SCPY 371: Solid State Physics **1^{st} Semester 2021**

Lecture 5: Phonons and thermal properties

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In this chapter, we will try to explain thermal properties that are due to lattice vibrations or phonons. In order to archive this task, we will have to first consider the energy of lattice vibration. Classically, this energy is proportional to the amplitude squared, which implies that its energy can be any value. You have proved this relation in the homework. However, similar to photons, phonons are quantum-mechanical particles and its energy is quantized. In the previous chapter, we have learned that we can model the crystal as atoms connected by springs. Therefore, the Hamiltonian for this system is the same as that of the simple harmonic oscillators, to which we know the answer. Quantum mechanically, the energy of phonons with the frequency ω is equal to:

$$E_n = \hbar\omega_{\vec{K},\sigma}\left(n+\frac{1}{2}\right),$$

where $\omega_{\vec{K},\sigma}$ is the normal mode frequency of phonons and σ indicates phonon modes. The total energy is equal to $\sum_{\vec{K},\sigma}\langle n_{\vec{K},\sigma}\rangle\,\hbar\omega_{\vec{K},\sigma}$, where $\langle n_{\vec{K},\sigma}\rangle$ is the Planck distribution function indicating how many phonons of a particular energy there are at a given temperature. The statistics used to derive this expression is the Boson statistics, which is the same as in the case of photons. We will use this knowledge of phonon energy to study the thermal properties of solids.

5.1 Phonon heat capacity

The first thermal quantity that we will study is the heat capacity, which is defined as

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V,$$

where the subscript V implies the heat capacity at constant volume, which is theoretically more fundamental than the heat capacity at constant pressure C_P even though the latter is experimentally measured. The difference between them are quite small at a finite temperature and goes to zero as temperature approaches zero.

We will here only consider the heat capacity that is due to phonons, which we sometimes call the **lattice heat capacity** to differentiate it from the **electronic heat capacity** which is due to electrons. We will come back to the electronic heat capacity later in the course.

First, we have to calculate the total energy of phonons for a **single branch** (acoustics or optical), which is equal to

$$U = \sum_{\vec{K}}\sum_{p}\left\langle n_{\vec{K},p}\right\rangle\hbar\omega_{\vec{K},p}, \tag{5.1}$$

where $\sum_p$ denotes the sum over the phonon polarizations and $\left\langle n_{\vec{K},p}\right\rangle$ is the Planck distribution function, which is equal to

$$\left\langle n_{\vec{K},p}\right\rangle = \frac{1}{e^{\beta\hbar\omega}-1},$$

where $\beta = \frac{1}{kT}$, where k (or k_B) is the Boltzmann constant, and the $\langle ... \rangle$ denotes the thermal average. Knowing $\left\langle n_{\vec{K},p} \right\rangle$, we can rewrite Eq. 5.1 as

$$U = \sum_{\vec{K}} \sum_{p} \frac{\hbar\omega_{\vec{K},p}}{e^{\beta\hbar\omega} - 1}. \tag{5.2}$$

Since we will consider a very large system, that is, the number of particles or atoms in the system is close to infinity, we can treat $\vec{K}$ as a continuous variable. Therefore, we will replace $\sum_{\vec{K}}$ with the integral over $\vec{K}$. Then, we also have to know the density of the modes $D_p(\vec{K})$ or $D_p(\omega)$, that is, the number of states for a given value of $\vec{K}$ or ω. This density of states can be calculated from the dispersion relation.

Density of states in three dimensions We will start by first considering the simple case of one dimensional lattice. Let us consider the one-dimensional lattice of $N+1$ atoms with the separation distance between the nearest neighbors a and hence the total is $L = Na$. We will assume that the boundary condition of this system is periodic, that is, $u_s(sa) = u_s(sa+L)$ where $u_s(sa) \propto \sin Ksa$. One could think of this system as a circular lattice that closes on itself so that the two ends of the lattice are connected. This boundary condition can only be satisfied if

$$K = 0,\ \pm\frac{2\pi}{L},\ \pm\frac{4\pi}{L},\ \pm\frac{6\pi}{L}, ..., \pm\frac{N\pi}{L}.$$

In fact, the number of $\vec{K}$ is equal to the number of atoms in the lattice that are allowed to move. Note that the two atoms at the two ends are the same atom that is located at the origin. We can immediately see that $\Delta K = \frac{2\pi}{L}$. This means that in the interval $\frac{2\pi}{L}$ there can only be one state or one $\vec{K}$ value. The density of state in this case is, therefore, one per $\frac{2\pi}{L}$ or $\frac{L}{2\pi}$.

Similarly, in the two- or three dimensional space, we can apply the periodic boundary condition and found that $\Delta K = \frac{2\pi}{L}$ along two or three orthogonal directions, respectively. Therefore, there can only be one state in the area (in the reciprocal space) of $\dfrac{4\pi^2}{L^2} = \dfrac{4\pi^2}{A}$ in two dimensions and in the volume of $\dfrac{8\pi^3}{L^3} = \dfrac{8\pi^3}{V}$ in three dimensions, and hence the densities are equal to $\dfrac{A}{4\pi^2}$ and $\dfrac{V}{8\pi^3}$ in 2D and 3D, respectively. For N states in three dimensions, we find that

$$N = \frac{V}{8\pi^3} \cdot \frac{4}{3}\pi K^3,$$

where K denotes the radius of a sphere in the reciprocal space. Therefore, the density of states in three dimensions in terms of ω is

$$D(\omega) = \frac{dN}{d\omega} = \frac{V}{8\pi^3} \cdot 4\pi K^2 \frac{dK}{d\omega}.$$

In order to calculate $\frac{dK}{d\omega}$, we need to the dispersion relation $\omega(K)$. This expression is for one polarization of phonons. Since in three dimensions each branch has three polarizations, we have to multiply three to the equation, which gives

$$D(\omega) = 3 \cdot \frac{VK^2}{2\pi^2} \frac{dK}{d\omega}.$$

Debye Model for Density of States The Debye model is used to approximate the heat capacity at small temperature, at which only low-energy phonons are excited. From the dispersion relation of phonons, we can see that the Debye approximation focusses on the acoustic branch at small $\vec{K}$ where the dispersion relation is linear, that is,

$$\omega = vK \quad \Rightarrow \quad \frac{d\omega}{dK} = v,$$

where v is the sound velocity. Therefore, the density of states in terms of ω becomes

$$D(\omega) = \frac{3V}{2\pi^2}\frac{\omega^2}{v^3}.$$

This function is monotonically increasing and goes to infinity as ω becomes large. However, in the real system, we know that the number of modes is equal to $3N$, where N is a number of atoms, which is finite. Therefore, there must be a cut-off frequency to prevent $D(\omega)$ from becoming too large. This constraint can be expressed by the following equation:

$$\begin{aligned}
\int_0^\infty D(\omega) d\omega &= \frac{3V}{2\pi^2 v^3}\int_0^{\omega_D} \omega^2 d\omega = 3N \\
\Rightarrow \quad \frac{V}{2\pi^2 v^3}\omega_D^3 &= 3N \\
\Rightarrow \quad \omega_D = v\left(6\pi^2\frac{N}{V}\right)^{1/3} &= v\left(6\pi^2 n\right)^{1/3},
\end{aligned}$$

where $n \equiv \frac{N}{V}$ is the density.

Now we are ready to calculate the total of energy of phonons. Therefore, for the Debye approximation we have

$$\begin{aligned}
U &= \int_0^{\omega_D} \hbar\omega\, D(\omega)\, \langle n(\omega)\rangle\, d\omega \\
&= \frac{3V\hbar}{2\pi^2 v^3}\int_0^{\omega_D} \frac{\omega^3\, d\omega}{e^{\hbar\omega/kT}-1}.
\end{aligned}$$

We then take the derivative of this equation with respect to temperature while keep V fixed to obtain the heat capacity at constant volume.

$$C_V = \frac{3V\hbar}{2\pi^2 v^3}\int_0^{\omega_D} \frac{\omega^3\, d\omega}{\left(e^{\hbar\omega/kT}-1\right)^2}\cdot e^{\hbar\omega/kT}\cdot\frac{\hbar\omega}{kT^2}.$$

Let $x = \frac{\hbar\omega}{kT}$ and rewrite the equation for C_V as

$$\begin{aligned}
C_V &= \frac{3V\hbar^2}{2\pi^2 v^3}\cdot\frac{1}{kT^2}\cdot\left(\frac{kT}{\hbar}\right)^5 \int_0^{x_D} \frac{e^x\, x^4\, dx}{(e^x-1)^2}. \\
&= \frac{3Vk}{2\pi^2 v^3}\left(\frac{kT}{\hbar}\right)^3 \int_0^{x_D} \frac{e^x\, x^4\, dx}{(e^x-1)^2}. \qquad (5.3)
\end{aligned}$$

First, we can consider this expression in the low-temperature limit where $T \to 0$, which means $x \to \infty$. Therefore, the integral becomes

$$\int_0^\infty \frac{e^x\, x^4\, dx}{(e^x-1)^2} = \frac{4\pi^4}{15}.$$

The expression for C_V becomes

$$C_V = \frac{3Vk}{2\pi^2 v^3}\left(\frac{kT}{\hbar}\right)^3\cdot\frac{4\pi^4}{15} = \frac{2\pi^2 Vk}{5v^3}\left(\frac{kT}{\hbar}\right)^3$$

We will write this expression in terms of the Debye temperature θ, which is defined as

$$\begin{aligned}
\hbar\omega_D &= \hbar v\left(6\pi^2 n\right)^{1/3} = k\theta \\
\Rightarrow \quad \theta^3 &= \left(\frac{\hbar}{k}\right)^3\cdot 6\pi^2 v^3\frac{N}{V} \\
\Rightarrow \quad C_V &= \frac{12\pi^4}{5}Nk\left(\frac{T}{\theta}\right)^3 \qquad (5.4)
\end{aligned}$$

This expression for C_V shows that at low temperature the heat capacity is proportional to T^3, which is in agreement with the experiment.

We could understand this T^3 dependence in a more physical way. First, we have to realize that not all phonon modes are excited at a given temperature and only those with energy $\hbar\omega < kT$ will be excited. That means, the fraction of the three dimensional K-space with phonons that can be excited is proportional to $(\omega/\omega_D)^3 = (T/\theta)^3$. Note that if T is equal to the Debye temperature θ, then all phonon modes will be excited. Since the total number of phonons is $3N$ and each phonon has energy of kT, the total energy is approximately equal to $3N \cdot (T/\theta)^3 \cdot kT$. Therefore, the heat capacity is equal to $12Nk(T/\theta)^3$, which is the same order as what we calculate above. In the real system, in order to observe this T^3 dependence, we have to go to much lower temperature than the Debye temperature; $T < \theta/50$.

Now, we will consider the limit where temperature is large, that is, $T \to \infty$ or $x_D \ll 1$. That means, $e^x \approx 1$ and $e^x - 1 \approx x$. Therefore, the integral in Eq. 5.3 becomes

$$\int_0^{x_D} \frac{e^x\, x^4\, dx}{(e^x-1)^2} \approx \int_0^{x_D} \frac{x^4}{x^2}\, dx = \frac{x_D^3}{3}.$$

And, the heat capacity becomes

$$C_V = \frac{3Vk}{2\pi^2 v^3}\left(\frac{kT}{\hbar}\right)^3 \frac{x_D^3}{3} = \frac{3Vk}{2\pi^2 v^3}\left(\frac{kT}{\hbar}\right)^3 \frac{1}{3}\left(\frac{\hbar\omega_D}{kT}\right)^3 = \frac{Vk}{2\pi^2 v^3}\cdot 6\pi^2 v^3 \cdot \frac{N}{V} = 3kN.$$

This value is known as the Dulong and Petit value and it is the heat capacity at the high-temperature limit where all $3N$ phonons mode are excited with each mode having energy of kT.

Einstein Model for the Density of States There is another model for the density of states of phonons. In this model, we will again start with N simple harmonic oscillators in the three-dimensional lattice. However, now we will assume that all of these N oscillators have the same vibrational frequency ω_0. Therefore, the density of states in this case is the $\delta-$function $D(\omega) = 3N\delta(\omega - \omega_0)$, where $3N$ is the total number of modes in three dimensions.

We can plug in this expression back the our equation for the total energy and obtain

$$\begin{aligned} U &= \int_0^{\omega_D} \hbar\omega\; 3N\delta(\omega-\omega_0)\; \langle n(\omega)\rangle\; d\omega \\ &= 3N\langle n(\omega_0)\rangle \hbar\omega_0 \\ &= 3N\frac{\hbar\omega_0}{e^{\hbar\omega_0/kT}-1}. \end{aligned} \quad (5.5)$$

Therefore, the heat capacity is equal to

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = 3Nk\left(\frac{\hbar\omega_0}{kT}\right)^2 \frac{e^{\hbar\omega_0/kT}}{\left(e^{\hbar\omega_0/kT}-1\right)^2}$$

Einstein first came up with this expression to describe the heat capacity in a solid. This model does not agree with the experiment at low temperature, which show the T^3 dependence as aforementioned. However, it can describe the heat capacity of a solid quite well in the intermediate temperature range. Furthermore, as $T \to \infty$ this expression for C_V goes to $3N$ in agreement with the experiment at high temperature. This fact implies that this model corresponds to high energy phonons, whose dispersion is quite flat, which is the characteristic of optical phonons. Therefore, the Einstein model is applied to the optical mode in the phonon dispersion relation.

For the low temperature limit ($T \to 0$) or $e^{\hbar\omega/kT} \gg 1$, we have

$$C_V \approx 3Nk\left(\frac{\hbar\omega_0}{kT}\right)^2 \cdot e^{-\hbar\omega_0/kT}.$$

which exponentially goes to zero, faster than the T^3 dependence.

On the other hand, in the high temperature limit $T \to \infty$ which mean $e^{\hbar\omega/kT} \approx 1 + \hbar\omega_0/kT$, we have

$$C_V \approx 3Nk\left(\frac{\hbar\omega_0}{kT}\right)^2 \cdot \frac{1}{(\hbar\omega_0/kT)^2} = 3Nk.$$

which is the Dulong and Petit value as we expect.

5.2 Effects of Anharmonic Terms

So far, we have done the calculations on the assumptions that

1. the displacement from the equilibrium separation is small, that is, the amplitude of the oscillations is small.
2. the higher-order terms in the expansion of binding energy is ignored, that is, we assume that the oscillations is purely harmonic.

However, in the real system the displacement does not necessarily small and the higher-order term could contribute significantly to the properties of solid. In fact, there are properties that cannot be explained based only the harmonic approximation and the anharmonic terms (which proportional to u^3 and u^4) are required. For example,

- Phonon-phonon interaction
- Thermal expansion which linearly proportional to T
- Saturated heat capacity at high temperature smaller than the Dulong and Petit value
- Finite thermal conductivity (harmonic model gives an infinite thermal conductivity for a perfect crystal)

We will not try to explain all these phenomena using the anharmonic model. In stead, we will pick only two phenomena, the thermal expansion and thermal conductivity.

Thermal expansion In order to include the anharmonic terms, we will have to rewrite the expansion of binding energy and keep higher-order terms. Assuming that the equilibrium position is at $x = 0$, we can write the series expansion as

$$U(x) = cx^2 - gx^3 - fx^4,$$

where c, g, and f are all positive. g denotes the asymmetric mutual repulsion between atoms and f denotes the softening of the vibration; hence the negative sign.

The thermal expansion is proportional to the change of the equilibrium separation or average separation as a function of temperature. As we might have already known that in the harmonic approximation (with only the quadratic term in the expansion) the average separation remains constant as a function of temperature. We can easily prove this by calculating the average separation $\langle x\rangle$.

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty} dx\, x\, e^{-\beta cx^2}}{\int_{-\infty}^{\infty} dx\, e^{-\beta cx^2}}.$$

However, as you might want to verify for yourself that $\int_{-\infty}^{\infty} dx\, x\, e^{-\beta cx^2} = 0$, since $xe^{-\beta cx^2}$ is an odd function. Therefore, for the harmonic approximation $\langle x\rangle = 0$ and hence the thermal expansion cannot occur.

Now, if we include the x^3 and x^4 term, we will have

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty} dx\, x\, e^{-\beta U}}{\int_{-\infty}^{\infty} dx\, e^{-\beta U}}.$$

Now, we will again assume that x is small, that is, we can rewrite $e^{-\beta U}$ as

$$e^{-\beta\left(cx^2-gx^3-fx^4\right)} = e^{-\beta cx^2} e^{-\beta\left(-gx^3-fx^4\right)} \approx e^{-\beta cx^2}\left[1+\beta(gx^3+fx^4)\right].$$

We then have

$$\int_{-\infty}^{\infty} dx\, x\, e^{-\beta U} = \int_{-\infty}^{\infty} dx\, e^{-\beta cx^2}\left[x+\beta gx^4+\beta fx^5\right] = \frac{3\pi^{1/2}}{4}\frac{g}{c^{5/2}}\beta^{-3/2}.$$

Note that the x and x^5 terms are odd, so they vanish after the integration and only the second term contributes to the integral. For the denominator, we have

$$\int_{-\infty}^{\infty} dx\, e^{-\beta U} = \int_{-\infty}^{\infty} dx\, e^{-\beta cx^2} = \left(\frac{\pi}{\beta c}\right)^{1/2}.$$

Therefore, the average separation becomes

$$\langle x\rangle = \frac{3g}{4c^3}kT,$$

which is linear proportional to T.

Thermal conductivity There are two processes that determine the thermal conductivity. The first process is the scattering of phonons by other phonons and the second process is the scattering of phonons by imperfections in the crystal lattice. The more often the scattering of phonons, the less the thermal conductivity. The anharmonic term will play a role in the phonon-phonon scattering process, which will lower the thermal conductivity of the perfect crystal. In fact, for the perfect crystal if there is no the anharmonic terms the thermal conductivity would go to infinity, which is in contrast with the experimental result since the thermal conductivity is always finite.

It turns out that the thermal conductivity is proportional to the temperature gradient and **mean free path** of phonons. The mean free path is large if there is less scattering with other phonons and imperfections. Since the number of phonons depends on temperature. The higher the temperature, the more the phonons. We would expect that as the temperature decreases, the number of phonons also decreases, and hence the mean free path should become larger. In fact, the mean free path l is inversely proportional to T, that is, $l \propto \frac{1}{T}$. We will not go into detail on how to derive this relation here.

In order to derive the thermal conductivity, we will consider the heat flux that is transferred between regions with different temperature, where there is temperature gradient. The net flux of heat energy j_U can be written as

$$j_U = -\frac{1}{3}n\langle v\rangle c\Delta T,$$

where n is the density of molecules, v is the phonon velocity, c is the specific heat or heat capacity per molecule, the $\frac{1}{3}$ factor represents the average among three orthogonal directions in three dimensions, and the minus sign denotes that the direction of the energy flux that is opposite to ΔT, from the high-temperature to low-temperature regions. We can write ΔT as

$$\Delta T = l\frac{dT}{dx},$$

where l is the mean free path of phonons. Therefore, we obtain

$$j_U = -\frac{1}{3}ncvl\frac{dT}{dx} = -\frac{1}{3}Cvl\frac{dT}{dx},$$

where $C = nc$ is the heat capacity per unit volume and we have omitted $\langle ... \rangle$ for v. Using the definition of the thermal conductivity

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

where K is the conductivity, we arrive at the final expression for K

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

We can write l as $l = v\tau$, where τ is the mean free time, that is, time between the collisions and rewrite the expression for K as

$$K = \frac{1}{3}Cv^2\tau.$$

In a crystal, there are two processes of phonon collisions that give rise to the thermal resistivity.

1. **Normal Process** In the normal process, the change of momentum of phonons after the collision is small and the momentum after the collision stays within the first Brillouin zone. There is no loss of phonon energy in this process and the thermal resistivity is zero. The normal process dominates at low temperature where the number of phonons and their energies are low.
2. **Umklapp Process** In the umklapp process, the change of the momentum after the collision is large and the final momentum of phonons is outside the first Brillouin zone, which can be mapped back to the zone. Therefore, the phonons lose energy in the collision giving rise to the non-zero thermal resistivity. The umklapp process dominates at high temperature where there are a lot of high energy phonons.

Although at low temperature the thermal resistivity is dominated by the normal process, the experiment shows that the thermal resistivity indeed does not vanish. This is because even at very low temperature, the umplapp can occur and degrade the thermal current.

References

[1] Kittel, C.: Introduction to Solid State Physics 7th Edition (Chapter 3), John Wiley & Sons, Inc. (1996).

[2] Ashcroft, N. W. and Mermin, N. D.: Solid State Physics (Chapter 20), Thomson Learning, Inc. (1976).