Unit 3-6: The Quantized Harmonic Oscillator as Bosons, the Debye Model for the Specific Heat of a Solid

<u>Review</u>

Partition function for *non-interacting* particles:

<u>Quantum:</u> $\ln \mathcal{L} = \pm \sum_i \ln \left(1 \pm e^{-\beta(\epsilon_i - \mu)}\right) = \pm \sum_i \ln \left(1 \pm z e^{-\beta \epsilon_i}\right)$ with $+$ for FD, $-$ for BE.

<u>Classical:</u> $\ln \mathcal{L} = \sum_i e^{-\beta(\epsilon_i - \mu)} = z \sum_i e^{-\beta \epsilon_i}$

The sum is over all *single particle* states i – for the quantum system, these are the single particle energy eigenstates.

If $\epsilon_{\min}$ is the smallest single particle energy level, from the above we see that the quantum result $\to$ classical result in the limit $z e^{-\beta \epsilon_{\min}} \ll 1$, since $\ln(1 + \delta) \approx \delta$ for $\delta \ll 1$. In this case $z e^{-\beta \epsilon_{\min}} = e^{\beta(\mu - \epsilon_{\min})} \ll 1 \Rightarrow \beta(\mu - \epsilon_{\min}) \ll 0$. For free point particles where $\epsilon_{\min} = 0$, this means that the chemical potential is negative, $\mu < 0$, in the classical limit.

Occupation numbers for *non-interacting* particles:

<u>Quantum:</u> $\langle n_i \rangle = \dfrac{1}{z^{-1} e^{\beta \epsilon_i} \pm 1} = \dfrac{1}{e^{\beta(\epsilon_i - \mu)} \pm 1}$ with $+$ for FD, $-$ for BE

<u>Classical:</u> $\langle n_i \rangle = z e^{-\beta \epsilon_i} = e^{-\beta(\epsilon_i - \mu)}$

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

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

Harmonic Oscillator vs Boson

Recall our earlier analysis of the quantized harmonic oscillator at the end of Notes 3-1. With energy levels $\epsilon_n = \hbar\omega(n + 1/2)$ we found for the average excitation level,

$$\langle n \rangle = \frac{\sum\limits_n e^{-\beta\hbar\omega n} n}{\sum\limits_n e^{-\beta\hbar\omega n}} = \frac{-\dfrac{1}{\hbar\omega}\dfrac{\partial}{\partial\beta}\left(\sum\limits_n e^{-\beta\hbar\omega n}\right)}{\sum\limits_n e^{-\beta\hbar\omega n}} = -\frac{1}{\hbar\omega}\frac{\partial}{\partial\beta}\ln\left[\frac{1}{1 - e^{-\beta\hbar\omega}}\right] = \frac{1}{\hbar\omega}\left[\frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}\right] \tag{3.6.1}$$

$$\langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1} \tag{3.6.2}$$

Compare this to the occupation number for a boson of energy ϵ,

$$\langle n \rangle = \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \tag{3.6.3}$$

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

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

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

For the harmonic oscillations involved in the elastic vibrations (sound modes) of solids, these quanta are called *phonons*.

For the harmonic oscillations of electromagnetic waves, these quanta are called *photons*.

Sound modes in solids

$\omega = c_s|\mathbf{k}|$ with c_s the speed of sound, $\mathbf{k}$ the wavevector of the sound mode

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

Electromagnetic waves

$\omega = c|\mathbf{k}|$ with c the speed of light, $\mathbf{k}$ the wavevector of the light wave

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

A physical way to understand why $\mu = 0$ for the bosons which describe the excitations of harmonic oscillators, is that these bosons are not conserved particles – they can be created or destroyed as the oscillator transitions between different levels of excitation.

As an example, consider an electron being scattered by absorbing or emitting a phonon. We can regard that as a chemical reaction, $e +$ phonon $\leftrightarrow e$. From our discussion of chemical equilibrium, we know that the equilibrium system of electrons and phonons should then satisfy the following relation for the chemical potentials: $\mu_e + \mu_{\text{phonon}} = \mu_e \Rightarrow \mu_{\text{phonon}} = 0$.

**Ionic Contribution to the Specific Heat of a Solid – the Debye Model**

In Notes 2-13 we discussed the classical model for the contribution of ionic vibrations to the specific heat of a solid. This led to the *Law of Dulong and Petit*. Since there are $6N$ harmonic degrees of freedom ($3N$ momenta and $3N$ normal coordinates), the equipartition theorem gave,

$$C_V = (6N)\left(\frac{1}{2}k_B\right) = 3Nk_B \quad \Rightarrow \quad \frac{C_V}{V} = 3nk_B \quad \text{with } n = \frac{N}{V} \text{ the density of ions.} \tag{3.6.4}$$
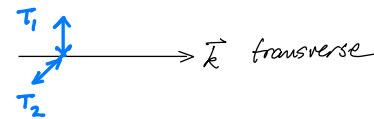
In quantum mechanics, the $3N$ momenta and the $3N$ normal coordinates can be thought of as $3N$ harmonic oscillators. These oscillations are the sound waves of vibration in the solid. We can approximate the dispersion relation of these sound waves as,

$$\omega = c_s|\mathbf{k}|, \qquad \mathbf{k} \text{ is the wavevector,} \qquad c_s \text{ is the speed of sound} \tag{3.6.5}$$

and there are three different wave polarizations s for each $\mathbf{k}$,
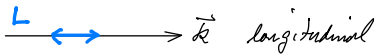
$$s = L \qquad \text{longitudinal mode where the ion displacement is } || \text{ to } \mathbf{k} \tag{3.6.6}$$
$$s = T_1, T_2 \quad \text{transverse modes where the ion displacement is } \perp \text{ to } \mathbf{k} \tag{3.6.7}$$

For a solid of volume $V = L^3$, we will take the sound modes to obey periodic boundary conditions. Then, just like with particle-in-a-box wavefunctions, the wavevectors of the sound modes must satisfy,

$$k_\mu = \left(\frac{2\pi}{L}\right)n_\mu, \qquad n_\mu = 0, \pm 1, \pm 2, \cdots \pm \text{integer} \qquad \mu = x, y, z \tag{3.6.8}$$

For simplicity, we will assume that all three polarizations of sound waves have the same speed of sound c_s.

The total number of sound modes must equal the total number of oscillators, which is $3N$. This sets an upper bound on $|\mathbf{k}|$. Let the maximum allowed value of $|\mathbf{k}|$ be denoted as k_D, the *Debye wavenumber*. Oscillations with $k > k_D$ would have wavelengths smaller than the spacing between the atoms of the solid, and so are not physical. The maximum k_D also means that the phonon modes have a maximum frequency, $\omega_D = c_s k_D$, known as the *Debye frequency*.

Since all the quantities we will want to compute depend on $\mathbf{k}$ only via $|\mathbf{k}| = \omega/c_s$, it is convenient to define a *phonon density of states* $g(\omega)$.

$g(\omega)d\omega$ is defined as the number of phonon modes, *per unit volume*, with frequencies between ω and $\omega + d\omega$. With $g(\omega)$ we can then compute for any quantity X that is independent of polarization s, and depends on wavevector only via $|\mathbf{k}|$,

$$\frac{1}{V} \sum_{s=1}^{3} \sum_{\mathbf{k}=0}^{k_D} X(|\mathbf{k}|) = \int_0^{\omega_D} d\omega\, g(\omega) X(\omega/c_s) \tag{3.6.9}$$

To find $g(\omega)$ let us first compute $G(\omega)$, the number of modes per unit volume with frequency less than or equal to ω. Each mode corresponds to a wavevector $\mathbf{k}$, with $\omega = c_s|\mathbf{k}|$. The volume of k-space that corresponds to each allowed $\mathbf{k}$ mode is $(\Delta k)^3$, with $\Delta k = 2\pi/L$ the spacing between allowed values of any given component of $\mathbf{k}$ from Eq. (3.6.8). So the number of modes with frequency $\leq \omega$ is just the number of modes contained within a sphere in k-space of radius $k = \omega/c_s$. For each $\mathbf{k}$ there are also 3 models of polarization, so we conclude that the number of modes per unit volume is roughly,

$$G(\omega) = \frac{3}{V} \frac{(\text{volume of sphere of radius } k = \omega/c_s)}{(\text{volume per mode})}$$

$$= \frac{3}{V} \frac{\frac{4}{3}\pi k^3}{(\Delta k)^3} = \frac{3}{V} \frac{\frac{4}{3}\pi k^3}{(2\pi/L)^3} = \frac{k^3}{2\pi^2} = \frac{\omega^3}{2\pi^2 c_s^3} \tag{3.6.10}$$

This becomes exact as the system gets infinitely large with $L \to \infty$, and so $\Delta k \to 0$.

The density of states per unit volume $g(\omega)$ is then obtained from $g(\omega)d\omega = G(\omega + d\omega) - G(\omega)$, or,

$$\boxed{g(\omega) = \frac{dG}{d\omega} = \frac{3}{2\pi^2} \frac{\omega^2}{c_s^3}} \tag{3.6.11}$$

nodes of grid lines locate allowed values of **k**
each allowed value of **k** occupies volume $(\Delta k)^3$
number of boxes within sphere of radius k is the
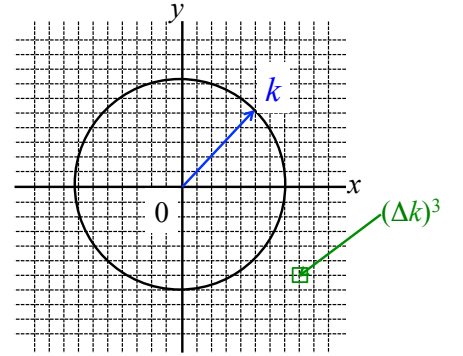number of allowed **k** values with $c_s k \leq \omega$.

Now, as we said earlier, since there are only a finite number $3N$ of sound modes, there is a maximum phonon frequency, $\omega_D = c_s k_D$, the *Debye frequency*. The total number of modes per unit volume is thus $3N/V$, and we can now determine ω_D by the condition,

$$\frac{3N}{V} = G(\omega_D) = \int_0^{\omega_D} d\omega\, g(\omega) = \frac{1}{2\pi^2} \frac{\omega_D^3}{c_s^3} \tag{3.6.12}$$

$$\Rightarrow \quad \omega_D = \left[6\pi^2 c_s^3 \frac{N}{V}\right]^{1/3} = \left[6\pi^2 c_s^3 n\right]^{1/3} \sim n^{1/3} \tag{3.6.13}$$

where $n = N/V$ is the density of ions in the solid. The Debye wavenumber is then,

$$k_D = \frac{\omega_D}{c_s} = \left[6\pi^2 n\right]^{1/3} \tag{3.6.14}$$

The Debye frequency ω_D is the frequency of the most energetic phonons.

Now the average energy per unit volume due to the thermal excitation of phonons is,

$$\frac{\langle E \rangle}{V} = \frac{1}{V} \sum_s \sum_{\mathbf{k}} \hbar \omega_{\mathbf{sk}} \left[\langle n_{\mathbf{sk}} \rangle + 1/2 \right] = \int_0^{\omega_D} d\omega \, g(\omega) \hbar \omega \left[\frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right] \tag{3.6.15}$$

The specific heat at constant volume, per unit volume, is then,

$$\frac{C_V}{V} = \frac{1}{V} \left(\frac{\partial \langle E \rangle}{\partial T} \right)_{V,N} = \int_0^{\omega_D} d\omega \, g(\omega) \, \hbar \omega \, \frac{\partial}{\partial T} \left[\frac{1}{e^{\beta \hbar \omega} - 1} + \frac{1}{2} \right] = \int_0^{\omega_D} d\omega \, g(\omega) \, \hbar \omega \, \frac{\left(\frac{\hbar \omega}{k_B T^2} \right) e^{\beta \hbar \omega}}{\left[e^{\beta \hbar \omega} - 1 \right]^2} \tag{3.6.16}$$

$$= \frac{3}{2\pi^2 c_s^3} \int_0^{\omega_D} d\omega \, \omega^2 \, k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\beta \hbar \omega}}{\left[e^{\beta \hbar \omega} - 1 \right]^2} \tag{3.6.17}$$

Now let $x \equiv \hbar \omega / k_B T = \beta \hbar \omega$. Then,

$$\frac{C_V}{V} = \frac{3 k_B}{2\pi^2 c_s^3} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{x_D} dx \, \frac{x^4 \, e^x}{\left[e^x - 1 \right]^2} \quad \text{where } x_D = \beta \hbar \omega_D \tag{3.6.18}$$

Consider the prefactor of the integral,

$$\frac{3 k_B}{2\pi^2 c_s^3} \left(\frac{k_B T}{\hbar} \right)^3 = \frac{3 k_B}{2\pi^2} \left(\frac{k_B T}{k_D c_s \hbar} \right)^3 (6\pi^2 n) = 9 k_B n \left(\frac{k_B T}{\hbar \omega_D} \right)^3 \tag{3.6.19}$$

where we used $k_D^3 = 6\pi^2 n$ from Eq. (3.6.14), and $\omega_D = c_s k_D$.

Define $\Theta_D \equiv \hbar \omega_D / k_B$, the *Debye temperature*. We will see that Θ_D sets the temperature scale for the appearance of quantum effects.

The specific heat per volume is then,

$$\frac{C_V}{V} = 9 n k_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} dx \, \frac{x^4 \, e^x}{\left[e^x - 1 \right]^2} \tag{3.6.20}$$

where $x_D = \beta \hbar \omega_D = \Theta_D / T$.

Now we can evaluate the integral above in different limits.

1) At high temperatures, $T \gg \Theta_D$, $x_D = \Theta_D / T$ gets very *small*. So we can expand the integrand for small values of x,

$$\frac{x^4 \, e^x}{\left[e^x - 1 \right]^2} \approx \frac{x^4}{x^2} = x^2 \quad \Rightarrow \quad \int_0^{x_D} dx \, x^2 = \frac{x_D^3}{3} = \frac{1}{3} \left(\frac{\Theta_D}{T} \right)^3 \tag{3.6.21}$$

So at large $T \gg \Theta_D$, we have,

$$\frac{C_V}{V} = 9 n k_B \left(\frac{T}{\Theta_D} \right)^3 \frac{1}{3} \left(\frac{\Theta_D}{T} \right)^3 = 3 n k_B \tag{3.6.22}$$

This is just the classical Law of Dulong and Petit! So the classical result remains correct provided $T \gg \Theta_D$, i.e. at high temperatures.

Note, if we wanted to find the high temperature corrections to the Law of Dulong and Petit, all we need to do is to continue the expansion of the integrand in Eq. (3.6.21) to higher order,

$$\frac{x^4 \, e^x}{\left[e^x - 1 \right]^2} = x^2 - \frac{x^4}{12} + \frac{x^6}{240} + \cdots \quad \text{(I cheated and used Mathematica ...)} \tag{3.6.23}$$

and then the integral becomes,

$$\frac{x_D^3}{3} - \frac{x_D^5}{60} + \frac{x_D^7}{1680} + \cdots = \frac{x_D^3}{3}\left(1 - \frac{x_D^2}{20} + \frac{x_D^4}{560} + \cdots\right) = \frac{1}{3}\left(\frac{\Theta_D}{T}\right)^3\left[1 - \frac{1}{12}\left(\frac{\Theta_D}{T}\right)^2 + \frac{1}{560}\left(\frac{\Theta_D}{T}\right)^4 + \cdots\right] \quad (3.6.24)$$

and then,

$$\frac{C_V}{V} = 3nk_B\left[1 - \frac{1}{12}\left(\frac{\Theta_D}{T}\right)^2 + \frac{1}{560}\left(\frac{\Theta_D}{T}\right)^4 + \cdots\right] \quad (3.6.25)$$

2) At low temperatures, $T \ll \Theta_D$, $x_D = \Theta_D/T$ gets very large and so we can approximate the integral by taking the upper limit $x_D \to \infty$. We then have,

$$\frac{C_V}{V} = 9nk_B\left(\frac{T}{\Theta_D}\right)^3\int_0^\infty dx\, \frac{x^4\, e^x}{[e^x - 1]^2} \quad (3.6.26)$$

The integral is now just a pure number – evaluating the integral gives $(4/15)\pi^4$. So at low temperatures $T \ll \Theta_D$, we have,

$$\frac{C_V}{V} = \frac{12}{5}\pi^4\, n\, k_B\left(\frac{T}{\Theta_D}\right)^3 \quad \propto\ T^3 \quad (3.6.27)$$

The crossover between the high and low temperature limits is roughly $T \sim \Theta_D$. In common solids, $\Theta_D \sim 100-300\mathrm{K}$, so the effect of quantum mechanics on the specific heat of a solid can be seen at *room temperature!* This is an example of a situation where we can see quantum effects in a macroscopic system at room temperature.
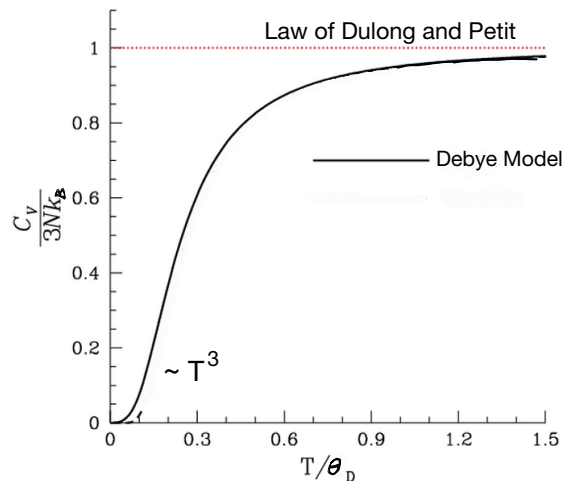
Originally Einstein treated this problem quantum mechanically by assuming that all phonon modes had the same k-independent frequency ω_0. This is called the "Einstein model" and it gives a specific heat that decreases exponentially as $e^{-\hbar\omega_0/k_B T}$ as T decreases. The Debye model is more physically correct.

This explanation of the specific heat of solids, as to why the Law of Dulong and Petit fails, was one of the early successes of quantum mechanics.