May 26th-28th, 2025 - Vienna, Austria

7th International Workshop on Models and Data for Plasma-Material Interactions in Fusion Devices (MoD-PMI)

Multiscale modeling of diffusion phenomena in nuclear fuels: from the atomic scale to phase-field polycristalline microstructure evolution simulations

Luca MESSINA [1],

Tommaso BARANI [1], Clément INTROINI [1], Petra OSPITAL [1], Maciej J. KARCZ [1], Thomas SCHULER [2], Eiji KAWASAKI [3], Frédéric SOISSON [2], Marjorie Bertolus [1], Emeric BOURASSEAU [1]

[1] CEA IRESNE, DEC, Cadarache, France

[2] CEA ISAS & Université Paris-Saclay, France

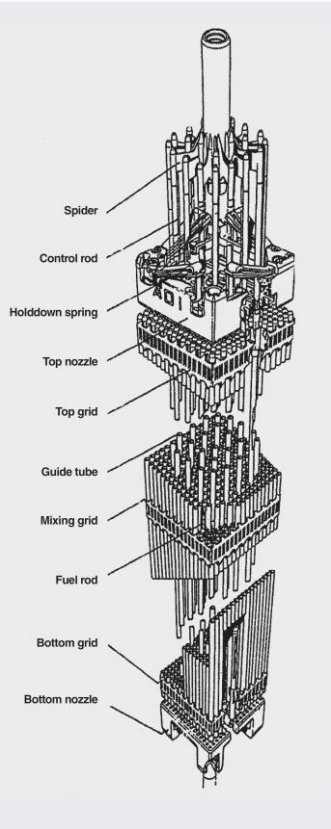
[3] CEA LIST & Université Paris-Saclay, France

luca.messina@cea.fr

Outline

1. Nuclear fuels and fission gases
2. Phase-field modeling of gas and microstructure evolution
3. Atomic-scale diffusion coefficients
4. AI approach to the partition function of disordered compounds
5. Conclusions and possible applications to fusion materials

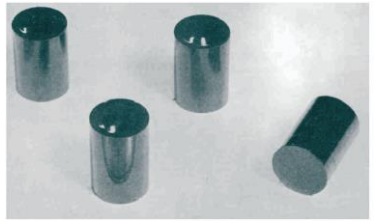
Nuclear fuels



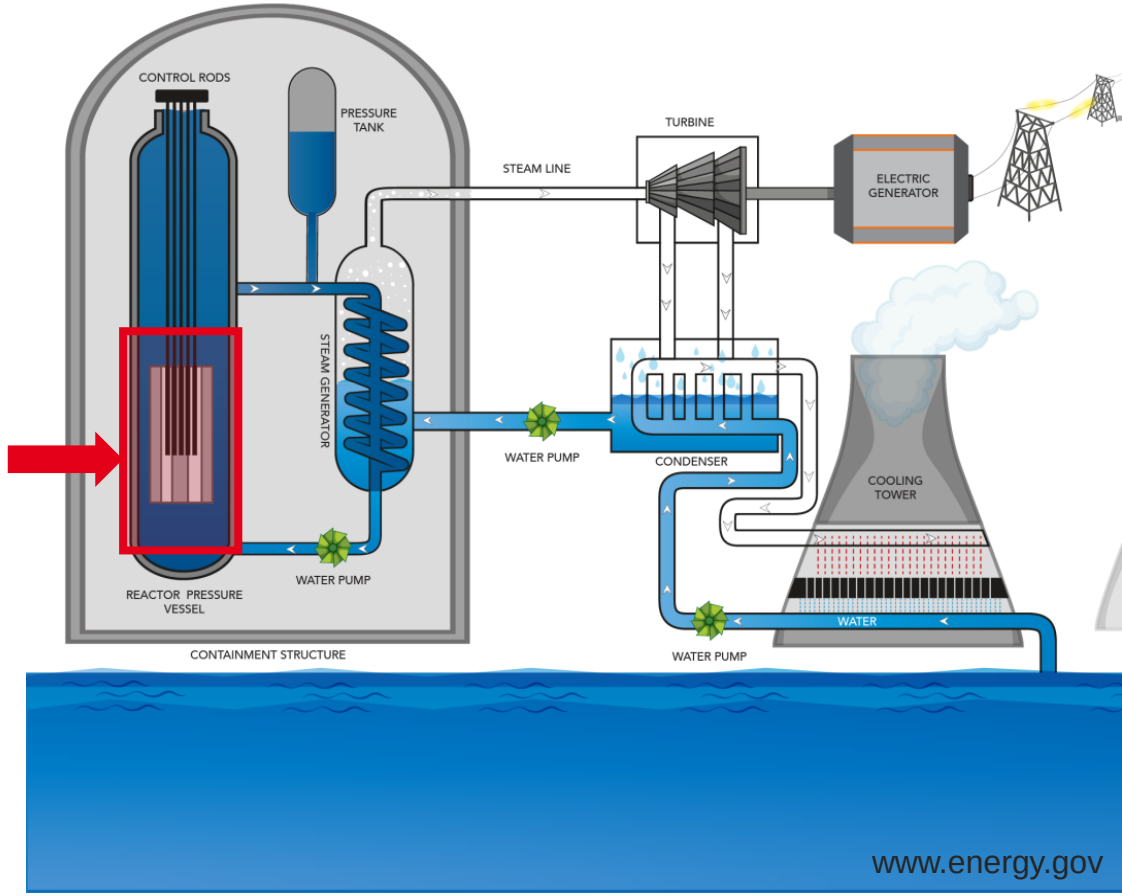
PWR Fuel assembly[1]

- Development of nuclear fuels: safety, efficiency, resources optimization, waste minimization
- Complex behaviour of fuel and fission products, with coupled multi-physics and multiscale phenomena
- Operational margins mainly determined by thermomechanical behavior of fuel elements
- Consequences of accidents depend on physico-chemical fuel behaviour (potential release of radioactive material)

⇨ **Important to understand and be able to predict the fuel behavior under irradiation**

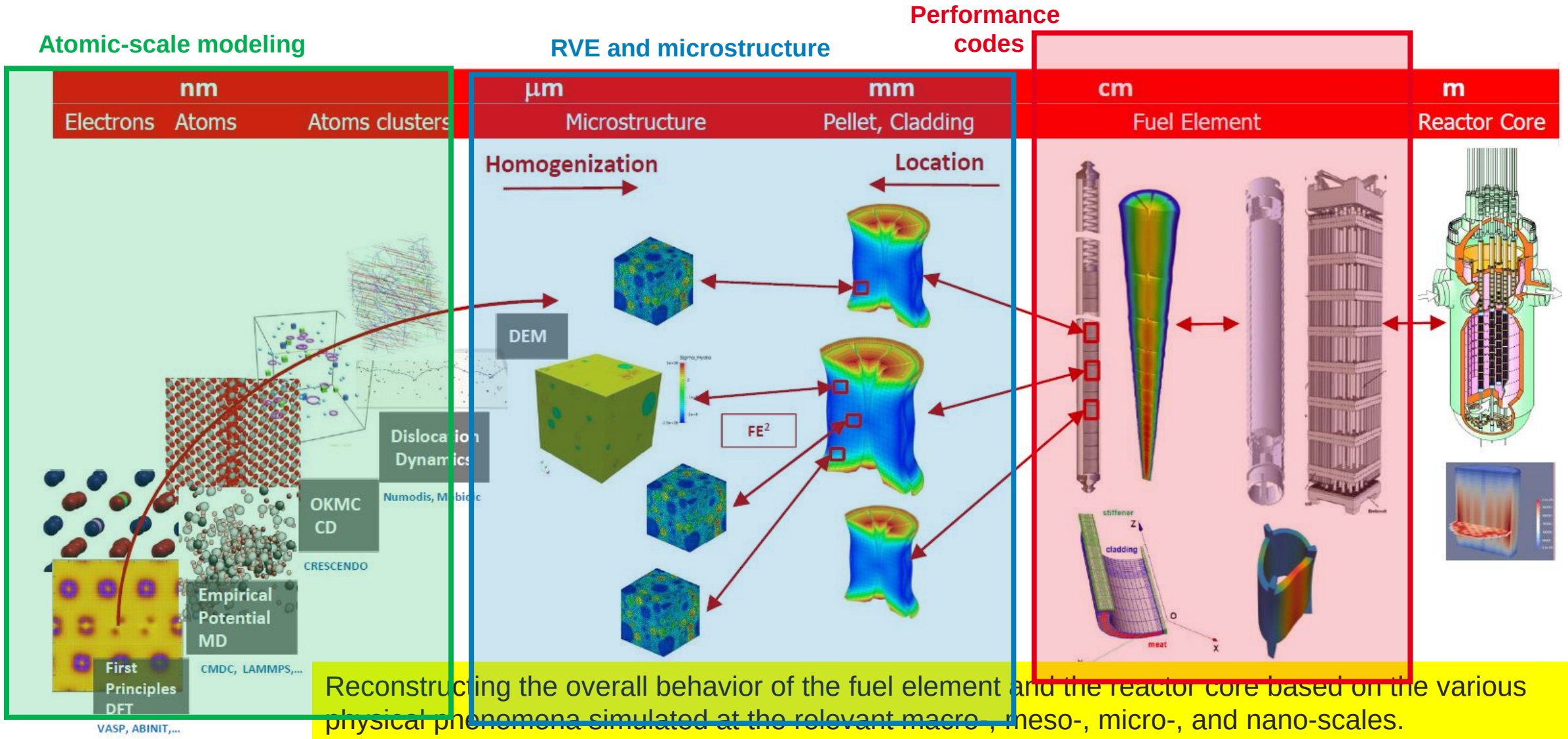


Fuel pellets[1]



[1] Nuclear Fuels, CEA, ISBN 978-2-281-11345-7 (2008)

Multiscale modeling approach to nuclear fuels

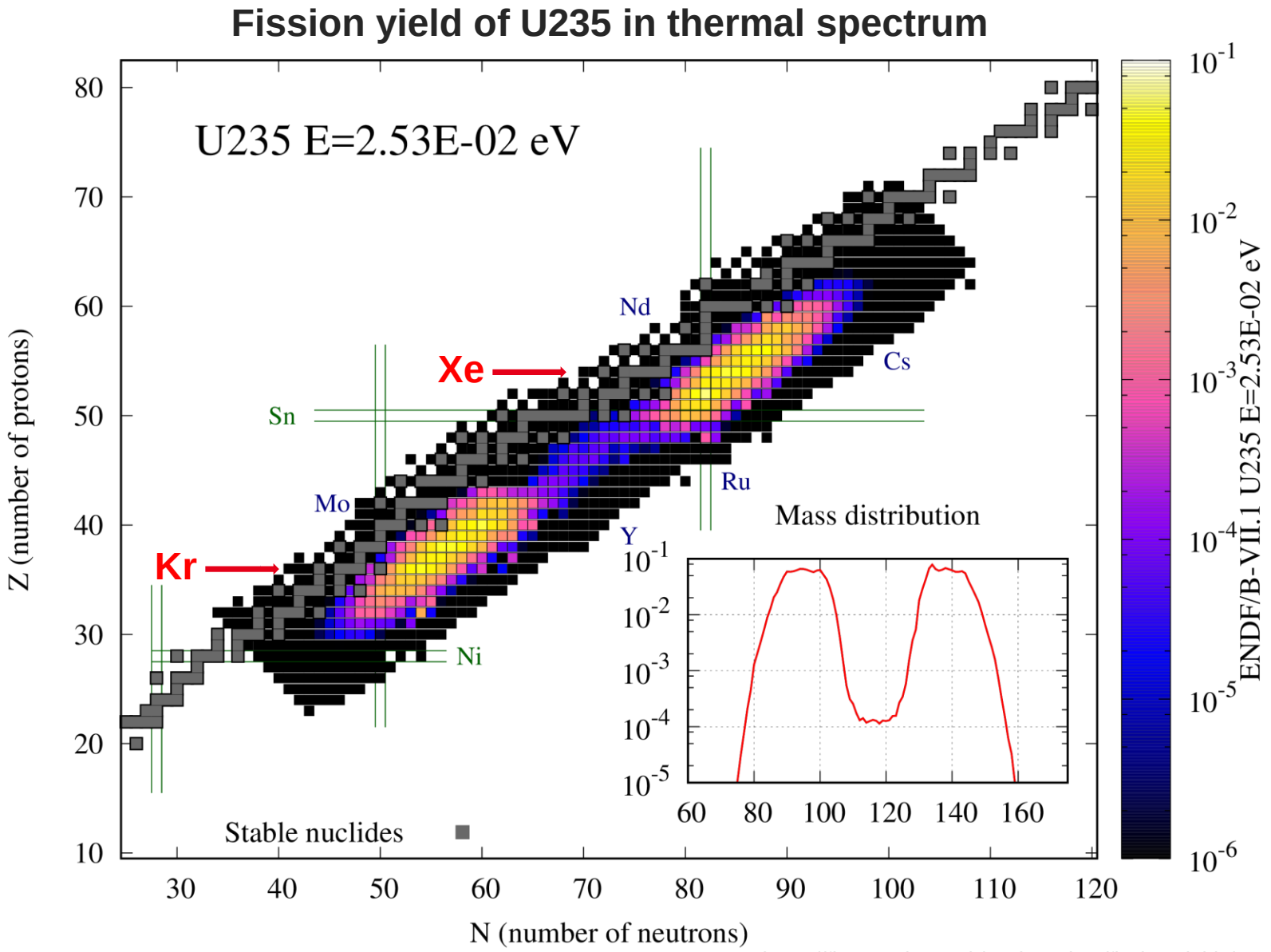


Reconstructing the overall behavior of the fuel element and the reactor core based on the various physical phenomena simulated at the relevant macro-, meso-, micro-, and nano-scales.

Fission gases

- Accumulation of inert gases during irradiation
  - Xenon (about 20%)
  - Krypton (about 10%)
  - Helium (by (n, α) reactions and α decay)

- Relevant impact on fuel behavior

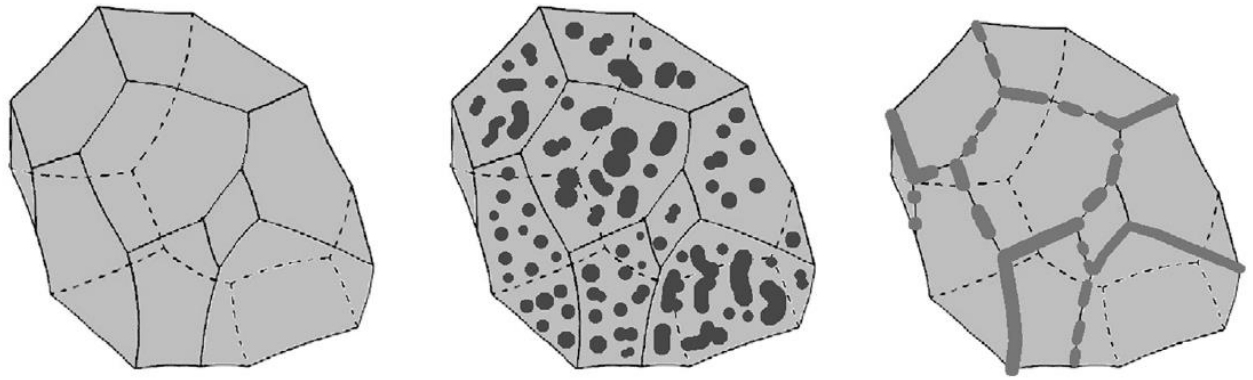


https://fispact.ukaea.uk/nuclear-data/fission-yields/

Fission gas phenomenology

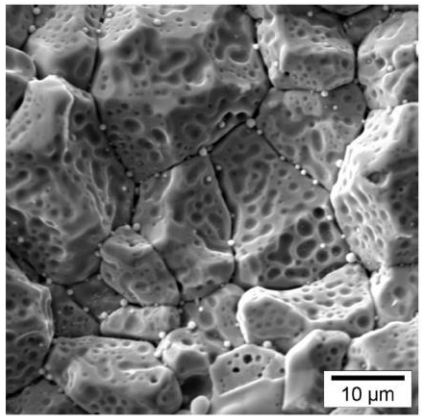
- Fission gas production (Xe, Kr, He) => atomic-scale intra-granular diffusion
- Intra-granular bubble formation and coalescence
- Gas accumulation on grain boundaries => inter-granular bubbles
- Growth and interconnection of inter-granular bubbles => gas release in fuel rod free volumes

M. Tonks et al., J. Nucl. Mater. 504 (2018), 300

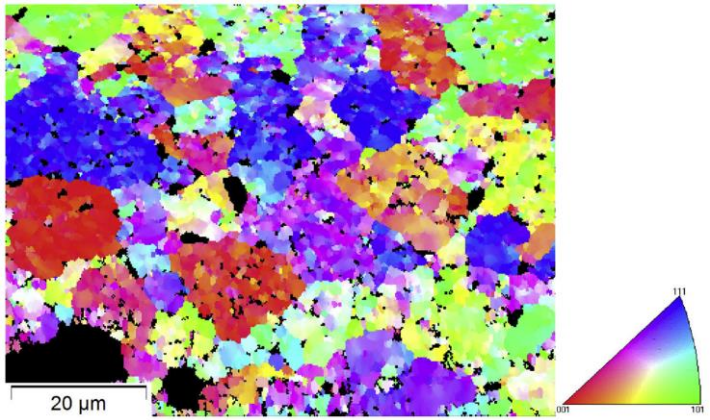


- Fission gas evolution ⇔ microstructure evolution
- Fission gas evolution ⇔ fuel pellet thermomechanical behavior

J. Noirot et al., Nucl. Eng. Tech. 50 (2018), 259



Sub-grain formation in the central area with gas bubble network



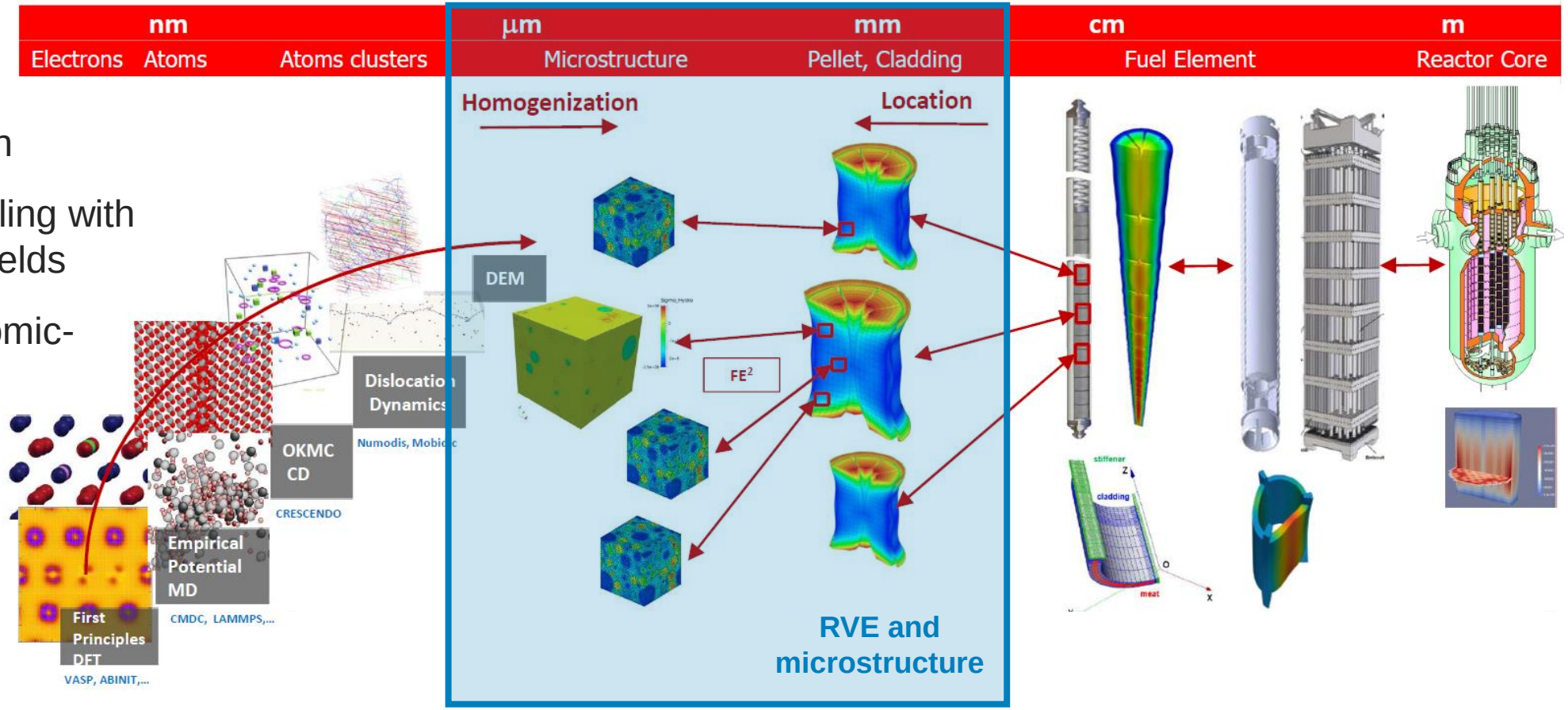
FIB/SEM electron backscattered diffraction (EBSD) inverse pole figure map of the polished surface

- Deformation, swelling
- Restructuring phenomena
  - high-burnup structures (periphery)
  - formation of sub-grains (central area)

Objective

Development of 3D simulation tool for fission gas behavior in polycristalline microstructures, integrated with evolution of thermomechanical fields

- Phase field approach
- Self-consistent coupling with thermomechanical fields
- Parameters from atomic-scale modeling



Outline

1. Nuclear fuels and fission gases
2. Phase-field modeling of gas and microstructure evolution
3. Atomic-scale diffusion coefficients
4. AI approach to the partition function of disordered compounds
5. Conclusions and possible applications to fusion materials

Phase-field model of gases in polycrystalline microstructures

L. Aagesen et al., Phys. Rev. E 98 (2018), 023309
L. Aagesen et al., Comp. Mater. Sci. 161 (2019), 35

- 2 phases (matrix/bubbles), with *p* grains and *n* bubbles
- One order parameter $\eta_1, \dots, \eta_p$ for each matrix grain, one unique order parameter η_b for bubbles
- Chemical potential (⇔ concentrations) fields of U-vacancies c_v and substitutional gas atoms c_g
- Diffuse interfaces (continuous variation of each field from 0 to 1)

$$\Omega = \int_V \left[f_{\text{chem}} + f_{\text{interface}} + \frac{\kappa}{2} |\nabla \eta|^2 (+ f_{\text{el}} + \cdots) \right]$$

ENERGY MINIMIZATION

- Evolution of order parameters : Allen-Cahn equation

$$\frac{\partial \eta_{\alpha i}}{\partial t} = -L(\boldsymbol{r}) \left[m \left(\eta_{\alpha i}^3(\boldsymbol{r}) - \eta_{\alpha i}(\boldsymbol{r}) + 2\eta_{\alpha i}(\boldsymbol{r}) \sum_{\beta=1}^{N} \sum_{j=1, \alpha i \neq \beta j}^{p_\beta} \gamma_{\alpha i \beta j} \eta_{\beta j}^2(\boldsymbol{r}) \right) - \kappa \nabla^2 \eta_{\alpha i}(\boldsymbol{r}) + \sum_{\beta=1}^{N} \frac{\partial h_\beta}{\partial \eta_{\alpha i}} \omega_\beta(\boldsymbol{r}) \right]$$

- Evolution of chemical potentials: Cahn-Hilliard equation

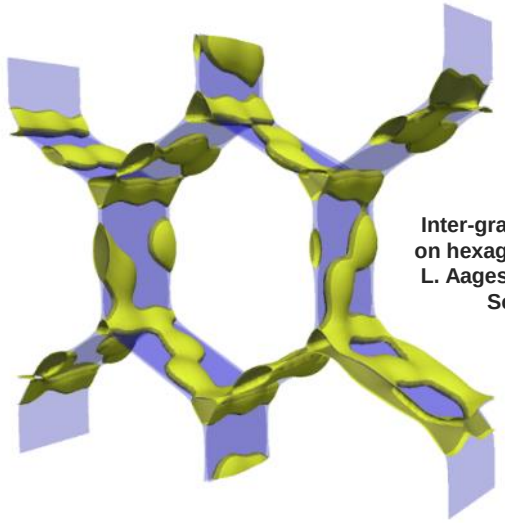
$$\frac{\partial \mu_I(\boldsymbol{r})}{\partial t} = \frac{1}{\mathrm{X}_{II}(\boldsymbol{r})} \left(\nabla \cdot M_{II}(\boldsymbol{r}) \nabla \mu_I(\boldsymbol{r}) - \sum_{\beta=1}^{N} \sum_{i=1}^{p_\beta} \frac{\partial \rho_I(\boldsymbol{r})}{\partial \eta_{\beta i}} \frac{\partial \eta_{\beta i}(\boldsymbol{r})}{\partial t} + s_I(\boldsymbol{r}) \right)$$

Physics ingredients

- **Grain interface/surface energy => evolution of grain/bubble shapes**
- **Gas/defect irradiation source terms**
- **Gas/defect diffusion towards grain boundaries (effective diffusion neglecting intragranular heterogeneities)**
- **Phase free energies and non-equilibrium conditions**

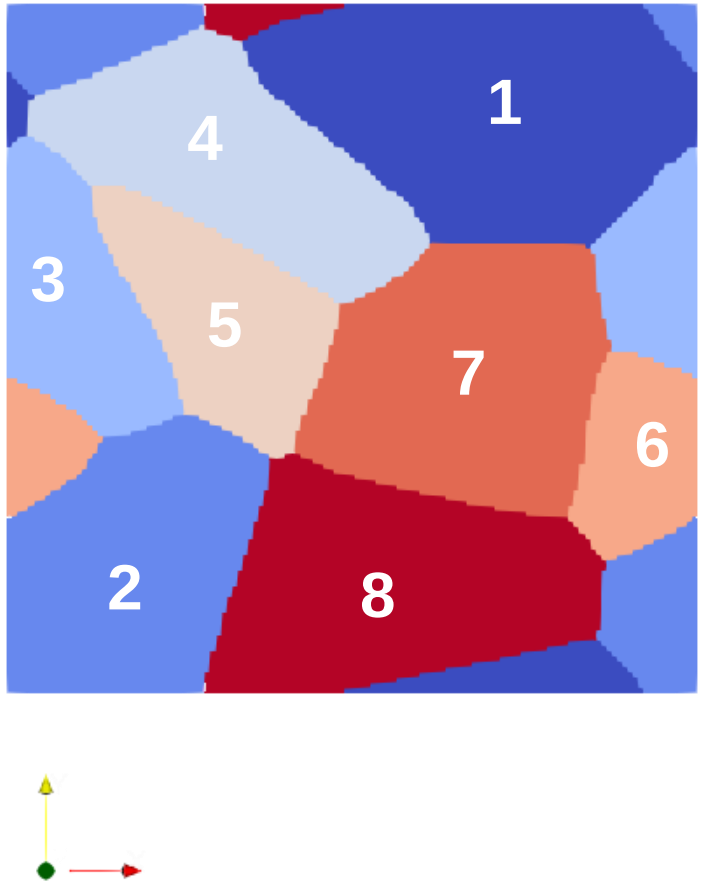
Input parameters

• Solid/gas phase free energies	• Gas/defect source term
• Gas/defect formation energies	• Grain boundary properties
• Gas/defect diffusion coefficients	• Restructuring onset criteria

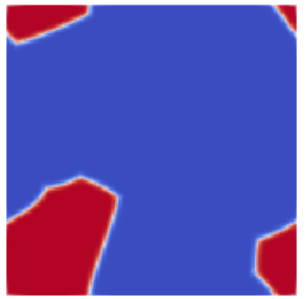


Inter-granular bubble evolution on hexagonal regular polycristal L. Aagesen et al., Comp. Mater. Sci. 161 (2019), 35

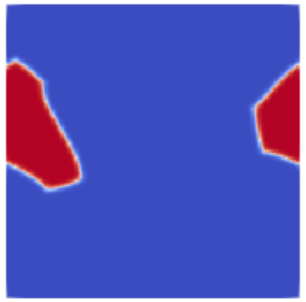
Polycrystal representation in phase field



φ_1 (grain 1)



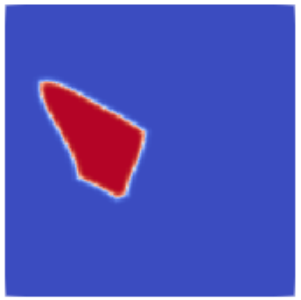
φ_2 (grain 2)



φ_3 (grain 3)

φ_4 (grain 4)

φ_5 (grain 5)

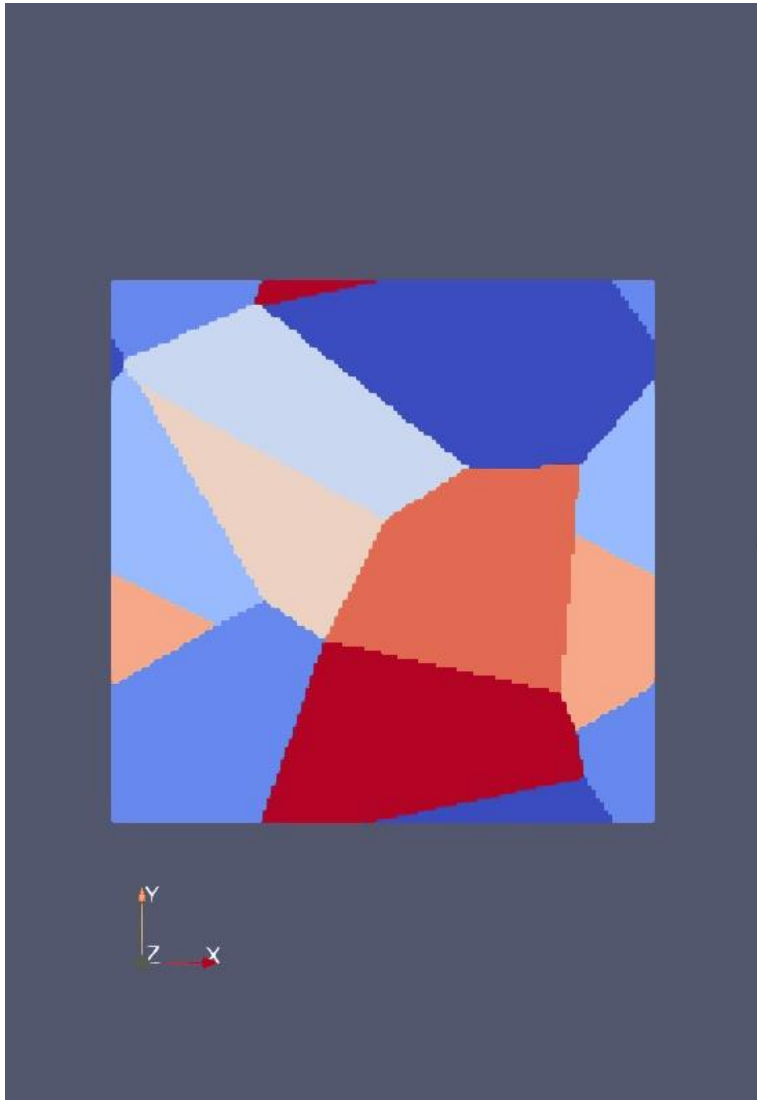


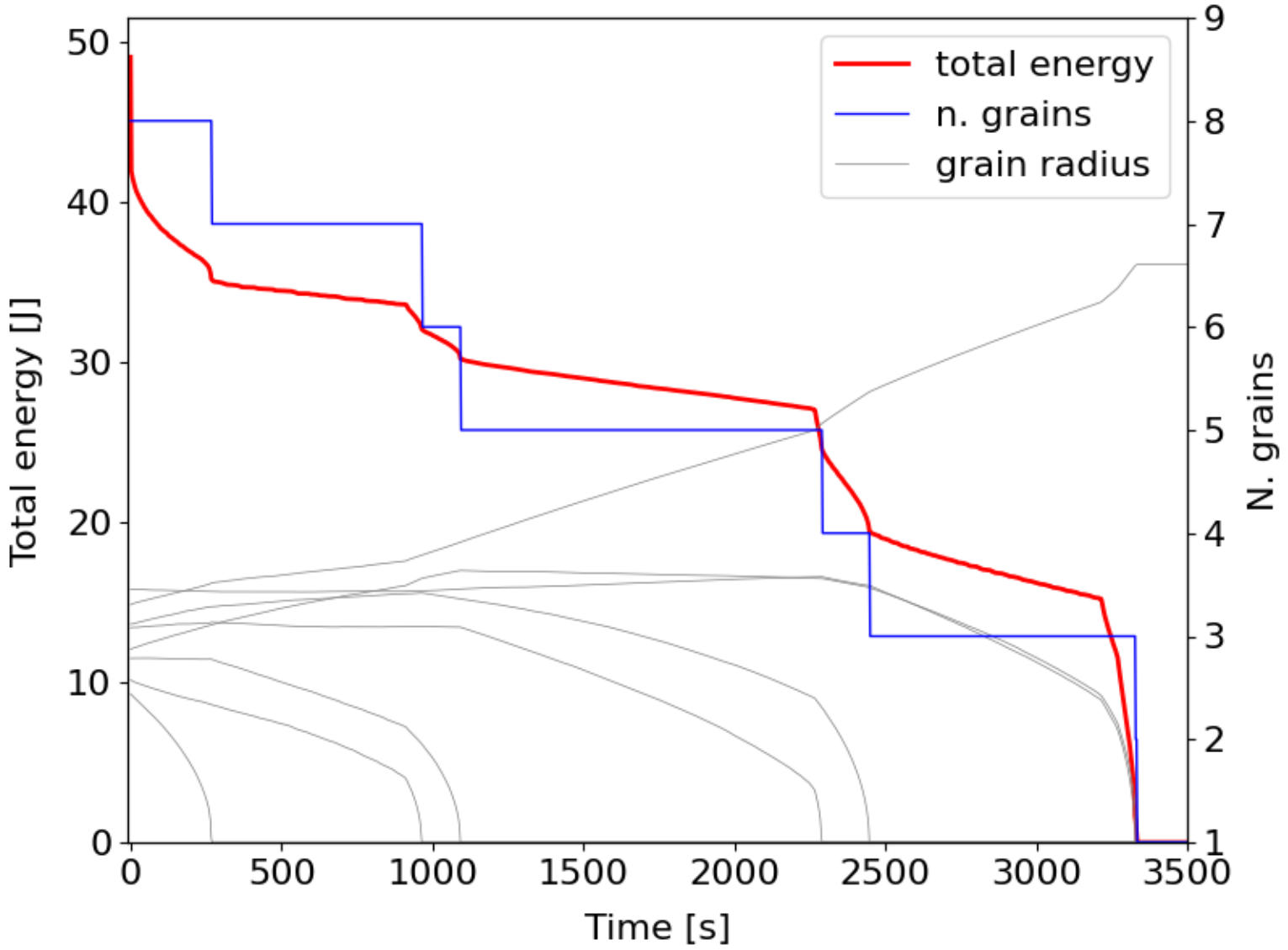
φ_6 (grain 6)

φ_7 (grain 7)

φ_8 (grain 8)

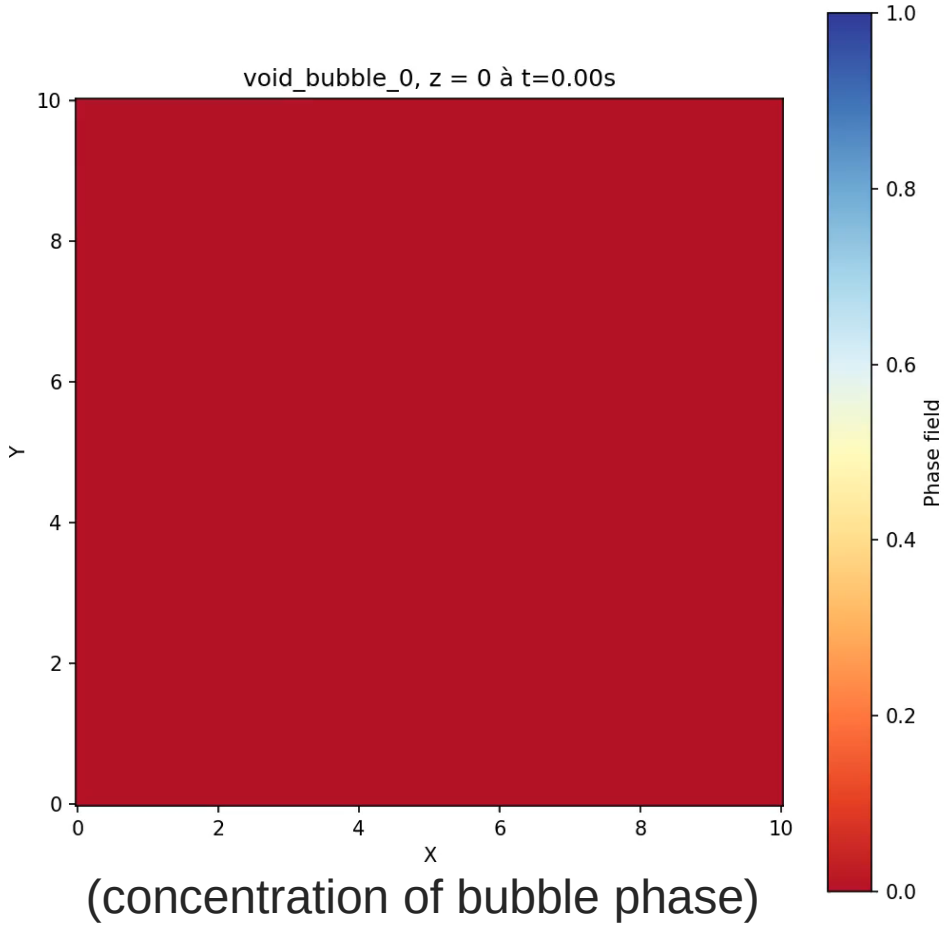
Example - Grain growth (2D)





Example – Intragranular bubble nucleation

Non-homogeneous random fission source
(generation of gas and point defects)

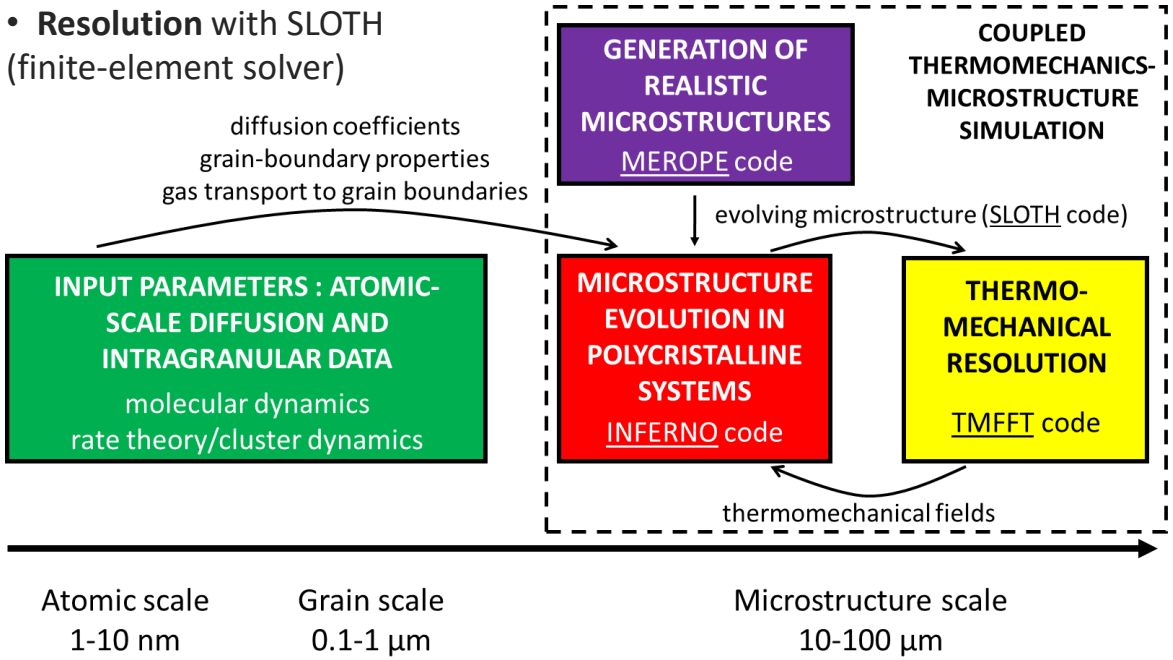


(concentration of bubble phase)

The INFERNO code

Coupled microstructure-mechanics resolution

- **Phase-field guided microstructure evolution**, receiving at each time step information about **mechanical fields** from FFT thermomechanics codes.
- **Initial microstructure** generated by **MEROPE** from experimentally observed microstructures.
- **Resolution** with SLOTH (finite-element solver)



Dedicated computational platform to solve custom multiphase-field models

- Fission gases
- Sintering
- Porosity evolution
- …

$$\Omega = \int_V \left[f_{\text{chem}} + f_{\text{interface}} + \frac{\kappa}{2} |\nabla \eta|^2 + f_{\text{elastic}} + f_{\text{viscoplastic}} \right]$$

provided at each time step by independent solver of mechanics equations

Code coupling

MEROPE — Microstructure generator for initial conditions of phase field simulations

TMFFT — Fast-Fourier transform solver for thermo-mechanics equations

SLOTH — 3D HPC finite-element phase-field solver based on the MFEM* library

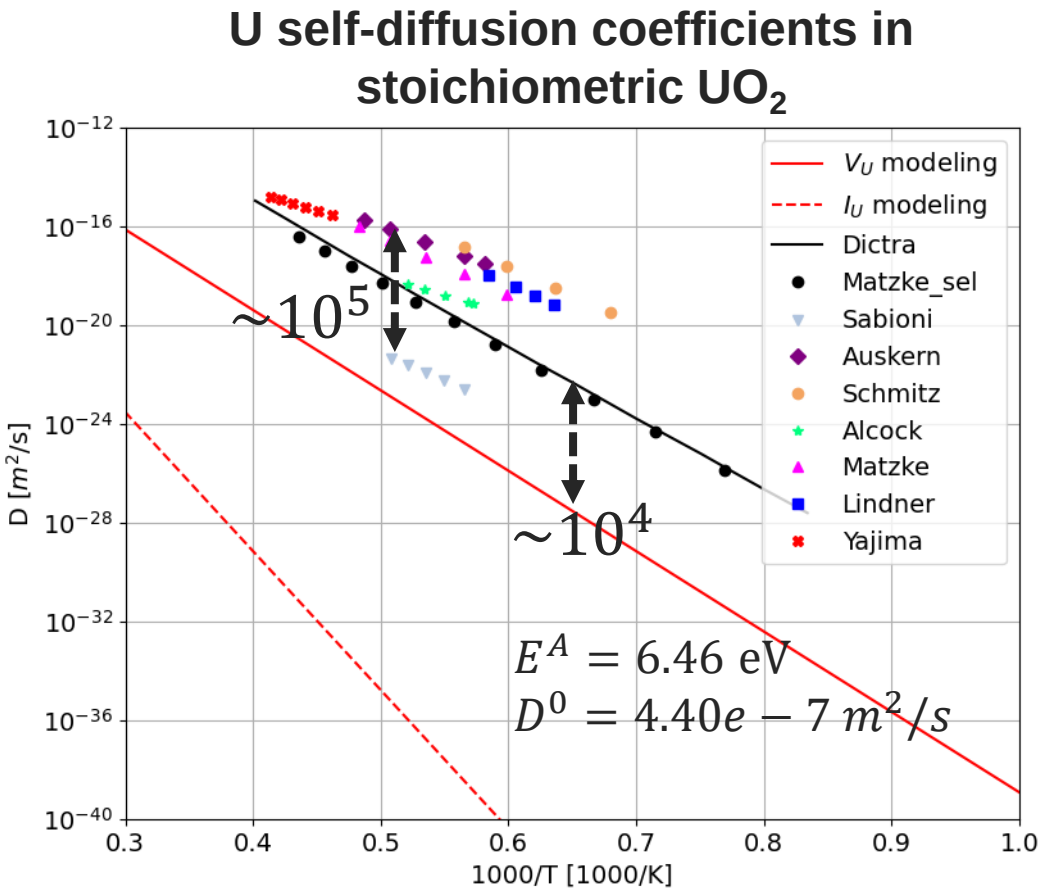
*mfem.org

Outline

1. Nuclear fuels and fission gases
2. Phase-field modeling of gas and microstructure evolution
3. Atomic-scale diffusion coefficients
4. AI approach to the partition function of disordered compounds
5. Conclusions and possible applications to fusion materials

Cationic self-diffusion in UO_2

- Dispersion among experimental values
  - Mainly explained by difficulty to control stoichiometry
- Large gap between modeling (lines) and experimental values (points) for isolated defects
- Gap could be explained by:
  - Thermal-expansion effect on migration energies [1]
  - Contribution of vacancy clusters



Moore, J. Solid State Chem. 203 (2013)

[1] W. D. Neilson *et al.*, J. Phys. Chem C **128**, 21559 (2024)

How to obtain a diffusion coefficient?

- Experimentally:
  - Direct measurements (ex. tracers)
  - Indirect measurements (ex. from gas release experiments during thermal ramps)
- Based on modeling:
  - Mean square displacement in Molecular Dynamics (MD) or Kinetic Monte Carlo (KMC) simulations
  - Analytical methods (KineCluE [1] and other methods)
    - MD => needs interatomic forces based on interatomic potentials or ab initio MD
    - KMC / analytical methods => need atomic-scale input such as:
      - Activation energies (defect formation + migration)
      - Prefactors

Defect activation free energy

Formation free energy

Migration free energy

$$D = g\nu \exp\left(-\frac{G^{\mathrm{act}}}{k_{\mathrm{B}}T}\right) = g \underbrace{\exp\left(-\frac{G^{\mathrm{for}}}{k_{\mathrm{B}}T}\right)}_{\text{DEFECT CONCENTRATION}} \underbrace{\nu \exp\left(-\frac{G^{\mathrm{mig}}}{k_{\mathrm{B}}T}\right)}_{\text{JUMP FREQUENCY}}$$

Attempt frequency (prefactor)

[1] T. Schuler *et al.*, Comput. Mater. Sci. 172 (2020)

Self-diffusion by small vacancy clusters

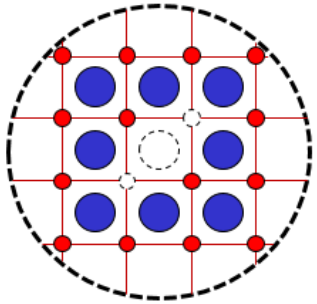
- **Dilute limit hypothesis :** The material defect clusters are low enough in concentrations to consider them non interacting at least until they achieve thermodynamic equilibrium
- The diffusion coefficient can be expressed with KineCluE [1] (KINetic CLUster Expansion) as:

$$D_{U^*} = \sum_c P_c \frac{L_{U^*U^*}(c)}{c_U^*} \quad ; \quad P_c = \frac{[c]}{\sum_{c'}[c']}$$

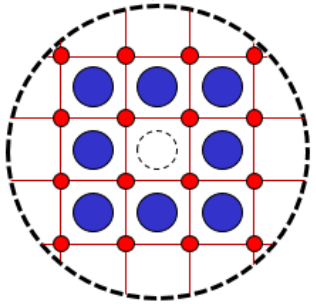
- We need to determine for each cluster :
  - **1)** The probability P_c for the U tracer to be in cluster c : *Which defect cluster is the most probable ?*
  - **2)** The cluster transport coefficient $D_{U^*}(c)$: *How fast do the defect clusters transport the U tracer atoms*

Studied defect clusters :

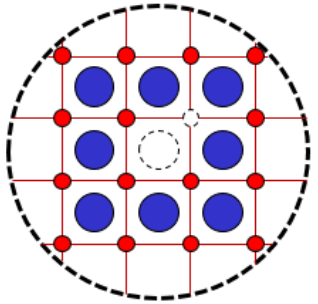
(and their multiple internal configurations)



Schottky defect (SD or $V_U V_O V_O$)



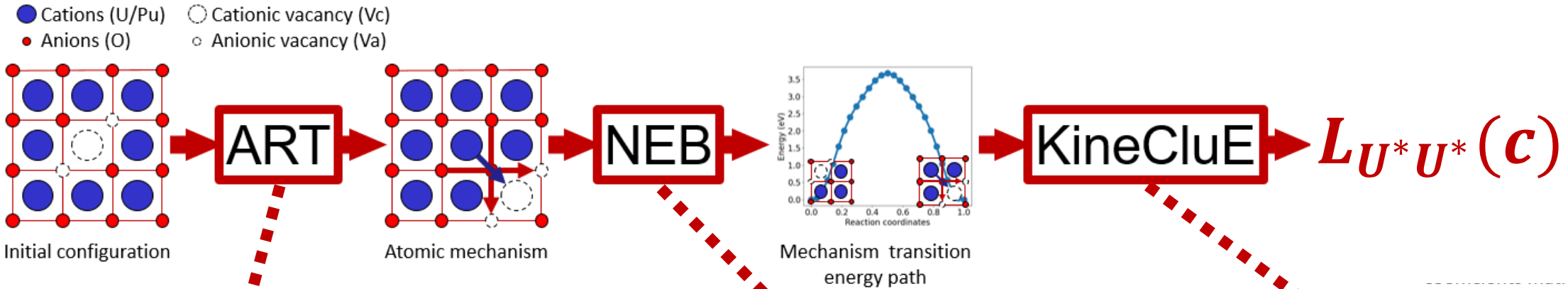
UO divacancy ($V_U V_O$)



U vacancy (V_U)

[1] T. Schuler *et al.*, Comput. Mater. Sci. 172 (2020)

Cationic self-diffusion coefficients with combined ART + KineCluE approach



ART (Activation Relaxation Technique)

- Searches energetic transitions by random explorations of the potential energy surface

Mousseau, N. J. Phys. B 2012 (2012)

NEB (Nudged Elastic Band)

- Breaks down energy transitions into migration mechanisms
- Computes the migration barriers of the mechanisms based on the initial and final atomic configurations

Jonsson, H. Classical and Quantum Dynamics in Condensed Phase Simulations p.385-404 (1998)

KineCluE (Kinetic Cluster Expansion)

- Computes the cluster transport coefficient

Schuler, T. Messina, L. Nastar, M. Comput. Mater. Sci. 172 (2020)

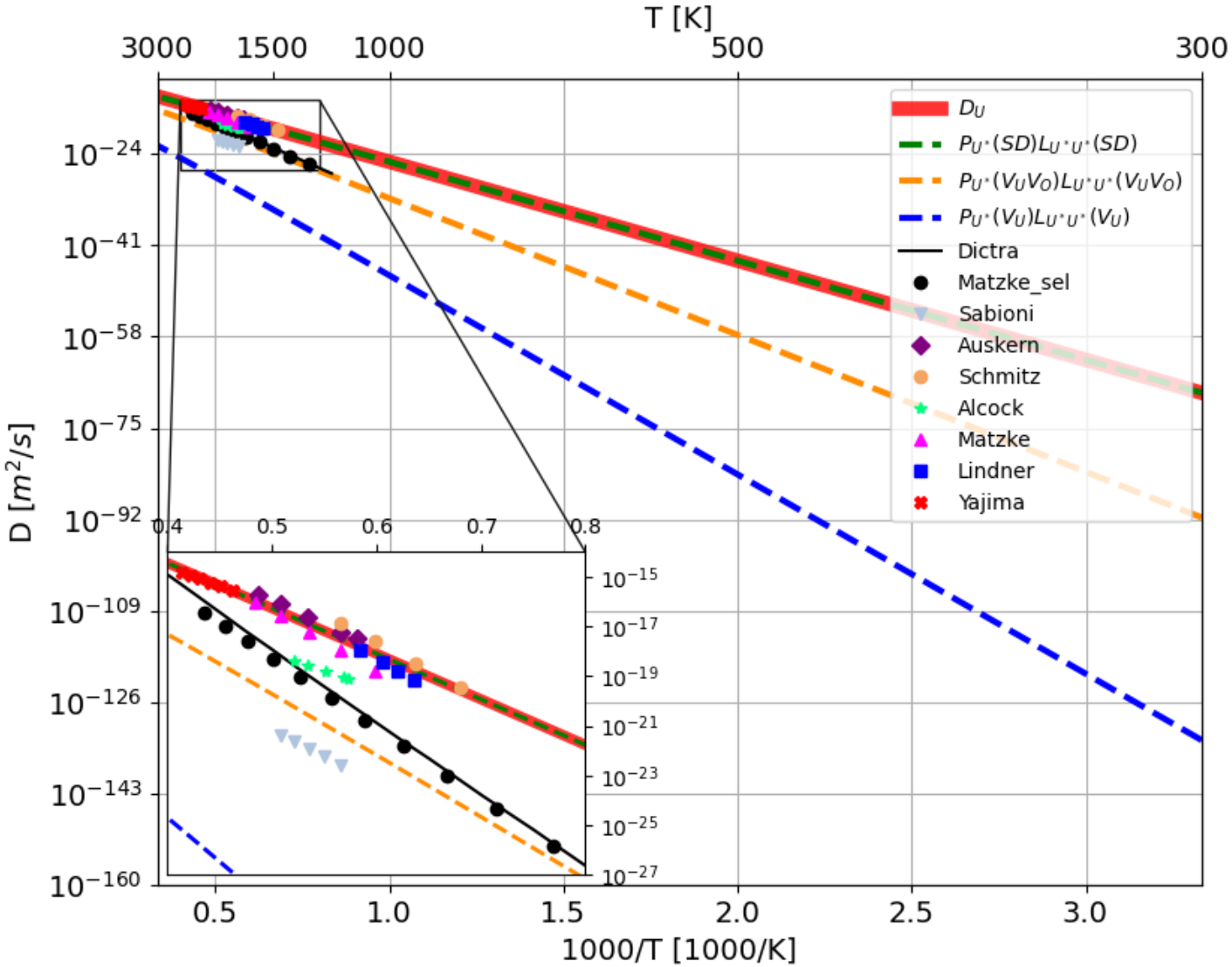
Cationic self-diffusion coefficients with combined ART + KineCluE approach

- Transport by Schottky defect is dominant
  - To be confirmed with refinement of defect model
- Satisfactory match with experiments at high temperatures
  - Thanks to several Schottky migration mechanisms found by ART and characterized by lower migration energies than isolated vacancies

D_U Arrhenian parameters	
E^A [eV]	D^0 $[m^2/s]$
3.65	8.41×10^{-8}

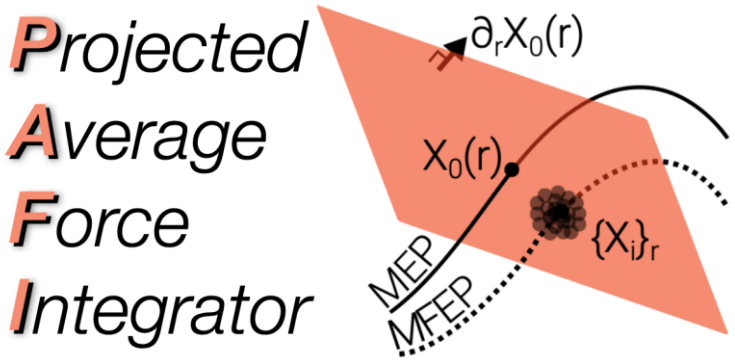
P. Ospital et al., manuscript under preparation

D_U diffusion coefficient : computed and experimental values



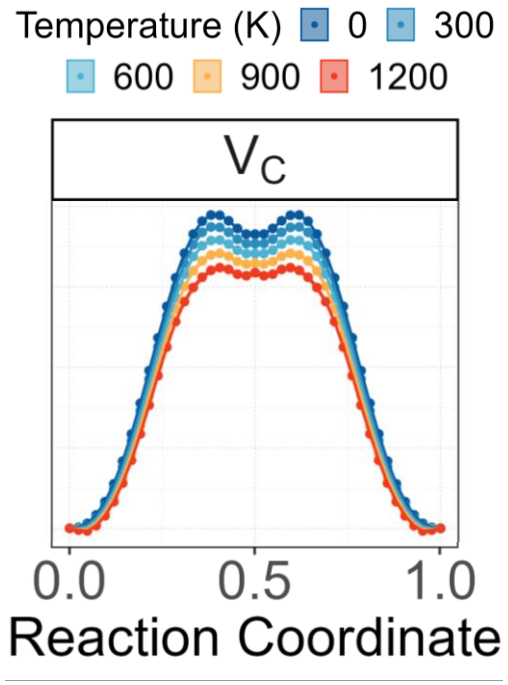
Effect of finite temperature on migration barriers with the PAFI method

T. Swinburne, M. C. Marinica, Phys. Rev. Lett. 120, 135503 (2018)

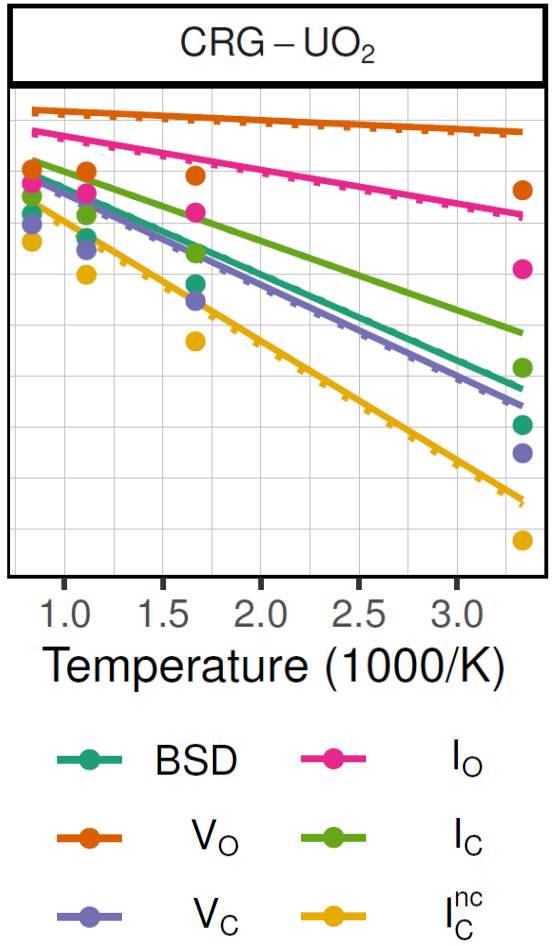


- Method to analytically determine minimum free energy path (MFEP) at finite temperature with full accounting of non-harmonic effects
- Based on adaptive biasing force method and stratified sampling of configuration space
- Starts from ground state MFEP
- Gives exact expression for free energy gradient

Cationic vacancy free energy barrier



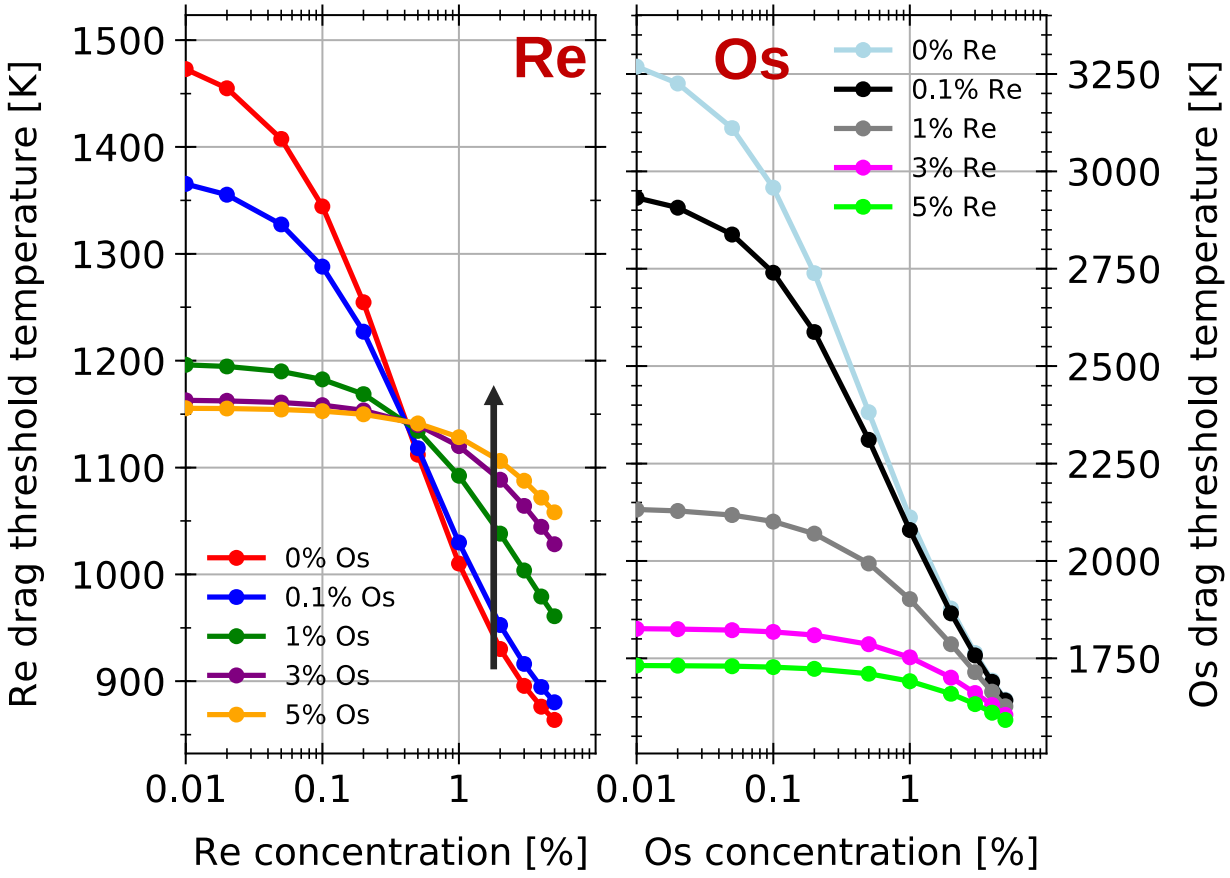
Jump frequency vs harmonic approximation



D. Frost et al., manuscript under preparation

Kinetic coupling of defects and transmutation products in W

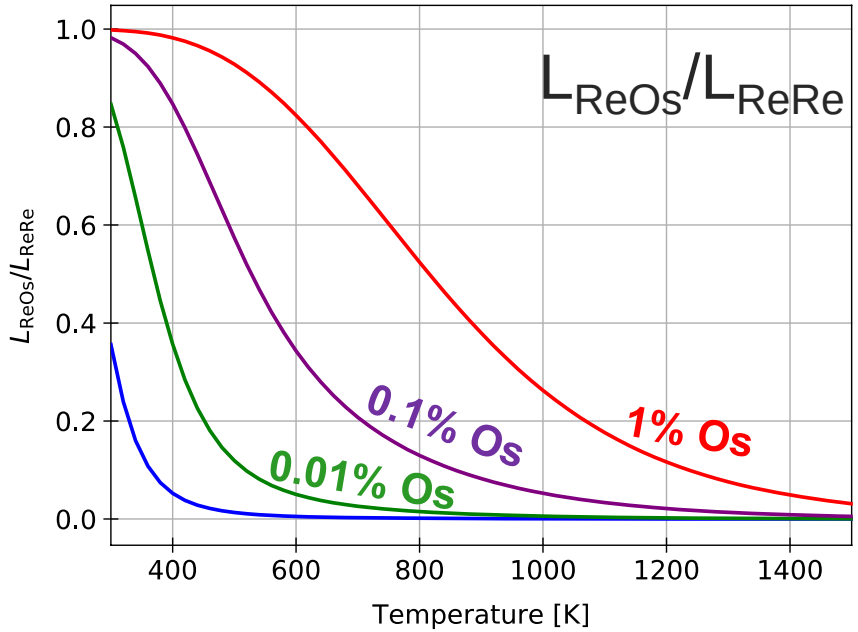
Variation of drag threshold temperature with Re/Os concentration



L. Messina, final report of EUROfusion Researcher Grant MEATBALL (2017-2019)

- Re (Os) drag weakens with increasing Re (Os) concentration
- Appearance of Os in W-Re (>0.5%Re) enhances Re drag
- Due to Re-Os coupling: as Os appears, Re diffusion can occur only through the $v_1Re_1Os_1$ cluster

Re drag by Os atoms

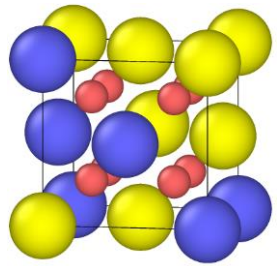


Outline

1. Nuclear fuels and fission gases
2. Phase-field modeling of gas and microstructure evolution
3. Atomic-scale diffusion coefficients
4. AI approach to the partition function of disordered compounds
5. Conclusions and possible applications to fusion materials

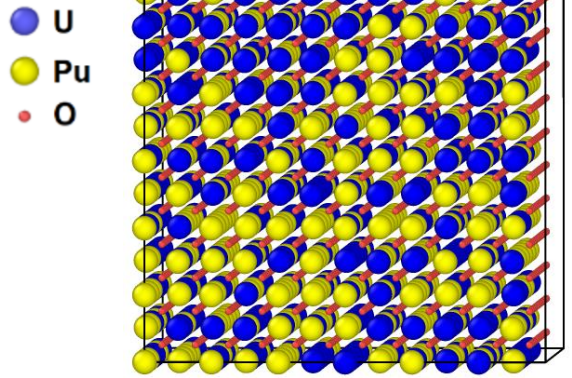
Chemical disorder

- Chemically disordered compounds: negligible mixing enthalpy
- From cristallographic point of view: multiple species sharing the same lattice/sublattice randomly (or pseudo-randomly)
- Various degrees of disorder, possible local order…
- Examples: $(U,Pu)O_2$ fuels, high-entropy alloys (HEA)

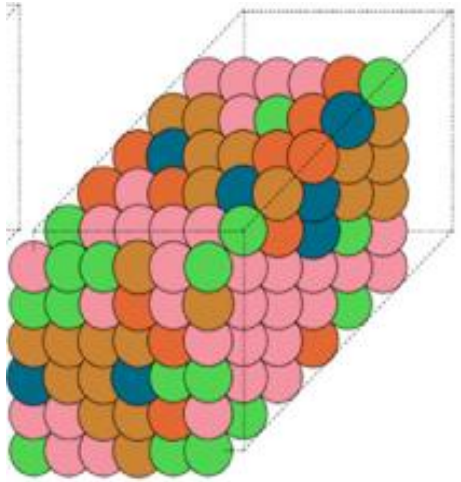


Fluorite
$(U,Pu)O_2$ cell

$(U,Pu)O_2$ supercell



HEA CoCuFeNiPd supercell



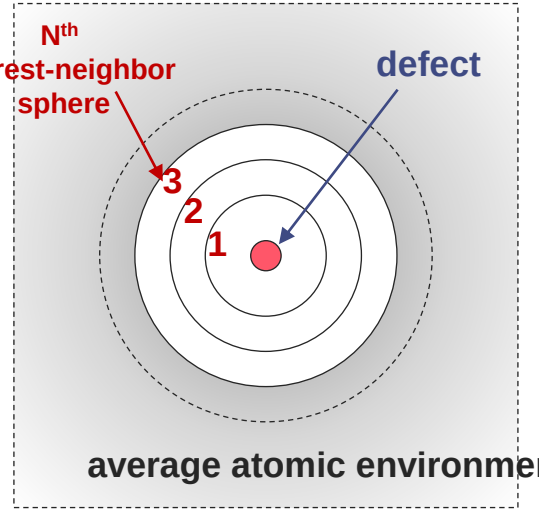
- Objective: atomic-scale properties of disordered materials that depend on atomic composition (i.e., distribution of chemical species on shared lattice)
- Needs sampling of (one or several) partition function(s)
- Example : point-defect equilibrium concentration:

$$C_d = \left\langle \exp\left(-\frac{G_{k,d}^{\mathrm{form}}}{k_{\mathrm{B}}T}\right)\right\rangle = \sum_{k=1}^{N_{\mathrm{conf}}} w_k \exp\left(-\frac{G_{k,d}^{\mathrm{form}}}{k_{\mathrm{B}}T}\right) \qquad w_k = \frac{\exp\left(-\frac{G_k}{k_{\mathrm{B}}T}\right)}{\sum_{k=1}^{N_{\mathrm{conf}}} \exp\left(-\frac{G_k}{k_{\mathrm{B}}T}\right)}$$

Limitation of traditional approaches to chemical disorder

- Brute-force approach not envisageable due to extremely large number of configurations (10^{16} with 4nn)
- Traditional approaches:
  - Special Quasi-Random Structures (SQS): generates supercells with maximized disorder, but no information on exploration exhaustivity (and not suited for locally ordered compounds)
  - Monte Carlo sampling (MCMC): demands a very high number of configurations, depending on target property
- For $(U,Pu)O_2$: very high computational cost (DFT+*U*, inaccurate interatomic potentials for certain properties)
- We propose 3 approaches:
  - Systematic approach limited to nearest-neighbor atoms
  - Statistical approach based on limited number of random configurations
  - Generative AI approach to optimize exploration

Generation of local atomic configurations around a central point, up to the Nth neighbor sphere



D. Bathellier et al., J. Appl. Phys. 132, 175103 (2022)

M. C. Notarangelo et al., under preparation

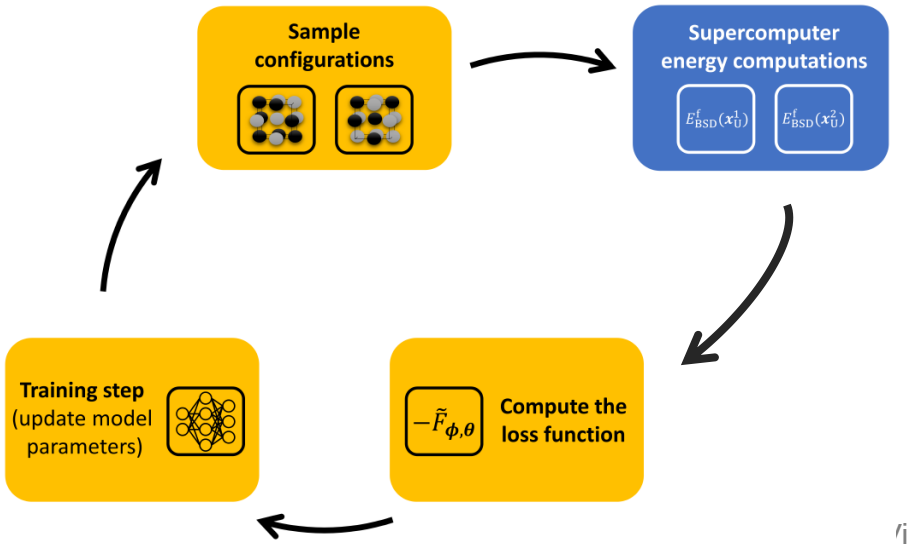
M. Karcz et al., Phys. Chem. Chem. Phys., 25, 23069-23080 (2023)
M. Karcz et al., arXiv:2408.14928

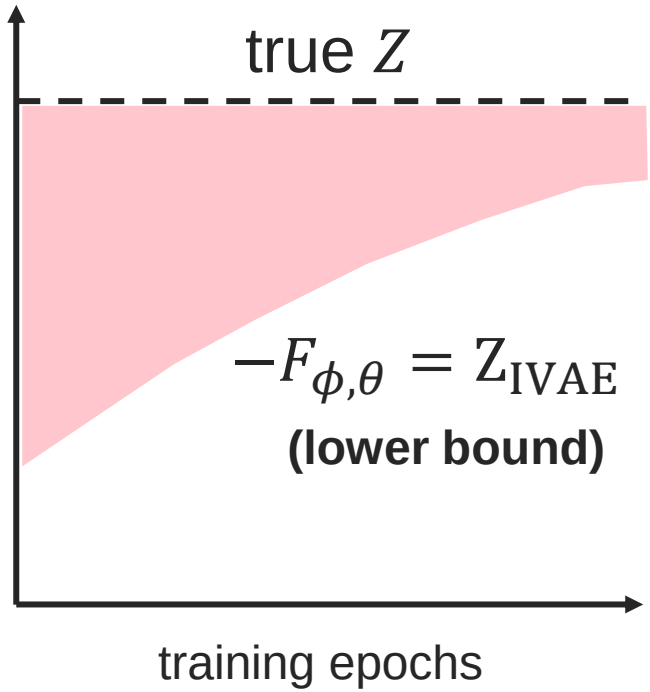
AI-driven partition function estimation and sampling: the PULSE method

PULSE : Partition function Unsupervised Learning Sampling and Evaluation for disordered compounds

- Non-supervised generative model that **builds its own training database** with an iterative **active learning approach**, with two simultaneous tasks:
  - Generation of representative atomic configurations
  - Estimation of a partition function, giving access to target property
- Requiring the lowest possible amount of training configurations (to reduce computational time needed for energy/force calculations)

M. Karcz *et al.*, arXiv:2408.14928





Outline

1. Nuclear fuels and fission gases
2. Phase-field modeling of gas and microstructure evolution
3. Atomic-scale diffusion coefficients
4. AI approach to the partition function of disordered compounds
5. Conclusions and possible applications to fusion materials

Conclusions

- Phase-field modeling of gas (He, Kr) evolution in polycristalline microstructures
- Coupled solution of phase-field and thermomechanical equations allows for simulation of complex microstructure phenomena such as fuel restructuring
- Calculation of point defect cluster contribution to transport/diffusion coefficients by combination of ART & KineCluE
- Full non-harmonic calculation of free-energy barriers with PAFI method
- AI-based PULSE method to sample and evaluation partition function of disordered compounds

Diffusion phenomena

Inert gas behavior

High-entropy alloys & oxides

Thank you

CEA CADARACHE
13115 Saint Paul Lez Durance Cedex
France
luca.messina@cea.fr
+ 33 4 42 25 61 80

iresne@cea.fr

Site internet CEA IRESNE

LinkedIn CEA IRESNE