5. Primary damage production from many-body nuclear collisions

Nota bene: if you read these notes on your own, you cannot see the many animations. However, some of them are available in the web in http://www.acclab.helsinki.fi/~knordlun/anims.html
5.1. Many-body collisions

- The final stage of irradiation almost always includes many-body collisions between atoms.
- Due to both nuclear and electronic stopping, the high-energy ions and recoils slow down and eventually reach thermal velocities (< 1 eV).
- At this stage they collide with several atoms at the same time = many-body collisions.
5.2. How to simulate the many-body collisions: The molecular dynamics method

- The molecular dynamics (molekyldynamik / molekyylyidynamiikka) (MD) simulation method is ideally suited for simulating many-body collisions.
- The MD method is normally a standard tool in materials physics, chemistry and biochemistry for simulating atom motion.
- Very basic example: motion of atoms in Cu at 600 K.
History of molecular dynamics

- MD is solving the Newton’s (or Lagrange or Hamilton) equations of motion to find the motion of a group of atoms
- Originally developed by Alder and Wainwright in 1957 to simulate atom vibrations in molecules
  - Hence the name “molecular”
  - Name unfortunate, as much of MD done nowadays does not include molecules at all
- Already in 1960 used by Gibson to simulate radiation effects in solids [Phys. Rev. 120 (1960) 1229]
  - A few hundred atoms, very primitive pair potentials
  - But found replacement collision sequences!
MD algorithm

Give atoms initial \( r^{(t=0)} \) and \( v^{(0)} \), choose short \( \Delta t \)

Get forces \( F = -\nabla V(r^{(i)}) \) or \( F = F(\Psi) \) and \( a = F/m \)

Move atoms: \( r^{(i+1)} = r^{(i)} + v^{(i)} \Delta t + \frac{1}{2} a \Delta t^2 + \) correction terms

Update velocities: \( v^{(i+1)} = v^{(i)} + a \Delta t + \) correction terms

Move time forward: \( t = t + \Delta t \)

Repeat as long as you need
MD – the time step limit

- Time step selection is a crucial part of MD
  - Choice of algorithm for solving equations of motion and time step are related
- Way too long time step: system completely unstable, “explodes”
- Too long time step: total energy in system not conserved
- Too short time step: waste of computer time
  - Pretty good rule of thumb: the fastest-moving atom in a system should not be able to move more than 1/20 of the smallest interatomic distance per time step – about 0.1 Å typically
- This leads to time steps of the order of fs in equilibrium simulations, and for high-energy recoils even down to as (attoseconds)!
- This severely limits the time scale MD can handle
MD – Periodic boundary conditions

- A real lattice can be extremely big
  - E.g. 1 cm^3 of Cu: 2.1e22 atoms => too much even for present-day computers
  - Hence desirable to have MD cell as segment of bigger real system
- Standard solution: **periodic boundary conditions**
  - This approach involves “copying” the simulation cell to each of the periodic directions (1–3) so that the initial system “sees” another system, exactly like itself, in each direction around it. So, one can create a “virtual infinite” crystal.
MD – Boundary conditions

- There are alternatives, though:

  - **Open boundaries** = no boundary condition, atoms can flee freely to vacuum
    - Obviously for surfaces

  - **Fixed boundaries**: atoms fixed at boundary
    - Unphysical, but sometimes needed for preventing a cell from moving or making sure pressure waves are not reflected over a periodic boundary

  - **Reflective boundaries**: atoms reflected off boundary, “wall”

- Combinations of these for different purposes
MD – Temperature and pressure control

- Controlling temperature and pressure is often a crucial part of MD
- “Plain MD” without any T or P control is same as simulating NVE thermodynamic ensemble
  - In irradiation simulations NVE only correct approach to deal with the collisional phase !!
- NVT ensemble simulation: temperature is controlled
- NPT ensemble simulation: both temperature and pressure is controlled
Nonequilibrium extensions to MD

- The standard MD algorithms are not suitable for high-energy interactions, and does not describe electronic stopping at all.
- But over the last ~25 years augmentations of MD to be able to handle this have been developed.
  - We will here discuss the most central ones.
What is needed to model irradiation effects?

**keV and MeV-energy collisions between nuclei**

- To handle the high-E collisions, one needs to know the high-energy repulsive part of the interatomic potential
  - We have developed DFT methods to obtain it to within ~1% accuracy for all energies above 10 eV
  - The so Universal ZBL potential described in chapter 4 accurate to ~5% and very easy to implement
- Simulating this gives the **nuclear stopping** explicitly from MD!

What is needed to model irradiation effects?

Energy loss to electronic excitations

- The electronic stopping can be included as a frictional force in MD
- The nice thing about this is that it can be compared directly to experiments via BCA or MD range or ion transmission calculations
- Examples of agreement:

What is needed to model irradiation effects?

**MD irradiation temperature control**

- For irradiation simulations the central part where the high-E collisions occur has to be in NVE ensemble, but on the other hand extra energy/pressure wave introduced by the ion or recoil needs to be dissipated somehow.

- Exact approach to take depends on physical question:
  a) surface, b) bulk recoil, c-d) swift heavy ion, e) nanocluster, f) nanowire

What is needed to model irradiation effects?

Realistic equilibrium interaction models

Finally one also needs the **normal equilibrium part** of the interaction model, and a **smooth joining** of the high-energy and equilibrium part.

Since we start out with the extremely non-equilibrium collisional part, all chemical bonds in system can break and reform and atoms switch places => one needs so called ‘reactive’ interatomic potentials.
Importance of potentials in MD

- The reliability of the interatomic potential is a **major issue** in MD, and non-equilibrium effects are especially demanding.
  - For common pure elements many good potentials exist, but even these are not always good enough for irradiation simulations.
  - For some common compounds potentials exist – but not nearly all.
  - To assess reliability needs an expert in the field.

- When a potential is used, the MD is called **classical MD**.
  - With parallel computers, classical MD can be done with hundreds of millions of atoms.

- Nowadays it is also possible to obtain the forces from quantum mechanical calculations, typically the approximate so called Density Functional Theory (DFT) approach.
  - But then system size limited to $\sim 1000$ atoms.

- **For more on MD, we have a course for it at our department.**
Cross-sectional views of MD simulation results

- For illustrating MD simulations it is very common to use a 2D cross sections of a true 3D view.
  - Typically 2-4 atom layers thick.
5.3. Damage from MD near the threshold $E$

- If the ion energy is just barely above the threshold, the damage production is easy to understand: the atom which receives a kick from a passing particle (e.g. electron, gamma, low-mass ion) or a nuclear decay process can enter an interstitial site and leave behind a vacancy

- Shown here: Atom given 20 eV recoil energy in Si just above the threshold energy in 111 crystal direction
  - Final state: single vacancy + single interstitial $\Rightarrow$ simple

Concept of primary damage

What this animation, and all other MD simulations, show is the production of **primary damage** *(primära skador / primäärit säteilyvauriot)*

This is the damage produced initially in a cascade on sub-nanosecond timescales, not counting any possible damage recombination by thermally activated processes.

In many cases the thermally activated recombination is actually very important, especially when diffusion occurs.

Physically the mechanisms of the two varieties are quite different and fairly well separated in time, so it makes sense anyway to describe them independently.
Damage from MD near threshold in graphene

- Low-energy recoil in a single sheet of graphene
  (Defect created is a topological defect known as the Stone-Wales one)

[J. Kotakoski et al]
Damage from MD at about 10x threshold energy: 500 eV Au -> Cu

- Many-body collisional effects clearly visible
- Nota bene: this animation has actually been done for school visits, and hence to make it look better there is a minor physical cheat in there – can you figure out what?
5.3. The dynamics of high-energy (keV) cascades from MD; Transition from ballistic collisions to thermodynamics: 10 keV recoil in Au
Development of maximum $E_{\text{kin}}$ and $T$

- Plot of maximum energy of any atom in the system and the temperature in the system vs. time.
- Note that there is of course a huge temperature gradient in the simulation system: the center is very hot, the edges close to 0 K.
- The dips in the beginning of the plots correspond to strong binary collisions: during the collision kinetic energy for a moment is converted into potential energy, decreasing the apparent temperature.
Transition to thermodynamics

- Ergo: the initial stages of the cascade are a linear collision cascade that can be well treated with the binary collision approximation.

- Towards the end, the system thermalizes (termaliseras / termalisoituu) and equilibrium thermodynamics comes into play.

- A detailed analysis [Zhu et al; Phil. Mag. A 71 (1995) 735] showed that after roughly 1 ps, the kinetic energy of the atoms follows a Maxwell-Boltzmann distribution, i.e. the system is thermal!
Temperature in cascade

- After thermalization, the center of the cascade is initially still very hot, ~ 10000 K
- However, it cools down very rapidly, with a cooling rate of the order of $10^{15}$ K/s
- The structure factor of the material follows closely that of a liquid at the same temperature

Cooling down mechanisms, 1

- The high temperature in the center (atoms with high kinetic energies) can cool down in the bulk by two mechanisms:
  - Lattice heat conductivity (phonons)
  - Electronic heat conductivity (free electrons)
- In addition, if a cascade intersects a surface, the sputtered particles will also carry away energy
- In case of a good insulator, the lattice heat conductivity of course dominates as there are no free electrons
  - The cascade itself may excite some electrons, but their contribution is likely small
Cooling down mechanisms, 2

However, in metals (and possibly semiconductors) some of the high lattice energy may transfer to the electrons via **electron-phonon coupling** (EPC) (elektroni-fononi-kytkentä/elektron-fonon-koppling) which may speed up the cooling down.

- This is because the electrons move much faster than atoms, and hence electronic heat conductivity is much more efficient than that of atoms.

The role of the EPC is not very clear, but the fact that ion beam mixing coefficients of atoms can be well reproduced by MD simulations without any EPC, indicates it is not overly important [K. Nordlund et al, Phys. Rev. B (Rapid Comm.) 57, 13965 (1998)].

Concept of a thermal spike

- This very high temperature region is known as a **thermal spike** or **heat spike** (*termisk pik / kuumuuspiikki*)
- Sometimes also as a Brinkman spike or displacement spike
- This was originally predicted in 1954(!) but whether they really exist was debated for a long time as it is difficult to determine the cooling rates of materials on nm length and ps time scales
Thermal spike is underdense in middle

- Key evidence for thermal spikes came from molecular dynamics simulations
- These also showed the cascade core is underdense for a while, as predicted by Brinkman in 1954

5 keV cascade in Cu

10 keV cascade in Au

Experimental evidence for thermal spikes

Also several experiments provide strong evidence for the existence of thermal spikes. A couple of key examples:

Experiments on irradiation of certain ceramics showed that after irradiation, new phases appear that are otherwise known to form only at high temperatures


A special nuclear physics measurement technique gave a lifetime of about 6 ps for a liquid phase in Fe


Strålingsskador 2014 – Kai Nordlund
Thermal spikes exist only in dense materials

- However, the thermal spikes are not always formed.
- In very light materials (say Li or C) there is *never* a thermal spike in the sense of a pocket of metastable liquid material.
- Spike formation probability depends on density and structure of material.
- Example: comparison of hot atoms by 10 keV recoils in Si, Al, Ge, Au: much denser cascade in the FCC metal Al, Au than in the diamond-structured Si, Ge.
  - Atomic packing fraction $\sim \frac{1}{2}$ in diamond compared to FCC.

FIG. 2. Liquid atoms in 10 keV cascades in silicon (upper left), germanium (upper right), aluminum (lower left), and gold (lower right) (Ref. 61). The snapshots were chosen at times when the number of atoms in large continuous liquid regions was at a maximum.

Cascade in Si vs. Au

- Widely different atomic mass and density
- Colors and size are kinetic energy of atoms, red=hot

Cascade in Ge vs. Cu

- Almost same atomic mass, but different crystal structure and density

**Damage recombination**

- Looking at these animations, it appears that many of the liquid atoms regenerate into perfect crystal, i.e. do not produce damage!
  - E.g. from the figure below it is obvious there are hundreds of liquid atoms just in this cross section, but only a few small vacancies remain in the end.
Damage recombination

- Analysis of defects (e.g. by counting empty lattice sites) confirms this visual observation
- The effect is known as **athermal defect recombination**
  - *(atermisk defektrekombination / aterminen kidevirherekombinaatio)*
  - “athermal” means that the effect occurs without any thermal activation
- It is a very strong effect in metals!

Damage recombination

- The reason to the recombination can be understood to be simply recrystallization.
- To what extent it occurs depends on the recrystallization rate of the material: if it is fast, the damage has time to recombine, if it is slower, not => liquid zone ‘freezes in’ into a disordered or amorphous region.
- The latter is typical in semiconductors, and also seen experimentally in at least Si, Ge and GaAs.

Si, TEM expt


Si, MD

[Diaz de la Rubia and Gilmer, Phys. Rev. Lett. 1995]
Damage recombination in ionic materials

- Ionic/ceramic materials are often somewhere in between metals and semiconductors
- Some recombination of damage, but disordered regions remain
- Large variations between different ionic materials!
  - Attempt to explain this:

### Damage in ceramics

#### Primary radiation damage in W vs. WC

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>5 keV</td>
<td>0.00014 ps</td>
</tr>
<tr>
<td>WC</td>
<td>5 keV</td>
<td>0.00014 ps</td>
</tr>
</tbody>
</table>

*Images showing the structure of W and WC at different times after a radiation event.*

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**Kai Nordlund (2010)**

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*Strålingsskador 2014 – Kai Nordlund*
Vacancy clustering in center

- The original picture of Brinkman is valid in one respect: the ballistic processes do press interstitial atoms to the outside of the cascade.
- At the end of the cascade, the behaviour can be understood by the recrystallization front of the cascade pressing the vacancies towards the center, resulting in the fact that one tends to have vacancy clusters in the center.
- This was shown explicitly in simulations of a Co/Cu bilayer system; vacancies tend to go to the side with the lower melting point (Cu), impurities on the other side (Co).

[Brinkman, 1954]

Surface effects: adatoms and sputtering

- For any irradiation event near the surface, a recoiling atom can instead of going into an interstitial atom, become an extra atom on the surface, an **adatom** (adatom/adatomi), or leave the material, **sputter** (förstoftas / sputrautua)

- Both effects are visible here:
Sputtering

The study of sputtering is a big topic in itself, and this is actually the oldest known radiation effect; it was first reported in [W. R. Grove. On the electro-chemical polarity of gases. Phil. trans. Roy. Soc. London, 142:87, 1852] and occurred regularly in cathode-ray tubes already in the 1800’s.

The sputtering is described by the sputtering yield (cf. section 2) = number of outcoming atoms / number of incoming particles.

Sputtering can also occur by electrons, especially in ionic materials, and even neutrons (although then the yields are extremely small).

Sputtering is in regular industrial use e.g. for making coatings.
Vacancy and interstitial clustering

- Thus there is a natural mechanism for vacancy clustering
- Interstitials also tend to cluster, but not as clearly
- Both vacancies and interstitial clusters can in some materials collapse directly into dislocation structures (more on these later)
- Now we can finally understand what is going on in this animation:
Resulting damage production

- If the damage production is counted purely by number of defects, it increases with nuclear damage energy (=recoil energy minus energy lost to electronic stopping)
- But due to recombination, increase is initially sublinear:

![Graph showing the number of Frenkel pairs vs. nuclear damage energy]
Resulting damage production

- Due to the athermal recombination, the damage production in metals is at high energies typically ~ a factor of 3 lower than that given by the Kinchin-Pease / NRT equations.
- This explains the behaviour shown in section 4:

![Simulations vs. Experiments](image)

[Strålningsskadorna 2014 – Kai Nordlund] [Nordlund et al, OECD PRD working group final report, in press]
Damage efficiency

- The difference between the true damage production and the NRT prediction is known as the cascade efficiency

- The new arc-dpa equation describes exactly this:

\[
N_{d,\text{arc-dpa}}(E) = \begin{cases} 
0 & \text{when } E < E_d \\
1 & \text{when } E_d < E < 2E_d / 0.8 \\
\frac{0.8E}{2E_d} \xi(E) & \text{when } 2E_d / 0.8 < E < \infty
\end{cases}
\]

\[
\xi(E) = \frac{1-c_{\text{arc-dpa}}}{(2E_d/0.8)^{b_{\text{arc-dpa}}}} E^{b_{\text{arc-dpa}}} + c_{\text{arc-dpa}}
\]

[Nordlund et al, OECD PRD working group final report, in press]
Alloy effects: mixing

- In an alloy, the heat spike can cause lots of mixing: it is very improbable that a liquid atom returns to its original position. If it does not, this is called (ion beam) mixing (*blandning* / *sekoitus*).

- Example:
  10 keV cascade in initially ordered Cu₃Au alloy
Mixing vs. damage production

- The result is that a cascade displaces a huge lot of atoms, but creates fairly few actual defects.
- The NRT value disagrees with both in metals!
  - The name “displacements-per-atom” for dpa is highly misleading, as it does not correspond to either damage or actual displaced atoms.

<table>
<thead>
<tr>
<th>Recoil energy (keV)</th>
<th># Frenkel pairs*</th>
<th>NRT damage (E_d = 25 eV)</th>
<th># Displaced atoms (mixing)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>1.8</td>
<td>6</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>6.4</td>
<td>26</td>
<td>370</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>126</td>
<td>3000</td>
</tr>
</tbody>
</table>

*Factors of 8 and 200 difference!*

*[MD data from: Nordlund et al, PRB 57 (1998) 7556]*
Surface effects by heat spikes

- If a heat spike intersects a surface, this can cause liquid flow of matter to the surface, and sputtering of massive clusters.
- It can also cause cratering or coherent displacement of atoms (dislocation loop punching towards the surface).

Ghaly and Averback, PRL 1994
Nordlund et al., Nature 1999
Nordlund, Physics World 2001
Surface effects by clusters

Cluster ion irradiation can lead to truly massive cratering
Breakup into subcascades

Finally, when the ion energy increases, the ion path starts to be so long due to the decreasing cross section, that there are regions with virtually no damage.

This behaviour is known as subcascade formation, and can also be deduced from BCA simulations.

Example: SRIM simulation of a single 100 keV Ar ion impact on Au, with a threshold energy of 10 eV.

Green regions are subcascades in between very little damage.
Subcascade breakdown threshold?

- The energy at which cascades supposedly fully break up into subcascades is known as the subcascade threshold energy.
- It is not entirely well defined, is stochastic, and depends on melting point and what quantity is measured (e.g. mixing or damage).
- In general, however, it clearly increases with density of material: e.g. in Si already 10 keV cascades are split into subcascades, whereas in W or Pt the threshold may be \( >\sim 100 \text{ keV} \).

Research ongoing

Swift heavy ion regime

- Finally, when the ion energy gets to the 100 keV/amu range
- Example: 100 MeV Xe -> Au, single SRIM trajectory
  - The swift heavy ion damage mechanism is dominated by the electronic stopping, and was discussed in section 4.
What should you have learned from this section?

- You understand how many-body collisions can be simulated with molecular dynamics (MD)
- You understand the basics of the MD algorithms
- You understand how many-body collisions lead to damage production
- You know the concept of thermal spikes and how damage is produced and recombined in them
- You understand qualitatively how damage is produced in different energy ranges
- You know the concepts of sputtering and surface cratering
- You know what subcascades are