Nanoscale thermal transport

Lecture 2

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1. Define (and understand) the phonon band structures
2. Learn how to read a phonon band structure
3. Introduction to the phonon gas model
4. Derive the phonon density of states two ways

Phonon band structures

Most solid-state physics classes will derive an analytical dispersion for a 1D chain.

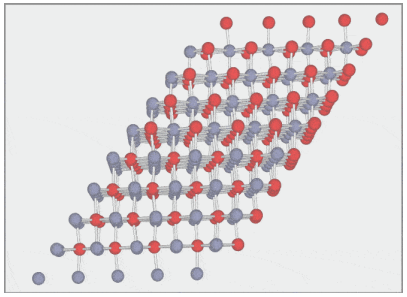
- If you haven't seen this, read **Kittel, Intro. to Solid State physics Chapter 4.**
- Much of the intuition gained from the 1D case extends to 3D

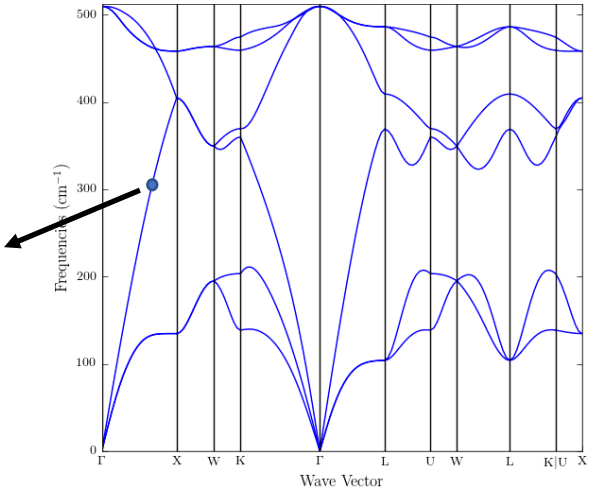
The math for a 3D crystal, which is used to calculate real dispersion relations is given in:

- **Wallace, Thermodynamics of Crystals, Chapter 3.10.**
- **Hanus, Thesis, Section 2.2.1 and Appendix B.**

Here we will outline the procedure for computing phonon properties:

- frequencies →
- eigenvectors (mode shape) →

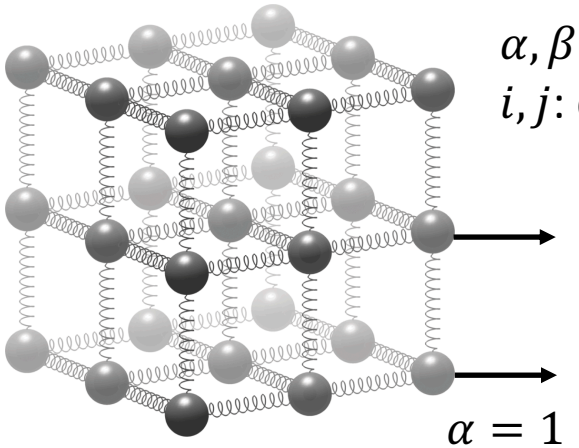




Phonon band structures Set up

Simply solve the equations of motion (Newton's law)

$$F = -\Phi x$$
$$F = ma$$



α, β: atom label
i, j: direction

$\beta = 2$
$j = x$

$\alpha = 1$
$i = x$

$$-\Phi x = ma$$

$$-\sum_{j\beta} \Phi_{ij}^{\alpha\beta} u_j^{\beta} = m^{\alpha} \ddot{u}_i^{\alpha}$$

We know $\Phi_{ij}^{\alpha\beta}$ and m^{α} , solve for u_i^{α}.

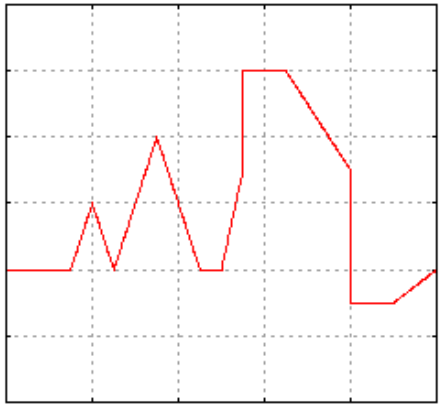
Databases for interatomic force constants (IFCs) $\Phi_{ij}^{\alpha\beta}$:

- Phonopy: http://phonondb.mtl.kyoto-u.ac.jp/
- almaBTE: http://www.almabte.eu/index.php/database/

Required math

Expressing a function as a Fourier Series:

$$f(x) = \sum_{N=-\infty}^{\infty} c_N e^{iNx}$$



Matrix diagonalization:

$$D_{ij} = \begin{bmatrix} 0 & 1 & -2 \\ 0 & 1 & 0 \\ 1 & -1 & 3 \end{bmatrix}$$

↓ Diagonalize

$$\lambda \epsilon_i = \sum_j D_{ij} \epsilon_j \qquad (\lambda = \omega^2 \text{ for phonons})$$

Find λ's and ϵ_i 's that obey this equation
(There are 3 combinations in this case since D_{ij} is 3 x 3)

$\lambda = 2$ and $\epsilon_i = \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}$ work

$$2\begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & -2 \\ 0 & 1 & 0 \\ 1 & -1 & 3 \end{bmatrix}\begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}$$

$$\begin{bmatrix} 2 \\ 0 \\ -2 \end{bmatrix} = \begin{bmatrix} 0+0+2 \\ 0+0+0 \\ 1+0-3 \end{bmatrix} = \begin{bmatrix} 2 \\ 0 \\ -2 \end{bmatrix}$$

as do

$\lambda = 1,1$ and $\epsilon_i = \begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} 0 \\ 2 \\ 1 \end{bmatrix}$

Phonon band structures

Lattice Dynamics

1. Express u_i^α as a Fourier Series (the Fourier coefficients "c_N" are a bit more complicated here)

$$u_i^\alpha = \frac{1}{\sqrt{m_\alpha}} \sum_{\mathbf{k}} A_{\mathbf{k}} \epsilon_{i,\mathbf{k}}^\alpha e^{\mathrm{i}(\mathbf{k}\cdot\mathbf{R}_\alpha - \omega t)}.$$

2. Solve equation of motion ($-\Phi x = ma$)

$$-\sum_{j\beta} \Phi_{ij}^{\alpha\beta} u_j^\beta = m^\alpha \ddot{u}_i^\alpha$$

2a. In solving we find its convenient to define the **Dynamical Matrix**

$$\mathbf{\Phi}_{ij}^{\alpha\beta}(\mathbf{k}) = \frac{\Phi_{ij}^{\alpha\beta}}{\sqrt{m_\alpha m_\beta}} e^{\mathrm{i}\mathbf{k}\cdot\mathbf{R}_\beta},$$

2b. Phonon 'eigenstates' are the solutions you get when you diagonalize the Dynamical Matrix

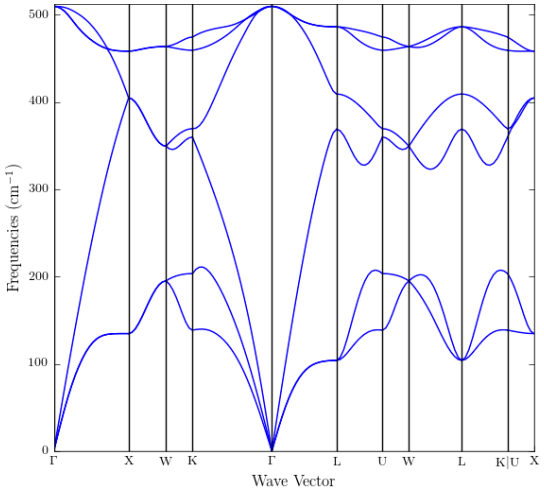
$$\omega^2(\mathbf{k}s)\epsilon_i^\alpha(\mathbf{k}s) = \sum_{j\beta} \mathbf{\Phi}_{ij}^{\alpha\beta}(\mathbf{k})\epsilon_j^\beta(\mathbf{k}s).$$

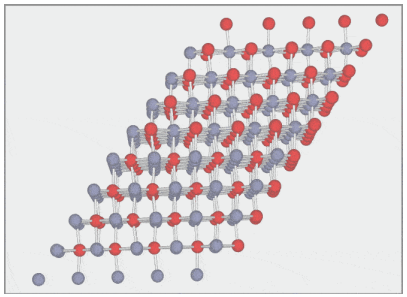
N = # of atoms in unit cell $\quad s = 1, \ldots, 3N$

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

scalar $\quad 3N$ length vector $\quad 3N$ x $3N$ matrix $\quad 3N$ length vector

$3N$ distinct $\quad \omega^2 \quad$ and $\quad \epsilon_i^{\alpha} \quad$ solutions





Lattice dynamics quiz

N: number of atoms in the unit cell

1. Define interatomic force constants (IFCs).
2. How many IFCs are there?
3. Define the Dynamical Matrix.
4. What is its dimensions?
5. Define an eigenstate.
6. How many eigenstates are there at a given k-point?
7. Define an eigenvector.
8. What is its dimensions?
9. Define an eigenvalue
10. What is its 'dimensions'?

a) 3N x 3N
b) The frequency squared of the eigenstate
c) A vector denoting the atomic displacements in each cartesian direction of each atom in the unit cell (mode shape)
d) An eigenvalue/eigenvector set which diagonalizes the dynamical matrix
e) A matrix governing the dynamic (vibrational) properties of crystals
f) Ideally, you would have an infinite number.
g) The spring constants between all atoms in the crystal
h) 3N
i) It's a vector of length 3N (3N x 1)
j) It's a scalar (so 1 x 1?)

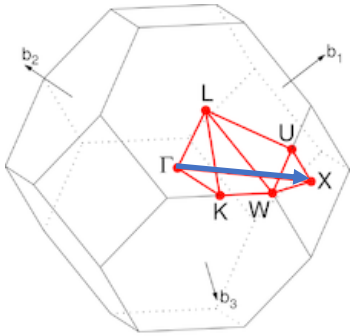
key: 1g, 2f, 3e, 4a, 5d, 6g, 7c, 8i, 9b, 10j

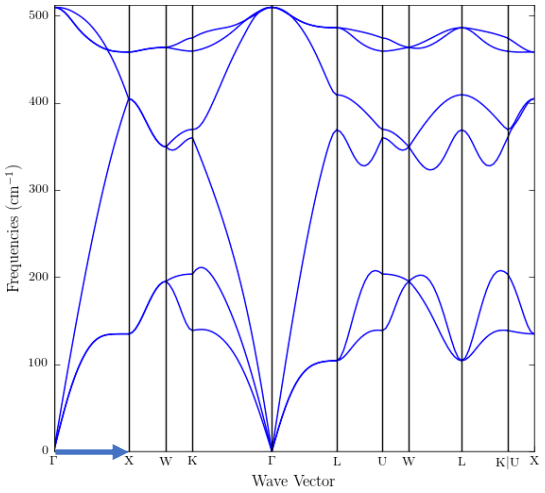
Phonon band structures In practice

Find solutions (diagonalize the Dynamical Matrix)

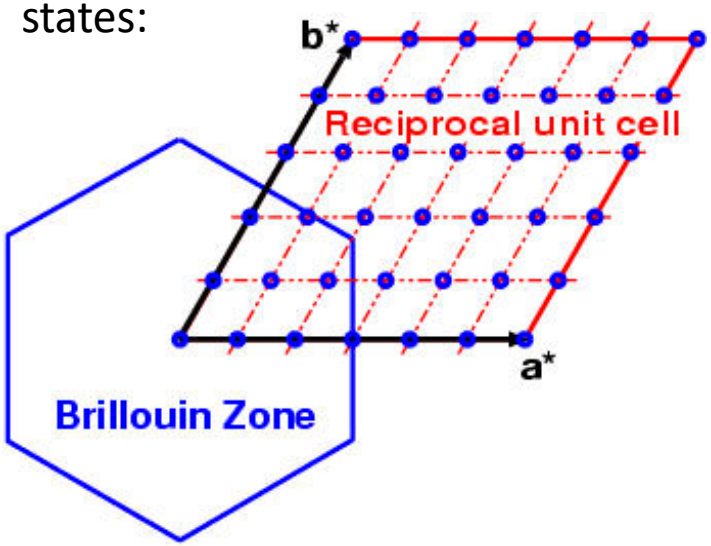
$$\omega^2(\mathbf{k}s)\epsilon_i^{\alpha}(\mathbf{k}s) = \sum_{j\beta} \mathbf{\Phi}_{ij}^{\alpha\beta}(\mathbf{k})\epsilon_j^{\beta}(\mathbf{k}s).$$

Along special directions to plot pretty band structures:





On a mesh to sample the entire Brillouin Zone, when we want transport properties of density of states:

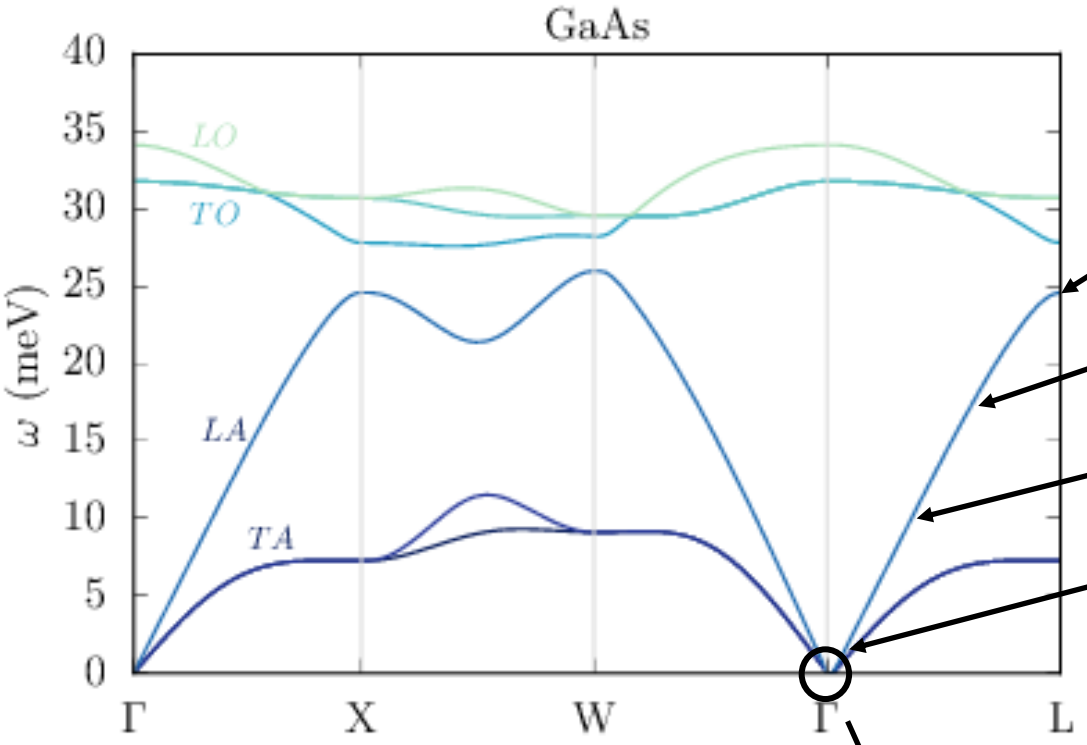


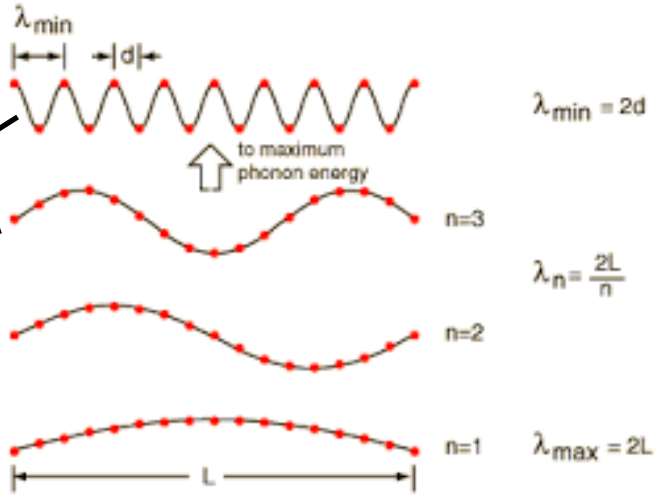
Computational suites that do this:
phonopy: https://atztogo.github.io/phonopy/
almaBTE: http://www.almabte.eu/
shengBTE: http://www.shengbte.org/

Reading a phonon band structure

3 **acoustic modes** ($\omega \to 0$ at Γ)
$3n-3$ **optical modes** ($\omega \neq 0$ at Γ)

n is the number of atoms in the unit cell





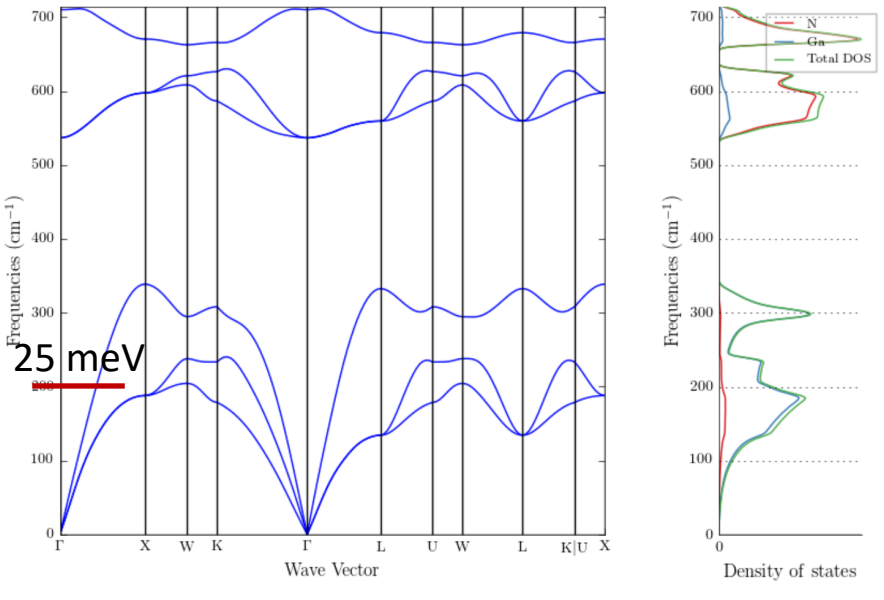
$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & c_{44} \end{pmatrix} \cdot \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ 2\varepsilon_{yz} \\ 2\varepsilon_{xz} \\ 2\varepsilon_{xy} \end{pmatrix}.$$

Ultrasound, speed of sound,
Elastic tensor and moduli,
Bulk modulus, Young's modulus,
etc.

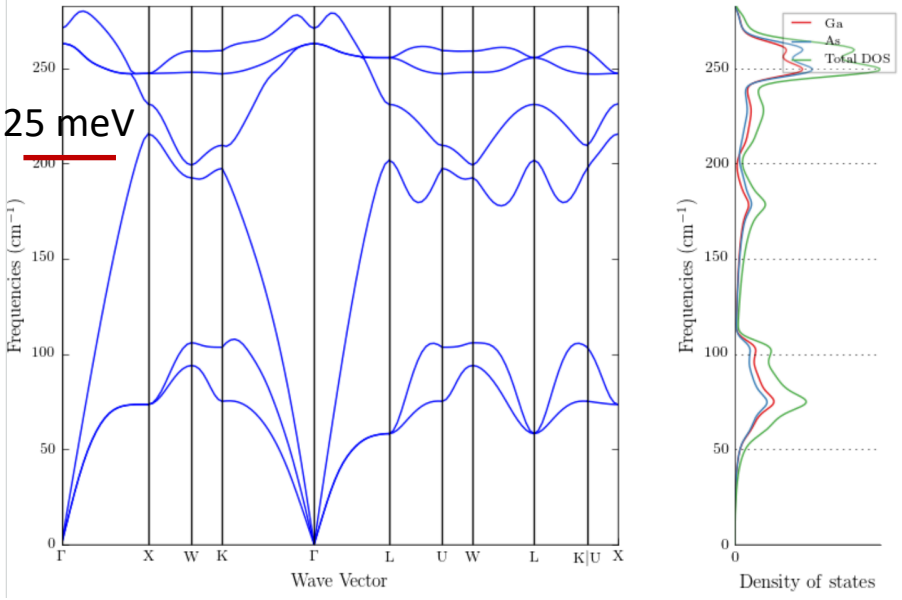
Reading a phonon band structure

Effect of atomic mass and the phonon band gap.

Cubic GaN: N mass = 14 amu



Cubic GaAs: As mass = 75 amu



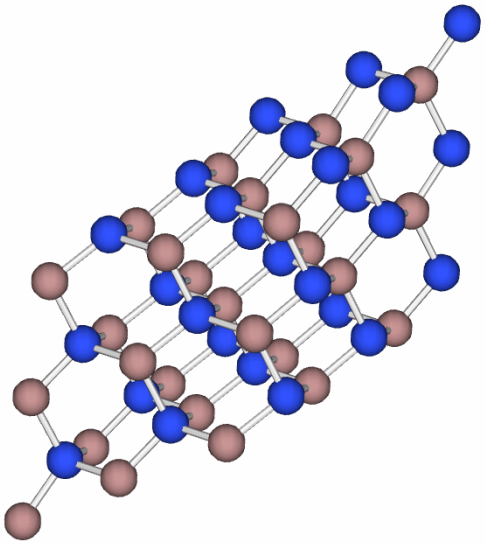
Units for vertical (energy) axis:

- some use 'angular' frequency $\omega = 2\pi f$ [rad THz] (they won't show the rad though)
- some use 'ordinal' frequency f [THz]
- some use frequency in [cm^{-1}]
- some use energy $E = \hbar\omega$ [meV]

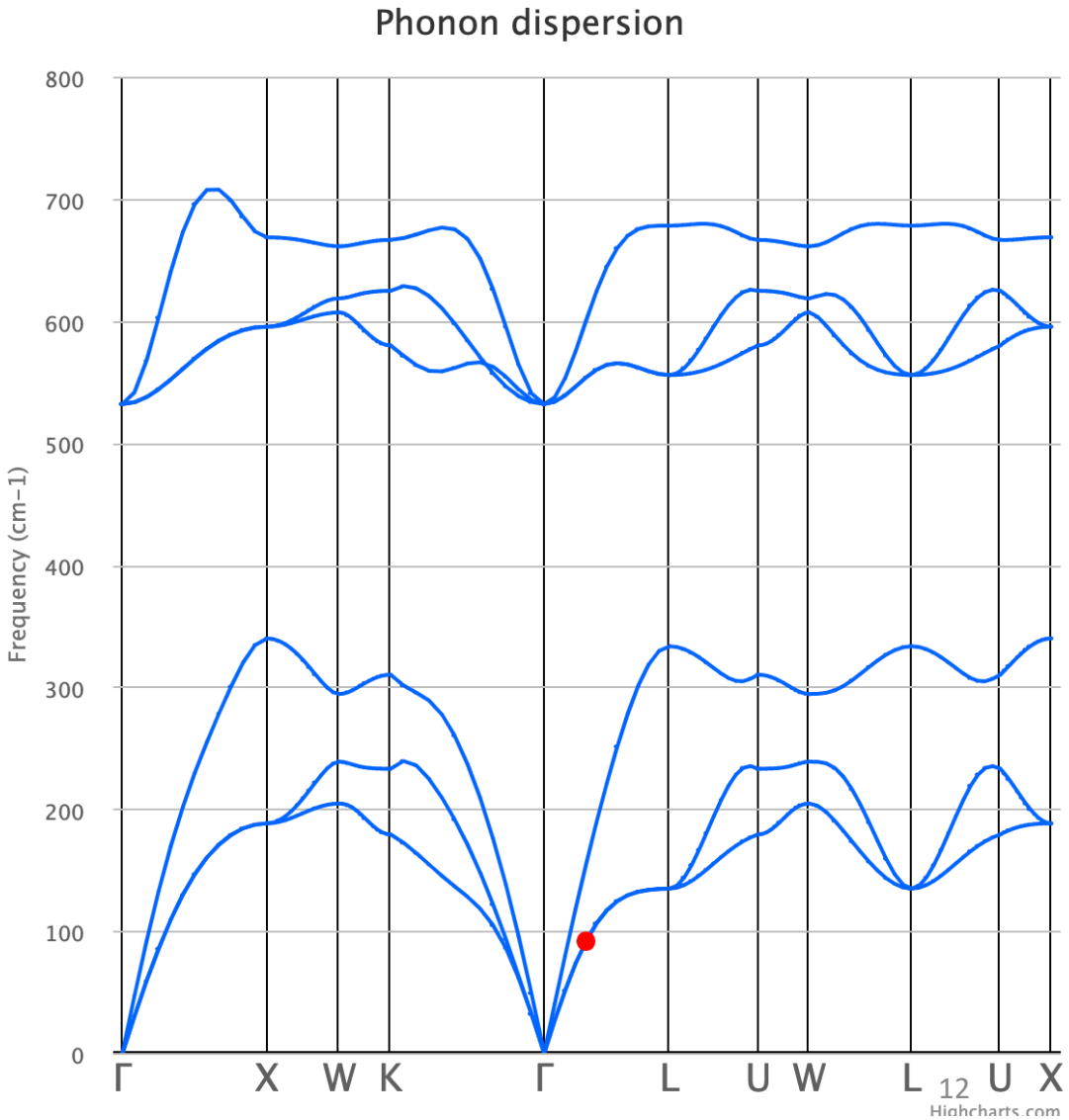
(f)	(f)	(ω)	(E)
$200\ \mathrm{cm}^{-1}$	≈ 6 THz	≈ 40 THz	≈ 25 meV

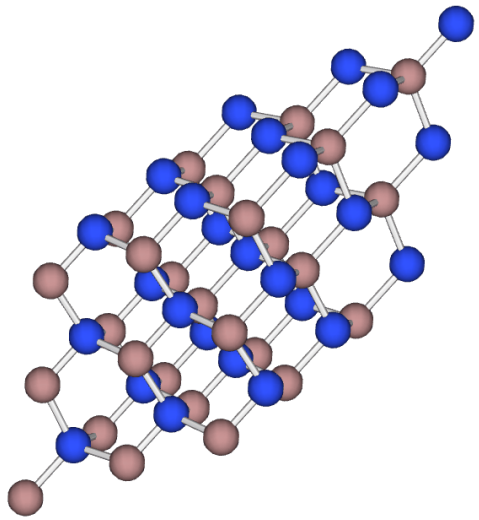
Ga: Brown
N: Blue

https://henriquemiranda.github.io/phononwebsite/phonon.html



magnitude of atomic displacement dramatically exaggerated





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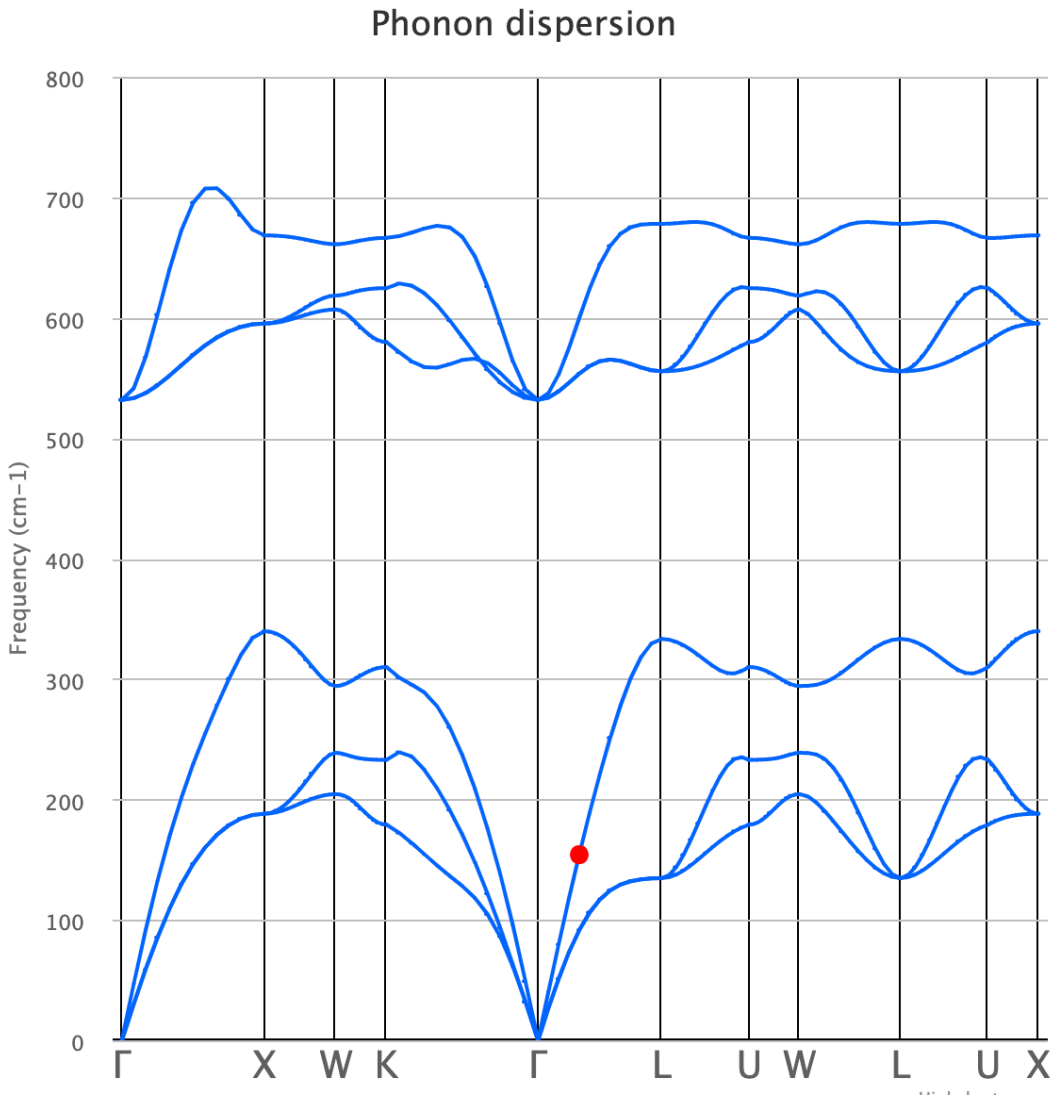
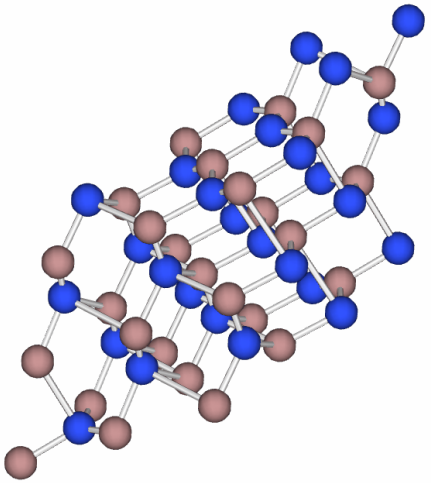
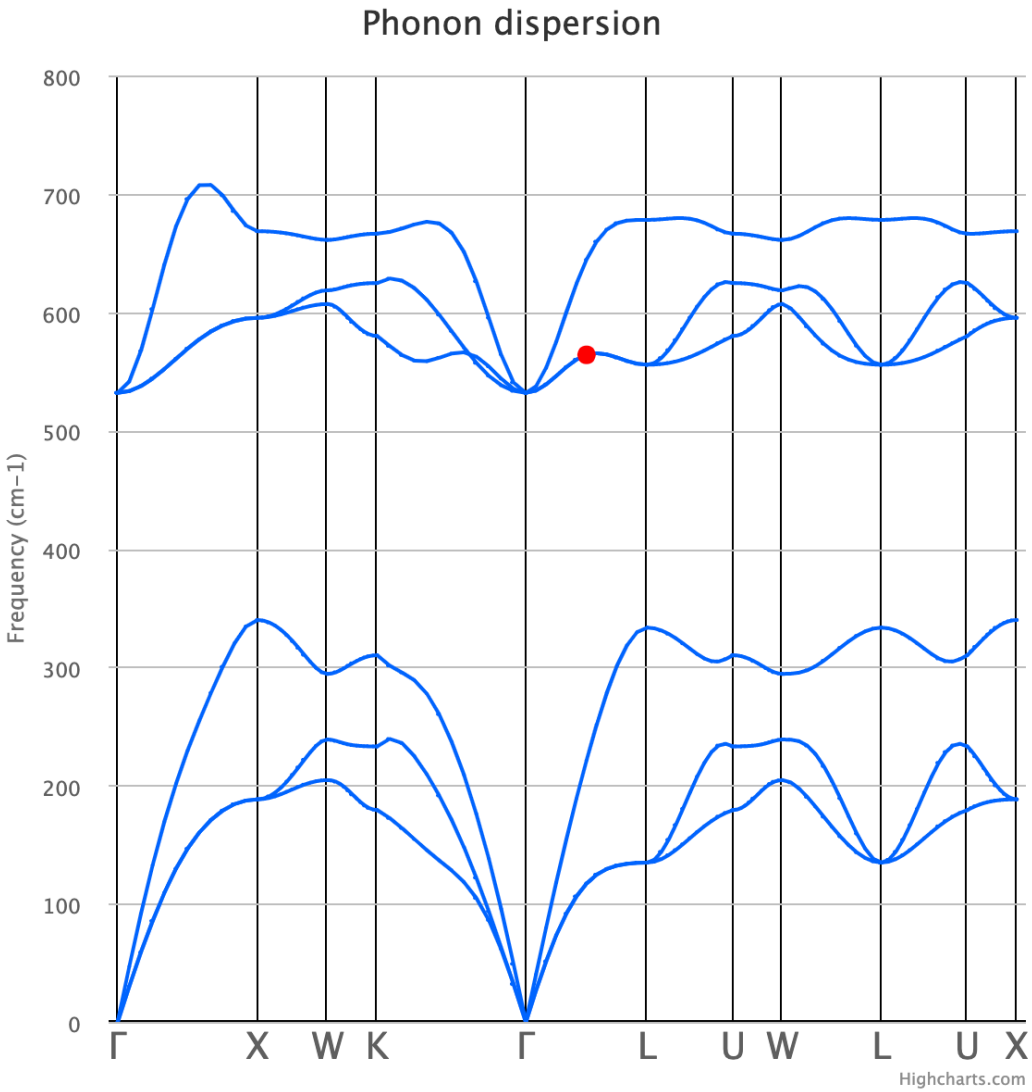


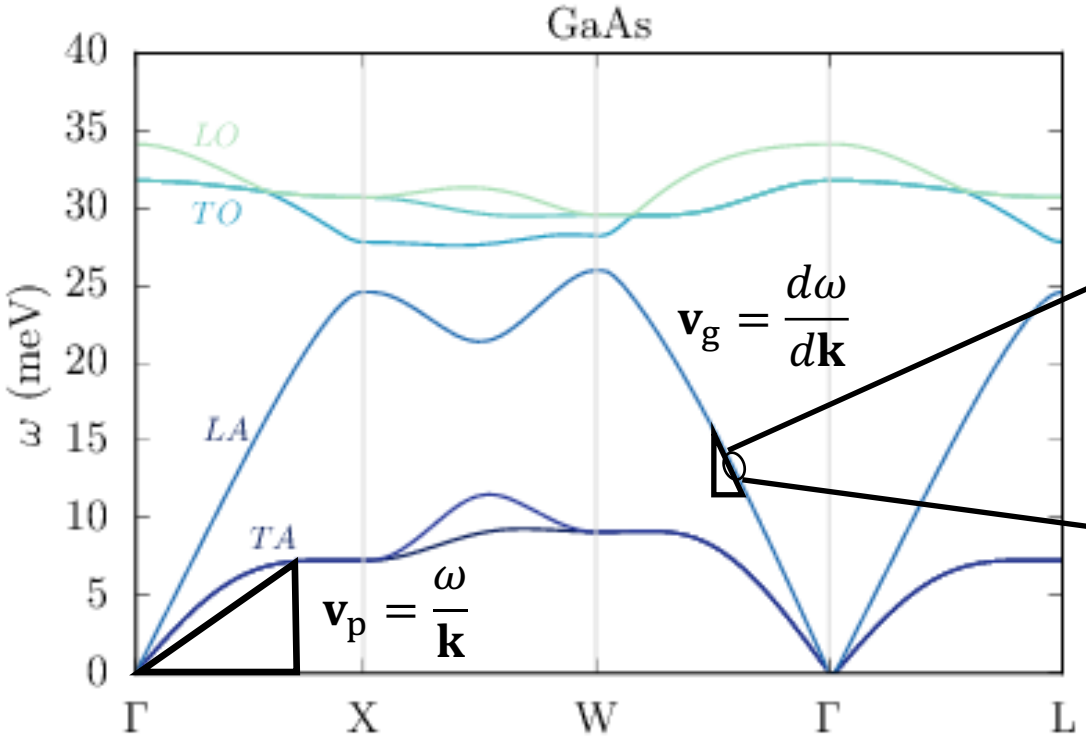


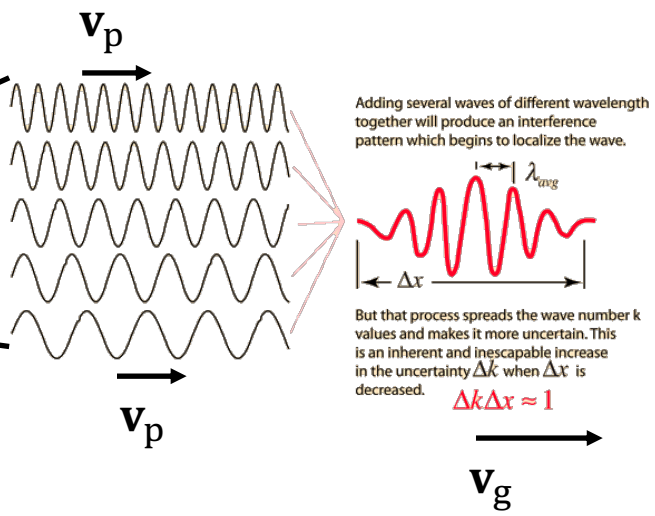
magnitude of atomic displacement
dramatically exaggerated



Reading a phonon band structure

Group velocity and phase velocity

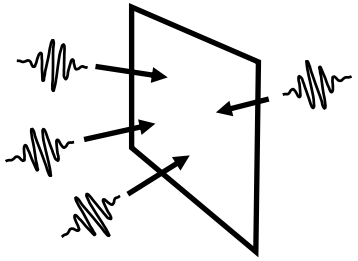




$$\text{flux} = \text{energy density} \times \text{velocity} \times \text{number} = \frac{\text{Energy}}{\text{Area} \times \text{time}}$$

Phonon-gas model for heat flux:

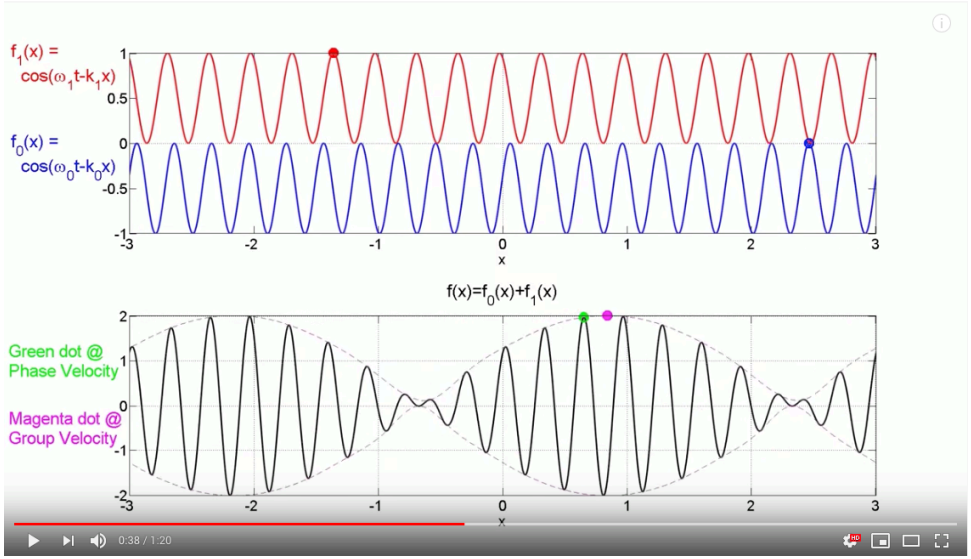
$$j^i = \frac{1}{V} \sum_{\mathbf{k}s} \hbar\omega(\mathbf{k}s)\, v_\mathrm{g}^i\, n(\mathbf{k}s)$$



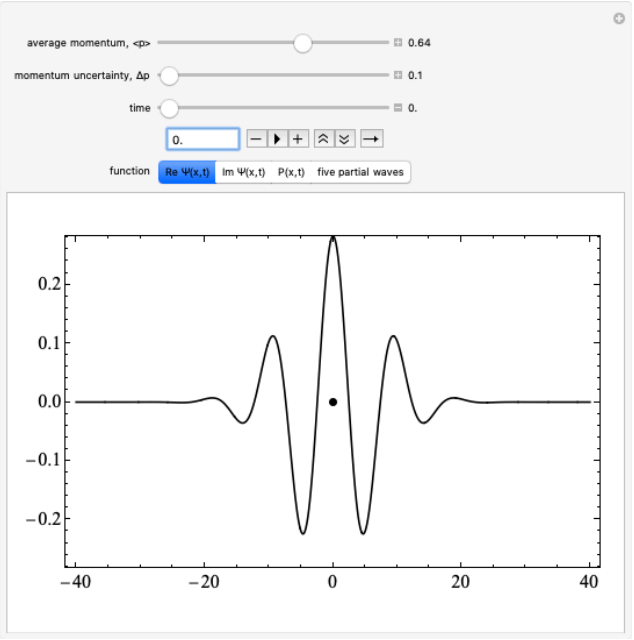
Wave packets

Group and phase velocity

https://www.youtube.com/watch?v=tlM9vq-bepA



https://demonstrations.wolfram.com/WavepacketForAFreeParticle/

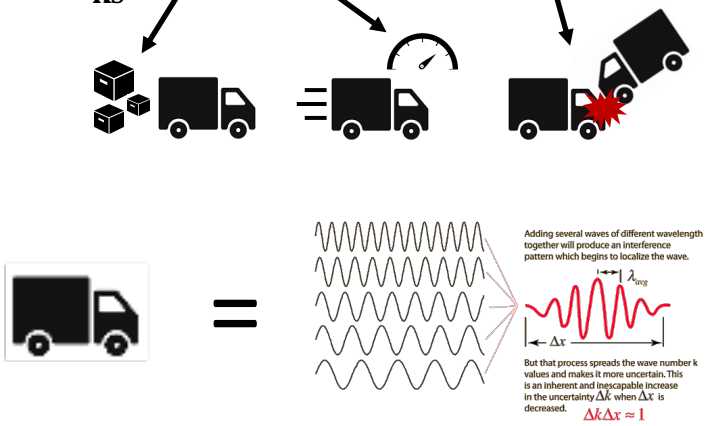


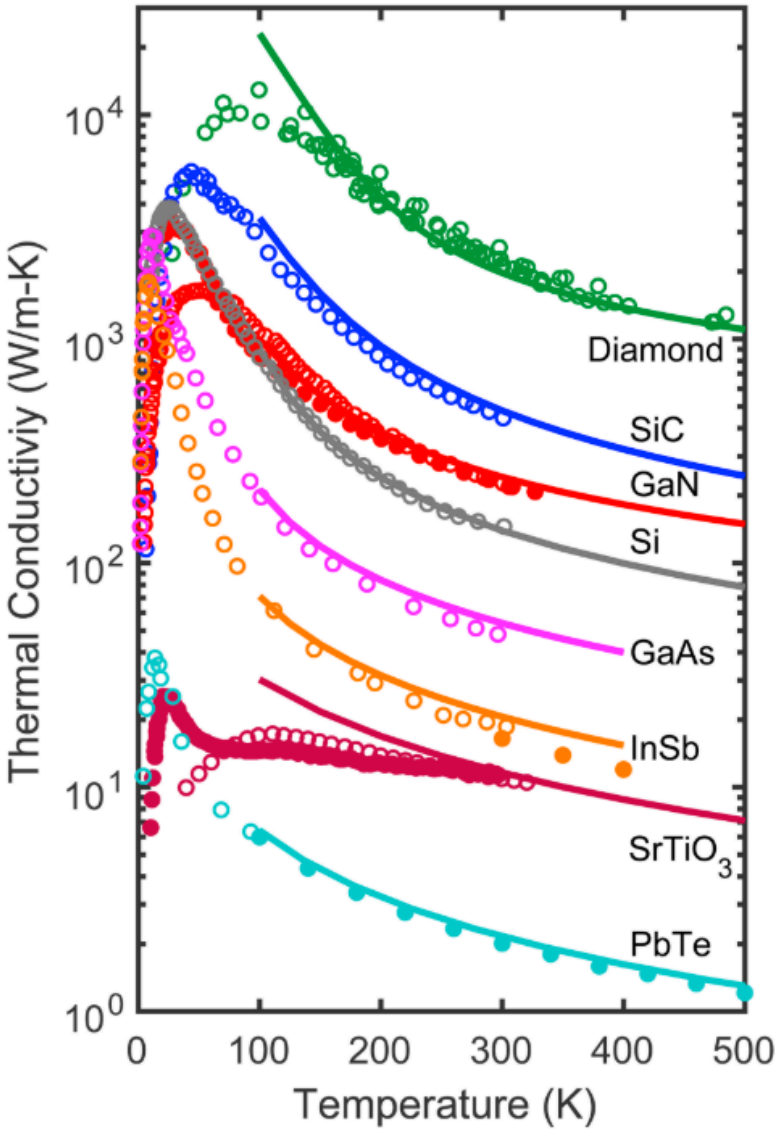
The phonon gas model

Lines are all:

- DFT obtained interatomic force constants ($\Phi_{ij}^{\alpha\beta}$ and $\Phi_{ijk}^{\alpha\beta\gamma}$)
- Phonon properties from lattice dynamics
- Thermal conductivity from the phonon gas model
- First principles simulation, no adjustable parameters… but there are choices

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





McGaughey, A. J. H., Jain, A. & Kim, H. Phonon properties and thermal conductivity from first principles, lattice dynamics, and the Boltzmann transport equation. *J. Appl. Phys.* **125**, 011101 (2019).

The phonon gas model

Mode specific treatment:
(computational approach)

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

Spectral treatment:
(Callaway modeling)

$$\kappa = \frac{1}{3}\int_{0}^{\infty} C(\omega)\, v_{\mathrm{g}}(\omega)^2\, \tau(\omega)\; d\omega$$

Where we define:

$$C(\omega) = \sum_{\mathbf{k}s} C(\mathbf{k}s)\delta(\omega - \omega(\mathbf{k}s))$$

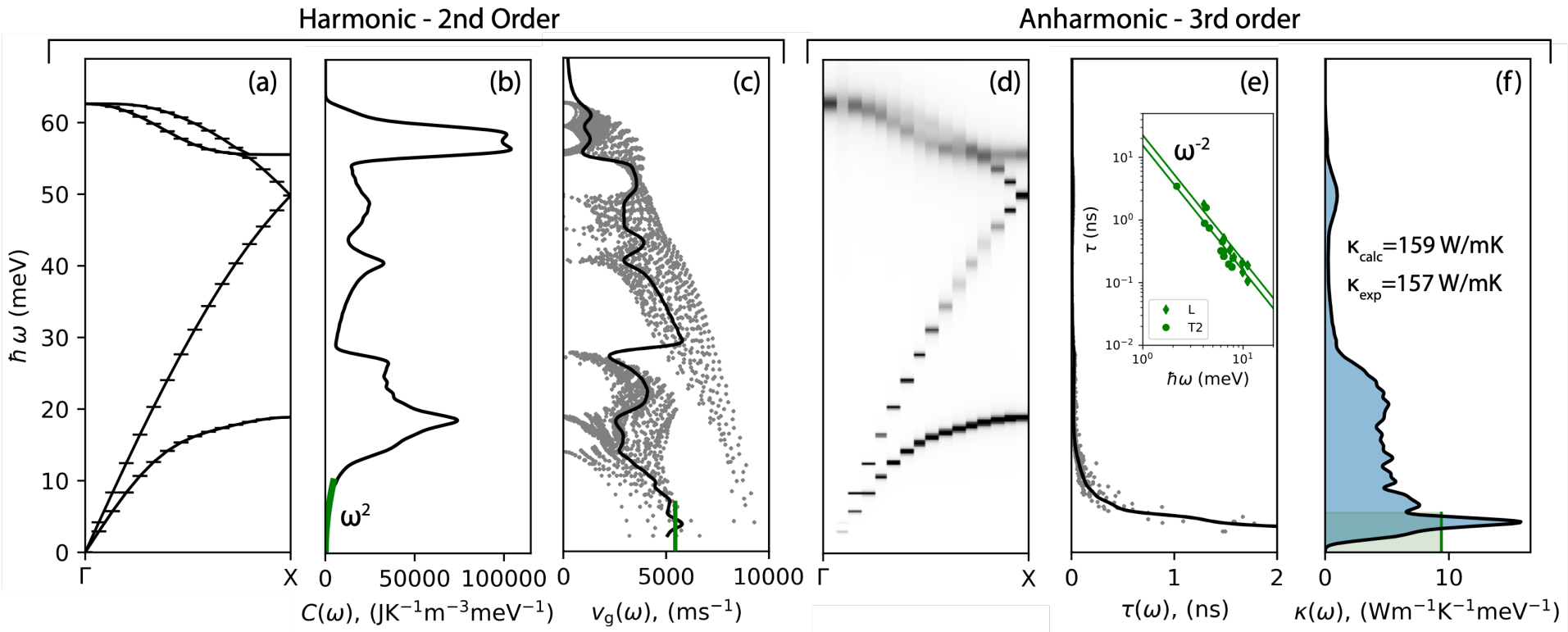
$$v_{\mathrm{g}}(\omega) = \frac{\sum_{\mathbf{k}s} v_{\mathrm{g}}(\mathbf{k}s)\, \delta(\omega - \omega(\mathbf{k}s))}{\sum_{\mathbf{k}s} \delta(\omega - \omega(\mathbf{k}s))}$$

$$\tau(\omega) = \frac{\sum_{\mathbf{k}s} \tau(\mathbf{k}s)\, \delta(\omega - \omega(\mathbf{k}s))}{\sum_{\mathbf{k}s} \delta(\omega - \omega(\mathbf{k}s))}$$

The spectral model can be thought as containing the mode specific properties “under the hood”.

Often, in real (defective) materials, we don’t have access to full mode specific properties, and therefore use the spectral treatement.

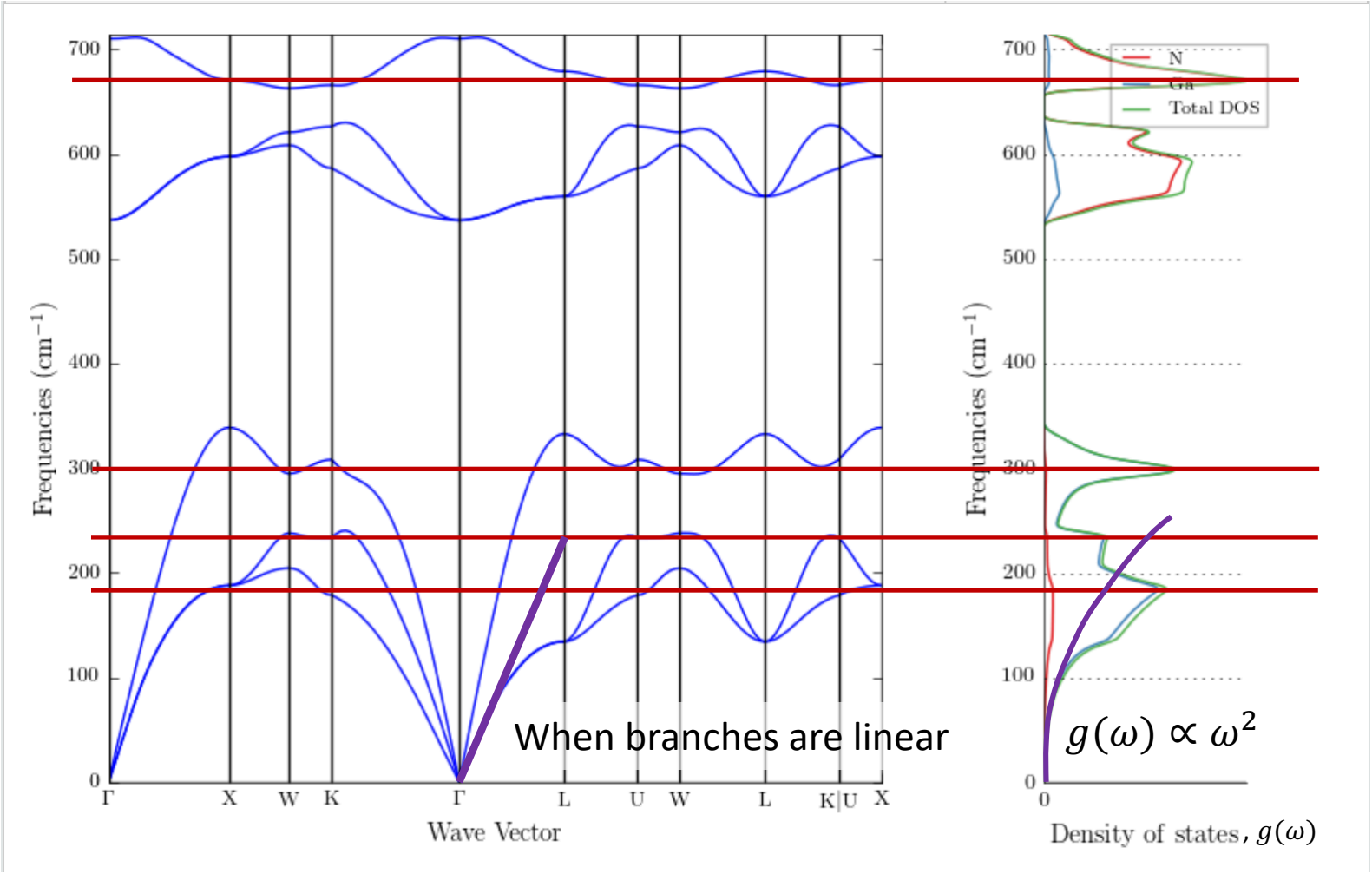
The phonon gas model



Density of states

How many states are at given energy?

Cubic GaN



where group velocity goes to zero at the BZ edge = “Van Hove singularity” = peak in density of states

Density of states

Probably the most common derivation.

We will just examine one branch.

N: number of states
V: crystal volume
k: magnitude of the k-vector
$(2\pi)^3/V$: volume of k-space

$$N(\omega)\frac{(2\pi)^3}{V} = \frac{4}{3}\pi\, k^3$$

$n(\omega) = \frac{N(\omega)}{V}$: number of states per volume

$g(\omega) = \frac{dn(\omega)}{d\omega}$: a definition of the phonon density of states

assert a Debye model for phonon dispersion relation (band structure): $\omega = v_s k$

$$n(\omega) = \frac{1}{6\pi^2}\frac{\omega^3}{v_s^3} \qquad g(\omega) = \frac{dn(\omega)}{d\omega} = \frac{1}{2\pi^2}\frac{\omega^2}{v_s^3}$$

Notice:
This derivation does not predict Van Hove singularities

Density of states

Another derivation which is a more informative and will introduce us to some math which is important in scattering theory

Required math:

Converting sums to integrals:

$$\frac{1}{N_{\mathbf{k}}}\sum_{\mathbf{k}} f(\mathbf{k}) \rightarrow \frac{V}{(2\pi)^3}\iiint f(\mathbf{k})dk_x dk_y dk_z$$

$$\frac{1}{N_{\mathbf{k}}}\sum_{\mathbf{k}} f(\mathbf{k}) \rightarrow \frac{V}{(2\pi)^3}\int f(\mathbf{k})d^3\mathbf{k}$$

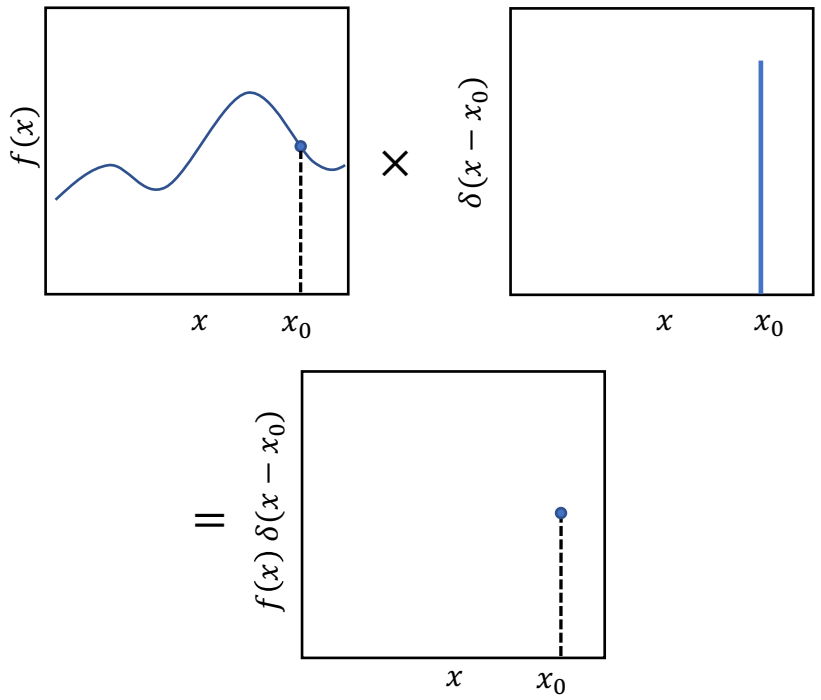
$N_{\mathbf{k}}$: number of k-vectors considered in the sum
V: is the volume of the unit cell

The sum introduces no units.
The integral comes with $d^3\mathbf{k}$, which has a value of $(2\pi)^3/V$ after integrating over the FBZ.

Instructive exercise:
Pretend $f(\mathbf{k}) = 1$ and compute both.
Hint: $\int d^3\mathbf{k} = (2\pi)^3/V$

Integrating over delta functions:

$$\int f(x)\,\delta(x - x_0)\,dx = f(x_0)$$

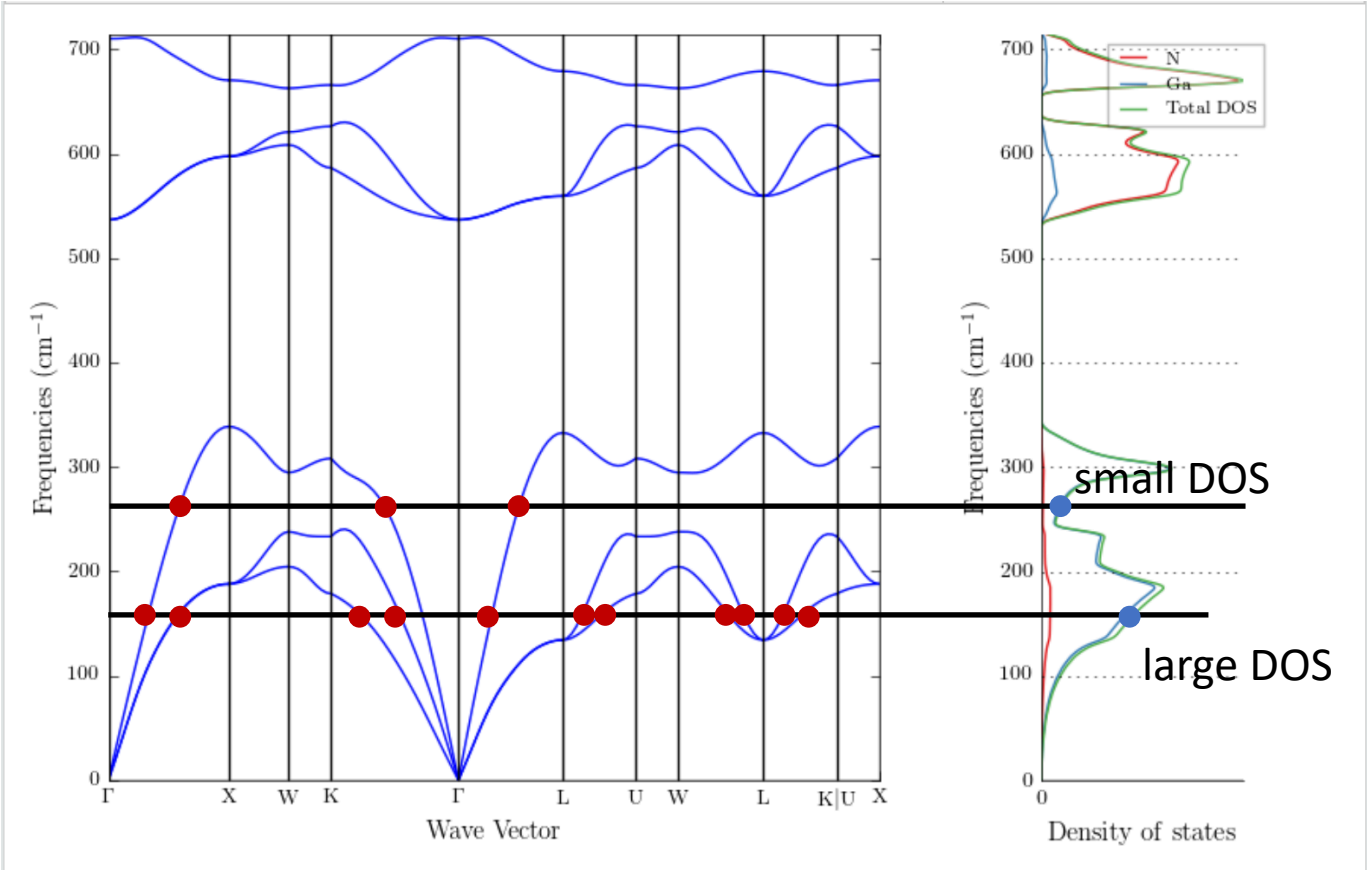


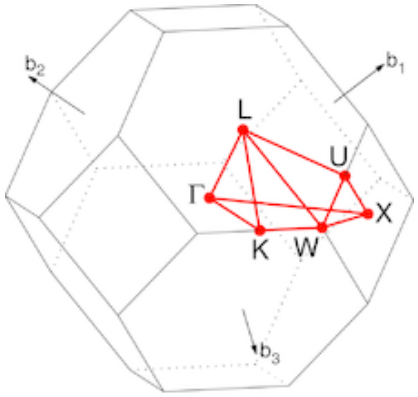
Note the units:
if x (and therefore dx) has units of $[\mathrm{m}]$
then $\delta(x)$ has units of $\left[\frac{1}{\mathrm{m}}\right]$

Density of states

A second definition of the density of states:

$$g(\omega) = \frac{1}{VN_{\mathbf{k}}} \sum_{\mathbf{k}s} \delta(\omega - \omega(\mathbf{k}s))$$





(1) pick a frequency/energy

(2) search through the whole FBZ and count all modes at that energy

on board

Density of states

$$g(\omega) = \frac{1}{VN_{\mathbf{k}}} \sum_{\mathbf{k}s} \delta(\omega - \omega(\mathbf{k}s))$$

For comparison we will only look at one branch, so only $s = 1$.
Therefore, we don't need the sum over s.

$$g(\omega) = \frac{1}{VN_{\mathbf{k}}} \sum_{\mathbf{k}} \delta(\omega - \omega(\mathbf{k}))$$

Convert sum to an integral

$$g(\omega) = \frac{1}{V} \frac{V}{(2\pi)^3} \int \delta\big(\omega - \omega(\mathbf{k})\big) d^3\mathbf{k}$$

Cancel V, and switch to spherical coordinates.

$$g(\omega) = \frac{1}{(2\pi)^3} \iiint_{-\infty\ 0\ 0}^{\infty\ \pi\ 2\pi} \delta\big(\omega - \omega(\mathbf{k})\big) \sin\theta\ k^2\ d\phi d\theta dk$$

on board

Density of states

$$g(\omega) = \frac{1}{(2\pi)^3} \iiint_{0\,0\,0}^{\mathbf{k}_{\max}\,\pi\,2\pi} \delta\big(\omega - \omega(\mathbf{k})\big) \sin\theta \; k^2 \, d\phi d\theta dk$$

Now we make the isotropic assumption, by saying that $\omega(\mathbf{k})$ no longer depends on the direction $\mathbf{k}$ is pointing, but only on its magnitude $\omega(k)$.

After this, we can take the integrals over θ and ϕ: $\iint \sin\theta \; d\phi \; d\theta = 4\pi$

$$g(\omega) = \frac{4\pi}{(2\pi)^3} \int_0^{k_{\max}} \delta(\omega - \omega(k)) \, k^2 dk$$

Need to convert the integral such that its over ω so we can take advantage of that δ-function. We use our definitions of group and phase velocity to do this.

$$v_{\mathrm{g}} = \frac{d\omega}{dk} \qquad v_{\mathrm{p}} = \frac{\omega}{k}$$

$$g(\omega) = \frac{1}{2\pi^2} \int_0^{\omega_{\max}} \delta(\omega - \omega(k)) \frac{\omega^2}{v_{\mathrm{p}}^2} \frac{d\omega}{v_{\mathrm{g}}}$$

Finally, we take the integral.

$$g(\omega) = \frac{1}{2\pi^2} \frac{\omega^2}{v_{\mathrm{p}}^2 v_{\mathrm{g}}}$$

on board

Density of states

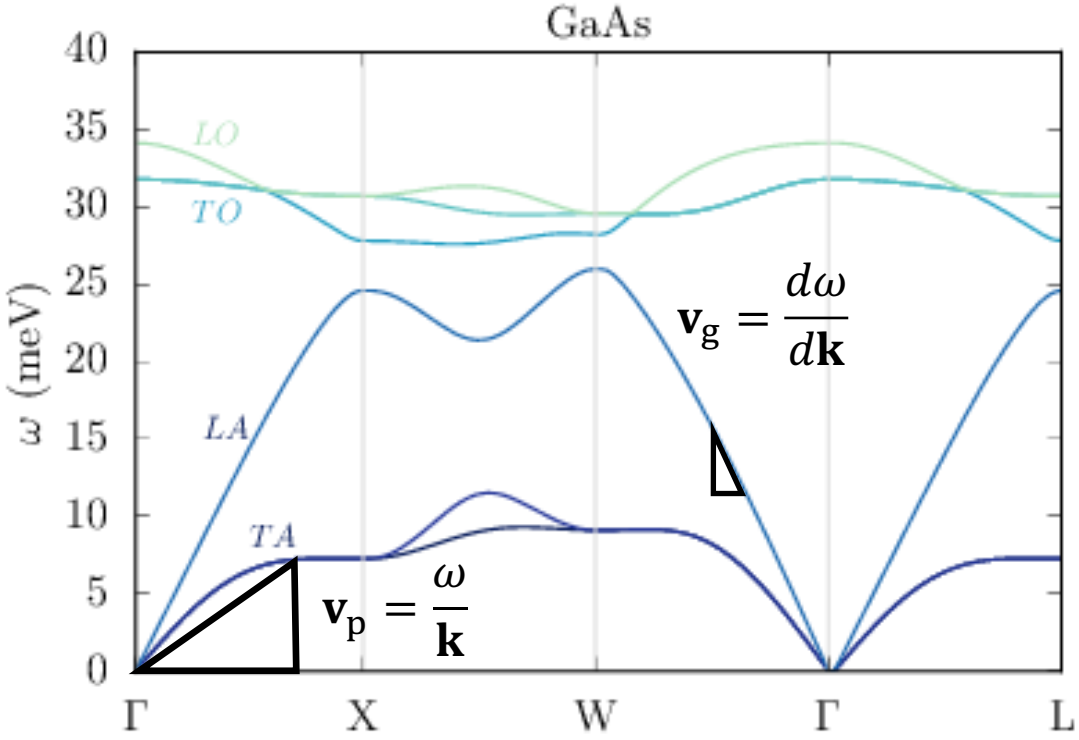
For a linear dispersion $v_g = v_p = v_s$

$$g(\omega) = \frac{1}{2\pi^2}\frac{\omega^2}{v_s^3}$$ (same as first derivation)

$$g(\omega) = \frac{1}{2\pi^2}\frac{\omega^2}{v_p^2 v_g}$$

Currently we are only looking at only one branch. Sometimes we approximate all three acoustic branches as one branch with average group and phase velocities.

$$g(\omega) \cong \frac{3}{2\pi^2}\frac{\omega^2}{v_p^2 v_g}$$



keep in mind v_g and v_p can change with ω

$$g(\omega) = \frac{3}{2\pi^2}\frac{\omega^2}{v_p(\omega)^2 v_g(\omega)}$$

When $v_g(\omega) = 0$, $g(\omega) = \infty$ and that is our Van Hove singularity