Nanoscale thermal transport

Lecture 1

Riley Hanus

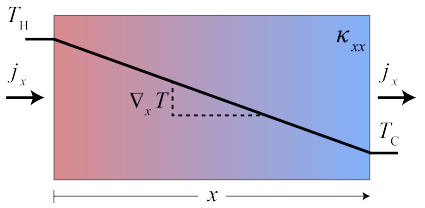
http://rileyhanus.com/science.html

Two rules

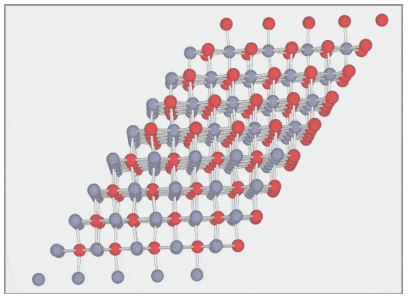
1. Use your imagination
    - You should be actively building a picture in your head.
    - I'll do my best to provide good pictures, but the pictures will fall short.

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

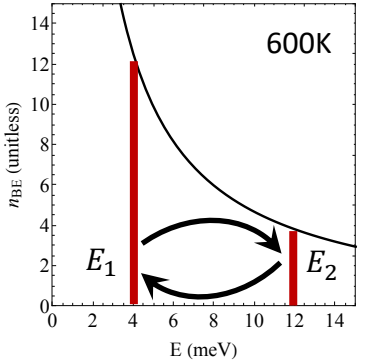
1. Define thermal conductivity, κ



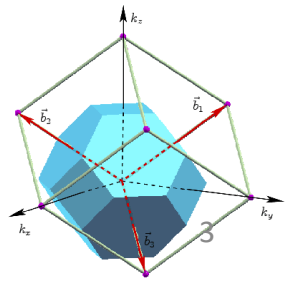
2. Overview of heat conduction mechanisms
   - electrons
   - bipolar
   - atomic vibrations

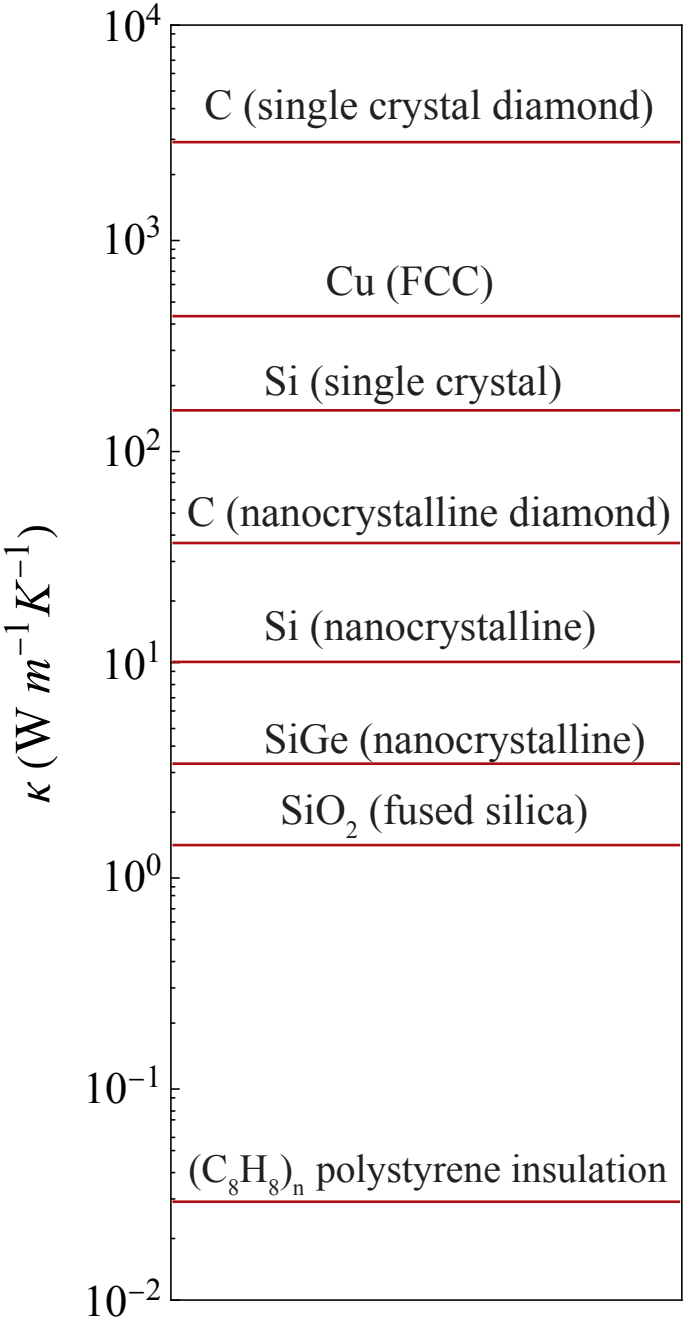


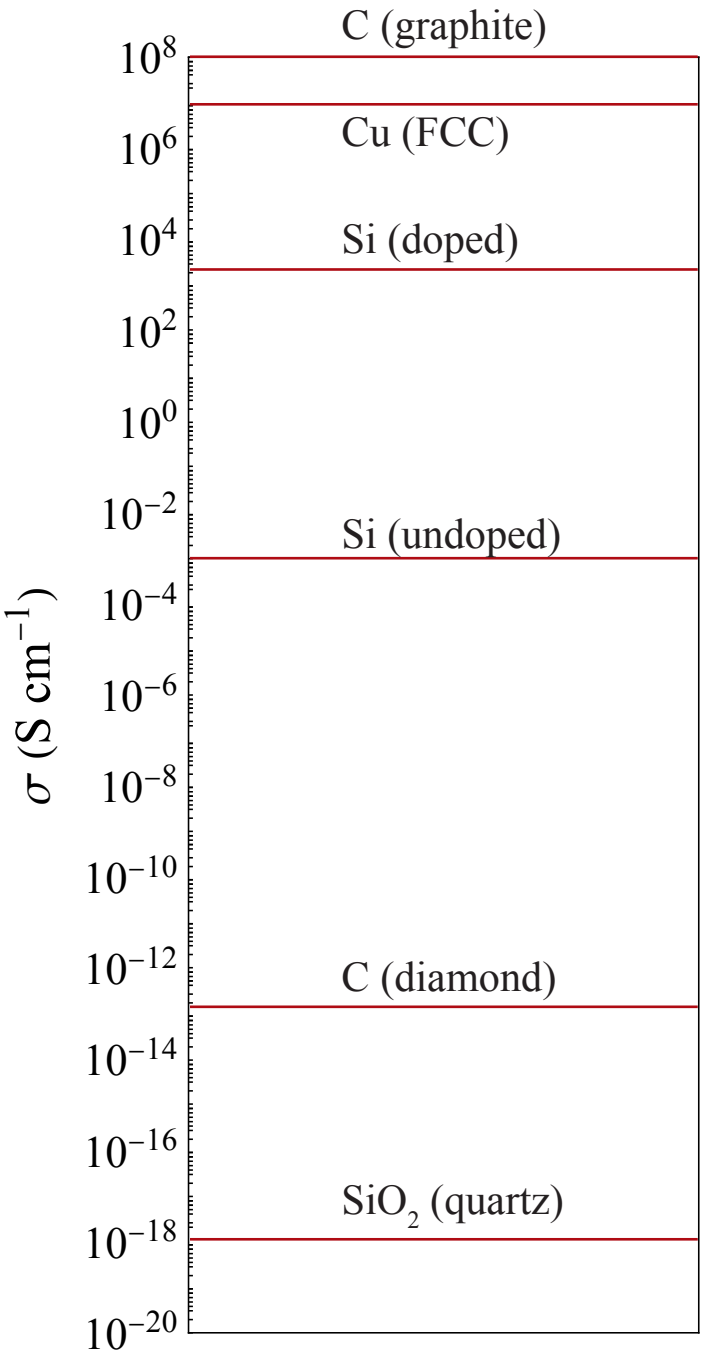
3. Define (and understand) temperature



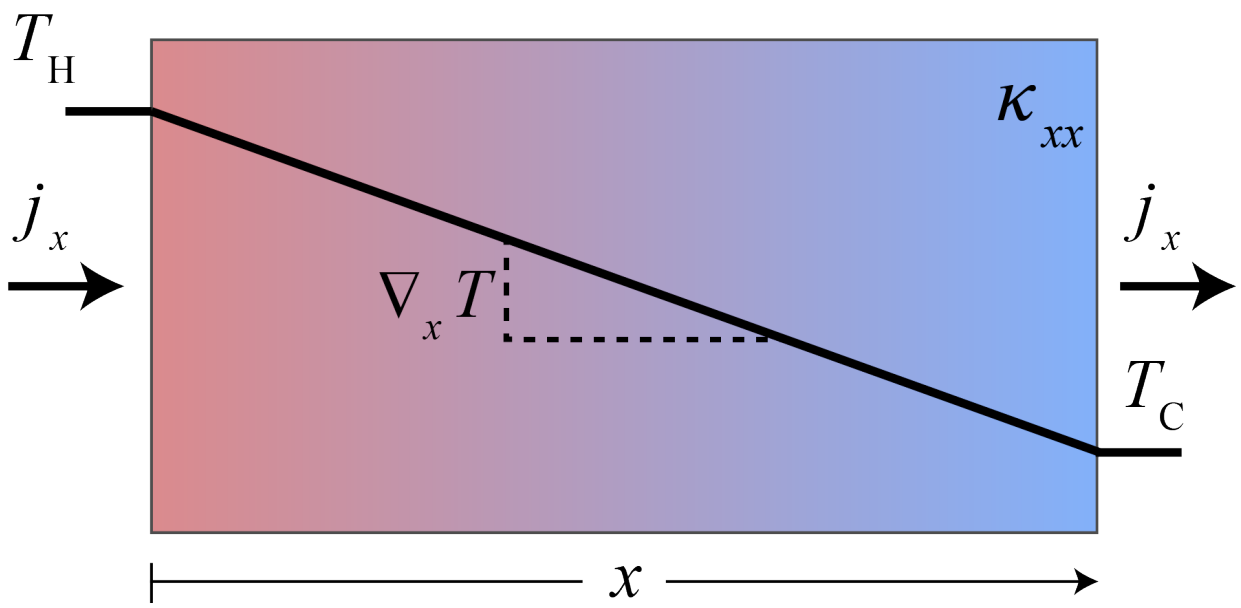
4. Define (and understand) reciprocal space
   - First Brillouin Zone
   - Band structures




10^4
C (single crystal diamond)
10^3
Cu (FCC)
Si (single crystal)
10^2
C (nanocrystalline diamond)
Si (nanocrystalline)
10^1
SiGe (nanocrystalline)
SiO_2 (fused silica)
10^0
10^{-1}
$(C_8H_8)_n$ polystyrene insulation
10^{-2}
κ (W $m^{-1} K^{-1}$)


C (graphite)
10^8
10^6
Cu (FCC)
10^4
Si (doped)
10^2
10^0
10^{-2}
Si (undoped)
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
C (diamond)
10^{-14}
10^{-16}
SiO_2 (quartz)
10^{-18}
10^{-20}
σ (S cm^{-1})

Fourier's Law $j = -\kappa \nabla T$



Let's be explicit:

vector notation: $\mathbf{j} = -\overline{\overline{\boldsymbol{\kappa}}}\, \nabla T$

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

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

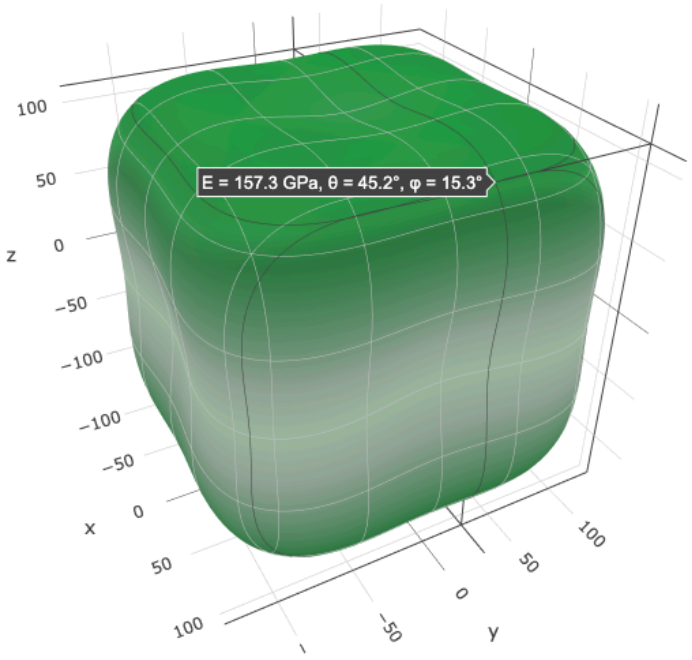
κ_{ij} : thermal conductivity (3x3 matrix) $\left[\frac{\mathrm{W}}{\mathrm{mK}}\right]$

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

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

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

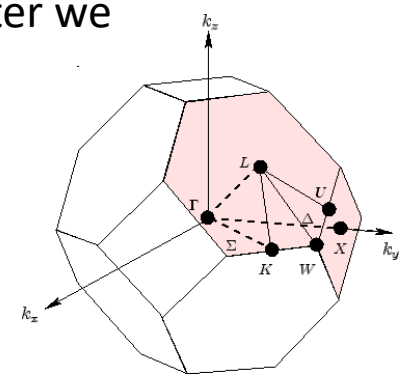
Young's Modulus contour of Si from Materials Project



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

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

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

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?

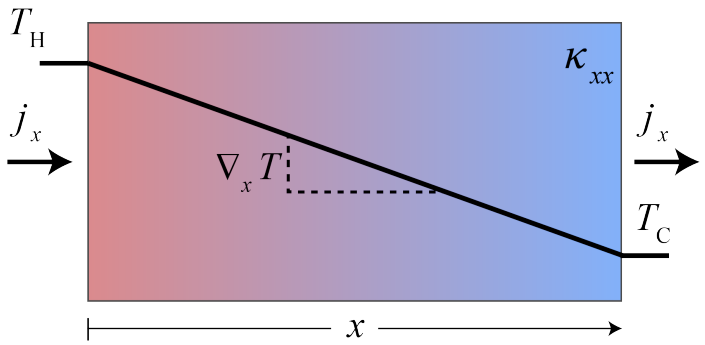
$$\kappa = \kappa_{\mathrm{vib}} + \kappa_{\mathrm{e}} + \kappa_{\mathrm{BP}} + \cdots$$

Electrons (Wiedemann-Franz Law)

$$\kappa_{\mathrm{e}} = L\sigma T$$

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

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



For metals and degenerate semiconductors

$$L = 2.45\times10^{-8}\ \mathrm{W\Omega K^{-2}}$$

e^- →

- 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

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).

Note: (worth remembering)

What conducts heat?

$$\kappa = \kappa_{\mathrm{vib}} + \kappa_{\mathrm{e}} + \kappa_{\mathrm{BP}} + \cdots$$

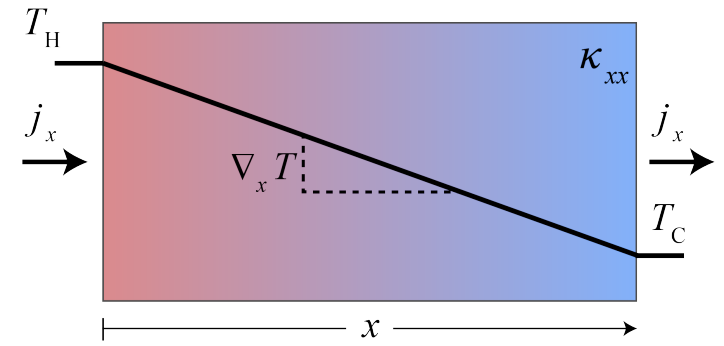
Bipolar conduction:

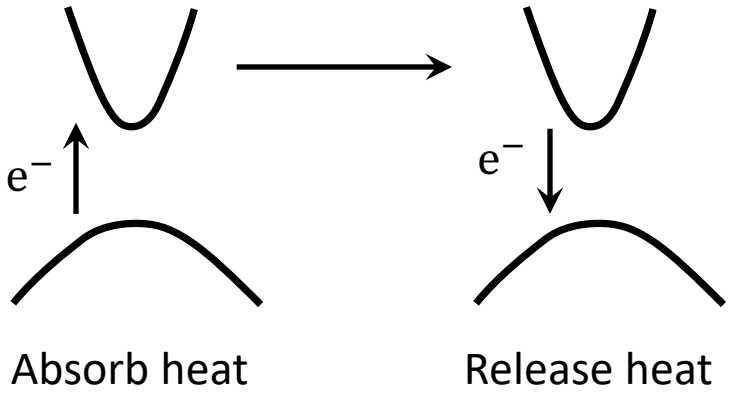
$$\kappa_{\mathrm{BP}} = \frac{\sigma_{\mathrm{e}}\sigma_{\mathrm{h}}}{\sigma_{\mathrm{e}}+\sigma_{\mathrm{h}}}(S_{\mathrm{e}} - S_{\mathrm{h}})^2 T$$

in the intrinsic regime

$$\kappa_{\mathrm{BP}} \propto \exp\left(-\frac{E_{\mathrm{g}}}{2k_{\mathrm{B}}T}\right)$$

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



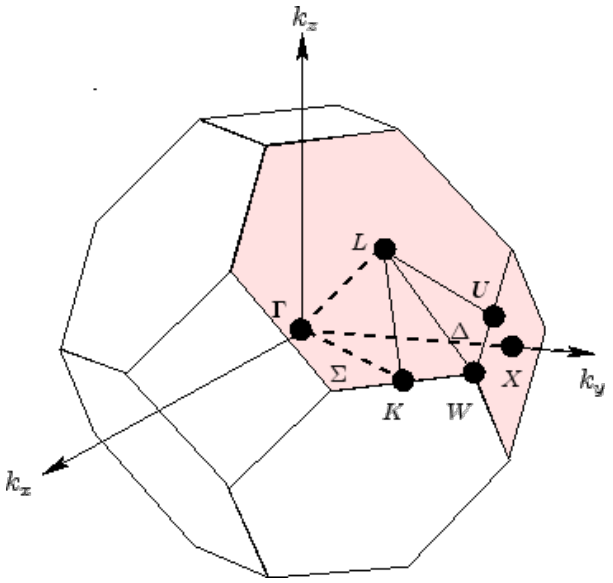


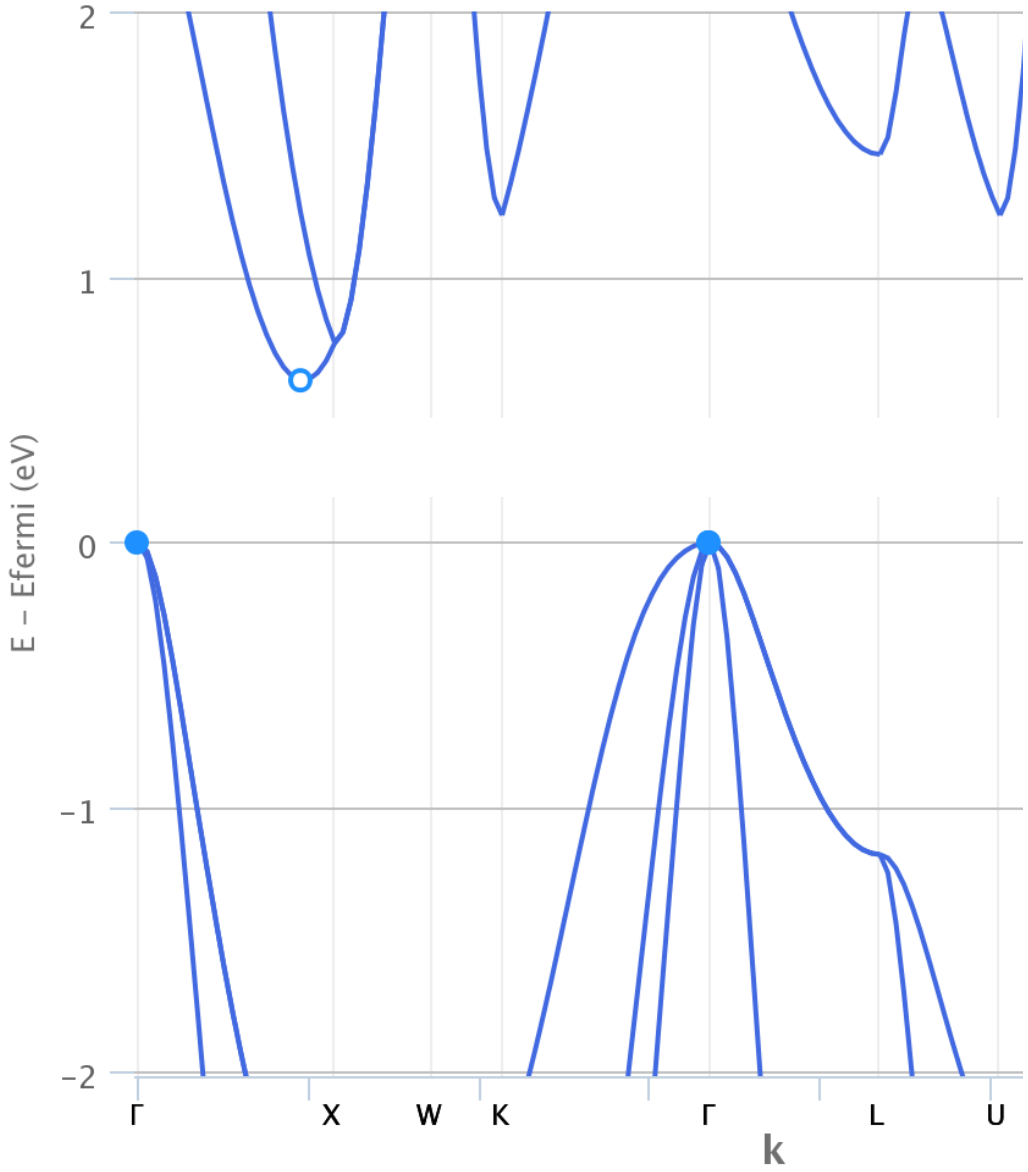
At 300 K
$k_{\mathrm{B}}T = 25$ meV

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

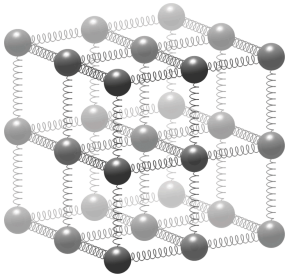
DFT usually gets the band gap wrong

What conducts heat?

$$\kappa = \kappa_{\mathrm{vib}} + \kappa_{\mathrm{e}} + \kappa_{\mathrm{BP}} + \cdots$$

Atomic vibrations:

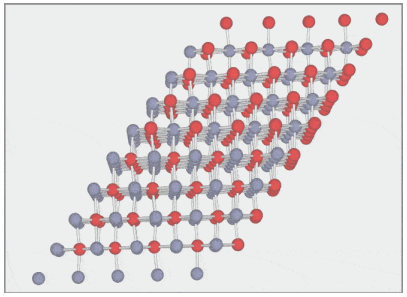
- Interatomic force constants (IFCs)
  - think ball and spring

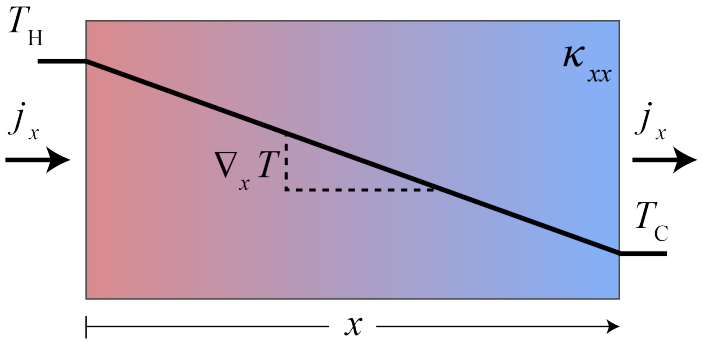


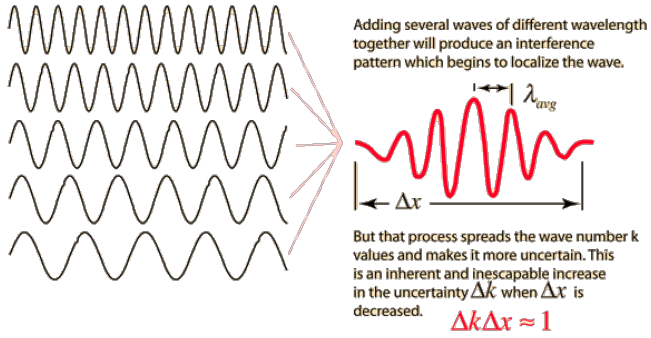
$$F = -\Phi x$$

IFCs atomic masses structure

normal modes of vibration

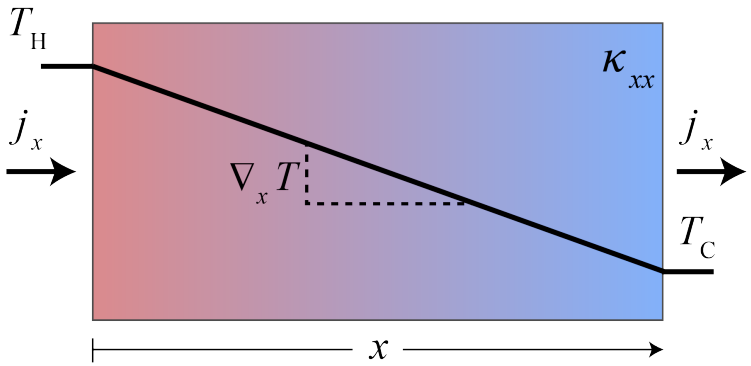






Phonons!

What is temperature?



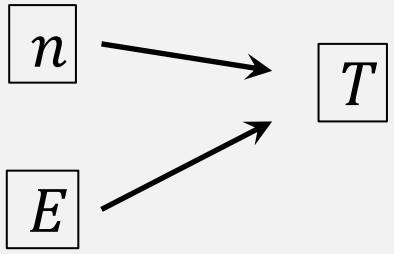
Measure of ‘hotness’.

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.

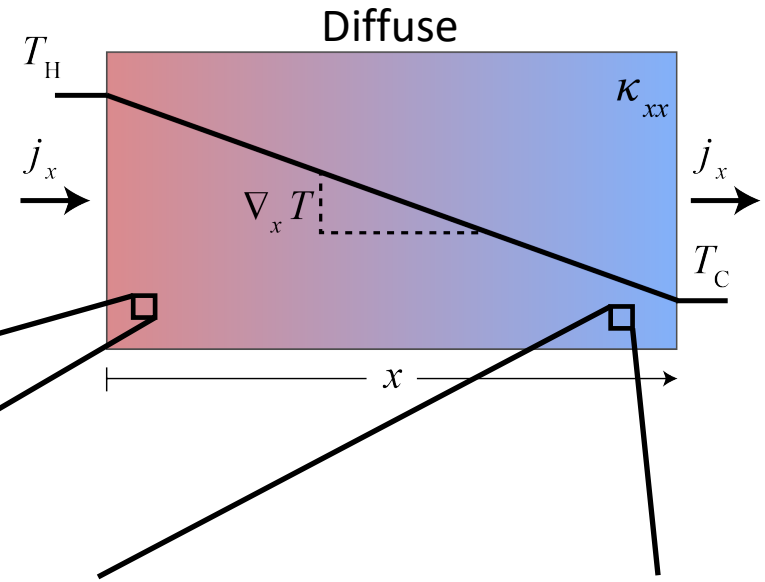
$$n_{\mathrm{BE}}(E,T) = \frac{1}{e^{E/k_{\mathrm{B}}T} - 1}$$

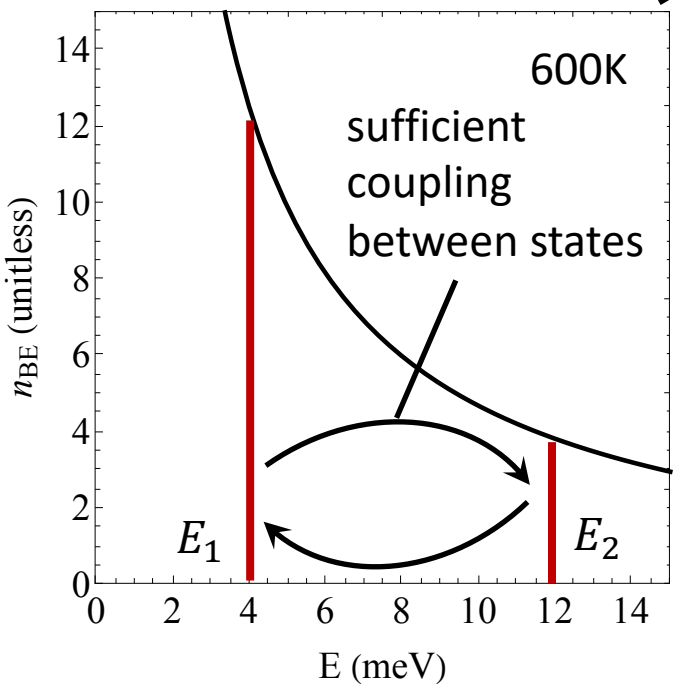
If I know the energy of all states E and the number of (quasi-) particles in those states n, I know T.

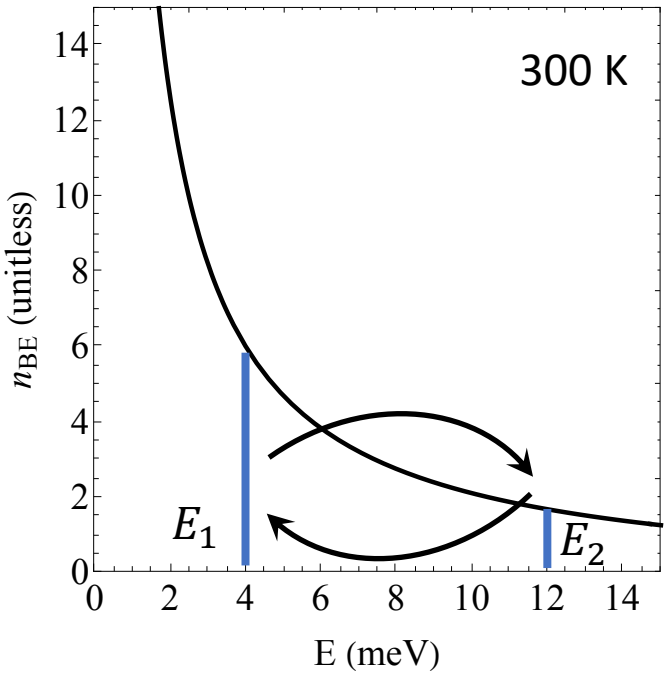


What is temperature?

$$n_{\mathrm{BE}}(E,T) = \frac{1}{e^{E/k_{\mathrm{B}}T} - 1}$$







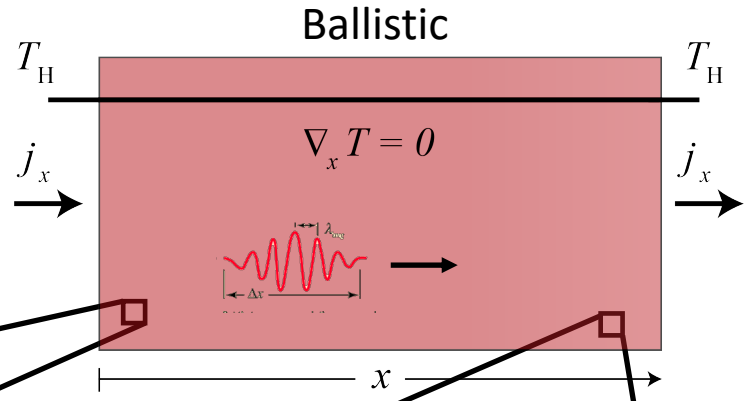
Coupling → phonon lifetime, relaxation time, mean free path

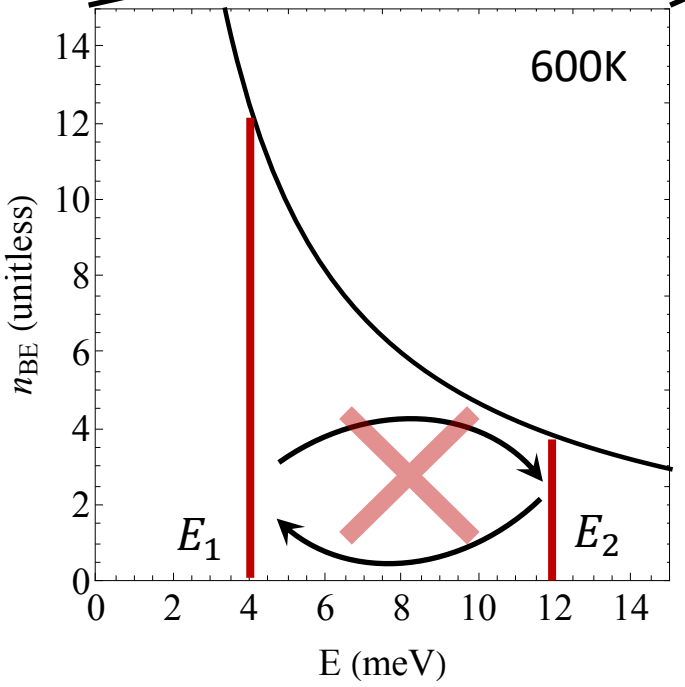
What is temperature?

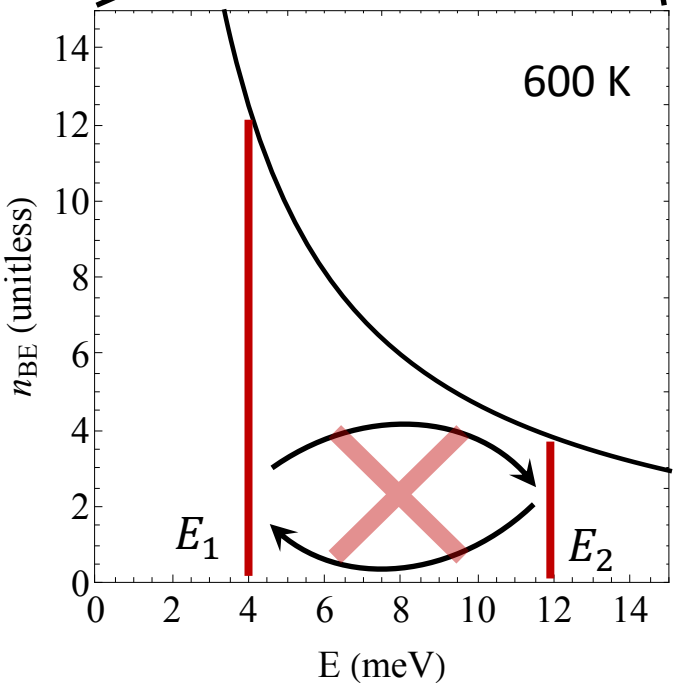
What's going on? $j_x = -\kappa_{xx} \nabla_x T$

$\nabla_x T = 0$

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 $\kappa_{xx} = \infty$)

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

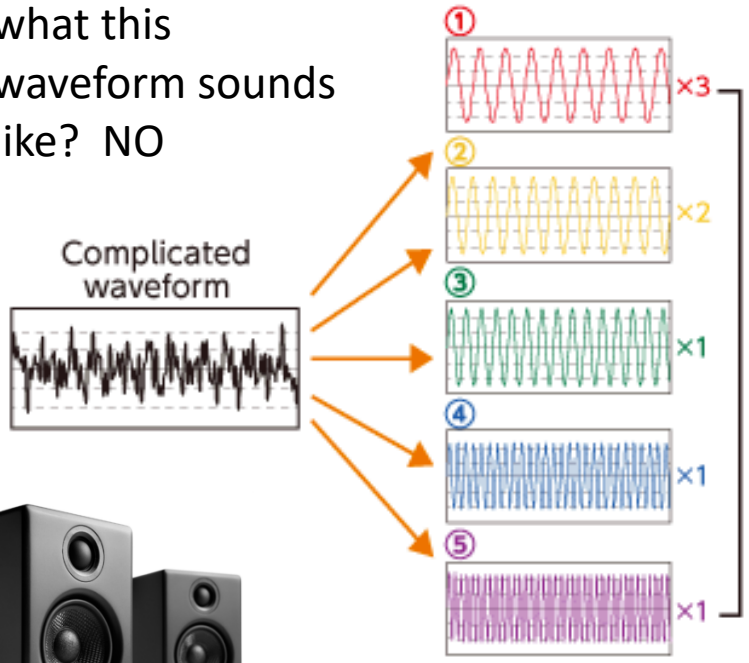
'Effective' κ is lower in ballistic transport than it is in diffuse

Reciprocal space

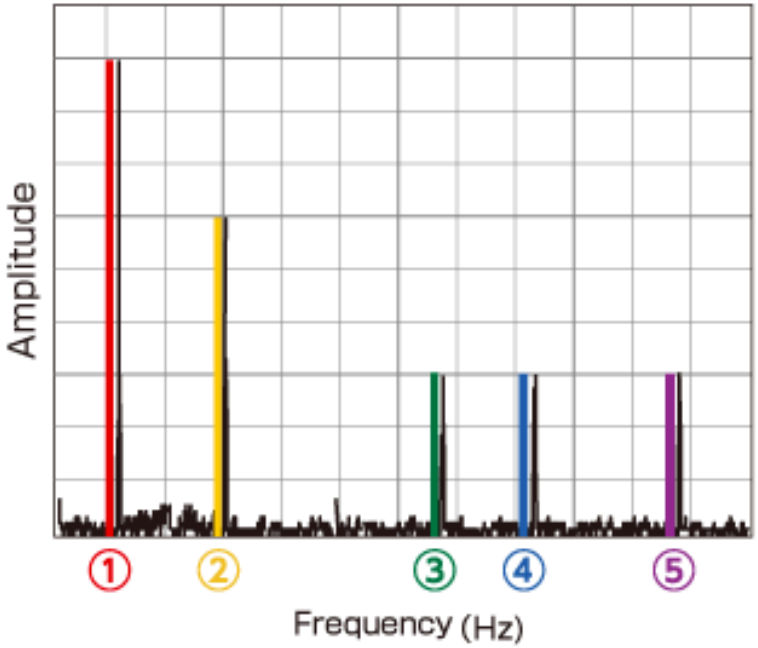
k-space

Why do we work in reciprocal space?

Can you tell me what this waveform sounds like? NO



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

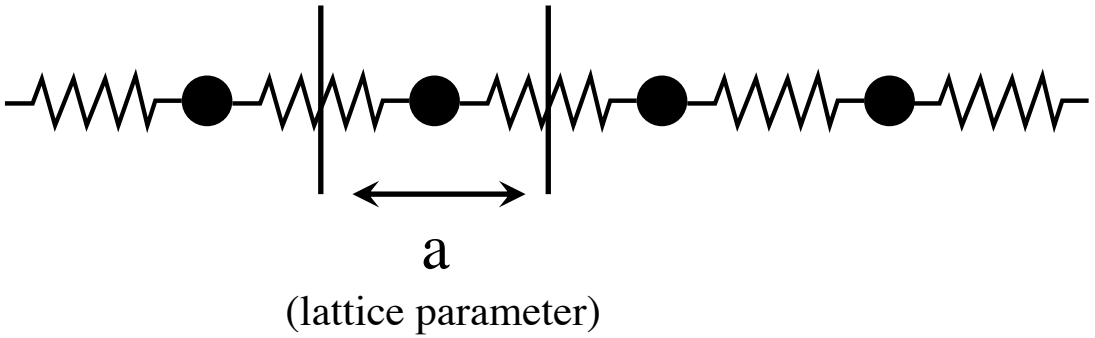
time → frequency space

$$t\ [\mathrm{s}] \quad \rightarrow \quad \omega \ \left[\frac{2\pi}{\mathrm{s}}\right]$$

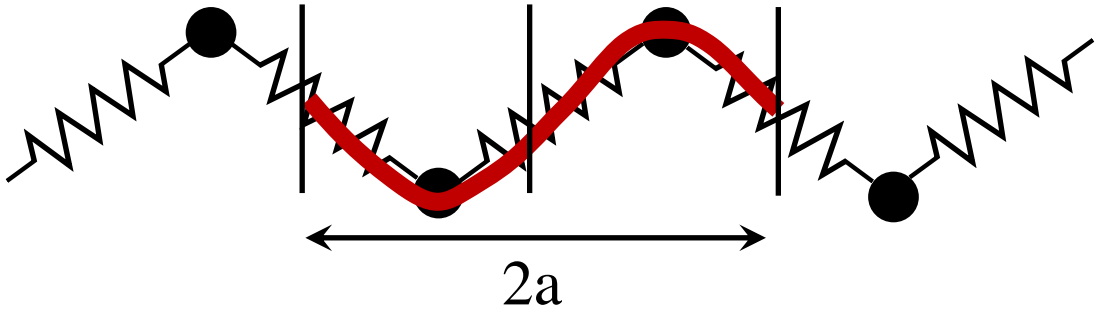
wavelength → reciprocal space

$$\lambda\ [\mathrm{m}] \quad \rightarrow \quad k \ \left[\frac{2\pi}{\mathrm{m}}\right]$$

Start in 1D



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



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

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

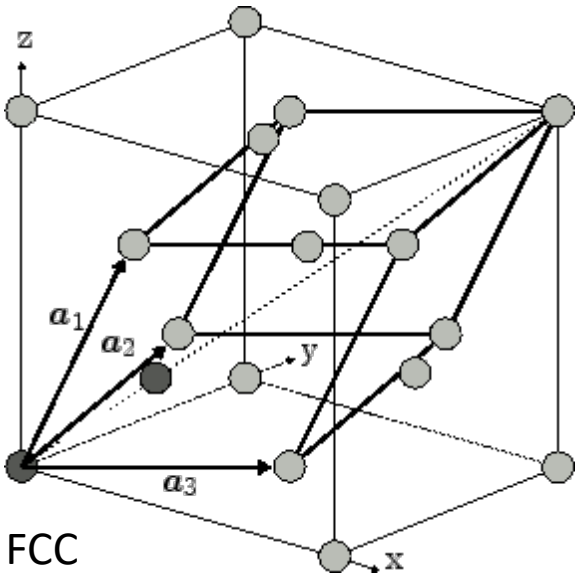
Reciprocal space
k-space

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 1
Start with unit cell vectors:
$\mathbf{a}_1, \mathbf{a}_2,$ and $\mathbf{a}_3$
(typically we work with primitive unit cells)

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



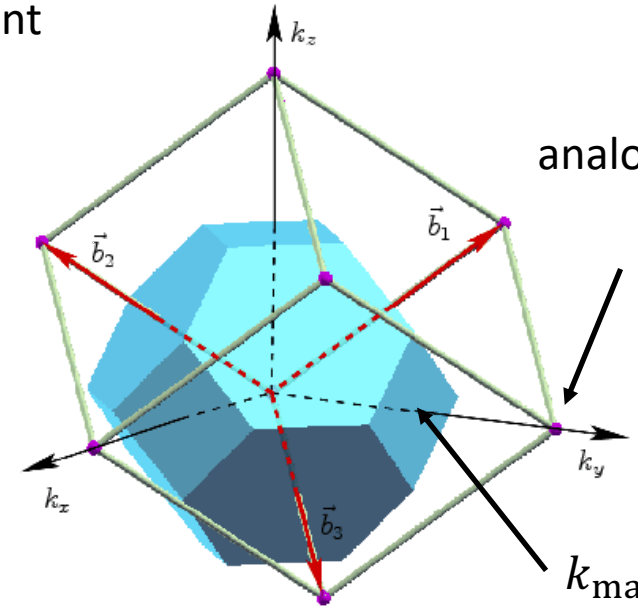
FCC

Step 2
Define reciprocal lattice vectors:

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

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

Step 3
Draw planes halfway between each reciprocal lattice point



analogous to $\frac{2\pi}{a}$

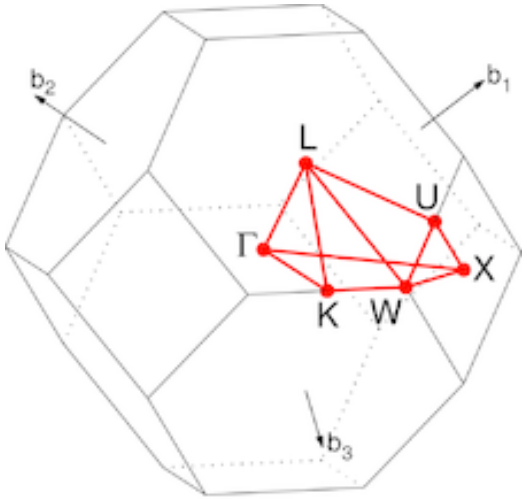
$k_{\max} = \frac{\pi}{a}$

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

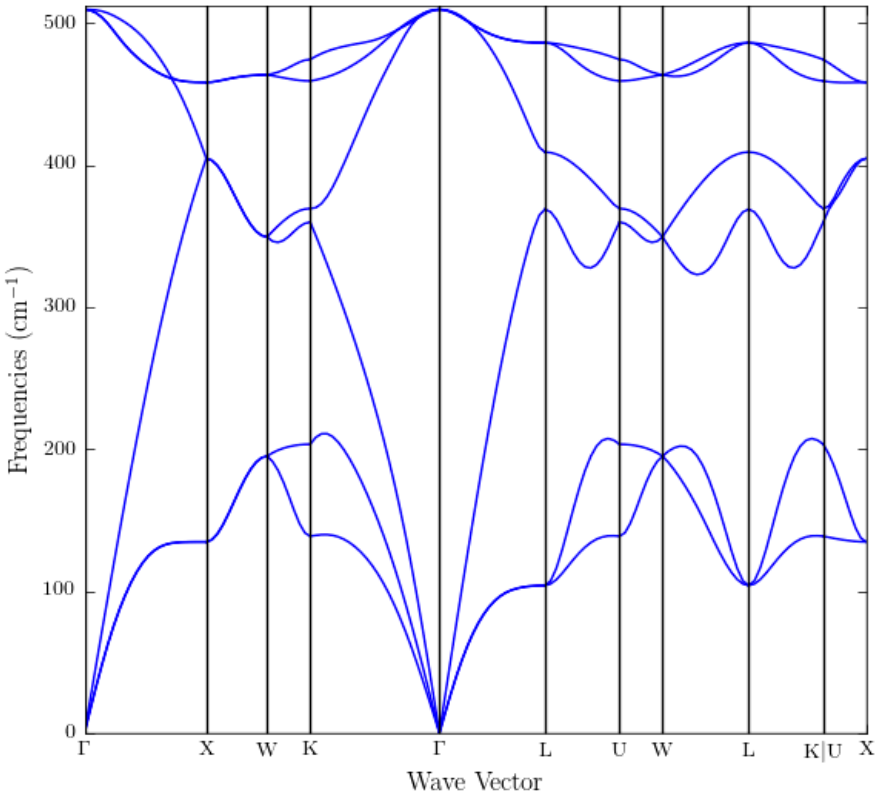
Step 4
Give certain k-points fancy names



https://www.cryst.ehu.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?

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/