Review — Partition Functions

Quantum
$$\ln \mathcal{Z} = \pm \sum_i \ln \left(1 \pm e^{-\beta(\epsilon_i - \mu)} \right) \quad \begin{array}{l} + \, FD \\ - \, BE \end{array}$$

$$= \pm \sum_i \ln \left(1 \pm z\, e^{-\beta \epsilon_i} \right)$$

Classical
$$\ln \mathcal{Z} = \sum_i z\, e^{-\beta \epsilon_i}$$

sum "i" is over all single particle energy levels
Let ϵ_{min} be the $\min_i [\epsilon_i]$ i̇ smallest single particle energy level
from above we see that quantum result → classical result
in the limit $z\, e^{-\beta \epsilon_{min}} \ll 1$, since $\ln(1+\delta) \approx \delta$,
when $\delta \ll 1$. $z\, e^{-\beta \epsilon_{min}} = e^{\beta(\mu - \epsilon_{min})} \ll 1 \Rightarrow \beta(\mu - \epsilon_{min}) \ll 0$
for free point particle where $\epsilon_{min} = 0$, chemical potential is negative in the classical limit

Occupation numbers

quantum
$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1} \quad \begin{array}{l} + \, FD \\ - \, BE \end{array}$$

classical
$$\langle n_i \rangle = e^{-\beta(\epsilon_i - \mu)}$$

we see that quantum → classical for states i
such that $e^{\beta(\epsilon_i - \mu)} \gg 1 \Rightarrow \beta(\epsilon_i - \mu) \gg 0$
$$\Rightarrow (\epsilon_i - \mu) \gg k_B T$$

Note: Since $\langle n_i \rangle$ must always be positive, and
for bosons $\langle n_i \rangle = 1/[e^{\beta(\epsilon_i - \mu)} - 1]$ it therefore
follows that we must always have $(\epsilon_i - \mu) > 0$
for any state i, for bosons. For free particles the smallest ϵ_i
is usually $\epsilon_i = 0$, so we conclude that $\mu < 0$
always must hold for bosons (or $\mu < \epsilon_{min}$)

Harmonic Oscillator vs boson

Recall our earlier result for the quantized harmonic oscillator

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

We found:

average $\longrightarrow$ level of excitation

$$\langle n \rangle = \frac{\sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})}\, n}{\sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})}} = \frac{\sum_n e^{-\beta\hbar\omega n}\, n}{\sum_n e^{-\beta\hbar\omega n}}$$

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

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

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

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 $\longleftrightarrow$ "phonons"
oscillation of electromagnetic waves $\longleftrightarrow$ "photons"

<u>Sound modes in solid</u>
$$\omega = c_s |\vec{k}| \qquad c_s = \text{speed of sound}, \; \vec{k} = \text{wave vector}$$

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

<u>electromagnetic waves</u>
$$\omega = c|\vec{k}|, \qquad c = \text{speed of light}, \; \vec{k} = \text{wave vector}$$

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

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

$$e + ph \rightarrow e \qquad \text{electron scattered by absorbing a phonon}$$

chemical equilib $\Rightarrow \mu_e + \mu_{ph} = \mu_e \Rightarrow \mu_{ph} = 0$ chemical pot of phonon

Specific Heat of a Solid — Ionic Contribution   Debye Model

Classical Law of Dulong & Petit

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

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

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

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

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

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

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

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

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, called the Debye wave number. Oscillations with $k > k_D$ would have wavelengths smaller than the spacing between the atoms of the solid and so are not physical

For simplicity we will assume that all 3 polarizations have the same speed of sound 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 $\omega + d\omega$

To count these modes, let $k = \frac{\omega}{c_s}$ and $dk = \frac{d\omega}{c_s}$. Then the number of modes with frequency ω' such that $\omega < \omega' < \omega + d\omega$ is

$$\underset{\substack{s \\ \nearrow \\ \text{polarizations}}}{\sum} \underset{\substack{\vec{k}' \\ \text{such that} \\ k < |\vec{k}'| < k+dk}}{\sum} (1) \quad = 3 \underset{\substack{\vec{k}' \\ \text{such that} \\ k < |\vec{k}'| < k+dk}}{\sum} (1) \quad = 3 \frac{1}{(\Delta k)^3} \underset{\substack{k < |\vec{k}'| < k+dk'}}{\int} d^3 k'$$

$$= 3 \frac{1}{(\Delta k)^3} \int_{k}^{k+dk} dk' \, 4\pi (k')^2 = 3 \frac{4\pi}{(\Delta k)^3} k^2 dk$$

$$= \frac{3V}{(2\pi)^3} 4\pi k^2 dk \qquad \text{using } \Delta k = \frac{2\pi}{L}$$

$$= \frac{3V}{(2\pi)^3} 4\pi \frac{\omega^2}{c_s^2} \frac{d\omega}{c_s} \qquad \text{using } k = \frac{\omega}{c_s}, \quad dk = \frac{d\omega}{c_s}$$

$$= g(\omega) d\omega \qquad \Rightarrow \qquad \boxed{g(\omega) = \frac{3V}{2\pi^2} \frac{\omega^2}{c_s^3}}$$

Since the total number of modes is $3N$, we have

$$3N = \int_0^{\omega_D} d\omega \, g(\omega) \qquad \text{where } \omega_D = c_s k_D \text{ is the}$$
"Debye frequency"

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

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

where $n = \frac{N}{V}$ is the density of atoms in the solid

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

ω_D is frequency of most energetic phonons.

Now the average energy due to thermal excitation of phonons is

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

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

Specific heat is

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

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

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

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

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

Consider the prefactor of the integral

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

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

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

$\Rightarrow$ specific heat per volume is

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

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

Now we evaluate the integral in various limits

i) 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

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

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

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

$$= 3nk_B \qquad \text{This is the classical}$$
Law of Dulong + Petite!

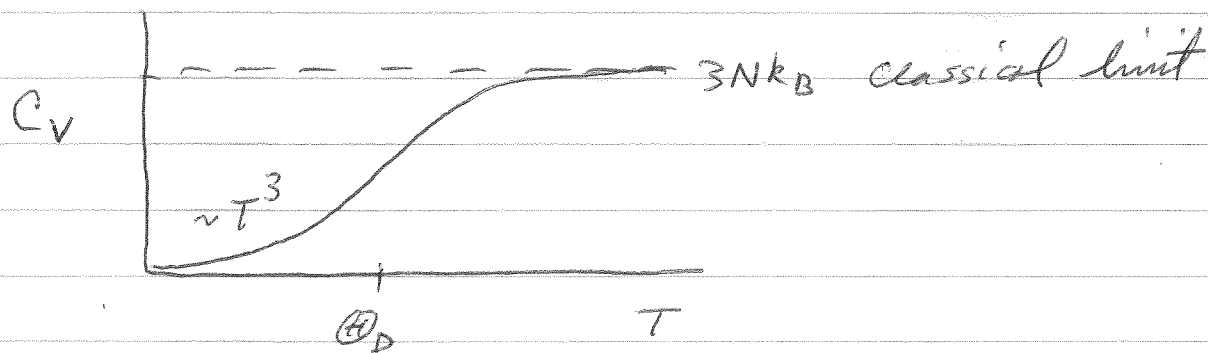So classical result remains correct provided
$T \gg \Theta_D$ ie high temperature

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

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

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

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

$\propto T^3$ at low temperatures

C_V ⎯ ⎯ ⎯ ⎯ ⎯ ⎯ $3Nk_B$ classical limit

$\sim T^3$

Θ_D T

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
$e^{-\hbar \omega_0 / k_B T}$ specific heat at low T.
The Debye model is more physically correct.