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Atomistic Fuels Modeling

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01/25/2017

Advanced Reactor Modeling and Simulation Workshop #2

This work was funded by the NEAMS program.

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Gap analysis

- **What M&S Tools are needed?**
  - "Atomistic modeling tools for fuel and materials" (for reactor design and safety analysis).
    - Yesterday: Specific question about the diffusion of fission products.
  - Fuel performance analysis code covering the full fuel life cycle and under accident scenarios.
    - Atomistic support for developing materials models.
- **Examples from LWR fuel**
  - UO_2 (main focus) and U_3Si_2 (recent accident tolerant fuel concept).
  - Although not the focus of this talk, Zr cladding (CASL) and FeCrAl (accident tolerant fuel concept).
- **The approach taken for the LWR fuels can be extended to other fuel and reactor systems.**
  - Example: Extending the approach originally developed for UO_2 + Zr cladding to U_3Si_2 + FeCrAl (ATF HIP).
  - Fuels: TRISO, metal, UN, UC, etc.,
  - Cladding: Zr+coatings, SiC, etc.

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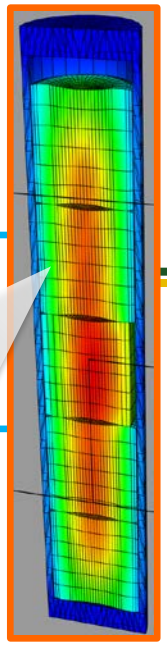
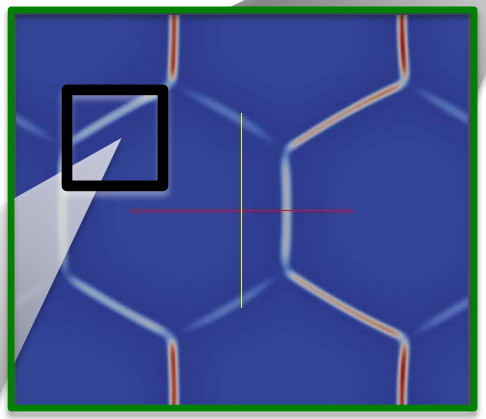
Role of atomistics in multiscale simulations

Atomistic simulations to inform meso-scale simulations of microstructure and property evolution in irradiated nuclear fuels. Enables mechanistic materials models in BISON fuel performance simulations.

Hierarchical multi-scale approach

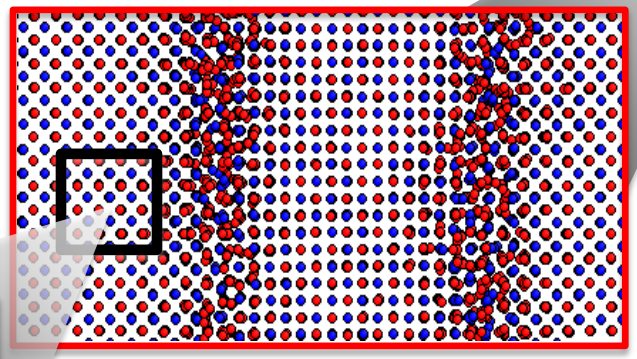
Validation is an integral part at each length scale.





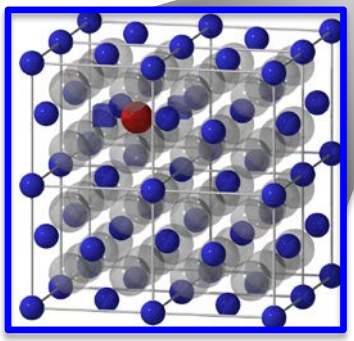
BISON fuel performance simulations (FEM)

MARMOT material model development based on state variables (phase field)



Microstructure evolution and role of microstructure in mass and thermal transport (MD)

Bulk properties and behavior of point defects (DFT)



All codes are available, but the lower length scale work requires experienced/expert users.

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Atomistic simulations methods: Density Functional Theory (DFT)

- **No input from experiments (except for validation), empirical correlations or fitting parameters - predictive power.**
- **Calculate the properties of materials from the laws of quantum mechanics – high accuracy but computationally demanding.**
- **Density functional theory (DFT):**
  - The original many-electron problem is transformed into a set of one-electron problems that can be solved self-consistently.
  - The difficult many-body effects are contained in the so-called exchange correlation energy, which requires special attention for uranium compounds due to the U 5f electrons.
  - Open source or commercial package with lots of features are available, e.g. VASP used in our studies.
- **Studies limited to a few hundred atoms and static calculations or MD simulations with short time scales.**

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Atomistic simulations methods: Empirical potentials

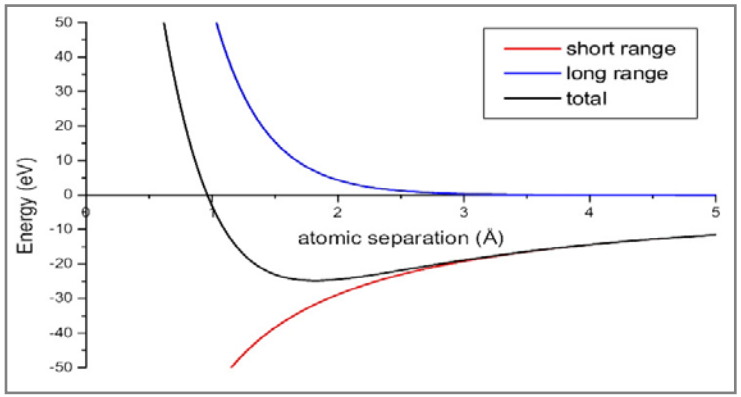
- **Empirical potentials or force-fields describe the interaction between atoms according to parametrized equations.**
- **Fitted to experiments and/or DFT calculations.**
- **High computational efficiency (>100 million atoms and much longer time scales than DFT), but also lower accuracy and strictly not predictive outside the fitting range.**
- **Many MD packages are available, e.g. LAMMPS from SNL.**

For ionic materials (UO_2):

$$\mathrm{E_{lattice}} = \frac{1}{8\pi\epsilon_o}\left(\sum_i \sum_{j\neq i} \frac{q_i q_j}{r_{ij}}\right) + \frac{1}{2}\Phi_{\mathrm{s-r}}$$

Buckingham potential (1938):

$$\Phi_{ij} = Ae^{-\frac{r}{\rho}} - \frac{C}{r^6}$$



Additional terms may be added for improved accuracy. Metals such as U_3Si_2 require a different potential due to the drastic difference in electronic structure and bonding.

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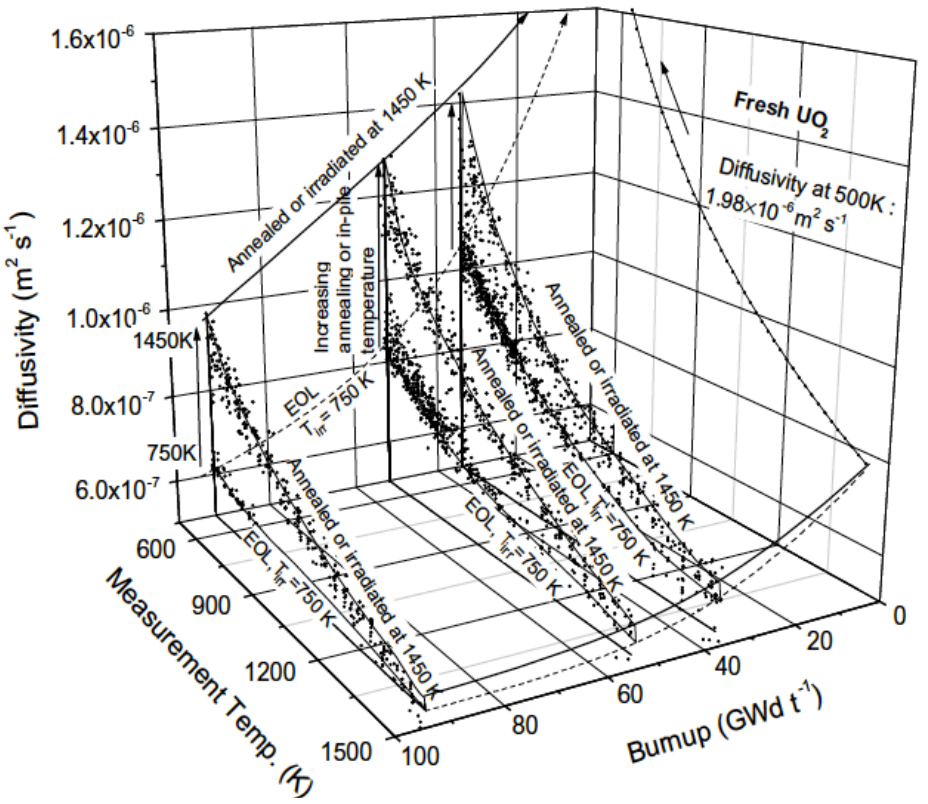
UO_2 thermal conductivity (κ) as function of fuel microstructure

C. Ronchi, *et al*., *J. Nucl. Mater.* **58** (2004) 327.



$$\lambda = [A(T_{irr}, T_{ann}, bu) + B(T_{irr}, T_{ann}, bu)\,T]^{-1}$$

P.G. Lucuta *et al*., *J. Nucl. Mater.* **232** (1996) 166.

$$\kappa = \kappa_0\, \kappa_1(\beta)\, \kappa_2(p)\, \kappa_3(x)\, \kappa_4(\tau)$$

where:

κ_0 is the unirradiated thermal conductivity

$\kappa_1(\beta)$ is the burnup (fission product) factor

$\kappa_2(p)$ is the porosity/bubble contribution

$\kappa_3(x)$ accounts for the O/M composition

$\kappa_4(\tau)$ refers to radiation damage from neutrons, α-decay and fission

Current models highly empirical. Rather attempt to quantitatively catalog contributions from individual defects and upscale using state variables (see Y. Zhang's talk).

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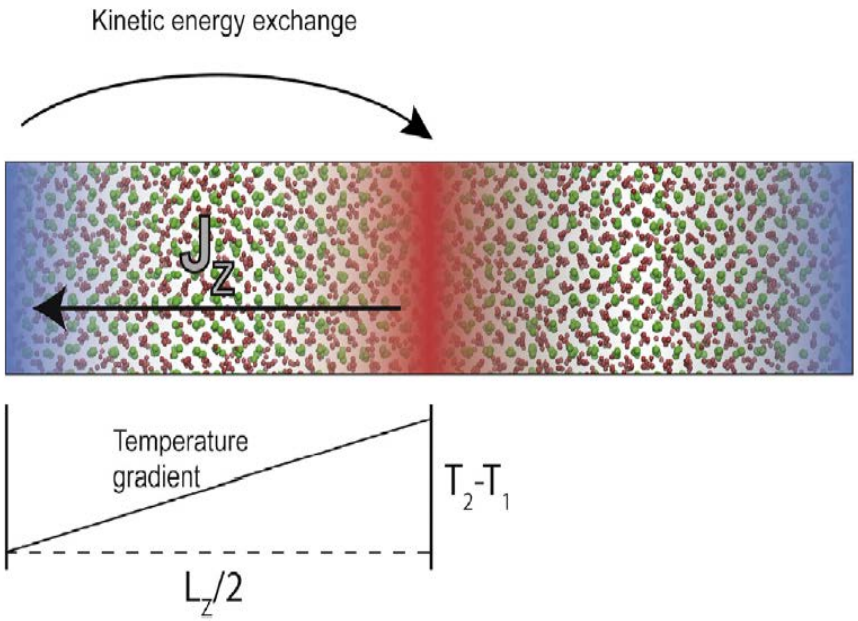
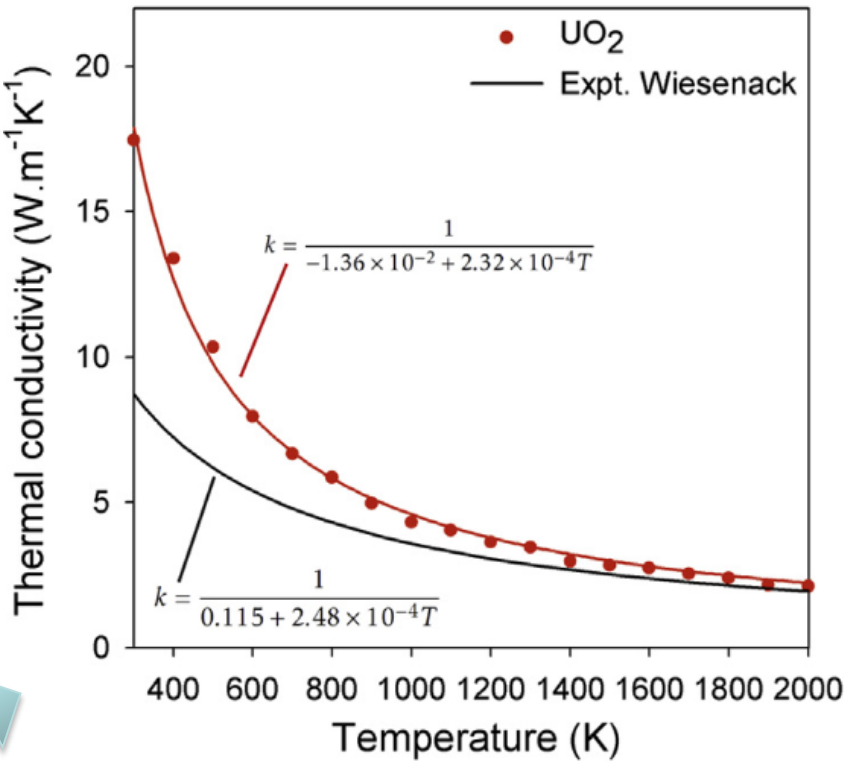
Challenges to accurately predict UO_2 thermal conductivity

Molecular dynamics (MD) to calculate thermal conductivity via direct method.



Values are significantly overestimated



- **Use accurate force description (many-body CRG potential[1]).**
- **Must account for missing physics (phonon-spin scattering[2,3]).**

[1]M.W.D. Cooper *et al. J. Nucl. Mater.* 466 43-50 (2015).
[2]K. Gofryk et al. *Nature Comm.* 5, 4551 (2014).
[3]J. Moore and D. McElroy, J. Am. Ceram. Soc. 54, 40 (1971).

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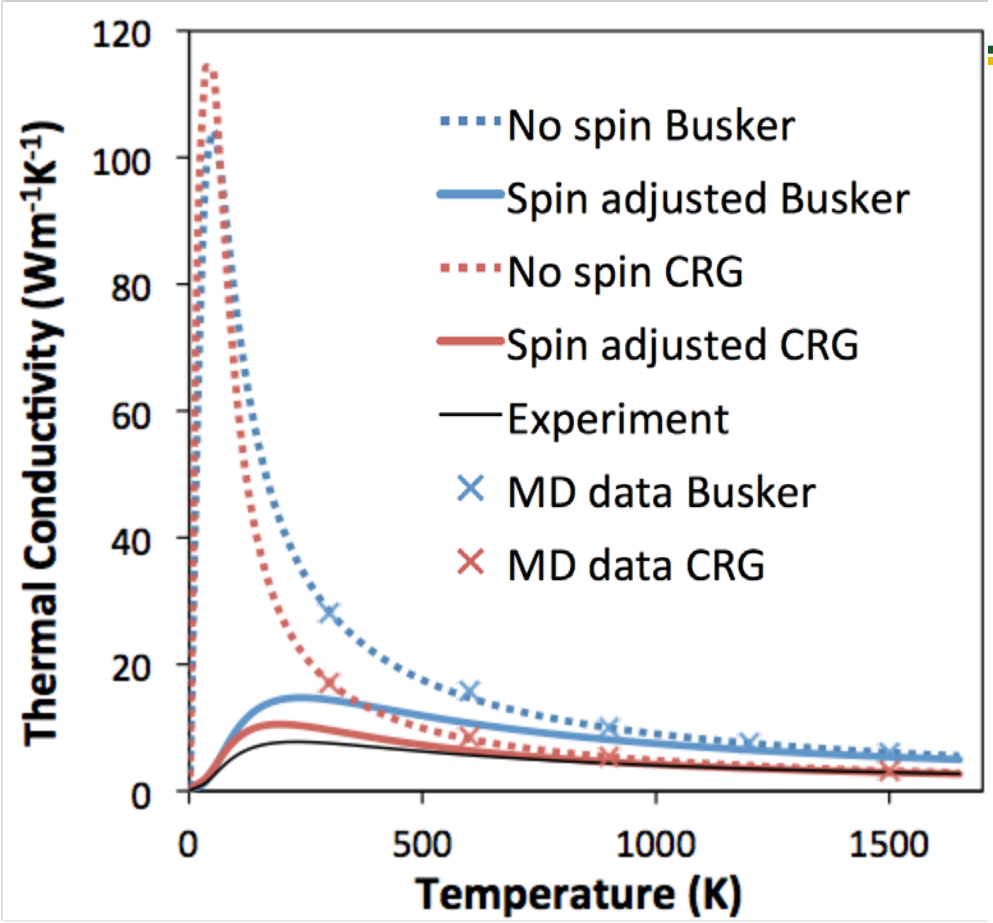
Including spin scattering term for UO_2 thermal conductivity



$$\kappa = \frac{k_B}{2\pi v}\left(\frac{k_B T}{\hbar}\right)\int_0^{\Theta_D/T}\frac{\tau_p x^4 e^x}{(e^x-1)^2}dx$$

$$x = \hbar\omega/k_B T$$

$$\tau_D^{-1} = Dx^4T^4 = D\left(\frac{\hbar\omega}{k_B}\right)^4$$

$$\tau_B^{-1} = B$$

$$\tau_U^{-1} = UT^3x^2e^{-\Theta_D/bT} = UT\left(\frac{\hbar\omega}{k_B}\right)^2 e^{-\Theta_D/bT}$$

$$\tau_S^{-1} = \sum_i \frac{C_i\omega^4}{(\omega^2-\omega_{S,i})}F_i(T)$$

Spin scattering resolves the difference between the CRG empirical potential and experiment.

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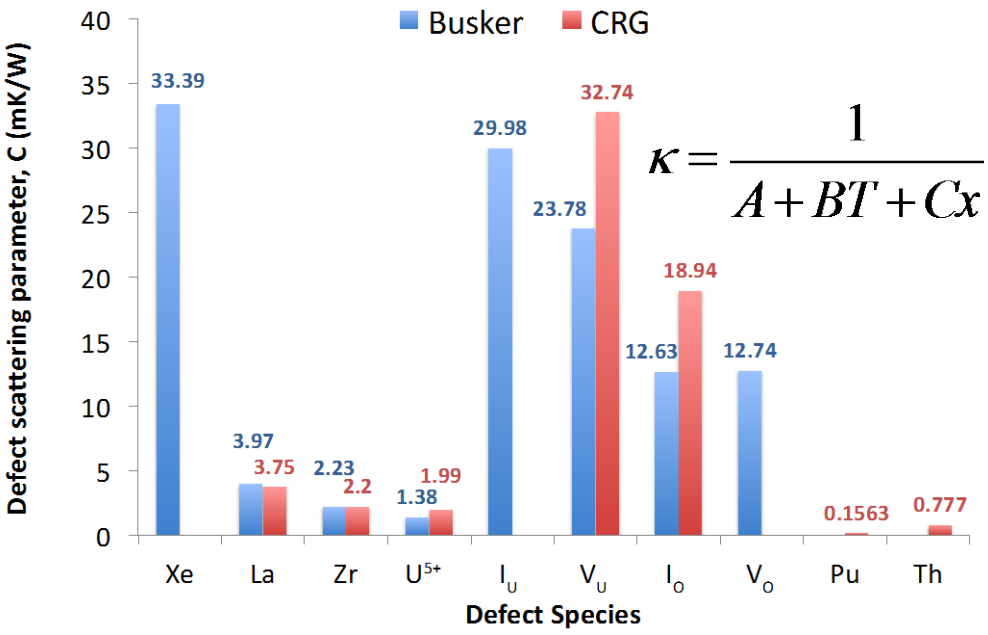
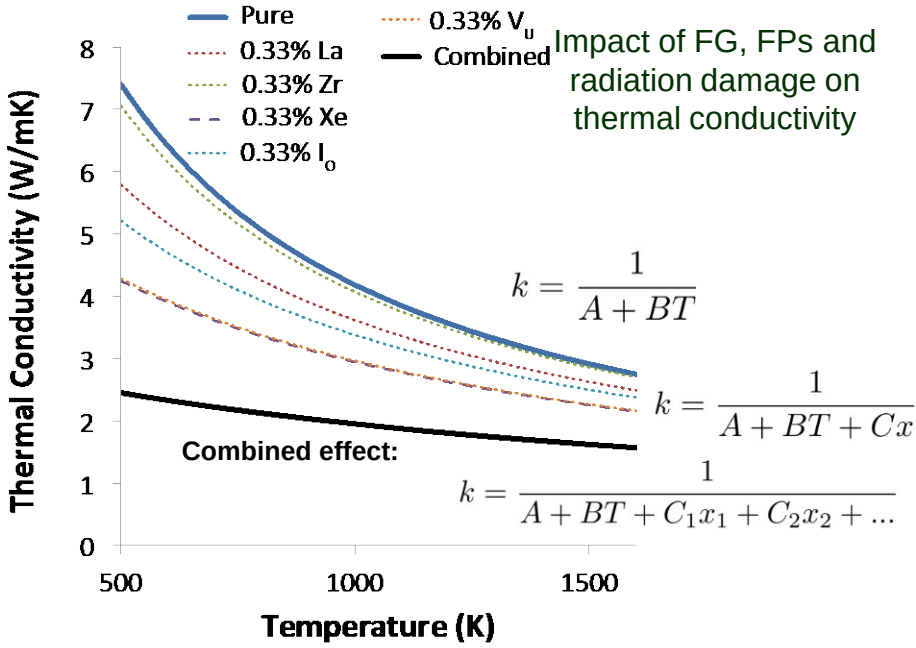
Simplified defect scattering model for BISON

- **Simple analytical expression of defect scattering[1] for application in MARMOT/BISON following M. Tonks et al[2] .**

Defect scattering parameters





Impact of FG, FPs and radiation damage on thermal conductivity

[1]Liu et al., Phys. Rev. Appl. 6, 044015 (2016).

[2]M. Tonks, et al., J. Nucl. Mater. **469**, 89 (2016).

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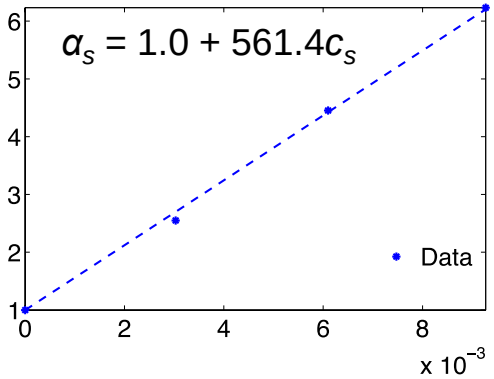
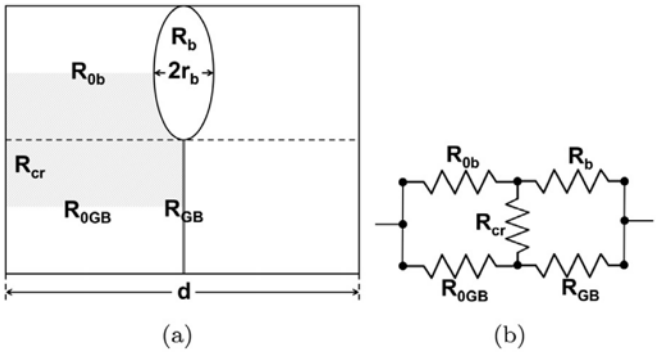
Mechanistic UO_2 thermal conductivity model

From M. Tonks, et al., "Development of a Multiscale Thermal Conductivity Model for Fission Gas in UO_2" *J. Nucl. Mater.* 469 (2016) 89.

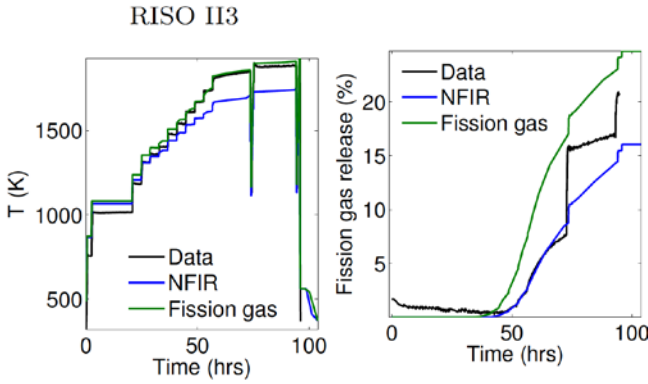
Xe scattering parameter from MD



MARMOT to model the impact of bubbles+grain boundaries



BISON simulation (Xe only)*



- Demonstrated mechanistic thermal conductivity model to treat the impact of Xe as well as microstructure (grain boundaries and bubbles).
- Similar analysis can be performed for other defects and fuels, though metals require a different simulation methodology due the change in transport mechanism (electrons vs. phonons).

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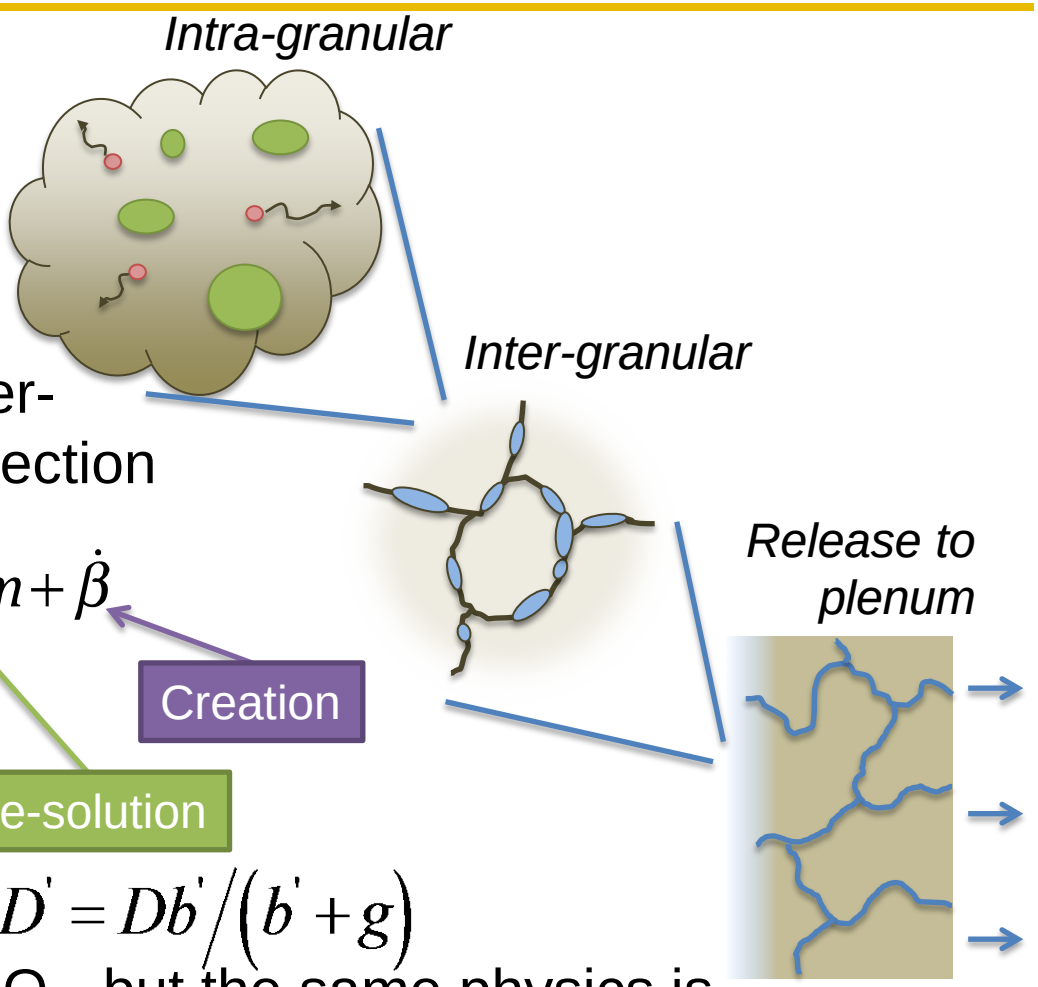
Fission gas behavior

- Fission gas located:
  - Mobile single gas atoms
  - *Intra*-granular bubbles
  - *Inter*-granular bubbles
- Gas release driven by inter-granular bubble interconnection



$$\frac{\partial c}{\partial t} = D\nabla^2 c - gc + b'm + \dot{\beta}$$

Diffusion | Absorption | Re-solution | Creation

- Effective diffusion rate: $D' = Db' / (b' + g)$
- Our focus has been on UO_2, but the same physics is relevant to most fuels (recent application to U_3Si_2).

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Diffusion of fission gas in UO_2

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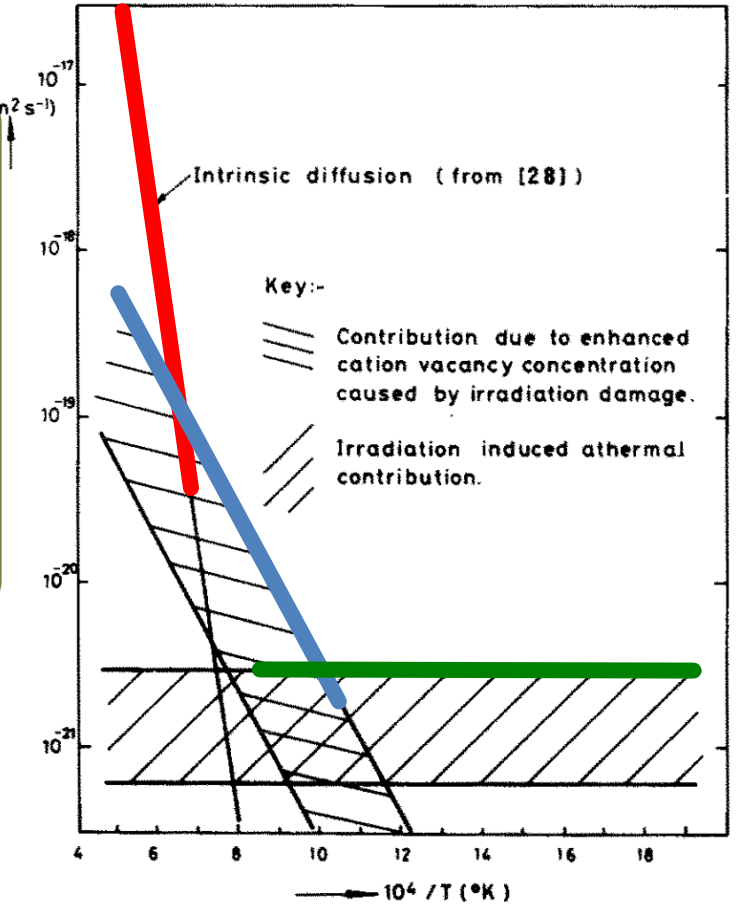
Current empirical model:

Total: $D_{xe} = D_1 + D_2 + D_3$

Intrinsic: $D_1 = 7.6 \cdot 10^{-10} \times \exp\left(-3.04 / k_B T\right) \left[\mathrm{m}^2/\mathrm{s}\right]$

Irr. Enhanced: $D_2 = 4 \times 1.4 \cdot 10^{-25} \times \sqrt{\dot{F}} \exp\left(-1.2 / k_B T\right) \left[\mathrm{m}^2/\mathrm{s}\right]$

Athermal: $D_3 = 4 \times 2 \cdot 10^{-40} \times \dot{F} \left[\mathrm{m}^2/\mathrm{s}\right]$



J. A. Turnbull et al., JNM **107,** 168 (1982)

- Empirical relationships.
- The mechanisms for D_1, D_2, and D_3 are not fully understood, which complicates development of predictive models.
- D_1 and D_2 driven by vacancy population.
- D_3 is believed to be caused directly by damage.

Goal: Calculate D_1 and D_2 fission gas diffusion through simulation using ***point defect dynamics*** and D_3 by direct MD simulations.

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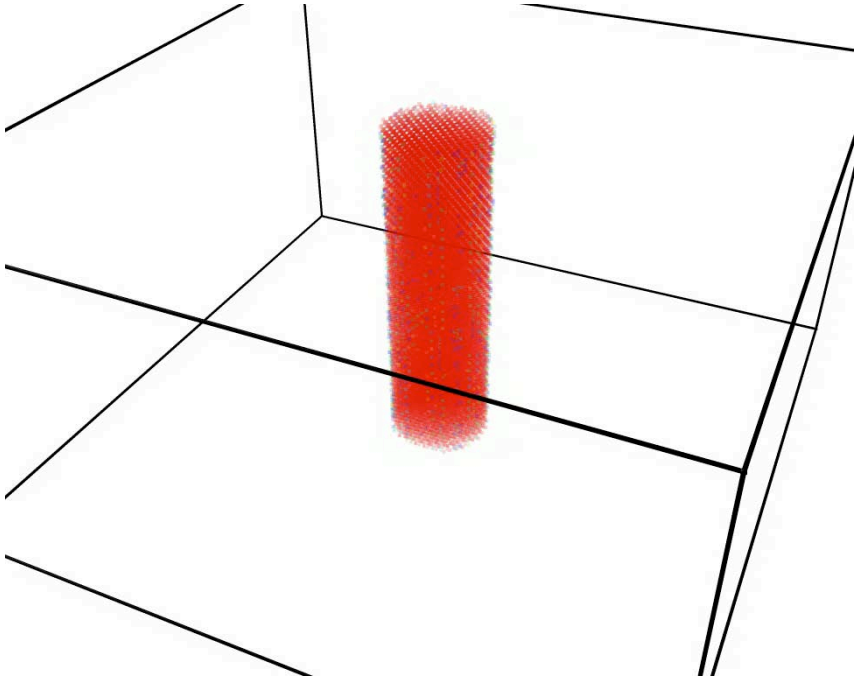
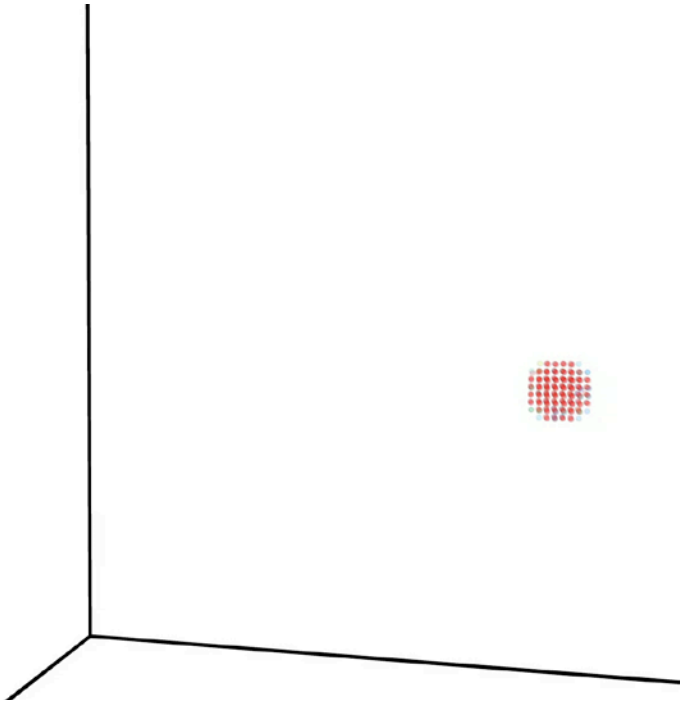
Radiation driven diffusion of fission gas (D_3): Simulations



Electronic stopping



Ballistic stopping

For each fission event a finite amount of displacement is generated. This is related to the diffusion coefficient by the fission rate. In UO_2 the majority of the energy is deposited through electronic stopping, but that is not the case for most other fuels.

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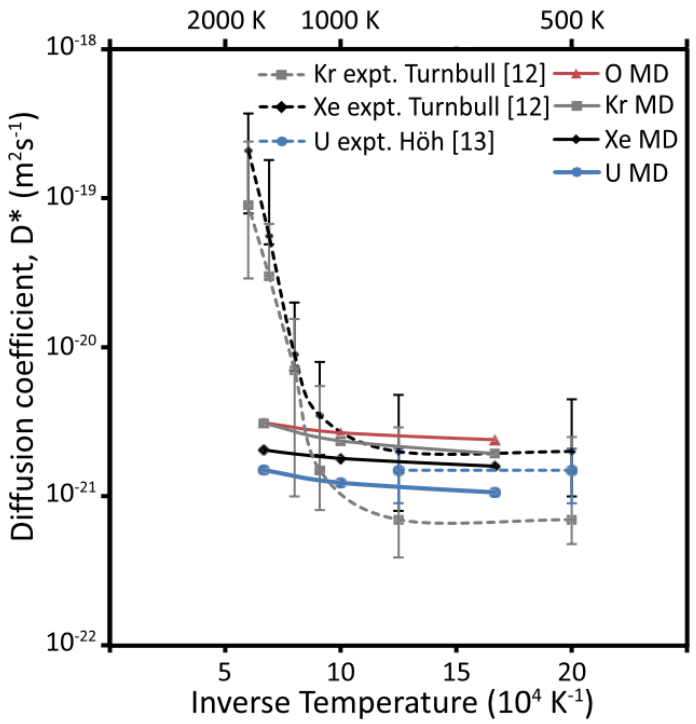
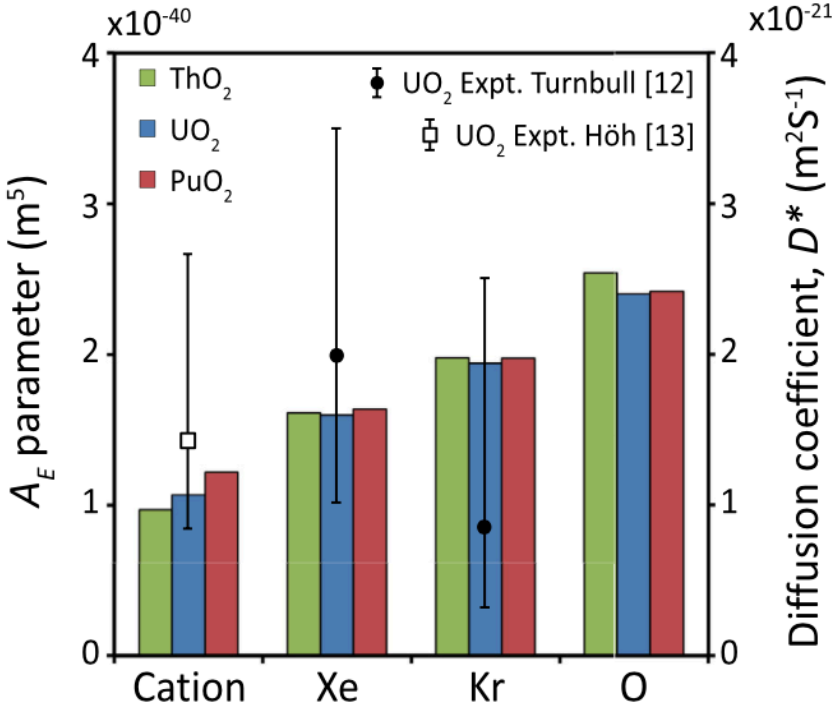
Radiation driven diffusion of fission gas (D_3): Diffusivities





- Near-athermal mechanism and within scatter of experiment. Ratio of 10:1 for ratio of electronic to ballistic contribution. Little difference between actinide oxides.
- Currently extending these simulations to U_3Si_2 using a new U-Si potential.

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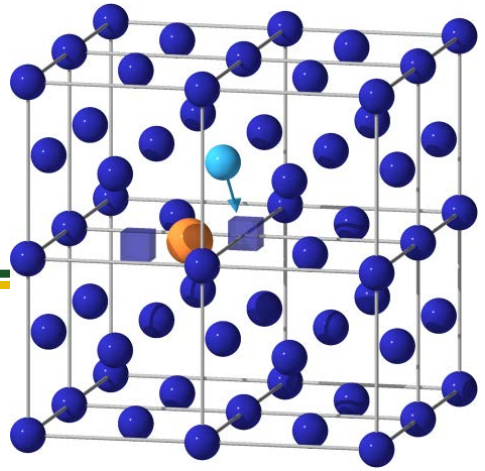
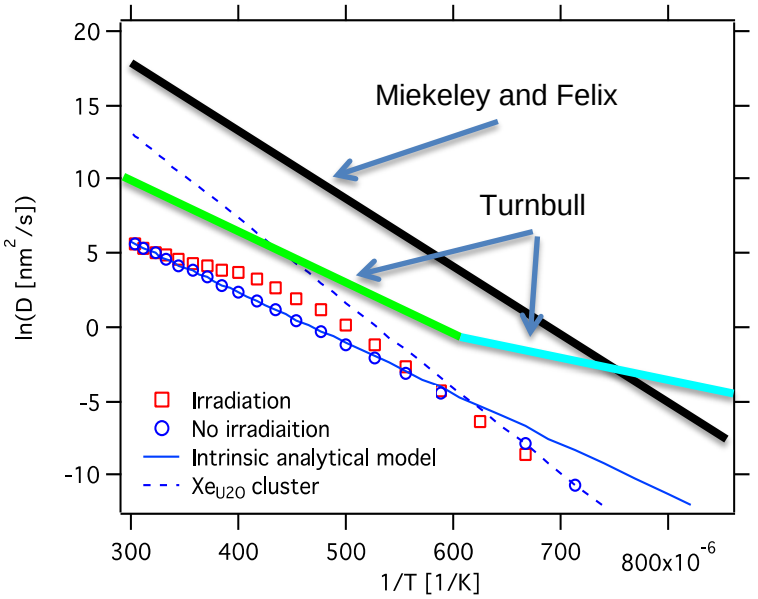
Xe diffusion by point defects in irradiated UO_2 (D_1 and D_2)



- Initial point defect dynamics model:
  - U vacancies (mono- and di-)
  - U interstitials
  - Equilibrium O (stoichiometric)
  - Xe residing in uranium single vacancy(+O) and diffusing as a di-vacancy
  - Damage source term (U interstitials, vacancies)
  - Sinks (static bubble population)
- Xe/Vacancy cluster dominates low temperature diffusion.



Xe+2Va diffusion behavior does not capture experiments

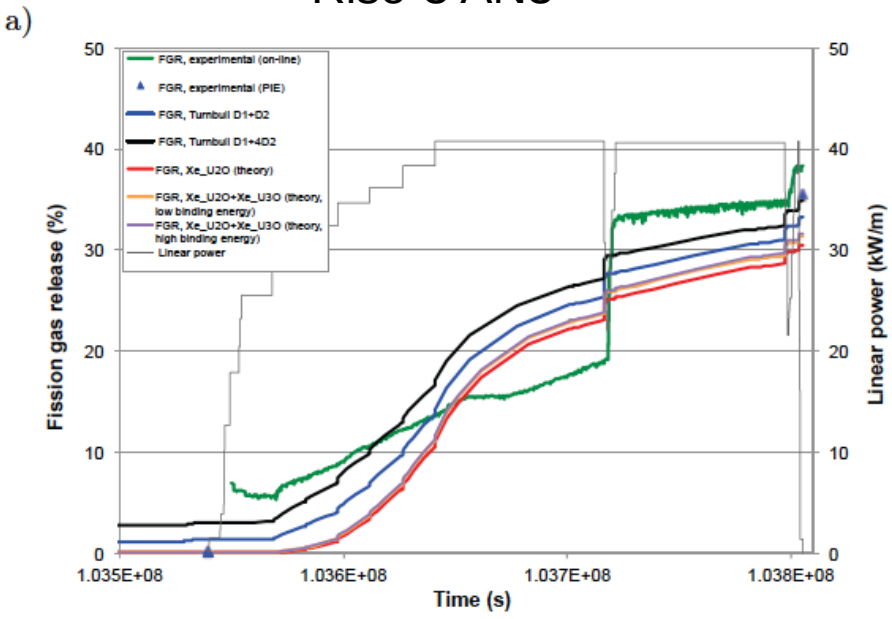
Investigate extended Xe-Va clusters

M. R. Tonks, et al., Comput. Mater. Sci. 51 20 (2012)
D. A. Andersson, et al., JNM **451**, 225 (2014)
D. A. Andersson et al., Phys. Rev. **84**, 054105 (2011)
D. A. Andersson et al., JNM **462**, 15 (2015)

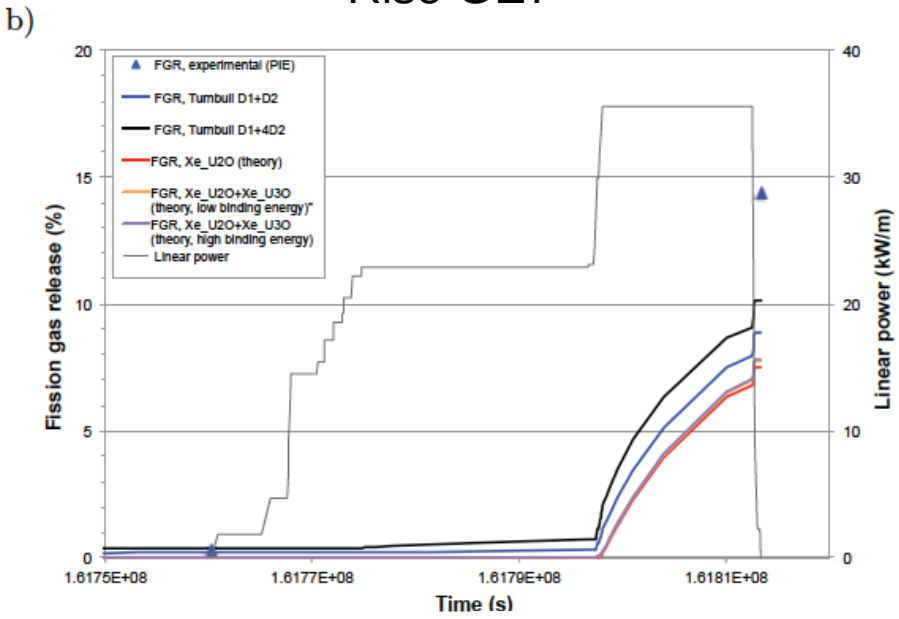
Testing the models in BISON

- The Xe diffusion models were used in BISON to simulate fission gas release for a few irradiation experiments.
- The lower release compared to empirical models follows from lower values for irradiation enhanced diffusion.

Risö-3 AN3



Risö GE7



G. Pastore, INL.

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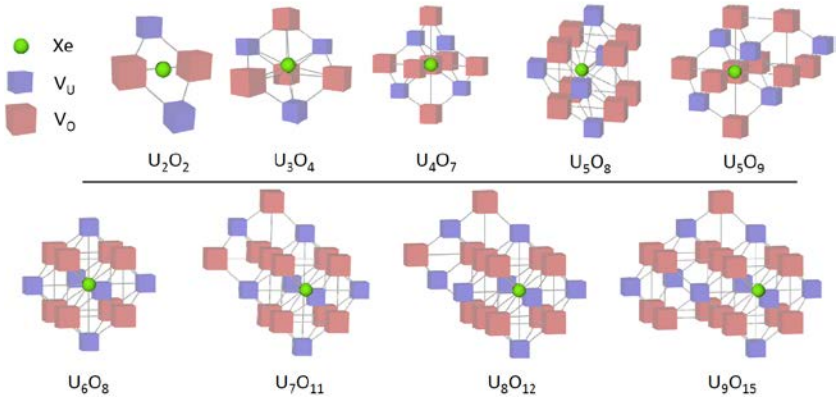
MARMOT free energy cluster dynamics for irradiated UO_2

- **Formulation of cluster dynamics using the change in *total free energy* as the "driving force" for reactions**
  - Naturally follows phase-field methods
  - Built upon existing framework in MARMOT



- **Requires many parameters from empirical potentials and DFT**
  - Formation energies of point defects
  - Binding energies of clusters
  - Migration energies
  - Database of $Xe+U_xO_y$ vacancy clusters
- **Many different variables and reactions requires custom automatic input file creation**
  - 17 non-linear variables, 60 reactions, ~200 kernels
- **Generic coding framework can be extended to other fuels or fission products.**

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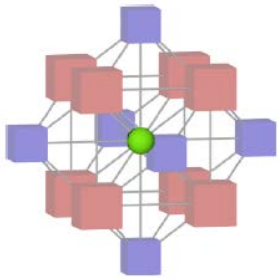
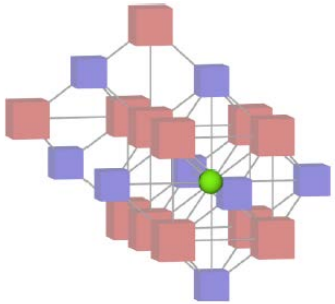
Results for Xe-Va cluster diffusion

- **Xe almost entirely within Xe+Uv6**
- **Reaction between divacancy and 6-vacancy cluster drives creation of fast moving 8-vacancy clusters.**
- **Shift from Xe+Uv8Ov12 → Xe+Uv8Ov11 →Xe+Uv8Ov10 follows the general trend of diffusivity data.**

Xe+Uv6:

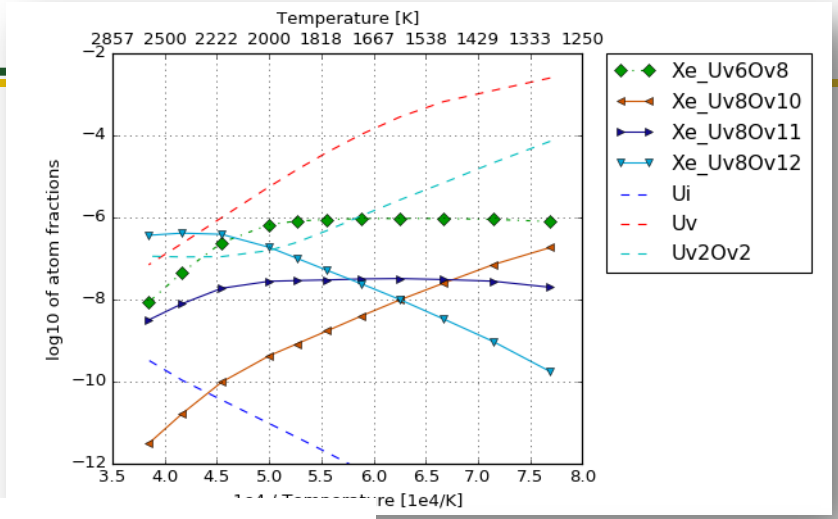


Xe+Uv6Ov12:

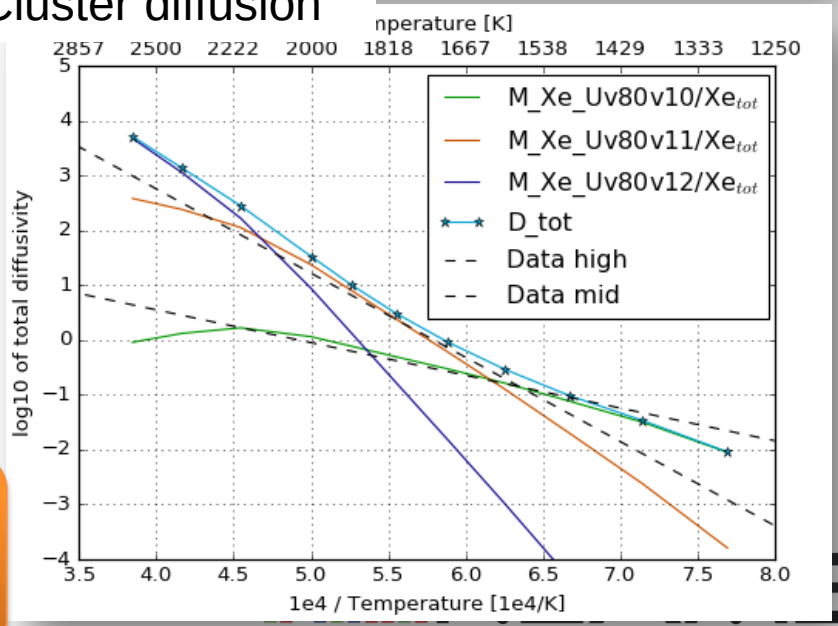


This conclusion (D_1 and D_2) breaks with long-standing Xe diffusion models. Important consequences for fission gas behavior.

Cluster concentrations



Cluster diffusion



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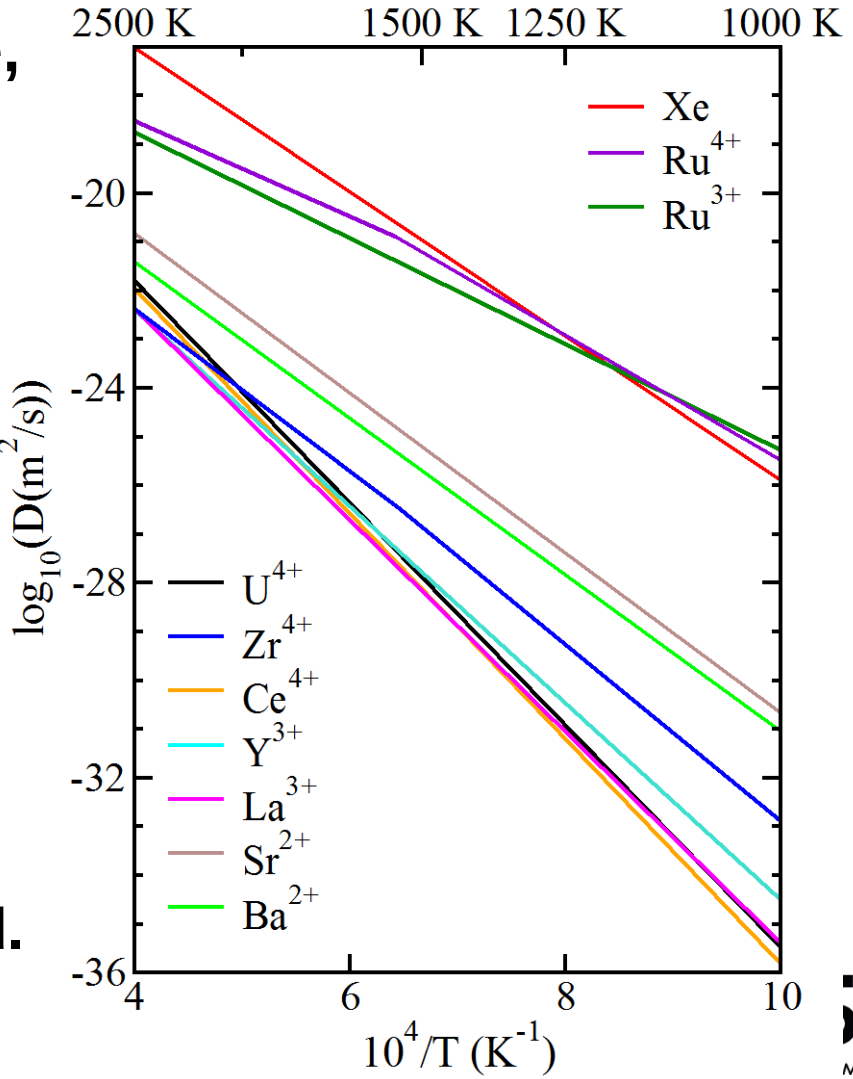
Fission product diffusivities

- Following the approach for Xe, calculated D for Zr^{4+}, Ru^{4+}, Ru^{3+}, Ce^{4+}, Y^{3+}, La^{3+}, Sr^{2+}, and Ba^{2+} in UO_2.
- Occupy single vacancy traps sites (FP_U).
- $Ru^{3+/4+}$ exhibit fast diffusion, comparable to Xe.
- Sr^{2+}, Ba^{2+} follow.
- Ce^{4+}, Zr^{4+}, La^{3+}, and Y^{3+} diffuse slower, rate ~ U self-diffusion.
- Example of how the modeling approach can easily be extended.



R. Perriot, et al., submitted to J. Nucl. Mater. (2014).

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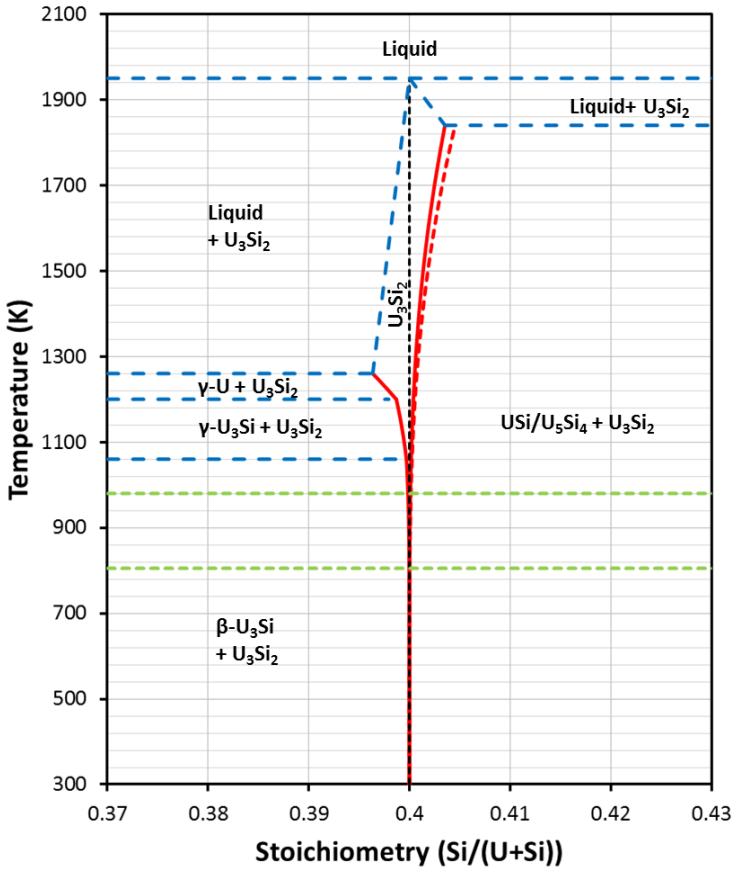
DFT study of stoichiometry deviation in U_3Si_2

Collaboration with S. Middleburgh at Westinghouse.

- **UO_2 fuel performance benefits from the ability to accommodate non-stoichiometry (UO_{2+x}).**
- **Much smaller non-stoichiometry in U_3Si_2, in agreement with the accepted phase diagram.**

Defect reactions for non-stoichiometry

Deviation type	Defect type	Reaction #	Detail	Enthalpy (eV)
Excess Si from USi	Interstitial	1	-	0.19
	Vacancy	2	-	0.68
	Substitutional	3	-	0.16
Excess Si from U_5Si_4	Interstitial	4	-	0.40
	Vacancy	5	-	1.38
	Substitutional	6	-	0.35
Excess U from U_3Si	Interstitial	7	From α-U_3Si	0.77
	Interstitial	7	From β-U_3Si	0.77
	Interstitial	7	From γ-U_3Si	0.72
	Vacancy	8	From α-U_3Si	1.59
	Vacancy	8	From β-U_3Si	1.59
	Vacancy	8	From γ-U_3Si	1.54
	Substitutional	9	From α-U_3Si	0.35
	Substitutional	9	From β-U_3Si	0.35
	Substitutional	9	From γ-U_3Si	0.31
Excess U from U(m)	Interstitial	10	From α-U	0.51
	Interstitial	10	From γ-U	0.41
	Vacancy	11	From α-U	1.06
	Vacancy	11	From γ-U	0.96
	Substitutional	12	From α-U	0.24
	Substitutional	12	From γ-U	0.14



S. C. Middleburgh, et al., "Non-stoichiometry in U_3Si_2", J. Nucl. Mater. **482**, 300 (2016).

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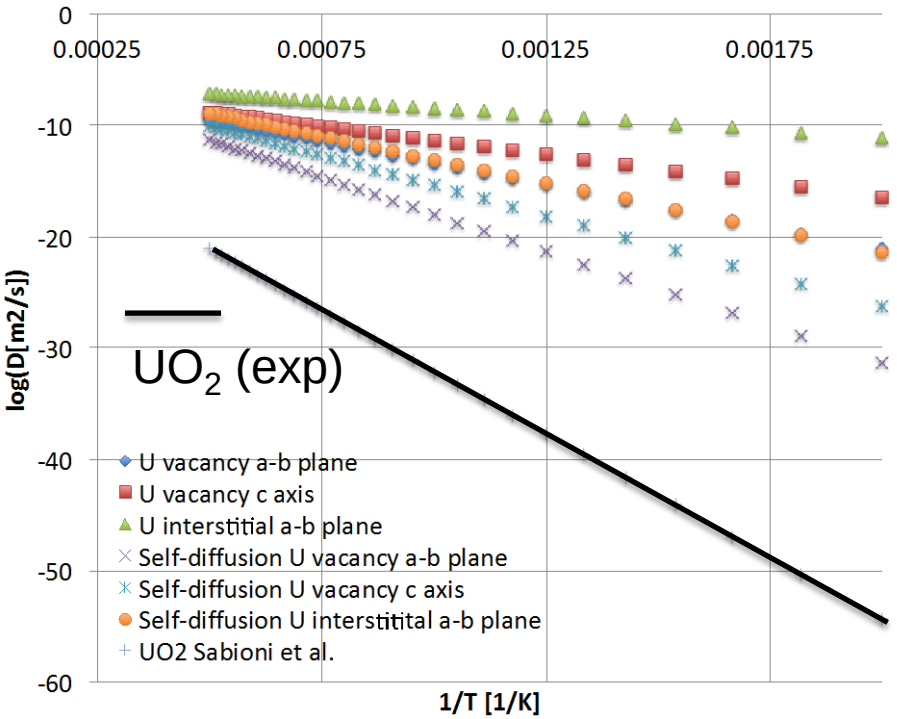
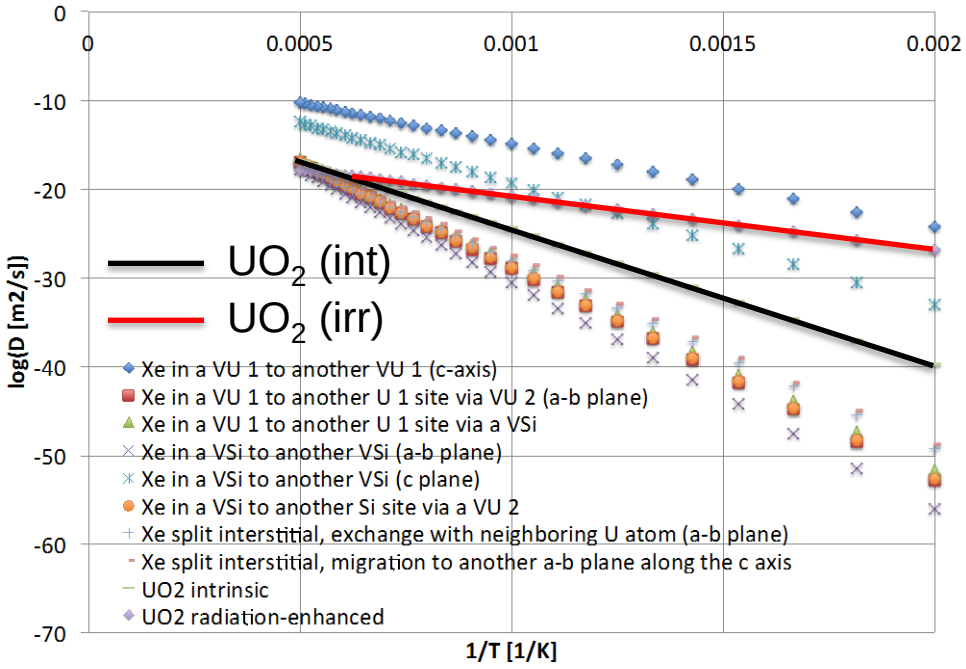
DFT study of defect and Xe diffusion in U_3Si_2

Uranium self- and defect diffusion



Intrinsic Xe diffusion



- Very few if any data points available from experiments.
- The fastest mechanisms exceed those in stoichiometric UO_2.
- These results feed models for swelling and fission gas release in fuel performance simulations (BISON).

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Hierarchical approach: Cladding (NEAMS: FeCrAl and CASL: Zr)

Type I

MOOSE Code

Interface VPSC-MOOSE gives dimensional changes & strength of cladding under complex conditions of dose, stress & temperature

Type II

VPSC Code

Polycrystal model of creep accounting for crystallo-graphic mechanisms, texture, processing conditions

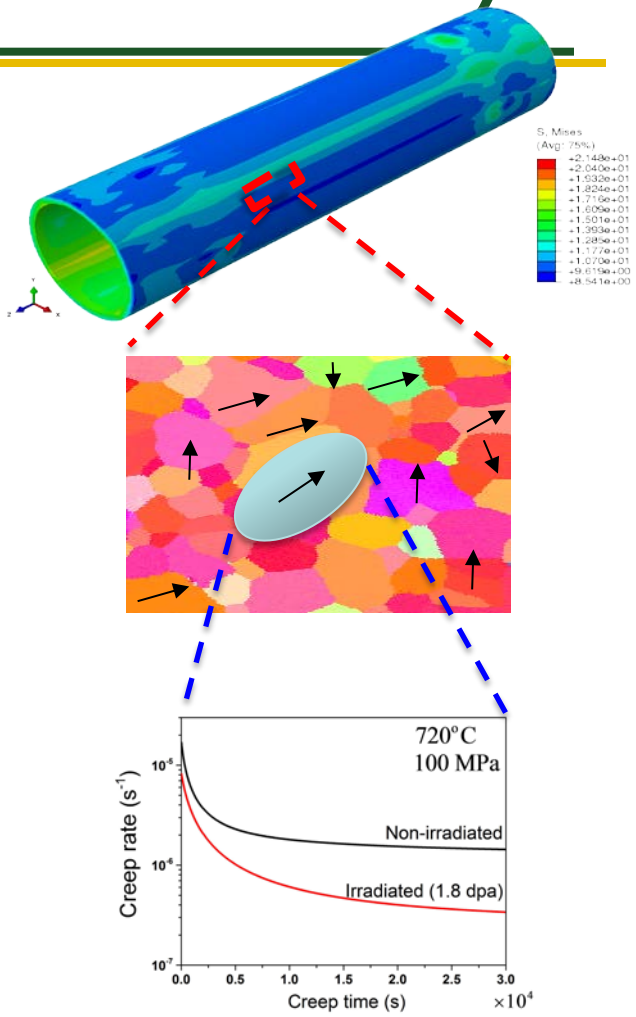
Type III

Thermal creep crystallographic model
→ climb assisted glide of dislocation

Irradiation creep crystallographic model
→ evolution of dislocation loops by climb

Radiation hardening model
→ dislocation-dislocation & dislocation-loop interactions

Molecular Dynamics and Discrete Dislocation Dynamics
Interaction between dislocation and irradiation induced defects



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NUCLEAR ENERGY ADVANCED MODELING & SIMULATION PROGRAM

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Additional possibilities for atomistics to inform nuclear fuel performance modeling

- **We (NEAMS) have focused work on the problems highlighted here (fission gas and thermal conductivity) based on UQ/sensitivity analysis for UO_2 (=impact).**
- **These methods can be used for other fuel types (TRISO, metal, UN, UC, etc.), cladding and other physics/chemistry problems:**
  - Fuel mechanical properties (creep).
  - Fuel fracture.
  - Fuel swelling.
  - Fuel grain growth.
  - High-burnup-structures.
  - Fuel-cladding chemical interaction.
  - Corrosion (CASL).
  - Cladding hydriding (CASL).
  - Cladding oxidation (CASL).
  - …
- **Few (=none) of these examples are simple, but there is a value added proposition to be made for each case.**

Thanks for your attention!

Questions?

Discussion