In Chapter 5 we discussed the total energy contained in a solid, i.e. the thermal energy of the phonons, the heat capacity, and in the latter part of the chapter the heat conduction done by phonons.

An expression for the energy contained in all phonons, U, is given by:

$$U = \sum_K \sum_p U_{K,p} = \sum_K \sum_p \langle n_{K,p} \rangle \hbar \omega_{K,p} = \sum_K \sum_p \frac{\hbar \omega_{K,p}}{e^{\hbar \omega/(k_B T)} - 1}$$ [1]

Where $U_{K,p}$ is the total energy of a phonon mode with wavevector K and polarization p which is equal to the thermal equilibrium occupancy of that particular phonon mode, $<n_{K,p}>$ times the energy of a single phonon in that particular phonon mode, i.e. $\hbar \omega$. The thermal equilibrium occupancy follows from statistical mechanics, so please review the statistical mechanics handout. To add over the modes we often assume that there are three different polarizations for each different wavevector K. To make the counting easier we furthermore replace the summation over K with an integral over the density of states $D(\omega)$. $D(\omega)d\omega$ is the number of states between ω and $\omega+d\omega$. Equation [1] can now be written as:

$$U = 3 \int d\omega \, D(\omega) \frac{\hbar \omega}{e^{\hbar \omega/(k_B T)} - 1}$$ [2]

The boundaries of the integral should be so it contains all the modes. What we are shooting for is the heat capacity (C), i.e. how much energy do we need to add in order to raise the temperature with 1 degrees Kelvin. Two different heat capacities are often considered, i.e. the heat capacity at constant pressure which is loved by experimentalists as it is easy to determine that in the lab, and the heat capacity at constant volume, which is loved by theoreticians as it does not include work that needs to be done to expand for example a gas that is heated. The heat capacity at constant volume, C_V, can be calculated from the derivative of U, i.e.

$$C_V = \left(\frac{dU}{dT} \right)_V = 3 k_B \int d\omega \, D(\omega) \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\hbar \omega/(k_B T)}}{\left(e^{\hbar \omega/(k_B T)} - 1 \right)^2}$$ [3]

Note that at very high temperature the terms with w can be approximated by a Taylor expansion of the exponential function and that C_V becomes equal to $3k_B$ times the total number of phonon modes per polarization, i.e. N:

$$C_V \approx 3 k_B \int d\omega \, D(\omega) \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{1 + \frac{\hbar \omega}{k_B T}}{\left(1 + \frac{\hbar \omega}{k_B T} - 1 \right)^2} \approx 3 k_B \int d\omega \, D(\omega) = 3 k_B N$$ [4]

The value of the heat capacity at high temperatures is known as the Dulong and Petit value.

Note that equation (4) is true for any dispersion and any density of states function. To get more specific expressions for U and C$_V$ we need to know something about the density of states of our system. Both Einstein and Debye estimated U and CV of a solid from their own density of states function. We will first discuss Einstein's approach and then review the approach followed by Debye.

Einstein assumed that a solid containing N atoms can be modeled by N independent harmonic oscillators that all have the same eigen-frequency. In this model you assume that the atoms are not coupled to each other and will function as independent oscillators. Above expressions are still valid but rather than having different phonon modes with different polarization, now we have different harmonic oscillators that oscillate in the x, y, and/or z-direction. Of course I know from chapter 4 that this model is not completely correct, because a vibrating atom on the left side of my crystal will cause its neighbors to vibrate as well and will result in an elastic wave traveling towards the right. So it is definitely an approximations. Einstein furthermore assumed that all oscillators have the same eigen-frequency, so Einstein's density of states function is:

$$D(\omega) = N\delta(\omega - \omega_0)$$ [5]

As shown in class we can calculate U and C$_V$ from equation [2] and [3]:

$$U = 3\int d\omega\, N\delta(\omega - \omega_o)\frac{\hbar\omega}{e^{\hbar\omega/(k_BT)}-1} = 3N\frac{\hbar\omega}{e^{\hbar\omega/(k_BT)}-1}\Bigg|_{\omega=\omega_o} = \frac{3N\hbar\omega_o}{e^{\hbar\omega_o/(k_BT)}-1}$$ [6]

$$C_V = \left(\frac{dU}{dT}\right)_V = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^{\hbar\omega/(k_BT)}}{\left(e^{\hbar\omega/(k_BT)}-1\right)^2}$$ [7]

Note that for large values of T, equation [7] can be approximated by 3NkB (we proved this in class) which is equal to equation [4], i.e. the Dulong Petit value. Figure 11 in the text shows the heat capacity of diamond along with the Einstein model. In particularly at small temperatures, the difference between theory and experiment are large. So for small temperatures, one cannot describe the atoms as being independent oscillators and we have to consider the coupling between the oscillators and use the traveling elastic mode concept developed in chapter 4. Debye that the eigen-frequencies of a solid are standing or traveling wave, not individual vibrating atoms. So Debye assumed that solid is better described by a system of coupled mechanical oscillators. In class we derived the density of states function for the 1D and 3D system while you did the calculation for the 2D system at home.

For the 1D system we had two different approaches which lead to the same density of states function, i.e. a 1D system of N+1 atoms with a beginning and an end atom whose positions are fixed and a 1D system where N atoms are situated on a circle and there is no beginning or end atom.

We will first discuss the linear chain. Solutions of the wave equation of such system are standing waves and given by the following expression:

$$u_s = u(0)e^{-i\omega_{K,p}t}\sin(sKa)$$ [10]

Where u_s is the displacement of the sth atom and s is the atom number. Note that u_s is not a function, it is a series of numbers. The larger the wavelength of the mode the lower the ground state of that particular mode. Note that in chapter 4 we saw that the energy of a mode is quantized, i.e. a mode can have an energy equal to $\hbar\omega_{K,p}\left(\dfrac{1}{2}+n_{K,p}\right)$ where $n_{K,p}$ is an integer number reflecting the number of phonons in that particular mode. So the larger the wavelength of a mode the smaller the energy of the phonons, and the closer the states are together. The mode with the lowest energy is a standing wave for which just half a wavelength fits in the system length L, so K=2π/λ=2π/(2L)=π/L. The 2nd mode has a wavelength of L so its K value is K=2π/L, etc. so we have the following modes in such system:

$$K = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots \frac{(N-1)\pi}{L} \qquad\qquad [9]$$

Note that for K=Nπ/L the u_s is proportional to sin(sπ) which is everywhere zero since s is an integer. Note also that modes higher than K=Nπ/L such as for example K=(N+m)π/L can be described by a standing wave with wavevector smaller than Nπ/L, i.e. K=(N-m)π/L. For a system consisting of 5 atoms this is shown in the figure below. The first three phonon modes are unique. Note that the phonon mode indicated with 5π/L is basically the negative version of the phonon mode 3π/L. We discussed this effect for traveling waves in chapter 4 (Brillouin zone section, page 93). Looking to equation [9] we can see that there are N-1 modes, which means for each atom that can move there is one mode.
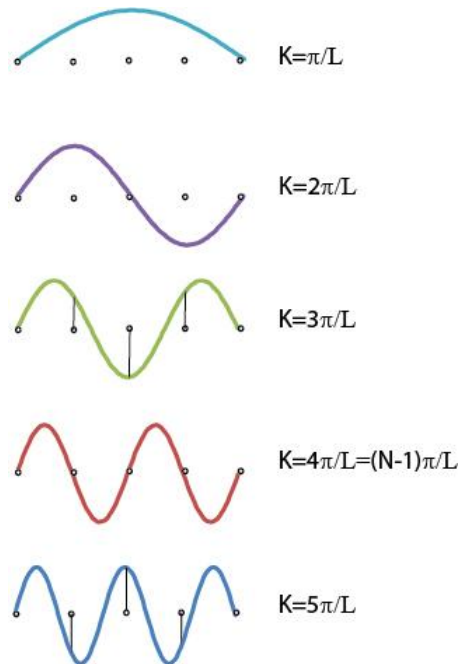
In K-space the distance between the modes is constant for such system, i.e. π/L. So for each π/L of K-space we have one mode, or we have a density of L/π modes per unit of K-space. Or the density of space in K-space is:

D(K)=L/π [10]

Note that we would need the density of space in w space to calculate U or CV. We can convert D(K) into D(ω) if we know the relation between ω and K. Using calculus we can write:

$$D(\omega)d\omega = D(K)\frac{dK}{d\omega}d\omega = \frac{L}{\pi}\frac{d\omega}{d\omega/dK}$$ [11]

Note that dω/dK is the group velocity and can be calculated from the dispersion relation. Debye assumed for his calculations that the phonon speed is constant, i.e. that the dispersion relation is given by:

$$\omega = vK$$ [12]

Where v is the speed of sound. So the density of states in 1 D (linear system) is given by:

$$D(\omega) = \frac{L}{\pi v}$$ [13]

Note that from equations [9] and [12] it follows that this function is valid for $0 < \omega < vK_{max} = v\pi(N-1)/L$.

Kittel discusses also the density of states for the 1D system of N atoms on a circle. This system has no real end points but has periodic boundary conditions since the wave-function needs to be single valued, differentiable and continuous:

$$u_s(sa) = u_s(sa+L)$$ [14]

Solutions of the wave equations for such system are traveling waves, i.e.

$$u_s(x) \sim e^{iKx}e^{-i\omega_{K,p}t}$$ [15]

Because of the periodic boundary conditions the following wave-vectors are allowed:

$$K = 0, \quad \pm\frac{2\pi}{L}, \quad \pm\frac{4\pi}{L}, \quad ..... \quad \frac{N\pi}{L}$$ [16]

Note that the mode K=-Nπ/L is similar as the negative of the mode K=Nπ/L (i.e. K'=K+/-2π/a=K+/-2Nπ/L) for traveling waves: see discussion on page 93). Note that we have again N modes. The distance between the modes is now 2π/L and thus D(K)=L/2π. Although it seems that D(K) of circular 1D system is half the value of the D(K) of the linear 1D system discussed above, allowed K-values extend now from -Nπ/L to Nπ/L so we still end up with the same number of states. For each ω there are two waves, a clockwise and a counter clockwise one. So D(ω) is equal to equation [13].

Kittel generalizes the periodic boundary condition approach to the 3D case. Let us assume we have N3 primitive cells within a cube of length L. The solutions of the wave-equations are:

$$u_s \sim e^{i\left(K_x x + K_y y + K_z z\right)} e^{-i\omega t} \tag{17}$$

Because of the periodic boundary conditions the components of the wave-vector can have the following values:

$$K_x, K_y, K_z = 0; \quad \pm\frac{2\pi}{L}; \quad \pm\frac{4\pi}{L}; \quad \dots \quad \frac{N\pi}{L} \tag{18}$$

So in K-space states are apart $2\pi/L$ in the x, y, and z-directions. Or one state for every $(2\pi/L)^3$ volume of K-space. To determine the density of states in K-space we count the number of states that has a K-vector with a magnitude smaller than K' and call that N. This is of course equal to the density of states per volume of K-space times the volume of a sphere with radius K', i.e.

$$N = \left(\frac{L}{2\pi}\right)^3 \frac{4}{3}\pi K^3 \tag{19}$$

The density of states in terms of w is now:

$$D(\omega) = \frac{dN}{d\omega} = \frac{VK^2}{2\pi^2}\frac{dK}{d\omega} \tag{19}$$

Assuming a constant velocity for the phonons now gives us:

$$D(\omega) = \frac{V\omega^2}{2\pi^2 v^3} \tag{20}$$

Debye used this density of states equation to determine the U and C_V. From equation [2] and [20] we can now derive the total thermal energy of the phonons. Note that we need to add up over all phonon modes but not more. There are only N acoustic phonon modes (N is the number of unit cells). So we can calculate the cut-off wave-vector K_D, or the cut off frequency ω_D from equations [12] and [20]:

$$\omega_D = \sqrt[3]{6\pi^2 v^3 \frac{N}{V}} \tag{21}$$

$$K_D = \sqrt[3]{6\pi^2 \frac{N}{V}} \tag{22}$$

And now it follows from equations [2] and [20] that

$$U = 3\int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 v^3} \frac{\hbar\omega}{e^{\hbar\omega/(k_B T)}-1} = \frac{3V\hbar}{2\pi^2 v^3}\int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/(k_B T)}-1} \tag{23}$$

After a substitution of $x = \dfrac{\hbar\omega}{k_B T}$, $dx = \dfrac{\hbar}{k_B T} d\omega$, $x_D = \dfrac{\hbar\omega_D}{k_B T}$ we get:

$$U = \frac{3Vk_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} dx\, \frac{x^3}{e^x - 1}$$ [24]

Note that the integral in both equation [23] and [24] depends on the temperature since x is temperature dependent. The temperature however is not the integration variable, x is the integration variable in [24] and we can factor out the T in front of the integral. It is not possible to determine the integral analytically which is a little disappointing. Similarly we can determined C_V from [3] and [20]:

$$C_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} d\omega\, \frac{\omega^4 e^{\hbar\omega/(k_B T)}}{\left(e^{\hbar\omega/(k_B T)} - 1\right)^2} = 9Nk_B \left(\frac{k_B T}{\hbar\omega_D}\right)^3 \int_0^{x_D} dx\, \frac{x^4 e^x}{\left(e^x - 1\right)^2}$$ [25]

Where for the last step the same substitution was used as for U. Also this integral cannot be solve analytically. Debye approximated [25] however for low temperature. In that case we can move the upper boundary of the integral to infinity. The idea is that at very low temperatures the higher energy phonon modes have a negligible occupancy. So for $k_B T \ll \hbar\omega$ the Planck distribution will become negligible. In statistical mechanics we say that the higher states are not accessible. So extending the upper boundary to infinity will not really change the calculated U or C_V. Mathematically notice that for small T, x_D will become very large. Applying 3 times integration by parts to the integral of [24] with an infinite upper boundary gives:

$$\int_0^\infty dx\, \frac{x^3}{e^x - 1} = \int_0^\infty dx\, x^3 \sum_1^\infty e^{-sx} = 6\sum_1^\infty \frac{1}{s^4} = \frac{\pi^4}{15}$$ [26]

Or the heat capacity at low temperatures is:

$$C_V = 234 Nk_B \left(\frac{k_B T}{\hbar\omega_D}\right)^3$$ [27]

This is the Debye T^3 law. It tells us that at low temperatures the heat capacity behaves like T^3. Although this is an approximation this is much more accurate than the Einstein heat capacity equation, i.e. equation [7]. The figure below on the left shows the comparison between experiment and theory for the Einstein model. Note that this is on a log-scale. One can see that in particularly for low T there is large difference between experimental results and theory. Note that the log temperature scale exaggerates the discrepancy at low temperatures.
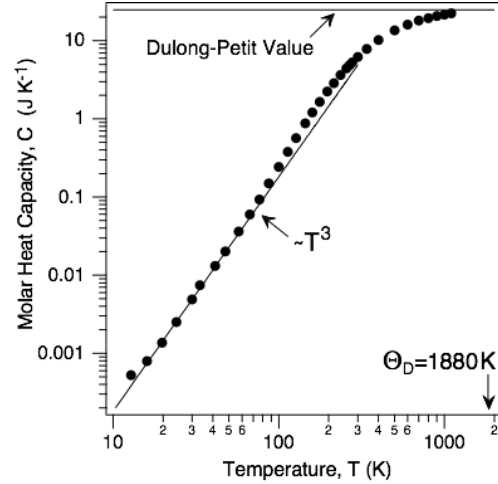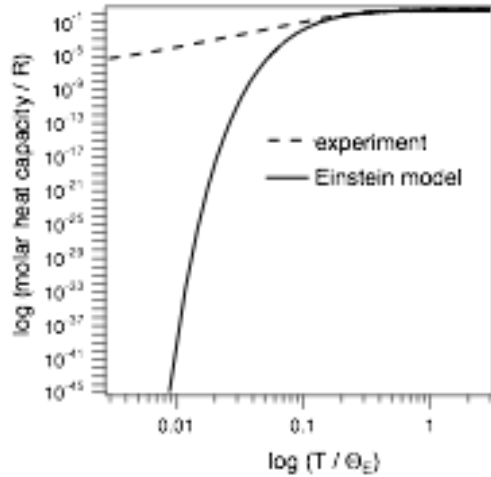
The figure on the right shows the comparison between experimental results and the Debye model. For low temperature is much better. Note that also this graph has a logarithmic temperature scale. The match is amazing considering the crude assumption that the speed of all phonons is the same. The saturation C_V value for high temperatures corresponds to the Dulong Petit value. The graphics below show the difference between both models. Note that the phonon energies are all the same in the Einstein model while for the Debye the distribution of low energy phonon states is almost continuous.
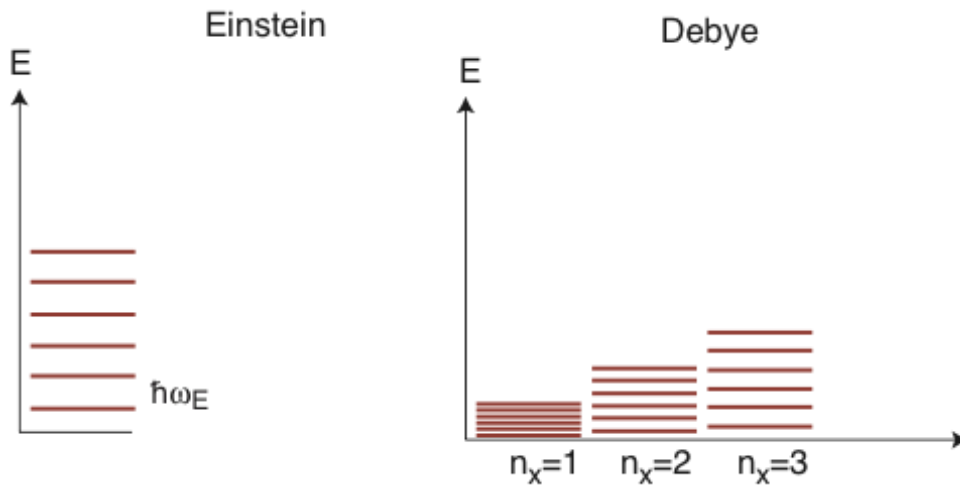
Note that the real density of states function of a particular lattice structure can differ quite a bit from equation [19]. The figure below shows the Debye and experimental density of state function for copper. Only at low temperature there is reasonable agreement.