Lattice Thermal Conductivity from Atomistic Simulations: ZrB_2 and HfB_2

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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
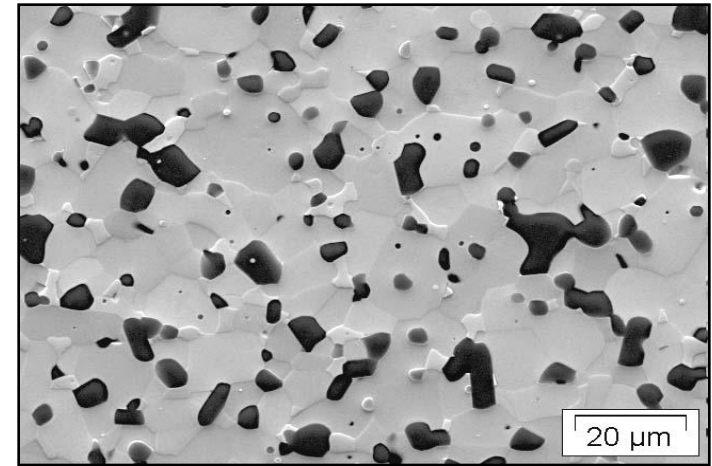- Improves safety

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
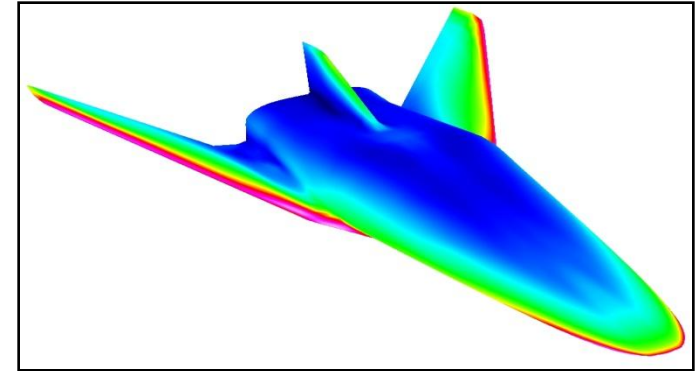

Leading edges of hypersonic vehicle

20 µm

SEM image of UHTC microstructure

Gasch, Johnson and Marschall, J. Am. Ceram. Soc. 91, 1423, (2008)

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
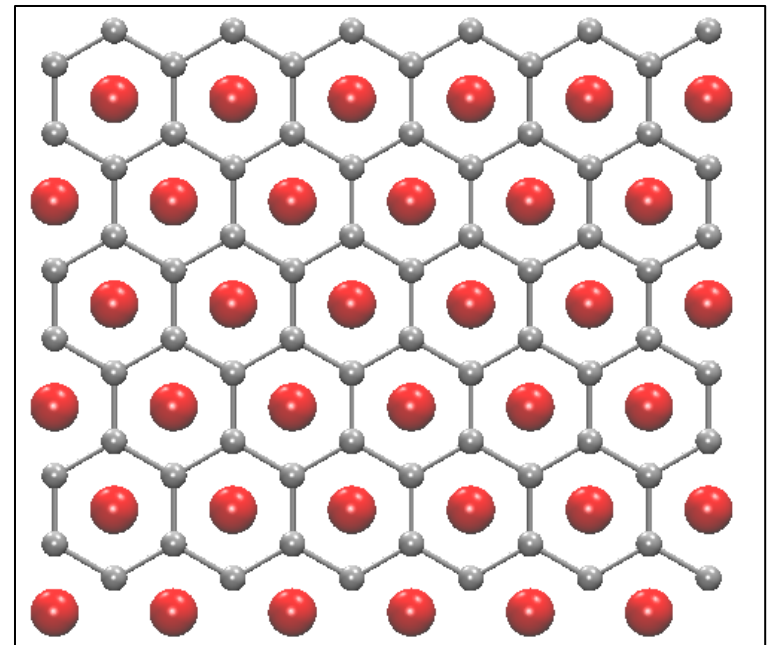 - Other topics presented elsewhere

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

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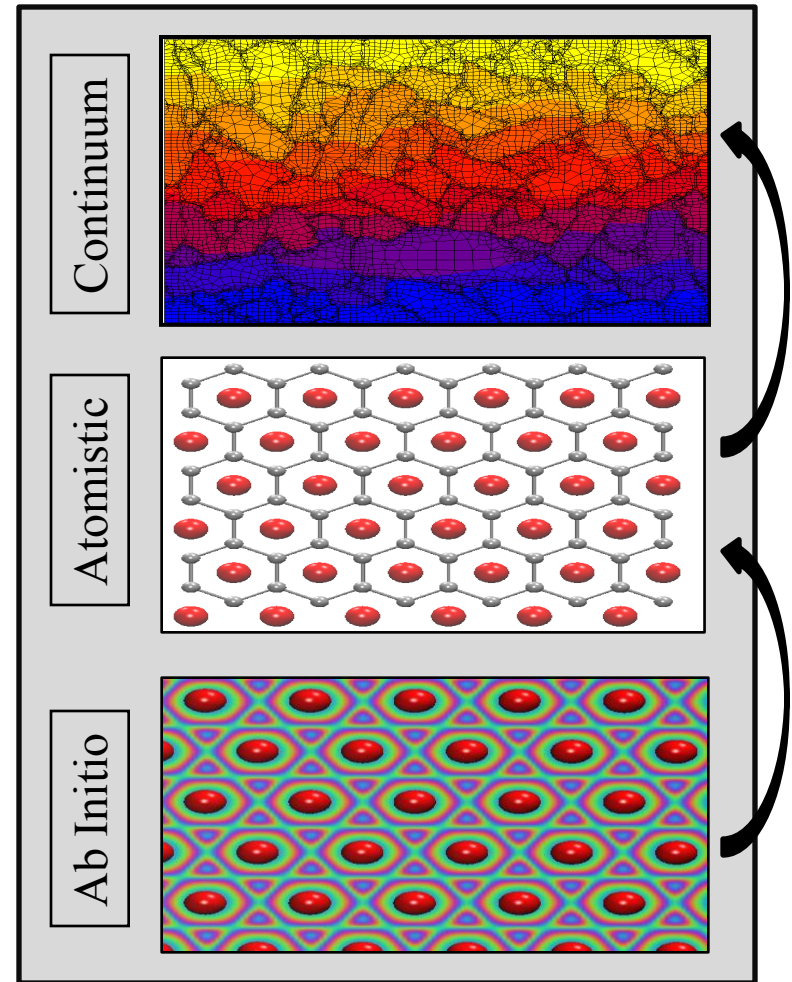
Atomic Structure: ZrB_2 and HfB_2
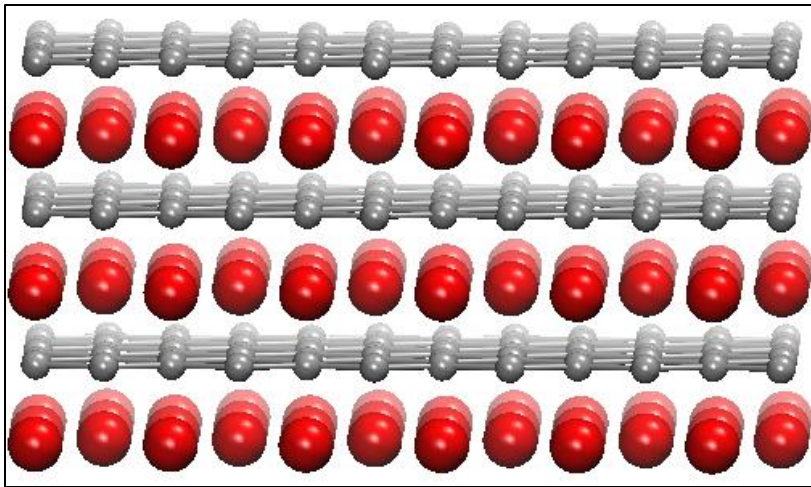
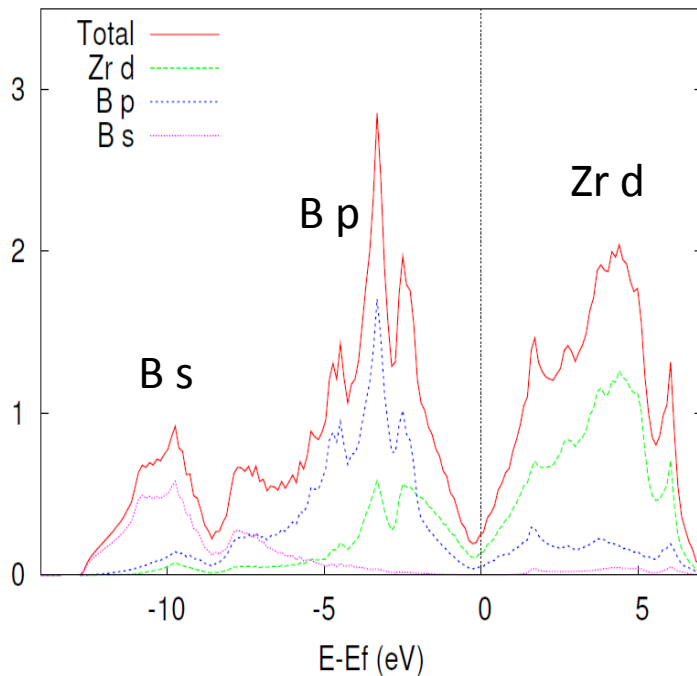Alternating layers of
Zr/Hf (red) and Boron (gray)

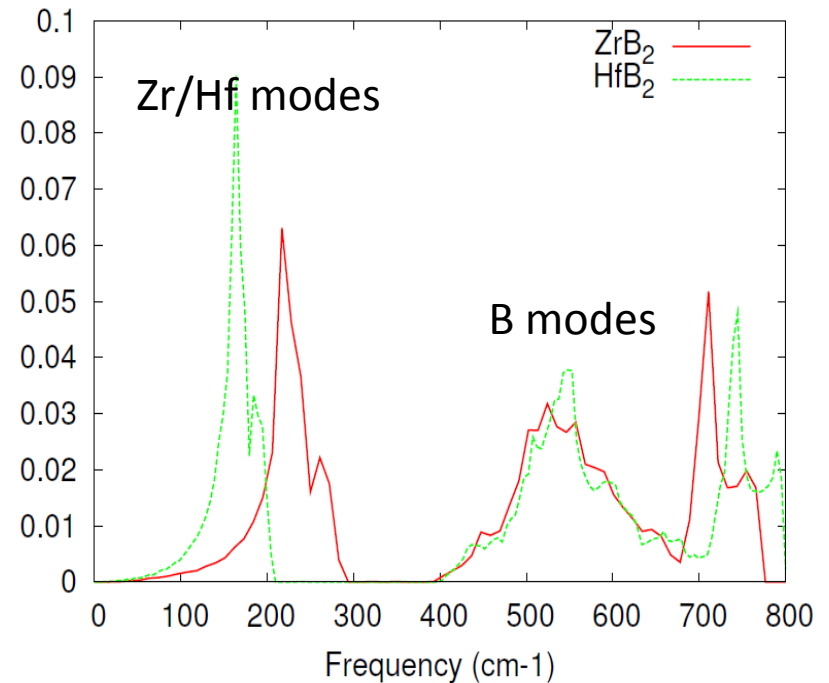Graphitic Boron layers
with Zr/Hf over each ring

Fundamental Properties: ZrB_2 & HfB_2

Electronic Spectra

Electronic properties essentially identical

Vibrational Spectra

Acoustic modes carry <u>heat</u>.
Optical modes are <u>resistive</u>.

JL, Bauschlicher and Daw, J. Am. Ceram. Soc., (2011)

Tersoff Bond Order Potential

- <u>Two body terms</u> (A, λ, B, μ) energy

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

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

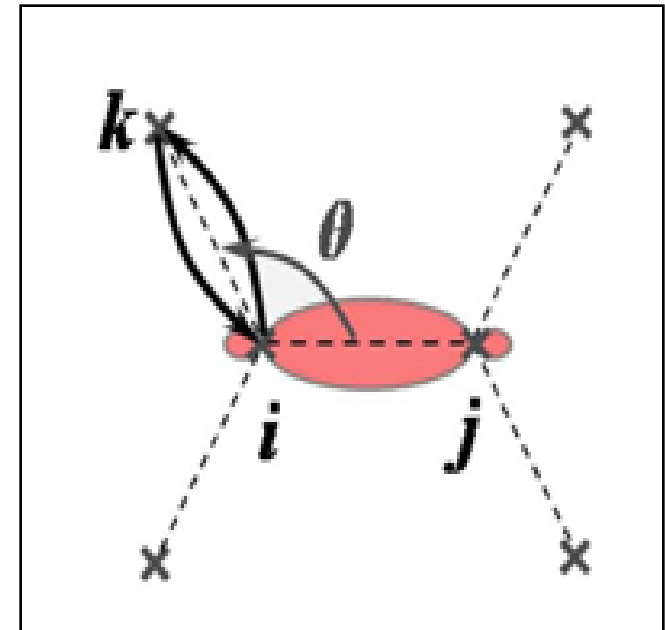$$f_A^{[ij]}(d) = -B_{ij} \exp(-\mu_{ij} d)$$

- <u>Bond order</u> (β, λ_3, n, m)

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

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

- <u>Angular function</u> (c, d, h)

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

Interatomic Energy

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

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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

FCC

HCP
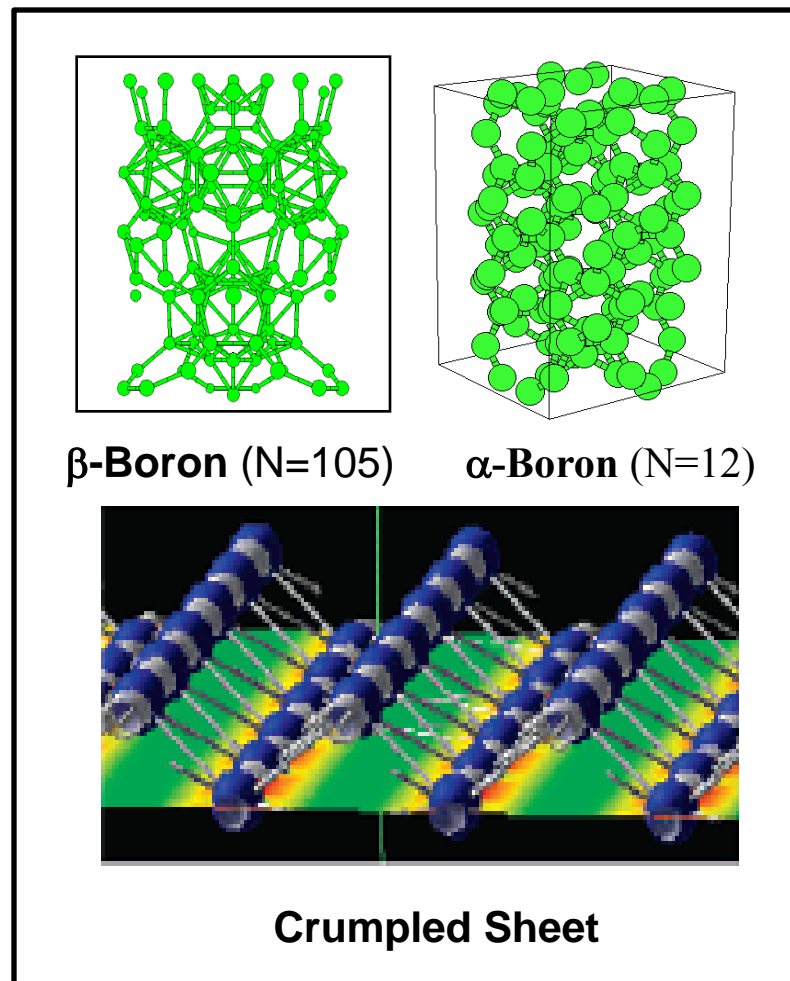
BCC

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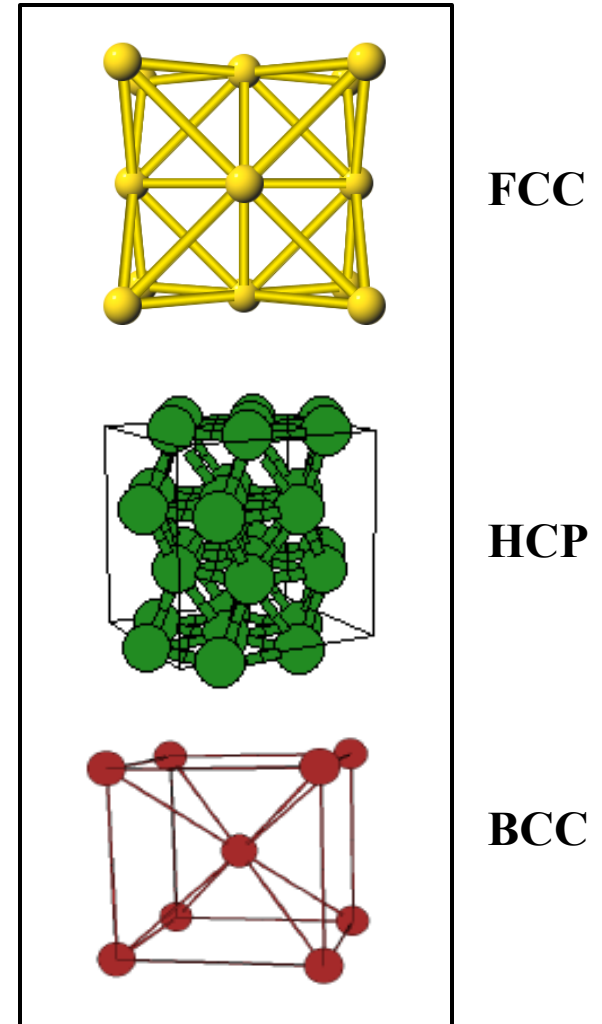
Second Step: Boron Potential

- No pubished Boron potentials
- Boron is *electron "deficient"*
- Boron may be *"frustrated"*
- Fit to simple structures

Structure	Property	Target	Fit
Hex sheet	a_0	2.91	2.89
	E_0	-5.15	-5.08
	E_0''	11.35	7.98
Tri sheet	a_0	1.70	1.81
	E_0	-5.71	-5.75
	E_0''	21.73	27.06
SC	a_0	1.88	1.84
	E_0	-5.33	-5.21
	E_0''	24.50	24.51
FCC	a_0	2.86	2.84
	E_0	-5.07	-5.22
	E_0''	21.85	12.28

β-**Boron** (N=105) α-**Boron** (N=12)

Crumpled Sheet
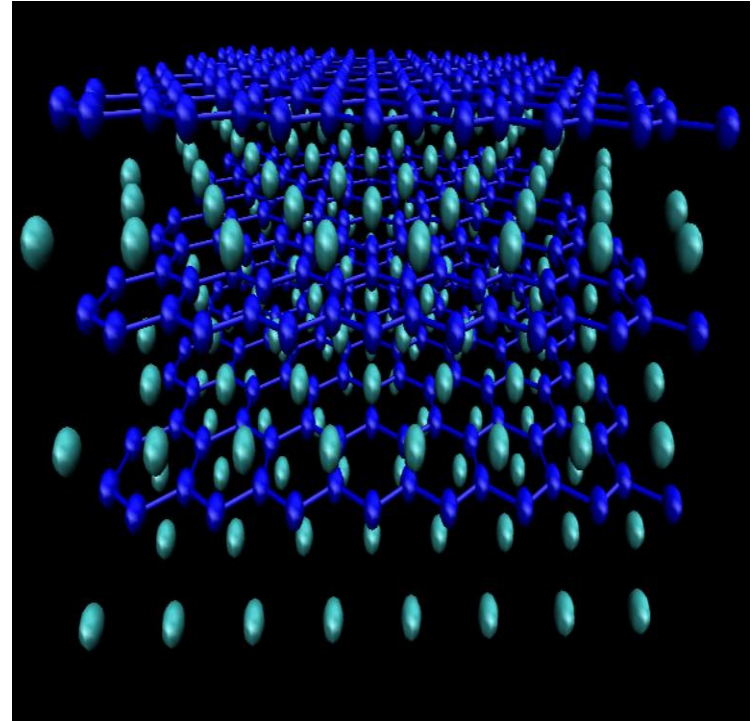
Ogitsu et al, JACS 131 (2009) 1903

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

Property	Target	Pot A	Pot B
a_0(A)	3.170	3.143	3.140
c_0(A)	3.550	3.547	3.547
E_0(eV)	-21.70	-21.29	-21.55

Stable, multilayered system
with **flat**, **hexagonal** Boron sheets!

● Boron ○ Zirconium

Lattice Thermal Conductivity
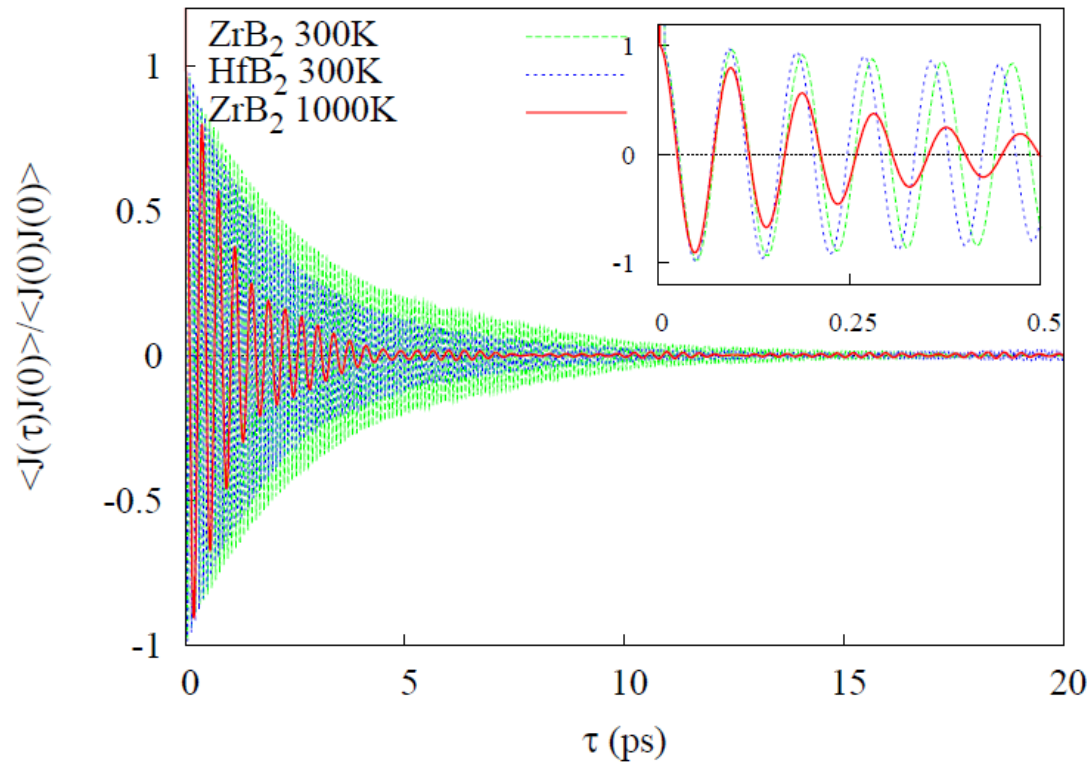
- Green-Kubo thermal conductivity tensor

$$\kappa_{\mu\nu} = \frac{1}{Vk_BT^2} \int_0^\infty \left\langle J_\mu(\tau)J_\nu(0) \right\rangle d\tau$$

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

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

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

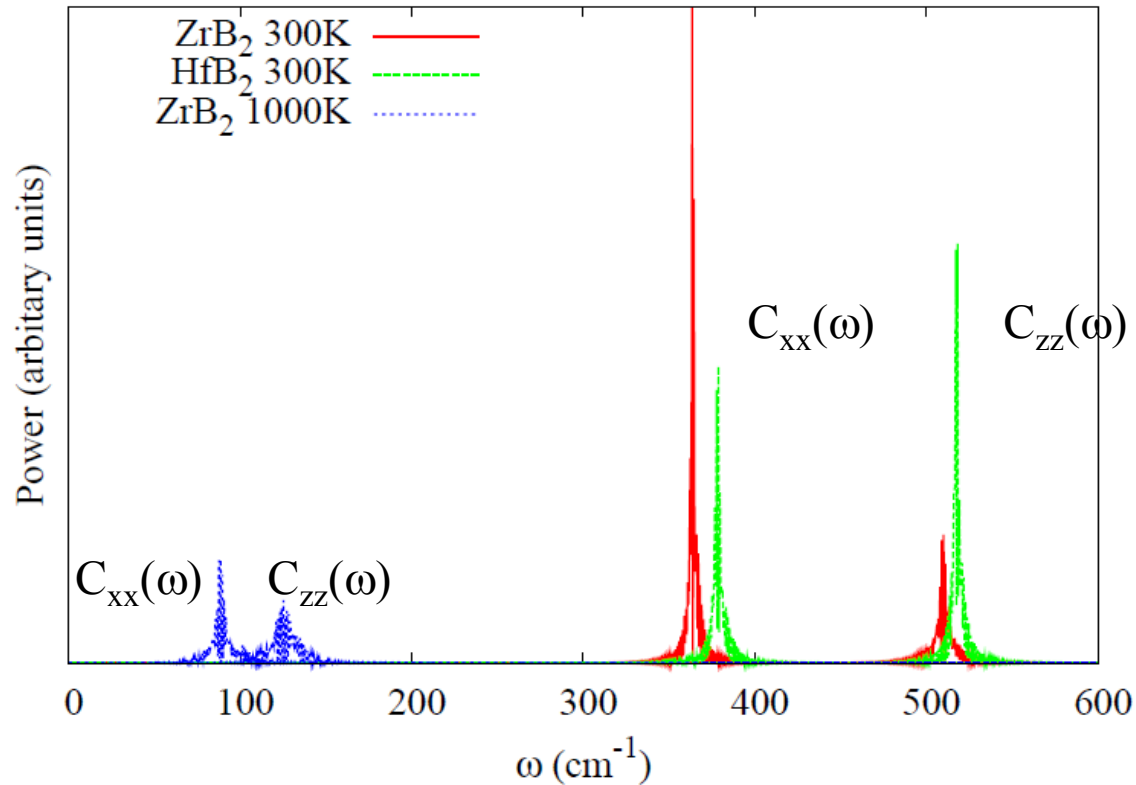JL, Daw and Bauschlicher, J. App. Phys, (2011)

Heat Current Correlation Function

- Monoatomic systems (e.g. Si) have monoatomic decay
- ZrB_2 has <u>longer</u> period than <u>HfB_2</u> at T=300K
- ZrB_2 at <u>T=1000K</u> has <u>longer</u> period than <u>T=300K</u>
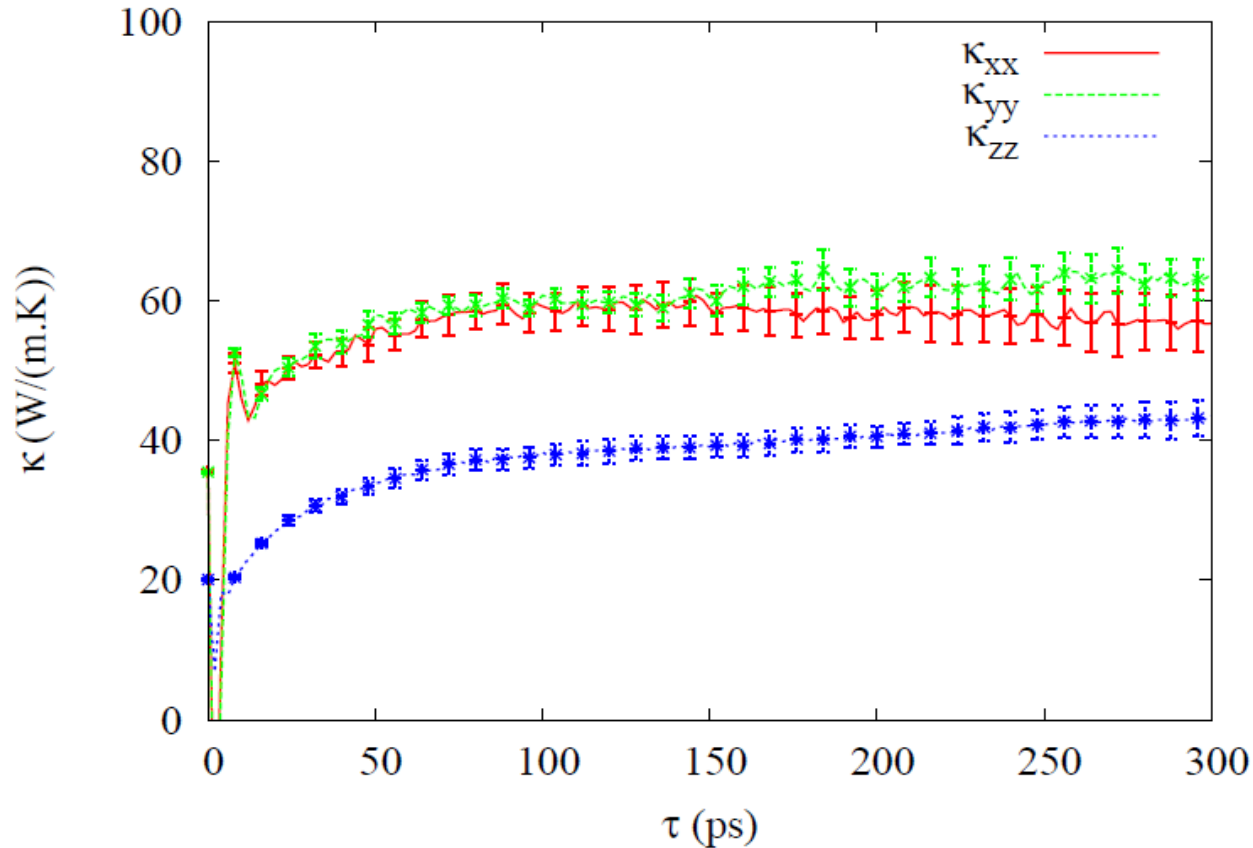
Correlation Function Power Spectra

- Correlations <u>oscillates</u> with metal-B <u>optical</u> modes
- C_{xx} and C_{yy} oscillate with <u>in-plane</u> mode frequency
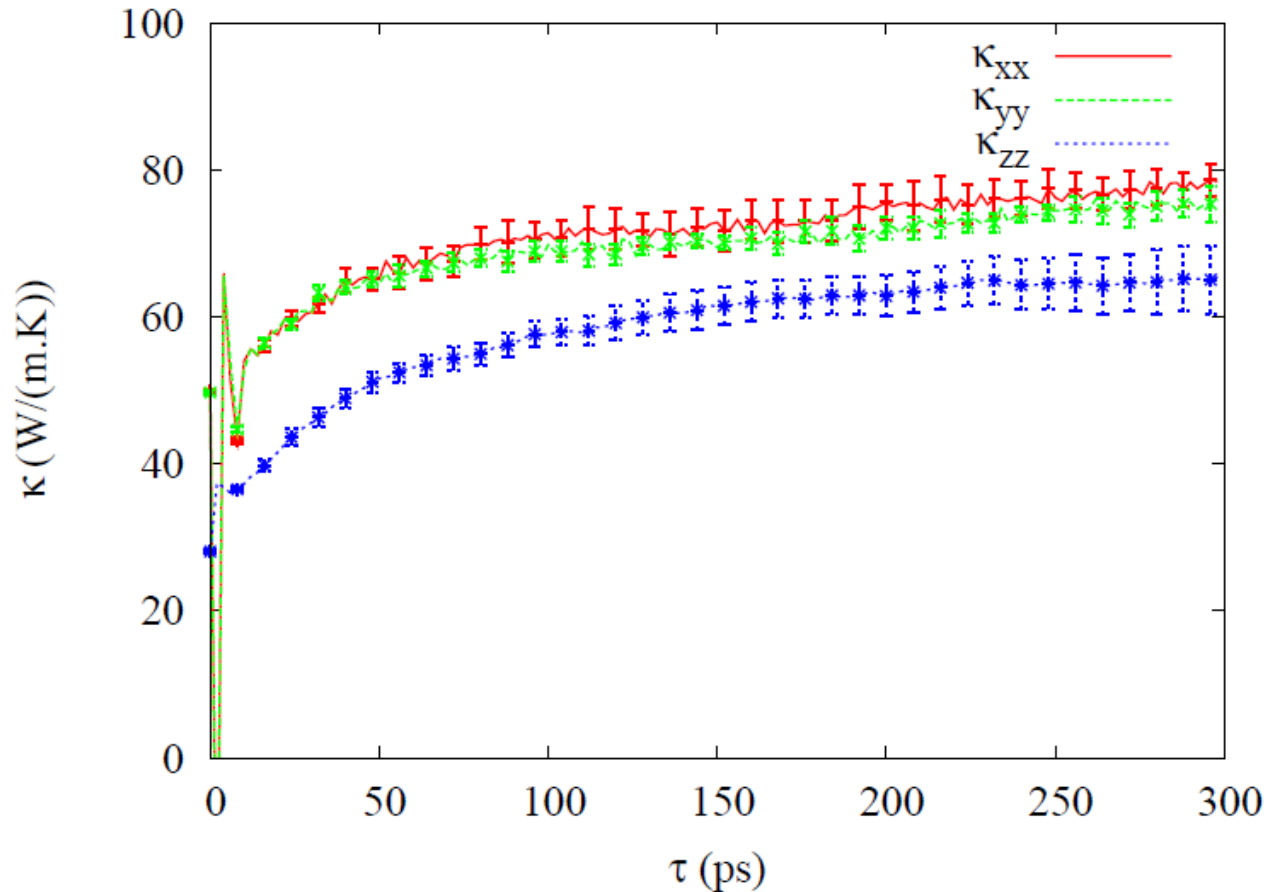- C_{zz} oscillates with <u>out-of-plane</u> mode frequency

Lattice Thermal Conductivity: ZrB$_2$

- 8 independent, 10 ns simulations, *T=300K*
- 8x8x16 unit cell, 12,255 atoms
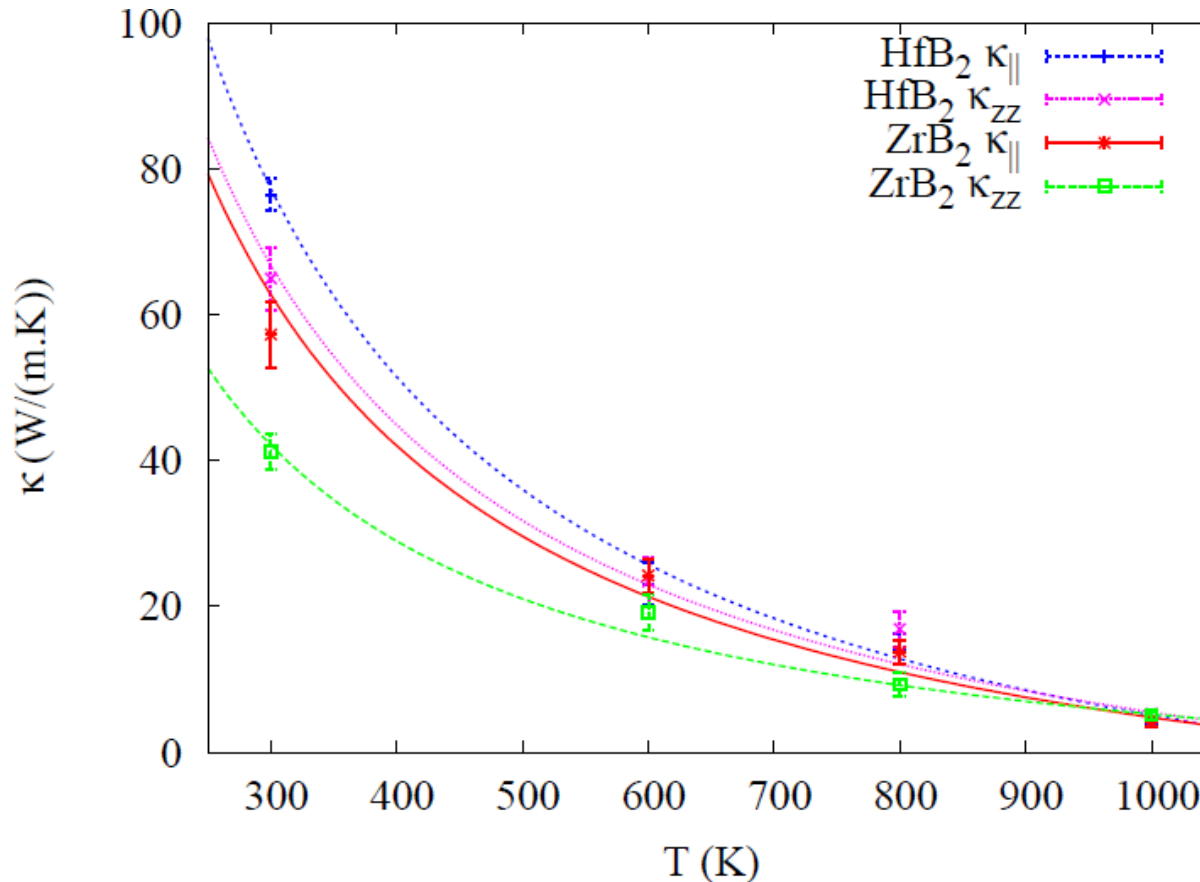- κ_{xx}*=60 W/(m.K)*, κ_{zz}*=40 W/(m.K)*

Lattice Thermal Conductivity: HfB$_2$

- 8 independent, 10 ns simulations
- 8x8x16 unit cell (12 atoms)= 12,255 atoms
- κ_{xx}=76 W/(m.K), κ_{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$_2$**
  - κ_e = 33 W/mK, $\boldsymbol{\kappa_{lat}}$ **= 22 W/mK**
  - $\kappa_{lat} \sim 0.3\kappa_{tot}$
- **Single crystal ZrB$_2$**
  - κ_{xx} = 140 W/mK, κ_{zz} = 100 W/mK
  - 1 sample, 1 measurement
  - defects uncharacterized
  - **$\boldsymbol{\kappa_{xx}}$ = 45 W/mK , $\boldsymbol{\kappa_{zz}}$ = 30 W/mK**
- Data needed for ZrB$_2$ and HfB$_2$
- *Simulation data reasonable at 300K but too low for higher T*

Polycrystalline ZrB$_2$
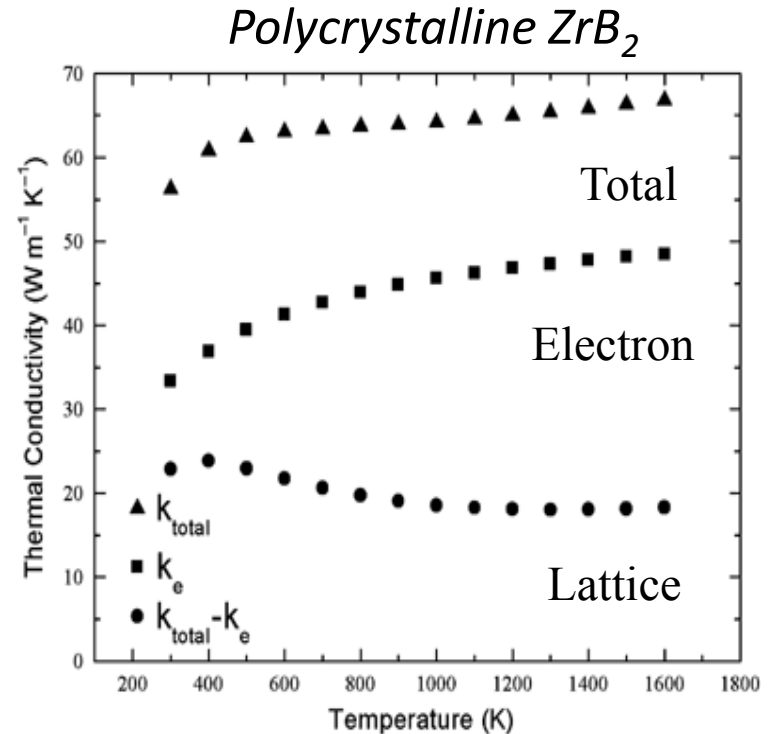
$$\kappa = \kappa_e + \kappa_{lat}$$

Zimmermann, Hilmas, Fahrenholtz Dinwiddie, Porter, Wang , J. Am. Ceram. Soc., (2008)

Kinoshita, Otani, Kamiyama, Amano, Akasaki, Suda, Matsunami, Japan. J. App. Phys., (2001)

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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
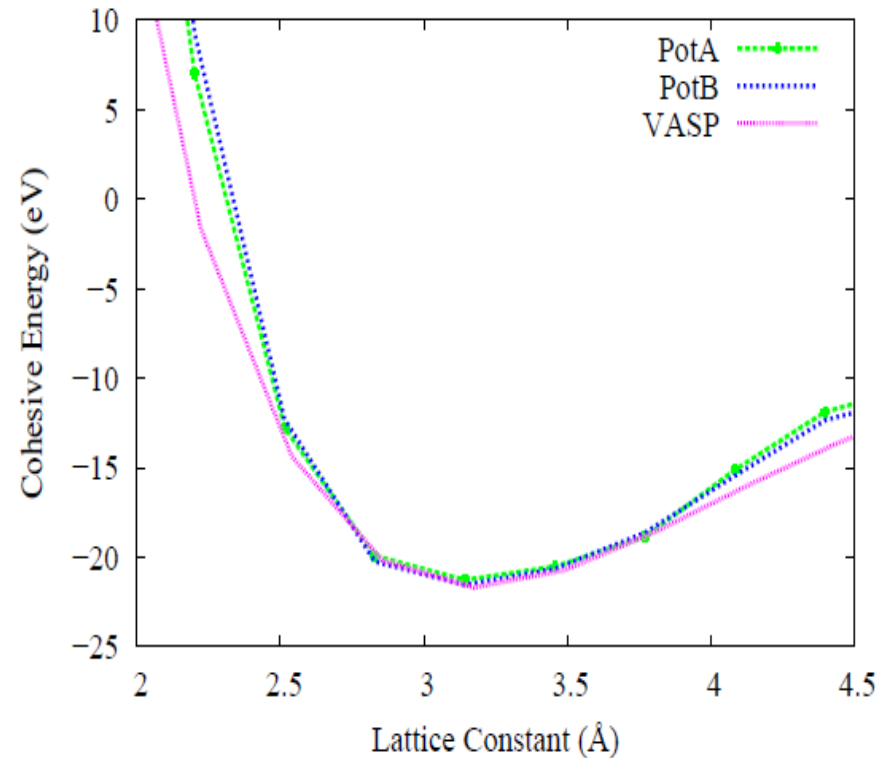
Extra Slides

ZrB$_2$ Potential Curves

Test Results

Properties	Ab Initio	Pot A	Pot B
C_{11}	556	365	422
C_{12}	57	156	156
C_{13}	113	173	171
C_{33}	419	307	320
C_{44}	234	106	119
B	233	227	240
G	226	98	118
A($=C_{33}/C_{11}$)	0.75	0.84	0.76

Properties <u>not</u> included in fit

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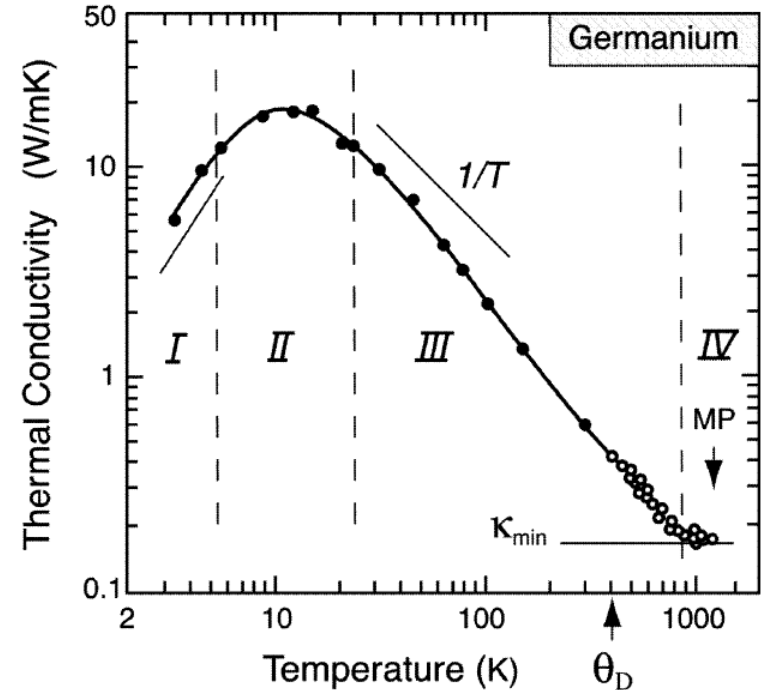
Physics of Lattice Thermal Conductivity

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

Clark, Surf. and Coat. Tech., (2003)

Summary

- <u>No</u> 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 <u>first</u> 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*