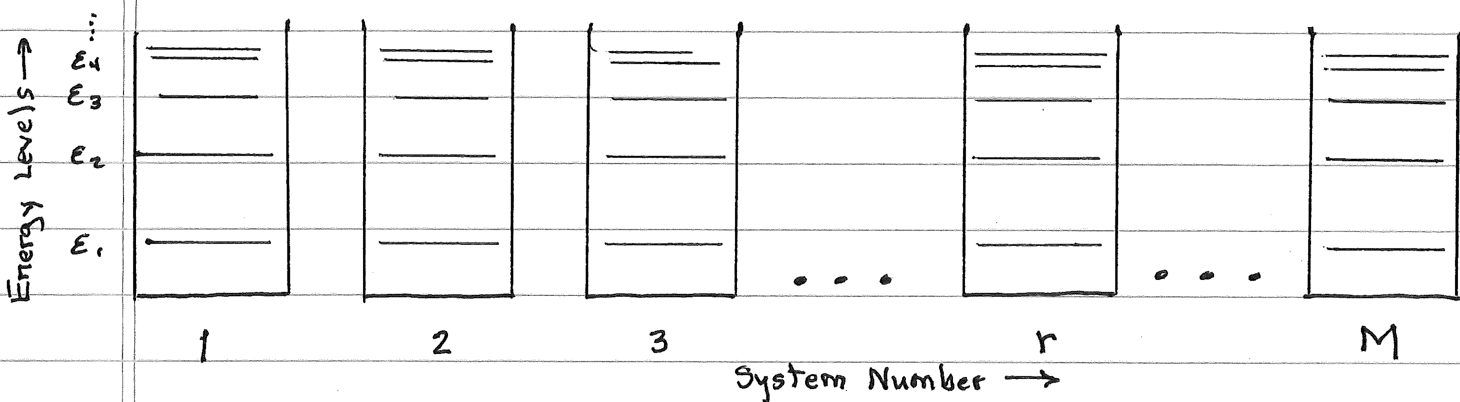
# Quantum Statistics

1. Maxwell - Boltzman statistics
2. Fermi - Dirac Statistics } Identical Particles
3. Bose - Einstein Statistics }

Ensemble of M identical systems : (i.e., atoms, potential wells, ....)




Single - particle energy states $\varepsilon_i$

Any state $\varepsilon_i$ of system r contains $n_i^{(r)}$ particles

$N_i = \sum_{r=1}^{M} n_i^{(r)}$ => The total number of particles at level $\varepsilon_i$ for all members of the ensemble $1 \to M$

Conditions:

1.) Each system has a total of exactly N particles (a vertical sum)

$$\sum_{i=1}^{\infty} n_i^{(r)} = N$$ (we're going to relax this condition)

$$\sum_{i=1}^{\infty} n_i^{(r)} = N^{(r)}$$ = the instantaneous # of particles in the $r^{th}$ system

2.) Since the average value of $N^{(r)}$ is N in each of the M systems

$$\boxed{\sum_{r=1}^{M} N^{(r)} = NM}$$

3.) Summing horizontally, the result is the number of particles $N_i$ in level $i$ for all members of the ensemble.

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TOPIC 2

# Quantum Statistics

That is: $\sum_{r=1}^{M} n_i^{(r)} = N_i$

The quantity of interest is the mean $n_i^{(r)}$ averaged over all the systems in the ensemble. The average is denoted simply by $n_i$.

$$\boxed{n_i = \frac{N_i}{M}}$$ → the most probable number of particles with energy, $\varepsilon_i$.

3.) What about the energy? Again, we're going to relax the ~~condition~~ restriction that each system have exactly energy E, and assume that it only has an average value → E.

System r has an actual value $E^{(r)}$ such that:

$$\sum_{j=1}^{\infty} n_j^{(r)} \varepsilon_j = E^{(r)} \quad \text{(a vertical sum)}$$

Since $\langle E^{(r)} \rangle = E$, we have $\boxed{\sum_{r=1}^{M} E^{(r)} = ME}$

## I. Maxwell-Boltzmann Statistics (Distinguishable Particles)

1.) How many ways can you distribute $N_i$ particles across M systems?

$$W_n^{(i)} = M^{N_i}$$

How about a different energy level? $W_n^{(j)} = M^{N_j}$

Repeat this process for all energy levels:

$$W_n = W_n^{(i)} W_n^{(j)} \quad \text{for 2 energy levels}$$

$$W_n = W_n^{(1)} W_n^{(2)} W_n^{(3)} \cdots$$

2.) Distributing the particles vertically or diagonally produces a a new configuration (or microstate).

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# Quantum Statistics

The total number of ways of interchanging $NM$ particles is $(NM)!$ However, this includes all the horizontal interchanges on each energy level $\varepsilon_i$, and these have already been considered in our calculation of $W_h$

So, $$W_{vd} = \frac{(NM)!}{N_1!\,N_2!\,N_3!\cdots}$$

vertical diagonal

Since there are $W_{vd}$ new configurations for each original one previously considered,

The total # of microstates that can occur for a fixed set of the numbers $N_1, N_2, N_3, \ldots$ is the product $W_h$ and $W_{vd}$.

$$W(N_1, N_2, N_3, \ldots) = W_h W_{vd} = (NM)!\,\frac{M^{N_1}}{N_1!}\,\frac{M^{N_2}}{N_2!}\cdots$$

$$\boxed{W(\underbrace{N_1, N_2, N_3, \ldots}_{\text{Macrostate}}) = (NM)! \prod_{i=1}^{\infty} \frac{M^{N_i}}{N_i!}}$$

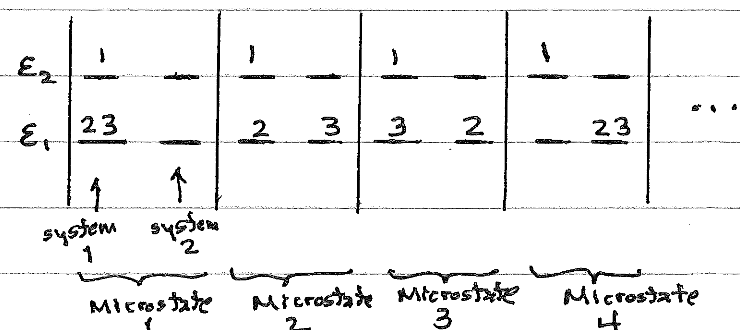
the number of microstates

Maxwell-Boltzmann Distribution.

Example: $M = 2$ systems

$MN = 3$ particles

$N_1 = 2 \quad N_2 = 1$




What is $W(2,1) = ?$

$$W(\underbrace{2,1}_{\text{Macrostate.}}) = (NM)! \prod_{i=1}^{2} \frac{M^{N_i}}{N_i!} = 3!\,\frac{2^2}{2!}\,\frac{2^1}{1!} = \frac{6(4)2}{2} = 24 \text{ microstates}$$

Quantum Statistics

Summing vertically, we get the following constraints:

(1) $$\sum_{j=1}^{\infty} N_j = \sum_{j=1}^{\infty}\sum_{r=1}^{M} n_j^{(r)} = \sum_{r=1}^{M}\sum_{j=1}^{\infty} n_j^{(r)} = \sum_{r=1}^{M} N^{(r)} = MN$$

(2) $$\sum_{j=1}^{\infty} \varepsilon_j N_j = \sum_{j=1}^{\infty} \varepsilon_j \sum_{r=1}^{M} n_j^{(r)} = \sum_{r=1}^{M}\sum_{j=1}^{\infty} \varepsilon_j n_j^{(r)} = \sum_{r=1}^{M} E^{(r)} = ME$$

$$\boxed{N = \frac{1}{M}\sum_{j=1}^{\infty} N_j}$$ and $$\boxed{E = \frac{1}{M}\sum_{j=1}^{\infty} N_j \varepsilon_j = \sum_{j=1}^{\infty} n_j \varepsilon_j}$$

Mean # of particles in each system

Mean energy of each system.

Which macrostate has the most microstates? $\frac{\partial W}{\partial N_j} = 0$

This doesn't take into account the constraints on energy (1) and the number of particles (2).

$\ln W(N_1, N_2, \ldots)$ peaks at the same macrostate as $W(N_1, N_2, \ldots)$

Use Lagrange multipliers to impose the 2 constraints:

Auxiliary function

$$F(N_1, N_2, \ldots, \alpha, \beta) = \ln W(N_1, N_2, \ldots) - \alpha\left(\sum_j N_j - NM\right) - \beta\left(\sum_j \varepsilon_j N_j - EM\right)$$

$$\ln(W) = \ln\left[(NM)!\right] + \ln M^{N_1} + \ln M^{N_2} + \cdots - \ln N_1! - \ln N_2! - \cdots$$
$$= \ln\left[(NM)!\right] + \sum_{j=1}^{\infty}\left(N_j \ln M - N_j \ln N_j + N_j\right)$$

# Quantum Statistics

The Auxiliary function becomes:

$$F(N_1, N_2, \ldots \alpha, \beta) = \ln\left[(MN)!\right] + \sum_i \left\{ N_i \ln M - N_i \ln N_i + N_i - \alpha N_i - \beta N_i \varepsilon_i \right\} + \alpha NM + \beta EM$$

Now, carry out the maximization: $\dfrac{\partial F}{\partial N_i} = 0$

$$0 = \frac{\partial F}{\partial N_i} = \ln M - \ln N_i - \alpha - \beta \varepsilon_i$$

Solve for $N_i \Rightarrow \quad N_i = M e^{-\alpha} e^{-\beta \varepsilon_i}$ $\qquad N = \frac{1}{M} \sum N_i$

$Z$ = partition function $\equiv \sum_i e^{-\beta \varepsilon_i}$ $\qquad N = e^{-\alpha} \sum_i e^{-\beta \varepsilon_i}$

$N = e^{-\alpha} Z \qquad e^{-\alpha} = \dfrac{N}{Z}$ $\qquad$ However, $N_i = M e^{-\alpha} e^{-\beta \varepsilon_i}$

$N_i = \dfrac{MN}{Z} e^{-\beta \varepsilon_i}$ $\qquad$ However, $n_i = \dfrac{N_i}{M}$

So, $\boxed{n_i = \dfrac{N}{Z} e^{-\beta \varepsilon_i}}$ $\qquad$ the Maxwell-Boltzmann Distribution

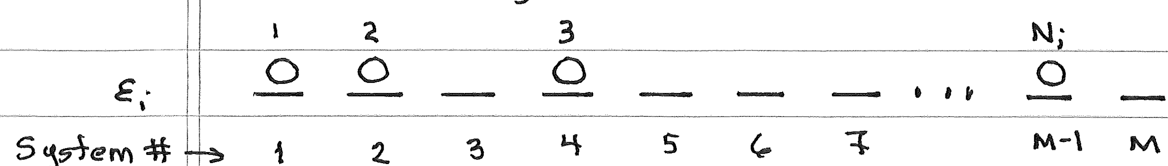
## II. Fermi - Dirac Statistics

Again, we spread out $MN$ particles over the levels such that:

1.) $N_1$ are in $\varepsilon_1$, $N_2$ are in $\varepsilon_2$, ...

2.) $M \geq N_i$ (Fermi - Dirac Statistics)

For any configuration, we have $N_i$ filled levels (particles) and $M - N_i$ empty ones (holes)



# Quantum Statistics

A new microstate is generated by exchanging "particles" and "holes" on the $i^{th}$ horizontal level.

$$W_h^{(i)} = \frac{M!}{N_i!\,(M-N_i)!}$$

In the Maxwell-Boltzmann case we also considered the number of vertical and diagonal rearrangements. However, exchanging identical particles between energy states $\varepsilon_i \leftrightarrow \varepsilon_j$ does not produce a new microstate. So, the total number of microstates is

$$W = W_h^{(1)}\,W_h^{(2)}\,W_h^{(3)}\cdots = \prod_{i=1}^{\infty} \frac{M!}{N_i!\,(M-N)!}$$

$$\boxed{\underset{\substack{\uparrow \\ \text{the number} \\ \text{of microstates}}}{W}\big(\underbrace{N_1, N_2, N_3, \ldots}_{\text{Macrostate}}\big) = \prod_{i=1}^{\infty} \frac{M!}{N_i!\,(M-N_i)!}}$$

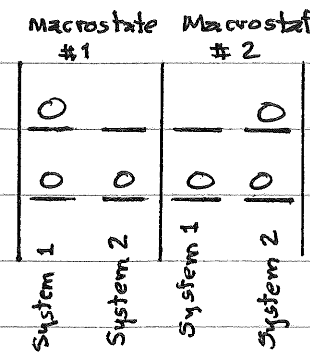
Fermi-Dirac Distribution

<u>Example:</u> Same as before $M=2$, $N_1=2$, and $N_2=1$

$$W(2,1) = \frac{2!}{2!\,(0!)}\,\frac{2!}{(1!)(1!)} = 2$$

From 24 microstates $\rightarrow$ 2 microstates

Maxwell-Boltzmann $\rightarrow$ Fermi-Dirac




What is the maximum of $\ln W$ subject to the constraints?

Using the Auxiliary function and the Stirling approximation, like before,

$$F(N_1, N_2, \ldots, \alpha, \beta) = \sum_{i=1}^{\infty} \Big\{ \ln M! - (M-N_i)\ln(M-N_i) + (M-N_i) - N_i \ln N_i + N_i - \alpha N_i - \beta \varepsilon_i N_i \Big\} + \alpha N M + \beta E M$$

# Quantum Statistics

Take the derivative as before: $\dfrac{\partial F}{\partial N_i} = 0 = \ln(M-N_i) - \ln N_i - \alpha - \beta\varepsilon_i$

$$\frac{M-N_i}{N_i} = e^{\alpha} e^{\beta\varepsilon_i} \qquad \frac{M}{N_i} = 1 + e^{\alpha} e^{\beta\varepsilon}$$

$$N_i = \frac{M}{1+e^{\alpha} e^{\beta\varepsilon_i}} \qquad \boxed{n_i = \frac{1}{e^{\alpha} e^{\beta\varepsilon_i} + 1}}$$

Fermi-Dirac Distribution

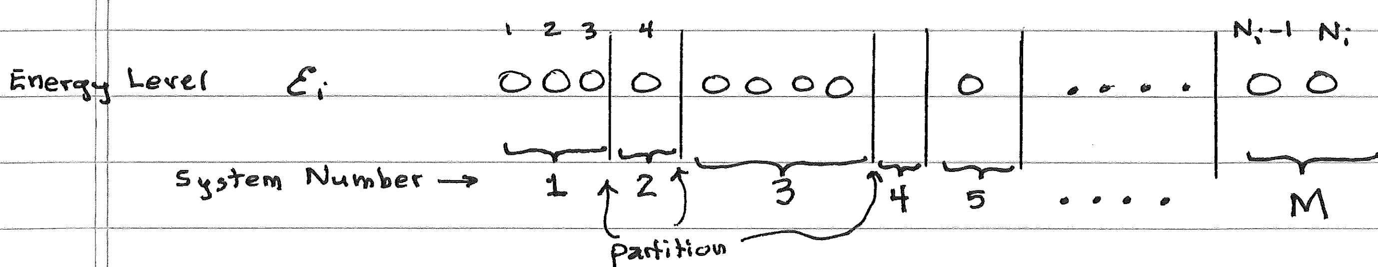
If $e^{+\alpha} e^{+\beta\varepsilon} \gg 1 \Rightarrow n_i \cong e^{-\alpha} e^{-\beta\varepsilon_i}$ the Boltzmann distribution.

$\boxed{e^{\alpha} e^{\beta\varepsilon_i} \text{ is always } \geq 0 \text{ .... so, } n_i \leq 1}$

## III. Bose-Einstein Statistics

Again we spread out MN particles over the energy levels $\varepsilon_i$

where: $N_i = 0, 1, 2, \ldots \leq NM$




$W_n^{(i)}$ = # of interchanges of particles and partitions that give a unique microstate. Remember, we're working with indistinguishable particles.

$(N_i + M-1)!$ = the number of ways of making interchanges of all $N_i$ particles and all $M-1$ partitions.

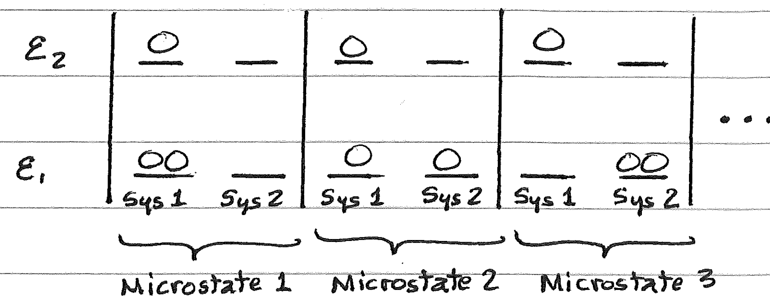
$$W_n^{(i)} = \frac{(N_i + M-1)!}{N_i!\,(M-1)!} \qquad \boxed{W(N_1, N_2, \ldots) = \prod_{i=1} \frac{(N_i+M-1)!}{N_i!\,(M-1)!}}$$

# Quantum Statistics

## Bose-Einstein (cont'd)

Example: Same as before → $M=2$, $N_1=2$, and $N_2=1$

$$W(2,1) = \frac{3!}{2!\,1!}\;\frac{2!}{1!\,1!} = 6$$




From 24 microstates → 6 microstates
(Maxwell-Boltzmann) → Bose-Einstein

What is the maximum $\ln W$ subject to the constraints?
Using the Auxiliary function and the Stirling approximation, like before,

$$F(N_1, N_2, \dots, \alpha, \beta) = \sum_i \left\{ (N_i + M - 1)\ln(N_i + M - 1) - N_i \ln N_i - \alpha N_i - \beta \varepsilon_i N_i \right\} + \alpha N M + \beta E M$$

Take the derivative as before:

$$\frac{\partial F}{\partial N_i} = 0 \qquad \frac{\partial F}{\partial N_i} = \ln(N_i + M - 1) - \ln N_i - \alpha - \beta\varepsilon_i = 0$$

$$\frac{N_i + (M-1)}{N_i} = e^{\alpha} e^{\beta\varepsilon_i}$$ Assume $M-1 \approx M$ (a large number of systems)

$$1 + \frac{M}{N_i} = e^{\alpha} e^{\beta\varepsilon_i} \qquad n_i \equiv \frac{N_i}{M} = \frac{1}{e^{\alpha} e^{\beta\varepsilon_i} - 1}$$

$$\boxed{n_i = \frac{1}{e^{\alpha} e^{\beta\varepsilon_i} - 1}}$$ Bose-Einstein Distribution

Bose-Einstein

The Lagrange multiplier $\alpha$ is determined by $N = \sum_i \frac{1}{e^{\alpha} e^{\beta\varepsilon_i} - 1}$

Let the lowest energy level $\varepsilon_1 = 0$, then

$$n_1 = \frac{1}{e^{\alpha} - 1}$$

# Quantum Statistics

At low temperatures, $\alpha$ becomes small and $n_1 \to$ increases. This sudden collection of particles into the ground state is what we call a <u>Bose - Einstein</u> <u>Condensation.</u>

$\Rightarrow$ Describes the properties of the superfluid liquid $^4He$ at low temperatures.

<u>In Summary:</u> $\beta = \dfrac{1}{k_B T}$

Define the chemical potential

$\mu(T) = -\alpha k_B T$

or $\alpha = -\beta\mu(T)$

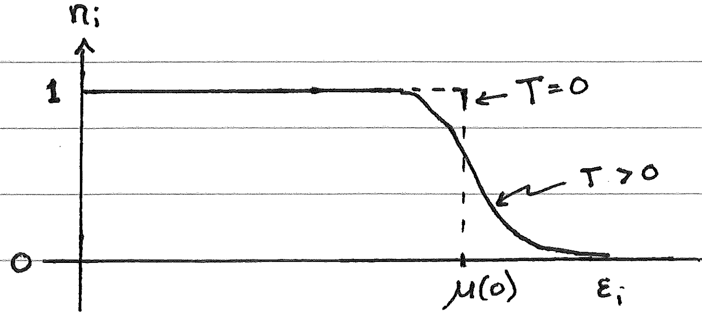
Maxwell - Boltzmann $\quad n_i = e^{-(\varepsilon_i-\mu)/k_B T}$

Fermi - Dirac $\quad n_i = \dfrac{1}{e^{(\varepsilon_i-\mu)/k_B T}+1}$

Bose - Einstein $\quad n_i = \dfrac{1}{e^{(\varepsilon_i-\mu)/k_B T}-1}$

The Fermi - Dirac distribution has a simple behavior as $T \to 0$

$$e^{(\varepsilon_i-\mu)/k_B T} \to \begin{cases} 0 & \text{if } \varepsilon_i < \mu(0) \quad \Rightarrow \quad n_i \to 1 \\ \infty & \text{if } \varepsilon_i > \mu(0) \quad \Rightarrow \quad n_i \to 0 \end{cases}$$




$\mu(0) = E_F$ fermi energy

# Blackbody Distribution

1. Standing electromagnetic waves in a cubical cavity $L^3$. $V = L^3$

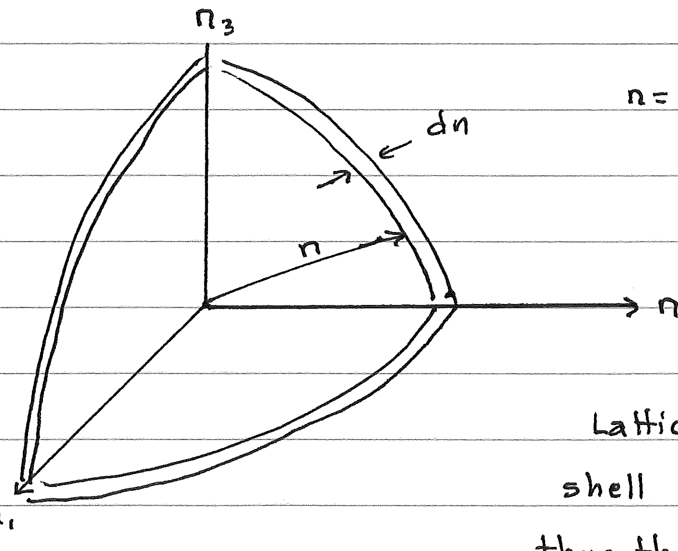
2. $f\lambda = c$ $\quad \lambda = \frac{2L}{n} \rightarrow \frac{2L}{\sqrt{n_1^2+n_2^2+n_3^2}}$ $\quad f = \frac{c}{2L}\sqrt{n_1^2+n_2^2+n_3^2}$

   where $\{n_1, n_2, n_3\} \overset{\text{e.g.}}{=} \{0, 1, 1\} \rightarrow f = \left(\frac{c}{2L}\right)\sqrt{2}$

   or $= \{1, 2, 3\} \rightarrow f = \left(\frac{c}{2L}\right)\sqrt{14}$

3. $\{n_1, n_2, n_3\}$ are points on a lattice and $n_1, n_2, n_3$ are integers.

4. What is the number of modes (i.e. lattice points) in a thin spherical shell of thickness $dn$?




$$n = \sqrt{n_1^2+n_2^2+n_3^2} = \frac{2Lf}{c}$$

$$dn = \frac{2L}{c}\,df$$

Lattice points in the thin spherical shell share the same frequency, thus the same energy.

Let $N_f\,df$ = # of modes with frequency $f$

The thin spherical shell of radius $n$ contains $\frac{1}{8}4\pi n^2\,dn$ lattice sites

# of lattice sites at radius $n$, thickness $dn = \frac{1}{8}4\pi\left(\frac{2L}{c}\right)^2 f^2 \left(\frac{2L}{c}\right) df$

The number of modes $= \underbrace{2\times}_{\text{polarization}}$ the # of lattice sites.

## Blackbody Distribution

The number of modes with frequency $f$:

$$N_f \, df = \frac{8\pi f^2 \, df}{c^3} L^3 \qquad \boxed{N_f \, df = \frac{8\pi f^2 V}{c^3} df}$$

$$N_f = \frac{\#\text{ of modes at frequency } f}{\text{per unit frequency}} = \frac{8\pi f^2 V}{c^3}$$

Energy Density $\quad u_f(T) = \left(\frac{N_f}{V}\right) \langle \varepsilon \rangle$

where $\langle \varepsilon \rangle$ = average total energy for each degree of freedom of a linear oscillator in a collection of particles at temperature T.

Classically: $\langle \varepsilon \rangle = \underbrace{\tfrac{1}{2} k_B T}_{\langle KE \rangle} + \underbrace{\tfrac{1}{2} k_B T}_{\langle PE \rangle} = k_B T$ for a harmonic oscillator

Classically: $u_f(T) = \frac{8\pi f^2}{c^3} (k_B T)$ ← ultraviolet catastrophe.

Quantum Mechanics + Quantum Statistics $\Rightarrow u_f = \frac{8\pi f^2}{c^3} \langle \varepsilon \rangle$

However, $\langle \varepsilon \rangle = n_f hf = \frac{hf}{e^{\beta hf} - 1}$

So, $u_f = \frac{8\pi f^2}{c^3} \left( \frac{hf}{e^{hf/kT} - 1} \right)$ $\qquad \boxed{u_f = \frac{8\pi f^3 h}{c^3} \frac{1}{e^{hf/kT} - 1}}$

⇑

The Planck Distribution for the energy density per freq.