Lattice Thermal Conductivity from Atomistic Simulations: ZrB$_2$ and HfB$_2$

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NASA Innovative Partners Program (IPP)
Overview

- Motivation and applications
- Multiscale materials modeling
- Atomic structure
- Interatomic potentials
- Simulations of lattice thermal conductivity for ZrB$_2$ and HfB$_2$
- Comparison to experiments
UHTC for Sharp Leading Edges

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

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

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

Multiscale Modeling of UHTC

- Framework integrates three methods
- Multiscale framework for ZrB$_2$ and HfB$_2$:
  - *Ab initio* – fundamental chemistry, electronic structure impact on basic material properties
  - *Atomistic* – thermal/mechanical properties, adhesion and thermal resistance of grain boundaries, fracture
  - *Continuum* – macro properties, thermal/mechanical analysis of microstructure
- This talk focuses on atomistic methods
  - Development of interatomic potentials
  - Lattice thermal conductivity simulations
  - Other topics presented elsewhere

JL, Daw, Squire and Bauschlicher, (2012), submitted
Atomic Structure: $\text{ZrB}_2$ and $\text{HfB}_2$

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

Graphitic Boron layers with Zr/Hf over each ring
Fundamental Properties: ZrB$_2$ & HfB$_2$

**Electronic Properties**
- Essentially identical

**Vibrational Spectra**
- Acoustic modes carry heat.
- Optical modes are resistive.

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** \((\beta, \lambda_3, n, m)\)

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

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

- **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)
First Step: Zr Potential

- Zr potential exists
- Developed new Zr potential
- Fit to *ab initio* database of crystal structures

### Property(units) | Target | New | WM2
--- | --- | --- | ---
$a_0$(FCC) (A) | 4.530 | 4.510 | 4.532
$E_0$(FCC) (eV) | -6.160 | -6.159 | -6.127
$B$(FCC) (eV/A$^3$) | 0.578 | 0.5899 | 0.6011
$B'$(FCC)(eV/A$^4$) | -0.8160 | -1.635 | -1.948
$C_{11}$(FCC)(eV/A$^3$) | 0.7740 | 0.6885 | 0.7404
$C_{12}$(FCC)(eV/A$^3$) | 0.4810 | 0.5405 | 0.5314
$C_{44}$(FCC)(eV/A$^3$) | 0.3560 | 0.5307 | 1.395
$E_{vac}$(FCC)(eV) | 2.500 | 6.072 | 8.338
$a_0$(HCP) (A) | 3.230 | 3.159 | 3.231
$E_0$(HCP) (eV) | -6.180 | -6.242 | -5.826
$E_0$(BCC) (eV) | -6.050 | -6.159 | -5.960

Williame and Massobrio, PRB 43 (1991), 11653
Second Step: Boron Potential

- No published Boron potentials
- Boron is *electron “deficient”*
- Boron may be “*frustrated”*
- Fit to simple structures

<table>
<thead>
<tr>
<th>Structure</th>
<th>Property</th>
<th>Target</th>
<th>Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hex sheet</td>
<td>$a_0$</td>
<td>2.91</td>
<td>2.89</td>
</tr>
<tr>
<td></td>
<td>$E_0$</td>
<td>-5.15</td>
<td>-5.08</td>
</tr>
<tr>
<td></td>
<td>$E_0''$</td>
<td>11.35</td>
<td>7.98</td>
</tr>
<tr>
<td>Tri sheet</td>
<td>$a_0$</td>
<td>1.70</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>$E_0$</td>
<td>-5.71</td>
<td>-5.75</td>
</tr>
<tr>
<td></td>
<td>$E_0''$</td>
<td>21.73</td>
<td>27.06</td>
</tr>
<tr>
<td>SC</td>
<td>$a_0$</td>
<td>1.88</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>$E_0$</td>
<td>-5.33</td>
<td>-5.21</td>
</tr>
<tr>
<td></td>
<td>$E_0''$</td>
<td>24.50</td>
<td>24.51</td>
</tr>
<tr>
<td>FCC</td>
<td>$a_0$</td>
<td>2.86</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>$E_0$</td>
<td>-5.07</td>
<td>-5.22</td>
</tr>
<tr>
<td></td>
<td>$E_0''$</td>
<td>21.85</td>
<td>12.28</td>
</tr>
</tbody>
</table>

Ogitsu et al, JACS 131 (2009) 1903
Third Step: ZrB$_2$ Potentials

- Zr-Zr parameters fixed
- B-B parameters fixed
- Zr-B fit to small database
- Pot A = “new Zr” + B
- Pot B = WM2 + B
- *Will Boron planes stay flat?*

### Fitting Results

<table>
<thead>
<tr>
<th>Property</th>
<th>Target</th>
<th>Pot A</th>
<th>Pot B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$(A)</td>
<td>3.170</td>
<td>3.143</td>
<td>3.140</td>
</tr>
<tr>
<td>$c_0$(A)</td>
<td>3.550</td>
<td>3.547</td>
<td>3.547</td>
</tr>
<tr>
<td>$E_0$(eV)</td>
<td>-21.70</td>
<td>-21.29</td>
<td>-21.55</td>
</tr>
</tbody>
</table>

Stable, multilayered system with **flat, hexagonal** Boron sheets!
Lattice Thermal Conductivity

• Green-Kubo thermal conductivity tensor

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

• 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
- $\text{ZrB}_2$ has longer period than $\text{HfB}_2$ at $T=300\text{K}$
- $\text{ZrB}_2$ at $T=1000\text{K}$ has longer period than $T=300\text{K}$
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
Experimental Data Comparison

- Polycrystalline ZrB$_2$
  - $\kappa_e = 33$ W/mK, $\kappa_{lat} = 22$ W/mK
  - $\kappa_{lat} \sim 0.3 \kappa_{tot}$
- Single crystal ZrB$_2$
  - $\kappa_{xx} = 140$ W/mK, $\kappa_{zz} = 100$ W/mK
  - 1 sample, 1 measurement
  - defects uncharacterized
  - $\kappa_{xx} = 45$ W/mK, $\kappa_{zz} = 30$ W/mK
- Data needed for ZrB$_2$ and HfB$_2$
- *Simulation data reasonable at 300K but too low for higher T*

\[ K = \kappa_e + \kappa_{lat} \]

Conclusions

• Atomistic simulations for ZrB$_2$ and HfB$_2$:
  • Developed first interatomic potentials for UTHC
  • Lattice thermal conductivity using Green-Kubo formalism
  • Heat current correlation function oscillations
  • Thermal conductivity versus temperature
  • Reasonable agreement with experiment

• Modeling unanswered questions:
  • Interatomic potential fidelity
  • Lattice TC without potentials (\textit{ab initio}, Boltzmann,…)
  • Conducting versus resistive vibrational modes
  • Isotope and defect effects
  • Interface thermal resistance: grain boundaries *

• Experimental unanswered questions:
  • Single crystal characterization and thermal conductivity
  • Electronic versus lattice thermal conductivity

* JL, Daw, Squire and Bauschlicher, (2012), submitted
Extra Slides
ZrB$_2$ Potential Curves

### Test Results

<table>
<thead>
<tr>
<th>Properties</th>
<th>Ab Initio</th>
<th>Pot A</th>
<th>Pot B</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{11}$</td>
<td>556</td>
<td>365</td>
<td>422</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>57</td>
<td>156</td>
<td>156</td>
</tr>
<tr>
<td>C$_{13}$</td>
<td>113</td>
<td>173</td>
<td>171</td>
</tr>
<tr>
<td>C$_{33}$</td>
<td>419</td>
<td>307</td>
<td>320</td>
</tr>
<tr>
<td>C$_{44}$</td>
<td>234</td>
<td>106</td>
<td>119</td>
</tr>
<tr>
<td>B</td>
<td>233</td>
<td>227</td>
<td>240</td>
</tr>
<tr>
<td>G</td>
<td>226</td>
<td>98</td>
<td>118</td>
</tr>
<tr>
<td>A(=C$<em>{33}$/C$</em>{11}$)</td>
<td>0.75</td>
<td>0.84</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Properties **not** included in fit

VASP = *ab initio* code
Physics of Lattice Thermal Conductivity

- \( \kappa = \rho \ C \ n \ l_{\text{mfp}} \)
  - scattering restricts \( l_{\text{mfp}} \)
- **Region I:** \( \kappa \sim T^3 \)
  - dilute phonons
  - boundary scattering
  - quantum statistics
- **Region II:** \( \kappa_{\text{max}} \)
- **Region III:** \( \kappa \sim 1/T \)
  - high phonon density
  - phonon, pt. defect scattering
- **Region IV:** \( \kappa_{\text{min}}, \ l_{\text{mfp}} = "a" \)

Summary

• No atomistic simulations for $\text{ZrB}_2$ due to lack interatomic potentials
• Potentials are prerequisite for atomistic simulations of mechanical and thermal properties
• We developed such potentials for ZrB$_2$
• $\text{ZrB}_2$ potentials give stable structures with flat, hexagonal $B$ planes
• We performed the first atomistic simulations for these materials
• Lattice thermal conductivity was evaluated for single crystals
• Reasonable agreement with experiments

• **Future/current work:**
  • Grain boundaries: energetics and thermal interface resistance
  • Integration into multiscale framework
  • Potentials and applications for Hf and HfB$_2$

JL, Daw, Squire and Bauschlicher, (2012), submitted