Thermoelectrics Quo Vadis?

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Energy issues

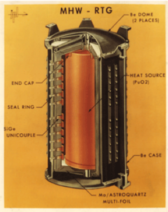
- Huge energy requirements
- CO_2 production, pollution...
- Renewables may cover *growth*
- EU is already reducing consumption
- But need more options...

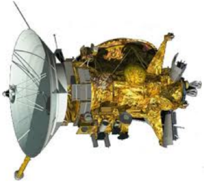
→ Save energy

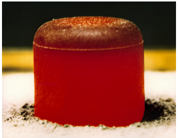
→ Recover waste heat
... with thermoelectrics

Space applications

- Solar flux too small
- Radioactive heat
- Robust energy source
- TEG → Voyager still going
- 5 kg of PuO_2 in Rover







Home applications

- Refrigerator/heater
- TE $\rightarrow$ no moving parts
- (Usually needs a fan)
- Limited efficiency
- Better for integrated apps:
- On-chip cooling
- On-board sensors, wifi...
- and camping!

Big applications?

- Where is the waste heat?
- Auto, aerospace, utilities
- Often $T_{op} \simeq 500$ C
- Needs: cheap, high volume
- large current, resistant...
- Still huge materials challenge

The game

Why is this talk in this school at all?

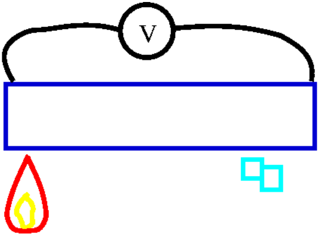
Spot surface/interface effects
Interrupt me
Have your name immortalized in pdf

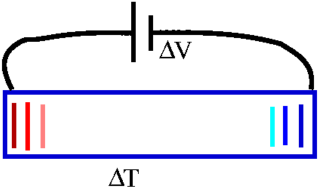
Outline

Outline

Peltier Seebeck and Thomson

- Make a thermocouple:
- Seebeck: ΔT produces ΔV
- $S = \Delta V / \Delta T$ (volt / Kelvin)
- Peltier: current produces ΔT
- Thomson(Kelvin):
- 2 effects are reciprocal
- Define single material S

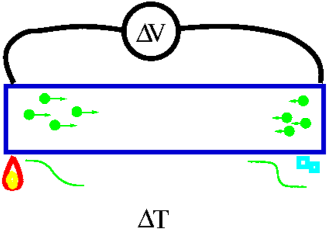


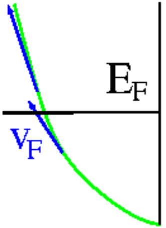


Microscopic view

- Hot side carriers diffuse (e^-, h^+)
- + equilibration mechanism
- m.f.p. or *relaxation time* τ
- microscopic: hom. Bloch solid
- mesoscopic: $T(r)$ or $V(r)$
- Need variation in DOS and v_F

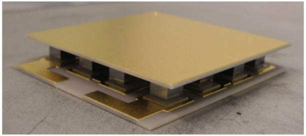
Electron gas: $n(\epsilon) \sim \sqrt{\epsilon}$ & $v_F \sim \sqrt{\epsilon}$
Above E_F more e^- diffuse $\rightarrow$ n type

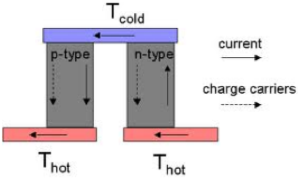




TE Devices

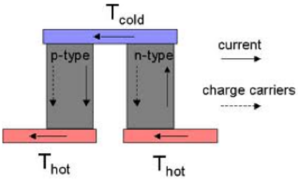
- Seebeck $\rightarrow$ power generation
- Peltier $\rightarrow$ heat/cool generation
- couple *p* and *n* materials
- thermally in parallel (κ)
- electrically in series (σ)





Device constraints

- Need compatible *n* and *p* materials
- Need to match them:
  - → chemically
  - → charge/thermal fluxes,
  - → metal junction, contacts
- Minimize thermal losses
- Maximize contact transparency



Efficiency

What do you want?

- Uses → Different efficiency
- Maximize power?
- Maximize current, heat flux?
- Figure(s) of Merit
- Coeff of Performance

Phonon Glass Electron Crystal
Slack Solid State Phys **34** 1 1979

$$
\begin{aligned}
P &= \sigma S^2 \\
z &= \frac{\sigma S^2}{\kappa} \\
z_{dev} &= \frac{(S_p - S_n)^2}{(\sqrt{\kappa_p/\sigma_p} + \sqrt{\kappa_n/\sigma_n})^2} \\
COP &= \frac{\gamma T_c - T_h}{(T_c - T_h)(1+\gamma)} \\
\gamma &= \sqrt{1 + zT}
\end{aligned}
$$

Outline

1 TE Concepts

2 TE Optimization

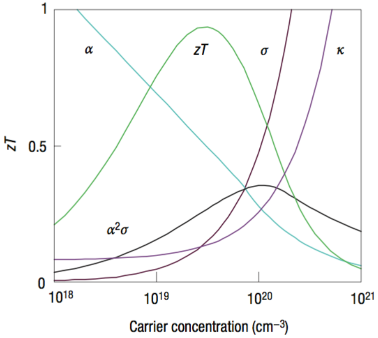
3 TE Calculations - “how to”

Orders of magnitude

- $10^{-16} < \sigma < 10^9 \;\; \Omega^{-1} m^{-1}$
- $0 < |S| <$ 100s – 1000s of μV / K
- $0.05 < \kappa <$ 1000s W / m / K
- metals: σ κ high, S small
- insulators: κ often high, $\sigma =$ S = 0
- ✓ doped dirty semiconductors

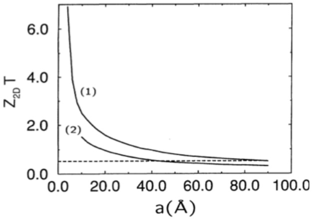
Trends in T and μ

- T increases phonons
- $\sigma, \kappa \searrow$
- $S \nearrow$
- μ increases $N(E_F)$
- $\sigma, \kappa \nearrow$
- $S \searrow$
- Historically: doping + disorder



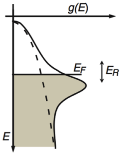
Novel attempts

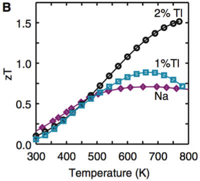
- Hicks and Dresselhaus
  Phys. Rev. B **47** 12727 (1993)
- zT vs QWell width *a*
- μ tuned by doping and *a*
- Boost: bands + phonon scattering
- Free e$^-$... usually wrong
  PRB **86** 195301 (2012)
- Few demonstrations of HD scaling
  but hugely inspirational

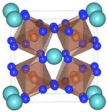


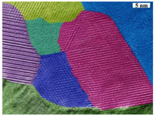
Novel attempts

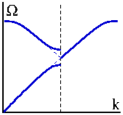
- Localized states
  Mahan PNAS **93** 7436 (1996)
  Heremans Science **321** 554 (2008)
- Rattlers, skutterudites, disorder...
- Nano alloying (e.g. MIT BiSbTe)
- LAST and related compounds

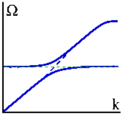






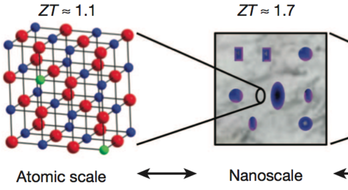


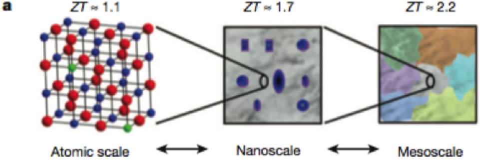


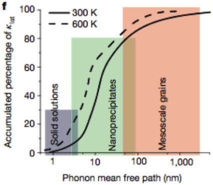


Novel attempts

- Biswas Nature **489** 414 (2012)
- Atomic doping Na
- Nanocluster doping
- Ball milling of grains
- Kill successive phonon wavelengths







Recap

- Most optimization on phonons and κ
- Doping and T have opposite effects
- S most difficult to control
- Devil is in the details:

$\rightarrow$ defects, doping sites

$\rightarrow$ band structure effects

$\rightarrow$ thermal effects

Outline

Need list

- Transport coefficients
- Functions of T and μ
- σ from electrons
- κ_L from phonons
- S from both
- + *many* scattering mechanisms:
  (charged) impurities, defects, *phonons*, boundaries, isotopes...

“Master” equations

Beyond simple models e.g. Slack $\kappa_L \simeq \bar{M}\theta_D^3(VN)^{1/3}/\gamma^2 T$
Broadly 3 ab initio approaches:

- Boltzmann equations
  Ziman *Electrons and Phonons* (1960)
- Green-Kubo relations (+MD)
  Green JPC **22** 398 (1954); Kubo JPS Japan **12** 570(1957)
- NEGF (too new for comfort)
  Jauho J. Phys.: Conf. Ser. **220** 012010 (2010)
  Wang Eur. Phys. J. B **62** 381 (2008)

  Sergueev Phys Rev B **83** 195415 (2011)

Boltzmann

- Classical stat mech "Hydrodynamic" approach

$$\frac{\partial f_{nk}}{\partial T} - eE \cdot \nabla_k f_{nk} + v_k \cdot \nabla_r f_{nk} = \frac{\partial f_{nk}}{\partial t}\Big|_{coll}$$

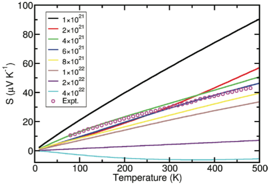
- Semi-classical: f_{FD}, N_{BE}, matrix elements in $\partial f / \partial t|_{coll}$
- Analogous equation for phonons
- Beyond lin resp $\rightarrow$ Monte Carlo solutions
- Relaxation time: $\partial f|_{coll} = \delta f / \tau_k$

$$\frac{1}{\tau} = \frac{1}{\tau_{imp}} + \frac{1}{\tau_{ph}} + \frac{1}{\tau_{iso}} + \frac{1}{\tau_{bdy}} ...$$

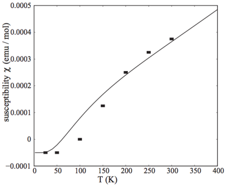
PB Allen *Contemp Concepts Cond Matt Sci* (2006)

Relaxation Time

- Constant relaxation time $\tau_k(T) = \tau$
  BoltzTrap Madsen CPC **175** 67 (2006)
  BoltzWann Pizzi arXiv:1305.1587
- ϵ_{nk} on dense k-point grid
- Gives $\sigma_{\alpha\beta}(\epsilon)$, S, σ, $\kappa_{el}(\mu, T)$
- Many DFT codes interface bands with BT and Wannier90/BW
- “Out of the box” but parameter τ
- We can do better...



OsSi Xu PRB **87** 134302 (2013)



$FeSb_2$ Diakhate PRB **84** 125210 (2011)

Elastic Variational

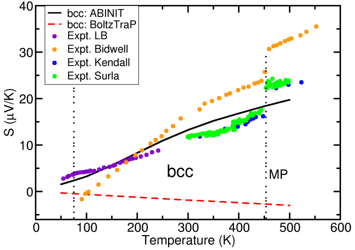
- Variational Approximation (lin resp) PB Allen PRB **17** 3725 (1978)

$$\rho \sim \frac{1}{\langle\tau\rangle} \sim \int (v_k - v_{k'})^2 |g_{kk'}|^2 f(\epsilon_k)[1 - f(\epsilon_{k'})] \times \{[N(\Omega)+1]\delta(\epsilon_k - \epsilon_{k'} - \Omega) + N(\Omega)\delta(\epsilon_k - \epsilon_{k'} + \Omega)\}$$

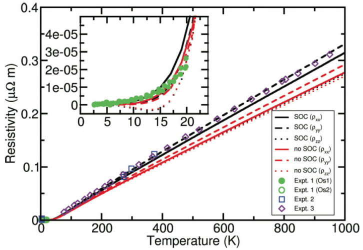
- (Elastic) Lowest Order VA: $\epsilon_k = \epsilon_{k'} = E_F$
- Much more work: phonons and integrations
- Phonons: *abinit*, QE, vasp, anything+phonopy
- In elastic LOVA $S = 0$!

Inelastic Variational

- Full inelastic treatment needed
- Allen decouples ϵ and k integrations
- For Li sign changes wrt RTA
- Limits: steady state, linear, not fully quantum



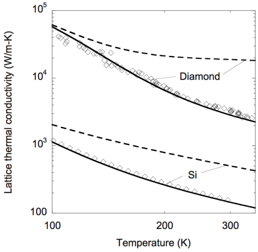
Lithium: Xu, Verstraete unpublished



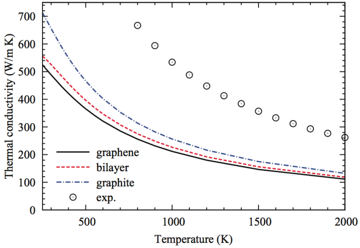
Osmium: Xu PRB **87** 134302 (2013)

Phonon Variational

- Variational phonon κ_L
- 3-phonon anharmonic scattering
- Energy conservation $\delta(\Omega_3 - \Omega_1 \pm \Omega_2)$
- DFPT Mingo PRB 84, 125426 (2011)



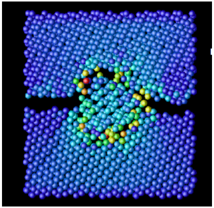
PRB 80 125203 (2009)

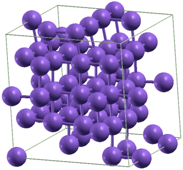


PRB 87, 214303 (2013)

Green-Kubo

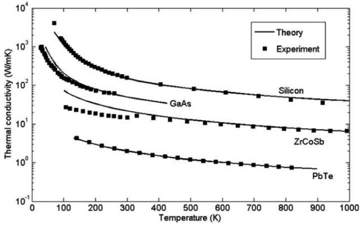
- $j =< j > +\Delta j$ (heat or charge)
- Universal Onsager-type relations: $\sigma \sim \int \langle j(0) j(t) \rangle dt$
- Charge current, classical heat current ok
- Molecular Dynamics: $v_{at}(t) \rightarrow j_Q(t) \rightarrow \kappa$
- Quantum heat = challenge: need energy density
- Trajectories from MD, TB, DFT...



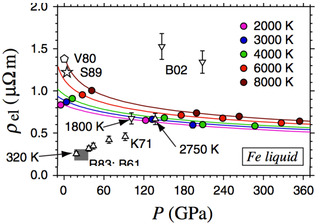


Green-Kubo

- Easy: many classical potential codes do this (GULP, LAMMPS...) + some TB and DFT codes
- Size effects: maximum λ, T_{max}
- Ergodicity issues
- Often fit a functional form to “safe” region in T or t



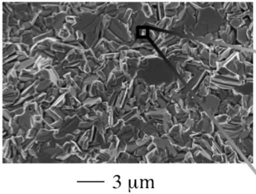
Zebarjadi En Env Sci (2011)



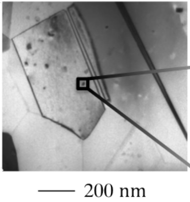
de Koker PNAS **190** 4070 (2012)

Multiscale needs

Macro(SEM image. Shades correspond to surface orientations, unrelated to grains. At this scale the material is homogeneous.)



Meso (TEM image showing grain boundaries and embedded nanoparticles. Transport at this scale is described by the BTE.)



Micro (TEM image of an embedded nanoparticle. Scattering at this scale requires an atomistic description.)

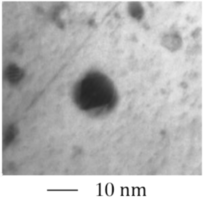


Fig 1: Bi2Te3 with embedded nanoparticles
(images by G. Bernard-Granger, CEA-Grenoble -Acta Materialia, 2012.-)

Multiscale todo list

- Atomistic $\rightarrow$ meso BTE $\rightarrow$ FE methods $\rightarrow$ device equation
- Which information to pass, how much, and how?
- Transport coefficients: anisotropic, T and μ dependent
- Add intermediate level grain/dopant/interface
  Empirical potentials? TB? Assemble DFT pieces?

Conclusions

- Most TE coefficients accessible from DFT
- System size, complexity are the problem
- Defects, explicit dopants only beginning to be treated
- Did I mention complex electronic structure?
- Intrinsically multiscale problem/solution

Acknowledgements

Ideas++

- Natalio Mingo
- Georg Madsen
- Nicola Marzari
- Bin Xu

Your name in lights

Preliminary list

Surface/interface effects
almost all neglected at present at ab initio level

- Contacts
- Grains, cluster doping, 2D defects
- Spontaneous nanoalloying
- Heterostructures
- Sample surface (+roughness)
- Interdiffusion of defects, impurities...