

$$K_E = \sum_i \phi''(r_i)$$

5.3.2 Debye Model

Use a continuum treatment of the oscillations of a solid to identify the normal modes and frequencies.

5.3.2.1 One Dimension

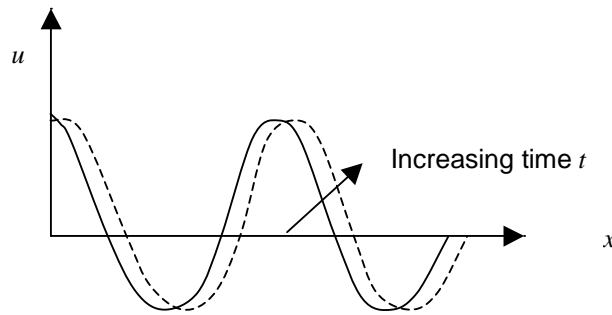
Start with the evolution equation for the longitudinal displacement field $u(x,t)$ in a thin rod.

$$\frac{\partial^2 u}{\partial t^2} = \frac{E_y}{\rho} \frac{\partial^2 u}{\partial x^2} \quad \text{the wave equation for acoustic waves (sound).}$$

E_y : Young's modulus. ρ : Mass density.

Solution: $u(x,t) = \text{Re}(A_k \exp i(kx - \omega t))$. $k = \text{wave vector} = 2\pi/\lambda$. $|A_k|$ is amplitude.

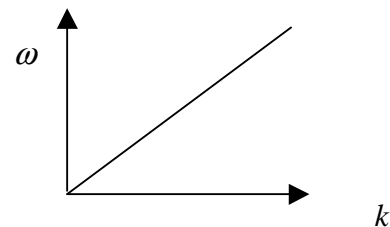
This is a propagating wave.



Put into wave equation:

$$-\omega^2 u = -\frac{E_y}{\rho} k^2 u$$

So
$$\omega = \left(\frac{E_y}{\rho}\right)^{1/2} k$$



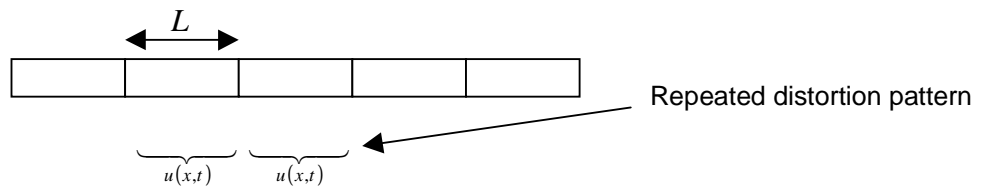
This is called the **dispersion relation**: relationship between the wavevector and frequency of a mode.

And the group velocity of the waves is: $\frac{d\omega}{dk} = \left(\frac{E_y}{\rho}\right)^{1/2} = v$, the speed of sound.

Debye took these propagating continuum waves to be the normal modes of vibration of the solid. The key **Debye approximation** is to use this dispersion relation for all frequencies.

Problem: apparently an infinite number of modes since there is a continuum of wavevectors. We have to limit the number in some way.

Instead of an infinite rod with displacements $u(x,t)$ for $-\infty \leq x \leq \infty$ we consider length $0 \leq x \leq L$ with a $u(x,t)$ with periodic boundary condition. Each length L contains N atoms and we'll eventually send both L and N to infinity.



Continuity of displacement between elements:

$$u(x=0,t) = u(x=L,t)$$

Implies that: $\exp(ikL) = 1$ so $k = n\Delta k$ with $n = \pm 1, \pm 2, \pm 3 \dots$ and $\Delta k = \frac{2\pi}{L}$

In 1-d; N atoms in length $L \Rightarrow N$ modes in total.

$\therefore k_{\max} = \frac{N}{2} \Delta k$: call this k_D , the Debye wavevector.

Define $\rho(k)$, the density of states in k space ($\rho(k)dk$ is the number of allowed wave vectors k in the range $|k| \rightarrow |k| + dk$). Separation between allowed k is Δk , so density of states is twice the inverse of this:

$$\rho = \frac{2}{\Delta k} \quad \leftarrow \text{factor of 2 for } \pm \text{ values of } k.$$

So
$$\rho = \frac{L}{\pi}$$

But we really want density of states in ω space $G(\omega)$. Relate through:

$$G(\omega)d\omega = \rho(k)dk \quad (\text{i.e. the same number of modes in the range } |k| \rightarrow |k| + dk \text{ as in } \omega \rightarrow \omega + d\omega)$$

so
$$G(\omega) = \rho \frac{dk}{d\omega} = \frac{\rho}{v} = \frac{L}{\pi v}$$
 where we have

inserted the Debye dispersion relation.

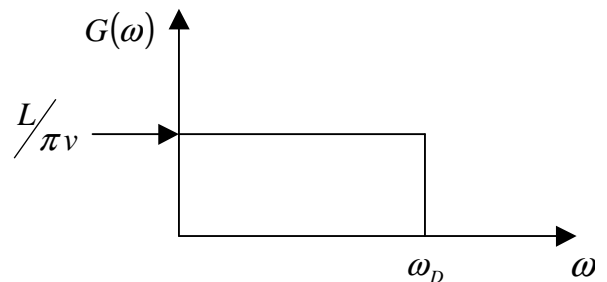
What is the maximum value of ω ?

$$\omega_D = k_D v = \frac{vN\pi}{L}. \text{ This is the Debye frequency (in}$$

1-d). Check number of modes:

$$\int_0^{\omega_D} G(\omega) d\omega = \int_0^{\omega_D} \frac{L}{\pi v} d\omega = \frac{L}{\pi v} \omega_D = \frac{L}{\pi v} \frac{v\pi N}{L} = N$$

as required for length L . Contrast this $G(\omega)$ with the Einstein frequency spectrum!



$$G(\omega)d\omega = 3\rho(k)dk$$

Hence
$$G(\omega) = \frac{3L^3 k^2}{2\pi^2} \frac{dk}{d\omega}$$

And according to the Debye approximation, we use $\omega = vk$ and set

$$\frac{d\omega}{dk} = v \quad \text{and so} \quad G(\omega) = \frac{3L^3 \omega^2}{2\pi^2 v^3}$$

and we use a weighted average speed of sound v given by

$$\frac{3}{v^3} = \frac{1}{v_l^3} + \frac{2}{v_t^3}$$

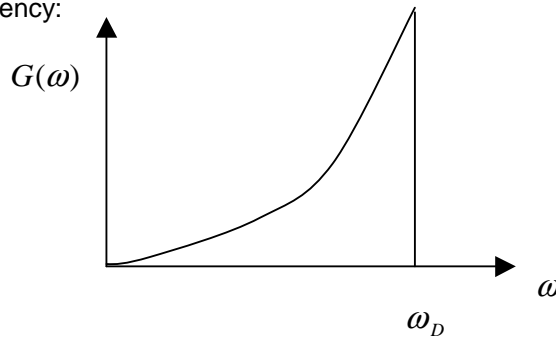
where v_l and v_t are the velocities of long wavelength longitudinal and transverse acoustic waves in the solid.

Now set the number of frequencies to $3N$, i.e. demand $\int_0^{\omega_D} G(\omega)d\omega = 3N$ with ω_D the maximum allowed frequency.

This requires:
$$\frac{3L^3}{2\pi^2 v^3} \int_0^{\omega_D} \omega^2 d\omega = 3N$$

So
$$\omega_D = v(6\pi^2 n_a)^{\frac{1}{3}} \quad \text{or} \quad k_D = v(6\pi^2 n_a)^{1/3} \approx 1/(\text{atomic spacing})$$

where n_a is the atomic density $= \frac{N}{L^3}$. This is the Debye frequency. The Debye density of states in 3-d is quadratic in frequency:



5.3.3 'Real' lattice dynamics

See handouts.

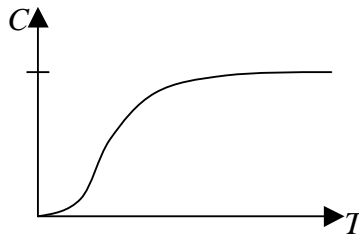
5.4 Thermal properties

Now employ these densities of states to obtain thermal properties.

5.4.1 Heat capacity

We calculate $C = \frac{dE}{dT}$ given $E = V_0 + \int d\omega G(\omega) \left[\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1 \right)^{-1} + \frac{1}{2} \right] \hbar\omega$.

Note that experimental heat capacity $C = \frac{dE}{dT}$ has the following dependence on T .



5.4.1.1 Law of Dulong and Petit

The $3N$ oscillators are excited classically and each possess an energy $k_B T$ (see section 5.1 on thermodynamics of SHO).

$$\text{So } E = V_0 + 3Nk_B T$$

$$\text{and } C = 3k_B \text{ per atom.}$$

No need to know $G(\omega)$: not a test of dynamical models.

This Dulong-Petit Law is based on the following assumptions:

- (i). Harmonic approximation is reasonable, i.e. displacements not too large (temperature not too high)
- (ii). Normal mode oscillators are excited classically (temperature not too low).

5.4.1.2 Einstein model

Insert $G(\omega) = 3N\delta(\omega - \omega_E)$:

$$\text{Heat Capacity: } \frac{d\langle E \rangle}{dT} = \frac{3Nk_B \left(\frac{\hbar\omega_E}{k_B T} \right)^2 \exp\left(\frac{\hbar\omega_E}{k_B T} \right)}{\left(\exp\left(\frac{\hbar\omega_E}{k_B T} \right) - 1 \right)^2} \quad \text{see eq. (5.6) in section 5.1.3}$$

$$\text{So } C_E = \frac{3Nk_B \left(\frac{\theta_E}{T} \right)^2 \exp\left(\frac{\theta_E}{T} \right)}{\left(\exp\left(\frac{\theta_E}{T} \right) - 1 \right)^2} \quad \text{where: } \theta_E = \frac{\hbar\omega_E}{k_B} \text{ Einstein temperature.}$$

Limits: $C_E \rightarrow 3Nk_B$ for $T \gg \theta_E$ Dulong-Petit limit
 $\rightarrow 3Nk_B \left(\frac{\theta_E}{T}\right)^2 \exp\left(-\frac{\theta_E}{T}\right)$ for $T \ll \theta_E$

But it vanishes too quickly as $T \rightarrow 0$ when compared with experiment.

5.4.1.3 Debye model

Insert Debye spectrum:

$$\langle E \rangle = \int_0^{\omega_D} G(\omega) \underbrace{\left(\frac{1}{\exp(\hbar\omega/kT) - 1} + \frac{1}{2} \right)}_{\text{Mean energy in mode at frequency } \omega} \hbar\omega d\omega$$

$$= N \left(3k_B T D(x_D) + \frac{9\hbar\omega_D}{8} \right)$$

with $D(x_D) = \frac{3}{x_D^3} \int_0^{x_D} \frac{x^3 dx}{\exp(x) - 1}$ with $x_D = \frac{\hbar\omega_D}{k_B T}$ (Debye integral)

Limits: $D(x_D) \rightarrow \frac{\pi^4}{5x_D^3}$ for $x_D \gg 1$
 $\rightarrow 1 - \frac{3x_D}{8}$ for $x_D \ll 1$

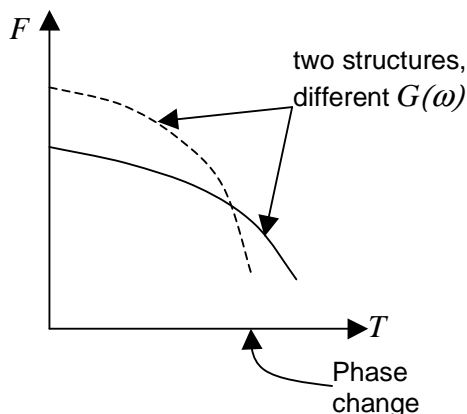
So heat capacity is: $C = 3Nk_B$ for high T . (Dulong-Petit limit).

while for low T , $C = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\theta_D}\right)^3$ where $\theta_D = \frac{\hbar\omega_D}{k_B}$ is the Debye Temperature,
 equal to $\frac{\hbar v}{k_B} (6\pi^2 n_a)^{1/3}$ where $n_a = \frac{N}{L^3}$ is the atomic density and v is the speed of sound.

This dependence on T^3 at low temperature is borne out by experiment.

5.4.2 Free Energy

Use $G(\omega)$ to calculate the free energy of a structure:



e.g. Iron.
 $T \leq 908^\circ\text{C}$ bcc.
 $908^\circ\text{C} \leq T \leq 1388^\circ\text{C}$ fcc.
 $1388^\circ\text{C} \leq T \leq 1535^\circ\text{C}$ bcc.
 $1535^\circ\text{C} \leq T$ liquid.
 all at one atmosphere pressure.

5.5 Phonons

We've represented the vibrations of a structure as a set of independent oscillators (normal modes in the form of propagating waves) and have quantised their energies. The quanta which populate these modes have a vibrational energy $\hbar\omega$, where ω is the angular frequency of the wave.

We can regard these elementary quanta as quasi-particles called phonons with energy $\hbar\omega$ and velocity given by the group velocity of the wave. The density of states $G(\omega)$ can then be viewed as a spectrum of allowed phonon energies.

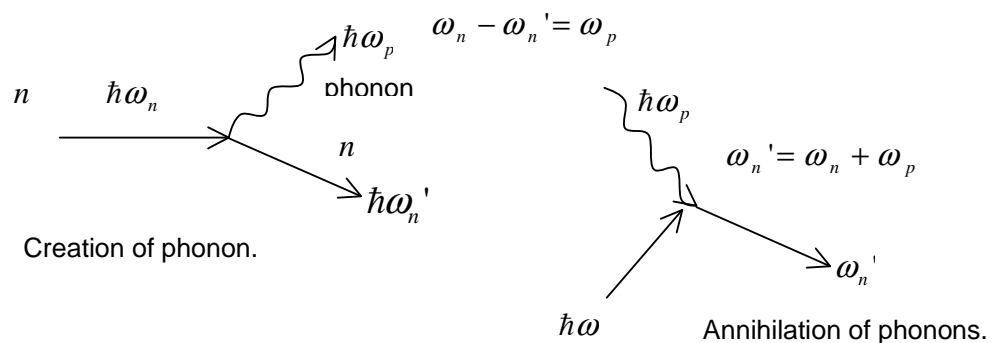
In the harmonic approximation, the phonons do not interact with each other. A solid can therefore be considered to possess both energy and entropy in the form of a gas of phonons propagating at various velocities in all directions within the material.

Phonons are quanta of the displacement field, just as photons are the quanta of the E-M field. Phonons are quanta of sound, photons are quanta of light.

Useful picture because:

- a) It allows us to interpret inelastic scattering results, e.g. a neutron hits a structure and loses or gains energy by creating or absorbing a phonon.

We can construct a theory of phonon-neutron interactions with 'Feynman diagrams'.



These experiments allow us to measure $G(\omega)$.

- b) Phonon-electron interactions give a picture of superconductivity.
- c) Phonons provide some understanding of thermal conductivity.

5.5.1 Thermal Conductivity

- a) Simple picture.

There are more phonons at the hotter end of a sample than at the cooler end,

since $\langle n \rangle \approx \frac{k_B T}{\hbar\omega}$ for an oscillator at frequency ω and at temperature T (classical limit). Phonon flow from dense to dilute regions carries energy and removes temperature differences.

- b) Heat flow is limited by scattering of phonons off: (i) defects in the material (impurities, vacancies (missing atoms), grain boundaries, dislocations), (ii) electrons, (iii) other phonons (through anharmonic interactions).

Use gas kinetic theory for the thermal conductivity of a phonon gas:

$$\kappa = \frac{1}{3} \lambda v c_1 n \quad \lambda = \text{mean free path.}$$

v = r.m.s. velocity.

c_1 = heat capacity per molecule of "gas species".

n = density of gas species.

For phonons:

v = speed of sound.

$c_1 n$ = heat capacity per unit volume.

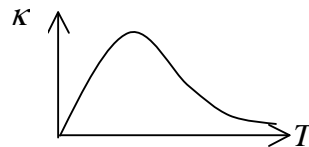
$$\rightarrow 3n_a k_B \quad (\text{large } T)$$

$$\propto \left(\frac{T}{\theta_D} \right)^3 \quad (\text{small } T)$$

At low T , $\lambda \sim$ distance between imperfections. (T independent).

$$\Rightarrow \kappa \propto T^3 \text{ at low } T.$$

Whereas at high T : $\lambda \sim$ phonon "spacing". (phonon-phonon collisions dominate) so $\lambda \downarrow$ as $T \uparrow$.
But $c_1 n$ is T independent (Dulong-Petit limit) so $\kappa \downarrow$. Overall temperature dependence is:



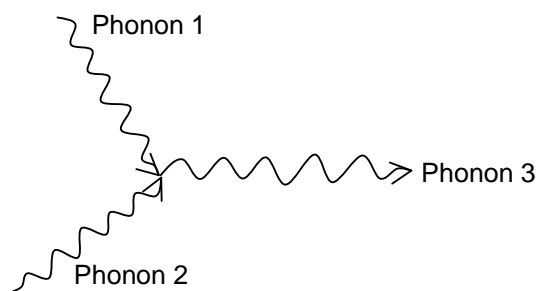
What are these phonon – phonon scattering processes?

Normal process

$$\omega_1 + \omega_2 = \omega_3$$

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

brought about by anharmonic terms in the Hamiltonian (neglected $O(u_i^3)$ terms).

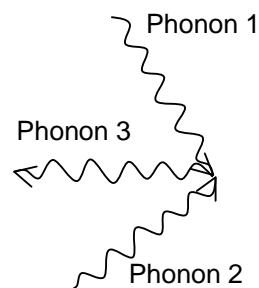


Umklapp process (German for "flip-over").

This occurs when $\vec{k}_1 + \vec{k}_2$ lies outside the Brillouin zone.

e.g. in 1-d, wavevector limited to $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$

Reverses direction of thermal energy flow!



5.6 Summary

- (i) The motion of atoms needs to be studied in order to understand the thermal properties of materials – energy and entropy.
- (ii) In the harmonic approximation (small amplitude oscillations) we can cast the Hamiltonian in the form of a set of SHOs. Normal modes are the eigenstates of the system. They are collective vibrational modes, each at a defined frequency, and they can be excited independently. Often it is useful to regard the normal modes as travelling waves.
- (iii) Key quantity is the density of states in frequency $G(\omega)$.
- (iv) The energy in each normal mode of oscillation can be quantised.
- (v) Quanta are phonons – can be regarded as particles with energy, related to the frequency of the mode, and velocity equal to the group velocity of the travelling wave.
- (vi) One can therefore construct a quantised theory of sound.