Specific Heat of a Solid - Ionic Contribution

Debye Model

Classical law of Dulong and Petit

\[ C_V = (6N)(\frac{1}{2}k_B) = 3Nk_B \quad \Rightarrow \quad C_V = \frac{3k_B}{V} \]

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

\[ \omega = c_s |k| \quad k \text{ is wave vector} \]

3 polarizations: \( S = \{ L \text{ longitudinal mode, ion displacement } k \}

\( T_1, T_2 \text{ transverse modes, ion displacement } \perp k \}

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

\[ \mu = x, y, z \quad k_\mu \cdot L = 2\pi \nu \mu \quad \nu \mu = 0, 1, 2, \ldots \text{ integer} \]

\[ k = \frac{2\pi}{L} \quad \text{integer} \]

The total number of sound modes = total number of oscillators = 3N. This sets an upper bound on 1|k|

Let the maximum value of 1|k| be denoted \( k_\text{D} \). Debye wave number.
For simplicity we will assume that all 3 polarizations have the same sound speed $c_s$

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

$$\sum_{s} \sum_{k} = \frac{3}{8} \sum_{k} \alpha_{s} \frac{1}{(2\pi k)^3} \int d^3k = \frac{3}{2\pi^3} \int dw \frac{e^{2\pi}}{4\pi}$$

$$= \int dw \ g(w)$$

So,

$$g(w)dw = \frac{3V}{(2\pi)^3} \frac{4\pi k^2}{2\pi^2 \frac{c_s^3}{C}} dw$$

$$g(w) = \frac{3V}{2\pi^2 \frac{c_s^3}{C}} \triangleq \text{phonon density of states}$$

Total number of modes is $3N$ so

$$3N = \int dw \ g(w) \quad \text{where } w_D = c_s k_D \text{ is the } \text{"Debye frequency"}$$

$$3N = \frac{3V}{2\pi^2 \frac{c_s^3}{C}} \int dw \ w^2 = \frac{V}{2\pi^2 \frac{c_s^3}{C}} \ w_D^3$$

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

$M = N/v$ is density of atoms in the solid.
$w_d$ is the frequency of most energetic phonons. Now the average energy due to thermal excitation of phonons is:

$$\langle E \rangle = \sum_s \sum_k \hbar \omega_k \langle n_k \rangle \left[ \langle n_{\text{sh}} \rangle + \frac{1}{2} \right]$$

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

Specific heat is:

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \int_0^{w_d} \omega g(\omega) \hbar \omega \frac{2}{e^{\beta \hbar \omega} - 1}$$

$$= \int_0^{w_d} \omega g(\omega) \hbar \omega \frac{(\hbar \omega/k_B)^2 e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

$$= \frac{3V}{2\pi^2 c_s^3} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{w_d} \omega \hbar \omega^2 \frac{(k_B T)^2}{(k_B T)^3} e^{\beta \hbar \omega}$$

Let $x = \frac{\hbar \omega}{k_B T}$

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

Consider the prefactor of the integral:

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

$$= 9V k_B m \left( \frac{k_B T}{\hbar \omega_d} \right)^3$$

where we used $\omega_d = c_s \left[ 6\pi^2 m \right]^{1/3}$
Define $\Theta_D = \frac{\hbar \omega_D}{k_B}$ the "Debye temperature".

The specific heat per volume is

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

where $x_D = \frac{\Theta_D}{T}$.

Now we evaluate the integral in various limits.

1) As $T \to \infty$, $\Theta_D/T = x_D$ gets very small.

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

$$\frac{x^4 e^x}{\left(e^x - 1\right)^2} \approx \frac{x^4}{x^2} = x^2$$

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

So

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

$$= 3 m k_B$$

This is the classical law of Dulong and Petit.

So classical result remains correct provided $T \gg \Theta_D$, i.e., high temperature.
For low $T \to 0$, $\Theta_D \to \infty$

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

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

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

$\propto T^3$ at low temperatures

For common solids, $\Theta_D \approx 100 - 300 K$

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 $T$-independent frequency $\omega_0$. This is called the "Einstein model" and it gives exponentially decreasing $e^{-\omega_0/\hbar \gamma T}$ 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 equilibrium radiation at fixed $T$?

EM waves with wave vector $\mathbf{k}$, freq $\omega = c |\mathbf{k}|$

two transverse polarizations for each $\mathbf{k}$.

Regard each mode as an oscillator. If excited to energy level $n$, the energy in the oscillator is

$E = n \hbar \omega = n \hbar c |\mathbf{k}| \Rightarrow n$ "photons" in this mode

Average energy in a given mode is therefore

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

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

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

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

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

average energy per volume at freq. \( \omega \)

\[ u(\omega) = \frac{g(\omega)}{V} \left( \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right) \text{ average energy in modes at freq. } \omega \]

\[ u(\omega) = \frac{\hbar \omega^3}{\pi^2 c^3 (e^{\beta \hbar \omega} - 1)} \quad \text{Black Body Spectrum Planck's formula} \]

Total energy density

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

\[ = \frac{\hbar}{\pi^2 c^3 (\beta \hbar)^4} \int_0^\infty dx \frac{x^3}{e^x - 1} \]

\[ x = \beta \hbar \omega \]

\[ U = \left( \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} \right) T^4 \]
Energy flux from a cavity, exiting from a hole

\[ \text{flux } \mathcal{F} = \left( \frac{U}{V} \right) C \langle \cos \theta \rangle \]

\[ \langle \cos \theta \rangle = \frac{1}{4\pi} \int_0^{2\pi} \int_0^\pi \sin \theta \cos \theta \, d\theta \, d\phi \]

\[ = \frac{2\pi}{4\pi} \left( \frac{\sin^2 \theta}{2} \right) \tfrac{\pi}{2} = \frac{1}{4} \]

\[ \mathcal{F} = \left( \frac{U}{V} \right) C = \sigma T^4 \quad \text{-- Stefan–Boltzmann law} \]

Where \( \sigma = \frac{\pi^2 k_B^4}{60 \, h^3 c^2} \approx 5.7 \times 10^{-8} \frac{W}{m^2 \cdot \text{K}^4} \)

Stefan's constant

We also have

\[ \frac{\mathcal{P}}{k_B T} = \ln \frac{\xi}{\lambda} = -\sum_k 2 \ln (1 - e^{-\beta \xi_k}) \]

\[ = -2 \frac{V}{(2\pi)^3} \int dk \, 4\pi k^2 \ln (1 - e^{-\beta \xi k}) \]

\[ = -\int_0^\infty dw \, g(w) \ln (1 - e^{-\beta \eta w}) \]

\[ = -\frac{V}{\pi^2 c^3} \int_0^\infty dw \, w^2 \ln (1 - e^{-\beta \eta w}) \]
Integrate by parts

\[
\frac{P}{k_B T} = -\frac{V}{\pi^2 c^3} \left[ \frac{\omega^3}{3} \ln(1-e^{-\beta \hbar \omega}) \right]_0^\infty + \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \frac{\omega^3}{3} \frac{\beta \hbar e^{-\beta \hbar \omega}}{1-e^{-\beta \hbar \omega}}
\]

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

Compare with computation of \( \frac{U}{V} \)

\[
= \frac{\beta}{3} U = \frac{1}{3} \frac{U}{k_B T}
\]

\[\Rightarrow \frac{1}{3} U = PV\]

Pressure of photon gas

Compare to non-relativistic ideal gas

\[U = \frac{2}{3} N k_B T, \quad PV = N k_B T \Rightarrow \frac{2}{3} U = PV\]
The previous examples of phonons in a solid and Black Body radiation were problems involving bosons with excitation spectrum
\[ E = \hbar \omega = \frac{\hbar c k}{c} \] (i.e. linear spectrum)
and zero chemical potential \( \mu = 0 \).

Now we want to turn to the problem of an ideal quantum gas (bosons or fermions) of physical particles with an excitation spectrum
\[ E = \frac{\hbar^2 k^2}{2m} \] (i.e. quadratic spectrum)
and \( \mu \neq 0 \).