Nanoscale thermal transport

Lecture 4

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1. A breakdown of phonon thermal conductivity

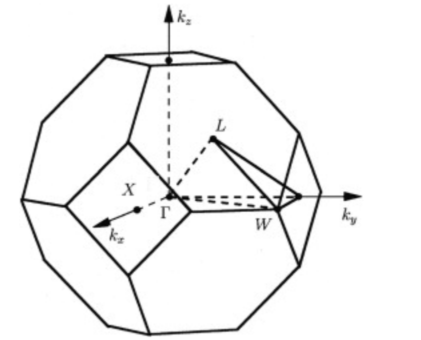
2. The vibrational (lattice) Hamiltonian
   a) The Harmonic Hamiltonian
   b) Types of phonon scattering

3. Scattering potential → Scattering Probability → Relaxation time (lifetime)
   a) point defects
   b) line defects
   c) planar defects

4. Phonon-phonon scattering

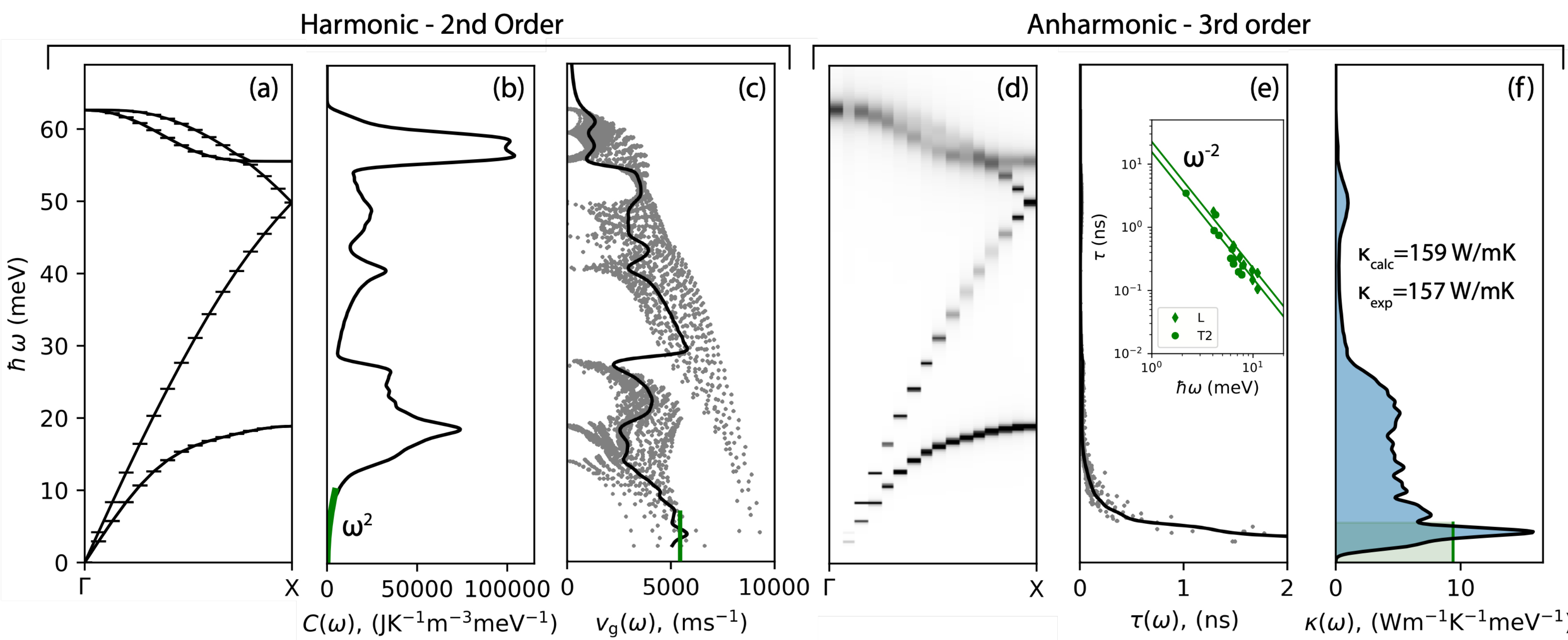
5. Low-frequency behavior of thermal conductivty

Phonon scattering and thermal conductivity



$$H = T + U_{\mathrm{2nd}} + U_{\mathrm{3rd}} + \cdots$$

T: kinetic energy of all atoms
$U = U_{\mathrm{2nd}} + U_{\mathrm{3rd}} + \cdots$: potential energy of all atoms expressed as a Taylor expansion



on board

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

$$KE = \frac{1}{2} m v^2$$

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

PE = ???
Taylor expand it:

reference energy, set this to zero

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

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

on board

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

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

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

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

$$H = \qquad T \qquad + \qquad U_{\mathrm{2nd}} \qquad + \qquad U_{\mathrm{3rd}}$$

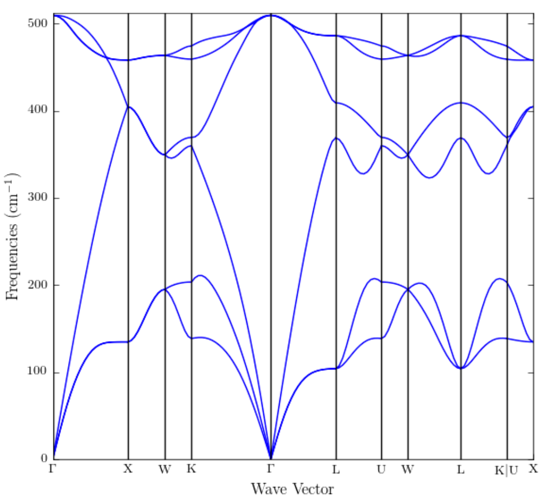
Harmonic Hamiltonian

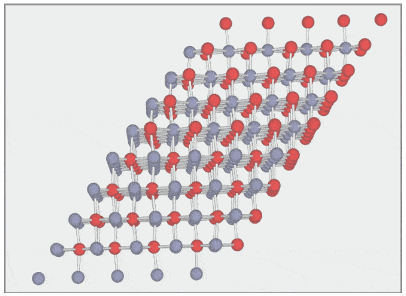
$$H_{\text{harm}} = \frac{1}{2}\sum_{\alpha}\sum_{i} m^{\alpha}(\dot{u}_i^{\alpha})^2 + \frac{1}{2!}\sum_{\alpha\beta}\sum_{ij} \Phi_{ij}^{\alpha\beta}\, u_i^{\alpha}\, u_i^{\beta}$$

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

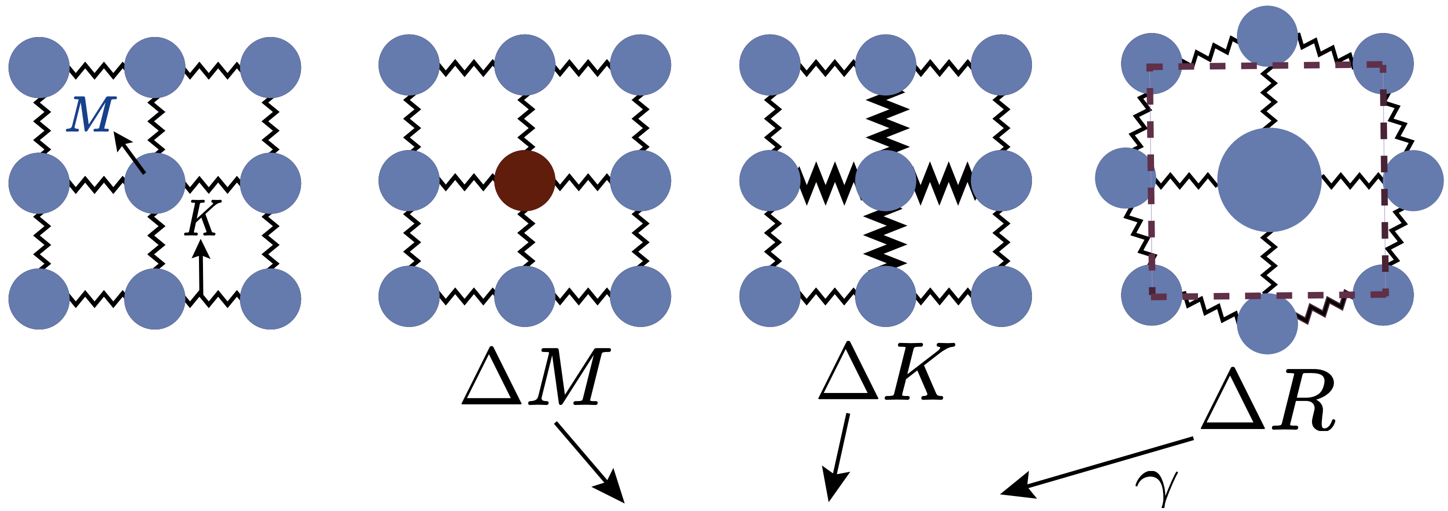
$$\omega^2(\mathbf{k}s)\epsilon_i^{\alpha}(\mathbf{k}s) = \sum_{j\beta} \mathbf{\Phi}_{ij}^{\alpha\beta}(\mathbf{k})\epsilon_j^{\beta}(\mathbf{k}s).$$

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





Types of perturbations



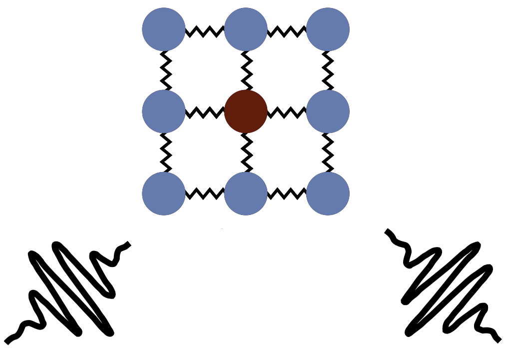
$$H = T + (U_{2\mathrm{nd}} + U_{3\mathrm{rd}})$$

$$H = \frac{1}{2}\sum_{\alpha}\sum_{i} \overset{M}{m^{\alpha}}(\dot{u}_i^{\alpha})^2 + \frac{1}{2!}\sum_{\alpha\beta}\sum_{ij} \overset{K}{\Phi_{ij}^{\alpha\beta}}\, u_i^{\alpha}\, u_i^{\beta} + \frac{1}{3!}\sum_{\alpha\beta\gamma}\sum_{ijk} \Phi_{ijk}^{\alpha\beta\gamma}\, u_i^{\alpha}\, u_i^{\beta}\, \overset{\Delta R}{u_k^{\gamma}}$$

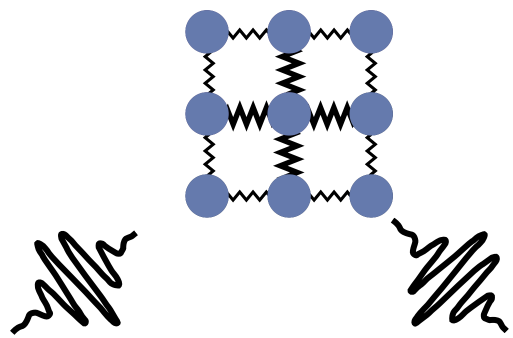
Mass (density) changes | Spring constant changes | Changes in strain

Types of perturbations

Mass contrast scattering

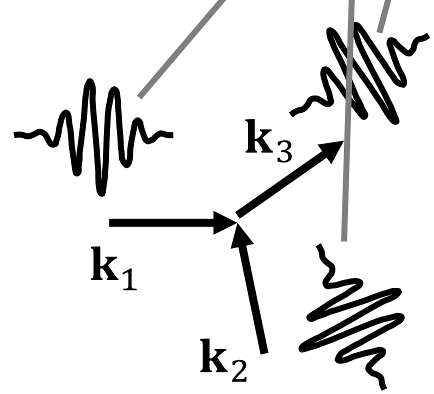


Bond strength contrast scattering



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

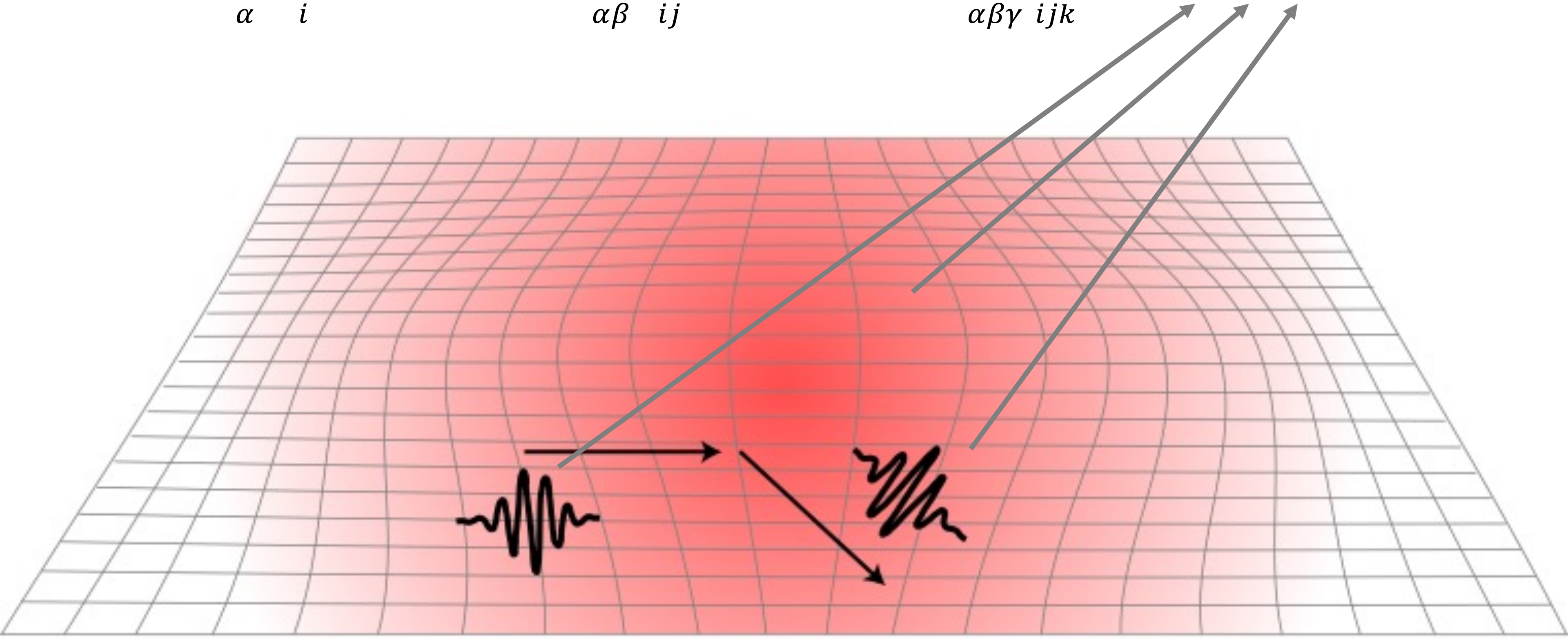
Phonon-phonon scattering



Types of perturbations

Static strain field scattering

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



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Scattering potential → relaxation time

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

You can find reference's in R. Hanus' thesis Appendix G.

Probability of scattering from state **k** into **k'** given by Fermi's Golden Rule:

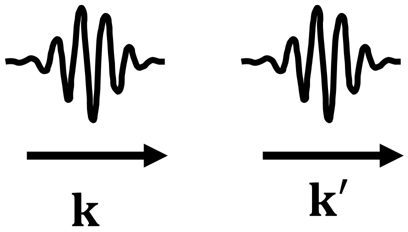
$$W_{\mathbf{k},\mathbf{k}'} = \frac{2\pi}{\hbar}|\langle\mathbf{k}'|V(\mathbf{r})|\mathbf{k}\rangle|^2\delta(\Delta E) \quad \text{units: } \left[\frac{1}{s}\right]$$

Total scattering rate is the sum over all possible **k'** states.

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

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

What if **k** = **k'** ? Does this scattering event impede heat conduction?



isotropic approximation, this becomes

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

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.

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

spatial density of defects

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

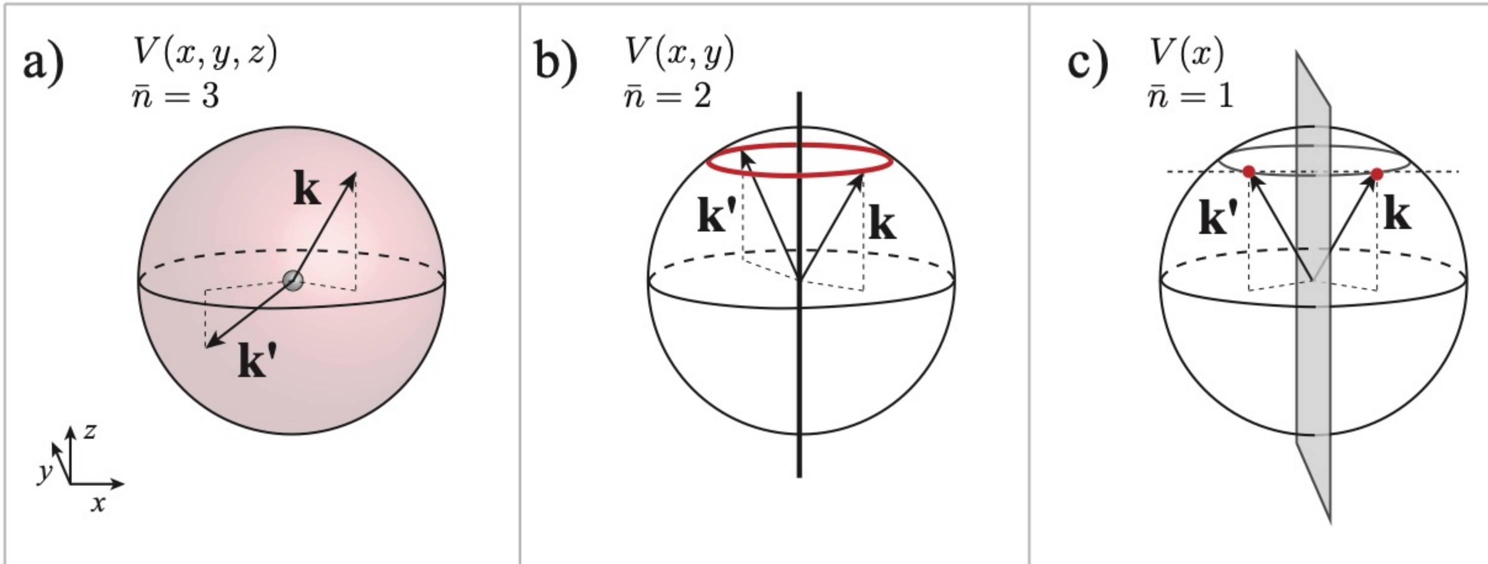
Matrix element contribution:
Magnitude squared of the Fourier transform of the scattering potential

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

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

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

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



	a)	b)	c)
Conserved quantities:	E	$E,\ k_z$	$E,\ k_z,\ k_y$
Phase space:	$g_{3\mathrm{d}} = \dfrac{\omega^2}{2\pi^2 v_\mathrm{g} v_\mathrm{p}^2}$	$g_{2\mathrm{d}} = \dfrac{\omega}{2\pi v_\mathrm{g} v_\mathrm{p}}$	$g_{1\mathrm{d}} = \dfrac{1}{\pi v_\mathrm{g}}$

Mass difference scattering potential

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

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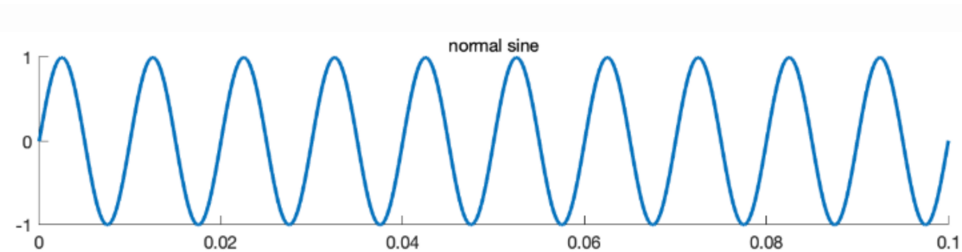
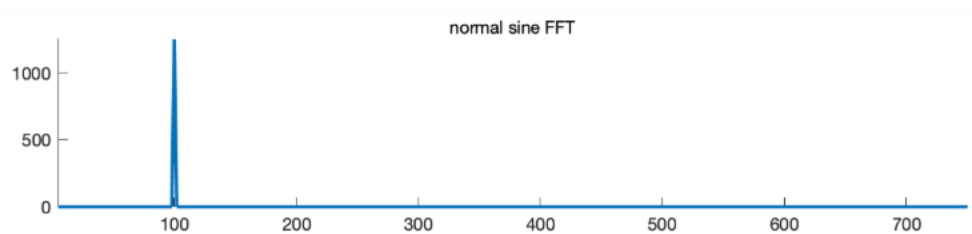
Scattering theory

Required Math

Integral definition of the Dirac δ-function

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





Some δ-function identities:

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

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

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

Example:

$$\delta\big(\hbar\omega(k) - \hbar\omega(k')\big) =$$

$$\frac{1}{\hbar}\delta\big(\omega(k) - \omega(k')\big) =$$

$$\frac{1}{\hbar|v_g|}\delta(k - k')$$

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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: $a_{\mathbf{k}s}|n_{\mathbf{k}s}\rangle = \sqrt{n_{\mathbf{k}s}+1}|n_{\mathbf{k}s}\rangle$

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

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Point defect – Mass contrast

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

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

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

$L_x L_y L_z$: 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:

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

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

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Point defect – Mass contrast

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

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

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

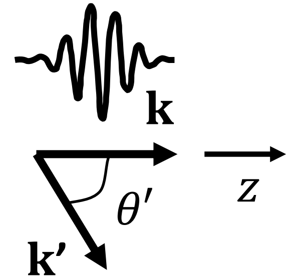
$$\delta(\Delta E) = \delta(\hbar\omega - \hbar\omega') = \frac{1}{\hbar}\delta(\omega-\omega') = \frac{1}{\hbar|v_{\mathrm{g}}|}\delta(k-k')$$

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

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

on board

Point defect – Mass contrast



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

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

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

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

$$\Gamma = \frac{n_{3\mathrm{d}}}{16\pi^2}\left(\frac{\Delta M}{M}\right)^2 V_0^2 \int_0^\infty\int_0^{2\pi}\int_0^\pi \omega^2 \frac{1}{|v_\mathrm{g}|}\delta(k-k')(1-\cos\theta')\, k'^2\sin\theta'\ d\theta' d\phi' dk'$$

$$\omega = v_\mathrm{p} k \qquad \int_0^{2\pi}\int_0^\pi \sin\theta'\ (1-\cos\theta')\, d\theta' d\phi' = 4\pi$$

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

Point defect – Mass contrast

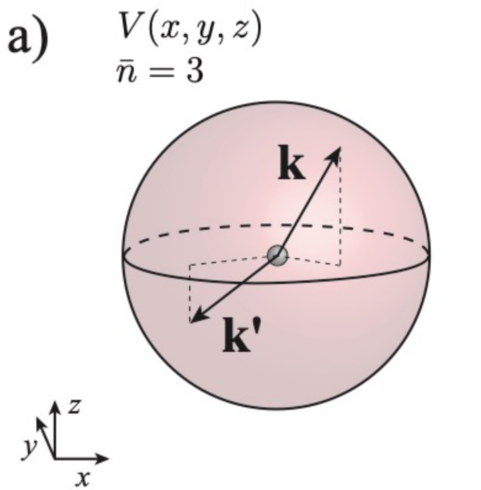
$$\Gamma = n_{3\mathrm{d}} \times \left(\frac{\omega^2}{2\pi^2 \, v_\mathrm{p}^2 |v_\mathrm{g}|} \right) \times \left(\frac{\pi}{2} \left(\frac{\Delta M}{M} \right)^2 \, V_0^2 \omega^2 \right)$$

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

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

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

a)



Conserved quantities:	E
Phase space:	$g_{3\mathrm{d}} = \frac{\omega^2}{2\pi^2 v_\mathrm{g} v_\mathrm{p}^2}$

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

Line defect – Mass contrast

details in supplemental slides

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

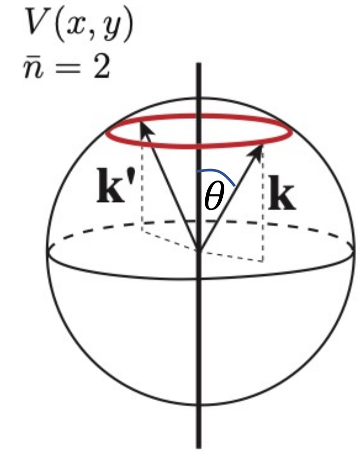
$$\tau(\mathbf{k})^{-1}=n_{\mathrm{2d}}\times\frac{\omega}{2\pi\, v_{\mathrm{p}}|v_{\mathrm{g}}|}\times\frac{\pi}{2}\left(\frac{\Delta M}{M}\right)^2 A_0^2\,\omega^2\sin(\theta)^2$$

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

$$\tau^{-1}=\Gamma=\frac{n_{\mathrm{2d}}A_0^2}{4\, v_{\mathrm{p}}|v_{\mathrm{g}}|}\left(\frac{\Delta M}{M}\right)^2\omega^3\sin(\theta)^2$$

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

b)



$E,\ k_z$

$$g_{\mathrm{2d}}=\frac{\omega}{2\pi v_{\mathrm{g}}v_{\mathrm{p}}}$$

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

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

Elastic defect scattering cheat sheet

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

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

$$g_{3\mathrm{d}} = \frac{\omega^2}{2\pi^2 v_\mathrm{g} v_\mathrm{p}^2}$$

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

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

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

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

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

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

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

$$g_{2\mathrm{d}} = \frac{\omega}{2\pi v_\mathrm{g} v_\mathrm{p}}$$

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

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

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

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

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

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

$$g_{1\mathrm{d}} = \frac{1}{\pi v_\mathrm{g}}$$

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

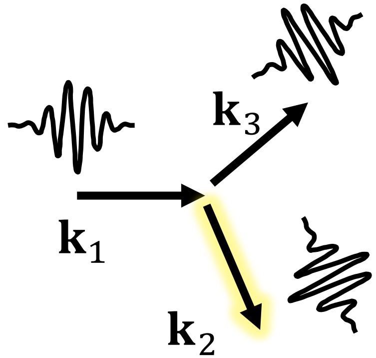
$$\overline{|M_{1\mathrm{d}}|^2} = \frac{\pi}{\hbar^2} \left[|M_{2d}|^2 \left(1 - \widehat{\mathbf{k}} \cdot \widehat{\mathbf{k}'}\right)\right]_{q_x = -2k_x}$$

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

Phonon-phonon scattering

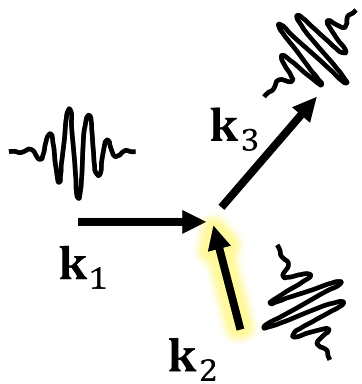
$\mathbf{b}$: any reciprocal lattice vector

Type I:
one phonon decomposes into two



$$\mathbf{k}_1 = \mathbf{k}_2 + \mathbf{k}_3 + \mathbf{b}$$
$$\hbar\omega_1 = \hbar\omega_2 + \hbar\omega_3$$

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.

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

$N(\mathbf{k}s)$: weighted joint density of states

$P(\mathbf{k}s)$: 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

$$n_{\mathrm{BE}} = \frac{1}{e^{\frac{\hbar\omega}{k_{\mathrm{B}}T}} - 1} \approx \frac{1}{1 + \frac{\hbar\omega}{k_{\mathrm{B}}T} - 1} = \frac{k_{\mathrm{B}}T}{\hbar\omega}$$

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

Togo, A., Chaput, L. & Tanaka, I. Distributions of phonon lifetimes in Brillouin zones. *Phys. Rev. B* **91**, 094306 (2015).

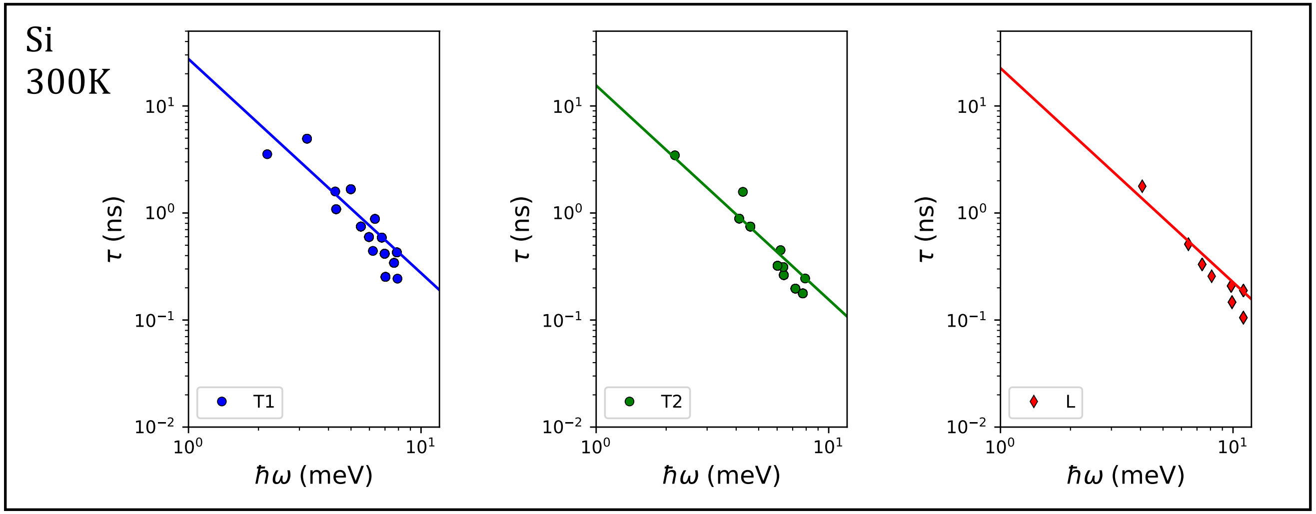
Phonon-phonon scattering

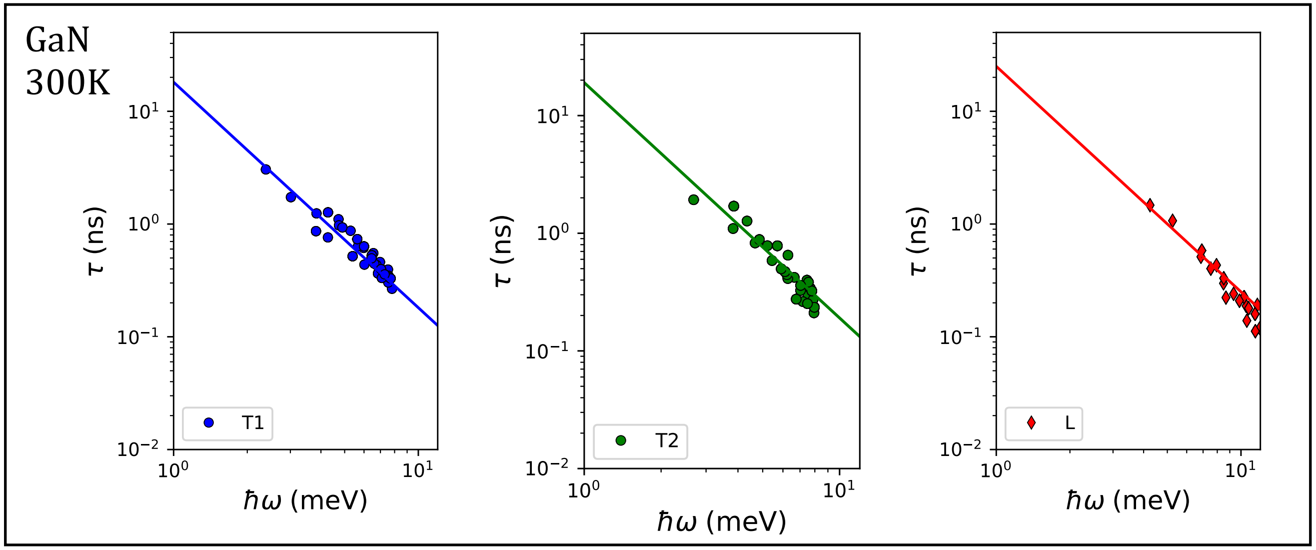
Common analytical form:

$$\tau_{\mathrm{pp}}^{-1} = C_1 \omega^2 T \exp(-C_2/T)$$

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

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





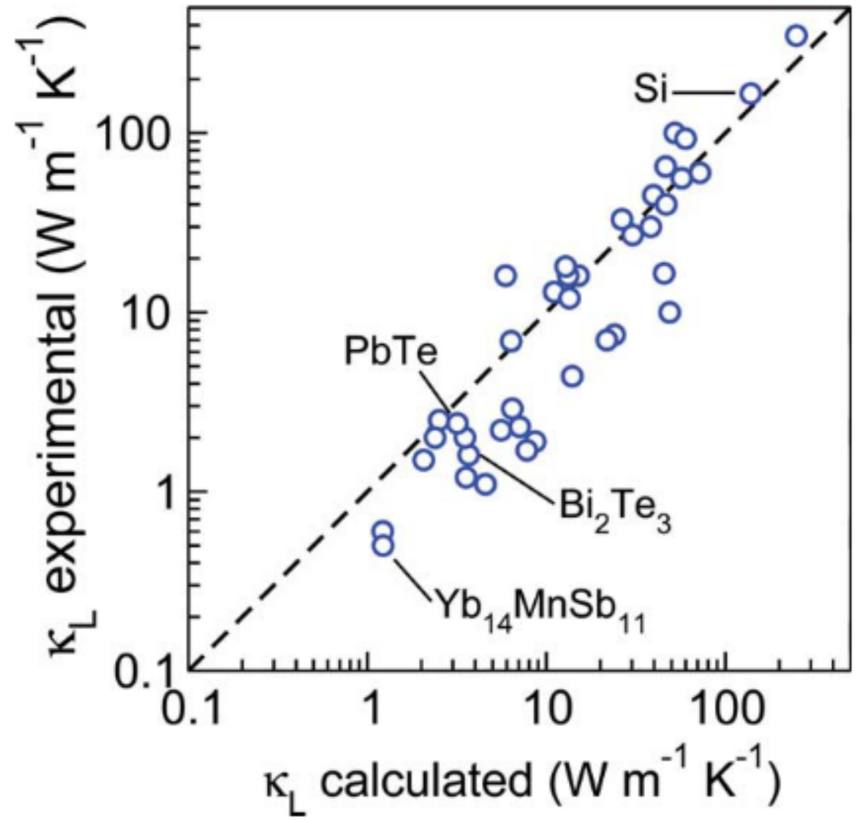
Phonon-phonon scattering

Analytical high-T phonon-phonon scattering model

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

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, probably not for detailed analysis within a material system.



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

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

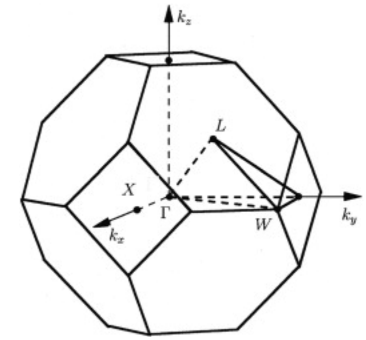
as $\omega \to 0$ $\qquad C(\omega) = \frac{k_B \cancel{\omega^2}}{2\pi^2 v_S^3} \qquad v_g(\omega)^2 = v_S^2 \qquad \tau(\omega) = \frac{A(T)}{\cancel{\omega^2}}$

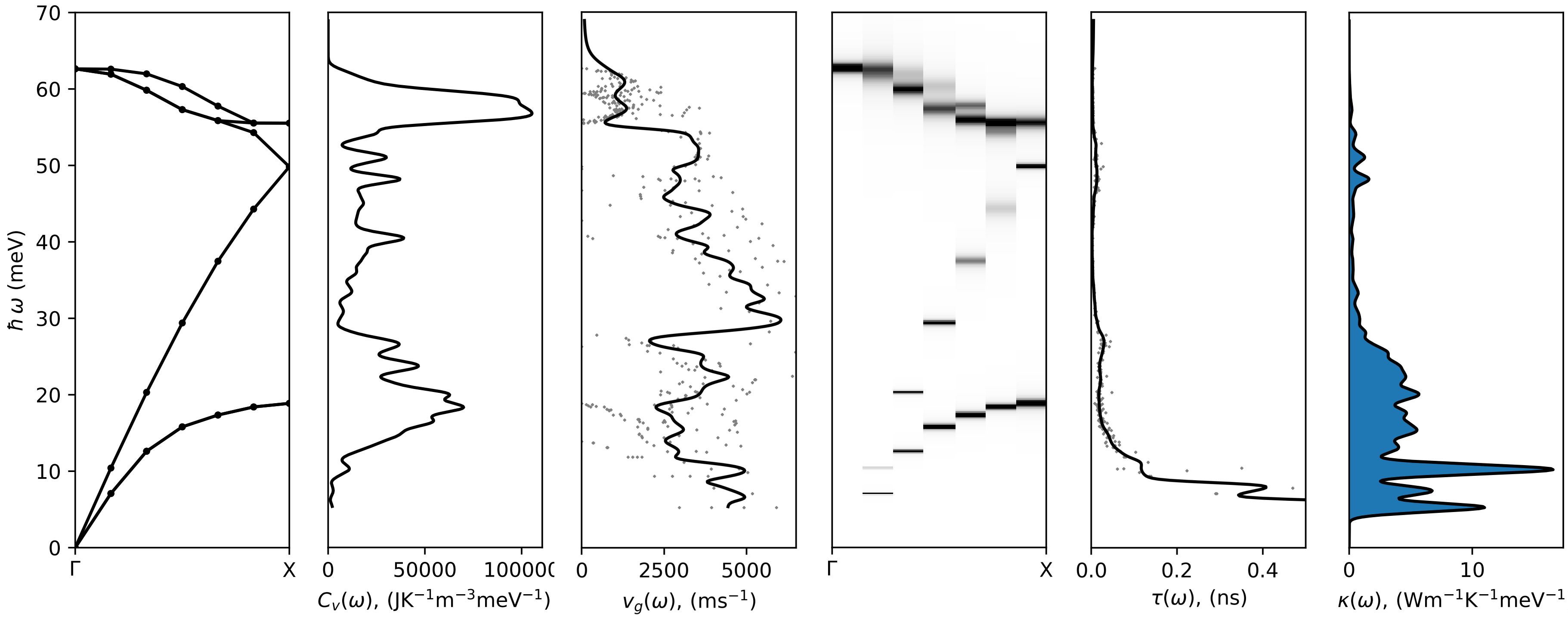
$$\lim_{\omega \to 0} \kappa(\omega) = \frac{k_B\, A(T)}{6\pi^2 v_S} \qquad \neq 0$$

BZ integration and k-meshing

Si at 300K

12x12x12

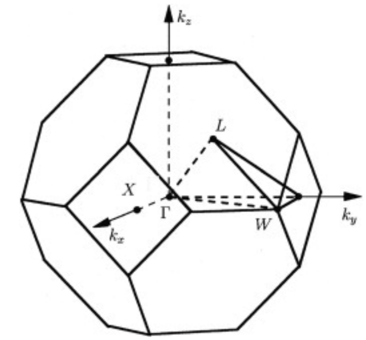


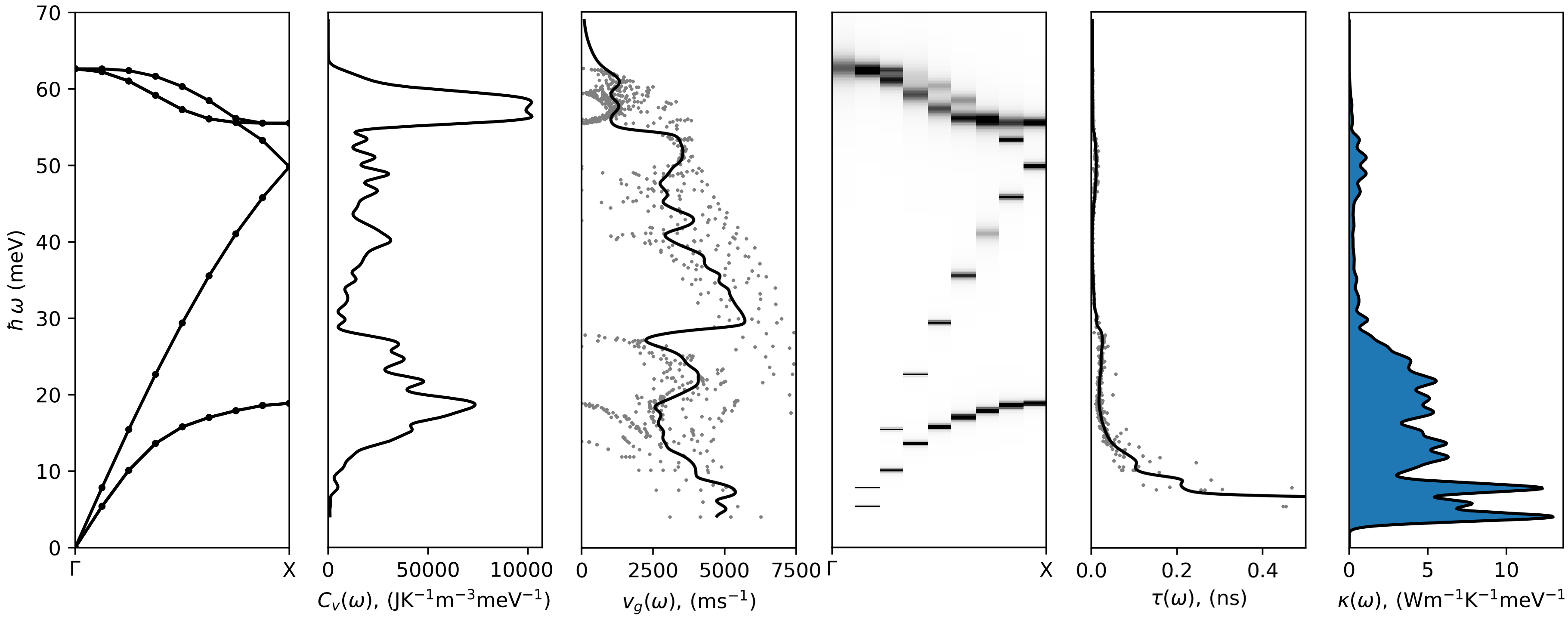


BZ integration and k-meshing

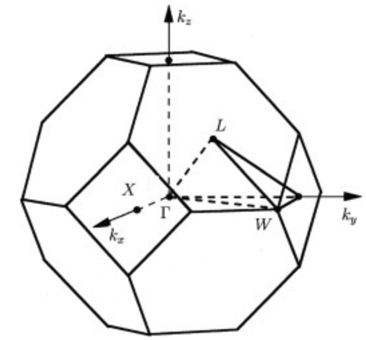
Si at 300K

16x16x16



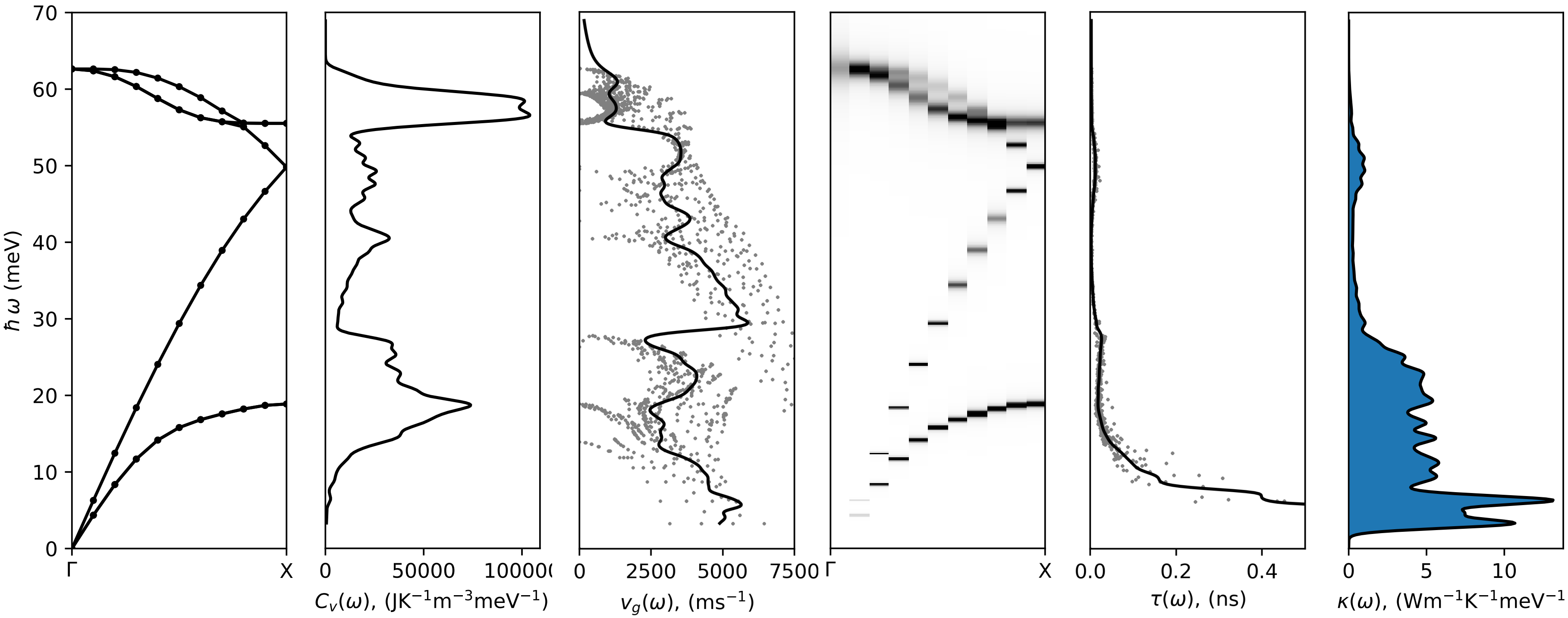


BZ integration and k-meshing



Si at 300K

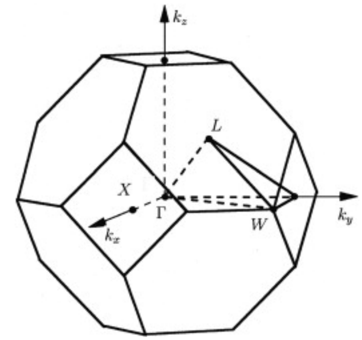
20x20x20

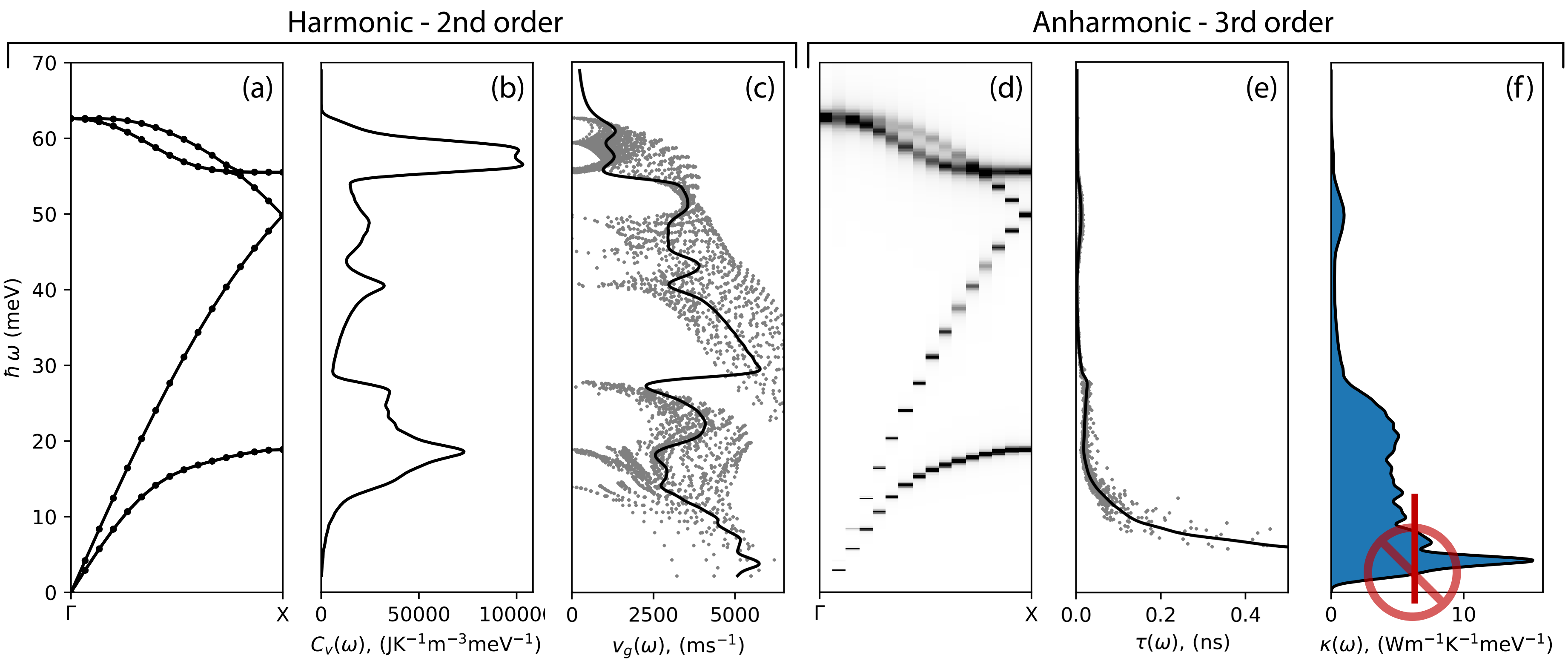


BZ integration and k-meshing

Si at 300K

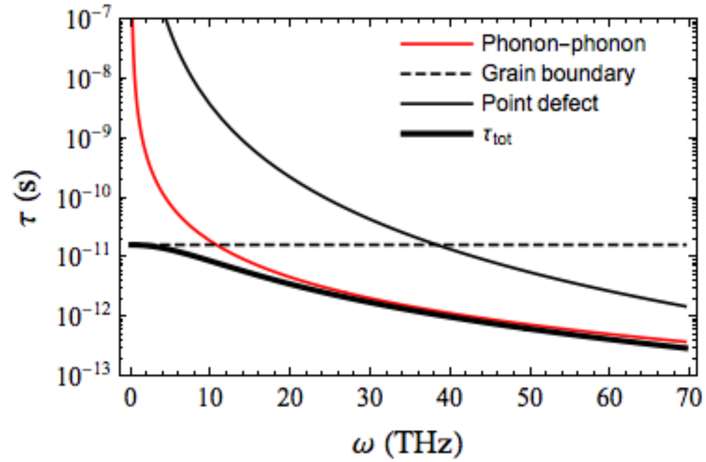
30x30x30

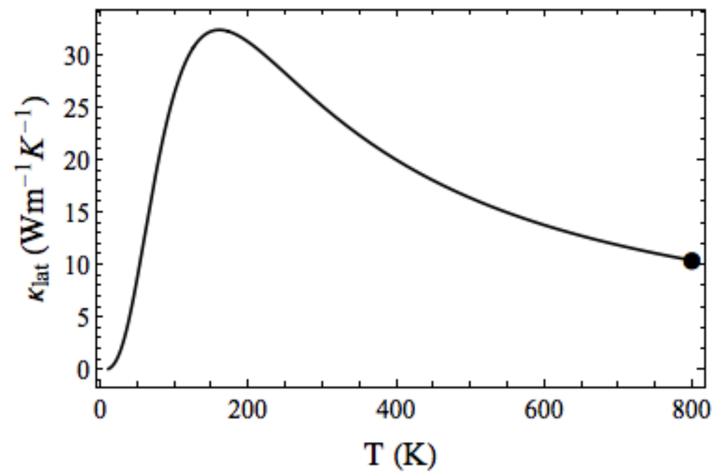


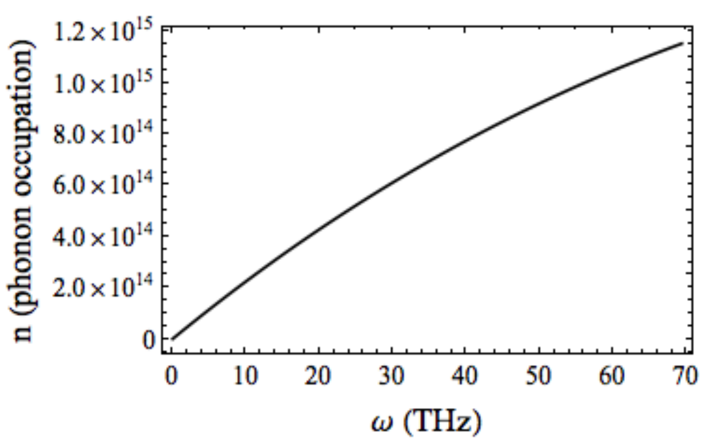


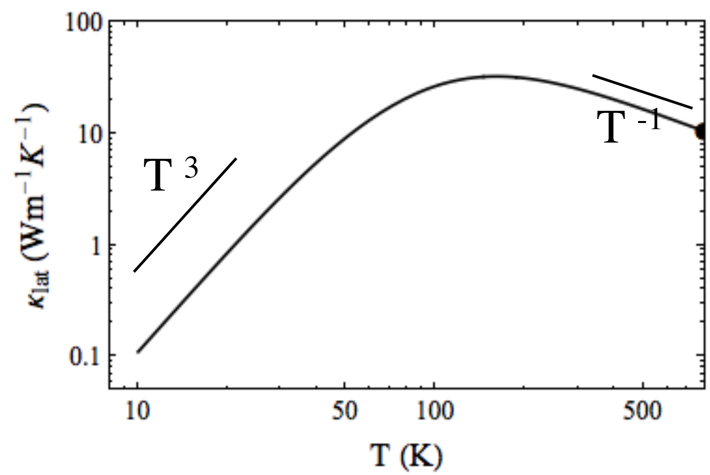
Example Callaway model

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









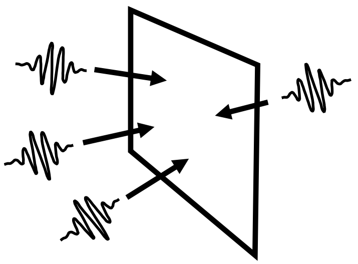
Relaxation time approximation

supplemental

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

Phonon-gas model for heat flux:

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



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

$$j^i = \underbrace{\frac{1}{V}\sum_{\mathbf{k}s} \hbar\omega(\mathbf{k}s)\;\, v_g^i\,(\mathbf{k}s) n_{\mathrm{BE}}(\mathbf{k}s)}_{=\,0} + \frac{1}{V}\sum_{\mathbf{k}s} \hbar\omega(\mathbf{k}s)\;\, v_g^i\,(\mathbf{k}s) n'(\mathbf{k}s)$$

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

compare to solve for κ^{ij}

need $n'(\mathbf{k}s)$, get it from BTE

supplemental

Relaxation time approximation

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

$$n = n(\mathbf{k}s, \mathbf{r}, t)$$
$$n_{\mathrm{BE}} = n_{\mathrm{BE}}(\mathbf{k}s, \mathbf{r})$$
$$n' = n'(\mathbf{k}s, t)$$

Boltzmann transport equation (BTE)

$$v_{\mathrm{g}}^{i}\, \nabla^{i} n + \underbrace{\frac{F^{i}}{\hbar}\, \frac{d\, n}{dk^{i}}}_{=0} = \left.\frac{dn}{dt}\right|_{\mathrm{coll}}$$

no external forces on phonons

$$v_{\mathrm{g}}^{i}\, \nabla^{i} n = \left.\frac{dn}{dt}\right|_{\mathrm{coll}}$$

Left side:
Only spatial (∇^{i} is real space gradient) dependence of $n(\mathbf{k}s)$ is through spatial dependence of T

$$v_{\mathrm{g}}^{i}\, \nabla^{i} n = v_{\mathrm{g}}^{i}\, \nabla^{i}(n_{\mathrm{BE}} + n')$$
$$= v_{g}^{i} \left(\frac{dn_{\mathrm{BE}}}{dT}\, \nabla^{i} T \right)$$

Right side:
Time dependence only through n'

Making the Relaxation Time Approx.

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

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

$$v_{\mathrm{g}}^{i}\, \frac{dn_{\mathrm{BE}}}{dT}\, \nabla^{i} T = -\frac{n'}{\tau} \quad \longrightarrow \quad n' = -\tau\, v_{\mathrm{g}}^{i}\, \frac{dn_{\mathrm{BE}}}{dT}\, \nabla^{i} T$$

Relaxation time approximation

supplemental

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

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

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

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

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

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

supplemental

Relaxation time and dispersion relation line width

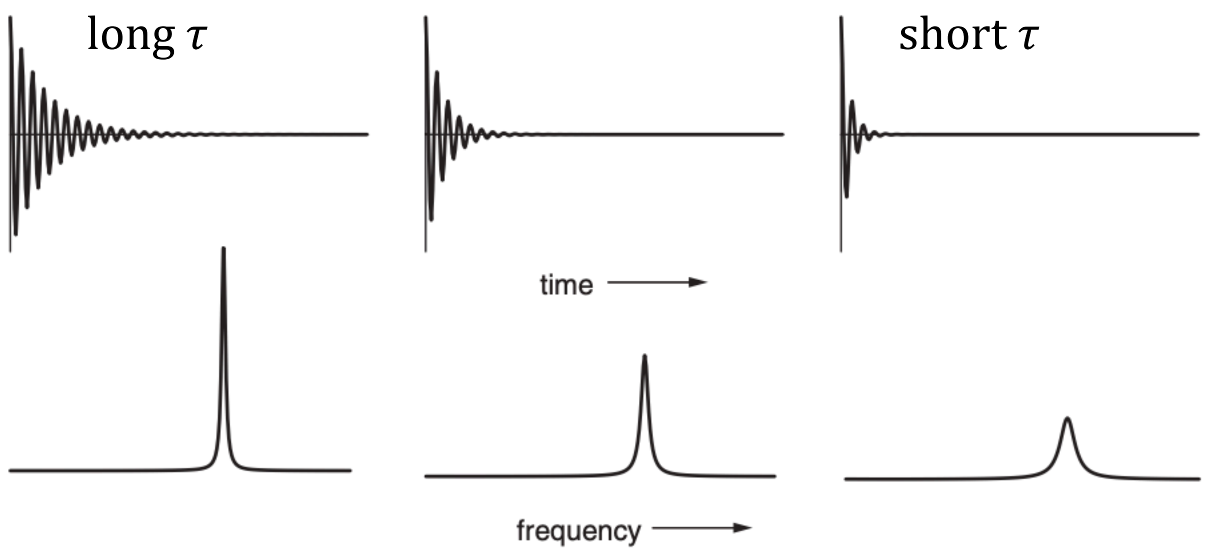
Vibrational amplitude as a function of time:

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

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 ($\left|\tilde{A}(t)\right|^2$) of Fourier transform are a Lorentzian function with FWHM = 2α



Line defect – Mass contrast

supplemental

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

A_0: cross-sectional area of line defect

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

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

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

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

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

supplemental

Line defect – Mass contrast

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

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

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

$$\Gamma = \frac{n_\mathrm{2d}}{8\pi}\left(\frac{\Delta M}{M}\right)^2\ A_0^2\int_0^\infty\int_0^{2\pi}\int_0^{\pi} k^2 v_\mathrm{p}^2\ \delta(k_z-k_z')\frac{1}{|v_\mathrm{g}|}\delta(k-k')\left(1-\hat{\mathbf{k}}\cdot\widehat{\mathbf{k}'}\right)k'^2\sin\theta'\,d\theta' d\phi' dk'$$

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

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

supplemental

$$\Gamma = \frac{n_{\mathrm{2d}}}{8\pi}\left(\frac{\Delta M}{M}\right)^2 A_0^2 \int_0^\infty\int_0^{2\pi}\int_0^{\pi} v_{\mathrm{p}}^2 \frac{k^2}{k|\sin\theta|}\delta(\theta-\theta')\frac{1}{|v_{\mathrm{g}}|}\delta(k-k')\left(1-\widehat{\mathbf{k}}\cdot\widehat{\mathbf{k}'}\right)k'^2\sin\theta'\,d\theta'\,d\phi'\,dk'$$

Can take the integrals over k' and θ'

$$\Gamma = \frac{n_{\mathrm{2d}}}{8\pi}\left(\frac{\Delta M}{M}\right)^2 A_0^2 \frac{k^3 v_{\mathrm{p}}^2}{|v_{\mathrm{g}}|}\int_0^{2\pi}\left(1-\widehat{\mathbf{k}}\cdot\widehat{\mathbf{k}'}\right)d\phi'$$

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

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

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