Structured chemical reactors: experimental analysis and simulation

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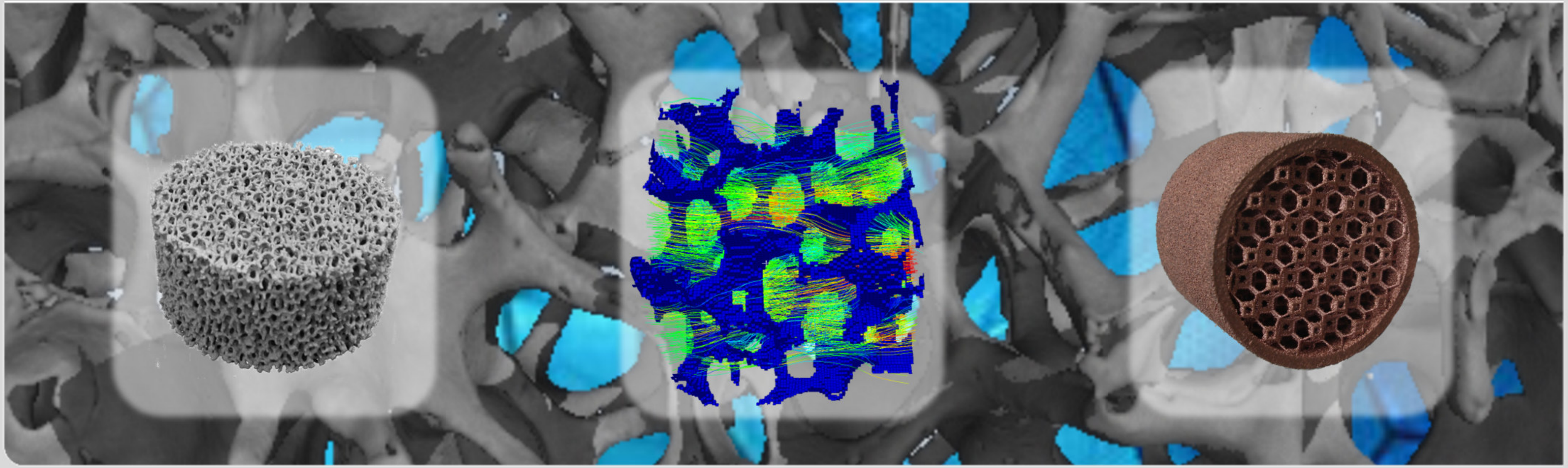
*INSTITUTE OF THERMAL PROCESS ENGINEERING and #INSTITUTE OF CATALYIS RESEARCH AND TECHNOLOGY



Outline

- Introduction
  - Structured reactors
  - Computational fluid dynamics (CFD)
- Solid sponge reactors
  - Single-phase flow and heat transfer
  - Gas-liquid flow
- Periodic open cell structures
  - Bubble structure interaction
- Monolith reactor
  - Taylor flow in a single channel
- Conclusions and outlook

Introduction

Typical structured elements for chemical reactors

	packed beds	honeycombs/monoliths
	 	

Main properties

	packed beds	honeycombs/monoliths
- Porosity	low (~ 40 %) (→high pressure drop)	high (~ 75 - 95 %) (→low pressure drop)
- Cross-mixing	good	not existing
- Heat transfer	high resistances (point contact)	low resistances (continuous solid phase)

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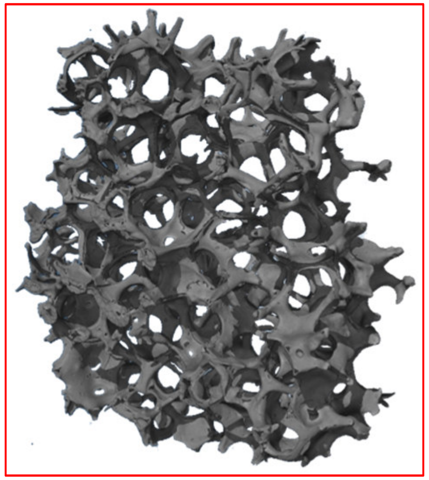
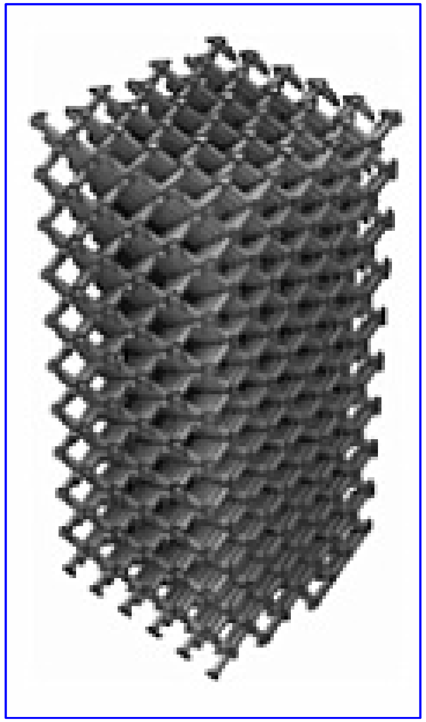
	(point contact)	(continuous solid phase)

Sponges and POCS

Open-cell foams (sponges) and periodic open cell structures (POCS) combine advantageous properties





- High porosity
  - Low pressure drop
  - Low weightiness
- High specific surface area
  - Advantageous for heterogeneous reactions and fluid-solid heat/mass transfer
- Continuous solid phase
  - Advantageous for heat transport
  - Possibility for utilizing heat of highly exothermic reactions in a separate process (→ *energy efficiency*)

For manufacturing, characterization and functionalization of sponges and POCS see the presentation of A. Inayat in this session

Modeling approaches

- Modeling is essential for …
  - A better understanding of the interactions of chemistry and physics (het./hom. chemical reactions ↔ mass and heat transport)
  - Support of reactor design and engineering
  - Optimization of the operation conditions (maximization of desired product yield, minimization of undesired side-products)
- Modeling hierarchies
  - Process simulations (Model-based design of optimal reactors and processes, FAU Erlangen)
  - Scale-reduced CFD simulations (Euler-Euler approach, HZDR)
  - **Scale-resolved CFD simulations (“Direct numerical simulation”, KIT)**
- Advantages/disadvantages of scale-resolved simulations
  - Getting insight in phenomena which are experimentally difficult accessible
  - Utilization of data for development of models on larger level of abstraction
  - High computational costs

CFD tools used here

Solution of the incompressible Navier-Stokes equations
(for two-phase flows with surface tension term)

- OpenFOAM®: open-source library for computational continuum mechanics
  - FOAM = Field Operation and Manipulation (not related to foam/sponge reactor)
  - simpleFoam (steady laminar flow)
  - porousSimpleFoam (steady laminar flow, multi-region approach)
  - buoyantBoussinesqSimpleFoam (steady laminar flow, Boussinesq approx. for heat tr.)
  - phaseFieldFoam (unsteady laminar two-phase flow)
    - Phase-field method for two-phase flows
    - Under development in cooperation with Dr. H. Marschall (TU Darmstadt)
- TURBIT-VOF: in-house code based on geometric volume-of-fluid method
  - Used for Taylor flow in single channel of monolith reactor

code for single-phase flow
code for two-phase flow

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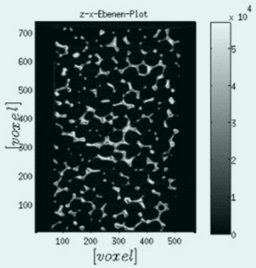
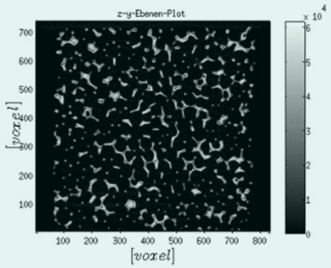
General procedure

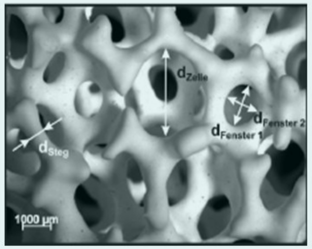
ψ = porosity
S_V = specific surface area

Δp = pressure drop
α = heat transfer coeff.

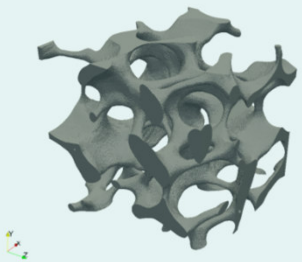




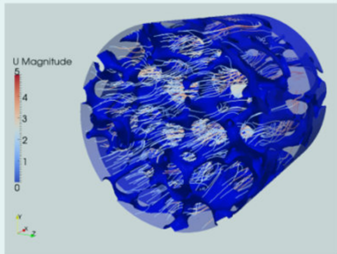
sponge structure data (CT)



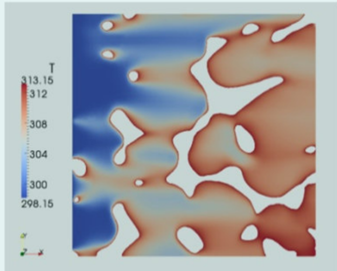
$\rightarrow \psi, S_V$



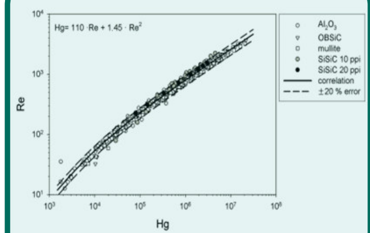
CFD geometries



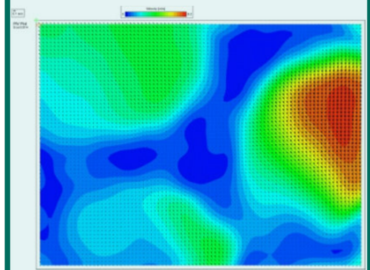
hydrodynamics



heat transfer



global (Δp, α)



local (µPIV)

first step:

- structural analysis
- reconstruction

second step:

- meshing
- simulation

third step:

- experimental validation

Multi-region approach

combined modeling approach for hydrodynamics and heat transfer in sponges:

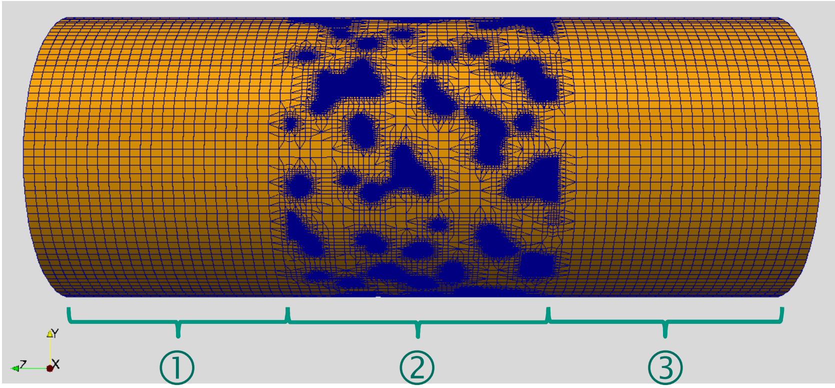
→ cylindrical representative elementary volume (**REV**) of the sponge to be investigated

→ **simulation geometry** consisting of ...

… inlet zone (①)

… resolved sponge REV (②)

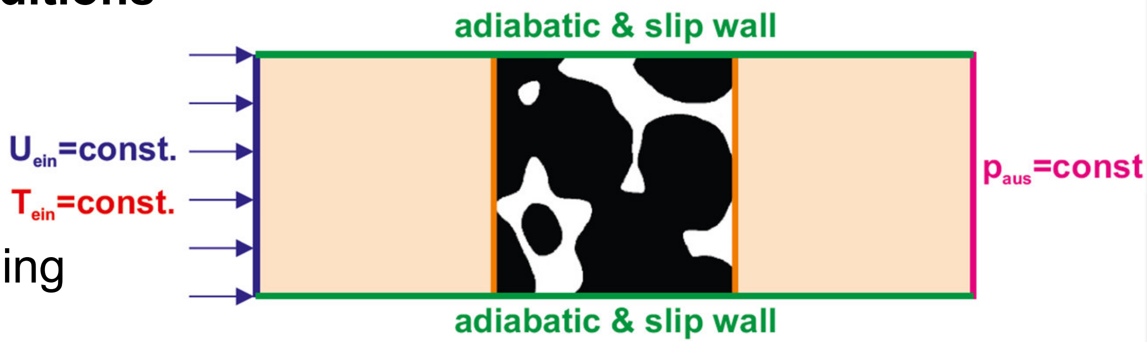
… outlet zone (③)



→ specification of **boundary conditions**

→ radially constant inlet/ outlet boundary values

→ embedding of sponge REV into hydrodynamic surrounding



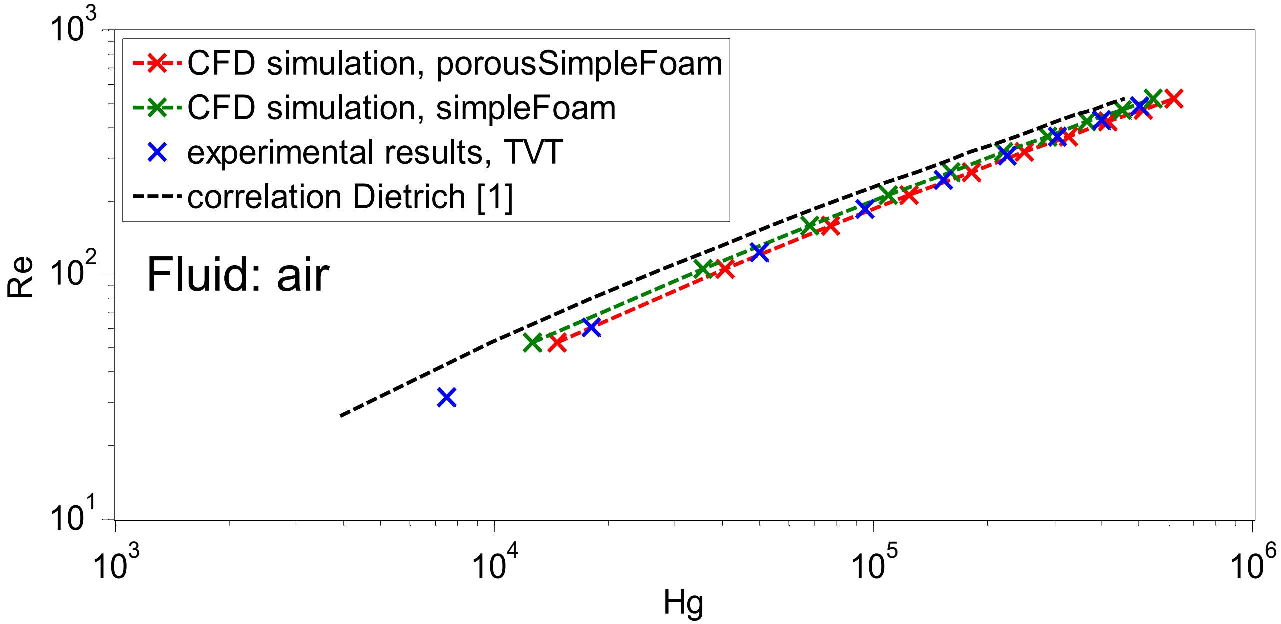
About 18 million mesh cells (cell size at sponge surface ≈ 25 µm)

Selected numerical results for single-phase pressure drop

→ focus on well-(heat-)conducting **SiSiC** sponges (e.g. 20 pores per inch, $\psi \approx 85\%$)

→ presentation of results in terms of **dimensionless numbers**:

$$Re_d = \frac{U_0 \cdot d_h}{\nu_F \cdot \psi} \qquad Hg = \frac{\Delta p}{\Delta z} \cdot \frac{{d_h}^3}{\rho_F \cdot {\nu_F}^2}$$ using hydraulic diameter $d_h = \frac{4\psi}{S_V}$



CFD model	RMS_{exp} [%]
simpleFoam	(-)6,70
porousSimpleFoam	(+)7,87

→ CFD simulation results obtained from different modeling approaches are in good agreement with literature data and experimental results (same sponge samples)

[1] Dietrich et al., Pressure drop measurements of ceramic sponges - determining the hydraulic diameter, Chem. Eng. Sci. 64 (2009) 3633-3640

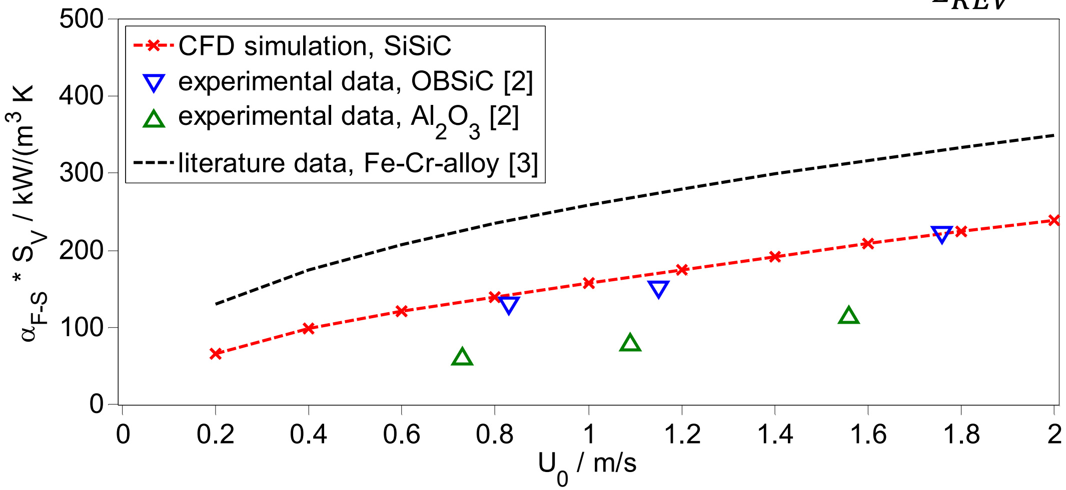
Selected numerical results for single-phase heat transfer

Karlsruhe Institute of Technology

→ simplifying assumption: **isothermal** sponge surface (e.g. T_S = 40 °C)

→ balancing of REV's energy gives term for **(volumetric) heat transfer coefficient**:

$$(\alpha \cdot S_V)_{CFD} = \frac{\rho_F \cdot U_0 \cdot c_{p,F} \cdot \ln\left(\frac{\overline{T_{F,in}} - T_S}{\overline{T_{F,out}} - T_S}\right)}{L_{REV}}$$



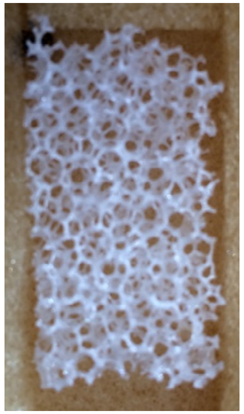
	ppi [-]	ψ [%]	S_V [m²/m³]	λ_S [W/(m K)]
CFD, SiSiC	20	84,75	962,04	→ ∞
exp., OBSiC	20	84,5	890	9,2
exp., Al_2O_3	20	85,4	974	27,5
Lit., Fe-Cr-alloy	12.8	93.7	767	≈ 80-90

→ acceptable agreement with reasonably comparable literature data and exp. results from similar (but transient) heat transfer coefficient measuring method

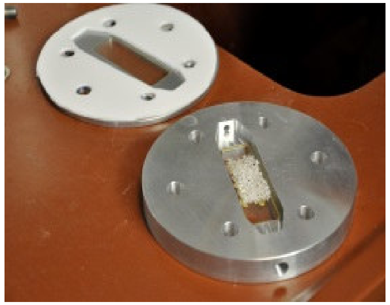
→ directly comparable experiments ongoing

[2] Dietrich, Heat transfer coefficients for solid ceramic sponges – Experimental results and correlation, Int. J. Heat Mass Transfer 61 (2013) 627-637
[3] Giani et al., Heat transfer characterization of metallic foams, Ind. Eng. Chem. Res. 44 (2005) 9078-9085

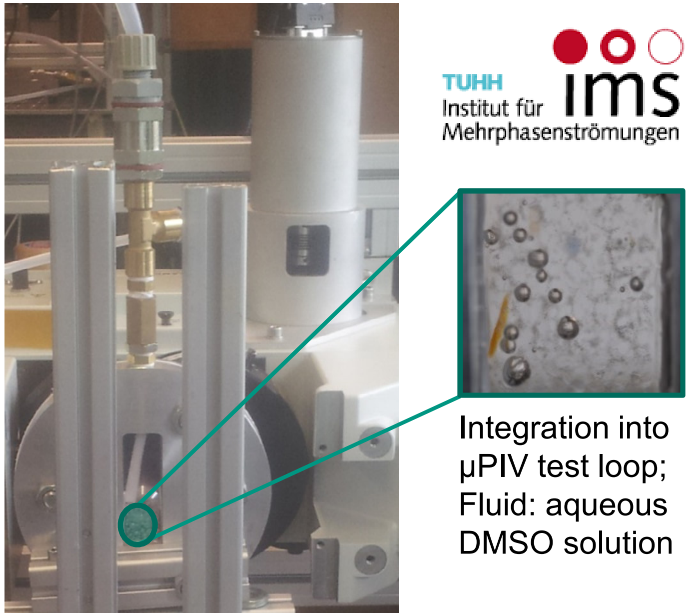
µPIV measurements as a novel validation technique for results of numerical simulations



SiO_2 glass sponge sample



insertion into flow channel



Integration into µPIV test loop; Fluid: aqueous DMSO solution

µPIV measurements as a novel validation technique for results of numerical simulations

SiO_2 glass sponge sample

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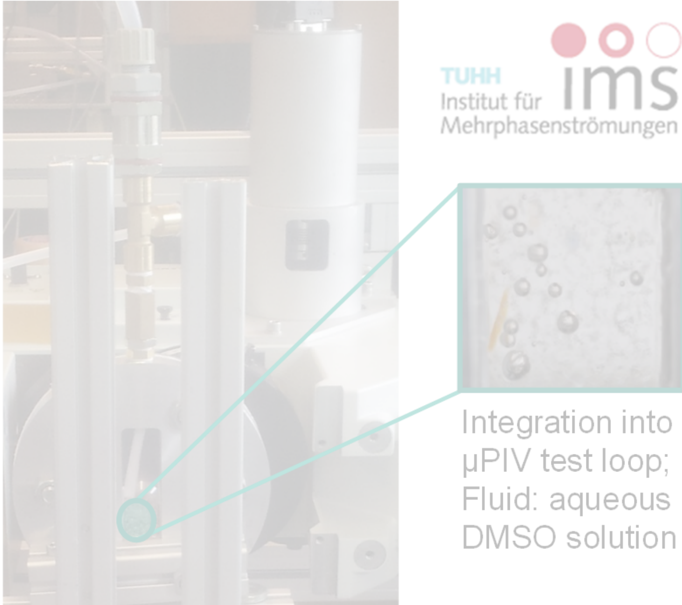

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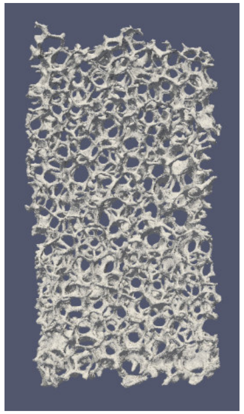


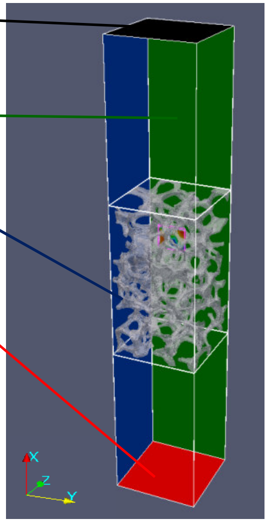
structural analysis (µCT)

p_{out} = const.

real channel wall → no slip wall

'internal' boundary → slip wall

$U_{x,in}$ = const.



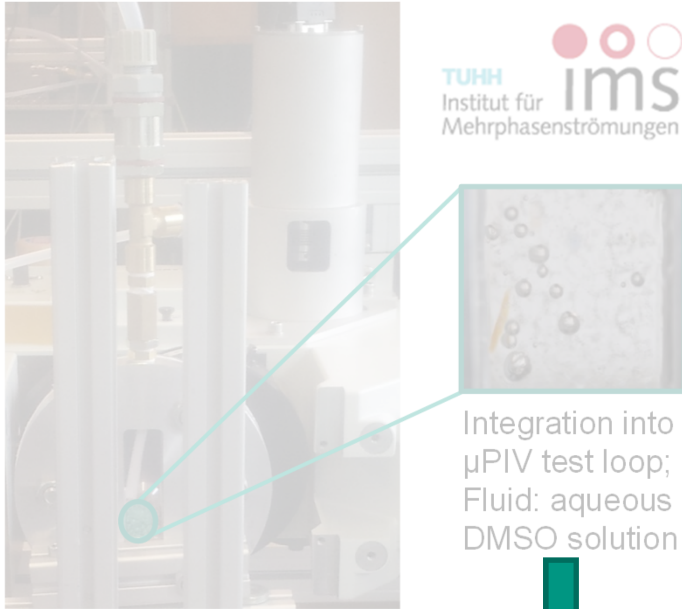
adapted CFD model set-up

µPIV measurements as a novel validation technique for results of numerical simulations

TUHH Institut für Mehrphasenströmungen ims

SiO_2 glass sponge sample

insertion into flow channel



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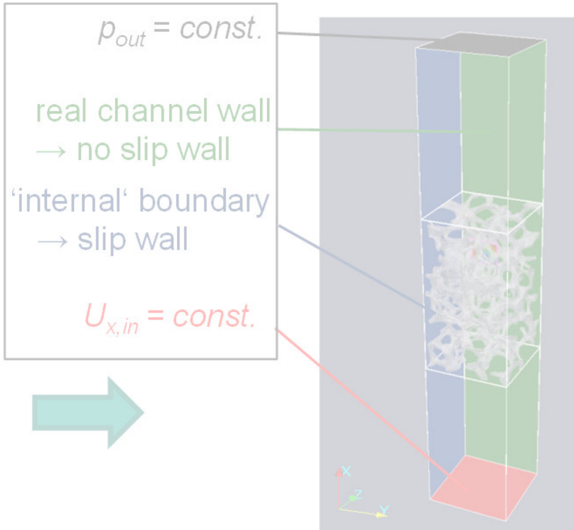

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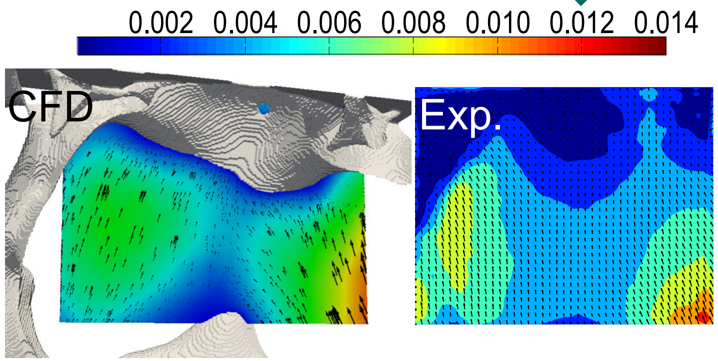

Comparison of calculated and measured local (time-averaged) velocity fields

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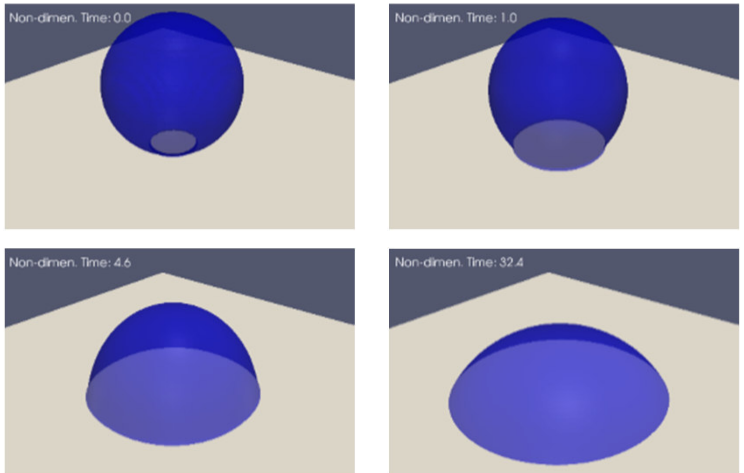
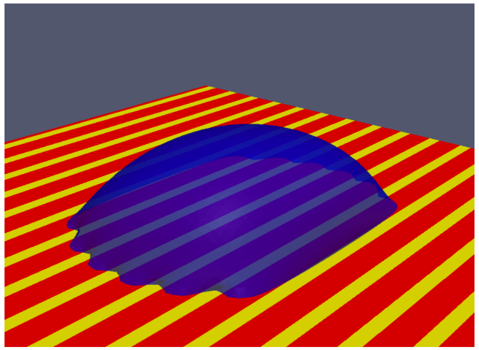
Two-phase flow – phase-field method

- The gas-liquid flow is influenced by the wettability of the sponge structure
- For dynamic wetting/dewetting processes accurate modeling of the **moving contact line** is necessary
- Development and implementation of a **phase-field method** in OpenFOAM with adaptive mesh refinement at the “diffusive” interface
- The (equilibrium) contact angle θ_e is an input parameter for the simulation
- Validation for various fundamental wetting phenomena [4]



$\theta_e = 60°$

Spreading on a chemically patterned surface (hydrophilic / hydrophobic)



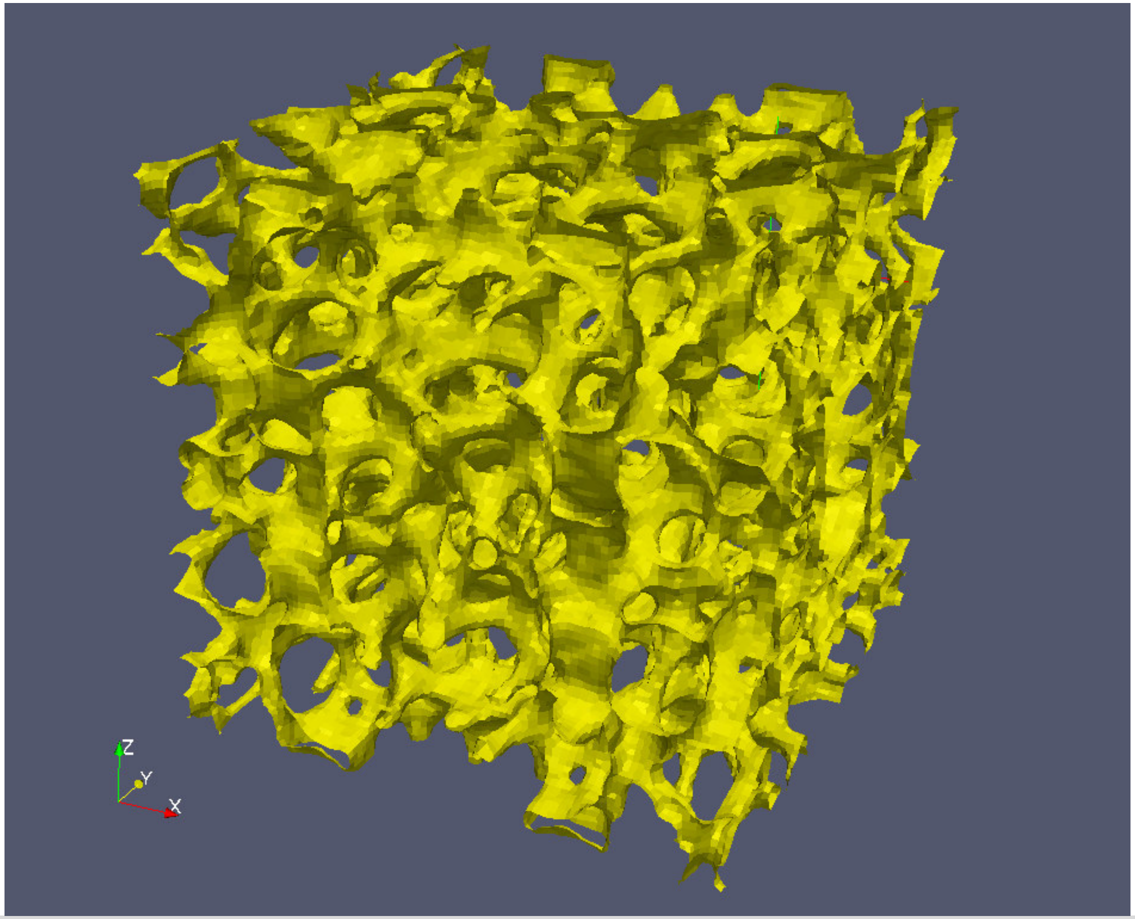
$\theta_e = 40°$

$\theta_e = 110°$

[4] Cai et al., Numerical simulation of wetting phenomena with a phase-field method using OpenFOAM®, Chem. Eng. Technol., submitted

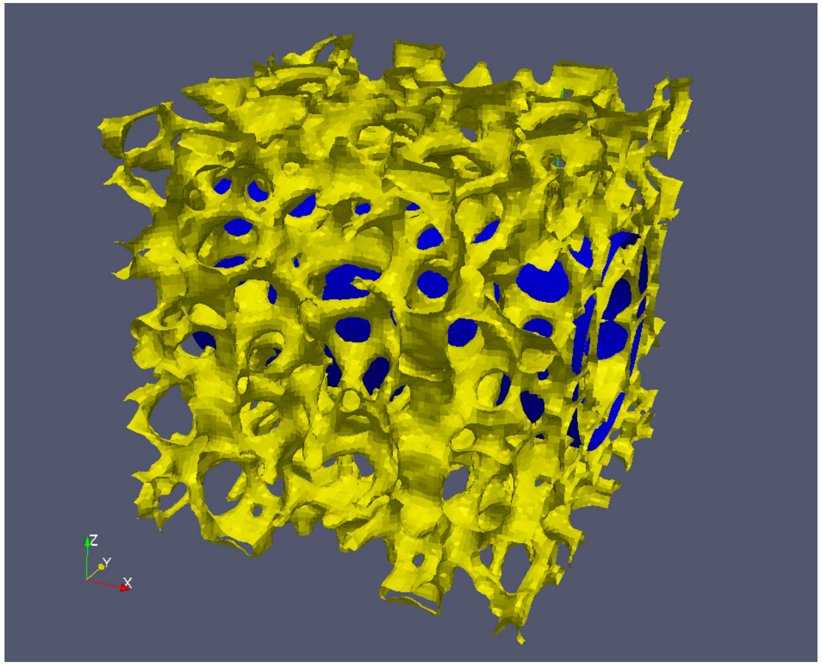
Two-phase flow in sponge – approach

- Problem: realistic inlet conditions for phase distribution
- Solution: mirror domain and use periodic boundary conditions



Two-phase flow in sponge – approach

- Specify initial phase distribution in domain and axial pressure drop which drives the flow (source term in N-S equation)
- Simulations for different parameters are under way
- <u>Goal:</u> derive closure relations for use in Euler-Euler model
  - Specific wetted surface area
  - Specific gas-liquid interfacial area
  - …
  - as function of superficial velocities
  - …
  - under variation of materials, porosity and pore size



(about one million mesh cells, θ_e = 90°)

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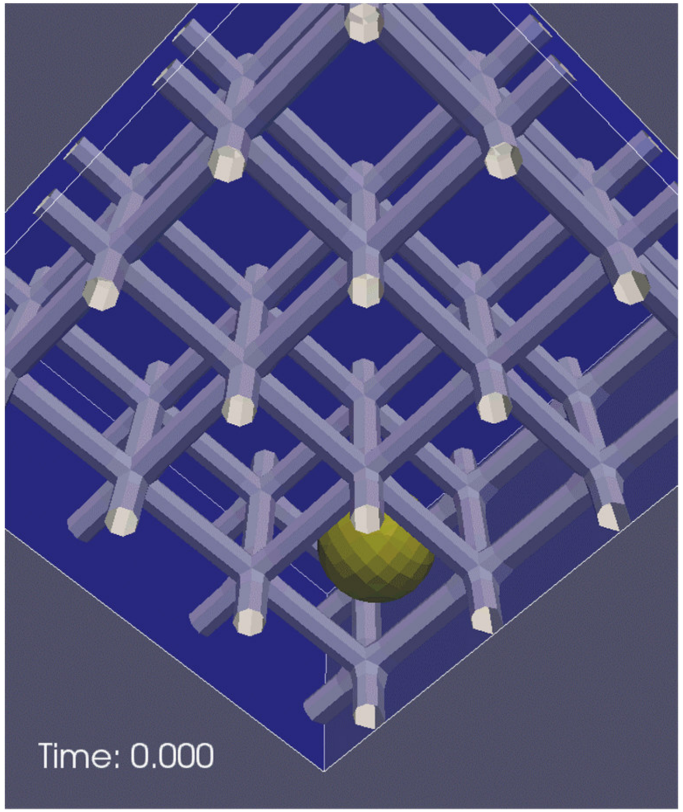
Bubble rise in POCS – results

POCS as internals in bubble column reactors can **enhance gas-liquid mass transfer** (by disturbing/renewing the liquid concentration boundary layer) while only slightly increasing the pressure drop (→ *energy efficiency*)

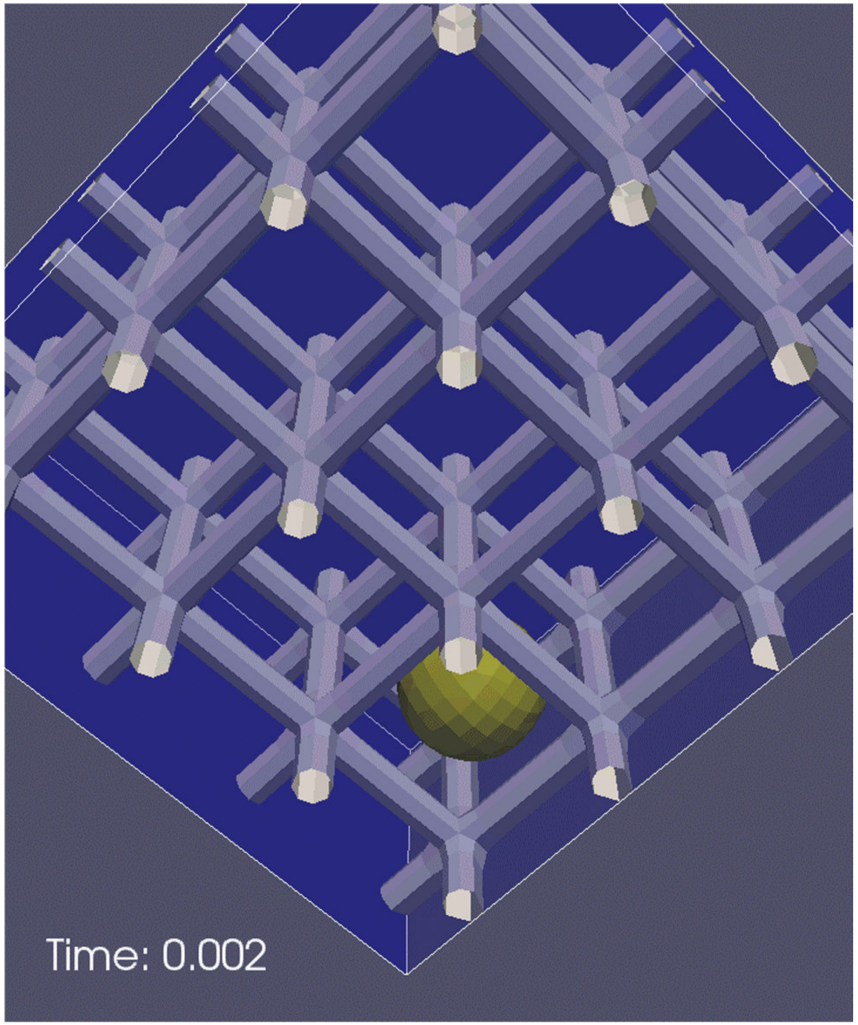
- POCS with window size 4 mm tilted by 45°
- Water and air are initially at rest
- Spherical bubble (diameter 4 mm) is placed so that it will hit the strut during its rise
- Structure is partially wetting (contact angle $\theta_e = 90°$)



POCS from FAU Erlangen

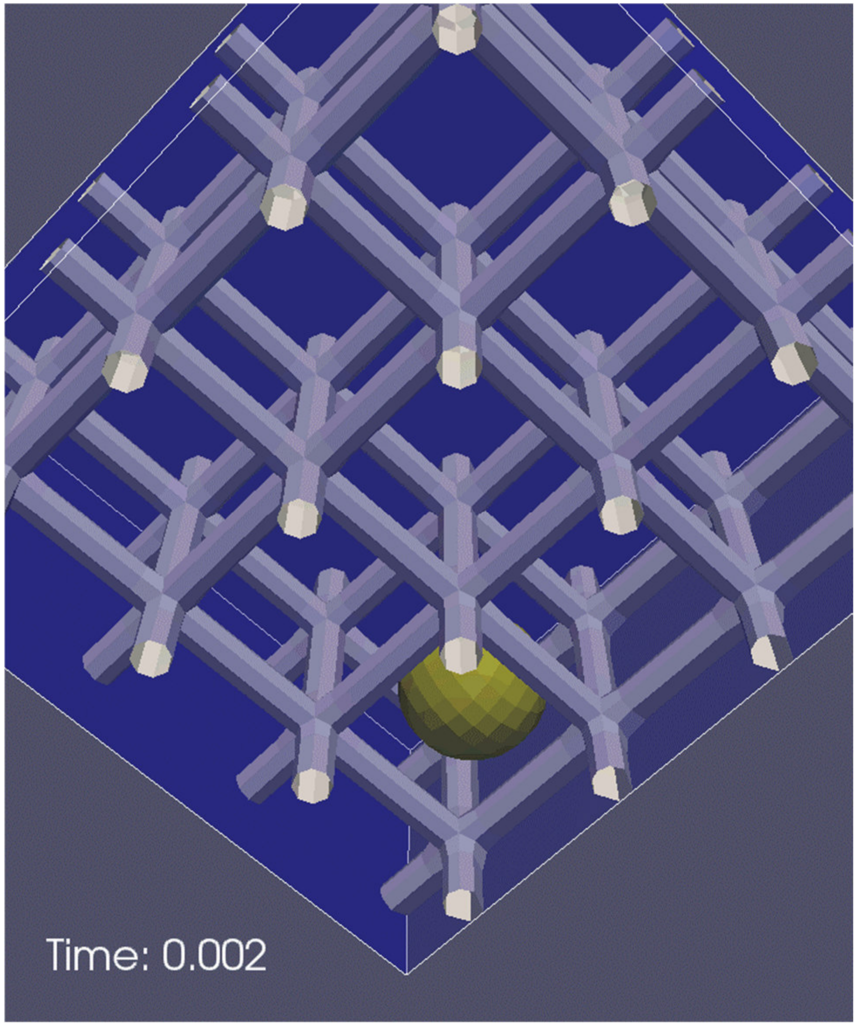
Bubble rise in POCS – results

- Structure is hydrophilic (contact angle $\theta_e = 0°$)



Bubble rise in POCS – results

- Structure is hydrophobic (contact angle $\theta_e = 135°$)
- Though at this stage, our simulations are qualitative, they show that the bubble interaction with the structure depends on wettability
- Planed cooperation with TU Hamburg-Harburg (O. Möller, Prof. M. Schlüter) to compare simulations with experiments



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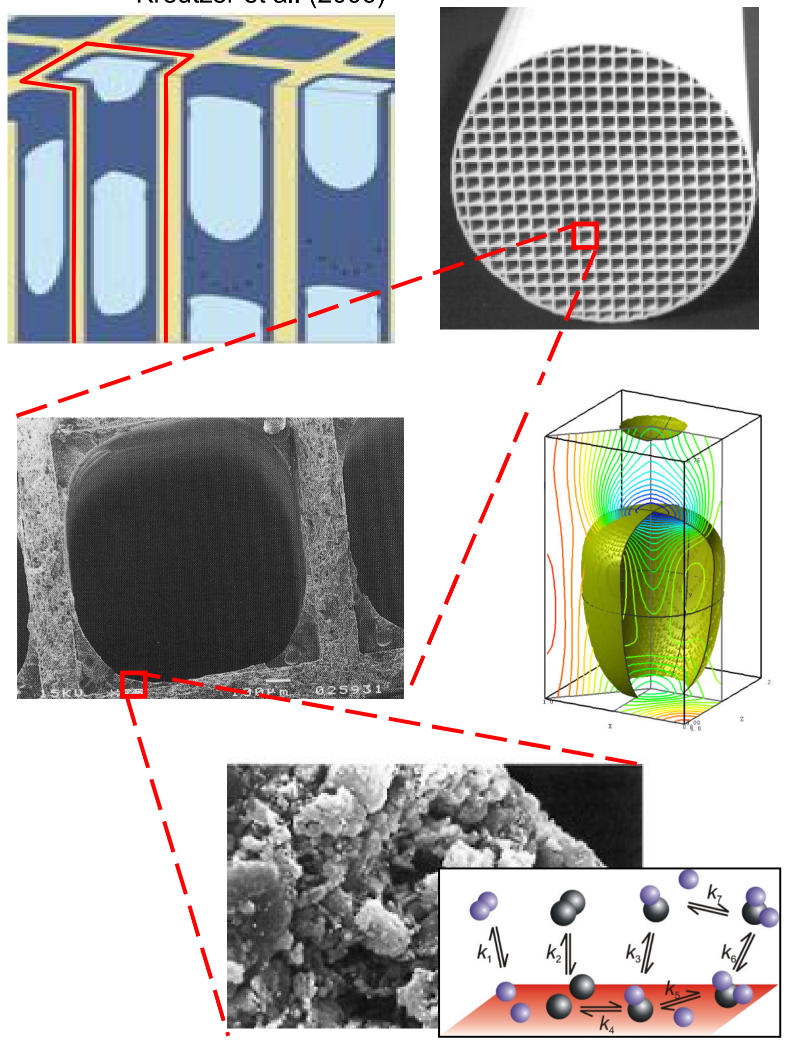
Taylor flow in a single channel of a monolith reactor

- Simulation of gas-liquid flow and mass transfer with TURBIT-VOF
- Modeling of elementary reactions in washcoat with DETCHEM^{TM} code
- Validation of coupled codes
  - Single- and multi-phase multispecies reactive-diffusive mass transfer (→ use effective diffusivity model)
- Simulations for hydrogenation of nitrobenzene to aniline
  - 2D simulations to determine flow regime map and range with Taylor flow
  - Simulations for interfacial mass transfer of hydrogen are in progress
  - *Simulations with detailed reaction kinetics to follow*

Kreutzer et al. (2006)



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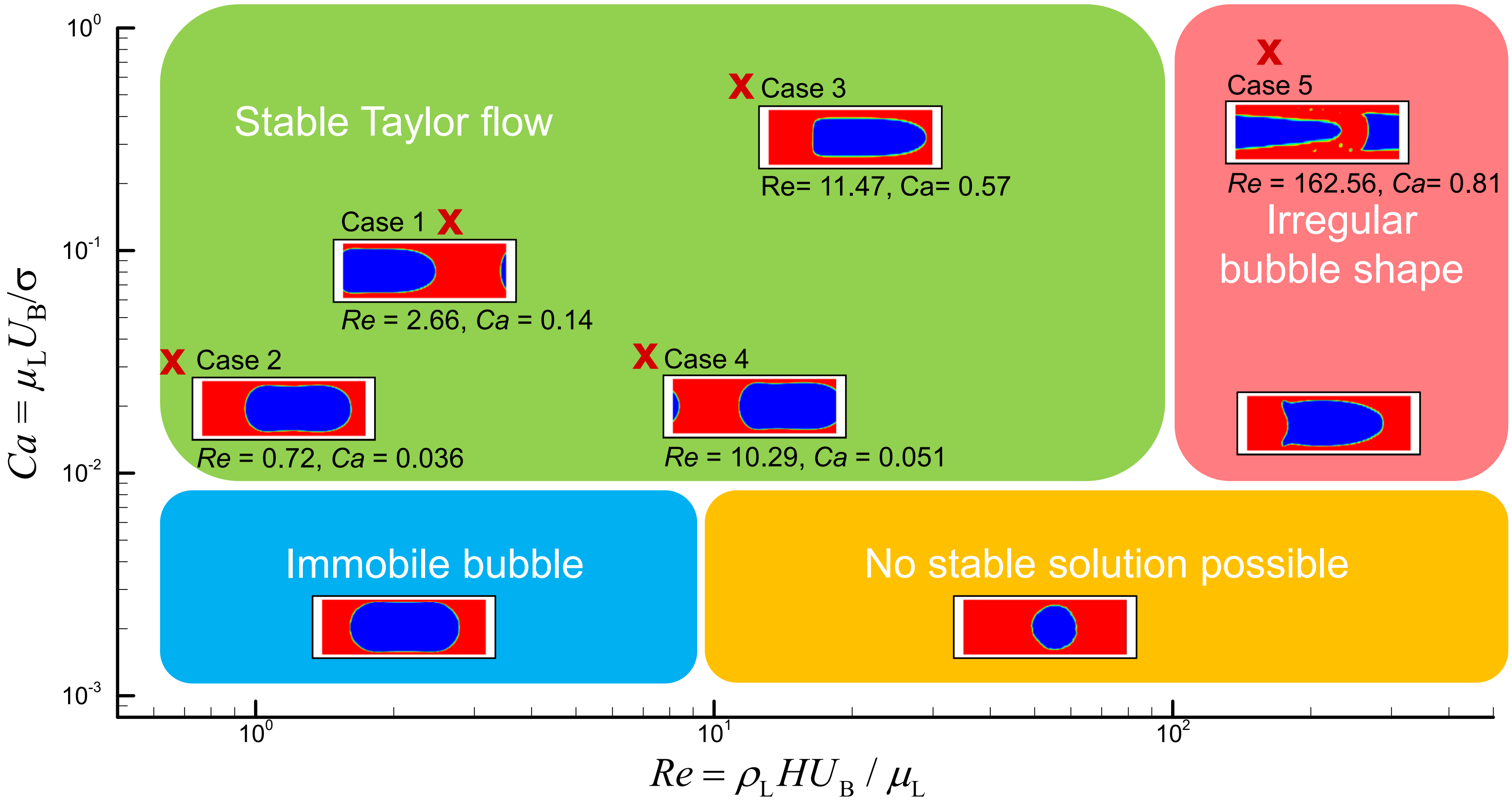
Flow regime map



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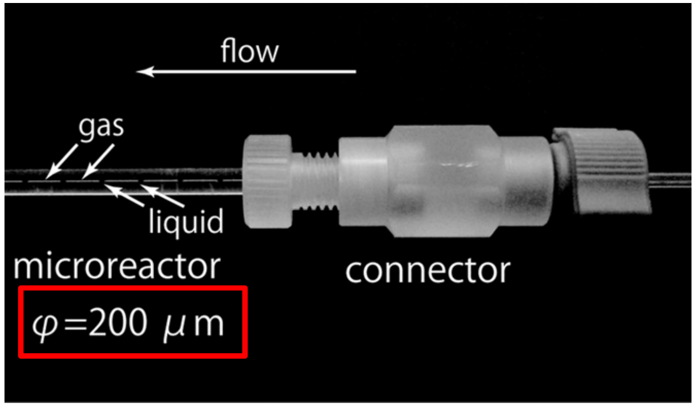
Reynolds no. for variable channel height and bubble velocity

Bubble velocity U_B [m/s]

Channel height H

	0.01	0.05	0.1	0.5	1	5	10
10 μm	0.082	0.41	0.82	4.1	8.2	41	82
50 μm	0.41	2.05	4.1	20.5	41	205	410
100 μm	0.82	4.1	8.2	41	82	410	820
500 μm	4.1	20.5	41	205	410	2050	4100
1 mm	8.2	41	82	410	820	4100	8200
5 mm	41	205	410	2050	4100	20500	41000
Ca	0.00036	0.0018	0.0036	0.018	0.036	0.18	0.36



Microreactor for hydrogenation of nitrobenzene from Kataoka et al., Applied Catalysis: General 427-428 (2012) 119-124

Ca > 0.01 *Re* < 200

→ small channel height required for Taylor flow

For Taylor flow in a capillary see also the presentation of H. Kryk in this session

Conclusions and outlook

- Single phase flow and heat transfer in sponges
  - Characterization of pressure drop (and heat transfer) by rather "universal" experimental correlations
  - Experimental pressure drop is very well recovered by CFD computations, exp. heat transfer coefficient till now less good
  - First steps towards a local validation (velocity field in a pore)
- Scale-resolved simulations for gas-liquid flows
  - Phase-field method is promising approach
  - Successful validation for *fundamental* wetting phenomena
  - Validation for *complex* wetting phenomena in sponges and POCS requires suitable experimental data
  - Potential to provide closure relations for Euler-Euler approach
  - Taylor flow simulations in monolith channel with detailed chemistry (hydrogenation of nitrobenzene) are underway

Thanks to …

- The Helmholtz Gemeinschaft for funding the Energy Alliance "Energy-efficient chemical multiphase processes"
- All partners within the alliance, especially
  - TU Hamburg-Harburg
- Cooperation partners outside the alliance
  - Dr. H. Marschall (TU Darmstadt)
  - Prof. P. Yue (Virginia Tech, USA)
  - Prof. H. Alla (USTO, Oran, Algeria)

… you, for your attention