

Nanoscale thermal transport

Lecture 4

Riley Hanus

<http://rileyhanus.com/science.html>

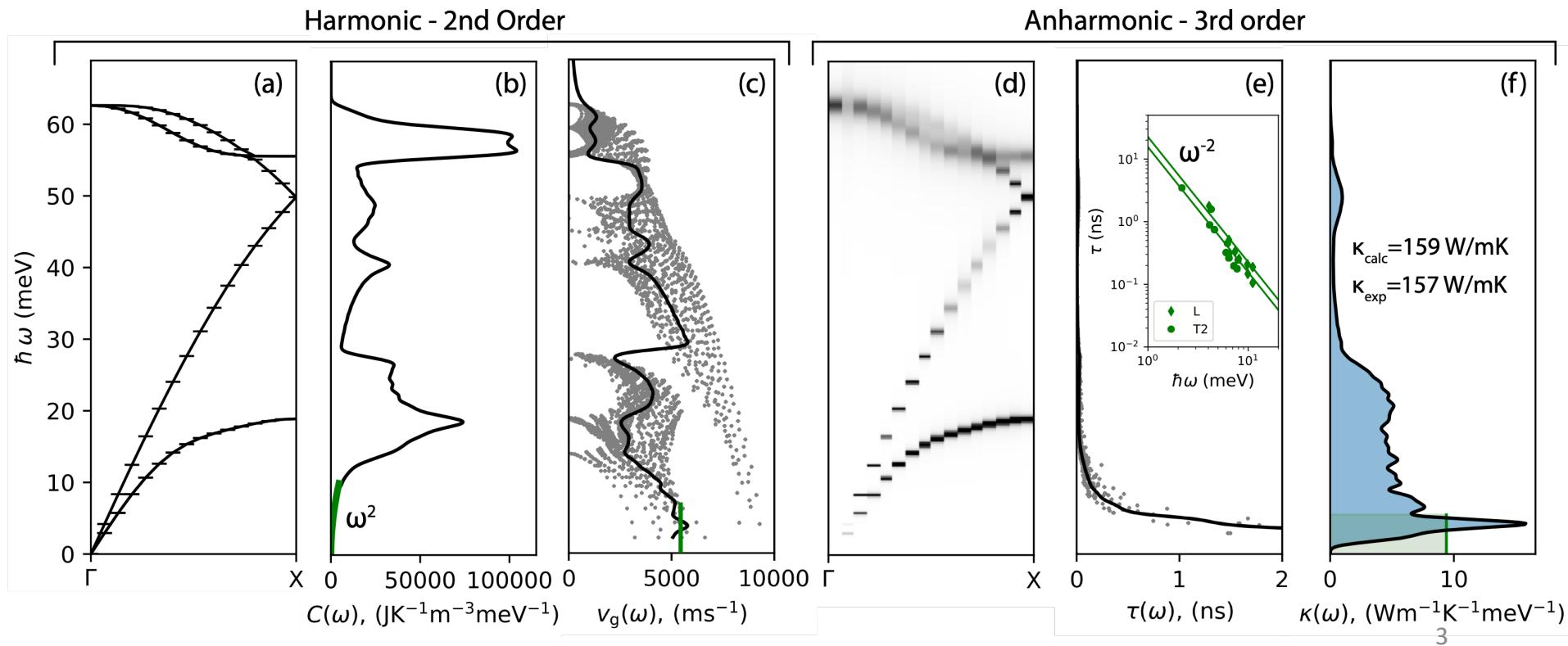
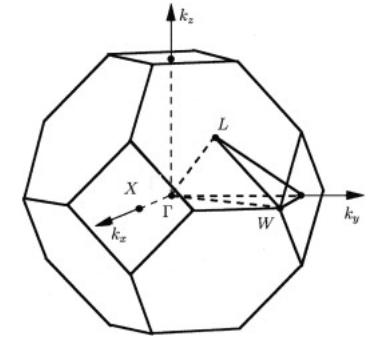
1. A breakdown of phonon thermal conductivity
2. The vibrational (lattice) Hamiltonian
 - a) The Harmonic Hamiltonian
 - b) Types of phonon scattering
3. Scattering potential → Scattering Probability → Relaxation time (lifetime)
 - a) point defects
 - b) line defects
 - c) planar defects
4. Phonon-phonon scattering
5. Low-frequency behavior of thermal conductivity

Phonon scattering and thermal conductivity

$$H = T + U_{\text{2nd}} + U_{\text{3rd}} + \dots$$

T : kinetic energy of all atoms

$U = U_{\text{2nd}} + U_{\text{3rd}} + \dots$: potential energy of all atoms expressed as a Taylor expansion



Hamiltonian

Energy of a solid is described by its *Hamiltonian*, H

$$H = T + U$$

T : kinetic energy of all atoms

U : potential energy of all atoms

$$KE = \frac{1}{2}mv^2$$

$$T = \frac{1}{2} \sum_{\alpha} \sum_i m^{\alpha} (\dot{u}_i^{\alpha})^2$$

PE = ???

Taylor expand it:

reference energy, set this to zero

$$U = U_0 + \sum_{\alpha} \sum_i \frac{\partial U}{\partial u_i^{\alpha}} u_i^{\alpha} + \frac{1}{2!} \sum_{\alpha\beta} \sum_{ij} \frac{\partial^2 U}{\partial u_i^{\alpha} \partial u_j^{\beta}} u_i^{\alpha} u_i^{\beta} + \frac{1}{3!} \sum_{\alpha\beta\gamma} \sum_{ijk} \frac{\partial^3 U}{\partial u_i^{\alpha} \partial u_j^{\beta} \partial u_k^{\gamma}} u_i^{\alpha} u_i^{\beta} u_k^{\gamma} + \dots$$



linear term is zero when all atoms are in their equilibrium positions

Hamiltonian

Energy of a solid is described by its *Hamiltonian*, H

$$H = T + U$$

T : kinetic energy of all atoms

U : potential energy of all atoms

$$U = \frac{1}{2!} \sum_{\alpha\beta} \sum_{ij} \frac{\partial^2 U}{\partial u_i^\alpha \partial u_j^\beta} u_i^\alpha u_i^\beta + \frac{1}{3!} \sum_{\alpha\beta\gamma} \sum_{ijk} \frac{\partial^3 U}{\partial u_i^\alpha \partial u_j^\beta \partial u_k^\gamma} u_i^\alpha u_i^\beta u_k^\gamma + \dots$$

$$U = \frac{1}{2!} \sum_{\alpha\beta} \sum_{ij} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_i^\beta + \frac{1}{3!} \sum_{\alpha\beta\gamma} \sum_{ijk} \Phi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_i^\beta u_k^\gamma + \dots$$

$$H = \frac{1}{2} \sum_{\alpha} \sum_i m^\alpha (\dot{u}_i^\alpha)^2 + \frac{1}{2!} \sum_{\alpha\beta} \sum_{ij} \Phi_{ij}^{\alpha\beta} u_i^\alpha u_i^\beta + \frac{1}{3!} \sum_{\alpha\beta\gamma} \sum_{ijk} \Phi_{ijk}^{\alpha\beta\gamma} u_i^\alpha u_i^\beta u_k^\gamma$$

$$H = \quad T \quad + \quad U_{2\text{nd}} \quad + \quad U_{3\text{rd}}$$

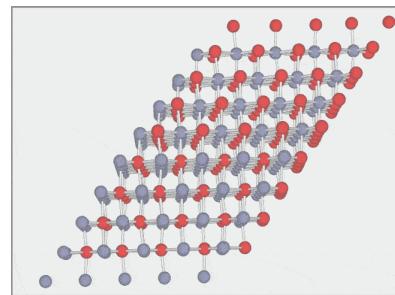
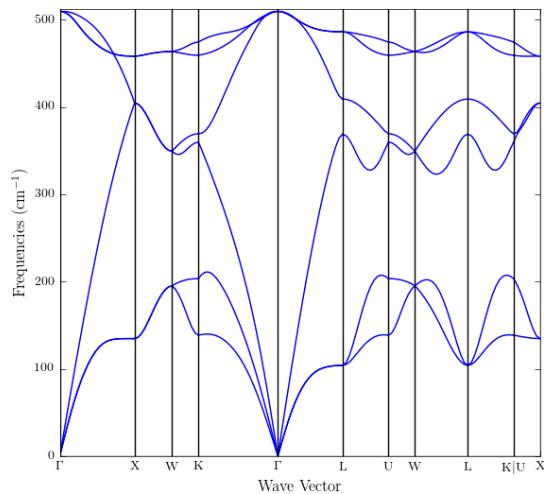
Harmonic Hamiltonian

$$H_{\text{harm}} = \frac{1}{2} \sum_{\alpha} \sum_i m^{\alpha} (\dot{u}_i^{\alpha})^2 + \frac{1}{2!} \sum_{\alpha\beta} \sum_{ij} \Phi_{ij}^{\alpha\beta} u_i^{\alpha} u_j^{\beta}$$

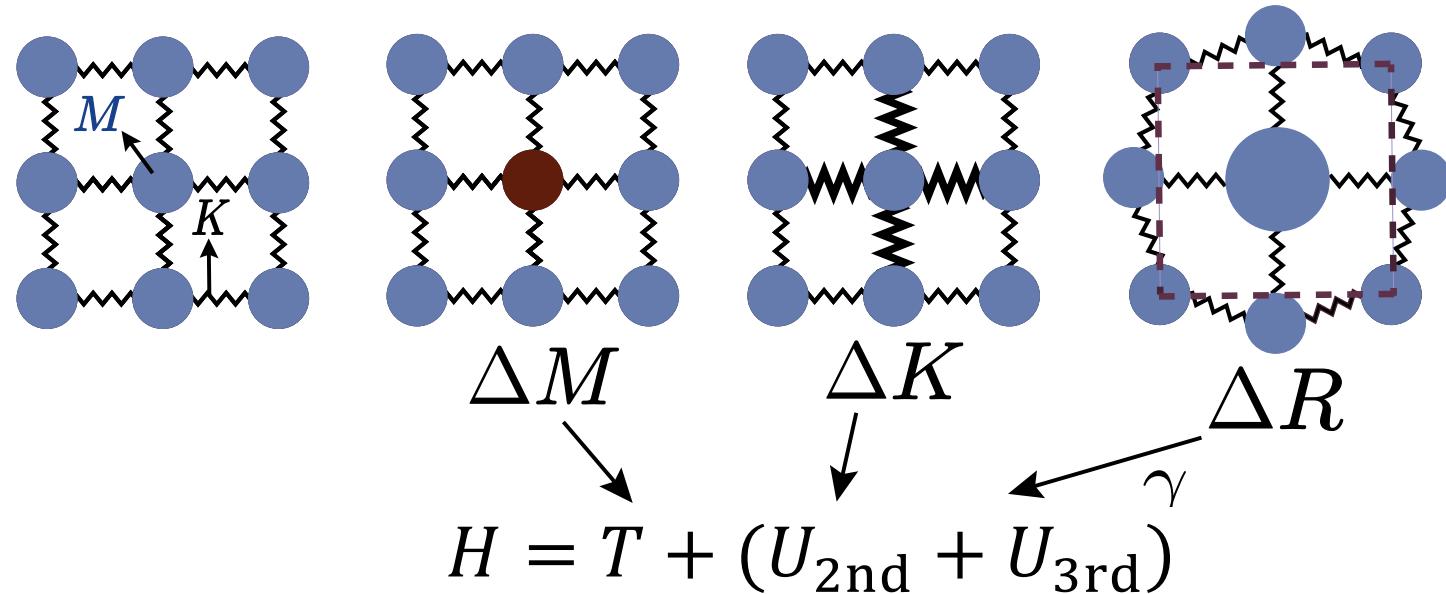
Allows us to write this equation of motion: $-\sum_{j\beta} \Phi_{ij}^{\alpha\beta} u_j^{\beta} = m^{\alpha} \ddot{u}_i^{\alpha}$

$$\omega^2(\mathbf{k}s) \epsilon_i^{\alpha}(\mathbf{k}s) = \sum_{j\beta} \Phi_{ij}^{\alpha\beta}(\mathbf{k}) \epsilon_j^{\beta}(\mathbf{k}s).$$

$3N$ distinct ω^2 and ϵ_i^{α} solutions



Types of perturbations



$$H = \frac{1}{2} \sum_{\alpha} \sum_i m^{\alpha} (\dot{u}_i^{\alpha})^2 + \frac{1}{2!} \sum_{\alpha\beta} \sum_{ij} \Phi_{ij}^{\alpha\beta} u_i^{\alpha} u_j^{\beta} + \frac{1}{3!} \sum_{\alpha\beta\gamma} \sum_{ijk} \Phi_{ijk}^{\alpha\beta\gamma} u_i^{\alpha} u_j^{\beta} u_k^{\gamma}$$

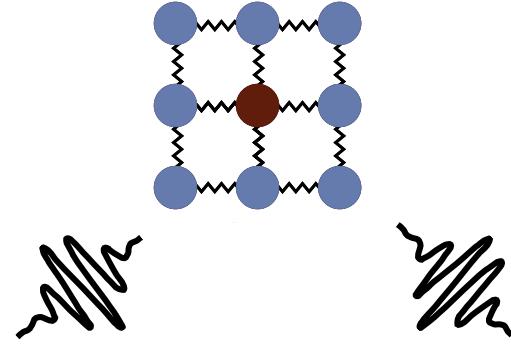
Mass (density) changes

Spring constant changes

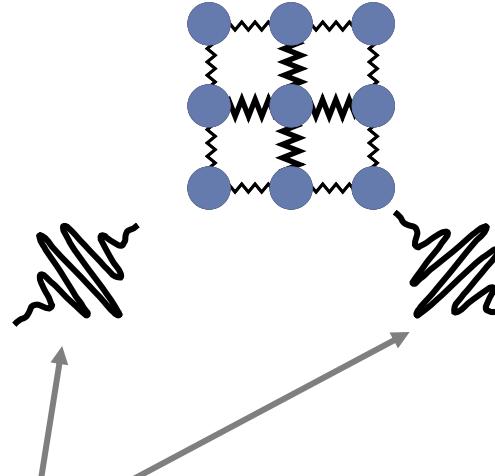
Changes in strain

Types of perturbations

Mass contrast
scattering

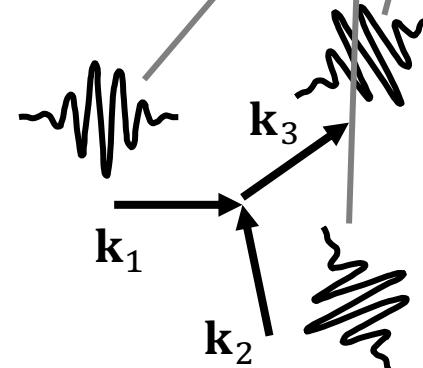


Bond strength
contrast scattering



$$H = \frac{1}{2} \sum_{\alpha} \sum_i m^{\alpha} \dot{u}_i^{\alpha} \dot{u}_i^{\alpha} + \frac{1}{2!} \sum_{\alpha\beta} \sum_{ij} \Phi_{ij}^{\alpha\beta} u_i^{\alpha} u_i^{\beta} + \frac{1}{3!} \sum_{\alpha\beta\gamma} \sum_{ijk} \Phi_{ijk}^{\alpha\beta\gamma} u_i^{\alpha} u_i^{\beta} u_k^{\gamma}$$

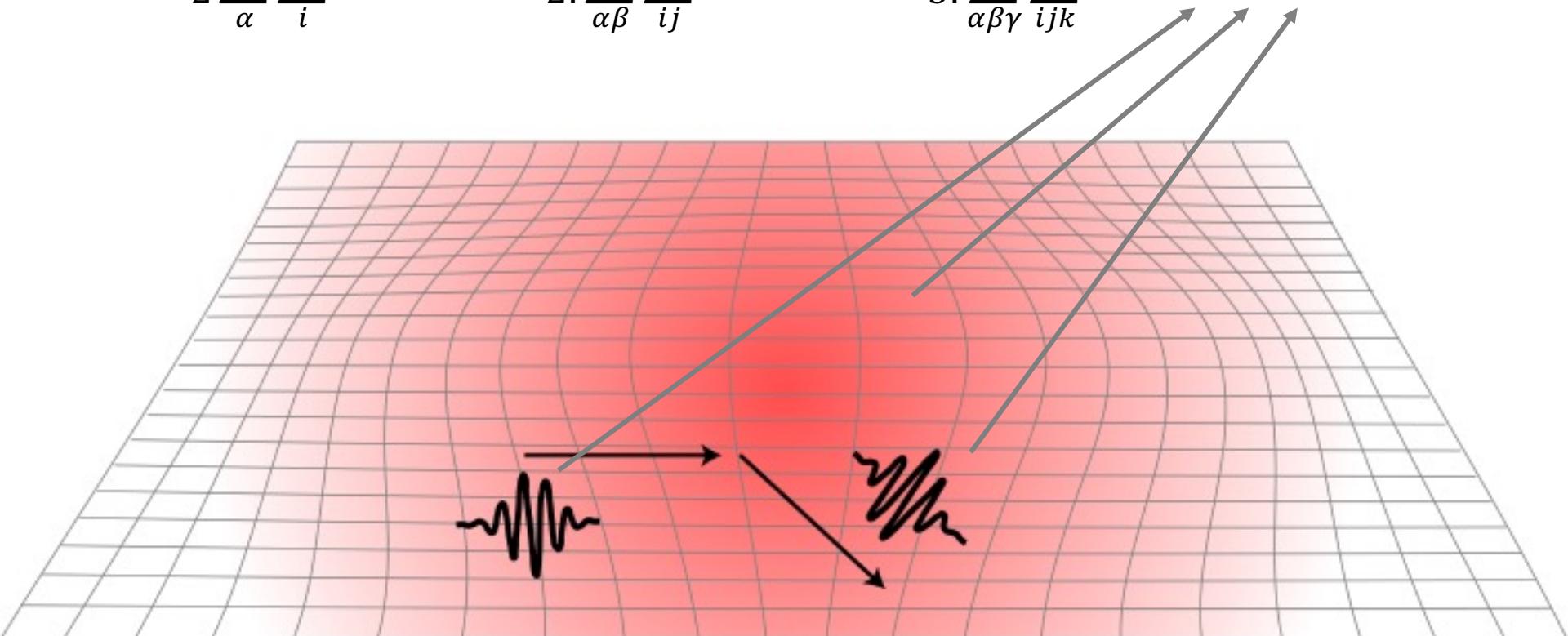
Phonon-phonon
scattering



Types of perturbations

Static strain field scattering

$$H = \frac{1}{2} \sum_{\alpha} \sum_i m^{\alpha} \dot{u}_i^{\alpha} \dot{u}_i^{\alpha} + \frac{1}{2!} \sum_{\alpha\beta} \sum_{ij} \Phi_{ij}^{\alpha\beta} u_i^{\alpha} u_i^{\beta} + \frac{1}{3!} \sum_{\alpha\beta\gamma} \sum_{ijk} \Phi_{ijk}^{\alpha\beta\gamma} u_i^{\alpha} u_i^{\beta} u_k^{\gamma}$$



Scattering potential → relaxation time

$$H(\mathbf{r}) = H_{\text{harm}} + V(\mathbf{r})$$

You can find reference's in R. Hanus' thesis Appendix G or Ashcroft and Mermin pg. 316

Probability of scattering from state \mathbf{k} into \mathbf{k}' given by Fermi's Golden Rule:

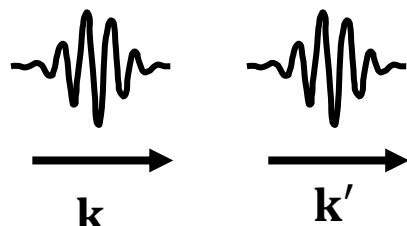
$$W_{\mathbf{k},\mathbf{k}'} = \frac{2\pi}{\hbar} |\langle \mathbf{k}' | V(\mathbf{r}) | \mathbf{k} \rangle|^2 \delta(\Delta E) \quad \text{units: } \left[\frac{1}{s} \right]$$

Inverse lifetime ($\Gamma(\mathbf{k})$) is the sum over all possible \mathbf{k}' states.

$$\text{inverse lifetime: } \Gamma(\mathbf{k}) = \sum_{\mathbf{k}'} W_{\mathbf{k},\mathbf{k}'}$$

$$\text{inverse relaxation time or scattering rate: } \Gamma(\mathbf{k}) = \sum_{\mathbf{k}'} (W_{\mathbf{k},\mathbf{k}'} - W_{\mathbf{k}',\mathbf{k}})$$

What if $\mathbf{k} = \mathbf{k}'$? Does this scattering event impede heat conduction?



isotropic approximation, this becomes

$$\tau(\mathbf{k})^{-1} = \Gamma(\mathbf{k}) = \sum_{\mathbf{k}'} W_{\mathbf{k},\mathbf{k}'} (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'})$$

See detail on Relaxation Time Approximation in supplemental slides

Contributions to the relaxation time

Elastic defect scattering can be expressed as the product of the three factors.

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

↓
spatial density of defects

↓
Phase space contribution:
Density of states into which
the phonon can scatter.

↓

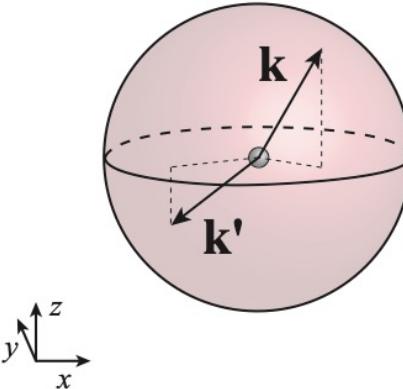
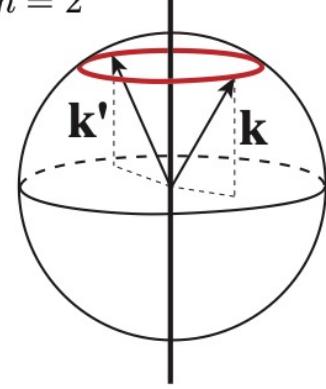
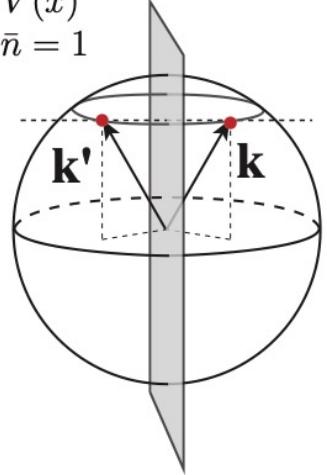
Matrix element contribution:
Magnitude squared of the Fourier
transform of the scattering potential

Codimension: $\bar{n} = 3 - d_{\text{defect}}$

Example:
line defect is 1D.
Need 2 dimensions to define it.
Mathematically this looks like:

$$\bar{n} = 3 - 1 = 2$$

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

a) $V(x, y, z)$ $\bar{n} = 3$ 	b) $V(x, y)$ $\bar{n} = 2$ 	c) $V(x)$ $\bar{n} = 1$ 
Conserved quantities: E	E, k_z	E, k_z, k_y
Phase space: $g_{3\text{d}} = \frac{\omega^2}{2\pi^2 v_g v_p^2}$	$g_{2\text{d}} = \frac{\omega}{2\pi v_g v_p}$	$g_{1\text{d}} = \frac{1}{\pi v_g}$

Mass difference scattering potential

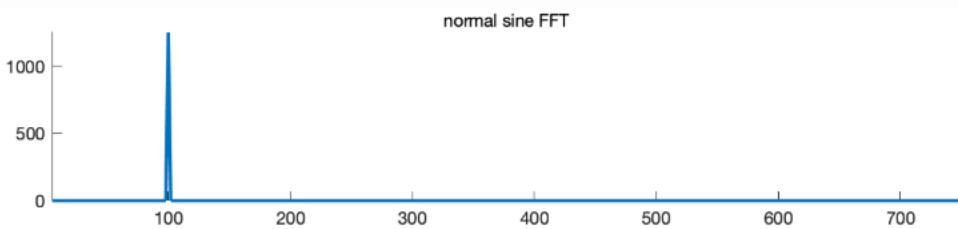
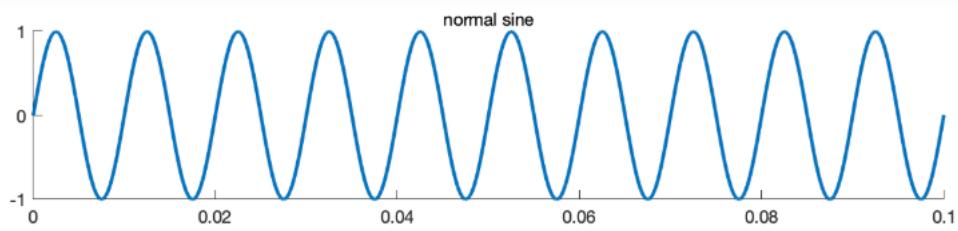
Matrix element: $\overline{ M_{3\text{d}} ^2} \propto \left(\frac{\Delta M}{M}\right)^2 \omega^2$	$\overline{ M_{2\text{d}} ^2} \propto \left(\frac{\Delta M}{M}\right)^2 \omega^2$	$\overline{ M_{1\text{d}} ^2} \propto \left(\frac{\Delta M}{M}\right)^2 \omega^2$
Scattering rate: $\tau^{-1} \propto \omega^4$	$\tau^{-1} \propto \omega^3$	$\tau^{-1} \propto \omega^2$

Scattering theory

Required Math

Integral definition of the Dirac δ -function

$$2\pi \delta(k_x) = \int e^{-ik_x x} dx$$



Some δ -function identities:

$$\delta(f(x)) = \sum_i \frac{\delta(x - x_i)}{|f'(x_i)|}$$

where $f(x) = 0$ at $x = x_i$

$$\delta(Ax) = \frac{1}{|A|} \delta(x)$$

Example:

$$\begin{aligned}\delta(\hbar\omega(k) - \hbar\omega(k')) &= \\ \frac{1}{\hbar} \delta(\omega(k) - \omega(k')) &= \\ \frac{1}{\hbar |v_g|} \delta(k - k')\end{aligned}$$

Scattering theory

Required Math

The square of a Dirac δ -function

$$\delta(k_x)^2 = \delta(k_x) \frac{1}{2\pi} \int e^{-ik_x x} dx$$

$$\delta(k_x)^2 = \delta(k_x) \frac{L_x}{2\pi}$$

Note: In the following examples we are building intuition about phase space and matrix element contributions and therefore we apply a ‘spectral’ treatment of scattering theory, making the *isotropic single mode approximation*.

Aside: Mode specific treatments can be done by expressing the factors of u_i^α in H in terms of creation and annihilation operators (Eq. L.14 in Ashcroft and Mermin) and computing the matrix element by following the creation and annihilation operator rules:

creation operator: $a_{\mathbf{k}s}|n_{\mathbf{k}s}\rangle = \sqrt{n_{\mathbf{k}s} + 1}|n_{\mathbf{k}s}\rangle$
annihilation operator: $a_{\mathbf{k}s}^\dagger|n_{\mathbf{k}s}\rangle = \sqrt{n_{\mathbf{k}s}}|n_{\mathbf{k}s} - 1\rangle$

Point defect – Mass contrast

$$V(\mathbf{r}, \omega) = \frac{1}{2} \left(\frac{\Delta M}{M} \right) \hbar \omega V_0 \delta(\mathbf{r})$$

$$W_{\mathbf{k}, \mathbf{k}'} = \frac{2\pi}{\hbar} |\langle \mathbf{k}' | V(\mathbf{r}) | \mathbf{k} \rangle|^2 \delta(\Delta E)$$

$$\langle \mathbf{k}' | V(\mathbf{r}, \omega) | \mathbf{k} \rangle = \iiint d^3 \mathbf{r} \frac{e^{-i(\mathbf{k}' \cdot \mathbf{r})}}{(L_x L_y L_z)^{1/2}} V(\mathbf{r}) \frac{e^{i(\mathbf{k} \cdot \mathbf{r})}}{(L_x L_y L_z)^{1/2}} = \frac{1}{L_x L_y L_z} \iiint d^3 \mathbf{r} V(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}}$$

$L_x L_y L_z$: volume of solid containing one defect who's scattering potential is given by $V(\mathbf{r}, \omega)$.

V_0 : volume of defect

Normalized plane wave:

$$|\mathbf{k}\rangle = \frac{e^{i(\mathbf{k} \cdot \mathbf{r})}}{(L_x L_y L_z)^{1/2}}$$

Scattering vector: $\mathbf{q} = \mathbf{k}' - \mathbf{k}$

Point defect – Mass contrast

$$\langle \mathbf{k}' | V(\mathbf{r}, \omega) | \mathbf{k} \rangle = \frac{1}{L_x L_y L_z} \left(\frac{1}{2} \left(\frac{\Delta M}{M} \right) \hbar \omega V_0 \right) \iiint d^3 \mathbf{r} \delta(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}}$$

$$= \frac{1}{L_x L_y L_z} \left(\frac{1}{2} \left(\frac{\Delta M}{M} \right) \hbar \omega V_0 \right) (1)$$

$$|\langle \mathbf{k}' | V(\mathbf{r}, \omega) | \mathbf{k} \rangle|^2 = \frac{1}{(L_x L_y L_z)^2} \left(\frac{1}{2} \left(\frac{\Delta M}{M} \right) \hbar \omega V_0 \right)^2$$

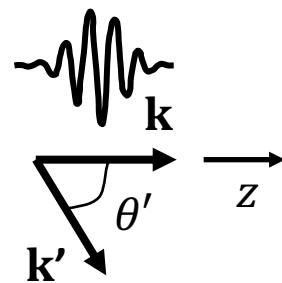
$$\delta(\Delta E) = \delta(\hbar \omega - \hbar \omega') = \frac{1}{\hbar} \delta(\omega - \omega') = \frac{1}{\hbar |v_g|} \delta(k - k')$$

$$W_{\mathbf{k}, \mathbf{k}'} = \frac{2\pi}{\hbar} \frac{1}{(L_x L_y L_z)^2} \left(\frac{1}{2} \left(\frac{\Delta M}{M} \right) \hbar \omega V_0 \right)^2 \frac{1}{\hbar |v_g|} \delta(k - k')$$

$$= \frac{1}{(L_x L_y L_z)^2} \frac{\pi}{2} \left(\frac{\Delta M}{M} \right)^2 V_0^2 \omega^2 \frac{1}{|v_g|} \delta(k - k')$$

Point defect – Mass contrast

$$(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) = (1 - \cos \theta')$$



we set \mathbf{k} to be in the z -direction so θ (angle between \mathbf{k} and \mathbf{k}') equals θ' the polar angle of \mathbf{k}' in spherical coordinates.

$$\tau^{-1} = \Gamma = \sum_{\mathbf{k}'} W_{\mathbf{k},\mathbf{k}'} (1 - \cos \theta') = \frac{L_x L_y L_z}{(2\pi)^3} \iiint W_{\mathbf{k},\mathbf{k}'} (1 - \cos \theta') d^3 \mathbf{k}'$$

$$\Gamma = \frac{L_x L_y L_z}{(L_x L_y L_z)^2} \frac{1}{16\pi^2} \left(\frac{\Delta M}{M}\right)^2 V_0^2 \iiint \omega^2 \frac{1}{|v_g|} \delta(k - k') (1 - \cos \theta') d^3 \mathbf{k}'$$

$$\Gamma = \frac{n_{3d}}{16\pi^2} \left(\frac{\Delta M}{M}\right)^2 V_0^2 \iiint_{0 0 0}^{\infty 2\pi \pi} \omega^2 \frac{1}{|v_g|} \delta(k - k') (1 - \cos \theta') k'^2 \sin \theta' d\theta' d\phi' dk'$$

$$\omega = v_p k$$

$$\iint_{0 0}^{2\pi \pi} \sin \theta' (1 - \cos \theta') d\theta' d\phi' = 4\pi$$

$$\Gamma = \frac{n_{3d}}{4\pi} \left(\frac{\Delta M}{M}\right)^2 V_0^2 \int_0^\infty k^2 v_p^2 \frac{1}{|v_g|} \delta(k - k') k'^2 dk' = \frac{n_{3d}}{4\pi} \left(\frac{\Delta M}{M}\right)^2 V_0^2 \frac{k^4 v_p^2}{|v_g|}$$

Point defect – Mass contrast

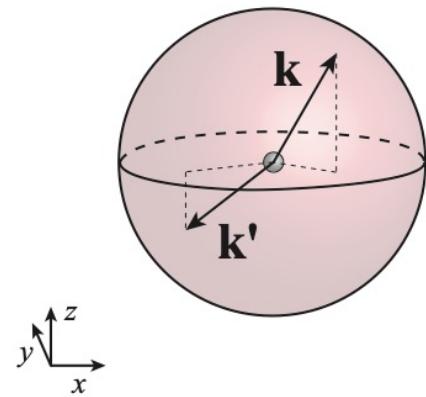
$$\Gamma = n_{3d} \times \left(\frac{\omega^2}{2\pi^2 v_p^2 |v_g|} \right) \times \left(\frac{\pi}{2} \left(\frac{\Delta M}{M} \right)^2 V_0^2 \omega^2 \right)$$

$$\Gamma = n_{3d} \times g_{3d} \times \overline{|M_{3d}|^2}$$

$$\tau(\omega)^{-1} = \Gamma = \frac{n_{3d} V_0^2}{4\pi |v_g| v_p^2} \left(\frac{\Delta M}{M} \right)^2 \omega^4$$

A localized scattering potential ($\delta(\mathbf{r})$ in V) results in $\overline{|M_{3d}|^2} \propto \omega^2$. The fact that it's a point defect (0d, $\bar{n} = 3$), means the phonon can scatter into the 3D density of states, $g_{3d} \propto \omega^2$. **Together we get the Raleigh scattering, ω^4 power law.**

a) $V(x, y, z)$
 $\bar{n} = 3$



Conserved
quantities: E

Phase
space: $g_{3d} = \frac{\omega^2}{2\pi^2 v_g v_p^2}$

Matrix
element: $\overline{|M_{3d}|^2} \propto \left(\frac{\Delta M}{M} \right)^2 \omega^2$

Scattering
rate: $\tau^{-1} \propto \omega^4$

Line defect – Mass contrast

details in
supplemental slides

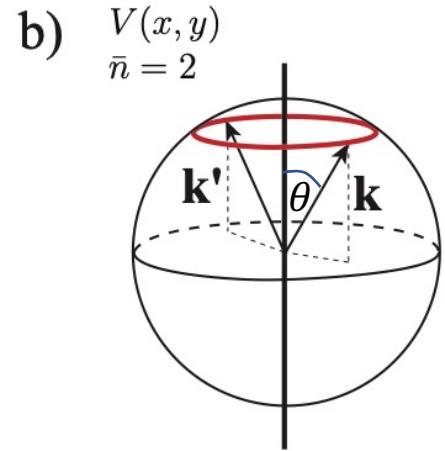
$$V(x, y, \omega) = \frac{1}{2} \left(\frac{\Delta M}{M} \right) \hbar \omega A_0 \delta(x) \delta(y)$$

$$\tau(\mathbf{k})^{-1} = n_{2d} \times \frac{\omega}{2\pi v_p |v_g|} \times \frac{\pi}{2} \left(\frac{\Delta M}{M} \right)^2 A_0^2 \omega^2 \sin(\theta)^2$$

$$\tau(\mathbf{k})^{-1} = n_{2d} \times g_{2d} \times \overline{|M_{2d}|^2}$$

$$\tau^{-1} = \Gamma = \frac{n_{2d} A_0^2}{4 v_p |v_g|} \left(\frac{\Delta M}{M} \right)^2 \omega^3 \sin(\theta)^2$$

A localized scattering potential ($\delta(x)\delta(y)$ in V) results in $\overline{|M_{3d}|^2} \propto \omega^2$. The fact that it's a line defect (1d, $\bar{n} = 2$), means the phonon can scattering into the 2D density of states, $g_{2d} \propto \omega$. **Together we get the ω^3 power law.**



E, k_z

$$g_{2d} = \frac{\omega}{2\pi v_g v_p}$$

$$\overline{|M_{2d}|^2} \propto \left(\frac{\Delta M}{M} \right)^2 \omega^2$$

$$\tau^{-1} \propto \omega^3$$

Elastic defect scattering cheat sheet

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

0D (point defect, $\bar{n} = 3$)

$$g_{3\text{d}} = \frac{\omega^2}{2\pi^2 v_g v_p^2}$$

$$M_{3\text{d}}(\mathbf{q}) = \iiint V(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}$$

1D (line defect, $\bar{n} = 2$)

$$g_{2\text{d}} = \frac{\omega}{2\pi v_g v_p}$$

$$M_{2\text{d}}(q_x, q_y) = \iint V(x, y) e^{-i(q_x x + q_y y)} dx dy$$

2D (planar defect, $\bar{n} = 1$)

$$g_{1\text{d}} = \frac{1}{\pi v_g}$$

$$M_{1\text{d}}(q_x) = \int V(x) e^{-i(q_x x)} dx$$

$$\overline{|M_{3\text{d}}|^2} = \frac{1}{2\hbar^2} \int |M_{3d}|^2 (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) d\Omega'$$

$$d\Omega' = \sin \theta' d\theta' d\phi'$$

$$\mathbf{q} = \mathbf{k}' - \mathbf{k}$$

$$\mathbf{k} = k(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$$

$$\mathbf{k}' = k(\sin \theta' \cos \phi', \sin \theta' \sin \phi', \cos \theta')$$

$$\overline{|M_{2\text{d}}|^2} = \frac{1}{\hbar^2} \int_0^{2\pi} |M_{2d}|^2 (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) d\phi'$$

$$q_x = k \sin \theta (\cos \phi' - \cos \phi)$$

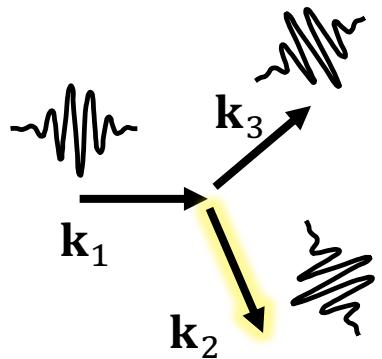
$$q_y = k \sin \theta (\sin \phi' - \sin \phi)$$

$$(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) = 2 \sin(\theta)^2 \sin\left(\frac{\phi' - \phi}{2}\right)^2$$

$$(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) = \frac{2k_x^2}{k^2}$$

Phonon-phonon scattering

Type I:
one phonon
decomposes into
two

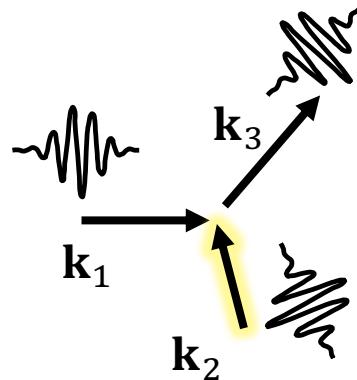


b: any reciprocal lattice vector

$$\mathbf{k}_1 = \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{b}$$

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

Type II:
two phonons
combine into one



$$\mathbf{k}_1 + \mathbf{k}_{2(3)} = \mathbf{k}_{3(2)} + \mathbf{b}$$

$$\hbar\omega_1 + \hbar\omega_{2(3)} = \hbar\omega_{3(2)}$$

Normal scattering process: $\mathbf{b} = 0$

Umklapp ("flip over") scattering process: $\mathbf{b} \neq 0$

Maznev, A. A. & Wright, O. B. Demystifying umklapp vs normal scattering in lattice thermal conductivity. *Am. J. Phys.* **82**, 1062–1066 (2014).

- Perturbation is $U_{3\text{rd}}$
- $|i\rangle$ and $|f\rangle$ are initial and final states (combinations of \mathbf{k}_1 \mathbf{k}_2 and \mathbf{k}_3)

$$W_{i,f} = \frac{2\pi}{\hbar} |\langle f | U_{3\text{rd}} | i \rangle|^2 \delta(\Delta E)$$

Phonon-phonon scattering

Phonon-phonon scattering has **phase space** and **matrix element contributions** as well.

$$\Gamma_{\text{pp}}(\mathbf{k}s) \approx \frac{18\pi}{\hbar^2} N(\mathbf{k}s) P(\mathbf{k}s)$$

↓
weighted joint density of states

↓
average anharmonic interaction
phonon $\mathbf{k}s$ has with all other phonons

$N(\mathbf{k}s)$ contains the number of other phonons in the material

$N(\mathbf{k}s) \propto T$ at high temperature

Stems from high-T behavior of Bose-Einstein distribution

$$n_{\text{BE}} = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \approx \frac{1}{1 + \frac{\hbar\omega}{k_B T} - 1} = \frac{k_B T}{\hbar\omega}$$

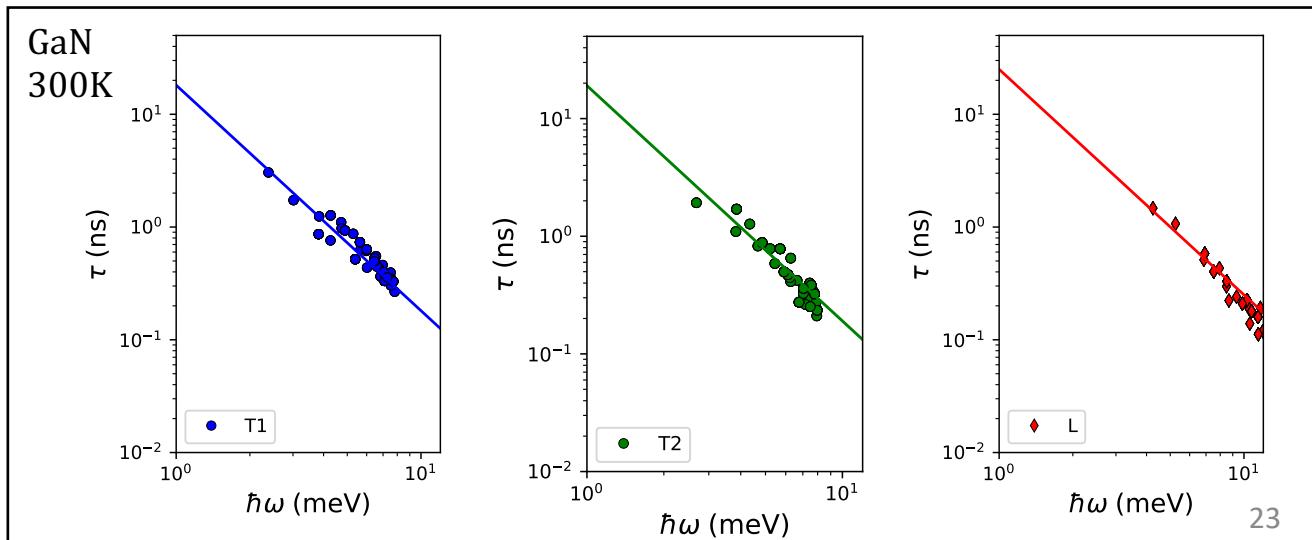
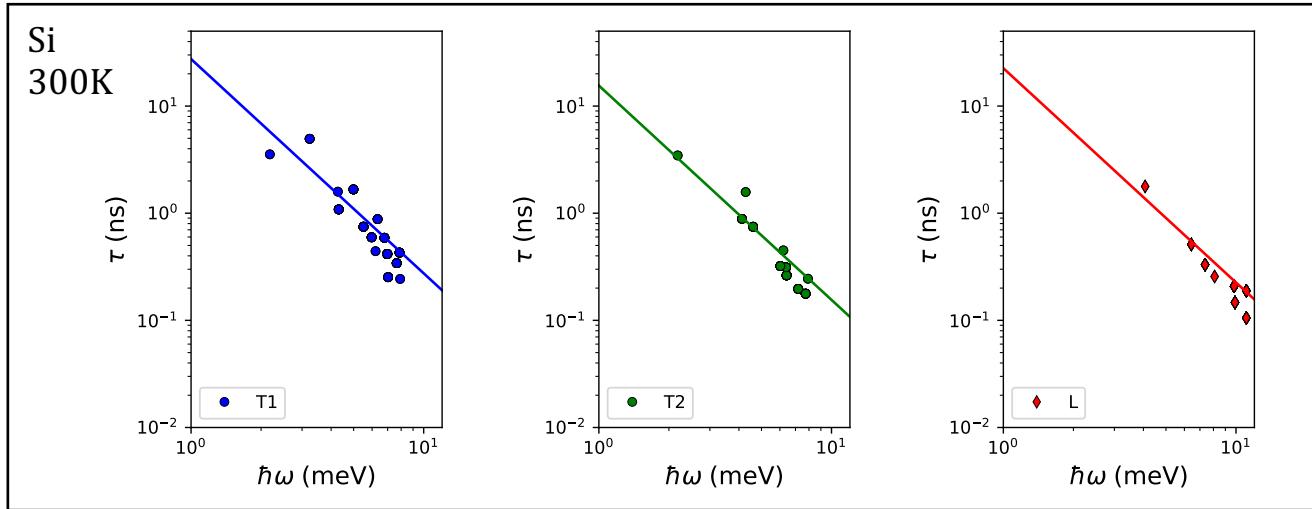
$$\Gamma_{\text{pp}} = \tau_{\text{pp}}^{-1} \propto T \text{ at high temperatures}$$

Phonon-phonon scattering

Common analytical form:
 $\tau_{\text{pp}}^{-1} = C_1 \omega^2 T \exp(-C_2/T)$

Low- ω behavior from DFT based lattice dynamics and phonon-phonon relaxation time.

lines show
 $\tau = A\omega^{-n}$
with $n = 2$



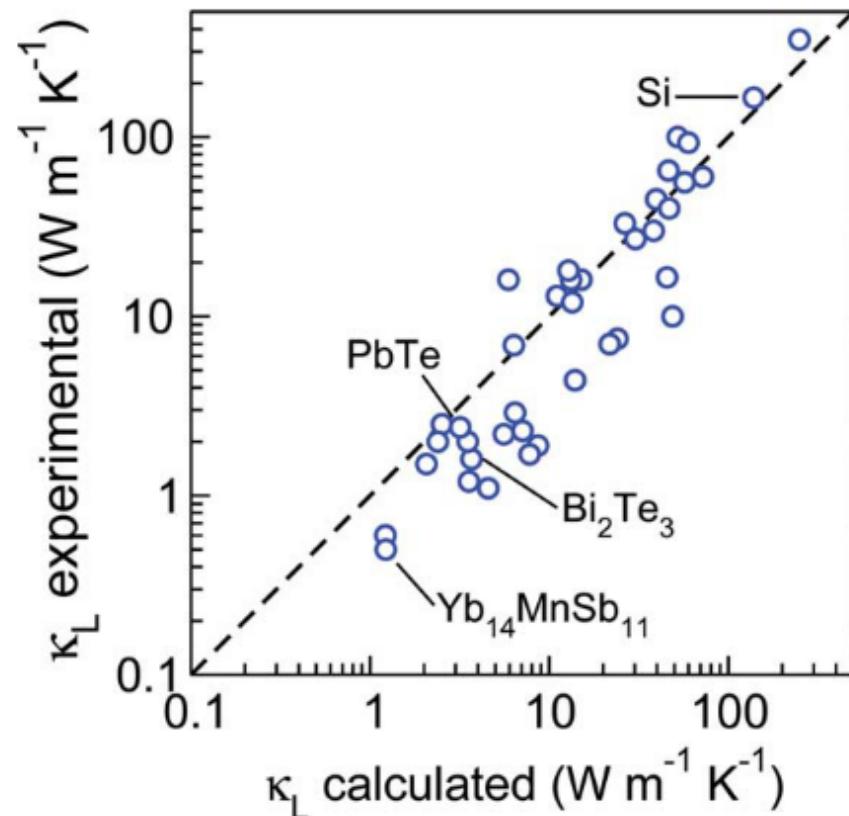
Phonon-phonon scattering

Analytical high-T phonon-phonon scattering model

$$\tau_{\text{pp}}^{-1} = \left(\frac{V}{6\pi^2} \right)^{\frac{1}{3}} \frac{2 k_B \gamma^2 \omega^2 T}{M v_g v_p^2}$$

Fully analytical thermal conductivity model using the above phonon-phonon scattering expression shows reasonable agreement with experiment across two orders of magnitude.

Good for broad screening across material systems.



Toberer, E. S., Zevalkink, A. & Snyder, G. J. Phonon engineering through crystal chemistry. *J. Mater. Chem.* **21**, 15843 (2011).

Low frequency behavior of spectral thermal conductivity

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

as $\omega \rightarrow 0$

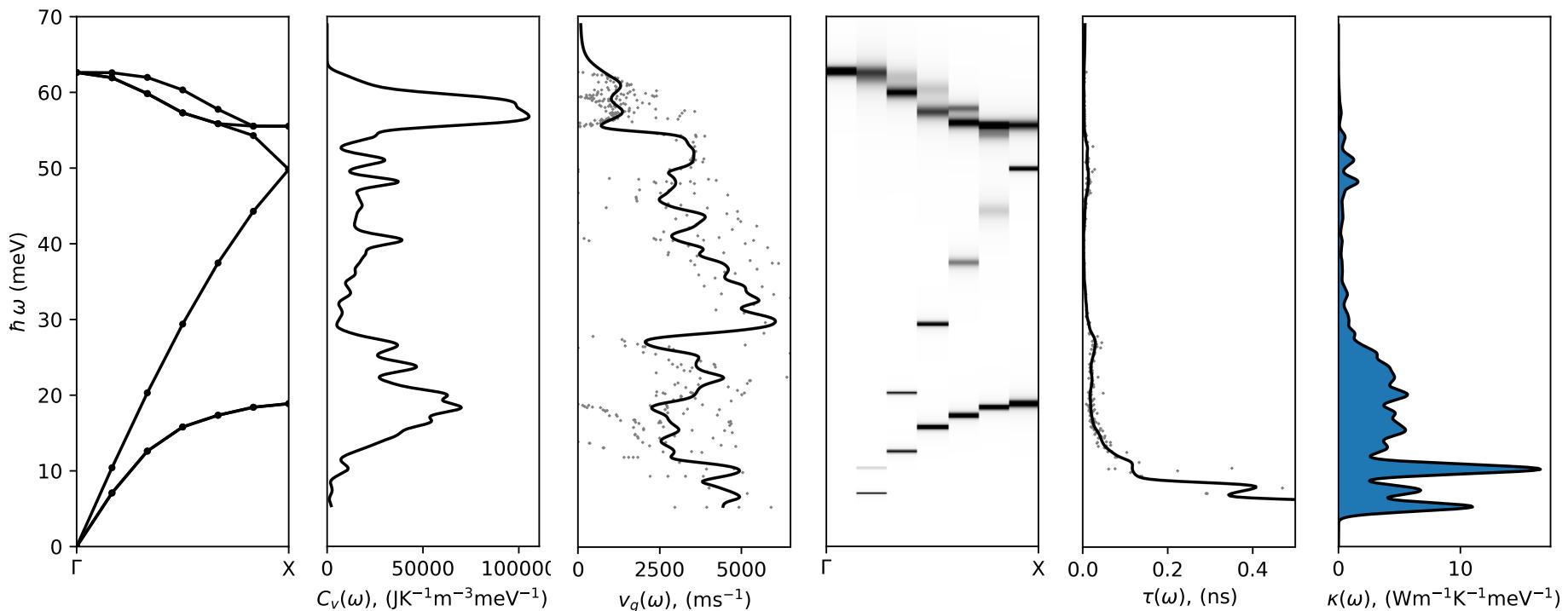
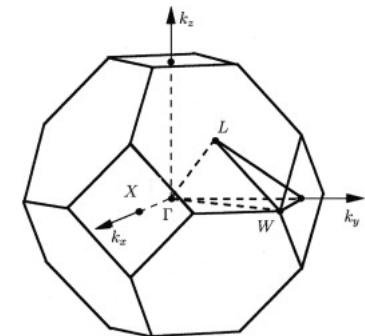
$$C(\omega) = \frac{k_B \cancel{\omega}^2}{2\pi^2 v_S^3} \quad v_g(\omega)^2 = v_S^2 \quad \tau(\omega) = \frac{A(T)}{\cancel{\omega}^2}$$

$$\lim_{\omega \rightarrow 0} \kappa(\omega) = \frac{k_B A(T)}{6\pi^2 v_S} \neq 0$$

BZ integration and k-meshing

Si at 300K

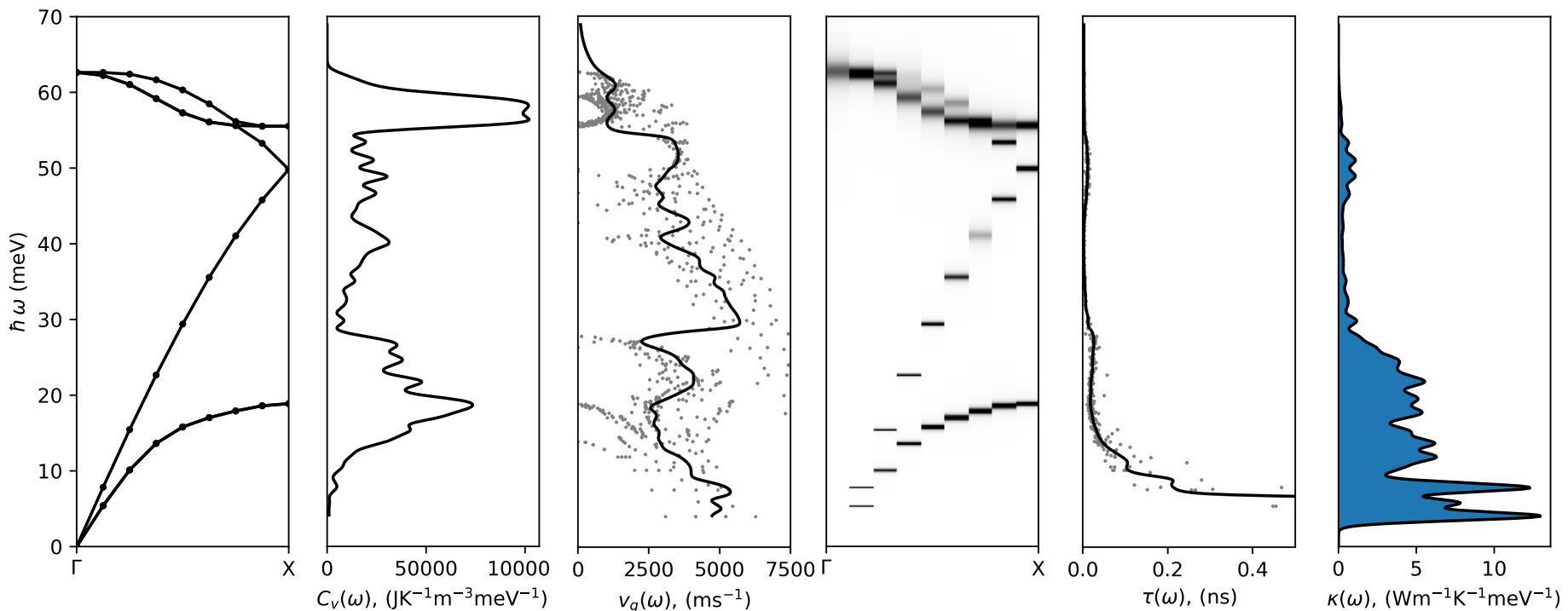
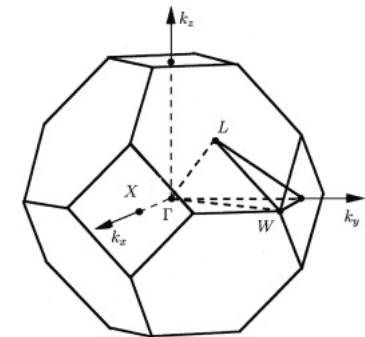
12x12x12



BZ integration and k-meshing

Si at 300K

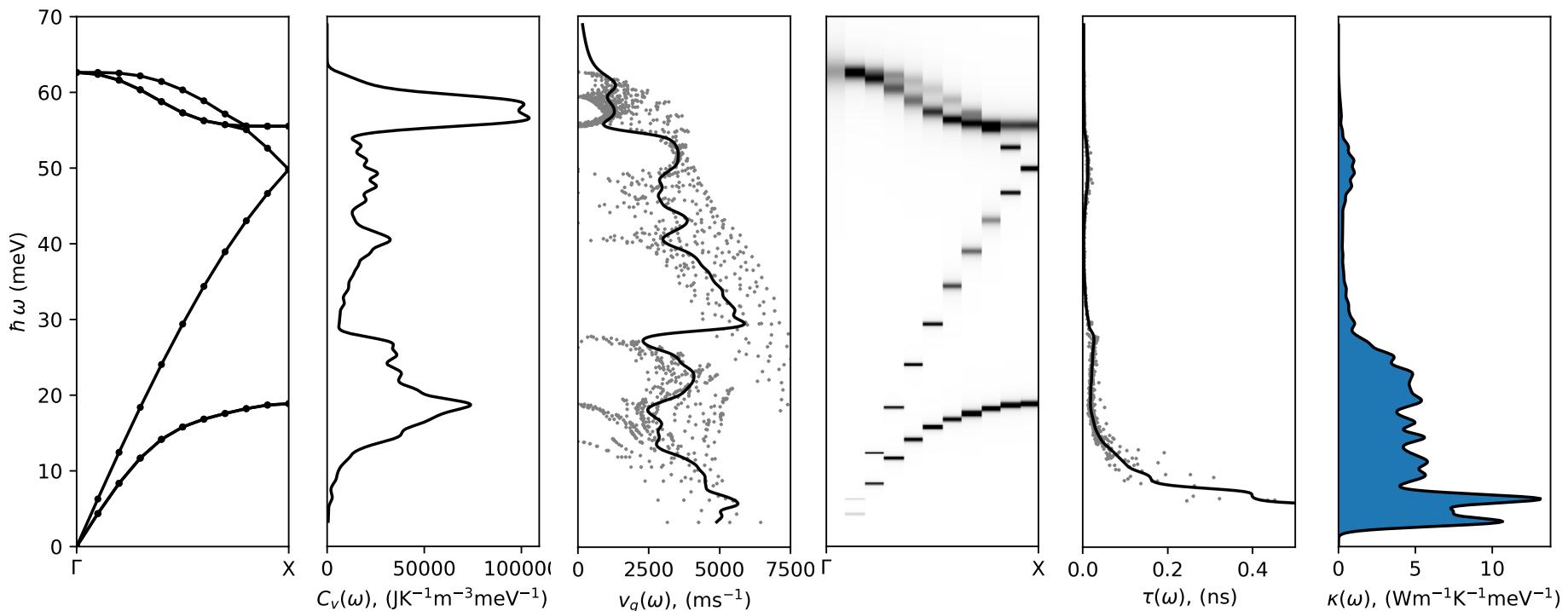
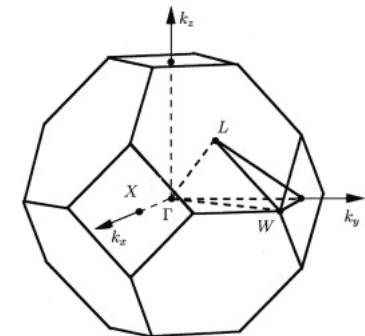
16x16x16



BZ integration and k-meshing

Si at 300K

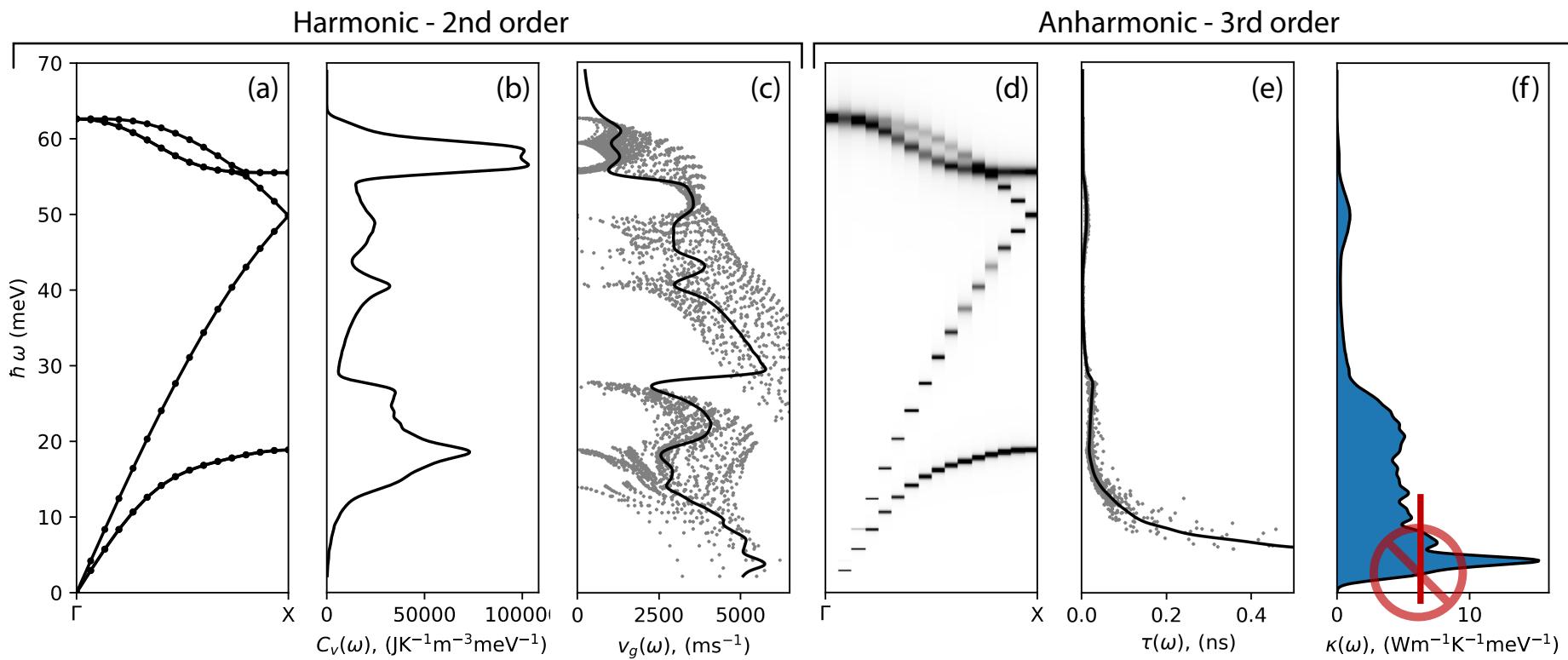
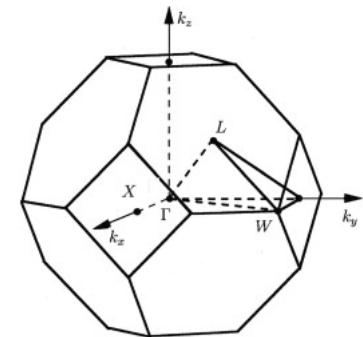
20x20x20



BZ integration and k-meshing

Si at 300K

30x30x30

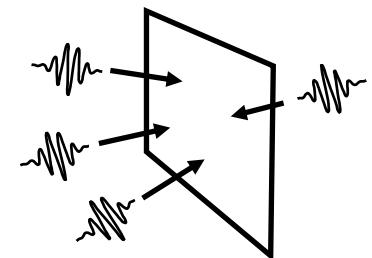


Relaxation time approximation

$$\text{flux} = \text{energy density} \times \text{velocity} \times \text{number} = \frac{\text{Energy}}{\text{Area} \times \text{time}}$$

Phonon-gas model
for heat flux:

$$j^i = \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega(\mathbf{k}s) v_g^i(\mathbf{k}s) n(\mathbf{k}s)$$



$$n(\mathbf{k}s) = n_{\text{BE}}(\mathbf{k}s) + n'(\mathbf{k}s)$$

$$j^i = \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega(\mathbf{k}s) v_g^i(\mathbf{k}s) n_{\text{BE}}(\mathbf{k}s) + \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega(\mathbf{k}s) v_g^i(\mathbf{k}s) n'(\mathbf{k}s)$$

$\underbrace{\qquad\qquad\qquad}_{= 0}$

$$j^i = \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega(\mathbf{k}s) v_g^i(\mathbf{k}s) n'(\mathbf{k}s) \longleftrightarrow j^i = -\kappa^{ij} \nabla^j T$$

compare to solve for κ^{ij}
need $n'(\mathbf{k}s)$, get it from BTE

Relaxation time approximation

Boltzmann transport equation (BTE)

$$\nu_g^i \nabla^i n + \underbrace{\frac{F^i}{\hbar} \frac{d n}{d k^i}}_{= 0} = \left. \frac{dn}{dt} \right|_{\text{coll}}$$

no external forces on phonons

suppress $\mathbf{k}, s, \mathbf{r}$, and t

$$n = n(\mathbf{ks}, \mathbf{r}, t)$$

$$n_{\text{BE}} = n_{\text{BE}}(\mathbf{ks}, \mathbf{r})$$

$$n' = n'(\mathbf{ks}, t)$$

$$\nu_g^i \nabla^i n = \left. \frac{dn}{dt} \right|_{\text{coll}}$$

Left side:

Only spatial (∇^i is real space gradient) dependence of $n(\mathbf{ks})$ is through spatial dependence of T

Right side:

Time dependence only through n'

Making the Relaxation Time Approx.

$$\begin{aligned} \nu_g^i \nabla^i n &= \nu_g^i \nabla^i (n_{\text{BE}} + n') \\ &= \nu_g^i \left(\frac{dn_{\text{BE}}}{dT} \nabla^i T \right) \end{aligned}$$

$$\left. \frac{dn}{dt} \right|_{\text{coll}} = \frac{d}{dt} (n_{\text{BE}} + n') = \frac{dn'}{dt} = -\frac{n'}{\tau}$$

$$n' \propto e^{-t/\tau}$$

$$\nu_g^i \frac{dn_{\text{BE}}}{dT} \nabla^i T = -\frac{n'}{\tau} \quad \longrightarrow \quad n' = -\tau \nu_g^i \frac{dn_{\text{BE}}}{dT} \nabla^i T$$

Relaxation time approximation

$$j^i = \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega(\mathbf{k}s) v_g^i(\mathbf{k}s) n'(\mathbf{k}s)$$

$$n' = -\tau v_g^j \frac{dn_{\text{BE}}}{dT} \nabla^j T$$

$$j^i = -\frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega v_g^i \tau v_g^j \frac{dn_{\text{BE}}}{dT} \nabla^j T \quad \longleftrightarrow \quad j^i = -\kappa^{ij} \nabla^j T$$

$$\kappa^{ij} = \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega v_g^i \tau v_g^j \frac{dn_{\text{BE}}}{dT} \quad C = \frac{1}{V} \frac{d(\hbar \omega n_{\text{BE}})}{dT}$$

$$\kappa^{ij} = \sum_{\mathbf{k}s} C v_g^i v_g^j \tau$$

$$\kappa^{ij} = \sum_{\mathbf{k}s} C(\mathbf{k}s) v_g^i(\mathbf{k}s) v_g^j(\mathbf{k}s) \tau(\mathbf{k}s)$$

Relaxation time and dispersion relation line width

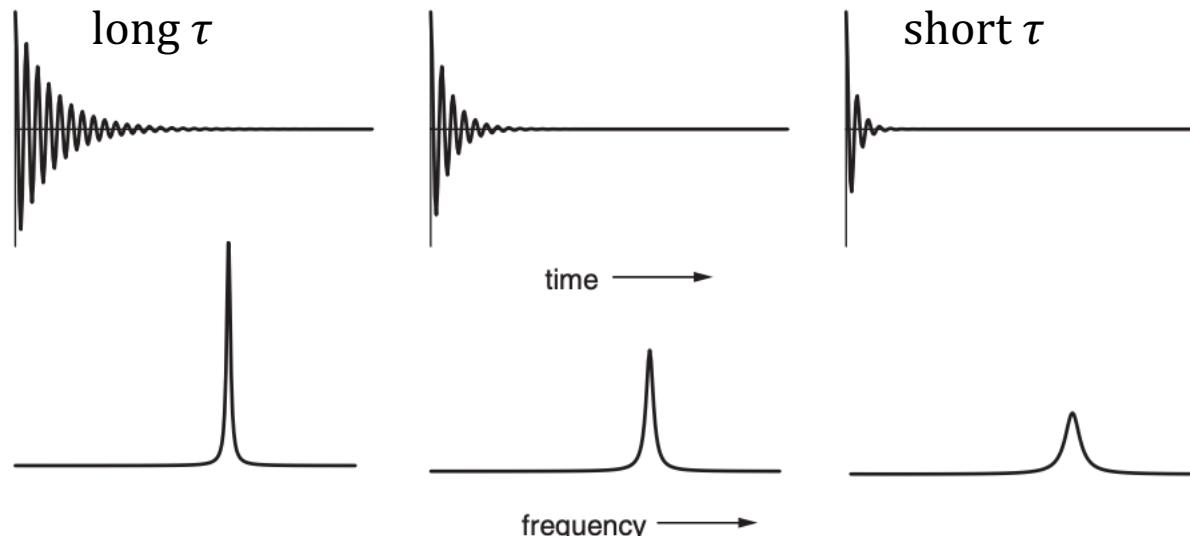
Vibrational amplitude as a function of time:

$$A(t) = e^{i(\omega_0 + i\alpha)t} = e^{-t\alpha} e^{i\omega_0 t} \quad t > 0 \quad \alpha = \frac{1}{\tau}$$

Note: τ has same units as $1/\omega$

$$\tilde{A}(t) = \int_0^{\infty} e^{i(\omega_0 + i\alpha)t} e^{-i\omega t} dt = \frac{1}{\alpha + i(\omega - \omega_0)}$$

Real part and magnitude squared ($|\tilde{A}(t)|^2$) of Fourier transform are a Lorentzian function with FWHM = 2α



Line defect – Mass contrast

$$V(x, y, \omega) = \frac{1}{2} \left(\frac{\Delta M}{M} \right) \hbar \omega A_0 \delta(x) \delta(y)$$

A_0 : cross-sectional area of line defect

$$\langle \mathbf{k}' | V(\mathbf{r}, \omega) | \mathbf{k} \rangle = \frac{1}{L_x L_y L_z} \left(\frac{1}{2} \left(\frac{\Delta M}{M} \right) \hbar \omega A_0 \right) \iiint \delta(x) \delta(y) e^{-i(q_x x + q_y y + q_z z)} dx dy dz$$

$$\langle \mathbf{k}' | V(\mathbf{r}, \omega) | \mathbf{k} \rangle = \frac{1}{L_x L_y L_z} \left(\frac{1}{2} \left(\frac{\Delta M}{M} \right) \hbar \omega A_0 \right) (1)(1) \int e^{-i q_z z} dz$$

$$\langle \mathbf{k}' | V(\mathbf{r}, \omega) | \mathbf{k} \rangle = \frac{1}{L_x L_y L_z} \left(\frac{1}{2} \left(\frac{\Delta M}{M} \right) \hbar \omega A_0 \right) 2\pi \delta(q_z)$$

$$|\langle \mathbf{k}' | V(\mathbf{r}, \omega) | \mathbf{k} \rangle|^2 = \frac{1}{(L_x L_y L_z)^2} \frac{1}{4} \left(\frac{\Delta M}{M} \right)^2 (\hbar \omega)^2 A_0^2 (2\pi)^2 \delta(q_z)^2$$

$$= \frac{1}{(L_x L_y L_z)^2} \frac{1}{4} \left(\frac{\Delta M}{M} \right)^2 (\hbar \omega)^2 A_0^2 2\pi \delta(q_z) L_z$$

Line defect – Mass contrast

$$W_{\mathbf{k}, \mathbf{k}'} = \frac{2\pi}{\hbar} \frac{1}{(L_x L_y)^2 L_z} \frac{1}{4} \left(\frac{\Delta M}{M} \right)^2 (\hbar\omega)^2 A_0^2 2\pi \delta(k_z - k'_z) \frac{1}{\hbar|v_g|} \delta(k - k')$$

$$\Gamma = \frac{L_x L_y L_z}{(2\pi)^3} \iiint W_{\mathbf{k}, \mathbf{k}'} (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) d^3 \mathbf{k}'$$

$$\Gamma = \frac{\pi^2}{8\pi^3} \frac{L_x L_y L_z}{(L_x L_y)^2 L_z} \left(\frac{\Delta M}{M} \right)^2 A_0^2 \iiint \omega^2 \delta(k_z - k'_z) \frac{1}{|v_g|} \delta(k - k') (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) d^3 \mathbf{k}'$$

$$\Gamma = \frac{n_{2d}}{8\pi} \left(\frac{\Delta M}{M} \right)^2 A_0^2 \iiint_0^{\infty} k^2 v_p^2 \delta(k_z - k'_z) \frac{1}{|v_g|} \delta(k - k') (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) k'^2 \sin \theta' d\theta' d\phi' dk'$$

$$\delta(k_z - k'_z) = \delta(k \cos \theta - k' \cos \theta')$$

since this is multiplied by $\delta(k - k')$, we can pull out the k

$$\delta(k \cos \theta - k' \cos \theta') = \frac{1}{k} \delta(\cos \theta - \cos \theta') = \frac{1}{k |\sin \theta|} \delta(\theta - \theta')$$

Line defect – Mass contrast

$$\Gamma = \frac{n_{2d}}{8\pi} \left(\frac{\Delta M}{M}\right)^2 A_0^2 \iiint_{0 \ 0 \ 0}^{\infty 2\pi \pi} v_p^2 \frac{k^2}{k|\sin \theta|} \delta(\theta - \theta') \frac{1}{|v_g|} \delta(k - k') (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) k'^2 \sin \theta' d\theta' d\phi' dk'$$

Can take the integrals over k' and θ'

$$\Gamma = \frac{n_{2d}}{8\pi} \left(\frac{\Delta M}{M}\right)^2 A_0^2 \frac{k^3 v_p^2}{|v_g|} \int_0^{2\pi} (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) d\phi'$$

with $\theta = \theta'$ $(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}'}) = 2 \sin(\theta)^2 \sin\left(\frac{\phi - \phi'}{2}\right)^2$

$$\int_0^{2\pi} 2 \sin(\theta)^2 \sin\left(\frac{\phi - \phi'}{2}\right)^2 d\phi' = 2\pi \sin(\theta)^2$$

$$\Gamma(\mathbf{k}) = \frac{n_{2d}}{4} \left(\frac{\Delta M}{M}\right)^2 A_0^2 \frac{k^3 v_p^2}{|v_g|} \sin(\theta)^2 = \frac{n_{2d}}{4} \left(\frac{\Delta M}{M}\right)^2 A_0^2 \frac{\omega^3}{v_p |v_g|} \sin(\theta)^2$$