Materials Chemistry III [IC 300]

Course Timings

Instructor: Dr. Satyajit Gupta
Grading: Relative
Course Credit: 2
Mode: Offline

Tuesday
2:30-3:30 PM MC III (L209)

Total 14 days; weekly 1 h; total 14 h

mid-semester break-21/10/2023-29/10/2023; Last teaching day 04/12/2023

1. ***Assignment***
2. ***Quiz***
3. ***Mid Semester exam (29/09/2023-06/10/2023) and Final Exam (05/12/2023-9/12/2023)***

- **Class representative?**

Please write your Name and ID number in all the pages of:

-Assignment

-Quiz

-Exam

The broad syllabus….

Light-matter interaction (black body radiation, photo-electric effect, wave-particle duality, concept of wave function, particle in 1D/2D box), concept of chemical bonding. ***(Detail Theory and Interpretation)***

Applications of semiconductor systems in 3G solar-cells, LEDs. Introduction to light harvesting materials (conjugated polymers, quantum dots and dyes and introduction to some advanced materials), electron-mater interaction. ***(Introductory Level)***

Objective of 20 h!!!

Theory (5L) → **Application (4L)**

Text-book ***In real life?***

Course Objective

- ✓ *To learn how certain quantum mechanical principles translates into applications in the area of materials science and advanced applications.*

- ✓ *The course will start with Pre-Quantum theory and then will move towards application of quantum mechanics in macroscopic world and in sub-atomic world.*

Basic Mathematics

- ***Standard Integration***
- ***Differentiation***
- ***Differential Equation***
- ***Operator Algebra***

- $\int_0^\infty \frac{X^3 dx}{e^x - 1} = (\pi^4/15)$

- $\lambda \times \nu = c$

  $\nu = (c/\lambda)$

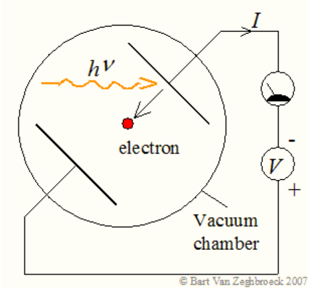
  $d\nu = - c(d\lambda/\lambda^2)$

Physical interpretation of the results will be important for this course!

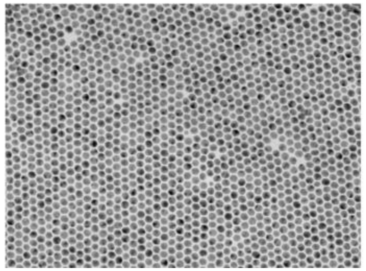
Physical Constants

- *Planks constant (h)=6.62618 × 10^{-34} J-sec*
- *Speed of light in vacuum (c): 2.99 ×10^{8} m/s*
- *Electron rest mass (m_e): 9.10953×10^{-31} Kg*
- *Boltzmann constant (K_B): 1.38066×10^{-23} J/K*

1) Black body radiation (~solar spectrum), ‘Photoelectric effect’-Light/Mater nteraction . (Concept of Work Function and Fermi level). UPS measurement.



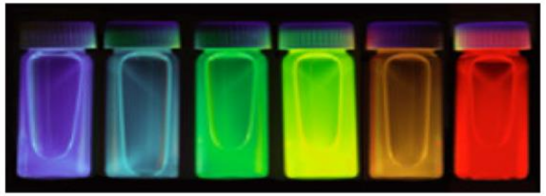
2) Wave-particle Duality, de Broglie’s equation: Application in real world and microscopic world. Emerging nanomaterials.
Heisenberg’s experiment and Uncertainty Principle.

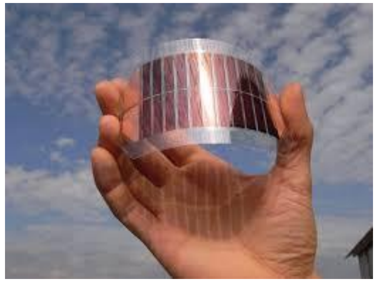


Nano Particles

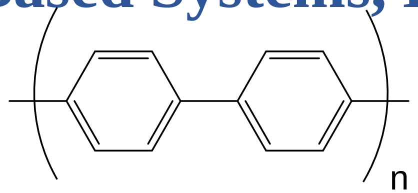
3) Understanding the Electron wavelength and principle of SEM.
(Electron mater interaction)

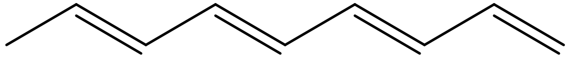
4) Particle in 1D Box and its implication in Materials world and the regime of nanoscale/Quantum dots, rainbow concept.
(Light mater interaction)





5) Conjugated Polymer Based Systems, Lead halide perovskites and Flexible Devices.





Day-Wise Plan

- Day 1/Problem day 2: Introduction and Black-body Radiation
- Day 3: Photo-electric effect, Application
- Day 4/Problem day 5: Wave-Particle Duality
- Day 6: Concept of wave function, Postulates, Operator Algebra
- Day 7/Problem day 8: Particle in 1D box (2D box and 3D box)
- Day 9: Electronic Transition
- Day 10: Quiz
- Day 11/Problem day 12: Simple Harmonic Oscillator
- Day 13: Quantum Confinement Effect
- Day 14: Applications

Study Materials

1. Quantum Chemistry, D. A. McQuarrie, Viva Books, New Delhi, 2003.

2. P. W. Atkins and R. Friedman, Molecular Quantum Mechanics, Oxford University Press, 2005.

3. K. L. Kapoor, A text book of Physical Chemistry.

4. A.K Chandra, Introductory Quantum Chemistry.

5. A textbook of nanoscience and nanotechnology, T. Pradeep

[All course materials/tutorials will be sent via email]

Materials Chemistry III

thus 'its' Chemistry of Materials Science

- ***Quantum Mechanics***

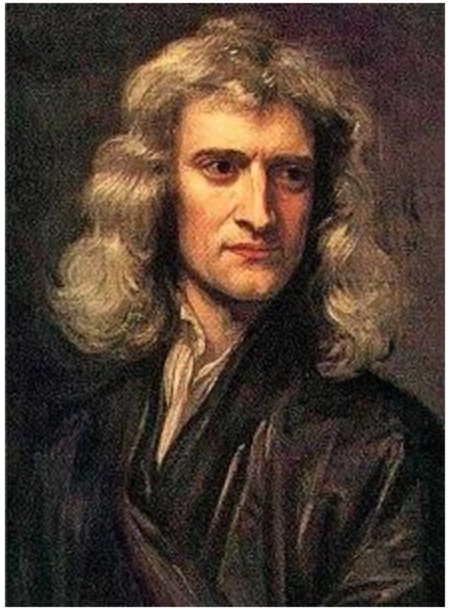
Newton's laws of motion: Solution of dynamic systems.

Lagrange's eqn, Hamilton's eqn are fundamental of classical mechanics, useful for complicated dynamical systems. Carnot, Gibbs's Thermodynamics. (Maxwell, Boltzmann)

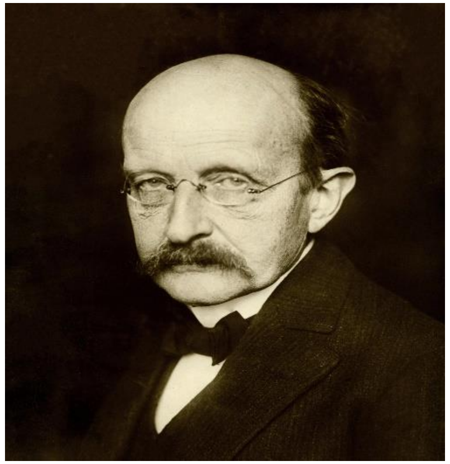
These can't explain certain properties of microscopic systems.

1st beginning was at German Physical Society by Max Plank

2nd stage initiation by Heisenberg and de Broglie



Newton



Plank
Noble
(Prize-1918)

Heisenberg
Noble Prize-1932

de Broglie
Noble Prize-1929

Erwin Schrödinger
Noble Prize-1933

Quantum Mechanics: the beginning…

Newton's laws of motion are the elementary equations of classical mechanics and these laws are suitable for the description motion of macroscopic bodies.

However, when we deal with very tiny particles (subatomic world - electrons) then these equations fail.

Quantum mechanics deals with the systems, that are not part of every day's macroscopic systems.

S.P Singh, M.K. Bagde, Quantum Mechanics, Published by S. Chand & Company.

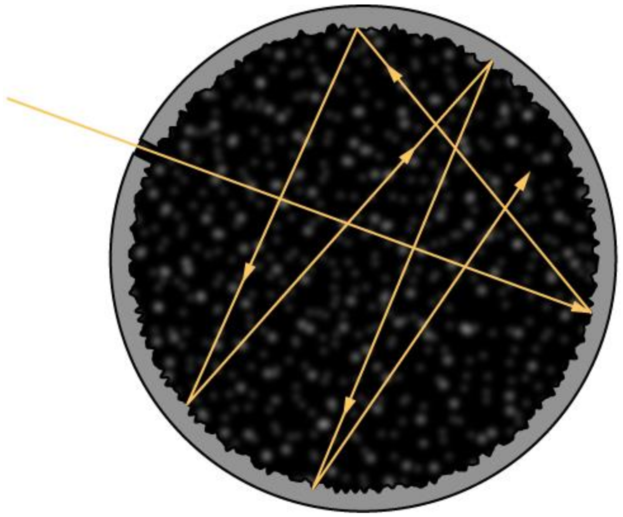
The followings are the example, where classical mechanics fails is Black-body radiation

- ***Black body radiation***
- ***Photoelectric effect***
- ***Compton effect***

Quantum mechanics….

Black Body Radiation

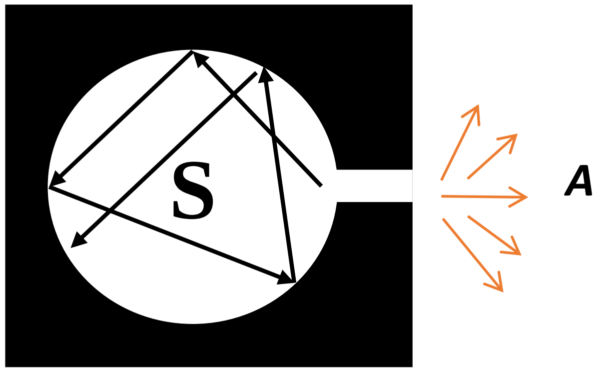
(Experimental data to Quantum theory)



Black body radiation

A black body is a body, which completely absorbs all the radiations falling on it and the radiation emitted by it called black body radiation.

A perfectly black-body absorbs all the radiations incident on it. [ideal condition]
Remember: There is no available surface that can absorb 100%!



S= Porcelain sphere
A= opening
Maintained at constant temperature

The emissive power is measured by means of 'Bolometer' and 'IR spectrophotometer'.

'Burner in an electrical stove-Red-White-Yellow'

Why black-body is important?

- **As the radiation level of a blackbody only depends on its temperature, blackbodies are used as optical reference sources for optical sensors.**

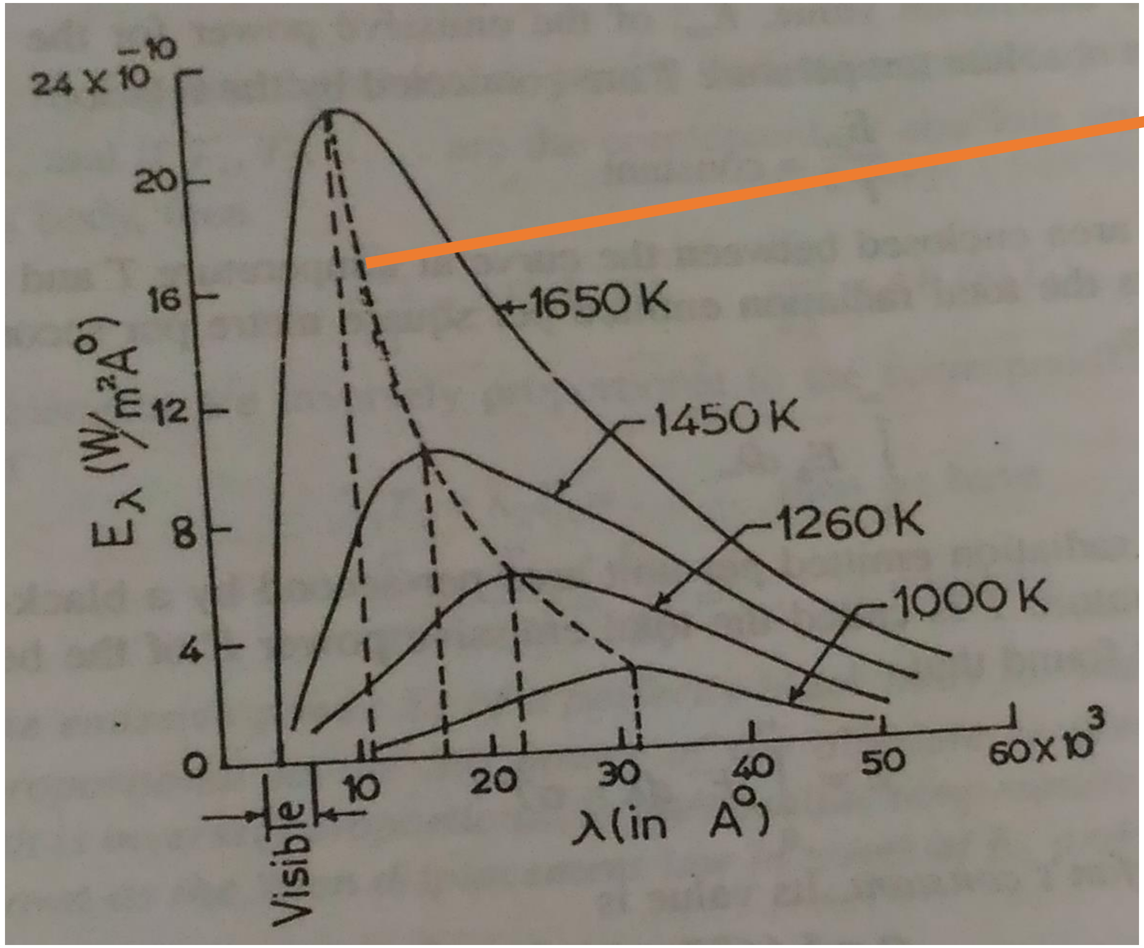
- **That's why blackbodies are also known as Infrared Reference Sources.**

- **The main applications are of course IR sensors calibration .**

  - **Applications in solar energy collectors**
  - **Anti-reflection surfaces (Telescope and cameras)**

https://www.hgh-infrared.com/FAQ/Blackbody/What-are-the-applications-of-a-blackbody

Lummer and Pringsheim - 1899



Wien's displacement law

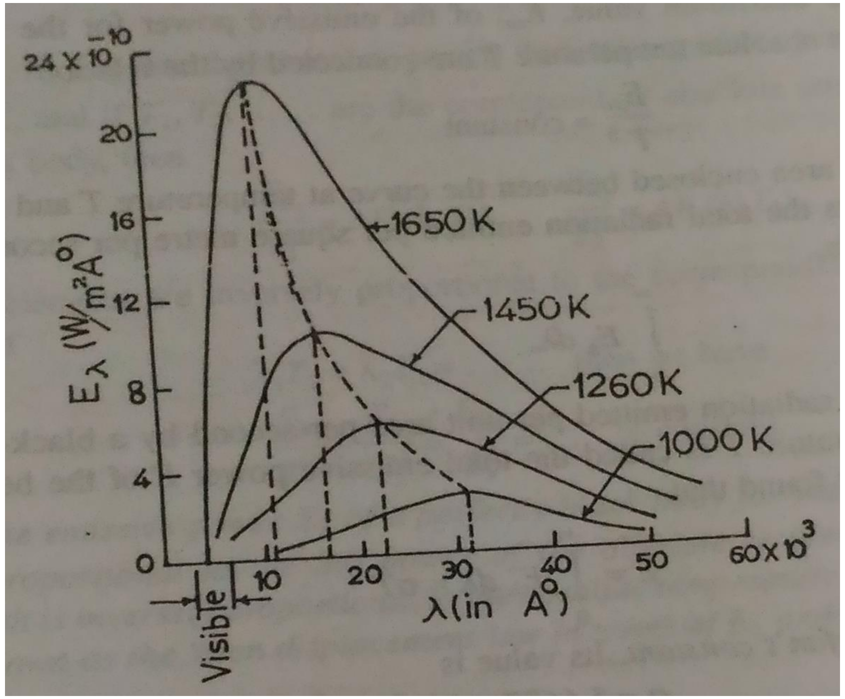
E(λ)dλ is the 'energy density' radiated, for wavelength in the range λ to λ+dλ. [J/m³]

Area under the curve: Total radiated energy

1) As T increases, E(λ) - emissive power for every wavelength increases.

2) At constant temperature, E(λ) increases and becomes maximum at a certain λ_{max} and then with further increase in λ, E(λ) decreases.

3) At higher temperature, E(λ) shifts towards shorter wavelength.



Features and the Laws……..

- λ_{max} and the corresponding temperature are related by **Wien's Displacement Law**

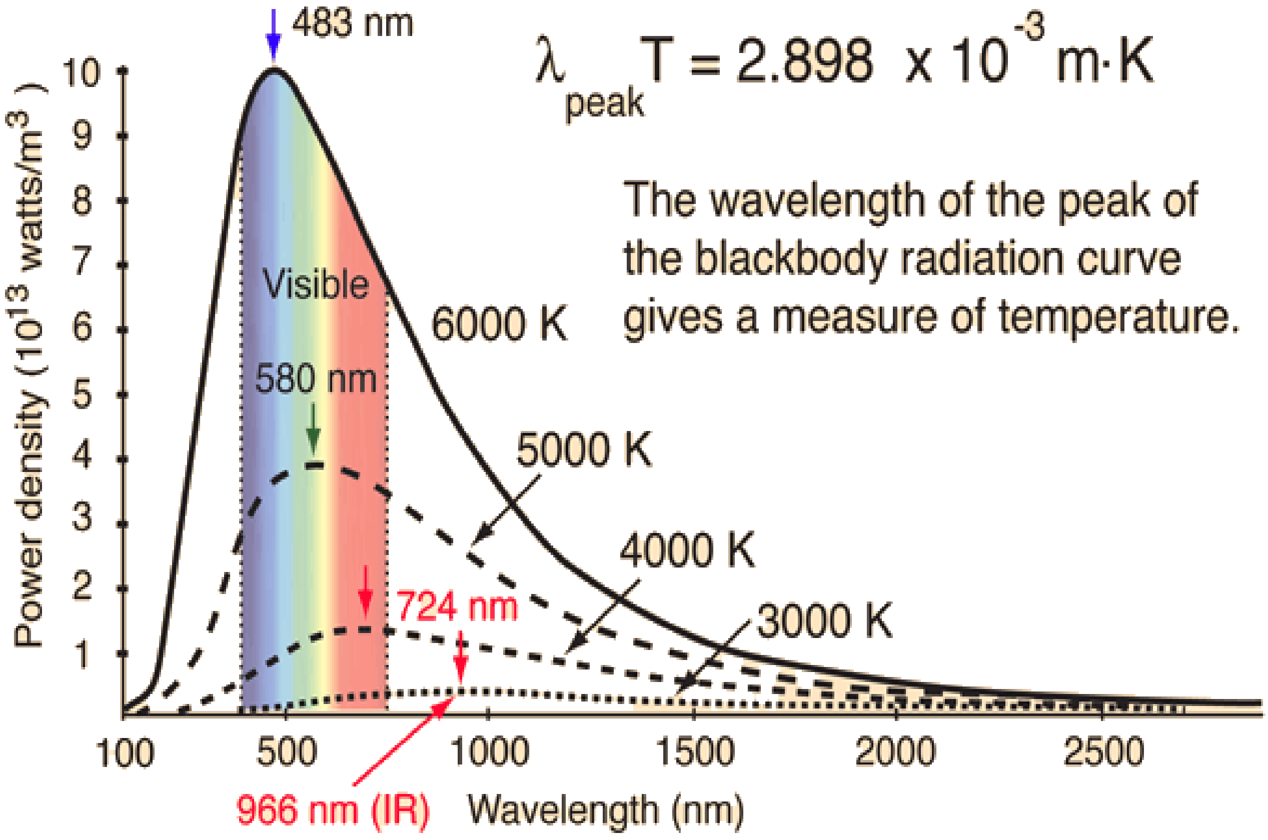
$$\boldsymbol{\lambda_{max}\mathrm{T} = \mathrm{constant} = 2.898\ \times 10^{-3}\mathrm{m.K}}$$

- The maximum value of E_{λ} is directly proportional to the fifth power of temperature: **E_m/T^5 = constant = 2.188 ×10^{-11} J K**

- The area enclosed between the curve at temperature T and the λ-axis represents the total radiation emitted per unit area per unit time over all wavelengths

- The total radiation emitted per unit area per unit time is directly proportional to the fourth power of temperature. This is called **Stefan's law**.

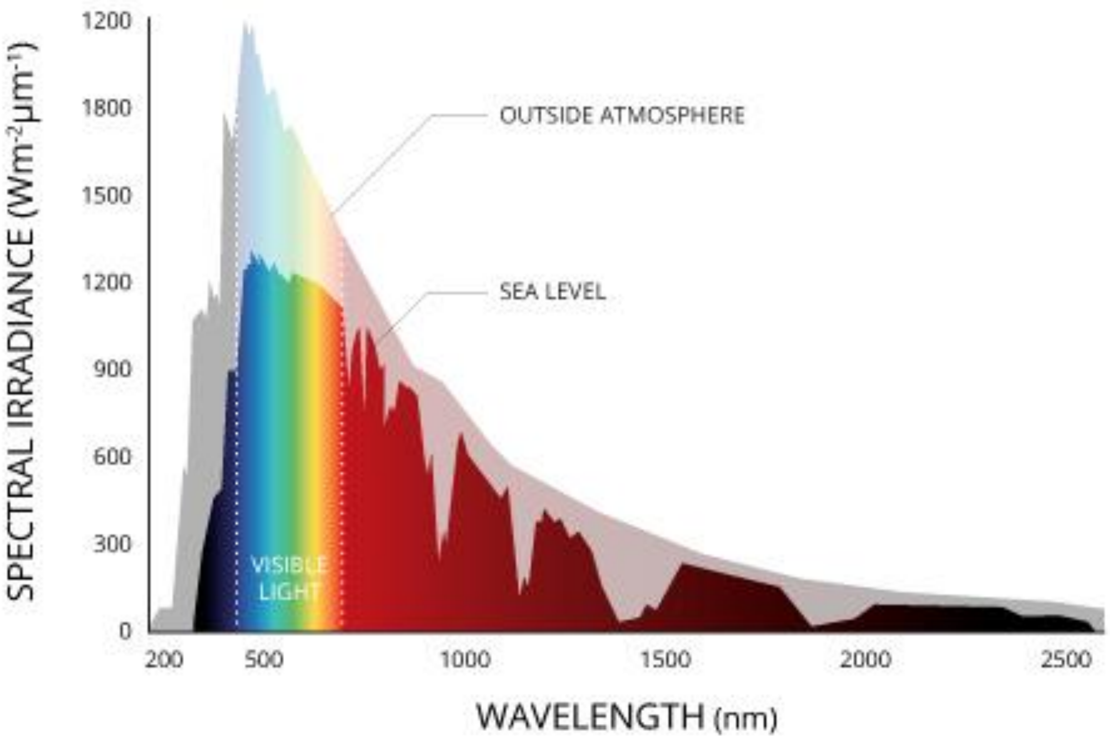
Total radiation from black body: $R_B = \int_0^{\infty} E(\lambda)\, d\lambda = \sigma T^4$; σ=Stefan's constant



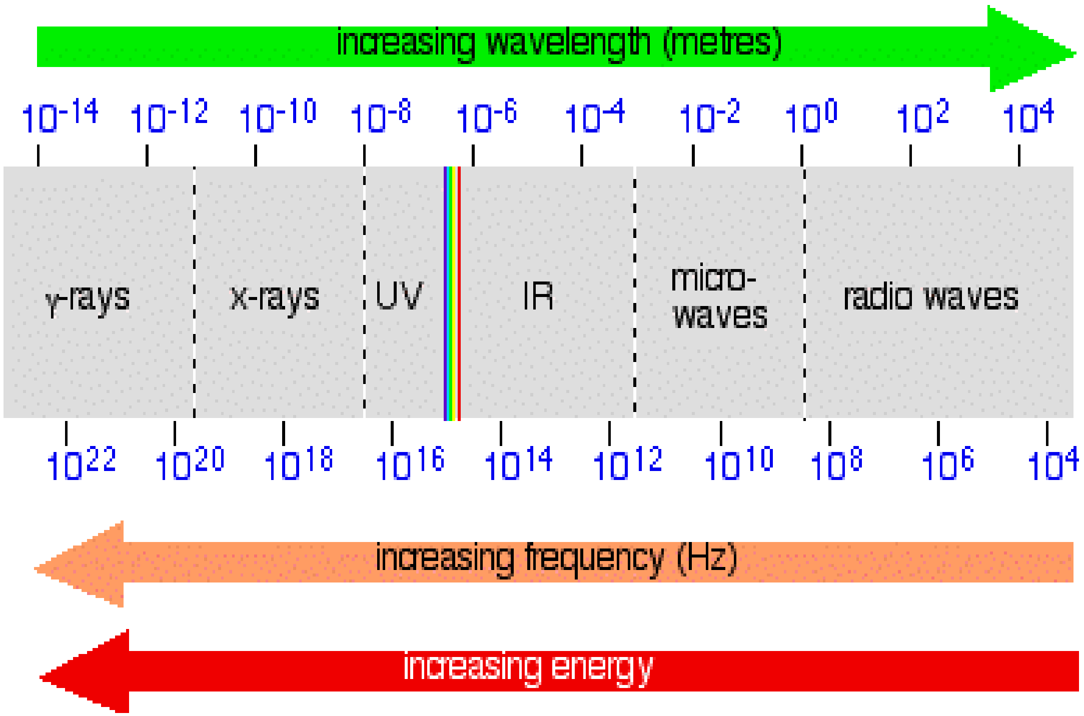
1) **Calculate the temperature of Sun, considering its radiation of the peak occurs at 500 nm.**

2) **Star Sirius appears blue, having a surface temperature of 11000 K. Find out its wavelength of radiation.**

Solar Radiation



$$C = \lambda \times \nu$$



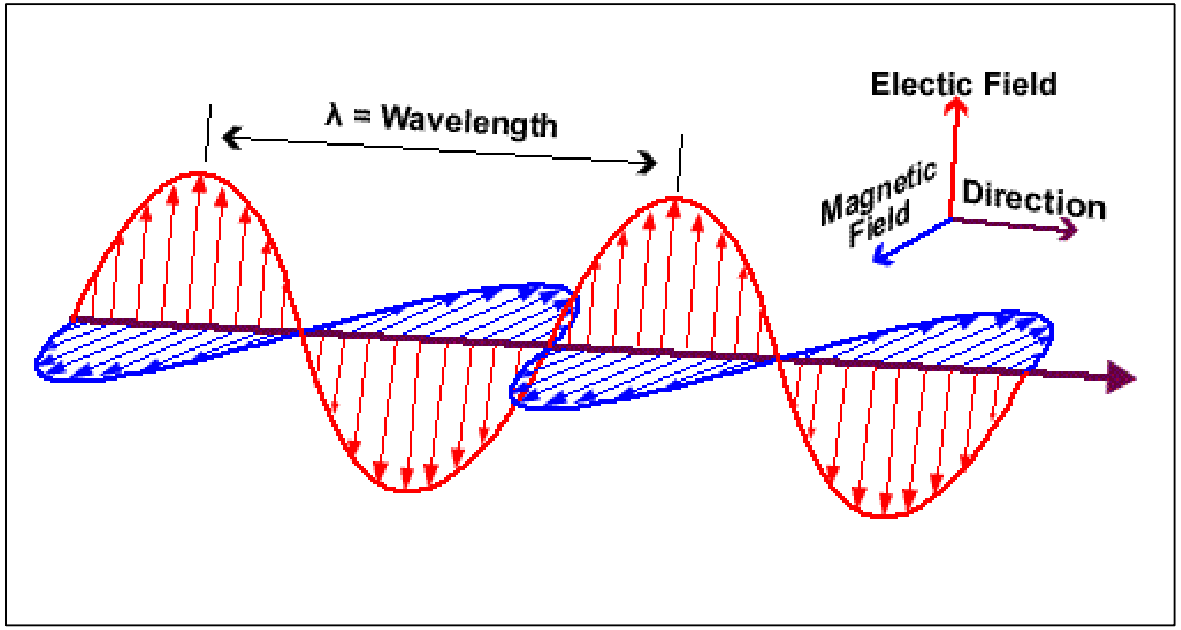
$$E = h \times \nu$$

Understanding Radiation

Radiation consists of electromagnetic waves.

Electric field is perpendicular to magnetic field
and they are perpendicular to the direction of propagation.

Diffraction and interference strongly evidenced that they have wave nature.



Classical mechanics:
Energy is proportional to Amplitude^2
And its Independent of frequency

Theoretical Laws of Black Body Radiation

- *Wien's displacement Law*
- *Stefan's law or Stefan-Boltzmann Law*
- *Wien's radiation Formula*
- *Rayleigh-Jeans Law*
- *Planck's Law*

Wien's Law and Radiation Formula

- Wien's displacement law: $\lambda_{max}\mathrm{T} = \mathrm{constant} = 2.898 \times 10^{-3}\mathrm{m.K}$
- Wien's radiation formula (derived in 1896):

$$\boldsymbol{E_\lambda d\lambda = \frac{C_1}{\lambda^5} e^{-\frac{C_2}{\lambda T}} d\lambda}$$

C_1 and C_2 are constants

Arbitrary assumptions:

1) **The radiation is produced by resonator of molecular dimensions.**
2) **Frequency of radiation is proportional to Kinetic Energy of the resonator.**

Outcome: It explained the experimental results at low values of λ.

Stefan Boltzmann Law

The area enclosed between the curve at temperature T and the axis of λ represents total radiation:

$$\int_0^\infty E(\lambda)d\,\lambda$$

The total radiation emitted /unit area/sec at temperature T is called black body radiant emittance R_B (Stefan's law for the total radiation from black body)

$$R_B=\int_0^\infty E(\lambda)d\,\lambda=\sigma T^4;\ \sigma=\text{Stefan's constant}$$

$$\sigma=5.6697\times10^{-8}\ \mathrm{w/m^2\,K^4}$$

Rayleigh-Jeans Law (1900)

Rayleigh-Jeans Law (1900)

$$E_\nu d\nu = \frac{8\pi\nu^2 kT}{c^3} d\nu$$

$$E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$$

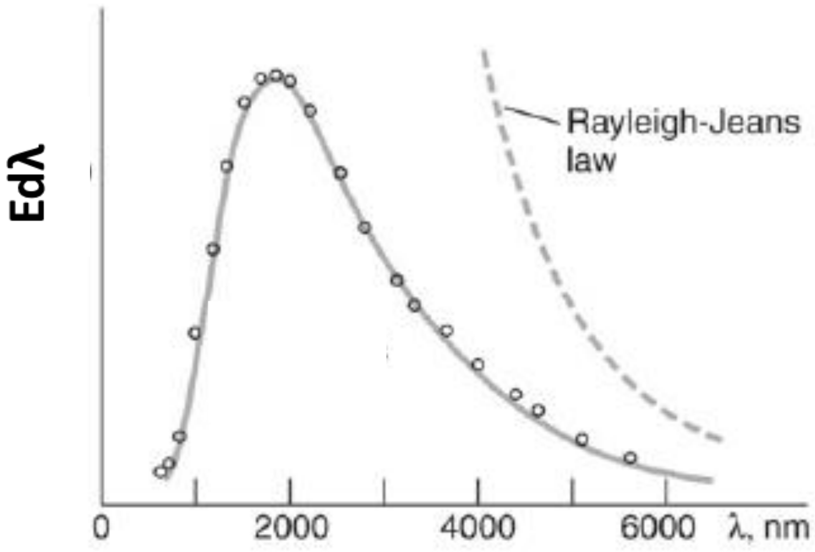
- This formula was derived by applying equipartition of energy of the electromagnetic vibration (classical treatment-each vibration mode posses on an average energy E_{avg}=KT; all oscillator have mean energy of this KT).
- If there are dn number of modes of oscillation in the wavelength λ and $\lambda + d\lambda$;

$$dn = \frac{8\pi}{\lambda^4}\ d\lambda$$

- The energy density $(E_\lambda d\lambda)$ =dn×E_{avg} $= \frac{8\pi kT}{\lambda^4} d\lambda$

It describes the black-body radiation in longer wavelength region but fails in shorter wavelength region as $\lambda \rightarrow 0$, E *approaches infinite.*

This is called ultraviolet catastrophe



Total energy of radiation per unit volume of the enclosure of all wavelength:

$$E = \int_0^\infty E_\lambda \, d\lambda$$

$$E = \int_0^\infty \frac{8\pi kT}{\lambda^4} d\lambda$$

$$= 8\pi kT \int_0^\infty \frac{1}{\lambda^4} d\lambda$$

$$= 8\pi kT \left[-1/3\lambda^3\right]_0^\infty$$

$$= \infty$$

Thus opening of shutter of the black body will lead to bombardment of shorter wavelength (X-ray/gamma ray). This is called as UV catastrophe. This absurd result is due to the assumption energy can be absorbed/emitted by the oscillators continuously by any amount.

Also in dark, all mater should emit radiation?

Ultraviolet Catastrophe

Rayleigh-Jeans Law: $$E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$$

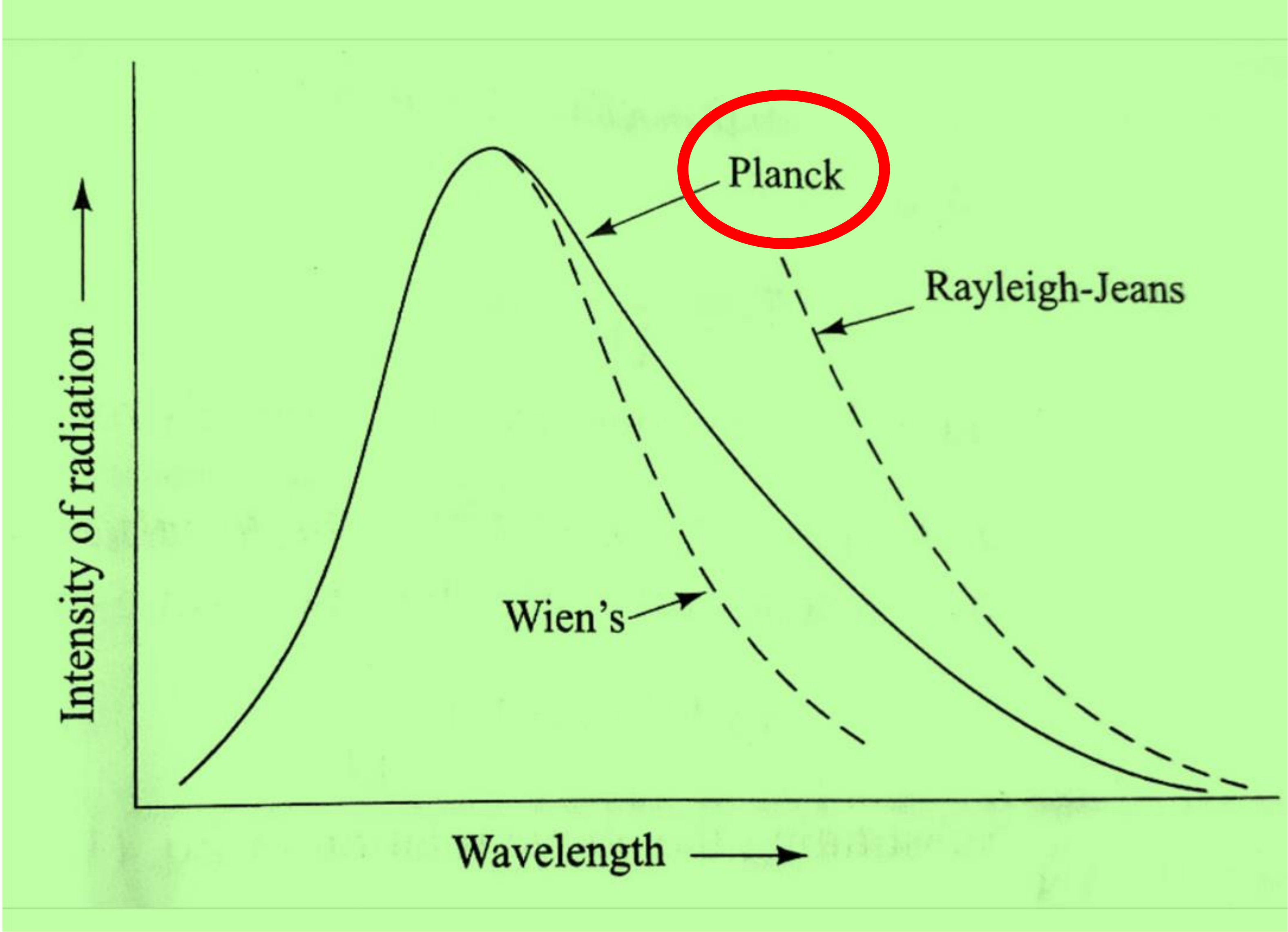
It describes the black-body radiation in longer wavelength region but fails in shorter wavelength region as $\lambda \rightarrow 0$, E *approaches* ***infinite*** *without passing through the maxima.*

Thus, the equation predicts that oscillators of very short wavelength (high frequency-$\nu \rightarrow$ high energy) radiation such as ***UV, X-Ray, γ-Ray*** *will come out even* ***at room temperature****. [It is impossible to generate* ***UV/X-Ray*** *at room temperature.*

This absurd result , which implies that a ***huge amount of energy*** *will be irradiated as we decrease λ is called Ultraviolet catastrophe.*

What is the significance of 'infinite'?

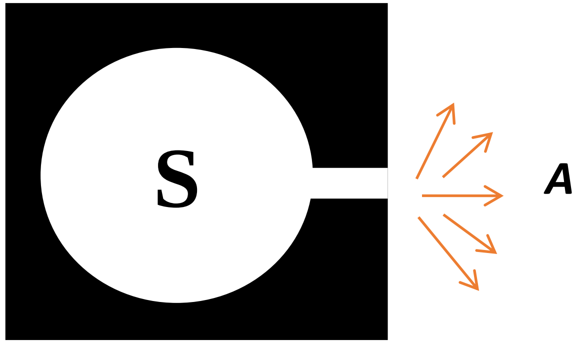
- According to classical physics a cool object should radiate in visible/UV region.
- Thus the object should glow in dark- signifying there is no darkness?


Planck
Rayleigh-Jeans
Wien's
Intensity of radiation
Wavelength

Planck's Law (1900)

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5\left(e^{\frac{hc}{\lambda kT}}-1\right)}d\lambda$$

- It perfectly describes the black-body radiation in whole range of wavelength
- All the laws (Wien, Rayleigh-Jeans and Stephan) can be arrived from this law. **(Tutorial)**
- **Energy of the oscillator has to be integral multiple of hν; E=nhν**



S= Porcelain sphere
A= opening

Atoms in the walls are like simple harmonic oscillators having a fixed frequency ν. 1901 Planks proposed the oscillator emits radiation in discrete amount.
(The electrons are pictured as oscillators like they oscillates in antenna to give radiowaves. But in black body they oscillates at a much higher frequency that why we see emission in visible/UV/IR ranges)

<u>Assumptions:</u>

1) Oscillators of black body can't have any amounts of energy but have a discrete energy. It can have only those values of total energy E, which satisfy the relation $E=nh\nu$. ($n=0,1,2\ldots$) $h\nu$ is the basic unit of energy. [$h=6.625\times10^{-34}$ J s]

2) The oscillator does not emits continuously. The emission/absorption only occurs when they jumps from one energy level to another.

Unit of radiant energy density

$$E_{\nu}d\nu = \frac{8\pi kT\nu^2}{c^3}d\nu$$

$$=[(\mathrm{J\ K^{-1}})\ (\mathrm{K})/(\mathrm{m\ s^{-1}})^3]\times\mathbf{(s^{-1})^2}\times\mathbf{(s^{-1})}$$

$$=\mathrm{J\ m^{-3}}$$

$$E_{\lambda}d\lambda = \frac{8\pi hc}{\lambda^5\left(e^{\frac{hc}{\lambda kT}}-1\right)}d\lambda$$

$$=\mathrm{J\ m^{-3}}$$

(Radiant energy density has units of energy per unit volume)

End of Lecture 1

The oscillator of the black-body cannot have any amount of energy but has a discrete energy equal to the integral multiple of some minimum energy ϵ=hν

$$\epsilon_i = n\epsilon, \text{where n} = 0, 1, 2, 3, \ldots$$

Energy Level	0	hν	2hν	2hν	3hν	4hν
E_i	E_0	E_1	E_2	E_3	E_4	E_5
N_i	N_0	N_1	N_2	N_3	N_4	N_5

Tutorial 1

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5\left(e^{\frac{hc}{\lambda kT}}-1\right)}d\lambda$$

Assuming 'λ' is small

1.Wien's radiation Formula

$$E_\lambda d\lambda = \frac{C_1}{\lambda^5}e^{-\frac{C_2}{\lambda T}}d\lambda$$

Integration

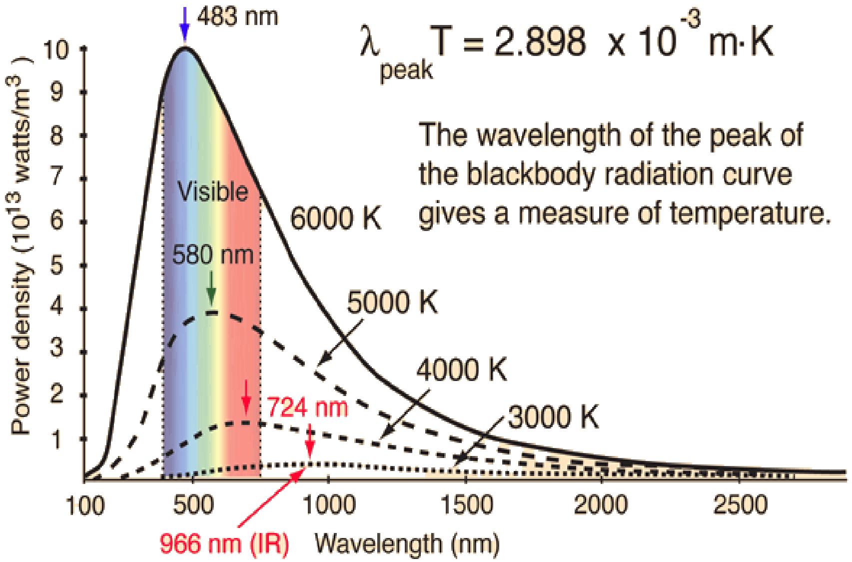
2. Stefan-Boltzmann Law

$$R_B = \int_0^\infty E(\lambda)d\lambda = \sigma T^4$$

Assuming 'λ' is large

3. Rayleigh-Jeans Law

$$E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4}d\lambda$$



Derivation of Planks Law!

1. $\left(1 + x + x^2 + \cdots\right) = 1/(1 - x)$

2. $\left(1 + 2\mathrm{x} + 3x^2 \ldots\right)$
$=d/dx(1+x+x^2+x^3+x^4+\ldots)$
$=d/dx[1/(1-x)]=1/(1-x)^2$

Thus:

$$\left(x + 2x^2 + 3x^3 \ldots\right) = x/(1 - x)^2$$

Derivation of Planck's Law

- **The total energy emitted per unit wavelength region is given by**

$$E_\lambda d\lambda = no.\,of\ oscillators\ per\ unit\ volume\ \times\ average\ energy\ of\ each\ oscillator$$
$$= dn\ \times Eavg$$

- **The number of oscillators per unit volume can be derived by the same way as done Rayleigh and Jeans:**

$$dn = \frac{8\pi}{\lambda^4} d\lambda$$

KL Kapoor, 5e

- **The oscillator of the black-body cannot have any amount of energy but has a discrete energy equal to the integral multiple of some minimum energy $\boldsymbol{\epsilon}$**

$$\boldsymbol{\epsilon_i = n\epsilon, \text{where n} = 0, 1, 2, 3, \ldots}$$

- **After this he used the Boltzmann expression to compute the average energy of the oscillator. According to which, the number of oscillators having energy $\boldsymbol{\epsilon_i}$ at temperature T is given by**

$$\boldsymbol{N_i = n_0 e^{-\frac{\epsilon_i}{kT}}}$$

- **Total number of oscillators, $\boldsymbol{N = \sum_i N_i}$**

E_{avg} can be derived in the following manner:

$$N_i = n_0 e^{-\frac{\epsilon_i}{kT}}$$

$$N = N_0 + N_1 + N_2 + \cdots = n_0 e^{-\frac{\epsilon_0}{kT}} + n_0 e^{-\frac{\epsilon_1}{kT}} + n_0 e^{-\frac{\epsilon_2}{kT}} + \cdots$$

$\epsilon_i = \mathrm{n}\epsilon$ [n = 0, 1, 2, 3 …]

$$N = N_0 + N_1 + N_2 + \cdots = n_0\left(1 + e^{-\frac{\epsilon}{kT}} + e^{-\frac{2\epsilon}{kT}} + \cdots\right) = n_0\left(1 + x + x^2 + \cdots\right)$$

Where, $x = e^{-\frac{\epsilon}{kT}}$

Remember: $\left(1 + x + x^2 + \cdots\right) = 1/(1 - x)$

Thus we get: $$N = \frac{n_0}{1 - x}$$

Average Energy of Oscillator

$$\bar{E} = \frac{\sum_i N_i \epsilon_i}{N}$$

$$= \frac{1}{N}[[n_0 \times \varepsilon_0 + n_1 \times \varepsilon_1 + n_2 \times \varepsilon_2 + n_3 \times \varepsilon_3 + ...]$$

$$= \frac{1}{N}[(n_0 \times 0) + n_1\epsilon + 2n_2\epsilon + 3n_3\epsilon \ldots]$$

$$= \frac{1}{N}\left[(n_0 \times 0) + e^{-\frac{\epsilon_1}{kT}}\epsilon + n_0 e^{-\frac{\epsilon_2}{kT}} 2\epsilon + \cdots\right]$$

$$= \frac{n_0 \epsilon x/(1-x)^2}{n_0/(1-x)} = \frac{\epsilon x}{(1-x)} = \frac{\epsilon}{\left(e^{\frac{\epsilon}{kT}} - 1\right)}$$

$$E_\lambda d\lambda = \frac{8\pi}{\lambda^4} \frac{\epsilon}{\left(e^{\frac{\epsilon}{kT}} - 1\right)} d\lambda$$

Remember:

$(1 + 2x + 3x^2 \ldots)$

$= d/dx(1+x+x^2+x^3+x^4+\ldots)$

$= d/dx[1/(1-x)] = 1/(1-x)^2$

Thus:

$(x + 2x^2 + 3x^3 \ldots) = x/(1-x)^2$

Where, $x = e^{-\frac{\epsilon}{kT}}$

$$3.\ \left(1 + x + x^2 + \cdots\right) = 1/(1 - x)$$

$$4.\ \left(1 + 2\mathrm{x} + 3x^2 \ldots\right)$$

$= d/dx(1+x+x^2+x^3+x^4+\ldots)$

$= d/dx[1/(1-x)] = 1/(1-x)^2$

Thus:

$$\left(x + 2x^2 + 3x^3 \ldots\right) = x/(1 - x)^2$$