

8. Lattice Vibrations of Solids

8.1 Classical Theory

Let $\underline{r}_1, \underline{r}_2, \dots, \underline{r}_n$ represent positions of atoms.

Need to solve Newton's law $M_i \ddot{\underline{r}}_i = F(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_n)$.

Denote $\underline{r}_i = \underline{R}_i + \underline{x}_i$, where $\underline{R}_i$ is the equilibrium position, and $\underline{x}_i$ is a small displacement from equilibrium. So;

$$M_i \ddot{\underline{x}}_i = -\sum_j A_{ij} x_j + \dots$$

We are looking at the potential $V(r)$ of the atom, i.e. that where it is at equilibrium – at its' lowest potential. $\underline{x}_i$ is a small displacement around this, i.e. that part of the curve which is mostly linear. If we increase the size of it, then we get into the non-linear part of the curve.

From $M_i \ddot{\underline{x}}_i = -\sum_j A_{ij} x_j + \dots$, we get $3N$ equations. We can solve them through

normal mode analysis, where we assume that all the atoms vibrate with the same frequency in the mode. In general, there are $3N$ normal modes of vibration. ω_i , $i = 1, 2, \dots, 3N$

8.2 Quantum Treatment

Here we have

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega,$$

but the same modes as in the classical case. In the classical treatment, we got the set of frequencies ω_i , $i = 1, 2, \dots, 3N$, but now we have to quantize.

8.3 Simplest Theory of Heat Capacity

This is a classical theory. It starts from the observation that each oscillator has classical equipartition energy $= k_B T$ (two degrees of freedom, KE and PE, each of which has $E = \frac{1}{2} kT$). There are $3N$ such oscillators.

Energy of the solid $= E = 3Nk_B T$.

So the heat capacity $C = \frac{dE}{dT} = 3Nk_B$.

So the heat capacity should be independent of temperature. It is often referred to as the Dulong and Petit law, and is only valid at high temperatures where classical ideas are valid.

8.4 Simplest Quantum Theory of Heat Capacity – Einstein Theory

This theory treats each normal mode as a quantum SHO, but Einstein assumed that all the oscillators, i.e. the $3N$ harmonic modes, have the same frequency ω_E .

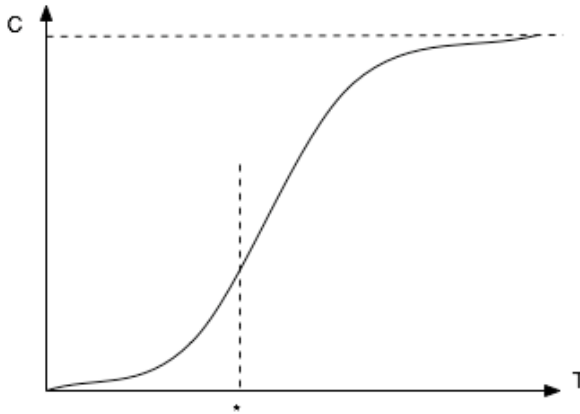
$$E = 3N \left[\bar{n} + \frac{1}{2} \right] \hbar \omega_E$$

where $\bar{n}$ is the average number of quanta that are associated with each mode, and is given by

$$\bar{n} = \frac{1}{e^{\frac{\hbar\omega_E}{k_B T}} - 1}$$

The quanta of lattice vibrations are called *Phonons*, c.f. the photons of EM radiation. So now we get:

$$C_v = \frac{dE}{dT} = 3Nk_B \left(\frac{\hbar\omega_E}{k_B T} \right)^2 \frac{e^{\frac{\hbar\omega_E}{k_B T}}}{e^{\frac{\hbar\omega_E}{k_B T}} - 1}$$



The * is at $\frac{\hbar\omega_E}{k_B T} \sim 1$. The curve starts off at $C \sim \frac{1}{T^2} e^{-\frac{\hbar\omega_E}{k_B T}}$, and reaches a maximum at $3Nk_B$.

Exponential fall off at low T – this is not seen in experiments.

$c_v \sim T^3$ at low T – not all of the 3N SHO have the same frequency. It works fairly well for diamonds, but not much else.

8.5 The Debye T^3 Law

Debye recognized that only low frequency modes would be thermally excited at low temperatures.

$$\bar{n} = \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1} \approx e^{-\frac{\hbar\omega}{k_B T}} \text{ for } \hbar\omega \gg k_B T, \text{ i.e. } \rightarrow 0.$$

We really need $\hbar\omega \sim k_B T$.

We know that the low energy (frequency) phonon modes are sound modes. So we need to innumerate the number of sound modes that might exist within a solid. Consider a cube with sides L. Sound waves are standing waves inside the cube.

Through the usual arguments, we have $\frac{V k^2 dk}{2\pi^2}$ values between k and $k + dk$.

There are 3 sound wave modes for each k value. There are 2 modes corresponding to transverse sound, where the displacement of the atoms is perpendicular to their direction of motion. There is one mode up, and one down, in this case. You can also have one mode corresponding to longitudinal sound, where the displacement is parallel to the k -vector.

In an isotropic solid, transverse modes have $\omega = V_t k$ where V_t is the velocity of the transverse waves (the same in an isotropic solid). Longitudinal have $\omega = V_\ell k$, where V_ℓ is the velocity of longitudinal sound.

In air and liquid, sound is always longitudinal. Transverse sound is only found in solids – it can be used as a definition of what a solid is. It only happens when the material can resist shear.

We can use these to count the number of modes between ω and $\omega + d\omega$.

$$= \left(\frac{2}{V_t^3} + \frac{1}{V_\ell^3} \right) \frac{V \omega^2}{2\pi^2} d\omega$$

Define effective average velocity $\frac{3}{\bar{V}^3} = \frac{2}{V_t^3} + \frac{1}{V_\ell^3}$. This has no physical significance – it just simplifies the equations.

$$\text{Energy of the modes at lower temperatures} = \int_0^\infty \left(\bar{n} + \frac{1}{2} \right) \hbar \omega \frac{3}{\bar{V}^3} \frac{V \omega^2}{2\pi^2} d\omega.$$

V here is volume.

Ignore the zero point energy. Upper limit over $\bar{n}$ can be taken to be infinite.

$$\bar{n} \rightarrow e^{-\frac{\hbar \omega}{k_B T}}.$$

$$\text{Define } x = \frac{\hbar \omega}{k_B T}$$

$$E = \frac{V \hbar}{2\pi^2} \frac{3}{\bar{V}^3} \left(\frac{k_B T}{\hbar} \right)^4 \int_0^\infty \frac{x^3}{e^x - 1} dx$$

$$\int_0^\infty \frac{x^3}{e^x - 1} dx \text{ is just a number, } = \frac{\pi^4}{15}$$

$$E = \frac{\pi^2}{10} \frac{\hbar \omega}{\bar{V}^3} \left(\frac{k_B T}{\hbar} \right)^4$$

This is very similar to what we had for black body radiation, with the exception of degeneracy of 3 rather than 2. For BBR, let $\bar{V} \rightarrow c$.

So the heat capacity at lower temperature is:

$$C_v = \frac{dE}{dT} = \frac{2\pi^2}{5} k_B V \left(\frac{k_B}{\hbar V} \right)^3 T^3$$

8.6 The Debye Interpolation Scheme

The above approach, the low temperature approach, fails for two reasons:

- 1) As ω increases, k increases, λ decreases. Eventually will get to the point where $\lambda \sim a$ the inter-atomic distance. Then the modes are no longer simple sound waves.
- 2) Put upper limit on the ω integral to infinity – this is wrong as it suggests that the number of modes is infinite. The correct number is $3N$.
(NB: for BBR, the number of modes is infinite.)

Debye put an upper limit on the integral.

$$3N = \int_0^{\omega_D} \frac{3}{\bar{V}^3} \frac{V \omega^2}{2\pi^2} d\omega$$

where $\frac{3}{\bar{V}^3} \frac{V\omega^2}{2\pi^2} d\omega$ is the number of modes between ω and $\omega + d\omega$.

$$\frac{3}{\bar{V}^3} = \frac{2}{V_t^3} + \frac{1}{V_\ell^3}$$

$$3N = \frac{3}{V} \frac{V}{2} \frac{1}{2\pi^2} \frac{\omega_D}{3}$$

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

where ω_D is the Debye cutoff frequency.

At ω_D , $\lambda_D = \frac{2\pi}{k_D} = \frac{2\pi}{\omega_D} \bar{V}$, where $\omega_D = \bar{V}k_D$.

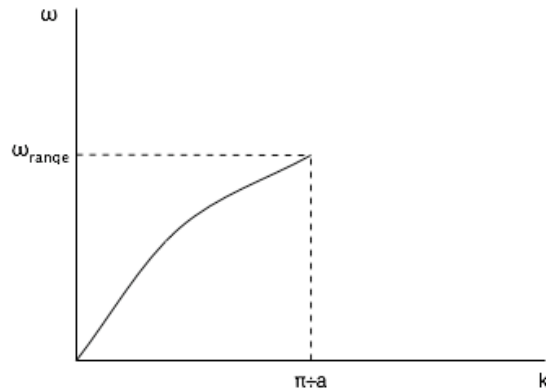
$$\lambda_D = \frac{2\pi}{(6\pi^2)^{1/3}} \left(\frac{V}{N} \right)^{1/3} = \left(\frac{4\pi}{3} \right)^{1/3} \left(\frac{V}{N} \right)^{1/3}$$

where $\frac{V}{N} \sim a^3$, where a is the interparticle spacing.

$\lambda_D \sim a$ (of the order of a) – the lattice spacing.

Therefore the cutoff wavelength $\lambda_D \sim$ interatomic spacing.

$\hbar\omega_D$ is of the order of the most energetic phonon energy.



$$E = \int_0^{\omega_D} \left(\frac{1}{e^{\hbar\omega\beta} - 1} + \frac{1}{2} \right) \hbar\omega \frac{3}{\bar{V}^3} \frac{V\omega^2}{2\pi^2} d\omega$$

Drop the ZPE as it is not temperature dependant and does not contribute to the specific heat.

$$E - ZPE = \frac{3V\hbar}{2\pi^2\bar{V}^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega\beta} - 1}$$

$$c_v = \frac{dE}{dT} = \frac{3V\hbar}{2\pi^2\bar{V}^3} \int_0^{\omega_D} \frac{\omega^2 e^{-\hbar\omega\beta}}{(e^{\hbar\omega\beta} - 1)^2} \frac{\hbar\omega}{k_B T^2}$$

Make the substitution $x = \hbar\omega\beta$. $dx = \hbar\beta d\omega$.

$$c_v = \frac{3V\hbar}{2\pi^2\bar{V}^3} \frac{\hbar\beta}{T} \left(\frac{1}{\hbar\beta} \right)^3 \int_0^{\hbar\omega_D\beta} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

The integral is just a number – it is a fraction of $\hbar\omega_D\beta$.

NB: as $T \rightarrow 0$ the upper limit can be approximated by infinity $\rightarrow$ then have a pure number $c_v \sim T^3$.

Define $\hbar\omega_D = k_B\Theta_D$, where Θ_D = Debye temperature.

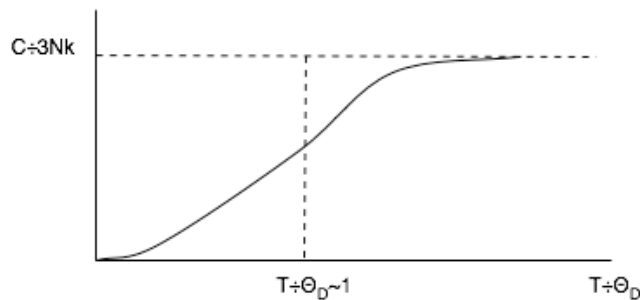
$$\hbar\omega_D\beta = \frac{\Theta_D}{T}.$$

$$\frac{3V}{2\pi^2\bar{V}^3} = \frac{N}{\omega_D^3}$$

$$c_v = 9Nk_B \left(\frac{1}{\hbar\omega_D\beta} \right)^3 f\left(\frac{T}{\Theta_D} \right)$$

$$\frac{c_v}{3Nk_B} = 3 \left(\frac{T}{\Theta_D} \right)^3 f\left(\frac{T}{\Theta_D} \right)$$

where $3Nk_B$ is the classical value. The RHS is a universal function of $\frac{T}{\Theta_D}$, and is the same for all materials.



T^3 at lower temperatures.

This agrees reasonably well with experiments for most solids.

Periodic Boundary Conditions

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi$$

a) Box Boundary Condition

$$\psi = 0 \text{ at } x = 0, x = L$$

$$\psi(x) = \sqrt{\frac{2}{L}} \sin kx \rightarrow \text{standing wave}$$

$$k = \frac{\pi n}{L} \quad n = 1, 2, 3, \dots$$

$$E = \frac{\hbar^2}{2m} \left(\frac{\pi n}{L} \right)^2$$

b) Periodic Boundary Conditions

$$\psi(x) = \psi(x + L)$$

$$\psi(x) = \frac{1}{\sqrt{L}} e^{ikx} \leftarrow \text{traveling waves.}$$

$$e^{ikL} = 1$$

$$k = \frac{2\pi n}{L}, \quad n = 0, \pm 1, \pm 2, \dots$$

K-Space

Box Boundary Condition:

0 missing. $\frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots$

Density of states $= \frac{L}{\pi}$.

Periodic boundary conditions:

Spacing is $\frac{2\pi}{L}$. Density of states is $\frac{L}{2\pi}$.

$\dots, -\frac{4\pi}{L}, -\frac{2\pi}{L}, 0, \frac{2\pi}{L}, \frac{4\pi}{L}, \frac{6\pi}{L}, \dots$

Periodic boundary conditions can be realized by bending the system into a ring of circumference L .

3D $\rightarrow$ periodic boundary conditions.

$$\psi(x+L) = \psi(x)$$

$$\psi(y+L) = \psi(y)$$

$$\psi(z+L) = \psi(z)$$

$$k_x = \frac{2\pi}{L} \ell, \quad k_y = \frac{2\pi}{L} m, \quad k_z = \frac{2\pi}{L} n.$$

$$\ell, m, n \rightarrow 0, \pm 1, \pm 2, \pm 3, \dots$$

Number of states between k and $k + dk$ = number of states in a shell of radius k and

thickness $dk = 4\pi k^2 dk \left(\frac{L}{2\pi} \right)^3 = \frac{V k^2}{2\pi^2} dk$. This is as for box boundary conditions.

$$\text{Box BC: } = \underbrace{\frac{1}{8} 4\pi k^2 dk}_{\text{positive octant}} \left(\frac{L}{\pi} \right)^3 = \frac{V k^2}{2\pi^2} dk$$