Multiscale Modeling of UHTC: Thermal Conductivity

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NASA Fundamental Aeronautics Program (FAP)
NASA Innovative Partners Program (IPP)
New materials modeling: interdisciplinary
  • Computational chemistry
  • Computational physics
  • Computational engineering

Ablative composites
  • Application: atmospheric re-entries
  • Materials: PICA, Avcoat, ...

Ultra high temperature ceramics (UHTC)
  • Applications: leading edges
  • Materials: ZrB$_2$ and HfB$_2$

UHTC modeling illustrate our approach
**UHTC for Sharp Leading Edges**

*Sharp leading edge for hypersonic aircraft*
- Enhances vehicle performance
- Improves safety

*Higher temperature requirements*
- Shuttle RCC leading edge: T~1650C
- Sharp leading edged vehicles: T>2000C

*UHTC advantages for sharp leading edges*
- Reasonable mechanical properties
- Oxidation resistance
- *High thermal conductivity*
  - Effective thermal radiation
  - Thermal shock resistance

Materials modeling will:
- Discover fundamental mechanisms
- Structure-property relationships
- Design new materials
- Accelerate material development

Framework integrates three methods:
- \textit{Ab initio} – fundamental chemistry
- \textit{Atomistic} – thermal/mechanical
- \textit{Continuum} – macro properties

This talk focuses on thermal conductivity
- Atomic structure and bonding
- Interatomic potential development
- Lattice thermal conductivity simulations
- Grain boundary thermal resistance
- Imaged based FEM of GB networks
UHTC: $\text{ZrB}_2$ and $\text{HfB}_2$

Alternating layers of Zr/Hf (red) and Boron (gray)

Graphitic Boron layers with Zr/Hf over each ring
Electron Localization Function (ELF)

**Covalent** bonding in Boron plane

**Metallic** bonding in Zr planes

**Ionic** bonding between Interlayers

Blue = High
Red = Low

Fundamental Properties: $\text{ZrB}_2 \& \text{HfB}_2$

Electronic properties essentially identical

Vibrational differences due to Zr/Hf mass difference
**Tersoff Bond Order Potential**

- **Two body terms** \((A, \lambda, B, \mu)\) energy

\[
E = \sum_{i \neq j} \left[ f_R^{[ij]}(d_{ij}) + b_{ij} f_A^{[ij]}(d_{ij}) \right]
\]

\[
f_R^{[ij]}(d) = A_{ij} \exp(-\lambda_{ij}d)
\]

\[
f_A^{[ij]}(d) = -B_{ij} \exp(-\mu_{ij}d)
\]

- **Bond order** \((\beta, \lambda_3, n, m)\)

\[
b_{ij} = (1 + \beta_i^n \zeta_{ij}^{n_i})^{-\frac{1}{2n_i}}
\]

\[
\zeta_{ij} = \sum_{k \neq i,j} f_C^{[ij]}(r_{ik}) \gamma_{ijk} g_i(\theta_{ijk}) \exp[\lambda_{3i}(d_{ij} - d_{ik})^{m_i}]
\]

- **Angular function** \((c, d, h)\)

\[
g_i(\theta) = 1 + c_i^2 / d_i^2 - c_i^2 /[d_i^2 + (h_i - \cos \theta)^2]
\]

Daw, JL and Bauschlicher, Comp. Mat. Sci., (2011)
Lattice Thermal Conductivity

• Green-Kubo thermal conductivity tensor

\[
\kappa_{\mu\nu} = \frac{1}{Vk_B T^2} \int_0^\infty \left\langle J_\mu (\tau) J_\nu (0) \right\rangle d\tau
\]

• Heat current \( J(x_i, v_i) \), energy \( e_i \), stress-tensor \( S_i \)

\[
J = \frac{1}{V} \left[ \sum_i e_i v_i - \sum_i S_i v_i \right]
\]

\[
J = \frac{1}{V} \left[ \sum_i e_i v_i + \frac{1}{2} \sum_{i<j} (f_{ij} \cdot (v_i + v_j)) \cdot x_{ij} \right]
\]

Monoatomic systems (e.g. Si) have monoatomic decay

- ZrB$_2$ has longer period than HfB$_2$ at T=300K
- ZrB$_2$ at T=1000K has longer period than T=300K

Correlation Function Power Spectra

- Correlations oscillates with metal-B optical modes
- $C_{xx}$ and $C_{yy}$ oscillate with in-plane mode frequency
- $C_{zz}$ oscillates with out-of-plane mode frequency
Lattice Thermal Conductivity: ZrB$_2$

- 8 independent, 10 ns simulations, $T=300K$
- 8x8x16 unit cell, 12,255 atoms
- $\kappa_{xx} = 60$ W/(m.K), $\kappa_{zz} = 40$ W/(m.K)
Lattice Thermal Conductivity: HfB$_2$

- 8 independent, 10 ns simulations
- 8x8x16 unit cell (12 atoms) = 12,255 atoms
- $\kappa_{xx} = 76 \text{ W/(m.K)}$, $\kappa_{zz} = 65 \text{ W/(m.K)}$
Thermal Conductivity vs Temperature

- 8 independent, 10 ns simulations for each point
- Data fit to 1/T curves
Single Crystal ZrB$_2$ Data

• Electron & lattice thermal conductivity

\[ K = K_e + K_{lat} \]

• \( K_{lat} \) is 0.3\( \kappa \) from polycrystalline data

• Single crystal data
  • \( \kappa_{xx} = 140 \text{ W/mK}, \kappa_{zz} = 100 \text{ W/mK} \)
  • 1 sample, 1 measurement
  • Defects uncharacterized
  • \( \kappa_{xx} = 45 \text{ W/mK}, \kappa_{zz} = 30 \text{ W/mK} \) (lattice)

• More data needed for ZrB$_2$ and HfB$_2$

UHTC Grain Boundaries

$\Sigma 7$ symmetric \textit{tilt} (graphene GB structure)

$\Sigma 7$ symmetric \textit{twist}

Full \textit{ab initio}/MD analysis of two \textit{tilt} and two \textit{twist} boundaries

Swap atoms to create heat source/sink

\[ Q = \sigma_K \Delta T \]

\( \sigma_K \) is the Kapitza conductance

Simulation Results

Interface Conductance

- Very high thermal conductance (very low resistance)
- Experimental data indicate much lower values
- Not surprising given pristine grain boundaries
- Need: improved processing for improved GB properties
- Need: modeling more complex boundaries

<table>
<thead>
<tr>
<th></th>
<th>$\gamma$ (meV/Å²)</th>
<th>$\Delta_z$ (Å)</th>
<th>$\gamma$ (meV/Å²)</th>
<th>$\Delta_z$ (Å)</th>
<th>$\sigma_K$ (GW/(m²·K))</th>
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<tr>
<td>c-tilt</td>
<td>153(369)</td>
<td>-</td>
<td>112(238)</td>
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<td>0.58</td>
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<td>107(1380)</td>
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<td>212(1230)</td>
<td>-</td>
<td>118(1430)</td>
<td>-</td>
<td>0.55/0.53</td>
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</table>

TABLE I: Energetics and thermal conductance for ZrB$_2$ grain boundary structures from empirical potentials (DLB/Pot 1) and ab initio/DFT. Units for $\gamma$ are meV/Å², $\Delta_z$ are Å and $\sigma_K$ are GW/(m²·K).
Experimental Results: Polycrystalline ZrB$_2$

At 300K, $\kappa_{\text{tot}} = 55$ W/mK, $\kappa_e = 33$ W/mK, $\kappa_{\text{lat}} = 22$ W/mK

Microstructural Model: ZrB$_2$

What is the effect of grain boundary network on thermal conductivity?

Estimate with Brick Layer Model

\[
\frac{1}{\kappa_{\text{eff}}} = \frac{1}{\kappa_0} + \frac{R_K}{d}
\]

- \( \kappa_{\text{eff}} = 48 \text{ W/mK} \)
- \( \kappa_0 = 50 \text{ W/mK} \)
- \( R_K = 1 \text{ m}^2\text{K/GW} \)
- \( d = 6 \mu\text{m} \)

Very small reduction using MD resistances and BLM!

Imaged based FEM

- Larger reduction with realistic structures and parameters?
- Realistic microstructure
- Finite element mesh from OOF2
- MD thermal conductivity for grains
- Experimental interface resistance

Development of Steady State

Uniform thermal gradient (UTG) applied vertically across structure
Effective Thermal Conductivity

- Boundary conditions
  - Uniform temperature gradient (UGT)
  - Uniform heat flux (UHF)
- Transport direction
  - Vertical
  - Horizontal
- Evaluate effective properties

\[
\langle q \rangle = -k_{\text{eff}} \cdot \langle \nabla T \rangle
\]

- Is microstructure “representative”???

\[
K_{\text{UHF}} \leq K \leq K_{\text{UTG}}
\]
### Effective Thermal Conductivity

<table>
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<tr>
<th>BC Type</th>
<th>Parameter</th>
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<th>Horizontal</th>
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<tr>
<td></td>
<td>$\kappa_{\text{eff}}$</td>
<td><strong>16.72</strong></td>
<td><strong>15.93</strong></td>
</tr>
</tbody>
</table>

**Comparison of results:**
- BLM $\kappa_{\text{eff}} = 15.4$ (series model)
- Rule of mixtures $\kappa_{\text{eff}} = 44.14$ (parallel model)
- FEM has series and parallel contributions
- BLM has very good agreement with FEM
Conclusions

• NASA ARC computational materials modeling:
  • Ablative composites
  • Ultra high temperature ceramics

• Multiscale framework for UHTC:
  • *Ab Initio* – bonding, electronic & vibrational spectra
  • Atomistic simulation – bulk and interfacial thermal conductivity
  • Continuum – microstructural modeling and effective properties
  • Iteration with experiment needed to “close” loop

• Modeling unanswered questions:
  • Interatomic potential fidelity
  • Complex grain boundary structural models and properties

• Experimental unanswered questions:
  • Single crystal thermal conductivity
  • Electronic vs lattice carrier breakdown
  • Grain boundary atomic structures and properties
  • Improved grain boundaries from improved processing