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Nuclear Energy

Lower Length Scale Simulations of Transport in Oxide Fuels

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Introduction

Motivation/Approach – context for results that follow

Results

Fission gas release

* first principles study of bulk Xe diffusion (compared to exp. data)
* atomistics study of fission gas interaction with microstructure
* "upscaling" both the above to meso- and engineering scale

Thermal conductivity

* atomistics: implementation of long range forces for consideration of microstructure
* Upscaling of atomistics to meso- and engineering scale

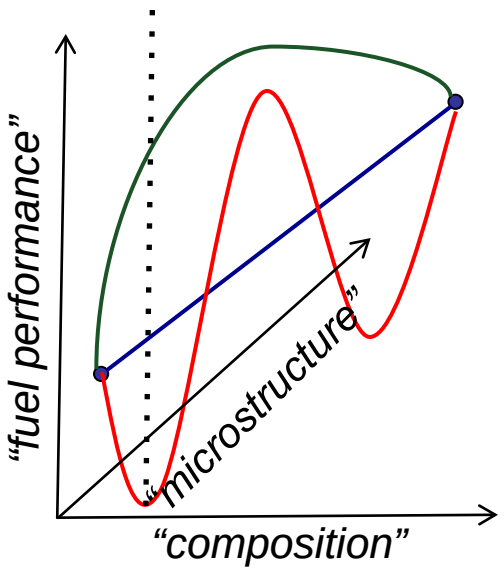
LLS work not discussed:

* Potts modeling of voids (ORNL)
* FG release in metal fuel (ANL)
* Radiation damage of clad (ORNL)
* VPSC of thermal and irradiation creep (and associated dislocation dynamics LANL + LLNL)

Lower length scale: *Motivation*

Many of the relevant nuclear fuels issues are problems of materials science

Goal: Extend IPSC to fuel compositions/conditions for which there is little or no experimental data.



(From a materials scientist's perspective) *Without improved materials (i.e. chemistry and physics) packages, IPSC may only be a marginal improvement over e.g. FRAPCON*

Simplified Roadmap:
Strategic Choice of Problem Enables Integration and Improves Relevance

EXPERIMENTAL CAMPAIGN

IPSC

microstructure

What?: *Informed simulation of effect of microstructure on fuel performance and synthesis*

How?: *mesoscale simulation techniques*

Single crystal
Idealized polycrystal

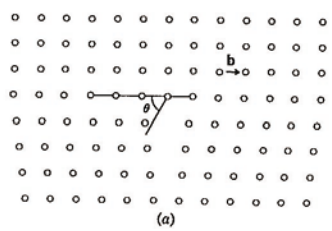
What?: *Thermal and mass transport as a function of composition, nonstoichiometry, GB structure, dislocation structure, etc.*

How?: *Atomistics (MD, DFT, etc), thermochemical models, etc. INDEPENDENT OF MESOSCALE APPROACH*

Upscaling via Consideration of Multidimensional Defects

In principle, all higher order defects can be considered as comprised of 0-D point defects

** one dimensional = dislocations*



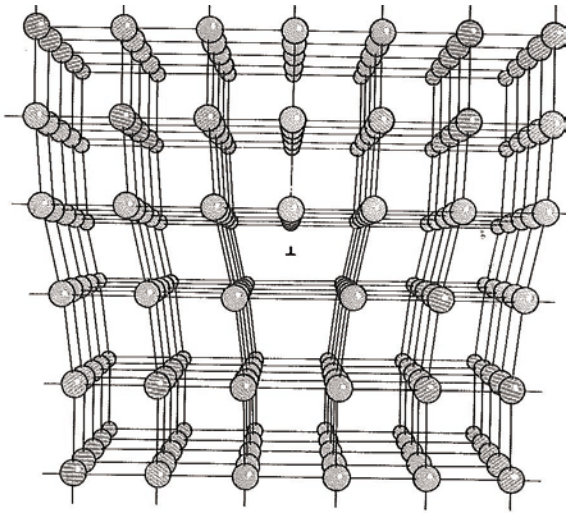


Figure 6-1 (*a*) Atomic arrangement of atoms in an edge dislocation (cross-section view); (*b*) perspective of atom arrangements about an edge dislocation in a simple cubic crystal.

From C.A. Wert and R.M. Thomson "Physics of Solids" (1964).

** two dimensional = surfaces, grain boundaries, interfaces*

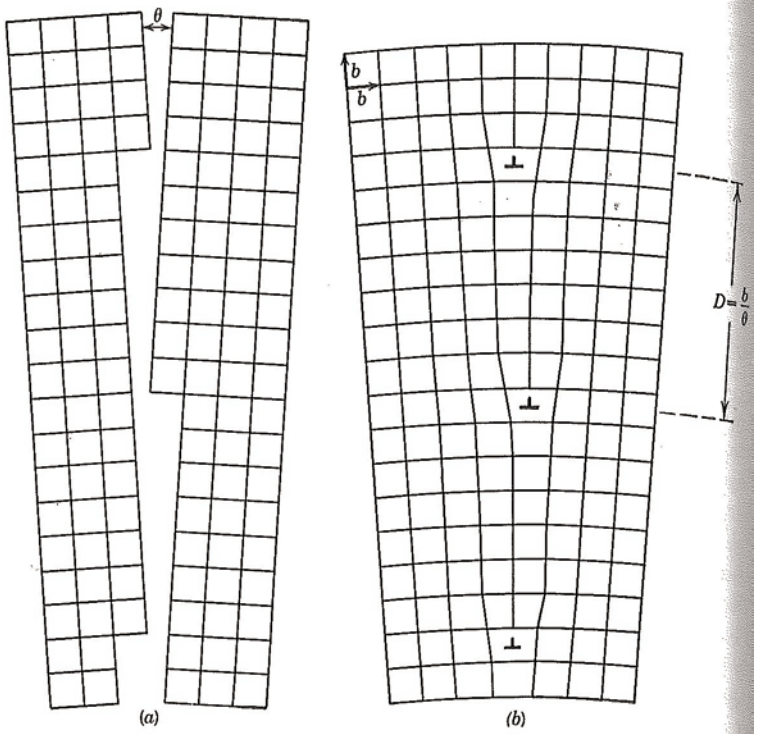


FIG. 1. Simple grain boundary showing (*a*) two grains with common crystal axis and (*b*) method of joining and dislocation model.

From W.T. Read Jr. and W. Shockley, in F. Seitz "Imperfections in Nearly Perfect Crystals" (1952).

** three dimensional = voids, bubbles*

Why Should We Care About Defects?

Defects are Responsible for Reliance on Empiricism

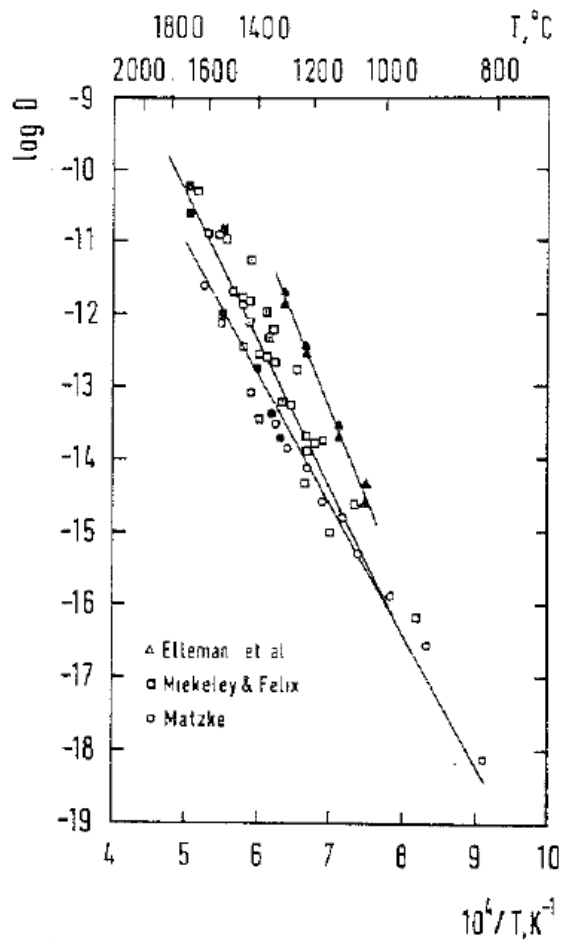
For example, it is not possible to make a connection between FG diffusion coefficient and FG release rates.

Reason, as stated by Olander, is defects.

D.R. Olander, "Fundamental Aspects of Nuclear Reactor Fuel Elements" (1976)

1. Natural defects:
   (a) Grain boundaries.
   (b) Dislocation lines.
   (c) Closed pores in the as-fabricated fuel.
   (d) Impurities in the solid.
2. Radiation-produced defects:
   (a) Vacancy clusters (perhaps stabilized by a few gas atoms). A fission track is especially rich in this type of trap.
   (b) Dislocation loops formed by condensation of excess interstitial atoms.
   (c) Fission-gas bubble.
   (d) Solid fission-product precipitates (e.g., the noble metal and alkaline earth oxide phases).

Hj. Matzke, *Radiation Effects* **53** (1980) 219



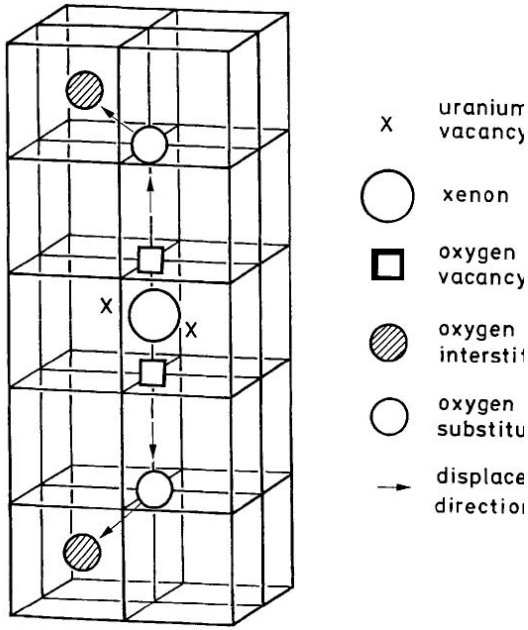
Why Now?

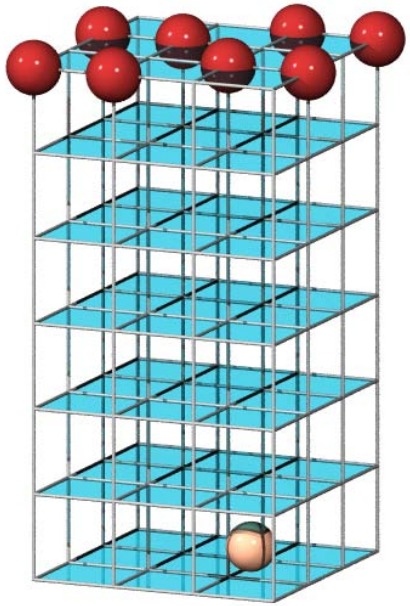
Olander elucidated many of the important issues over 30 years ago.

Original simulation study: Catlow, "Fission Gas Diffusion in Uranium Dioxide," *Proc. Roy. Soc. London A* **364** (1978) 473.

Xe diffusion mechanism proposed by Ball and Grimes (*J. Chem. Faraday Trans.* **86(8)** (1990) 1257) from **pair potentials**.

Surface segregation: C.R. Stanek, et al., *J. Phys.: Cond. Matter* **16** (2004) S2699.





Two important, recent advances – both benefit from high performance computing:

** DFT for improved quantification*

** Pair potentials for relevant microstructural features*

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FRAPCON Example of Fission Gas Release

Fuel performance codes are currently reliant on empirical data.

$$\frac{dC}{dt} = D(t)\Delta_r C(r, t) + \beta(t)$$

The diffusion coefficient is represented by one of three values depending on the T.

$$D = 1.09\ H\ 10^{-17} \exp(-6614/T),\ T > 1650\ K$$

$$D = 2.14\ H\ 10^{-13} \exp(-22884/T),\ 1381 < T < 1650\ K$$

$$D = 1.51\ H\ 10^{-17} \exp(-9508/T),\ T < 1381\ K$$

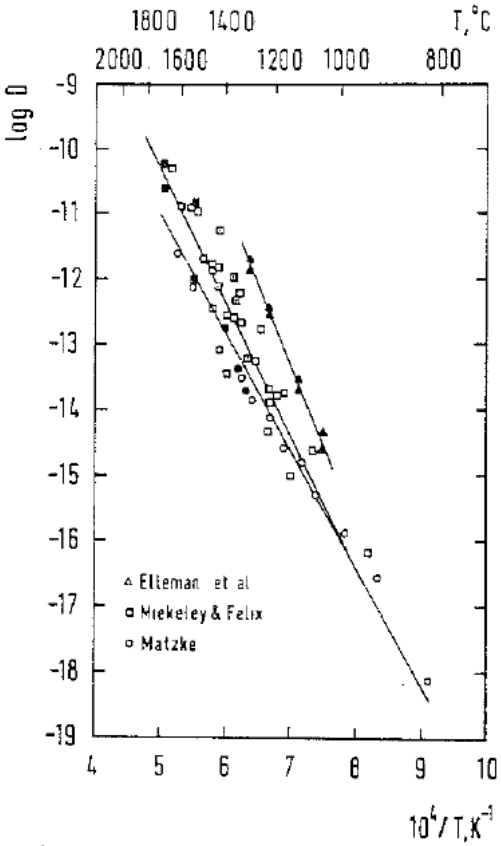
Impossible to capture fission gas behavior without understanding multidimensional defects – see Olander.

Useful to replace these D with compositionally and microstructurally aware functionals – results that follow begin to do that.

For IPSC: use well established LLS methods to generate inputs

Experimental activation energies for U and Xe diffusion in $UO_{2\pm x}$

Experiments, e.g. Hj. Matzke, Radiation Effects ***53*** *(1980) 219.*



ΔH_A Xe:

- *ΔH_A=6.0 eV UO_{2-x}.*
- *ΔH_A=3.9 eV UO_2.*
- *ΔH_A=1.7 eV UO_{2+x}.*

ΔH_A U:

- *ΔH_A=7.8 eV UO_{2-x}.*
- *ΔH_A=5.6 eV UO_2.*
- *ΔH_A=2.6 eV UO_{2+x}.*

Easier to form U vacancy for x>0 and x=0 than for x<0.

- *Effective activation energies determined decades ago, but mechanistic aspects not understood.*
- *Not of academic interest, but required for formulating accurate and predictive meso-scale diffusion models that account for irradiation.*

$$D = D_0 \exp\left(-\frac{\Delta H_A}{k_B T}\right)$$

First Principles Methodology for Xe Diffusion

- Simulations performed using DFT methodology including Hubbard U corrections for strong correlations and addressing issues regarding meta-stable electronic solutions that exist for this methodology.
- Calculation of migration barriers include effects of thermal expansion.
- The detailed charge compensation mechanism for intrinsic defects in $UO_{2\pm x}$ are included via so-called charged supercell calculations + appropriate corrections.
- All relevant defect cluster configurations were investigated for Xe, oxygen vacancies, uranium vacancies and combinations thereof.
- Good agreement with existing experimental validation data is only achieved when all of these steps are followed.
- Re-interpretation of experimental data based on diffusion mechanisms predicted from theory allows for improved estimates of elementary defect parameters.

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Comparison of First Principles Results to Experimental Values

	Calc.	Exp. [1]	Fitted
E_F	3.44	3.0-4.0	3.26
E_S	5.70	6-7	5.26
$E_B(Xe_{UO2})$	2.90	--	3.03
$E_B(Xe_{UO})$	1.60	--	1.87
$E_B(Xe_U)$	1.22	--	0.81
$E_M(V_U)$	3.77	2.4*	--
$E_M(V_{UO2})$	3.94	--	--
$E_M(V_{U2})$	2.18	--	--
$E_M(V_{U2O})$	2.67	--	--

	Calc.	Exp [1]
$E_a^U(UO_{2-x})$	8.15	7.8
$E_a^U(UO_2)$	6.03	5.6
$E_a^U(UO_{2+x})$	2.58	2.6
$E_a^{Xe}(UO_{2-x})$	6.57	6.0
$E_a^{Xe}(UO_2)$	4.42	3.9
$E_a^U(UO_{2+x})$	1.36	1.7

[3] Hj. Matzke, in Diffusion Processes in Nuclear Materials, ed. R. P. Agarwala, North-Holland, Amsterdam, 1992.

eeds

** Incorrect assignment.*

Bulk Diffusion Summary

Manuscript describing comprehensive bulk diffusion study available in Annual Report:

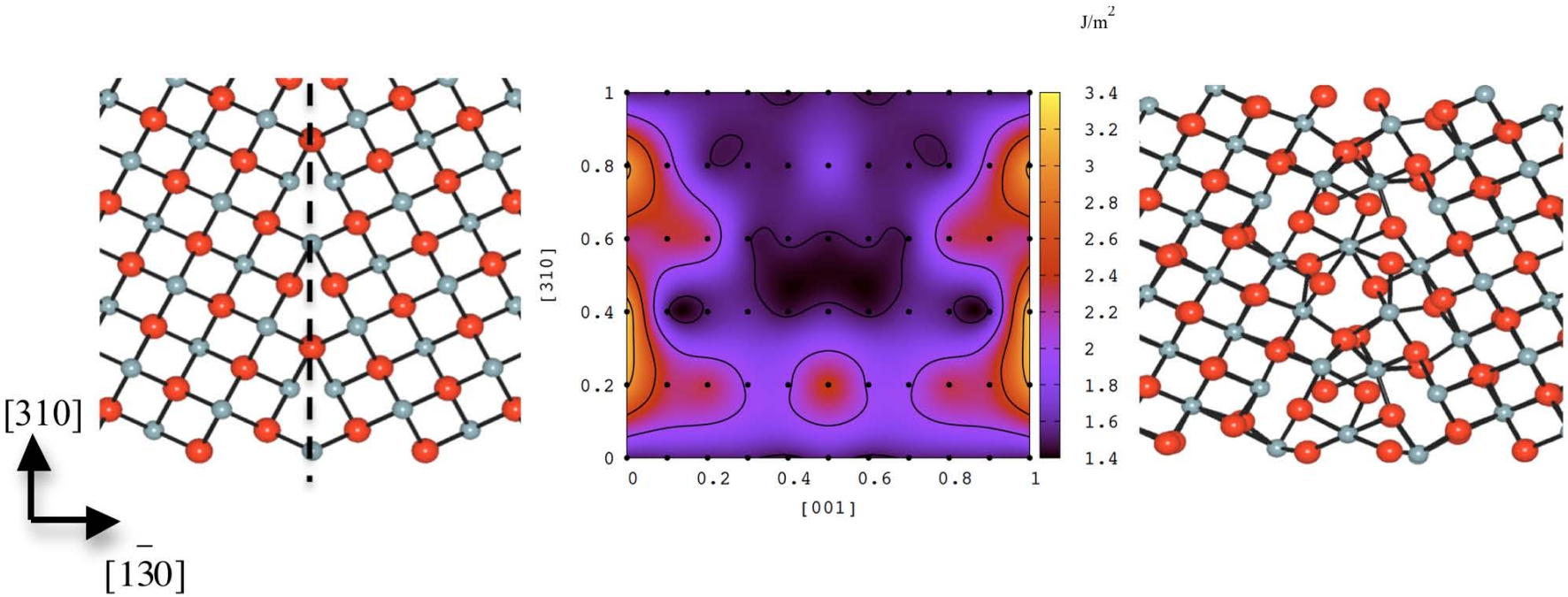
"Xe and U transport in $UO_{2\pm x}$: Density functional theory calculations," D.A. Andersson, B.P. Uberuaga, P.V. Nerikar, C. Unal and C.R. Stanek.

Will be submitted for publication after input from Hj. Matzke (ITU).

With improved understanding of bulk diffusion, now able to move on to consider microstructure.

Atomistic Simulation of UO_2 Grain Boundaries: *Lattice Statics and MD*

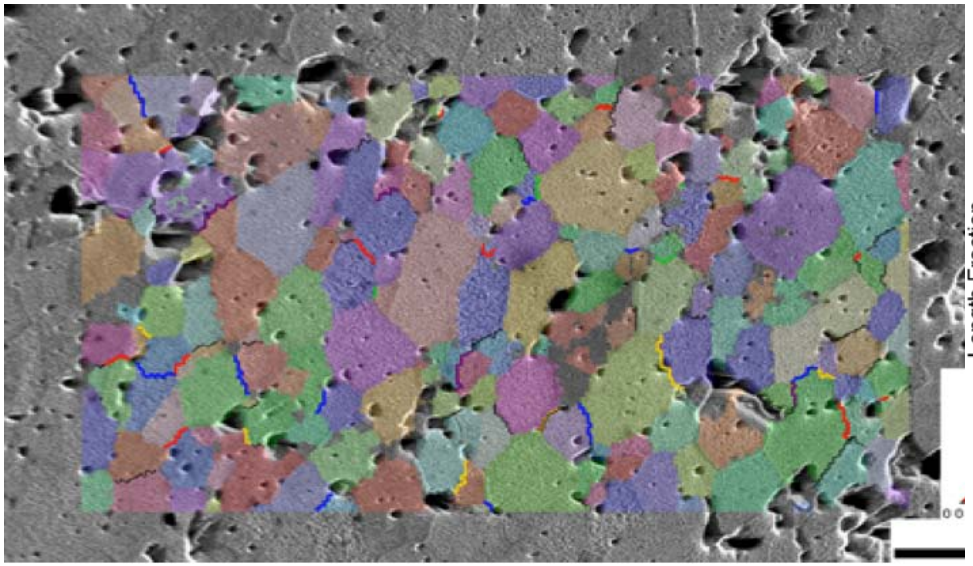
Lattice statics used to determine atomic scale structure of UO_2 grain boundaries

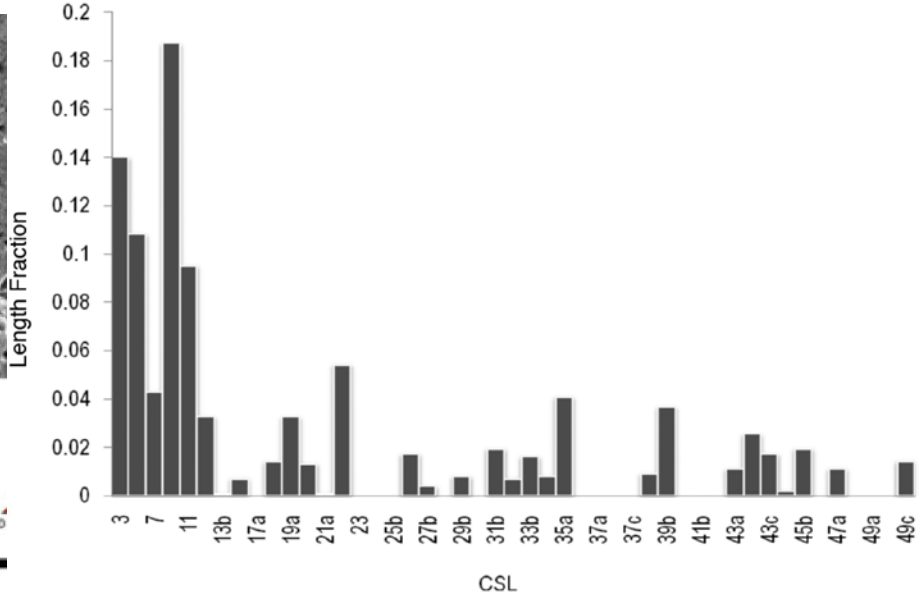


P.V. Nerikar, K. Rudman, T. G. Desai, D. Byler, C. Unal, K. J. McClellan, S. R. Phillpot, S. B. Sinnott, P. Peralta, B. P. Uberuaga, and C. R. Stanek, "Grain Boundaries in UO_2: Scanning Electron Microscopy Experiments and Atomistic Simulations," accepted in *J. Amer. Ceram. Soc.* (2010).

Microstructural Characterization of ATR Fuel Pellets (LANL + ASU)

Complementary characterization experiments on FCRD pellets focus atomistics





P.V. Nerikar, K. Rudman, T. G. Desai, D. Byler, C. Unal, K. J. McClellan, S. R. Phillpot, S. B. Sinnott, P. Peralta, B. P. Uberuaga, and C. R. Stanek, "Grain Boundaries in UO_2: Scanning Electron Microscopy Experiments and Atomistic Simulations," accepted in *J. Amer. Ceram. Soc.*

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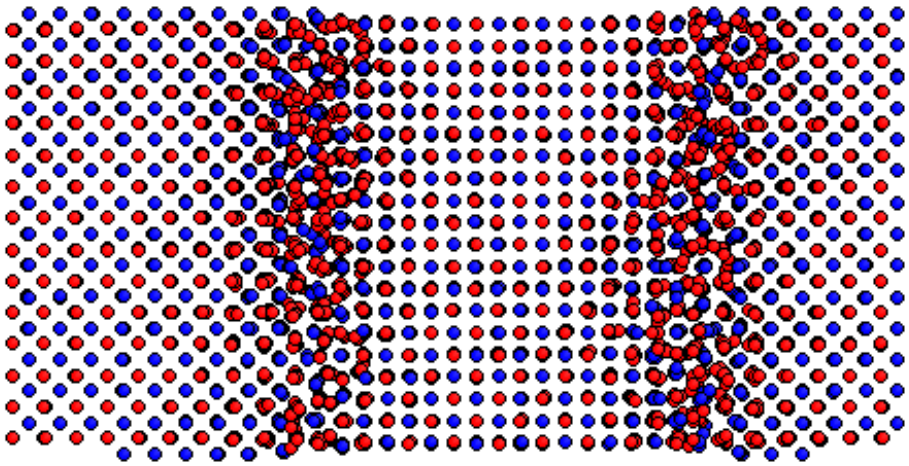
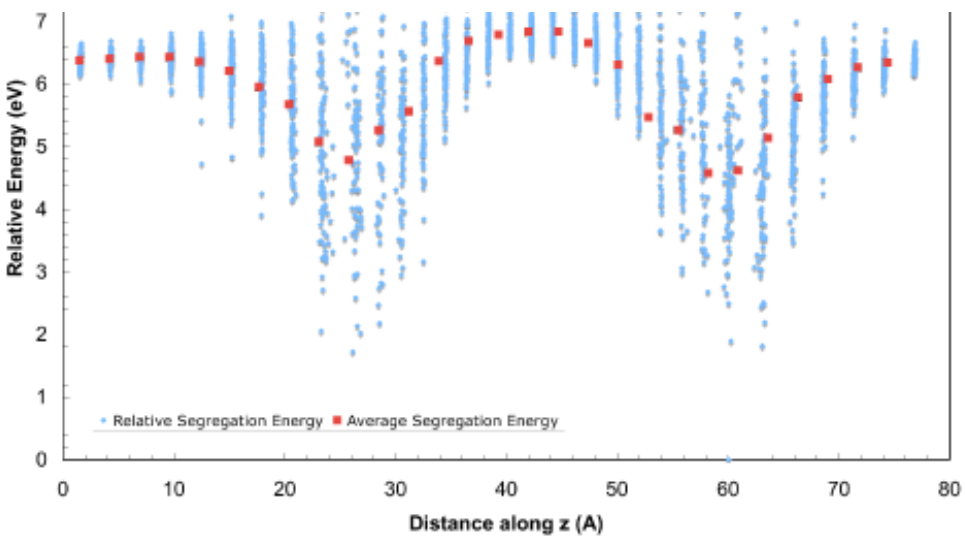
Xe Segregation to Grain Boundaries:

0-D Defect Interaction with 2-D





Modern simulation capability allows for consideration of **relevant** microstructural features – *e.g.* grain boundaries.

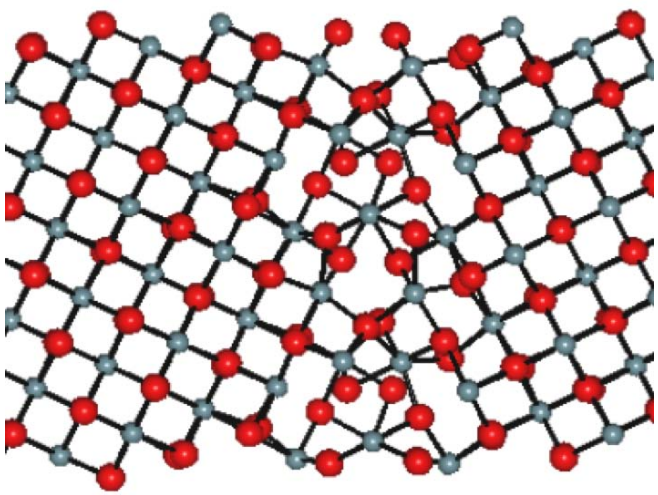
Recent results demonstrate that the atomistic structure of grain boundaries impacts fission gas segregation.

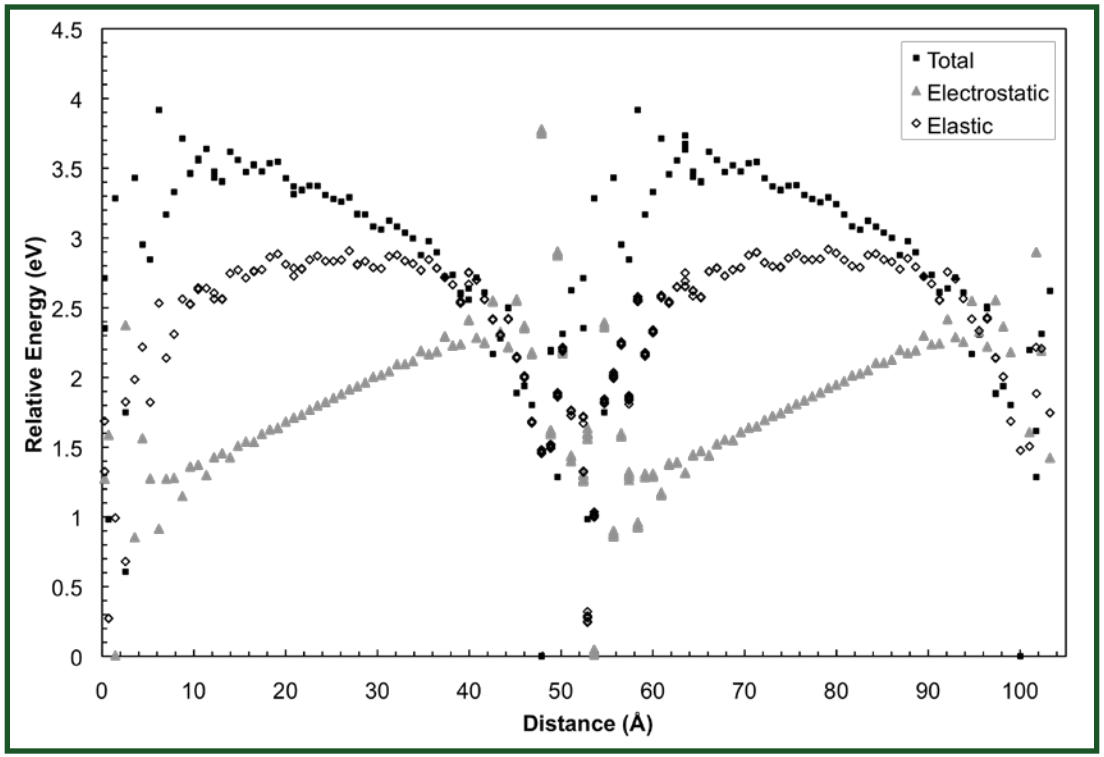
Results at left are for an amorphous boundary – also results for Σ3, Σ5 tilt and Σ5 twist.

"Xenon Segregation to Dislocations and Grain Boundaries," P.V. Nerikar, D. Parftt, D.A. Andersson, S.B. Sinnott, R.W. Grimes, B.P. Uberuaga and C.R. Stanek, submitted to *J. Nucl. Mater.*

Xe Segregation to Grain Boundaries:
Importance of Boundary Structure

For example, the relaxed structure of Σ5 tilt boundary leads to electrostatic effects that extend much further in to the bulk than other boundary types.





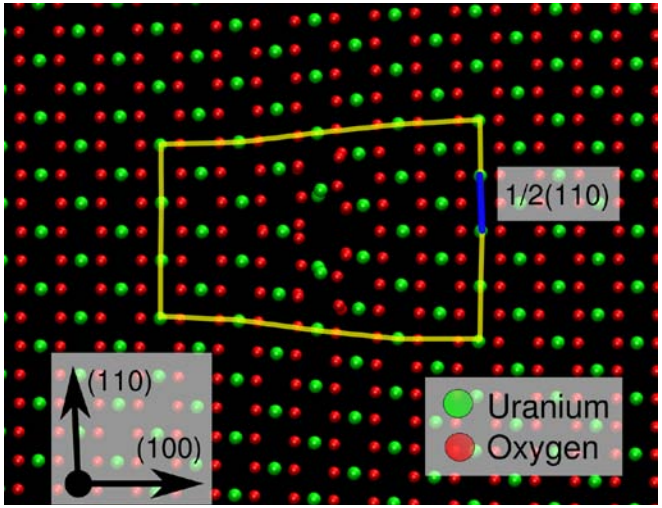
P. Nerikar, C. R. Stanek, S. R. Phillpot, S. B. Sinnott, and B. P. Uberuaga, "Intrinsic electrostatic effects in nanostructured ceramics," *Phys. Rev. B* **81** (2010) 064111.

Example of interaction with BES

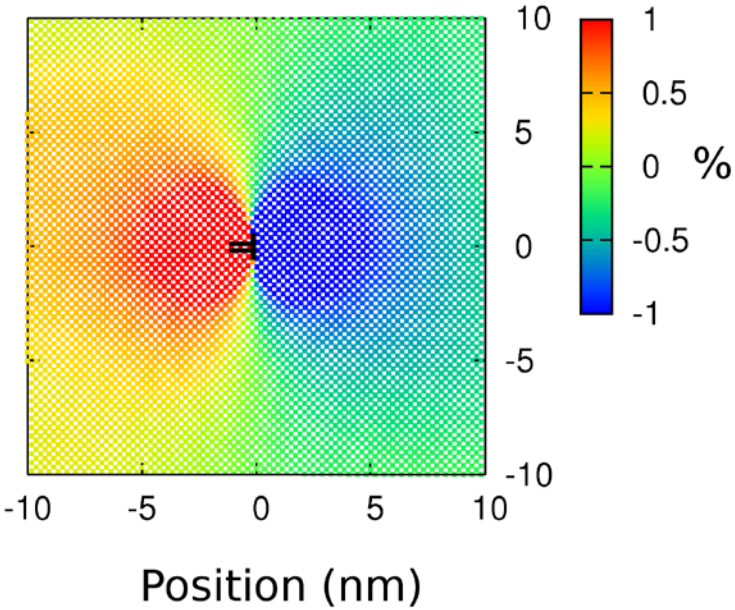
Xe Segregation to Dislocations (Imperial College):

0-D Defect Interaction with 1-D

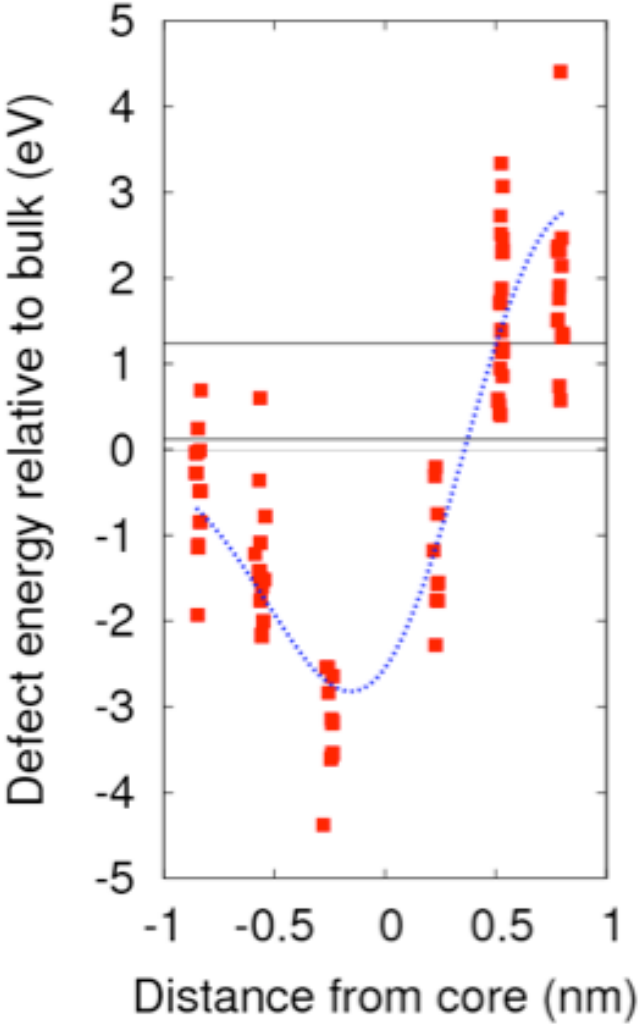
MD simulations of dislocation structure



Corresponding strain field (potentially important for mesoscale simulations)



Segregation of Xe near dislocation



Implementation of Atomistics to Improve Meso- and Engineering Scale

We have accumulated atomistic results for:

* bulk diffusion of Xe in UO_2

* Xe segregation to grain boundaries

* Xe segregation to dislocations

These results can be used to develop physics-based meso- and engineering-scale models

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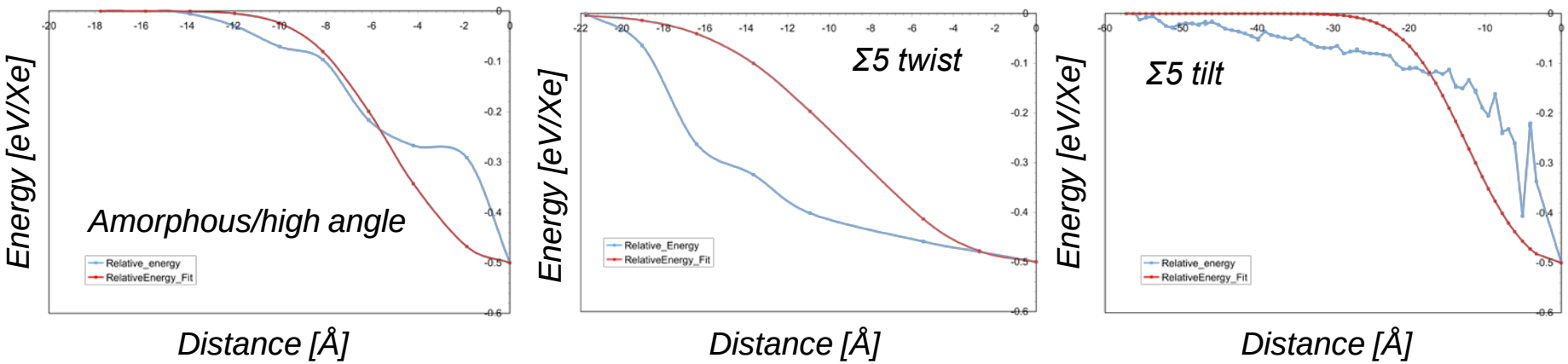
"Coarse Graining" of Segregation Data

Normalized Xe segregation energies from pair potentials (Buckingham + Morse) by Nerikar et al., separate analyses of elastic and electrostatic contributions underway.



$$f(r) = 1\Big/\left(1+\exp\left(-(r-r_0)^2/k^2\right)\right)-1$$

$$E_m(r) = 2C_1 f(r)$$

$$E_m^{gb}(x,r) = xE_m(r)$$

GB type	k (nm)	C_1 (eV)
∑5 Tilt	1.225	4.09
∑5 Twist	0.922	0.97
Amorphous	0.469	6.42

- *"Simplistic" approach designed to capture sink strengths and interaction range.*

Atomistically Informed Mesoscale

Thermodynamics:

$$G_m = y_{Xe}\,{}^oG_{Xe} + y_U\,{}^oG_U + y_{Va}\,{}^oG_{Va} + RT\left(y_{Xe}\ln\left(y_{Xe}\right) + y_U\ln\left(y_U\right) + y_{Va}\ln\left(y_{Va}\right)\right) +$$

$$+E^{excess} + \sum_i 2y_{Xe}\left(C_i - g_i\left(y_{Xe}\right)\right)\sum_j f_{ij}\left(r_{ij}\right)$$

Kinetics:

$$M_{XeVa}y_{Va} = \frac{D_0}{k_BT}\exp\left(-\frac{\Delta Q}{k_BT}\right) \qquad \Delta Q = \Delta Q_0 - \sum_i\sum_j q_i f_{ij}\left(r_{ij}\right) \qquad \Delta Q_0 = E_a^{Xe} = E_{VU}^F - E_B + E_m^{VU,C}\left(T\right)$$

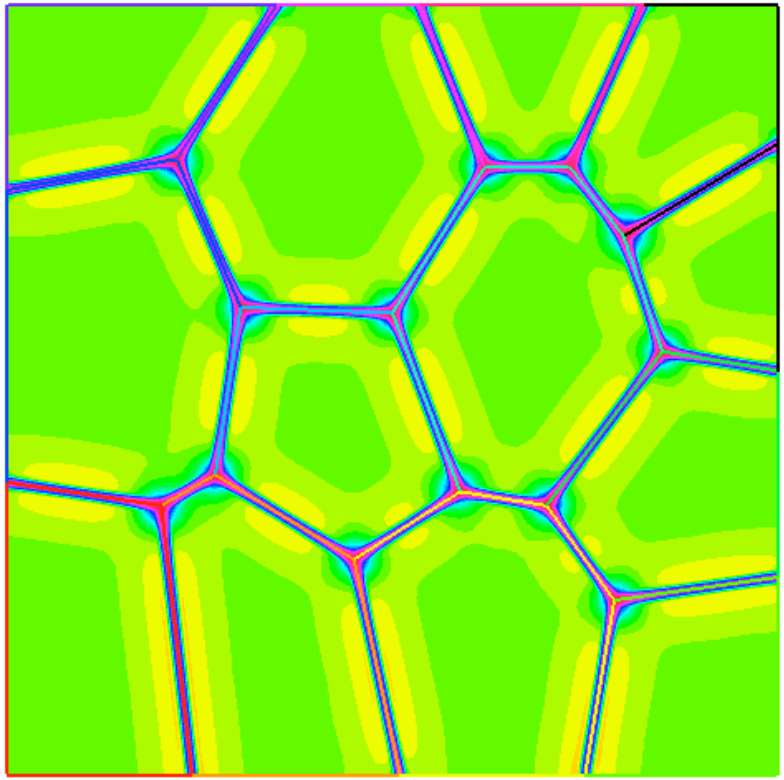
Thermodynamics + kinetics = Transport equations (μ_{Va}=0)

$$\frac{1}{V_m}\frac{\partial y_{Xe}}{\partial t} = \nabla\cdot\left(\frac{D_0}{V_m}\exp\left(-\frac{\Delta Q}{k_BT}\right)\nabla y_{Xe}\right) +$$

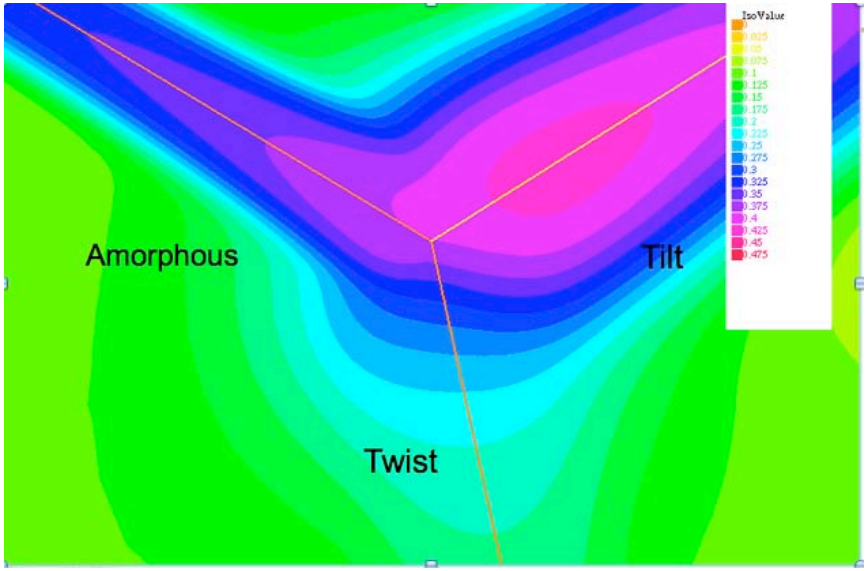
$$+\nabla\cdot\left(\frac{1}{k_BT}\frac{D_0}{V_m}y_{Xe}\exp\left(-\frac{\Delta Q}{k_BT}\right)\nabla\left(\sum_i 2\left(C_i - g_i\left(y_{Xe}\right)\right)\sum_j f_{ij}\left(r_{ij}\right) + \sum_i 2y_{Xe}\left(-\frac{\partial g_i\left(y_{Xe}\right)}{\partial y_{Xe}}\right)\sum_j f_{ij}\left(r_{ij}\right)\right)\right) +$$

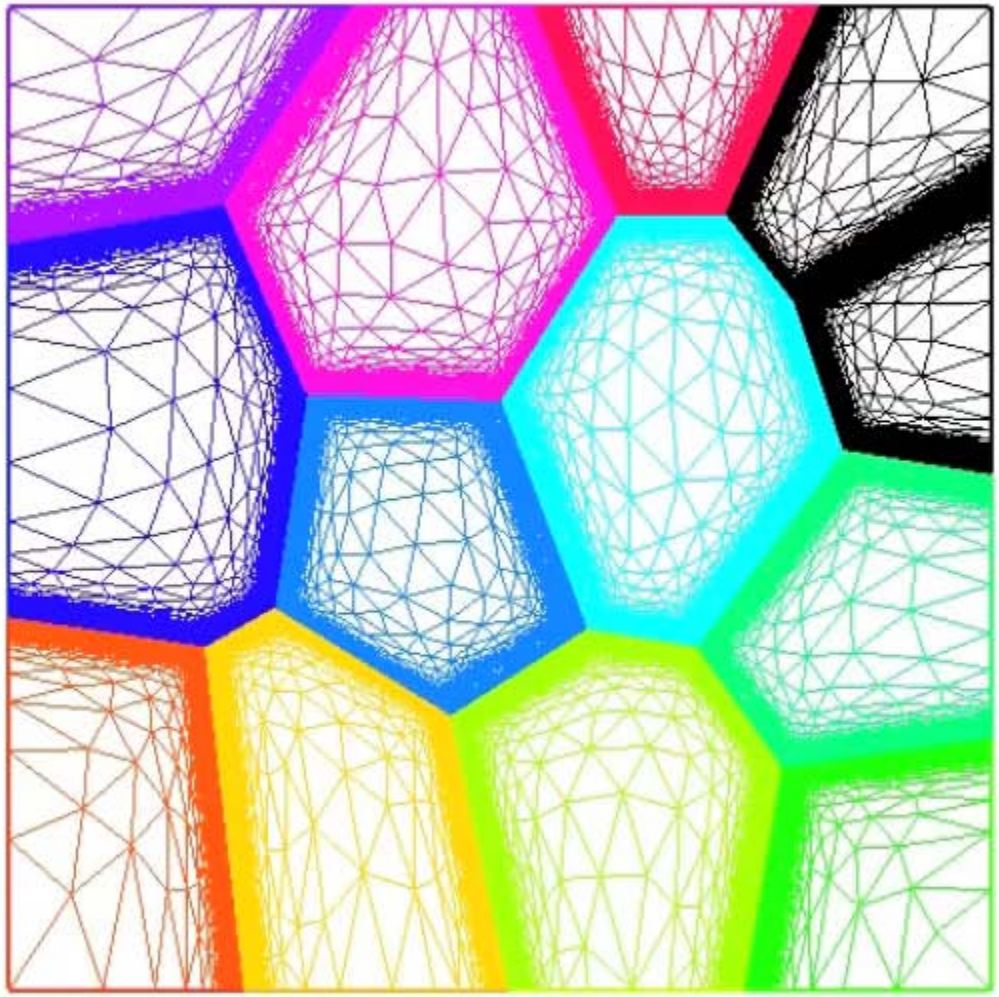
$$+\eta\left(t\right)$$

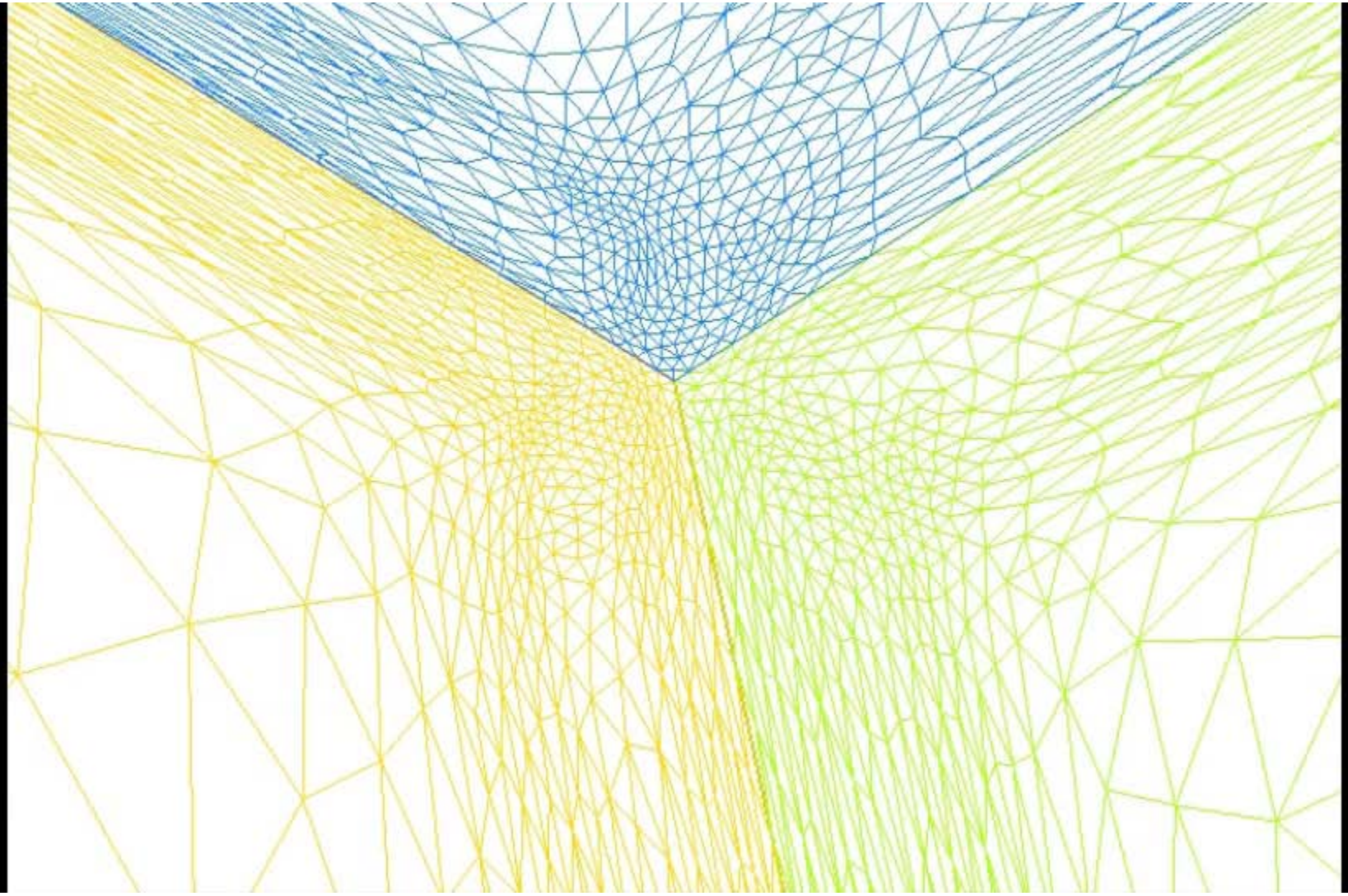
Implication of Atomistics for Mesoscale Simulations



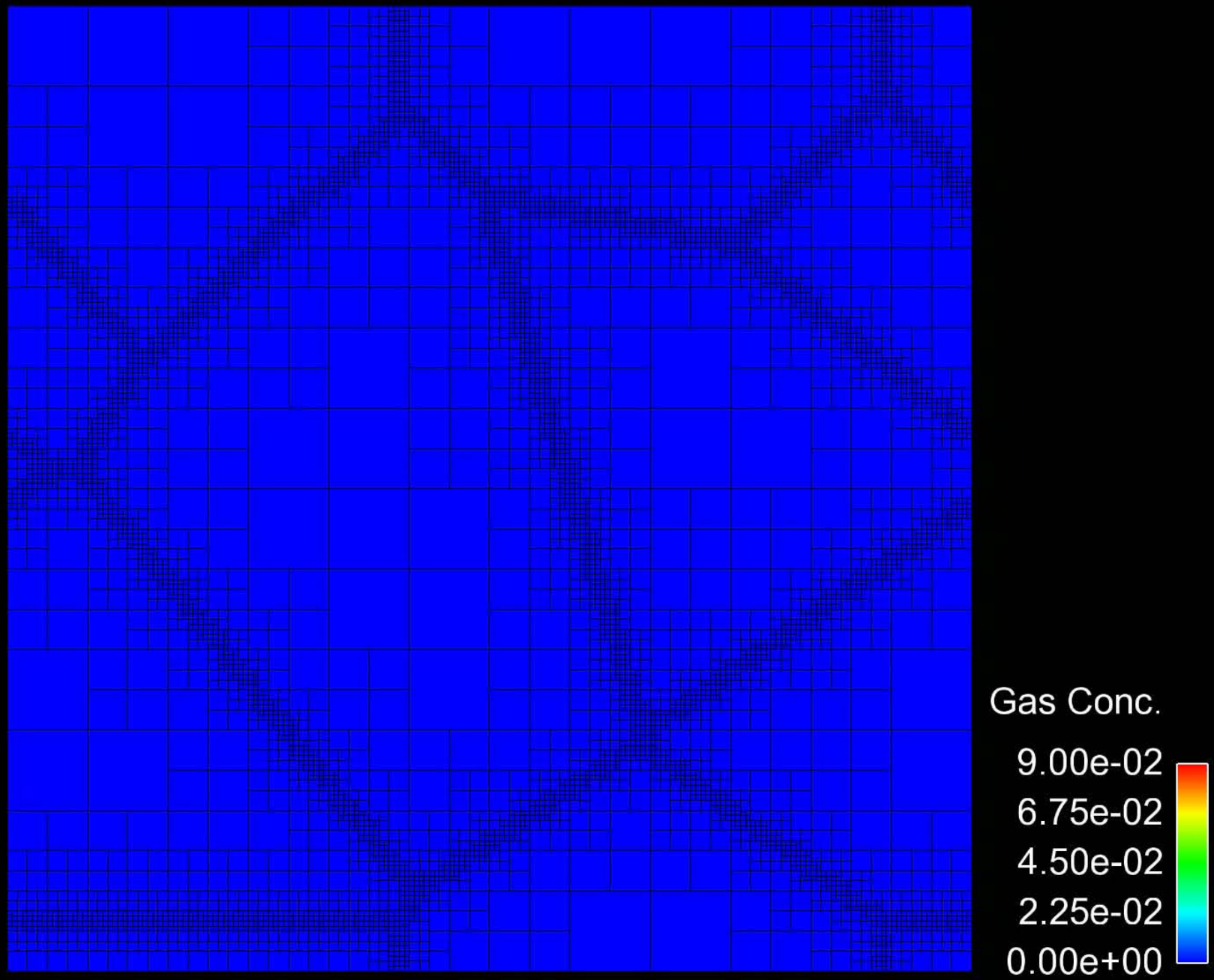
- *The larger interaction range of Σ5 tilt boundaries is clearly visible.*
- *Also the difference in Xe concentration at different boundaries is evident.*
- *May induce preferential gas bubble nucleation.*







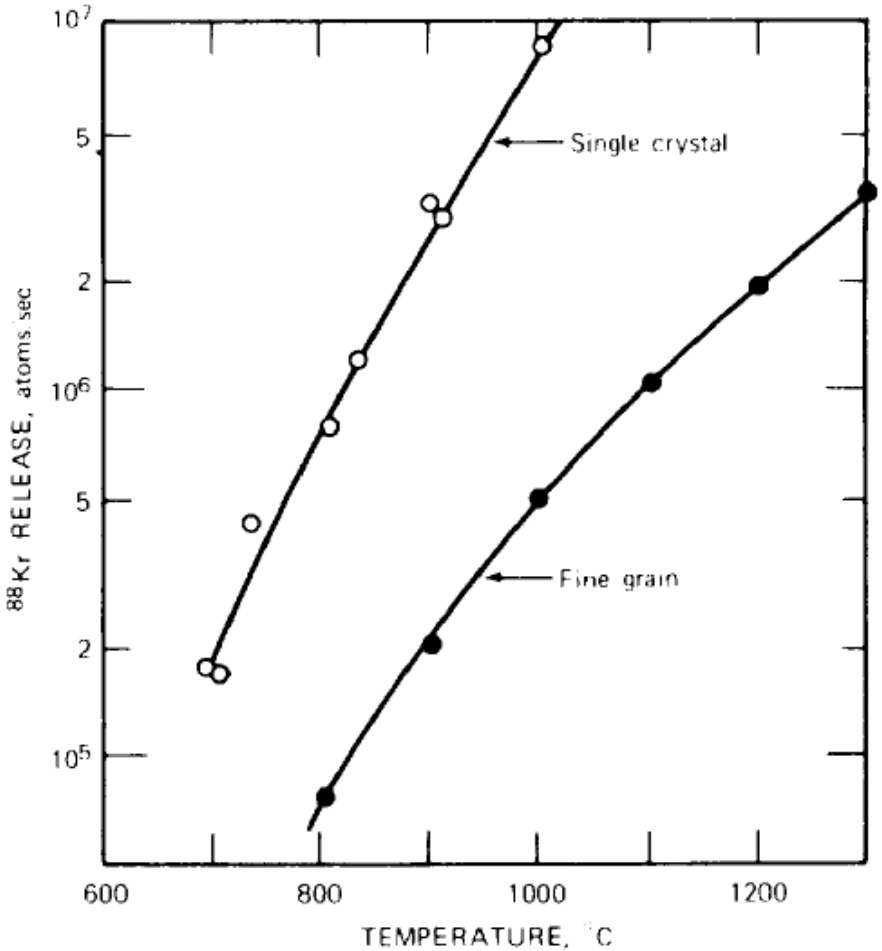
Gas Segregation with Grain Boundary Migration



Idaho National Laboratory

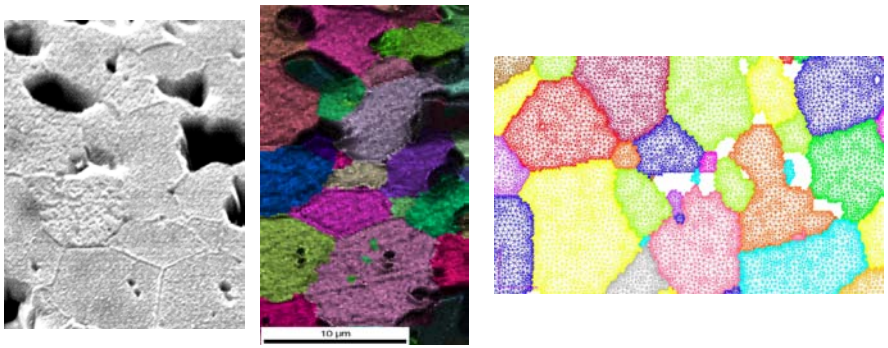
Link to Experiment:
Two Flavors of "Separate Effect Test"

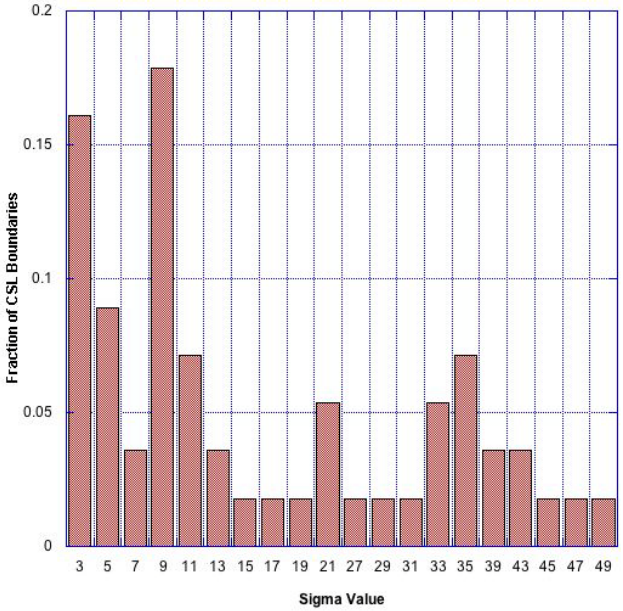
Validation: Kr release w.r.t. microstructure



R.M. Carroll and O. Sisman, Nucl. Appl. ***2*** *(1966) 142.*

Guidance/understanding: Microstructural characterization



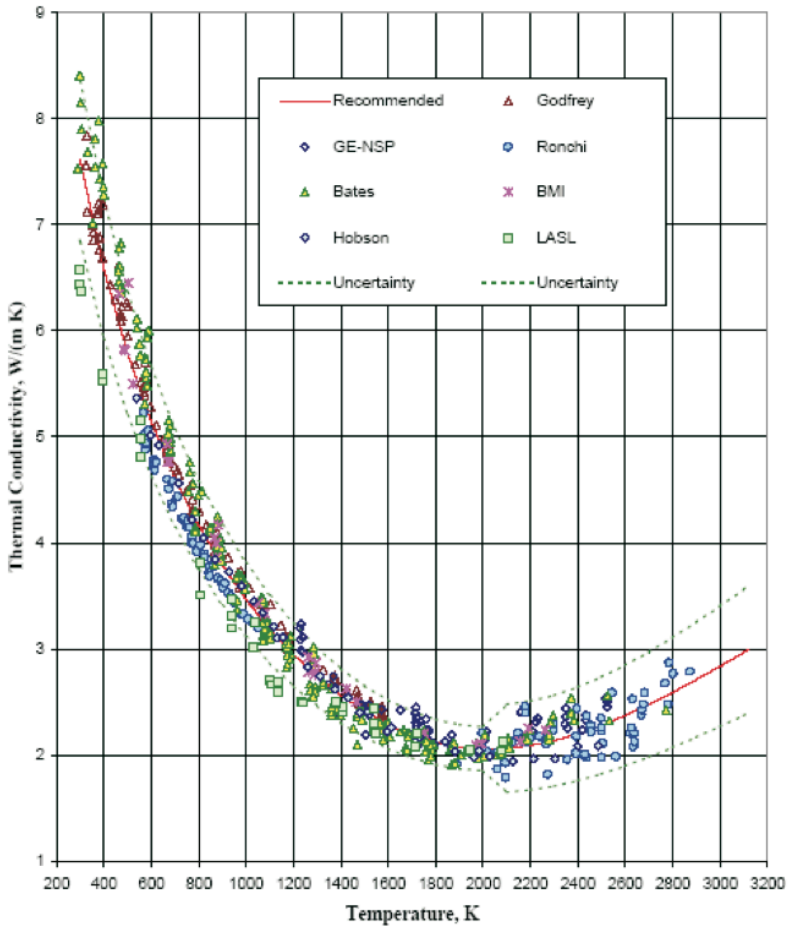


Thermal Conductivity

- **Shifting gears from fission gas release to thermal conductivity.**
- **Similar approach, different material property.**

A Pragmatic Approach to Thermal Conductivity of UO_2

*[P.G. Lucuta et al., J. Nucl. Mat. **232** (1996) 166]*



$$k = k_0\, \kappa_1(\beta)\, \kappa_2(p)\, \kappa_3(x)\, \kappa_4(\tau)$$

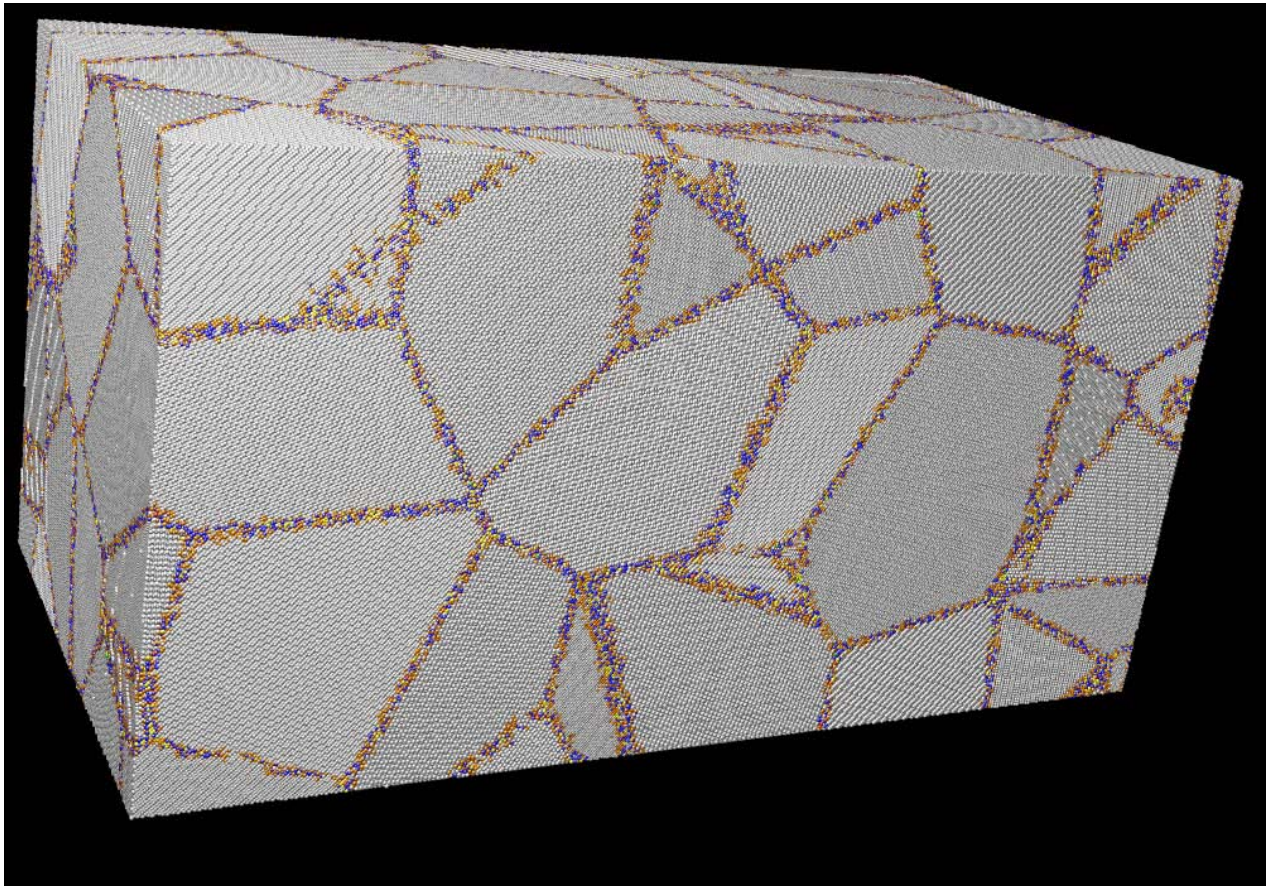
where:

- *k_0 is the unirradiated thermal conductivity*
- *$\kappa_1(\beta)$ is the burnup (fission product) factor*
- *$\kappa_2(p)$ is the porosity/bubbles contribution*
- *$\kappa_3(x)$ accounts for the O/M composition*
- *$\kappa_4(\tau)$ refers to radiation damage from neutrons, α-decay and fission*

Atomistic Simulation of Thermal Conductivity

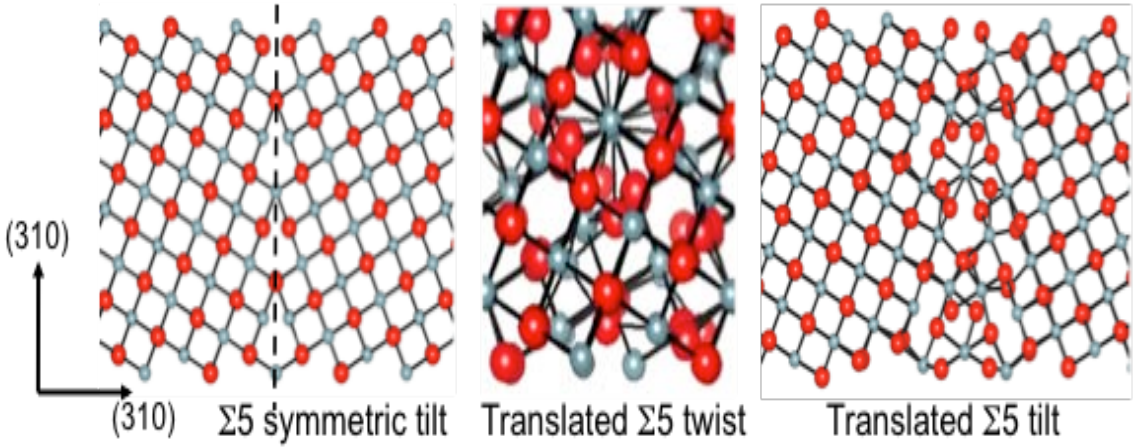
Inspired by large ASC of shock, implemented long range electrostatic forces in SPaSM MD code.

Allows for large atomistic simulations of thermal conductivity on HPC systems.



Dependence of Grain Boundary Structure on Kapitza Resistance

Preliminary results of the role of boundary on thermal conductivity



Boundary type	Grain size (nm)	K (W/mK)	Kapitza resistance (m^2K/W)	Kapitza length (nm)
Σ5 (310) symmetric tilt	21.6	7.62	2.05×10^{-9}	56
Σ5 (310) translated tilt	21.6	14.22	0.73×10^{-9}	20.13
Σ5 36.7° translated twist	20.24	9.38	1.00×10^{-9}	39

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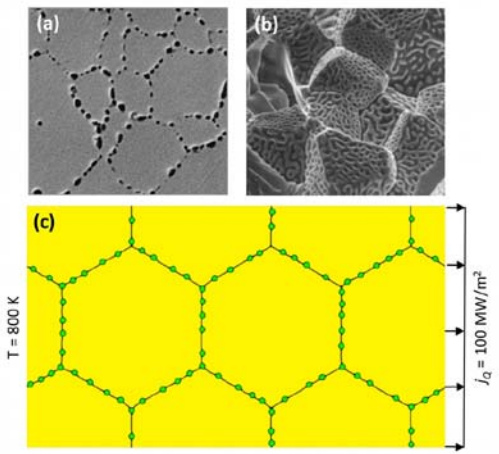
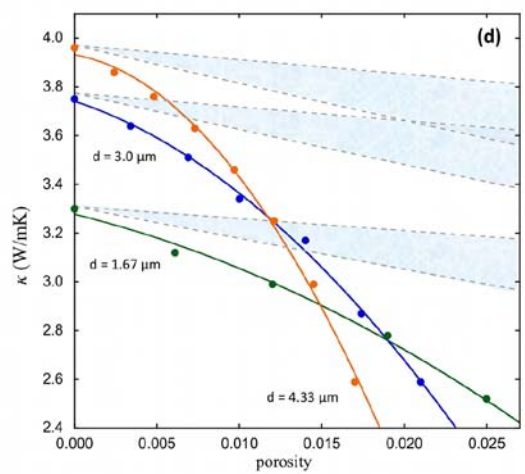
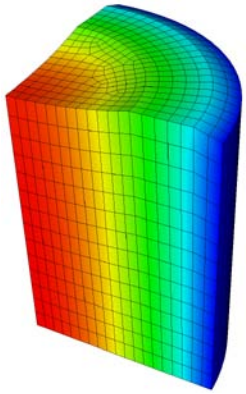
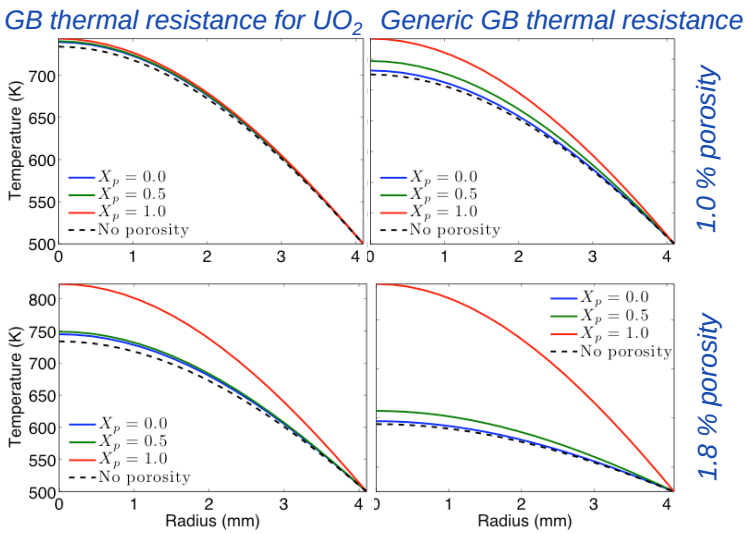
Multiscale Thermal Conductivity Model (from INL)





Mesoscale model of thermal conductivity in UO_2 with intergranular bubbles as a function of grain size d and porosity using the GB thermal resistance from MD





Small length scale information can have a significant impact on macroscale fuel performance

Radial temperature profiles in a UO_2 fuel pellet, where the fraction of intergranular bubbles X_p is varied from 0 to 1

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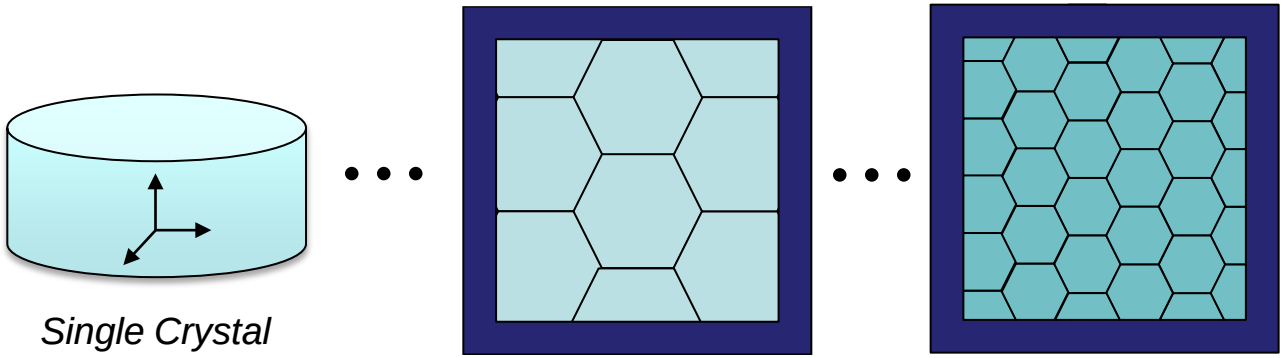
Thermal Transport: Linking Modeling and Experiment

The thermal conductivity of ceramic fuels represents one of the most critical yet only moderately understood properties impacting both current and future reactor operation and design

$\Lambda=(\alpha)(C_p)(\rho)$ *Thermal Conductivity = (Thermal diffusivity) x (Specific Heat) x (Density)*

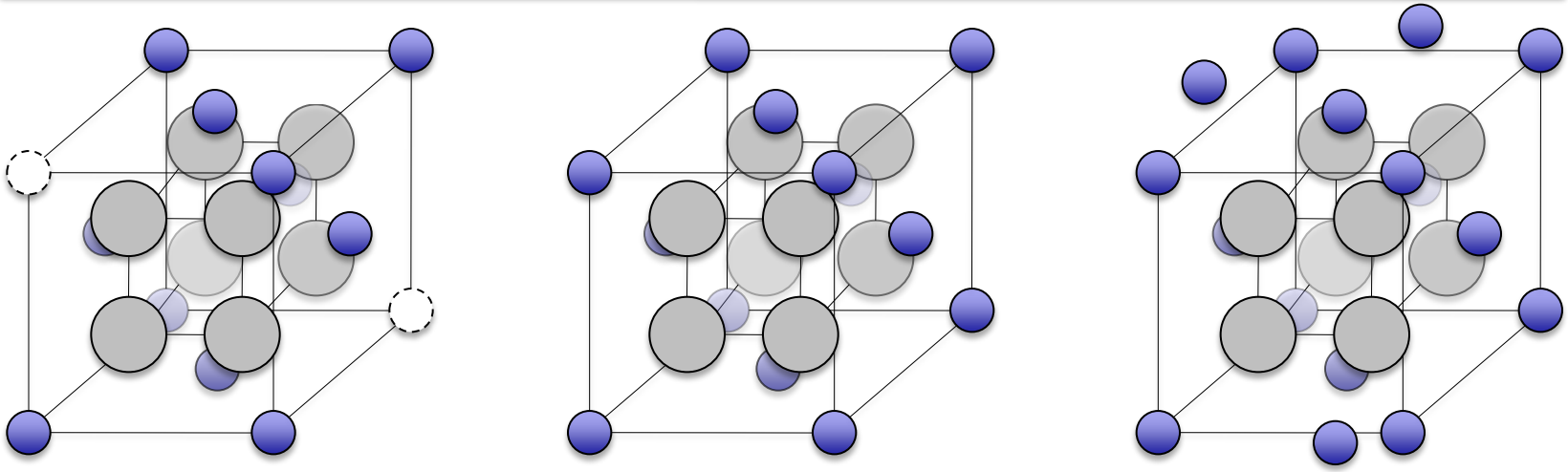
A. Study of thermal diffusivity as a function of basic microstructure (grain size) in UO_2



Beginning with single crystal urania (O/M driven to 2.00), the thermal diffusivity will be measured as a function of grain size (~100 µm - ~100 nm) from -150°C (LN) to 2400°C under vacuum

Thermal Transport: Linking Modeling and Experiment

B. Study of thermal diffusivity as a function of O/M (hypo/hyper stoichiometry) in $UO_{2\pm X}$



UO_{2-X} *UO_2* *UO_{2+X}*

Through dynamic Ar/Ar-H/H_2O atmosphere controls, P_{O2} can be dictated and maintained constant (thus driving O/M) throughout an entire temperature range for diffusivity / dilatometry measurement

Experiment: $\Lambda = f$ (O/M, Temp)

DFT defect structure

→

Theory-based models linking phonon scattering to oxygen defect structures

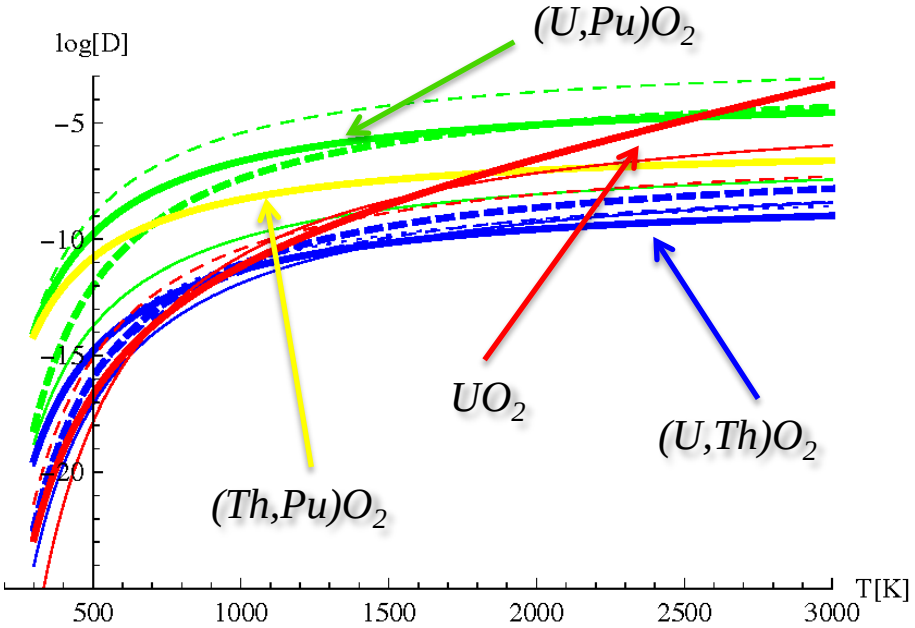
Summary – Future Work

Atomistic simulation results shown for mass and thermal transport in UO_2.

For both mass and thermal transport, initial upscaling steps have been taken.

In both cases, link to experiment has either been made or path forward is defined.

Not done yet- additional detail and fidelity required of the atomistics.

Upscaling has only just begun.

Oxygen diffusion is yet another example of where not all fluorites are the same.