Atomistic modeling of carbon fibers: Structural characterization and mechanical properties

Kaushik Joshi, Mikhail Arefev and Leonid Zhigilei
University of Virginia

Multiscale Modeling of Carbon Materials
August 20, 2018, Charlottesville, Virginia
Outline

• Carbon fiber properties and its processing
• Atomistic simulations of carbon fiber: brief review
• Atomistic approach for generating 2D and 3D microstructures of carbon fibers
• Computational tools for characterization of carbon fiber microstructures
  o Hybridization state of carbon and ring analysis
  o X-ray diffraction, crystallite size
  o Pore size-pore volume distribution
  o Graphitic and turbostratic nature of carbon fiber
• Atomistic simulations for prediction of mechanical properties of carbon fiber
• Future plans
Carbon fiber for vehicle technologies

- Growing use in automobile, aircraft, space and military applications
- Attractive alternative to metals
  - Lightweight
  - High strength to weight ratio
  - Excellent tensile strength and fatigue resistance
  - Excellent corrosion resistance and chemically stable
- Can be produced from different precursors like Polyacrylonitrile (PAN), pitch and cellulose
  - Carbon fibers from PAN
    - Highest in quality and most widely used
    - Expensive and complex chemical processing
  - Fiber from other precursors is lower in cost, but inferior in mechanical properties when compared with PAN fiber
Chemical processing involves multiple steps like oxidation, cyclization, carbonization and graphitization.

Ladder-like intermediate structures formed which further link to create fiber microstructure.

Fiber microstructure and mechanical properties sensitive to precursor and chemistry.

**How to use atomistic simulations to predict microstructure and mechanical properties of carbon fiber?**

Atomistic simulations of carbon fiber chemistry and properties

- ReaxFF reactive molecular simulations to investigate chemistry of PAN derived fibers
  - Formation of carbon sheets from PAN polymer
  - Chemistry of formation of different gases like $\text{NH}_3$, $\text{H}_2\text{O}$, $\text{O}_2$
  - Interactions between CNT and carbon fiber (physisorption and chemisorption)

- Molecular simulations to investigate effect of structural faults on strength of PAN derived fibers
  - Strength of fiber decreases with increase in misalignment
  - Fracture initiation occurs near misoriented crystallites

Saha, Furmanchuk, Dzenis, Schatz; *Carbon*, 94, 1015
Penev, Artyukhov, Yakobson; *Carbon*; 85; 2015
Atomistic simulations of carbon fiber microstructure

- Simplified models that assume ladder-like structures formed during chemical processing
- Ladder-like structure with saturated (sp\(^2\)) and unsaturated (reactive) carbon atoms
  - Non-reactive MD simulation for 2D microstructure
  - Reactive atoms converted into sp\(^2\) by creating bonds based on distance and angle-based cut-offs

![Ladder unit with reactive and non-reactive carbon atoms](image)

Randomly placed ladders

Cross-section of simulated microstructure

HRTEM image of carbon fiber cross-section

Desai, Li, Shen, Strachan; *J. Chem. Phys.*; 2017, 147, 224705

Kumar, Anderson, Grasto; *J. Mat. Sci.*; 28, 1993

- XRD pattern in reasonable agreement with experiments
2D microstructure of carbon fibers: Reactive ladders

- Ladder-like structure with saturated and unsaturated (reactive) carbon atoms

\[
\begin{align*}
\text{sp}^2 \text{ C atom} & \quad \text{Reactive C atom} \\
\end{align*}
\]

800 ladder units placed inside periodic box using PACKMOL

- 2.5 nm \times 14.5 \text{ nm} \times 14.5 \text{ nm}
- \rho \approx 1.76 \text{ g/cm}^3

- Instead of selectively forming bonds, reactive NPT-MD simulation using AIREBO potential

\[
\begin{align*}
14.2 \text{ nm} \times 14.3 \text{ nm} & \quad \rho \approx 1.78 \text{ g/cm}^3 \\
\end{align*}
\]

Kumar, Anderson, Grasto; J. Mat. Sci.; 28, 1993

XRD from AIREBO simulation

Desai, Li, Shen, Strachan; J. Chem. Phys.; 2017, 147, 224705
2D microstructure of carbon fibers: Hydrogenated ladders

- Generating 3D microstructure with reactive ladders still a challenge

2D microstructure of carbon fiber can be generated using idealized hydrogenated ladders
Generating 3D microstructure using hydrogenated ladders

- Change size, shape and orientation of ladder units to obtain different microstructure samples
- Perform 300 K MD-NPT simulation to obtain starting configuration

L1
L2

Ladders aligned along x-axis
No rotational constraints during packing

L1_L2_ns_na

XY view

21.5 nm × 7.1 nm × 7.1 nm
ρ = 1.37 g/cm³

YZ view

L1_L2_ns_xa

XY view

20.2 nm × 7.5 nm × 7.5 nm
ρ = 1.39 g/cm³

YZ view
Generating 3D microstructure using hydrogenated ladders

**L1_L2_s_xa**

XY view

24.6 nm × 8.1 nm × 6.8 nm  \( \rho = 1.33 \text{ g/cm}^3 \)

**L1_L2_s_xyza**

XY view

22.2 nm × 8.0 nm × 7.3 nm  \( \rho = 1.39 \text{ g/cm}^3 \)
Generating 3D microstructure using ReaxFF ring structures

- ReaxFF reactive MD simulation on cyclization and carbonization of PAN (from Dr. van Duin’s group, PSU)
- Screen out carbon structures with rings, 5-, 6-, 7- and 9-member rings
Simulation procedure for generation of 3D microstructures of carbon fibers

- Increase temperature from 300 K to 900 K and pressure to 0.3 GPa (compression)
- Remove H atoms at 900 K in following steps
  - First, delete armchair H atoms and perform NPT-MD for 50 ps to allow ladders to link along longitudinal/axial direction, allow pressure to relax to 1 atm along X-direction
  - Then, delete zig-zag hydrogen atoms. Perform MD-NVT for 50 ps, relax pressure from 0.3 GPa to 1 atm in Y and Z-direction
- After removing all hydrogen atoms, perform annealing simulation at 1 atm
  - Heat from 900 K to 2000 K in 125 ps
  - MD-NPT at 2000 K for next 250 ps
  - Quench from 2000 K to 300 K in 200 ps
Changes in carbon fiber structure and chemical state during MD simulation

- Density increases by 23% during deletion and annealing of fiber structure
- Experimental fiber density 1.74 - 1.96 g/cm³
- Development of analysis tools
  - Builds connection table using domain decomposition approach (indirect graph of the system),
  - Identify sp, sp² and sp³ carbons
  - For identifying cycles/rings, modified form of Depth First Search (DFS) algorithm. Currently, maximum ring size set to 9 edges
- During deletion of H atoms, increase in density due to conversion of sp carbon into sp² carbon
- sp² to sp³ conversion during high temperature annealing, significant amount sp³ corresponds to cross-linking

![Graphs showing changes in density and sp² to sp³ conversion over time](image)

**L1_L2_s_xa**

- Graphs showing changes in density (ρ) and sp², sp³ carbon content over time (T (ps))
- Graphs showing evolution of 6-member and non-6-member rings over time (T (ps))
3D microstructures of carbon fibers

- Atoms that are part of only 6-member rings are colored as green. Atoms that have at least one non 6-member ring colored as blue.

![ReaxFF_structure](image1)

1.63 g/cm³

![L1_L2_ns_na](image2)

1.64 g/cm³

![L1_L2_ns_xa](image3)

1.82 g/cm³

![L1_L2_s_xa](image4)

1.80 g/cm³

![L1_L2_s_xyza](image5)

1.93 g/cm³
Microstructure characterization: XRD

- XRD for identifying crystal structure and crystallite size
- Calculate structure factor (SF) by integrating radial distribution function, $g(r)$

$$g(r) = \frac{1}{4\pi N r^2 \rho_0} \sum_{i,j} \delta(r - r_{ij})$$

$$SF(Q) = 1 + 4\pi \int_0^\infty (g(r) - 1) r^2 \sin \left( \frac{Qr}{Qr} \right) W(r) dr$$

- SF of aligned 3D microstructures show $d_{002}$ peak which corresponds to interlayer separation in graphitic phase
- XRD in reasonable agreement with experiments
- Initial arrangement of ladders is important for generating better fiber samples

Kumar, Anderson, Grasto; J. Mat. Sci.; 28, 1993
Microstructure characterization: interlayer spacing $d_{002}$ and crystallite size

- Identify $d_{002}$ using Bragg’s law

$$d_{002} = \frac{\lambda}{2 \sin \theta}$$

- Calculate crystallite size ($L_c$) using Scherrer equation

$$L_c = \frac{\lambda}{\beta_s \cos \theta}$$

Measures crystallite size, $L_c$ along planes $d_{002}$

$\beta_s$ = full width at half peak maximum
$\theta$ = location of $d_{002}$ peak

- Estimated $d_{002}$ spacing higher than graphite (3.36 Å), indicates presence of turbostratic carbon

- For experimental samples with comparable densities (1.73-1.96 g/cm$^3$), crystallite size varies in range of 14 - 48 Å

- Bigger samples might provide bigger crystals

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Density (g/cm$^3$)</th>
<th>$2\theta$</th>
<th>$d_{002}$ (Å)</th>
<th>$L_c$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1_L2_ns_xa</td>
<td>1.82</td>
<td>24.91</td>
<td>3.64</td>
<td>12.96</td>
</tr>
<tr>
<td>L1_L2_s_xa</td>
<td>1.80</td>
<td>25.04</td>
<td>3.57</td>
<td>14.34</td>
</tr>
<tr>
<td>L2_L2_s_xyza</td>
<td>1.93</td>
<td>25.12</td>
<td>3.55</td>
<td>19.78</td>
</tr>
</tbody>
</table>
Microstructure characterization: pore size estimation

• Discretize simulated sample into rectangular grid, each cell 4Å × 4Å × 4Å (cell size can be varied if desired)
• Using atomic positions, identify empty cells and then perform cluster analysis to identify clusters of empty cells
• Tagged as a void only if two or more adjacent bins are empty

• Hard to estimate shape and size of voids from empty bin centers, additional analysis is needed
Microstructure characterization: pore size estimation

- To improving analysis further, identify edge bins of each void and then represent every void by edge surfaces.

[Diagram showing the process of identifying and connecting faces of voids and edge bins]
Microstructure characterization: pore size estimation

- To improving analysis further, identify edge bins of each void and then represent every void by edge surfaces

- Considerable amount of voids aligned along fiber axis

- Mixture of cylindrical voids and irregular shaped voids, bigger voids more likely irregular shaped
Microstructure characterization: pore size estimation

Snapshots of some individual voids

- Modified version of Breshenham’s line algorithm to identify pore size (commonly used for ray tracing in computer graphics)
- Faces of void edges used as extremities (can be replaced with atom coordinates closest to the face)

Characteristics:
- 0.4 nm³
- 0.9 nm³
- 6.1 nm³ (biggest void in sample)

Line passes through non-empty bins

Characteristic pore size
Microstructure characterization: Pore size distribution

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Density (g/cm³)</th>
<th>Maximum Pore Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1_L2_ns_na</td>
<td>1.64</td>
<td>4.4</td>
</tr>
<tr>
<td>L1_L2_ns_xa</td>
<td>1.82</td>
<td>6.0</td>
</tr>
<tr>
<td>L1_L2_s_xa</td>
<td>1.80</td>
<td>8.4</td>
</tr>
<tr>
<td>L1_L2_s_xyz</td>
<td>1.93</td>
<td>5.2</td>
</tr>
<tr>
<td>ReaxFF_structure</td>
<td>1.63</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Experimental pore size distribution

Ozcan, Vautard, Naskar; *Polymer Precursor-Derived Carbon*, 215; 2014
Microstructure characterization: Degree of graphitization

- Carbo fiber composed of graphitic and turbostratic carbon

\[
\text{Degree of graphitization, } g_p = \frac{d_{tc} - d_{002}}{d_{tc} - d_{gr}} \quad \text{ where: } \\
\begin{align*}
    d_{tc} &: \text{ d-spacing in turbostratic carbon} \\
    d_{002} &: \text{ d-spacing in graphite} \\
    d_{gr} &: \text{ d-spacing in graphite}
\end{align*}
\]

- Estimating d-spacing in turbostratic carbon is a challenge, varies in range 3.44 - 3.67 Å
- Alternatively, amount of graphitic carbon can be estimated using per atom energy

Hexagonal graphite crystal

- 3D microstructure was cooled to 1K
- Performed energy minimization for obtaining per atom energy
- Distribution obtained by calculating histogram with 100 bins

Energy of each carbon at 0K = -7.45 eV

Energy distribution for sample L1_L2_s_xa

- Per atom energy of C in graphite
Microstructure characterization: Degree of graphitization

- How to choose a cut-off for per atom energy for identifying graphitic carbon?
- Interaction energy as a function of interlayer separation in bilayer graphite

Interaction energy $\approx 30$ meV

O’Connor, Andzelm and Robbins;
*J. Chem. Phys*; 142; 2015
Microstructure characterization: Degree of graphitization

- How to choose a cut-off for per atom energy for identifying graphitic carbon?
- Interaction energy as a function of inter-layer separation in bilayer graphite

Interaction energy $\approx 30$ meV

Test 30 meV cut-off for ladder system (non-hydrogenated)

For ladder with stacked sheets, most of the carbon atoms get tagged as graphitic carbon

O’Connor, Andzelm and Robbins; *J. Chem. Phys*; 142; 2015
Microstructure characterization: Degree of graphitization

- How to choose a cut-off for per atom energy for identifying graphitic carbon?
- Interaction energy as a function of inter-layer separation in bilayer graphite

Interaction energy $\approx 30$ meV

Test 30 meV cut-off for ladder system (non-hydrogenated)

For ladder with stacked sheets, most of the carbon atoms get tagged as graphitic carbon

For ladder with single sheet of carbon, no graphitic carbon

Energy cut-off of 30 meV reasonable for identifying graphitic phase in carbon fiber microstructures

O'Connor, Andzelm and Robbins; J. Chem. Phys; 142; 2015
Microstructure characterization: Degree of graphitization

- Graphitic carbon atoms shown by blue color. Other carbon atoms shown as transparent for visualization purposes

\[ L1_{-}L2_{-}ns_{-}xa \]

\[ L1_{-}L2_{-}s_{-}xa \]

\[ L1_{-}L2_{-}s_{-}xyza \]

\[ \text{turbostratic carbon} = \text{sp}^2 \text{ carbon} - \text{Graphitic carbon} \]

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Density (g/cm(^3))</th>
<th>% Graphitic carbon</th>
<th>% sp(^2) carbon</th>
<th>% Turbostratic carbon</th>
<th>(L_c (\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L1_{-}L2_{-}ns_{-}na)</td>
<td>1.82</td>
<td>14.7</td>
<td>92.7</td>
<td>78.0</td>
<td>12.96</td>
</tr>
<tr>
<td>(L1_{-}L2_{-}s_{-}xa)</td>
<td>1.80</td>
<td>18.5</td>
<td>92.5</td>
<td>74.0</td>
<td>14.34</td>
</tr>
<tr>
<td>(L1_{-}L2_{-}s_{-}xyza)</td>
<td>1.93</td>
<td>31.2</td>
<td>95.0</td>
<td>63.8</td>
<td>19.78</td>
</tr>
</tbody>
</table>

- Graphitization in generated microstructures within experimental range (2\%- 34\%)
- Higher degree of graphitization for structures with stacked ladders than non-stacked ladders
- Degree of graphitization increases with increase in alignment
- Degree of graphitization correlated with crystallite size
Estimating longitudinal tensile strength of 3D microstructure

- Tensile testing of simulated sample
- Longitudinal modulus by stretching in x-direction, strain rate of $2.5 \times 10^8$ s$^{-1}$
Estimating longitudinal tensile strength of 3D microstructure

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Density (g/cm³)</th>
<th>Tensile modulus (GPa)</th>
<th>Tensile strength (GPa)</th>
<th>Tensile strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1_L2_ns_xa</td>
<td>1.82</td>
<td>230.4</td>
<td>18.2</td>
<td>7.9</td>
</tr>
<tr>
<td>L1_L2_s_xa</td>
<td>1.80</td>
<td>262.5</td>
<td>16.8</td>
<td>6.4</td>
</tr>
<tr>
<td>L1_L2_s_xyza</td>
<td>1.93</td>
<td>280.8</td>
<td>14.6</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Experimental measurements on PAN fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm³)</th>
<th>Filament diameter (µm)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
<th>Strain at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS4</td>
<td>1.79</td>
<td>6.1</td>
<td>4330</td>
<td>231</td>
<td>1.8</td>
</tr>
<tr>
<td>T700</td>
<td>1.80</td>
<td>7.0</td>
<td>4900</td>
<td>230</td>
<td>2.1</td>
</tr>
<tr>
<td>T1000</td>
<td>1.80</td>
<td>5.0</td>
<td>6370</td>
<td>294</td>
<td>2.2</td>
</tr>
<tr>
<td>IM10</td>
<td>1.79</td>
<td>4.2</td>
<td>6964</td>
<td>310</td>
<td>2.0</td>
</tr>
<tr>
<td>UHMS</td>
<td>1.88</td>
<td>5.0</td>
<td>3730</td>
<td>440</td>
<td>1.1</td>
</tr>
</tbody>
</table>

- Predicted tensile modulus within experimental range, modulus increases with increase in stacking and alignment
- Both tensile strength and tensile strain are higher than experiments
- Both nonaligned structures have Young’s modulus that is at least 3x lower than other samples
- Stress-strain curve indicates different failure mechanics for nonaligned microstructures
Structure-property relationship in carbon fibers

• Current computational capabilities can calculate microstructure parameters and mechanical properties

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Density (g/cm³)</th>
<th>(d_{002}(\text{Å}))</th>
<th>(L_c(\text{Å}))</th>
<th>% Graphitic carbon</th>
<th>% (sp^2) carbon</th>
<th>% Turbostratic carbon</th>
<th>Maximum pore size (nm)</th>
<th>Tensile modulus (GPa)</th>
<th>Tensile strength (GPa)</th>
<th>Tensile strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1_L2_ns_xa</td>
<td>1.82</td>
<td>3.64</td>
<td>12.96</td>
<td>14.7</td>
<td>92.7</td>
<td>78.0</td>
<td>6.0</td>
<td>230.4</td>
<td>18.2</td>
<td>7.9</td>
</tr>
<tr>
<td>L1_L2_s_xa</td>
<td>1.80</td>
<td>3.57</td>
<td>14.34</td>
<td>18.5</td>
<td>92.5</td>
<td>74.0</td>
<td>8.4</td>
<td>262.5</td>
<td>16.8</td>
<td>6.4</td>
</tr>
<tr>
<td>L1_L2_s_xyza</td>
<td>1.93</td>
<td>3.55</td>
<td>19.78</td>
<td>31.2</td>
<td>95.0</td>
<td>63.8</td>
<td>5.2</td>
<td>280.8</td>
<td>14.6</td>
<td>5.2</td>
</tr>
</tbody>
</table>

• Identify structure-property relationship in carbon fibers
• In-depth analysis on failure mechanism of each microstructure
Hybrid MD-kMC for incorporating chemistry in microstructure generation

- Currently, developing kMC tool that will allow us to include chemistry into atomistic calculations
- As a first step, delete atoms based on distance criteria

Perform MD simulation → Calculate distances ($r_{HH}$) between all H pairs → If $r_{HH} < \text{cut\_off}$, delete that pair

Current approach: Delete all H atoms at once

Hybrid MD-kMC approach: Delete only those H atoms for which $r_{HH} < \text{cut\_off}$

Can be used to delete $\text{H}_2$, $\text{O}_2$, $\text{N}_2$, NO and NH species
Hybrid MD-kMC for incorporating chemistry in microstructure generation

- Starting structure consists of stacked, aligned ladders, simulation procedure similar to earlier approach up to heating to 900K
- For kMC, 1.8 Å cut-off distance for atom deletion, distance checking after every 2.5 ps of NPT-MD at 900 K

Starting configuration

Configuration after 620 ps

Future directions:
- In addition to distance cut-off, incorporate kinetic effects using Arrhenius equation, $k = \frac{-\Delta E}{kT}$
- Compare microstructures obtained from previous approach and from hybrid MD-kMC approach
- Perform simulations on ladder containing C, N, O and H atoms
Summary

• We have developed the computational framework for generating 3D realistic microstructures of carbon fibers

• Computational tools for characterizing microstructures:
  o Hybridization state of carbon and ring analysis
  o X-ray diffraction pattern, crystallite size and d-spacing
  o Pore size-pore volume distribution
  o Graphitic and turbostratic carbon

• Tested generated samples for mechanical properties like Young’s modulus, tensile strength and tensile strength

• Future directions
  o Identify the structure-property relationship and identify the mechanics of failure of different microstructures
  o Development of hybrid MD-kMC approach to incorporate reaction chemistry in generation of 3D microstructures from different precursors
Questions??