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~1650C
- Sharp leading edged vehicles: T>2000C

*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: ZrB$_2$ and 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 Spectra**

- Total
- Zr d
- B p
- B s

Electronic properties essentially identical

**Vibrational Spectra**

- Zr/Hf modes
- B modes

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** \((\beta, \lambda_{3}, n, m)\)

\[
b_{ij} = (1 + \beta_{i}^{n_{i}} \zeta_{ij}^{n_{i}})^{-\frac{1}{2n_{i}}}
\]

\[
\zeta_{ij} = \sum_{k \neq i, j} f_{C}^{[ik]}(r_{ik}) \gamma_{ijk} g_{i}^{(\theta_{ijk})} \exp[\lambda_{3i}(d_{ij} - d_{ik})^{m_{i}}]
\]

- **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

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

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>

\(\beta\)-Boron (N=105)  \(\alpha\)-Boron (N=12)  Crumpled Sheet

Ogitsu et al, JACS 131 (2009) 1903
**Third Step: ZrB₂ 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?*

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**Fitting Results**

<table>
<thead>
<tr>
<th>Property</th>
<th>Target</th>
<th>Pot A</th>
<th>Pot B</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₀(A)</td>
<td>3.170</td>
<td>3.143</td>
<td>3.140</td>
</tr>
<tr>
<td>c₀(A)</td>
<td>3.550</td>
<td>3.547</td>
<td>3.547</td>
</tr>
<tr>
<td>E₀(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

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

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

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

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

Heat Current Correlation Function

- 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
- $\kappa_{xx}=60 \, \text{W/}(\text{m.K})$, $\kappa_{zz}=40 \, \text{W/}(\text{m.K})$
Lattice Thermal Conductivity: HfB$_2$

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

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

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 (*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 = \textit{ab initio} code
Physics of Lattice Thermal Conductivity

\[ \kappa = \rho C v l_{\text{mfp}} \]
- 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: \( \kappa_{\text{min}} \), \( l_{\text{mfp}} = \text{a} \)

Summary

- No atomistic simulations for ZrB$_2$ due to lack interatomic potentials
- Potentials are prerequisite for atomistic simulations of *mechanical* and *thermal* properties
- We developed such potentials for ZrB$_2$
- 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