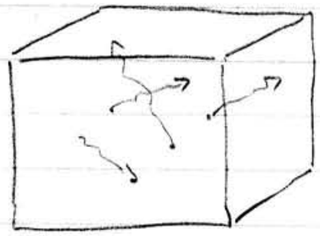
Lecture 8

Thermodynamics of a photon gas – black body radiation

Consider a cavity of volume $V = L_x L_y L_z$ at temperature T that contains electromagnetic radiation



EM radiation is quantized = photons
EM wave of frequency ω has energy

$$\varepsilon_s = \hbar\omega\left(s + \frac{1}{2}\right)$$

where $s = 0, 1, 2 \cdots$ is the number of quanta (photons) in that oscillation (called a mode)

Partition f'n for that EM wave is:

$$Z = \sum_{s=0}^{\infty} e^{-\beta\varepsilon_s} = e^{-\beta\hbar\omega/2} \sum_{s=0}^{\infty} e^{-\beta\hbar\omega s}$$

$$= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \qquad \sum_{s=0}^{\infty} x^s = \frac{1}{1-x}$$

$$U = \langle\varepsilon\rangle = -\frac{\partial}{\partial\beta}\ln Z = -\frac{\partial}{\partial\beta}\left[-\beta\frac{\hbar\omega}{2} - \ln\left(1 - e^{-\beta\hbar\omega}\right)\right]$$

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

$$= \hbar\omega\left[\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2}\right] = \hbar\omega\left(\langle s\rangle + \frac{1}{2}\right)$$

$\langle s\rangle = \dfrac{1}{e^{\beta\hbar\omega} - 1}$ is the average # of photons in that EM wave of frequency ω

Look at high T limit $(\beta \to 0)$

$$\langle s \rangle \approx \frac{1}{\cancel{1} + \frac{\hbar\omega}{k_B T} \cdots - \cancel{1}} = \frac{k_B T}{\hbar\omega}$$

$$U \approx \hbar\omega\left(\frac{k_B T}{\hbar\omega} + \frac{1}{2}\right) = k_B T + \frac{\hbar\omega}{2}$$

Ignoring zero-pt energy, this is the equipartition result

$$U = \underset{\substack{\uparrow \\ \#\text{ degrees of freedom}}}{2} \cdot \frac{1}{2} k_B T$$

Spacing between levels $\ll k_B T$

$\frac{\hbar\omega}{2}$ is just an additive constant, it is standard to <u>omit it</u>

This is all for a single EM wave of frequency ω. To get total U, we need to sum up over all possible ω. <u>Not all ω</u> are allowed; the cavity imposes boundary conditions, such that $\bar{E}_{\text{tangent}}\big|_{\text{walls}} = 0$

Solutions are standing waves of the form:

$$E_x = E_{x0}\, e^{-i\omega t} \cos\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

$$E_y = E_{y0}\, e^{-i\omega t} \sin\left(\frac{n_x \pi x}{L_x}\right) \cos\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi z}{L_z}\right)$$

$$E_z = E_{z0}\, e^{-i\omega t} \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \cos\left(\frac{n_z \pi z}{L_z}\right)$$

i.e. standing waves with $k_x = \frac{n_x \pi}{L_x}$, $k_y = \frac{n_y \pi}{L_y}$, $k_z = \frac{n_z \pi}{L_z}$

$n_x, n_y, n_z = 0, +1, +2, \ldots$

Each configuration n_x, n_y, n_z is called a <u>mode</u>

Each satisfies the wave equation so:

$$\nabla^2 \bar{E} = \frac{1}{c^2}\frac{\partial^2 \bar{E}}{\partial t^2} \quad \text{gives}$$

$$k_x^2 + k_y^2 + k_z^2 = \left(\frac{\omega}{c}\right)^2$$

$$\Rightarrow \quad \omega_n = ck = c\sqrt{k_x^2 + k_y^2 + k_z^2} = c\pi\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)^{1/2}$$

Only certain mode energies $\hbar\omega_n$ are allowed

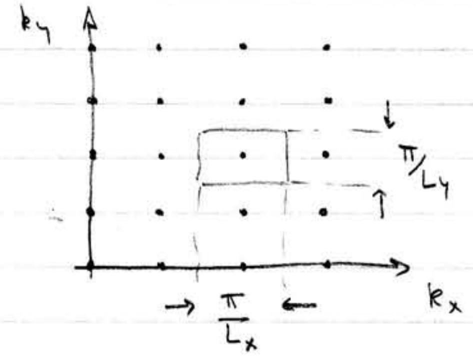
$$\therefore \quad Z_{tot} = \prod_n \left(1 - e^{-\beta\hbar\omega_n}\right)^{-1} \qquad n = \{n_x, n_y, n_z\}$$

Note that we omitted contribution from zero-pt. energy

$$\therefore \quad U_{tot} = \sum_n \frac{\hbar\omega_n}{e^{\beta\hbar\omega_n} - 1}$$

$$\left(\text{Note} \quad \sum_n = \sum_{n_x=0}^{\infty}\sum_{n_y=0}^{\infty}\sum_{n_z=0}^{\infty}\right)$$

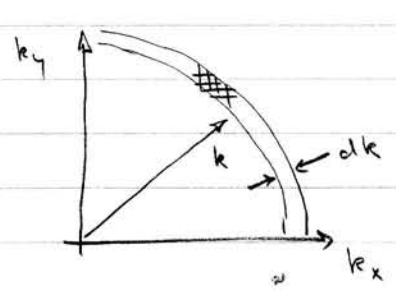
To carry out this sum, we'll use the same approach we used for the ideal gas in <u>Lecture 4</u> $(\Omega(E))$



Each mode occupies a volume in k-space of $\left(\frac{\pi}{L_x}\right)\left(\frac{\pi}{L_y}\right)\left(\frac{\pi}{L_z}\right) = \frac{\pi^3}{V}$

To count modes, integrate over k-space and divide by π^3/V

Assume $n_x, n_y, n_z \gg 1$



modes with frequency between ω, $\omega + d\omega$:

$$N(\omega)\,d\omega = \underset{\substack{\uparrow \\ *}}{2} \cdot \frac{V}{\pi^3} \cdot V_{shell} = 2 \cdot \frac{V}{\pi^3} \, \frac{4\pi k^2 dk}{8}$$

$k_x, k_y, k_z \geq 0$ so shell is $\frac{1}{8}$ of a sphere $\frac{4\pi k^2 dk}{8}$

(Note: we could have used periodic boundary conditions for the cavity, in which the solutions would have been <u>traveling</u> waves with $k_x = \frac{2\pi}{L_x} n_x \cdots$ $n_x = 0, \pm 1, \pm 2 \cdots$

Then each mode takes a volume of k-space $\frac{(2\pi)^3}{V}$
<u>But</u> we would have to use $V_{shell} = 4\pi k^2 dk$ since k_x, k_y, k_z can be negative.

Get the <u>same</u> answer regardless)

* Factor of two included to account for 2 polarization states of EM wave

$$N(\omega)\,d\omega = 2 \cdot \frac{V}{(2\pi)^3} 4\pi k^2 dk$$

$$= \frac{V}{\pi^2} \frac{\omega^2 d\omega}{c^3}$$

Similar expression as ideal gas, except
$\varepsilon = \hbar\omega = \hbar c k$

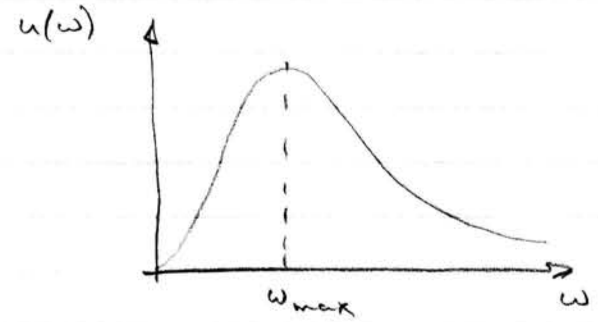
$$\therefore \; U_{tot} = \sum_n \frac{\hbar\omega_n}{e^{\beta\hbar\omega_n} - 1} = \int_0^\infty N(\omega)\,d\omega \, \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

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

Consider energy density instead $u = \frac{U}{V}$

$$u_{tot} = \int_0^\infty d\omega \; u(\omega) = \int_0^\infty d\omega \; \frac{\hbar \omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1}$$

$u(\omega)\,d\omega$ is the energy density in a frequency band $\omega, \omega + d\omega$
Called the Planck radiation law



Spectrum $u(\omega)$ entirely determined by temperature of cavity T

Spectrum has a peak so object at temperature T has a characteristic color

$$\frac{du(\omega)}{d\omega} = 0 \quad \Rightarrow \quad \frac{d}{dx}\left(\frac{x^3}{e^x - 1}\right) = 0 \qquad \text{with } x \equiv \beta\hbar\omega$$

$$\frac{3x^2}{e^x - 1} - \frac{x^3 e^x}{(e^x - 1)^2} = 0$$

Two trivial sol'ns are $x = 0, \infty$

$$\Rightarrow \quad 3 = \frac{x e^x}{e^x - 1}$$

$$\text{or} \quad 3 - 3e^{-x} = x$$

solve numerically $x = 2.82$

Peak at $\boxed{\hbar\omega_{max} = 2.82\, k_B T}$

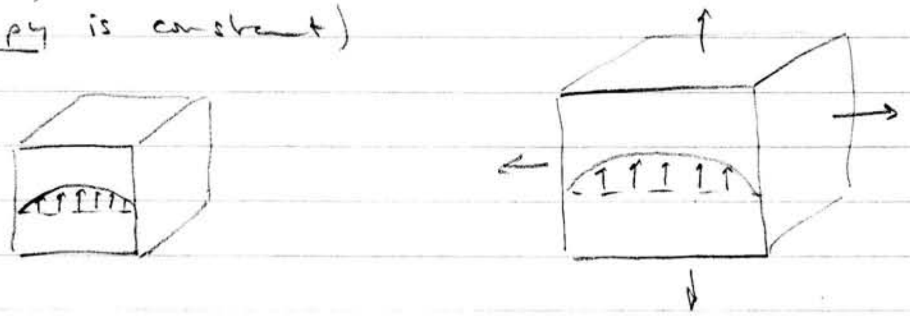
Ex: Our sun $T = 5800\,K$ $\quad \hbar\omega_{max} = 1.41\, eV$ $\quad \lambda = 880\, nm$
near infrared

Much of sun's energy emitted in visible spectrum $\sim 400 - 700\, nm$

Ex: Cosmic background radiation

In the early universe, universe was filled with ionized gas at high-T that interacted strongly with EM radiation. Photon gas at thermal equilibrium, $T \sim 3000K$

Since then, the universe expanded and photon λ stretched (Doppler-shift). One way to think of this is the universe (the cavity) expanded maintaining the same states (i.e. photon entropy is constant)



So $\lambda \uparrow$

Remnant of this thermal photon gas is seen today, but with $T = 2.73K$ (discovered in 1965 by Penzias + Wilson)

$\hbar\omega_{max} = 2.82\, k_B T$ gives $\lambda_{peak} = 1\,mm$

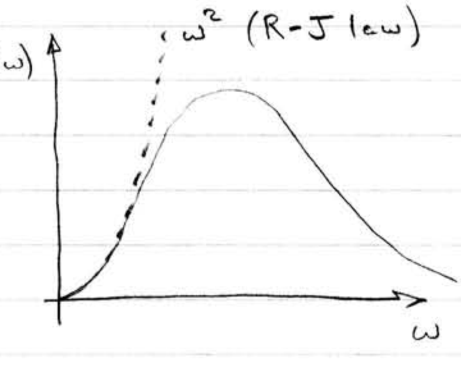
An object that exhibits Planck radiation law is called an ideal blackbody

Most objects show deviations from $u(\omega)$, but cosmic background is as close to an ideal blackbody as you can find in nature

How does $u(\omega)$ behave in classical regime $\hbar\omega \ll k_B T$

$$u(\omega) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1} \approx \frac{\cancel{\hbar}\omega^{\cancel{3}\,2}}{\pi^2 c^3} \frac{k_B T}{\cancel{\hbar\omega}} = \frac{\omega^2 k_B T}{\pi^2 c^3}$$

This is the Raleigh - Jeans law. Without QM (notice $\hbar$ disappears) would predict $u(\omega) \sim \omega^2$



But then $u_{tot} = \int_0^\infty d\omega\, u(\omega) \to \infty$

This was called the ultraviolet catastrophe. Predicted that if we'd open an oven, X-rays would come out!

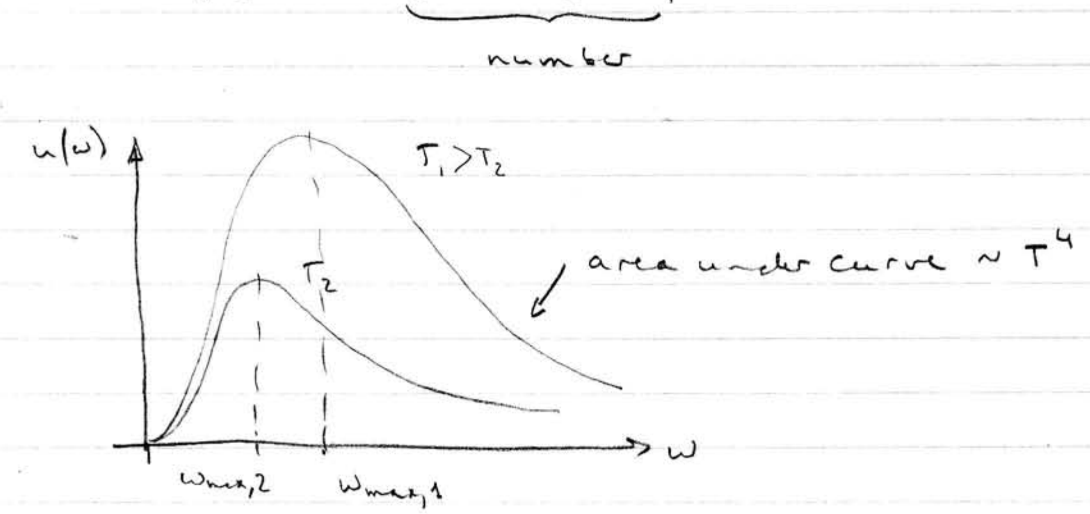
This failure of classical treatment / Equipartition theorem lead to idea of photon and QM.

What is u_{tot} with correct $u(\omega)$?

$$u_{tot} = \int_0^\infty d\omega \, \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\beta\hbar\omega} - 1}$$

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

$$= \frac{(k_B T)^4}{\hbar^3 c^3} \frac{1}{\pi^2} \underbrace{\int_0^\infty dx \, \frac{x^3}{e^x - 1}}_{\text{number}} = \alpha T^4$$



We will encounter integrals of the form:

$$\int_0^\infty dx \, \frac{x^n}{e^x - 1} = \int_0^\infty dx \, \frac{x^n e^{-x}}{1 - e^{-x}}$$

$$= \int_0^\infty dx \, x^n e^{-x} \sum_{k=0}^{\infty} e^{-kx}$$

$$= \int_0^\infty dx \, x^n \sum_{=1}^{\infty} e^{-kx}$$

$$= \sum_{k=1}^{\infty} \underbrace{\int_0^\infty dx \, x^n e^{-kx}}_{\frac{\Gamma(n+1)}{k^{n+1}}}$$

$\Gamma(n+1) = n!$ for integer

$$= \Gamma(n+1) \sum_{k=1}^{\infty} \frac{1}{k^{n+1}} \equiv \Gamma(n+1)\,\zeta(n+1)$$

$$\zeta(n) = \sum_{k=1}^{\infty} \frac{1}{k^n} = 1 + \frac{1}{2^n} + \frac{1}{3^n} \cdots$$

Riemann zeta function
Look up in a table

For $n=3$ $\zeta(4) = \frac{\pi^4}{90}$, $\Gamma(4) = 3! = 6$ so $\boxed{u_{tot} = \frac{\pi^2}{15} \frac{(k_B T)^4}{\hbar^3 c^3}}$

Stefan – Boltzmann Law of radiation ↑