Thermoelectricity: From Atoms to Systems

Week 5: Recent Advances in Thermoelectric Materials and Physics

Lecture 5.5: Ideal Thermoelectrics, Carnot vs. Curzon-Ahlborn limits, Some open questions

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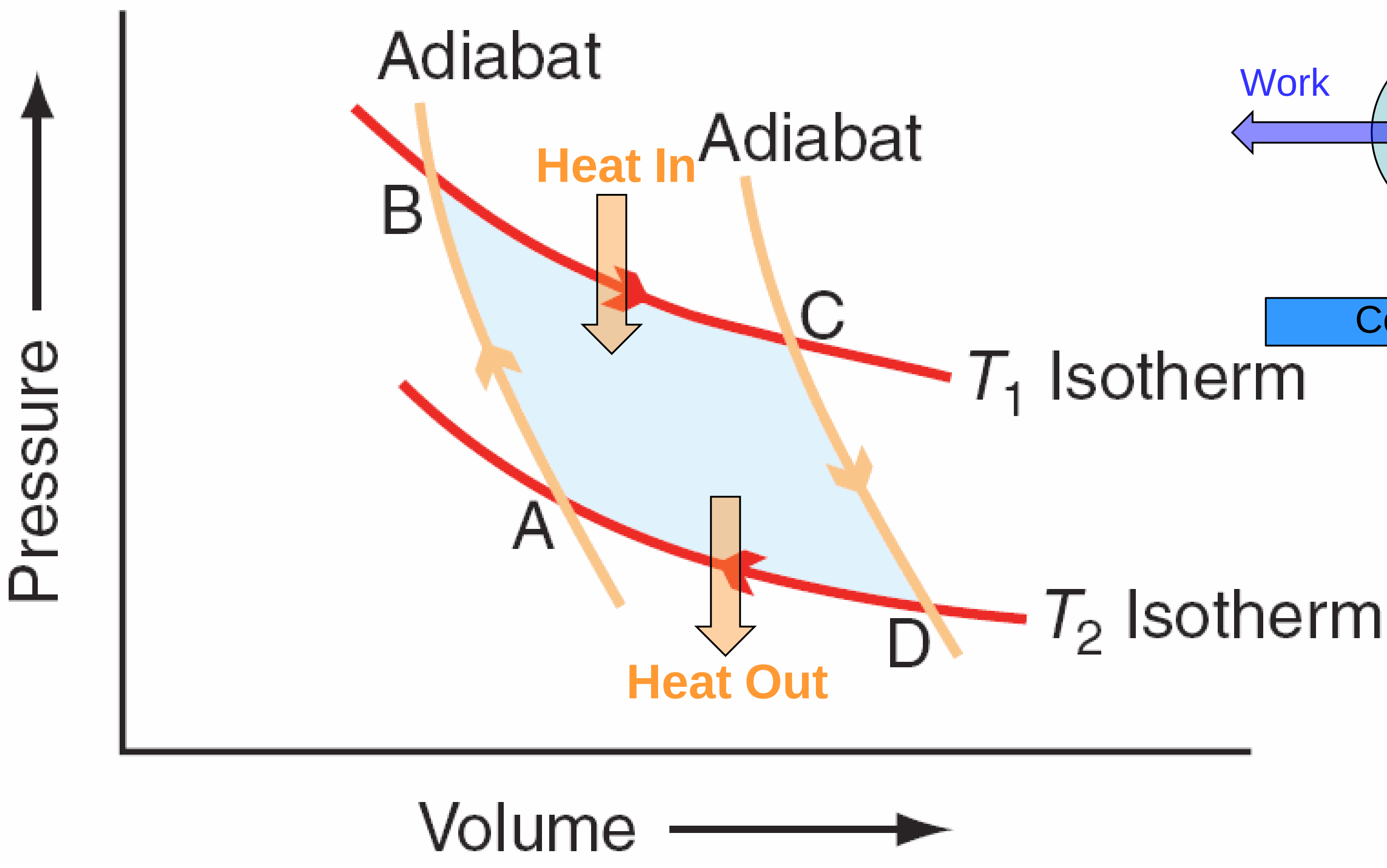
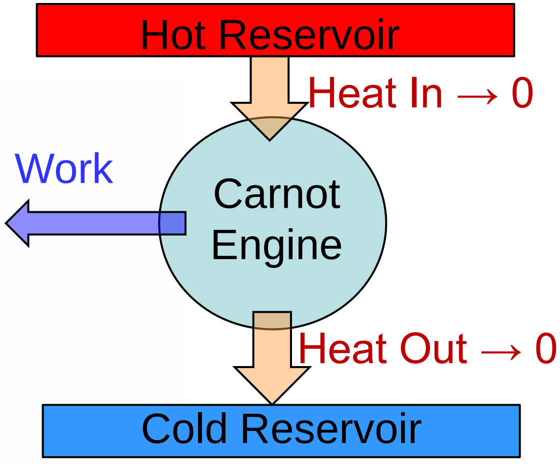
Carnot Cycle (reversible)





Carnot efficiency for heat engines

The production of motive power is then due in steam-engines not to an actual consumption of caloric, but *to its transportation from a warm body to a cold body*, that is, to its re-establishment of equilibrium.

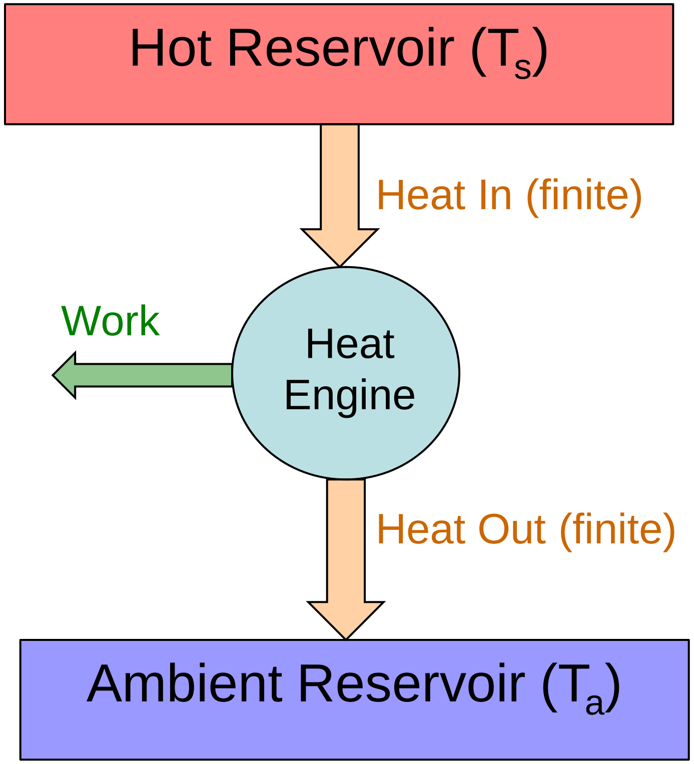
in the bodies employed to realize the motive power of heat there should not occur any change of temperature which may not be due to a change of volume. Reciprocally, ...

Reflections on Motive Power of Fire, *Sadi Carnot*, 1824

Curzon-Ahlborn Limit

F.L. Curzon and B. Ahlborn, *Am. J. Phys*. **43**, 22 (1975)

K. Yazawa and A. Shakouri, J. Appl. Phys. 111, 024509 (2012)



Finite thermal resistances with hot and cold reservoirs

$\Rightarrow$ Finite output power

$\Rightarrow$ Curzon-Ahlborn efficiency at maximum output power:

$$\eta_{\text{limit}} \rightarrow 1 - \sqrt{\frac{T_a}{T_s}}$$

The Best Thermoelectric

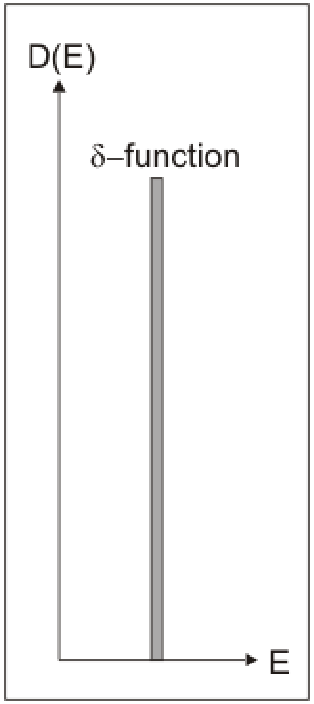
G. D. Mahan and J. O. Sofo, *Proc. Nat. Acad. Sci.* **93**, 7436 (1996).

$$\sigma = e^2 \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \Sigma(\varepsilon),$$

$$T\sigma S = e \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \Sigma(\varepsilon)(\varepsilon - \mu),$$

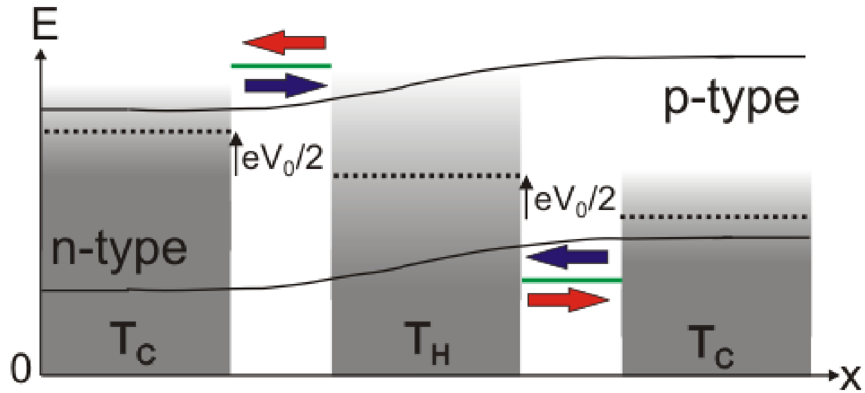
$$T\kappa_0 = \int_{-\infty}^{+\infty} d\varepsilon \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \Sigma(\varepsilon)(\varepsilon - \mu)^2$$

$$\Sigma(\varepsilon) = N(\varepsilon) v_x(\varepsilon)^2 \tau(\varepsilon),$$



Limitation: regime of validity of Boltzmann transport equation
Single energy level → Localized state (zero coupling with reservoirs)

Physics of reversible thermoelectrics



One energy at which current reverses:

$$\left[\exp\left(\frac{E_0}{k_B T_H}\right)+1\right]^{-1} = \left[\exp\left(\frac{E_0 - eV_{OC}/2}{k_B T_C}\right)+1\right]^{-1}$$

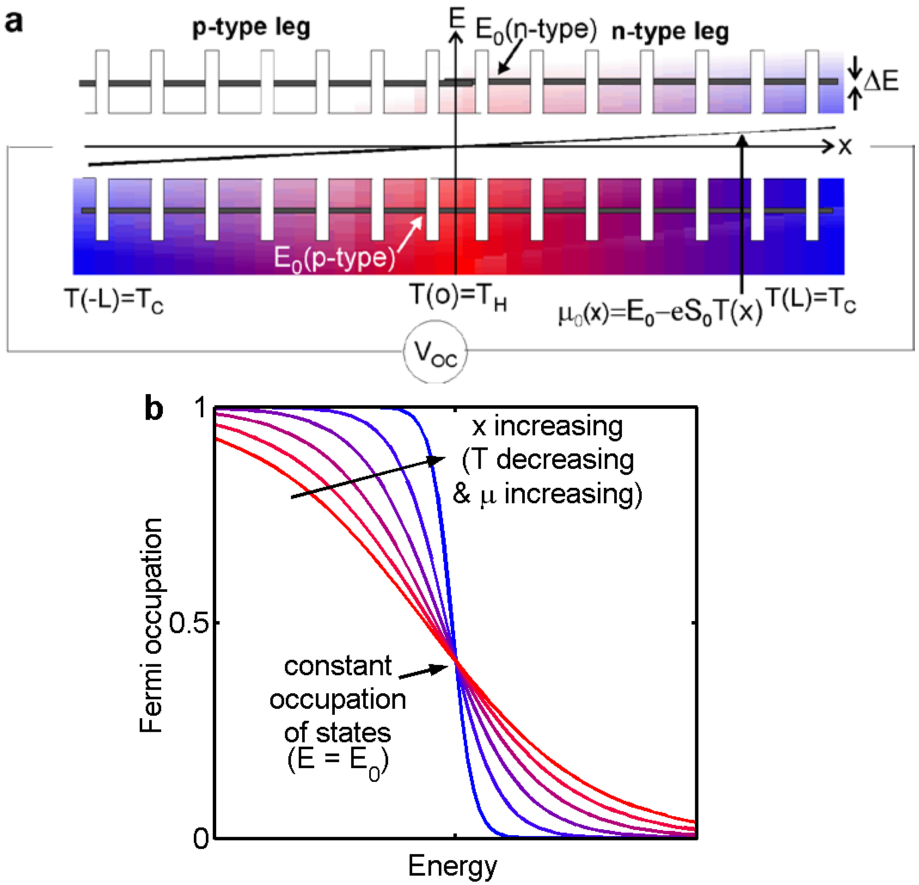
$$\frac{eV}{E_G} = 1 - \frac{T_C}{T_H} \quad \text{(Carnot limit)}$$

Constant occupation of states = Equilibrium

(despite temperature and electrochemical potential gradients)

T. E. Humphrey and H. Linke, *Phys. Rev. Lett.* **94**, 096601 (2005)

Physics of reversible thermoelectrics



T. E. Humphrey and H. Linke, *Phys. Rev. Lett.* **94**, 096601 (2005)

Thermodynamic analysis of single level thermoelectrics

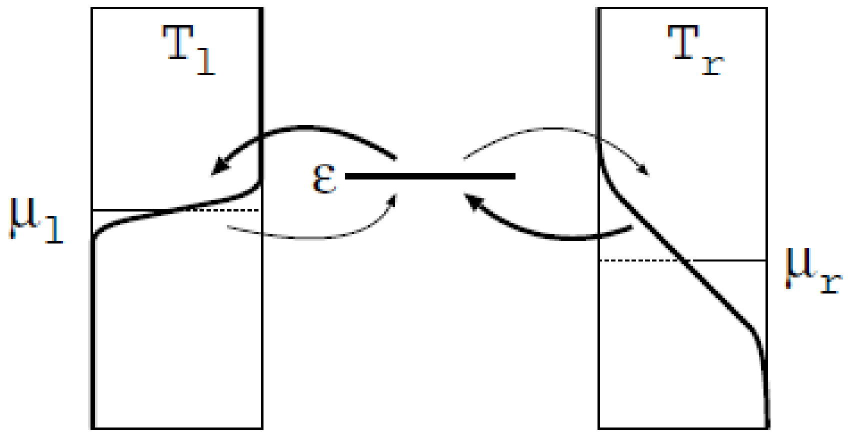


Fig. 1: Sketch of the nanothermoelectric engine consisting of a single quantum level embedded between two leads at different temperatures and chemical potentials. We choose by convention $T_l < T_r$. Maximum power is observed in the regime $\varepsilon > \mu_l > \mu_r$.

Abstract – We identify the operational conditions for maximum power of a nanothermoelectric engine consisting of a single quantum level embedded between two leads at different temperatures and chemical potentials. The corresponding thermodynamic efficiency agrees with the Curzon-Ahlborn expression up to quadratic terms in the gradients, supporting the thesis of universality beyond linear response.

M. Esposito, K. Lindenberg and C. Van den Broeck; EPL, 85 (2009) 60010

TE efficiency at maximum power (level broadening) Nakpathomkun et al., Phys. Rev. B 82, 235428, 2010

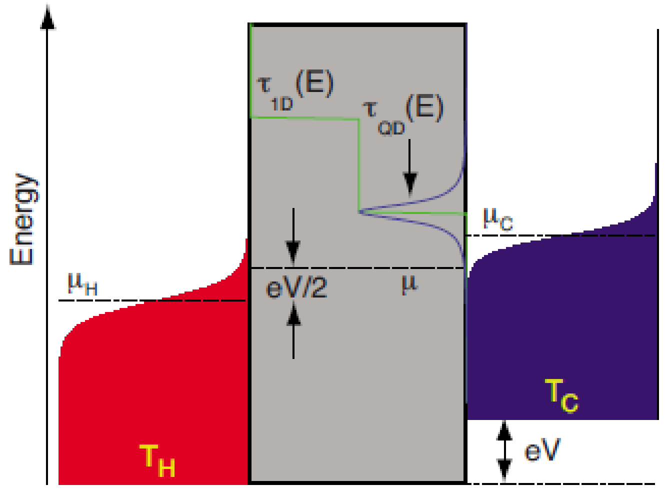
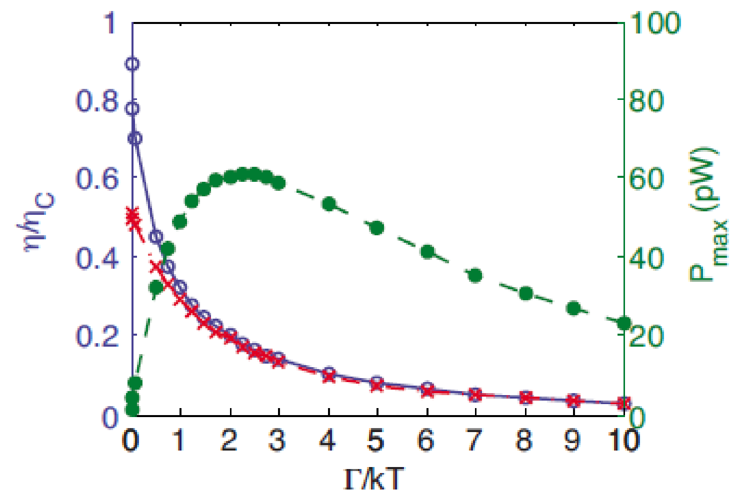


FIG. 1. (Color online) The basic setup considered here consists of a device described by its transmission function $\tau(E)$ (τ_{QD} and τ_{1D} are sketched as examples), with contact leads that act as the hot and cold electron reservoirs. A bias voltage, V, is applied symmetrically with respect to the average chemical potential μ, which can be tuned relative to the transmission function, using a gate voltage.

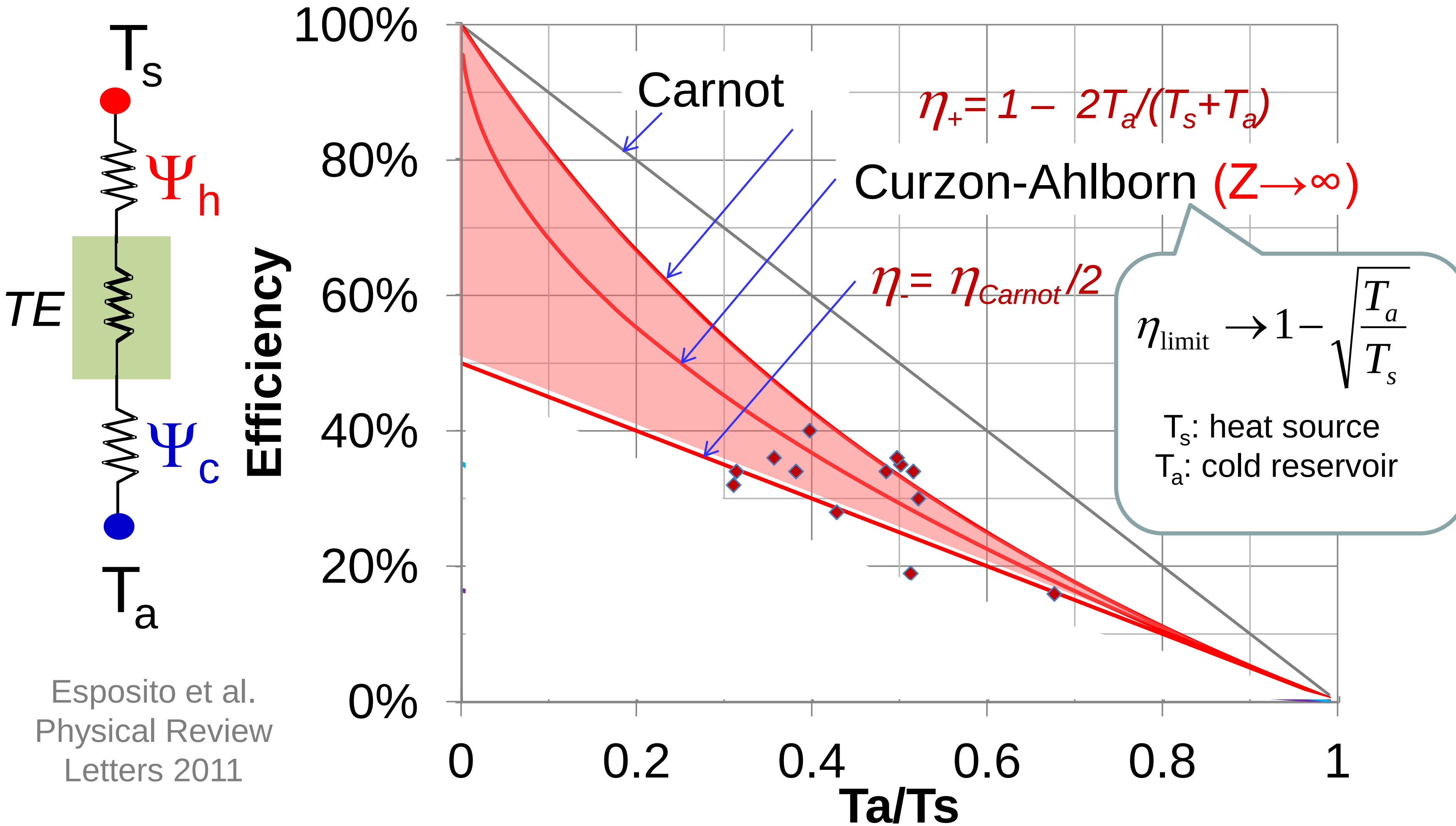
Neglect phonon mediated heat flow.
The efficiency at maximum power is independent of temperature and a careful tuning of relevant energies is required to achieve maximal performance.



Quantum dots perform relatively poorly under maximum power conditions.
Ideal one-dimensional conductors offer the highest efficiency at maximum power 36% of the Carnot efficiency.

FIG. 4. (Color online) $\eta_{max\ P}$ (red, crosses) and η_{max} (blue, open dots), both normalized by Carnot efficiency, and maximum power (green, full dots) of a quantum dot as a function of Γ/kT for T_C =300 K and T_H=330 K. Maximum power peaks around Γ/kT =2.25. Efficiency at maximum power $\eta_{max\ P}$ approaches η_{CA} =51% for small Γ and is always smaller than η_{max}.

Efficiency at maximum output power



Esposito et al. Physical Review Letters 2011

K. Yazawa and A. Shakouri, J. Appl. Phys. 111, 024509 (2012)

TE vs. conventional refrigerator

If we could create 1st order phase transition (latent heat) in "transported" electron gas, the efficiency of thermoelectric energy conversion could be significantly increased.

C. Vining, "Thermo-electric Process", MRS Spring 1997 (Vol. 478, p.3)

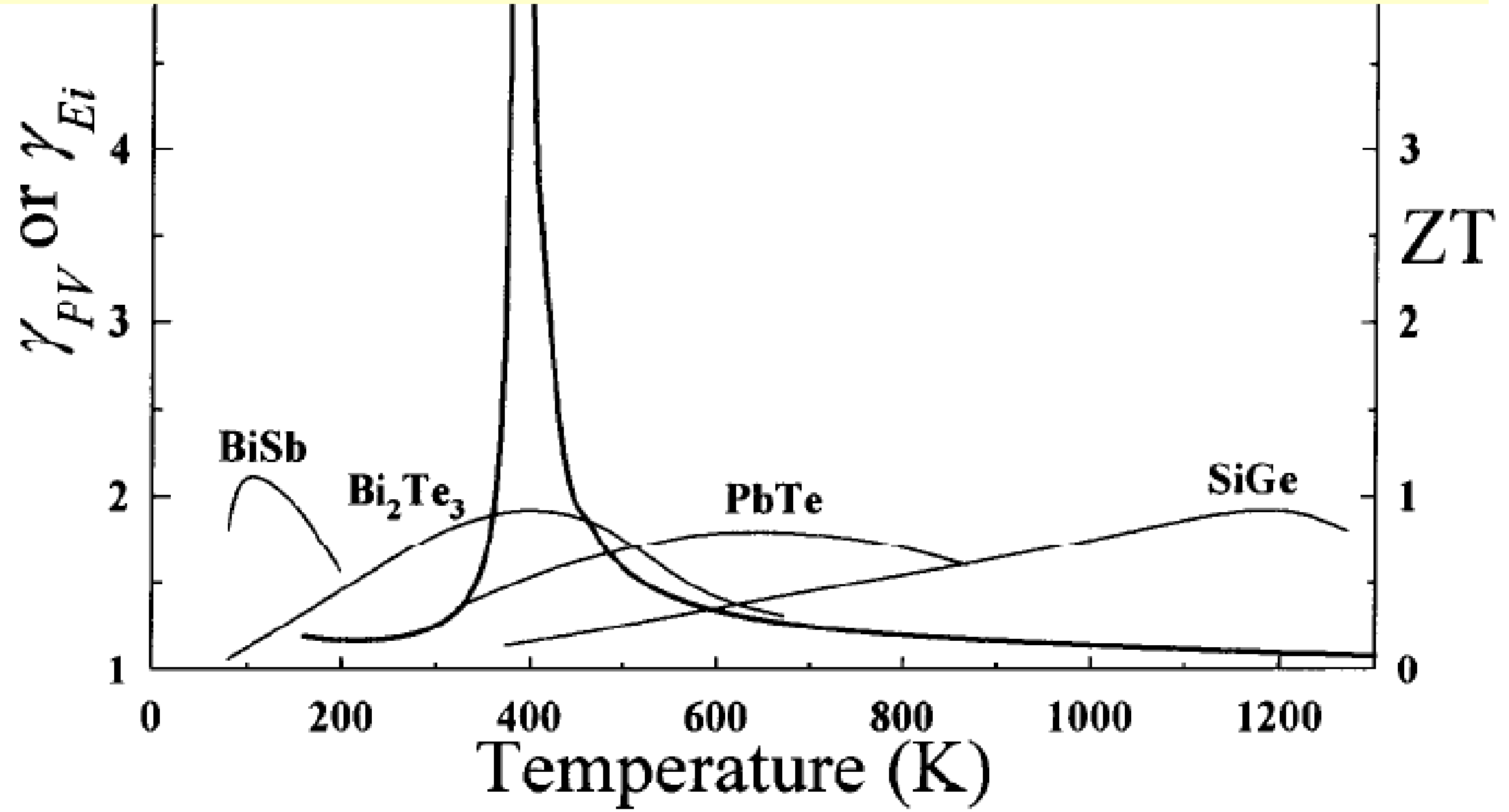


Fig. 4: Specific heat ratios, γ_{PV} for a *PV* system (Freon 12) and thermal conductivity ratios, γ_{Ei}=1+ZT, for selected n-type semiconductor alloys as a function of temperature.

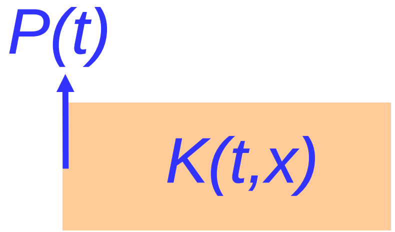
Energy density propagation in TE materials

N_2: The Green's function of the total energy density propagation $K(t,x)$ in a solid material when there is delta-function excitation $P(t)$

$$N_2(\omega,q)=\frac{\delta K(\omega,q)}{\overline{P}(\omega)}=\frac{i}{\omega}-\frac{q}{\omega}M_2$$

$$M_2=-\frac{D_Q q}{\Delta}\left[\omega-i\omega\tau_q+i(1-\xi)D_C q^2\right]$$

$$\Delta=\left(\omega-i\omega\tau_q+iD_Q q^2\right)\left(\omega-i\omega\tau_q+iD_C q^2\right)+\xi D_Q D_C q^4$$

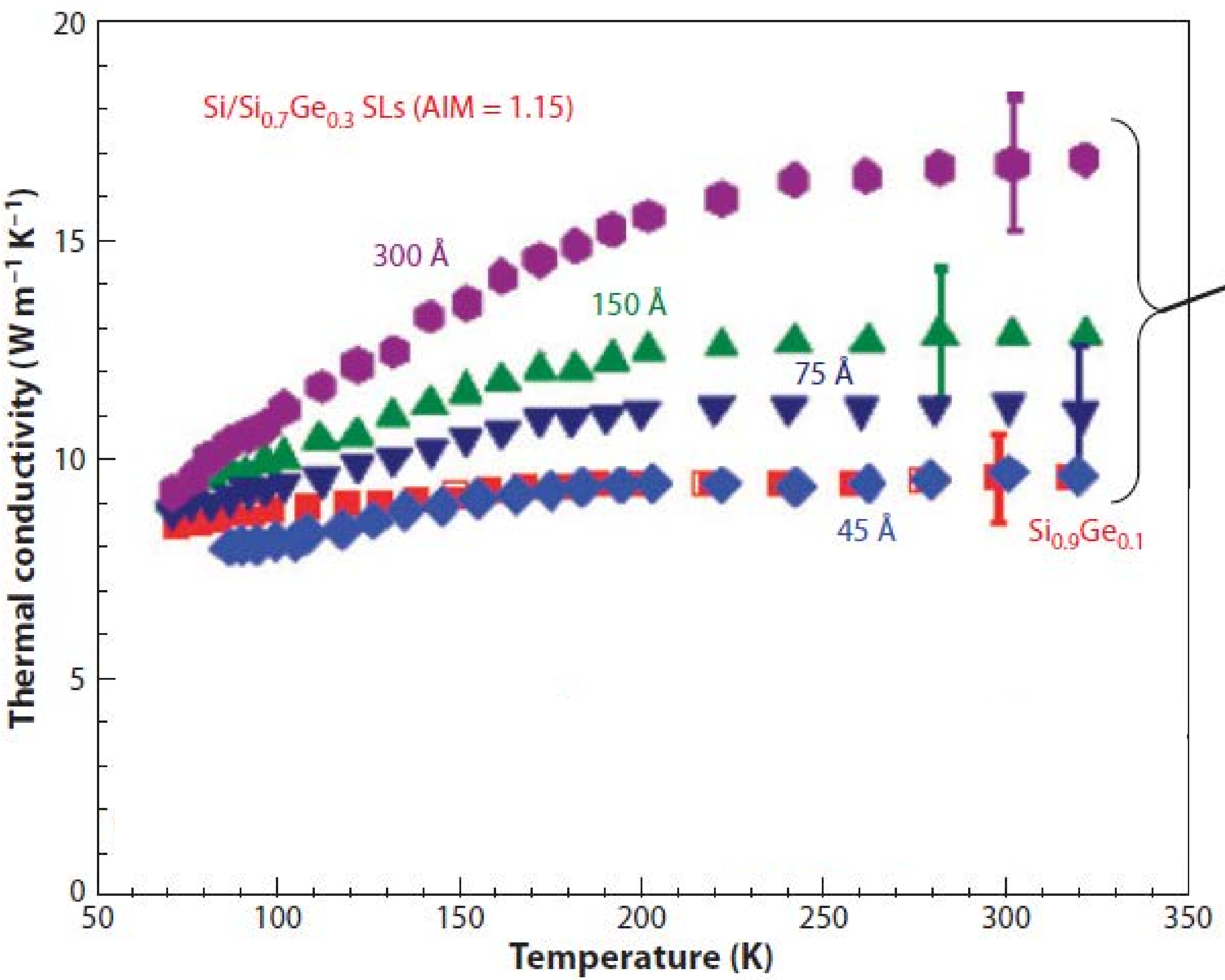


- τ_q total relaxation time of energy carriers (funct. of wavevector q)
- D_Q heat diffusion constant
- D_C charge diffusion constant
  - ξ coupling factor between charge and energy density
  - Z^* high frequency limit of figure of merit

$$\xi=\frac{Z^*T}{1+Z^*T}$$

- *B. S. Shastry, Rep, Prog, Phys **72**, 016501, (2009)*
- *Y. Ezzahri and A. Shakouri; Phys. Rev. B, 79, 184303, (2009)*

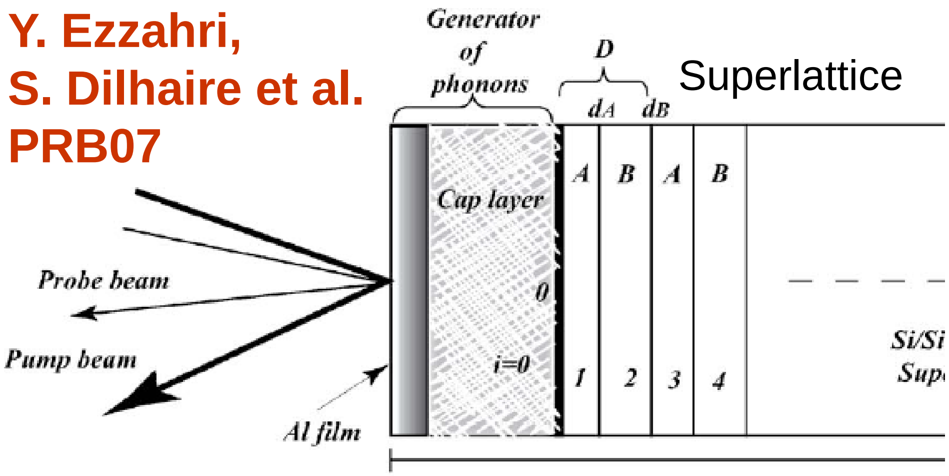
SiGe/Si superlattice thermal conductivity

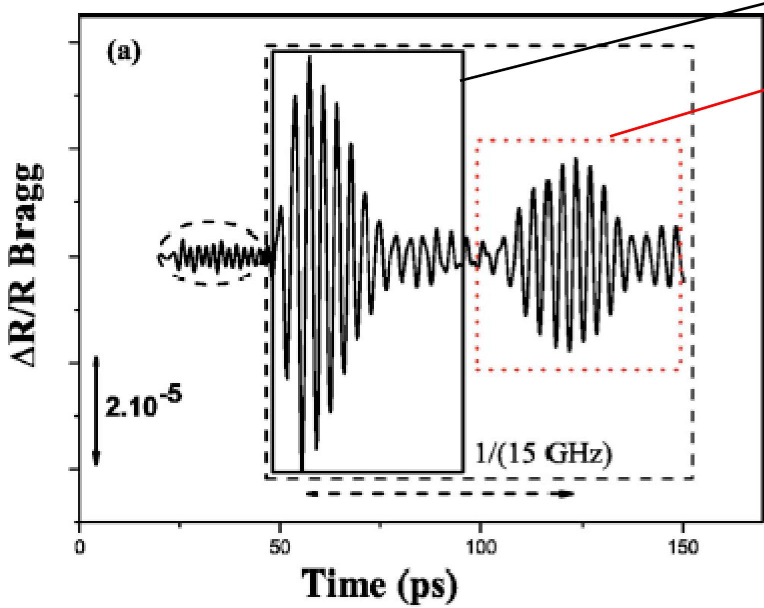


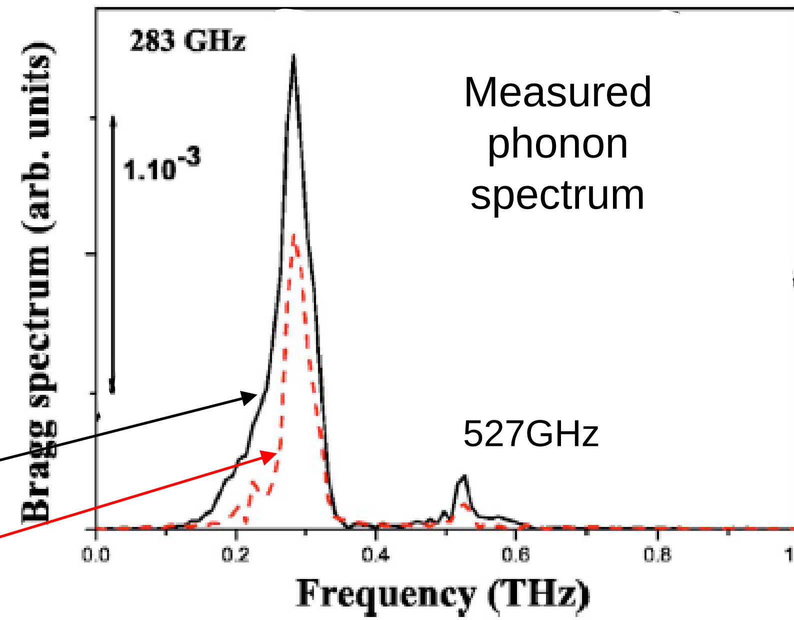
S. Huxtable, A. Majumdar, E. Croke, et al. (1999-2003)

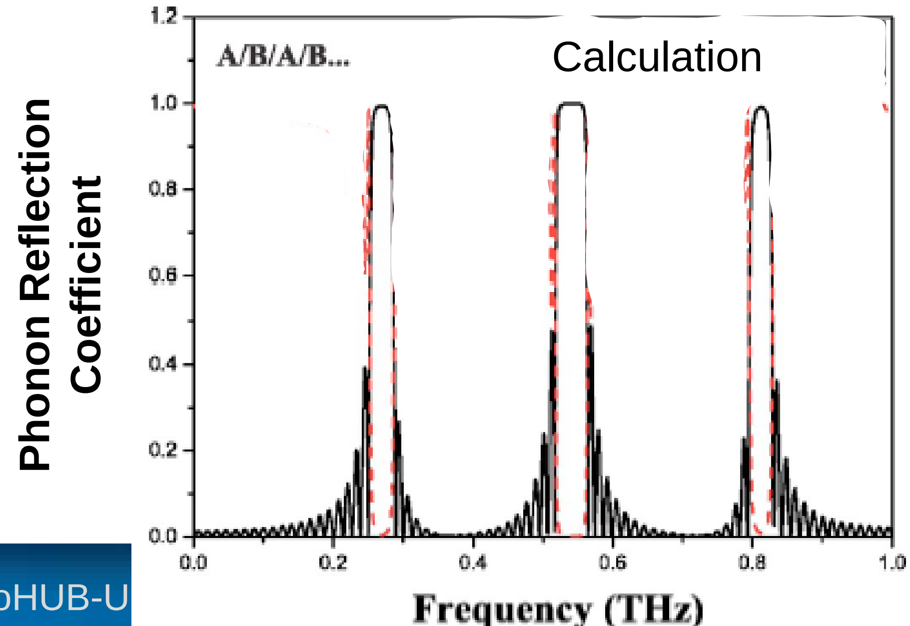
Phonon minibands in SiGe superlattices

Y. Ezzahri,
S. Dilhaire et al.
PRB07



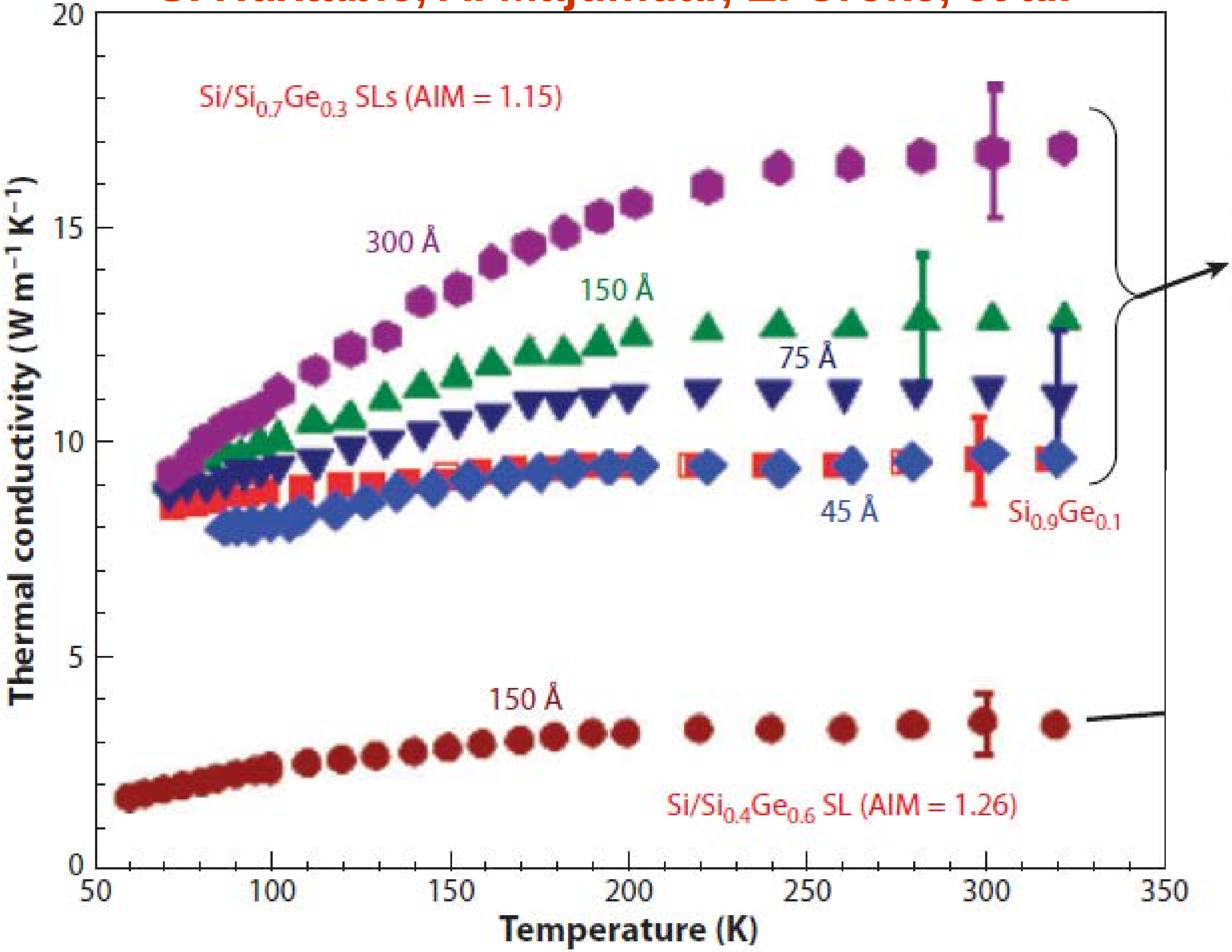




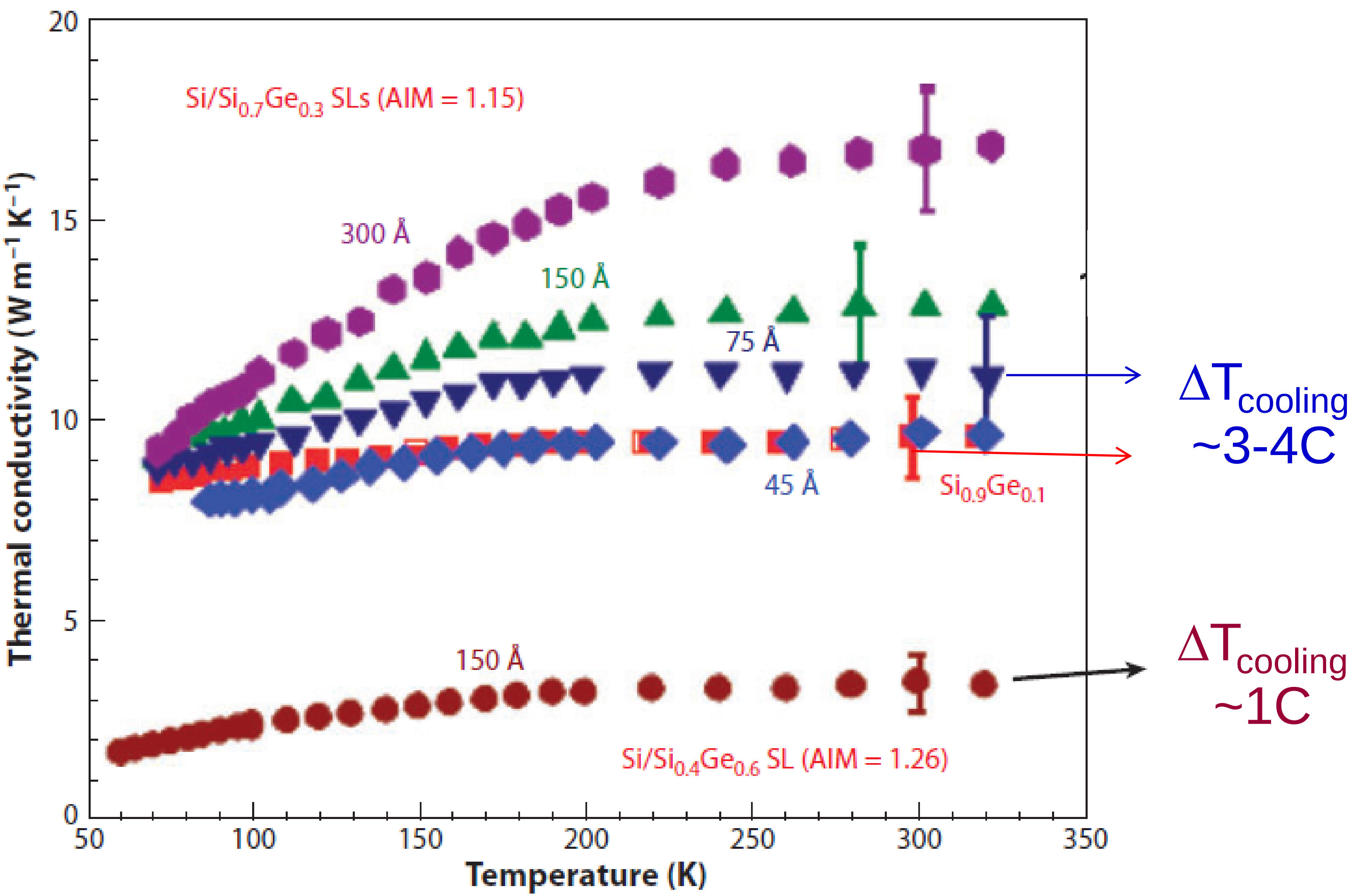


SiGe/Si superlattice thermal conductivity

S. Huxtable, A. Majumdar, E. Croke, et al.

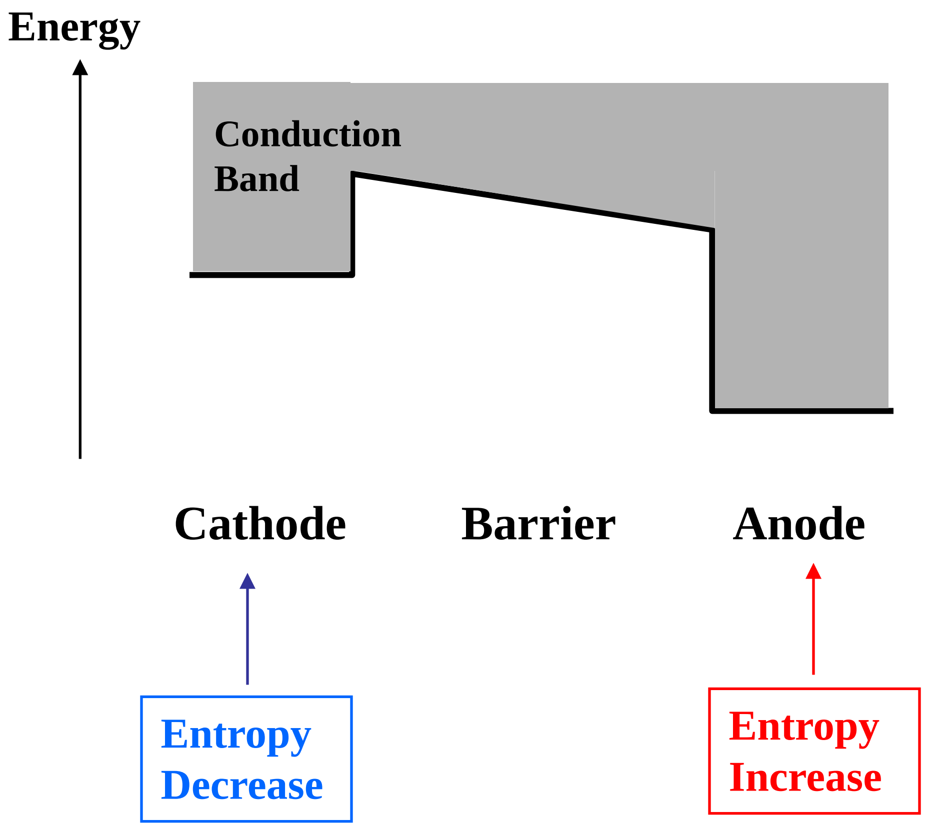


SiGe/Si superlattice thermal conductivity



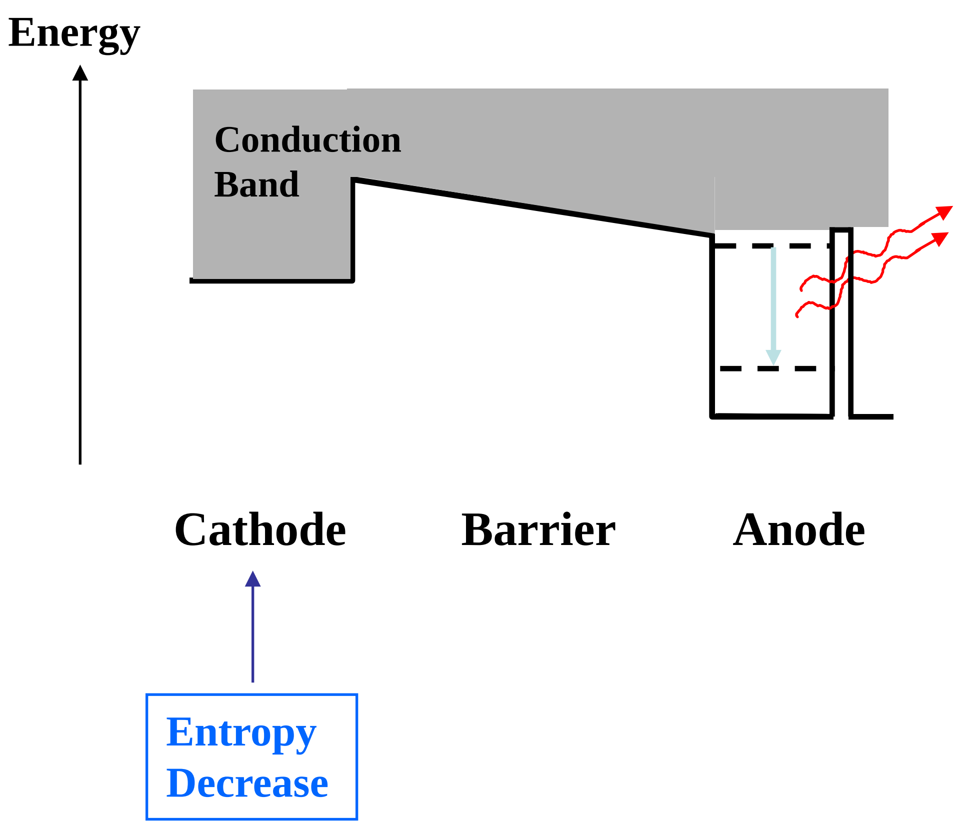
A. Shakouri, *Annual Review of Materials Research* (July 2011)

Miniature Refrigerator



Ali Shakouri and John E. Bowers, “*Heterostructure integrated thermionic refrigeration*“, **International Conference on Thermoelectrics**, Dresden, Germany, August 1997

Second Law of Thermodynamics?



Ali Shakouri and John E. Bowers, "*Heterostructure integrated thermionic refrigeration*", **International Conference on Thermoelectrics**, Dresden, Germany, August 1997

Week 5: Lecture 5 Summary

- Carnot vs. Curzon-Ahlborn efficiencies
- Single level thermoelectrics (-revisit Prof. Datta's lectures)
  - Sofo and Mahan vs. Humphrey and Linke
  - Thermodynamic argument, optimum broadening
- Some open questions
  - Phase transition in electron gas (latent heat)
  - Coupled charge/energy transport
  - Superlattice thermal conductivity
  - Opto thermo electric devices