



KATHOLIEKE UNIVERSITEIT
LEUVEN



Crystallization of oxide melts

Phase field model coupled with ChemApp

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Preface

- Start of PhD project in september 2007
 - Funding by IWT (Innovation Scholarship)
- Currently finishing a PhD in Materials Engineering at Katholieke Universiteit Leuven
 - Promotors: prof. Nele Moelans and prof. Bart Blanpain
 - Most important assessor: prof. Klaus Hack
- Since August 2011: Project Leader at Umicore R&D



Outline

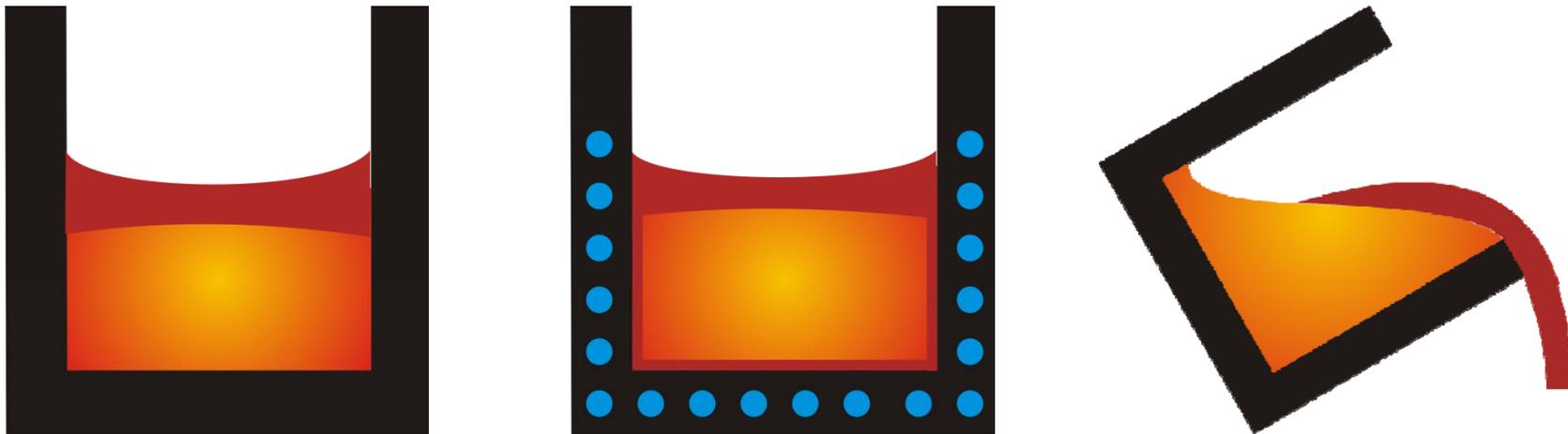
- Introduction
- Phase field model
 - Concepts of phase field modeling
 - Thermodynamic data for oxide melts
 - Other specific features for oxide systems
 - Numerical implementation
- Applications of the model
 - Dendritic crystallization of a silicate melt
 - Faceted crystallization of a geological melt
- Conclusions

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- Oxide melt = silicate liquid = metallurgical slag
- **Problem statement**
 - Microstructure evolution of metallurgical slags controls many aspects of pyrometallurgical processes
 - e.g. freeze lining, refractory wear, tapping and cooling
- **Research goals of the PhD**
 - Develop a multiphase and multicomponent model to simulate microstructure evolution in slags
 - Perform *in-situ* high temperature experiments for benchmarking of the simulation

Industrial relevance

- Process slag in contact with furnace refractories
- Freeze lining formed by solidification of process slag
- Tapping slag at high temperature and cooling down



Modeled physical phenomena

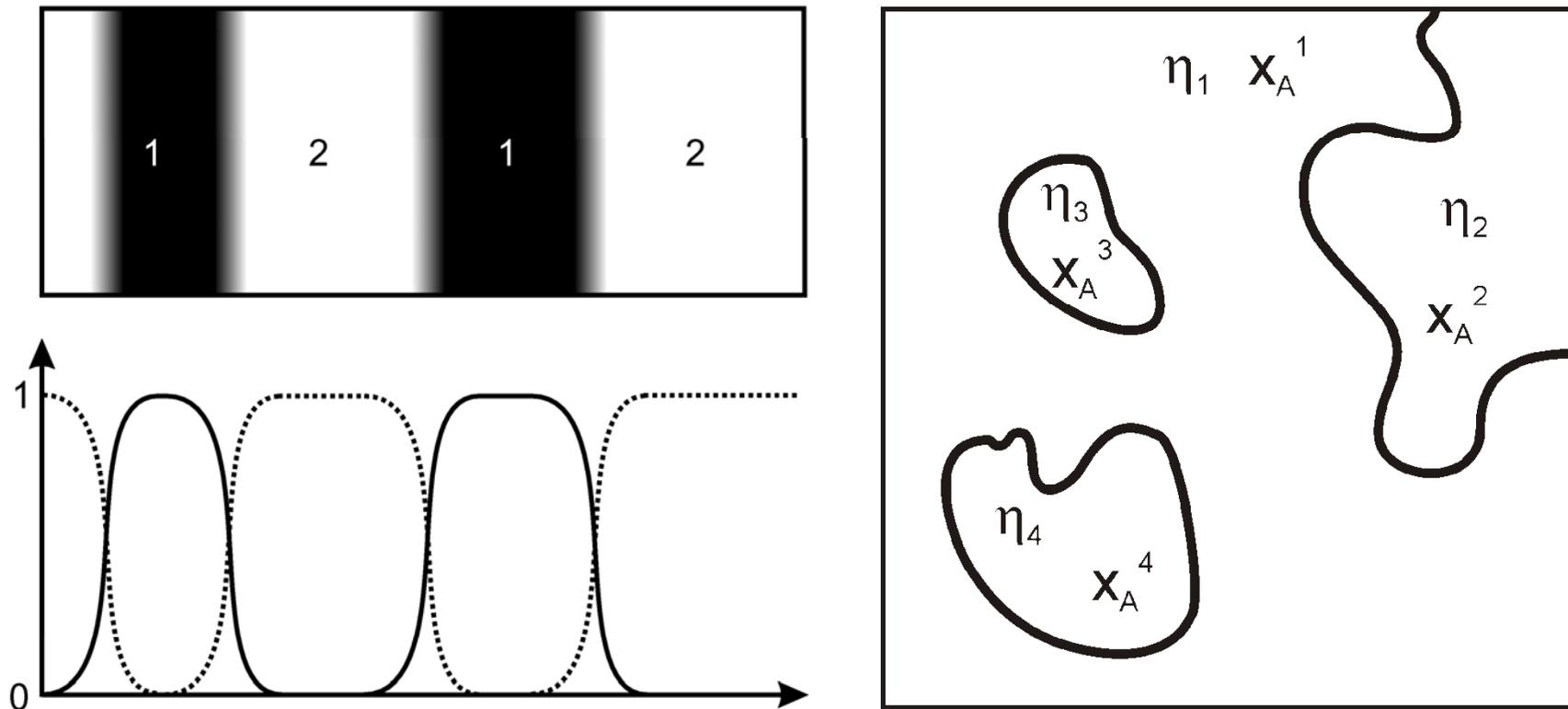
- Surface energies of all interfaces
- Interface anisotropy (kinetics or energy)
- Diffusion coefficients
(all components in all phases)
- Chemical potentials
(all components in all phases)
- Flow in the liquid phase
(convection, forced ...)

Acc.V Spot Magn Det WD |-----| 100 μ m
12.0 kV 5.0 250x Solidifying CAS slag (L.CS.C₂AS)

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Concepts of phase field modeling

- Diffuse interfaces between different phases can treat arbitrary interface shapes



Equations for microstructure evolution

- System of p phases and c components
- Phase fields evolve by energy minimization:

$$\frac{\partial \eta_i}{\partial t} = -L \frac{\delta}{\delta \eta_i} \left(\int_V \left(mf_0 + \frac{\kappa}{2} \sum_{r=1}^p |\nabla \eta_r|^2 + f_{chem} \right) dV \right)$$

- **Interfacial energy** (Double well and gradient term)
 - **Chemical energy** (Gibbs energies of phases)
- Diffusion equation for every component k :

$$\frac{\partial x_k}{\partial t} = \nabla \cdot \left(\sum_{i=1}^p \phi_i \sum_{r=1}^{c-1} M_{rk}^i \nabla \tilde{\mu}_r^i \right) \quad \tilde{\mu}_r^i = \mu_r^i - \mu_{SiO_2}^i$$

Coupling with thermodynamic database

- Local (volumetric) chemical energy is calculated as:

$$f_{chem} = \sum_{i=1}^p \phi_i f^i$$

- Equality of diffusion potentials of $c-1$ components in p phases:

$$\tilde{\mu}_k^1 = \dots = \tilde{\mu}_k^i = \dots = \tilde{\mu}_k^p \quad i = 1..p$$

- Mass balance to link phase concentrations to x_k :

$$x_k = \sum_{i=1}^p \phi_i x_k^i \quad k = 1..c-1$$

- Set of equations is solved for phase concentrations x_k^i

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Thermodynamic data in the model

- The phase field model uses:
 - Gibbs energies of all phases (solid and liquid)
 - $f_i(x_k, T)$ depends on local composition and temperature
 - 2nd order Taylor expansion for local approximation
 - Diffusion potentials of all components
 - $\mu_k(x_k, T)$ depends on local composition and temperature
 - Second derivative of Gibbs energies
- This data can be calculated using ChemApp
 - Converting c chemical potentials into $c-1$ diffusion potentials
 - Carefully assess and use reference states for $\mu_k(x_k, T)$

Local approximation of Gibbs energy

- Gibbs energy of phase i is approximated by:

$$\hat{f}^i = \sum_{k=1}^{c-1} \left(\frac{A_{kk}^i}{2} (x_k^i - \hat{x}_k^i)^2 + \sum_{l \neq k} A_{kl}^i (x_k^i - \hat{x}_k^i)(x_l^i - \hat{x}_l^i) + B_k^i (x_k^i - \hat{x}_k^i) \right) + C^i$$

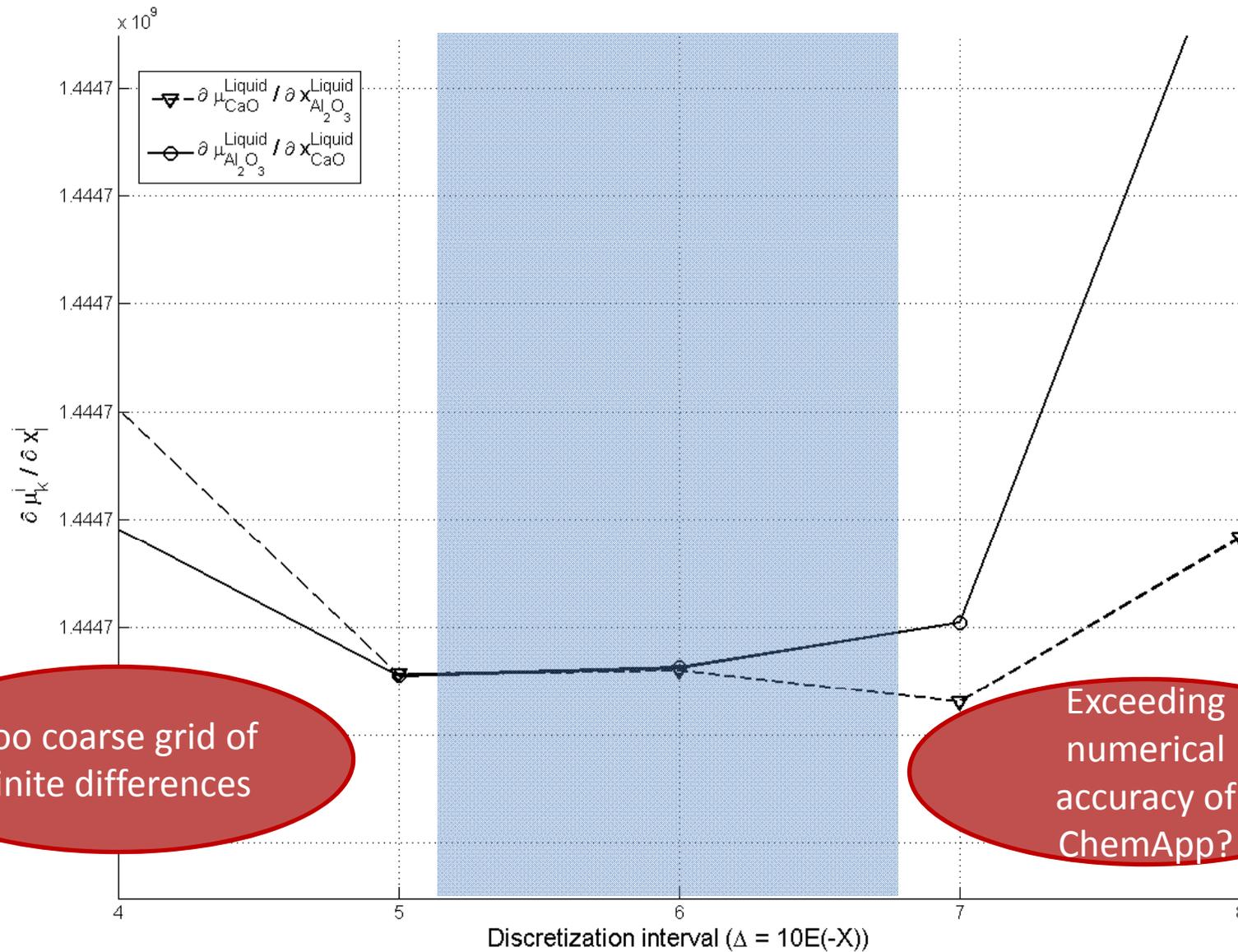
$$A_{kl}^i = \frac{\partial^2 f^i}{\partial x_k^i \partial x_l^i} \quad B_k^i = \frac{\partial f^i}{\partial x_k^i} = \tilde{\mu}_k^i \quad C^i = f^i$$

- **A**, **B** and **C** are retrieved by ChemApp and stored in an array to load in the phase field code
 - No link with ChemApp at run-time, but before simulation
- Diffusion potentials are linear in concentrations, which greatly reduces computational effort

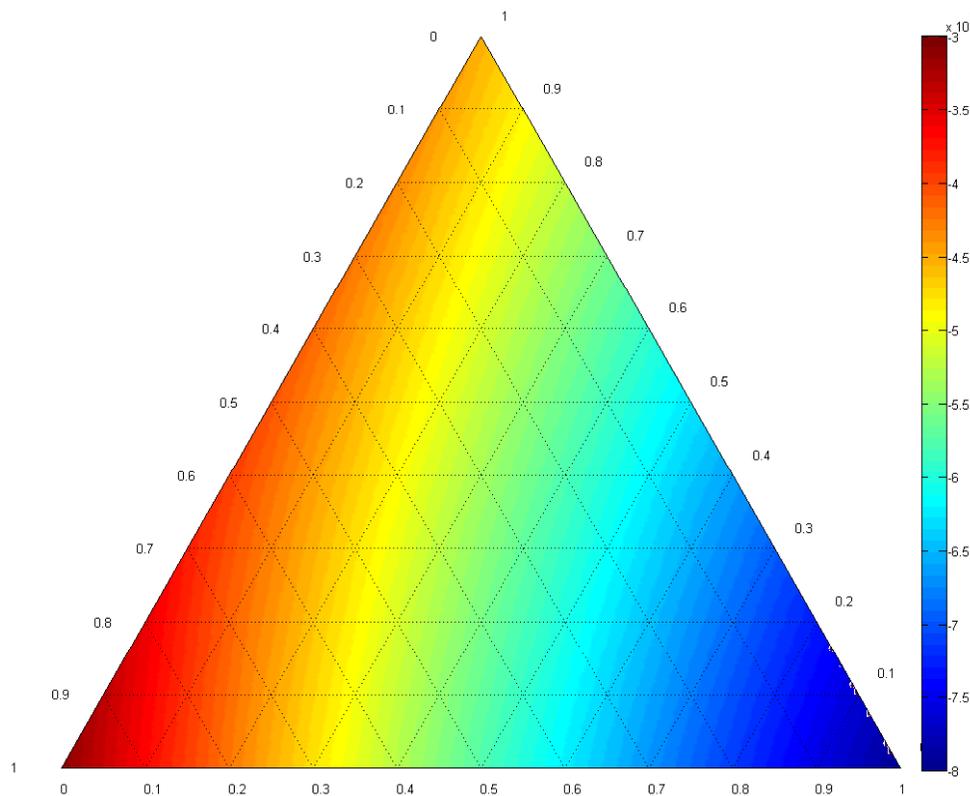
Retrieval of thermodynamic data

- Molar Gibbs energy
 - call `tqgetr('GM', 0, 0, F, noerr)`
- Diffusion potential of CaO (reference SiO₂)
 - `G_SiO2_0` and `G_CaO_0` (*standard states in liquid at certain T*)
 - call `tqgetr('MU', i_liquid, i_SiO2, mu_SiO2, noerr)`
`mu_SiO2 = G_SiO2_0 + mu_SiO2`
 - call `tqgetr('MU', i_liquid, i_CaO, mu_CaO, noerr)`
`mu_CaO = ((G_CaO_0 + mu_CaO) - mu_SiO2)/Vm`
- Second derivative of Gibbs energy
 - call `tqsetc('IA ', i_liquid, i_CaO, x_CaO±dr, numcon, noerr)`
 - `dmu_dCaO = (mu2-mu1)/(2.d0*dr)/Vm`

Second derivative of Gibbs energy



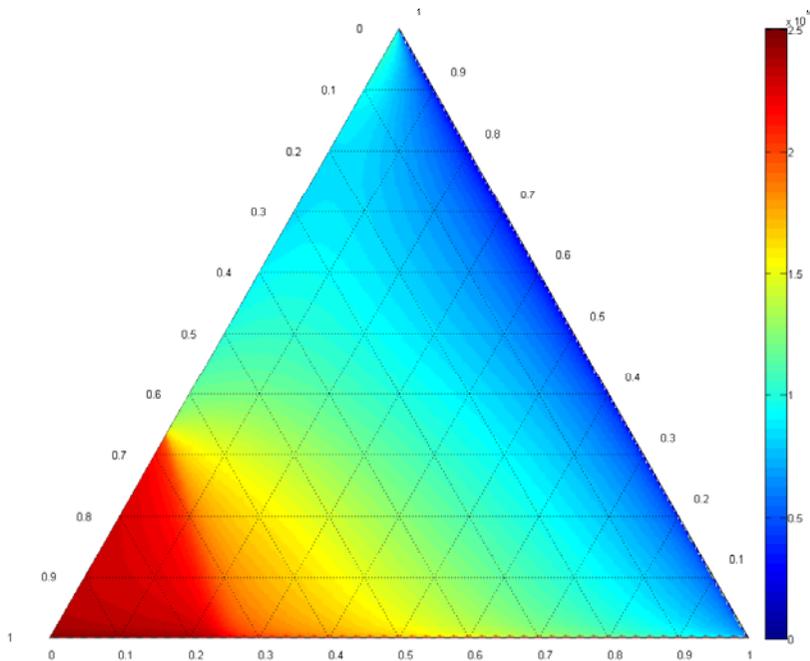
Gibbs energy of liquid oxide melt



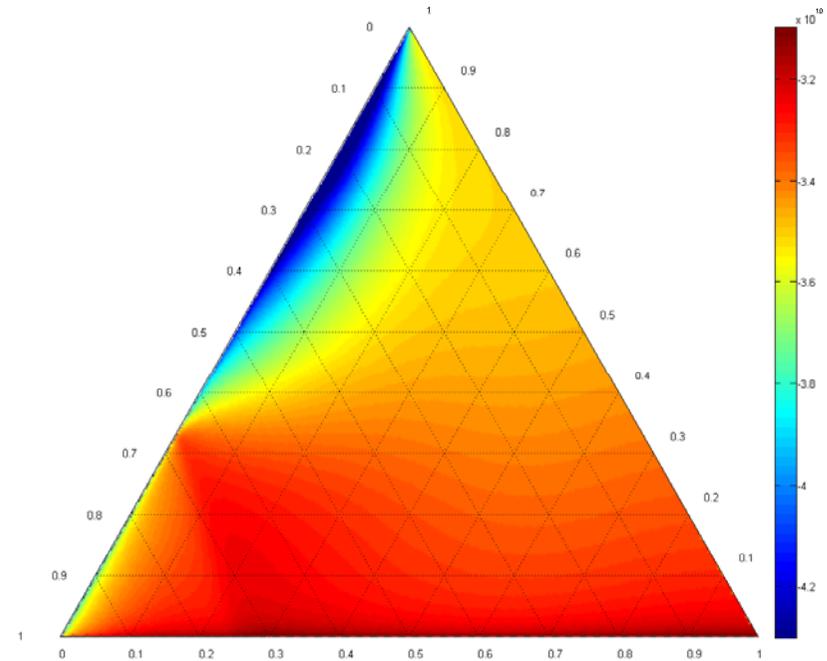
- All phases suspended
- Liquid phase is entered
- Stored in an array with $\Delta = 0.001$ spacing
- Locally approximated with 2nd order Taylor expansion
 - First derivatives
 - *Second derivatives*

Diffusion potentials in oxide melt

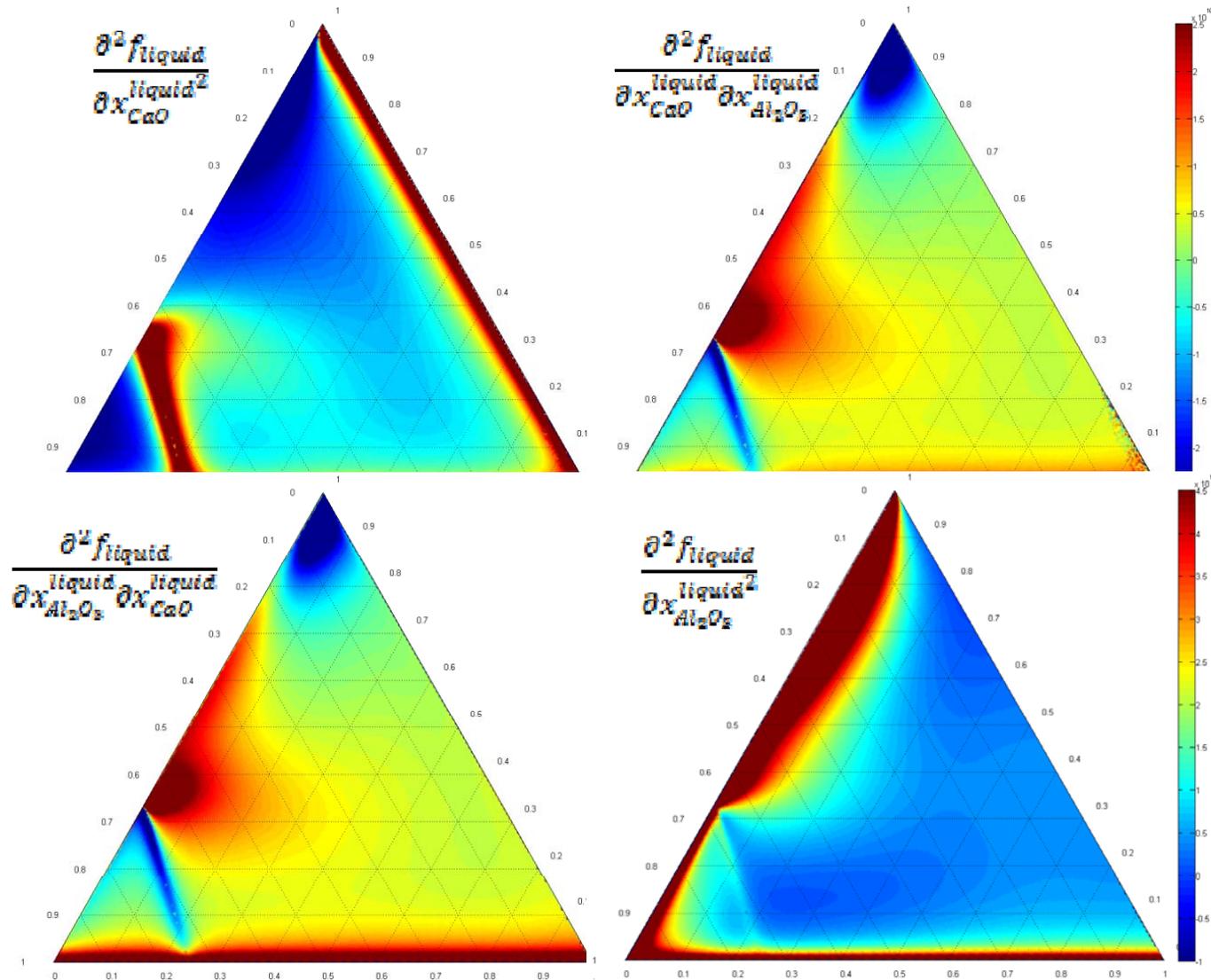
$$\tilde{\mu}_{CaO}^{liquid} = \mu_{CaO}^{liquid} - \mu_{SiO_2}^{liquid}$$



$$\tilde{\mu}_{Al_2O_3}^{liquid} = \mu_{Al_2O_3}^{liquid} - \mu_{Al_2O_3}^{liquid}$$



Second derivatives of Gibbs energy



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Slag specific features of the model

- Coupling with FACT database for oxides
- Many solid stoichiometric phases (e.g. $\text{CaO}\cdot\text{SiO}_2$)
 - Artificial Gibbs energy for stoichiometric phase
- Diffusion mobilities matrix **M**
 - No mobility database available
 - Interdiffusion coefficients matrix **D** from literature
 - Thermodynamic factor matrix **G** from ChemApp
- Wide variety of interface anisotropy
 - Faceted growth (strong anisotropy in interface mobility)
 - Dendrite growth (weak anisotropy in interface energy)

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Numerical implementation

- Partial Differential Equations (PDE's) are solved
 - using a finite difference scheme on a square grid
 - using a higher order Laplacian to ensure correct anisotropy
 - using ghost nodes for the boundary conditions
- The program is written in Fortran90
- The code is parallelized using the MPI-2 standard
- All relevant simulations run on a computer cluster
 - Distributed memory architecture (using MPI-2 standard)
 - Mostly 100 cpu's for 5 days for a single simulation
- Numerical efficiency is currently low
 - No adaptive meshing or no advanced solvers are used
- The code is still under scientific development

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Applications of the model

- **Dendritic crystallization of a mineral in silicate melt**
 - Acta Materialia 59(5), 2156-2165, 2011
- **New insights into two-phase ternary diffusion couples**
 - Acta Materialia 59(10), 3946-3954, 2011
- **Comparison with in-situ experiments**
 - Journal of the Eur. Ceramic Society 31(10), 1873-1879, 2011
- **Crystallization of a Fe bearing geological melt**
 - Chemical Geology, in press, 2011

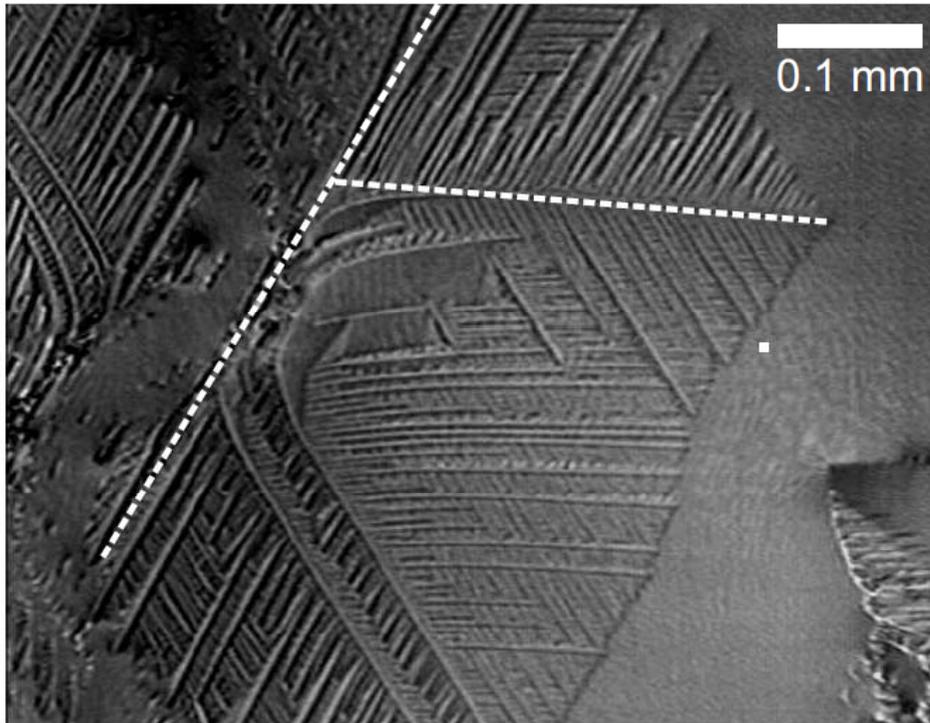
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Comparison with *in-situ* experiment

- In-situ experiments of dendritic crystallization of CaSiO_3 in a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melt
 - Dendrite tip velocity
- Large-scale phase field simulations incorporating all relevant properties of the solid and liquid phases
 - Except the solid-liquid interfacial energy
- Comparing simulation and experiment
 - High fidelity estimation of the interfacial energy, which is notoriously difficult to measure

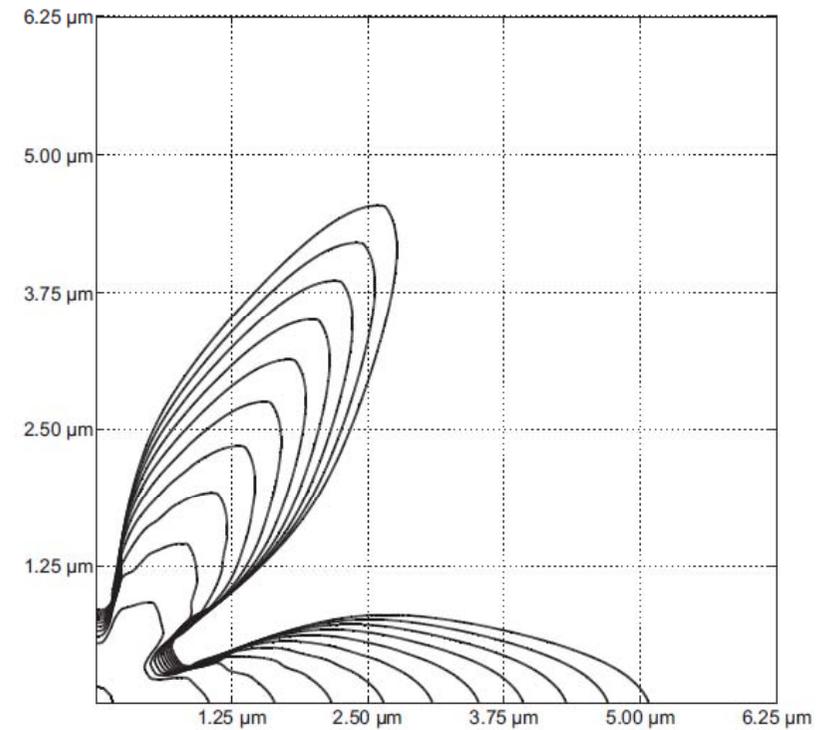
Experiment versus simulation

Experiment



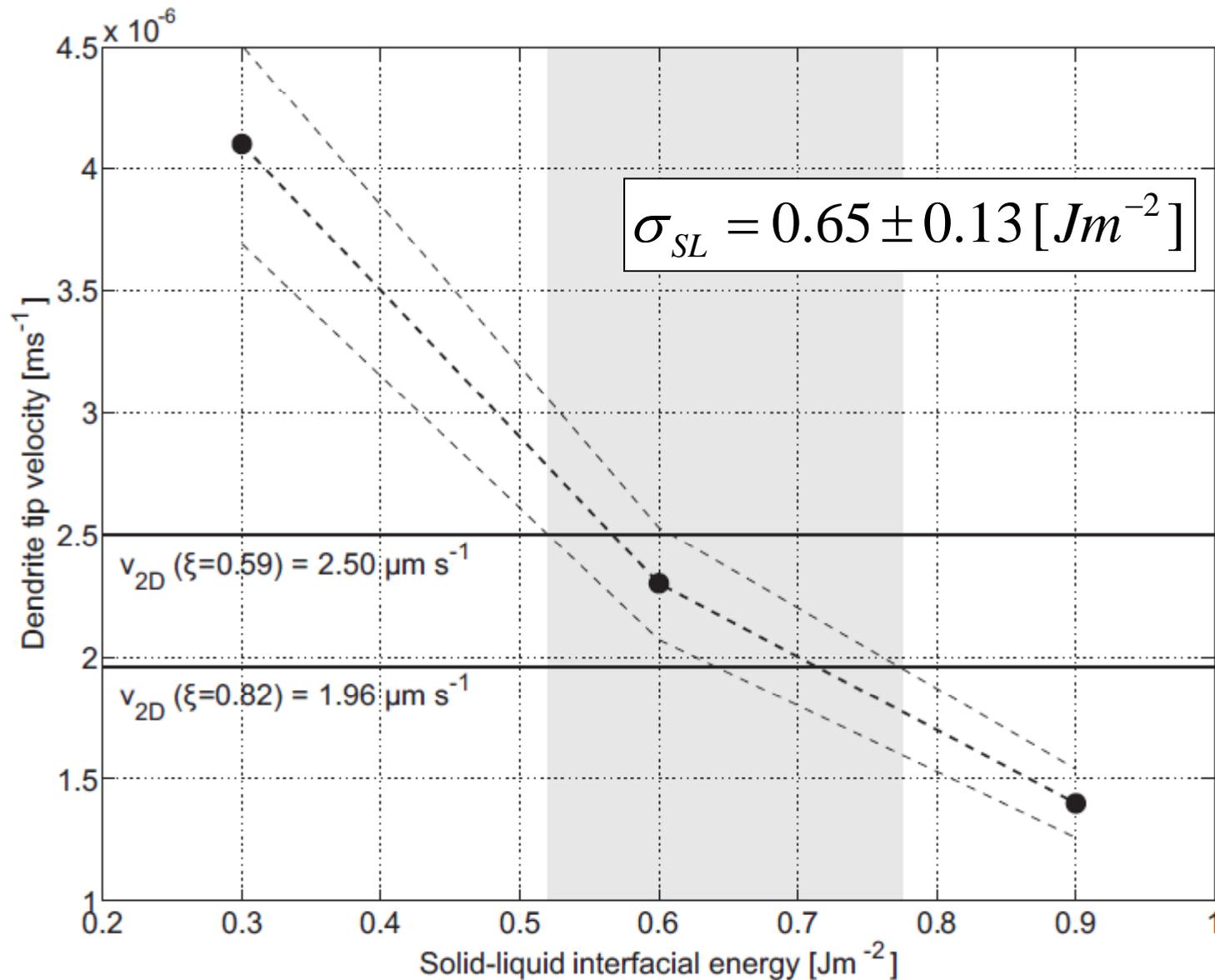
(a)

Simulation



(b)

Estimation of the S-L interfacial energy

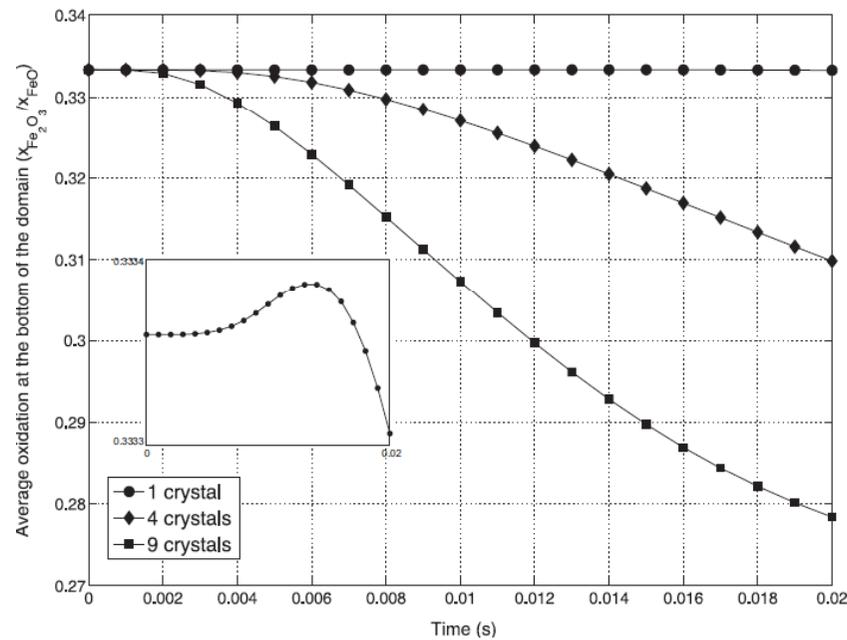
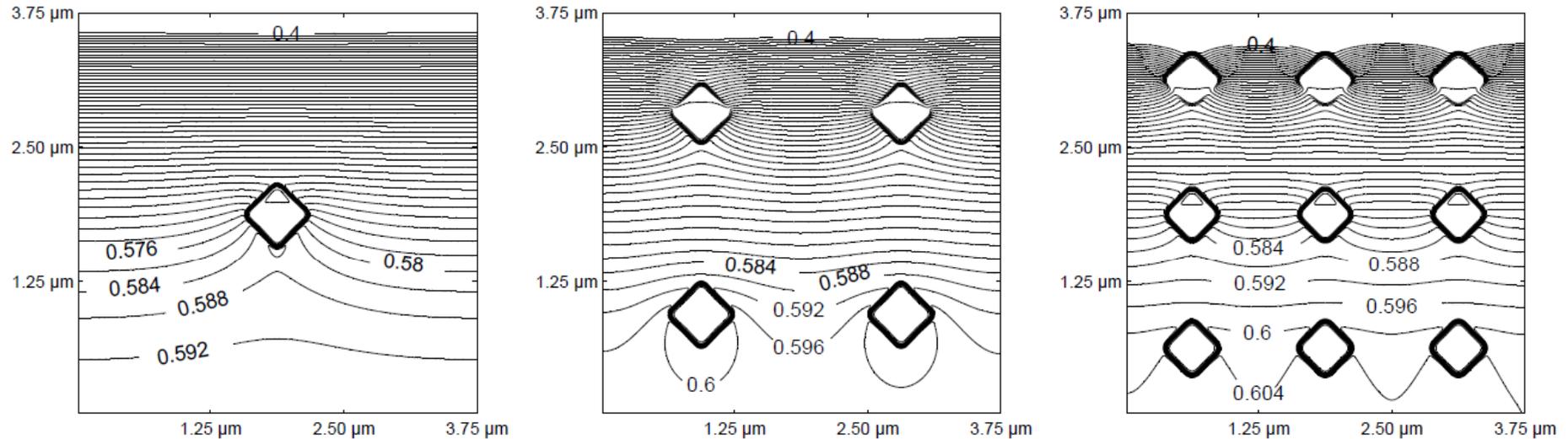


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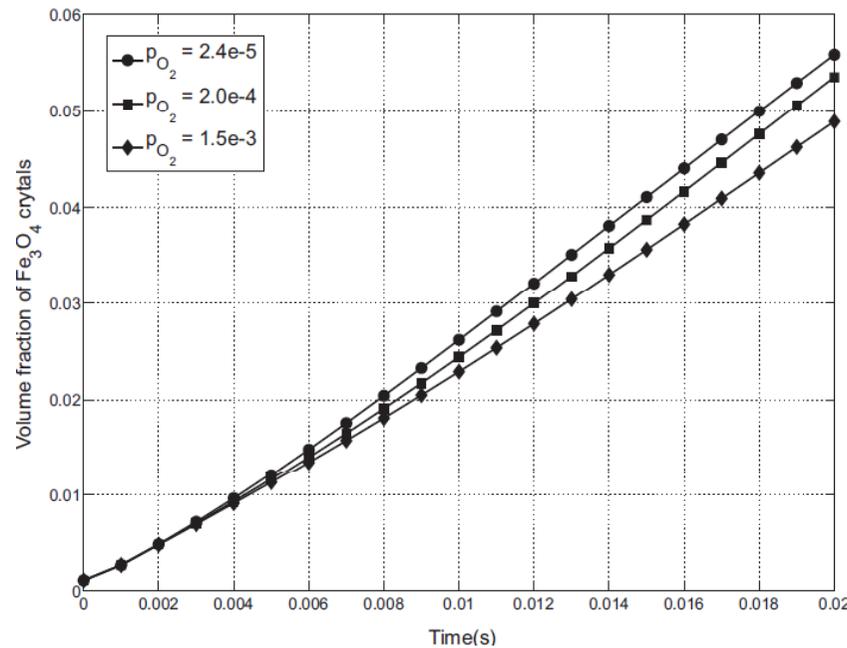
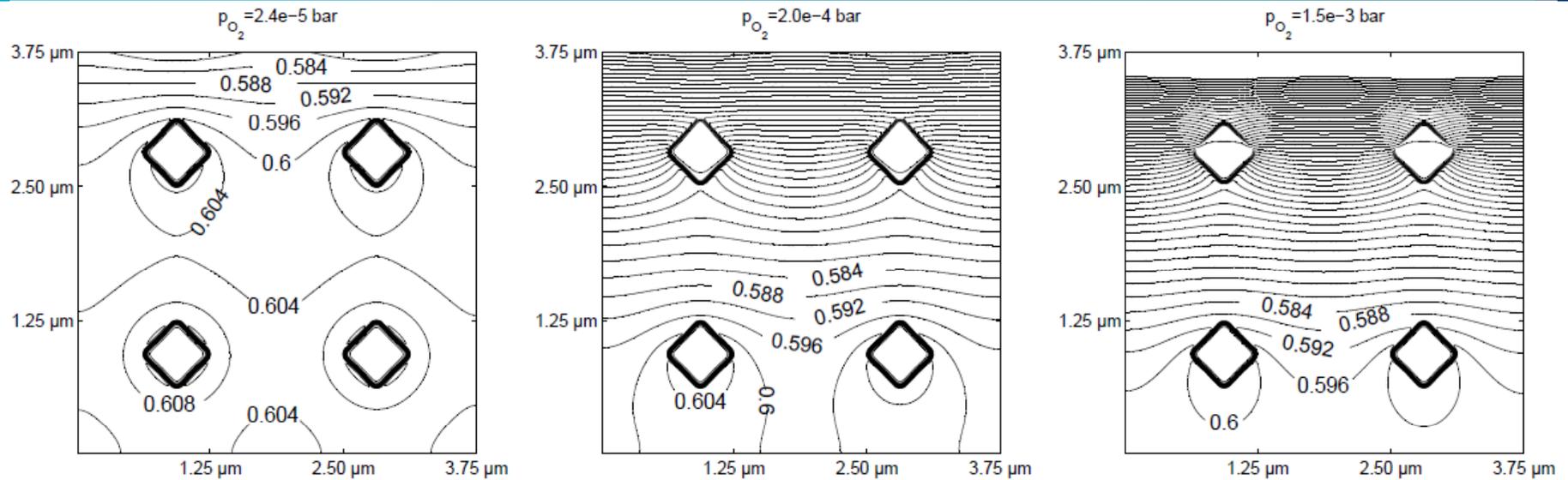
Crystallization of a geological melt

- Oxygen dependent system
 - FeO-Fe₂O₃-SiO₂
- Open system with at least one boundary in contact with O₂ atmosphere (with fixed p_{O_2})
- Assumptions made regarding to redox reactions
 - Redox equilibria are locally always in equilibrium
 - Fe³⁺ / Fe²⁺ is a direct measure for local oxygen potential
 - O₂ can only diffuse into the slag by changing the local multivalent composition
- Special boundary condition to preserve Fe but not O

Different nucleation densities



Different oxidizing conditions



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Conclusions

- Phase field model for crystallization of slags
 - Thermodynamic properties from FACT databases
 - Diffusion properties from literature
 - Arbitrary interface kinetics and anisotropies
- Agreement between simulation and experiment
- Two applications were shown
 - Pyrometallurgy and geology
 - Model proofs to be a succesful tool for microstructure evolutiong in these melts