

# THERMAL CONDUCTIVITY

## 1. Introduction:

Thermal **conduction** is a measure of how much heat energy is transported through a material per time. We expect that the thermal conduction will depend on the cross-sectional area,  $A$  (the more area, the more heat conducted); the length,  $s$  (the more length, the less heat conducted); the temperature difference,  $\Delta T$  (the higher the temperature difference, the more heat conducted); and the material. The parameter that covers the material we call the **thermal conductivity,  $K_T$** :

$$\text{Energy/time} = \text{Power} = A K_T (\Delta T / \Delta s),$$

and in the limit as  $\Delta T \rightarrow 0$  and  $\Delta s \rightarrow 0$ ,

$$\text{Power} = A K_T (-dT/ds),$$

where we have included the minus sign to indicate that the energy flows from high to low temperature ( $\Delta T / \Delta s$  was considered positive, but  $dT/ds$  is negative).

We can further **define a power density** (also called an energy flux):  $\mathbf{j}_U \equiv \text{Power/Area} = -K_T dT/ds$ .

## 2. How is the heat energy transported?

Our previous theory on heat capacity suggests that the heat energy can be carried by phonons (particles of wave energy) where the energy of the phonon is  $\epsilon = \hbar \Omega$ . Heat (radiation) on one end can create phonons on that end, and these phonons can then travel through the solid, and on the other end the phonons can convert their energy back into radiation (usually in the infrared). Thus we can think of the energy flux as equal to a particle flux times the energy per particle. [Flux = amount flowing per area.]

The particle flux is defined to be the number of particles passing through an area per second, but if we multiply through by  $\text{distance}_\perp / \text{distance}_\perp$  (where this distance is perpendicular to the area):

$$\text{particle flux} = (\text{number/area}) / \text{time} = (\text{number}/[\text{area} \bullet \text{distance}_\perp]) (\text{distance}_\perp / \text{time}) = \mathbf{n} \mathbf{v}_\perp,$$

where  $n$  is the number of phonons per volume and  $v_\perp$  is the speed of the phonons in the direction of the heat flow. But not all the particles are going in the same direction at the same speed (we assumed in the Debye approximation that  $v_g \approx v_p \approx \text{constant}$ ), but we must also account for three dimensions, so  $v_\perp$  does not necessarily equal the full  $v_p$ . Thus we must use an average for  $v_\perp$ . It might at first seem that the average for  $v_\perp$  would be close to zero; but we are interested in the energy flux which means the particle flux must be weighted by the energy/particle as we do next.

The extra energy carried by the particle in the  $+\perp$  direction over that carried in the  $-\perp$  direction can be specified by the **heat capacity per particle,  $c$** , times the temperature difference,  $\Delta T$ . Further, the temperature difference,  $\Delta T$ , is related to the temperature gradient,  $dT/ds$ , by the length that the particle travels before it collides (this is called the **mean free path,  $l$** ); further, this mean free path is equal to the speed of the wave (or phonon) times the average time between collisions,  $\tau$ :

$$\text{extra energy/particle} = c \Delta T = c (-dT/ds) l_\perp = \mathbf{c} (-dT/ds) \mathbf{v}_\perp \tau.$$

This then allows us to write:

$$\mathbf{j}_U = (\mathbf{n} \mathbf{v}_\perp) (\mathbf{c} \mathbf{v}_\perp \tau) (-dT/ds) = -ncv_\perp^2 \tau (dT/ds) = -K_T (dT/ds).$$

Hence we can say that  $K_T = ncv_\perp^2 \tau$ .

Further, since on average  $v_x^2 \approx v_y^2 \approx v_z^2$ , and from the 3-D Pythagorean theorem:

$v^2 = v_x^2 + v_y^2 + v_z^2 \approx 3v_x^2$ , we can say that  $v_\perp^2 \approx \frac{1}{3}v^2 \approx \text{constant}$  (as in the Debye approximation), so that:

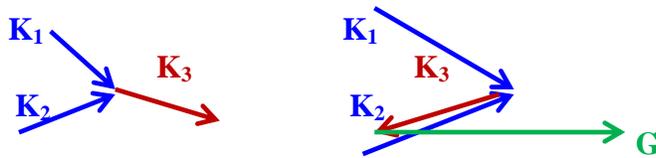
$$K_T = \frac{1}{3}ncv^2 \tau = \frac{1}{3}(nc)v(v\tau) = \frac{1}{3}Cv l;$$

where we have used  $C = nc$  as the total heat capacity per volume (recall  $n$  was number of particles per volume and  $c$  the heat capacity per particle),  $l$  is the mean free path ( $l = v\tau$ ), and  $v$  is the speed of the waves (speed of sound).

*In homework problem 28 in part 3 you will be asked to do something similar for the thermal conductivity due to electrons (instead of phonons as done here).*

### 3. Temperature dependence of $K_T$

In the harmonic approximation, two phonons will not “collide” – the two waves will travel right through one another just like any other type of wave. However, there can be an interaction between two phonons if we consider higher order terms in the PE function. This allows two phonons to interact and become a third phonon:  $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$ . This collision conserves momentum and energy (remember  $\mathbf{p} = \hbar\mathbf{K}$  and  $E = \hbar\Omega$  and  $v = \Omega/K$ ) and so the flow of heat energy in the form of phonon flow continues without change. However, if  $\mathbf{K}_3 > \mathbf{G}$ , then we get transfer of momentum to the crystal and a reverse flow of momentum (and energy flow) via  $\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3 + \mathbf{G}$ . Recall that a  $\mathbf{G}$  oscillation is that of a standing wave, so it has energy but does not have that energy flow one way or the other.



#### 3a) High temperature limit:

We start with  $K_T = \frac{1}{3}Cv l$ . At high temperatures ( $T > \Theta_{\text{Debye}}$ ), we have seen that  $C \approx \text{constant}$ ,  $v \approx \text{constant}$ , but what about  $l$ ? What causes the particles (the phonons) to be scattered (this is what causes the mean free path not to be infinite)? **The phonons will run into other phonons!** However, if two phonons collide there will be no net momentum change and no net energy transport change – unless the two phonons have combined  $\mathbf{K}$ 's such that  $\mathbf{K}_1 + \mathbf{K}_2 > \mathbf{G}$ . In this case, we do get energy in the form of a phonon reflected back. At high  $T$ 's we will have plenty of phonons with high enough energy so the probability of losing momentum and energy transport will be proportional to the total number of phonons. Hence the mean free path will depend on the number of phonons present: the more the number of phonons, the less the mean free path:  $l \propto (1/n)$  (here  $\propto$  stands for proportional to); and from the Planck distribution:  $\langle n \rangle = 1/[e^{\hbar\Omega/kT} - 1]$ ; and at high temperature the exponent of the exponential is small and so the exponential can be expanded in a Taylor series:  $e^{\hbar\Omega/kT} \approx 1 + \hbar\Omega/k_B T$ ; therefore:

$$l \propto 1/\langle n \rangle = [e^{\hbar\Omega/kT} - 1] \approx \{1 + \hbar\Omega/k_B T\} - 1 = \hbar\Omega/k_B T$$

which says that:  $l \propto 1/T$ ; this means then that  $K_T \propto (1/T)$ . We can further define a thermal resistivity as  $1/K_T$  so that the thermal resistivity is proportional to  $T$  (at high temperatures).

#### 3b) Low temperature limit:

At low temperatures,  $v$  is still constant; but  $C \propto (T/\Theta)^3$ , and  $l \propto 1/\langle n \rangle$ . The low temperature limit for  $\langle n \rangle = 1/[e^{\hbar\Omega/kT} - 1]$  now has a big exponent in the exponential, so that the  $-1$  term in the denominator can be neglected, and  $\langle n \rangle \approx e^{-\hbar\Omega/kT}$  and hence  $l \propto e^{+\hbar\Omega/kT}$ . Hence:

$$K_T \propto (T/\Theta)^3 e^{+\hbar\Omega/kT}.$$

This still isn't of the final form since we have a strong dependence on  $\Omega$ . At low  $T$ 's we don't have many phonons with sufficient energy to have a collision where  $\mathbf{K}_1 + \mathbf{K}_2 > \mathbf{G}$ . Such higher energy phonons are

created with a Boltzmann probability, and so we need  $\mathbf{K}$ 's (momenta) that are roughly  $\frac{1}{2}\mathbf{G}$  and this means we need  $\Omega$ 's that are roughly  $\frac{1}{2}\Omega_{\text{Debye}}$ . But recall that  $\hbar\Omega_{\text{Debye}}/k_B = \Theta$ . Therefore, we would expect that:

$$\mathbf{K}_T \propto (T/\Theta)^3 e^{+\Theta/2T} .$$

A plot of this function is on the supplemental excel spreadsheet containing several graphs of different functions of  $(x=T/\Theta)$ .

A further note is that as  $T$  gets very small, the part due to the mean free path gets very large - so large that it would be greater than the size of the crystal. In this case the phonons would scatter off the crystal boundaries or imperfections in the crystal rather than off other phonons. This means that the size and purity of the crystal would impose more of a restriction on the thermal conductivity than the mean free path due to phonon collisions. This then means that the mean free path restriction would no longer depend on  $T$ . Hence in this case the thermal conductivity temperature dependence would simply depend on the temperature dependence of the  $C$  term [that is, the  $(T/\Theta)^3$  term].

#### 4. Numerical values

Let's use values we have used before for Copper:  $a = 2.2 \times 10^{-10}$  m,  $v = 4,600$  m/s. When  $\mathbf{K}$  is near the zone boundary,  $\mathbf{K} \approx \frac{1}{2}\mathbf{G} = \pi/a$ , we have  $\mathbf{K} \approx \pi/(2.2 \times 10^{-10} \text{ m}) = 1.4 \times 10^{10}/\text{m}$ , and so using  $v = \Omega/\mathbf{K}$ ,  $\Omega = v\mathbf{K} = (4,600 \text{ m/s})(1.4 \times 10^{10}/\text{m}) = 6.4 \times 10^{13}$  rad/sec. This gives the energy for this phonon of  $\epsilon = \hbar\Omega = (6.63 \times 10^{-34} \text{ J-s} / 2\pi)(6.4 \times 10^{13} \text{ rad/s}) = \mathbf{6.7 \times 10^{-21} \text{ J}}$ .

This compares to the thermal energy/mode of  $k_B T$  at room temperature  $= (1.38 \times 10^{-23} \text{ J/K})(300 \text{ K}) = \mathbf{4.1 \times 10^{-21} \text{ J}}$ . The probability (Boltzmann) of exciting a phonon of one and half times the thermal energy will be small. Only lower  $\Omega$  frequencies with lower  $\mathbf{K}$ 's with longer  $\lambda$ 's will be excited (acoustical branch).

According to the Planck distribution,  $\langle n \rangle = 1/\{e^{\hbar\Omega/kT} - 1\}$ , for the phonons near the zone boundary at room temperature,  $\langle n \rangle = 1 / \{\exp[6.7 \times 10^{-21} \text{ J} / 4.1 \times 10^{-21} \text{ J}] - 1\} = 0.242$ .

Note: Since photon wavevectors (and frequencies) are continuous rather than discrete like those of phonons, the distribution of thermal energy for light is different. It is considered in the derivation of blackbody radiation – see the section in Physics III (PHYS 252) and/or Quantum Mechanics (PHYS 447). From the blackbody radiation analysis, the peak of the light (E&M) radiation occurs at a wavelength of  $\lambda_{\text{peak}} = b/T = 2.9 \times 10^{-3} \text{ m} \cdot \text{K} / 300 \text{ K} = 9.67 \times 10^{-6} \text{ m}$  (which is in the infrared region) and corresponds to a frequency ( $f=c/\lambda$ ) of  $3.1 \times 10^{13}$  rad/sec (compared to the  $6.4 \times 10^{13}$  rad/sec for phonons near the zone boundary).

At temperatures close to the melting temperature of 1,350 K, the thermal energy/mode is about 3 times that of the zone boundary  $\mathbf{K}=\pi/a$  phonon, and so these phonons near the zone boundary will have a decent probability of being excited. According to the Planck distribution,  $\langle n \rangle = 1/\{e^{\hbar\Omega/kT} - 1\}$ , for the phonons near the zone boundary at temperatures near the melting point,  $\langle n \rangle = 1/\{\exp[6.7 \times 10^{-21} \text{ J} / 1.9 \times 10^{-20} \text{ J}] - 1\} = 2.4$ . This is about 10 times more probable than at room temperature.