

Nanoscale thermal transport

Lecture 1

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

Two rules

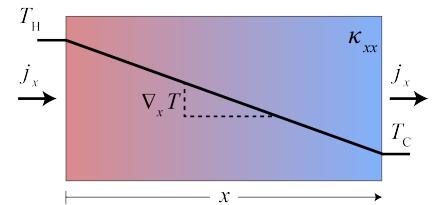
1. Use your imagination

- You should be actively building a picture in your head.
- I'll do my best to provide good pictures, but the pictures will fall short.

2. Don't be afraid of the math

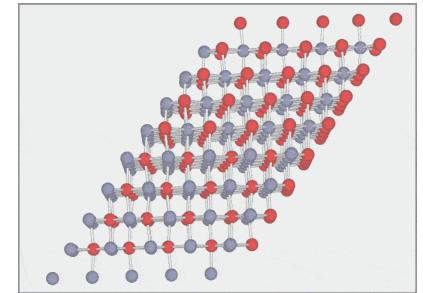
- It's (almost) impossible to know every bit of math that is thrown at you.
- You will need to learn math as you go.
- All math can be learned, it just might take some patience.

1. Define thermal conductivity, κ

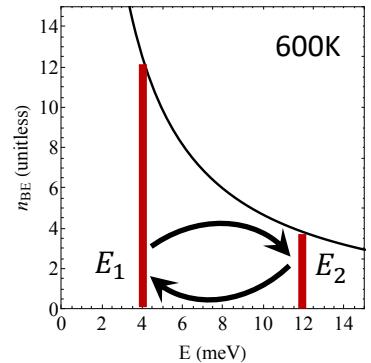


2. Overview of heat conduction mechanisms

- electrons
- bipolar
- atomic vibrations

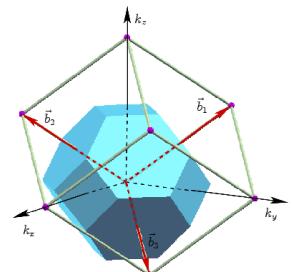


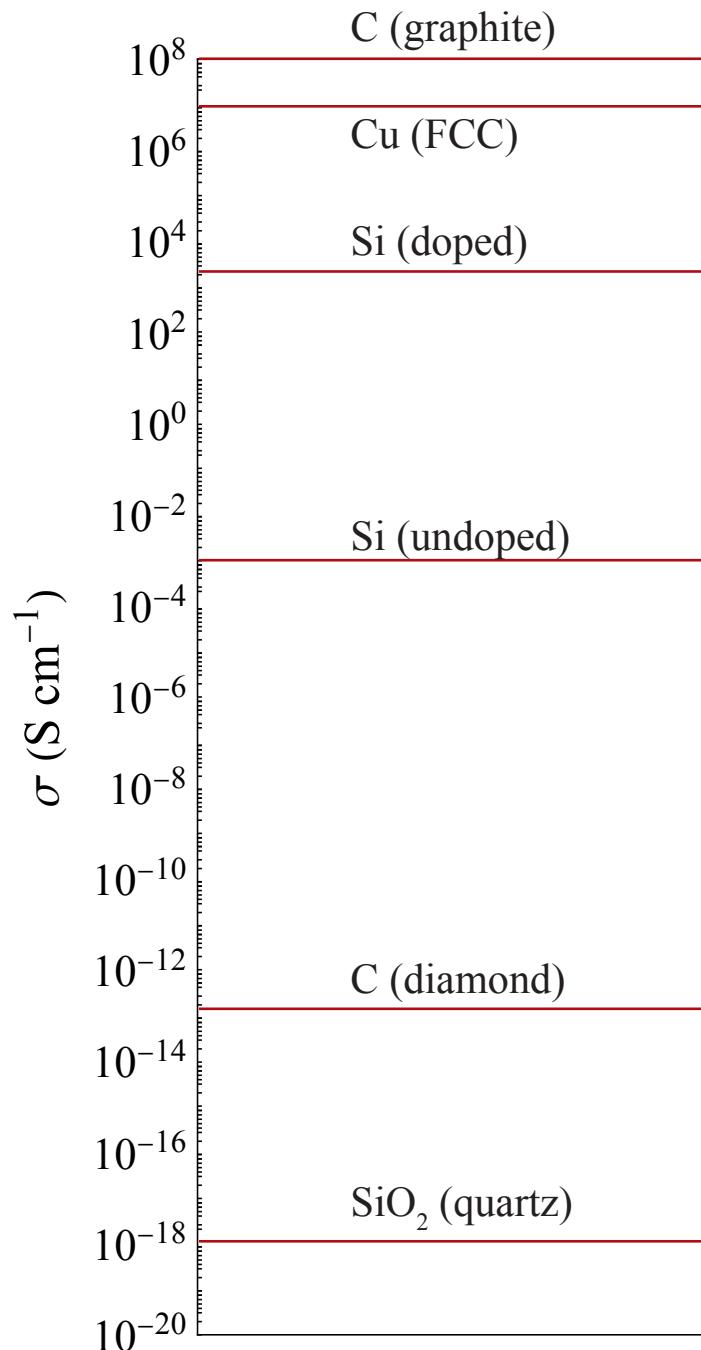
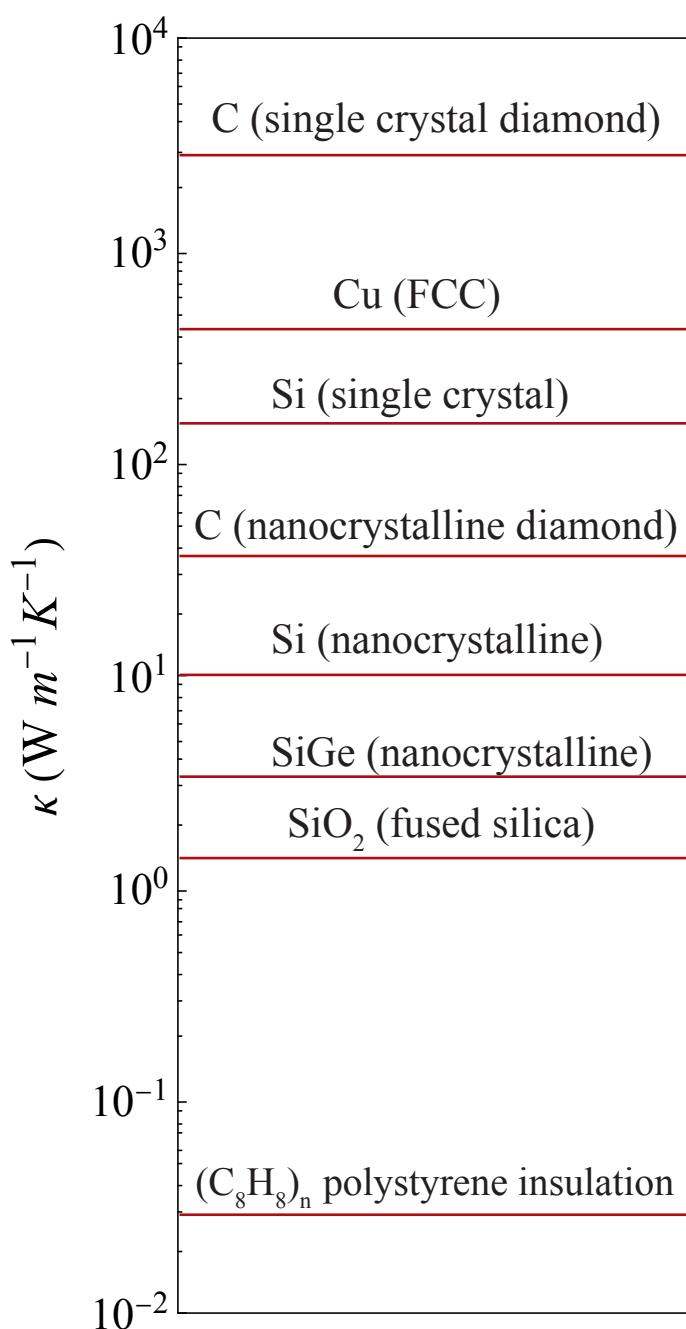
3. Define (and understand) temperature



4. Define (and understand) reciprocal space

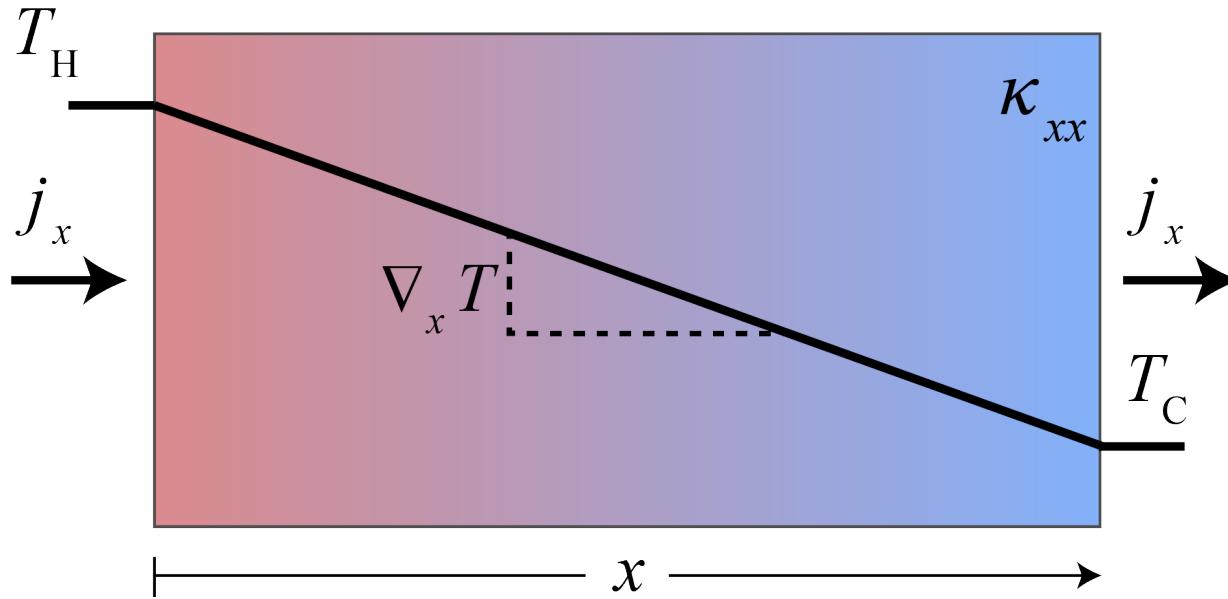
- First Brillouin Zone
- Band structures





Fourier's Law

$$j = -\kappa \nabla T$$



Let's be explicit:

$$j_i : \text{heat flux (3x1 vector)} \left[\frac{\text{J}}{\text{s m}^2} \right] = \left[\frac{\text{W}}{\text{m}^2} \right]$$

vector notation: $\mathbf{j} = -\bar{\kappa} \nabla T$

$$\kappa_{ij} : \text{thermal conductivity (3x3 matrix)} \left[\frac{\text{W}}{\text{mK}} \right]$$

Einstein notation: $j_i = -\kappa_{ij} \nabla_j T$

$$\nabla_i T : \text{gradient of temperature (3x1 vector)} \left[\frac{\text{K}}{\text{m}} \right]$$

For a cubic material κ is isotropic, even though elastic properties, speed of sound, and phonon dispersion is not!

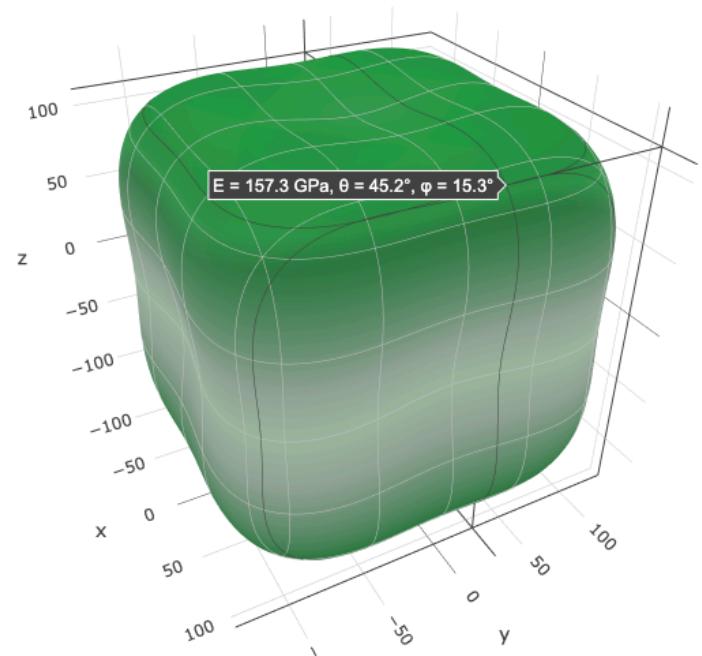
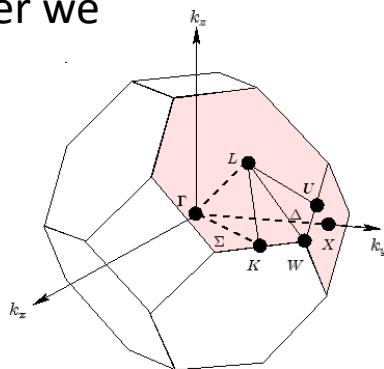
$$\kappa_{ij} = \begin{bmatrix} \kappa & 0 & 0 \\ 0 & \kappa & 0 \\ 0 & 0 & \kappa \end{bmatrix} \rightarrow \kappa$$

Young's Modulus contour of Si
from [Materials Project](#)

Why?

κ is the result of an integration over the first Brillouin zone (FBZ)

This will make more sense after we cover reciprocal space.



Einstein (index) notation

Rule: sum over repeated indices in a term, sometimes called a ‘dummy’ index

$$j_i = -\kappa_{ij} \nabla_j T = -(\kappa_{ix} \nabla_x T + \kappa_{iy} \nabla_y T + \kappa_{iz} \nabla_z T)$$

$$\mathbf{j} = -\bar{\kappa} \nabla T \quad \rightarrow \quad \begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = - \begin{bmatrix} \kappa_{xx} & \kappa_{xy} & \kappa_{xz} \\ \kappa_{yx} & \kappa_{yy} & \kappa_{yz} \\ \kappa_{zx} & \kappa_{yx} & \kappa_{zz} \end{bmatrix} \begin{bmatrix} \nabla_x T \\ \nabla_y T \\ \nabla_z T \end{bmatrix}$$

Why worry about Einstein notation?

Einstein notation makes tensor math much cleaner and is really the best (only?) way to do tensor math in dimensions higher than 3 (tensors rank 4 and up).

Elastic properties (involves 4th rank tensors) ↔ Thermal properties

What conducts heat?

$$\kappa = \kappa_{\text{vib}} + \kappa_e + \kappa_{\text{BP}} + \dots$$

Electrons (Wiedemann-Franz Law)

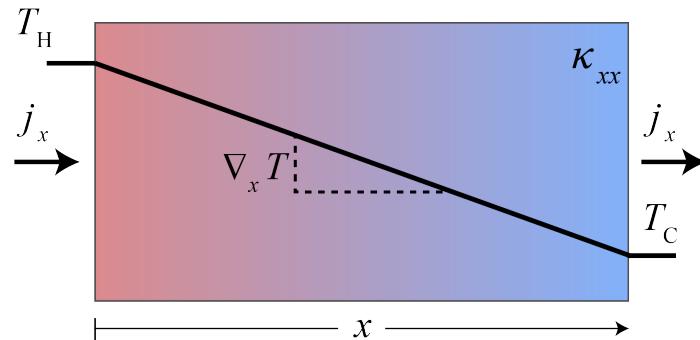
$$\kappa_e = L\sigma T$$

σ : electrical conductivity $\left[\frac{1}{\Omega\text{m}}\right]$

L : Lorenz number $\left[\frac{W\Omega}{K^2}\right]$

For metals and degenerate semiconductors

$$L = 2.45 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$$



- Depends on electronic band structure
- Varies in semiconductors, but typically no more than 20%
- This value held for doped, metallic like conducting polymer [PEDOT:PSS](#)
- Weird things happening in VO_2

Note: (worth remembering)

Band modeling for better estimation of L in semiconductors, and a simple formula for it:

[Kim, H.-S., et al. Characterization of Lorenz number with Seebeck coefficient measurement. *APL Mater.* **3**, 041506 \(2015\).](#)

What conducts heat?

$$\kappa = \kappa_{\text{vib}} + \kappa_e + \kappa_{\text{BP}} + \dots$$

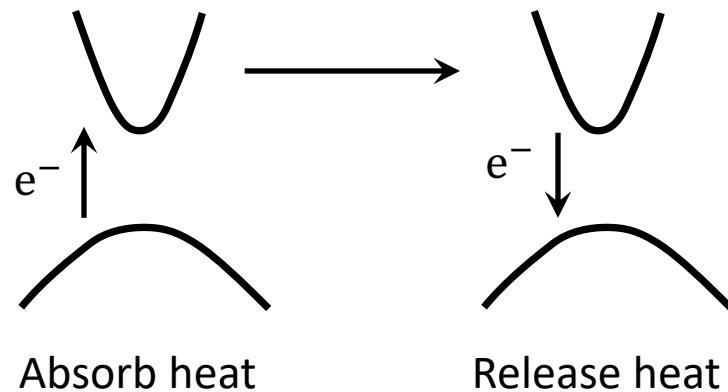
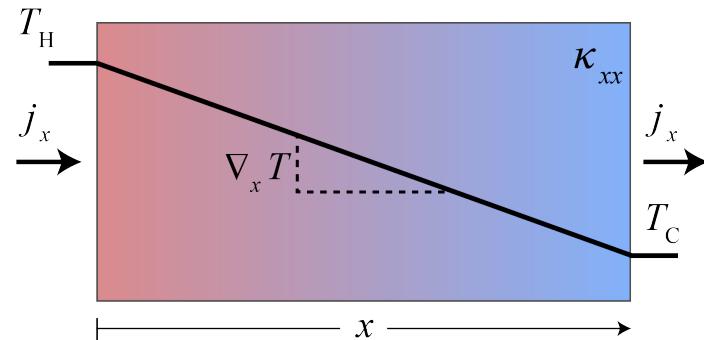
Bipolar conduction:

$$\kappa_{\text{BP}} = \frac{\sigma_e \sigma_h}{\sigma_e + \sigma_h} (S_e - S_h)^2 T$$

in the intrinsic regime

$$\kappa_{\text{BP}} \propto \exp\left(-\frac{E_g}{2k_B T}\right)$$

- Occurs when electronic conduction is happening in both conduction and valence bands

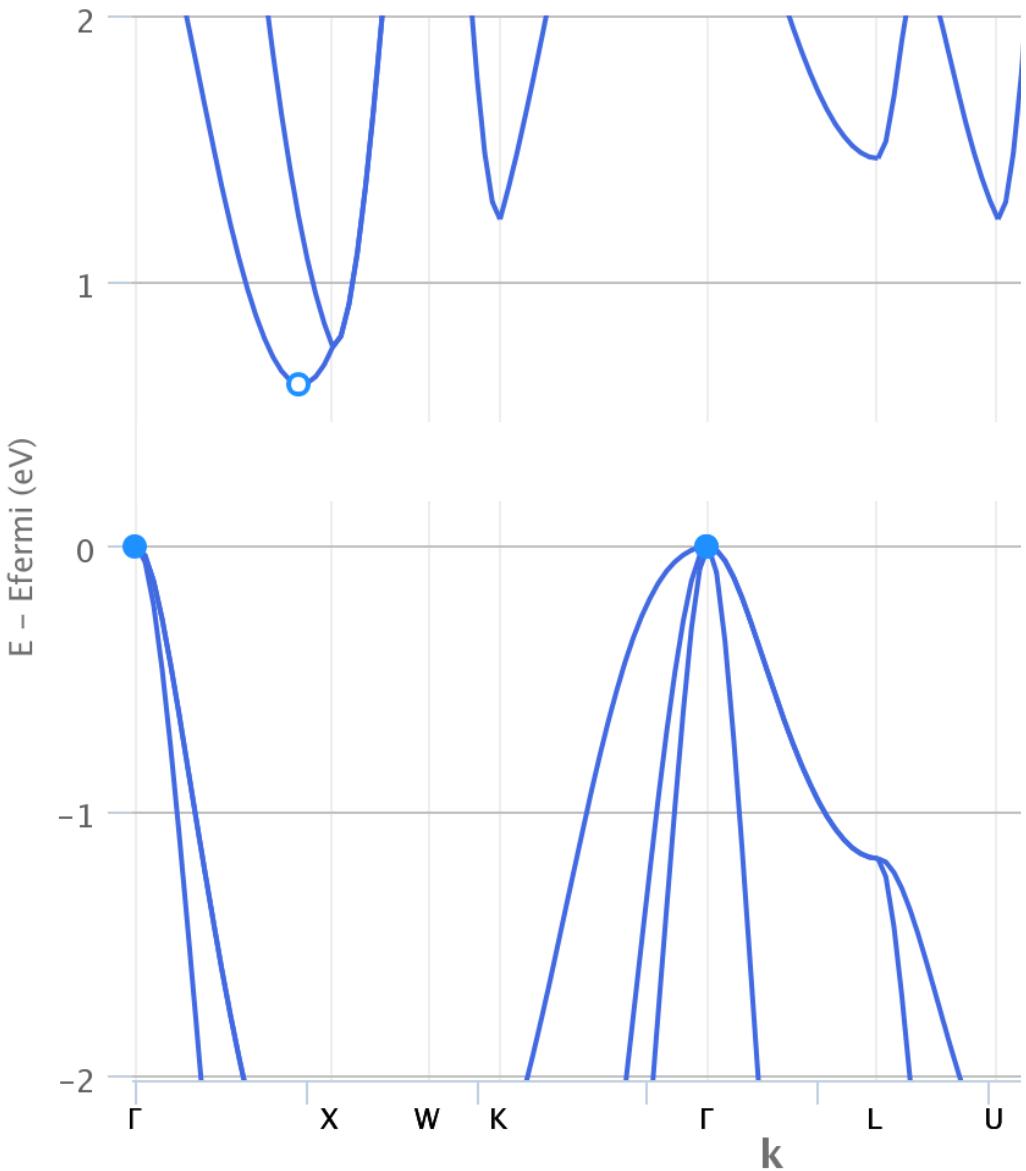
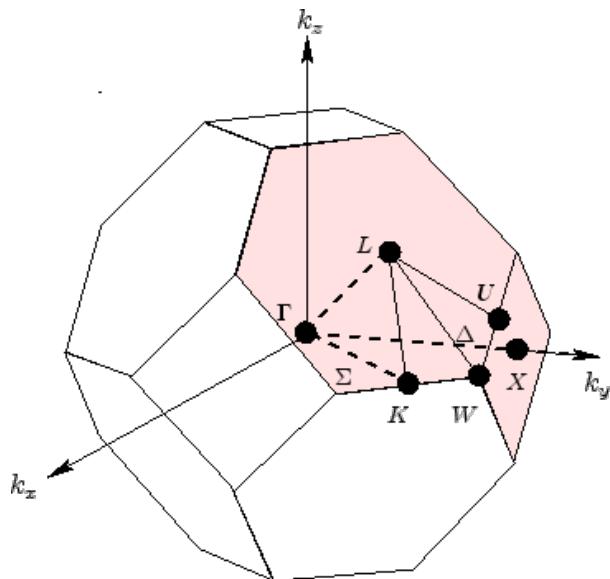


At 300 K
 $k_B T = 25 \text{ meV}$

Paper discussing bipolar thermal conductivity, lots of good references:

[Bahk, J. H. & Shakouri, A. Appl. Phys. Lett. 105, 6–11 \(2014\).](#)

Aside: Electronic band structure of Si from DFT, [Materials Project](#)



Anything wrong?

Si bandgap is 1.1 eV

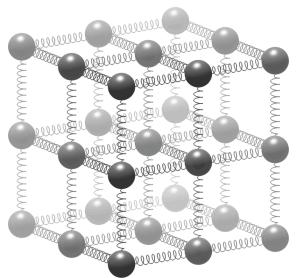
DFT usually gets the band gap wrong

What conducts heat?

$$\kappa = \kappa_{\text{vib}} + \kappa_e + \kappa_{\text{BP}} + \dots$$

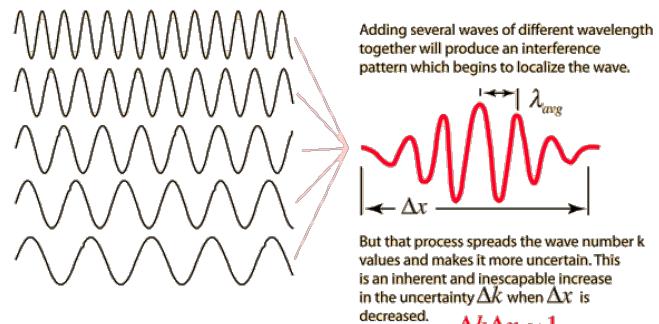
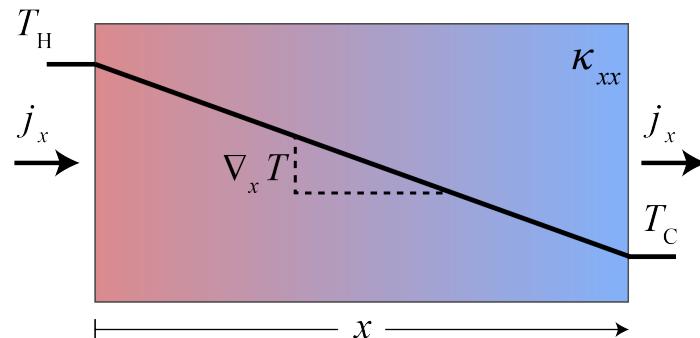
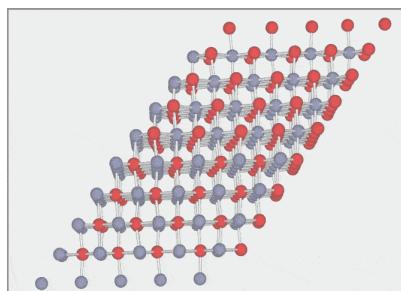
Atomic vibrations:

- Interatomic force constants (IFCs)
 - think ball and spring



$$F = -\Phi x$$

IFCs atomic masses structure
↓ ↓ ↓
normal modes of vibration



Phonons!

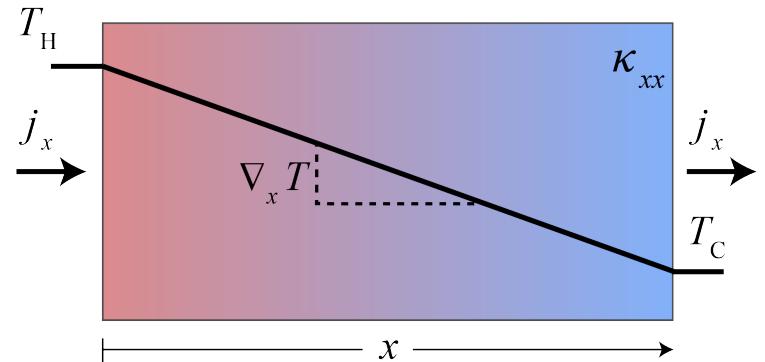
What is temperature?

Measure of ‘hotness’.

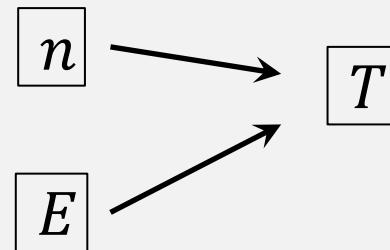
Temperature (T) of a ‘state’ at energy (E) in a material is given by its occupation number (n).

If the ‘state’ represents a boson, we use the Bose-Einstein distribution.

$$n_{\text{BE}}(E, T) = \frac{1}{e^{E/k_B T} - 1}$$

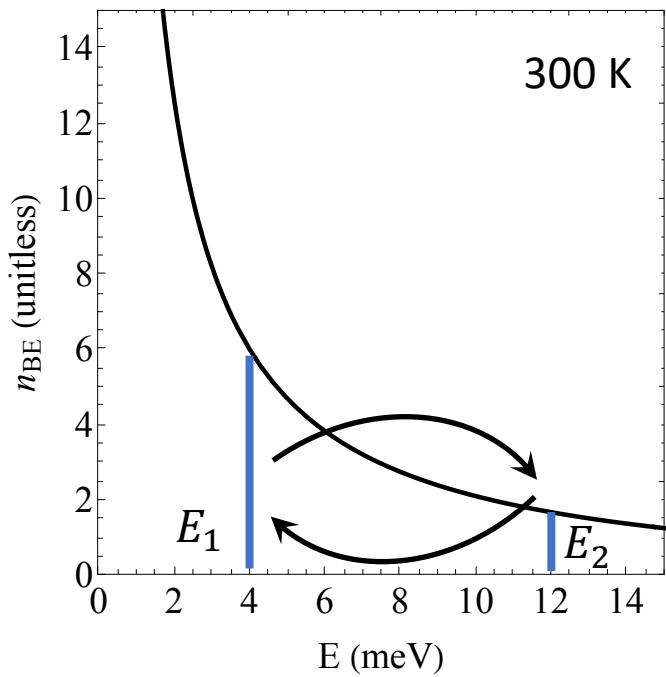
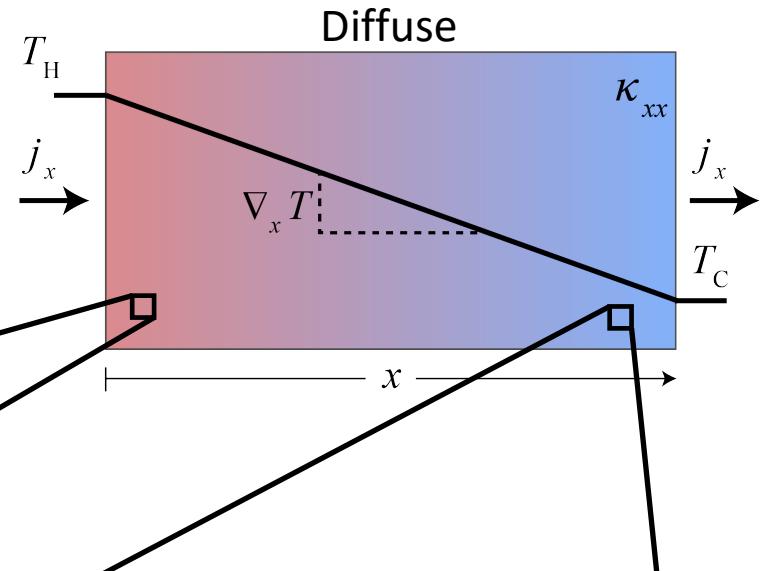
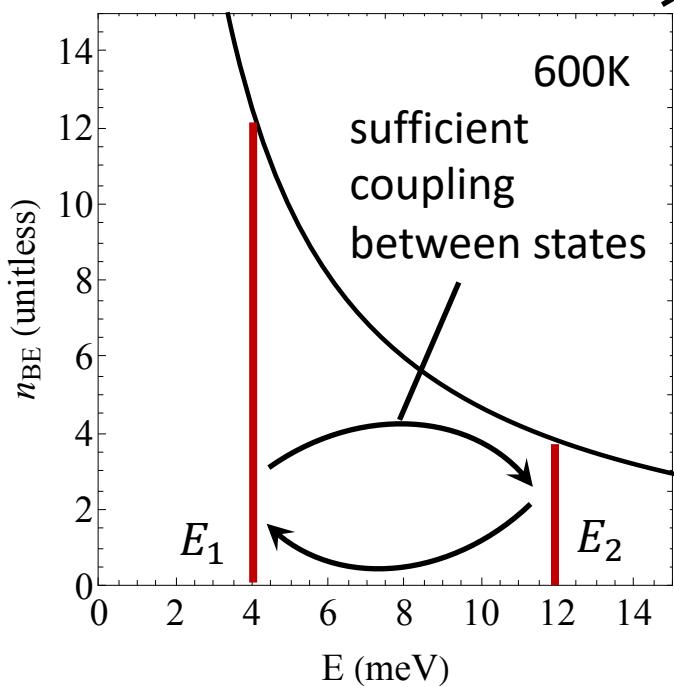


If I know the energy of all states E and the number of (quasi-) particles in those states n , I know T .



What is temperature?

$$n_{\text{BE}}(E, T) = \frac{1}{e^{E/k_B T} - 1}$$

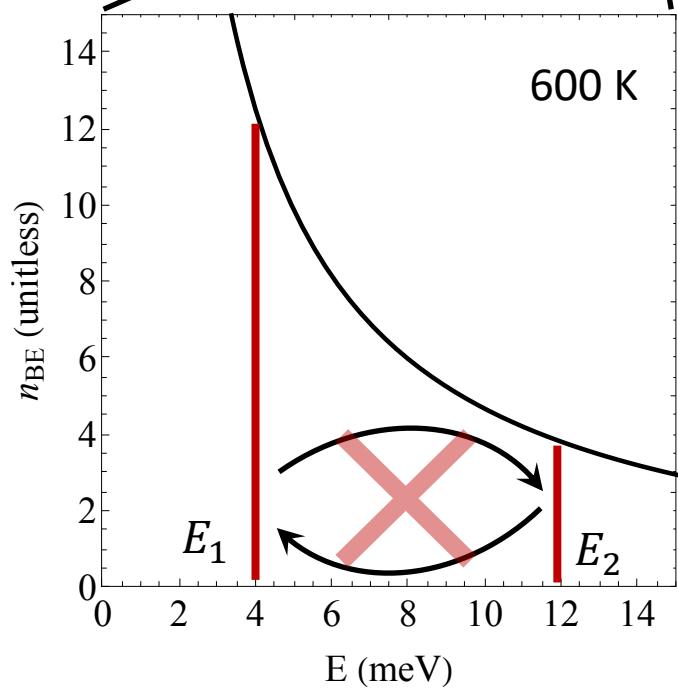
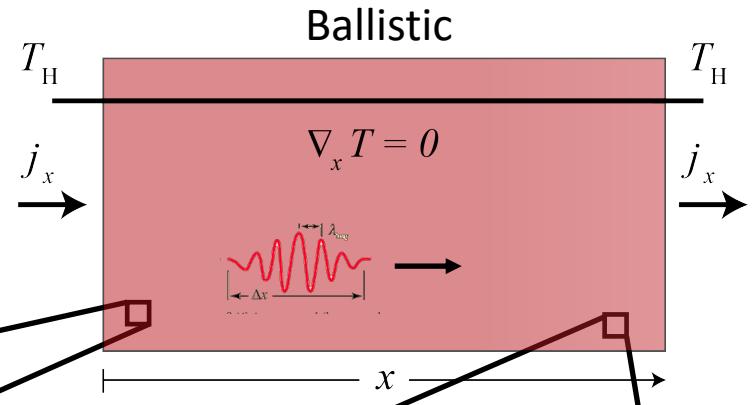
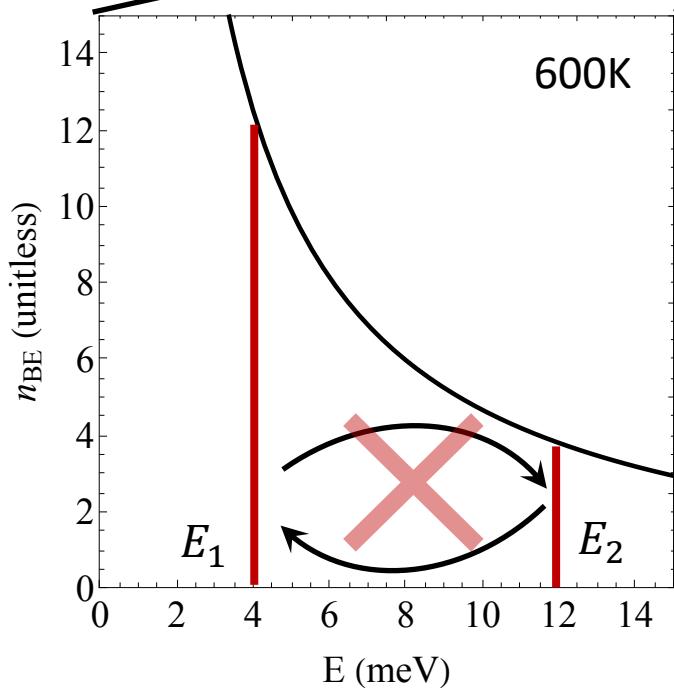


Coupling → phonon lifetime, relaxation time, mean free path

What is temperature?

What's going on? $j_x = -\kappa_{xx} \nabla_x T$

$\nabla_x T = 0$ But we are still pumping heat through, $j_x > 0$!



Fourier's law breaks down for ballistic transport!
(I say κ_{xx} not defined, some will say $\kappa_{xx} = \infty$)

$$j_x = -\kappa_{xx} \nabla_x T$$

'Effective' κ is lower in ballistic transport than it is in diffuse

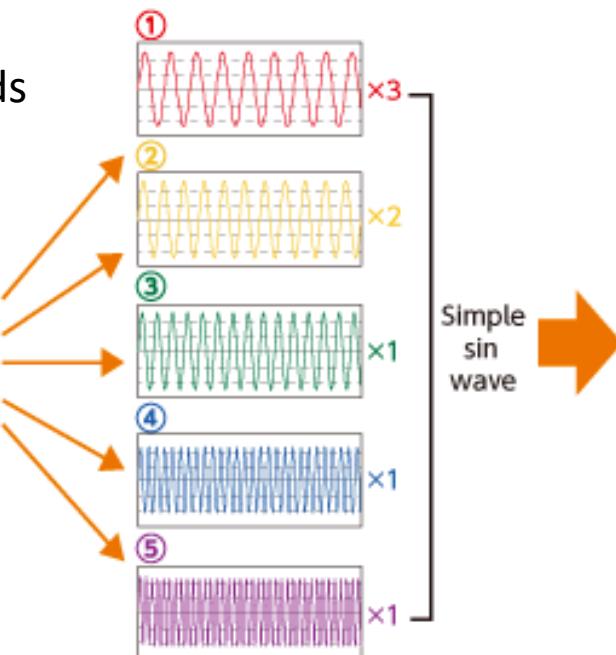
Reciprocal space

k-space

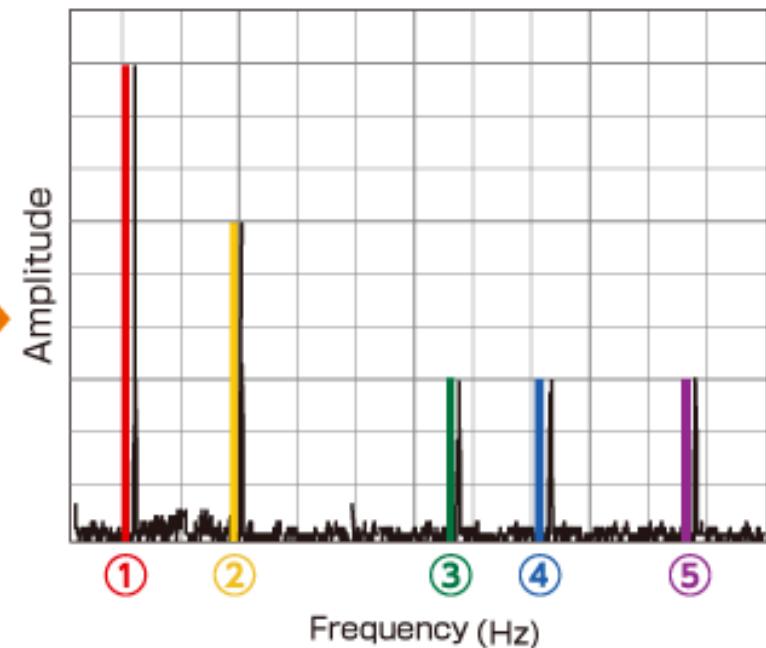
Can you tell me what this waveform sounds like? NO



Why do we work in reciprocal space?



Once you see its Fourier transform in **reciprocal space**? MAYBE



*generic example

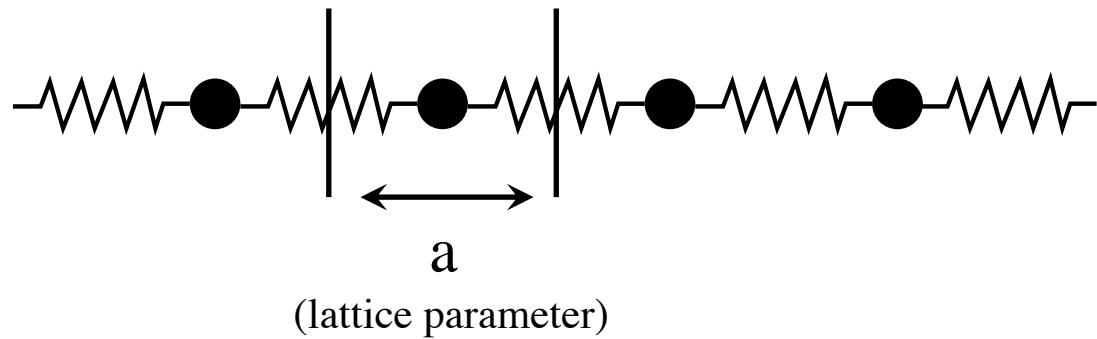
It's more natural to examine waves in reciprocal space.

Reciprocal space k-space

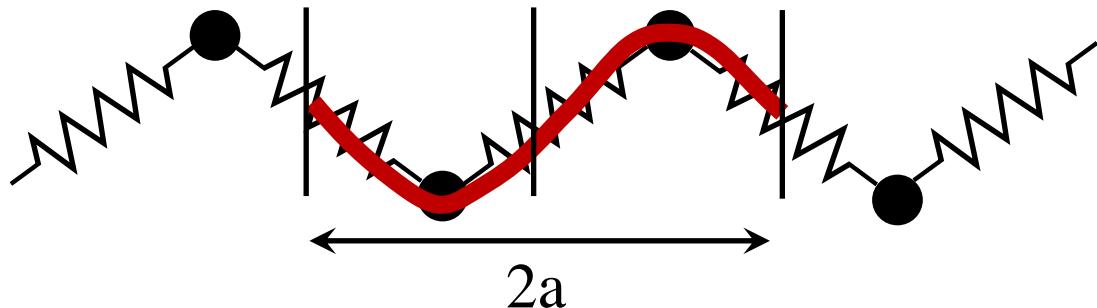
Let's apply the same concept to a crystal

$$\begin{array}{ccc} \text{time} \rightarrow \text{frequency space} & & \text{wavelength} \rightarrow \text{reciprocal space} \\ t \text{ [s]} \rightarrow \omega \left[\frac{2\pi}{\text{s}} \right] & & \lambda \text{ [m]} \rightarrow k \left[\frac{2\pi}{\text{m}} \right] \end{array}$$

Start in 1D



The crystal structure will set a minimum λ , or a maximum k



$$\lambda_{\min} = 2a$$

$$k_{\max} = \frac{2\pi}{2a} = \frac{\pi}{a}$$

Reciprocal space

k-space

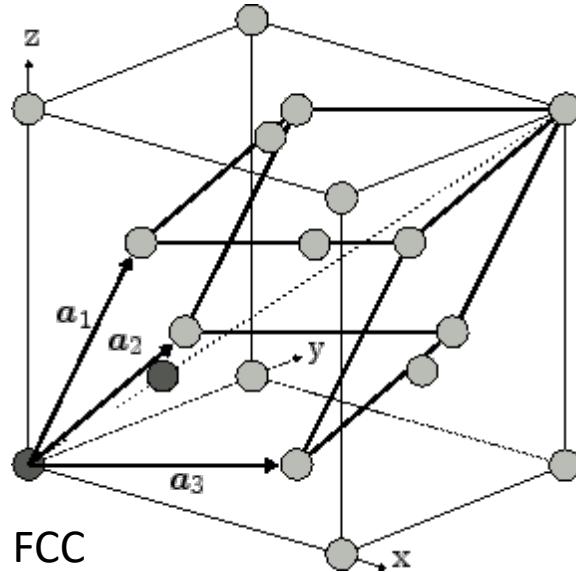
Step 1

Start with unit cell vectors:

$\mathbf{a}_1, \mathbf{a}_2$, and \mathbf{a}_3

(typically we work with primitive unit cells)

$$\text{volume: } V = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$



Defining the First Brillouin Zone, FBZ

(pronounced BREE – you – on with a soft ‘n’, its French)

See Kittle, Introduction to Solid State Physics, pg. 26 to 41

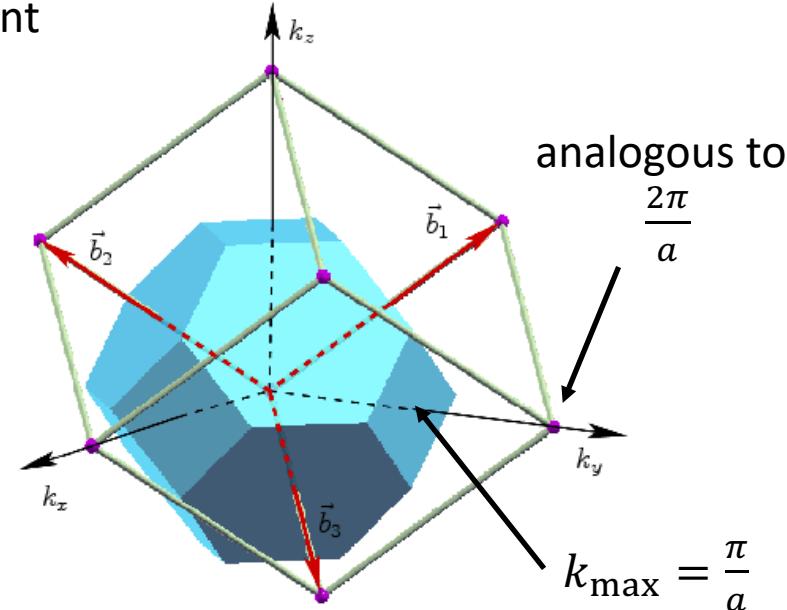
Step 2

Define reciprocal lattice vectors:

$$\mathbf{b}_1 = \frac{2\pi}{V} (\mathbf{a}_2 \times \mathbf{a}_3), \quad \mathbf{b}_2 = \frac{2\pi}{V} (\mathbf{a}_3 \times \mathbf{a}_1), \\ \mathbf{b}_3 = \frac{2\pi}{V} (\mathbf{a}_1 \times \mathbf{a}_2)$$

Step 3

Draw planes halfway between each reciprocal lattice point



Note: be mindful of your 2π 's. Some define k-space with 2π , a lot of codes don't.

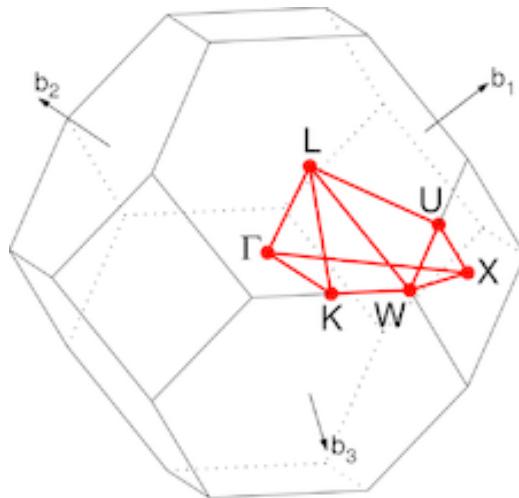
Reciprocal space

k-space

Defining the First Brillouin Zone, FBZ

Step 4

Give certain k-points fancy names

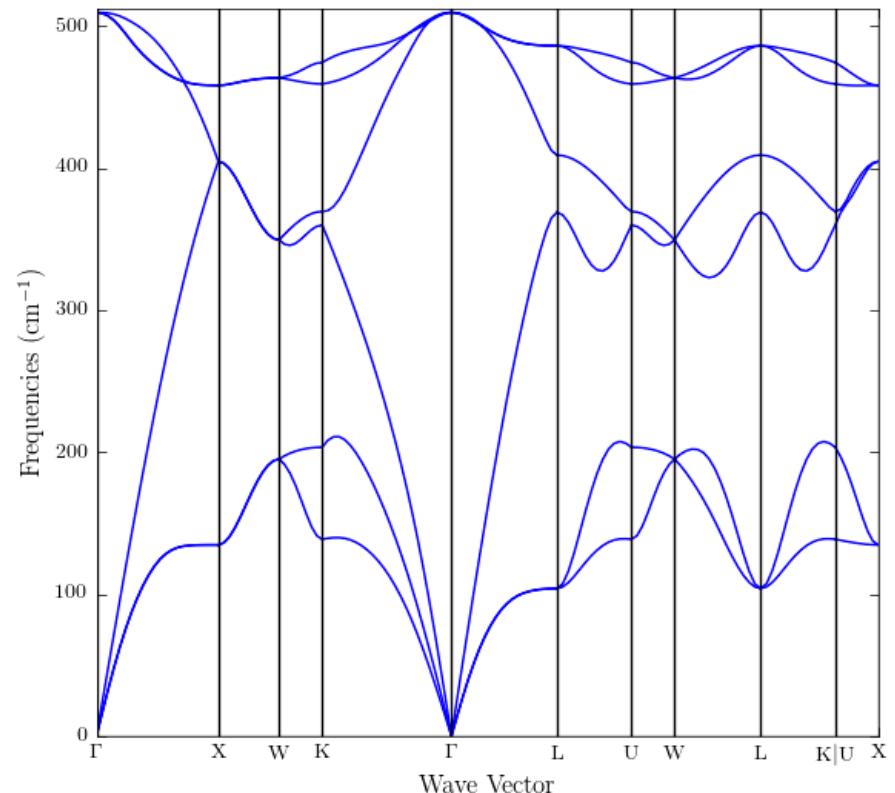


<https://www.crys.ceu.es/>

You can think of a phonon band structure (roughly) as the Fourier transform of the interatomic spring constants, weighted by the atomic masses.

Step 5

Walk from point to point and map energies of phonons, or electrons



What's the wavelength at Γ ? What about X ?

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:

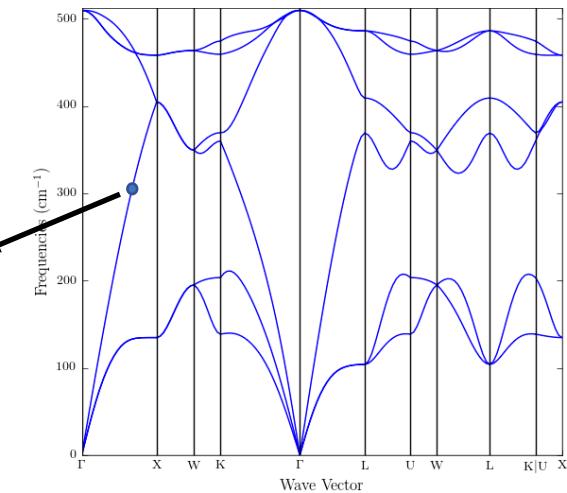
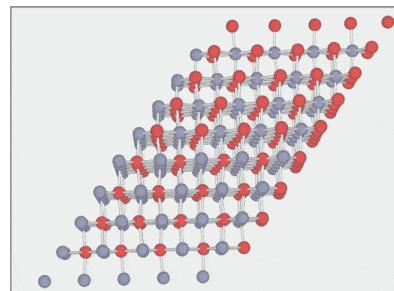
- **Wallace, Thermodynamics of Crystals, Chapter 3.10.**
- [Hanus, Thesis, Section 2.2.1 and Appendix B.](#)

Here we will outline the procedure for computing phonon properties:

- frequencies



- eigenvectors
(mode shape)

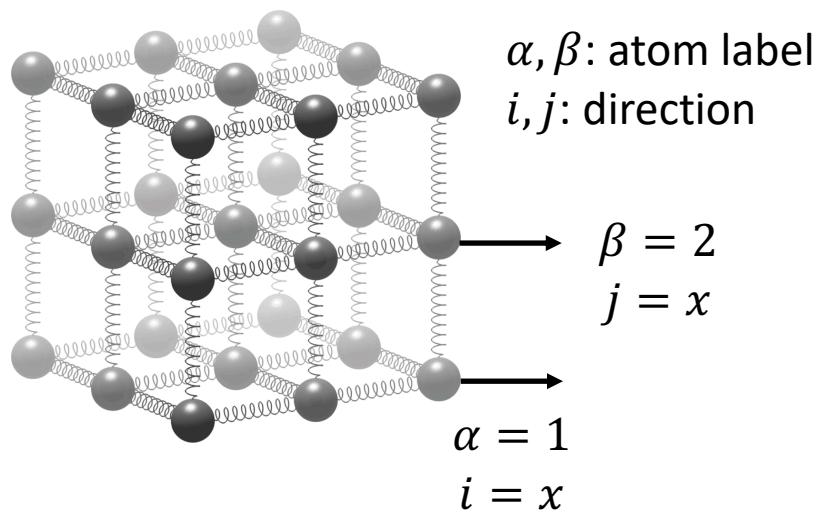


Phonon band structures

Set up

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

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



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

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/>

Phonon band structures

1. Express u_i^α as a Fourier Series

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

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 it's convenient to define the **Dynamical Matrix**

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

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

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

scalar

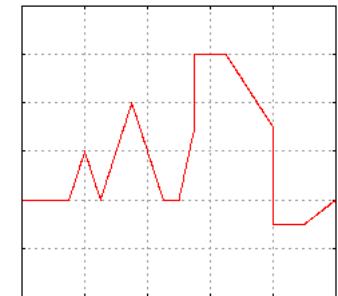
3n length vector

3n x 3n matrix

3n length vector

Expressing a function as a Fourier Series

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



3n distinct ω^2 and ϵ_i^α solutions

$n = \# \text{ of atoms in unit cell}$

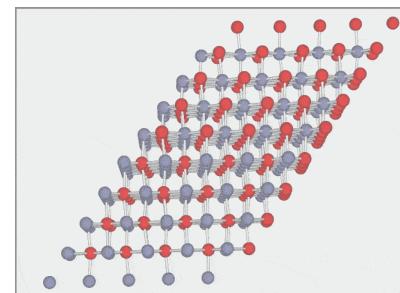
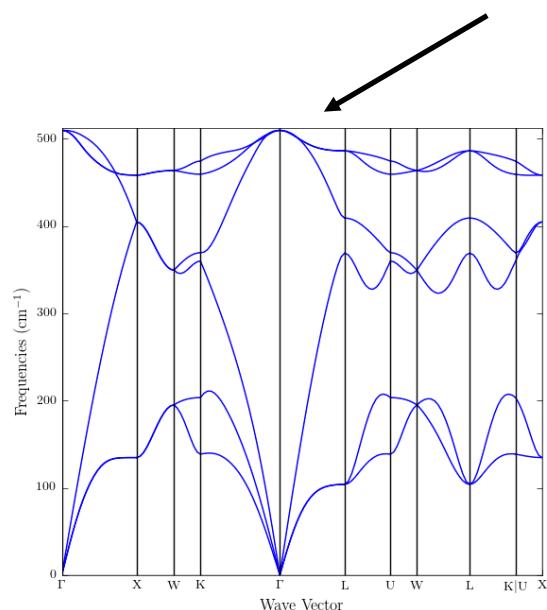
$s = 1, \dots, 3n$

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

scalar $3n$ length vector $3n \times 3n$ matrix $3n$ length vector

$3n$ distinct ω^2 and

ϵ_i^α solutions



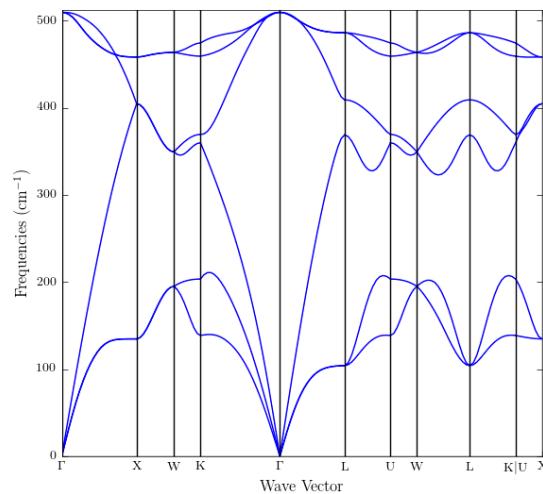
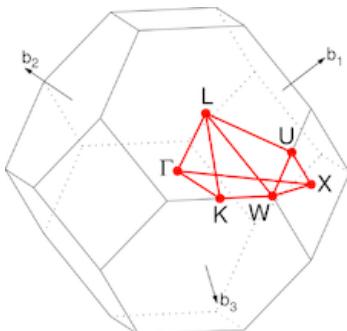
Phonon band structures

In practice

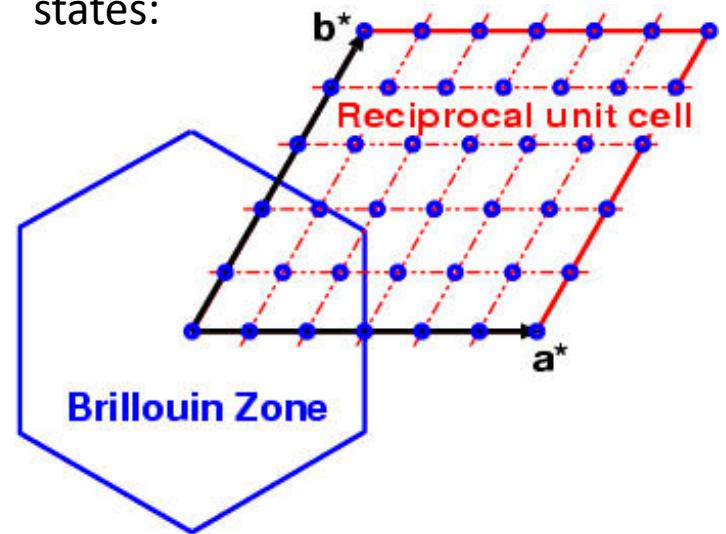
Find solutions (diagonalize the Dynamical Matrix)

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

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:

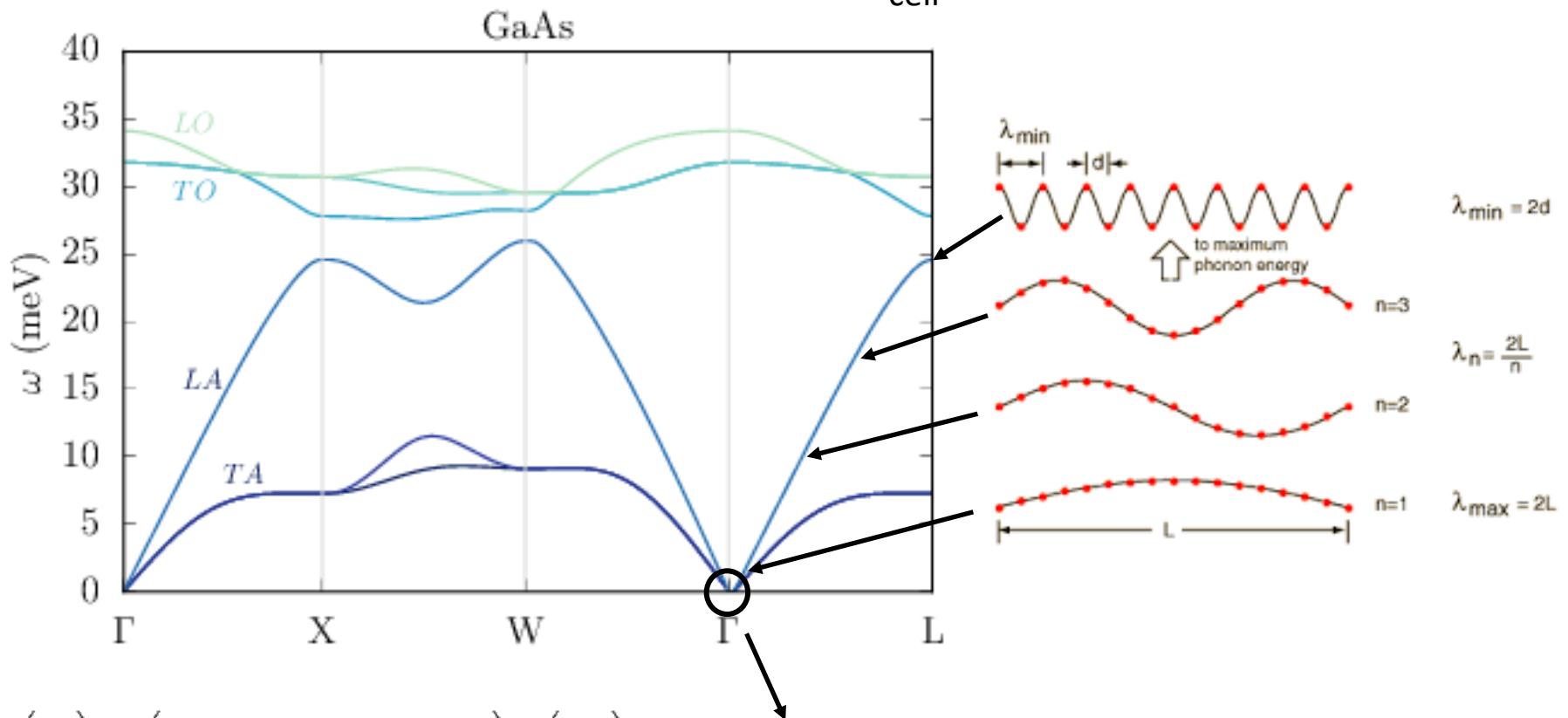


Computational suites that do this:

phonopy: <https://atztogo.github.io/phonopy/>
almaBTE: <http://www.almabte.eu/>
shengBTE: <http://www.shengbte.org/>

Reading a phonon band structure

3 acoustic modes ($\omega \rightarrow 0$ at Γ)
 $3n - 3$ optical modes ($\omega \neq 0$ at Γ)
 where n is the number of atoms in the unit cell

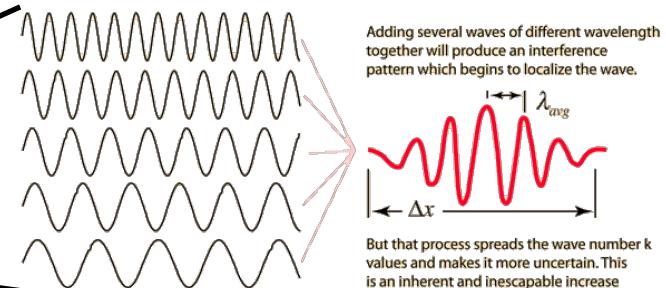
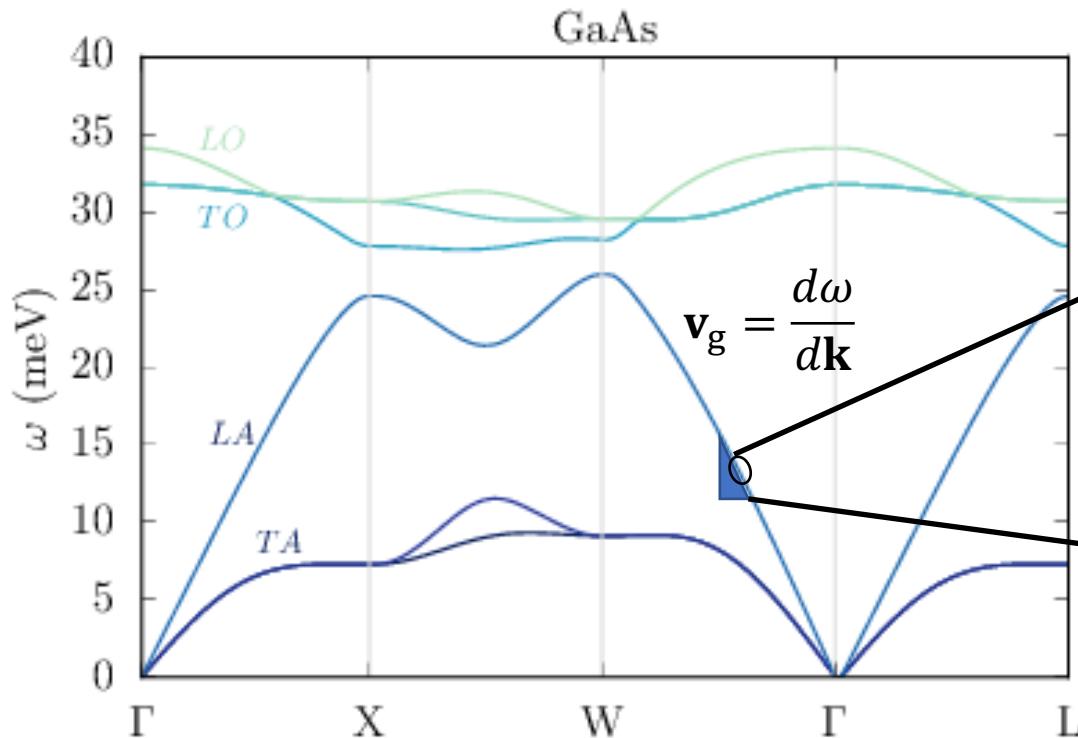


$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{11} & c_{12} & 0 & 0 & 0 \\ c_{12} & c_{12} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0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

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

Reading a phonon band structure

Group velocity



Adding several waves of different wavelength together will produce an interference pattern which begins to localize the wave.

But that process spreads the wave number k values and makes it more uncertain. This is an inherent and inescapable increase in the uncertainty Δk when Δx is decreased.

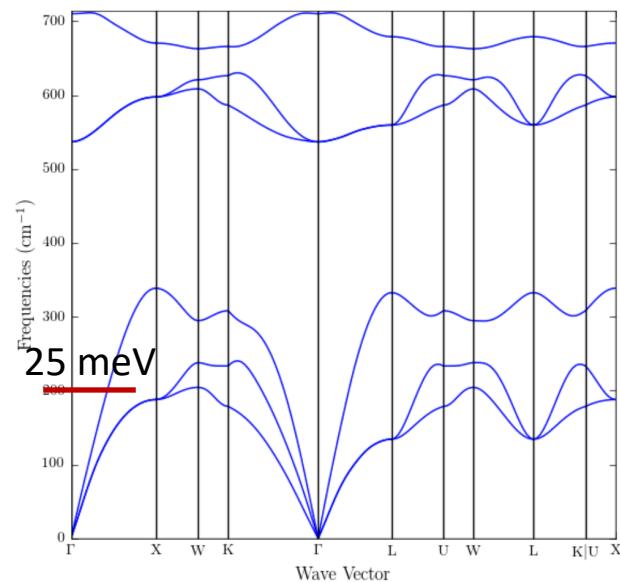
$$\Delta k \Delta x \approx 1$$

$$v_g$$

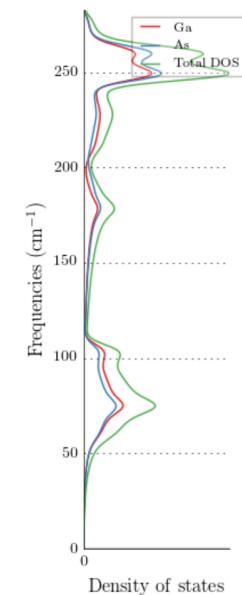
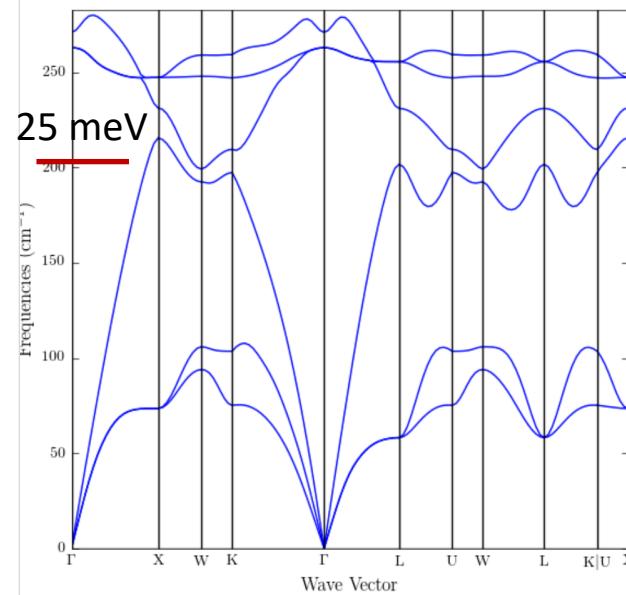
Reading a phonon band structure

Effect of atomic mass and the phonon band gap.

Cubic GaN



Cubic GaAs



$$200 \text{ cm}^{-1} \approx 25 \text{ meV}$$

Resources

bilbao crystallographic server

<https://www.cryst.ehu.es/>

- space-group symmetry
 - KVEC
 - type in space group # (FCC Si, Fd-3m, no. 227)
 - click Brillouin zone

Phonon simulation software and databases:

phonopy: <https://atztogo.github.io/phonopy/>

almaBTE: <http://www.almabte.eu/>

shengBTE: <http://www.shengbte.org/>

Elastic properties:

Elastic tensors: materials project

averaging: <https://github.com/JanJaeken/christoffel>