Combining molecular dynamics and on-the-fly kinetic Monte Carlo to investigate radiation damage in solids

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Overview

• **Introduction into radiation damage.**
  ▶ Motivation.
  ▶ Time-scale problem.
  ▶ Requirement for atomistic simulation.
  ▶ General methodology.

• **Applications:**
  ▶ Simulating self-irradiation effects of plutonium\(^1\)\(^-\)\(^3\).
    - Defect formation and migration in Ga-stabilised \(\delta\)-Pu.
  ▶ The effect of structure on radiation damage\(^4\).
    - Comparison of radiation response of the rutile, brookite and anatase polymorphs of TiO\(_2\).

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Materials for nuclear applications must all share one important property:

“The ability to maintain functionality during exposure to extreme levels of irradiation”

Two key goals:
- To develop new ‘nuclear materials’ for future reactors or waste forms.
- To determine the life expectancy and failure mechanisms of materials currently in service.

Requires an in-depth understanding of the atomistic processes that attribute to macroscopic changes in properties.

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Time scale problem

Ballistic Phase
- High Energy ~keV
- Collision Cascade
- Thermal Spike

Time scales:
up to ~20 ps

Recovery Phase
- Defect migration and recombination.
- Activated processes - “Rare Events”

Time scales:
ns up to seconds, d/w/y

but events may overlap...
Ballistic Phase

- Recoil event from a **Primary Knock-on Atom (PKA)**
- High energies, typically ~keV (dependent on the simulated process)
- Requires dynamics
  - \textit{Ab initio} methods unsuitable.
- Requires atomistic lattice effects
  - Phase field or continuum models inappropriate.
- Molecular dynamics is well suited to modelling the ballistic phase:
  - Time-scales: \( \sim O \) (ns)
  - Length scale: \( \sim O \) (nm)
  - Ensembles (thermo/barostats)

*Simulation*: 5 keV cascade in fcc Pu @ 300 K. 1.1M atoms 15 ps
Molecular Dynamics

• Molecular Dynamics (MD) is a powerful tool that can be used to investigate the ballistic phase at the atomic level response.

• In addition, MD has allowed in depth studies into all areas of radiation damage
  ▶ Self-irradiation effects (decay).
  ▶ Ion implantation (e.g SWIFT heavy ion).
  ▶ Sputtering.
  ▶ Defect aggregation at grain boundaries or interfaces.
  ▶ Dislocation dynamics and diffusion.
  ▶ Bubble formation.

• Serves as an alternative to analytical models of defect production (KP, NRT) or models based on the binary collision approximation (SRIM)
Ballistic Phase

- Important requirements for modelling the ballistic phase using MD:
  - **Interatomic potential**
    - Must **depict nuclei-nuclei interactions** correctly - i.e. ZBL screened coulomb potential.
  - **Variable time-step**
    - Due to the **high atomic velocities**.
  - **Sampling**
    - Due to the **chaotic nature** of the atomic collisions, important to gain a high level of sampling of PKA **energies**, initial **directions** of impact, **thermal vibrations**, atomic specie.
  - **Defect analysis**
    - Vacancy/Interstitial (Frenkel pairs), Anti-sites, Dislocations, Schottky defects
Recovery Phase

• Modelling the recovery phase is made significantly harder by the highly inhomogeneous nature of the residual lattice:
  ▶ After the ballistic phase, the remaining lattice is potentially highly disordered.
    - Frenkel pairs, voids, dislocations.
  ▶ The presence of impurities or fission products.
    - Bubble formation (H, He, Xe, Kr).
  ▶ Nuclear materials and fuels are typically complex and multi-component
    - Structural vacancies, partial occupancy (i.e. disordered Pyrochlores/Fluorites).
    - Interfaces or grain boundaries (ODS steels, fuel cladding).

• Removes the possibility of using on-lattice KMC due to the variation in local environment surrounding each defect.
Recovery Phase

- The recovery phase itself can be broken down into:
  - Transitions where the **end state is known**.
    - Examples:
      - Simple vacancy/interstitial hops.
      - Direct recombination.
    - Methods:
      - Climbing image NEB\(^1\), String methods
  - Transitions where the **end state is unknown**
    - Examples:
      - Complex defect migration.
      - Long range recombination.
    - Methods:
      - Dimer\(^2\), ART\(^3\), RAT\(^4\)
  - These techniques can also be used in on-the-fly KMC methods.
    - Migration and recombination pathways.

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Application 1

Simulating radiation damage in Ga-stabilised Pu.
Simulating radiation damage in Ga-stabilised δ-Pu.

- Understanding the aging due to self-irradiation in fcc plutonium.
- FCC plutonium is unstable at RT so is alloyed with a small percentage of Ga (up to ~12%)

Aim

- To study the radiation response of Ga-stabilised Pu.
  - Cascade simulations, displacement threshold energy calculations
- To investigate the effect of Ga on defect diffusion.
  - Transitions barrier calculations and OTF-KMC of defect migration.

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Application - Ga stabilised Pu

- Methodology:
  - MD cascades
    - Modified Embedded Atom Method (MEAM) for PuGa in LBOMD.
    - 0.2 - 10 keV PKA energies.
    - 10 lattices equilibrated to 300K for between 10-15 ps.
    - 12 PKA directions chosen from the FCC irreducible volume.
    - Thermal and periodic boundaries.
    - MD runs of 20 ps.
  - LTSD
    - Simple transitions, manual setup, MEP defined using CNEB.
    - Transition searches using Dimer/RAT methods
    - On-the-fly KMC - Dimer/RAT followed by CNEB

**Application - Ga stabilised Pu**

- **Lattice Structure**
  - FCC phase Pu with arbitrary 5% substitutional Ga.

  ![Ga-Pu lattice structure](image)

  Substitutional Ga lowers the PE of surrounding Pu matrix

- Ga ordering determined using lattice Monte Carlo
  - Results in no 1st nearest neighbour (1NN) Ga-Ga bonds

  ![Ga-Ga radial distribution function](image)

**Impact on LTSD techniques - resultant crystal structure highly inhomogeneous**
Application - Ga stabilised Pu

- A first look at the ballistic phase
- The effect of Ga on: Threshold displacement energy $E_d$.
  “Minimum energy required to displace an atom as to create a Frenkel (vacancy-interstitial) Pair”
  - Low energy cascades (< 200 eV) initiated in an irreducible volume.

- Overall increase in $E_d$ for the Ga PKA
Application - Ga stabilised Pu

- Cascade Results

<table>
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<th>Pu 5 at. % Ga 5 keV Cascades Defect Analysis</th>
<th>Ga</th>
<th>Pu</th>
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</table>

Table 6.1: Analysis of outlying defect clusters in Pu-Ga outside the core region after 3 pseudospinor cascades into Pu-Ga at 5 keV. Note the small number of Ga vacancies or interstitials yet the abundance of anti-site defects suggesting nearly all Ga displaced during the cascade finish occupying lattice sites.

Large build up of 1NN mixed specie anti-site defects.
- Interstitial barriers << vacancy barriers
- The creation of vacancies by the displacement of Ga atoms is highly unfavourable.
Application - Ga stabilised Pu

- On-the-fly KMC of Pu split-interstitial

- Due to the low energy barriers associated with split-interstitials, diffusion occurs quickly $\sim$ns.

- Defect migrates through a succession of Pu atomic replacements

- But what about the effect of the substitutional Ga? ...
Application - Ga stabilised Pu

- On-the-fly KMC of Pu split-interstitial

- Due to the low energy barriers associated with split-interstitials, diffusion occurs quickly ~ns.

- Defect migrates through a succession of Pu atomic replacements

- But what about the effect of the substitutional Ga? ...

Simulated time: 842.24 ns
Application - Ga stabilised Pu

- On-the-fly KMC of Pu split-interstitial

- By rendering the Ga-Pu polyhedra, it becomes clear that the interstitial migration is confined to Pu rich regions.
Application - Ga stabilised Pu

- On-the-fly KMC of Pu split-interstitial

- By rendering the Ga-Pu polyhedra, it becomes clear that the interstitial migration is confined to Pu rich regions.
Application - Ga stabilised Pu

- On-the-fly KMC of Pu mono-vacancy.
  - The same is also true for vacancy migration, with the migration pathway avoiding Ga-rich regions.
  - As the lowest energy barriers for vacancy transitions are higher than interstitial, the time scale for migration is significantly increased.
Conclusions:

- We have built up a picture of radiation damage in Ga-stabilised Pu, showing the effect of Ga on:
  - Ballistic phase - Threshold displacement energies.
    - Higher value of $E_d$ for the Ga PKA.
  - Ballistic phase - Cascade damage.
    - No outlying Ga defects
    - Build up of 1NN ‘anti-sites’ i.e. Pu-Ga switching during the cascade
  - Recovery phase - Transition barriers.
    - High energy barriers associated with introducing vacancies and interstitials intro Ga rich regions.
  - Recovery phase - Diffusion mechanisms.
    - Pu defect migrations is confined to Pu-rich zones, bounded by Ga-Pu polyhedra.

Todo: Cascade overlap, effect of GB, varying at.% Ga, migration of complex defect structures. - requires robust LTSD methods!
Application 2

The effect of structure on radiation damage: A case study in TiO$_2$
**Application - TiO$_2$**

- **Rutile** application as a nuclear waste form, i.e. Synroc, and has a high tolerance to radiation damage.

- The **Anatase** and **Brookite** polymorphs behave differently with **Anatase** exhibiting a much higher susceptibility to radiation damage.

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Application - Ga stabilised Pu

**Aim**

- To study the low energy radiation response of the low pressure polymorphs of TiO$_2$
  - Reproduce trends found in experiments.
  - Investigate the atomic level differences in radiation response.

- A transferable and generalised method of simulation and analysis of low energy radiation events.
  - As a method of calculating the threshold displacement energy, $E_d$.
  - To determine defect production mechanisms and recovery processes.
  - Quantitative insight into resultant defect structures.
  - To generate comparable results between crystal structures and/or potentials.
Methodology:

- **MD cascades**
  - **Matsui-Akaogi (MA)** buckingham potential\(^1\) with ZBL in the DL_POLY3 MD code.
  - Low energy cascades < 200 eV.
  - 10 lattices equilibrated to **300K** for between 10-15 ps.
  - 100 PKA directions chosen from a **uniform spherical distribution**.
  - Thermal and periodic boundaries.
  - MD runs of **20 ps**.

- **LTSD**
  - Simple transitions, manual setup, MEP defined using CNEB.
  - Transition searches using Dimer/RAT methods
  - On-the-fly KMC - Dimer/RAT followed by CNEB

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\(^1\) M. Matsui and M. Akaogi, Molecular Simulation 6, 239-244 (1991).
One of the goals was to produce a **generalized and transferable** methodology to study initial defect formation and extracting quantities such as threshold displacement energy $E_d$.

- Main area to automate: the determination of **PKA directions**

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**The Thomson Problem**

"Minimum energy configuration of point charges on the surface of a conducting sphere"

No analytical solution for large $N$, requires **numerical constrained minimisation**.
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**The Thomson Problem**

"Minimum energy configuration of point charges on the surface of a conducting sphere"

**No analytical solution** for large $N$, requires **numerical constrained minimisation**.
• Finding solutions to the Thomson Problem.
  ▶ Steepest Decent
  ▶ MD
  ▶ Conjugate Gradient
  ▶ Broyden–Fletcher–Goldfarb–Shanno (BFGS & LBFGS)

• Exponential Increase in local minima as N increases
  ▶ Requires basin-hopping techniques to find global minima.
Application - TiO$_2$

- Finding solutions to the Thomson Problem.
  - Steepest Decent
  - MD
  - Conjugate Gradient
  - Broyden–Fletcher–Goldfarb–Shanno (BFGS & LBFGS)

- Exponential Increase in local minima as N increases
  - Requires basin-hopping techniques to find global minima.
Relax and thermalise \( N_l \) lattices to \( T \) Kelvin.

Determine unique PKAs: \((\text{Ti, O}_1, \text{O}_2)\)

Choose \( E_{\text{min}}, E_{\text{max}} \) and step size \( \Delta E \).

Generate \( N_d \) PKA directions from solutions to the Thomson Problem

In each lattice, for each unique PKA, energy and direction, run MD collision cascades for \( t \) ps.

Analysis of recovery time as a function of PKA energy/specie

Transition searches / OTF-KMC

Post analysis: DFP, FP separations ...

On-the-fly analysis: Frenkel pairs, replacements ...

Application - \( \text{TiO}_2 \)
The importance of high sampling to generate representative results

- Defect formation probability (DFP) - The probability of defect formation at a given PKA energy over all directions and lattices.

*Error bars represent 95% confidence interval in SEM
**Application - TiO_2**

- Quantitative analysis of the ballistic phase:
  - DFP as a function of PKA energy

**Rutile**

\[
DFP(E_{pka}) = \begin{cases} 
\frac{1}{\beta}(E_{pka}^\alpha - E_d^\alpha) & \text{if } E_{pka} > E_d \\
0 & \text{if } E_{pka} \leq E_d 
\end{cases}
\]

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>O PKA</th>
<th>Ti PKA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_d)</td>
<td>(E_{0.5})</td>
</tr>
<tr>
<td>Rutile</td>
<td>19</td>
<td>201</td>
</tr>
<tr>
<td>Brookite</td>
<td>19</td>
<td>105</td>
</tr>
<tr>
<td>Anatase</td>
<td>15</td>
<td>121</td>
</tr>
</tbody>
</table>

*Energies in eV

*\(E_{0.5}\) - the energy required to achieve 50% DFP

- Defect formation is **probabilistic over a large energy range**, up to at least 300-400 eV.
- Although the \(E_d\) is lower for O, defect formation is more probable from Ti displacements at higher energies.
- **Defect formation requires more energy** in Rutile over the energy range studied - particularly from Ti PKAs.
Application - TiO2

- Taking an in-depth look into Rutile - Defect cluster analysis

- Highlights the differences in sublattice response.
- Provides a good foundation for studies of defect migration and FP recombination \textit{i.e.} KMC

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• **DFP** categorised by the **atomic specie** of the defects.

**Across all polymorphs**

- Predominantly **O defects** created by **O PKAs**.
- Even proportion of **Ti and O defects** from **Ti PKAs**

• **Implications for TRCS** (or other methods that rely on anion vacancies)
  - Method traditionally only detects **first emission** i.e. **O defects from O PKAs**
  - Second emission relating to **O defects from Ti PKAs**.
  - *Only if energy gap is sufficiently large*
Application - TiO$_2$

- Quantitative analysis of the ballistic phase - Comparison with experiment:
  - Experimental values of $E_d$ for the O PKA are significantly lower than observed from the MD simulations, for example:
    - TEM
      - $\sim 33$ eV$^1$
    - TRCS (Time-resolved Cathodoluminescence Spectroscopy)
      - $\sim 39$ eV rutile 45-50 eV for other oxides$^2$.

- Reasons for discrepancies
  - TEM
    - Relies on observable defect structures (saturation of point defects)
    - Always overestimate $E_d$.
  - TRCS
    - Displaces O atoms with electron beam - observes decay of excited F-centers.

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Application - TiO$_2$

- What can happen in 25 ns? (Rutile)
  - Simple O Frenkel pair annihilation - separation around 4 Å

- At small separations O FP recombination occurs on the ps time scale.
- At what separation do we see a marked increase in FP recombination barrier?
Application - TiO$_2$

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- At small separations O FP recombination occurs on the ps time scale.
- At what separation do we see a marked increase in FP recombination barrier?

Single barrier process 0.07 eV
O Frenkel pair annihilation - separation of around 6 Å.

Migration along the c-axis

Single barrier process 0.18 eV
Application - TiO$_2$

- O Frenkel pair annihilation - separation of around 6 Å.

Migration along the c-axis

Single barrier process 0.18 eV
Application - TiO$_2$

- O Frenkel pair annihilation - separation of around 6 Å.

Migration along the c-axis

Single barrier process 0.18 eV
Mechanism of O split-interstitial migration in rutile

- Migration through the shared edge of the polyhedra along the c direction (z axis).

• TODO: Is this migration possible in anatase and brookite?
In the presence of a local vacancy, the mechanism has a very low single barrier for annihilation.

- In bulk the transition is a two stage process with barriers around 0.12 eV.

- 0.12 eV

- CNEB

- 0.16 eV

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In the presence of a local vacancy, the mechanism has a very low single barrier for annihilation.

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In the presence of a local vacancy, the mechanism has a very low single barrier for annihilation.

In bulk the transition is a **two stage process** with barriers around 0.12 eV.

![Graph showing energy vs separation with a peak at 0.16 eV](image)
In the presence of a local vacancy, the mechanism has a very low single barrier for annihilation.

- In bulk the transition is a two stage process with barriers around 0.12 eV.

![Diagram of TiO₂ structure and energy levels](image)
Application - TiO$_2$

- In contrast, Ti octahedral interstitials migrate at much higher barrier down the Z-axis channels.
  - Migration passes through 2 symmetrically equivalent octahedral sites with a barrier of 0.85 eV.

- Unlike the O split-interstitials that migrate through a concerted motion, the mechanism for the Ti interstitial is a simple linear transition.
Current conclusions:

- **Ballistic phase - Displacement threshold energy**
  - Reiterates the probabilistic nature of defect formation at low energy
  - \(O\) values of \(E_d\) were found to be lower than experimental, but can be attributed to low energy recombination barriers.

- **Ballistic phase - Quantitative defect cluster analysis**
  - Different response from each sublattice, \(O\) PKA generates strictly \(O\) defects, Ti PKA produces a multitude of defects
  - Representative defect proportions useful for future long time scale simulations

- **Recovery phase - Transition barriers / Diffusion mechanisms**
  - Relatively long range and low barrier \(O\) FP recombination transitions.
  - \(O\) split-interstitial migration along the rutile c-axis, with very low energy barriers.

TODO:

- The effect of the connectivity of the \(\text{TiO}_6\) polyhedra on defect migration:
  - Is migration impeded by change from edge to corner sharing?
  - Is the presence of the z-axis channel in rutile the main factor behind its increase in tolerance?

- Full scale OTF-KMC in each polymorph on the resultant defect clusters - particularly the di-vacancies and di-interstitials.
Requirements for Future Work

- A robust method of accessing time-scales beyond MD.
  - Automated
  - Handle multiple complex defect structures
  - Highly disordered lattices
  - Large systems (as PKA energy increases)

Thanks to ...