Lecture 7 Phonons and Thermal Properties

*Simon: Chapter 10 p 89-96, Chapter 2 p7-15; Kittel: Chapters 4 and 5*

Two atom basis per lattice point

Many crystal structures have two atoms in their basis e.g. salts, NaCl, semiconductors (Si, GaAs, ZnS). etc. When there are two atoms in the basis the atomic motion is more complex and the phonon dispersion curve shows more features. The two atoms often have different masses.

When there is a two atom basis we find that for a given direction in the crystal the $\omega(K)$ relation has two branches. These are called the *optical* and *acoustic* modes. For different wave types we have the *longitudinal* and *transverse* acoustic modes and optic modes (TA, LA) and (TO LO).

Figure 7 Optical and acoustical branches of the dispersion relation for a diatomic linear lattice, showing the limiting frequencies at $K = 0$ and $K = K_{\max} = \pi/a$. The lattice constant is a.
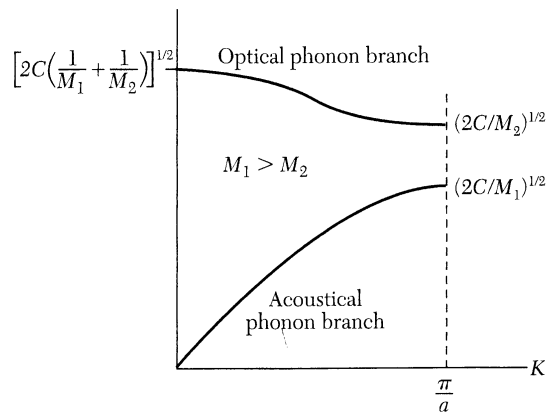
The number of branches in the phonon dispersion relation is related to the number of degrees of freedom. The *optic modes* are due to the two atoms in the basis moving *out of phase*, the *acoustic modes* are due to the two atoms in the basis moving *in phase*.

To derive the dispersion relation we consider a cubic crystal with atoms of mass M_1 on one set of planes and atoms of mass M_2 on a plane interleaved between the first set. The assumption is that the masses M_1 and M_2 are different. The period of separation between the lattices is a.

We consider waves that propagate in a symmetry direction such that a single plane contains only one type of ion, for example [111] in NaCl and [100] in CsCl.

The equations of motion assume that only nearest neighbour interactions are considered and that the force constants are identical between all nearest neighbour pairs of planes.

This gives two equations describing the motion of atoms M_1 and M_2 in planes u_s and v_s respectively:

$$M_1 \frac{d^2 u_s}{dt^2} = C(v_s + v_{s-1} - 2u_s)$$
$$M_2 \frac{d^2 v_s}{dt^2} = C(u_{s+1} + u_s - 2v_s)$$

The solution, as before, is in the form of a travelling wave which will have different amplitudes u, v on alternative planes.

$$u_s = u \exp(isKa) \exp(-i\omega t) \; ; \; v_s = v \exp(isKa) \exp(-i\omega t)$$

The distance a is defined as the distance between identical planes not nearest neighbour planes. This definition used by Kittel is different from many other texts who define a as the separation of adjacent planes.

Substituting the travelling wave solution into the equations of motion gives:

$$-\omega^2 M_1 u = Cv[1 + \exp(-iKa)] - 2Cu$$

$$-\omega^2 M_2 v = Cu[1 + \exp(-iKa)] - 2Cv$$

These are homogeneous linear equations. Writing as a matrix equation, the only solution is when the determinant of the coefficients for the variables u, v vanishes:

$$\begin{vmatrix} 2C - M_1\omega^2 & -C[1 + \exp(iKa)] \\ -C[1 + \exp(iKa)] & 2C - M_2\omega^2 \end{vmatrix} = 0$$

This gives:

$$M_1 M_2 \omega^4 - 2C(M_1 + M_2)\omega^2 + 2C^2(1 - \cos Ka) = 0$$

This equation is quadratic in ω^2 and can be solved for ω^2

$$\omega^2 = \frac{C(M_1+M_2)}{M_1 M_2} \pm \frac{C(M_1+M_2)}{M_1 M_2} \sqrt{1 - \frac{2M_1 M_2((1-\cos Ka))}{(M_1+M_2)^2}}$$

This equation describes the total behaviour illustrated in Figure 7 above.

The overall behaviour is best illustrated by considering the **two limits**
1. when $Ka \ll 1$ (*long wavelength* or small K) and
2. $Ka = \pm\pi$ at the zone boundary. (i.e. at the limits of the x axis on Figure 7 previous page).

For small Ka we have:

$$\cos Ka \cong 1 - \frac{1}{2} K^2 a^2$$

The two solutions (roots) are then:

(optical branch) $\boxed{\omega^2 \cong 2C\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}$ (note that ω is independent of K)

(acoustic branch $\boxed{\omega^2 \cong \frac{C/2}{M_1+M_2} K^2 a^2}$ (note that ω is proportional to K)
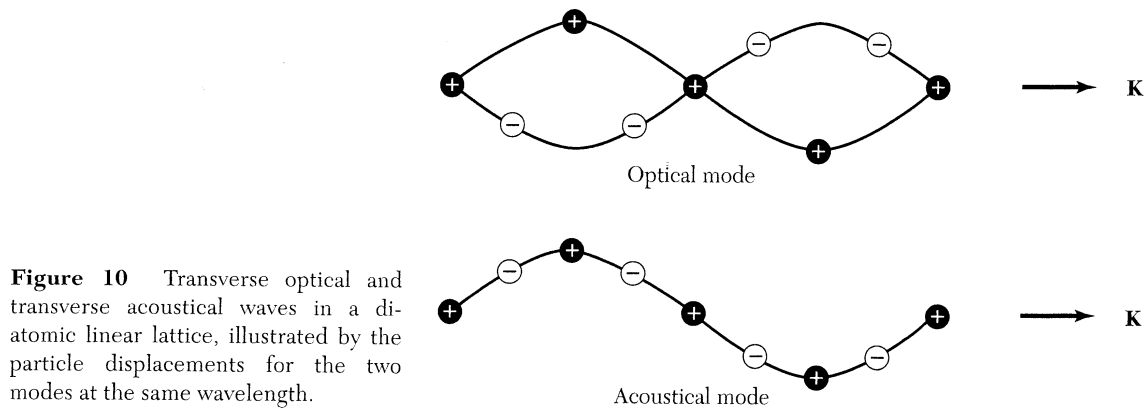
The first Brillouin zone extends from $-\pi/a \leq K \leq \pi/a$ where a is the lattice repeat distance (separation between identical planes). Remember that the first Brillouin zone can be considered the unit cell in reciprocal space.

At the maximum value of K namely: $K_{\max} = \pm {}^\pi/_a$ the roots are:

$$\omega^2 = 2C/M_1 \; ; \; \omega^2 = 2C/M_2$$

The result is shown in Figure 7 (above) for $M_1 > M_2$.

The atom motion for Transverse Acoustic (TA) and Transverse Optic (TO) modes is shown in figure 10.

Figure 10 Transverse optical and transverse acoustical waves in a diatomic linear lattice, illustrated by the particle displacements for the two modes at the same wavelength.

Considering the optical branch at $K = 0$ we find that:

$$\frac{u}{v} = -\frac{M_2}{M_1}$$

The physical picture is that the atoms vibrate out of phase but the centre of mass of the two atom basis is fixed. If the two atoms have different charge (which is often the case) the motion can be excited by an electromagnetic waves (because there will be a local electric dipole associated with the out of phase motion). This is why this is called the optical branch. At any non-zero K value the ratio u/v will be complex.

A second valid solution at $K = 0$ gives $u = v$. In this case the atoms move in phase, in this case also in phase with the centre of mass. This is equivalent to long wavelength acoustic vibrations (sound waves) hence the name acoustic branch.

The figure also shows that there is a frequency gap where there is no valid solutions for the equations of motion. The frequency gap lies between $(2C/M_1)^{1/2}$ and $(2C/M_2)^{1/2}$. This is a characteristic behaviour for elastic waves in polyatomic crystal structures. The frequency gap is at the boundary of the first Brillouin zone.

We can now use this description of phonon modes to predict the thermal properties of crystals.

Thermal Properties

The properties of phonons and the framework developed to describe lattice vibrations is now used to explain the **thermal properties of crystals**.
When describing the properties of phonons we used the concept of a "phonon gas" to describe the properties. This term recognises that in certain circumstances phonons exist in a sufficiently low density that the interactions between them can be neglected (rather like the situation of molecules in a dilute gas).

Classical thermodynamics provides a relationship between heat and work in a body through the first and second laws of thermodynamics and the equation of state for

the system. It is not possible however to determine the other thermal properties of the system (such as specific heat, thermal conductivity, and thermal expansion). For this we need an expression for the internal energy of the system U.

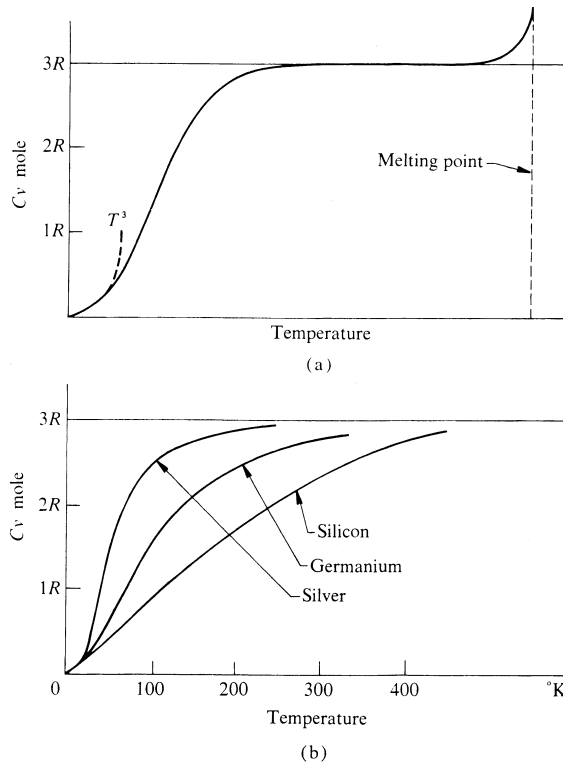In a solid the model of the vibrating lattice (dynamical lattice) provides a framework for this.

Experimentally it is observed that at higher temperatures the specific heat capacity at constant volume C_V is constant with temperature and equivalent to $3R$ per mole for all solids. This is the *Dulong and Petit law*. This remains valid to just below the melting point of a solid.

At low temperatures C_V falls off towards zero and is observed to be a T^3 law.

This is explained in part by recognising that the specific heat is related to the number of degrees of freedom in a system. Each degree of freedom is able to absorb a given amount of energy (kinetic or potential). For the model of a dynamical lattice where the atoms are vibrating this can become a complex problem.

Fig. 4.1 (a) General temperature dependence of specific heat of solids. (b) Experimental curve of specific heat for silver, germanium, and silicon.

Phonon Heat Capacity

This is assumed to be the heat capacity at constant volume. The quantity C_V is more fundamental than C_P. (At constant volume no work is done on the system)

From thermodynamics, the ideal gas equation and considering a piston at constant pressure we get $C_V \equiv \frac{dU}{dT}$ (the rate of change of internal energy with temperature as no work is done). For an ideal gas it can also be shown that $C_P = C_V + nR$

We define $C_V \equiv \left(\frac{\partial U}{\partial T} \right)_V$

Phonons contribute to the heat capacity of the crystal. The assumption is that supplying more thermal energy to a lattice increases the internal energy U, this in turn **increases the number of phonons** (and **does not alter the phonon frequency** or energy). This contribution is called the lattice heat capacity C_{lat}. The total energy of all phonons at a temperature T is given by the sum over all phonon modes (summing over wavevector K and longitudinal and transverse modes p):

$$U_{lat} = \sum_K \sum_p U_{K,p} = \sum_K \sum_p \langle n_{K,p} \rangle \hbar\omega_{K,p}$$

where $\langle n_{K,p} \rangle$ is the thermal equilibrium occupancy (number) of phonons with wavevector and polarisation K and p.

The functional form of $\langle n_{K,p} \rangle$ is given by the Planck distribution function:

$$n = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$
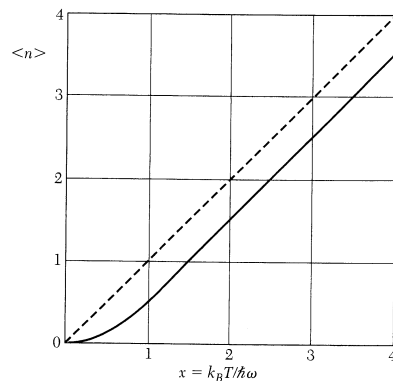
Figure 1 Plot of Planck distribution function. At high temperatures the occupancy of a state is approximately linear in the temperature. The function $\langle n \rangle + \frac{1}{2}$, which is not plotted, approaches the dashed line as asymptote at high temperatures.

The figure shows a plot of this function. At high temperatures the function is linear when $k_B T \ll \hbar\omega$

A full derivation (*not needed*) is given on pages 107/108 of Kittel.
In summary – the derivation consider the energy difference between the nth and (n+1)th states – which is $\hbar\omega$, The ratio $n/n+1$ is given by the classical Boltzmann factor $\exp\left(\frac{\hbar\omega}{k_B T}\right)$.

Substituting these expressions above finally gives us:

$$U_{lat} = \sum_K \sum_p U_{K,p} = \frac{\hbar\omega_{K,p}}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

In evaluating this, it is usual to replace the summation by an integral with respect to K. In evaluating the integral we need to know the number of modes of a given polarisation p in the frequency range from ω to $\omega + d\omega$. This is written as $D(\omega)d\omega$ and is called the **density of states**. This is a key quantity in condensed matter physics.

The density of states for each polarisation is then given by: (*details of calculation not required*):

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

The density of states function describes the number of phonon modes in a given frequency or energy range.

We now introduce **two models** to describe phonons. These are the **Debye model** and the **Einstein model**. These models replace the curves on Figure 7 with two straight lines. (One at constant velocity (gradient), the other at constant energy.)

Debye Model for Density of States

In the Debye model the assumption made is that the velocity of sound is a constant for each polarisation (i.e. the slope of the $\omega(K)$ dispersion relation does not change). This is a classical approximation for an elastic medium. The dispersion relation is then written as

$$\omega = vK$$

where v is the velocity of sound.

ω

Einstein approximation

Optical branch

Debye approximation

Acoustical branch
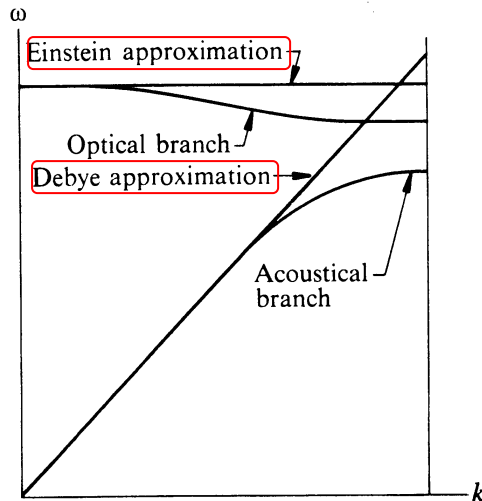
Fig. 4.5 Comparison of Einstein and Debye approximations for the dispersion relation of lattice waves, referred to a linear diatomic lattice.

k

The density of states then becomes:

$$D(\omega) = V\omega^2 / 2\pi^2 v^3$$

in other words, the number of phonons $D(\omega) \propto \omega^2$

It is assumed that there are N acoustic phonon modes where N is the number of unit cells in the system.

There is a cut off frequency (maximum frequency) determined from the expression for N as:
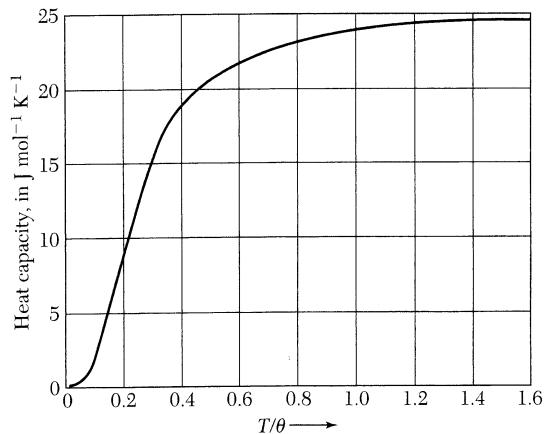
$$\omega_D^3 = 6\pi^2 v^3 N \big/ V$$

This corresponds to a wavevector in $\textbf{K}$ space – the Debye wavevector

$$K_D = \frac{\omega_D}{v} = \left(6\pi^2 \frac{N}{V}\right)^{\frac{1}{3}}$$

The Debye model does not allow any modes with a wavevector larger than K_D.

The number of modes with $K \leq K_D$ is the same as the total number of degrees of freedom of a monatomic lattice.

The result is plotted in:

Figure 7 Heat capacity C_V of a solid, according to the Debye approximation. The vertical scale is in J mol^{-1} K^{-1}. The horizontal scale is the temperature normalized to the Debye temperature θ. The region of the T^3 law is below 0.1θ. The asymptotic value at high values of T/θ is 24.943 J mol^{-1} deg^{-1}.
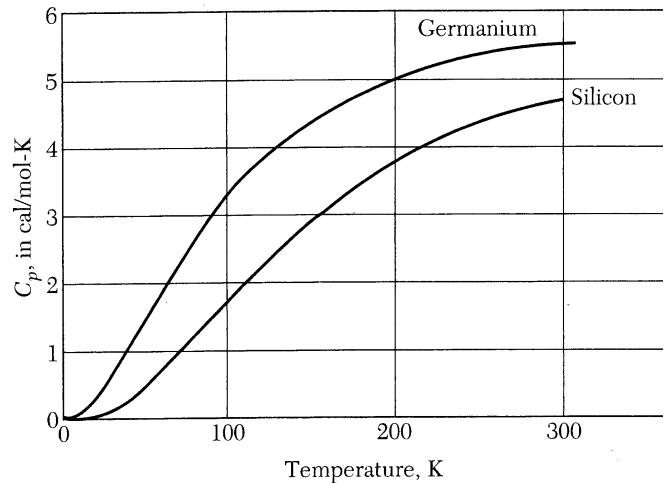
Figure 8 Heat capacity of silicon and germanium. Note the decrease at low temperatures. To convert a value in cal/mol-K to J/mol-K, multiply by 4.186.

When $T \gg \theta$ (where θ is the Debye Temperature) the heat capacity approaches the classical value of $3Nk_B$.

Einstein Model of Density of States

The Einstein model treats the oscillators as having the same quantised energy (see Figure 4.5 page 6). To develop this approach, consider N oscillators of the same frequency ω_E which for simplicity we assume to be in just one dimension. The Einstein density of states is then given by the expression: $D(\omega_E) = N\delta(\omega-\omega_0)$ where the delta function is centred at ω_E.
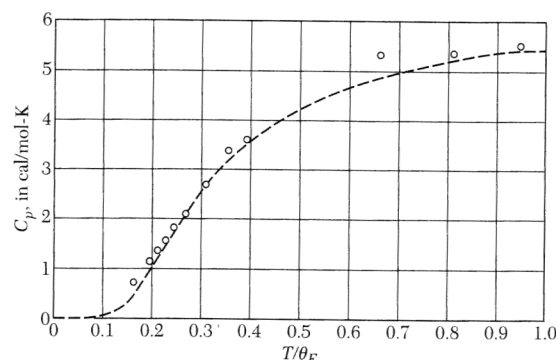
The thermal energy of the system is

$$U = N\langle n\rangle \hbar\omega_E = \frac{\hbar\omega_E}{\exp(\hbar\omega_E/k_BT) - 1}$$

The heat capacity of this ensemble of oscillators is then

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = Nk_B \left(\frac{\hbar\omega_E}{k_BT}\right)^2 \frac{\exp(\hbar\omega_E/k_BT)}{(\exp(\hbar\omega_E/k_BT) - 1)^2}$$

Function plotted in Kittel:

Figure 11 Comparison of experimental values of the heat capacity of diamond with values calculated on the earliest quantum (Einstein) model, using the characteristic temperature $\theta_E = \hbar\omega/k_B = 1320$ K. To convert to J/mol-deg, multiply by 4.186.

This result shows the contribution of N identical oscillators to the heat capacity of a solid. In three dimensions N becomes $3N$ as there are three modes per oscillator (one longitudinal and two transverse). The high temperature limit becomes $3Nk_B$ (or $3R$ where R is the ideal gas constant) – this the Dulong and Petit law.

At low temperatures this Einstein relation decreases as exp($-\hbar\omega_E/k_BT$) whereas the experimental data confirms the T^3 behaviour as described by the Debye approximation above.

The Einstein model is more useful in approximating the behaviour of the optical phonon modes with its fixed energy.

In practice the real measured phonon properties required a combination of the Debye and Einstein models for a full description. (see Figure 4.11 below)
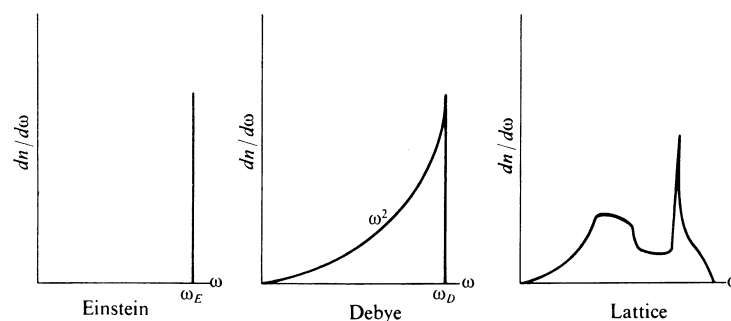
Fig. 4.11 Mode spectra for the Einstein and Debye approximations and a lattice. A combination of Einstein and Debye frequencies (acoustic and optical) can result in a good estimate of the mode spectrum for real crystals.

Anharmonic Crystal Interactions (Something covered in future years – *details not required here*)

The theory developed has assumed that potential energy is proportional to the atomic displacement squared (quadratic). (This implies Hooke's Law and linear elastic constants)

The consequences of this approximation are:
- Two different lattice waves do not interact
- A single wave does not change or decay with time
- There is no thermal expansion (mean atomic position does not change)
- Adiabatic and isothermal elastic constants are equal
- The elastic constants are independent of temperature and pressure
- The heat capacity becomes a constant at high temperatures above the Debye Temperature $T > \theta_D$.

None of the above are true in real crystals. The incorporation of higher order terms above quadratic is required to fully describe real crystals.