Pore – Scale Mesoscopic Modeling of Reactive Mixtures in the Porous Media for SOFC Application: Physical Model, Numerical Code Development and Preliminary Validation

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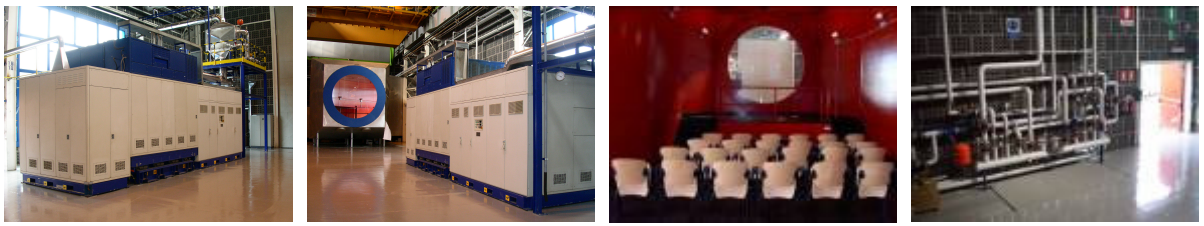

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Problem Definition

- Modeling is a very powerful tool for SOFC technology because
  - it allows one to go deeply in the reaction core for investigating fuel cell portions, which are actually not accessible by direct measurement (spatial distribution of the concentration polarization, local fluid flow,…),
  - it allows one to test different configurations concerning both the stack packaging and the balance of plant (BoP) design.
- However the reliability of numerical results strongly depends on
  - the reliability of the input parameters, particularly the transport coefficients effecting the reaction rate,
  - the reliability of the macroscopic models for the considered application, since the general purpose model does not exist.
- Otherwise modeling becomes simply numerical data fitting, which is useless for designing new devices !!

Gas Permeation and Diffusion Coefficients

- Mass transport models inside the porous SOFC anode must be applied to estimate gas concentrations at the anode – electrolyte interface.
- Such a mass transport model needs to be sophisticated enough so that it can take into account parameters such as complex functions of temperature, pressure, gas concentrations, and the physical properties of SOFC materials like porosity, tortuosity and pore size of the electrode materials.
- Popular models are:
  - the extended Fick model (EFM);
  - the dusty-gas model (DGM);
  - the Stefan–Maxwell model (SMM), obtained by eliminating out the effect of Knudsen diffusion yields.

Macroscopic vs. Mesoscopic Approach

Continuous Kinetic Theory by Boltzmann Equation (CKT)

D_{12} Molecular diffusivity

$D_{1,k}$ Knudsen diffusivity

Macroscopic Approach

Corrections due to porous topology

D_{12}^{eff} $D_{1,k}^{\text{eff}}$

Diffusion model

EFM	DGM
$D_1^{\text{eff}} = \left(\frac{1}{D_{12}^{\text{eff}}} + \frac{1}{D_{1,k}^{\text{eff}}} \right)^{-1}$	$\frac{N_1}{D_{1,k}^{\text{eff}}} + \frac{y_2 N_1 - y_1 N_2}{D_{12}^{\text{eff}}} =$
$N_1 = -\frac{D_1^{\text{eff}} P}{R T} \frac{\mathrm{d}y_1}{\mathrm{d}z}$	$-\frac{P}{R T} \frac{\mathrm{d}y_1}{\mathrm{d}z}$

Mesoscopic Approach

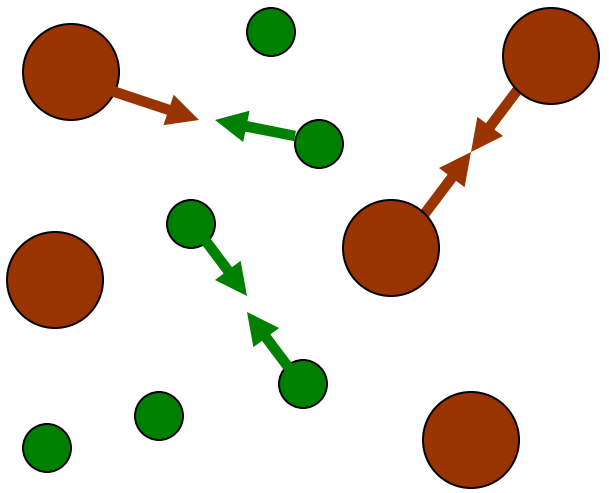
Pseudo-Kinetic Model: BGK Hamel

> The mesoscopic approach aims to solve directly the fluid flow of reactive mixtures by a simplified kinetic description (1) in virtual topologies which mimic the actual porous media (2).

$$\frac{\partial f_\sigma}{\partial t} + \mathbf{v}\cdot\nabla f_\sigma + \mathbf{g}_\sigma\cdot\nabla_{\mathbf{v}} f_\sigma = -\frac{1}{\tau_\sigma}\left[f_\sigma - f^e_\sigma\right] - \frac{1}{\tau_{m\sigma}}\left[f_\sigma - f^e_{\sigma(m)}\right]$$

The Hamel model (original) is a good example of pseudo-kinetic modeling:

- self collisions involving particles of the same type and cross collisions involve particles of different type are independently taken into account;
- two tunable parameters are not enough for good stability



Pseudo-Kinetic Model: MRT Gross & Krook

> Multiple-relaxation-time model (MRT) derived by Gross & Krook (original): it shares the same advantages of the previous model, but the maximum number of tunable parameters are considered.

$$\frac{\partial \mathbf{f}_\sigma}{\partial t} + \mathbf{V} \cdot \nabla \mathbf{f}_\sigma = \mathbf{A}_m \left(\mathbf{f}_m^e - \mathbf{f}_\sigma \right)$$

> Designing properly the ortho-normal basis for the calculation of the effects due to collisions among particles is possible to increase the efficiency of the model (flops reduction).

$$\mathbf{A}_m = \mathbf{M}_D^{-1} \mathbf{D}_m \mathbf{M}_D$$

> Phenomenological parameters and stability parameters are clearly distinct.

$$diag(\mathbf{D}_m) = [\lambda_m^0, \lambda_m^I, \lambda_m^I, \lambda_{m\,1}^{II}, \lambda_{m\,2}^{II}, \lambda_{m\,3}^{II}, \lambda_m^{III}, \lambda_m^{III}, \lambda_m^{IV}]^T$$

Numerical Method: SILBE – LBM

> The previous models can be discretized by means of any numerical technique, but the lattice Boltzmann method (LBM) is particularly suitable for this task, because it is formulated in terms of discretized probability distribution function (native quantity).

> A very popular formulation of LBM is based on forward Euler rule (FE) because it is very simple and explicit in time.

$$\mathbf{f}_\sigma(\hat{t}_c, \hat{\mathbf{x}}_c) - \overline{\mathbf{f}}_\sigma(\hat{t}_c - 1, \hat{\mathbf{X}}_c - \hat{\mathbf{V}}) = \hat{\mathbf{A}}_* \left[\mathbf{f}_*^{e\,0}(\hat{t}_c, \hat{\mathbf{x}}_c) + \mathbf{f}_*^{e\,1}(\hat{t}_c, \hat{\mathbf{x}}_c) + \mathbf{f}_*^{e\,2}(\hat{t}_c - 1, \hat{\mathbf{x}}_c) - \mathbf{f}_\sigma(\hat{t}_c, \hat{\mathbf{x}}_c) + \mathbf{k}_b(\hat{t}_c, \hat{\mathbf{x}}_c) \right] .$$

> When very large particle ratios (M-H2O/M-H2=9) must be considered, the implicit schemes ensure better performances. This is the reason why a semi-implicit-linearized formulation of the backward Euler rule (SIL-BE) was proposed (original).

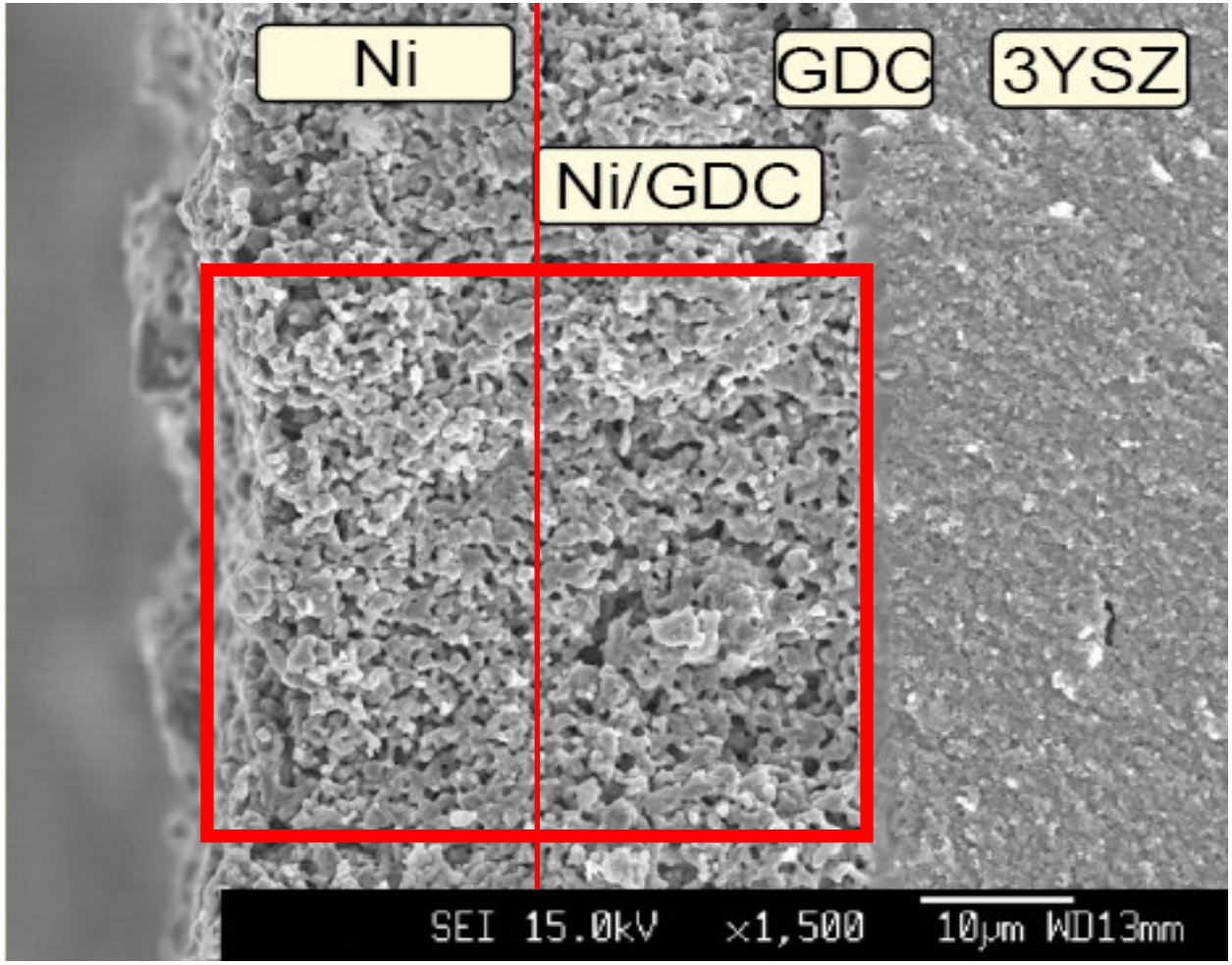
Implementation and Code Development

- An original numerical code has been developed from scratch, based on the previous schemes (roughly 10,000 lines).
- Essential features:
  - completely 3D capability (D3Q19 lattice);
  - optimized memory management for dealing with randomly-generated porous media;
  - parallel implementation by MPI package.
- Main computational facilities at Virginia Polytechnic Institute and State University (VA, U.S.A.):
  - SYSTEM – X, 1100 Apple XServe G5 dual processor nodes (2200 CPUs, 2.3 GHz, 4 GB RAM, 80 GB HD), the fastest supercomputer at any academic institution in the world with 12.25 Teraflops ("Top500 Data" for 2004);
  - ANANTHAM, 64 AMD Dual Opteron nodes (128 CPUs, 1.3 GHz, 1 GB RAM, 10 GB HD).

Code Validation and Performances

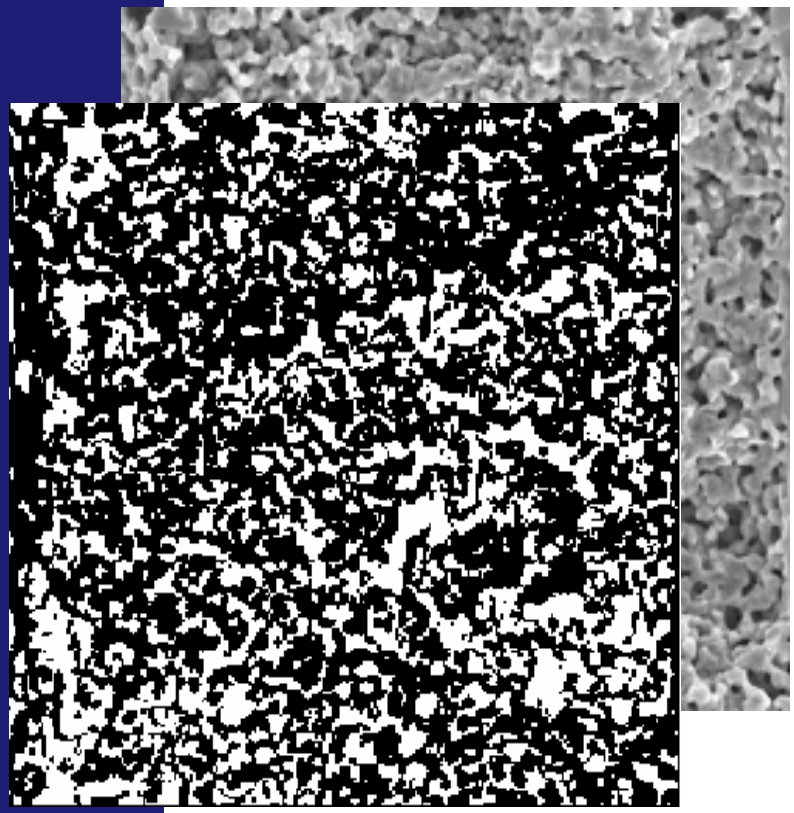
- Test reference cases
  - For the diffusion phenomena: time decay of single and multiple concentration waves (advection + mixing);
  - For viscous dynamics: time decay of kinetic energy for ideal flows (like the Green – Taylor vortex).
- Speed performance
  - A useful index is MLUPS, which means the millions of lattice sites (computational cells) completely updated (streaming and collision) per second. This index allows one to compare the performances of an LB code with other numerical techniques and/or with other codes.
  - Actual performance: 0.3 MLUPS for a binary mixture dynamics due to an initial concentration field in a 64^3 computational domain.

Topology Definition in SOFC Anode Cermet



Courtesy of “Energy Centre of the Netherlands (ECN)”, 2005

SOFC Anode Cermet Reconstruction

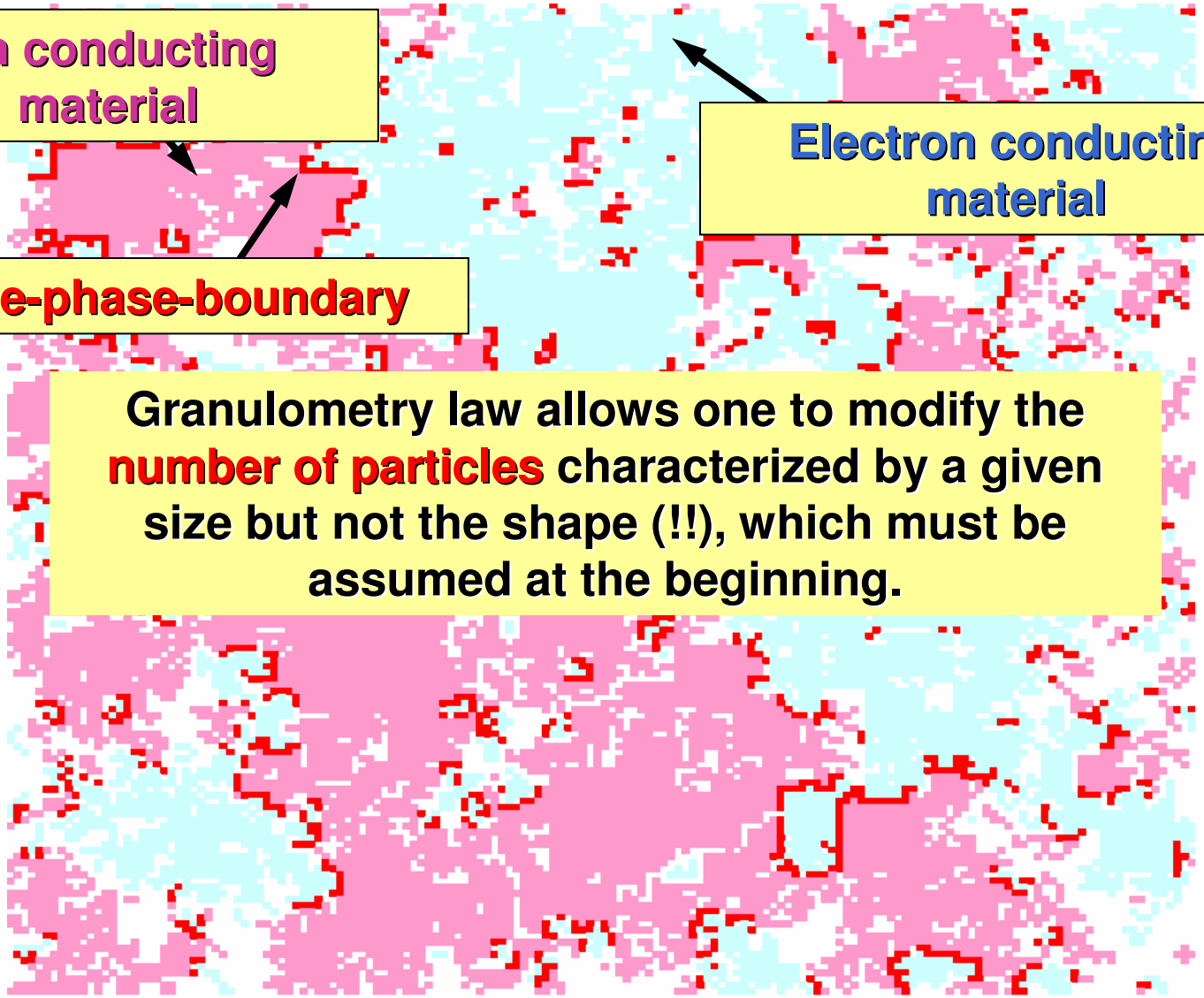


Non-destructive X-ray computed micro-tomography directly produces 3D pore space at resolutions of around a micron. For SOFC application, this resolution is not sufficient → reconstructions from reliable 2D techniques, such as standard and back scanning electron microscopy (SEM/BSEM), is the only viable alternative.

(1) granulometry law → grain shapes are assumed;

(2) multiple–point statistics → neighboring information are processed for more reliable reconstruction.

Limits: Fixed Cluster Shape



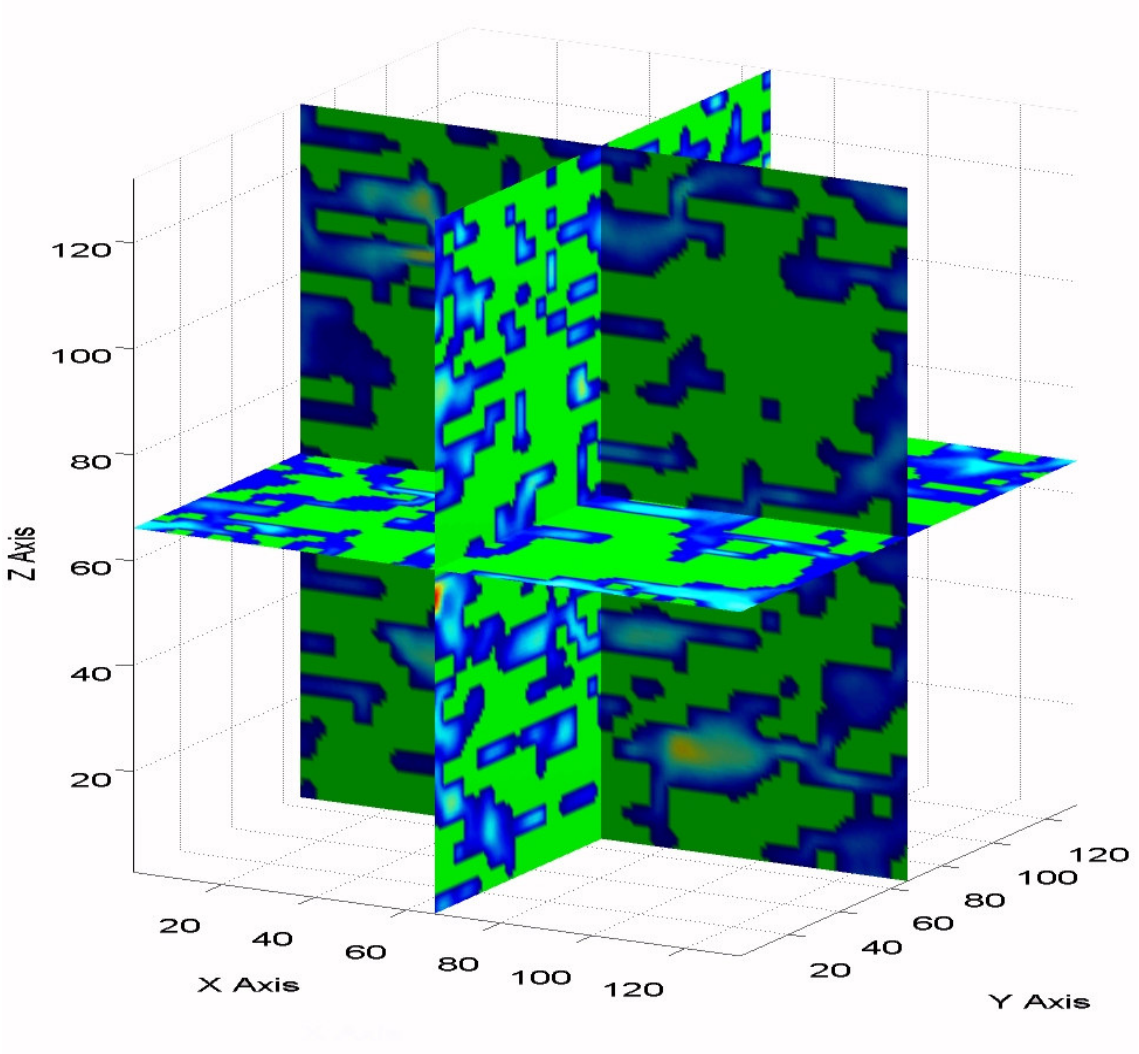
Granulometry law allows one to modify the **number of particles** characterized by a given size but not the shape (!!), which must be assumed at the beginning.

Multiple – point Statistics

- Multiple-point statistics is used, based on two-dimensional (2D) thin sections as training images, to generate 3D pore space representations.
- Assuming that the medium is isotropic, a 3D image can be generated that preserves typical patterns of the void space seen in the thin sections
- The use of multiple-point statistics predicts long-range connectivity of the structures better than granulometry law
- Essentially the algorithm is based on three steps:
  - Borrowing multiple-point statistics from training images
  - Pattern reproduction
  - Image processing-noise reduction and smoothing
- Currently under development by Vikram Kasula, who is a PhD student of Prof. Michael R. von Spakovsky at Virginia Tech.

Simulation of Fluid Flow in Cermet

Fluid flow due to electro–chemical reactions (constant current flow) of hydrogen / water mixture at 1000 °C in a reconstructed SOFC porous anode (132^3 = 2.3 Mcells and 330^3 = 35.9 Mcells domains were considered, meaning 9.2 Mdofs and 143.6 Mdofs respectively).



Conclusions

- LBM for mixing phenomena:
  - it is possible to formulate reliable mesoscopic models for simulating mixing phenomena, if consistent mathematical tools distinguishing the effects on diffusivity and those on mixture kinematic viscosity are considered;
  - MRT formulation proved to be effective in achieving the previous goals and improving the stability of the code.
- LBM for reactive mixtures in SOFC porous media:
  - the practical relevance of simulating fluid flow in SOFC anode porous media strongly depends on the reliability of the reconstructed microscopic topologies;
  - Multiple-point statistics seems to effectively catch long-range connectivity of the structures.

Acknowledgements and Main Publications

Prof. Michael R. von Spakovsky – Center for Energy Systems Research, Mechanical Engineering Department, Virginia Polytechnic Institute and State University (VA, U.S.A.)

Prof. Li-Shi Luo – Department of Mathematics and Statistics, Old Dominion University and National Institute of Aerospace (VA, U.S.A.)

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- P. Asinari, "Asymptotic analysis of multiple-relaxation-time lattice Boltzmann schemes for mixture modeling", **International Journal Modern Physics C**, 2005 (in press).
- P. Asinari, "Semi-implicit-linearized Multiple-relaxation-time formulation of Lattice Boltzmann Schemes for Mixture Modeling", submitted to **Physical Review E**, 2005.