Nanoscale thermal transport

Lecture 5

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http://rileyhanus.com/science.html

1. Wavelength, coherence length, mean free path, and relaxation time

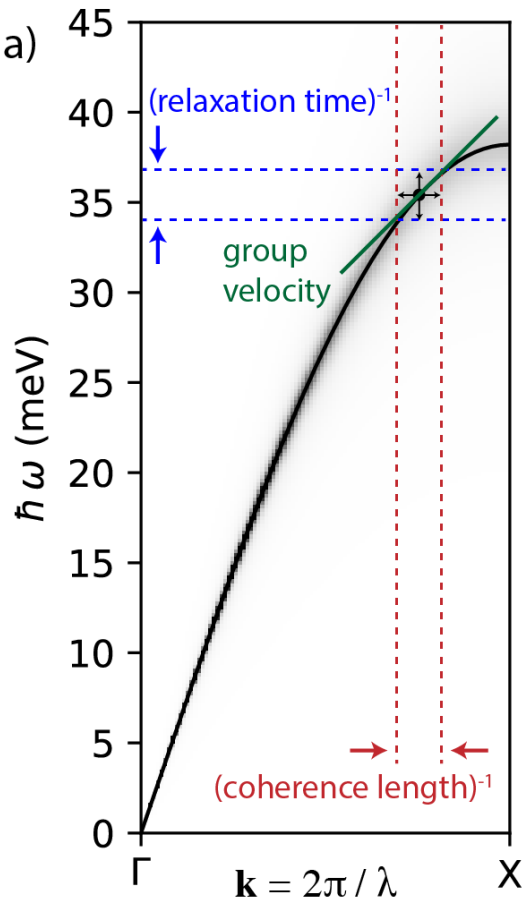
2. Example Callaway model

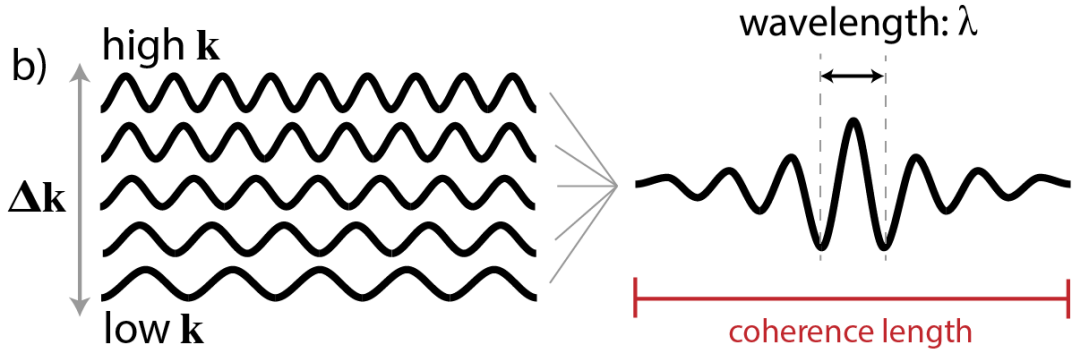
3. Explore how different scattering mechanisms influence thermal conductivity versus temperature
   a. Point defects
   b. Interfaces

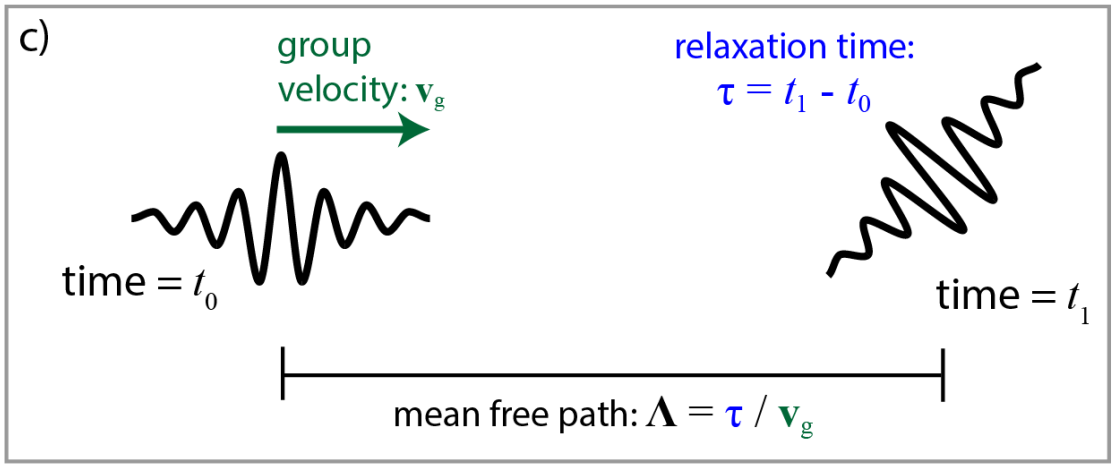
4. Explore low and high temperature limits
   a. Lattice softening

5. Mean free path accumulation

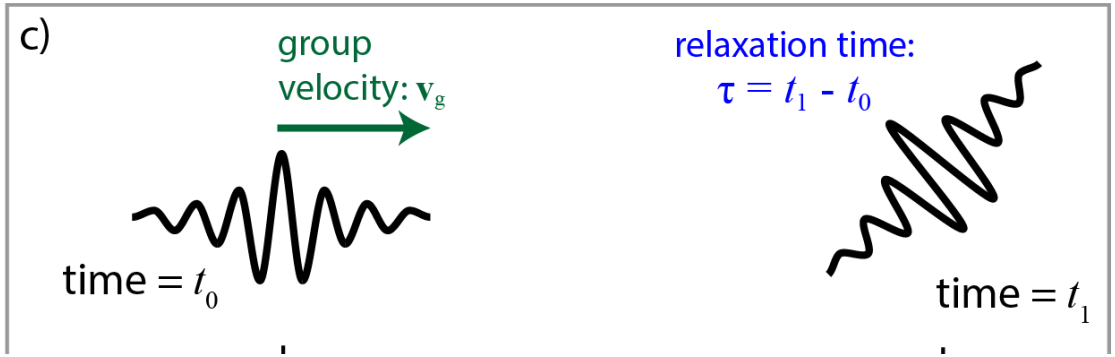
Review wave packet basics





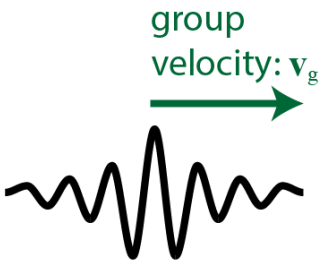


Review wave-packet basics



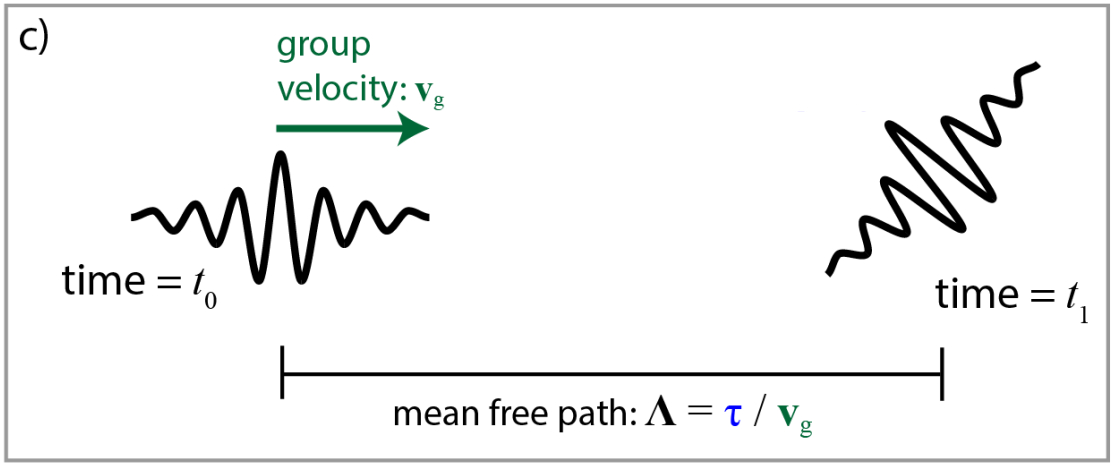
Relaxation time, τ (scalar): The time between scattering events of a phonon wave-packet.

Review wave-packet basics



Group velocity, $\mathbf{v_g}$ (vector)**:** The speed and direction the wave-packet travels.

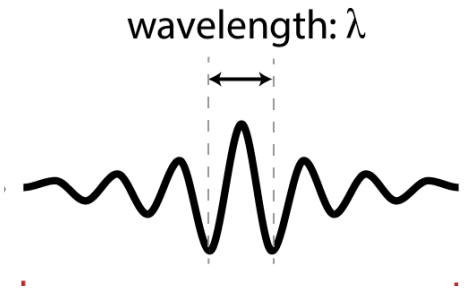
Review wave-packet basics



Mean free path, $\Lambda = \mathbf{v_g}\,\tau$ (vector): The distance a phonon wave-packet travels before scattering.

Λ determines how closely defects must be space for them to significantly reduce thermal conductivity. For example, defects that are spaced significantly farther apart than the phonon wave-packets phonon-phonon scattering mean free path, will not significantly reduce the heat carried by the wave-packet.

Review wave-packet basics



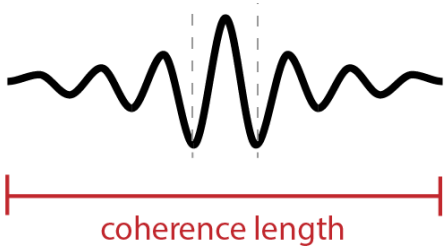
$$\tau(\mathbf{k})^{-1} = \Gamma(\mathbf{k}) = n_{\bar{3}\mathrm{d}}\, g_{\bar{3}\mathrm{d}}(\omega)\, \overline{|M_{\bar{3}\mathrm{d}}|^2}$$

$$M_{3\mathrm{d}}(\mathbf{q}) = \iiint V(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r} \qquad \mathbf{q} \propto \frac{1}{\lambda}$$

Wavelength, $\boldsymbol{\lambda}$ (vector)**:** The wavelength of the wave-packet.

λ, influences how strongly the phonon wave-packet will interact with a defect of a given physical size. This is intuitive when one remembers the scattering rate involves the real space Fourier transform of scattering potential (Lecture 4).

Review wave-packet basics



Coherence length (vector)**:** The distance over which the atomic vibrations are correlated to one another.

Ideal plane waves have an infinite coherence length. These do not exist in nature. In reality, there is a distance beyond which the vibration of atoms are uncorrelated.

Callaway Modeling

We've derived each part of this model in previous lectures.
The spectral version is listed here for reference.
A similar procedure can be performed on a mode specific basis.

$$\kappa = \frac{1}{3}\int_0^{\omega_{\max}} C(\omega)\, v_{\mathrm{g}}(\omega)^2\, \tau(\omega)\; d\omega$$

$$C(\omega) = \frac{3}{2\pi^2}\frac{\omega^4}{v_{\mathrm{g}} v_{\mathrm{p}}^2}\frac{\hbar^2}{k_{\mathrm{B}} T^2}\frac{e^{\hbar\omega/k_{\mathrm{B}}T}}{(e^{\hbar\omega/k_{\mathrm{B}}T}-1)^2}$$

$$k_{\max} = \left(\frac{6\pi^2}{V}\right)^{1/3}$$

only acoustic modes
V: volume per primitive unit cell
all modes
V: volume per atom

Dispersion relation:
1) Debye

$$v_{\mathrm{s}} = \left(\frac{1}{3v_{\mathrm{L}}^3} + \frac{2}{3v_{\mathrm{T}}^3}\right)^{-1/3}$$

$$\omega = v_{\mathrm{s}} k \qquad \omega_{\max} = v_{\mathrm{s}}\, k_{\max} \qquad v_{\mathrm{g}} = \frac{d\omega}{dk} = v_{\mathrm{s}} \qquad v_{\mathrm{p}} = \frac{\omega}{k} = v_{\mathrm{s}}$$

2) Born von Karman

$$\omega = \omega_{\max} \sin\left(\frac{\pi}{2}\frac{k}{k_{\max}}\right) \qquad \omega_{\max} = \frac{2}{\pi}\, v_{\mathrm{s}}\, k_{\max} \qquad v_{\mathrm{g}} = \frac{d\omega}{dk} = v_{\mathrm{s}} \cos\left(\frac{\pi}{2}\frac{k}{k_{\max}}\right) \qquad v_{\mathrm{p}} = \frac{\omega}{k}$$

$$k = \frac{2}{\pi}\, k_{\max} \arcsin\left(\frac{\omega}{\omega_{\max}}\right)$$

Anderson, O. L. *J. Phys. Chem. Solids* **24**, 909–917 (1963).

Example Callaway model

Materials values required to reproduce this model (roughly based on Si)

$$V = 4\times10^{-29}\ \mathrm{m}^{-3}$$
$$v_\mathrm{s} = 6084\ \ \mathrm{m/s}$$

$$\omega = v_\mathrm{s} k$$

$$\tau^{-1} = \tau_\mathrm{pp}^{-1} + \tau_\mathrm{pd}^{-1} + \tau_\mathrm{b}^{-1}$$

phonon-phonon scattering

$$\tau_\mathrm{pp}^{-1} = \frac{\omega^2\, T}{A\, v_\mathrm{s}^3} \exp\left(-\frac{B}{T}\right)$$

$$A = 0.135\,\frac{\mathrm{m}^3}{\mathrm{Ks}^2}$$
$$B = 220\ \mathrm{K}$$

point defect scattering

$$\tau_\mathrm{pd}^{-1} = \frac{V_\mathrm{atom}\omega^4}{4\,\pi\, v_\mathrm{s}^3} f\left(1-\frac{\Delta M}{M}\right)^2$$

$$M_1 = 28.09\times10^{-3}\ \mathrm{kg/mol}$$
$$M_2 = 30.97\times10^{-3}\ \ \mathrm{kg/mol}$$
$$\Delta M = M_2 - M_1$$
$$M = fM_1 + (1-f)M_2$$
$$f = 0.005$$
$$V_\mathrm{atom} = \frac{V}{2}$$

boundary scattering

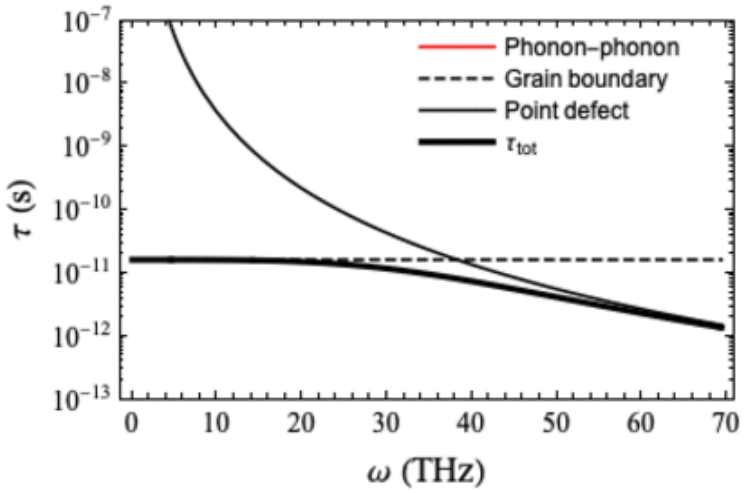
$$\tau_\mathrm{b}^{-1} = \frac{v_\mathrm{s}}{d}$$

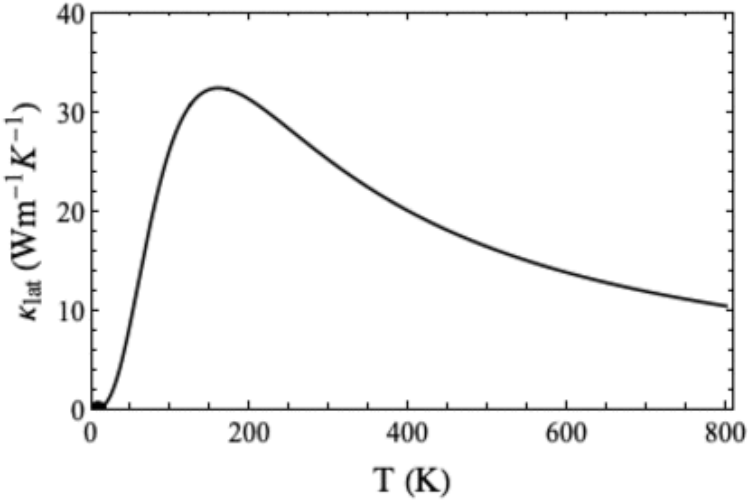
$$d = 0.1\ \mu\mathrm{m}$$

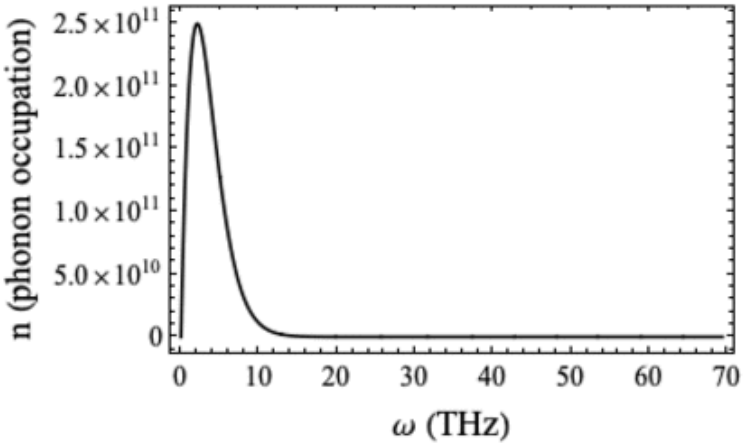
Tan, G. *et al*. *ACS Energy Lett.* **3**, 705–712 (2018).
Hanus, R., Garg, A. & Snyder, G. J. *Commun. Phys.* **1**, 78 (2018).

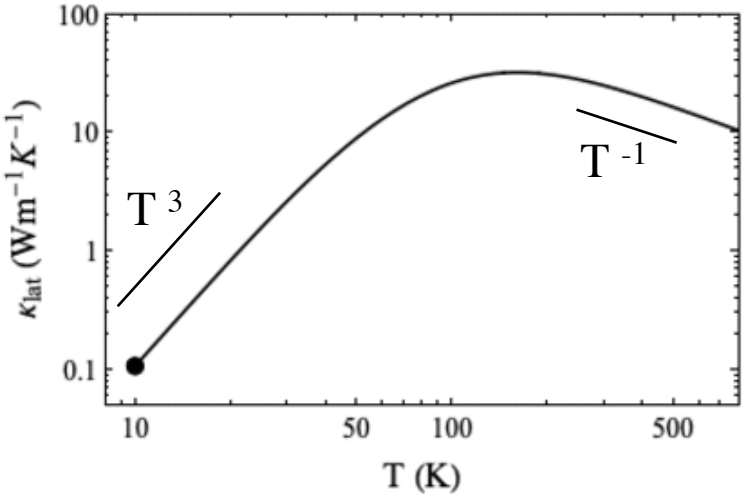
Example Callaway model

1. Low-T gives information about microstructural scattering
2. High-T, $\kappa \propto T^{-1}$ behavior stems from phonon-phonon scattering



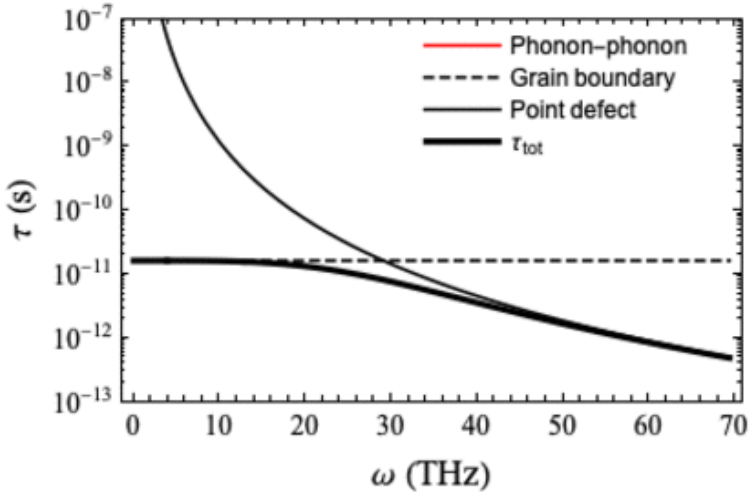


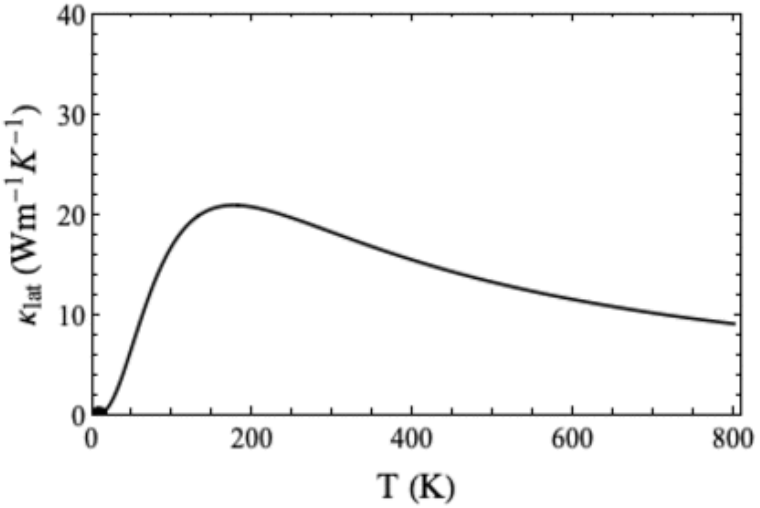


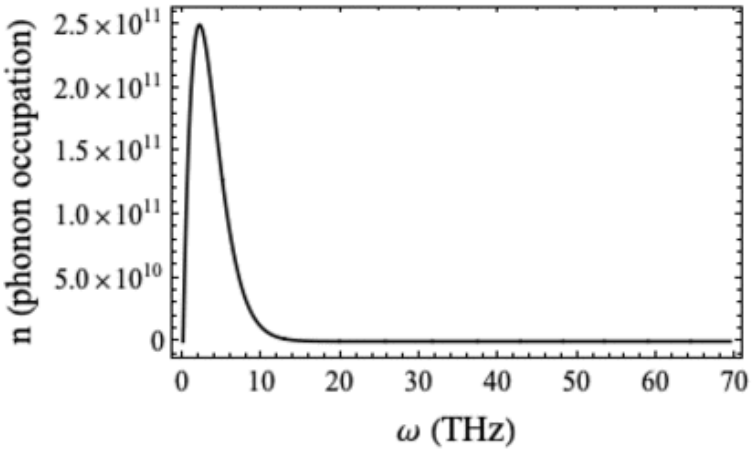


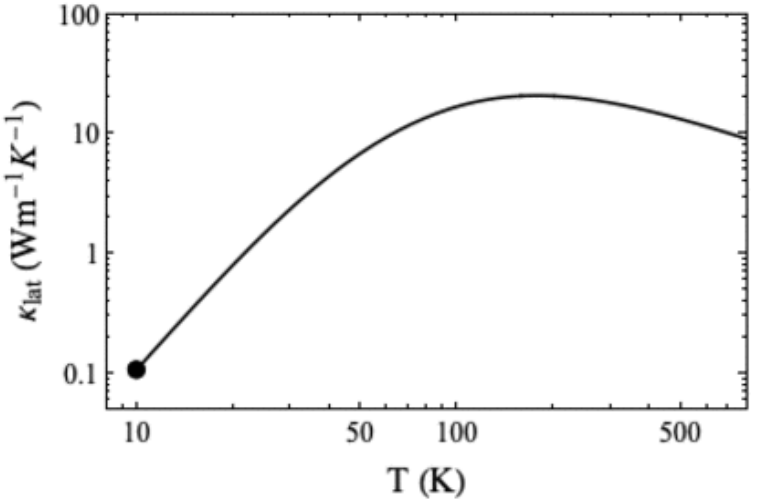
Example Callaway model

Increased point defect scattering
$f = 0.005 \rightarrow 0.015$



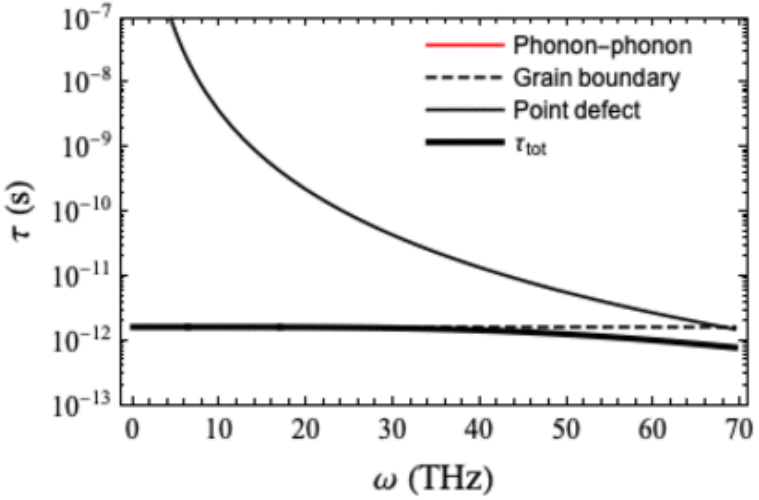


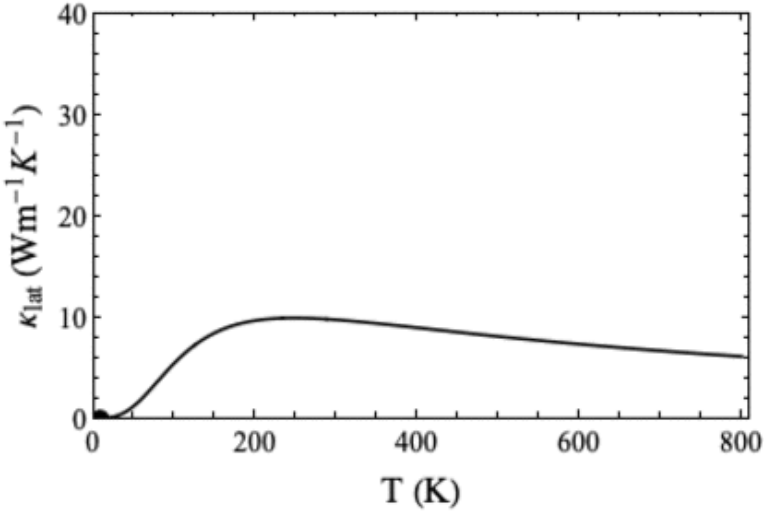


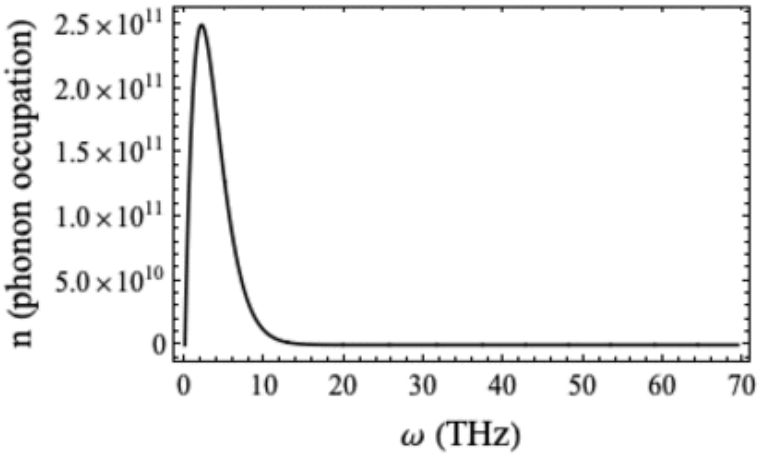


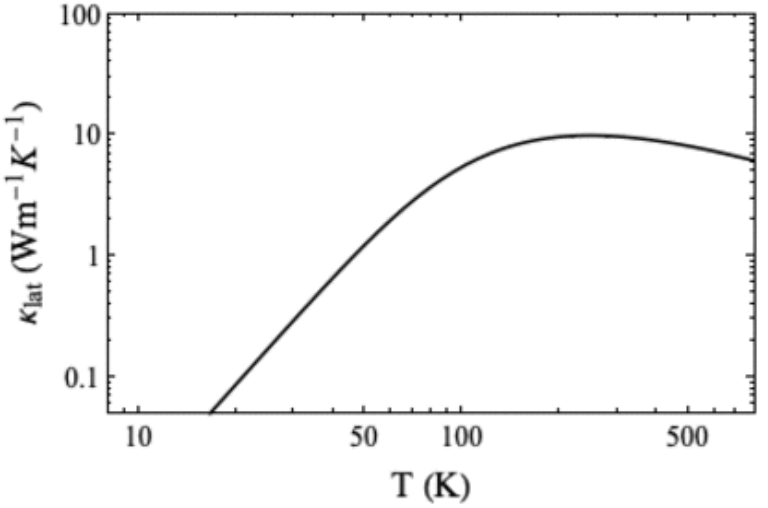
Example Callaway model

Increased microstructural scattering
$d = 100\ \text{nm} \rightarrow 10\ \text{nm}$





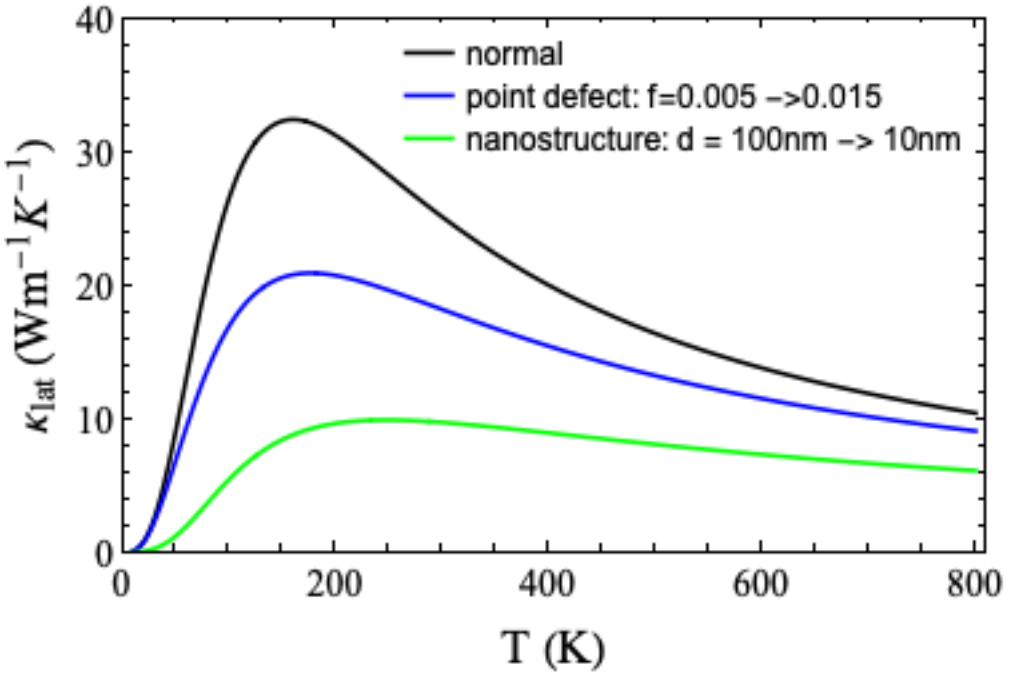


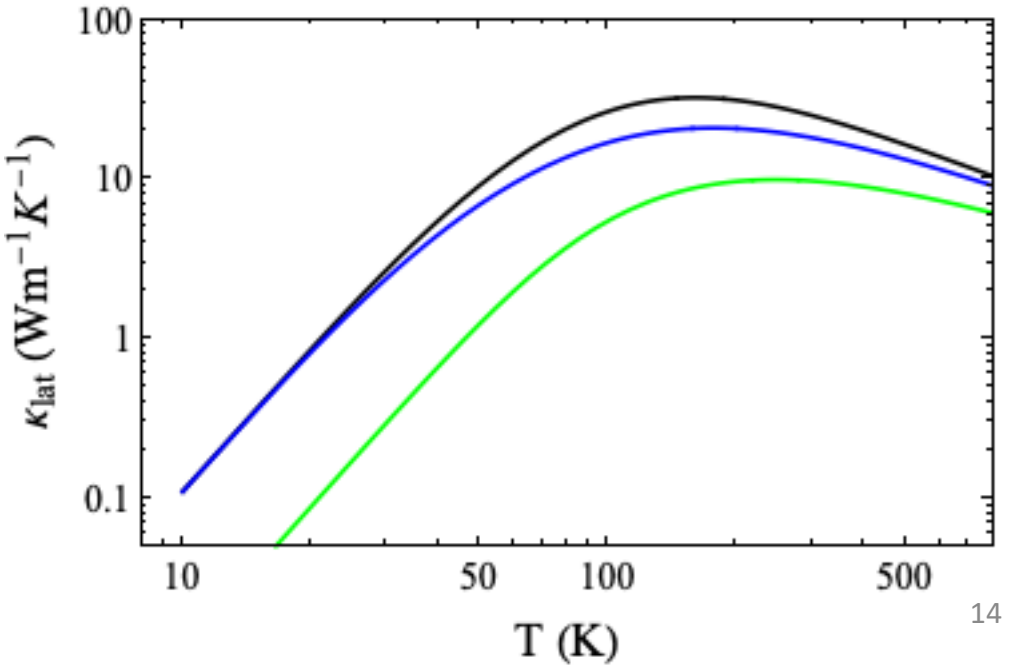


Example Callaway model

Comparing the previous two models

increased point defect scattering vs. increased microstructural scattering





Low-temperature limit

Callaway (spectral) model:

$$\kappa = \frac{1}{3} \int_0^{\omega_{\max}} C(\omega)\, v_{\mathrm{g}}(\omega)^2\, \tau(\omega)\; d\omega$$

assert Debye dispersion:

$\omega = v_{\mathrm{S}}\, k$

$v_{\mathrm{g}} = v_{\mathrm{S}}$

exercise

Debye-Callaway model:

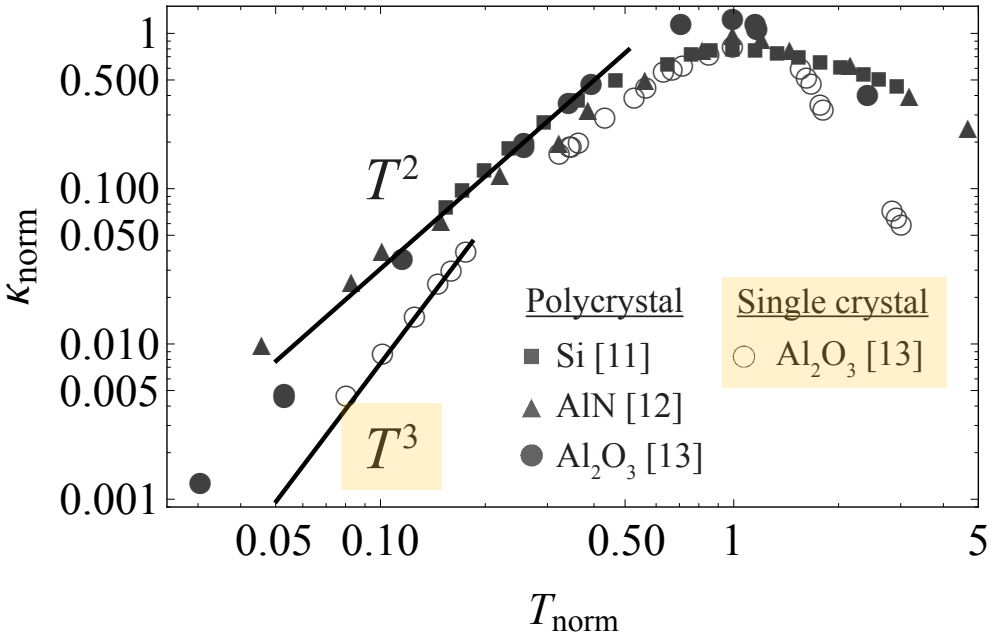
$$\kappa_{\mathrm{L}} = k_{\mathrm{B}} \frac{(k_{\mathrm{B}}\, T)^3}{2\pi^2 v_{\mathrm{S}} \hbar^3} \int_0^{\theta_{\mathrm{D}}/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx \qquad x = \frac{\hbar\omega}{k_{\mathrm{B}} T}$$

on board

Low-temperature limit

$$x = \frac{\hbar\omega}{k_B T}$$

$$\kappa_L = k_B \frac{(k_B T)^3}{2\pi^2 v_S \hbar^3} \int_0^{\theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx$$



Case 1: $\tau = \text{cst}$

$$\kappa_L = k_B \frac{(k_B T)^3}{2\pi^2 v_S \hbar^3} \tau \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

cst @ low-T

$$\tau = \text{cst} \longrightarrow \kappa_L \propto T^3$$

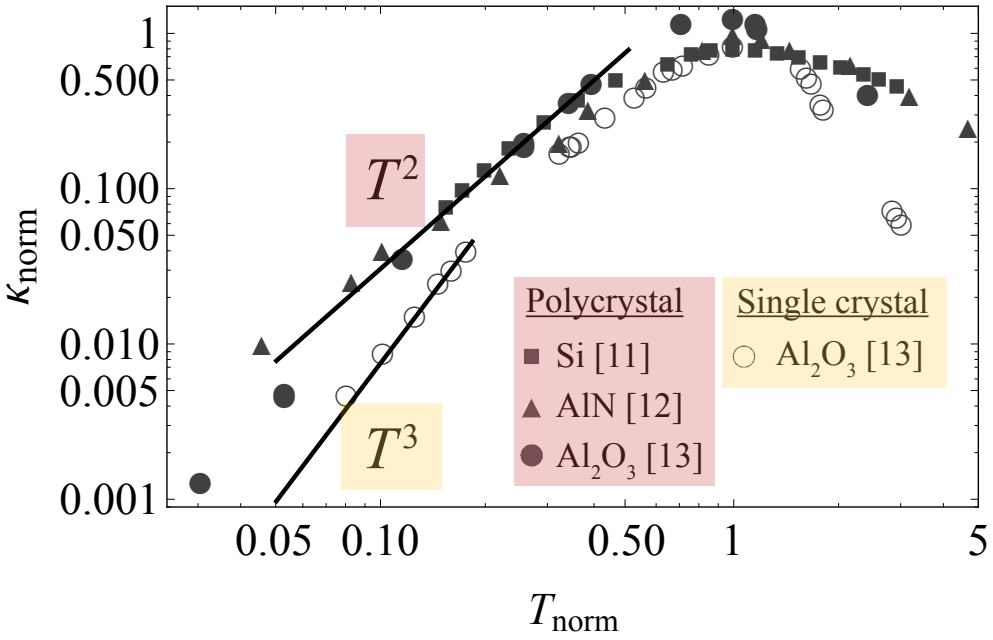
Hanus, R., Garg, A. & Snyder, G. J. Phonon diffraction and dimensionality crossover in phonon-interface scattering. *Commun. Phys.* **1**, 78 (2018).

on board

Low-temperature limit

$$x = \frac{\hbar\omega}{k_B T}$$

$$\kappa_L = k_B \frac{(k_B T)^3}{2\pi^2 v_S \hbar^3} \int_0^{\theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx$$



Case 2: $\tau = \frac{A}{\omega} \longrightarrow \tau(x) = \frac{A\hbar}{x(k_B T)}$

$$\kappa_L = k_B \frac{(k_B T)^3}{2\pi^2 v_S \hbar^3} \int_0^{\theta_D/T} \frac{A\hbar}{x(k_B T)} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$\kappa_L = k_B \underbrace{\frac{A(k_B T)^2}{2\pi^2 v_S \hbar^2} \int_0^{\theta_D/T} \frac{x^3 e^x}{(e^x - 1)^2} dx}_{\text{cst @ low-T}}$$

$\tau = \text{cst} \longrightarrow \kappa_L \propto T^3$

$\tau = \frac{A}{\omega} \longrightarrow \kappa_L \propto T^2$

Hanus, R., Garg, A. & Snyder, G. J. Phonon diffraction and dimensionality crossover in phonon-interface scattering. *Commun. Phys.* **1**, 78 (2018).

High-temperature limit

Assert the following form of phonon-phonon scattering, and Debye dispersion

$$\tau_{\mathrm{pp}} = \left(\frac{6\pi^2}{V}\right)^{1/3} \frac{\bar{M}\, v_{\mathrm{s}}^3}{2k_{\mathrm{B}}\gamma^2\omega^2 T}$$

Refs: Slack, G. A. & Galginaitis, S. *Phys. Rev.* **133**, (1964).
Toberer, E. S., et al. *J. Mater. Chem.* **21**, 15843 (2011).

Make high temperature approximation ($T > \Theta_{\mathrm{D}}$) for $C(\omega)$

$$C(\omega) \approx \frac{3\, k_{\mathrm{B}}\, \omega^2}{2\, \pi^2 v_{\mathrm{s}}^3}$$

$$\kappa = \frac{1}{3}\int_0^{\omega_{\max}} C(\omega)\, v_{\mathrm{g}}(\omega)^2\, \tau(\omega)\; d\omega \quad \xrightarrow{\text{exercise}}$$

$$\kappa = \left(\frac{6\pi^2}{V}\right)^{2/3} \frac{\bar{M}}{4\pi^2\gamma^2}\frac{v_{\mathrm{s}}^3}{T}$$

$$\kappa \propto \frac{v_{\mathrm{s}}^3}{T}$$

Hanus, R. *et al.* Lattice Softening Significantly Reduces Thermal Conductivity and Leads to High Thermoelectric Efficiency. *Adv. Mater.* **1900108**, 1900108 (2019).

Phonon scattering vs. Elastic (lattice) softening

Phonon thermal conductivity

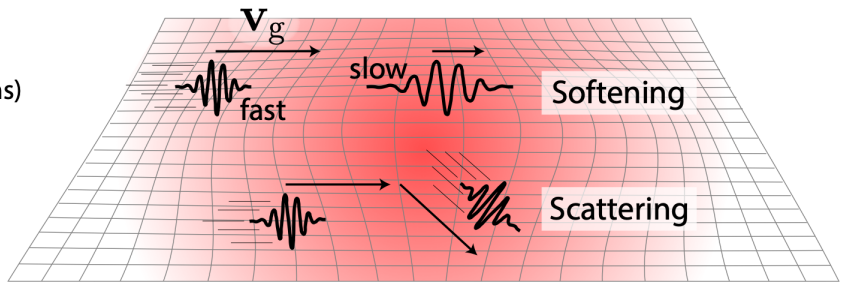
(a)

Heat Capacity (amount of heat)

Group Velocity (speed of phonon)

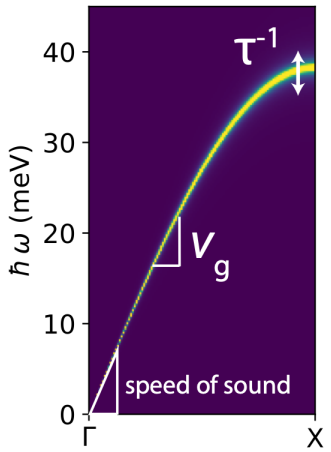
Relaxation Time (time between collisions)

$$\kappa_L = \frac{1}{3}\int_0^{\omega_{max}} C(\omega)\, v_g^2(\omega)\, \tau(\omega)\, d\omega$$



Pristine

(b)



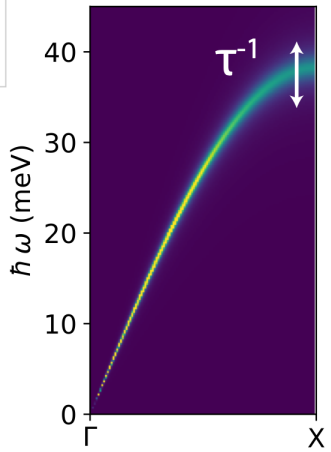
Scattering

(c)

Matthiessen's rule

$$\tau^{-1} = \tau_{pp}^{-1} + \tau_{PD}^{-1} + \tau_{GB}^{-1} + \ldots$$

- Phonons scattered by lattice defects
- Increased scattering rate (decrease in relaxtion time)



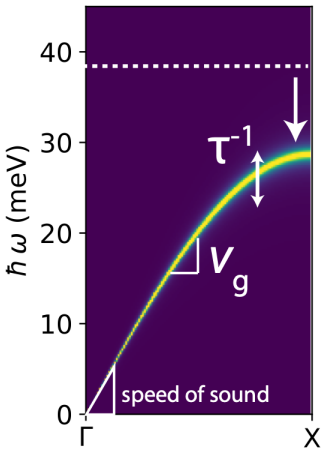
Softening

(d)

Simplifies at high-T

$$\kappa = A\, v_s^3/T$$

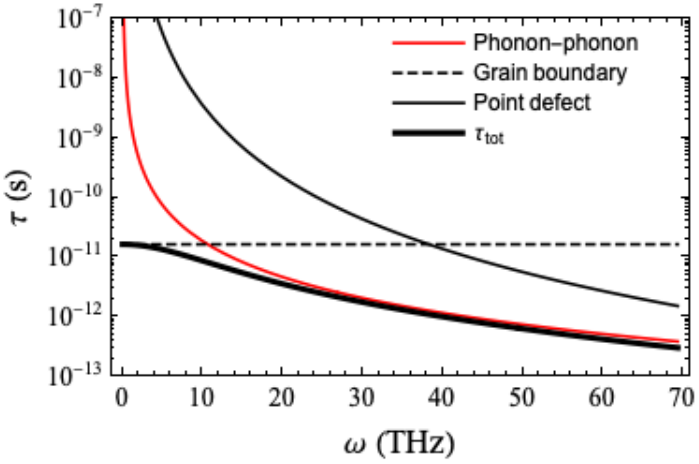
- Decrease in elastic moduli
- Decrease in speed of sound (phonons slow down)
- Increased phonon scattering (increase in scattering phase space)

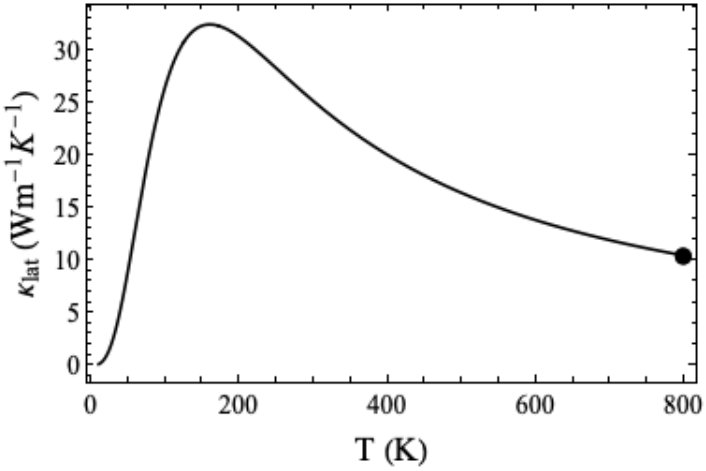


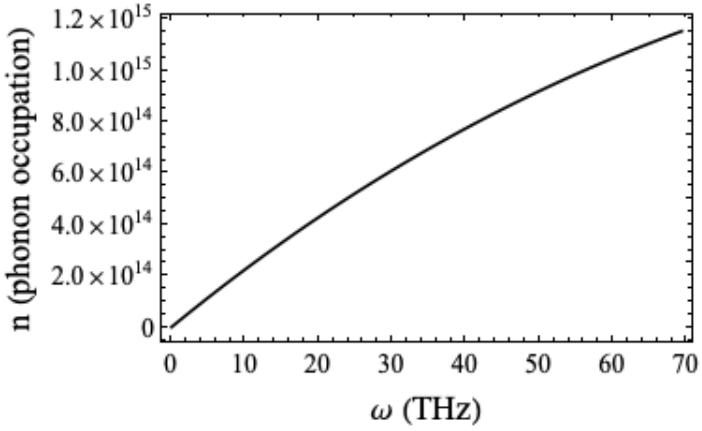
When is softening expected to be important?

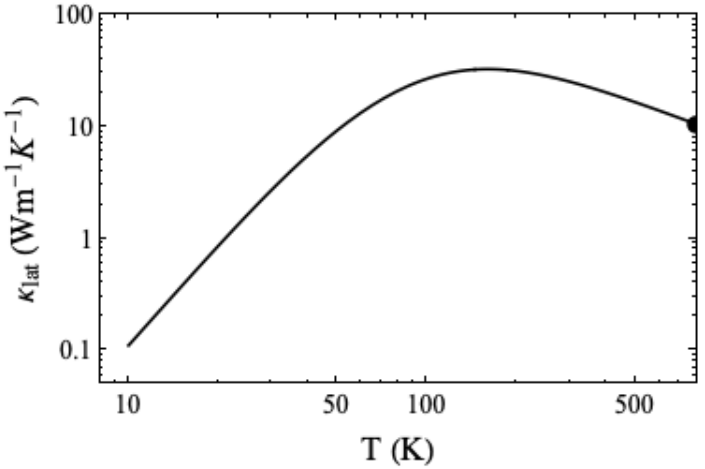
1. Anharmonic materials
2. High temperatures

800 K, phonon-phonon scattering dominates









on board

Accumulation plots

$$\kappa = \frac{1}{3}\sum_{s}\int_{0}^{\omega_{\max}} C(\omega)\, v_{\mathrm{g}}(\omega)\, \Lambda(\omega)\; d\omega$$

If I know $\Lambda(\omega)$, then I can rewrite the integral over ω to one over Λ.
Note, $\Lambda(\omega)$ usually decreases with increasing ω.
So we label $\Lambda(\omega_{\max}) = \Lambda_{\min}$ and $\Lambda(0) = \Lambda_{\max}$.

$$\kappa = \frac{1}{3}\sum_{s}\int_{\Lambda_{\max}}^{\Lambda_{\min}} C\; v_{\mathrm{g}}\, \Lambda \left(\frac{d\Lambda}{d\omega}\right)^{-1} d\Lambda$$

Flip the limits, which spits out a negative sign, and package up the integrand into K_Λ

$$\kappa = \int_{\Lambda_{\min}}^{\Lambda_{\max}} K_\Lambda\; d\Lambda \qquad\qquad K_\Lambda = -\frac{1}{3}\sum_{s} C\; v_{\mathrm{g}}\, \Lambda \left(\frac{d\Lambda}{d\omega}\right)^{-1}$$

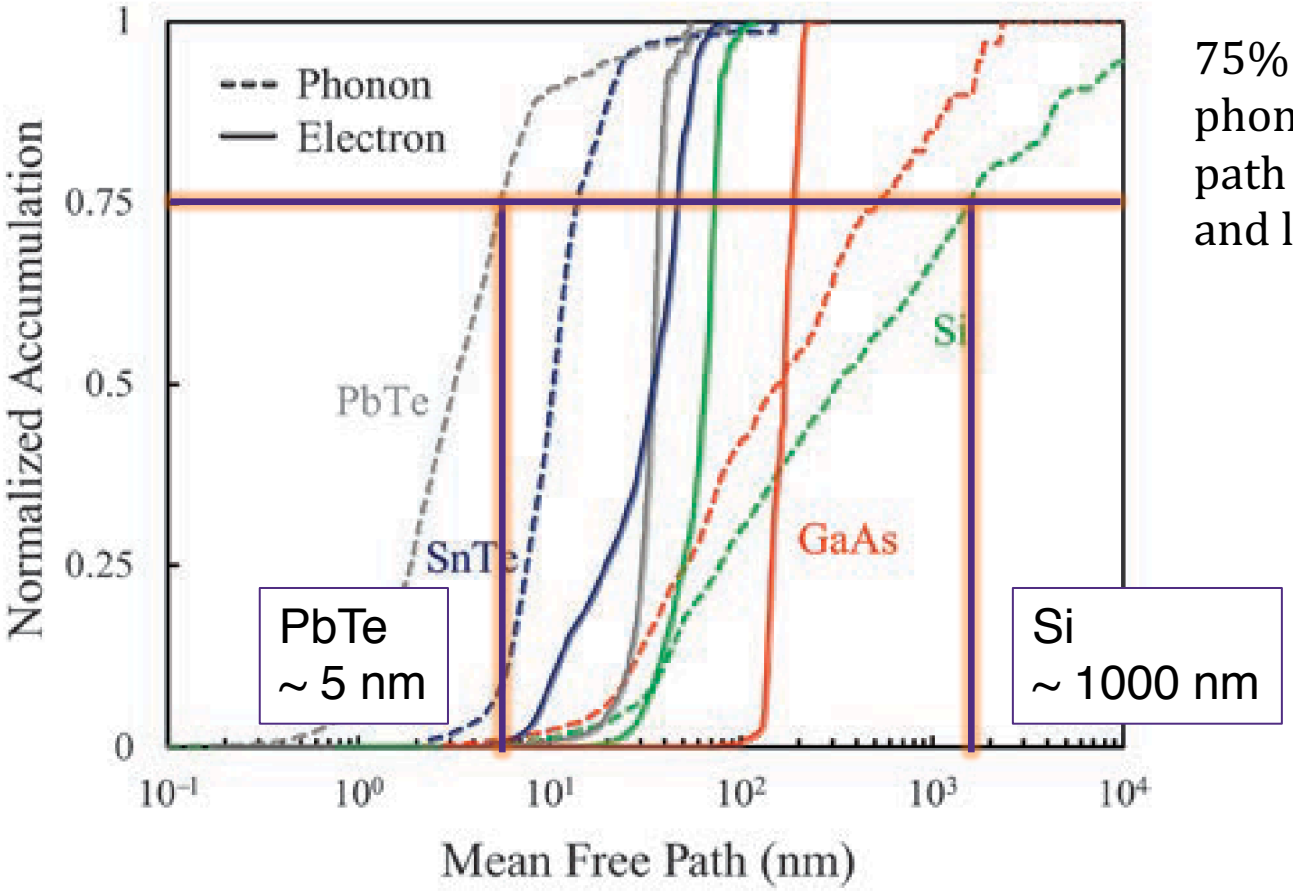
Now define the "Normalized accumulation function"

$$\alpha(\Lambda_\alpha) = \frac{1}{\kappa}\int_{\Lambda_{\min}}^{\Lambda_\alpha} K_\Lambda\, d\Lambda \qquad\qquad \text{plot from } \Lambda_\alpha = \Lambda_{\min} \text{ to } \Lambda_{\max}$$

Yang, F. & Dames, C. Mean free path spectra as a tool to understand thermal conductivity in bulk and nanostructures. *Phys. Rev. B - Condens. Matter Mater. Phys.* **87**, 1–12 (2013).

Accumulation plots

Example



75% of the heat is carried by phonons with a mean free path less than 1000 nm in Si, and less than 5 nm in PbTe

Liu, Z., Mao, J., Liu, T.-H., Chen, G. & Ren, Z. *MRS Bull.* **43,** 181–186 (2018).