Specific Heat of a Solid – Ionic Contribution Debye Model

Classical Law of Dulong & Petit

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

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

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

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

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

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

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

ie $\frac{L}{\lambda} = n$ integer

$$\vec{k} = \frac{2\pi}{L}\vec{m}$$

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 ~~k_{max}~~ "Debye wavenumber"

$$\cancel{3N = 3\sum_{|\vec{k}|<k_{max}} 1 = \frac{3V}{(2\pi)^3}\int_{|\vec{k}|<k_{max}} d^3k = \frac{3V}{(2\pi)^3}\int_0 dk\, 4\pi k^2}$$

~~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 $\omega + d\omega$

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

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

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"

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

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

$n = N/V$ 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

$$\langle E \rangle = \sum_s \sum_{\vec{k}} \hbar\omega_s(\vec{k}) \left[\langle n_{sk} \rangle + 1/2 \right]$$

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

Specific heat is

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \int_0^{\omega_D} d\omega\, g(\omega)\, \hbar\omega\, \frac{\partial}{\partial T}\left[\frac{1}{e^{\beta\hbar\omega}-1} \right]$$

$$= \int_0^{\omega_D} d\omega\, g(\omega)\, \hbar\omega\, \frac{\left(\frac{\hbar\omega}{k_B T^2}\right) e^{\beta\hbar\omega}}{\left[e^{\beta\hbar\omega}-1\right]^2}$$

$$= \frac{3V}{2\pi^2 c_s^3} \int_0^{\omega_D} d\omega\, \omega^2\, k_B \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\beta\hbar\omega}}{\left[e^{\beta\hbar\omega}-1\right]^2}$$

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

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

Consider the prefactor of the integral

$$\frac{3V k_B}{2\pi^2} \left(\frac{k_B T}{c_s \hbar}\right)^3 = \frac{3V k_B}{2\pi^2} \left(\frac{k_B T}{\hbar\omega_D}\right)^3 \frac{6\pi^2 n}{}$$

$$= 9 V k_B n \left(\frac{T}{\hbar\omega_D}\right)^3$$ where we used $\omega_D = c_s [6\pi^2 n]^{1/3}$

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

$\Rightarrow$ specific heat per volume is

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

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

Now we evaluate the integral in various limits

1) as $T \to \infty$, $\Theta_D / T = x_D$ gets very <u>small</u>

$\Rightarrow$ we can expand the integrand for small values of x

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

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

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

$$= 3 n k_B$$ This is the classical Law of Dulong + Petite

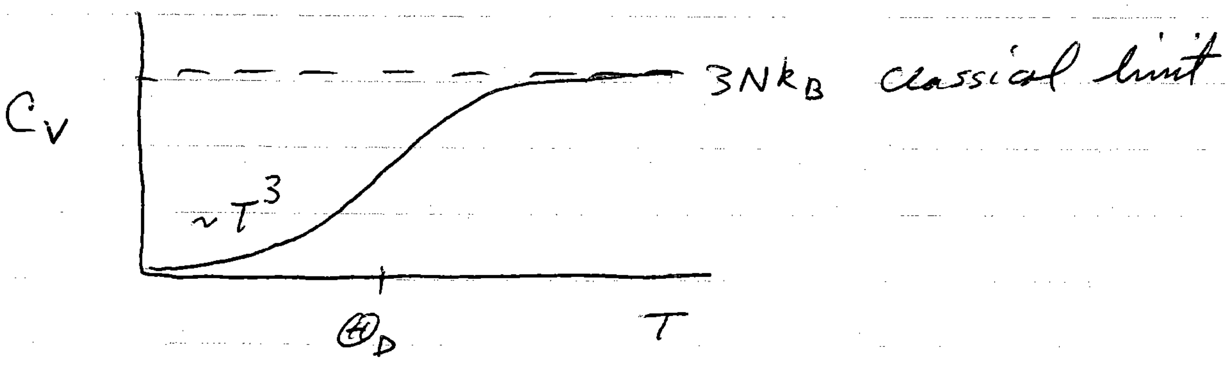
So classical result remains correct provided $T \gg \Theta_D$ ie high temperature

For low $T \to 0$, $x_D \to \infty$

$$\frac{C_V}{V} \simeq 9 n k_B \left(\frac{T}{\Theta_D}\right)^3 \underbrace{\int_0^\infty dx \, \frac{x^4 e^x}{(e^x - 1)^2}}_{\text{this integral is just a pure number.} \; = \frac{4}{15}\pi^4}$$

$$\frac{C_V}{V} \simeq \frac{12}{5}\pi^4 n k_B \left(\frac{T}{\Theta_D}\right)^3$$

$\propto T^3$ at low temperatures



For common solids, $\Theta_D \sim 100 - 300\,K$
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 $\vec{k}$-independent frequency ω_0. This is called the "Einstein model" and it gives exponentially decreasing $e^{-\hbar\omega_0/k_BT}$ 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
$$\epsilon = n\hbar\omega = n\hbar ck \Rightarrow n \text{ "photons" in this mode}$$
average energy in a given mode is therefore
$$\langle \epsilon \rangle = \hbar\omega \langle n \rangle = \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

(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 $\vec{k} = \frac{2\pi}{L}\vec{m}$ $\quad m_x, m_y, m_z$ integers

Density of states $g(\omega)$

two polarizations for each $\vec{k}$

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

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

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

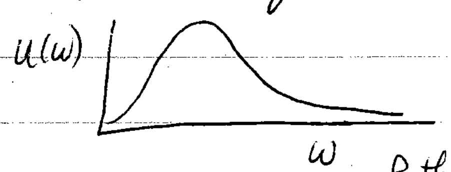
average energy per volume at freq ω is

modes at freq ω

average energy in a given mode at freq ω

$$u(\omega) = \frac{g(\omega)}{V}\left(\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right)$$

$$u(\omega) = \frac{\hbar\,\omega^3}{\pi^2 c^3 (e^{\beta\hbar\omega}-1)}$$ ← Black Body Spectrum Plancks formula



Pathria fig 7.7

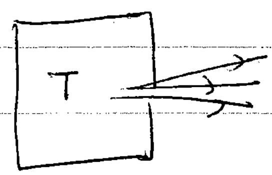
<u>Total energy density</u>

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

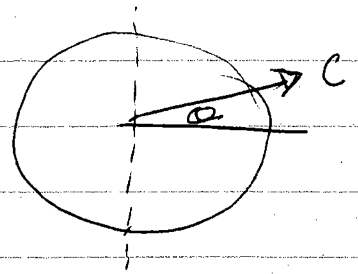
$$= \frac{\hbar}{\pi^2 c^3}\frac{1}{(\beta\hbar)^4}\underbrace{\int_0^\infty dx\,\frac{x^3}{e^x-1}}_{\frac{\pi^4}{15}} \qquad x = \beta\hbar\omega$$

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

- energy flux from a cavity, exiting from a hole



$$\text{flux } \mathcal{F} = \underbrace{\left(\frac{U}{V}\right)}_{\text{energy density}} \underbrace{c}_{\text{speed}} \underbrace{\langle \cos\theta \rangle}_{\text{projection of velocity in outwards direction}}$$



$\pi/2$ ← only in outward direction

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

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

- $$\mathcal{F} = \left(\frac{U}{V}\right)\frac{c}{4} = \sigma T^4 \quad \leftarrow \text{Stefan Boltzman Law}$$

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

↑ Stefan's constant

We also have

$$\frac{pV}{k_B T} = \ln \mathcal{L} = -\sum_k \underbrace{2}_{\text{polarizations}} \ln\left(1 - e^{-\beta\epsilon_k}\right)$$

$$= -\frac{2V}{(2\pi)^3} \int dk\, 4\pi k^2 \ln\left(1 - e^{-\beta\hbar c k}\right)$$

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

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

integrate by parts

$$\frac{pV}{k_BT} = \frac{-V}{\pi^2c^3}\underbrace{\left[\frac{\omega^3}{3}\ln\left(1-e^{-\beta\hbar\omega}\right)\right]_0^\infty}_{=\,0} + \frac{V}{\pi^2c^3}\int d\omega\,\frac{\omega^3}{3}\,\frac{\beta\hbar e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

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

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

$$= \frac{\beta}{3}U = \frac{1}{3}\frac{U}{k_BT}.$$

$$\Rightarrow \boxed{\frac{1}{3}U = PV}$$ pressure of photon gas

compare to non relativistic ideal gas

$U = \frac{3}{2}Nk_BT$, $PV = Nk_BT \Rightarrow \frac{2}{3}U = PV$