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Paper: C14T (Statistical Mechanics)
Topic: Classical Theory of Radiation (Part-II)

Having learnt the basics of blackbody radiation in the previous E-material, we are going to discuss now the following topics:

- *Radiation Pressure*
- *Stefan-Boltzmann Law and its Thermodynamic Proof*
- *Wien's Law of Energy Distribution*
- *Wien's Displacement Law*
- *Rayleigh-Jeans' Law*
- *Saha's Ionization Formula*
- *Ultraviolet Catastrophe*

Radiation Pressure

Radiation pressure is the mechanical pressure exerted by the electromagnetic radiation upon any surface on which it is incident. It is due to the exchange of momentum between the object and the electromagnetic radiation which consists of photons.

The forces generated by radiation pressure are generally very small to be realized in our everyday life. But, they are important in some physical processes. For example, in outer space force due to radiation pressure is usually the main force acting on objects besides gravity. There the net effect of a tiny force can have a large cumulative effect over a long period of time. Let's see it through an example - had the effects of the sun's radiation pressure on the spacecraft of the "Viking Program" been ignored, the spacecraft would have missed Mars' orbit by about 15,000 km.

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Let's define radiation pressure using the quantum theory of electromagnetic radiation. According to the quantum theory, electromagnetic radiation consists of photons, each photon having energy $h\nu$ and speed c where ν is the frequency of the photon. By the mass-energy relation of Einstein, energy $E = mc^2$.

Therefore, $E = h\nu = mc^2$.

mass of the photon, $m = h\nu / c^2$

and momentum of the photon $= mc = h\nu / c$.

If this photon is incident normally on a surface and gets absorbed then the photon will transfer the momentum **$h\nu/c$** to the surface.

The total pressure exerted by the radiation on the surface is **$p = \sum h\nu / c$** where summation is over all the frequency of the photons incident per second on the surface.

Therefore, **radiation pressure,** $p = \sum h / c = I / c$ -------- (3)

where $I = \sum h\nu$ is the intensity of the radiation.

Stefan-Boltzmann Law

The total radiation energy emitted per unit surface area per unit time from a blackbody is proportional to the fourth power of the absolute temperature of the blackbody. Mathematically,

$$Q = \sigma T^4 \qquad \text{-------- (4)}$$

where σ is called Stefan constant.

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Thermodynamic Proof of Stefan-Boltzmann Law:

Let us consider an enclosure of volume V containing blackbody radiation at a constant absolute temperature T. Let 'u' be energy density of radiation and 'p' be the radiation pressure. So, the total energy of radiation in the enclosure U = uV and the radiation pressure p = u/3 (refer to any book for the derivation of it).

According to the first law of thermodynamics, we have

$$\begin{aligned} dQ &= dU + pdV \\ &= d(uV) + (u/3)\, dV \\ &= u\, dV + V\, du + (u/3)\, dV \\ &= V\, du + (4u/3)\, dV \qquad \text{-------- (5)} \end{aligned}$$

From the second law thermodynamics,

$$dQ = T\, dS \qquad \text{-------- (6)}$$

Using eqn.(5) and (6), we get

$$dS = \frac{V}{T}\, du + \frac{4}{3}\frac{u}{T}\, dV \qquad \text{-------- (7)}$$

As entropy S is a function of u and V, we can write

$$S \equiv S\,(u, V)$$

$$\therefore \quad dS = \left(\frac{\partial S}{\partial u}\right)_V du + \left(\frac{\partial S}{\partial V}\right)_u dV \qquad \text{--------}$$

(8)

Comparing eqn.(7) with eqn.(8) we get

$$\left(\frac{\partial S}{\partial u}\right)_V = \frac{V}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_u = \frac{4}{3}\frac{u}{T} \qquad \text{-------- (9)}$$

Since dS is a perfect differential,

$$\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial u}\right) = \frac{\partial}{\partial u}\left(\frac{\partial S}{\partial V}\right)$$

$$\Rightarrow \frac{\partial}{\partial V}\left(\frac{V}{T}\right) = \frac{\partial}{\partial u}\left(\frac{4}{3}\frac{u}{T}\right) \qquad \text{———} (10)$$

Now as the temperature T is independent of V and u is a function of T only, eqn.(10) becomes

$$\frac{1}{T} = \frac{4}{3}\left(\frac{1}{T} - \frac{u}{T^2}\frac{dT}{du}\right)$$

$$\Rightarrow -\frac{1}{3}\cdot\frac{1}{T} = -\frac{4}{3}\cdot\frac{u}{T^2}\frac{dT}{du}$$

$$\Rightarrow \frac{du}{dT} = 4\frac{u}{T}$$

$$\Rightarrow \frac{du}{u} = 4\frac{dT}{T}$$

Integrating this equation we get

$$\ln u = 4\ln T + \ln k$$

$$\Rightarrow u = kT^4 \qquad \text{---------} (11)$$

where k is the constant of integration. So the radiant energy density (u) is proportional to the fourth power of T. Now the total energy (Q) of the radiation is proportional to the energy density u and hence Q is also proportional to the fourth power of the absolute temperature (T) i.e **Q =** $\boldsymbol{\sigma}$ **T**^{4}, where $\boldsymbol{\sigma}$ being the Stefan's constant. This is ***Stefan-Boltzmann law***.

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Wien's Law of energy distribution

We have learnt how total energy of the blackbody radiation is related to the temperature of the source through Stefan-Boltzmann law. The emitted radiation is spread over a continuous spectrum. But, how is the total energy of the radiation distributed amongst the different wavelengths? The attempts to find the answer to this question have a long story of development of physics including the revolutionary concept of quanta by Planck and eventually the quantum theory.

The answer to the above question is easy to find considering the quantum theory. It essentially becomes the problem of finding out how many quanta having energy between ϵ and ϵ+dϵ or frequency between ν and ν+dν are contained per unit volume in an enclosure of blackbody radiation at temperature T. But, it is the present day concept and it came after a long struggle.

Before the quantum theory was developed, the researchers of this field like Wien, Rayleigh, Jeans, Planck et. al were not aware of the mechanism of emission and absorption of radiation. In fact, this mechanism came to be known only through the work of Planck on blackbody radiation. They had to start with the existing knowledge on the laws of classical thermodynamics and electromagnetism. We will now chronologically discuss how these scientists found the solution to the problem of energy distribution in blackbody radiation.

The first development came from Wien in1893. From the thermodynamic consideration Wien found the energy distribution over the different wavelengths of emitted radiation from a blackbody at a temperature T to be as following

$$u_\lambda d\lambda = C\lambda^{-5} f(\lambda T) d\lambda \qquad \text{-------- (12)}$$

where $u_\lambda d_\lambda$ is the energy density of radiation between wavelengths λ and λ+dλ, C is a constant and f(λT) is a function of the product λT. This spectral distribution is known as **Wien's distribution law.**

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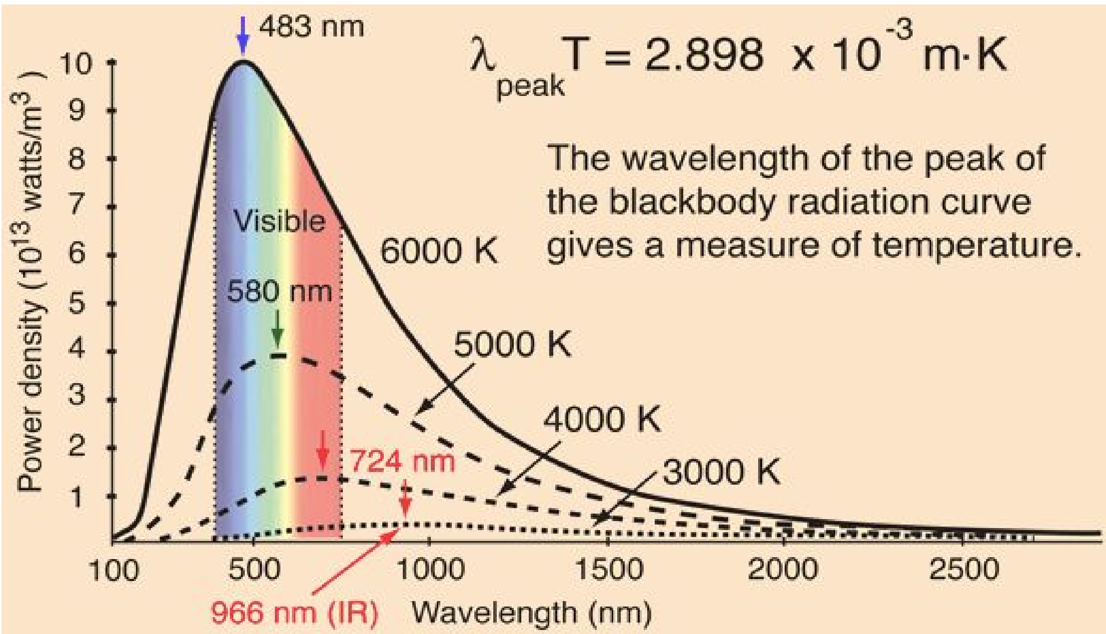
Wien's Displacement Law

Wien also showed that the blackbody radiation curve for different temperatures will have peaks at different wavelengths following an inverse relation with the temperature. As the temperature increases the whole radiation spectrum of the radiation shifts toward shorter wavelengths. These behaviors are depicted in the figure below.



Wien's displacement law formally states that the spectral radiance of black-body radiation has peaks at wavelengths that are inversely proportional to the absolute temperature of the blackbody. Mathematically it says,

$$\lambda_{peak} = \frac{b}{T} \quad \text{-------- (13)}$$

where b is the Wien's displacement constant = 2.8977×10^{-3} and T is the absolute temperature. This law is useful in determining the temperatures of hot radiant objects, such as stars, whose temperatures are far above that of their surroundings.

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Rayleigh-Jeans' Law

As Wien's law fails to account for the experimental results at longer wavelengths, Rayleigh and Jeans came up with another approximation to the spectral radiance of electromagnetic radiation from a blackbody on the basis of two classical ideas of - (i) stationary waves in a hollow enclosure and (ii) law of equipartition of energy.

Blackbody radiation in an enclosure is composed of electromagnetic waves of wavelengths between 0 and ∞. These waves are reflected back and forth from the walls of the enclosure and form stationary waves in space. Rayleigh showed that the possible number of independent vibrations between the wavelengths $\boldsymbol{\lambda}$ and $\boldsymbol{\lambda}+d\boldsymbol{\lambda}$ per unit volume is proportional to $(1/\boldsymbol{\lambda}^4)d\boldsymbol{\lambda}$. Also, according to the law of equipartition of energy, the energy corresponding to each vibrational mode will be K_BT (kinetic energy ½ K_BT and potential energy ½ K_BT). Using these classical concepts, Rayleigh and Jeans derived the distribution of energy for blackbody radiation in an enclosure at temperature T as

$$u_\lambda d\lambda = \frac{8\Pi K_B T}{\lambda^4} d\lambda \qquad \text{-------- (14)}$$

This is the ***Rayleigh-Jeans' law*** of spectral distribution of energy of Blackbody radiation.

To complete the story we should talk about ***Planck's law of radiation*** but it's beyond our topic of discussion which is only classical theory of radiation. Hopefully, it has been (or will be) discussed by the teacher who is teaching quantum theory of radiation. Anyway, you must go through Planck's law of radiation carefully and learn to derive the laws discussed here from it and compare them with their shortcomings and advantages.

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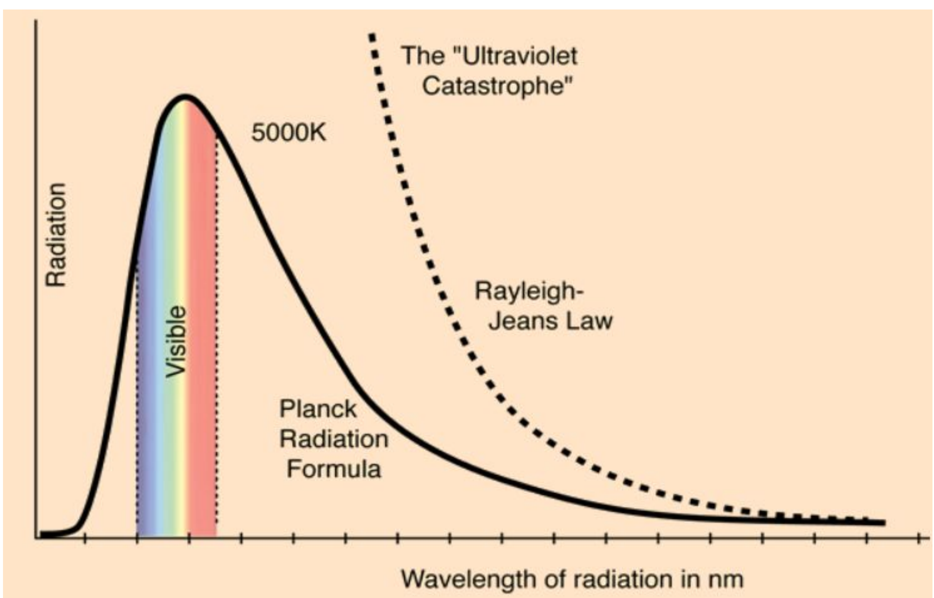
Ultraviolet Catastrophe

Ultraviolet catastrophe is basically the failure of the classical theory of Rayleigh and Jeans to predict the spectral distribution of blackbody radiation. Though Rayleigh-Jeans' law matches the experimental results at higher wavelengths quite well, it fails miserably at lower wavelengths (or higher frequencies) i.e. at the ultraviolet range. According to Rayleigh-Jeans law, a blackbody at thermal equilibrium will emit radiation in all wavelength ranges, emitting extraordinarily more energy at lower wavelengths. The radiation energy diverges as $1/\lambda^4$ as the wavelength decreases. This suggests that all matter would radiate all its energy instantaneously contradicting the experimental facts. This is known as ***ultraviolet catastrophe*** or ***Rayleigh-Jeans' catastrophe***.



The ultraviolet catastrophe results from the use of the classical equipartition theorem and the classical electromagnetism in the derivation of spectral energy by Rayleigh and Jeans. This problem was resolved by Planck in 1900 through a groundbreaking assumption.

Planck's assumption was that electromagnetic radiation can be emitted or absorbed only in discrete packets, called quanta, of energy $E = h\nu = \frac{hc}{\lambda}$, where h is the Planck constant with the value 6.626×10^{-34} J s. This assumption by Planck not only led to the correct form of the spectral distribution of blackbody radiation but also to the successful theory of quantum mechanics.

Saha's Ionization Formula

Saha's ionization formula describes the ionization state of a gas in thermal equilibrium. It is a pioneer work by scientist Meghnad Saha. This work combines the ideas of quantum mechanics and statistical mechanics to explain the spectral classification of stars.

The thermal collisions of the atoms in a gas at a very high temperature will ionize some of the atoms making it an ionized gas. When many such electrons which are normally bound to the atoms are freed, they form an electron gas cloud co-existing with the surrounding gas of ions and neutral atoms. This generates an electric field and the motion of the electric charges generates current and hence a localized magnetic field. This forms a state of the matter called plasma.

Saha's formula describes the degree of ionization of a gas in thermal equilibrium as a function of the temperature, density and ionization energies of the constituting atoms of the gas. It holds good for weakly ionized plasmas for which Debye length is large.

Saha's formula for an ionized gas consisting of one atomic type at an absolute temperature T is given by

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$$\frac{n_{i+1}n_e}{n_i} = \frac{2}{\lambda^3}\frac{g_{i+1}}{g_i}\, exp\left[-\frac{(\varepsilon_{i+1}-\varepsilon_i)}{K_B T}\right] \quad \text{-------- (15)}$$

where,

- n_i is the density of atoms with the *i*-th state of ionization i.e. with *i* no. of electrons removed
- n_e is the electron density
- **λ** is the thermal de Broglie wavelength of an electron
- g_i is the degeneracy of states for the *i*-ions
- ε_i is the energy required to remove *i* electrons from a neutral atom.

This equation is a very important equation for the development of a branch of physics called Astrophysics. It also acted as a milestone in the study of Plasma physics.

References:

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(3) https://en.wikipedia.org/wiki/Saha_ionization_equation
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[Figures taken from the above websites are used for teaching purposes only.]