Thermal and Electric Conduction in Nanostructures

Nick Fang

Course Website: **nanoHUB.org**
Compass.illinois.edu

First Midterm

- Friday, Sept 25 1-2PM
- Coverage:
  - Scaling
  - Quantum Effects
  - Molecular Dynamics of Transport
  - Nanoscale Solid Mechanics

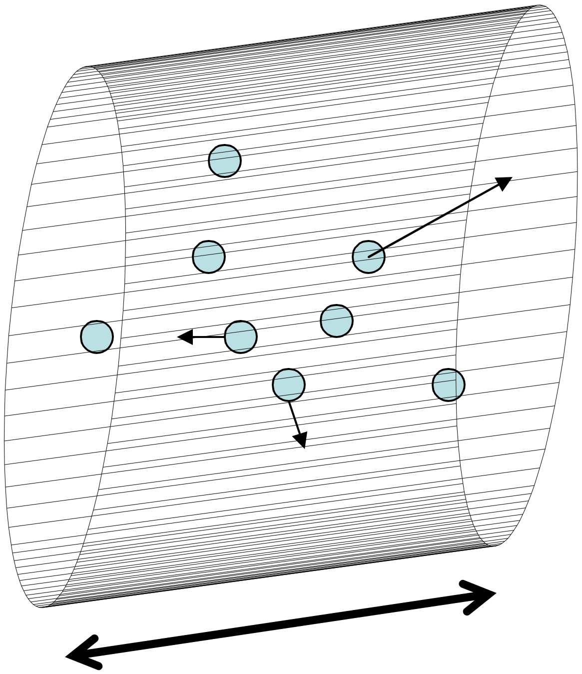
- A Review Lecture on Monday, Sept 21

Back to Constitutive Equations

- Hooke's Law $\sigma = E\varepsilon$
- Fourier's Law $\mathbf{q} = -\boldsymbol{k}\nabla T$
- Fick's Law of Diffusion $\mathbf{J} = -\boldsymbol{D}\nabla \boldsymbol{C}$
- Newton's law on shear stress $\tau = -\mu\ (\mathbf{du/dy})$
- Ohm's Law $\boldsymbol{J} = \sigma E$

How are they correlated in the nanoscale?

Calculating Current Density



Current = # electrons through A per second

$$I = e \times \underbrace{n(r,k)}_{\textbf{Average number of electrons}} \times \underbrace{Adr/dt}_{\textbf{Average velocity}}$$

Current density:

$$J = e \times n(r,k) \times v(r,k)$$

Power density:

$$Q = E(r,k) \times n(r,k) \times v(r,k)$$

Net Charge/Energy Flux

In order to find the net charge/energy flux (net current/power density), we need to consider all possible states at thermal equilibrium

$$J = \int_k e \times n(r,k) \times v(r,k) dk$$

$$Q = \int_k E(r,k) \times n(r,k) \times v(r,k) dk$$

Note: $$n(r,k)dk = \underbrace{D(r,k)}_{\text{Density of States}} \underbrace{p(r,k)}_{\text{Boltzmann Distributions}} dk$$

Boltzmann Transport Equation

$$\frac{\partial}{\partial t} p = -\vec{v} \cdot \nabla_r p - \frac{\vec{F}}{\hbar} \cdot \nabla_k p$$

“**Convection**” “**Acceleration**”

So how to estimate reaction?

Locally, the system that is away from thermal equilibrium has a tendency to relax toward equilibrium state:

$$\frac{\partial}{\partial t} p = -\frac{p - p_0}{\tau}$$

Equilibrium Distribution

Current Density and Mobility

$$J = \int_k e \times n(r,k) \times v(r,k) dk$$

$$J = \int_E e \times D(r,E) \times v(r,E) \times (\tau \vec{v} \cdot (\nabla_r p_0 + \frac{\vec{F}}{\hbar} \frac{\partial p_0}{\partial E})) dE$$

Assume F along z direction, we find:

$$J = \frac{\partial}{\partial z}(e \frac{k_B T n_e \langle \tau \rangle}{m}) + F_z \frac{e n_e \langle \tau \rangle}{m}$$

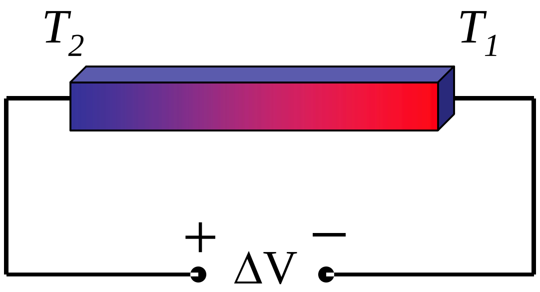
Electron diffusion

Migration under external field

Coupled Heat and Electron Conduction

- Seebeck effect (1821)

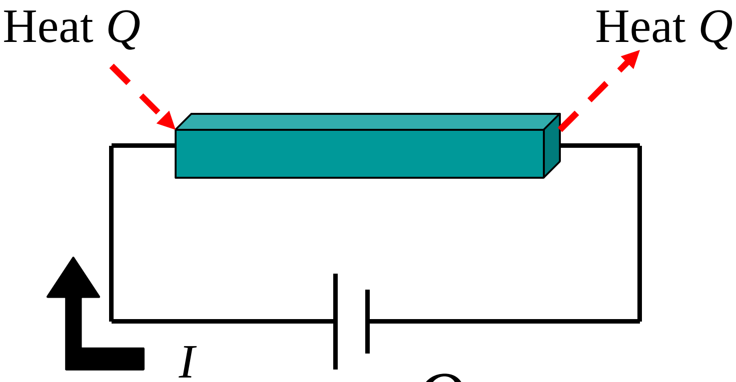
(Heat to electricity)



$$S = -\frac{\Delta V}{T_2 - T_1} \quad [\mathrm{V/°K}]$$

- Peltier effect (1834)

(Electric cooling)



$$\pi = \frac{Q}{I}$$

Thermoelectric Cooling

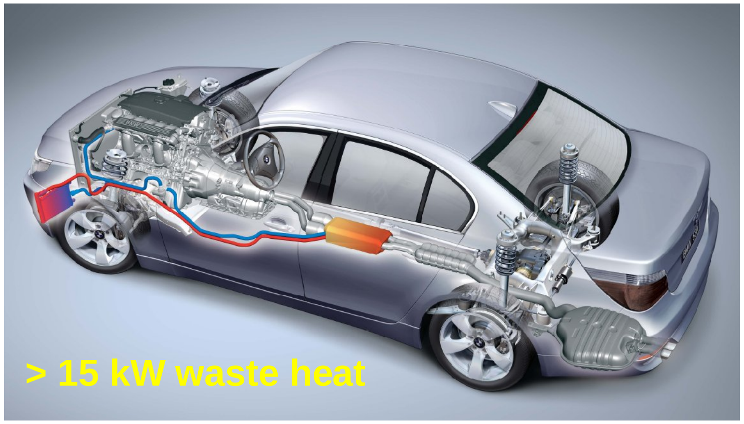
- No moving parts
- Environmentally friendly
- No loss of efficiency with size reduction
- Can be integrated with electronic circuits (e.g. CPU)
- Localized cooling with rapid response

Koolatron Kool Sport Cooler

Major Opportunities in Energy Industry

- Large scale waste heat recovery of industrial processes
  - Benefit from higher energy costs and reduction of fossil fuel pollution
- Hybrid low cost power sources
  - Hybrid solar cell/thermoelectric/battery
    - Day & night operation
    - Flexible, easy deployment

Industrial Waste Heat Recovery



Automobile Exhaust Waste Heat Recovery

Principle of Thermoelectric Effect

Electron Current by BTE:

$$\mathbf{J}_e = \sigma_e \mathbf{E} + \frac{k_B \sigma_e}{e} \nabla \left(T_e \ln n_e \right)$$

Thermoelectricity:

$$\mathbf{E} = \frac{k_B}{e} \nabla \left(T_e \ln n_e \right)$$

Seebeck coefficient:

$$S = \frac{\partial \mathbf{E}}{\partial T} = -\frac{k_B}{e} \boxed{\left(\ln n_0 + \frac{E_a}{k_B T} \right)}$$

86μV/K

- Density of electrons (n)

- Activation energy (Ea)

Thermoelectric Figure of Merit

Electronic current

$$\mathbf{J}_e = \sigma_e(\mathbf{E} + S\nabla T)$$

Electronic current

$$\mathbf{J}_Q = \kappa\nabla T - \pi\sigma\mathbf{E} = \kappa\nabla T - (ST)\sigma\mathbf{E}$$

Seebeck Coefficient

Conductivity

Temperature

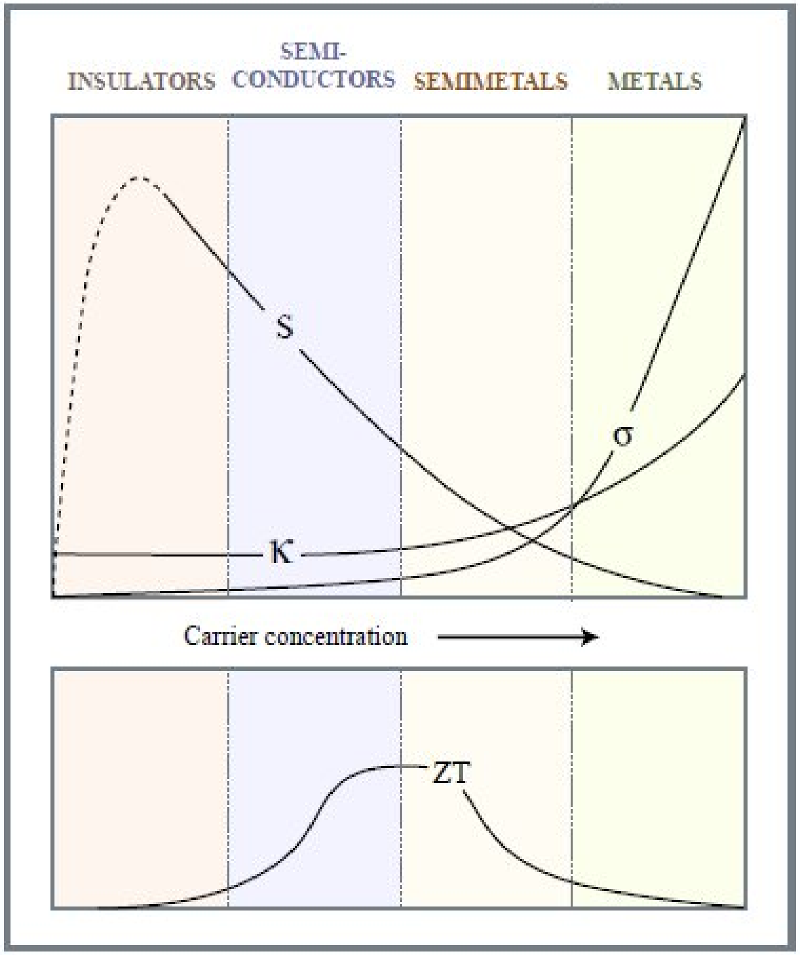
Figure of Merit

$$ZT = \frac{S^2\sigma T}{\kappa}$$

Thermal Conductivity (from electron+phonon)

Comparison of Different Materials

Material	***Typical Seebeck Coefficient (µV/°K)***
Metal	< 10
Semiconductors	200~600 (Heavy Doping)
Ionized Hydrogels	250~400
Electrolyte	200-1000 ($AgBr/CdBr_2$)

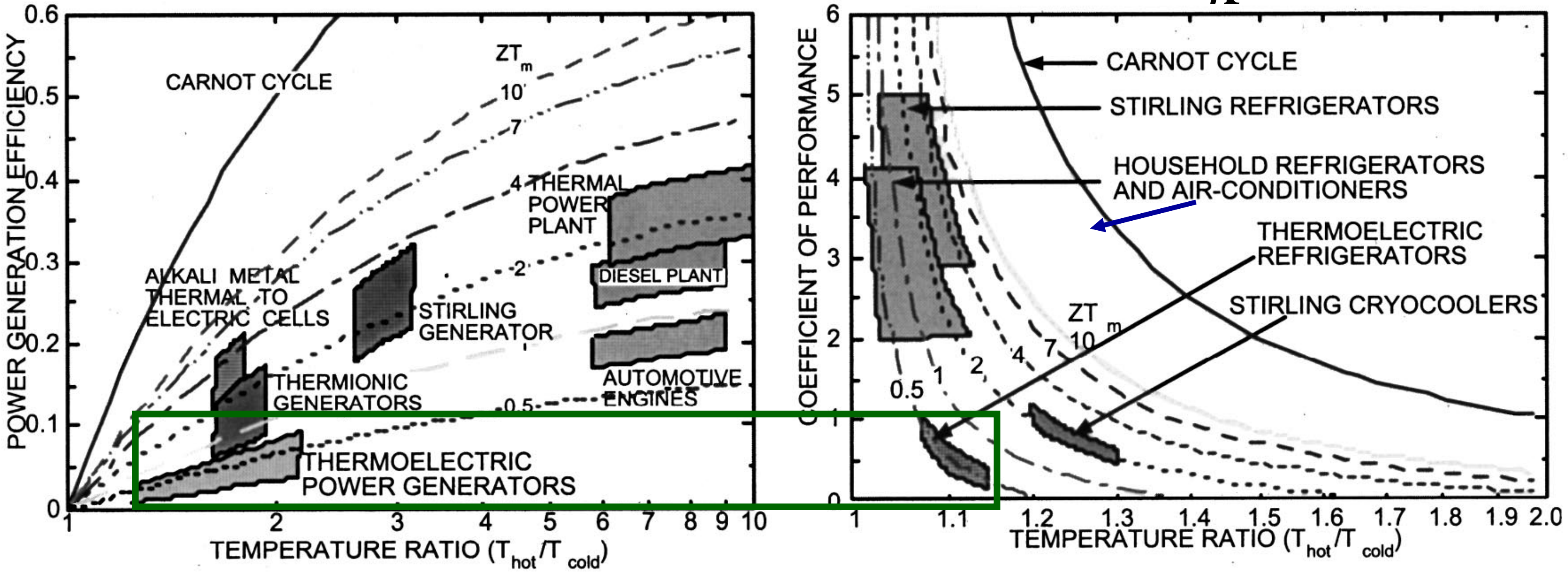


$$ZT = \frac{\sigma S^2 T}{\kappa}$$

Challenges in Efficiency

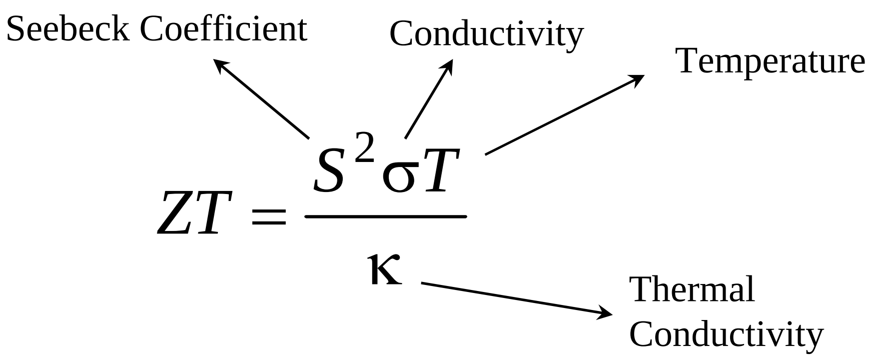
Existing thermo-electric devices operate in limited temperature range and suffer from lower efficiency

$$ZT = \frac{\sigma S^2 T}{\kappa} < 1$$



from G. Chen et al, JOURNAL OF HEAT TRANSFER, 2002(124)242-252

Nanoscale Thermoelectricity?


Seebeck Coefficient

Conductivity

Temperature

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

Thermal Conductivity

ZT ~ 3 for desired goal

Difficulties in increasing *ZT* in bulk materials:

$S \uparrow \Longleftrightarrow \sigma \downarrow$

$\sigma \uparrow \Longleftrightarrow S \downarrow$ and $\kappa \uparrow$

⇒ A limit to *Z* is rapidly obtained in conventional materials

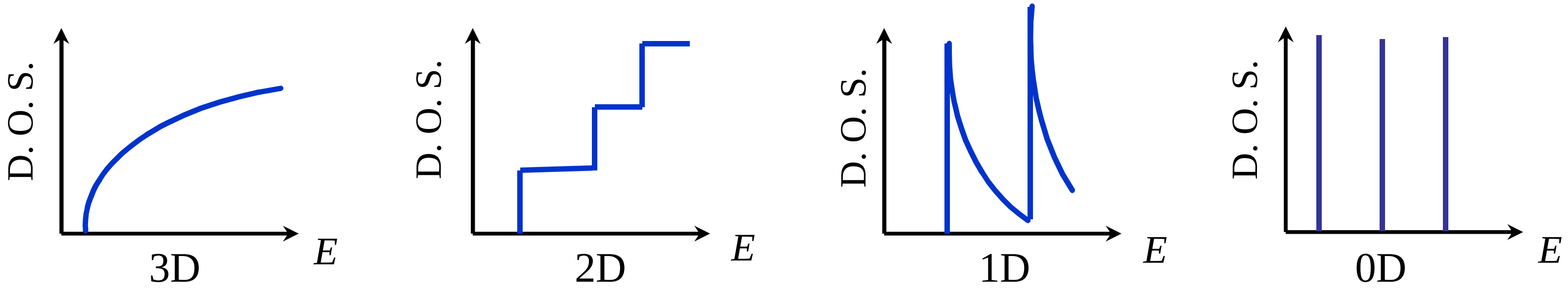
⇒ So far, best bulk material ($Bi_{0.5}Sb_{1.5}Te_3$) has *ZT* ~ 1 at 300 K

Low dimensions give additional control:

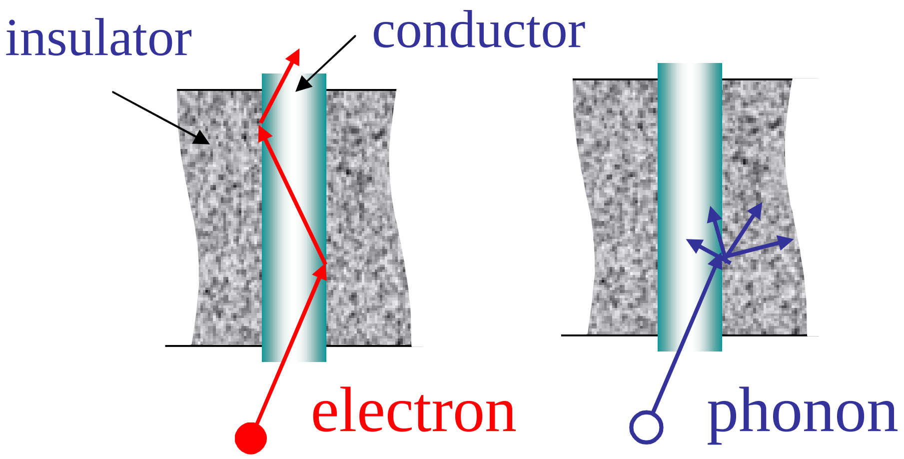
- Enhanced density of states due to quantum confinement effects
  - ⇒ Increase *S* without reducing σ
- Boundary scattering at interfaces reduces κ more than σ
- Possibility of materials engineering to further improve *ZT*

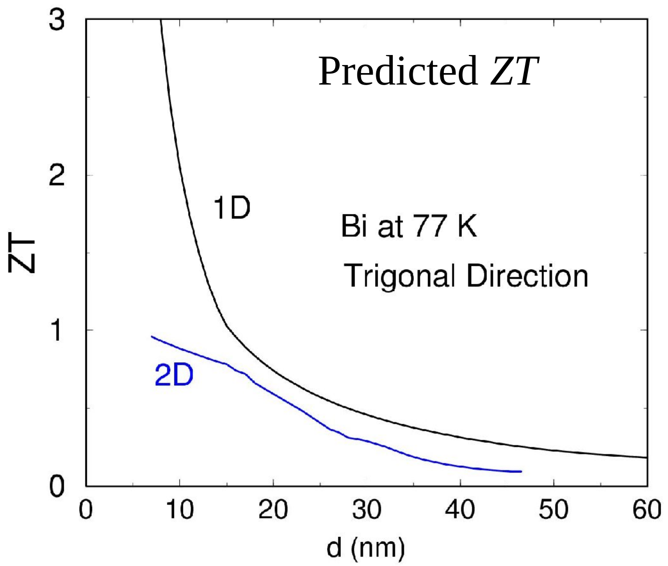
New Directions for Nano- Thermoelectricity

- Electronic properties may be dramatically modified due to the electron confinement in nanostructures which exhibit low-dimensional behaviors

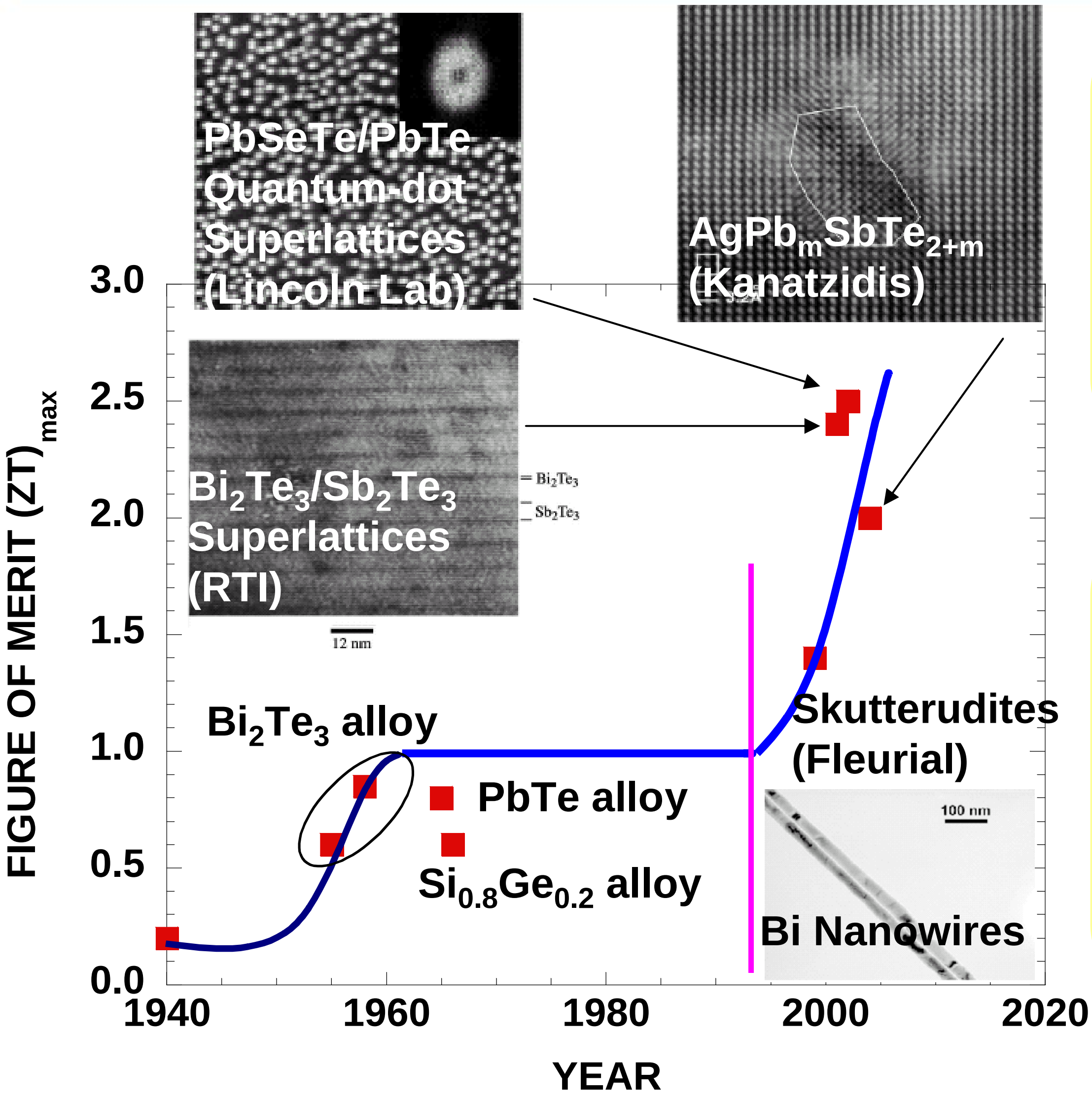


- Thermal conductivity can be significantly reduced by the preferential scattering of phonons at the interfaces





State-of-the-Art in Thermoelectrics



PbTe/PbSeTe	Nano	Bulk
$S^2\sigma$ ($\mu W/cmK^2$)	32	28
k (W/mK)	0.6	2.5
ZT (T=300K)	1.6	0.3

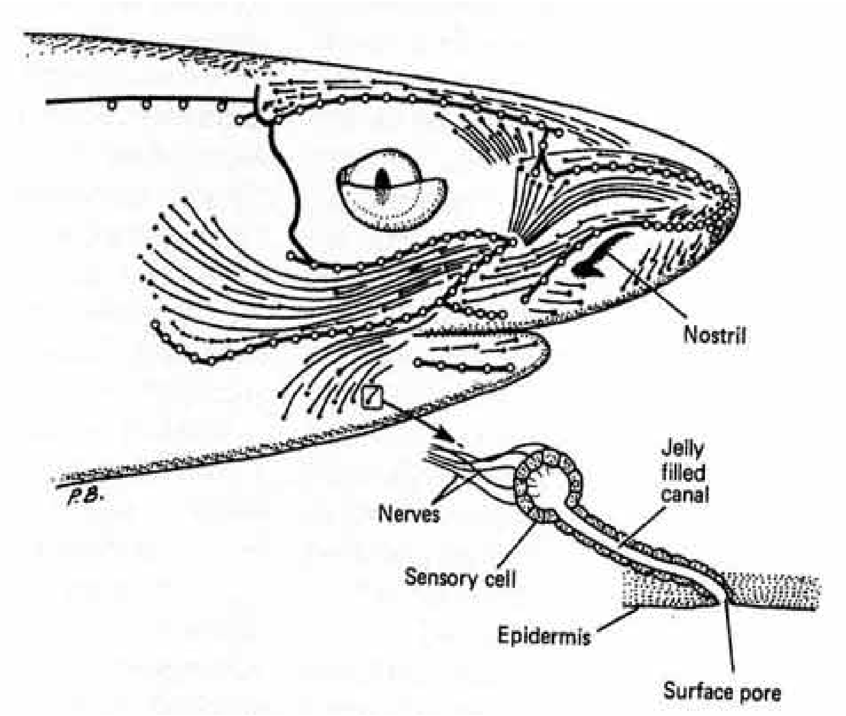
Harman et al., Science (2003)

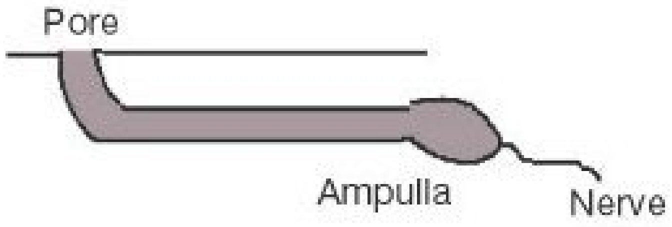
Bi_2Te_3/Sb_2Te_3	Nano	Bulk
$S^2\sigma$ ($\mu W/cmK^2$)	40	50.9
k (W/mK)	0.6	1.45
ZT (T=300K)	2.4	1.0

Venkatasubramanian et al., Nature, 2002.

A Natural Thermo-electric Sensor in Shark

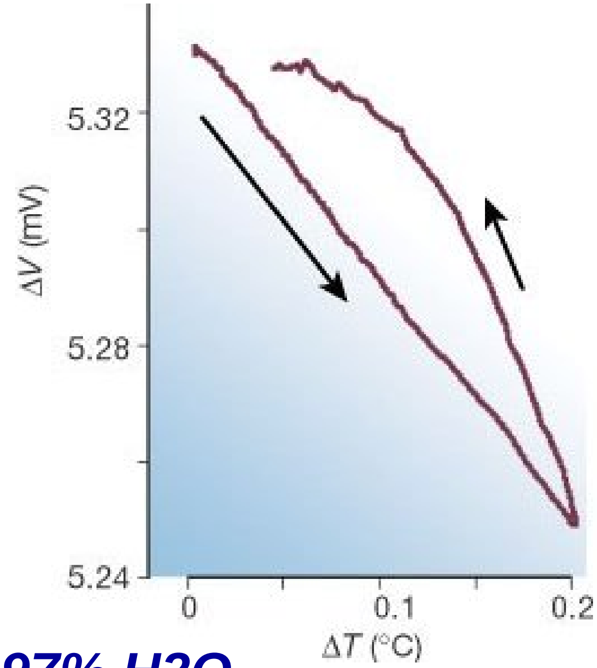
Brown, Nature, 2003





Extreme sensitivity to temperature changes

~0.001°C !!

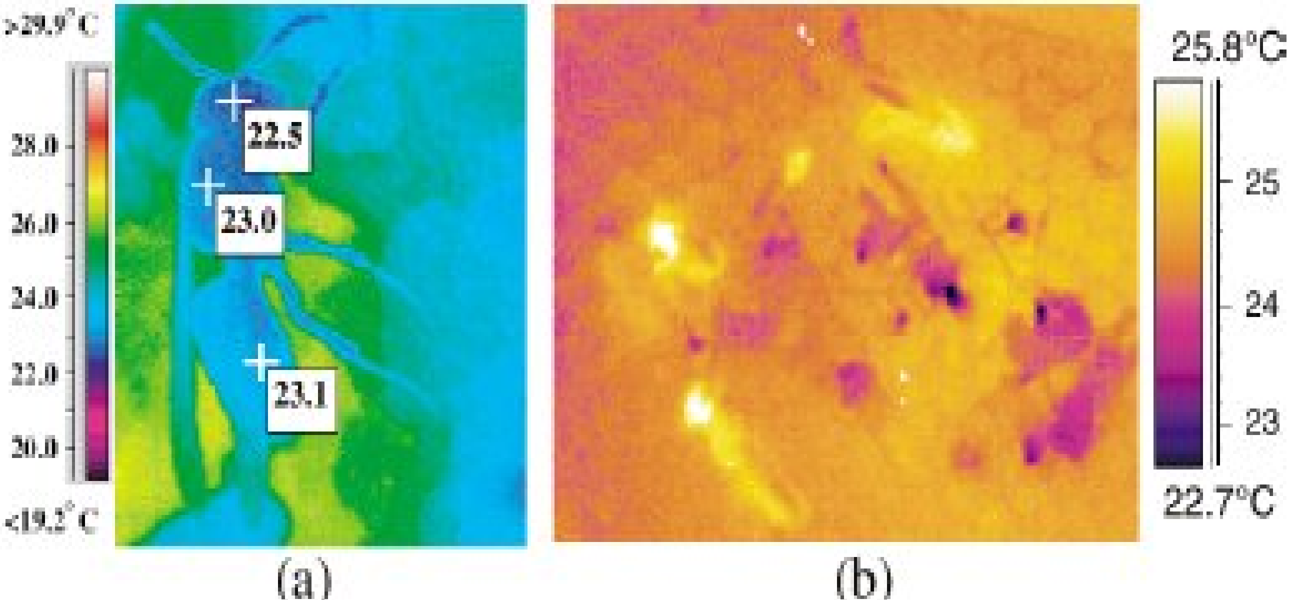


97% $H2O$

Sulfated glycoprotein

Na, Ca, Cl, and K ions.

Hornet skin: a natural heat pump?

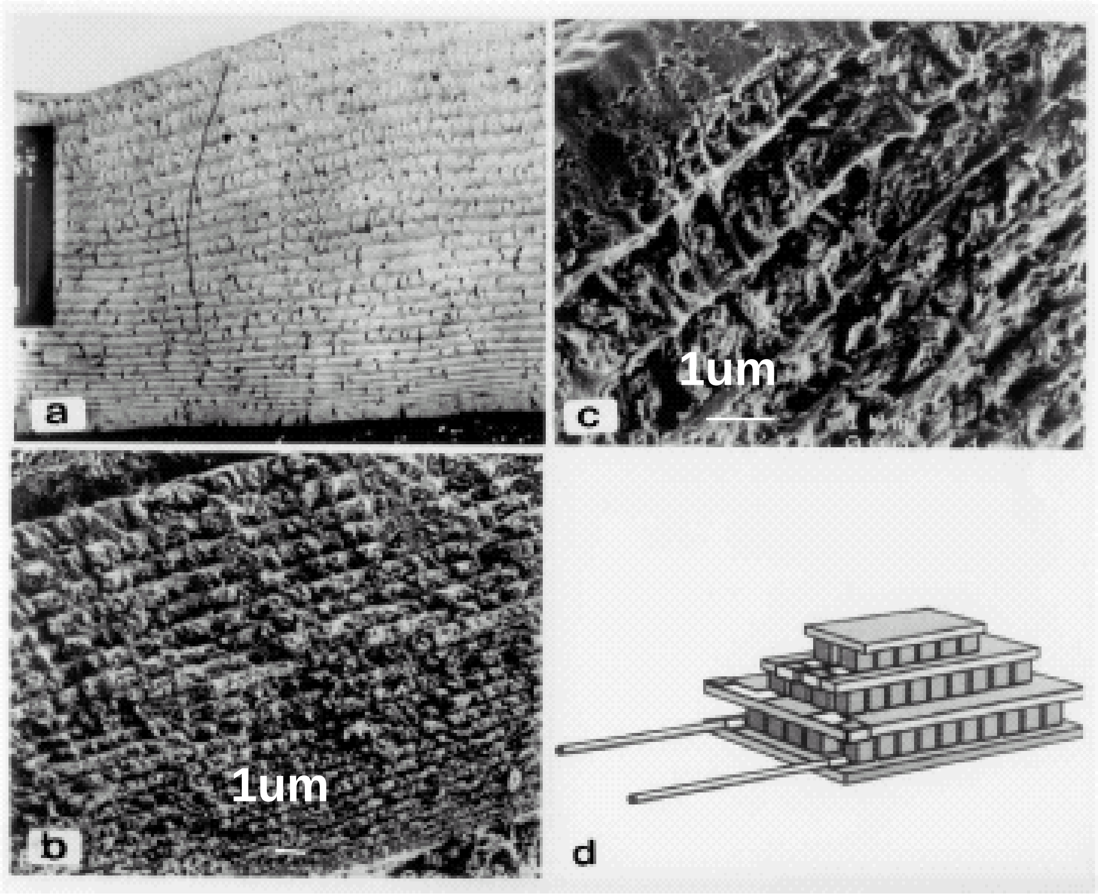


IR image of the hornets

Hornets keep their body temperature lower by 3-4 degrees when they are active outside the nest in daytime, where the ambient temperature can be as high as 40–60 C.

(Ishay et al, PRL, 2003)

Hornet skin: a natural heat pump?



Indirect measurement suggests

- ☐ σ=0.16 *S*/m and
- *S*~ **2mV/K**!
- ☐ κ~ 0.01W/(mK)

Shimony and Ishay, J. Theo. Bio, 1981

Additional Readings

- G. Chen and A. Shakouri, “Heat Transfer in Nanostructures for Solid-State Energy Conversion”, JOURNAL OF HEAT TRANSFER**,** 2002(124)242-252

- J.S. Ishay et al, “Natural Thermoelectric Heat Pump in Social Wasps”, Physical Review Letters, 2003 (90)218102.

- Theme Issue, “Harvesting Energy through Thermoelectrics: Power Generation and Cooling”, MRS Bulletin, March 2006 (36).