Multiscale Modeling of UHTC: Thermal Conductivity

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NASA Fundamental Aeronautics Program (FAP)
NASA Innovative Partners Program (IPP)

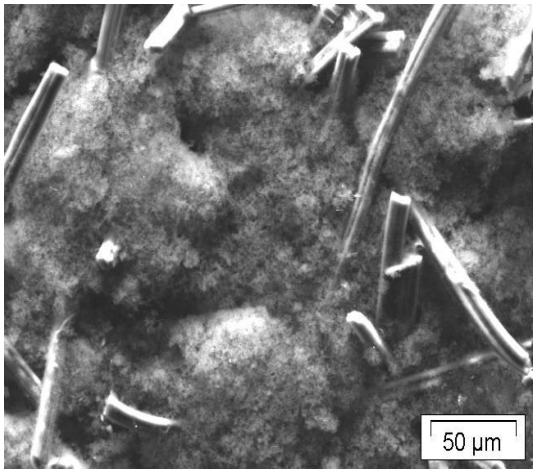
Materials Modeling at NASA ARC

New materials modeling: interdisciplinary
- Computational chemistry
- Computational physics
- Computational engineering

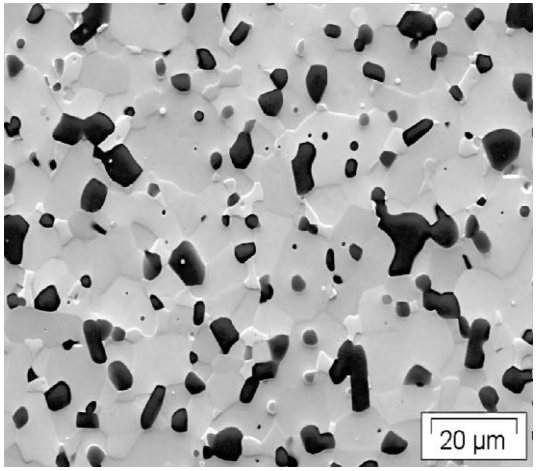
Ablative composites
- Application: atmospheric re-entries
- Materials: PICA, Avcoat,…

Ultra high temperature ceramics (UHTC)
- Applications: leading edges
- Materials: ZrB_2 and HfB_2

UHTC modeling illustrate our approach



PICA: fibers w/ phenolic



UHTC: HfB_2 w/ 20% SiC

UHTC for Sharp Leading Edges

Sharp leading edge for hypersonic aircraft

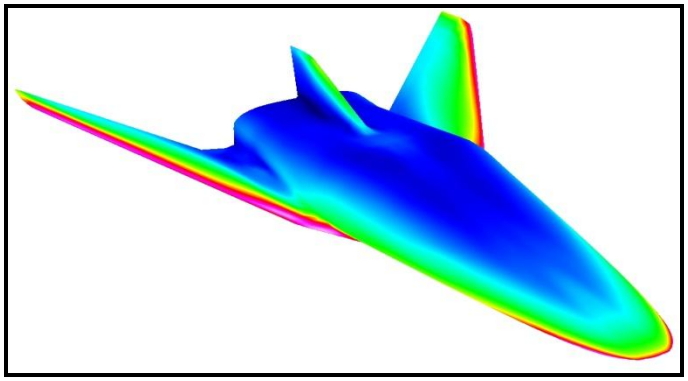
- Enhances vehicle performance
- Improves safety

Higher temperature requirements

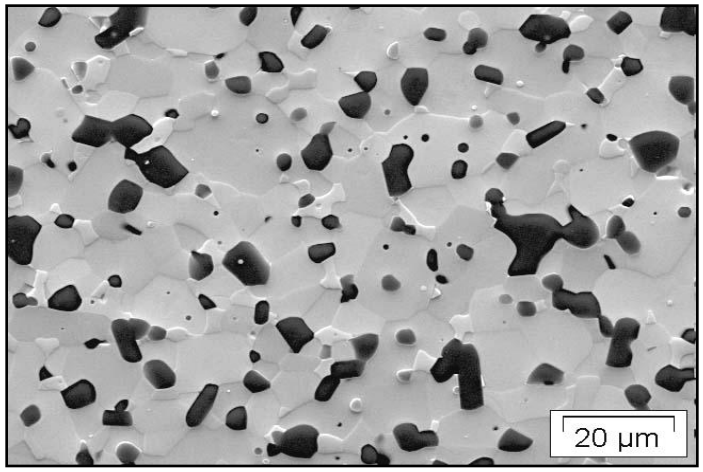
- Shuttle RCC leading edge: T~1650C
- Sharp leading edged vehicles: T>2000C

UHTC advantages for sharp leading edges

- Reasonable mechanical properties
- Oxidation resistance
- *High thermal conductivity*
  - Effective thermal radiation
  - Thermal shock resistance



Leading edges of hypersonic vehicle

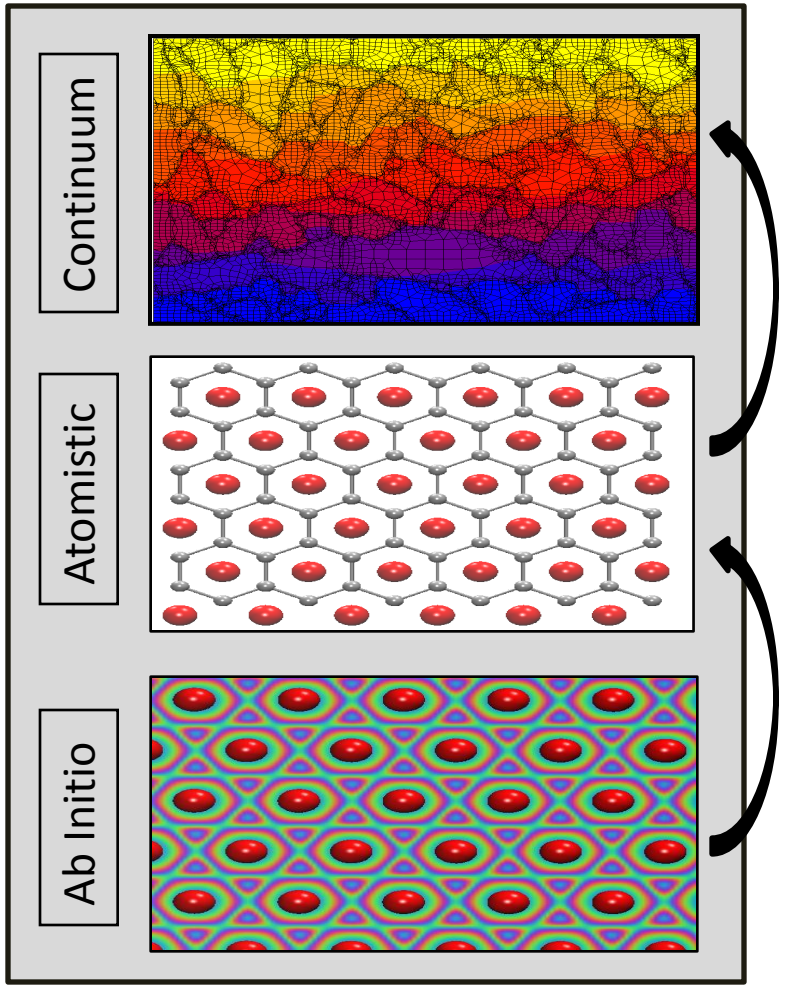


SEM image of UHTC microstructure

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

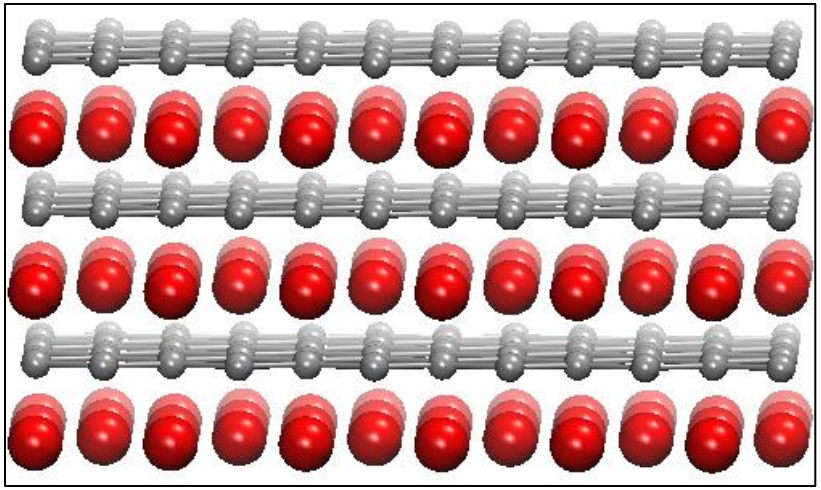
Multiscale Modeling of UHTC

- **Materials modeling will**:
  - Discover fundamental mechanisms
  - Structure-property relationships
  - Design new materials
  - Accelerate material development
- **Framework integrates three methods:**
  - *Ab initio* – fundamental chemistry
  - *Atomistic* – thermal/mechanical
  - *Continuum* – macro properties
- **<u>This talk focuses on thermal conductivity</u>**
  - Atomic structure and bonding
  - Interatomic potential development
  - Lattice thermal conductivity simulations
  - Grain boundary thermal resistance
  - Imaged based FEM of GB networks

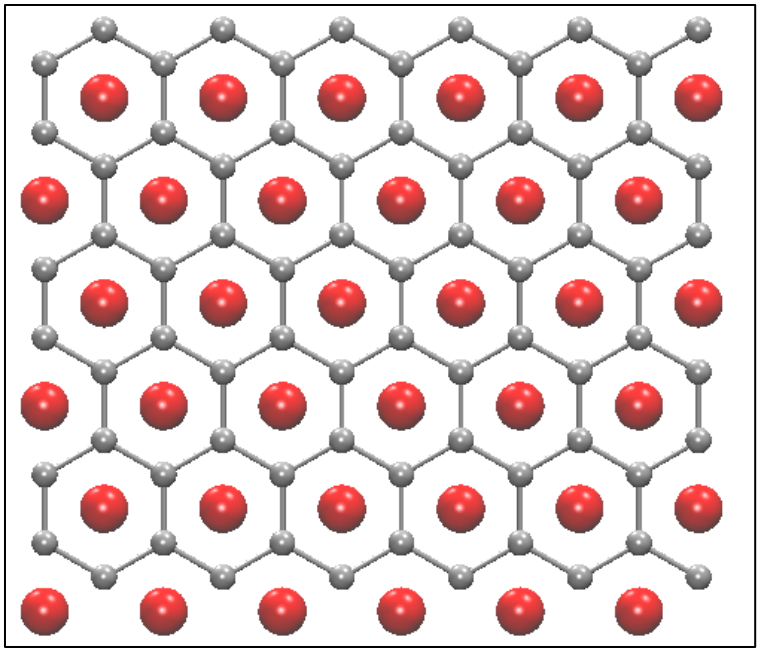


JL, Daw, Squire and Bauschlicher, (2012), submitted

UHTC: ZrB_2 and HfB_2

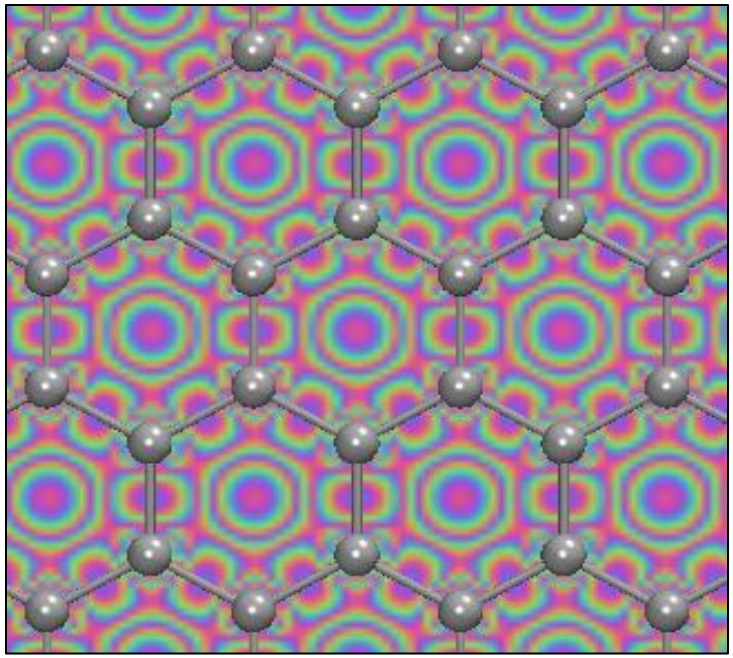


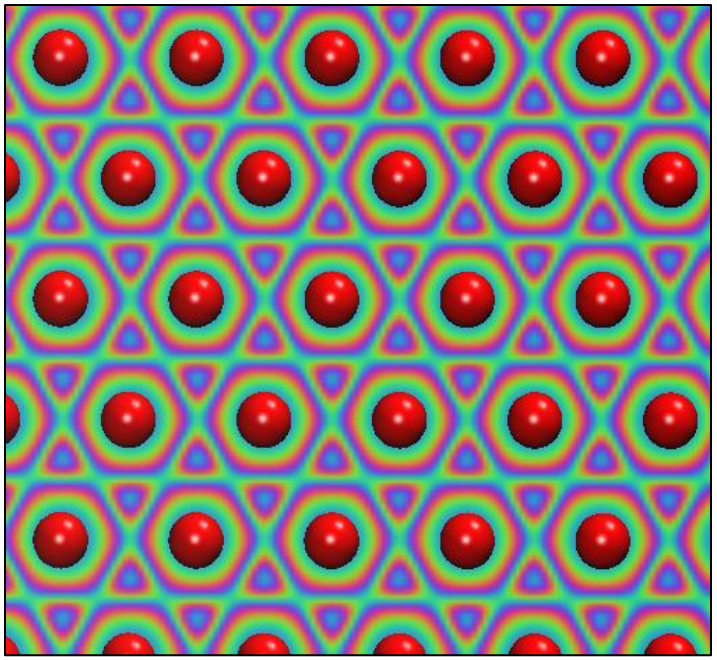
Alternating layers of
Zr/Hf (red) and Boron (gray)



Graphitic Boron layers
with Zr/Hf over each ring

Electron Localization Function (ELF)





Covalent bonding in Boron plane

Metallic bonding in Zr planes

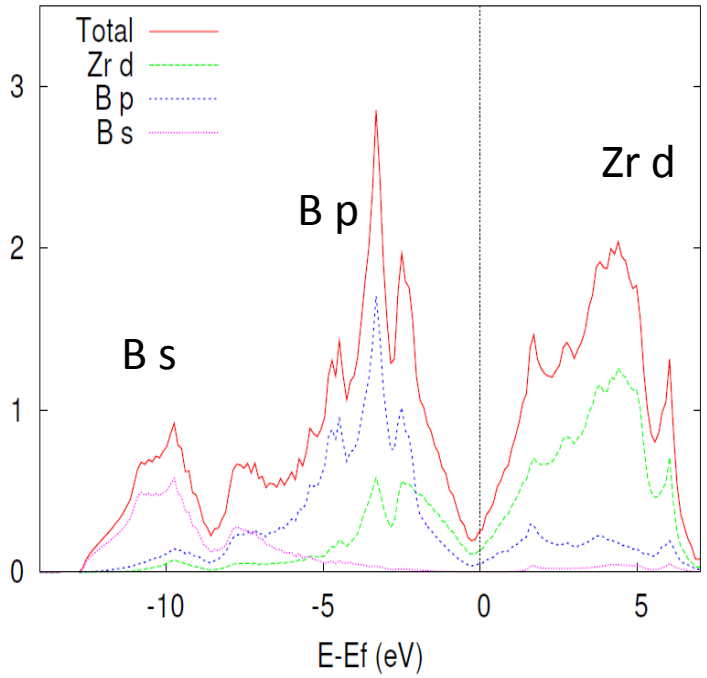
Blue = High
Red = Low

Ionic bonding between Interlayers

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

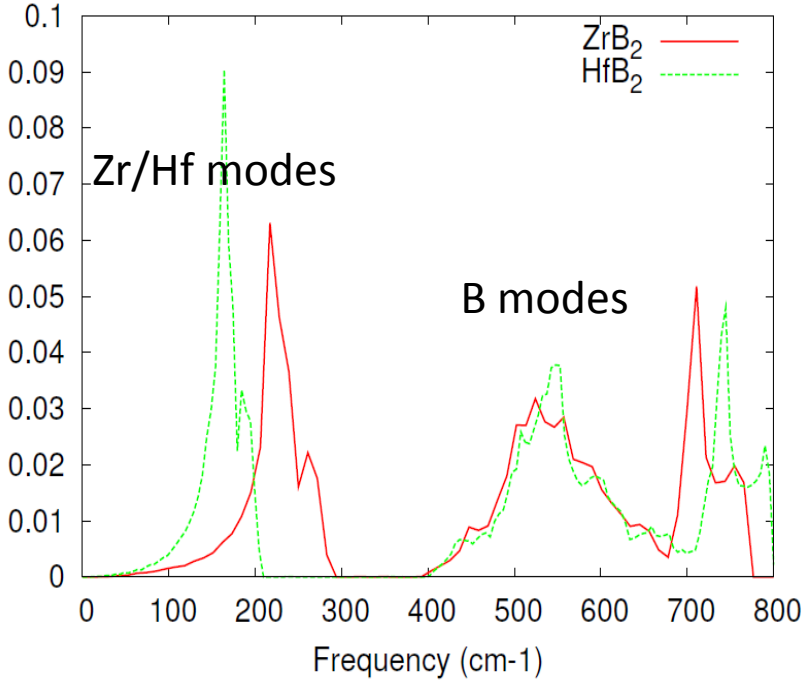
Fundamental Properties: ZrB_2 & HfB_2

Electronic Spectra



Electronic properties essentially identical

Vibrational Spectra



Vibrational differences due to Zr/Hf mass difference

Tersoff Bond Order Potential

- Two body terms (A,λ, B, μ) energy

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

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

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

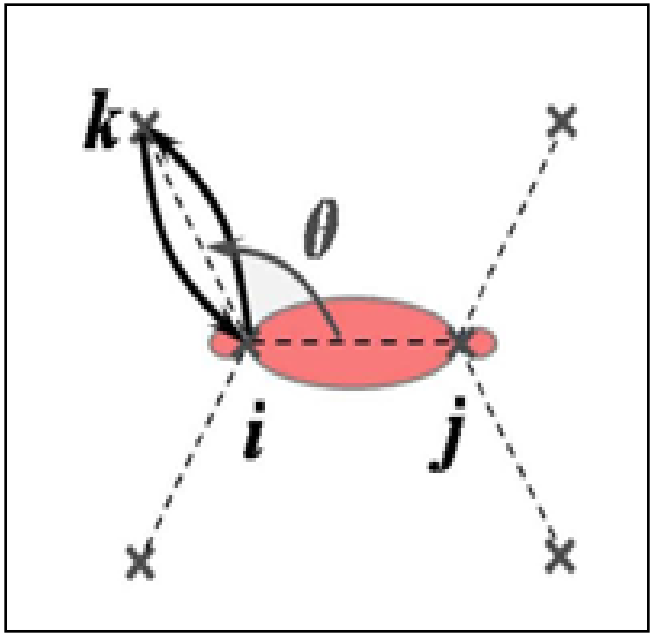
- Bond order (β, λ_3, n, m)

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

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

- 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

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

Lattice Thermal Conductivity

- Green-Kubo thermal conductivity tensor

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

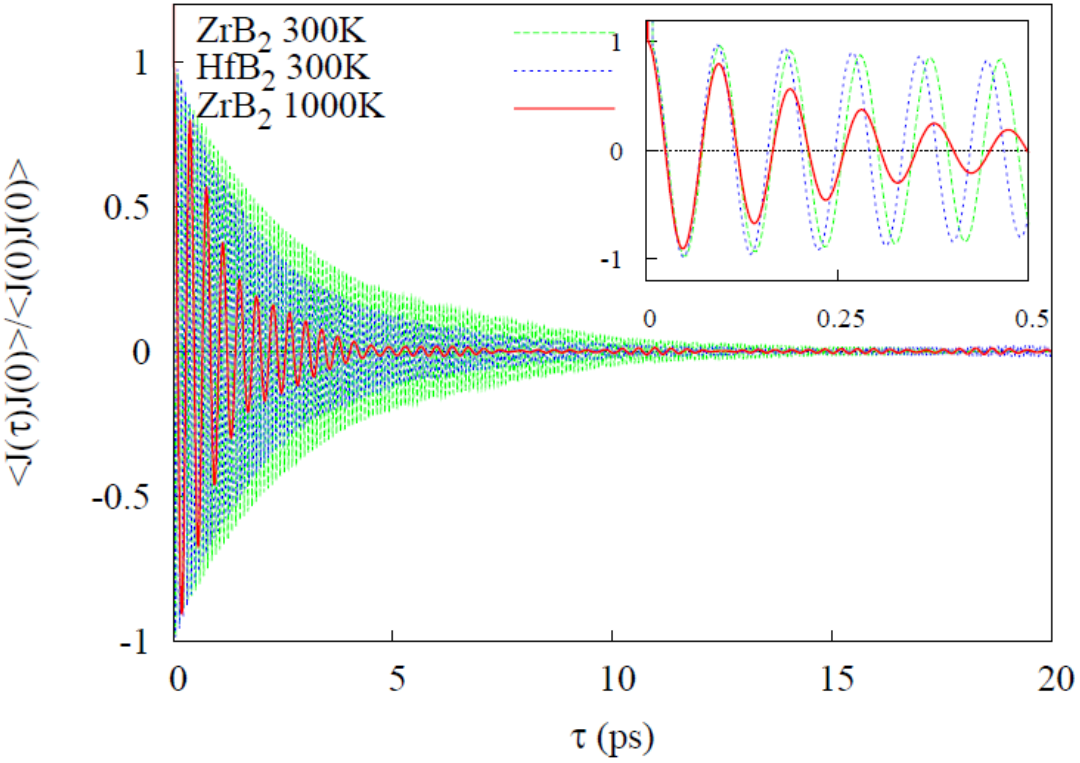
- Heat current J(x_i,v_i), energy e_i, stress-tensor S_i

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

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

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

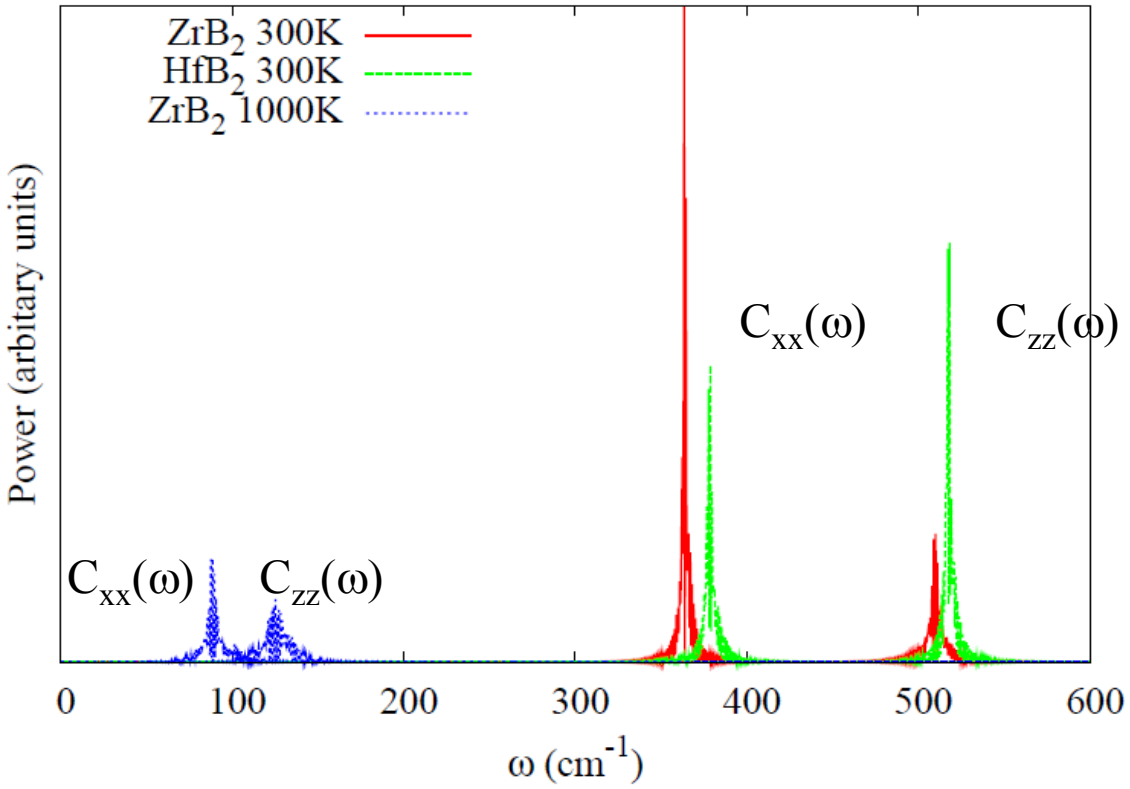
Heat Current Correlation Function



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

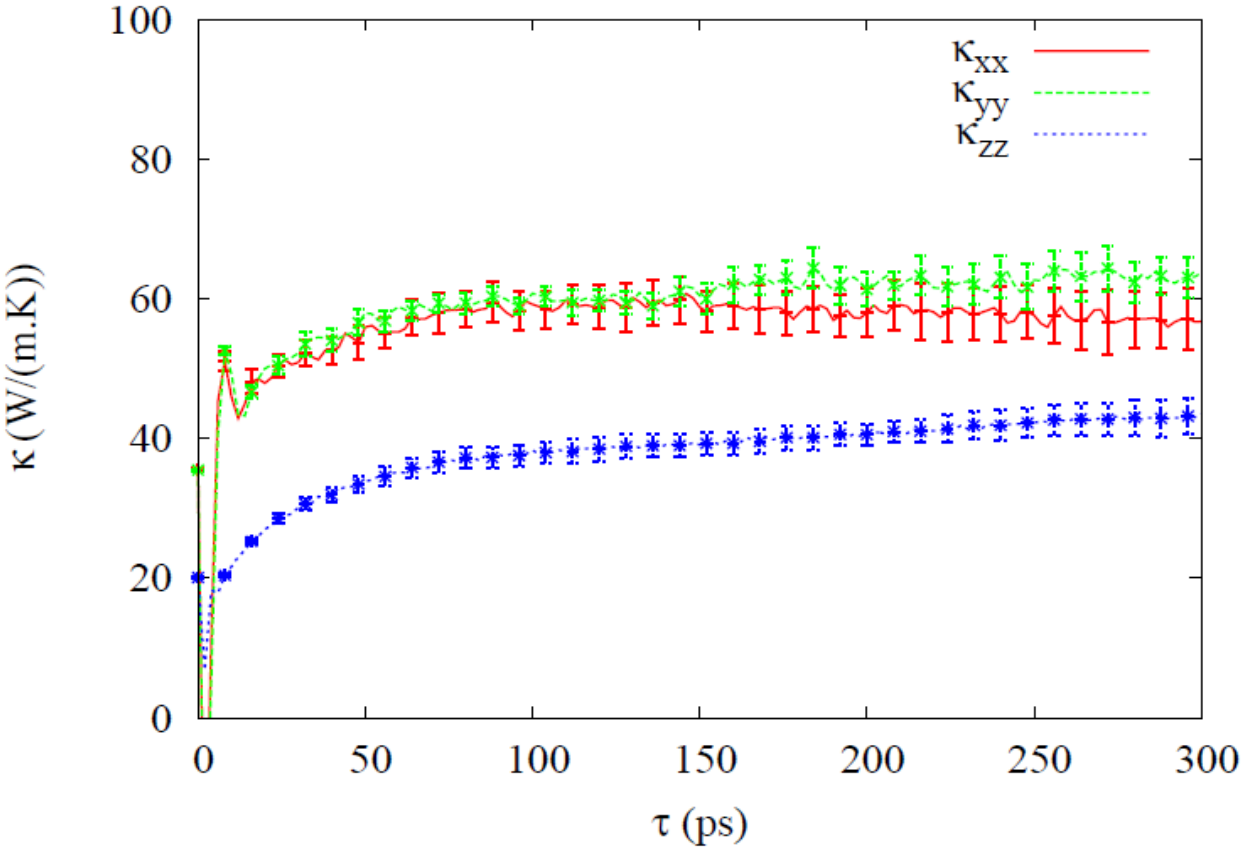
JL, Daw and Bauschlicher, J. App. Phys, (2011)

Correlation Function Power Spectra



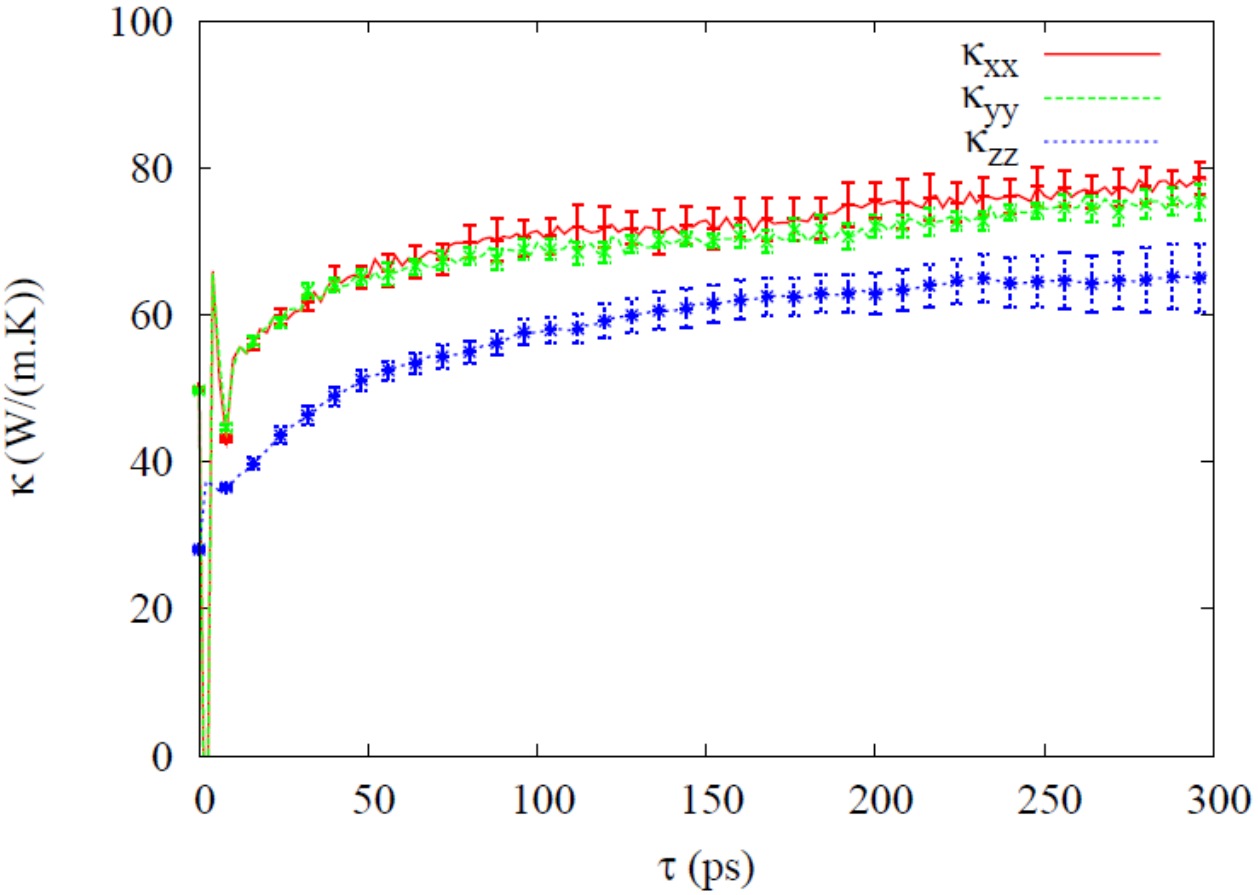
- Correlations oscillates with metal-B optical modes
- C_{xx} and C_{yy} oscillate with in-plane mode frequency
- C_{zz} oscillates with out-of-plane mode frequency

Lattice Thermal Conductivity: ZrB_2



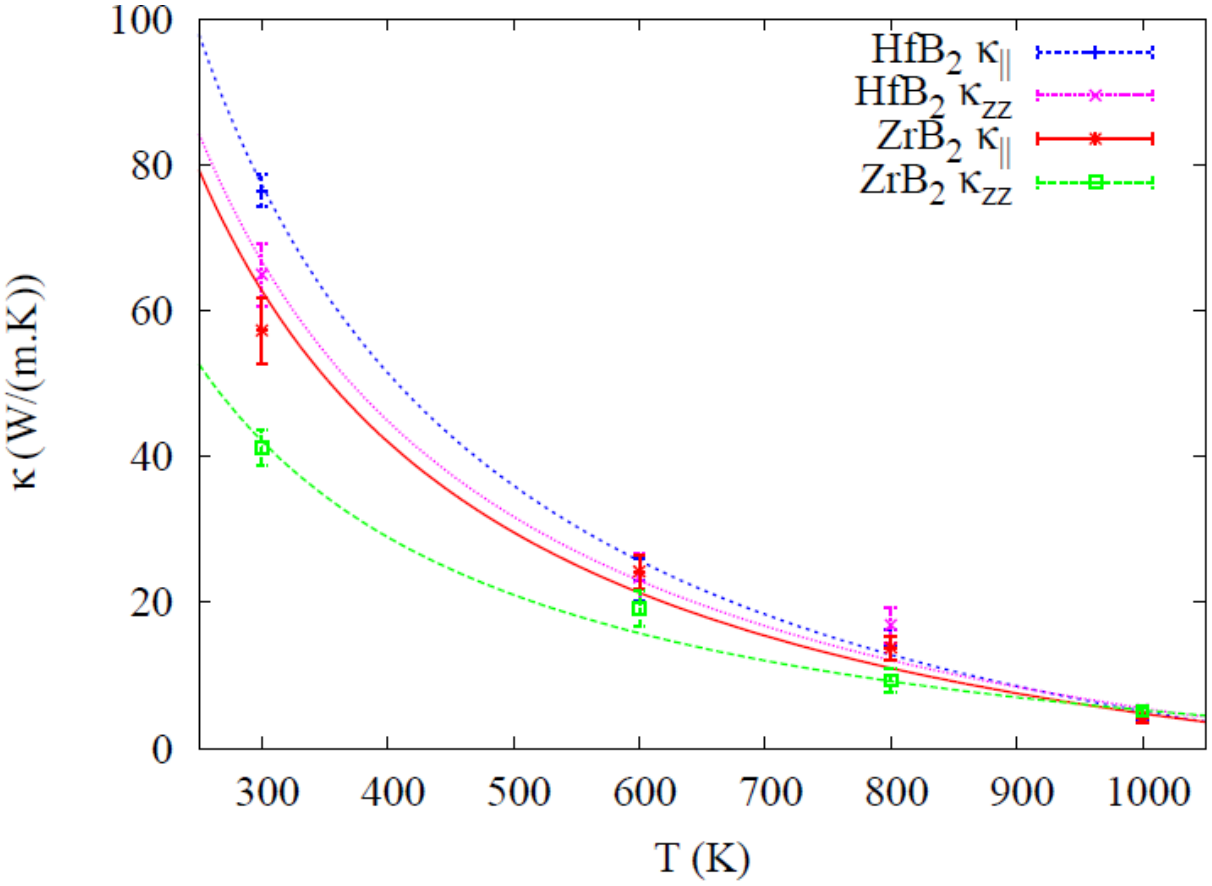
- 8 independent, 10 ns simulations, ***T=300K***
- 8x8x16 unit cell, 12,255 atoms
- ***κ_{xx}=60 W/(m.K), κ_{zz}=40 W/(m.K)***

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*

Single Crystal ZrB_2 Data

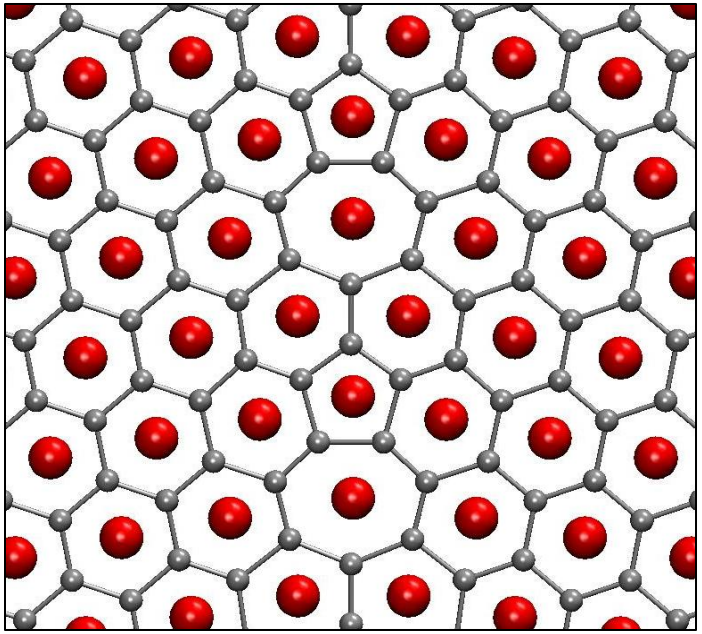
- Electron & lattice thermal conductivity

$$\kappa = \kappa_e + \kappa_{lat}$$

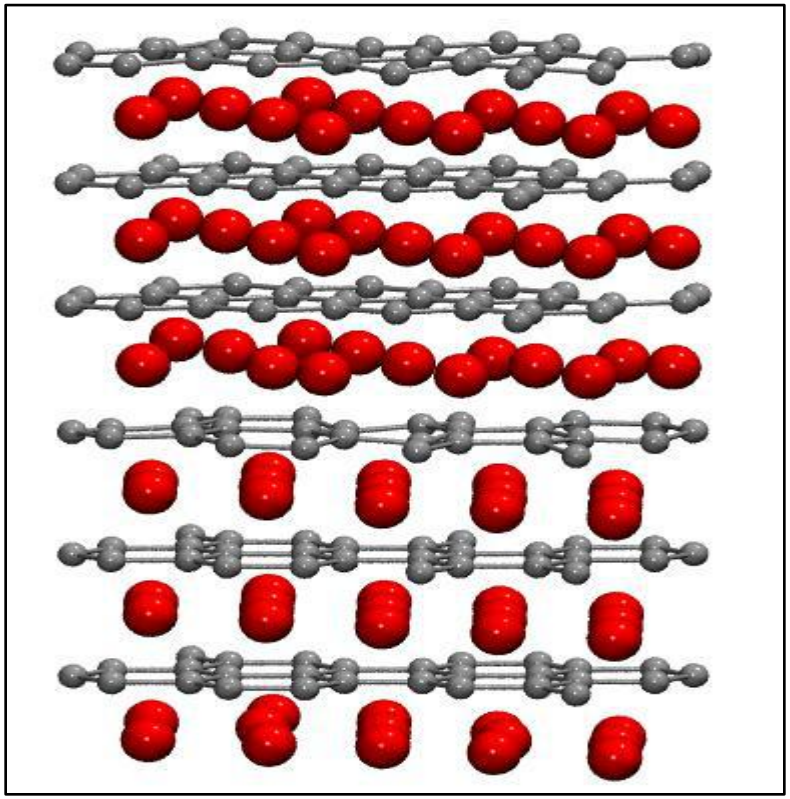
- κ_{lat} is 0.3κ from polycrystalline data
- Single crystal data
  - **κ_{xx} = 140 W/mK, κ_{zz} = 100 W/mK**
  - 1 sample, 1 measurement
  - Defects uncharacterized
  - **κ_{xx} = 45 W/mK , κ_{zz} = 30 W/mK** (lattice)
- More data needed for ZrB_2 and HfB_2

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

UHTC Grain Boundaries



Σ7 symmetric *tilt*
(graphene GB structure)

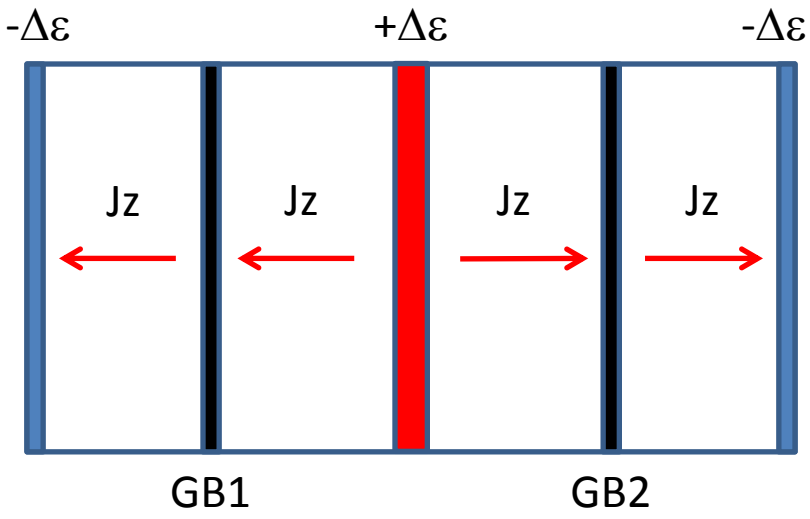


Σ7 symmetric *twist*

Full *ab initio*/MD analysis of two *tilt* and two *twist* boundaries

JL, Daw, Squire and Bauschlicher, J. Am. Ceram. Soc, submitted, (2012)

Interface Thermal Resistance

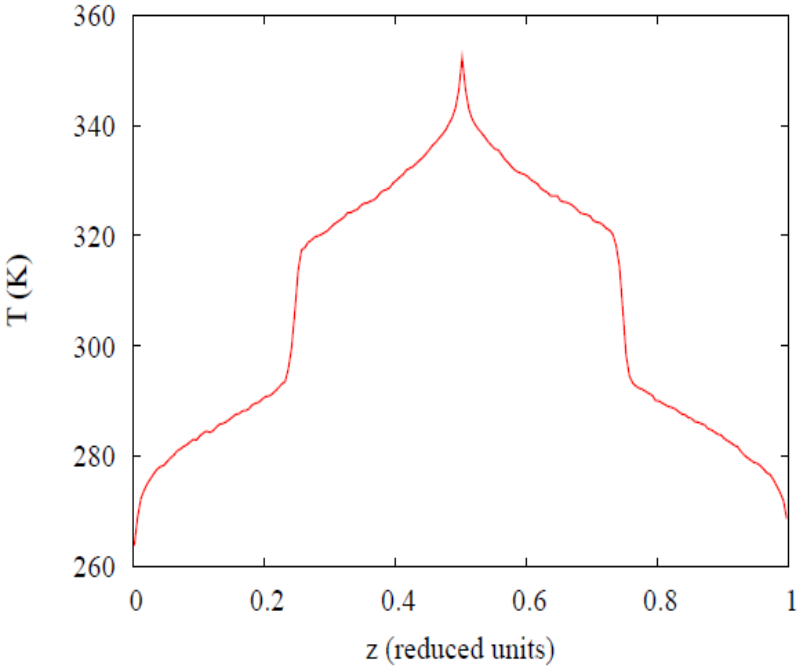


Swap atoms to create heat source/sink

$$Q = \sigma_K \Delta T$$

σ_K is the Kapitza conductance

Temperature Profile



GB at z = 0.25 and 0.75

Muller-Plathe, J. Chem. Phys. 106 (1997), p 6082

Simulation Results

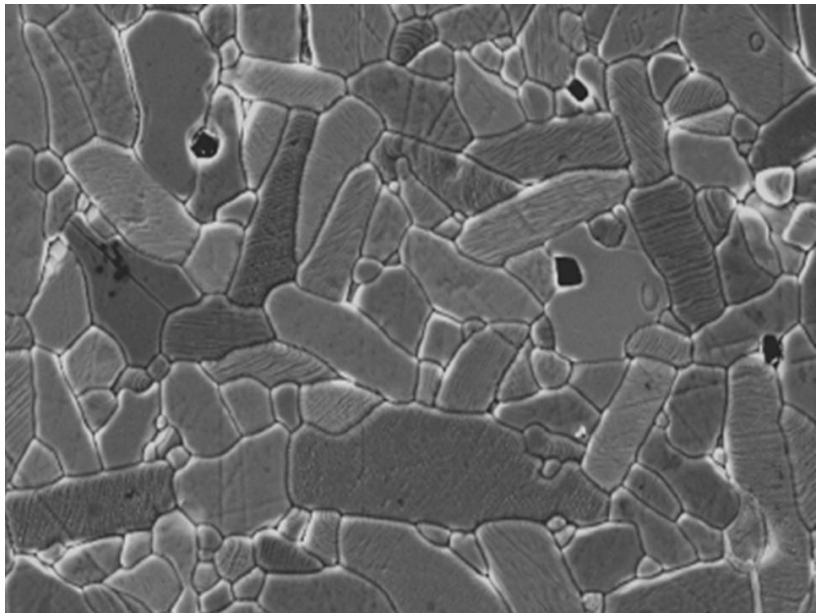
Interface Conductance

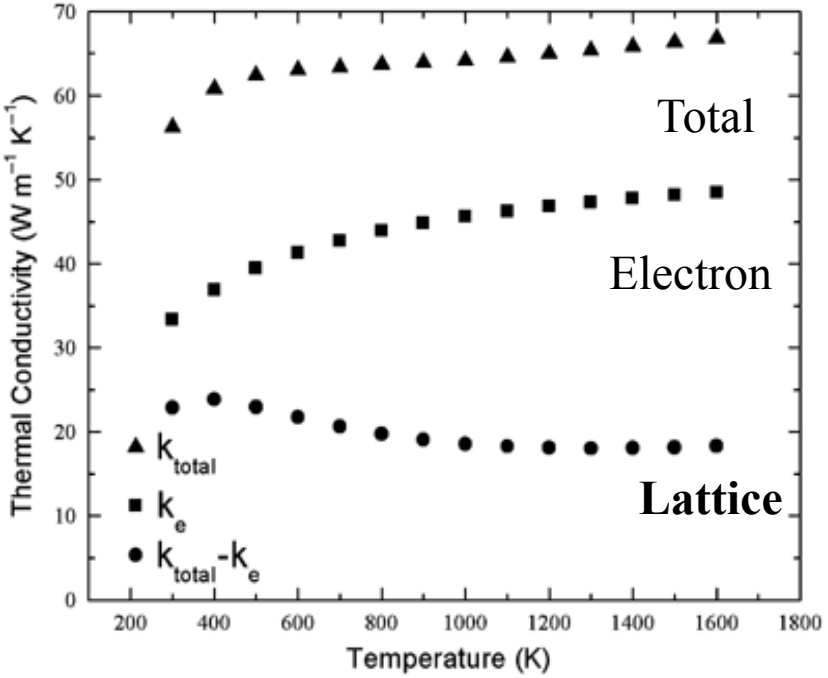
	Ab Initio		DLB/Pot 1		
	γ (meV/Å^2)	Δ_z (Å)	γ (meV/Å^2)	Δ_z (Å)	σ_K $(GW/(m^2 \cdot K))$
c-tilt	153(369)	-	112(238)	-	1.77
c-twist	157(375)	0.29	111(258)	0.29	0.58
a-tilt	227(1040)	-	107(1380)	-	0.38/0.31
a-twist	212(1230)	-	118(1430)	-	0.55/0.53

TABLE I: Energetics and thermal conductance for ZrB_2 grain boundary structures from empirical potentials (DLB/Pot 1) and *ab initio*/DFT. Units for γ are meV/Å^2, Δ_z are Å and σ_K are $GW/(m^2 \cdot K)$.

- 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

Experimental Results: Polycrystalline ZrB_2



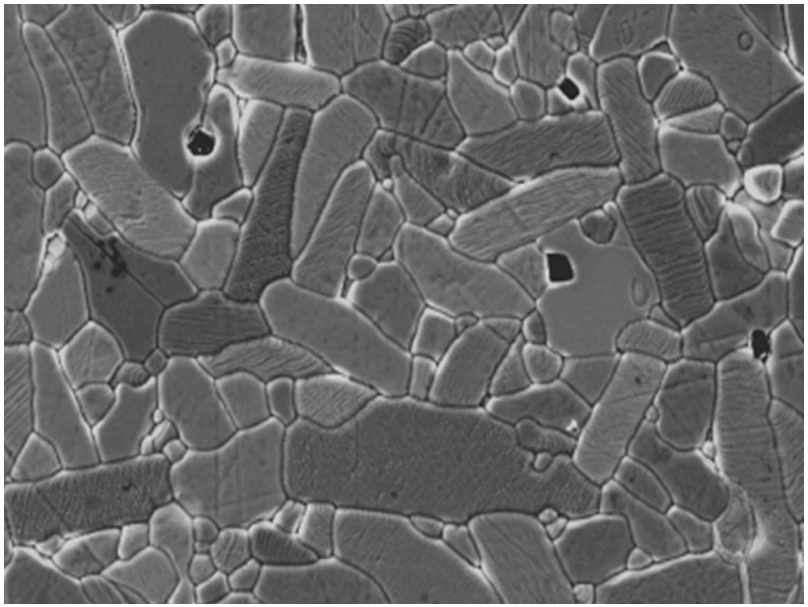


At 300K, κ_{tot} = 55 W/mK, κ_e = 33 W/mK, κ_{lat} = **22 W/mK**

Fahrenholtz, Hilmas, Talmy and Zaykoski, J. Am. Ceram. Soc., (2007)

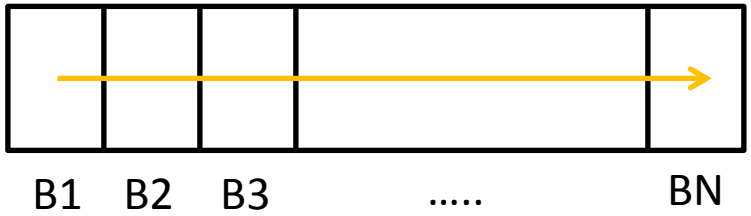
Zimmermann, Hilmas, Fahrenholtz Dinwiddie, Porter, Wang , J. Am. Ceram. Soc., (2008)

Microstructural Model: ZrB_2



What is effect of grain boundary network on thermal conductivity?

Estimate with Brick Layer Model



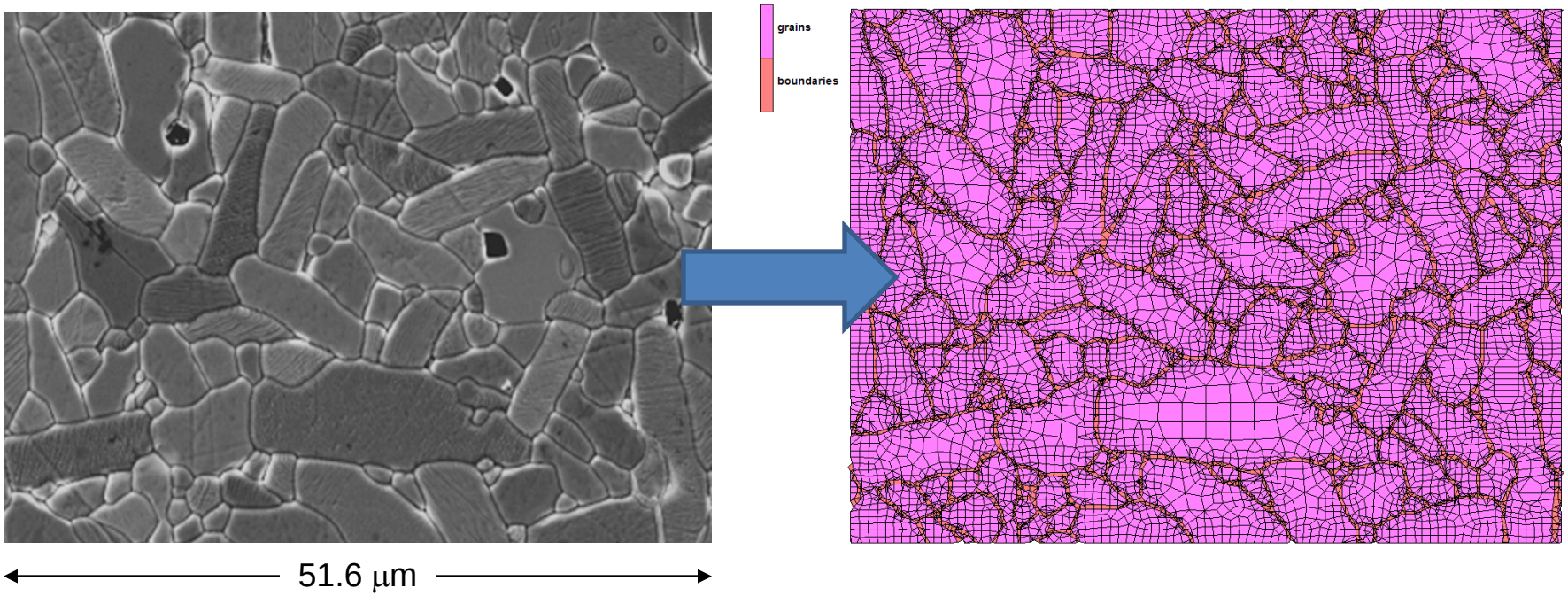
$$\frac{1}{\kappa_{eff}} = \frac{1}{\kappa_0} + \frac{R_K}{d}$$

κ_{eff} = 48 W/mK using **κ_0 = 50 W/mK**, R_K = 1 m^2K/GW, d = 6μm

Very small reduction using MD resistances and BLM!

Fahrenholtz, Hilmas, Talmy and Zaykoski, J. Am. Ceram. Soc., (2007)

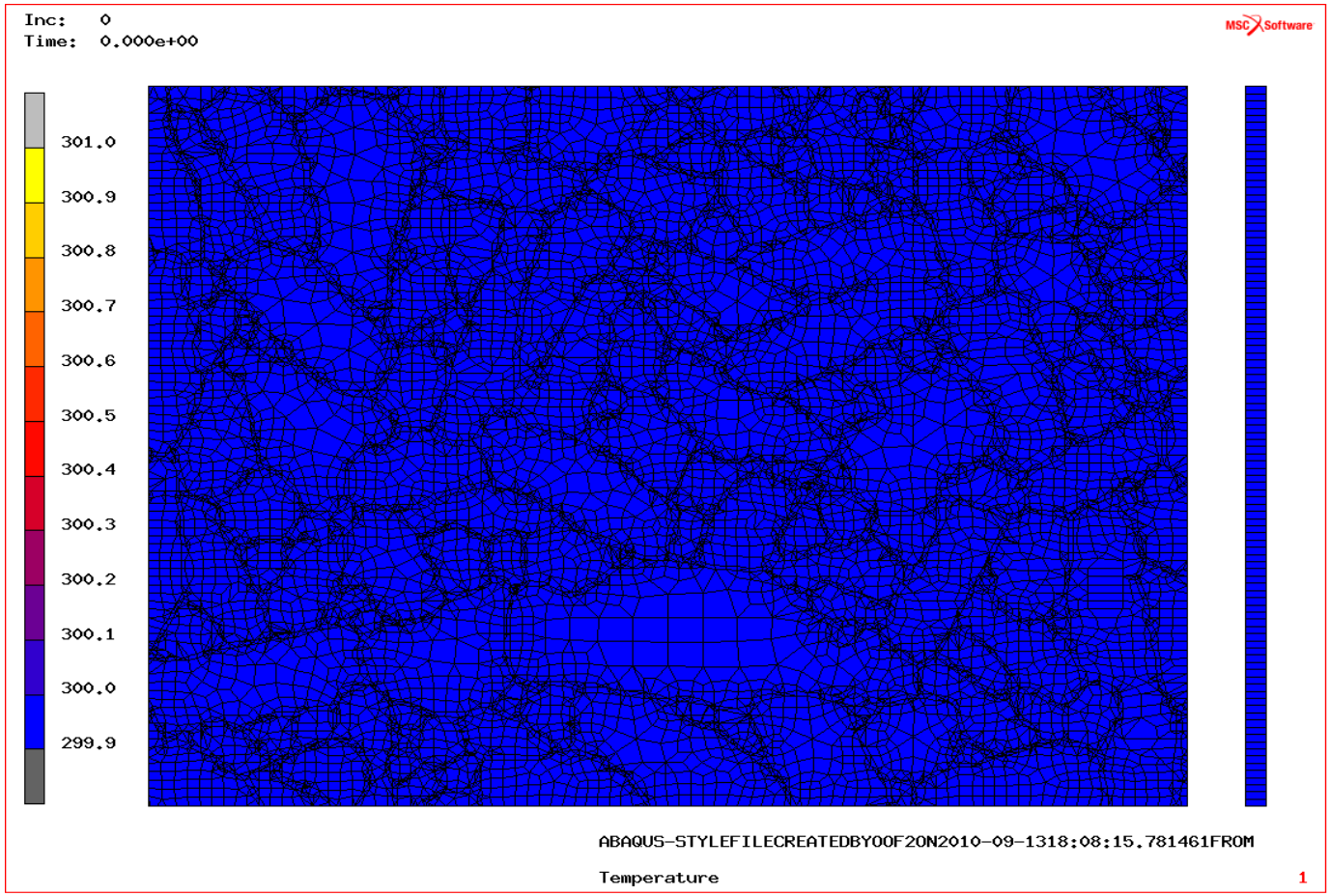
Imaged based FEM



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

Reid, Lua, Garcia, Coffman, Langer, *Int. J. Mat. and Prod. Tech.*, 2009

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

$$\langle q \rangle = -k_{eff} \cdot \langle \nabla T \rangle$$

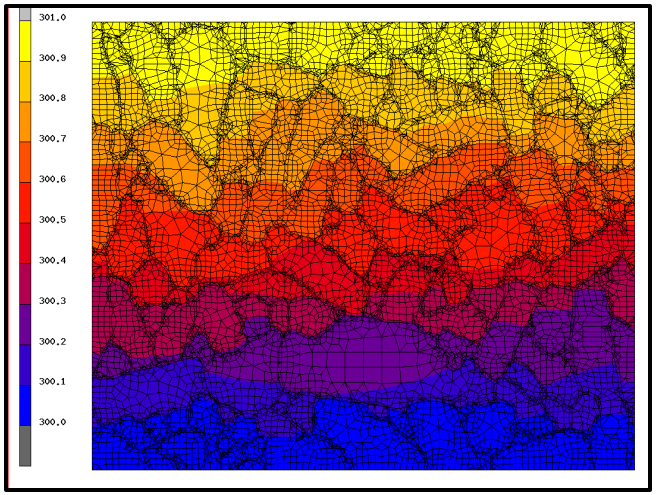
k_{eff} = effective thermal conductivity

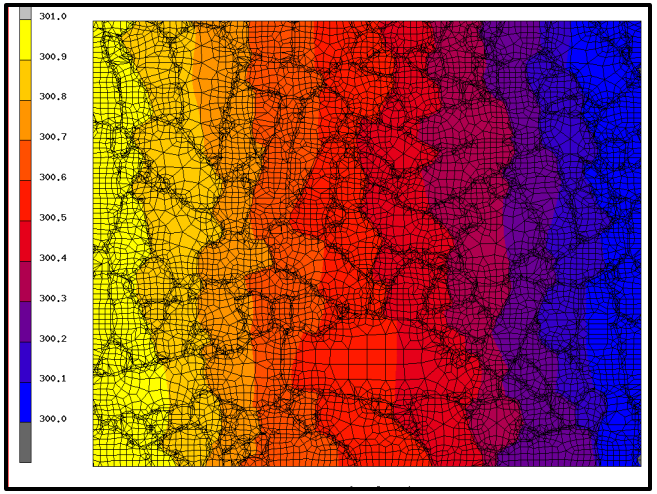
$\langle q \rangle$ = volume averaged heat flux

$\langle \nabla T \rangle$ = volume averaged temperature gradient

- Is microstructure "representative"???

$$\kappa_{UHF} \leq \kappa \leq \kappa_{UTG}$$





Effective Thermal Conductivity

BC Type	Parameter	Vertical	Horizontal
UGT	<q>	-27.32	19.05
	<dT/ds>	1.56	-1.17
	κ_{eff}	**17.48**	**16.24**
UHF	<q>	-28.13	28.05
	<dT/ds>	1.68	-1.76
	κ_{eff}	**16.72**	**15.93**

Comparison of results:

- BLM κ_{eff} = 15.4 (series model)
- Rule of mixtures κ_{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