Harmonic Oscillator vs boson

Recall our earlier result for the quantized harmonic oscillator

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

We found:

$$\text{average level of excitation} \longrightarrow \langle n\rangle = \frac{\sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})}\, n}{\sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})}} = \frac{\sum_n e^{-\beta\hbar\omega n}\, n}{\sum_n e^{-\beta\hbar\omega n}}$$

$$= \frac{-\frac{1}{\hbar\omega}\frac{\partial}{\partial\beta}\left(\sum_n e^{-\beta\hbar\omega n}\right)}{\sum_n e^{-\beta\hbar\omega}} = -\frac{1}{\hbar\omega}\frac{\partial}{\partial\beta}\ln\left[\frac{1}{1-e^{-\beta\hbar\omega}}\right]$$

$$= \frac{1}{\hbar\omega}\frac{\partial}{\partial\beta}\ln\left(1-e^{-\beta\hbar\omega}\right) = \frac{1}{\hbar\omega}\,\frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

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

Compare to occupation number of a boson of energy ϵ

$$\langle n\rangle = \frac{1}{e^{\beta(\epsilon-\mu)}-1}$$

We see that average level excitation of the harmonic oscillator has exactly the same form as the average ~~number~~ number of bosons with energy $\epsilon = \hbar\omega$, if the boson chemical potential is taken to be $\mu=0$.

$\Rightarrow$ quantized harmonic oscillators obey same statistics as bosons, with $\mu = 0$

we say that excitation level n of the oscillator is the same as n quanta or n "particles" of excitation.

Applies to: elastic oscillations of a solid $\leftrightarrow$ "phonons"
oscillation of electromagnetic waves $\leftrightarrow$ "photons"

<u>Sound modes in solid</u>

$\omega = c_s|\vec{k}|$ c_s = speed of sound, $\vec{k}$ = wave vector

$$\Rightarrow \text{phonon modes } \langle n_k \rangle = \frac{1}{e^{\beta\hbar c_s k} - 1}$$

<u>electromagnetic waves</u>

$\omega = c|\vec{k}|$, c = speed of light, $\vec{k}$ = wave vector

$$\text{photon modes } \langle n_k \rangle = \frac{1}{e^{\beta\hbar c k} - 1}$$

Another way to see $\mu = 0$. Phonons and photons are not conserved particles - they can be created and destroyed

$e + \gamma \to e$ electron scattered by absorbing a photon

chemical equilib $\Rightarrow \mu_e + \mu_\gamma = \mu_e \rightarrow \mu_\gamma = 0$ chemical pot of photon

Specific Heat of a Solid – Ionic Contribution Debye Model

Classical Law of Dulong & Petit

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

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

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

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

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

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 wavenumber" ~~k_{max}~~

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

~~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 <u>phonon density of states</u> $g(\omega)$ 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

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

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

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

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

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

Consider the prefactor of the integral

$$\frac{3Vk_B}{2\pi^2}\left(\frac{k_BT}{c_s\hbar}\right)^3 = \frac{3Vk_B}{2\pi^2}\left(\frac{k_BT}{\hbar\omega_D}\right)^3 \frac{6\pi^2 n}{\text{[illegible]}}$$

$$= 9Vk_B n\left(\frac{k_BT}{\hbar\omega_D}\right)^3$$

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

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

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

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

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

$$= 3 n k_B$$

This is the classical Law of Dulong + Petite

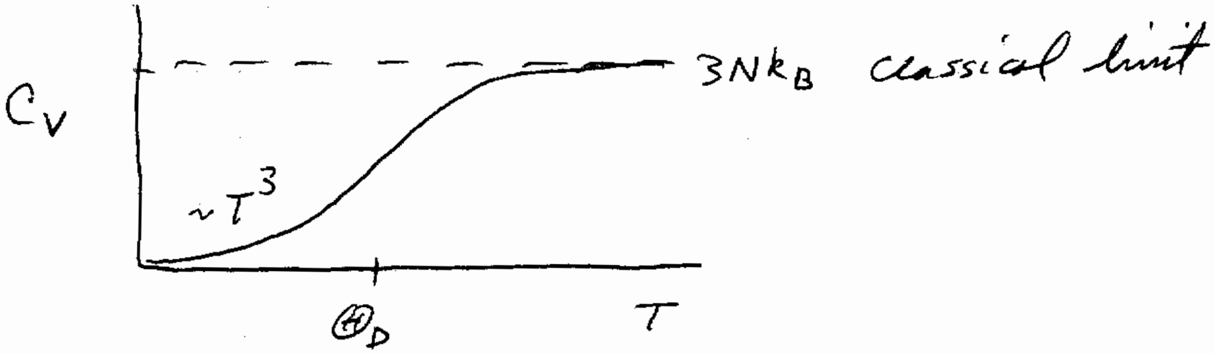
So classical result remains correct provided $T \gg \Theta_D$ ie high temperature

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 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

$$\epsilon = n\hbar\omega = n\hbar c k \quad \Rightarrow \quad n \text{ "photons" in this mode}$$

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 $\vec{k}$

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

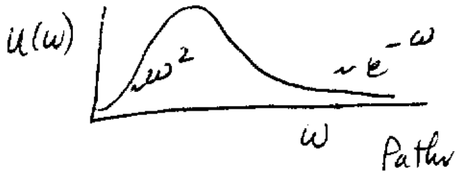
$$\Rightarrow \quad g(\omega)\,d\omega = \frac{2V}{(2\pi)^3}4\pi k^2 dk = \frac{V}{\pi^2}\frac{\omega^2 d\omega}{c^3}$$

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

average energy per volume at freq ω is

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

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



Pathria
fig 7.7

Total energy density

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

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

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