Atomistic Fuels Modeling

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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$_3$Si$_2$ (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$_3$Si$_2$ + FeCrAl (ATF HIP).
- Fuels: TRISO, metal, UN, UC, etc.,
- Cladding: Zr+coatings, SiC, etc.
Role of atomistics in multiscale simulations

Validation is an integral part at each length scale.

Hierarchical multi-scale approach

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.

BISON fuel performance simulations (FEM)

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

Bulk properties and behavior of point defects (DFT)

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

All codes are available, but the lower length scale work requires experienced/expert users.
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.
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 (UO₂):

\[ E_{\text{lattice}} = \frac{1}{8\pi\varepsilon_0} \left( \sum_i \sum_{j \neq i} \frac{q_i q_j}{r_{ij}} \right) + \frac{1}{2} \Phi_{s-r} \]

Buckingham potential (1938):

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

Additional terms may be added for improved accuracy. Metals such as U₃Si₂ require a different potential due to the drastic difference in electronic structure and bonding.
UO$_2$ thermal conductivity ($\kappa$) as function of fuel microstructure

\[
\kappa = \kappa_0 \kappa_1(\beta) \kappa_2(p) \kappa_3(x) \kappa_4(T)
\]

where:

- $\kappa_0$ 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
- $\kappa_4(T)$ refers to radiation damage from neutrons, $\alpha$-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).
Challenges to accurately predict UO$_2$ thermal conductivity

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

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

Values are significantly overestimated

Including spin scattering term for UO$_2$ thermal conductivity

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

\[ \tau_D^{-1} = D x^4 T^4 = D \left( \frac{\hbar \omega}{k_B} \right)^4 \]
\[ \tau_B^{-1} = B \]
\[ \tau_U^{-1} = U T^3 x^2 e^{-\Theta_D/bT} = U T \left( \frac{\hbar \omega}{k_B} \right)^2 e^{-\Theta_D/bT} \]
\[ \tau_S^{-1} = \sum_i \frac{C_i \omega^4}{(\omega^2 - \omega_{S,i})} F_i(T) \]

Spin scattering resolves the difference between the CRG empirical potential and experiment.
Simplified defect scattering model for BISON

Simple analytical expression of defect scattering\(^1\) for application in MARMOT/BISON following M. Tonks et al\(^2\).

\[ \kappa = \frac{1}{A + BT + Cx} \]

Defect scattering parameters

Impact of FG, FPs and radiation damage on thermal conductivity

\[ k = \frac{1}{A + BT} \]

Combined effect:

\[ k = \frac{1}{A + BT + C_1x_1 + C_2x_2 + \ldots} \]


**Xe scattering parameter from MD**

\[ \alpha_s = 1.0 + 561.4 c_s \]

**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).
Fission gas behavior

- Fission gas located:
  - Mobile single gas atoms
  - *Intra*-granular bubbles
  - *Inter*-granular bubbles

- Gas release driven by inter-granular bubble interconnection

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

- 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\(_3\)Si\(_2\)).
Diffusion of fission gas in UO₂

Current empirical model:

Total: \[ D_{xe} = D_1 + D_2 + D_3 \]

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

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

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

- 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.
Radiation driven diffusion of fission gas \((D_3)\): Simulations

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.
- 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 U₃Si₂ using a new U-Si potential.
Xe diffusion by point defects in irradiated UO₂ (D₁ and D₂)

- 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

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)
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.
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.
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 \rightarrow Xe+Uv8Ov11 \rightarrow Xe+Uv8Ov10 follows the general trend of diffusivity data.

This conclusion (D1 and D2) breaks with long-standing Xe diffusion models. Important consequences for fission gas behavior.
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.

DFT study of stoichiometry deviation in U₃Si₂

- UO₂ fuel performance benefits from the ability to accommodate non-stoichiometry (UO₂₊ₓ).
- Much smaller non-stoichiometry in U₃Si₂, in agreement with the accepted phase diagram.

Defect reactions for non-stoichiometry

<table>
<thead>
<tr>
<th>Deviation type</th>
<th>Defect type</th>
<th>Reaction #</th>
<th>Detail</th>
<th>Enthalpy (eV)</th>
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<tr>
<td>Excess Si from USi</td>
<td>Interstitial</td>
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<td>-</td>
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<tr>
<td></td>
<td>Vacancy</td>
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<td>-</td>
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<tr>
<td></td>
<td>Substitutional</td>
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<td>-</td>
<td>0.16</td>
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<tr>
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<tr>
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<td>-</td>
<td>1.38</td>
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<tr>
<td></td>
<td>Substitutional</td>
<td>6</td>
<td>-</td>
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<tr>
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<td>7</td>
<td>From α-U₃Si</td>
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<tr>
<td></td>
<td>Interstitial</td>
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<td>From β-U₃Si</td>
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<tr>
<td></td>
<td>Interstitial</td>
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<td>From γ-U₃Si</td>
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<tr>
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<td>From β-U₃Si</td>
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<tr>
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<td>Vacancy</td>
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<td>From γ-U₃Si</td>
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<td>Substitutional</td>
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<td>From α-U₃Si</td>
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<tr>
<td></td>
<td>Substitutional</td>
<td>9</td>
<td>From γ-U₃Si</td>
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<tr>
<td>Excess U from U(m)</td>
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<td>From α-U</td>
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<tr>
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</tbody>
</table>

Very few if any data points available from experiments.

The fastest mechanisms exceed those in stoichiometric UO₂.

These results feed models for swelling and fission gas release in fuel performance simulations (BISON).
Hierarchical approach: Cladding (NEAMS: FeCrAl and CASL: Zr)

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

VPSC Code
Polycrystal model of creep accounting for crystallographic mechanisms, texture, processing conditions

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

Type II
Polycrystal model of creep accounting for crystallographic 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
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 UO₂ (=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