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Physics 141A: Solid State Physics

Homework 1

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Question 1: Show that the Bose occupation factor for the number $\langle N \rangle$ of excited vibrational "particles" (modes) is

$$\frac{1}{e^{\hbar\omega\beta} - 1}$$

where $\beta = 1/k_B T$ and $\hbar\omega$ is the energy of this vibrational mode.

Solution:

In the Einstein model of a solid, an excited vibrational "particle" or mode can have energies quantized as

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

so the probability that a mode N is occupied is proportional to

$$e^{-\beta E_n} = e^{-\beta(N+1/2)\hbar\omega}$$

The normalization factor would be the partition function

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\hbar/2}\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}$$

i.e.

$$P\left(\text{Mode } N \text{ is occupied}\right) = \frac{e^{-\beta E_n}}{Z} = \frac{e^{-N\beta\hbar\omega} \cdot e^{-\beta\hbar/2}}{e^{-\beta\hbar/2} \cdot \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}} = \frac{e^{-N\beta\hbar\omega}}{\sum_{n=0}^{\infty} e^{-n\beta\hbar\omega}}$$

and the sum in the denominator is a geometric series so we have

$$P\left(\text{Mode } N \text{ is occupied}\right) = e^{-N\beta\hbar\omega} \cdot \left(1 - e^{-\beta\hbar\omega}\right)$$

Now, the expected number of occupied vibrational modes can be expressed as

$$\begin{aligned}
\langle N \rangle &= \sum_{N=0}^{\infty} N \cdot P(\text{Mode } N \text{ is occupied}) \\
\implies \langle N \rangle &= \sum_{N=0}^{\infty} N \cdot \frac{e^{-\beta E_N}}{Z} \\
&= \frac{1}{Z_1} \sum_{N=0}^{\infty} N e^{-\beta \hbar \omega (N)} \\
&= \frac{1}{Z_1} \cdot \left(-\frac{1}{\hbar \omega} \frac{\partial Z_1}{\partial \beta} \right)
\end{aligned}$$

where

$$Z_1 = \sum_{N=0}^{\infty} e^{-N\beta\hbar\omega} = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

and we can use this since the $-\beta\hbar\omega(1/2)$ factor is in both the boltzmann factor and the partition function Z so it can be cancelled.

Then,

$$\begin{aligned}
\frac{\partial Z_1}{\partial \beta} &= \left(-\frac{1}{(1 - e^{-\beta\hbar\omega})^2} \right) \cdot \left(\hbar\omega e^{-\beta\hbar\omega} \right) \\
&= -\hbar\omega \left(\frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2} \right)
\end{aligned}$$

Thus,

$$\begin{aligned}
\langle N \rangle &= -\frac{1}{\hbar\omega} \cdot \frac{1}{Z_1} \cdot \frac{\partial Z_1}{\partial \beta} \\
&= -\frac{1}{\hbar\omega} \cdot \left(1 - e^{-\beta\hbar\omega} \right) \cdot (-\hbar\omega) \left(\frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2} \right) \\
&= \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}
\end{aligned}$$

So, multiplying the numberator and denominator by $e^{+\beta\hbar\omega}$ we get

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

Question 2: Use the Debye approximation to determine the heat capacity of a two dimensional solid as a function of temperature.

- State your assumptions.
  You will need to leave your answer in terms of an integral that one cannot do analytically.
- At high T, show that the heat capacity goes to a constant and find that constant.
- At low T, show that $C_v = KT^n$ and find n. Find K in terms of a definite integral.
  If you are brace, you can try to evaluate the integral, but you will need to leave your result in terms of the Riemann Zeta function.

Solution:

Assumptions:

1. Energy is carried in waves and the energy of a given mode is described as
$$E_n = \hbar\omega(\mathbf{k})\left(n + \frac{1}{2}\right)$$
2. We have the dispersion relation $\omega = v|\mathbf{k}|$ where $\mathbf{k} = k_x\mathbf{x} + k_y\mathbf{y}$
3. We use periodic boundary-conditions with box length L, which restricts our k_x, k_y values so that
$$\vec{k} = \frac{2\pi}{L}(n_x, n_y)$$
where n_x, n_y are integers.
4. We can take the continuum limit and convert the sum into an integral
$$\sum_k \to \left(\frac{L}{2\pi}\right)^2 \int \mathrm{d}\mathbf{k}$$

So, since we have two modes for the sound wave now, we have

$$\langle E\rangle = 2\cdot\left(\frac{L}{2\pi}\right)^2 \int \mathrm{d}\mathbf{k}\ \hbar\omega(\mathbf{k})\left(n_B(\omega(\mathbf{k})) + \frac{1}{2}\right)$$

We can convert to polar coordinates are get

$$\begin{aligned}
\langle E\rangle &= 2\cdot\left(\frac{L}{2\pi}\right)^2 \int_0^{2\pi}\int_0^{\infty} k\mathrm{d}k\mathrm{d}\theta\ \hbar\omega(k)\left(n_B(\omega(k)) + \frac{1}{2}\right) \\
&= 2\cdot\left(\frac{L}{2\pi}\right)^2 \int_0^{2\pi}\mathrm{d}\theta\int_0^{\infty} k\mathrm{d}k\ \hbar\omega(k)\left(n_B(\omega(k)) + \frac{1}{2}\right) \\
&= 4\pi\cdot\left(\frac{L}{2\pi}\right)^2 \int_0^{\infty} k\mathrm{d}k\ \hbar\omega(k)\left(n_B(\omega(k)) + \frac{1}{2}\right)
\end{aligned}$$

We can use the dispersion relation $\omega = vk$ to write everything in terms of ω:

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

and since we're actually interested in the heat capacity, we can drop the temperature independent term we get from the $+\frac{1}{2}$ i.e. we'll abuse notation and write

$$\langle E \rangle = \frac{L^2}{\pi} \int_0^\infty \left(\frac{\omega}{v}\right) \left(\frac{\mathrm{d}\omega}{v}\right) \hbar\omega \left(n_B(\omega)\right)$$

or, in other words, we have

$$\langle E \rangle = \frac{L^2}{\pi} \int_0^\infty \mathrm{d}\omega \; g(\omega) \; \hbar\omega \left(n_B(\beta\hbar\omega)\right)$$

where

$$g(\omega) = \frac{L^2\omega}{\pi v^2}$$

is the density of states.

Now, physically, it doesn't make sense for infinitely many modes to be occupied, so we introduce a cutoff-frequency ω_c defined as

$$2N = \int_0^{\omega_c} g(\omega)\mathrm{d}\omega$$

(there should be $2N$ modes of oscillation)

In any case, using the cut-off frequency and substituting in the Bose-Einstein distribution, we have

$$\langle E \rangle = \frac{L^2\hbar}{\pi v^2} \int_0^{\omega_c} \mathrm{d}\omega \; \frac{\omega^2}{e^{\beta\hbar\omega} - 1}$$

<u>High-Temperature limit:</u>
In the limit $T \to 0$, we have $\beta \to 0$ so

$$\begin{aligned} \frac{1}{e^{\beta\hbar\omega} - 1} &\approx \frac{1}{(1 + \beta\hbar\omega) - 1} \\ &= \frac{1}{\beta\hbar\omega} \\ &= \frac{k_B T}{\hbar\omega} \end{aligned}$$

So,

$$\begin{aligned}\langle E\rangle &= \frac{L^2\hbar}{\pi v^2}\int_0^{\omega_c}\omega^2\cdot\frac{k_BT}{\hbar\omega}\mathrm{d}\omega \\ &= \int_0^{\omega_c}\frac{L^2\omega}{\pi v^2}\hbar\omega\frac{k_BT}{\hbar\omega}\mathrm{d}\omega \\ &= k_BT\int_0^{\omega_c}g(\omega)\mathrm{d}\omega \\ &= k_BT\cdot 2N\end{aligned}$$

Therefore, the Heat Capacity in the high-temperature limit is

$$\boxed{C_v = 2Nk_B}$$

Low-Temperature limit: In the low-temperature limit, introducing the cut-off frequency ω_c doesn't impact the integral much because the bose-factor will cause the integrand to vanish before we even reach ω_c. Thus, we can integrate all the way to infinity instead.

So,

$$\langle E\rangle = \frac{L^2\hbar}{\pi v^2}\int_0^{\infty}\frac{\omega^2}{e^{\beta\hbar\omega}-1}\mathrm{d}\omega$$

Using the substitution $x=\beta\hbar\omega$ we have

$$\begin{aligned}\langle E\rangle &= \frac{L^2\hbar}{\pi v^2}\int_0^{\infty}\left(\frac{\mathrm{d}x}{\beta\hbar}\right)\left(\frac{x}{\beta\hbar}\right)^2\frac{1}{x^x-1} \\ \langle E\rangle &= \frac{L^2\hbar}{\pi v^2}\left(\frac{1}{\beta\hbar}\right)^3\int_0^{\infty}\mathrm{d}x\frac{x^2}{x^x-1} \\ \langle E\rangle &= \frac{L^2\hbar}{\pi v^2}\left(\frac{k_BT}{\hbar}\right)^3\int_0^{\infty}\mathrm{d}x\frac{x^2}{x^x-1}\end{aligned}$$

Thus, the heat capacity is given by

$$\begin{aligned}C &= \frac{d\langle E\rangle}{dT} \\ &= \frac{L^2\hbar}{\pi v^2}\left(\frac{k_B}{\hbar}\right)^3\cdot(3T^2)\cdot\int_0^{\infty}\mathrm{d}x\frac{x^2}{x^x-1} \\ &= KT^n\end{aligned}$$

where

$$\boxed{K = \frac{3L^2\hbar}{\pi v^2}\left(\frac{k_B}{\hbar}\right)^3\cdot\int_0^{\infty}\mathrm{d}x\frac{x^2}{x^x-1}}$$

and

$$\boxed{n=3}$$

Question 3:

- What is the mean kinetic energy in eV at room temperature of a gaseous (a) He atom (b) Xe atom (c) Ar atom and (d) Kr atom? The gas is classical.
- Explain the following values of the molar heat capacity $JK^{-1}mol^{-1}$ all measured at constant pressuer at $298K$:

$$\mathrm{Al} = 24.35, \mathrm{Pb} = 26.44, \mathrm{N_2} = 29.13, \mathrm{Ar} = 20.79, \mathrm{O_2} = 29.36$$

Solution:

- The mean kinetic energy is given by the Equipartition Theorem:

$$\mathrm{KE} = \frac{f}{2} k_B T$$

  Since He, Xe, Ar, Ke are all mono-atomic and have 3 degrees of freedom they all have the same mean kinetic energy at $T = 298K$

$$\mathrm{KE} = \frac{3}{2} k_B T = 0.03852eV$$

- Since Kinetic Energy (of one atom) is $\frac{f}{2} k_B T$, the heat capacity of an ideal gas atom is $C = \frac{f}{2} k_B$. For an entire mole, we have $C = \frac{f}{2} N k_B = \frac{f}{2} R$ where R is the universal gas constant.

  Since $\mathrm{N_2}, \mathrm{O_2}$ are diatomic they have more degrees of freedom (it has quadratic degrees of freedom) than Ar and thus have higher molar heat capacity.

  Al and Pb are metals so they cannot be treated accurately by the Ideal Gas model because many-particle interactions are important in metals.