MICROSTRUCTURAL EVOLUTION OF GRAPHITE UNDER IRRADIATION:
Large scale molecular dynamics simulations

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Framework: decommissioning of graphite from "UNGG"
- Graphite = moderator in "UNGG" → neutrons, temperature
- In 11 years of exploitation 2.6 dpa
- Activation of some impurities
  
i-graphite contains $^{14}\text{C}$ & $^{36}\text{Cl}$ (½ life: 5 500 & $3\times10^5$ years)

Foreseen Solutions:
- Decommissioning under water
- Treatment to eliminate $^{14}\text{C}$ & $^{36}\text{Cl}$, ($^3\text{H}$) interaction: graphite ↔ H$_2$O, O$_2$, CO$_2$…
- Graphite microstructure evolution under irradiation?

INTRODUCTION

Simulation of the primary damage with molecular dynamics simulations
1. Irradiated Graphite – state of the art

2. Primary damage: Displacement Cascades

3. Dose Effect: Point Defects Accumulations

4. Summary – Ongoing works
Question: Neutron damages in nuclear graphite?

Answers:
- Some review articles
  Heggie (2007)
  Marsden, Burchell and Fachinger (2012)

However, few data on Primary Damage State

- Two main scenarii proposed to describe radiation damages:
  1. Creation of point defects, then clustering via diffusion and dislocation formation
  2. Creation of point defects, then wrinkling, sliding, and dislocation formation (Heggie & Telling)
Study of Primary Damage with Molecular Dynamics

- **Code**: LAMMPS
- **Empirical potential**: LCBOP (bond-order)

- **Primary Damage**: *Displacement Cascades*
  - Primary Knock-on Atom: C
  - \( E_{\text{PKA}} = 0.5 \rightarrow 10 \text{ keV} \)
  - \( T = 300 \rightarrow 1000 \text{ K} \)
  - Statistics: 16 cascades / \( E_{\text{PKA}} \)

- **Dose Effects**: *Point Defects Accumulation*
  - Creation of random Frenkel pairs
  - Dose rate: \( 10^{10} \text{ dpa/s} \)
  - Dose: \( 0.1 \rightarrow 1 \text{ dpa} \)
  - \( 300 \rightarrow 1000 \text{ K} \) (relaxation NPT) \( \rightarrow \) Swelling
Example: Cascade with 5 keV PKA
Projectile C - direction [100] – 300 K

Three Steps:
1. Collision Stage : 2 ps
2. Thermal Spike : 5 ps
3. Relaxation : 10 ps

Damage:
- No Amorphisation
- Numerous Point defects
- Few Recombination
- No influence of the initial PKA orientation
- Number of vacancies ≈ interstitials

→ Point Defect Accumulation method
Dose effect from MD – Analysis from curvature criterion, HRTEM, SAED and XRD calculations

→ Visualization of defects in graphene planes (MD and HRTEM)
→ Visualization of wrinkles (MD analysis)
→ Swelling from size of box (not easy from XRD)
→ amorphisation at 0.10 dpa (SAED and XRD)
FRENKEL PAIR ACCUMULATION – DOSE EFFECT

Perfect graphene sheets in red and point defects in blue

Three Steps:

1. Point Defects

2. Pinning on small disordered cluster and Wrinkling of graphene sheets

3. Growth of amorphous pockets → Amorphisation
Common explanation: Decrease of graphene sheet’s size with increasing dose

→ small graphene sheets in “noodles shape”

Simulations show good agreement with experiments
SWELLING UNDER RADIATION

Expansion along the c-axis and shrinking of the graphene sheets

Interstitials pushing graphene sheets

Wrinkling of graphene sheets:

\[ c^4 \propto a \]

Tapasztó 2012 Nature Physics Letters
**Primary Damage**: Displacement Cascades

- Point Defects (large variety)
- Localized along PKA track
- \# Vacancies \approx \# Interstitials \rightarrow Frenkel pairs

**Dose effects**: Frenkel Pair Accumulation method

- Alternative scenario for Amorphisation in 3 steps:
  1. Point Defects
  2. Pinning + Wrinkling of graphene sheets
  3. Growth of amorphous pockets \rightarrow Amorphisation
- Swelling explained by both defects + wrinkling of graphene sheets

Carbon 91 (2015) 395-407
Study of radiation damages in polycrystalline graphite

- Interface and Porosity effect
- System approaching Nuclear Graphite

Result of a displacement cascade simulation in scale 1 crystallite of nuclear graphite. Formations of strongly wrinkled graphene sheets areas.

Schematic of the real nuclear graphite by Mironov et al. [Carbon 83 (2015) 106]
Thank you for listening

Questions ?

Challenge project – mtt7073
Basic principle

- Solve for every time steps and for all the particles the motion equations:

\[
M_i \frac{d^2 \vec{R}_i(t)}{dt^2} = \vec{F}_i(t) = \sum_{j \text{neighbour}} \frac{\partial V(R)}{\partial \vec{R}_{ij}}
\]

- \( V(r) \) interaction potential = modeling of the material

- \( \Rightarrow \) trajectories of all the particles in a thermodynamic ensemble (NVE, NVT, NPT)

- Characteristic Variables
  - \( \delta t = 10^{-15} \text{ sec} \rightarrow \sim 10 \text{ ns max} \)
  - \( 10^3 - 10^7 \) particles
LCBOP potential

Account for all the C-C hybridization: \( sp, sp^2, sp^3 \) and bond rotation

\[
E^{AIREBO} = \frac{1}{2} \sum_i \sum_{j \neq i} \left[ E^{REBO} + E^{LJ} + \sum_{k \neq i,j} \sum_{l \neq j,k} E^{torsion} \right]
\]

- Covalent bond
- Long range VdW
- Torsion

\[
E^{REBO} = V^{\text{Repulsive}}(r_{ij}) + b_{ij}(r_{ij}, N_{ijkl}, \theta_{ijk})V^{\text{Attractive}}(r_{ij})
\]

- \( b_{ij} \) term (bond-order) reveals the chemical surrounding of the i-j bond up to the 2\textsuperscript{nd} neighbor
Comparison between AIREBO and LCBOP potentials

<table>
<thead>
<tr>
<th></th>
<th>LCBOP</th>
<th>AIREBO</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>graphite</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_{CC}$ graphene (Å)</td>
<td>1,420</td>
<td>1,396</td>
<td>1,415 [1]</td>
</tr>
<tr>
<td>$r_{inter-layer}$ (Å)</td>
<td>3,354</td>
<td>3,354</td>
<td>3,354 [1]</td>
</tr>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>1049</td>
<td>1150</td>
<td>1060(20) [2]</td>
</tr>
<tr>
<td>$C_{66}$ (GPa)</td>
<td>445</td>
<td>-</td>
<td>439,96 [2]</td>
</tr>
<tr>
<td>$E_{bond}$ (eV)</td>
<td>7,374</td>
<td>7,472</td>
<td>7,374 [3]</td>
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<tr>
<td><strong>diamond</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$r_{CC}$ (Å)</td>
<td>1,544</td>
<td>1,540</td>
<td>1,544 [1]</td>
</tr>
<tr>
<td>$C_{11}$ (GPa)</td>
<td>1076</td>
<td>1120</td>
<td>1073(5) [4]</td>
</tr>
<tr>
<td>$C_{44}$ (GPa)</td>
<td>577</td>
<td>770</td>
<td>578(2) [4]</td>
</tr>
<tr>
<td>$E_{bond}$ (eV)</td>
<td>7,349</td>
<td>7,419</td>
<td>7,349 [3]</td>
</tr>
</tbody>
</table>

POINT DEFECTS WITH AIREBO

### Formation Energies - Vacancy (eV)

<table>
<thead>
<tr>
<th></th>
<th>AIREBO</th>
<th>VdW-DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(α)</td>
<td>8.13</td>
<td>8.62</td>
</tr>
<tr>
<td>V(β)</td>
<td>8.08</td>
<td>8.58</td>
</tr>
<tr>
<td>V2</td>
<td>10.75</td>
<td>13.7</td>
</tr>
</tbody>
</table>

$$E_f(X) = E_X - E_{bulk} - N\mu$$

Results AIREBO in agreement with VdW-DFT
Vacancies (~ sp) in small clusters
Interstitials (~ sp³) isolated, large variety

After 1 cascade:
only point defects
→ point defects accumulation method
**DISPLACEMENT CASCADES - DEFECTS**

- **Evolution of the damage zone's size**
  
  \[
  \text{Size (nm)} = 23 \times E^{1/2}
  \]

- **Evolution of the number of defects**
  
  - Damaged zone \( \propto \sqrt{E} \) \( \Rightarrow 40 \text{ keV} \approx 20 \text{ nm} \)
  - Ratio \( \text{sp} / \text{sp}^3 \approx 3 \) Frenkel pairs creation
  - Number of defects follows a linear law with energy (NRT) \( 40 \text{ keV} \approx 300 \) Frenkel pairs
  
  \( \rightarrow \) Frenkel Pair Accumulation Method can be used
Plains pinned by disordered amorphous zones

Graphene sheets are discriminated by local curvature
  → average curvature radius
  → size of graphene clusters
0.05 dpa

Vue of the basal plane

Basal plane with vacancies

Apply curvature criterion

Remaining graphene clusters
Apply curvature criterion

Observation of graphene sheets during damage accumulation

Damaged zone removed
Apply curvature criterion

Amorphous System
Three steps:
1. Point Defects
2. Pinning + Wrinkling
3. Amorphization
Defects / Wrinkling and Swelling

Deformation along axis \( c^4 \propto a \)

\( \rightarrow \) ondulations of graphene sheets

\[ Z^4 \propto X \]

Tapaszto 2012 Nature Physics Letters
Swelling → defects + wrinkling of graphene sheets
TEM images experimental & calculated

Experimental observation

Computation from atomic positions \((x_i, y_i, z_i)\) from simulations

Observed TEM Image

Calculated TEM Image

Experiment: Leyssale et al., Carbon 2012 and calculated with NCEMSS