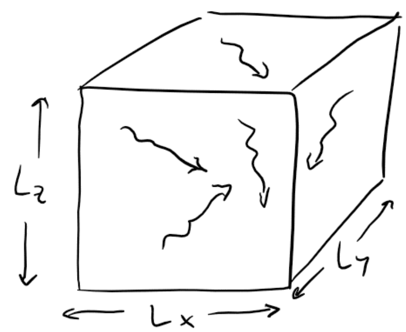
Lecture 13 – Photon gas (blackbody radiation)



PREVIOUSLY: we analyzed statistical mechanics of Einstein solid & ideal gas using quantum mechanics

TODAY: Statistical mechanics of a thermal photon gas

Consider a cavity of volume $V = L_x L_y L_z$ at temperature T that contains electromagnetic radiation due to vibrations of atoms in cavity (e.g. an oven, a star)

Review of electromagnetic (EM) waves:

Classically, EM waves are solutions to wave equation $\nabla^2 \mathbf{E} = \frac{1}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2}$ from Maxwell's equations.

The electric field of an EM wave has the form

$$\mathbf{E} = \mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}$$

The wavevector **k** gives the EM waves propagation direction and wavelength ($k = 2\pi/\lambda$) and ω is the oscillation angular frequency. EM wave can have two transverse polarizations $\perp$ to **k** given by **E**. The wave equation gives the following relation between **k** and ω:

$$|\mathbf{k}|^2 = k^2 = \frac{\omega^2}{c^2}$$

In a cavity, only certain wavenumbers k are allowed. Each allowed EM wave is called a mode.

Quantum mechanics shows that an EM wave of frequency ω has energy quantized according to

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

where $s = 0, 1, 2\cdots$ is the number of quanta, or photons, in that oscillation. The zero-point energy $\frac{1}{2}\hbar\omega$ is conventionally dropped.

The partition function for one EM wave (or mode) is:

$$Z = \sum_{s=0}^{\infty} e^{-\beta\varepsilon_s} = \sum_{s=0}^{\infty} e^{-\beta\hbar\omega s} = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

using $\sum_{s=0}^{\infty} x^s = \frac{1}{1-x}$, true when $|x| < 1$.

As we showed before from the Einstein model, the average energy U is:

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

omitting the $\frac{1}{2}\hbar\omega$. $\langle s\rangle = \dfrac{1}{e^{\beta\hbar\omega}-1}$ is the average number of photons in an EM mode at temperature *T*.

At high temperatures $\hbar\omega \ll k_B T$, $\langle s\rangle \approx k_B T/\hbar\omega$, and $U \approx k_B T$, as expected from equipartition.

This is for a <u>single</u> EM mode of frequency *ω*. For U_{tot} we need to sum up over <u>all</u> possible *ω*. Not all *ω* are allowed; the cavity imposes boundary conditions, such that $\mathbf{E}_{\parallel}\big|_{\text{walls}} = 0$.

Solutions are standing waves of the form:

$$E_x = E_{x0}e^{-i\omega t}\cos\left(\frac{n_x\pi}{L_x}x\right)\sin\left(\frac{n_y\pi}{L_y}y\right)\sin\left(\frac{n_z\pi}{L_z}z\right)$$
$$E_y = E_{y0}e^{-i\omega t}\sin\left(\frac{n_x\pi}{L_x}x\right)\cos\left(\frac{n_y\pi}{L_y}y\right)\sin\left(\frac{n_z\pi}{L_z}z\right)$$
$$E_z = E_{z0}e^{-i\omega t}\sin\left(\frac{n_x\pi}{L_x}x\right)\sin\left(\frac{n_y\pi}{L_y}y\right)\cos\left(\frac{n_z\pi}{L_z}z\right)$$

with $n_{x,y,z} = 1,2,3\cdots$, i.e. standing waves with $k_x = \dfrac{n_x\pi}{L_x}$, $k_y = \dfrac{n_y\pi}{L_y}$, and $k_z = \dfrac{n_z\pi}{L_z}$.

Each mode of oscillation is given by set of integers $\{n_x, n_y, n_z\}$. So,

$$\omega_n = c\sqrt{k_x^2+k_y^2+k_z^2} = \pi c\sqrt{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}}$$

i.e. only certain energies $\hbar\omega_n$ are allowed (using the shorthand $n = \{n_x, n_y, n_z\}$):

$$Z_{tot} = \prod_{\text{modes } n}\left(1-e^{-\beta\hbar\omega_n}\right)^{-1}$$
$$U_{tot} = \sum_{\text{modes } n}\frac{\hbar\omega_n}{e^{\beta\hbar\omega_n}-1} = \sum_{\text{modes } n}\hbar\omega_n\langle s_n\rangle$$

(where $\displaystyle\sum_{\text{modes } n} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty}$)

(Note: this is a difference with the Einstein model. In the Einstein model, we assumed all the oscillators are <u>identical</u>. Here the oscillators are all different $\hbar\omega_n$ due to the different modes.)

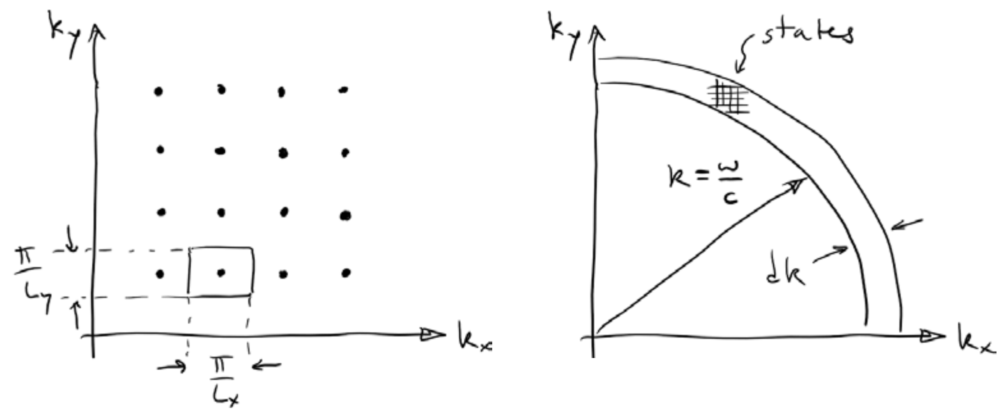
KEY CONCEPT: density of states

There is no analytic expression for this sum. We use approximation from Lect. 4, turning the sum into an integral over angular frequency ω (basically equivalent to energy since $\varepsilon = \hbar\omega$):

$$\sum_{\text{modes } n} \rightarrow \int_0^\infty d\omega\, D(\omega)$$

The sum enumerates modes. In the integral we need the number of modes that have angular frequency in the range ω to $\omega+d\omega$. This is related to the <u>density of states</u> $D(\omega)$, which we first encountered in Lect. 4

Each mode can be represented as a point on a lattice in *k*-space



Each mode occupies $\frac{\pi}{L_x}\frac{\pi}{L_y}\frac{\pi}{L_z} = \frac{\pi^3}{V}$ volume in *k*-space*

States of constant ω lie on a spherical shell in *k*-space with radius $k = \omega / c$

Question 1: Write down an expression for the density of states of the photon gas $D(\omega)$

$$\begin{array}{r}\text{\# of modes with frequency} \\ \text{between } \omega \text{ and } \omega+d\omega\end{array} \approx \frac{\text{volume of shell in } k\text{-space with radius } k = \omega / c}{\text{volume in } k\text{-space per state}}$$

$$D(\omega)d\omega \approx \underset{\uparrow}{2}\frac{4\pi k^2 dk/8}{\pi^3/V} = \frac{V}{\pi^2}k^2 dk = \frac{V}{\pi^2}\frac{\omega^2 d\omega}{c^3}$$

*We also need to account for 2 polarization states of each mode

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Note that this is equivalent to writing:

$$2\times\sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \rightarrow 2\times\int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z = 2\frac{L_x L_y L_z}{\pi^3}\int_0^\infty dk_x \int_0^\infty dk_y \int_0^\infty dk_z = 2\frac{V}{\pi^3}\frac{4\pi}{8}\int_0^\infty dk\, k^2$$

Note: we could have used periodic boundary conditions for the cavity instead, in which the solutions would have been traveling waves with

$$k_x = \frac{n_x \pi}{L_x},\ k_y = \frac{n_y \pi}{L_y},\ \text{and}\ k_z = \frac{n_z \pi}{L_z}\ \text{ and }\ n_{x,y,z} = 0, \pm 1, \pm 2 \cdots$$

In this case, each mode takes a volume in k-space of $(2\pi)^3/V$, but we would have to integrate over a complete shell (instead of 1/8 of a shell) because $k_{x,y,z}$ can now be negative. We get the same answer – factor of 2^3 for volume per mode cancels with 8× larger shell volume.

KEY CONCEPTS: Planck radiation law, blackbody

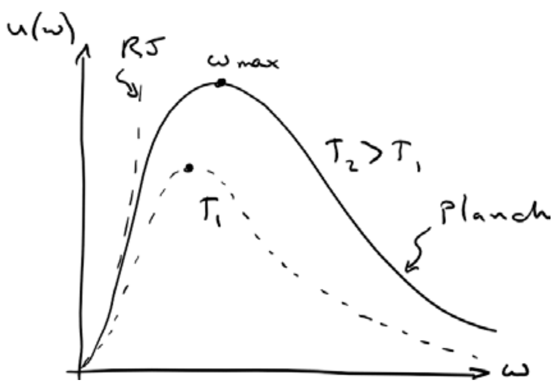
Putting it all together,

$$U_{tot} = \sum_n \frac{\hbar\omega_n}{e^{\beta\hbar\omega_n} - 1} \approx \int_0^\infty d\omega\, D(\omega) \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = \int_0^\infty d\omega \frac{V}{\pi^2} \frac{\omega^2}{c^3} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

Considering the energy density $u = U/V$ instead

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

$u(\omega)$ is the energy density in a frequency band ω, $\omega + d\omega$ – 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

Where is the peak? Define $x = \beta\hbar\omega = \frac{\hbar\omega}{k_B T}$

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

Gives trivial solutions $x = 0, \infty$, and a nontrivial solution:

$$3 = \frac{x e^x}{e^x - 1} \quad \text{or} \quad 3(1 - e^{-x}) = x$$

which is solved numerically by $x_{max} = 2.82$, so

$$\hbar\omega_{\max} = 2.82 k_B T$$

also called Wien's displacement law

<u>Blackbody</u> – idealized object that absorbs all EM radiation (at all ω or λ). In thermal equilibrium at temperature T, a blackbody emits radiation according to the Planck radiation law $u(\omega)$.

Ex: Cosmic microwave background (CMB)
Early universe was filled with hot ionized gas interacting strongly with EM radiation – photon gas at thermal equilibrium at $T \approx 3000$ K ($\lambda_{peak} \sim$ µm). Universe expanded (can think of this as isentropic expansion) and photon λ was stretched or Doppler-shifted ~1000×. Today, remnant looks like blackbody at $T = 2.73$ K ($\lambda_{peak} \sim$ mm), although photon gas is no longer at equilibrium.

CMB is as close to an ideal blackbody as you can find in nature. Most objects (e.g. celestial bodies) show deviations from $u(\omega)$, but Planck radiation law is a good first approximation.

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

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

This is called the <u>Raleigh-Jeans law</u>. This is a classical result (notice $\hbar$ disappeared from expression). Without QM, predicts $u(\omega) \propto \omega^2$ (see curve above)

Notice that Raleigh-Jeans law would predict that

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

This was called the <u>ultraviolet catastrophe</u>. RJ model predicted that if we'd open an oven, high energy EM radiation (ultraviolet, X-rays, etc.) would come out!

The failure of the classical model / equipartition theorem lead to idea of photon and QM.

KEY CONCEPT: Stefan-Boltzmann law
What is u_{tot} with correct $u(\omega)$?

Question 2: Show that the correct u_{tot} scales as T^γ and find the value of γ.

The correct expression for the total energy is

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

Define $x \equiv \beta\hbar\omega = \frac{\hbar\omega}{k_B T}$, so $dx = \frac{\hbar}{k_B T} d\omega$

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

i.e. the area under curve is proportional to T^4. Notice the difference with an ideal gas: $U \sim T$.

Let's evaluate the integral in *x*. We will encounter many integrals of the form:

$$\int_0^\infty dx \frac{x^n}{e^x - 1} = \int_0^\infty dx \frac{x^n e^{-x}}{1 - e^{-x}} = \int_0^\infty dx\, x^n e^{-x} \sum_{k=0}^\infty e^{-kx} = \int_0^\infty dx\, x^n \sum_{k=1}^\infty e^{-kx}$$

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

where the Gamma function $\Gamma(n+1) = n!$ for integers, and

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

is called the Riemann zeta function. We can look this up in a table:

$$\varsigma(4) = \frac{\pi^4}{90} \text{ and } \Gamma(4) = 3! = 6$$

Putting it all together, we get the <u>Stefan-Boltzmann law</u> of radiation:

$$u_{tot} = \frac{\pi^2}{15} \frac{(k_B T)^4}{(\hbar c)^3}$$

Question 3: Find an expression for the entropy *S* of the photon gas given $u_{tot} = \alpha T^4$

Hint: use the thermodynamic identity.

The cavity has a fixed volume *V* so $dU = TdS - \cancel{pdV}$

$$dS = \frac{dU}{T} = 4\alpha V \frac{T^{\cancel{3}2} dT}{\cancel{T}} = 4\alpha V T^2 dT$$

$$S = \int dS = \frac{4}{3}\alpha V T^3 + \text{const.}$$

The constant of integration is zero by the third law of thermodynamics, i.e. $S(T \to 0) = 0$. So,

$$S(T,V) = \frac{4}{3}\alpha V T^3 \quad \text{or} \quad S(U,V) = \frac{4}{3}(\alpha V)^{1/4} U^{3/4}$$

Notice the difference in dependence compared to an ideal gas: $S \sim \ln U$
