Quantum transport simulations for understanding the thermoelectric effect in nanocomposites

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Thermoelectricity - basics

Electrical conductivity
Seebeck coefficient

\[ ZT = \frac{\sigma S^2 T}{K_e + K_l} \]

Electronic thermal conductivity
Lattice thermal conductivity

- 15 TW of heat is lost worldwide, but
- State of the art: \( ZT \approx 1.5 \) (need \( ZT \approx 4 \))
- Rare earth, toxic, expensive materials

Abundance issues with good TE materials

http://pubs.usgs.gov/fs/2002/fs087-02/

Abundance issues for Te, toxicity for Pb
What nanomaterials offer to TEs

Sharp peaks in $DOS(E)$

\[ S \sim \frac{d}{dE} DOS(E) \]

- Low dimensionality – improves $S$

\[ ZT = \frac{\sigma S^2 T}{k_e + k_l} \]

- Nanostructuring - phonon engineering
- Scatter phonons only

Hicks and Dresselhaus - 1993, Dresselhaus - 2001

Hochbaum, Nature 2008
Recent advancements - How to proceed further?

Case for Si:
Bulk: 140 W/mK, ZT=0.01
NWs: 1-2 W/mK, ZT≈1

- $\kappa_f$ reduction benefits are reaching their limits (easily)
- we need to look into $\sigma S^2$

Vineis et al., Adv. Mater. 22, 3790, 2010
Nanostructured thermoelectrics

0D
- nano-dots in lattices
  - ZT ~ 1.8
    - Kanatzidis, Rogl, Bauer

1D
- SL NWs
  - ZT ~ 1
    - Boukai, Hochbaum
- core-shell NWs

2D
- in-plane SLs
  - ZT ~ 2.4
    - Venkatasubramanian
- cross-plane SLs

Most of these originates from $\kappa_l$ reduction
$\sigma S^2$ benefits are yet to be observed
Superlattices as a first step for large PFs

Make $S$ and $\sigma$ really independent – energy filtering for $S$? How to increase both simultaneously?

Barriers:
- $S \sim \eta_F$ 
- $\sigma \sim \exp(-\eta_F)$

Wells:
- $S \sim E_F$
- $\sigma \sim \exp(-E_F)$
Nanocomposites with very high PFs

Very high PF:
- 2-phase materials: 15 mW/K²m⁻¹
- 3-phase materials: 22 mW/K²m⁻¹
  (~7x compared to bulk Si)

Nanocomposite multi-phase materials
~30nm grains + 2nm boundaries

Quantum / thermionic transport

Simultaneous improvement in $\sigma$ and $S$

Nanocomposites can indeed provide large PF gains

But they are tricky to realize…

Outline

- Introduction – nanomaterials for thermoelectrics
- The method: Non-equilibrium Green’s function
- Quantum transport - NEGF
  - Example 1: Superlattices
  - Example 2: Nanocomposites
- Towards hierarchical geometry simulations
  - Monte Carlo for phonons/electrons
  - Infrastructure development
- Conclusions
Non-Equilibrium Green’s Function (NEGF)

\[ G(E) = \left[ (E + i0^+)I - H - \Sigma_1 - \Sigma_2 \right]^{-1} \]

- Device Green’s function:

- Transmission:

\[ T(E) = \text{Trace}(\Gamma_1 G \Gamma_2 G^\dagger) \]

\[ D(E) = \frac{1}{2\pi} \text{Trace}(G \Gamma G^\dagger), \quad \Gamma = i(\Sigma - \Sigma^\dagger) \]

- TE coefficients:

\[ I^{(j)} = \int_{-\infty}^{+\infty} \left( \frac{E - E_F}{k_B T} \right)^j T(E) \left( -\frac{\partial f}{\partial E} \right) dE \]

\[ G = \left( \frac{2q^2}{h} \right) I^{(0)} \quad [1/\Omega] \]

\[ S = \left( -\frac{k_B}{q} \right) \frac{I^{(1)}}{I^{(0)}} \quad [V/K] \]
Electron-Phonon Scattering within NEGF

- Device Green’s function:

\[ G(E) = \left[ (E + i0^+) I - H - \Sigma_1 - \Sigma_2 - \Sigma_{\text{scatt}} \right]^{-1} \]

- Electron-phonon scattering self-energies (optical here, for acoustic \( h\omega = 0 \))

\[ \Sigma_{\text{scatt}}^{\text{in}} (j, j, m, E) = D_0 \left( n_\omega + 1 \right) G^{\text{n}} (j, j, m, E + \hbar \omega) + D_0 n_\omega G^{\text{n}} (j, j, m, E - \hbar \omega) \]

\[ \Sigma_{\text{scatt}}^{\text{out}} (j, j, m, E) = D_0 \left( n_\omega + 1 \right) G^{\text{p}} (j, j, m, E - \hbar \omega) + D_0 n_\omega G^{\text{p}} (j, j, m, E + \hbar \omega) \]

phonon emission  \quad  \text{phonon absorption}

\[ G^{\text{n}} (E) = G \left( \Sigma_{\text{scatt}}^{\text{in}} + \Sigma_{\text{scatt}}^{\text{in}} \right) G^{\dagger} \]

\[ G^{\text{p}} (E) = G \left( \Sigma_{\text{scatt}}^{\text{out}} + \Sigma_{\text{scatt}}^{\text{out}} \right) G^{\dagger} \]
Ballistic vs phonons results

**Coherent transport:**
- Usually NOT appropriate – can lead to `unphysical` localization
- PF is limited by the G of the barrier region

**Incoherent transport:**
- Smoothened resonances
- The different regions can be decoupled
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Example 1: 1D superlattice - all features captured

\[ S = -\frac{k_B}{q} \frac{E - E_F}{k_B T} = -\frac{E - E_F}{qT} \]

Current flow variations and \( \lambda_E \)

Tunneling is detrimental to PF

Variation in \( V_B \) reduces PF

(Perhaps explains why filtering improvements have not been realized experimentally?)

Features for PF improvement

How to design such structures?

- $E_F$ should be high into the bands to improve $\sigma_w$
- $L_B$ should be large enough to prevent tunneling
- Barrier height $V_B$ should be 1-2kT above $E_F$
- $L_W$ should be similar to $\lambda_E$ (somewhat larger)
- Good to have large current energy variations in barriers and wells

*No flexibility*

*Some flexibility here*
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Seebeck has very week dependence on $V_B$: limited possibilities for filtering

Mostly nano-inclusions reduce the PF (from an optimal case), unlike in SLs

For large $V_B$, the influence of both $V_B$ and $E_F$ on the PF is reduced
Explaining the Seebeck behavior

- Seebeck proportional to the average energy of the current

\[ S = \frac{\langle E \rangle - E_F}{qT} \]
Increasing porosity

- For small $V_B$:
  *Porosity has a weak effect on the PF*

- Porosity has a stronger effect at higher $V_B$

- Characteristics saturate for barriers beyond $E_F + k_B T$
Influence of diameter

- Larger diameter has greater effect on G
- Negligible change in S for the smaller diameter – no power factor peak
- Quantum tunnelling renders the smaller nanoinclusions semi-transparent and the energy filtering effect disappears
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Numerical issues in NEGF

- Single simulation of 60x30 nm channel ~ 10 hrs
- Length dimension scales linearly, but...
- Width scales ~ $W^3$
- Geometries of microns by microns simply not possible
Simulations of superlattices in Monte Carlo

Superlattice

➢ Include all relevant scattering parameters (next Ionised Impurities)
Include additional effects

**ELECTROSTATICS**

- Given $n \rightarrow U_{scf}$
- Poisson
- Iterate until convergence
- Given $U_{scf} \rightarrow n$

**TRANSPORT**

Self-consistent electrostatics

Quantum tunneling
Thermal conductivity – nanocomposites/nanomeshes

Need something more multi-physics based!

- **Geometry:** boundaries, nanoinclusions, voids,…
- **Physics:** particle + wave effects
- Scale to realistic micron sizes
- Couple phonon and electronic systems

**Boundary scattering**

boundary specularity \( \frac{1-p}{1+p} \)

\[ p(q) = \exp(-q^2 \Delta_{rms}^2) \]

**Grain boundary scattering**

\[ p_{GB} = \exp\left(-4q^2 \Delta_{rms}^2 \sin^2 \theta_{in}\right) \]

- Transmission probability \( p_{GB} \)
- Reflected diffusively with \( (1-p_{GB}) \)
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Conclusions

- Electronic transport in low-D and nanocomposite TE materials
- NEGF quantum transport for nanocomposites
- Extend to large geometries
- Perform realistic simulations
- Incorporate all important transport effects
- Improve thermoelectric power factor in nanomaterials

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