Lecture 14: Thermal conductivity

Review: phonons as particles

In chapter 5, we have been considering quantized waves in solids to be **particles** and this becomes very important when we discuss thermal conductivity. In discussing thermal conductivity, we often think of a 'gas' of phonons, and the table below makes this more concrete via a comparison to a classical gas.

	Classical gas (molecules)	Phonon gas
Number	fixed	Population depends on frequency of mode and temperature: $\langle n\rangle = \frac{1}{e^{\hbar\omega/k_BT}-1}$ (What are the limits of this expression for very small T and for very large T)? Small T: $e^{\hbar\omega/k_BT} \gg 1 \rightarrow$ $\langle n\rangle \sim e^{-\hbar\omega/k_BT}$ Large T: $e^{\frac{\hbar\omega}{k_BT}} \sim 1+\frac{\hbar\omega}{k_BT}$ $\langle n\rangle \sim k_BT/\hbar\omega$
Relationship between energy and momentum	$KE = p^2/2m$ For each particle	Depends on which branch you are considering (see chapter 4), but for acoustic phonons near k=0, $\omega \sim v_s k$ where k is crystal momentum and v_s is speed of sound
Relationship between temperature and total internal energy	For an N-particle gas $U = 3Nk_BT$	$U = \sum_K \sum_p < n_{K,p} > \hbar\omega_{K,p}$= $= \sum_K \sum_p \frac{\hbar\omega_{K,p}}{e^{\hbar\omega_{K,p}/k_BT}-1}$
Collisions	Molecules collide with each other and with walls of vessel	Phonons collide with each other, with surface of crystal, and with impurities
Energy conserved in collisions?	Yes	Yes
Momentum conserved in collisions?	Yes, except for at walls	Yes, modulo a reciprocal lattice vector **G**
Number of particles conserved in collision?	Yes	No

Thermal conductivity

Thermal conductivity is defined as heat flow in response to a **temperature gradient**

$$j_U = -K\frac{dT}{dx}$$

j_U is the energy transmitted across a unit area per unit time and K is the thermal conductivity coefficient. The negative sign reflects the intuitive fact that 'heat' flows from hot regions into cold regions.

We encounter thermal conductivity in many ways in the real world

- When we heat up a large pan on a tiny electric burner and we have to wait for the edges to reach the same temperature as the center
- When we touch two different materials in thermal equilibrium with the same room, such as wood and marble, and the latter feels cooler to the touch (the higher thermal conductivity of marble draws heat away from your fingers to the 'cooler' side which you are not touching)
- A challenge in modern electronics is to draw heat away from the processor, and appropriate materials with high thermal conductivity can serve this purpose

Temperature is an incoherent phenomenon—changes in temperature of a system are associated with changes in entropy. Thus, heat flow is not a ballistic process, but rather, involves a lot of collisions. As a starting point, we continue with a particle-like treatment of phonons. As shown earlier, at higher temperature, there is higher occupation or population of phonons modes with energy less than or comparable to the temperature. As these phonons diffuse to the cooler side of a solid, they will scatter many times and the value of the thermal conductivity coefficient will depend on how often they scatter.

$$K = \frac{1}{3} C v \ell$$

C is the heat capacity (at constant volume, per unit volume), v is the average particle velocity, and ℓ is the mean free path between collisions. The factors of v and ℓ are fairly intuitive (why?), but C needs some explaining.

When a particle moves from a region with temperature $T + \Delta T$ to a region with temperature T¸it will give up $c\Delta T$ of energy.

If this particle moves a distance of one mean free path in this process,

$$\Delta T = \frac{dT}{dx} \ell_x = \frac{dT}{dx} v_x \tau$$

Where τ is the average time between collisions. The subscript x has been added because the temperature gradient is only in the x-direction for now

The net flux of energy is:

$$j_u = nc < v_x^2 > \tau \frac{dT}{dx} = \frac{1}{3} nc \langle v^2 \rangle \tau \frac{dT}{dx}$$

There is a factor of v_x^2 because the first factor of v_x comes from the amount of energy the particle gives up and the second factor comes from the rate of flow of these particles. The number of particles is denoted by n and nc=C is the heat capacity per unit volume (n is particle density, number/volume).

Thus, $j_U = -\frac{1}{3} C v \ell \frac{dT}{dx}$ and the previous 'assertion' for the expression for K is confirmed

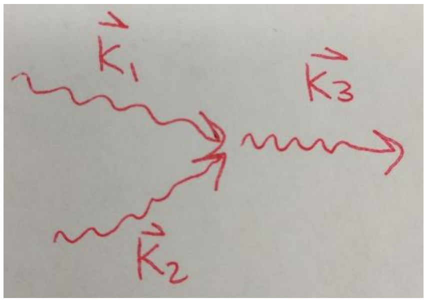
Causes of thermal resistivity

Phonons are **not** conducted ballistically from one end of the sample to another (if this were the case, thermal conductivity would solely be determined by sound velocity). Instead, a number of scattering processes introduce a 'thermal resistivity' (resistivity is inverse of conductivity). These include:

- Imperfections in the crystal such as impurities, inhmogeneities, and crystal grain boundaries
- The edge or surface of the crystal
- Scattering off another phonon (this requires an *anharmonic* potential, which typically holds for real materials because the atomic potential is *not perfectly* quadratic)

We begin by considering the latter:

Imagine a process where two phonons of momentum $\boldsymbol{K_1}$ and $\boldsymbol{K_2}$ collide and produce a third phonon with momentum $\boldsymbol{K_3}$**.** Another way to say this is that two phonons annihilate and produce a new one with momentum $\boldsymbol{K_3} = \boldsymbol{K_2} + \boldsymbol{K_1}$.



Following this process, the occupation numbers of these three modes is as follows:

$$n_{\boldsymbol{K_1}} \rightarrow n_{\boldsymbol{K_1}} - 1 = n_{\boldsymbol{K_1}}{}'$$

$$n_{\boldsymbol{K_2}} \rightarrow n_{\boldsymbol{K_2}} - 1 = n_{\boldsymbol{K_2}}{}'$$

$$n_{\boldsymbol{K_3}} \rightarrow n_{\boldsymbol{K_3}} + 1 = n_{\boldsymbol{K_3}}{}'$$

Energy conservation requires that:

$$n_{\boldsymbol{K_1}}\hbar\omega(\boldsymbol{K_1}) + n_{\boldsymbol{K_2}}\hbar\omega(\boldsymbol{K_2}) + n_{\boldsymbol{K_3}}\hbar\omega(\boldsymbol{K_3}) = n_{\boldsymbol{K_1}}{}'\hbar\omega(\boldsymbol{K_1}) + n_{\boldsymbol{K_2}}{}'\hbar\omega(\boldsymbol{K_2}) + n_{\boldsymbol{K_3}}{}'\hbar\omega(\boldsymbol{K_3})$$

$$= n_{\boldsymbol{K_1}}\hbar\omega(\boldsymbol{K_1}) - \hbar\omega(\boldsymbol{K_1}) + n_{\boldsymbol{K_2}}\hbar\omega(\boldsymbol{K_2}) - \hbar\omega(\boldsymbol{K_2}) + n_{\boldsymbol{K_3}}\hbar\omega(\boldsymbol{K_3}) + \hbar\omega(\boldsymbol{K_3})$$

$$0 = -\hbar\omega(\boldsymbol{K_1}) - \hbar\omega(\boldsymbol{K_2}) + \hbar\omega(\boldsymbol{K_3})$$

Momentum conservation requires that:

$$\boldsymbol{K_1} + \boldsymbol{K_2} = \boldsymbol{K_3} + \boldsymbol{G}$$

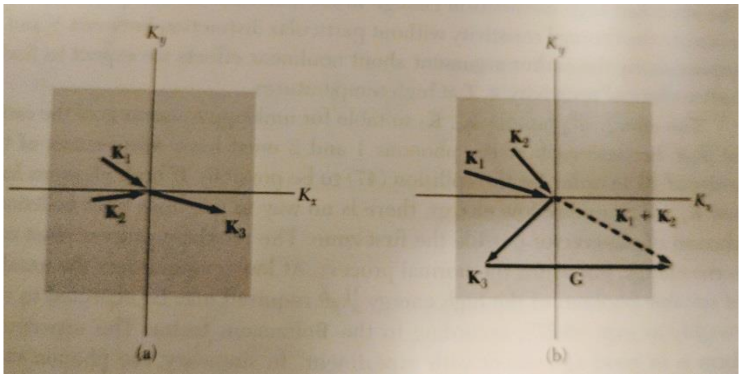
Where G is a reciprocal lattice vector.

To make both of these expressions completely generic, we can write:

- Energy conservation:$\sum_p \hbar\omega_p(\boldsymbol{K}) n_{\boldsymbol{K},p,initial} - \sum_p \hbar\omega_p n_{\boldsymbol{K},p,final} = 0$
- Momentum conservation: $\sum_p \boldsymbol{K} n_{\boldsymbol{K},p,initial} = \sum_p \boldsymbol{K} n_{\boldsymbol{K},p,final} + \boldsymbol{G}$

Where the sum over p denotes a sum over all phonon branches ("polarization branches").

The factor of G is needed because phonon momentum is only defined modulo a reciprocal lattice vector, so if the sum of two phonon momenta is located outside the first Brillouin zone, it is mapped onto an equivalent momentum in the first Brillouin zone by translating by a reciprocal lattice vector. If $\boldsymbol{G} \neq 0$ is needed to make the equality above hold, the scattering is called an **Umklapp process.** If **G**=0, it is called a normal scattering process. It should be noted that **only Umklapp** processes contribute to a material's thermal resistivity.



Comparison of normal (left) and umklapp(right) processes. The grey square marks the first Brillouin zone in two dimensions, and for a square lattice, the intersection points between the first Brillouin zone and the K_x, K_y *axes are at* $\pm\frac{\pi}{a}$

To show that only umklapp processes contribute to thermal resistivity, we consider the sum over all phonon scattering processes

$$\boldsymbol{K}_{tot} = \sum_{p} \sum_{K \in 1st\ Brillouin\ zone} \boldsymbol{K} n_s(\boldsymbol{K})$$

The outer sum sums over all phonon branches (e.g. all acoustic and optical dispersions) and the inner sum counts all momenta in the first Brillouin zone. The terms being added together include the momentum (vector) of each phonon mode being considered (**K**) multiplied by how many of them there are ($n_p(\boldsymbol{K})$).

If only normal scattering processes are included $\boldsymbol{K}_{tot} = 0$ because for every **K**, there is a **–K** in the first Brillouin zone and $n_p(\boldsymbol{K}) = n_s(-\boldsymbol{K}) = \frac{1}{e^{\hbar\omega_p/k_B T} - 1}$

In the context of thermal conductivity, what this means is that if you heat up one side of a rod, you will change the **occupation numbers** of phonon modes, but if these phonons can only scatter via **normal** processes, they will propagate down the length of the rod with no thermal resistance.

Now consider a situation where Umklapp processes are allowed.

$$\boldsymbol{K}_{tot} = \boldsymbol{K_{initial}} - \boldsymbol{K_{final}} = \sum_{p} \boldsymbol{K} n_{\boldsymbol{K},p,initial} - (\sum_{p} \boldsymbol{K} n_{\boldsymbol{K},p,final} + \boldsymbol{G})$$

$\boldsymbol{G} = v_1 \boldsymbol{b_1} + v_2 \boldsymbol{b_2} + v_3 \boldsymbol{b_3}$ is *any* reciprocal lattice vector, so when we have many terms contributing to **G**, we accommodate this by making the integers v_1, v_2, v_3 as large as needed

When we consider Umklapp processes, we do not have the same cancellation as we did without and $\boldsymbol{K_{tot}} = \boldsymbol{G}$.

Even if we fold this back into the first Brillouin zone, we are still left with a non-zero net momentum ($\boldsymbol{K}'$) which contributes a **net** drift velocity between collisions which is not zero.

Consider two temperature regimes:

1) **Temperature much larger than the Debye temperature ($\boldsymbol{T \gg \theta}$)** :
   at high temperature $n_p(\boldsymbol{K}) = \frac{1}{e^{\hbar\omega/k_B T} - 1} \approx \frac{k_B T}{\hbar\omega_p(\boldsymbol{K})}$ (from taylor expanding exponent to first order)
   Using $K = \frac{1}{3}Cv\ell = \langle v^2 \rangle \tau$, C is independent of temperature in this high temperature regime, but τ is not.
   The collision frequency ($\frac{1}{\tau}$) should be proportional to the number of phonons that a given phonon can collide with and thus $K \propto \tau \propto \frac{1}{n} \propto \frac{1}{T}$. In reality, $K \propto 1/T^x$ where x is between 1 and 2.
   High temperature not only ensures that C is constant as a function of temperature, but it also ensures that Umklapp processes have a reasonable probability of happening because it allows for sufficient thermal population of higher momentum (which are also higher frequency) acoustic phonons.
2) $\boldsymbol{T \ll \theta}$
   At low temperature, only low energy (and low momentum) acoustic modes will have substantial thermal population, so Umklapp processes will be unlikely and phonon-phonon scattering will not contribute to thermal resistivity

Imperfections

Geometric effects can decrease the thermal conductivity if they increase a length scale shorter than ℓ.

For instance, if the material is in a reduced geometry (e.g. a thin film or a nanowire) with minimum dimension length D

$$K \approx CvD$$

This also holds if the material consists of small crystallites of dimension D—phonons can scatter at the boundary between crystallites of different orientations and reduce the thermal conductivity

Example:

Thermal conductivity of insulating solids at room temperature (insulating so we don't have to deal with electrons' contribution to thermal conductivity)

Material	K (W/m K)	v (m/s)	Debye T
Diamond	2200	12,000	1320K
Silicon	130	5000	645K
KCl	6.5	2273	240K
SiO2	130	3962	470K

- This table illustrates the general scaling between thermal conductivity, sound velocity, and Debye temperature, which makes sense since both K and θ depend on v
- Diamond is characterized by a high thermal conductivity, and this is how one tests to see if a material is a diamond. Physically, the large sound velocity, which produces high thermal conductivity and Debye temperature, originates from very light atoms (carbon) connected by very stiff covalent bonds

Overview of Chapter 5

It is common knowledge that atoms "vibrate more" at higher temperature, and in this chapter we quantified this aphorism using the quantum nature of atomic lattice vibrations.

A key step in doing this is recognizing/believing/decreeing that phonons are bosons, and thus any number of particles can occupy a given 'state' which is defined by a momentum, frequency, and 'polarization' (a polarization is a distinct dispersion branch).

For a state with a given **frequency**, its expected occupation number is given by the Planck distribution

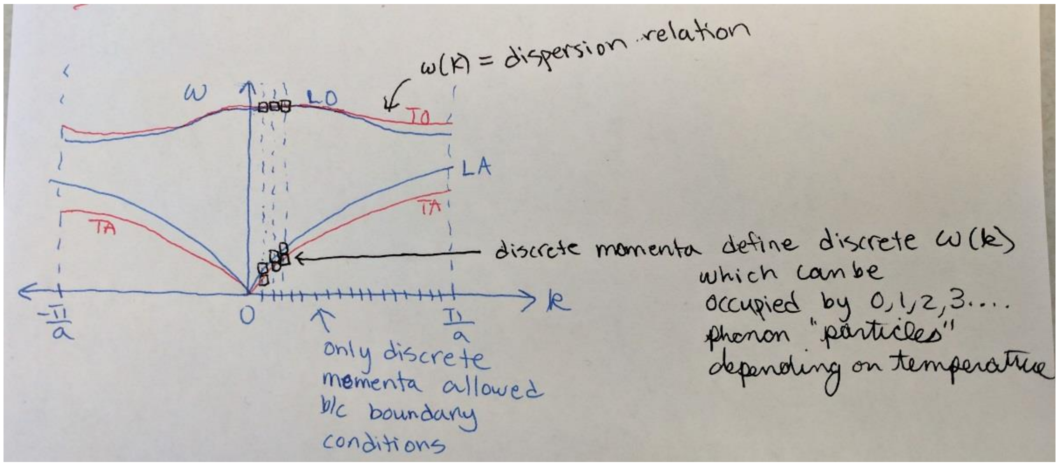
$$\langle n \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

This occupation number allows us to derive heat capacity, thermal expansion (if we were to do a more rigorous derivation than the textbook), and thermal conductivity.

A state with a given **frequency** also has an associated **crystal momentum** because elastic waves in crystalline solids have specific relationships between frequency and momentum called **dispersion relations.**

Using boundary conditions, we can show that **crystal momentum is quantized**, with permissible momenta (in 1 dimension) given by: $0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \dots \pm\frac{N\pi}{L}$ where N is the number of atoms in the chain, and L is the length of the chain.

Because any given **K** only allows specific frequencies to satisfy the equations of motion (this is what we solved for in Ch. 4), the statement above also means that only certain specific ω are allowed for each K. The number of permissible ω for each K is determined by how many phonon branches exist in the material. For a D dimensional solid with p atoms in the basis, there are D acoustic branches and D(p-1) optical branches. Each unique combination of $\omega, K, \text{and } polarization$ defines a 'normal mode' or a 'state' that can be occupied by n phonons. Although K and polarization (again, polarization is a term the book uses, and it is not exactly the same as light polarization…it is just an index to count all the phonon branches you have) help define the state you are considering, only the frequency, ω, relative to the temperature will determine the occupation of each state.



The **density of states**, $D(\omega)$ is a concept that we use to convert $\omega(K)$ dispersion relations into information we can use to determine occupation numbers. The density of states, as the name implies, is the number of states available between frequency ω and frequency $\omega + d\omega$. Density of states depends on the details of the dispersion relation and the dimensionality, but it **does not** depend on temperature (unless temperature changed the dispersion relations). Occupation number is a separate issue from the density of states.

In three dimensions, a generic expression for the density of states is: $D(\omega) = \frac{K^2 V}{2\pi^2}\frac{dK}{d\omega}$

If we had an analytic or computational expression for $\omega(K)$ we could invert it to get $K(\omega)$ and take a derivative to get $dK/d\omega$ and the density of states. But sometimes it is equally useful to make a physically motivated approximation, and the **Debye model** is such an approximation which works well for predicting behavior of real materials. The Debye model only considers **acoustic phonons** and approximates all acoustic branches as having the same group velocity v. There is also a cutoff frequency, ω_D, which defines the highest frequency phonon which is allowed in the debye model. This frequency also defines a momentum $k_D = \omega_D/v$ and a Debye temperature $\theta = \hbar\omega_D/k_B$. The Debye temperature is physically significant because it represents roughly the temperature at which a 'phonon gas' starts acting like a classical gas.

The Debye model gives a closed-form approximation for heat capacity in the limit of low temperature and high temperature (low and high relative to θ).

Low T: $C_V \approx \frac{12\pi^4}{5} N k_B \left(\frac{T}{\theta}\right)^3$ (This is consistent with experiments)

High T: $C_V \approx 3Nk_B$ (This is also consistent with experiments and with a classical gas)

In almost every concept we have discussed in this chapter, a particle 'velocity' has come into play, and this is essentially the speed of sound. Thus, the speed of sound in a solid, technically given by $\partial\omega/\partial k$ near k=0, is a crucial parameter determining how non-electromagnetic (e.g. thermal, but also vibrational and elastic wave) information is transmitted from one end of a solid to another.