Up to now we assumed that the potential energy between two atoms is a quadratic function of the distance between the atoms. In chapter 3 we saw though that this is not the case. The Lennard Jones potential or the potential of an ionic crystal contains both an attractive and repulsive term. The attractive term was caused by Coulomb interaction (ionic potential) or Van der Waals interaction (Lennar Jones potential) and had a different x dependence from the repulsive term that originated from Pauli-exclusion's principle. The sum or the attractive and repulsive potential resulted in a minimum in the U(x) function where x is the distance from the equilibrium position. It should be clear from the discussion in chapter 3 that U(x) is not purely parabolic but contains odd and higher order components. Those anharmonic terms are described higher order terms in the potential energy function:

$$U(x) = cx^2 - gx^3 - fx^4 + \ldots\ldots \qquad [1]$$

The presence of those anharmonic terms result in:

1. The lattice constant will depend on the temperature, i.e. thermal expansion exists. This effect is illustrated in the figure below. At higher temperatures the intensity of the vibrational energy of the atoms will be higher resulting in larger vibrational aplitudes. If the potential contains asymmetric terms, a higher energy will result in different turning points on both sides of the equilibrium position. The average distance between the atoms will now increase. Note that for the Lennard-Jones potential shown in the figure below, the left turning point of T_2 is almost the same as the left turning point of T_1. The right turning point shift much more than the left turning point.

   The effect of the temperature on the average equilibrium position can be calculated using statistical mechanics, i.e. weighted average of the position using the Boltzman factor divided by the partition function (similar to how we calculated the thermal equilibrium occupancy of a certain phonon mode in the statistical mechanics primer (equation 18) but now the integral form):

   $$\langle x \rangle = \frac{\int\limits_{-\infty}^{\infty} x e^{-U(x)/(k_B T)} dx}{\int\limits_{-\infty}^{\infty} e^{-U(x)/(k_B T)} dx} \qquad [2]$$

   Using equation [1] you calculated <x> for the chapter 5 homework and found:

 $$\langle x \rangle = \frac{3g}{4c^2} k_B T \qquad [3]$$

   Note that in classed we discussed that only the odd terms of the potential energy should show up in this expression.

2. Elastic constants will depend on temperature and pressure. To understand this relation note that the derivative of the potential energy towards position gives a force, so taking the derivative of equation [1] gives:

   $$F = \frac{dU}{dx} = 2Cx - 3gx^2 - 4fx^3 + \ldots. \qquad [4]$$

So in other words Hooke's law is no longer obeyed and higher order force terms are there reducing the force between the atoms. We can also see from the potential function in the graph below that the coupling between the atoms decreases for higher vibrational amplitudes. Similar effects happen when you apply tensile stress to the material. The atoms are pulled farther apart from each other and the average slope of the U(x) graph goes down resulting in less coupling between the atoms reducing the elastic constants. Applying a compressive stress to the material does the opposite and will increase the coupling between the atoms. Note that this effect originates from the higher order odd terms in equation [1]: the attractive and repulsive terms in the potential energy function have a different x dependence.

3. The heat capacity at high temperature does not become constant: at higher temperatures the elastic constant will go down, see above. From equation (8) of chapter 4 we can conclude that $\omega(K)$ will go down, so the group velocity will go down, so the density of states goes up so the heat capacity goes up slightly.
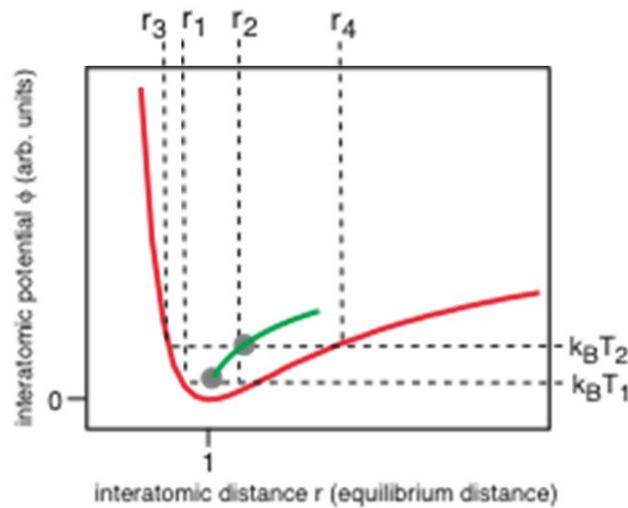

4. Two phonons can interact with each other and create a third phonon. Of course energy and momentum needs to be conserved. Kittel explains this process as the presence of one phonon causes a periodic elastic strain which modulates the elastic constant. The second phonon perceives the modulation of the elastic constant and is scattered to produce a third phonon. This process is shown in the diagram below. Notice that phonon phonon scattering becomes very probable at higher temperatures when there are a lot of phonons. It is the main mechanism that limits the mean free path of the phonons at high temperatures. In a perfect single crystal the phonon-phonon interaction is the mechanism that results in a final thermal conductivity due to flow of phonons.
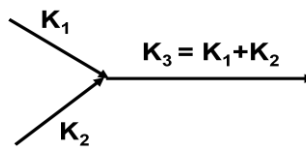
Just like an electric field (read a gradient of the electric potential) causes transport of charge in a conductor, a temperature gradient will cause transport of heat j_U, i.e.

$$j_U = -K_{thermal} \frac{dT}{dx}$$

[5]

Where $K_{thermal}$ is the thermal conductivity of the solid and j_U is the flux of thermal energy (energy transmitted across unit area per unit time). This equation suggests that phonons diffuse by a random process where phonons move from one side of the object to the other side of the object in a random path. Phonon collide with other phonons, crystal defects, and grain boundaries and get scattered, i.e. change direction. Similar to electrical conduction models we use the concepts of mean free path, i.e. the mean distance a phonon travels between two scattering events, and mean time between collisions (l), i.e. the mean time before the phonon scatters again (τ). Of course these two parameters are related by the phonon speed (see figure below).
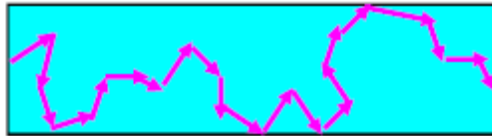

In class we derived an expression for the thermal conductivity:

$$K = \frac{1}{3} Cvl$$

[6]

Where l is the mean free path of the phonons, v is their speed and C is the heat capacity per unit volume. If you assume that we have n particles per volume unit and that the particles have an average velocity of $<v_x>$ in the x-direction than you can calculate the flux of particles (number of particles per unit area) to be:

$$\Phi_{particles} = \frac{1}{2} \frac{nA\langle |v_x| \rangle}{A} = \frac{1}{2} n \langle |v_x| \rangle$$

[7]

The factor half originates from the fact that half of the particles move towards the left and half towards the right. Note that A<|vₓ|> is a volume of a cylinder with a cross sectional area of A, and that half of the particles in this volume will have moved through on beyond the cylinder after 1 second. See also the figure below. The number of particles in that volume is equal to nA<|vₓ|>.
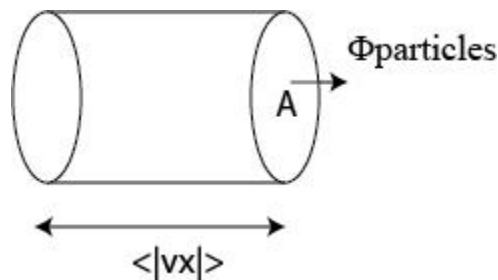
In order to find an expression for $K_{thermal}$ we need the thermal flux, so we need to multiply the particle flux $\Phi_{particles}$, by the thermal energy of a phonon. Let us consider phonons that travel a distance equal to the mean free path l_x from an area with high local temperature $T+\Delta T$ to and area of low local temperature T. Of course ΔT is given by:

$$\Delta T = \frac{dT}{dx} l_x = \frac{dT}{dx} v_x \tau \qquad [8]$$

Where v_x is the speed of the phonon and τ is the average time between two successive collisions of the same phonon. We assume that after the phonon scatters it is again in equilibrium with the local temperature. If we assume the heat capacity per phonon to be c, than $c\Delta T$ will be carried by each phonon. Also notice that we have phonon coming from the left and phonons coming from the right at location T. So putting that all together gives:

$$j_{U1} = -2\left(\frac{1}{2}n\langle|v_x|\rangle\right)(c\Delta T) = -n\langle v_x^2\rangle c\tau \frac{dT}{dx} = -\frac{1}{3}n\langle v^2\rangle c\tau \frac{dT}{dx} \qquad [9]$$

For the last step we average over all directions of the speed. It can be shown that $<v_x^2>=1/3<v^2>$. We can do one more simplification by replacing $<v>\tau$ by l, where l is the magnitude of the mean free path vector. So this will give us:

$$j_U = -\frac{1}{3}n\langle v\rangle lc \frac{dT}{dx} = -\frac{1}{3}\langle v\rangle lC \frac{dT}{dx} = -K_{thermal}\frac{dT}{dx} \qquad \text{QED} \qquad [10]$$

Where cn is replaced by C (C is the heat capacity per unit volume, c is the heat capacity per phonon, and n is the concentration of phonons).

Notice that the thermal conductivity is proportional to the mean free path l. The mean free paths of the phonon is determined by two different mechanisms, i.e. phonon-phonon scattering and the scattering of phonons by the geometry of the sample. The former effect is expected to limit the mean free path of the phonons at high temperature. Note that the number of phonons increases with the temperature and that the probability for phonon-phonon scattering increases with T, i.e.

$$l \sim \frac{1}{T} \qquad [11]$$

At low temperature the l will be determined by the size of the system, i.e. crystal size or sample size. The thermal conductivity will still depend on the temperature since C varies at low T according to T^3. Notice that the thermal conductivity is also proportional to the average speed of the phonons, so the contribution of optical phonons or transverse acoustical phonons that have a small group velocity (read small slope in the dispersion plot (see Fig. 8a from chapter 4)) will be negligible and those contributions can be ignored for a rough estimate.

The whole picture is a little bit more complicated than sketched above. We have assumed that the phonons in the material are in equilibrium with the local temperature. As the local temperature changes the distribution of the energy over the various phonon modes changes from position to position. In

order for a phonon that travels a certain distance through the crystal to get in equilibrium with the local temperature, a mechanism needs to exist for the phonons to redistribute the energy over all available phonon modes. Elastic collisions of phonons with imperfections will not change the energy of the scattered phonon. We saw that some three phonon processes will modify the total wave-vector. Kittel considered the following two three phonon processes:

1. Normal 3 phonon process (N-process) where the total momentum of the produced phonon is equal to the momentum of the original two phonons and this sum also lays in the first Brillouin zone, so

$$\vec{k}_3 = \vec{k}_1 + \vec{k}_2$$

See the figure on the left below. The pink box outlines the first Brillouin zone. Note that the total momentum and the total energy is not changed by the normal 3 phonon process. Normal 3 phonon processes will result in zero thermal resistance.
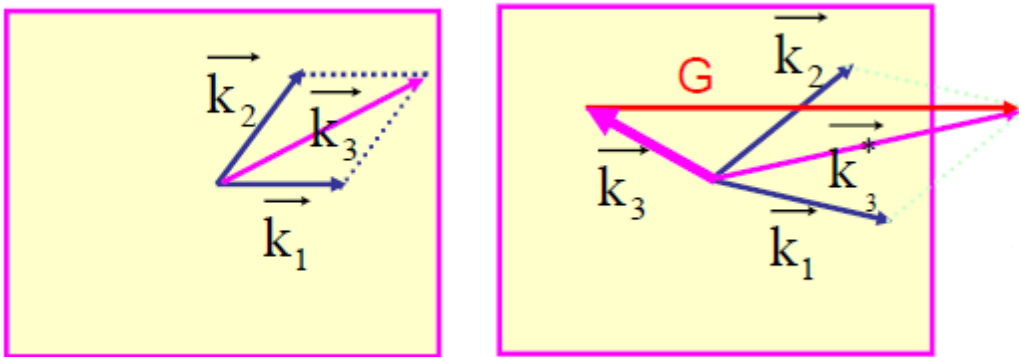
2. Umklapp 3 phonon process (U-process): this is a process were the sum of the wave-vectors of the two original phonons lays outside the first Brillouin zone. Note that a phonon whose wave-vector lays outside the first Brillouin zone can be described by a phonon inside the first Brillouin zone: so we can transfer the phonon back in the first Brillouin zone by substracting a reciprocal lattice vector. See also discussion on page 93 of chapter 4 of Kittel. This process is illustrated in the figure on the right above. Note that k_3 is pointing in the opposite direction of k_1+k_2. Umklapp is the German word for flipping. So Umklapp 3 phonon processes will allow for a redistribution of the energy over the different phonon modes and are crucial for establishing thermal equilibrium of the phonon. Notice that U-processes only occur at high temperature since you need two phonons with a rather large K so the sum vector falls outside the first Brillouin zone. A large K-vector means a high ω (see also dispersion plot on page 96 of Kittel).

Also other scattering processes with grain boundaries or defects can contribute to some extent to a redistribution of the energy. Although I'm surely not an expert on thermal conductivity, it looks like the mean free path increases for lower temperature, and at low temperature the mean free path is limited by the sample size. The graphics below show how the phonon mean path varies with a

function of the temperature. Note that also the heat capacity is temperature dependent and that therefore the thermal conductivity has a maximum value for a certain temperature.
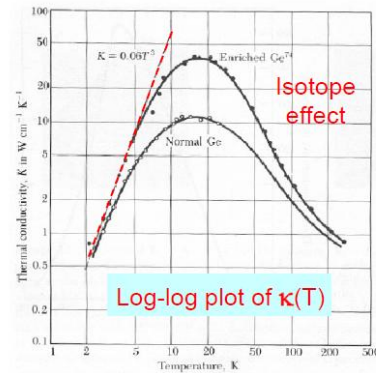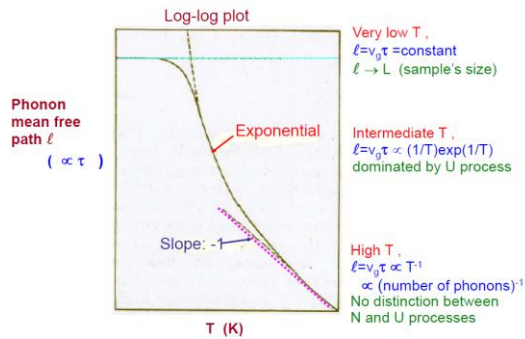
Last of all a vivid picture of a phonon that I definitely wanted to share with you and a couple of references that I want you to look at if you want to learn more about thermal properties.

○ Normal lattice positions for atoms
● Positions displaced because of vibrations
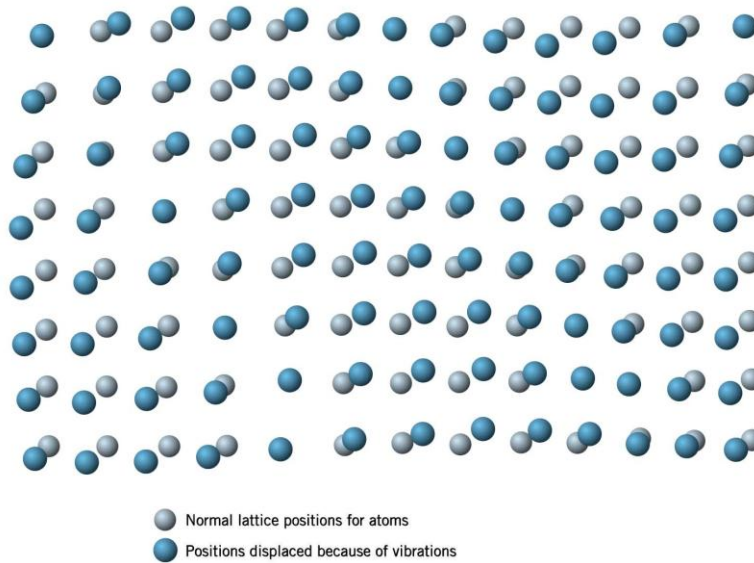
[1] Website of Solid State Physics class of Charley Myles of Texas Tech University and posted presentation on that website.

[2] Electroncs and Phonons, J.M. Ziman