Solids

In this chapter we will study solids that can be described
in terms of simple cubic lattice crystals.
The side of cubic cell is denoted a

Dulong and Petit's Law from Equipartition Theorem

Consider a cubic lattice crystal. Interatomic spacing between
equilibrium positions of atoms is a.

Atoms oscillate around equilibrium position. The number
of degrees of freedom of the lattice is $3N$. The number
of internal degrees of freedom is $3N -$ (number of macroscopic motions)

The number of macroscopic motions are the sum of rigid translations,
rotations, compressions and dilations, which is 6.

So number of internal degrees of freedom is $3N-6$ but
since $3N \gg 6$, we say it is $M \sim 3N$

For example, for a simple "3-atom solid" ⬤m⬤m⬤ , the
solid has $3N-6 = 3\times3-6 = 3$ internal degrees of freedom. The
N value is the 3 coordinates the solid can move.
We can arrive at 3 internal d.o.f. conceptually be realising
the central atom can vibrate around its equilibrium position in
3 ways: 1 longitudinal and 2 transverse.

If we consider just the longitudinal vibration, the energy
to a first approximation is that of a harmonic
oscillator
$$E(p, x) = \frac{p^2}{2M} + \frac{K}{2}x^2 \quad \text{where } K \text{ is spring constant.}$$

what about for $N \gg 1$? A real macroscopic solid?

The hamiltonian becomes much more complicated:

$$E = H(p,q) = \sum_{i}^{3N} \frac{p_i^2}{2M} + \frac{1}{2} \sum_{i,j=1}^{3N} K_{ij} \, q_i \, q_j$$

using a classical mechanics variable transformation $(p,q) \rightarrow (P,Q)$:

$$Q_\alpha = \sum_i b_i^\alpha \sqrt{M} \, q_i \, ; \qquad P_\alpha = \frac{\partial H}{\partial \dot{Q}_\alpha}$$

$$E = \frac{1}{2} \sum_{\alpha=1}^{3N} (P_\alpha^2 + \omega_\alpha^2 Q_\alpha^2) \qquad \text{where} \quad \omega = \sqrt{\frac{K}{M}}$$

Each vibrational mode has a frequency ω. The number of vibrational modes is equal to the number of degrees of freedom. $3N-6 \approx 3N$ We consider each mode uncoupled and independent from others. Each vibrational mode contributes with 2 quadratic terms to energy (One kinetic and one potential energy term). So using Equipartition theorem, we can say:

$$U = \langle E \rangle = 6N \frac{k_B T}{2} = 3N k_B T$$

The heat capacity of the system is:

$$C_p \approx C_v = C = \left(\frac{\partial U}{\partial T} \right)_v = 3N k_B \left[= 3R \text{ for one mole} \right]$$

This is Dulong-Petit rule and seems to work for ~ 12 solids at room temperature and above, and for most solids at room temperature.

Einstein's Model

In the limit $T \to 0$, classically we expect C to remain constant but experimentally, we find it vanishes. This is actually expected from the 3rd Law of TD since if $S \to 0$, it can be shown $C \to 0$. But how do we fix the classical prediction?

Einstein attempted to do this by considering the $3N$ harmonic oscillators of the solid to be QHO with frequency ω_α
Each harmonic oscillator (labelled α) has:

$$E_{n_\alpha}(\omega_\alpha) = \hbar \omega_\alpha \left(\tfrac{1}{2} + n_\alpha \right)$$

Since all vibrational modes are uncoupled and independent:

$$U = \langle E \rangle = \sum_{\alpha=1}^{3N} \langle E_{n_\alpha}(\omega_\alpha) \rangle$$

remembering for one harmonic oscillator we found:

$$\langle E \rangle = \hbar \omega \left[\tfrac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1} \right] \quad \text{we can write:}$$

$$\langle E_{n_\alpha}(\omega_\alpha) \rangle = \hbar \omega_\alpha \left[\tfrac{1}{2} + \frac{1}{e^{\beta \hbar \omega_\alpha} - 1} \right]$$

Analogously for total heat capacity:

$$C = \left(\frac{\partial U}{\partial T} \right)_V = \sum_{\alpha=1}^{3N} C_\alpha(\omega_\alpha)$$

where C_α is heat capacity of single QHO given by:

$$C_\alpha(\omega_\alpha) = K_B (\beta \hbar \omega_\alpha)^2 \frac{e^{\beta \hbar \omega_\alpha}}{(e^{\beta \hbar \omega_\alpha} - 1)^2}$$

we showed previously $C_\alpha \to 0$ as $T \to 0$ irrespective of ω_α
so we can intuitively see $C \to 0$ as $T \to 0$

But now we wonder, what is the dependence of C on T?

To know this, we would have to know how many oscillators have a certain ω_α, for every value of ω_α.

Einstein made the assumption that all harmonic oscillators have same frequency ω_E, the einstein frequency.
With this assumption:

$$U = \langle E \rangle = \sum_{\alpha=1}^{3N} \langle E(\omega_E) \rangle = 3N \langle E(\omega_E) \rangle$$
$$= 3N \hbar \omega_E \left[\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega_E} - 1} \right]$$

and:

$$C = 3 N k_B (\beta \hbar \omega_E)^2 \frac{e^{\beta \hbar \omega_E}}{(e^{\beta \hbar \omega_E} - 1)^2}$$

if we introduce Einstein Temperature: $\Theta_E = \frac{\hbar \omega_E}{k_B}$
we can rewrite this:

$$C = 3 N k_B \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E / T}}{(e^{\Theta_E / T} - 1)^2} \qquad (*)$$

Which gives the same behaviour for $T \to 0$ as a single harmonic oscillator, but we replace ω with ω_E.

The disadvantages of Einstein's Approach are:

- It does not predict any particular value of ω_E, these must be found experimentally for each substance.

- Although $(*)$ gives $C \to 0$ as $T \to 0$, (check with l'hopital!), it does not give the dependence we see experimentally: $C \propto T^3$ as $T \to 0$

We will focus on this 2nd problem.

Debye Model

The Debye Model makes no assumption about the distribution of the frequencies. The distribution is taken to be that for em waves in the case of thermal radiation:

$$dW_k = 2V \frac{4\pi k^2 dk}{8\pi^3} = \frac{Vk^2 dk}{\pi^2}$$

But unlike for em waves, the number of polarisations for each mode is 3 instead of 2 (since em has 2 transverse polarisations but no longitudinal). So we need to multiply by $3/2$:

$$dW_k^{VM} = \frac{3Vk^2}{2\pi^2} dk = g_k dk \qquad \text{let's reexpress in terms of } \omega$$

$$dW_\omega^{VM} = g_\omega(\omega) d\omega = g_k(k) dk$$

$$\therefore \quad g_\omega(\omega) = \frac{3Vk^2}{2\pi^2} \left| \frac{dk}{d\omega} \right| = \frac{3V\omega^2}{2\pi^2 v_s^2} \left| \frac{dk}{d\omega} \right| \qquad \text{After some algebra:}$$

$$\Rightarrow \quad \frac{dk}{d\omega} = \frac{1}{v_s} \left(1 - \frac{\omega}{v_s} \frac{dv_s(\omega)}{d\omega} \right)$$

But we see a problem. In order to evaluate this, we need to know $\omega(k)$ for $v_s(\omega)$. We need to know dispersion relation. It is assumed that we have $v_s(\omega) = $ constant (which actually holds at low frequencies). So we have $\frac{dv_s(\omega)}{d\omega} = 0 \Rightarrow \frac{dk}{d\omega} = \frac{1}{v_s}$

so $\quad g_\omega(\omega) = \frac{3Vk^2}{2\pi^2 v_s^3}$

In contrast to thermal radiation, there will be a cut off at high frequency, because there are a finite number of modes $(3N)$. So we impose $\int_0^{\omega_D} g_\omega(\omega) d\omega = 3N$

Evaluating the integral, we get:

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

where ω_D is the Debye Frequency.

We also define debye temperature $\Theta_D = \frac{\hbar\omega_D}{K_B}$

$g_\omega(\omega)$ is the density in frequency of vibrational modes and can be recast:

$$\underline{g_\omega(\omega) = \frac{9N}{\omega_D^3}\omega^2}$$

which is valid for $\omega \leq \omega_D$ and $=0$ for $\omega > \omega_D$

$$U = \langle E \rangle = \int_0^{\omega_D} g(\omega)\langle \mathcal{E}(\omega)\rangle\, d\omega = \int_0^{\omega_D} g(\omega)\,\hbar\omega\left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right]d\omega$$

$$C = \int_0^{\omega_D} g(\omega) C(\omega)\, d\omega = \int_0^{\omega_D} g(\omega) K_B(\beta\hbar\omega)^2 \frac{e^{\hbar\omega\beta}}{(e^{\beta\hbar\omega}-1)^2}\, d\omega$$

If we focus on C, we can simplify it with $x = \beta\hbar\omega$

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

$$\therefore \quad C = \frac{9NK_B}{x_D^3}\int_0^{x_D}\frac{x^4 e^x}{(e^x-1)^2}\, dx$$

For $T\to 0$, $x_D \to \infty$ and we have $C \propto T^3$ as we require.
and $C\to 0$

For $T\to\infty$, $x_D \to 0$ and we have $C \to 3NK_B$ the classical limit (equipartition theorem)

If we consider the volume of a single cell in the lattice $a^3 = \frac{V}{N}$,

we can rewrite Debye Frequency:

$$\omega_D = \left(\frac{6\pi^2 v_s^3}{a^3}\right)^{1/3} \approx (6\pi^2)^{1/3}\left(\frac{v_s}{a}\right)$$

The maximum frequency ω_D corresponds to a minimum wavelength:

$$\lambda_{min} = \frac{2\pi v_s}{\omega_D} \approx \frac{2\pi}{(6\pi^2)^{1/3}} a \approx \underline{\underline{a}}$$