WCPM/CSC, University of Warwick

Quantum transport simulations for understanding the thermoelectric effect in nanocomposites

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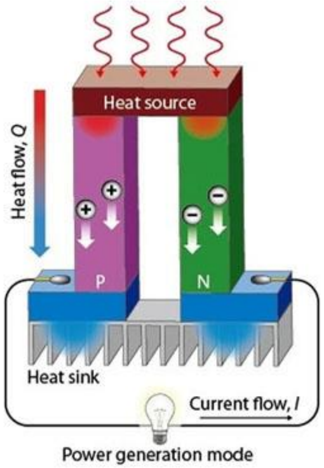
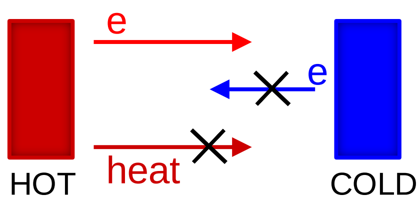
Thermoelectricity - basics





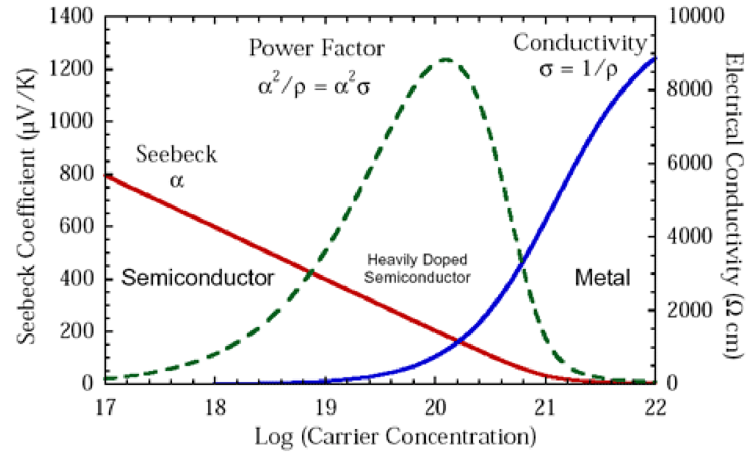
Electrical conductivity

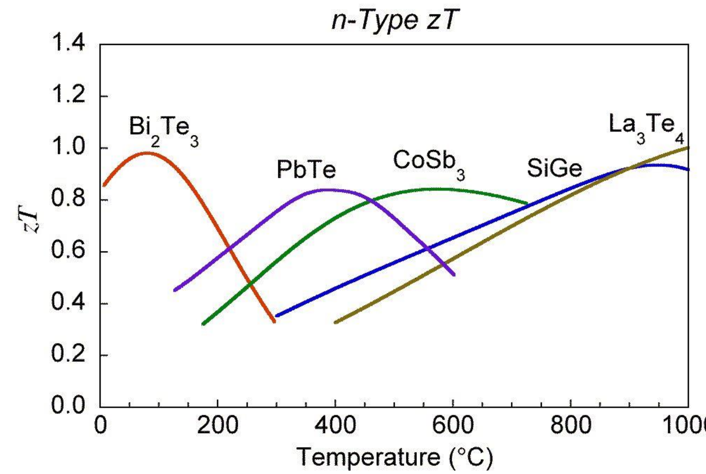
Seebeck coefficient

$$ZT = \frac{\sigma S^2 T}{\kappa_e + \kappa_l}$$

Electronic thermal conductivity

Lattice thermal conductivity

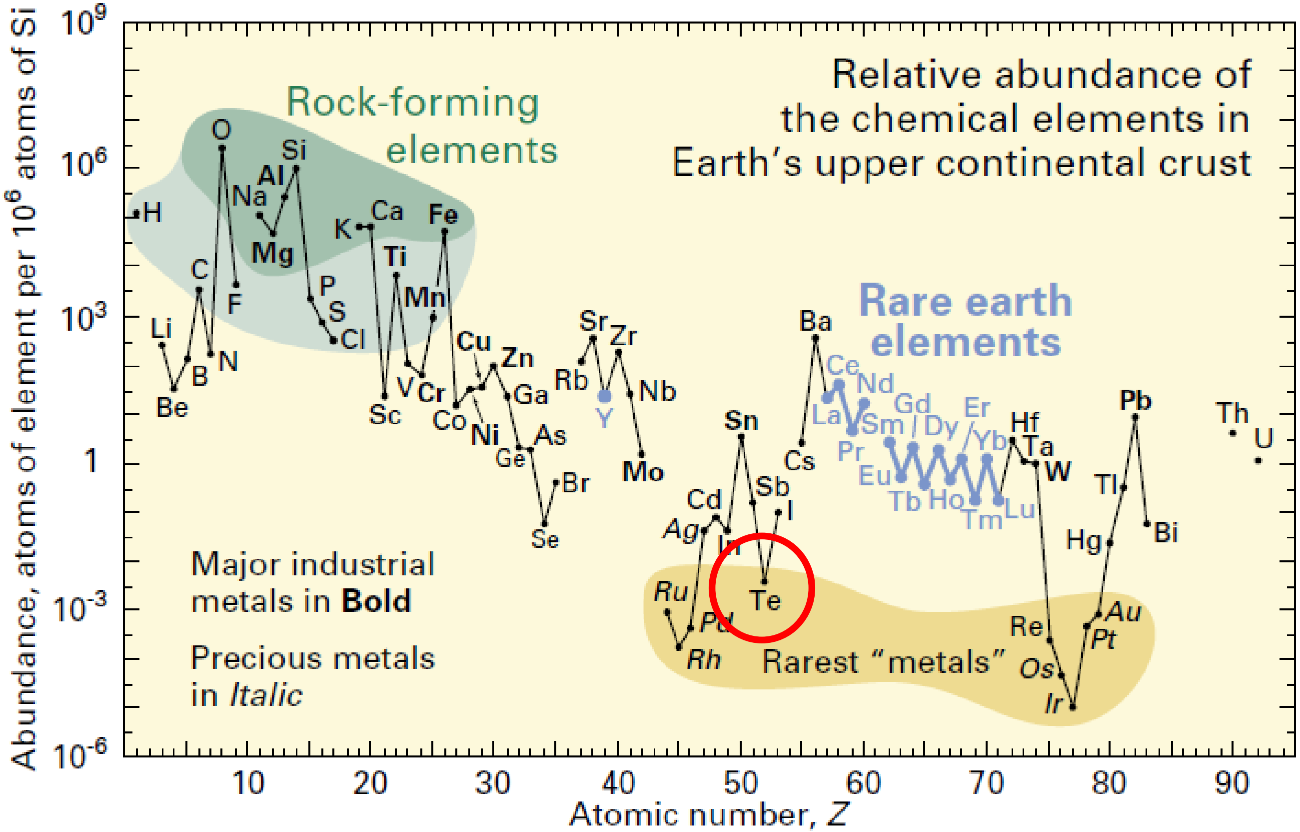




Snyder *et al*., Science, 2008, Nat. Mat., 2008.

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

Abundance issues with good TE materials



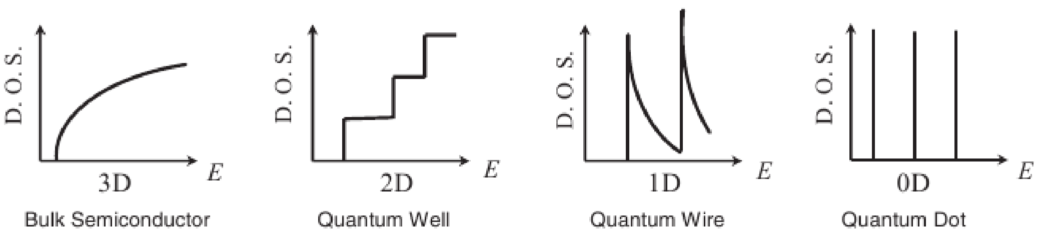
http://pubs.usgs.gov/fs/2002/fs087-02/

Abundance issues for Te, toxicity for Pb

What nanomaterials offer to TEs

<u>Sharp peaks in *DOS(E)*</u>

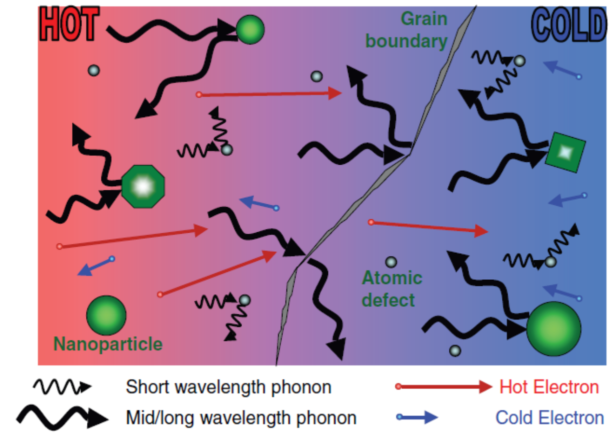
$$S \sim \frac{d}{dE} DOS(E)$$

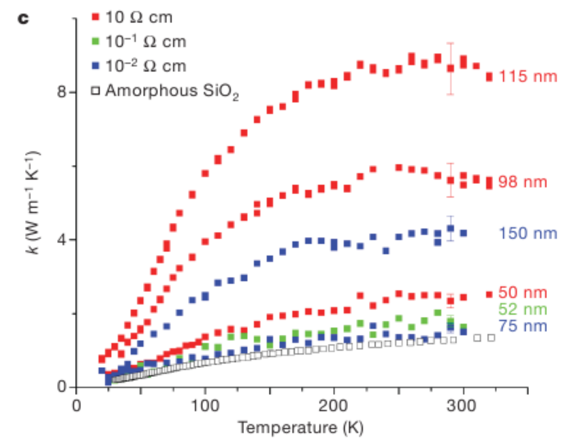


Hicks and Dresselhaus -1993, Dresselhaus - 2001

- Low dimensionality – improves *S*

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

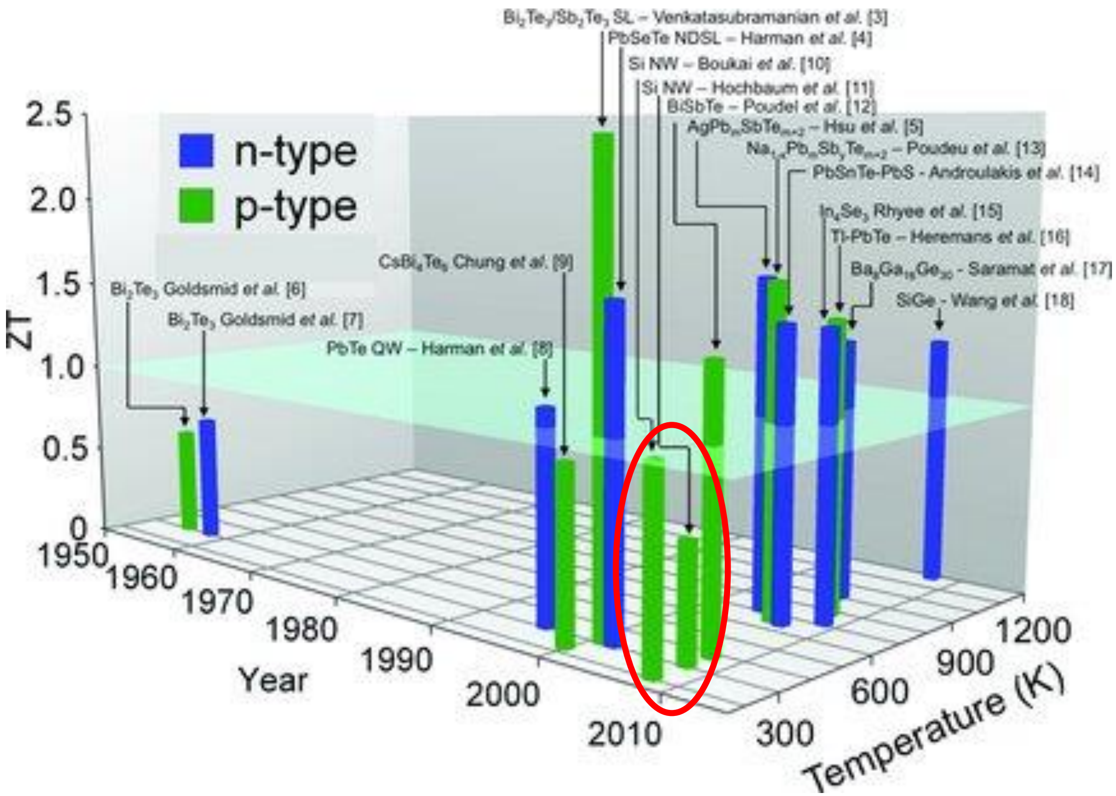




Hochbaum,Nature 2008

- Nanostructuring - phonon engineering
- Scatter phonons only

Recent advancements - How to proceed further ?



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

Case for Si:

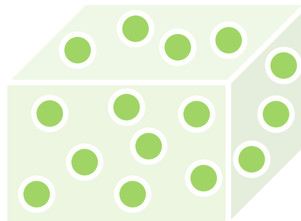
Bulk : 140 W/mK, ZT=0.01

NWs: 1-2 W/mK, ZT~1

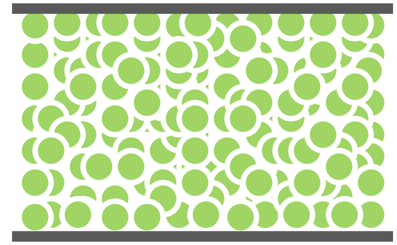
- κ_l reduction benefits are reaching their limits (easily)
- we need to look into σS^2

Nanostructured thermoelectrics

0D



nano-dots
in lattices

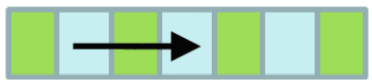


Nanograins

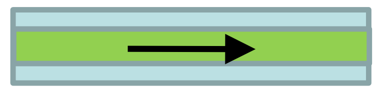
$ZT \sim 1.8$

Kanatzidis, Rogl, Bauer

1D



SL NWs

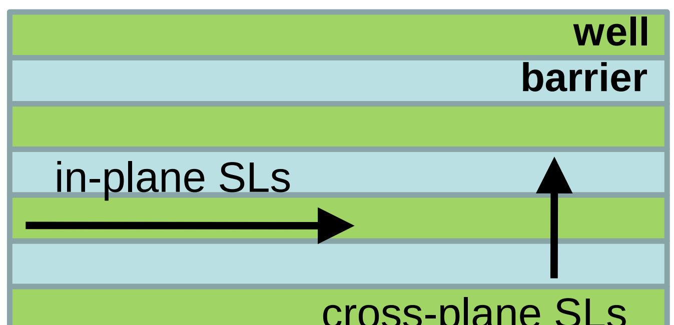


core-shell NWs

$ZT \sim 1$

Boukai, Hochbaum

2D



$ZT \sim 2.4$

Venkatasubramanian

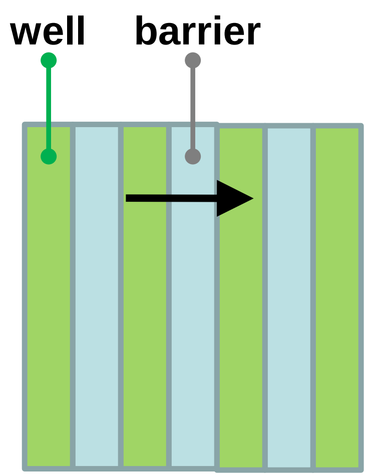
Most of these originates from κ_l reduction

σS^2 benefits are yet to be observed

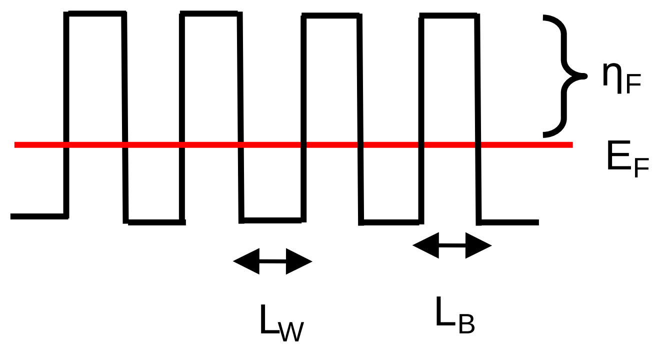
Superlattices as a first step for large PFs

Make S and σ really independent – energy filtering for S ?

How to increase both simultaneously?



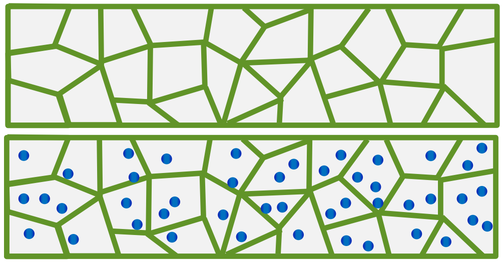
superlattices

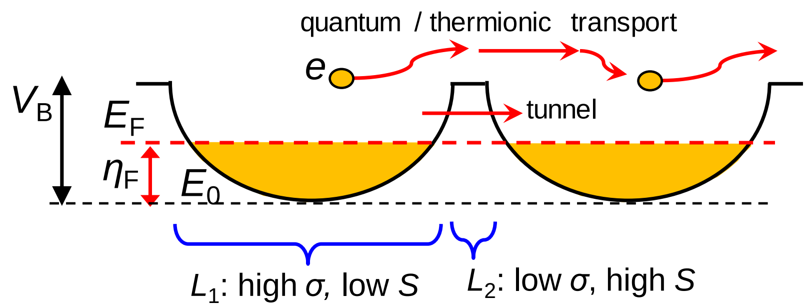


Barriers: $S \sim \eta_F$ ↑↑ $\sigma \sim \exp(-\eta_F)$ ↓

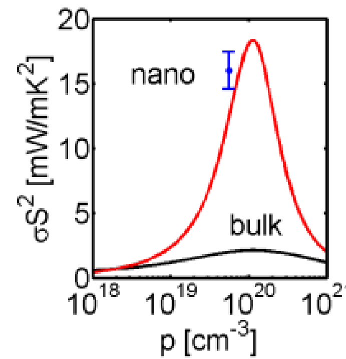
Wells: $S \sim E_F$ ↓ $\sigma \sim \exp(-E_F)$ ↑↑

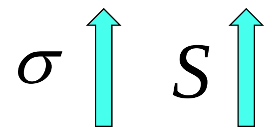
Nanocomposites with very high PFs





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





Simultaneous improvement in σ and S

Very high PF:
2-phase materials: 15 mW/K^{2}m^{-1}
3-phase materials: 22 mW/K^{2}m^{-1}
(~7x compared to bulk Si)

- *Nanocomposites can indeed provide large PF gains*
- *But they are tricky to realize…*

Neophytou, Zianni, Kosina, Frabboni, Lorenzi, Narducci, ***Nanotechnology***, 24, 205402, 2013.
Lorenzi, Narducci, Totini, Frabboni, Gazzadi, Ottaviani, Neophytou, Zianni, ***J. Electr. Mat.***, 43, 3812, 2014

Outline

- Introduction – nanomaterials for thermoelectrics
- The method: Non-equilibrium Green's function
- Quantum transport - NEGF
  - Example 1: Superlattices
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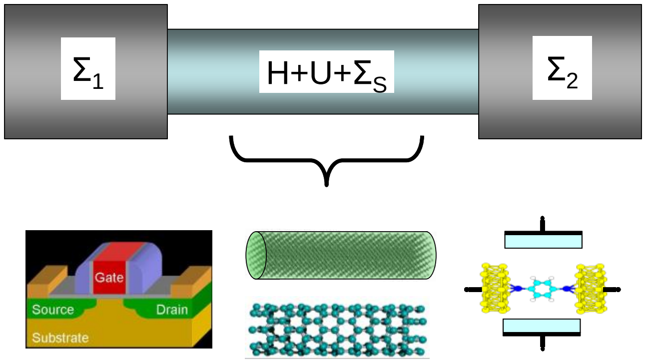
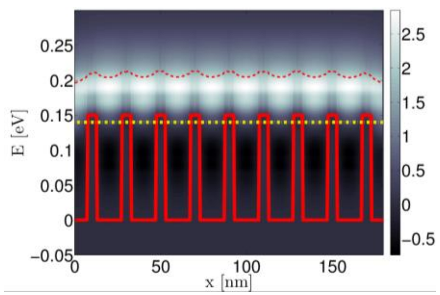
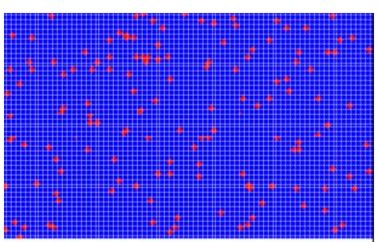
Non-Equilibrium Green's Function (NEGF)

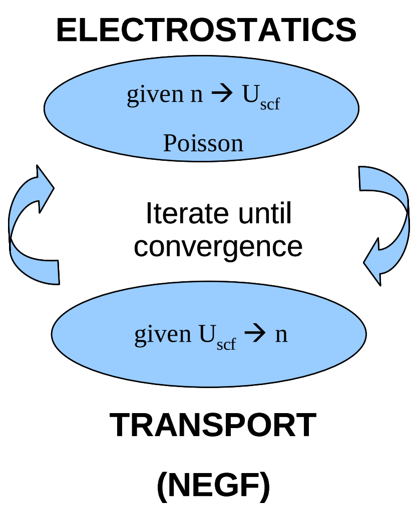




superlattices



nano-inclusions



- Device Green's function:

$$G(E) = [(E + i0^{+})I - H - \Sigma_{1} - \Sigma_{2}]^{-1}$$

- Transmission:

$$T(E) = Trace(\Gamma_{1} G \Gamma_{2} G^{\dagger})$$

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

- TE coefficients:

$$I^{(j)} = \int_{-\infty}^{+\infty} \left(\frac{E - E_{F}}{k_{B} T} \right)^{j} T(E) \left(-\frac{\partial f}{\partial E} \right) dE$$

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

$$S = \left(-\frac{k_{B}}{q} \right) \frac{I^{(1)}}{I^{(0)}} \qquad [V/K]$$

Electron-Phonon Scattering within NEGF

- Device Green's function:

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

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

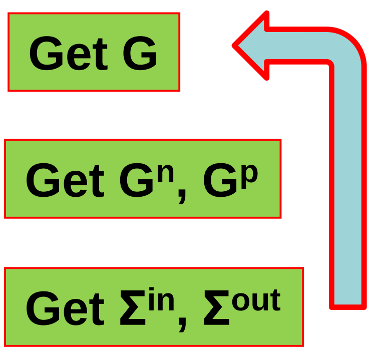
$$\Sigma^{\text{in}}_{\text{scatt}}\left(j,j,m,E\right) = D_0\left(n_\omega + 1\right)G^{\text{n}}\left(j,j,m,E+\hbar\omega\right) + D_0 n_\omega G^{\text{n}}\left(j,j,m,E-\hbar\omega\right)$$

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

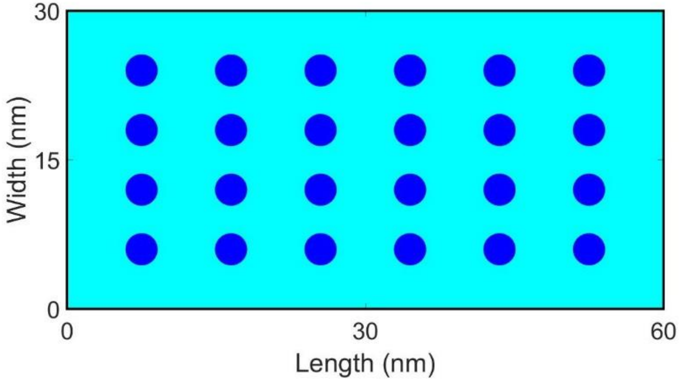
phonon emission phonon absorption

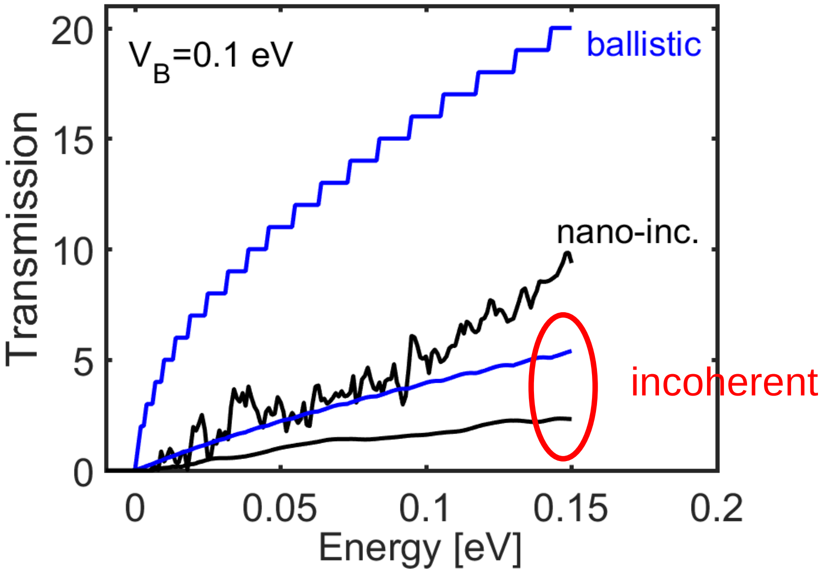
$$G^{\text{n}}\left(E\right) = G\left(\Sigma^{\text{in}}_1 + \Sigma^{\text{in}}_2 + \Sigma^{\text{in}}_{\text{scatt}}\right)G^\dagger$$

$$G^{\text{p}}\left(E\right) = G\left(\Sigma^{\text{out}}_1 + \Sigma^{\text{out}}_2 + \Sigma^{\text{out}}_{\text{scatt}}\right)G^\dagger$$



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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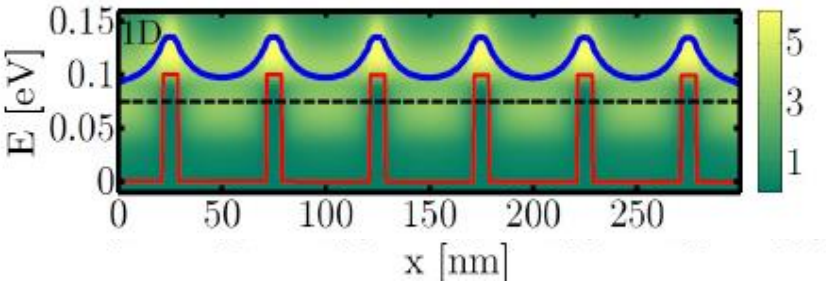
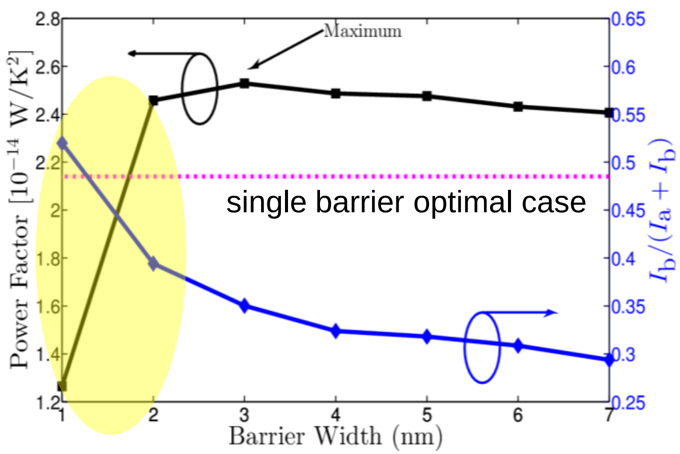
Example 1: 1D superlattice - all features captured

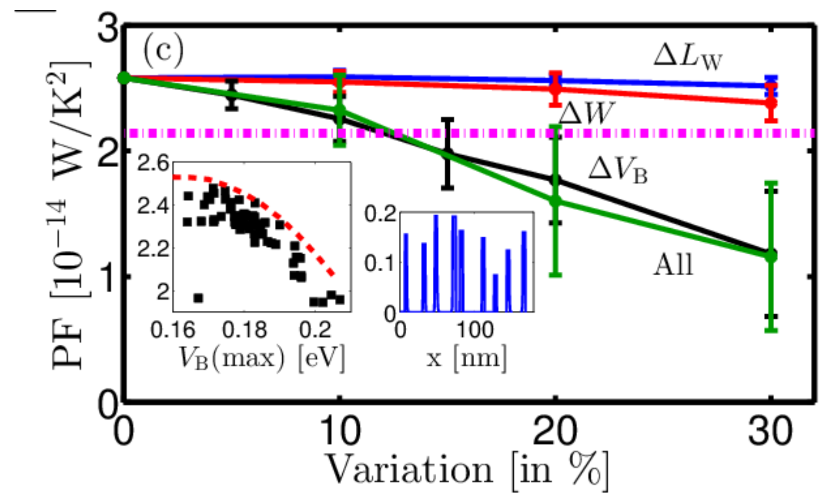


$$S = -\frac{k_B}{q}\left\langle \frac{E - E_F}{k_B T} \right\rangle = -\frac{\langle E - E_F \rangle}{qT}$$

current flow variations and λ_E



Tunneling is detrimental to PF



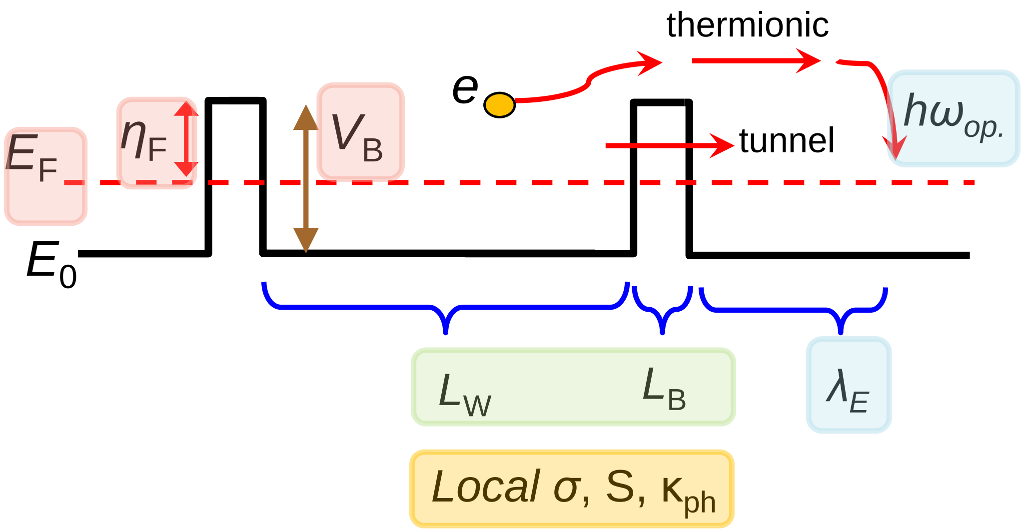
Variation in V_B reduces PF

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

Thesberg, Kosina, Neophytou, ***J. Appl. Phys.***, 118, 224301, 2015

Features for PF improvement

How to design such structures ?



- E_F should be high into the bands to improve σ_W
- L_B should large enough to prevent tunneling
- Barrier height V_B should be 1-2kT above E_F → *No flexibility*
- L_W should be similar to λ_E (somewhat larger) → *Some flexibility here*
- Good to have large current energy variations in barriers and wells

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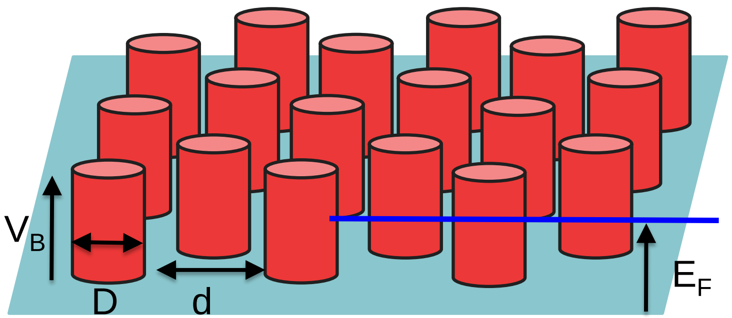
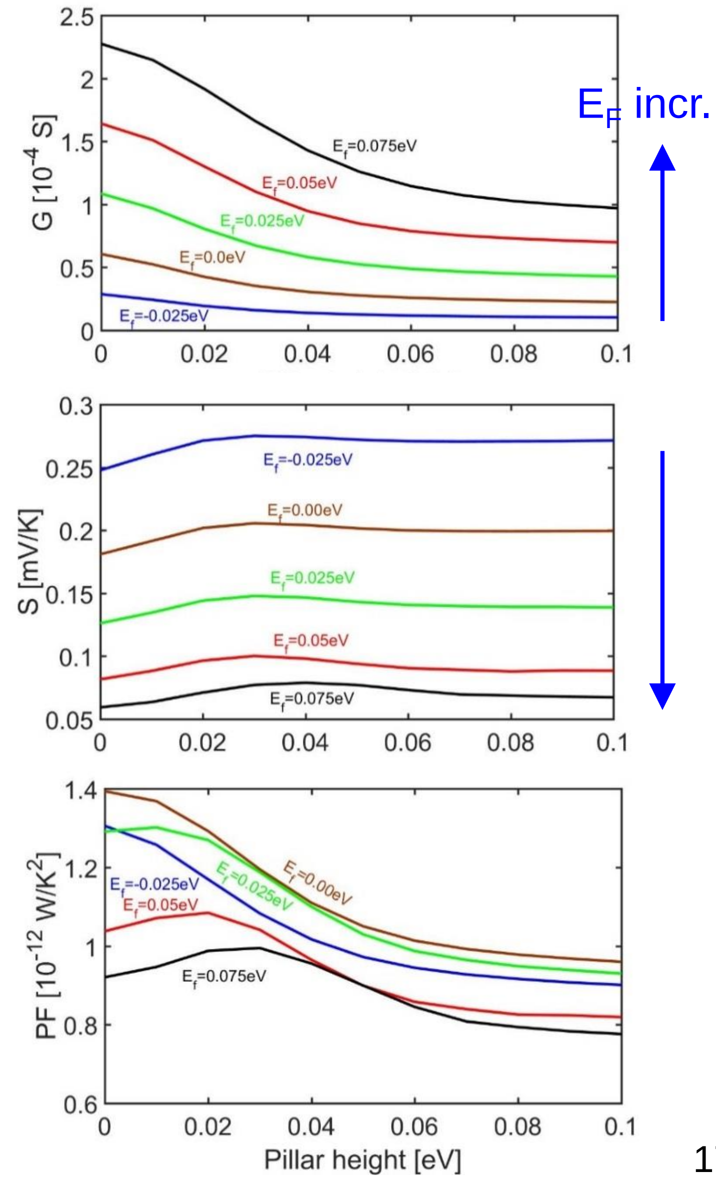
Materials with nano-inclusions: E_F, and V_B dependences



Vary E_F and V_B

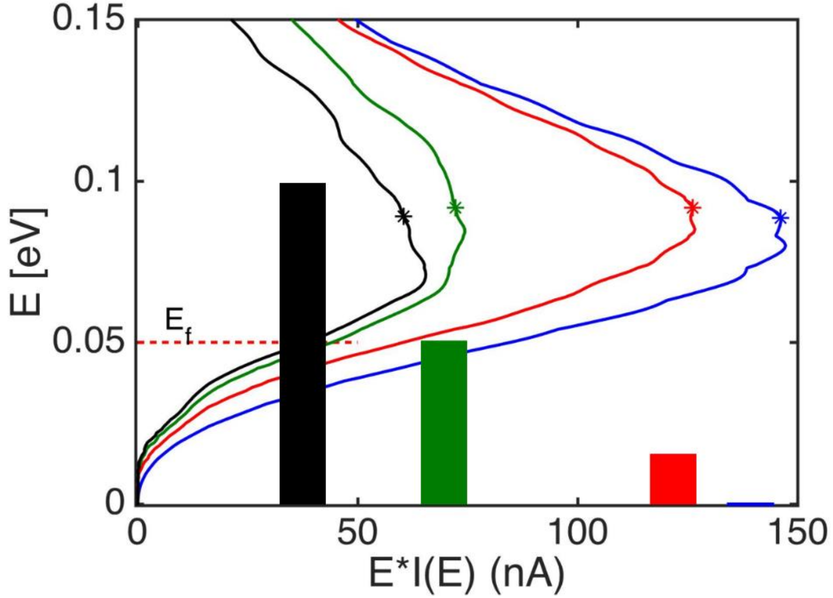


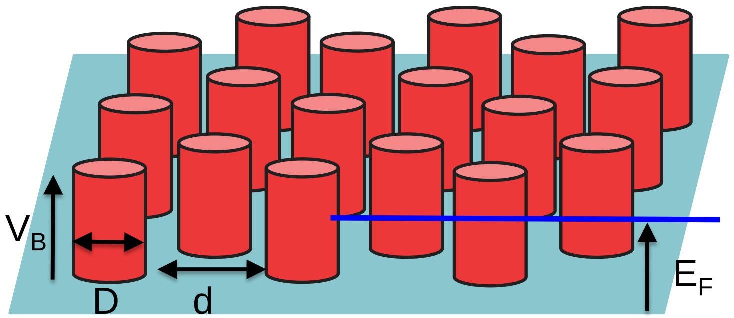
- Seebeck has <u>very week </u>dependence on V_B : limited possibilities for filtering
- *Mostly nano-inclusions reduce the PF (from an optimal case), unlike in SLs*
- For large V_B, the influence of both V_B and E_F on the PF is reduced

Explaining the Seebeck behavior

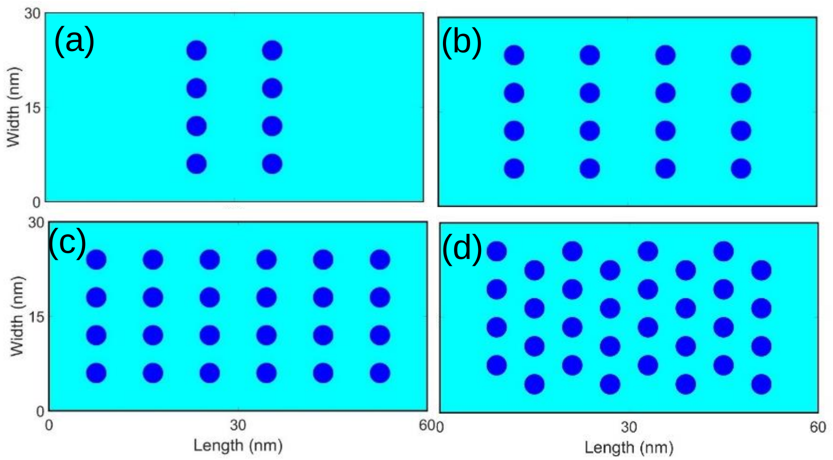
- Seebeck proportional to the average energy of the current

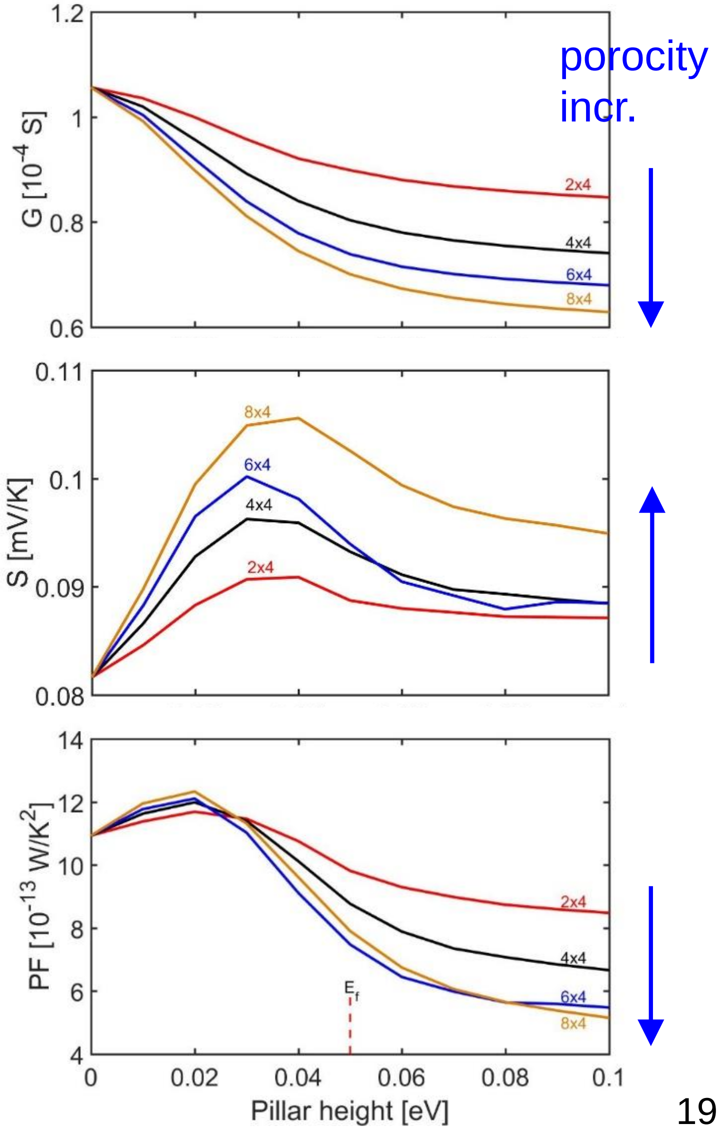
$$S = \frac{< E > - E_F}{qT}$$





Increasing porosity

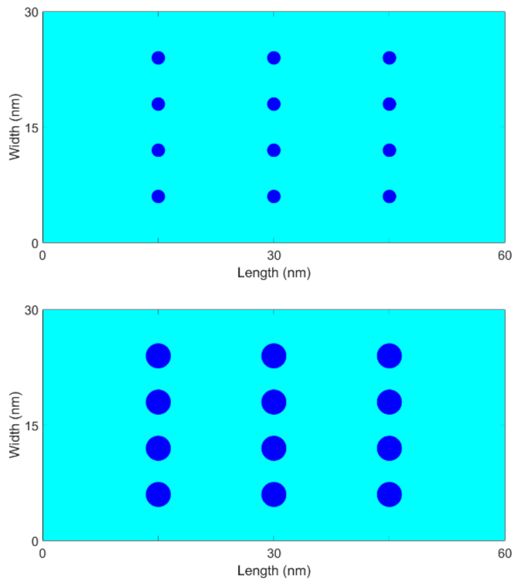


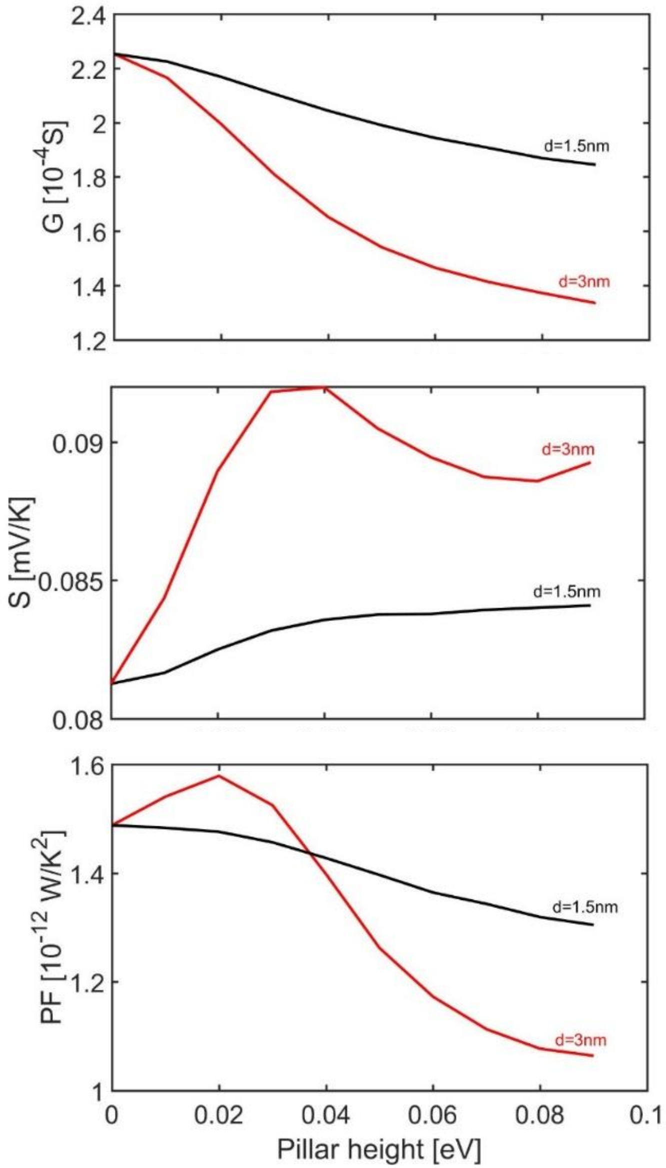


- <u>For small V_B:</u>
  Porosity has a weak effect on the PF
- Porosity has a stronger effect at higher V_B
- Characteristics saturate for barriers beyond E_F+k_BT

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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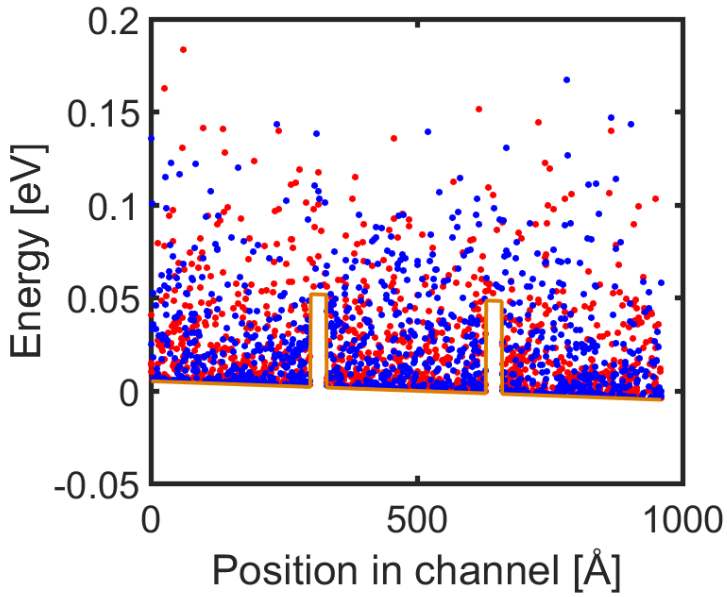
Numerical issues in NEGF

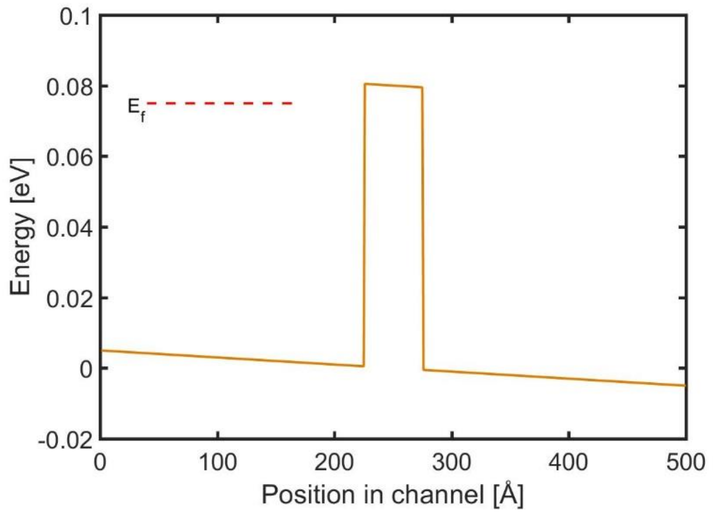
- Single simulation of 60x30 nm channel ~ 10 hrs
- Length dimension scales linearly, but…
- Width scales ~ W^3
- Geometries of microns by microns simply not possible

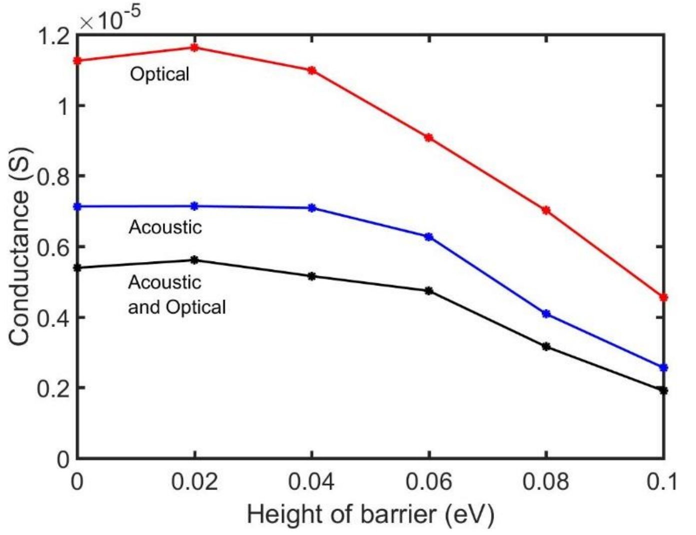
Simulations of superlattices in Monte Carlo



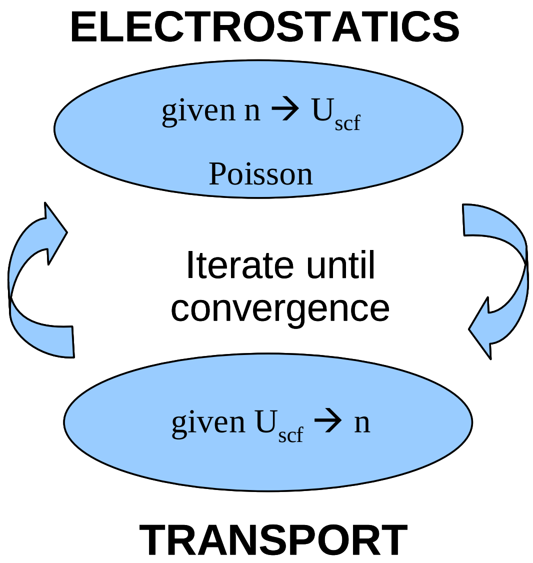
Superlattice

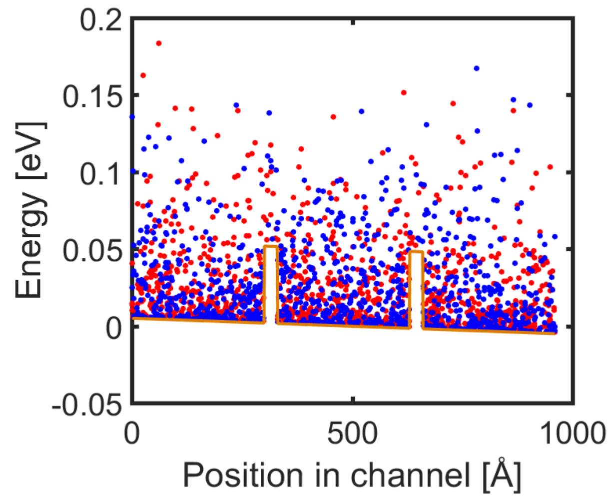
➢Include all relevant scattering parameters (next Ionised Impurities)

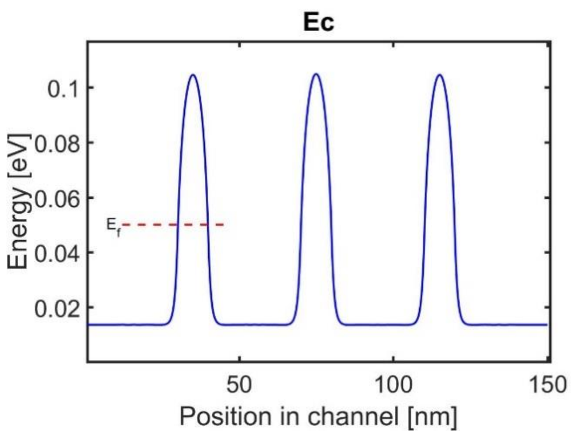


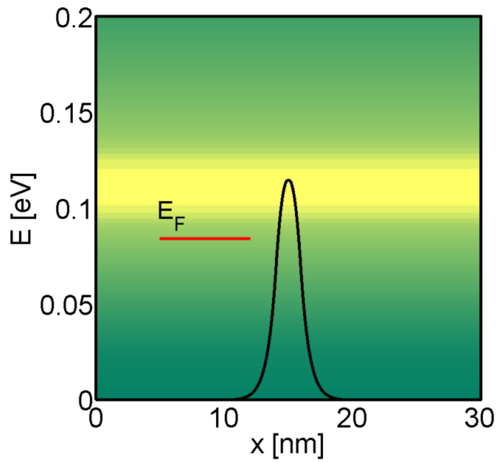


Include additional effects





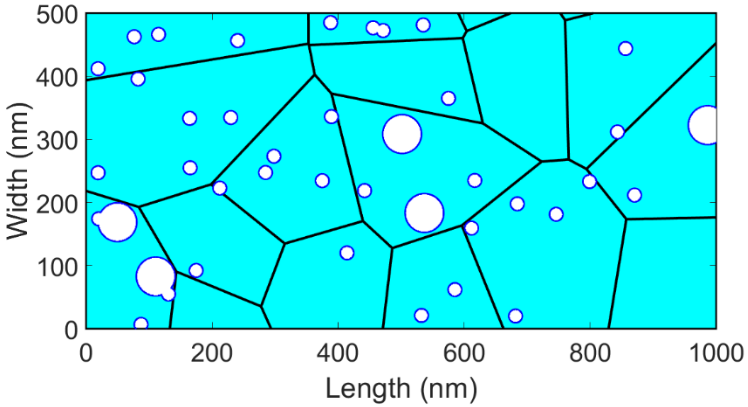




Self-consistent electrostatics

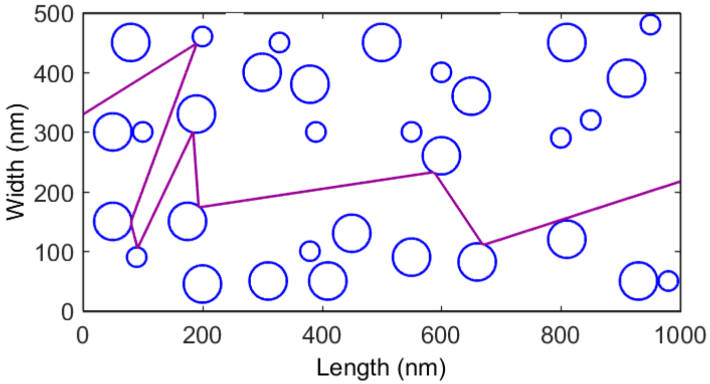
Quantum tunneling

Thermal conductivity – nanocomposites/nanomeshes



Need something more multi-physics based !

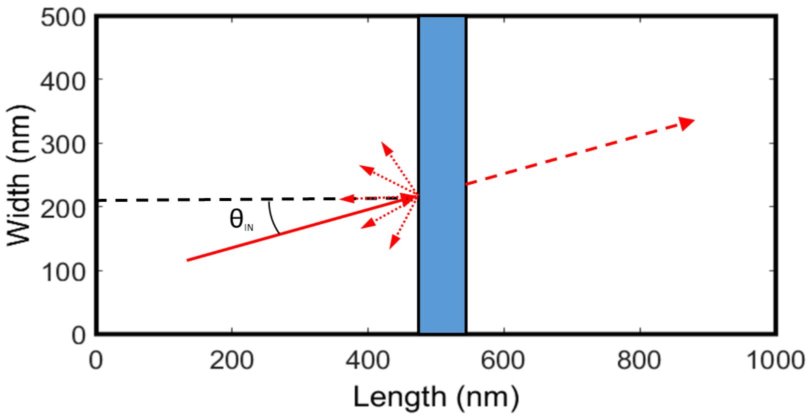
- <u>Geometry:</u> boundaries, nanoinclusions, voids,…
- <u>Physics:</u> particle + wave effects
- Scale to realistic micron sizes
- Couple phonon and electronic systems



boundary scattering

$$\text{boundary specularity} = \frac{1-p}{1+p}$$

$$p(q) = \exp\left(-q^2 \Delta_{\text{rms}}^2\right)$$



grain boundary scattering

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

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

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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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FFG FWF SEVENTH FRAMEWORK PROGRAMME HORIZON 2020 erc

ERC StG: NANOthermMA