School of Mechanical Engineering

PURDUE UNIVERSITY Discovery Park

Predicting Thermal Transport in Bismuth Telluride: From Bulk to Nanostructures

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Why Bi_2Te_3?

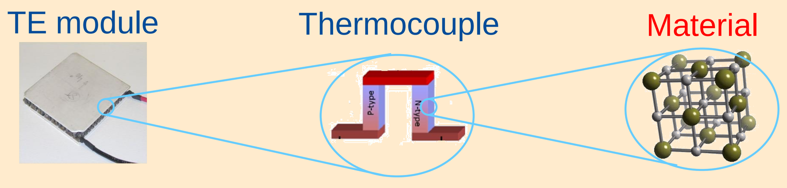
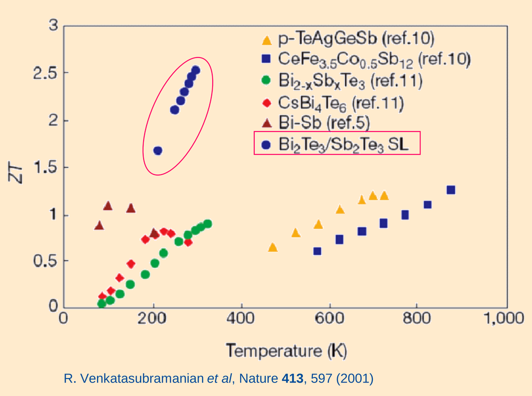


Figure of Merit $ZT = S^2\sigma T/\kappa = \sigma S^2 T/(\kappa_e + \kappa_l)$

Good = high ZT = High σS^2 + Low κ



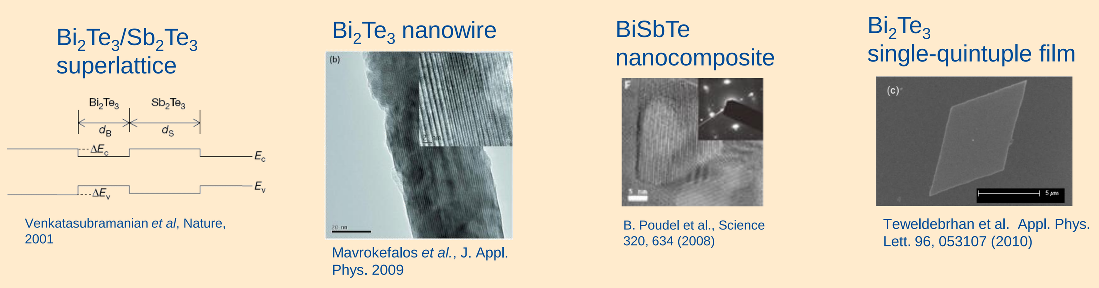
R. Venkatasubramanian et al, Nature 413, 597 (2001)

Highest ZT achieved in Bi_2Te_3 based materials

Reduction in κ_l can almost always bring up *ZT*

To further reduce κ_l: Knowledge of thermal transport in Bi_2Te_3 is required

Experiments in literature

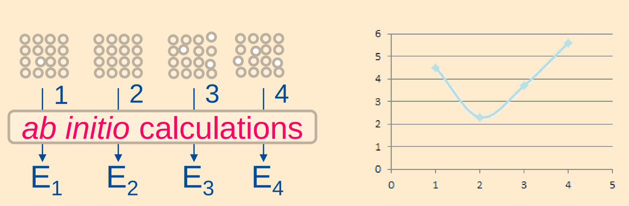


Venkatasubramanian et al, Nature, 2001; Mavrokefalos et al., J. Appl. Phys. 2009; B. Poudel et al., Science 320, 634 (2008); Teweldebrhan et al., Appl. Phys. Lett. 96, 053107 (2010)

Methodology

- Classical potential development

Configuration creation ⇒ Energy surface generation ⇒ Potential parameterization



$$V(r) = D_e(1 - e^{-\alpha(r - r_e)})^2$$

$$D_e = ?, \alpha = ?, r_e = ?$$

- Molecular dynamics simulations
  - Green-Kubo method

MD simulations → Heat current → HCACF → Lattice thermal conductivity

General: $\mathbf{S} = \frac{d}{dt}\sum_i r_i E_i$

Two-body: $\mathbf{S} = \sum_i e_i \mathbf{v}_i + \frac{1}{2}\sum_{i,j}(\mathbf{F}_{ij}\cdot\mathbf{v}_i)\mathbf{r}_{ij}$

$$< S_i(t)\cdot S_i(0) >$$

$$k_l = \frac{1}{k_B T^2 V}\int_0^\infty < S_i(t)\cdot S_i(0) > dt$$

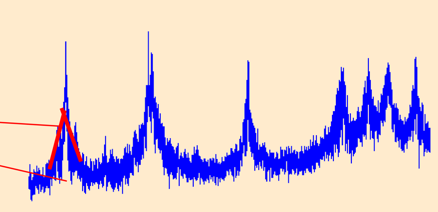
  - Spectral energy density approach

MD simulations → Atomic velocities → Spectral energy density function → Fit to Lorentzian form → Phonon frequency, Relaxation time

$$\dot{u}_\alpha^{b,l}(t)$$

$$\Psi(\mathbf{k},\omega) = \frac{1}{4\pi\tau_0 N_T}\sum_\alpha^3\sum_b^{n_b} m_b \left|\int_0^{\tau_0}\sum_l^{N_T}\dot{u}_\alpha^{b,l}(t) \times \exp[i\mathbf{k}\cdot\mathbf{r}_0^l - i\omega t]dt\right|^2,$$

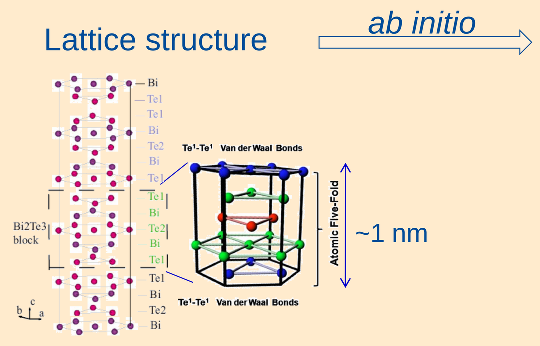
$$= \sum_\nu^{3n} C_0(\boldsymbol{\kappa}_\nu) \frac{\Gamma(\boldsymbol{\kappa}_\nu)/\pi}{[\omega_A(\boldsymbol{\kappa}_\nu) - \omega]^2 + \Gamma^2(\boldsymbol{\kappa}_\nu)}$$



Classical potential for Bi_2Te_3

- Development of two-body classic interatomic potential

Lattice structure —*ab initio*⇒ Morse potential



$$\varphi_s(r_{ij}) = D_e[\{1 - e^{[-a(r_{ij} - r_0)]}\}^2 - 1]$$

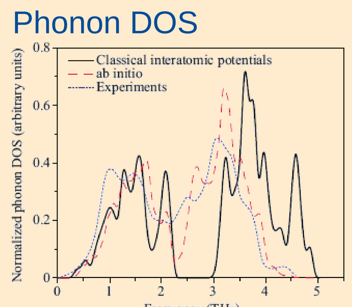
Interaction	D_e (eV)	a (1/Å)	r_0 (Å)	r_c (Å)
Te1-Bi	0.975	1.285	3.089	4.0
Te2-Bi	0.582	1.257	3.251	4.0
Te1-Te1	0.076	1.675	3.642	5.0
Bi-Bi	0.085	2.212	4.203	5.5
Te2-Te2	0.066	2.876	4.312	5.0
Te1-Te2	0.807	0.731	4.497	5.5

- Validation of developed potential

Elastic properties

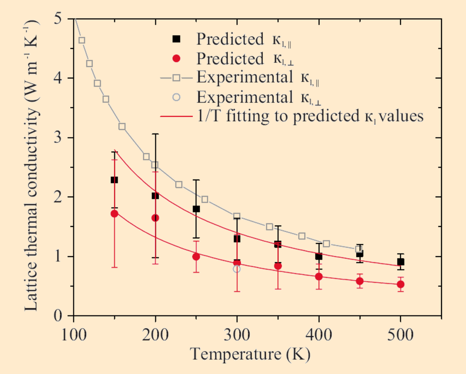
	Ultrasonic experiment[a]	Many-body potential MD[b]	This work
C_{11}	74.4	69.0	75.4
C_{12}	29.2	21.6	23.7
C_{14}	15.4	12.3	11.0
C_{33}	51.6	54.8	49.3
C_{44}	29.2	28.8	23.5
C_{66}	26.2	26.7	25.8
B	39.5	34.4	37.3

Phonon DOS



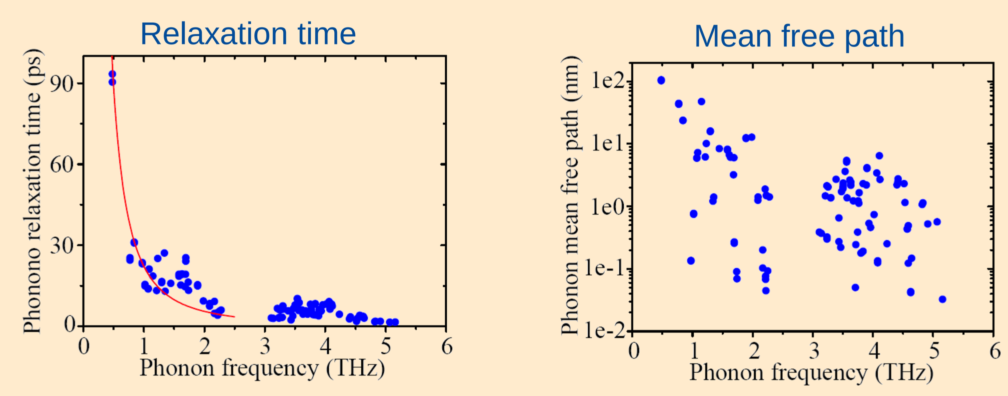
Bi_2Te_3 bulk lattice thermal conductivity

- MD simulation (Green-Kubo) of lattice thermal conductivity



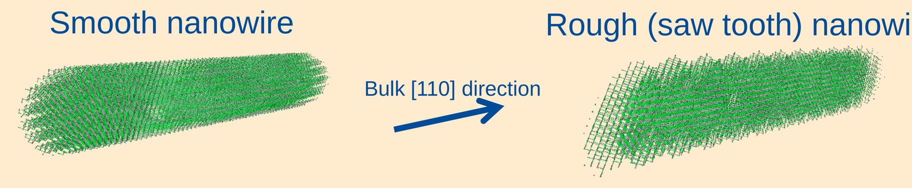
- Agreement with experiments
- 1/T dependence due to Umklapp phonon scattering
- Lattice thermal conductivity
  - Low : Weak bonding
  - Anisotropic: Anisotropic elastic and anharmonic properties

Spectral analysis for Bi_2Te_3 bulk



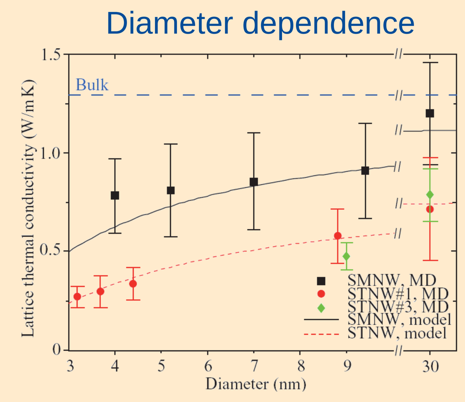
- Phonon relaxation time roughly follow $\tau \sim \omega^{-2}$
- Majority of mean free path : 0.1-100 nm, much smaller than silicon 40 nm – 5 μm (Henry and Chen, J. Comput. Theor. Nanosci. 5,1 (2008))

Bi_2Te_3 nanowires



- MD simulation (Green-Kubo) of lattice thermal conductivity

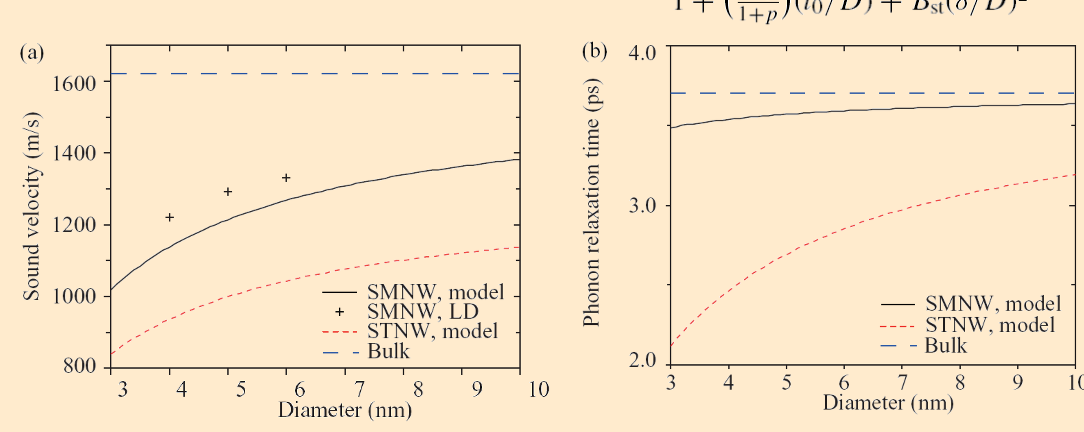
Diameter dependence



- Reduction from bulk
- More reduction in rough nanowires
- Smaller for thinner nanowires
- Minor reduction when D>30 nm

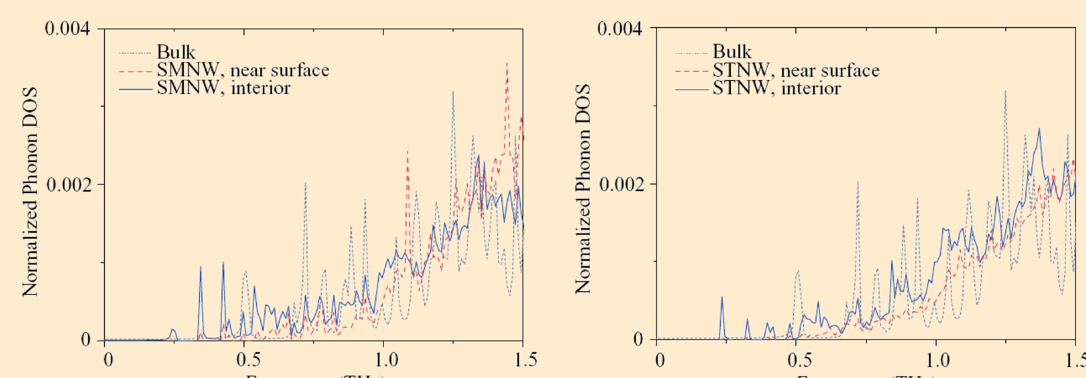
- What leads to reduction from bulk?

Empirical model $\kappa_l = \kappa_0 p \exp(-\alpha l_0/D) \times \dfrac{\left(1 - \frac{1}{12D/L_0 - 1}\right)\exp\left(-\frac{2S_m}{3R}\frac{1}{12D/L_0 - 1}\right)}{1 + \left(\frac{1-p}{1+p}\right)(l_0/D) + B_a(\delta/D)^2}$



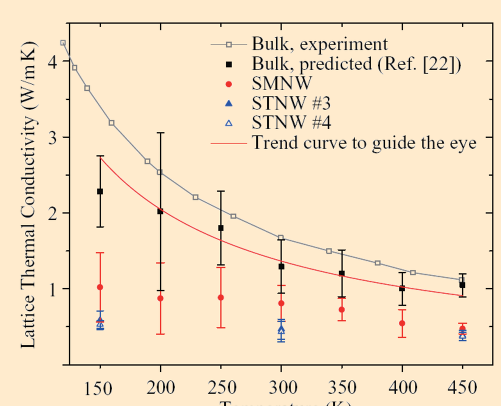
- Smooth nanowire : reduction of sound velocity (phonon softening)
- Rough nanowire : reduction of sound velocity & relaxation time (stronger scattering)

- Why κ_l is lower in rough nanowires?



- Stronger phonon softening in rough nanowires
- Less interior phonon states in rough nanowires to carry heat

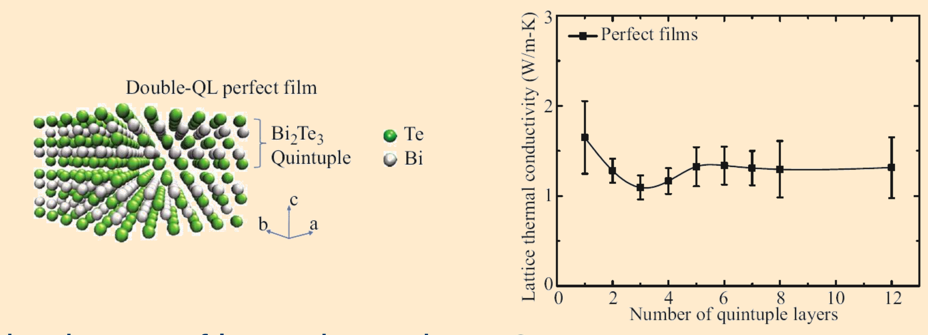
- Temperature dependence



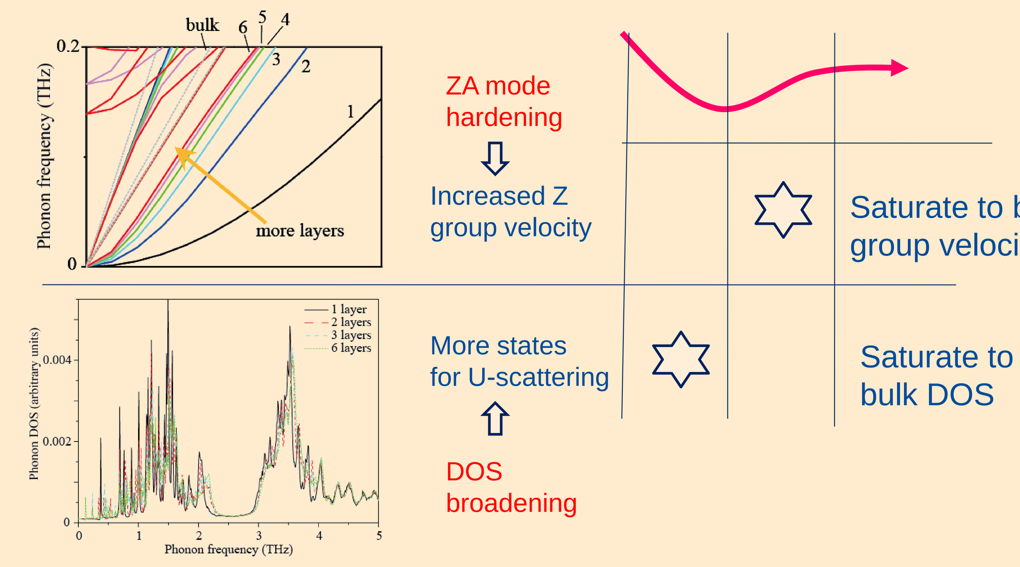
- Weakens from bulk 1/T : boundary scattering
- Weaker for rough nanowires : rough-surface scattering

Few-quintuple Bi_2Te_3 thin films

- Change of thermal conductivity with film stacking



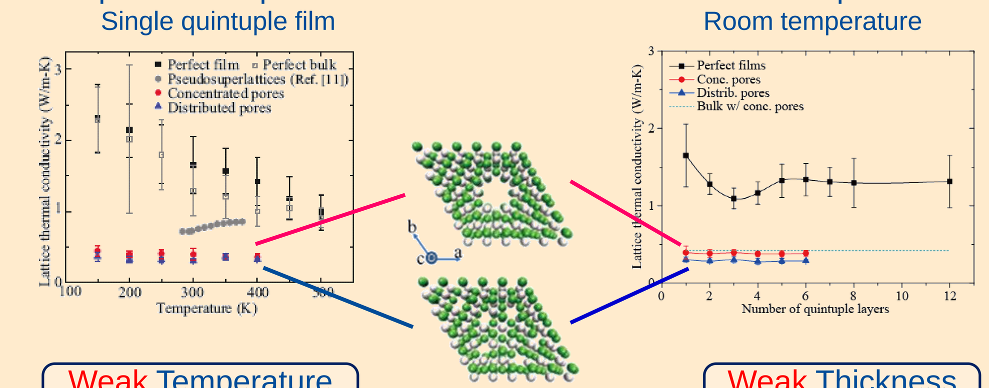
- Why the no. of layer dependence?



ZA mode hardening ⇩ Increased Z group velocity → Saturate to bulk group velocity

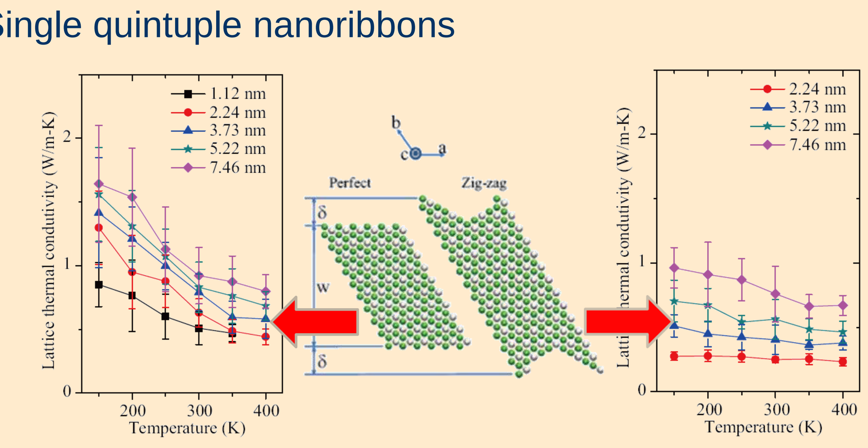
More states for U-scattering ⇧ DOS broadening → Saturate to bulk DOS

- Nanoporous films



Weak Temperature dependence; Weak Thickness dependence ⇒ Constant Low thermal conductivity < 0.5 W/m-K — Good for thermoelectrics!

- Single quintuple nanoribbons



Stronger T dependence, Larger thermal conductivity; Weaker Thickness dependence, Smaller thermal conductivity ⇒ Rough edge leads to low thermal conductivity with weak T dependence — Good for thermoelectrics!

Conclusions and Future work

- Two-body classical potentials developed for Bi_2Te_3, enabling MD simulation of thermal transport
- Bulk thermal conductivity: low value ; anisotropic transport
- Spectral analysis : majority phonons with MFP 0.1-100 nm
- Nanowires with smooth and rough surfaces
  - Strong reduction in thin and rough nanowires
  - Thermal conductivity reduces with decreasing diameter
  - Phonon softening and roughness scattering
- Few-quintuple thin films
  - Interplay between phonon hardening and DOS broadening
  - Porous film and nanoribbon are good candidates for thermoelectrics
- Future work
  - Phonon spectral properties for Bi_2Te_3 bulk and nanostructures
  - Experimental investigation: few-quintuple porous film and nanoribbons

Selected Publications

- Bo Qiu, Lin Sun and Xiulin Ruan, Phys. Rev. B 83, 035312 (2011)
- Bo Qiu and Xiulin Ruan, Appl. Phys. Lett. 97, 183107 (2010)
- Bo Qiu and Xiulin Ruan, Phys. Rev. B 80, 165203 (2009)

Nanoscale Energy Transport and Conversion Laboratory