Thermoelectricity: From Atoms to Systems

Week 2: Thermoelectric Transport Parameters
Lecture 2.5: **Lattice Thermal Conductivity**

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review: coupled charge and heat currents

electrical current:

$$\mathcal{E}_x = \rho J_x + S\frac{dT}{dx}$$

heat current (electronic):

$$J_{Qx} = \pi J_x - \kappa_e \frac{dT}{dx}$$

heat current (lattice):

$$q_x = -\kappa_L\left(\frac{dT}{dx}\right)$$

$$\sigma = \frac{2q^2}{h}\langle M_{el}/A\rangle\langle\langle\lambda_{el}\rangle\rangle = n_0 q\mu_n$$

$$S = -\left(\frac{k_B}{q}\right)\left(\frac{E_J - E_F}{k_B T}\right)$$

$$\pi = TS$$

$$\kappa_e = T\sigma\mathcal{L}$$

$$\kappa_L = \frac{\pi^2 k_B^2 T}{3h}\langle M_{ph}/A\rangle\langle\langle\lambda_{ph}\rangle\rangle$$

heat flux and thermal conductivity

1) Electrons can carry heat, and we have seen how to evaluate the electronic thermal conductivity.

2) In metals, **electrons** carry most of the heat.

3) But in semiconductors and insulators, lattice vibrations (***phonons***) transport most of the heat.

Lecture 5 topics

1) Phonons

2) Landauer approach to phonon transport

3) Thermal conductivity vs. temperature

1) Electron vs. phonon transport

electron dispersion

Electrons in a solid behave as both particles (quasi-particles) and as waves.

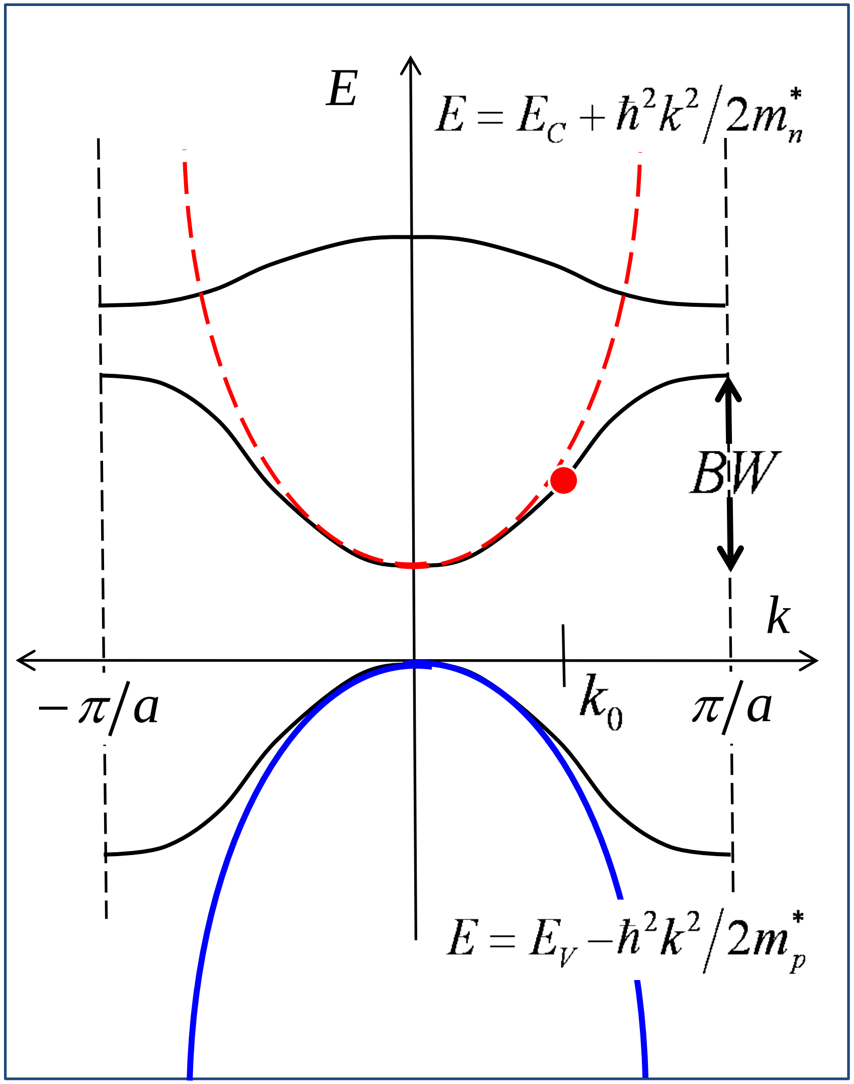
Electron waves are described by a "dispersion:" $E(\vec{k}) = \hbar\omega(\vec{k})$

Because the crystal is periodic, the dispersion is periodic in *k* (Brillouin zone).

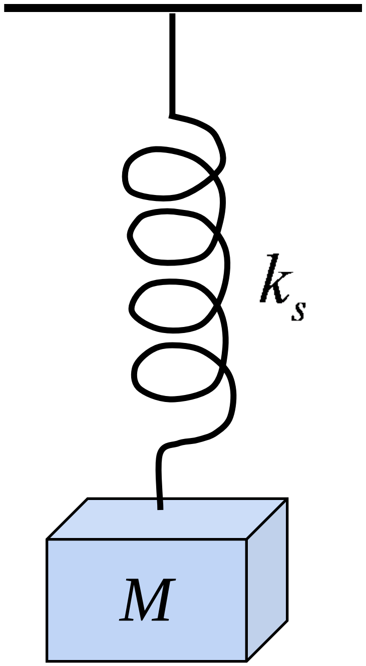
Particles described by a "wavepacket."

The "group velocity" of a wavepacket is determined by the dispersion:

$$\vec{\upsilon}_g(\vec{k}) = \nabla_k E(\vec{k})/\hbar$$



mass and spring



$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$U = \frac{1}{2}k_s\left(x - x_0\right)^2$$

$$F = -\frac{dU}{dx} = -k_s\left(x - x_0\right)$$

$$M\frac{d^2x}{dt^2} = -k_s\left(x - x_0\right)$$

$$x(t) - x_0 = Ae^{i\omega t}$$

$$\omega = \sqrt{k_s/M}$$

phonon dispersion

Lattice vibrations behave both as particles (quasi-particles) and as waves.

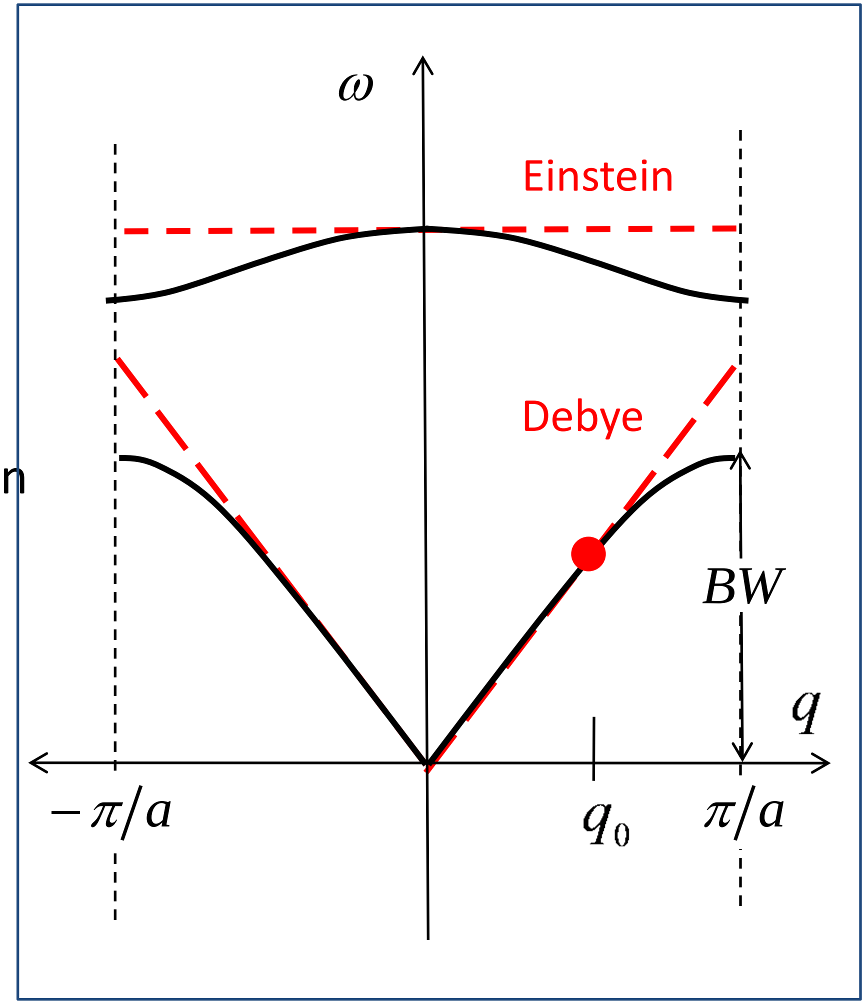
Lattice vibrations are described by a "dispersion:" $\omega(\vec{q}) = E(\vec{q})/\hbar$

Because the crystal is periodic, the dispersion is periodic in *k* (Brillouin zone).

Particles described by a "wavepacket."

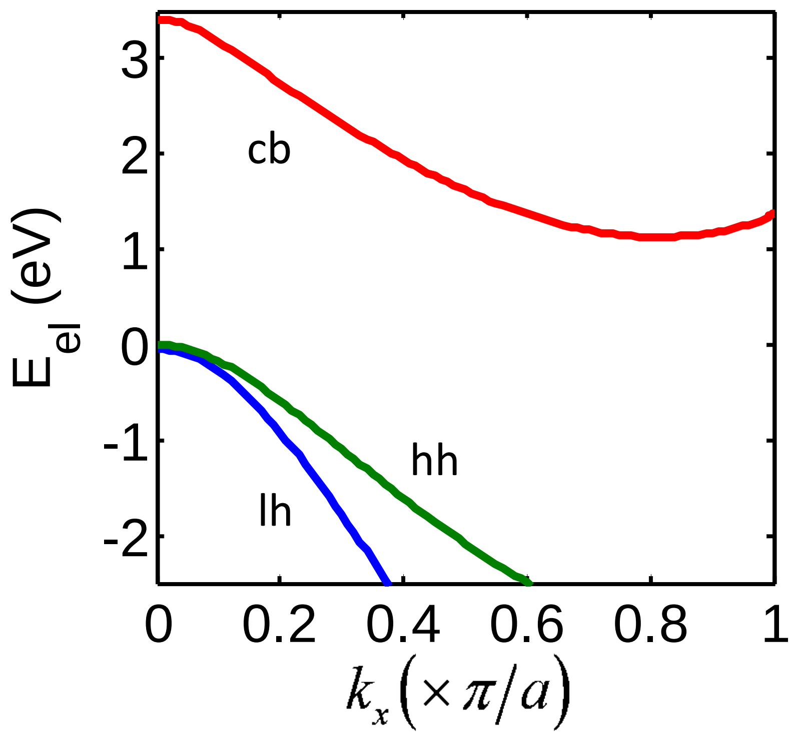
The "group velocity" of a wavepacket is determined by the dispersion:

$$\vec{\upsilon}_g(\vec{q}) = \nabla_q \omega(\vec{q})$$

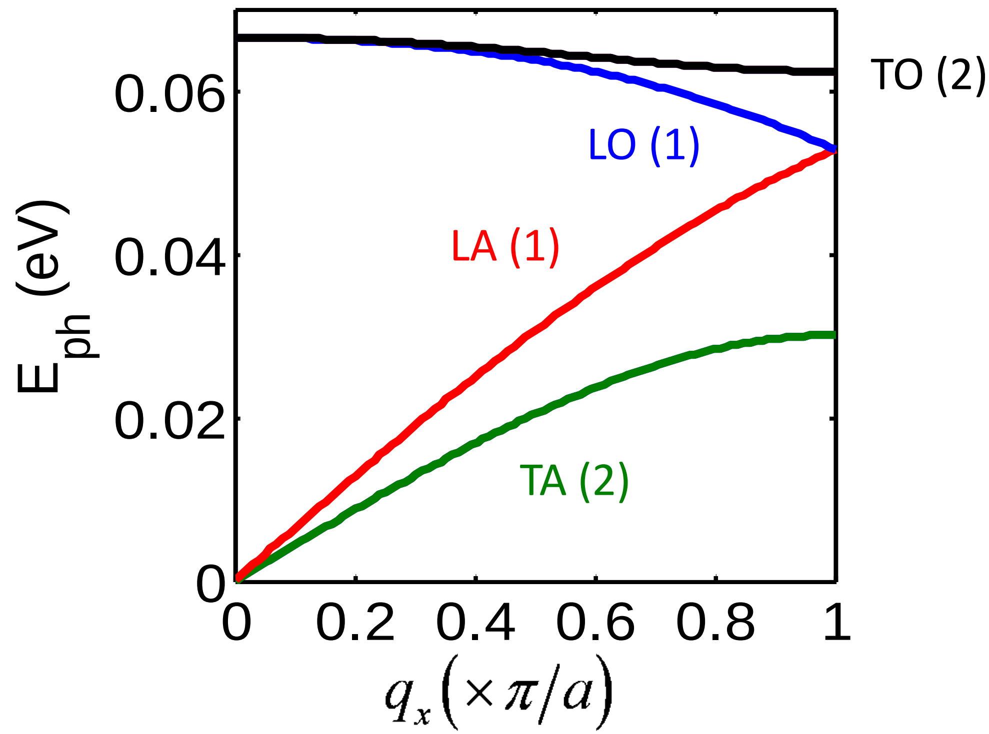


real dispersions

$BW \gg k_B T$



$BW \sim k_B T$



note the different energy scales!

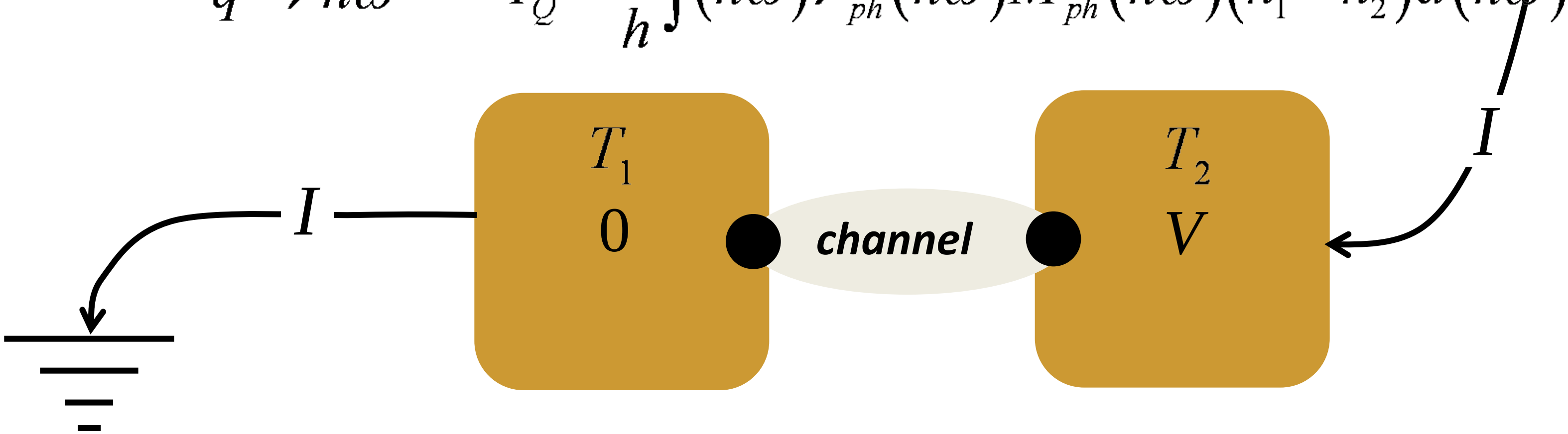
electrons in Si (along [100])

phonons in Si (along [100])

general model for **lattice thermal** conduction

$$I = \frac{2q}{h}\int \mathcal{T}_{el}(E) M_{el}(E)\left(f_1 - f_2\right) dE$$ (electrons)

$$q \rightarrow \hbar\omega \qquad I_Q = \frac{1}{h}\int (\hbar\omega)\mathcal{T}_{ph}(\hbar\omega) M_{ph}(\hbar\omega)\left(n_1 - n_2\right) d(\hbar\omega)$$



$$n_1(E) = \frac{1}{e^{\hbar\omega/k_B T_1} - 1} \qquad n_2(E) = \frac{1}{e^{\hbar\omega/k_B T_2} - 1}$$

near-equilibrium heat flux

$$I_Q = \frac{1}{h}\int (\hbar\omega)\mathcal{T}_{ph}(\hbar\omega)M_{ph}(\hbar\omega)(n_1 - n_2)\,d(\hbar\omega)$$

$$(n_1 - n_2) \approx -\frac{\hbar\omega}{T}\left(-\frac{\partial n_0}{\partial(\hbar\omega)}\right)\Delta T$$

$$\boxed{I_Q = -K_L \Delta T}$$

watts = (watts/K) x K

thermal conductance

window functions

$$I_Q = -K_L \Delta T \quad K_L = \frac{k_B^2 T}{h} \int \mathcal{T}_{ph}(\hbar\omega) M_{ph}(\hbar\omega) \left\{ \left(\frac{\hbar\omega}{k_B T} \right)^2 \left(-\frac{\partial n_0}{\partial(\hbar\omega)} \right) \right\} d(\hbar\omega)$$

Recall the electrical conductance:

$$G = \frac{2q^2}{h} \int \mathcal{T}_{el}(E) M_{el}(E) \left(-\frac{\partial f_0}{\partial E} \right) dE$$

"window function":

$$W_{el}(E) = \left(-\partial f_0 / \partial E \right) \qquad \int_{-\infty}^{+\infty} \left(-\partial f_0 / \partial E \right) dE = 1$$

heat conduction

1) Fourier's Law of heat conduction: $I_Q = -K_L \Delta T$

2) Thermal conductance: $K_L = \dfrac{\pi^2 k_B^2 T}{3h} \int \mathcal{T}_{ph}(\hbar\omega) M_{ph}(\hbar\omega) W_{ph}(\hbar\omega) d(\hbar\omega)$

3) Quantum of heat conduction: $\dfrac{\pi^2 k_B^2 T}{3h}$

4) Window function for phonons: $W_{ph}(\hbar\omega) = \left\{ \dfrac{3}{\pi^2} \left(\dfrac{\hbar\omega}{k_B T} \right)^2 \left(-\dfrac{\partial n_0}{\partial(\hbar\omega)} \right) \right\}$

electrical conduction

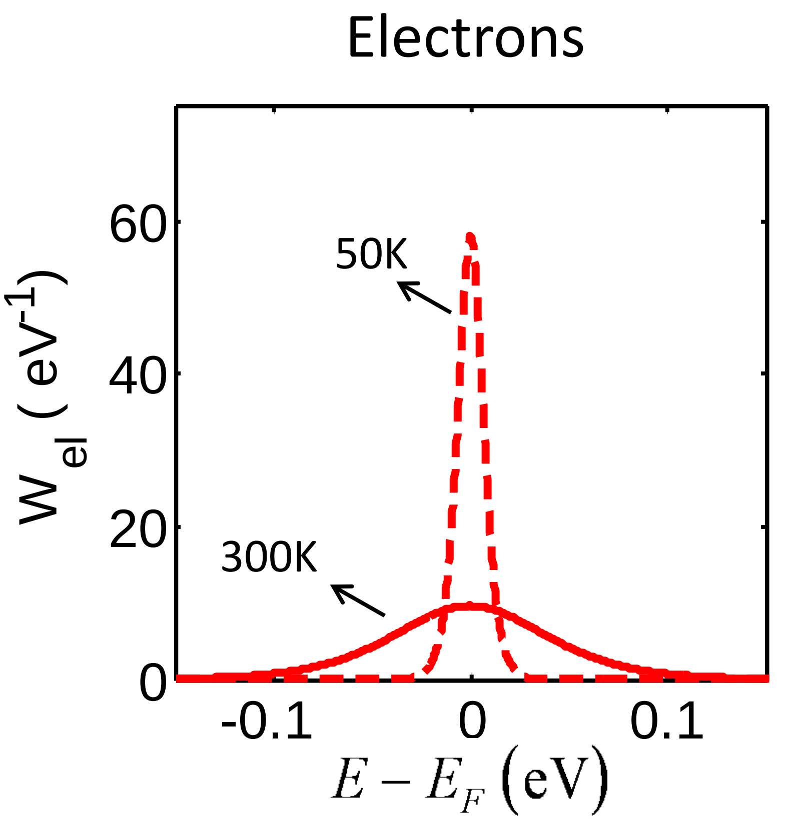
1) Electrical current: $I = G\Delta V$

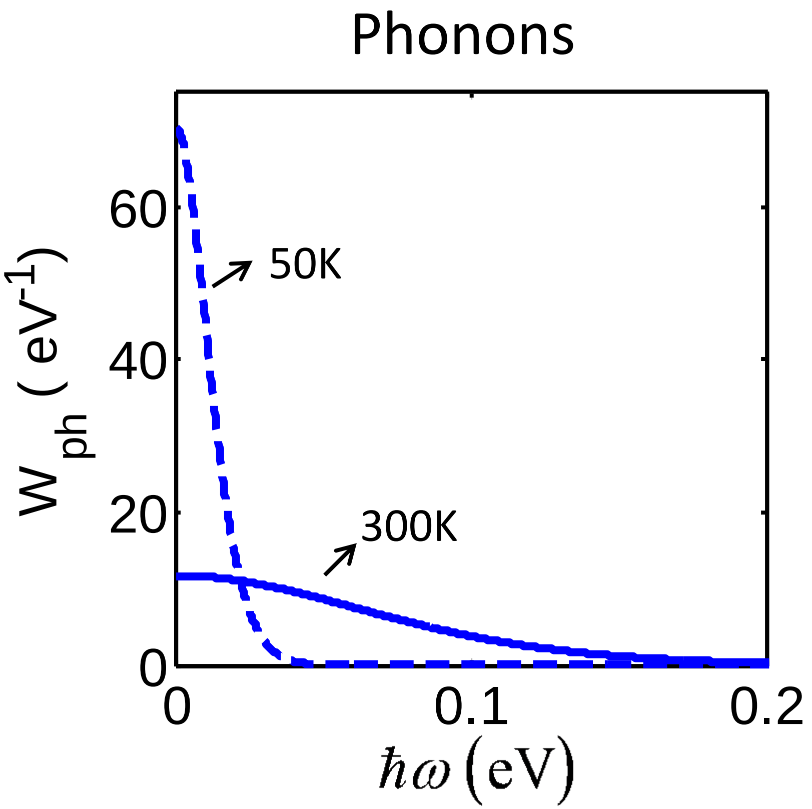
2) Electrical conductance: $G = \dfrac{2q^2}{h}\int \mathcal{T}_{el}(E) M_{el}(E) W_{el}\, dE$

3) Quantum of electrical conduction: $\dfrac{2q^2}{h}$

4) Window function for electrons: $W_{el}(E) = \left(-\partial f_0/\partial E\right)$

window functions: electrons vs. phonons





$$W_{el}(E) = \left(-\partial f_0 / \partial E\right)$$

$$W_{ph}(\hbar\omega) = \left\{ \frac{3}{\pi^2} \left(\frac{\hbar\omega}{k_B T} \right)^2 \left(-\frac{\partial n_0}{\partial(\hbar\omega)} \right) \right\}$$

diffusive heat transport (3D)

$$I_Q = -K_L \Delta T \qquad \text{(Watts)}$$

$$K_L = \frac{\pi^2 k_B^2 T}{3h} \int \mathcal{T}_{ph}(\hbar\omega) M_{ph}(\hbar\omega) W_{ph}(\hbar\omega)\, d(\hbar\omega) \qquad \text{(Watts/K)}$$

$$\mathcal{T}_{ph}(\hbar\omega) = \frac{\lambda_{ph}(\hbar\omega)}{\lambda_{ph}(\hbar\omega) + L} \rightarrow \frac{\lambda_{ph}(\hbar\omega)}{L} \qquad \text{(diffusive phonon transport)}$$

$$q_x = I_Q / A = -K_L \frac{L}{A} \frac{\Delta T}{L} = -\kappa_L \frac{dT}{dx} \quad \text{(Watts)}$$

$$\kappa_L = K_L \left(\frac{L}{A} \right) \qquad \text{(Watts/m-K)}$$

diffusive heat transport (3D)

$$q_x = -\kappa_L \frac{dT}{dx}$$ (Watts / m^2)

$$\kappa_L = \frac{\pi^2 k_B^2 T}{3h} \int \lambda_{ph}(\hbar\omega) \frac{M_{ph}(\hbar\omega)}{A} W_{ph}(\hbar\omega) d(\hbar\omega)$$ (Watts/m-K)

$$J_x = \sigma \frac{d(F_n/q)}{dx}$$ (Amperes / m^2)

$$\sigma = \frac{2q^2}{h} \int \lambda_{el}(E) \frac{M_{el}(E)}{A} W_{el}(E) dE$$ (1/Ohm-m)

diffusive heat transport (3D)

$$q_x = -\kappa_L \frac{dT}{dx}$$ (Watts / m^2)

$$\kappa_L = \frac{\pi^2 k_B^2 T}{3h} \langle M_{ph}/A \rangle \langle\langle \lambda_{ph} \rangle\rangle$$ (Watts/m-K)

$$J = \sigma \frac{d(F_n/q)}{dx}$$ (Amperes / m^2)

$$\sigma = \frac{2q^2}{h} \langle M_{el}/A \rangle \langle\langle \lambda_{el} \rangle\rangle$$ (1/Ohm-m)

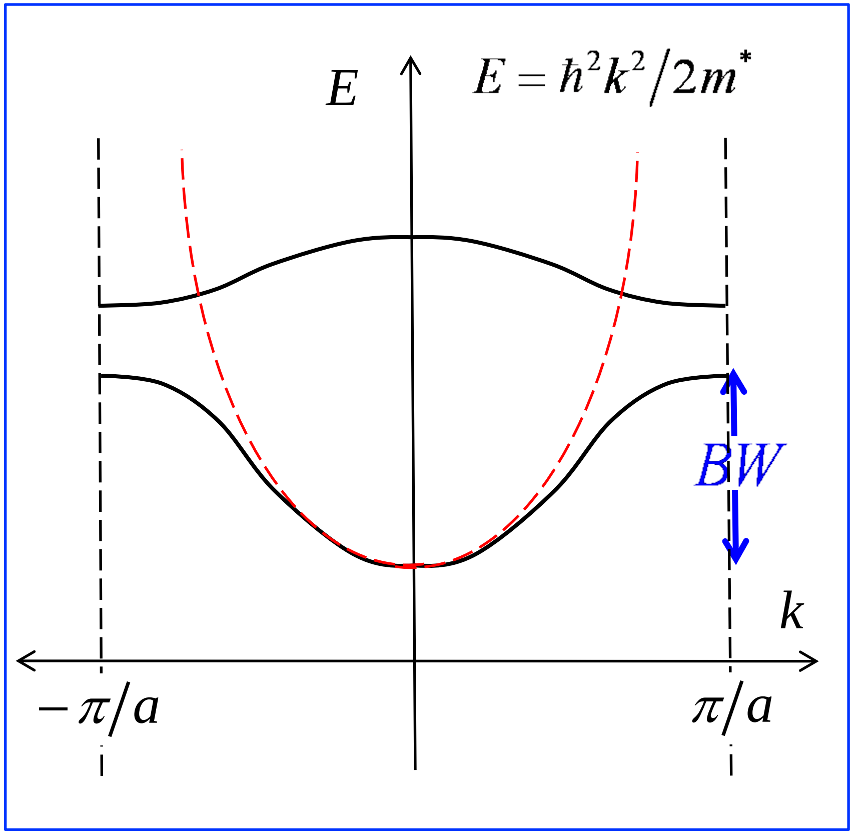
connection to traditional view

$$\sigma = \frac{2q^2}{h}\langle M_{el}/A\rangle\langle\langle\lambda_{el}\rangle\rangle \leftrightarrow n_0 q\mu_n$$ (1/Ohm-m)

$$\kappa_L = \frac{\pi^2 k_B^2 T}{3h}\langle M_{ph}/A\rangle\langle\langle\lambda_{ph}\rangle\rangle \leftrightarrow \frac{1}{3}\langle\langle\Lambda_{ph}\rangle\rangle\langle\upsilon_{ph}\rangle C_V$$ (Watts/m-K)

$$E_L = \int_0^\infty (\hbar\omega) D_{ph}(\hbar\omega) n_0(\hbar\omega) d(\hbar\omega) \qquad C_V = \left.\frac{\partial E_L}{\partial T}\right|_V$$

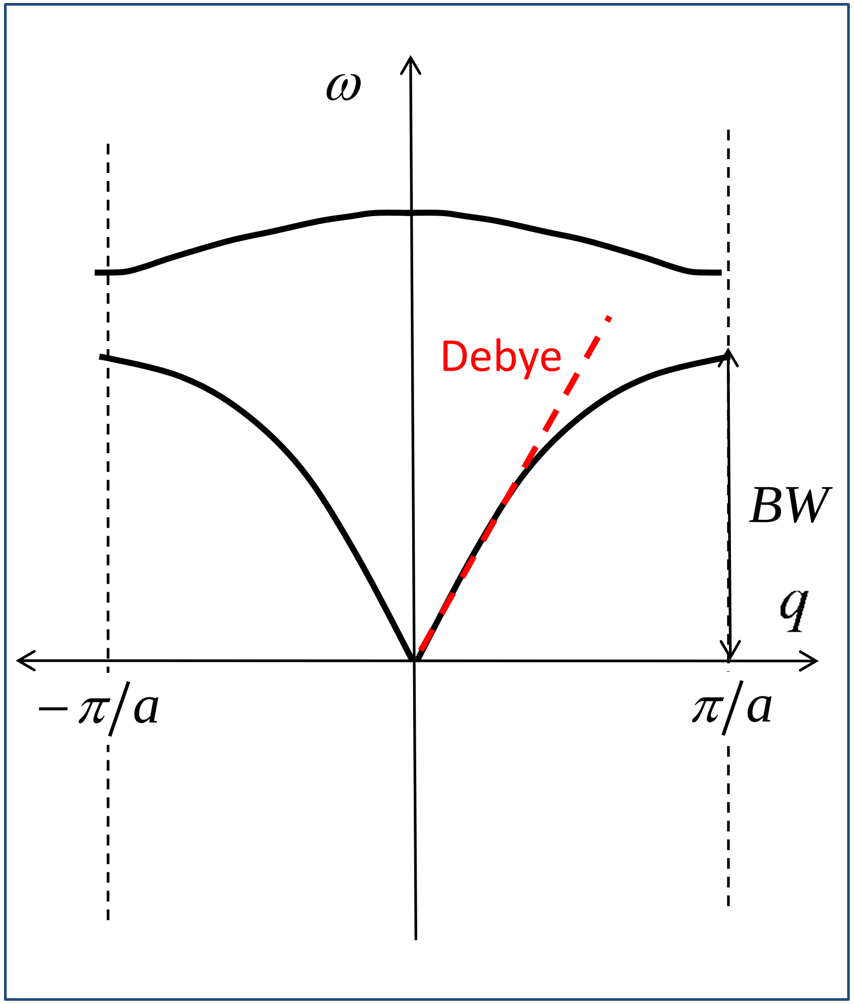
effective mass model for electrons



As long as the BW >> $k_B T$, the effective mass model generally works ok.

Typically, only states near the band edge matter, and these regions can be described by an effective mass approximation.

Debye model for acoustic phonons



Linear dispersion model

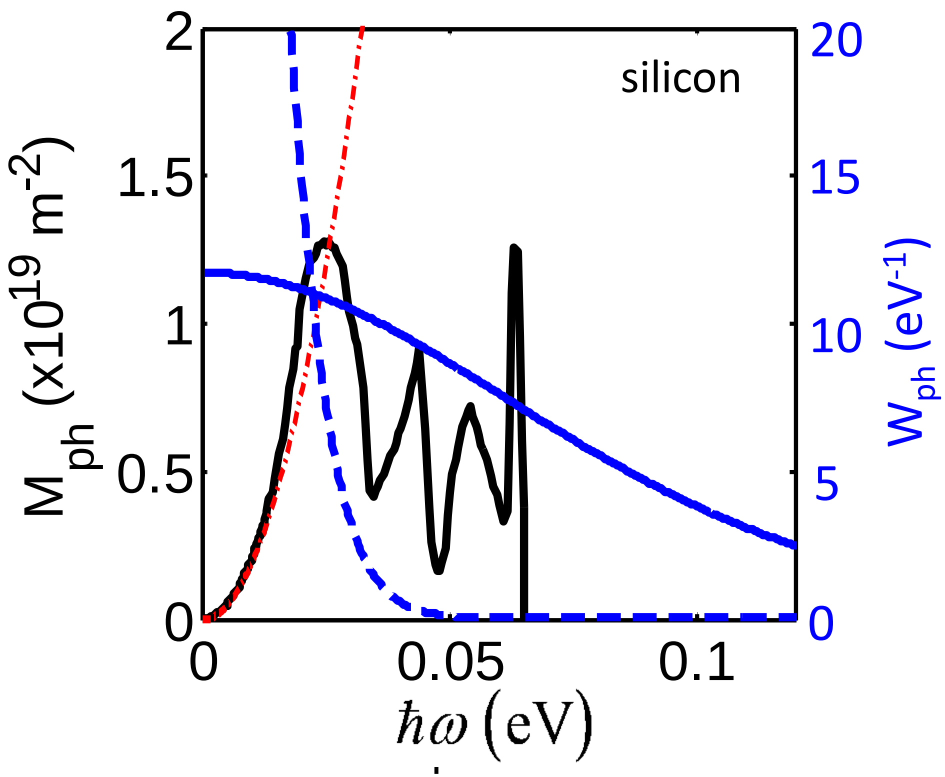
$$\omega = \upsilon_D q$$

$$D_{ph}(\hbar\omega) = \frac{3(\hbar\omega)^2\,\Omega}{2\pi^2(\hbar\upsilon_D)^3} \quad (\text{no.}/\text{J})$$

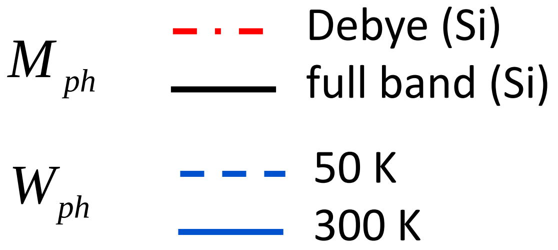
$$M_{ph}(\hbar\omega) = \frac{3(\hbar\omega)^2\,A}{2\pi\hbar\upsilon_D^2} \quad (\text{no.}/\text{J})$$

If acoustic phonons near q =0 mostly contribute to heat transport, Debye model works work well.

limitation of Debye model



$$\kappa_L = \frac{\pi^2 k_B^2 T}{3h} \int \lambda_{ph} \frac{M_{ph}}{A} W_{ph} \, d(\hbar\omega)$$



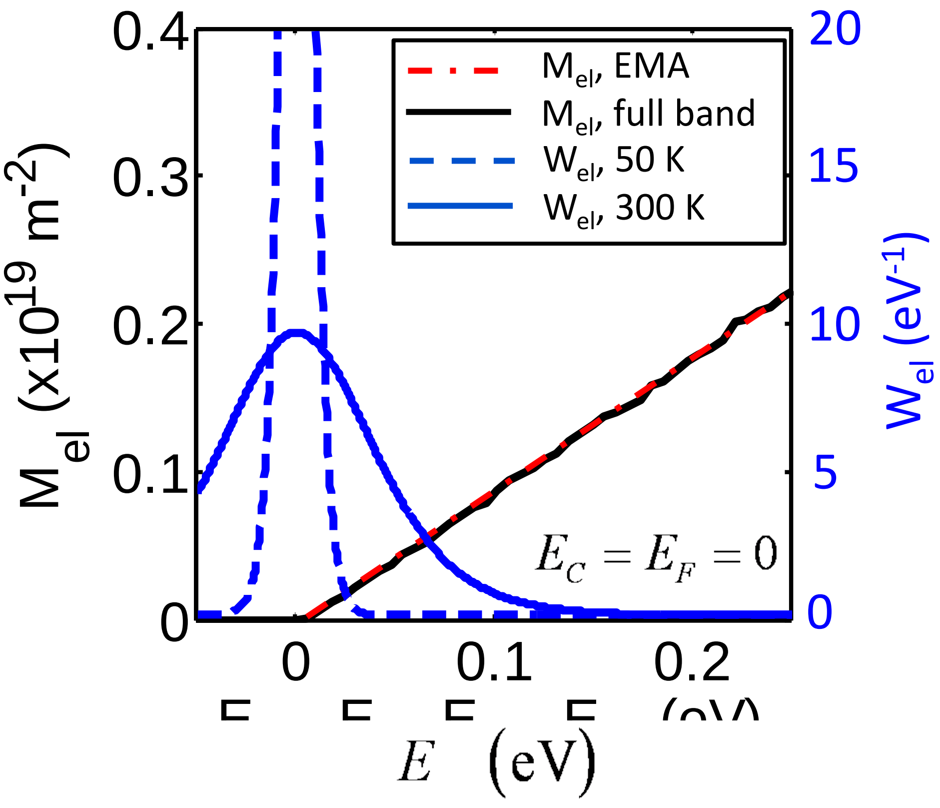
Window function spans the entire BZ at room temp.

Debye model works well **at low temperatures.**

effective mass model for electrons

Parabolic dispersion assumption for electrons works well at room temperature.

electrons in Si



lattice thermal conductivity

$$\kappa_L = \frac{\pi^2 k_B^2 T}{3h} \left\langle M_{ph}/A \right\rangle \left\langle\left\langle \lambda_{ph} \right\rangle\right\rangle$$

scattering

Electrons scatter from:

1) defects
   -e.g. charged impurities, neutral impurities, dislocations, etc.

2) phonons

3) surfaces and boundaries

4) other electrons

Phonons scatter from:

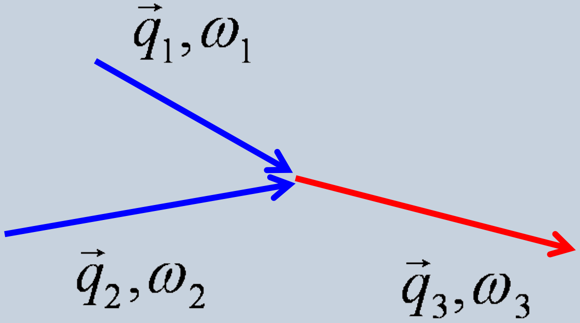
1) defects
   -e.g. impurities, dislocations, isotopes, etc.

2) other phonons

3) surfaces and boundaries

4) electrons ("phonon drag")

phonon-phonon scattering



i) momentum conservation:

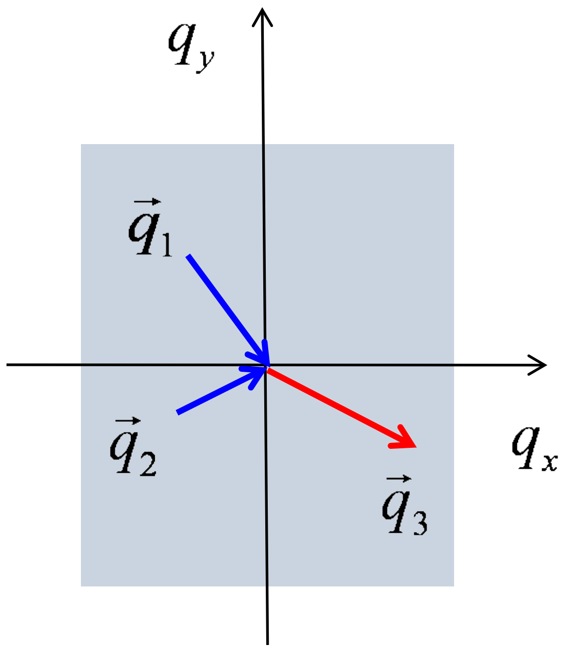
$$\hbar \vec{q}_3 = \hbar \vec{q}_1 + \hbar \vec{q}_2$$

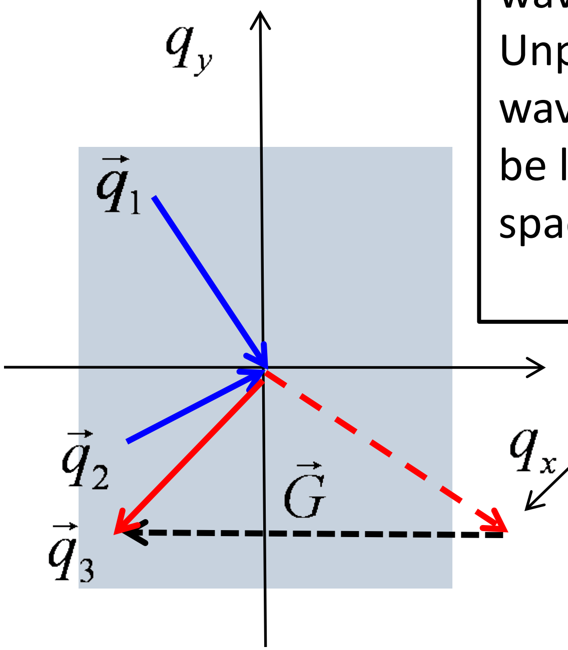
ii) energy conservation:

$$\hbar \omega_3 = \hbar \omega_1 + \hbar \omega_2$$

little effect on thermal conductivity!

N and U processes





High *q* implies short wavelength. Unphysical because wavelength would be less than lattice spacing.

Normal (N) process (momentum conserved) Little effect on κ_L.

Umklapp (U) process (momentum not conserved). Lowers κ_L.

scattering summary

$$\frac{1}{\tau_{ph}(\hbar\omega)} = \frac{1}{\tau_D(\hbar\omega)} + \frac{1}{\tau_B(\hbar\omega)} + \frac{1}{\tau_U(\hbar\omega)}$$

$$\frac{1}{\lambda_{ph}(\hbar\omega)} = \frac{1}{\lambda_D(\hbar\omega)} + \frac{1}{\lambda_B(\hbar\omega)} + \frac{1}{\lambda_U(\hbar\omega)}$$

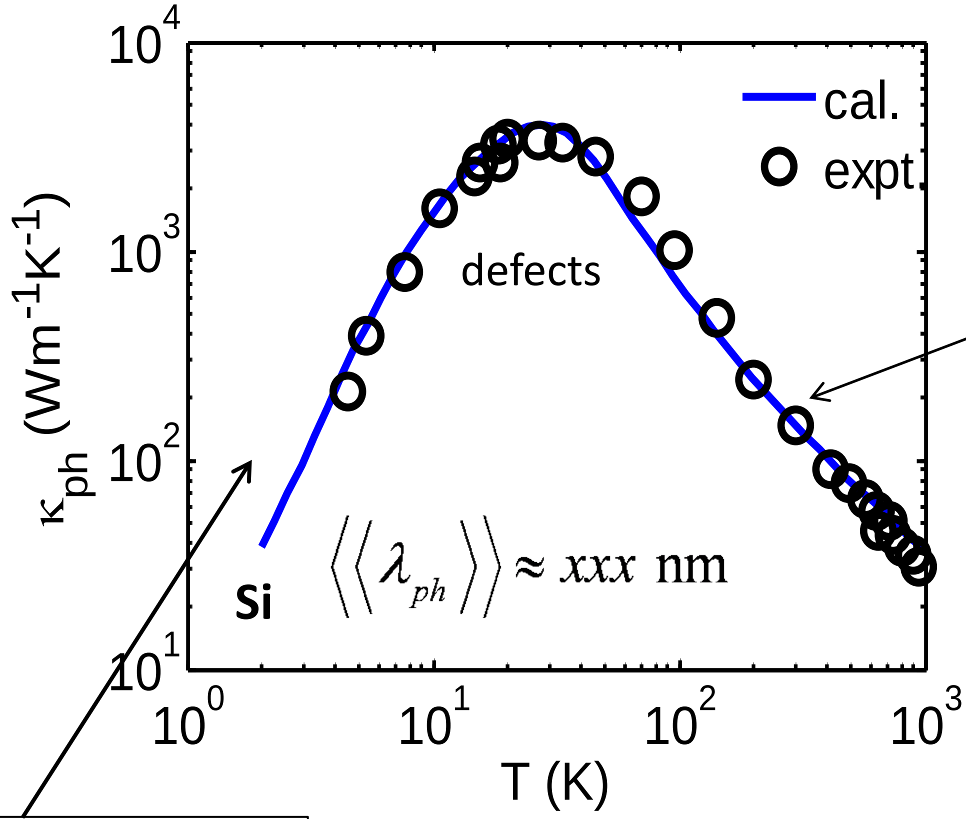
$$\lambda_{ph}(\hbar\omega) \propto \upsilon_{ph}(\hbar\omega)\tau_{ph}(\hbar\omega)$$

1) point defects and impurities: $1/\tau_D(\hbar\omega) \propto \omega^4$ "Raleigh scattering"

2) boundaries and surfaces: $1/\tau_B(\hbar\omega) \propto \upsilon_{ph}(\hbar\omega)/t$

3) Umklapp scattering: $1/\tau_U(\hbar\omega) \propto T_L$ $\left\{1/\tau_U(\hbar\omega) \propto e^{-T_D/bT_L} T_L^3 \omega^2\right\}$

temperature-dependent thermal conductivity



phonon scattering by U-processes

population of modes and boundary scattering

$$\kappa_L = \frac{\pi^2 k_B^2 T_L}{3h} \langle M_{ph} \rangle \times \langle\langle \lambda_{ph} \rangle\rangle$$

electron vs. phonon conductivities

The expressions look similar:

$$\kappa_L = \frac{\pi^2 k_B^2 T}{3h} \langle M_{ph}/A \rangle \langle\langle \lambda_{ph} \rangle\rangle \qquad \sigma = \frac{2q^2}{h} \langle M_{el}/A \rangle \langle\langle \lambda_{el} \rangle\rangle$$

In practice, the mfps often have similar values. **The difference is <*M*>**.

For electrons, the location E_F can vary <*M*> over many orders of magnitude.

But even when $E_F = E_C$, <*M*> is much smaller for electrons than for phonons because for electrons, the BW >> $k_B T_L$ while for phonons, BW ~ $k_B T_L$. Most of the modes are occupied for phonons but only a few for electrons.

electron vs. phonon conductivities

$$\frac{\kappa_L}{\left(\pi^2 k_B^2 T / 3h\right)} = \tilde{\kappa}_L = \langle M_{ph}/A \rangle \langle\langle \lambda_{ph} \rangle\rangle \qquad \frac{\sigma}{\left(2q^2/h\right)} = \tilde{\sigma} = \langle M_{el}/A \rangle \langle\langle \lambda_{el} \rangle\rangle$$

Example 1: Bi_2Te_3:

$$\frac{\tilde{\sigma}}{\kappa_L'} = \frac{\langle M_{el}/A \rangle}{\langle M_{ph}/A \rangle} \times \frac{\langle\langle \lambda_{el} \rangle\rangle}{\langle\langle \lambda_{ph} \rangle\rangle} = \frac{9.2 \times 10^{16}\,\mathrm{m}^{-2}}{53 \times 10^{16}\,\mathrm{m}^{-2}} \times \frac{21\ \mathrm{nm}}{9\ \mathrm{nm}} = 0.41$$

Phonon MFP engineering

Large mass, low sound velocity → small BW

n-type Bi_2Te_3 vs. Si

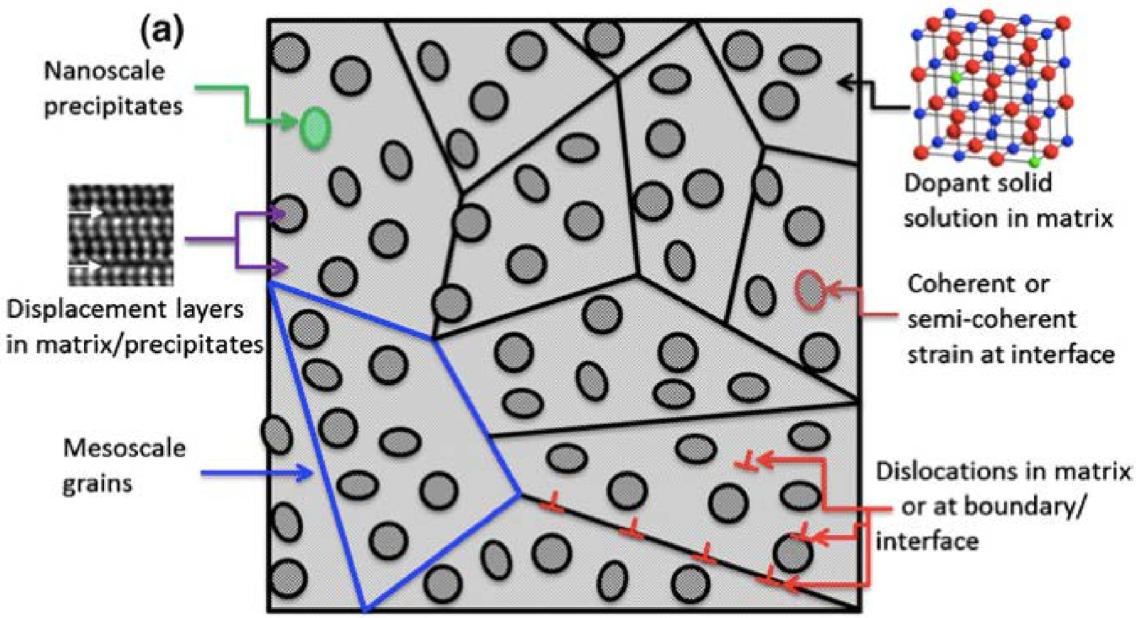
Example 1: Bi_2Te_3:

$$\frac{\tilde{\sigma}}{\kappa_L'} = \frac{\langle M_{el}/A \rangle}{\langle M_{ph}/A \rangle} \times \frac{\langle\langle \lambda_{el} \rangle\rangle}{\langle\langle \lambda_{ph} \rangle\rangle} = \frac{9.2 \times 10^{16}\,\text{m}^{-2}}{53 \times 10^{16}\,\text{m}^{-2}} \times \frac{21\text{ nm}}{9\text{ nm}} = 0.41$$

Example 2: Si:

$$\frac{\tilde{\sigma}}{\kappa_L'} = \frac{\langle M_{el}/A \rangle}{\langle M_{ph}/A \rangle} \times \frac{\langle\langle \lambda_{el} \rangle\rangle}{\langle\langle \lambda_{ph} \rangle\rangle} = \frac{14 \times 10^{16}\,\text{m}^{-2}}{360 \times 10^{16}\,\text{m}^{-2}} \times \frac{10\text{ nm}}{140\text{ nm}} = 0.003$$

Phonon MFP engineering



Jiaqing He, Mercouri G. Kanatzidis, and Vinayak P. Dravid, "High performance bulk thermoelectrics via a panoscopic approach," *Materials Today*, **16**, 166-176, 2013.

summary

1) Model for electrical conduction can readily be extended to phonons. The mathematics are very similar. Lattice heat conduction is quantized just as electronic conductivity is.

2) The different BW's of the electron and phonon dispersions have important consequences. For electrons, a simple dispersion (effective mass) is often adequate, but for phonons, the simple dispersion (Debye model) is not very good.

3) There is no Fermi level for phonons, so the lattice thermal conductivity cannot be varied across several orders of magnitude like the electrical conductivity, but MFPs can be engineered.