Specific Heat of Insulating Solids

Heat capacity is given by -

$$C = 3k_B \quad \text{per atom}$$

$$C = 3R \quad \text{per mole}$$

Material	C/R
Aluminum	2.91
Antimony	3.03
Copper	2.94
Gold	3.05
Silver	2.99
Diamond	0.735

This law holds fairly well at room temperature for many materials (exception being Diamond)

At low temperature this law deviates from the experimental behavior for all materials

Einstein's Treatment of Specific Heat

He started wondering why Dulong-Petit law does not hold at low temperatures (For Diamond RT seems to be low temperature)

Quantum mechanical treatment of vibrations was essential

Each atom in the solid is bound to neighboring atoms. Each atom is in a harmonic potential well formed by interaction with its neighbors.

Einstein further assumed that every atom is in an identical harmonic well and has an oscillation frequency ω [Einstein freq.]

The problem then reduces to quantum mechanical problem of a simple harmonic oscillator which is well known

We will treat here for one-dimensional harmonic oscillator

Einstein's Treatment of Specific Heat

In one dimension, the eigenstates of a simple harmonic oscillator -

$$E_n = \hbar\omega(n + 1/2)$$

The partition function is then -

$$Z_{1D} = \sum_{n \geqslant 0} e^{-\beta\hbar\omega(n+1/2)} \qquad [\text{Here } \beta = \frac{1}{k_B T}]$$

$$= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2\sinh(\beta\hbar\omega/2)}$$

The expectation energy is -

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

Einstein's Treatment of Specific Heat

So the expectation energy is -

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right) = \hbar\omega\left(n_B(\beta\hbar\omega) + \frac{1}{2}\right)$$

Here n_B is the Bose occupation number -

$$n_B(x) = \frac{1}{e^x - 1}$$

Interpretation – The mode ω is an excitation that is excited on average n_B times

Differentiating the above energy expression w.r.t T, we get the heat capacity for a single oscillator

Einstein's Treatment of Specific Heat

So the heat capacity is -

$$C = \frac{\partial \langle E \rangle}{\partial T} = k_B (\beta \hbar \omega)^2 \frac{e^{\beta \hbar \omega}}{(e^{\beta \hbar \omega} - 1)^2}$$

The high temperature limit $k_B T \gg \hbar \omega$ of the above expression is

$$C = k_B$$

Generalizing to three dimensional case -

$$E_{n_x, n_y, n_z} = \hbar \omega [(n_x + 1/2) + (n_y + 1/2) + (n_z + 1/2)]$$

And -

$$Z_{3D} = \sum_{n_x, n_y, n_z \geqslant 0} e^{-\beta E_{n_x, n_y, n_z}} = [Z_{1D}]^3$$

Einstein's Treatment of Specific Heat

Again since -

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

We get -

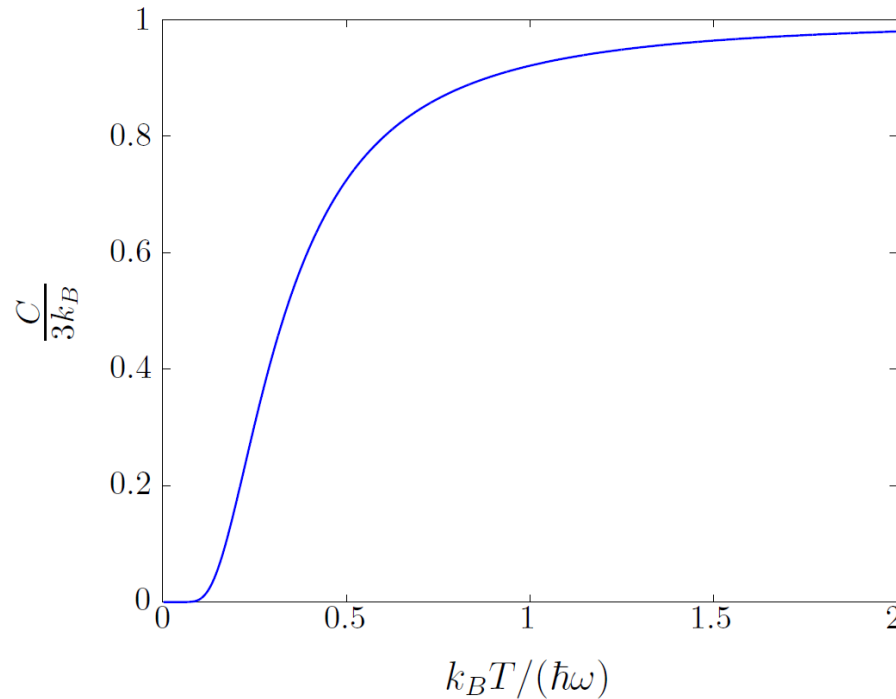$$\langle E_{3D} \rangle = 3\langle E_{1D} \rangle$$

And -

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

Thus, the high temperature limit $k_B T \gg \hbar\omega$ for specific heat in the three-dimensional case is - $C = 3k_B$

which is in agreement with Dulong – Petit law of specific heat
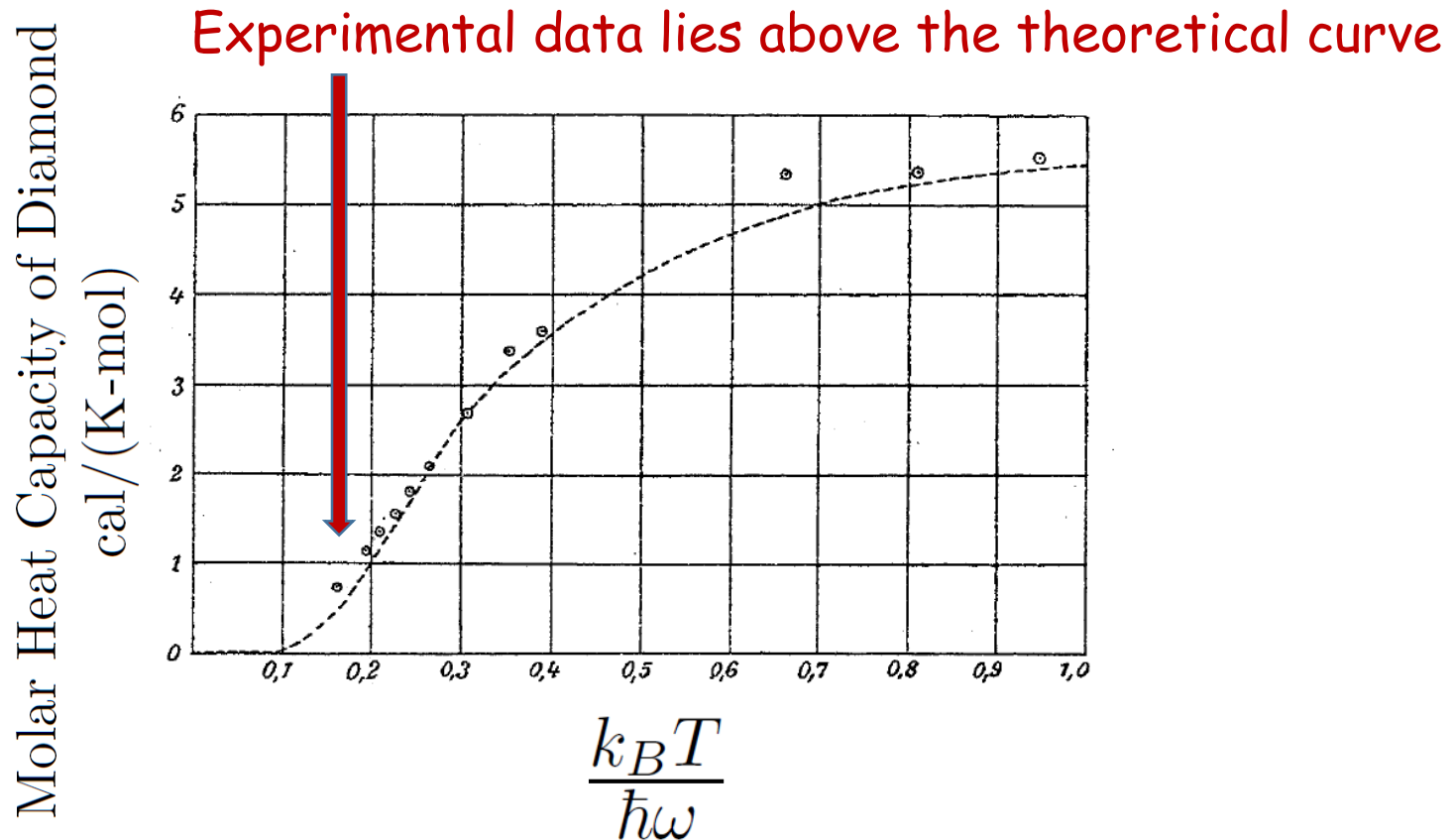
Einstein's Treatment of Specific Heat

The plot of

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

At low temperature, the degrees of freedom "freeze out" and the system remains in the ground-state eigenstate, and the heat capacity vanishes rapidly

Einstein's Treatment of Specific Heat

Comparison to experimental data of specific heat -

Experimental data lies above the theoretical curve

w is used as a fitting parameter in Einstein's theory

Einstein's Treatment of Specific Heat

Einstein *frequency w,* for most materials, is low compared to room temperature

However, for diamond, *w* is high compared to room temperature, so the heat capacity is lower than 3R at room temperature

In diamond bonding between atoms is very strong and atomic mass is relatively low and since oscillation frequency depends on spring constant and *m* as –

$$\omega = \sqrt{\kappa/m}$$

As a result Einstein frequency is very high for diamond. This is also a reason why diamond is an exceptionally hard material

Debye's treatment of specific heat

Debye's Treatment of Specific Heat

The deviation seen in the experimental data at low temperatures from Einstein's theoretical curve is actually important

Most materials at low temperatures have a heat capacity proportional to T^3 (Metals have an additional contribution αT)

Einstein's theory at low temperature is exponentially small in T

Peter Debye could explain the T^3 dependence of specific heat at low temperatures

He realized that oscillation of atoms is the same thing as sound, and since it is a wave as light, it should be quantized

For sound there are three modes for each k, a longitudinal mode where atomic motion is in the same direction of k and two transverse modes where the motion is perpendicular to k. We will take the sound velocity to be same for these modes

Debye's Treatment of Specific Heat

The oscillation modes were considered as waves with frequencies

$$\omega(\mathbf{k}) = v|\mathbf{k}|$$

Here v is the sound velocity and for each k there are three modes

So the expectation of energy is -

$$\langle E \rangle = 3 \sum_{\mathbf{k}} \hbar\omega(\mathbf{k}) \left(n_B(\beta\hbar\omega(\mathbf{k})) + \frac{1}{2} \right)$$

Invoking the Born-Von-Karmen boundary conditions -

$$\langle E \rangle = 3 \frac{L^3}{(2\pi)^3} \int \mathbf{dk}\, \hbar\omega(\mathbf{k}) \left(n_B(\beta\hbar\omega(\mathbf{k})) + \frac{1}{2} \right)$$

L^3 is the volume of the solid

Debye's Treatment of Specific Heat

Using $\int \mathbf{dk} \to 4\pi \int_0^\infty k^2 dk$ and $k = \omega/v$ we get

$$\langle E \rangle = 3\frac{4\pi L^3}{(2\pi)^3} \int_0^\infty \omega^2 d\omega (1/v^3)(\hbar\omega)\left(n_B(\beta\hbar\omega) + \frac{1}{2}\right)$$

Again using $nL^3 = N$ and the concept of density of states

$$\langle E \rangle = \int_0^\infty d\omega\, g(\omega)(\hbar\omega)\left(n_B(\beta\hbar\omega) + \frac{1}{2}\right)$$

The density of states here is given by -

$$g(\omega) = N\left[\frac{12\pi\omega^2}{(2\pi)^3 nv^3}\right] = N\frac{9\omega^2}{\omega_d^3} \quad \text{where} \quad \omega_d^3 = 6\pi^2 nv^3$$

ω_d is known as the Debye frequency

Debye's Treatment of Specific Heat

$g(\omega)d\omega$ corresponds to total number of oscillation modes between frequencies ω and $\omega + d\omega$

We thus have

$$\langle E \rangle = \frac{9N\hbar}{\omega_d^3} \int_0^\infty d\omega \ \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \quad + \text{T independent const.}$$

By defining $x = \beta\hbar\omega$, we have

$$\langle E \rangle = \frac{9N\hbar}{\omega_d^3(\beta\hbar)^4} \int_0^\infty dx \ \frac{x^3}{e^x - 1} \quad + \text{T independent const.}$$

Debye's Treatment of Specific Heat

Invoking integration formula using Riemann Zeta function -

$$\langle E \rangle = 9N \frac{(k_B T)^4}{(\hbar \omega_d)^3} \frac{\pi^4}{15} \quad + \text{T independent const.}$$

So the heat capacity becomes -

$$C = \frac{\partial \langle E \rangle}{\partial T} = N k_B \frac{(k_B T)^3}{(\hbar \omega_d)^3} \frac{12 \pi^4}{5} \sim T^3$$

Sometimes the Debye frequency is replaced by Debye temperature

$$\hbar \omega_d = k_B T_{Debye}$$

$$C = \frac{\partial \langle E \rangle}{\partial T} = N k_B \frac{(T)^3}{(T_{Debye})^3} \frac{12 \pi^4}{5}$$

Debye's Interpolation

$$C = \frac{\partial \langle E \rangle}{\partial T} = N k_B \frac{(T)^3}{(T_{Debye})^3} \frac{12\pi^4}{5}$$

The formula predicts T^3 dependence of specific heat upto arbitrarily high temperature !

The heat capacity should level off to $3 K_B N$ at high temperature

The problem lies in the assumption that there are infinite number of sound wave modes upto arbitrarily large k

There should be only as many modes as degrees of freedom in the system

For N particles total number of modes should be $3N$

Necessity to define a cutoff freq. - $3N = \int_0^{\omega_{cutoff}} d\omega \, g(\omega)$

Debye's Interpolation

Thus, the energy dropping the zero-point contribution -

$$\langle E \rangle = \int_0^{\omega_{cutoff}} d\omega \, g(\omega) \, \hbar\omega \, n_B(\beta\hbar\omega)$$

The low temperature property will not change since the Bose factor will very rapidly approach zero for frequencies well below the cut-off frequency

For high temperature we note -

$$n_B(\beta\hbar\omega) = \frac{1}{e^{\beta\hbar\omega} - 1} \rightarrow \frac{k_B T}{\hbar\omega}$$

Using this we can write for high temperatures -

$$\langle E \rangle = k_B T \int_0^{\omega_{cutoff}} d\omega g(\omega) = 3k_B T N$$

Debye's Interpolation

Thus, the specific heat at high temperatures become -

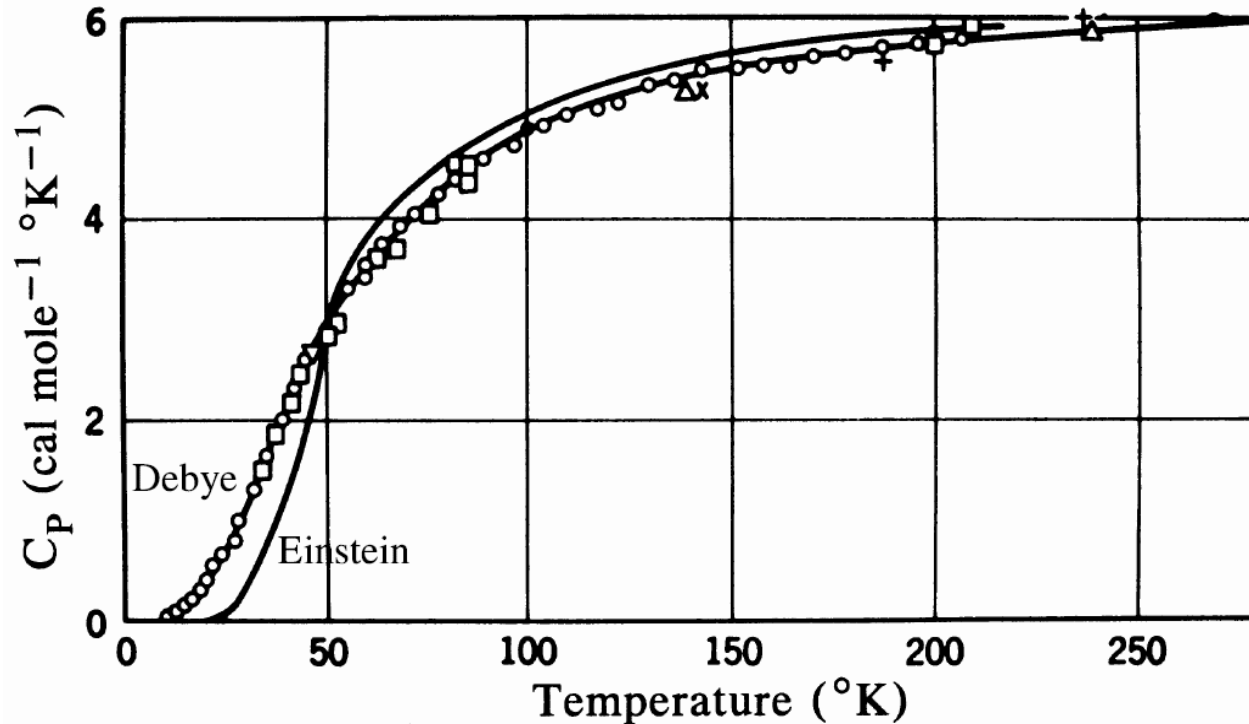$$C = \partial\langle E\rangle/\partial T = 3k_B N = 3k_B \text{ per atom}$$

Evaluating the cut-off frequency -

$$3N = \int_0^{\omega_{cutoff}} d\omega\, g(\omega) = 9N \int_0^{\omega_{cutoff}} d\omega \frac{\omega^2}{\omega_d^3} = 3N\frac{\omega_{cutoff}^3}{\omega_d^3}$$

which gives $\qquad \omega_{cutoff} = \omega_d$

Also $k = \omega_d/v = (6\pi^2 n)^{1/3}$ is of the order of inverse atomic

spacing in the solid

Comparison of the two results

The introduction of the cut-off frequency in Debye theory seems ad-hoc

The linearity of the dispersion $\omega = vk$ for arbitrarily high k also needs attention