Quantum statistics

" Till now we talked about distinguishable entities with classical or quantum description".

Density Matrix:

Ensemble : N identical systems

$\downarrow$

Common Hamiltonian $\hat{H}$

$\downarrow$

kth state description $\psi^k(\vec{r}_i, t)$

$\downarrow$

Time variation : $\hat{H}\psi^k(t) = i\hbar\dot{\psi}^k(t)$

$\downarrow$

Braking ψ^k : $\psi^k(t) = \sum_n a_n^k(t)\,\phi_n$

↳ orthonormal functions

$$a_n^k(t) = \int \phi_n^* \psi^k(t)\, d\tau$$

↳ Vol^n element

↳ Probability amplitude of k^{th} system being in ϕ_n state!

$$\sum_n |a_n^k(t)|^2 = 1 \quad \text{for all } k$$

$\downarrow$

Density operator: $\underbrace{\rho_{mn}(t)} = \frac{1}{N}\sum_{k=1}^{N}\left[a_m^k(t)\, a_n^{*k}(t)\right]$

↳ Ensemble average of the quantity $a_m(t)a_n^*(t)$

Diagonal element : $\rho_{nn} \to$ ensemble average of prob $\underbrace{|a_n(t)|^2}_{\text{quantum mechanical average}!}$

This is the double-averaging → (i) quantum mechanical aspect of the states (wave functions) (ii) statistical aspect of the ensemble.

Properties of $\rho \to \quad \sum_n \rho_{nn} = 1$

$$i\hbar \dot{\rho}_{mn} = (\hat{H}\hat{\rho} - \hat{\rho}\hat{H})_{mn} \quad \left(\text{or, } i\hbar \dot{\hat{\rho}} = [\hat{H}, \hat{\rho}] \right)$$

Special Case → $\hat{H}\phi_n = E_n \phi_n$

$\downarrow$

$H_{mn} = E_n \delta_{mn}, \quad \rho_{mn} = \rho_n \delta_{mn}$

Energy Repn.

Another general property → $\rho_{mn} = \rho_{nm}$

(If a system wants to switch from $m \to n$ should be balanced by that of $n \to m$)

Other properties → $\mathrm{Tr}(\hat{\rho}) = 1$

Any physical quantity → $\langle G \rangle = \mathrm{Tr}(\hat{\rho}\hat{G})$ if norm $= 1$

$$= \frac{\mathrm{Tr}(\hat{\rho}\hat{G})}{\mathrm{Tr}(\hat{\rho})} \quad \text{if norm} \neq 1$$

MCE : An ensemble of $\mathcal{N}$ identical systems with N, V and $E \to (E \pm \frac{1}{2}\Delta E)$, where $\Delta \ll E$.

$\Gamma(N, V, E; \Delta) \to$ Total # of distinct microstates

$\hookrightarrow$ Any one of them is as likely to be as the others (PEAP)

In energy Rep^{n}.

$$\rho_{mn} = \rho_n \delta_{mn}$$

with,

$$\rho_n = \begin{cases} 1/\Gamma & \text{for accessible microstates} \\ 0 & \text{all other states} \end{cases}$$

But this should be true for any other ~~stal~~ Rep^{n} as well!
((i) Non-diag elements to be zero. (ii) All diag elements are equal)
How do we ensure that?

Postulate of ~~a~~ random a priori phases $\to$
Random phases for probability amplitudes $a_n^k \Rightarrow \psi^k$ (for all k) is an incoherent superposition of the basis $\{\phi_n\}$

$$\rho_{mn} = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} a_m^k a_n^{k*} = \frac{1}{\mathcal{N}} \sum_{k=1}^{\mathcal{N}} |a|^2 e^{i(\theta_m^k - \theta_n^k)}$$

$$= c \left\langle e^{i(\theta_m^k - \theta_n^k)} \right\rangle$$

(To ensure no interference b/w member systems)

$$= c\,\delta_{mn}$$

CE →

Macro state → N, V, T

Probability that a system has energy E_r → $\exp(-\beta E_r)$

In energy repⁿ →

$$\rho_{mn} = \rho_n \delta_{mn}$$

with

$$\rho_n = C \exp(-\beta E_n) \qquad n = 0, 1, 2 ..$$

$$C = \frac{1}{\sum_n \exp(-\beta E_n)} = \frac{1}{Q_N(\beta)}$$

normalization condition

partition function

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Tr(e^{-\beta \hat{H}})}$$

$$\langle G \rangle = \frac{Tr(\hat{G} e^{-\beta \hat{H}})}{Tr(e^{-\beta \hat{H}})}$$

GCE :→

Both energy and # of particle can change!

Density operator →

$$\hat{\rho} = \frac{1}{\mathcal{Q}(\mu, V, T)} e^{-\beta(\hat{H} - \mu \hat{n})}$$

$$\mathcal{Q}(\mu, V, T) = \sum_{r,s} e^{-\beta(E_r - \mu N_s)}$$

$$= \mathrm{Tr}\left\{ e^{-\beta(\hat{H} - \mu \hat{n})} \right]$$

The ensemble average →

$$\langle G \rangle = \frac{1}{\mathcal{Q}(\mu, V, T)} \mathrm{Tr}\left(\hat{G} e^{-\beta \hat{H}} e^{\beta \mu \hat{n}} \right)$$

→ Canonical ensemble average

$$= \frac{\sum_{N=0}^{\infty} z^N \langle G \rangle_N \mathcal{Q}_N(\beta)}{\sum_{N=0}^{\infty} z^N \mathcal{Q}_N(\beta)}$$

→ Canonical partition function

$$z = e^{\beta \mu}$$ → fugacity / activity.

A free particle in a box $\rightarrow$

Hamiltonian $\rightarrow$ $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$

Eigenfunctions $\rightarrow$

B.C. $\rightarrow \Phi(x+L, y, z) = \Phi(x, y+L, z) = \Phi(x, y, z+L) = \Phi(x, y, z)$

Eigenstates $\rightarrow$ $\Phi_E(r) = \frac{1}{L^{3/2}} \exp(i\vec{k}\cdot\vec{r})$

Eigenvalues $\longrightarrow$ $E = \frac{\hbar^2 k^2}{2m}$

$$\vec{k} = (k_x, k_y, k_z) = \frac{2\pi}{L}(n_x, n_y, n_z)$$

co-ordinate rep^n. $\rightarrow \langle \vec{r} | e^{-\beta\hat{H}} | \vec{r}' \rangle = \sum_E \langle \vec{r} | E \rangle e^{-\beta E} \langle E | \vec{r}' \rangle$

$$= \sum_E e^{-\beta E} \Phi_E(\vec{r}) \Phi_E^*(\vec{r}')$$

$$= \left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2} \exp\left[-\frac{m}{2\beta\hbar^2}|\vec{r}-\vec{r}'|^2\right]$$

$$\mathrm{Tr}(e^{-\beta\hat{H}}) = V\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}$$

Density matrix $\longrightarrow$ So, $\langle \vec{r} | \hat{\rho} | \vec{r}' \rangle = \frac{1}{V}\exp\left[-\frac{m}{2\beta\hbar^2}|\vec{r}-\vec{r}'|^2\right]$

$\rightarrow$ diag $(\vec{r}' = \vec{r}) \Rightarrow \hat{P}_n = \frac{1}{V}$ [all are equally probable]

$\rightarrow$ non-diag $\rightarrow$ prob of "spontaneous transition" b/w co-ords.

A measure of 'intensity' of wave-packet at a relative distance $|\vec{r}-\vec{r}'|$ from the center of the wave packet.

→ uncertainty!

spatial extent of uncertainty $\sim \dfrac{\hbar}{(mkT)^{1/2}} = \dfrac{\hbar\beta^{1/2}}{m^{1/2}}$

as $\beta \to 0$ $\quad \rho_{mn} = \underbrace{\frac{1}{V}\delta_{mn}}_{}$

→ classical picture!
(High Temperature)

Linear Harmonic Oscillator →

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + \frac{1}{2}m\omega^2 q^2$$

$$E_n = (n+\tfrac{1}{2})\hbar\omega \qquad , n = 0,1,2 \ldots$$

$$\phi_n(q) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4}\frac{H_n(\xi)}{(2^n n!)^{1/2}}\, e^{-(1/2)\xi^2}$$

$\xi \to \left(\dfrac{m\omega}{\hbar}\right)^{1/2} q$

$$H_n(\xi) = (-1)^n e^{\xi^2}\left(\frac{d}{d\xi}\right)^n e^{-\xi^2}$$

Matrix elements of the operator $\exp(-\beta\hat{H})$ in the q-repⁿ. →

$$\langle q|e^{-\beta\hat{H}}|q\rangle = \sum_{n=0}^{\infty} e^{-\beta E_n}\phi_n(q)\phi_n(q')$$

$$= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-(1/2)(\xi^2+\xi'^2)} \times \sum_{n=0}^{\infty}\left[e^{-(n+\frac{1}{2})\beta\hbar\omega}\frac{H_n(\xi)H_n(\xi')}{2^n n!}\right]$$

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$$\langle q|e^{-\beta\hat{H}}|q\rangle = \left[\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)}\right]^{1/2} \times \exp\left[-\frac{m\omega}{4\hbar}\left[(q+q')^2\tanh\left(\frac{\beta\hbar\omega}{2}\right) + (q-q')^2 \times \coth\left(\frac{\beta\hbar\omega}{2}\right)\right]\right],$$

$$\downarrow$$

$$\mathrm{Tr}(e^{-\beta\hat{H}}) = \int_{-\infty}^{\infty} \langle q|e^{-\beta\hat{H}}|q\rangle\, dq$$

$$= \left[\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)}\right]^{1/2} \int_{-\infty}^{\infty} \exp\left[-\frac{m\omega q^2}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right] dq$$

$$= \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \rightarrow \text{Partition function}$$

Probability density for the oscillator co-ordinate to be in the vicinity of the value q →

$$\langle q|\hat{\rho}|q\rangle = \underbrace{\left[\frac{m\omega\tanh(\frac{1}{2}\beta\hbar\omega)}{\pi\hbar}\right]^{1/2} \exp\left[-\frac{m\omega q^2}{\hbar}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right]}_{\text{Gaussian distribution in } q},$$

mean value → 0

r.m.s deviation → $q_{r.m.s} = \left[\dfrac{\hbar}{2m\omega\tanh(\frac{1}{2}\beta\hbar\omega)}\right]$

Classical limit → Purely thermal distribution
$(\beta\hbar\omega \ll 1)$

$$\hookrightarrow \langle q|\hat{\rho}|q\rangle = \left(\frac{m\omega^2}{2\pi kT}\right)^{1/2}\exp\left[-\frac{m\omega^2 q^2}{2kT}\right]$$

↳ dispersion $= \left(\dfrac{kT}{m\omega^2}\right)^{1/2}$

Other extreme → Purely quantum mechanical
$(\beta\hbar\omega \gg 1)$

$$\hookrightarrow \langle q|\hat{\rho}|q\rangle = \left[\left(\frac{m\omega}{\pi\hbar}\right)^{1/2}\exp\left[-\frac{m\omega q^2}{\hbar}\right]\right.$$

↳ dispersion $= \left(\dfrac{\hbar}{2m\omega}\right)^{1/2}$

Oscillator in ground state

Systems composed of indistinguishable particles →

$$\hat{H}(\vec{q},\vec{p}) = \sum_{i=1}^{N} \hat{H}_i(q_i,p_i)$$

→ Hamiltonian of N non-interacting particles

→ identical Hamiltonian

$$\hat{H}\Psi_E(\vec{q}) = E\Psi_E(\vec{q})$$

→ Time-independent Schrodinger equation

Solution

$$\Psi_E(\vec{q}) = \prod_{i=1}^{N} u_{\varepsilon_i}(q_i)$$

$$\hat{H}_i u_{\varepsilon_i}(q_i) = \varepsilon_i u_{\varepsilon_i}(q)$$

and, $E = \sum_{i=1}^{N} \varepsilon_i$

Stationary state of the system →

Characterized by → $\{n_i\}$

→ How many particles are in the state signified by ε_i.

Conditions → $\sum_i n_i = N$

$$\sum_i n_i \varepsilon_i = E$$

Wave-function of the system →

$u_i(m) \equiv u_{\varepsilon_i}(q_m)$

$$\Psi_E(\vec{q}) = \prod_{m=1}^{n_1} u_1(m) \prod_{m=n_1+1}^{n_2} u_2(m) \dots$$

What if we make some permutations? (Reshuffle)

$$P\Psi_E(\vec{q}) = \prod_{m=1}^{n_1} u_1(Pm) \prod_{m=n_1+1}^{n_2} u_2(Pm) \dots$$

As a result, taking the Gibbs Paradox correction into account, the statistical weight factor →

$$W_c\{n_i\} = \frac{1}{n_1!\, n_2! \cdots}$$

Essentially corresponds to the fact that, exchange of two particles in the same energy state, leads to a new distinct state → distinguishable particles.

↳ Not the case for indistinguishable particles.

⊙ Can not label particles, so can not 'interchange' them!

So irrespective of the value of $\{n_i\}$ →

$$W_q\{n_i\} = 1$$

If it is not allowed → $W_q\{n_i\} = 0$.

↳ This means changing arguments of u_i to u_j $(i \neq j)$ does not change ~~the~~ anything!

So, $$|P\psi|^2 = |\psi|^2$$

Possibility - I : $P\psi = \psi$ for all P → symmetric (ψ_s)

Possibility - II : $P\psi = \begin{cases} +\psi & \text{if } P \text{ is an even perm} \\ -\psi & \text{if } P \text{ is an odd perm} \end{cases}$

↳ antisymmetric (ψ_A)

So, $$\psi_s(\vec{q}) = \text{const} \sum_P P\psi_{E(\text{Boltz})}(\vec{q})$$

$$\psi_A(\vec{q}) = \text{const} \sum_P \delta_P P\psi_{E(\text{Boltz})}(\vec{q})$$

δ_P ↳ +1 (even P)

↳ −1 (odd P)

Slater determinant →

$$\Psi_A(\vec{q}) = \text{const} \times \begin{vmatrix} u_i(1) & u_i(2) & \cdots & u_i(N) \\ u_j(1) & u_j(2) & \cdots & u_j(N) \\ \vdots & \vdots & \ddots & \vdots \\ u_\ell(1) & u_\ell(2) & \cdots & u_\ell(N) \end{vmatrix}$$

- Automatically takes care of δ_P (+1 or −1) when we expand it.
- Interchanging a pair of arguments (interchanging columns) just changes the sign of $\Psi_A(\vec{q})$
- If two or more particles are in the same single particle states, then corresponding rows will be same, so Ψ_A vanishes!

$P\Psi_A = \Psi_A$ if we change two particles in the same energy state.

$P\Psi_A = -\Psi_A$ because it is a odd permutation

So, $\boxed{\Psi_A = 0}$ → Pauli's exclusion principle.

So,

$$W_{F.D}\{n_i\} = \begin{cases} 1 & \text{if } n_i = 0, 1 \\ 0 & \text{if } n_i > 1 \end{cases}$$

$$W_{B.E}\{n_i\} = 1 \quad \text{for } n_i = 0, 1, 2 \ldots$$

Theory of gases

Considering systems with non-interacting distinguishable or indistinguishable particles.

From the MCE perspective:

Macrostate : $\Omega (N, V, E)$

# of Microstates : $\Omega (N, V, E)$

Large V, single particle energy levels are very close to each other, so we consider group of energy levels.
↳ energy cell.

avg energy of a level → ϵ_i (cell)

# of levels in ith cell → g_i

So,
$$\sum_i n_i = N$$

$$\sum_i n_i \epsilon_i = E$$

$$\Omega(N,V,E) = \sum_{\{n_i\}}{}' \underbrace{W\{n_i\}}$$
↳ # of distinct microstate associated with the distribution set $\{n_i\}$.

$$W\{n_i\} = \prod_i \underbrace{\omega(i)}$$
↳ # of distinct microstate associated with the ith cell. ⇒ # of unique ways in which n_i identical indistinguishable particles can be distributed among g_i levels of ith cell.

Bose-Einstein case:

$$\omega_{B.E}(i) = \frac{(n_i+g_i-1)!}{n_i!(g_i-1)!}$$ (No limit on the # of particles in one level)

Fermi-Dirac case:

$$\omega_{F.D}(i) = \cancel{\frac{g_i!}{n_i!(g_i-n_i)!}} \quad \frac{g_i!}{n_i!(g_i-n_i)!}$$ (in each level # of particles ~~are~~ is either 0 or 1)

Maxwell-Boltzman case: (Classical limit)

$$\omega_{M.B}(i) = \frac{(g_i)^{n_i}}{(n_i)!}$$

CE perspective →

Partition function, $Q_N(V,T) = \sum_E e^{-\beta E}$; $\beta \to 1/kT$

$$E = \sum_\varepsilon n_\varepsilon \varepsilon$$

n_ε → # of single particles in energy level ε.

ε → single particle energy

E → Total energy of the system. Eigenvalue.

Partition function can also be expressed as.

$$Q_N(V,T) = \sum_{\{n_\varepsilon\}} \underbrace{g\{n_\varepsilon\}}_{\text{statistical weight factor.}} e^{-\beta \sum n_\varepsilon \varepsilon}$$

Can come from the above formulae with $g_i = 1$ → individual energy level.

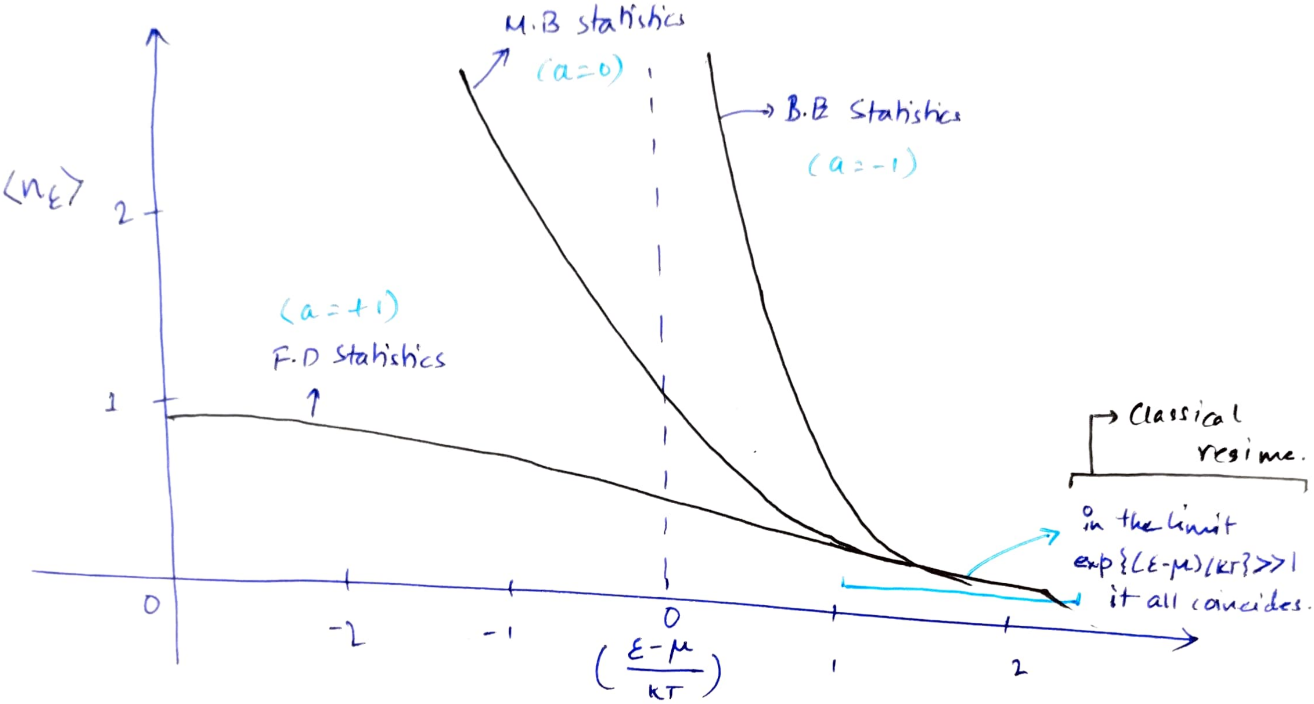
$$g_{B.E}\{n_\varepsilon\} = 1$$

$$g_{F.D}\{n_\varepsilon\} = \begin{cases} 1 & \text{if all } n_\varepsilon = 0 \text{ or } 1 \\ 0 & \text{otherwise} \end{cases}$$

$$g_{M.B}\{n_\varepsilon\} = \prod_\varepsilon \frac{1}{n_\varepsilon!}$$

Mean occupation number:

$$\langle n_\varepsilon \rangle = \frac{1}{e^{(\varepsilon-\mu)/kT} + a}$$



FD Case →

- $\langle n_\varepsilon \rangle$ never exceeds unity as n_ε is always either 1 or 0.
- for $\varepsilon < \mu$ and $|\varepsilon - \mu| \gg kT$, $\langle n_\varepsilon \rangle \to 1$

BE Case →

- $\mu <$ all ε
- when μ becomes equal to lowest value of ε, the occupancy of that perticulor level becomes infinitely high → B.E condenstate

MB Case →

- Classical, $\langle n_\varepsilon \rangle \propto \exp(-\varepsilon/kT)$

Thermodynamics of Black-body radiation (Bose gas)

Random cavity of vol^{m} V and temperature T.

Two identical but conceptually different point of view →

(i) An assembly of harmonic oscillators with quantized energies $(n_s + \frac{1}{2})\hbar\omega_s$.

(ii) A gas of identical and indistinguishable quanta with energy $\hbar\omega_s$. → photon

View point (i) →

$$\langle \mathcal{E}_s \rangle = \frac{\hbar\omega_s}{e^{\hbar\omega_s/kT} - 1}$$

→ Expectation value of the energy of a Planck oscillator of frequency ω_s

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

→ # of normal modes of vibration per unit volume of cavity in the frequency range $(\omega, \omega + d\omega)$

$$u(\omega)\, d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{e^{\hbar\omega/kT} - 1}$$

→ The energy density associated with the frequency range $(\omega, \omega + d\omega)$.

→ Planck formula for distribution of energy over a black-body spectrum.

View point (ii) →

$$\langle n_s \rangle = \frac{\sum_{n_s=0}^{\infty} n_s e^{-n_s\hbar\omega_s/kT}}{\sum_{n_s=0}^{\infty} e^{-n_s\hbar\omega_s/kT}}$$

→ Mean value of n_s following Boltzmannian statistics. (Bose's treatment, ~~[illegible]~~ inherently indistinguishable)

$$= \frac{1}{e^{\hbar\omega_s/kT} - 1}$$

$$\langle \mathcal{E}_s \rangle = \hbar\omega_s \langle n_s \rangle = \frac{\hbar\omega_s}{e^{\hbar\omega_s/kT} - 1}$$

→ mean value of energy.

# of photon states with momenta lying b/w $\frac{\hbar\omega}{c}$ and $\frac{\hbar(\omega+d\omega)}{c}$

$$g(\omega)\,d\omega \simeq 2\cdot\frac{V}{h^3}\left[4\pi\left(\frac{\hbar\omega}{c}\right)^2\left(\frac{\hbar\,d\omega}{c}\right)\right]$$

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

Distribution function →

$$u'(x) = \frac{\pi^2\hbar^3c^2}{(kT)^4}\,u(x)$$

$$u'(x)\,dx = \frac{x^3\,dx}{e^x - 1}$$

$$x = \frac{\hbar\omega}{kT}$$

long wavelength ($x \ll 1$)

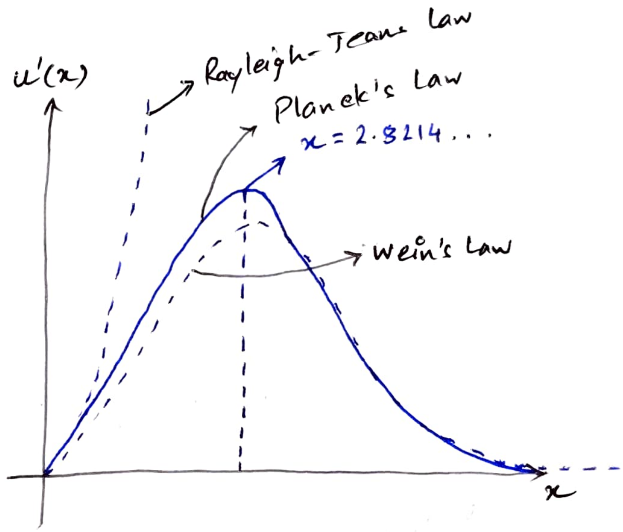
$$u'(x) \simeq x^2$$

Classical approx of Rayleigh and Jeans

Short wavelength ($x \gg 1$)

$$u'(x) \simeq x^3 e^{-x}$$

Wein's formula



Total energy density in the cavity →

$$\frac{U}{V} = \int_0^\infty u(x)\,dx = \frac{\pi^2 k^4}{15\hbar^3c^3}T^4$$

Net flow of radiation → (rate / unit area)

$$\frac{1}{4}\frac{U}{V}c = \frac{\pi^2k^4}{60\hbar^3c^2}T^4 = \sigma T^4 \rightarrow \text{Stefan-Boltzmann law}$$