

Specific Heat of a Solid - Ionic Contribution Debye Model

Classical Law of Dulong & Petit

$6N$ harmonic degrees of freedom - $\begin{cases} 3N \text{ momenta} \\ 3N \text{ normal coords} \end{cases}$

$$C_V = (6N) \left(\frac{1}{2} k_B \right) = 3Nk_B \Rightarrow \frac{C_V}{V} = 3k_B m \quad m = \frac{N}{V}$$

In QM treatment, the $3N$ momenta + $3N$ normal coords can be thought of as $3N$ harmonic oscillators. These oscillations are the sound waves of vibration in the solid. We can approx their dispersion relation as

$$\omega = c_s |\vec{k}| \quad \vec{k} \text{ is wave vector}$$

3 polarizations: $S = \begin{cases} L \text{ longitudinal mode, } \text{ion displacement} \parallel \vec{k} \\ T_1, T_2 \text{ transverse modes, } \text{ion displacement} \perp \vec{k} \end{cases}$
at each \vec{k}

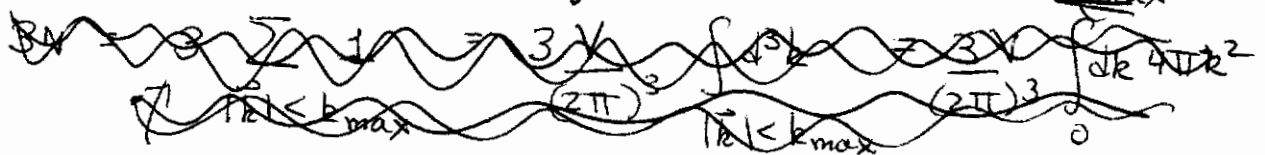
For a solid of volume V , the only sound modes are those that obey periodic boundary conditions

$$\mu = x, y, z \quad k_\mu L = 2\pi n_\mu \quad n_\mu = 0, 1, 2, \dots \text{ integer}$$

$$\vec{k} = \frac{2\pi}{L} \vec{m} \quad \text{ie } \frac{L}{\lambda} = n \text{ integer}$$

The total number of sound modes = total number of oscillators = $3N$. This sets an upper bound on $|\vec{k}|$

Let the maximum value of $|\vec{k}|$ be denoted k_D Debye wave number k_{max}



3 polarizations for each \vec{k}

For simplicity we will assume that all 3 polarizations have the same sound speed c_s

Since everything we want to compute depends on \vec{k} only via $|\vec{k}| = \omega/c_s$, it is convenient to define a phonon density of states $g(\omega)$ as follows.

$g(\omega)d\omega$ is the number of phonon modes with frequencies between ω and $\omega+d\omega$

$$\sum_s \sum_{\vec{k}} = 3 \sum_{\vec{k}} \approx 3 \frac{1}{(\Delta k)^3} \int d^3k = 3 \frac{V}{(2\pi)^3} \int dk k^2 4\pi$$

$$= \int d\omega g(\omega)$$

So

$$g(\omega)d\omega = \frac{3V}{(2\pi)^3} 4\pi k^2 dk = \frac{3V}{2\pi^2} \frac{\omega^2}{c_s^3} d\omega$$

$$\boxed{g(\omega) = \frac{3V}{2\pi^2} \frac{\omega^2}{c_s^3}} \leftarrow \text{phonon density of states}$$

Total number of modes is $3N$ so

$$3N = \int_0^{\omega_D} d\omega g(\omega)$$

where $\omega_D = c_s k_D$ is the "Debye frequency"

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

$$\omega_D = \left[6\pi^2 c_s^3 \frac{N}{V} \right]^{1/3} = \left[6\pi^2 c_s^3 M \right]^{1/3} \sim M^{1/3}$$

$M = N/V$ is density of atoms in the solid.

ω_D is frequency of most energetic phonons.

Now the average energy due to thermal excitation of phonons is

$$\begin{aligned}\langle E \rangle &= \sum_s \sum_{\vec{k}} \hbar \omega_s(\vec{k}) [\langle n_{s\vec{k}} \rangle + 1/2] \\ &= \int_0^{\omega_D} d\omega g(\omega) \hbar \omega \left[\frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right]\end{aligned}$$

Specific heat is

$$\begin{aligned}C_V &= \frac{\partial \langle E \rangle}{\partial T} = \int_0^{\omega_D} d\omega g(\omega) \hbar \omega \frac{\partial}{\partial T} \left[\frac{1}{e^{\beta \hbar \omega} - 1} \right] \\ &= \int_0^{\omega_D} d\omega g(\omega) \hbar \omega \frac{\left(\frac{\hbar \omega}{k_B T^2} \right) e^{\beta \hbar \omega}}{[e^{\beta \hbar \omega} - 1]^2} \\ &= \frac{3V}{2\pi^2 c_s^3} \int_0^{\omega_D} d\omega \omega^2 k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\beta \hbar \omega}}{[e^{\beta \hbar \omega} - 1]^2}\end{aligned}$$

$$\text{let } x \equiv \frac{\hbar \omega}{k_B T} = \beta \hbar \omega$$

$$C_V = \frac{3V k_B}{2\pi^2 c_s^3} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{[e^x - 1]^2}, \quad x_D = \beta \hbar \omega_D$$

Consider the prefactor of the integral

$$\begin{aligned}\frac{3V k_B}{2\pi^2} \left(\frac{k_B T}{c_s \hbar} \right)^3 &= \frac{3V k_B}{2\pi^2} \left(\frac{k_B T}{\hbar \omega_D} \right)^3 \frac{6\pi^2 m}{\cancel{\omega_D^3}} \\ &= 9V k_B m \left(\frac{k_B T}{\hbar \omega_D} \right)^3\end{aligned}$$

where we used $\omega_D = c_s [6\pi^2 m]^{1/3}$

Define $\Theta_D \equiv \hbar \omega_D / k_B$ the "Debye temperature"

→ specific heat per volume is

$$\frac{C_V}{V} = 9mk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} dx \frac{x^4 e^x}{[e^x - 1]^2}$$

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

Now we evaluate the integral in various limits

1) as $T \rightarrow \infty$, $\Theta_D/T = x_D$ gets very small
⇒ we can expand the integrand for small values of x

$$\frac{x^4 e^x}{[e^x - 1]^2} \approx \frac{x^4}{x^2} = x^2$$

$$\int_0^{x_D} dx x^2 \approx \frac{1}{3} x_D^3 = \frac{1}{3} \left(\frac{\Theta_D}{T}\right)^3$$

$$\text{So } \frac{C_V}{V} = 9mk_B \left(\frac{T}{\Theta_D}\right)^3 \cdot \frac{1}{3} \left(\frac{\Theta_D}{T}\right)^3$$

$$= 3mk_B$$

This is the classical Law of Dulong + Petit

So classical result remains correct provided
 $T \gg \Theta_D$ i.e. high temperature

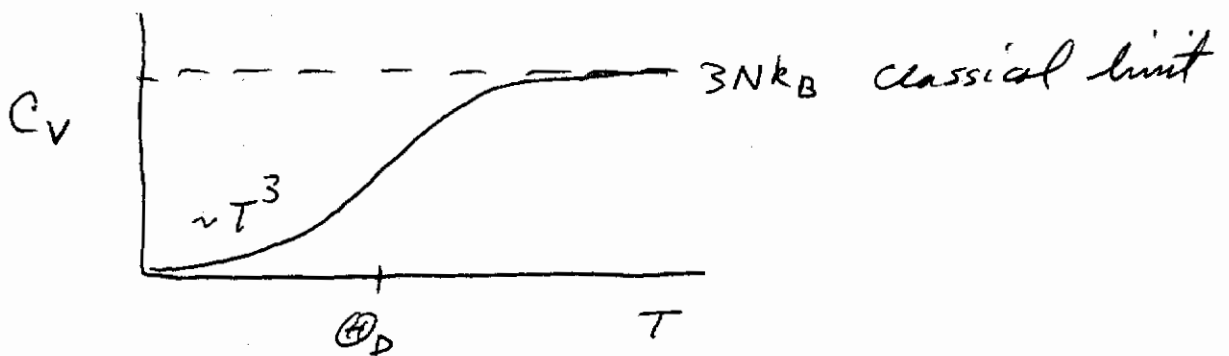
For low $T \neq 0$, $x_D \rightarrow \infty$

$$\frac{C_V}{V} \approx 9mk_B \left(\frac{T}{\Theta_D}\right)^3 \int_0^\infty dx \frac{x^4 e^{-x}}{(e^x - 1)^2}$$

This integral is just a pure number. $= \frac{4}{15} \pi^4$

$$\frac{C_V}{V} \approx \frac{12}{5} \pi^4 mk_B \left(\frac{T}{\Theta_D}\right)^3$$

$\propto T^3$ at low temperatures



For common solids, $\Theta_D \sim 100 - 300\text{K}$
so the effects of quantum mechanics on the specific heat of a solid can be seen at room temperature!

Originally, Einstein treated this problem quantum mechanically assuming that all phonon modes had the same T -independent frequency ω_0 . This is called the "Einstein-model" and it gives exponentially decreasing $e^{-\hbar\omega_0/k_B T}$ specific heat at low T .
The Debye model is more physically correct

Black Body Radiation

Cavity radiation - a volume V at fixed temp T absorbs + emits electromagnetic radiation. What are characteristics of this equilib radiation at fixed T ?

EM waves with wave vector \vec{k} , freq $\omega = c|\vec{k}|$
two transverse polarizations for each \vec{k} .

Regard each mode as an oscillator. If excited to energy level n , the energy in the oscillator is
 $E = n\hbar\omega = n\hbar ck \Rightarrow n$ "photons" in this mode
average energy in a given mode is therefore

$$\langle E \rangle = \hbar\omega \langle n \rangle = \frac{\hbar\omega}{e^{B\hbar\omega} - 1}$$

(Ignore ground state energy $\frac{1}{2}\hbar\omega$ as it is T -indep constant)

For a volume $V=L^3$, periodic boundary conditions give the allowed wave vectors $\vec{k} = \frac{2\pi}{L} \vec{m}$ m_x, m_y, m_z integers

Density of states $g(\omega)$ ↙ two polarizations for each \vec{k}

$$\int g(\omega) d\omega = 2 \sum_{\vec{k}} = \frac{2V}{(2\pi)^3} \int d^3k$$

$$\Rightarrow g(\omega) d\omega = \frac{2V}{(2\pi)^3} 4\pi k^2 dk = \frac{V}{\pi^2} \frac{\omega^2 d\omega}{c^3}$$

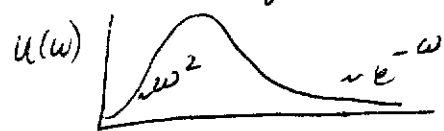
$$g(\omega) = \frac{V \omega^2}{\pi^2 c^3}$$

average energy per volume at freq ω is

$$u(\omega) = \frac{g(\omega)}{V} \left(\frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right) \begin{matrix} \leftarrow \# \text{ modes at freq } \omega \\ \leftarrow \text{ average energy in} \\ \text{ a given mode at freq } \omega \end{matrix}$$

$$u(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3 (e^{\beta \hbar \omega} - 1)}$$

← Black Body Spectrum
Planck's formula



Pathria
fig 7.7

Total energy density

$$\frac{U}{V} = \int_0^{\infty} u(\omega) d\omega = \frac{\hbar}{\pi^2 c^3} \int_0^{\infty} d\omega \frac{\omega^3}{e^{\beta \hbar \omega} - 1}$$

$$= \frac{\hbar}{\pi^2 c^3} \frac{1}{(\beta \hbar)^4} \underbrace{\int_0^{\infty} dx \frac{x^3}{e^x - 1}}_{\frac{\pi^4}{15}} \quad x = \beta \hbar \omega$$

$$\frac{U}{V} = \left(\frac{\pi^2 k_B^4}{15 \hbar^3 c^3} \right) T^4$$

energy flux from a cavity, exiting from a hole

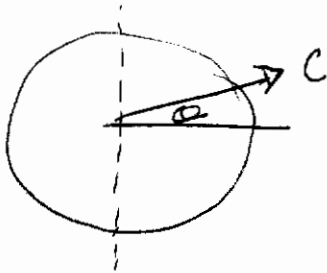


$$\text{flux } \mathcal{F} = \left(\frac{U}{V}\right) c \langle \cos \theta \rangle$$

↑
energy density

↑
speed

↑
projection of velocity
in outwards direction



$$\langle \cos \theta \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin \theta \cos \theta$$

← only in outward direction

$$= \frac{2\pi}{4\pi} \left(\frac{\sin^2 \theta}{2}\right) \Big|_0^{\pi/2} = \frac{1}{4}$$

$$\mathcal{F} = \left(\frac{U}{V}\right) \frac{c}{4} = \sigma T^4 \leftarrow \text{Stefan Boltzmann law}$$

$$\text{where } \sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} = 5.7 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \cdot \text{K}^4}$$

↑
Stefan's constant

We also have

$$\frac{pV}{k_B T} = \ln \mathcal{Z} = - \sum_{\mathbf{k}} 2 \ln (1 - e^{-\beta \epsilon_{\mathbf{k}}})$$

↖ polarizations

$$= - \frac{2V}{(2\pi)^3} \int d\mathbf{k} 4\pi k^2 \ln (1 - e^{-\beta \hbar c k})$$

$$= - \int_0^{\infty} d\omega g(\omega) \ln (1 - e^{-\beta \hbar \omega})$$

$$= - \frac{V}{\pi^2 c^3} \int_0^{\infty} d\omega \omega^2 \ln (1 - e^{-\beta \hbar \omega})$$

integrate by parts

$$\frac{PV}{k_B T} = -\frac{V}{\pi^2 c^3} \left[\frac{\omega^3}{3} \ln(1 - e^{-\beta \hbar \omega}) \right]_0^\infty + \frac{V}{\pi^2 c^3} \int d\omega \frac{\omega^3}{3} \frac{\beta \hbar e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

$$\frac{PV}{k_B T} = \frac{V \beta \hbar}{3 \pi^2 c^3} \int_0^\infty d\omega \left(\frac{\omega^3}{e^{\beta \hbar \omega} - 1} \right)$$

compare with computation of $\frac{U}{V}$

$$= \frac{\beta}{3} U = \frac{1}{3} \frac{U}{k_B T}$$

$$\Rightarrow \boxed{\frac{1}{3} U = PV}$$

pressure of photon gas

compare to non relativistic ideal gas

$$U = \frac{3}{2} N k_B T, \quad PV = N k_B T \Rightarrow \frac{2}{3} U = PV$$

The previous examples of phonons in a solid and Black Body radiation were problems involving bosons with excitation spectrum $E = \hbar\omega = \hbar c|k|$ (ie linear spectrum) and zero chemical potential $\mu = 0$.

non-interacting

→ Now we want to turn to the problem of an ideal quantum gas (bosons or fermions) of physical particles with an ~~excitation~~ an ordinary non-relativistic excitation spectrum

$$E = \frac{\hbar^2 k^2}{2m} \quad (\text{ie quadratic spectrum})$$

and $\mu \neq 0$.