PH20017/63 Condensed Matter Physics 1

Dr Simon Crampin

Department of Physics
University of Bath

Lecture notes set 5 - Crystal Dynamics

These are only summary notes – you should annotate, expand and supplement.

Crystal dynamics

1. Lattice vibrations

    - Continuum theory
    - Vibrations of a monatomic chain
    - Vibrations of a diatomic chain
    - Phonons and their experimental study

2. Heat Capacity

    - Classical theory
    - Einstein model
    - Debye model
    - Specific heat of metals and insulators

Crystal dynamics

Crystal structure as previously studied (i.e. regular array of stationary atoms) is a theoretical idealisation

   – e.g. it violates Heisenberg uncertainty principle $\Delta x \Delta p \geq \hbar$.

 ⇒ even at $T = 0$ K, atoms must vibrate about average locations: this is called zero point motion.

As T increases, vibrations will increase as atoms gain thermal energy – we call this atomic motion lattice vibrations.

We will study harmonic effects, which occur for small amplitude oscillations – when the restoring force is proportional to the displacement.

Other effects such as thermal expansion are the result of anharmonic effects.

# Continuum theory of longitudinal vibrations

For reference, we note continuum elasticity theory predicts longitudinal vibrations in a one-dimensional solid satisfy the equation of motion

$$\frac{\partial^2 u}{\partial t^2} = \frac{E}{\varrho} \frac{\partial^2 u}{\partial x^2},$$

$u(x, t)$ displacement field at position x, time t
ϱ mass density
E elastic modulus,

– a wave equation with solutions $u(x, t) = u_0 \cos(kx - \omega t + \phi)$ where the wave vector k and angular frequency ω are related by $\omega = \sqrt{E/\varrho}\, k$.
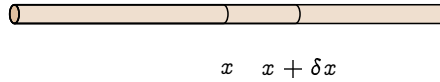
The phase velocity $v_p = \omega/k$ and the group velocity $v_g = \partial\omega/\partial k$ are both given by the constant $\sqrt{E/\varrho}$. This means there is no dispersion.
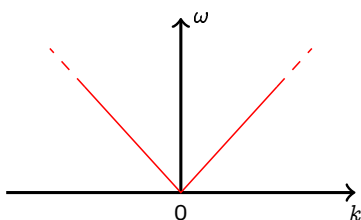
There is no restriction on ω or k — waves of arbitrarily small wavelength $\lambda = 2\pi/k$, and arbitrarily high frequency, may propagate in the solid.

Derivation [background]

Consider a long rod of elastic material, cross section A, density ϱ.

$$x \quad x + \delta x$$

A longitudinal vibration described by displacement field $u(x, t)$ passes along the rod: at time t, the plane at x is displaced to $x + u(x, t)$ and the plane at $x + \delta x$ displaced to

$$x + \delta x + u(x + \delta x, t) \simeq x + \delta x + u(x, t) + \frac{\partial u(x, t)}{\partial x} \delta x$$

This means element of length δx changes to length $\delta x + \frac{\partial u(x, t)}{\partial x} \delta x$

$$\text{The result is a strain} = \frac{\text{extension}}{\text{original length}} = \frac{\partial u(x, t)}{\partial x}$$

According to Hooke's law, stress is proportional to strain. Therefore

$$\text{stress} = \frac{\text{force}}{A} = E \frac{\partial u}{\partial x} \qquad E = \text{elastic modulus}, \ A = \text{area}.$$

As the vibration passes along the rod, the stress will vary with position. The net force F acting on element δx causes it to accelerate:
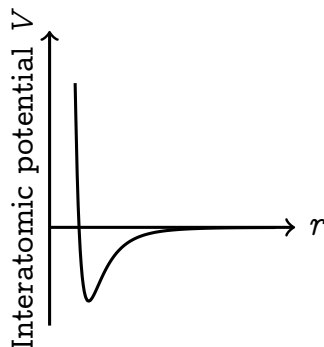
$$F(x + \delta x, t) - F(x, t) \simeq \frac{\partial F}{\partial x} \delta x = \frac{\partial}{\partial x} \left(AE \frac{\partial u}{\partial x} \right) \delta x = (\varrho A \delta x) \times \frac{\partial^2 u}{\partial t^2}$$

where the mass is $\varrho A \delta x$, with ϱ the mass density. Tidying, $\dfrac{\partial^2 u}{\partial t^2} = \dfrac{E}{\varrho} \dfrac{\partial^2 u}{\partial x^2}$

Atomistic picture

Real solids are made up of atoms held together by interatomic forces.

The equilibrium structure corresponds to atoms occupying minima of the potential energy function

For small displacements from equilibrium

$$V(r) = V(r_s) + (r - r_s) \frac{dV}{dr}\Big|_{r_s} + \frac{1}{2}(r - r_s)^2 \frac{d^2 V}{dr^2}\Big|_{r_s} + \dots$$

Ignoring anharmonic terms $\propto (r - r_s)^3$ and higher, we see

$$V(r) = V_0 + \frac{1}{2} K (r - r_s)^2 \qquad \Rightarrow \qquad \text{force } F(r) = -\frac{dV}{dr} = -K(r - r_s)$$

The forces between atoms behave like springs, with spring constant K that are related to the curvature of the potential.

Lattice vibrations

The interactions between atoms mean that when one atom moves, so too do its neighbours. The result is a collective vibration of the lattice.

As a simple model of lattice vibrations we consider a chain of atoms, each with mass M, and with equilibrium (average) spacing a.
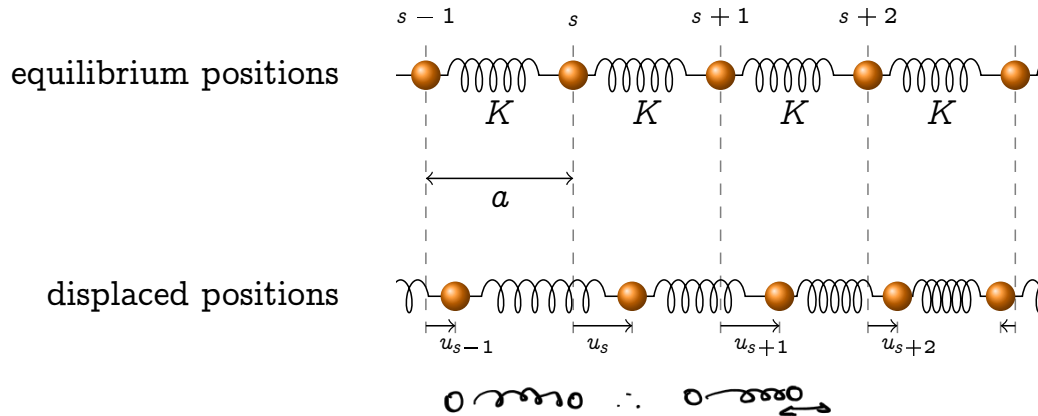
Let the displacement of atom s from its equilibrium position $x_s = sa$ be the quantity u_s.

We assume interactions exists between neighbouring atoms that can be described by a spring with spring constant K.

Equation of motion

The forces on atom s are [Hooke's law]

(i) $K(u_s - u_{s-1})$ to the left, due to the spring to the left; and
(ii) $K(u_{s+1} - u_s)$ to the right, due to the spring to the right

Equating total force to the right, (ii)-(i), to mass times acceleration gives the equation of motion of atom s:

EOM mass M atom s:

$$M\frac{d^2 u_s}{dt^2} = K(u_{s+1} + u_{s-1} - 2u_s).$$

We look for a wavelike solution, $u_s = ue^{i(kx_s - \omega t)}$.   Substituting
[*Note: complex exp. used for convenience; physical solution is Re(u$_s$)*]

$$-M\omega^2 ue^{i(ksa - \omega t)} = Ku\left(e^{i[k(s+1)a - \omega t]} + e^{i[k(s-1)a - \omega t]} - 2e^{i(ksa - \omega t)}\right)$$

$$\times e^{-i(ksa - \omega t)}: \quad -M\omega^2 u = 2Ku(\cos ka - 1)$$
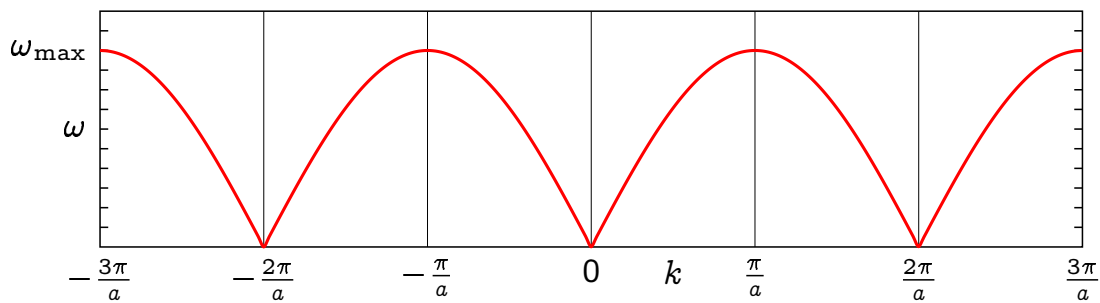
Dispersion relation

This equation has two possible solutions: either $u = 0$ (no vibration) or

$$\omega^2 = \frac{2K}{M}\left(1 - \cos ka\right) = \frac{4K}{M}\sin^2 \frac{ka}{2}$$

Hence wavelike solutions exist at frequencies

$$\omega = \omega(k) = \sqrt{\frac{4K}{M}}\left|\sin \frac{ka}{2}\right|$$

− this is a dispersion relation, giving the frequency of lattice vibrations that have wavevector k.

Cut-off frequency

In contrast to the elastic rod we see that there is a maximum frequency of any lattice vibrations: $\omega_{\text{max}} = \sqrt{\frac{4K}{M}}$. The chain of atoms can ony support oscillating waves with frequencies below this cut-off frequency.

What happens if we force an atom to oscillate more rapidly than this?

$$\omega > \omega_{\text{max}}$$
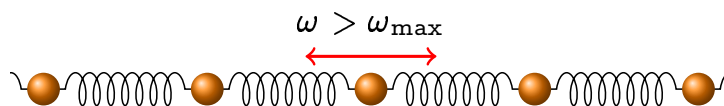
Solutions to

$$\omega^2 = \frac{4K}{M}\sin^2 \frac{ka}{2}$$

exist but with complex k, corresponding to vibrations $ue^{i(ksa-\omega t)}$ that decay as they move away from the atom undergoing forced motion − we get localised vibration.

Range of k

Also in contrast to the elastic rod, the allowed frequencies are a periodic function of wavevector k. This is because solutions with wavevectors k and $k + 2\pi/a$ actually correspond to exactly the same atomic displacements:
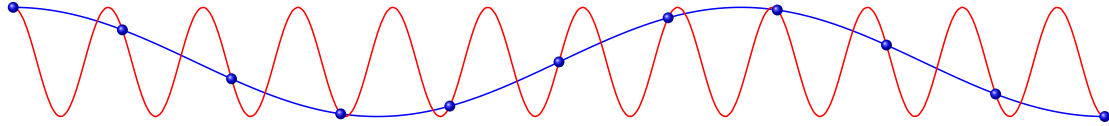
$\cos(kx)$ for: Blue: $k = 0.3\pi/a$ Red: $k = 0.3\pi/a + 2\pi/a$

Hence the allowed frequencies vary periodically with k, and we only need to describe ω for k spanning some period $2\pi/a$ to fully specify $\omega(k)$.

We choose the interval $-\pi/a$ to $+\pi/a$. This includes the origin, and negative values are needed to specify both possible directions of the wave.

This range of k corresponds to the Brillouin zone of the one-dimensional lattice.

Speed of sound

In the long wavelength limit ($\lambda \gg a$, or $ka \ll 1$) the dispersion relation simplifies to $\omega(k) = \sqrt{\frac{K}{M}}ka$ (using $\sin x \simeq x$ for small x). Therefore long wavelength lattice vibrations are dispersionless, with both the group velocity $d\omega/dk$ and phase velocity ω/k given by

$$v = \sqrt{\frac{K}{M}}a = \sqrt{\frac{Ka}{M/a}} = \sqrt{\frac{E}{\varrho}}$$

$-$ we recover the continuum result with density M/a, elastic modulus Ka.
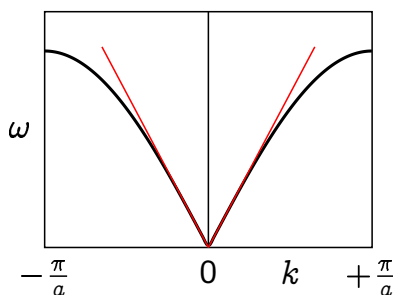
More generally, the group velocity $v_g = \partial\omega/\partial k$ varies with k.

$$v_g = \sqrt{\frac{Ka^2}{M}}\cos\frac{ka}{2}.$$

At $k = \pm\pi/a$, $v_g = 0$ $-$ we have a standing wave. [animations]

Counting lattice vibrations

How many different lattice vibrations (distinguished by k) are there?

To avoid surface effects, we take our macroscopic sample, length $L = Na$ where N is the number of atoms, and form it into a circle to create periodic boundary conditions.
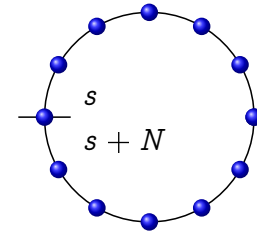
Now atom s and atoms $s + N$ are equivalent, and vibrate with the same amplitude and phase.

Recall atom s vibrates with amplitude $u_s = u e^{i(ksa - \omega t)}$.

Requiring $\qquad u_{s+N} = u_s \qquad \Rightarrow \quad u e^{ik(s+N)a} \quad = \quad u e^{iksa}$

$$\Rightarrow \quad e^{ikNa} \quad = \quad 1, \qquad \text{or} \qquad kNa = 2\pi \times integer$$

So the wavevectors are separated by $\Delta k = \dfrac{2\pi}{Na}$

Total no. of different modes $= \dfrac{\text{length of Brillouin zone}}{\text{spacing between points}} = \dfrac{2\pi/a}{2\pi/Na} = N$

The monatomic chain supports N different longitudinal lattice vibrations.

Transverse vibrations

As well as the longitudinal vibrations, the linear chain also supports transverse vibrations, with atomic motion perpendicular to the wave vector k. Two independent sets of transverse vibration exist (in perpendicular planes). These are degenerate, but in actual solids they can be different.

Transverse restoring forces are normally weaker, with the transverse branches lying below the longitudinal branch.
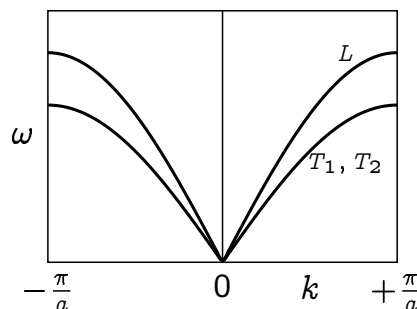
In total the chain has $3N$ different lattice vibrations, to be compared with the $3N$ degrees of freedom of N atoms. This is a general result for a monatomic lattice.

Dispersion curves for a real solid: Cu (fcc)

Although simple, the monatomic chain can be used to understand lattice vibrations in monatomic solids, where planes of atoms vibrate.
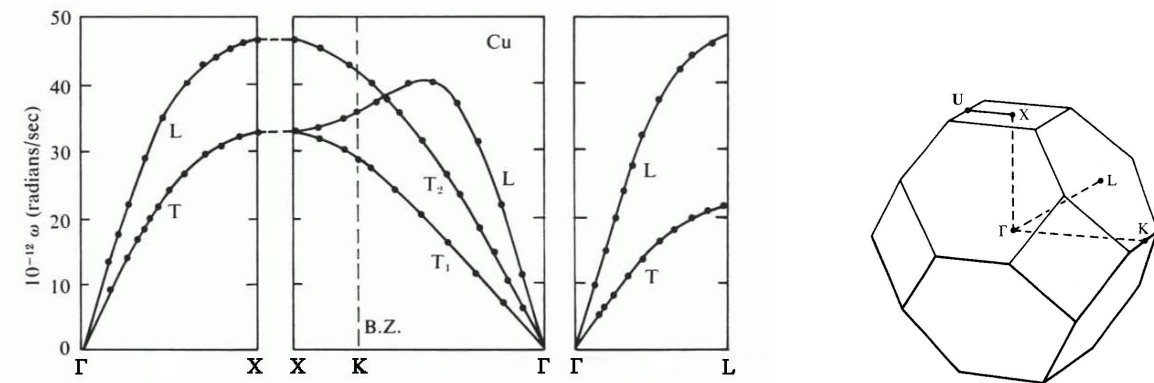
It is not easy to plot ω versus (k_x, k_y, k_z). Therefore dispersion plots for real materials are normally displayed with ω plotted against k for wavevectors in a small number of special directions within the Brillouin zone.

The end points are labelled using special letters. For fcc materials,
$\Gamma = \frac{2\pi}{a}(0,0,0)$, $X = \frac{2\pi}{a}(1,0,0)$, $L = \frac{2\pi}{a}(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $K = \frac{2\pi}{a}(\frac{3}{4}, \frac{3}{4}, 0)$.

Lattice planes in fcc structure
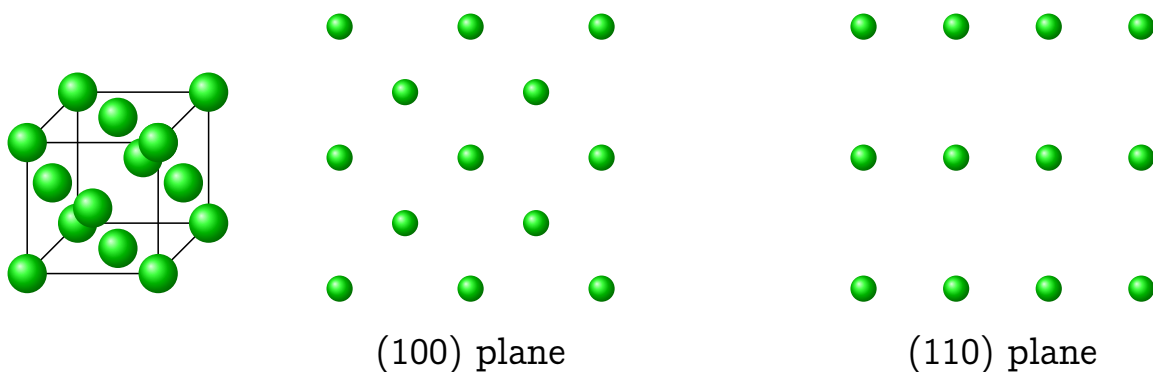
(100) plane   (110) plane

Transverse vibrations are degenerate for wavevectors along $\Gamma - X$ because these correspond to vibrations of the (100) planes, which have $x \to y$ symmetry.

Transverse vibrations along $\Gamma - K$ are not degenerate, because (110) planes do not have $x \to y$ symmetry.

Diatomic chain

As a simple model of lattice vibrations in more complex solids, we now consider an alternating chain of atoms, masses m and M, and with repeat length a.
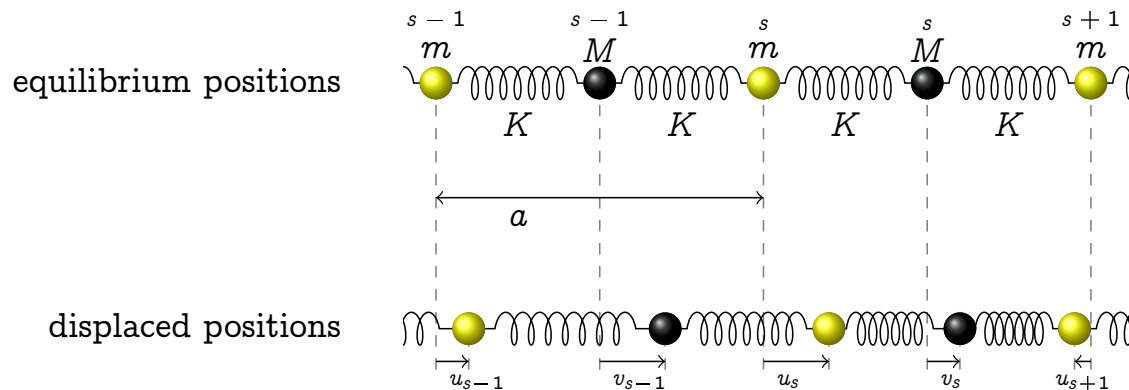
s'th atom of mass m is displaced from equilibrium position by an amount u_s. s'th atom of mass M is displaced from equilibrium position by an amount v_s.

Neighbouring atoms interact via springs with spring constant K.

Equation of motion

There are two (longitudinal) degrees of freedom (u,v) - we need two equations:

The forces on atom mass m in unit cell s are

   (i) $K(u_s - v_{s-1})$ to the left, due to the spring to the left; and
   (ii) $K(v_s - u_s)$ to the right, due to the spring to the right

The resulting equation of motion is $\quad m\dfrac{d^2 u_s}{dt^2} = K(v_s + v_{s-1} - 2u_s).$

The forces on atom mass M in unit cell s are

   (i) $K(v_s - u_s)$ to the left, due to the spring to the left; and
   (ii) $K(u_{s+1} - v_s)$ to the right, due to the spring to the right

The resulting equation of motion is $\quad M\dfrac{d^2 v_s}{dt^2} = K(u_{s+1} + u_s - 2v_s).$

Solution

The equations of motion are two coupled equations.

We look for wavelike solutions, $u_s = u e^{i(ksa - \omega t)}$, $v_s = v e^{i(ksa - \omega t)}$.

Substitute:

$$-m\omega^2 u e^{i(ksa - \omega t)} = K\left(v e^{i[ksa - \omega t]} + v e^{i[k(s-1)a - \omega t]} - 2u e^{i(ksa - \omega t)}\right)$$

$$-M\omega^2 v e^{i(ksa - \omega t)} = K\left(u e^{i[k(s+1)a - \omega t]} + u e^{i[ksa - \omega t]} - 2v e^{i(ksa - \omega t)}\right)$$

Simplify: $\times e^{-i(ksa - \omega t)}$

$$-m\omega^2 u = K\left([1 + e^{-ika}]v - 2u\right)$$

$$-M\omega^2 v = K\left([e^{ika} + 1]u - 2v\right)$$

Rearrange:

$$\begin{bmatrix} \frac{2K}{m} & -\frac{K}{m}\left(1 + e^{-ika}\right) \\ -\frac{K}{M}\left(e^{ika} + 1\right) & \frac{2K}{M} \end{bmatrix} \begin{bmatrix} u \\ v \end{bmatrix} = \omega^2 \begin{bmatrix} u \\ v \end{bmatrix}$$
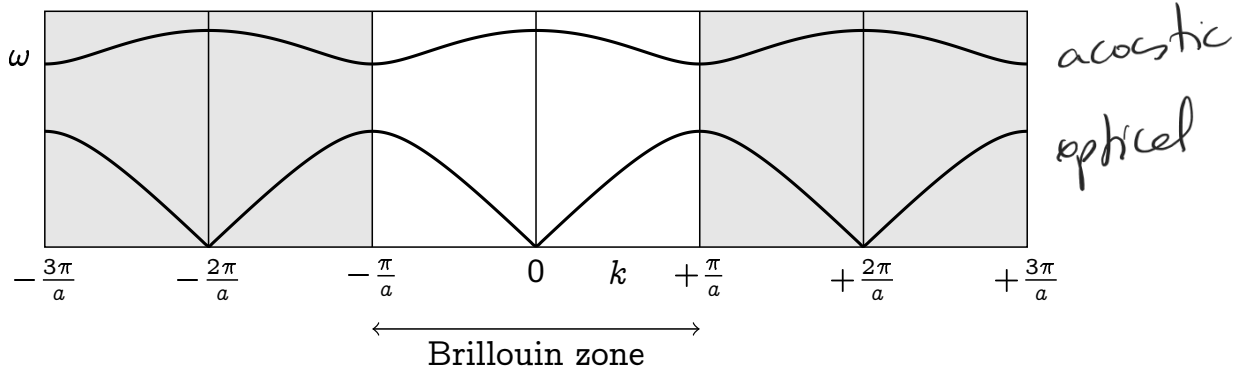
Dispersion

The frequencies are found by solving this matrix eigenvalue problem. The general result is [problem sheet]

$$\omega^2 = K\left(\frac{1}{m} + \frac{1}{M}\right) \pm K\sqrt{\left(\frac{1}{m} + \frac{1}{M}\right)^2 - \frac{4}{mM}\sin^2\frac{ka}{2}}$$

The dispersion is periodic, with period $ka/2 = \pi$ or $k = 2\pi/a$.

The diatomic chain supports two longitudinal modes for each k.

acoustic
optical

Brillouin zone

Special values

At $k = 0$ and $k = \pi/a$ the problem simplifies and we can gain insight into the general nature of the lattice vibrations.

e.g. at $k = \pi/a$

$$\begin{pmatrix} 2K/m & 0 \\ 0 & 2K/M \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix} = \omega^2 \begin{pmatrix} u \\ v \end{pmatrix}$$

k	solutions		
0	$\omega = 0, \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$		$\omega = \sqrt{\dfrac{2K}{\mu}}, \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} M \\ -m \end{pmatrix}$
$\dfrac{\pi}{a}$	$\omega = \sqrt{\dfrac{2K}{m}}, \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$		$\omega = \sqrt{\dfrac{2K}{M}}, \begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

μ is the reduced mass: $\dfrac{1}{\mu} = \dfrac{1}{m} + \dfrac{1}{M}$.

Acoustic and optical branches

For small k, one branch approaches zero as $k \to 0$. This is called the acoustic branch. For small k ($ka \ll 1$), ω is proportional to k and vibrations associated with this branch are dispersionless – these are long-wavelength sound waves, as described by the continuum theory.

The branch for which $\omega \neq 0$ for $k = 0$ is called the optical branch. This is because at $k = 0$ the atomic motions associated with this branch have the two atom types vibrating out of phase ($u \propto -v$). In ionic solids, positively charged atoms move in opposite direction to negatively charged atoms, creating an osillating dipole which can couple to an EM field (absorb infrared radiation).

At $k = \pi/a$, the two modes correspond to one or other atom type being stationary.

So we have the following dispersion diagram of longitudinal vibrations of a diatomic chain.
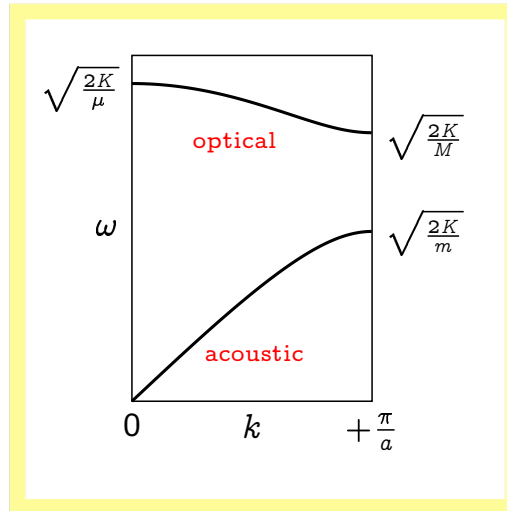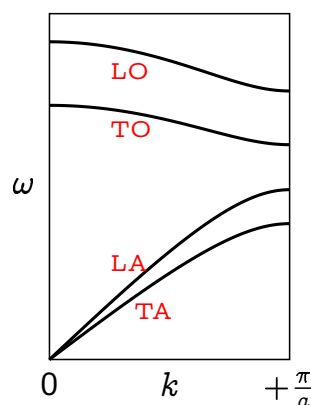

The plot assumes $m > M$.

The upper branch becomes flatter as the mass ratio increases.

Each branch contain N different modes (see earlier analysis).

Dispersion diagram for a diatomic chain

A diatomic chain also supports transverse vibrations

LA = longitudinal acoustic branch
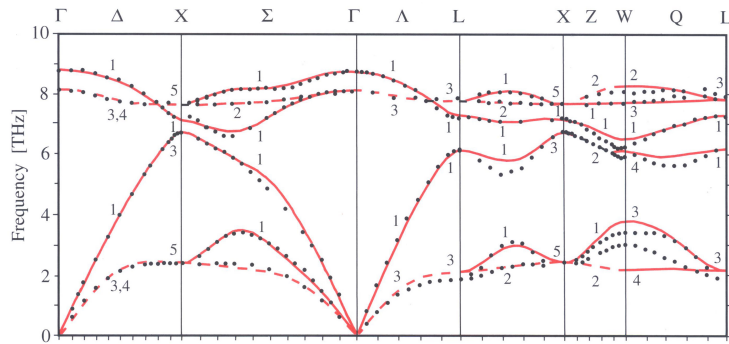TA = transverse acoustic (2-fold degenerate)
LO = longitudinal optical branch
TO = transverse optical branch (2-fold degenerate)

In total, there are $3N$ acoustic modes and $3N$ optical modes.

Dispersion curves for a real diatomic solid: GaAs

GaAs crystallises in the Zincblende structure, which has 2 atoms in the primitive fcc unit cell: Ga at $(0,0,0)$, and As at $(1/4,1/4,1/4)$.

Fig. 3.2. Phonon dispersion curves in GaAs along high-symmetry axes [3.5]. The experimental data points were measured at 12 K. The *continuous lines* were calculated with a 15-parameter rigid-ion model. The numbers next to the phonon branches label the corresponding irreducible representations
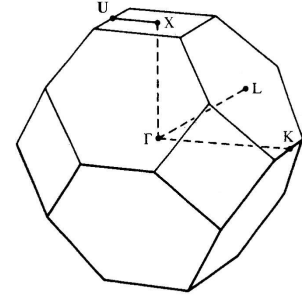
$\Gamma = \frac{2\pi}{a}(0,0,0)$, $X = \frac{2\pi}{a}(1,0,0)$, $L = \frac{2\pi}{a}(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $K = \frac{2\pi}{a}(\frac{3}{4},\frac{3}{4},0)$.

There are $3N$ acoustic modes and $3N$ optical modes. If a crystal has N unit cells, with n atoms in the basis, there will be $3N$ acoustic and $3N(n-1)$ optical modes.

Dispersion curves for a real solid: Si

Si crystallises in the diamond structure, which is Zincblende (as GaAs) but both atoms are the same element There are still 2 atoms in the primitive unit cell.
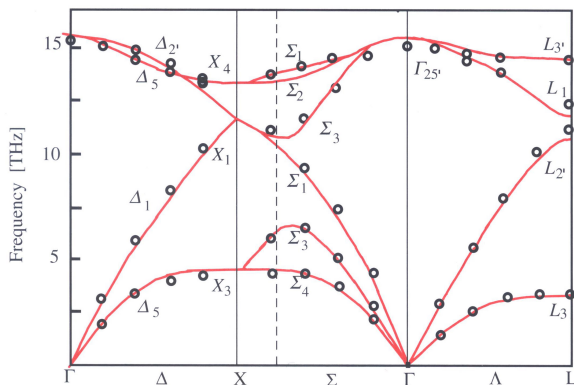
Fig. 3.1. Phonon dispersion curves in Si along high-symmetry axes. The *circles* are data points from [3.3]. The continuous curves are calculated with the adiabatic bond charge model of *Weber* [3.4]
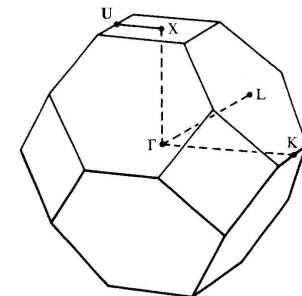
The upper branches are still called optical branches, although the atoms in Si will not be charged and will not behave like an oscillating dipole that couples to IR radiation.

Scattering experiments to study lattice vibrations

Lattice vibrations can be studied through scattering experiments.

Recall [Crystal structure topic 4] that the amplitude of radiation measured at a distance detector is [monatomic crystal]

$$A \propto e^{-i\omega_0 t} \sum_j e^{-i\mathbf{Q} \cdot \mathbf{r}_j}$$

where ω_0: frequency of radiation $\mathbf{Q} = \mathbf{k}' - \mathbf{k}$ scattering vector

       $\mathbf{k}$ wavevector of incident radiation $\mathbf{r}_j$: atomic positions

       $\mathbf{k}'$ wavevector of scattered radiation

Allowing for time-dependent atomic positions $\mathbf{r}_j(t) = \mathbf{r}_j + \mathbf{u}_j(t)$,

$$\begin{aligned} A \quad &\propto \quad e^{-i\omega_0 t} \sum_j e^{-i\mathbf{Q} \cdot \mathbf{r}_j(t)} \\ &\propto \quad e^{-i\omega_0 t} \sum_j e^{-i\mathbf{Q} \cdot \mathbf{r}_j} e^{-i\mathbf{Q} \cdot \mathbf{u}_j(t)} \\ &\propto \quad e^{-i\omega_0 t} \sum_j e^{-i\mathbf{Q} \cdot \mathbf{r}_j} \left[1 - i\mathbf{Q} \cdot \mathbf{u}_j(t) + \ldots \right] \end{aligned}$$

(assuming small $\mathbf{u}_j$).

The first term in square brackets gives rise to the elastic scattering intensity previously studied.

$$A_{\text{el}} \propto e^{-i\omega_0 t} \sum_j e^{-i\mathbf{Q} \cdot \mathbf{r}_j}.$$

For the second term in the square bracket we use $\mathbf{q}$ for the wavevector of the lattice vibration so

$$\mathbf{u}_j(t) = Re\left(\mathbf{u} e^{i(\mathbf{q} \cdot \mathbf{r}_j - \omega(\mathbf{q})t)} \right) \propto \mathbf{u} e^{i(\mathbf{q} \cdot \mathbf{r}_j - \omega(\mathbf{q})t)} + \mathbf{u} e^{-i(\mathbf{q} \cdot \mathbf{r}_j - \omega(\mathbf{q})t)}.$$

This term produces extra scattering

$$A_{\text{inel}} \propto e^{-i(\omega_0 \pm \omega(\mathbf{q}))t} \sum_j e^{-i(\mathbf{Q} \mp \mathbf{q}) \cdot \mathbf{r}_j}$$

i.e. scattered waves with

- frequency $\omega = \omega_0 \pm \omega(\mathbf{q})$

- significant amplitude only when the Laue condition $\mathbf{Q} \mp \mathbf{q} = \mathbf{G}$ is satisfied, where $\mathbf{G}$ is a reciprocal lattice vector.

Phonons

Multiplying by $\hbar$, these two classical equations become

$$\hbar\omega = \hbar\omega_0 \pm \hbar\omega(\mathbf{q})$$
$$\hbar\mathbf{k}' = \hbar\mathbf{k} \pm \hbar\mathbf{q} + \hbar\mathbf{G}$$

First equation is the quantum mechanical conservation of energy
- minus sign, excitation of lattice vibration
- plus sign, lattice vibration loses energy to incident wave

Second equation is conservation of quasimomentum, if $\hbar q$ is assumed to be the quasimomentum of the lattice vibration. Quasimomentum because
- only conserved to within reciprocal lattice vector, and
- $\sum_i m \frac{d}{dt} \mathbf{r}_j(t) = 0$ for general lattice vibration [see problem sheet].

These conservation equations suggest lattice vibrations behave like particles
- we call these phonons.

Requirements for experimental probe

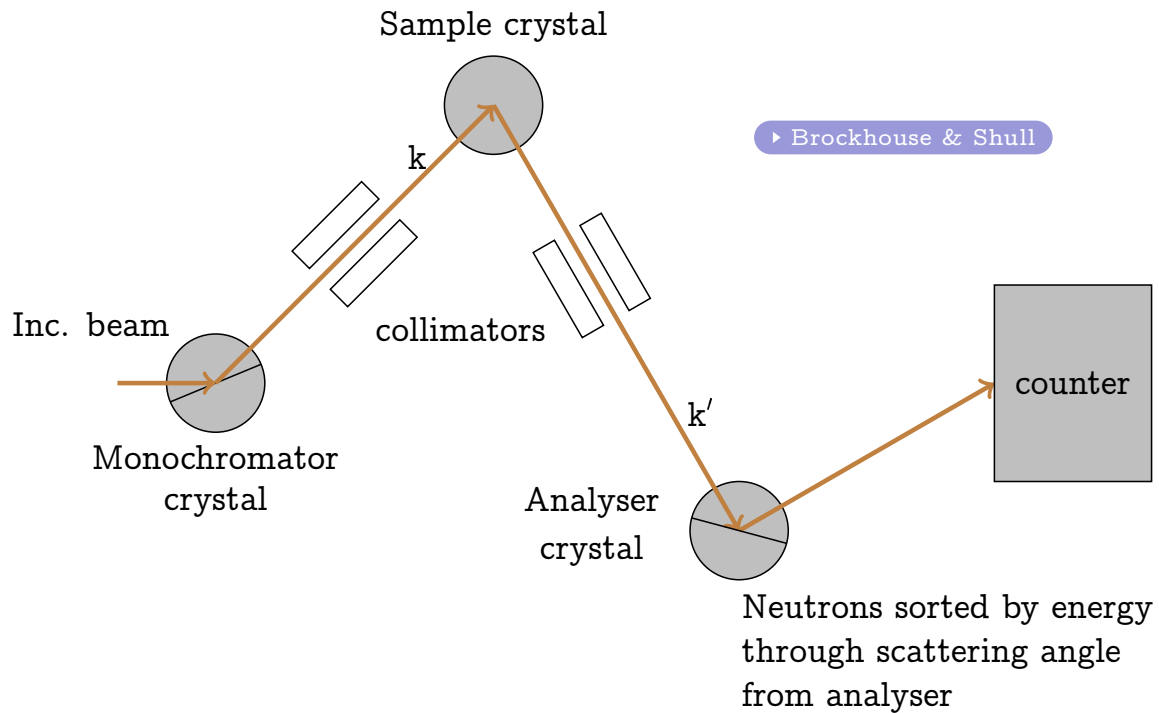Crystal structure is normally measured using X-rays or neutrons. What about lattice vibrations?

Raman spectroscopy uses inelastic scattering of light around the visible region. Maximum momentum transfer for visible light is $|\mathbf{Q_{max}}| = 2k = 4\pi/\lambda \sim 2 \times 10^{-3}$ Å, a small fraction of the Brillouin zone. Therefore Raman spectroscopy can only measure phonons near $q = 0$.

For X-rays this is not a problem: $\lambda \sim a$. But X-ray energies $\gg$ phonon energies (10 keV vs $1 - 100$ meV), and the energy change is swamped by the natural width ΔE of X-ray sources, preventing identification of ΔE
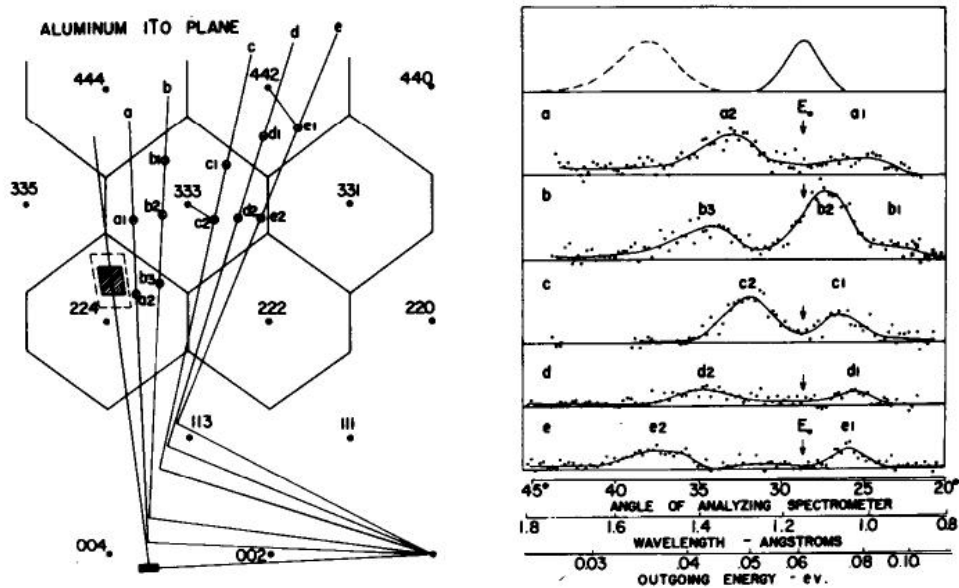
Neutrons and atoms are ideal probes – energies needed to give momentum transfer are in the $0.1 - 1$ eV range. Inelastic neutron scattering is the principle probe of phonons, with atom (e.g. Helium) scattering used for surface phonons.

Electrons can also be scattered by lattice vibrations – an important source of resistance, and the origin of conventional superconductivity [see Superconductivity unit].

Inelastic Neutron Scattering: experiment set-up

Sample crystal

k

▸ Brockhouse & Shull

Inc. beam

collimators

Monochromator crystal

Analyser crystal

k′

counter

Neutrons sorted by energy through scattering angle from analyser
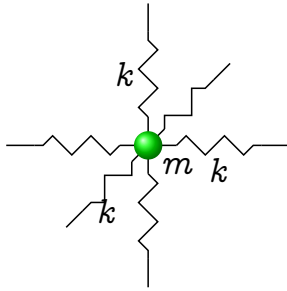
Neutron spectra for Al

Neutron counts (right) for wavevectors in different directions (left) [from Brockhouse's Nobel Prize acceptance speech].

Vibrational heat capacity

We now consider the contribution of lattice vibrations to the heat capacity of solids.

Classical theory:

Vibrating atom:

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}kx^2 + \frac{1}{2}ky^2 + \frac{1}{2}kz^2$$

Equipartition theorem (classical stat. mech.):
"*in thermal equilibrium, each quadratic term in E has an average energy $(1/2)k_B T$*"

$$\langle E \rangle = 6 \times \frac{1}{2}k_B T = 3k_B T$$

Law of Dulong and Petit

N_A vibrating atoms/oscillators: $\qquad \langle E \rangle / \text{mole} = 3N_A k_B T = 3RT$

(N_A – Avagadro's constant; R – gas constant)
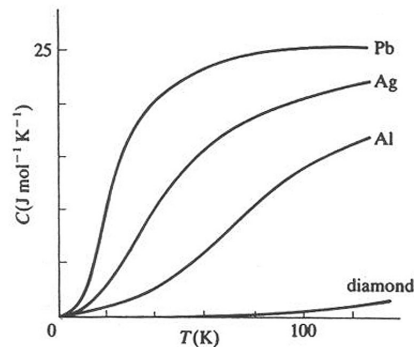
So heat capacity per mole at constant volume:
= rate change of energy of a solid with temp

$$C_V = \frac{\partial}{\partial T}\left(\frac{\langle E \rangle}{n}\right)_V = 3R \quad (\simeq 25\text{J mol}^{-1}\text{ K}^{-1})$$

This is the law of Dulong and Petit (1819).

Heat capacity of different materials

Law of Dulong and Petit is obeyed by most solids at high temperatures ...

... but not at low temperatures.

Also, C_V for diamond is very low. Why?

This was known by the middle of the 19th century – one of the "clouds of the 19th century" that prompted the development of quantum mechanics.

Einstein Model

Planck postulated that oscillators have quantised energies ▸ Planck

$$E_n = n\hbar\omega, \quad n = 0, 1, 2, \ldots$$

Einstein (1907) calculated the vibrational heat capacity assuming the solid comprised $3N$ independent oscillators with Planck's energies.

▸ Einstein

Note: it was later shown [see Quantum course] $E_n = (n + \frac{1}{2})\hbar\omega$ for vibrating oscillators.

Then prob. of oscillator being in state i is $P_i = \dfrac{e^{-E_i/k_B T}}{\sum_{n=0}^{\infty} e^{-E_n/k_B T}}$,

and the average energy of each oscillator is $\langle E_{\text{osc}} \rangle = \sum_{i=0}^{\infty} E_i P_i$

From thermal physics ...

Partition function Z $= \sum_{n=0}^{\infty} e^{-E_n/k_B T} = \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}$ here, where $\beta = \dfrac{1}{k_B T}$

$\qquad\qquad = 1 + r + r^2 + r^3 + \ldots$ where $r = e^{-\beta\hbar\omega}$

$\qquad\qquad = \dfrac{1}{1-r}$ geometric series $(r < 1)$

$\qquad\qquad = \dfrac{1}{1 - e^{-\beta\hbar\omega}}$

In terms of Z, the average energy is $\langle E_{\text{osc}} \rangle = -\dfrac{\partial}{\partial\beta} \ln Z$.

Check:

$$-\frac{\partial}{\partial\beta}\ln Z = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} \quad = \quad \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \equiv \frac{\sum_i E_i e^{-\beta E_i}}{\sum_n e^{-\beta E_n}}$$

$$= \sum_i E_i P_i \qquad \text{as required}$$

So $\langle E_{\text{osc}} \rangle = -\dfrac{\partial}{\partial\beta} \ln Z$. Here, we have

$$\ln Z \;=\; \ln \frac{1}{1 - e^{-\beta\hbar\omega}} = -\ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$\frac{\partial}{\partial\beta}\ln Z \;=\; -\frac{1}{1 - e^{-\beta\hbar\omega}}\frac{\partial}{\partial\beta}\left(1 - e^{-\beta\hbar\omega}\right) = -\frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

and so

$$\langle E_{\text{osc}} \rangle = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}.$$

Therefore, we find that the average vibrational energy of a solid in the Einstein model is

$$\langle E \rangle = 3N\langle E_{\text{osc}} \rangle = \frac{3N\hbar\omega}{e^{\hbar\omega/k_B T} - 1}$$

Limiting behaviour

At high temperatures $\hbar\omega \ll k_B T$, then $e^{\hbar\omega/k_B T} \simeq 1 + \hbar\omega/k_B T$, giving

$$\langle E \rangle = \frac{3N\hbar\omega}{\hbar\omega/k_B T} = 3Nk_B T = 3RT \quad \text{per mole}$$

and $\quad C_V = 3R, \quad$ as observed experimentally.

At low temperatures $\hbar\omega \gg k_B T$, then $e^{\hbar\omega/k_B T} \gg 1$, giving

$$\langle E \rangle = \frac{3N\hbar\omega}{e^{\hbar\omega/k_B T}} = 3N\hbar\omega\, e^{-\hbar\omega/k_B T},$$

and $\quad C_V = 3Nk_B \dfrac{\hbar^2\omega^2}{k_B^2 T^2} e^{-\hbar\omega/k_B T} = 3R\left(\dfrac{\theta_E}{T}\right)^2 e^{-\theta_E/T} \quad$ per mole
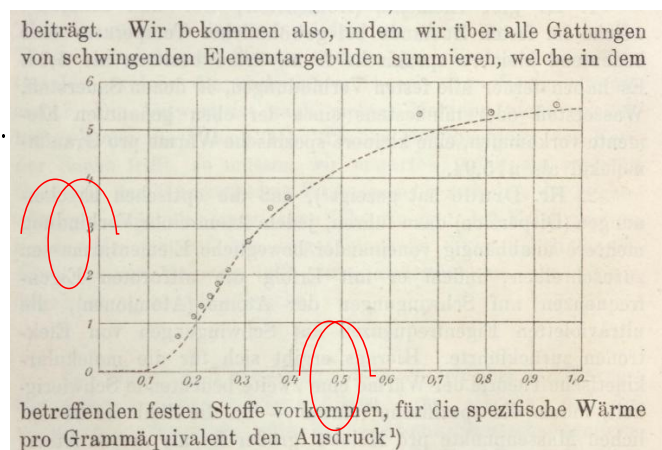
$\theta_E = \hbar\omega/k_B$ is the Einstein temperature, and characterises the solid.

Einstein model predicts $C_V \to 0$ as $T \to 0$, as observed experimentally.

Heat capacity of diamond

General expression:

$$C_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2}.$$

from: A. Einstein, Ann. d. Physik 22, 180 (1907).
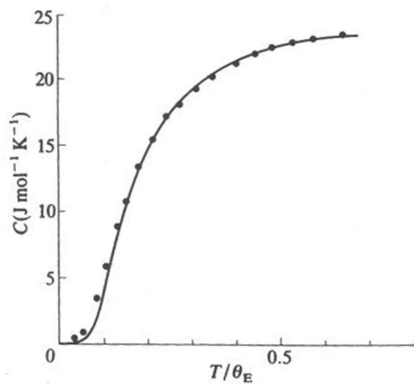
Note Einstein didn't label his axes!   horizontal axis: T/(1320 K)
vertical axis: cal K^{-1} mol^{-1}
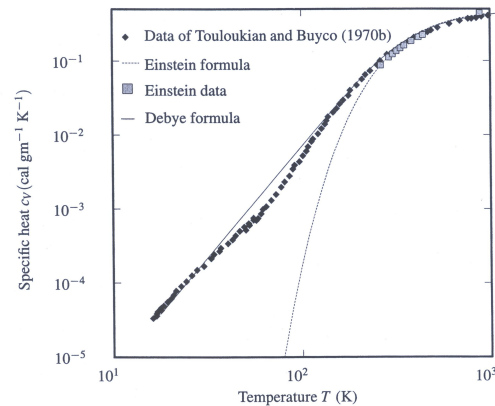
$3R = 5.96$ cal K^{-1} mol^{-1}

Heat capacity at low temperatures

The Einstein model fits experimental data well as a first approximation, but going to very low temperatures shows the theory does not work for all T.

Specific heat for Ag (silver) using $\theta_E = 160$ K.

Specific heat of diamond: Einstein data/formula and more recent data.

Einstein model drops to zero too quickly.

This failure is due to the assumption that there is only one frequency of vibration − as we know (and also appreciated by Einstein), interatomic forces couple together atoms leading to lattice vibrations with a range of frequencies. Including these is the Debye model.

Counting states in 3D

For vibrations of a monatomic chain, we noted that the allowed values of k were $k = (2\pi/L) \times integer$.

For a three-dimensional solid of volume $V = L^3$, the allowed k values are

$$\mathbf{k} = (k_x, k_y, k_z) \qquad k_i = \frac{2\pi}{L} \times n, \qquad \begin{cases} n = 0, \pm 1, \pm 2, \ldots \\ i = x, y, z \end{cases}$$
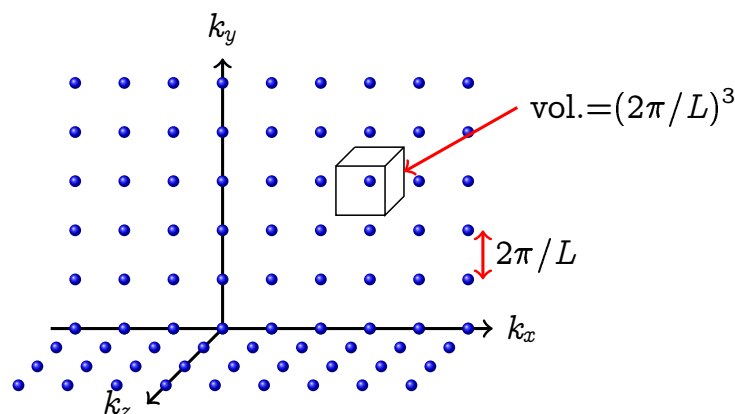
Each k-point corresponds to a different lattice vibration ("state"), and is associated with a volume $(2\pi)^3/V$ of k-space.

If $\omega = ck$, valid for the long-wavelength sound waves that we expect to exist at low temperatures, then the number of lattice vibrations with frequencies ω or less is the number of lattice vibrations with wavevector $k = \omega/c$ or less.

$$N(\omega) = \frac{\text{vol. of sphere, radius } k = \omega/c}{\text{vol. per } k \text{ point}} = \left.\frac{\frac{4}{3}\pi k^3}{(2\pi)^3/V}\right|_{k=\omega/c} = \frac{V}{6\pi^2}\left(\frac{\omega}{c}\right)^3$$

The density of states $g(\omega)$, the number of lattice vibrations per unit frequency with frequency ω, is then

$$\begin{aligned}
g(\omega)\,d\omega &= N(\omega + d\omega) - N(\omega) = \frac{dN(\omega)}{d\omega}\,d\omega \\
&= \frac{V}{2\pi^2}\frac{\omega^2}{c^3}\,d\omega
\end{aligned}$$

Thus $g(\omega) = \dfrac{V\omega^2}{2\pi^2 c^3}$.

Density of states in Debye model

A monatomic solid actually has one longitudinal and two transverse acoustic modes. So for low frequencies

$$g(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{c_L^3} + \frac{2}{c_T^3}\right) \equiv \frac{3V\omega^2}{2\pi^2 \bar{c}^3}$$

where c_L and c_T are the speed of longitudinal and transverse acoustic waves, and $\bar{c}$ an average speed.

Debye then assumed this expression held for higher frequencies too, dropping abruptly to zero at a cut-off frequency ω_D that ensured the solid has $3N$ phonons/lattice vibrations i.e.
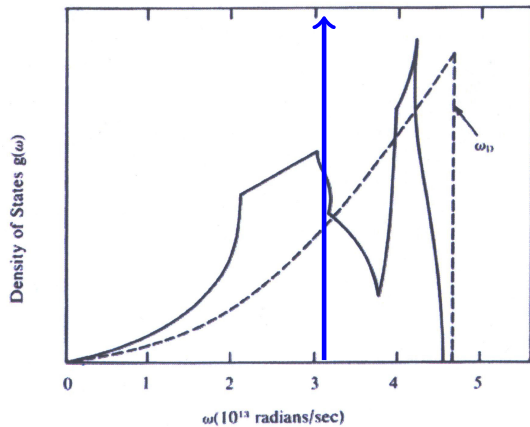
$$\int_0^{\omega_D} g(\omega)\,d\omega = 3N.$$

This gives [see problem sheet] $\omega_D = \bar{c}\left(6\pi^2 N/V\right)^{1/3}$.

Note ω_D is material dependent, due to $\bar{c}$ and the number density N/V.

Comparison of Debye, Einstein and real $g(\omega)$

Density of states
$$g(\omega) = 3N\frac{3\omega^2}{\omega_D^3}\vartheta(\omega_D - \omega) \qquad \text{Debye}$$

$$= 3N\delta(\omega - \omega_E) \qquad \text{Einstein}$$

Cu:

solid curve: from neutron scattering experiments

dashed curve: Debye approximation

delta function: Einstein model

[Note: the Einstein model is sometimes used to model optical branches.]

Average energy of solid in Debye model

Recall previous lecture, average energy of oscillator, frequency ω is

$$\langle E_{\text{osc}}\rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}.$$

[extra term is due to correct energy levels of oscillator being $(n + \frac{1}{2})\hbar\omega$].

So for the continuous distribution of frequencies present in the Debye model,

$$
\begin{aligned}
\langle E\rangle &= \int \langle E_{\text{osc}}\rangle g(\omega)\,d\omega \\
&= \int_0^{\omega_D} \left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right) \times 3N\frac{3\omega^2}{\omega_D^3} \\
&= \frac{9N\hbar}{2\omega_D^3}\int_0^{\omega_D} \omega^3\,d\omega + \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}d\omega
\end{aligned}
$$

The first term is independent of energy, and so it doesn't contribute to the heat capacity.
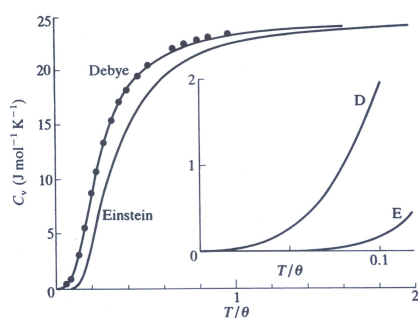
Heat Capacity

Differentiating,

$$
\begin{aligned}
C_V &= \frac{d\langle E\rangle}{dT} = \frac{d\langle E\rangle}{d\beta}\frac{d\beta}{dT} \\
&= -\frac{9N\hbar^2}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^4 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}\,d\omega \times \left(-\frac{1}{k_B T^2}\right) \\
&= \frac{9N\hbar^2}{\omega_D^3 k_B T^2}\int_0^{\omega_D}\frac{\omega^4 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}\,d\omega
\end{aligned}
$$

We introduce $\hbar\omega_D = k_B\theta_D$, where θ_D is called the Debye temperature. Then with $x = \beta\hbar\omega$ (so $dx = \beta\hbar\,d\omega$) we get [check!]

$$
C_V = 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^4 e^x}{(e^x-1)^2}\,dx
$$

This is the heat capacity in the Debye model.

Debye vs Einstein

Debye expression fitted to Ag data using

$\theta_D = 215$ K

Debye:

$$
C_V = 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^4 e^x}{(e^x-1)^2}\,dx
$$

Einstein:

$$
C_V = 3Nk_B\left(\frac{\theta_E}{T}\right)^2\frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2}.
$$

Both Debye and Einstein theories give C_V as a function of a single (temperature) parameter, θ_D or θ_E.

Both theories lead to a similar overall shape for C_V, but with different optimum fitting temperatures.

The differences are very pronounced at low temperatures.
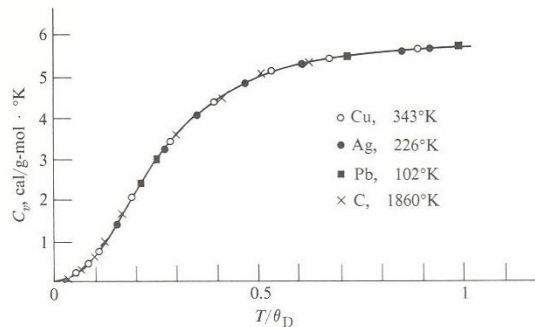
Debye vs Expt

Debye Temperatures			
Element	θ_D, °K	Compound	θ_D, °K
Li	335	NaCl	280
Na	156	KCl	230
K	91.1	CaF$_2$	470
Cu	343	LiF	680
Ag	226	SiO$_2$ (quartz)	255
Au	162		
Al	428		
Ga	325		
Pb	102		
Ge	378		
Si	647		
C	1860		

Better agreement than Einstein at low T

Univeral behaviour for all solids!

Debye temperature correlates with

"stiffness" of solid, as expected

Limiting behaviour

At high temperatures $T \gg \theta_D$, and x in the integrand is always small. Expanding $e^x \simeq 1 + x$ gives

$$C_V = 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} x^2\,dx = 3Nk_B = 3R \text{ per mole.}$$

The Debye model gives the Dulong-Petit value at high temperatures.

At low temperatures $T \ll \theta_D$ and we can write

$$\int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\,dx \simeq \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2}\,dx = \frac{4\pi^4}{15} \quad \text{using tables}$$

Then $C_V = \dfrac{12\pi^4}{5} Nk_B \left(\dfrac{T}{\theta_D}\right)^3$ and $C_V \to 0$ as $T \to 0$

− as observed experimentally. However, in contrast to the exponential variation of the Einstein model, the Debye model predicts $C_V \sim T^3$ at low temperatures.

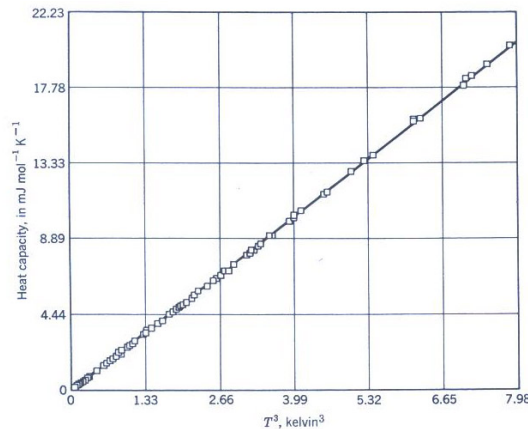# Heat capacity of Ar (argon)

C_V plotted against T^3.

Figure 11 Low temperature heat capacity of solid argon, plotted against T^3. In this temperature region the experimental results are in excellent agreement with the Debye T^3 law with $\theta_0 = 92.0$ K. (Courtesy of L. Finegold and N. E. Phillips.)

Data for Ar are in excellent agreement with the Debye model.

Theories of the heat capacity – essential details

Classical: Vibrational properties of a solid are modelled as those of N atoms, each with average energy corresponding to 6 quadratic degrees of freedom. This predicts $C_V = 3R$ per mole, for all temperatures.

Einstein: Vibrational properties of a solid are modelled as $3N$ (N atoms, 3 directions) identical oscillators with quantised energies. The model predicts $C_V \to 3R$ per mole at high temperatures, and C_V drops to zero exponentially as $T \to 0$.

Debye: Vibrational properties of a solid are modelled as $3N$ quantised oscillators, with frequencies satisfying the dispersion relation $\omega = ck$ of long-wavelength acoustic vibrations. The model predicts $C_V \to 3R$ per mole at high temperatures, and $C_V \propto T^3$ at low T.

Heat capacity of electron gas - reminder

Historically, this was another puzzle – electrons freely conduct, but C_V^{el} is a small fraction of that expected based upon classical gas.

The answer [found by Fermi] lies in quantum statistics.

Fermi occupation function
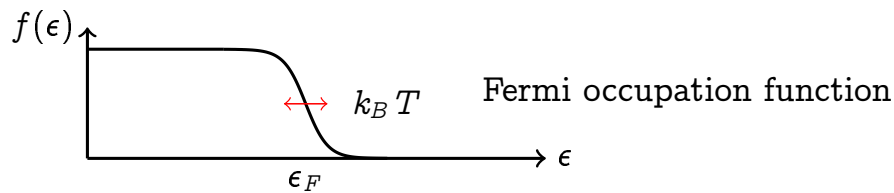
Heat electrons in solid; only states within $k_B T$ of Fermi level become thermally excited. These gain energy of order $k_B T$.

Therefore $\qquad \langle E(T) \rangle - \langle E(0) \rangle \sim N \left(\dfrac{T}{T_F} \right) k_B T \qquad \Rightarrow \qquad C_V^{\text{el}} \sim 2 N k_B \left(\dfrac{T}{T_F} \right).$

Quantitative derivation [Kittel p164] gives

$$C_V^{\text{el}} = \frac{\pi^2}{3} g(\epsilon_F) k_B^2 T = \frac{\pi^2}{2} N k_B \left(\frac{T}{T_F} \right) \quad \text{for free electron gas}$$
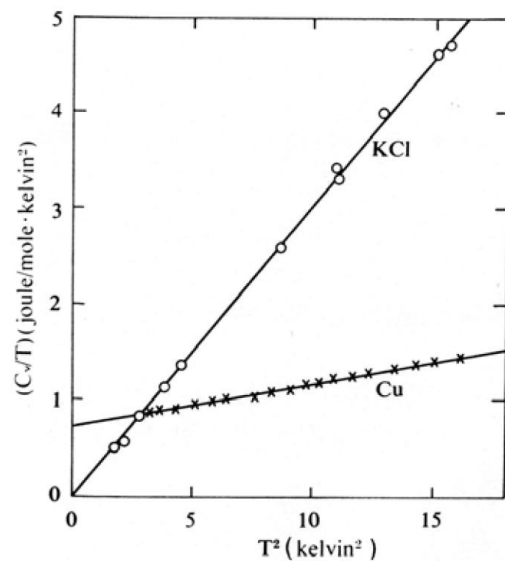
Insulators have no states at Fermi energy to be thermally excited: $C_V^{\text{el}} = 0$.

Low T heat capacity of metals and insulators

$$
\begin{aligned}
C_V &= \gamma T + \alpha T^3 &\quad& \text{metals} \\
&= \alpha T^3 &\quad& \text{insulators}
\end{aligned}
$$

so

$$
\frac{C_V}{T} = \begin{cases} \gamma + \alpha T^2 & \text{metals} \\ \alpha T^2 & \text{insulators} \end{cases}
$$

Suggested further reading

For alternative descriptions and explanations, often at a different level, plus further problems, see

Lattice vibrations

Hook and Hall	p33–49,348–350
Myers	p109–119,122–125
Kittel (5th ed.)	p107–124
Ibach & Lüth	p51–65
Ashcroft & Mermin	p430–437, p470–486

Heat capacity

Hook and Hall	p49–62
Myers	p105–109, 120–121
Kittel (5th ed.)	p127–139
Ibach & Lüth	p68–73
Ashcroft & Mermin	p452–468