



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

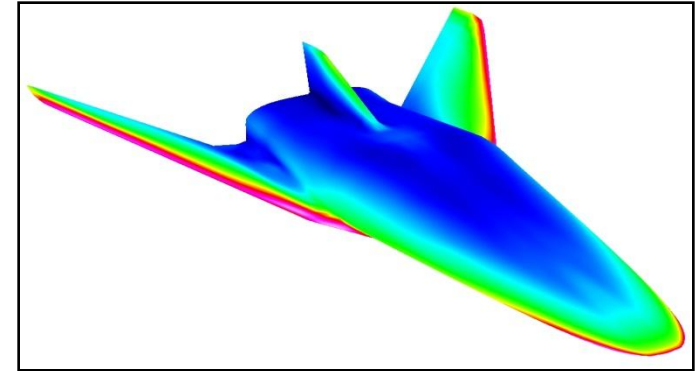
- Enhances vehicle performance
- Improves safety

Higher temperature requirements

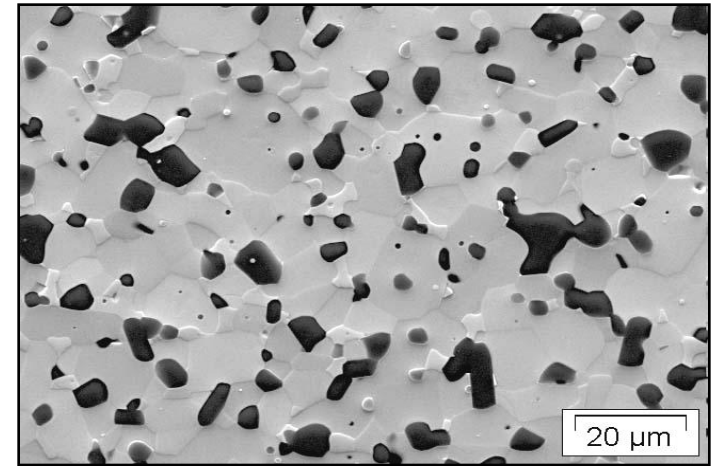
- Shuttle RCC leading edge: $T \sim 1650^\circ\text{C}$
- Sharp leading edged vehicles: $T > 2000^\circ\text{C}$

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

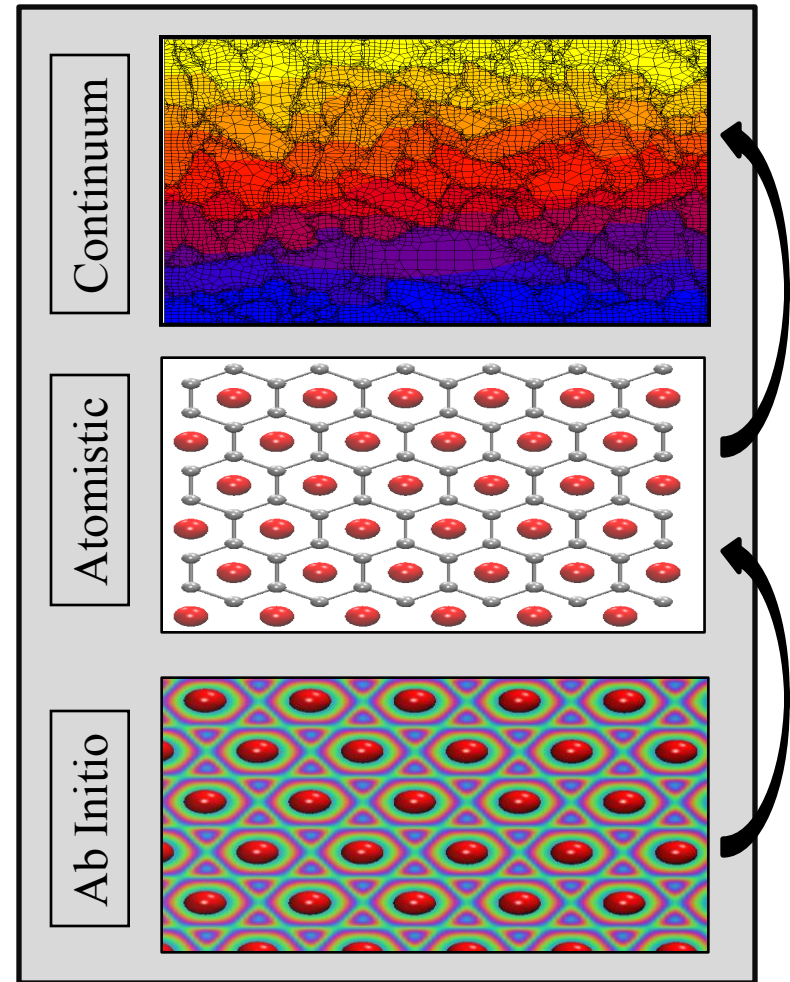


SEM image of UHTC microstructure



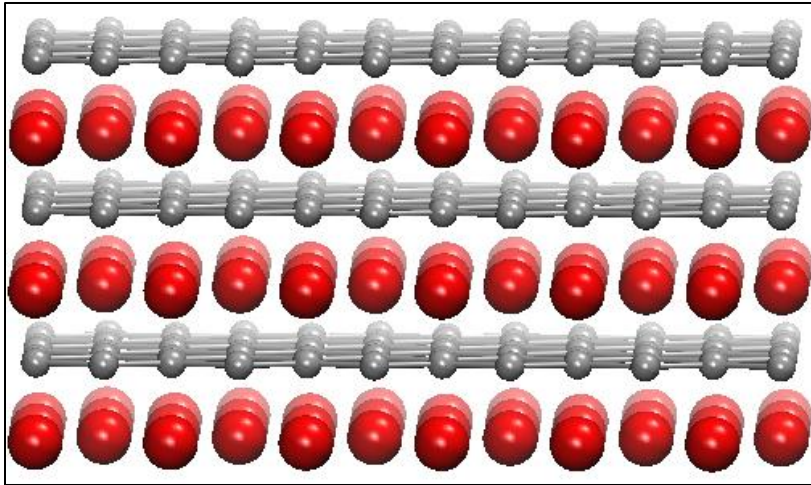
Multiscale Modeling of UHTC

- 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

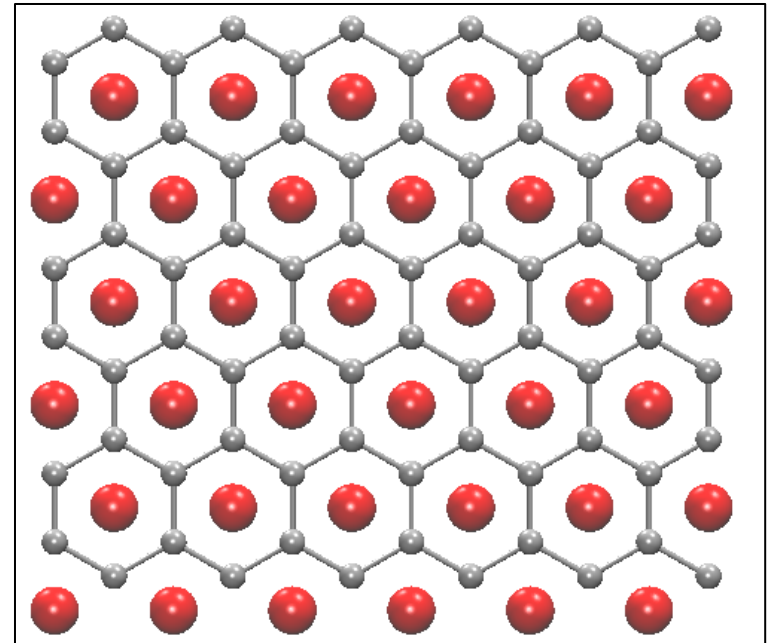




Atomic Structure: ZrB_2 and HfB_2



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

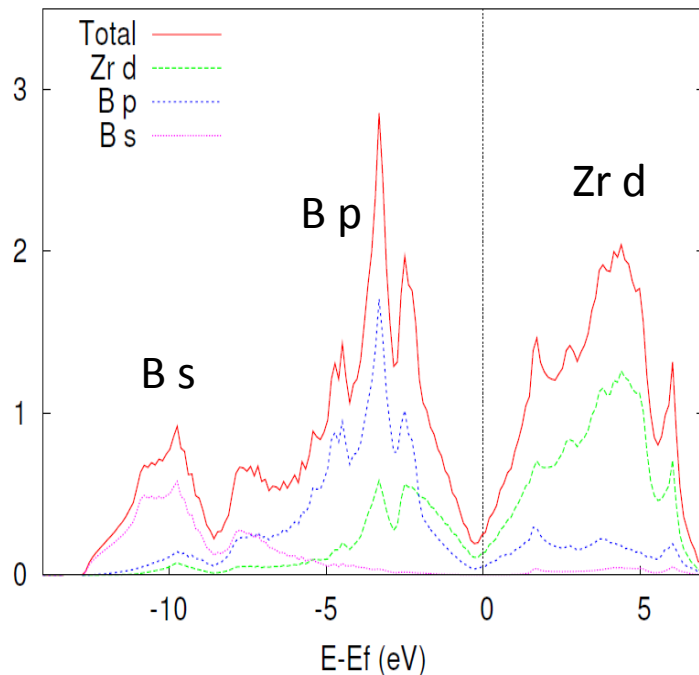


Graphitic Boron layers
with Zr/Hf over each ring



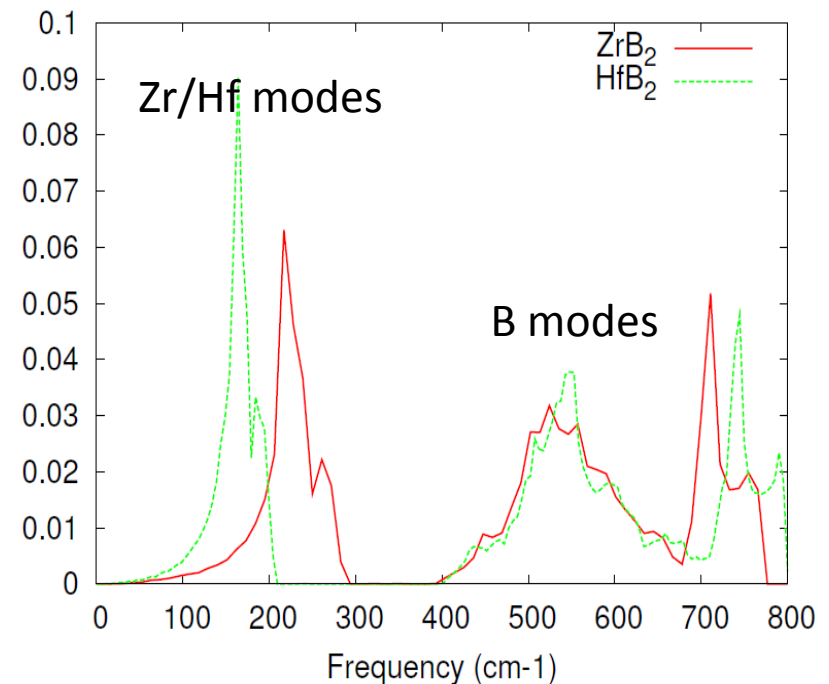
Fundamental Properties: ZrB_2 & HfB_2

Electronic Spectra



Electronic properties
essentially identical

Vibrational Spectra



Acoustic modes carry heat.
Optical modes are resistive.



Tersoff Bond Order Potential

- Two body terms (A, λ, B, μ) energy

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

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

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

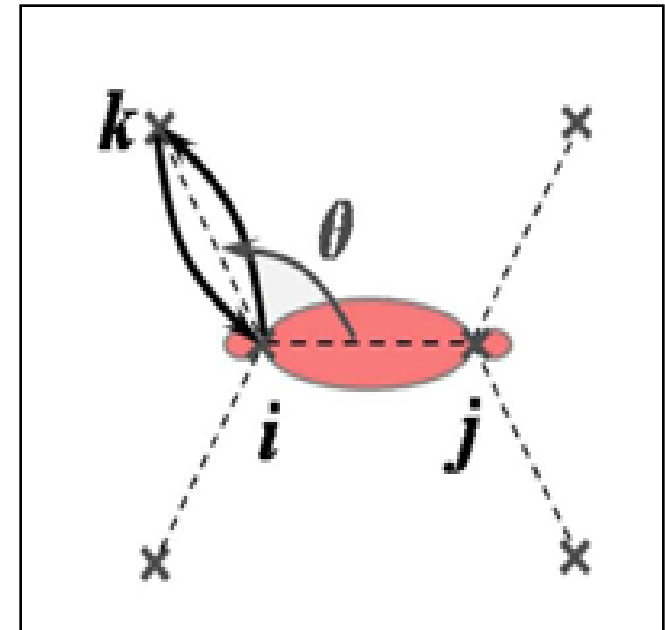
- Bond order (β, λ_3, n, m)

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

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

- Angular function (c, d, h)

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



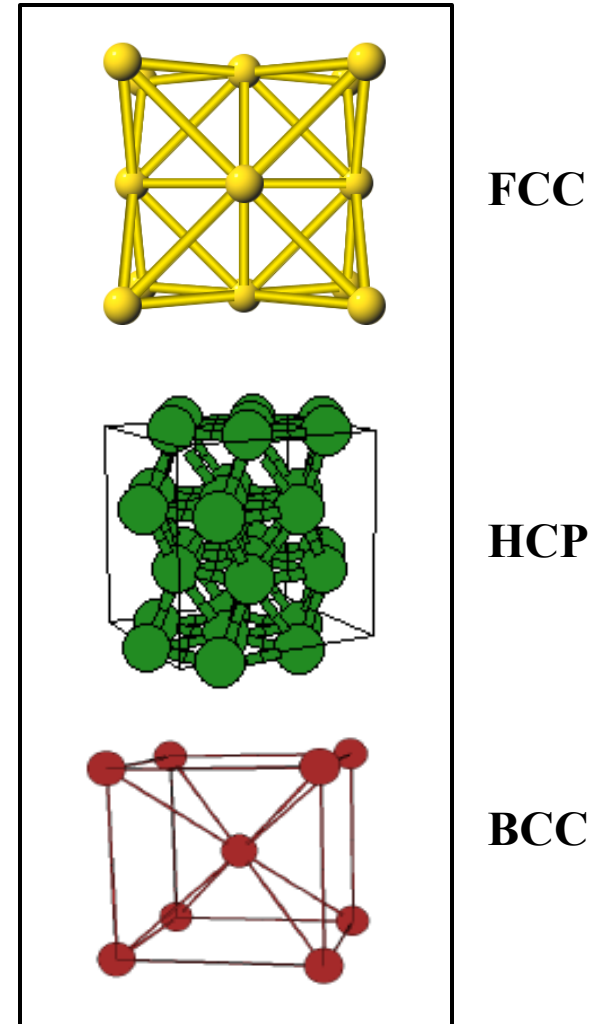
Interatomic Energy



First Step: Zr Potential

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

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

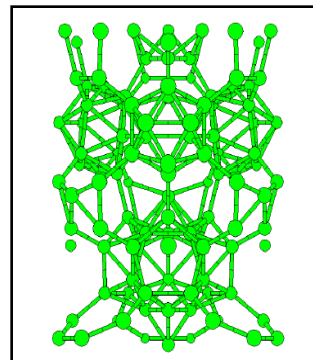




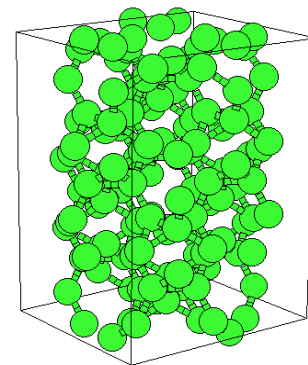
Second Step: Boron Potential

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

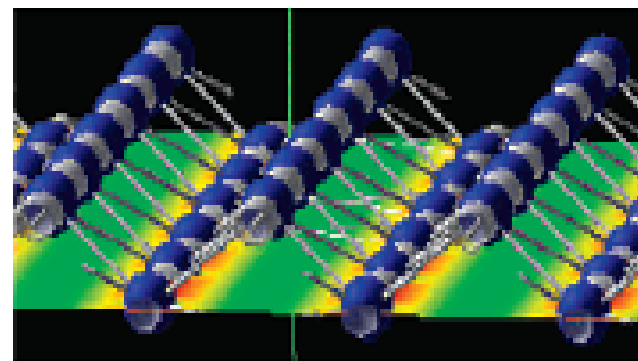
Structure	Property	Target	Fit
Hex sheet	a_0	2.91	2.89
	E_0	-5.15	-5.08
	E_0''	11.35	7.98
Tri sheet	a_0	1.70	1.81
	E_0	-5.71	-5.75
	E_0''	21.73	27.06
SC	a_0	1.88	1.84
	E_0	-5.33	-5.21
	E_0''	24.50	24.51
FCC	a_0	2.86	2.84
	E_0	-5.07	-5.22
	E_0''	21.85	12.28



β -Boron (N=105)



α -Boron (N=12)



Crumpled Sheet

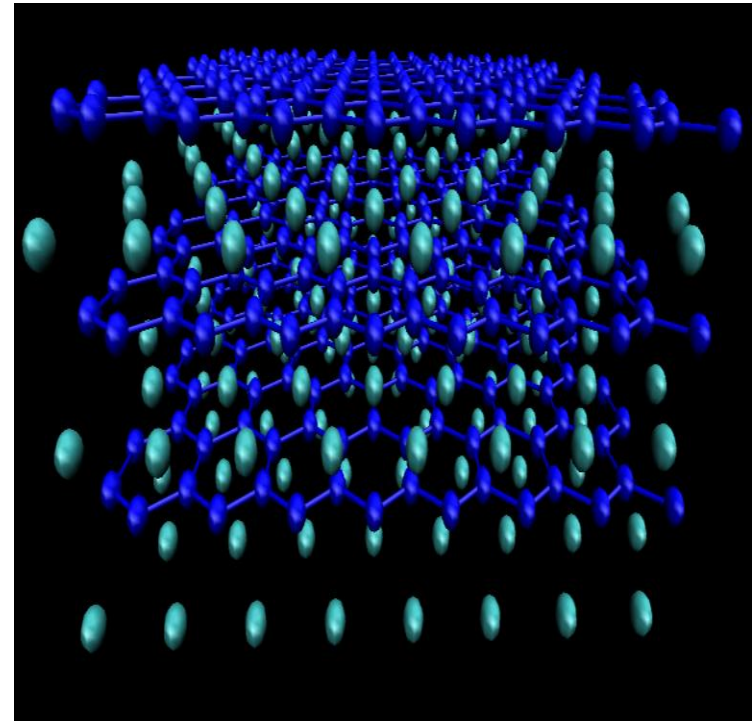


Third Step: ZrB_2 Potentials

- 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
$a_0(\text{\AA})$	3.170	3.143	3.140
$c_0(\text{\AA})$	3.550	3.547	3.547
$E_0(\text{eV})$	-21.70	-21.29	-21.55



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



Lattice Thermal Conductivity

- Green-Kubo thermal conductivity tensor

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

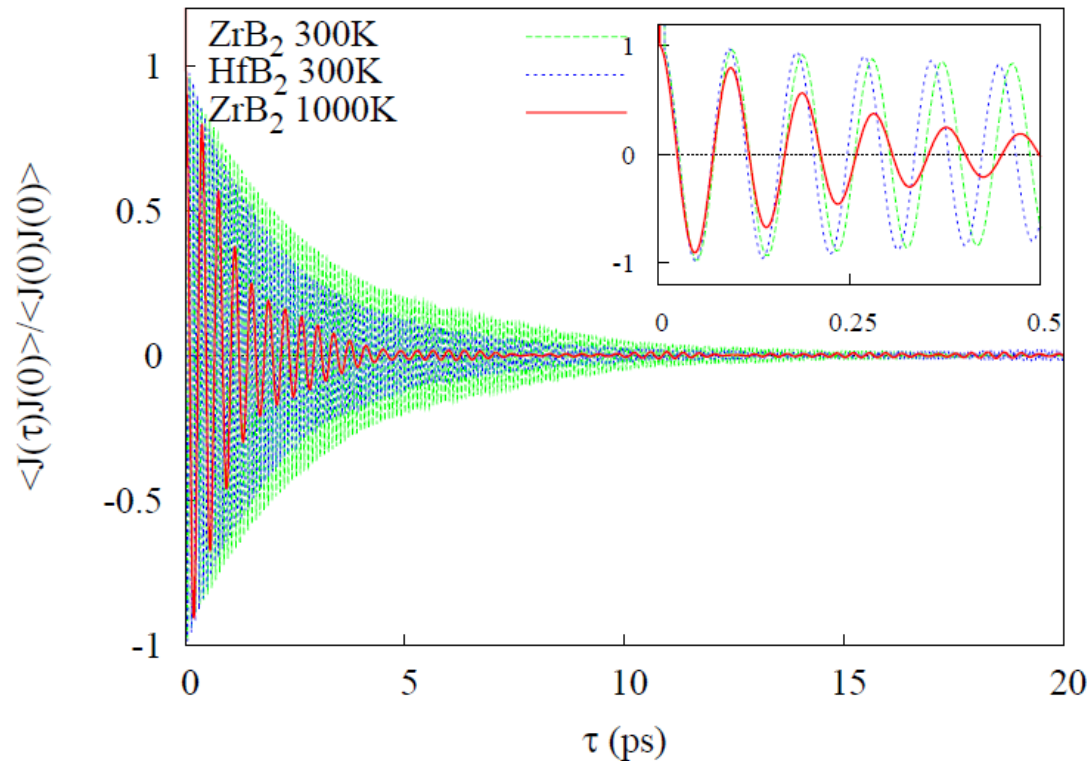
- Heat current $J(x_i, v_i)$, energy e_i , stress-tensor S_i

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

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



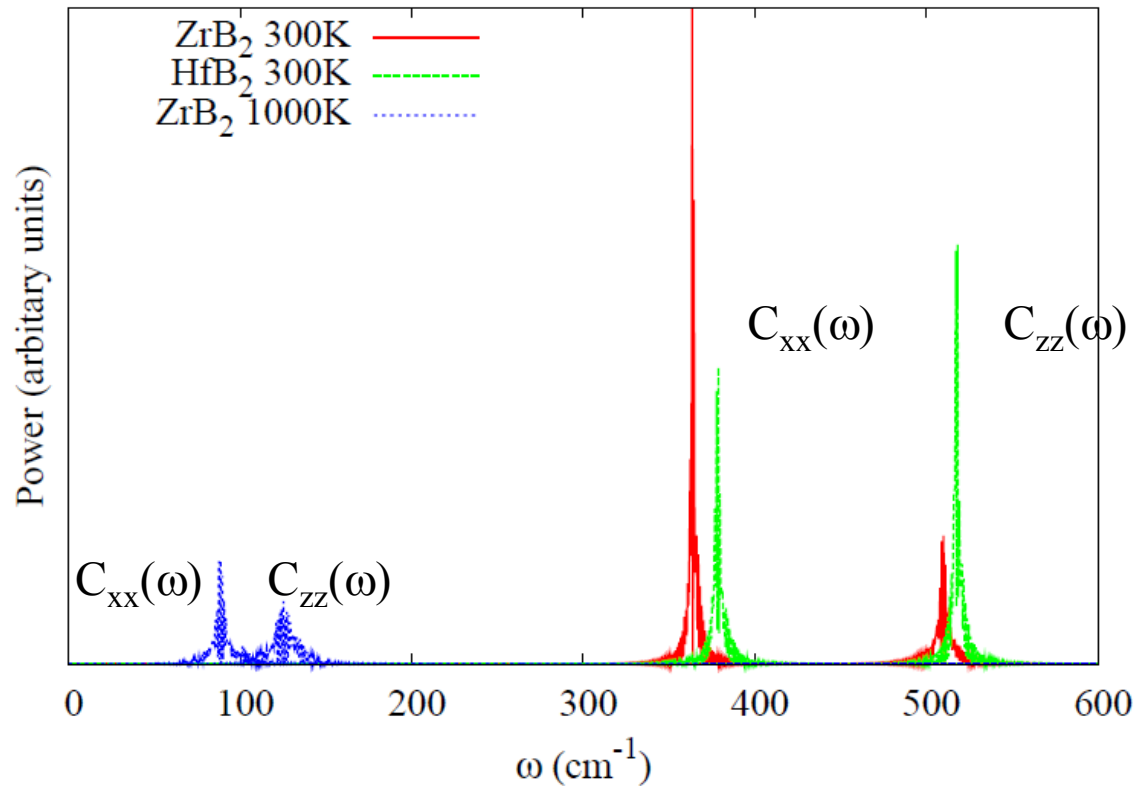
Heat Current Correlation Function



- Monoatomic systems (e.g. Si) have monoatomic decay
- ZrB_2 has longer period than HfB_2 at $T=300\text{K}$
- ZrB_2 at $T=1000\text{K}$ has longer period than $T=300\text{K}$



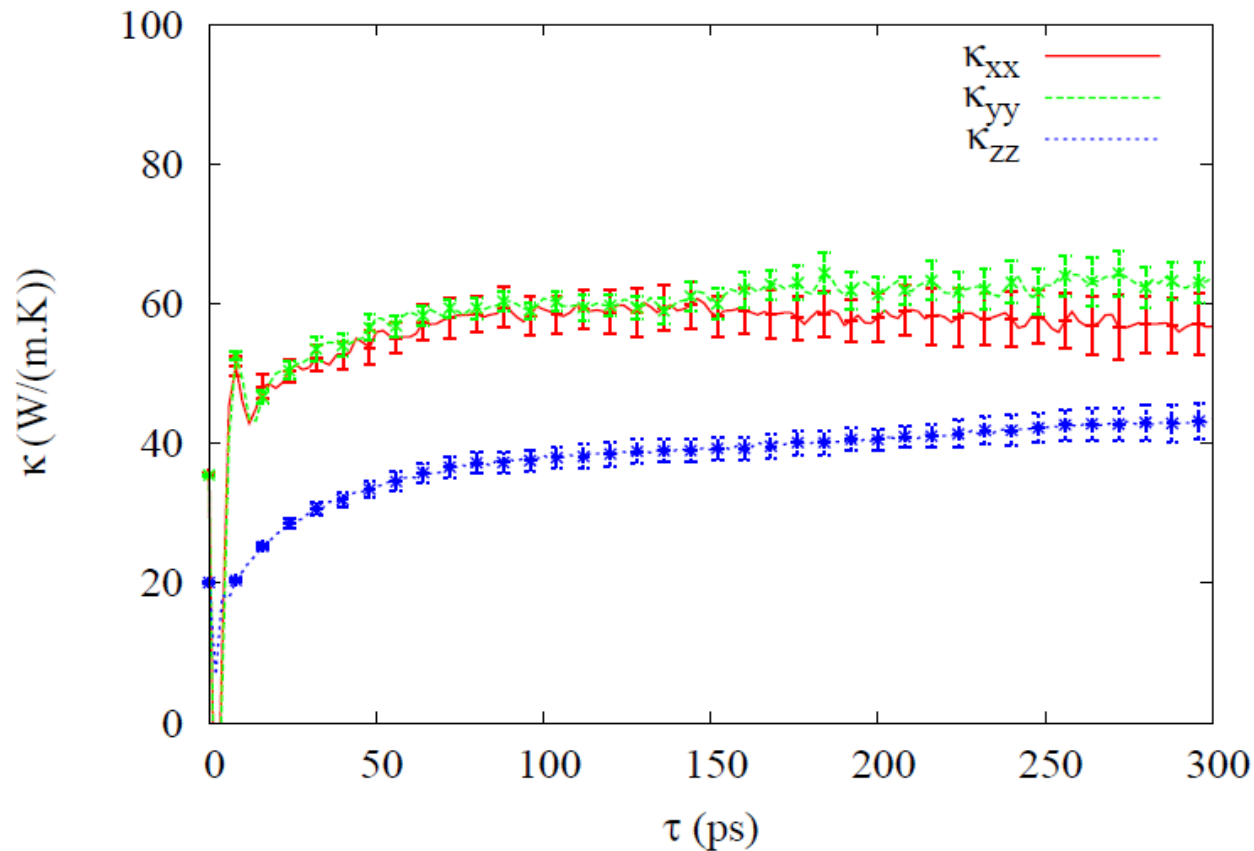
Correlation Function Power Spectra



- 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



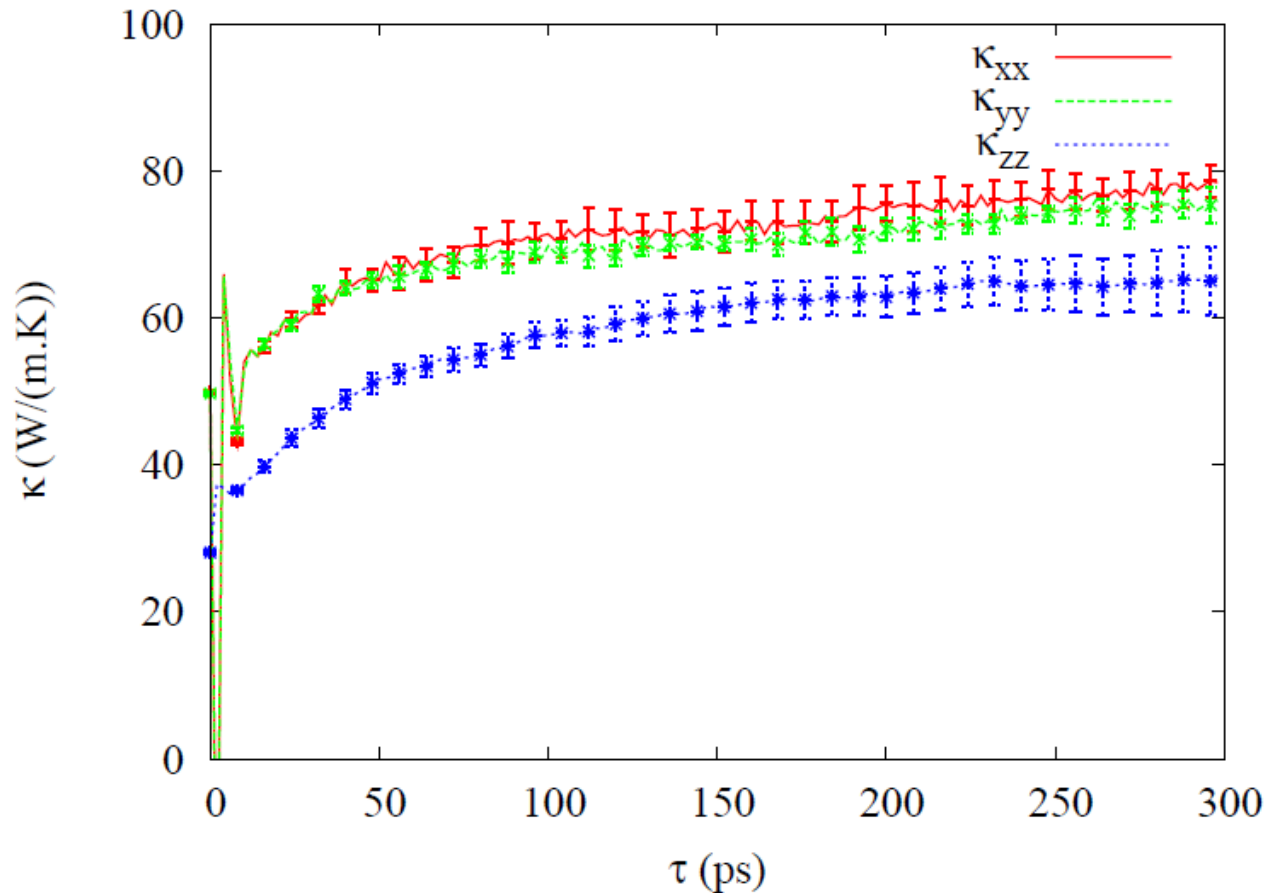
Lattice Thermal Conductivity: ZrB_2



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



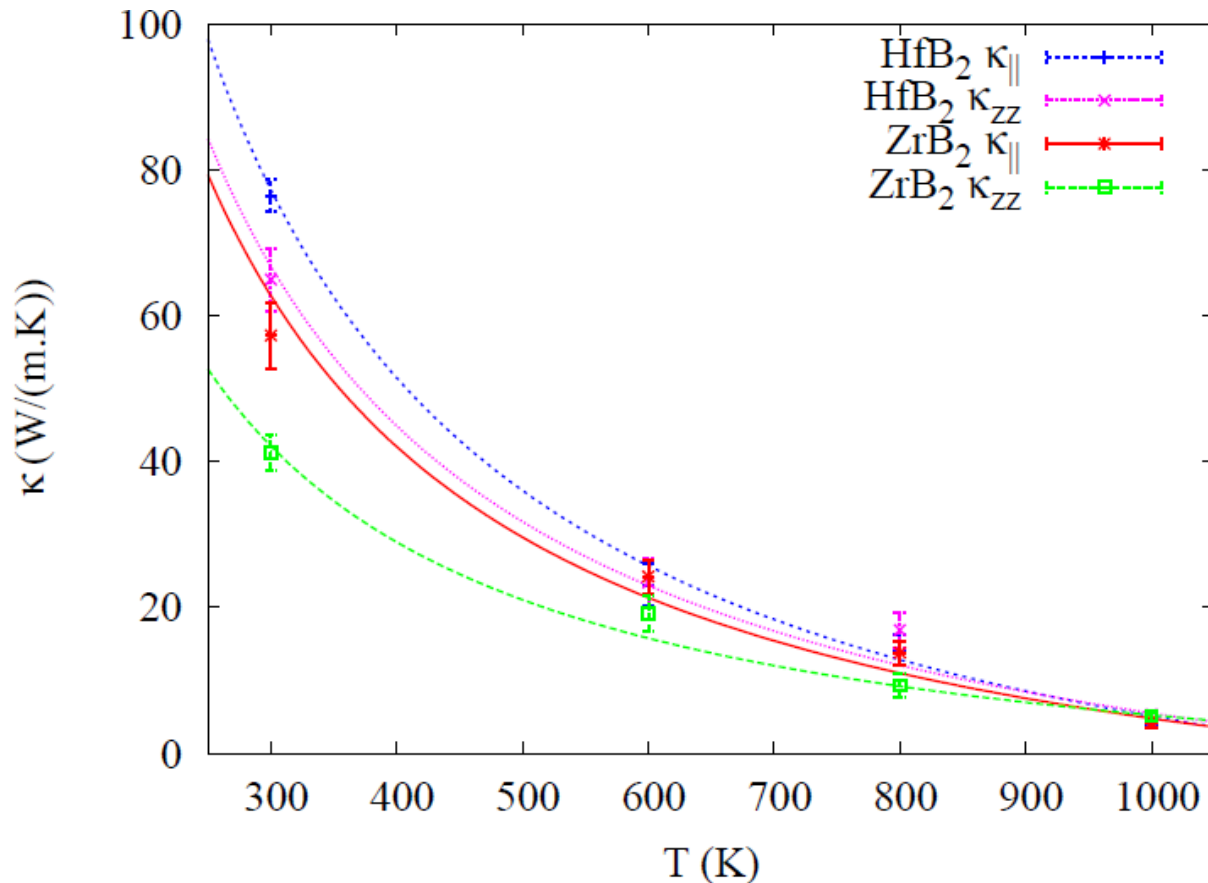
Lattice Thermal Conductivity: HfB₂



- 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

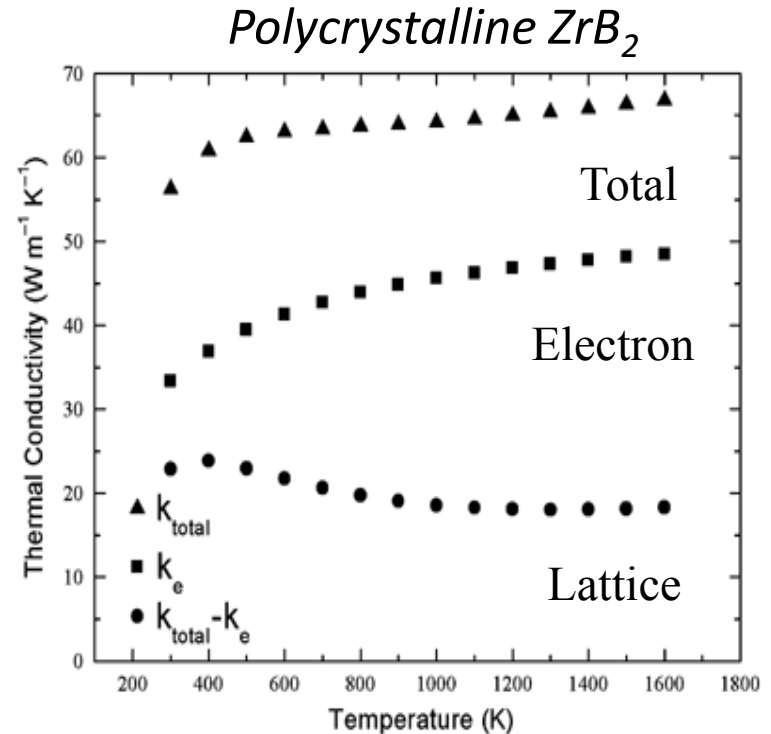


- 8 independent, 10 ns simulations for each point
- Data fit to $1/T$ curves



Experimental Data Comparison

- **Polycrystalline ZrB_2**
 - $\kappa_e = 33 \text{ W/mK}$, $\kappa_{\text{lat}} = 22 \text{ W/mK}$
 - $\kappa_{\text{lat}} \sim 0.3\kappa_{\text{tot}}$
- **Single crystal ZrB_2**
 - $\kappa_{xx} = 140 \text{ W/mK}$, $\kappa_{zz} = 100 \text{ W/mK}$
 - 1 sample, 1 measurement
 - defects uncharacterized
 - $\kappa_{xx} = 45 \text{ W/mK}$, $\kappa_{zz} = 30 \text{ W/mK}$
- Data needed for ZrB_2 and HfB_2
- *Simulation data reasonable at 300K but too low for higher T*



$$K = K_e + K_{\text{lat}}$$



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



Extra Slides

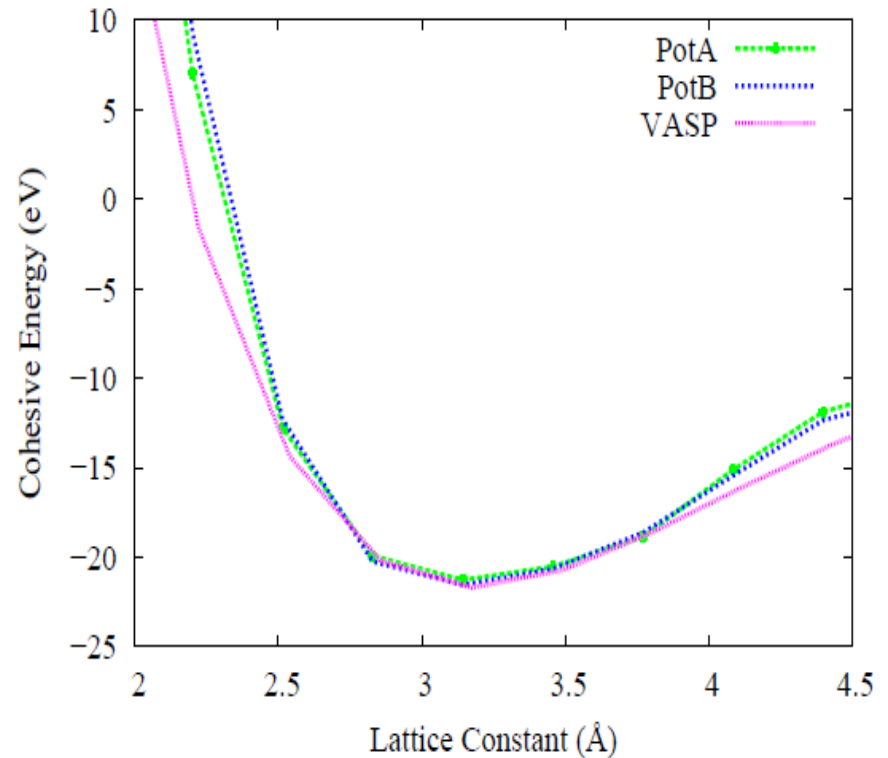


ZrB₂ Potential Curves

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

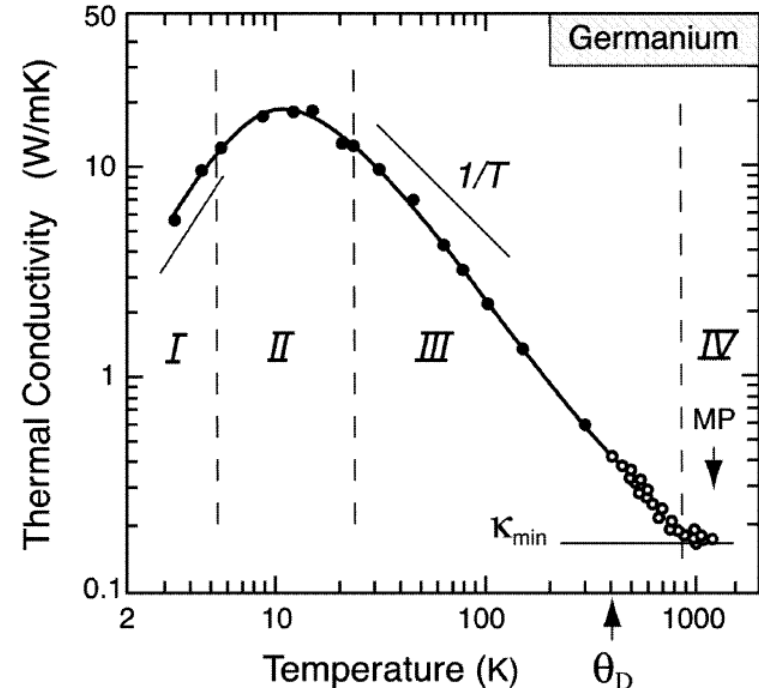
Properties not included in fit





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:** $\kappa_{\text{min}}, l_{\text{mfp}} = "a"$





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