Classical versus Quantum Systems

- Translational partition function for N ideal gas particles

$$Z_{3D} = \frac{1}{N!}\left(\frac{V}{\upsilon_Q}\right)^N \qquad \text{where } \upsilon_Q = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3$$

- Usually have very large number of states available and much smaller number of particles

- When $\upsilon_Q(=l_Q^3) << V/N$, there is very little chance for two particles to be in the same state (dilute gas, ideal gas…)

Bosons versus Fermions

- As we move to discussing more interesting systems, we need to consider quantum statistics

- So far, have assumed that two particles in our system could occupy the same state but it was unlikely

- However, some types of particles can share the same state but others cannot
  - Bosons (e.g. photons, He atoms) - can share same state
  - Fermions (e.g. electrons) - cannot share the same state (Pauli exclusion principle - two identical fermions cannot occupy the same state)

Blackbody Radiation

- Consider radiation given off by "object" when heated
  - Such as a stove burner, resistive heater element
- As temperature of "object" increases, peak in emitted frequencies increases
  - Exact shape of frequency spectrum depends on "object"
- Ideal is a "blackbody"
  - Emits and absorbs all frequencies of radiation perfectly
  - Radiation emitted is "blackbody radiation"

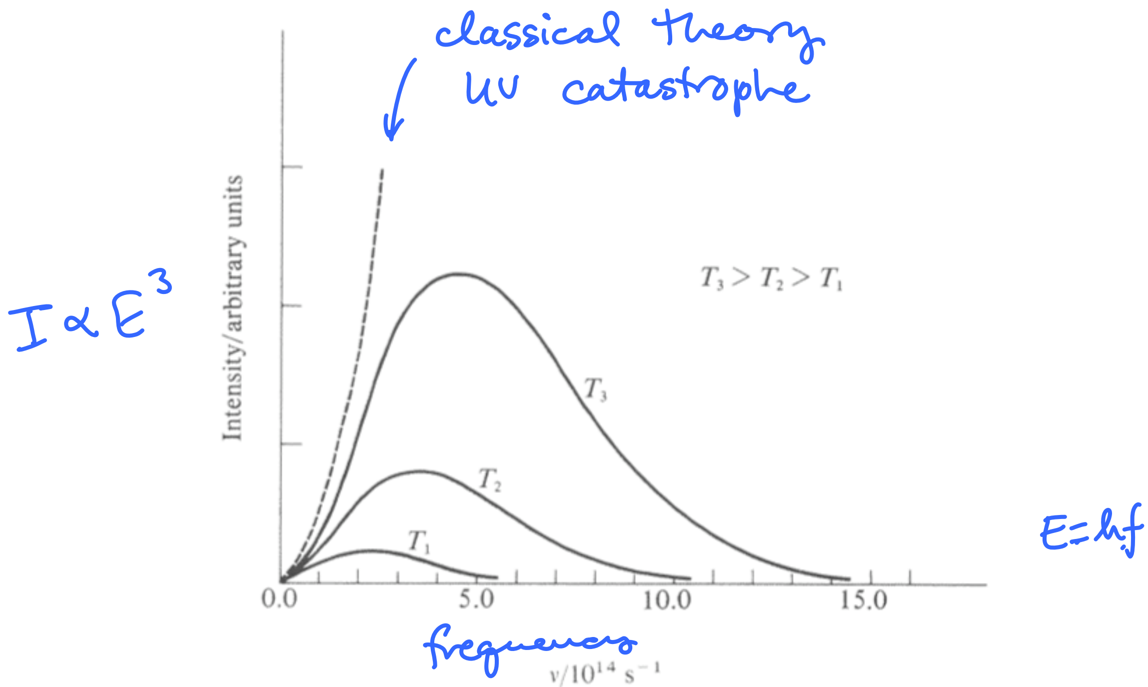
Description of Electromagnetic Field

Starting with a classical description of EM field:

- Radiation field exists inside a box at a given temperature
- Box can support various standing wave patterns and each acts as a harmonic oscillator ($f = c / \lambda$)
- In this classical description,
  - Each has average thermal energy, kT
  - Total thermal energy is infinite ← from number of modes can be supported

    $U = kT \cdot \infty$

Blackbody Radiation



From McQuarrie, Quantum Chemistry, 1e

Photons

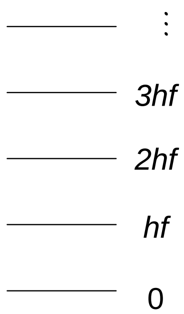
- Photons are bosons - consider as a photon gas
  - Number of photons is not conserved in system
  - Don't need to consider chemical potential (μ)
  - Special case of Bose-Einstein distribution

- Want to calculate total energy of photons in box
  - Count number of photons for given energy
  - Convert number distribution to energy distribution
  - Sum over all energies
  - Convert sum to integral and calculate integral

Planck Distribution

Quantum mechanical description is needed

- For a single wavelength (single mode)
  - photon $\Leftrightarrow$ harmonic oscillator



$E = nhf$

n = # of photons
f = frequency

$$Z = 1 + e^{-\beta hf} + e^{-2\beta hf} \ldots\ldots$$
$$= \frac{1}{1 - e^{-\beta hf}}$$

Average Energy

- For this mode, $\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$

$$\overline{E} = -(1 - e^{-\beta hf}) \cdot \frac{1}{(1 - e^{-\beta hf})^2} \cdot \left[-hf\, e^{-\beta hf}\right]$$

$$= \frac{hf e^{-\beta hf}}{1 - e^{-\beta hf}}$$

$$= \frac{hf}{e^{\beta hf} - 1} = hf\,\overline{n}$$

Planck Distribution

- Number of oscillators inside box that contribute to energy is finite

$$\bar{n}_{Pl} = \frac{1}{e^{hf/kT} - 1}$$

as $hf \gg kT$ → number of oscillators with this energy becomes small

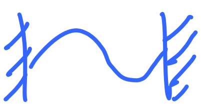
→ puts finite limit on total number of oscillators contributing to energy

→ avoids UV catastrophe

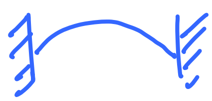
Allowed Frequencies for Photon Gas

Consider 1-D box of length L

- Allowed wavelengths and momenta for photons



$\lambda = L$



$\lambda = 2L$

$p = \frac{h}{2L} \cdot n$

n = mode label

$E = hf \quad f = c/\lambda$

$E = p \cdot c$

$= \frac{hcn}{2L}$

3D

$$E = p \cdot c = \sqrt{p_x^2 + p_y^2 + p_z^2} \cdot c$$

$$= \frac{hc}{2L}\sqrt{n_x^2 + n_y^2 + n_z^2}$$ ← magnitude of mode label vector

$$= \frac{hcn}{2L}$$

Total Energy

$$E \cdot \bar{n} = \bar{n} \cdot hf$$

$$U = \sum_f \bar{n}_f hf$$

$$= 2\sum_{n_x, n_y, n_z} \frac{hcn}{2L} \cdot \frac{1}{e^{hcn/2kTL} - 1}$$

need factor of two for independent polarizations of each mode

$$= \sum_{n_x, n_y, n_z} \frac{hcn}{L} \cdot \frac{1}{e^{hcn/2kTL} - 1}$$

$$n^2 = n_x^2 + n_y^2 + n_z^2$$

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

$$= \int dn_x \, dn_y \, dn_z \, \frac{hc}{L}\sqrt{n_x^2 + n_y^2 + n_z^2} \, \frac{1}{e^{hcn/2kTL} - 1}$$

to spherical coordinates

$n_x, n_y, n_z \longrightarrow n, \theta, \phi$

$dn_x dn_y dn_z \longrightarrow n^2 \sin\theta \, d\theta \, d\phi \, dn$

figure shown in fig 7.11

$$U = \int_0^\infty dn \, n^2 \frac{hcn}{L} \frac{1}{e^{hcn/2kTL} - 1} \underbrace{\int_0^{\pi/2} \sin\theta \, d\theta}_{1} \underbrace{\int_0^{\pi/2} d\phi}_{\pi/2}$$

$$= \frac{\pi}{2} \int_0^\infty dn \, n^2 \frac{hcn}{L} \frac{1}{e^{hcn/2kTL} - 1}$$

$$= \frac{\pi}{2} \int_0^\infty d\varepsilon \frac{2^4 L^3 \varepsilon^3}{h^3 c^3} \cdot \frac{1}{e^{hcn/2LTk} - 1}$$

$\varepsilon = \frac{hcn}{2L}$ $\quad d\varepsilon = \frac{hc}{2L} dn$

result is

$$U = \frac{8\pi L^3}{h^3 c^3} \int_0^\infty \frac{\varepsilon^3 d\varepsilon}{e^{\varepsilon/kT} - 1}$$

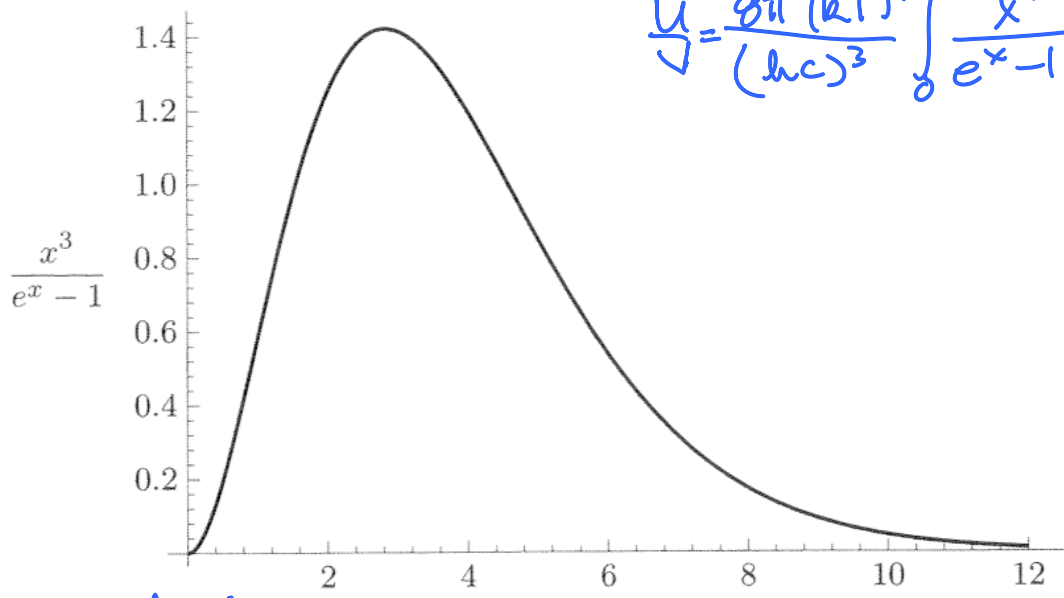
$L^3 = V$

$$\frac{U}{V} = \frac{8\pi}{h^3 c^3} \int_0^\infty \frac{\varepsilon^3 d\varepsilon}{e^{\varepsilon/kT} - 1}$$

spectrum of energy density $\left(\frac{U}{V}\right)$ per unit energy (ε)

Planck Spectrum

$$\frac{U}{V} = \frac{8\pi (kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1}\, dx$$



the peak in spectrum

$\varepsilon = 2.82\, kT$ ← Wien's Law