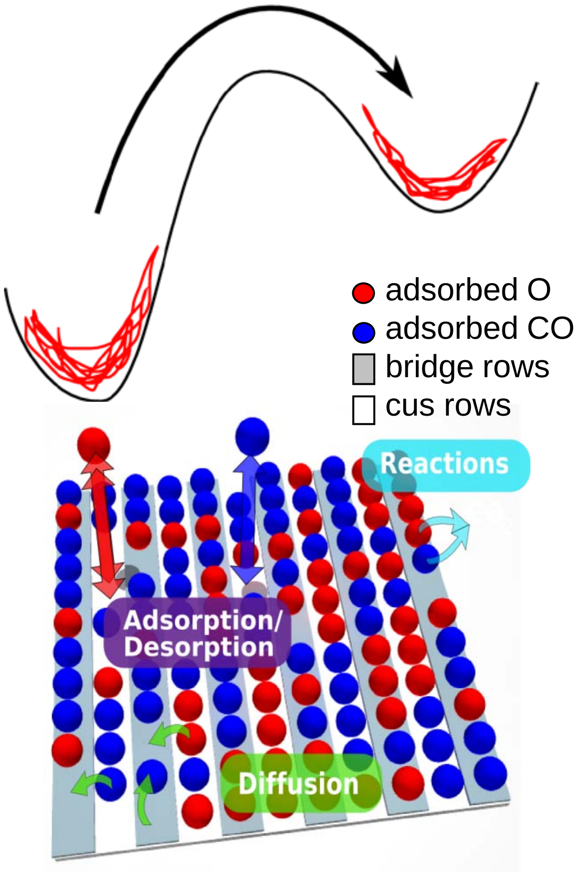


Image courtesy of Dr. S. Matera (TUM)

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

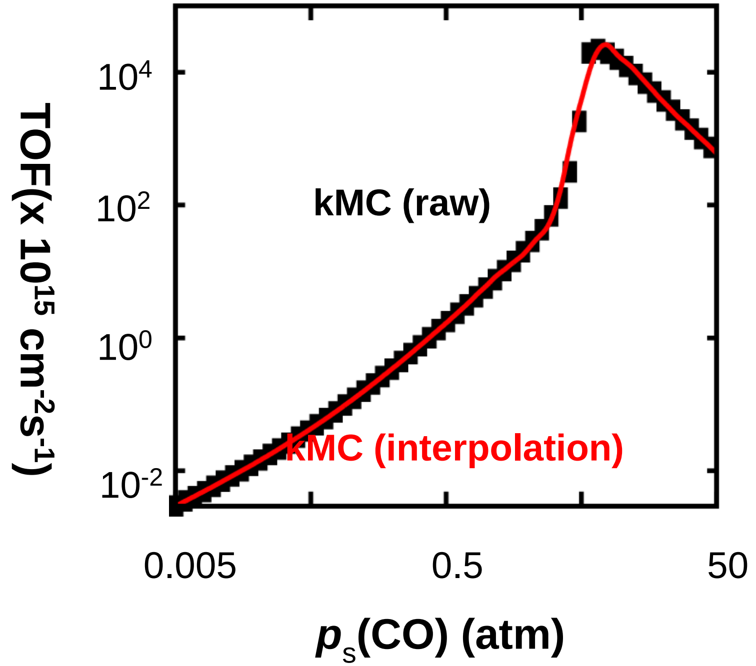
Linking the scales

- 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



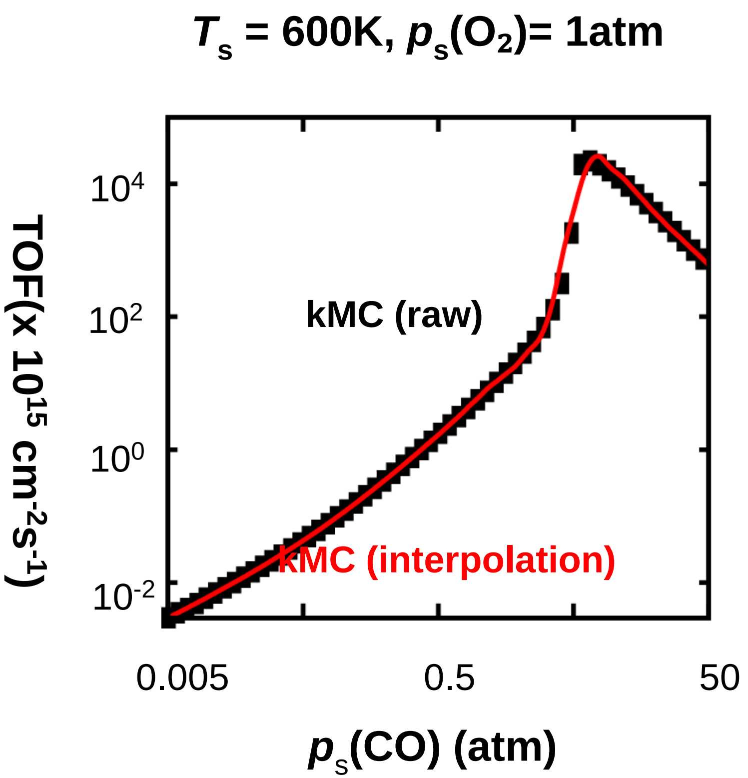
S. Matera and K. Reuter, *Catal. Lett.* **133**, 156-159 (2009); *Phys. Rev. B* **82**, 085446 (2010).

Linking the scales

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

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

- **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**



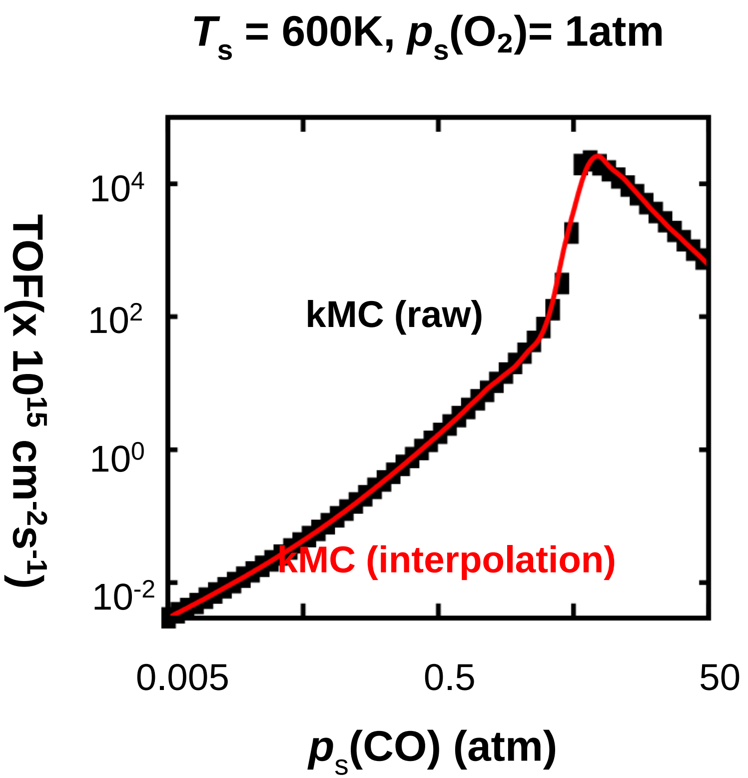
S. Matera and K. Reuter, *Catal. Lett.* **133**, 156-159 (2009); *Phys. Rev. B* **82**, 085446 (2010).

Linking the scales

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

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

- **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**



Karsten's tutorial this afternoon

Show-case: the “reactor STM”

REVIEW OF SCIENTIFIC INSTRUMENTS VOLUME 69, NUMBER 11 NOVEMBER 1998

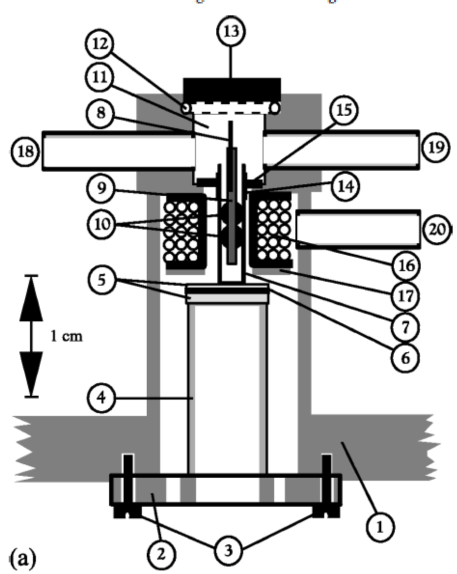
The “Reactor STM”: A scanning tunneling microscope for investigation of catalytic surfaces at semi-industrial reaction conditions

P. B. Rasmussen, B. L. M. Hendriksen,[a)] H. Zeijlemaker, and H. G. Ficke
FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

J. W. M. Frenken
Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands and FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

(Received 17 March 1998; accepted for publication 17 August 1998)

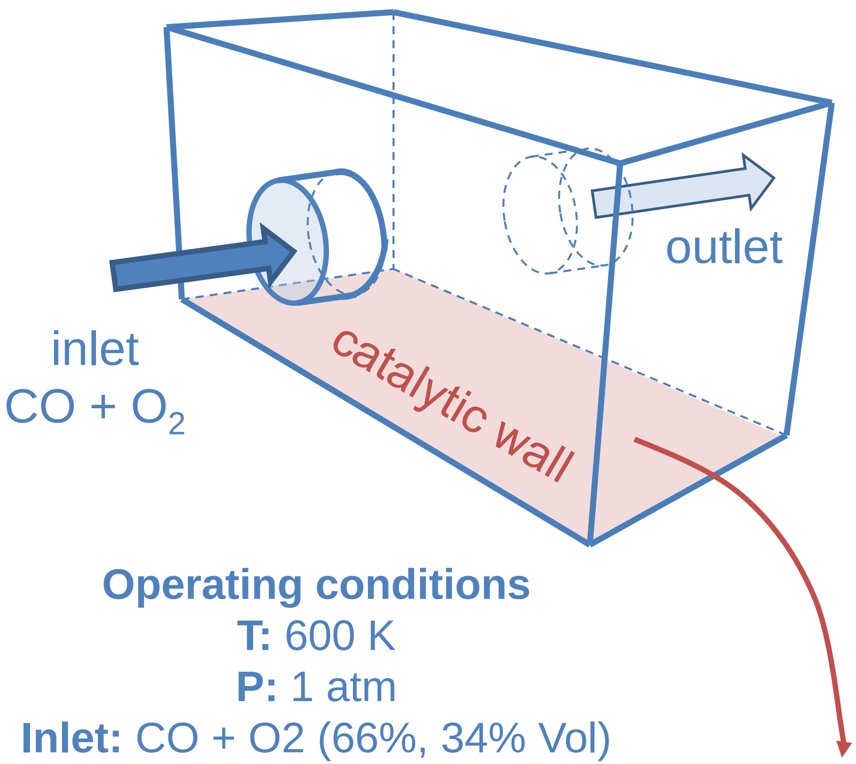
An instrument is introduced that combines a scanning tunneling microscope (STM) and a small volume (300 μl) flow reactor, for the *in situ* study of catalytic surfaces at *semi-industrial* conditions.



(a)

Show-case: the “reactor STM”

Rasmussen et al., Review of scientific instrument, 69 (1998) 3879



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

Catalytic Wall
Catalyst: Ru_2O

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)

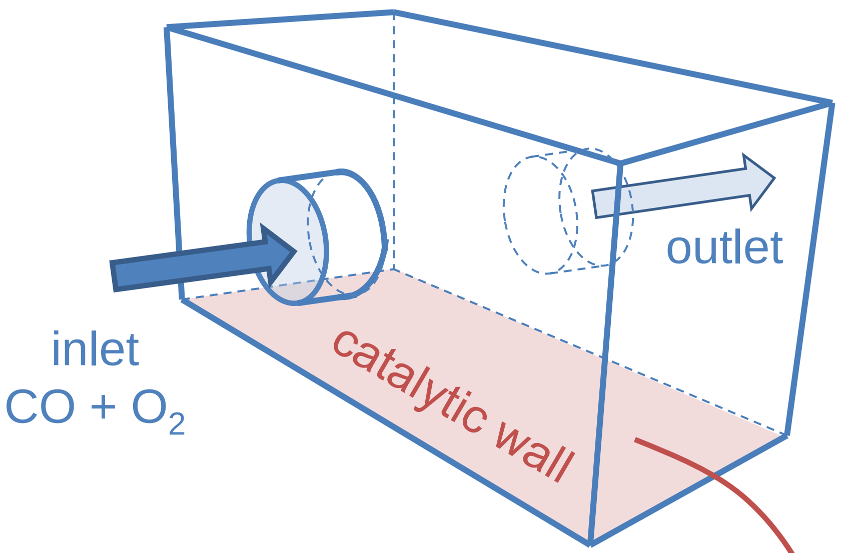
CatalyticFOAM

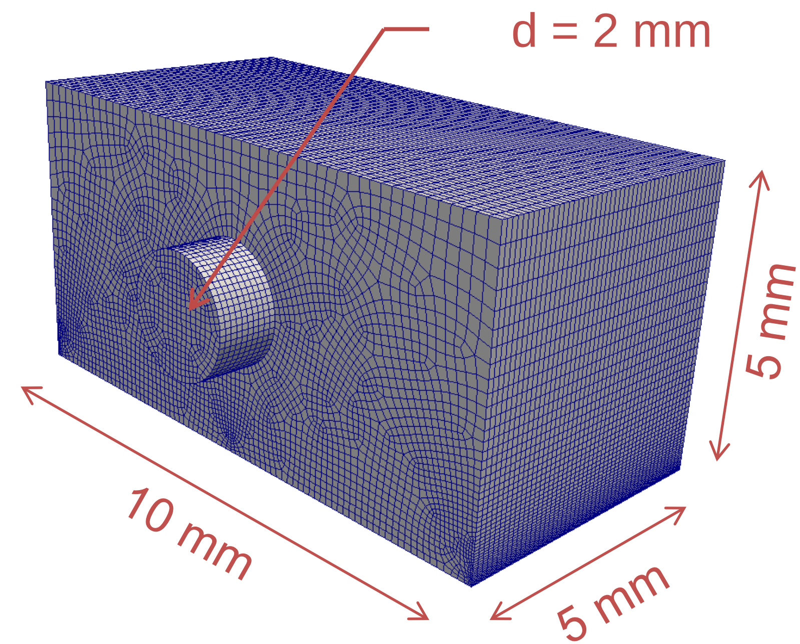
catalyticFOAM (interpolated kMC)

www.catalyticfoam.polimi.it

Show-case: the “reactor STM”

Rasmussen et al., Review of scientific instrument, 69 (1998) 3879





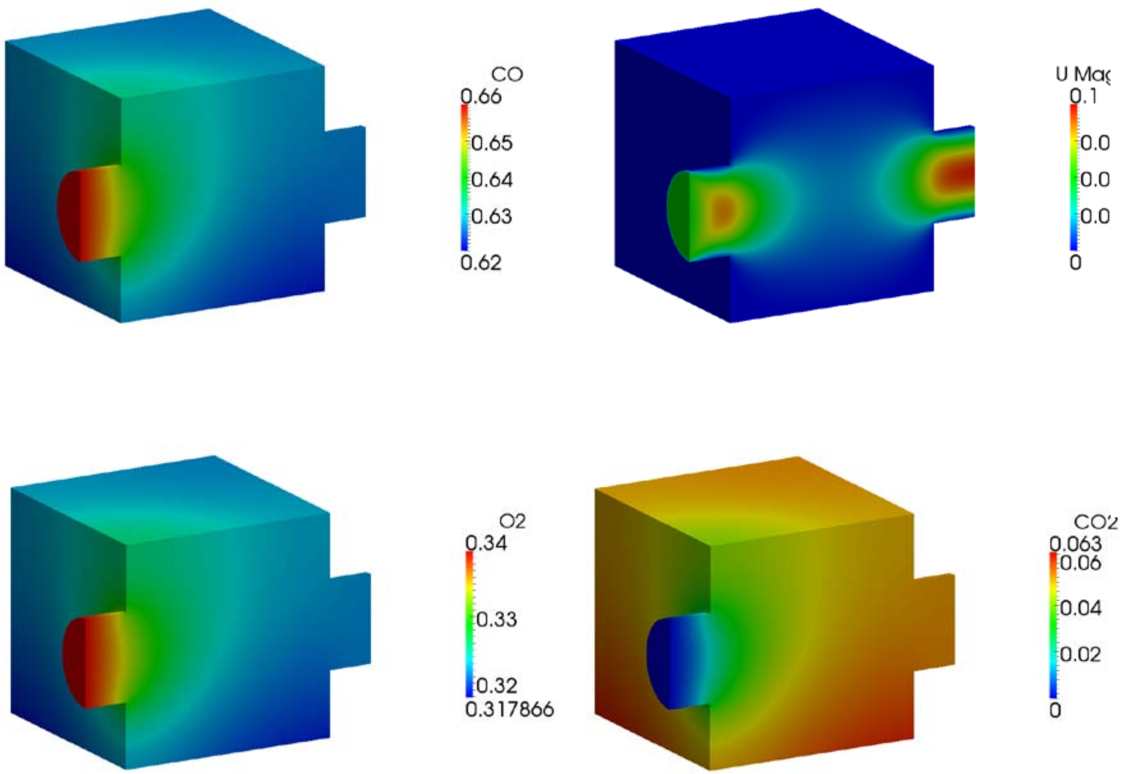
Operating conditions
T: 600 K
P: 1 atm
Inlet: CO + O2 (66%, 34% Vol)
Inlet velocity: 5 cm/s

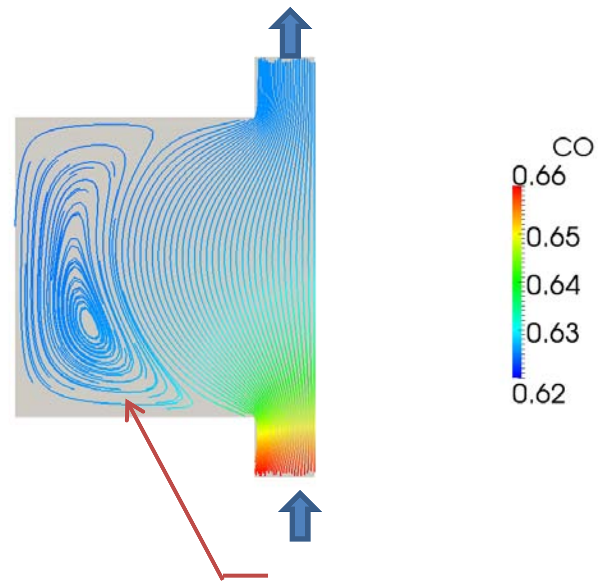
Catalytic Wall
Catalyst: Ru_2O

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

Results

Stream lines





Strong recirculations

Catalytic Wall
Catalyst: Ru_2O

Conclusions & perspectives

- ✓ Efficient coupling between heterogeneous microkinetic models and computational fluid dynamics (complex and fundamental chemistry with complex and general geometries)

- ✓ Description of the solid phase (diffusion/conduction and reaction within the solid: assessment of internal mass transfer limitation)

- ✓ Implementation of the interpolated kMC methodology in catalyticFOAM (in collaboration with K. Reuter/S. Matera, TUM)

- ✓ Multiscale framework for the first-principles analysis of catalytic processes

www.catalyticfoam.polimi.it

Acknowledgements

CatalyticFOAM@*polimi.it*

M. Maestri & **A. Cuoci**

Tiziano Maffei, G. Gentile, F. Manelli, S. Rebughini,

S. Goisis, A. Osio, M. Calonaci, F. Furnari, B. Baran, Y. Niyazi

University of Delaware | Max-Planck-Gesellschaft | Technische Universität München | Alexander von Humboldt Stiftung/Foundation | Politecnico Milano | Laboratory of Catalysis and Catalytic Processes LCCP

Politecnico di Milano

Thank you for your attention!

Raffaello, The school of Athens, 1509, Apostolic Palace, Roma

www.catalyticfoam.polimi.it CatalyticFOAM **matteo.maestri@polimi.it**