The Genesis of Quanta: 1890–1910

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In this article we discuss how the concept of quantum of energy came into being from the analysis of black-body spectrum. We start our discussion with the work of Wien who discovered the general form of black-body spectrum and on the basis of his discovery proposed a formula to obtain power radiated from a black body as a function of its temperature and the frequency of radiation. We then focus on the work of Planck who modified Wien's formula to bring it in close agreement with the experimental results. However, the real greatness of Planck is displayed in his interpretation of the modified formula that led him to introduce the revolutionary concept of the quantum of energy. How Planck arrived at this conclusion is described in detail. We conclude the article with a discussion of the generalization of the concept of quanta by Einstein to propose quantization of radiation as well as of mechanical vibrations.

Introduction

The story of the concept of quantum of energy is not only fascinating but also an epoch-making one as it completely changed the way we thought about Nature. What started as a simple interpolation formula for making theoretically derived result for the black-body spectrum match with its experimental counterpart was destined to change history when Planck made an attempt to understand what the formula meant. Planck's analysis implied that oscillators that generated electromagnetic radiation could have energies only in units of $h\nu$, where h is the Planck's constant and ν is the frequency

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of the oscillator. After this revolutionary idea was put forth, it was generalized and given a much wider meaning by Einstein who showed that even radiation came in packets of energy. Further, he proposed that not only oscillators connected with electromagnetic radiation but mechanical oscillators also take energy only in units of $h\nu$.

How did these ideas come into being? How did Planck make his initial breakthrough? These are the questions that we are going to address in this article. We start with a discussion of the background against which Planck came into the scene. We first discuss what the black-body spectrum signifies? We then briefly present the results from electromagnetic theory, thermodynamics and statistical mechanics that were known in the last decade of the nineteenth century and which are relevant to understanding the black-body spectrum. We then review the pathbreaking work that Wien had done in his analysis of the black-body spectrum; he was awarded the Nobel Prize for this work. However Wien's formula for the spectrum of black-body radiation, although accurate for large values of ν/T, deviated from experimental results for small values of ν/T. This set the stage for Planck to make his seminal contribution of introducing the concept of quanta. The work by Planck forms the major part of the article. The article concludes with a discussion of Einstein's contribution in making the concept of quanta general and concrete.

A Black Body and its Spectrum

When radiation is incident on an object, some part of it gets absorbed by the body, some part gets reflected and the rest gets transmitted. Let us define the absorptive power a of the body as the fraction of incident energy that is absorbed; similarly reflectivity r is the fraction of incident energy that is reflected and the transmission coefficient t is the fraction that is transmitted through

Perfect black body is defined to be the one that is a perfect absorber.

the body. Further, these quantities may also depend on the wavelength of radiation. For example, the ordinary glass in window panes lets visible light pass through it but absorbs ultraviolet radiation. We define the absorptive power, reflectivity and the transmission coefficient for each wavelength λ as a_λ, r_λ and t_λ. Thus, if radiation between wavelengths λ and $\lambda + \mathrm{d}\lambda$ with energy $\mathrm{d}Q_\lambda$ is incident on a body, the energy absorbed, reflected and transmitted will be given as follows:

$$\begin{aligned} \text{energy absorbed} &= a_\lambda \, \mathrm{d}Q_\lambda \\ \text{energy reflected} &= r_\lambda \, \mathrm{d}Q_\lambda \\ \text{energy transmitted} &= t_\lambda \, \mathrm{d}Q_\lambda \end{aligned} \tag{1}$$

It is evident that

$$a_\lambda + r_\lambda + t_\lambda = 1. \tag{2}$$

Definitions above are sufficient to describe a black body. The name might have come from the observation that black colour substances appear to absorb a lot of radiation. Thus a perfect black body is defined to be the one that is a perfect absorber. In other words, it absorbs all the radiation of any wavelength falling on it and no portion of it is reflected or transmitted. Thus for a black body

$$\begin{aligned} a_\lambda &= 1, \\ r_\lambda &= 0, \\ t_\lambda &= 0. \end{aligned} \tag{3}$$

Black soot of lamp absorbs about 96% of the visible light incident on it. Recently a new material has been made using carbon nanotubes that absorbs 99.955% of radiation falling on it and hence sets a record for being the darkest material.

One naturally occurring substance that comes close to being a black body is the black soot of a lamp that absorbs about 96% of the visible light although longer wavelength radiation passes through it. (Recently a new material has been made using carbon nanotubes that absorbs 99.955% of radiation falling on it and hence sets a record for being the darkest material (See Yang *et al.*, *Nano Letters*, 2008)). Thus a perfect black body has to be designed. This is done by taking a closed cavity with a small hole in it for radiation to enter and making sure that from the opposite side of the hole, the radiation gets reflected in some other direction, *Figure* 1. To make sure that no radiation is transmitted, i.e. $t_\lambda = 0$ for all wavelengths, the walls of the cavity are made thick. Thus for the walls of such a cavity, $a_\lambda + r_\lambda = 1$.

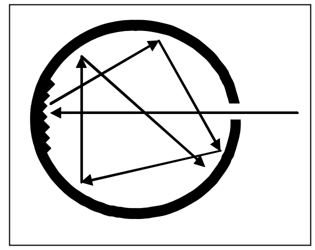

Figure 1. A cavity with a hole in it and jagged edges on the opposite sides to diffuse the radiation entering from the hole.

We now show that the cavity in *Figure* 1 acts as a black body. Consider radiation of wavelength λ entering from the hole, as shown by an arrow in *Figure* 1 and subsequently getting multiply reflected from the inner sides of the cavity. As it reflects, fraction a_λ of it gets absorbed and only fraction r_λ gets reflected. When reflected portion of the radiation strikes the walls again, a further fraction a_λ of it gets absorbed. Thus finally all the radiation entering the cavity gets absorbed in it.

Mathematically, this is seen easily by adding the fractions of radiation absorbed during each strike on the walls of the cavity. Thus,

total fraction of radiation absorbed

$$\begin{aligned} &= a_\lambda + r_\lambda a_\lambda + r_\lambda^2 a_\lambda + \cdots \\ &= a_\lambda(1 + r_\lambda + r_\lambda^2 + \cdots) \\ &= \tfrac{a_\lambda}{1-r_\lambda} \\ &= 1. \end{aligned} \tag{4}$$

In the above equation the fact that $a_\lambda + r_\lambda = 1$ is used. The prefect absorption of radiation discussed above is true for any wavelength. Thus the cavity makes a perfect black body. Further down, after defining the emissive power of a body, we will give another argument to show that the cavity considered here is indeed a black body.

A body heated to a certain temperature also emits radiation. Now we define the emissive power e_λ of a body. Consider a small area $\mathrm{d}A$ of a body shown in *Figure* 2. We measure energy $u_\lambda \mathrm{d}\lambda$ being emitted in the direction perpendicular to $\mathrm{d}A$ in a small solid angle $\mathrm{d}\Omega$ in time $\mathrm{d}t$

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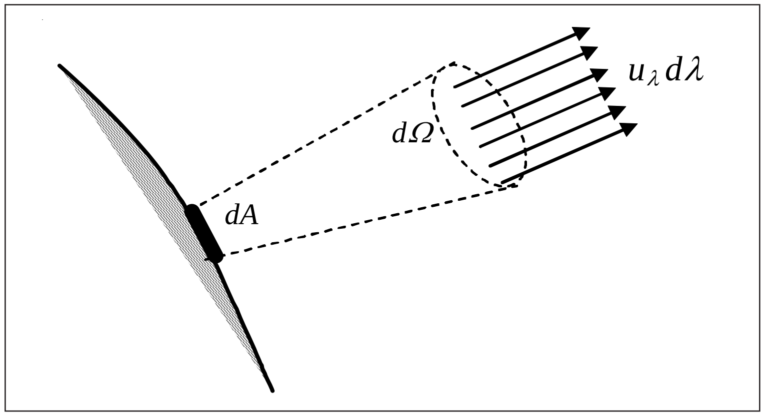

Figure 2: Radiation energy being emitted from a small area dA of a body in solid angle dΩ perpendicular to the area dA.

and define the emissive power e_λ by the relation

$$e_\lambda \mathrm{d}\lambda = \frac{u_\lambda \mathrm{d}\lambda}{\mathrm{d}t\,\mathrm{d}\Omega\,\mathrm{d}A} \tag{5}$$

In other words, emissive power of a body at wavelength λ is the energy emitted per unit time per unit area in a unit solid angle perpendicular to its area in the unit range of the wavelength. Having defined emissive power we now make observations about radiation inside a hollow cavity, e.g., the one shown in *Figure* 1, followed by an explanation:

(i) Radiation in a cavity is isotropic: Take a small body which has parts made up of materials of different emissive power and absorption coefficient. No matter how it is oriented inside the cavity, it will always be in equilibrium with the radiation inside. *This shows that radiation coming from any direction inside a cavity must have the same quality i.e., it is isotropic.*

Emissive power of a body at wavelength λ is the energy emitted per unit time per unit area in a unit solid angle perpendicular to its area in the unit range of the wavelength.

(ii) Nature of radiation is independent of the material and geometry of cavity: Take a small body with emissive power e_λ and absorption coefficient a_λ, and put it inside a cavity with temperature T. The body comes in equilibrium after some time, attaining the same temperature. If the radiation inside corresponds to that of a body with emissive power E_λ, then equilibrium condition – the radiation absorbed is the same as radiation given out by the body – gives (*Appendix* 1)

$$\frac{e_\lambda}{a_\lambda} = E_\lambda.$$

Equilibrium of the same body, when put inside another cavity at the same temperature but a different emissive power E'_λ will give

$$\frac{e_\lambda}{a_\lambda} = E'_\lambda,$$

which implies that $E_\lambda = E'_\lambda$. Thus, the nature of radiation inside a cavity has a universal character and is independent of the material it is made of or its geometry, and depends only on the temperature.

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(iii) Radiation in a cavity corresponds to that of a black body: After point (ii) this is quite easy to see. Take the body that is put inside the cavity to be a perfect black-body for which $a_\lambda = 1$. Then E_λ turns out to the same as e_λ for a black body. As a corollary, Kirchhoff's law for emissive power and absorption coefficient also follows: The ratio of emissive power of a body and its absorption coefficient is equal to the emissive power of a black body.

(iv) Universality of E_λ: Finally, as noted above and in *Appendix* 1, as a result of Kirchhoff's law, black-body radiation has a universal character about it and depends only on the temperature of the black body.

The properties of radiation in a cavity described above are easy to see in a collection of burning coals. If one looks at a pocket made by three or four coals, it looks brighter than the rest of the fire, demonstrating that the emissive power of a cavity is comparatively larger. In such a pocket it is difficult to make out the surface of the coal forming the cavity, indicating the isotropic nature of the radiation inside. Similarly, to observe Kirchhoff's law, all we need to do is to put our hands close to a piece of wood and a piece of iron at the same temperature;

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If we touch a piece of wood and a piece of iron lying in the sun for the same amount of time, we would find that iron is much hotter.

we will find that iron feels hotter because it emits more radiation. This is consistent with iron being a better absorber; if we touch a piece of wood and a piece of iron lying in the sun for the same amount of time, we would find that iron is much hotter.

Having understood how to obtain a nearly perfect black-body radiation (slight departure from absolute perfection may arise because of the hole made in the cavity), the properties of radiation coming from a black-body could now be studied. This was done in the later half of the nineteenth century. In 1879 Stefan deduced a formula for the dependence of the total power radiated from a black body. Accordingly, the total power (summed over all wavelengths) radiated from a black body is proportional to the fourth power of its temperature. Thus the intensity I of radiation (power per unit area) coming out of a black body is given as

$$I = \sigma T^4, \tag{6}$$

where σ is a constant with the value of 5.70×10^{-8} W m^{-2} K^{-4}. In 1884 this law was derived theoretically by Boltzmann using properties of electromagnetic radiation and thermodynamics as follows:

Consider the radiation in a cavity at temperature T. In an isothermal thermodynamic process where some heat is given to the cavity and its volume changes, the first law of thermodynamics gives

$$T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + p, \tag{7}$$

where S is the entropy of the radiation, U its internal energy, p its pressure and V the volume occupied by it (the volume of the cavity). Now $U = uV$ and $p = \frac{u}{3}$ in terms of the radiation density u inside the cavity (*Appendix* 2). Further by Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$. Substituting all these relations in equation (7) gives (u remains unchanged during an isothermal process)

$$T\left(\frac{\partial u}{\partial T}\right)_V = 4u, \tag{8}$$

which in turn implies that

$$u \propto T^4. \tag{9}$$

As shown in *Appendix* 2, intensity of radiation coming out of a cavity is $\frac{c}{4}u$. Thus the intensity also is proportional to T^4. This law is therefore known as Stefan–Boltzmann law. What occupied scientists a great deal at that time, however, and finally led to the revolutionary concept of quanta of energy, was the black-body spectrum. This forms the basis of this article and we describe it next.

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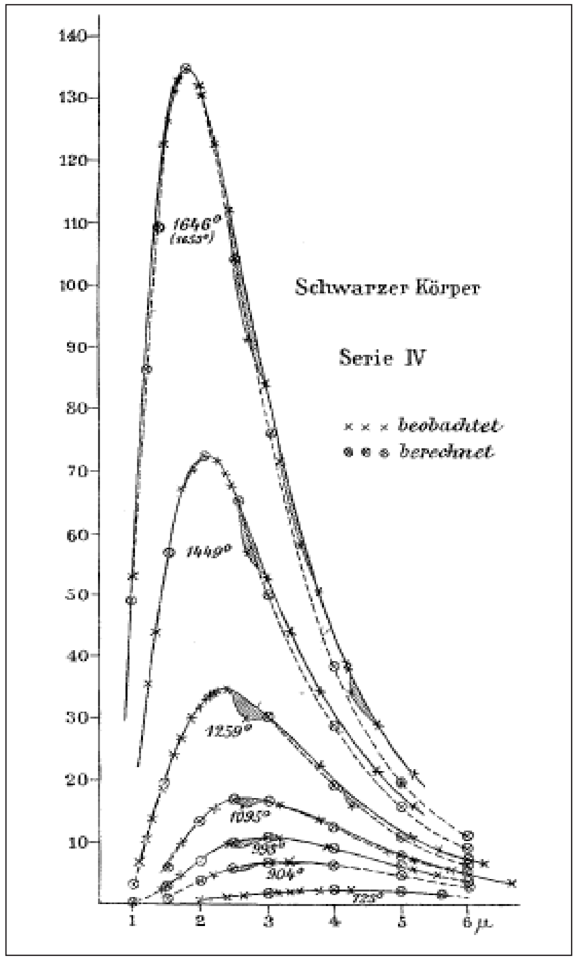
When we study the spectrum of a black body at temperature T, it is done by plotting the spectral density against the wavelength of the radiation. Let us describe how to measure spectral density and that would make its meaning also clear. Consider the radiation between wavelengths λ and $\lambda + \mathrm{d}\lambda$ coming out of a small area $\mathrm{d}A$ of a black body and measure the amount of energy $\mathrm{d}E$ that is radiated in time $\mathrm{d}t$. Dividing $\mathrm{d}E$ by $\mathrm{d}\lambda$, $\mathrm{d}A$ and $\mathrm{d}t$ gives the spectral density. Thus spectral density is the power per unit area per unit wavelength, i.e., it describes how the energy radiated from a black-body is distributed over different wavelengths. Sometimes one may ask, is it necessary to find energy per unit area or should the total power be used? Or should one measure energy per unit time (that is power) or energy radiated in a given time interval? The answer is that it does not matter as long as we are interested in measuring how much energy is radiated at a given wavelength. Dividing by the area or time just rescales this distribution. The spectral density of black-body radiation obtained by Lummer and Pringsheim (Lummer and Pringsheim, *Verhandl. der Deutschen Physikal. Gessellsch.* **Vol.1**,

Figure 3. Plot of black-body data obtained by Lummer and Prigsheim in 1899. Solid lines are the experimental data and dotted lines is the Wien's formula given by equation (24).



p.213, 1899) at several different temperatures is shown in *Figure* 3. On the y-axis is shown the total energy radiated at between λ and $\lambda + d\lambda$ plotted against the wavelength shown on the x-axis. Two observations are made regarding the spectral density:

(i) At a given temperature, small energy is radiated at short wavelengths. As the wavelength increases, so does the energy radiated but then it decreases again for longer wavelengths. Thus for a given temperature, maximum energy is radiated at a particular wavelength $\lambda_{\max}$.

(ii) As the temperature of a black body increases, the wavelength $\lambda_{\max}$ becomes shorter.

The challenge during the last decade of the nineteenth century – and our focus in this article – was to understand how this distribution arises.

The first successful attempt to understand the shape of the black-body spectrum was made by Wien that we now discuss.

To understand the shape of black-body spectrum, Wien analyzed how the black-body spectrum changes as the temperature of a cavity is changed.

Wien's Analysis (1893,1894)

To understand the shape of black-body spectrum, Wien analyzed how the black-body spectrum changes as the temperature of a cavity is changed. For this, he considered adiabatic change in the volume of a spherical cavity. Thus no heat is added to or taken away from the cavity. Let us take the cavity to be expanding. Since some work is done in the expansion, the cavity will cool down and the radiation inside will change to that corresponding to the new temperature. Thus if the radiation density is known at the initial temperature, we can figure out how it will look at the new temperature by analyzing the adiabatic expansion. Keep in mind that results derived on the basis of spherical cavity are absolutely general since the nature of radiation in a cavity does not depend on its shape or size. Let us take a cavity of radius R at temperature T. As it expands adiabatically, let the change in its volume and internal energy be $\mathrm{d}V$ and $\mathrm{d}U$, respectively. If the radiation density in it is u, the pressure $p = \frac{u}{3}$ and $\mathrm{d}U = V\mathrm{d}u + u\mathrm{d}V$. The application of the first law of thermodynamics, $\mathrm{d}Q = \mathrm{d}U + p\mathrm{d}V$ then gives:

$$0 = V\mathrm{d}u + u\mathrm{d}V + \frac{u}{3}\mathrm{d}V \quad \text{or} \quad \frac{\mathrm{d}u}{u} = -\frac{4}{3}\frac{\mathrm{d}V}{V}. \qquad (10)$$

Integration then leads to

$$uV^{\frac{4}{3}} = \text{constant}. \qquad (11)$$

Since $V \propto R^3$ and by Stefan–Boltzmann law $u \propto T^4$, equation (11) gives

$$T \propto R^{-1}. \qquad (12)$$

Thus as the radius of the cavity increases, its temperature goes down in inverse proportion to its radius. Further, as the cavity expands, the wavelength of each wave in it also increases due to Doppler shift during reflection from the moving cavity walls. If we calculate the increase in the wavelength, we can see how a portion of the spectral density curve shifts in wavelength as the temperature of a black body changes.

To calculate change in the wavelength, consider walls of the cavity moving slowly with speed v so that in time Δt, its radius increases by $\Delta R = v\Delta t$ (*Figure* 4). Since a wave travels a distance of $2R\cos\theta$ between two reflections, time taken for each reflection is $\frac{2R\cos\theta}{c}$. Thus in time Δt, the number of reflection that a wave undergoes is $\frac{c\Delta t}{2R\cos\theta}$. In each reflection, wavelength of the wave changes due to the Doppler shift by an amount $\frac{2\mathrm{v}\cos\theta}{c}\lambda$. Thus during time interval Δt, the total change in the wavelength is

$$\Delta\lambda = \frac{c\Delta t}{2R\cos\theta} \times \frac{2\mathrm{v}\cos\theta}{c}\lambda = \frac{\Delta R}{R}\lambda, \qquad (13)$$

which implies that

$$\lambda \propto R. \qquad (14)$$

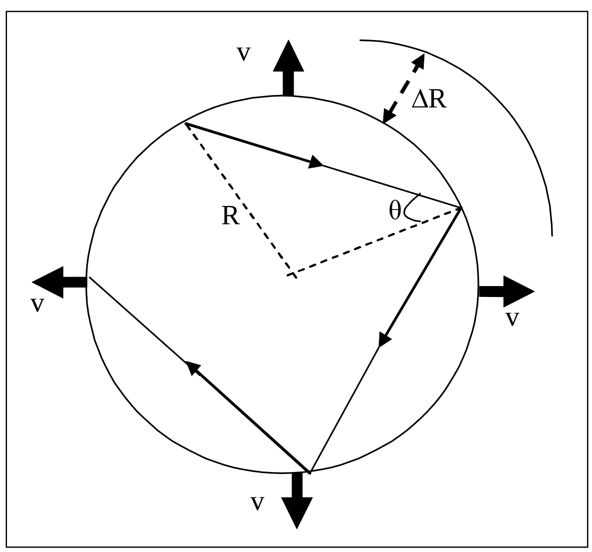


Figure 4: As radiation gets reflected from the moving walls of the cavity, its wavelength changes due to the Doppler shift.

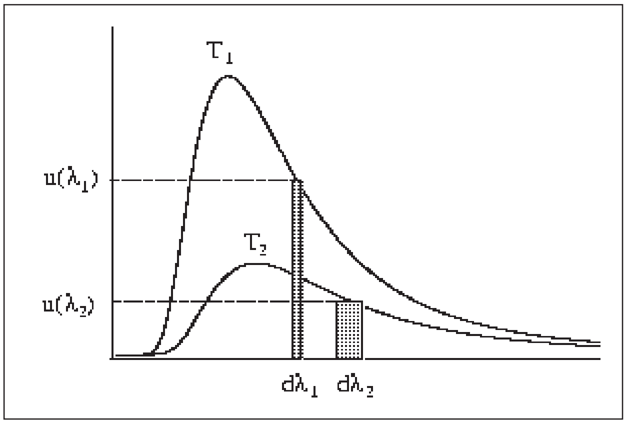


Figure 5. As a cavity at temperature T_1 expands, small portion of width $d\lambda_1$ of spectral density at λ_1 moves over to portion of width $d\lambda_2$ at wavelength λ_2 while the temperature of the cavity changes to T_2.

This combined with equation (12) gives

$$\lambda \propto T^{-1} \text{ or } \lambda T = \text{constant.} \tag{15}$$

Equation (15) is known as Wien's displacement law. It is interpreted as follows:

As the cavity expands, it cools down from temperature T_1 to temperature T_2, and a given section of width $\mathrm{d}\lambda_1$ of the spectral density at wavelength λ_1 moves to a section of width $\mathrm{d}\lambda_2$ at wavelength λ_2 (*Figure* 5). The relationship between T_1, T_2, λ_1, λ_2, $\mathrm{d}\lambda_1$ and $\mathrm{d}\lambda_2$ is given by Wien's displacement law as follows:

$$\begin{aligned} \lambda_1 T_1 &= \lambda_2 T_2, \\ \mathrm{d}\lambda_1\, T_1 &= \mathrm{d}\lambda_2\, T_2. \end{aligned} \tag{16}$$

Thus by Wien's displacement law, if we identify a specific feature of the spectral density curve at temperature T_1 that appears at wavelength λ_1, the same feature would appear at wavelength λ_2 for black-body spectrum at temperature T_2, with these wavelengths and temperatures related by Wien's displacement law. In particular, the wavelength $\lambda_{\max}$, where the maximum of the spectrum occurs, should shift with the temperature of the black body so that

$$\lambda_{\max} T = \text{constant.} \tag{17}$$

Table 1. Experimental verification of Wien's displacement law.

Temp K	λ_{max} (micron)	$\lambda_{max}T$(micron-K)
1646	1.78	2928
1449	2.05	2970
1259	2.33	2933
1095	2.61	2859
995	2.94	2925
904	3.17	2866
725	4.06	2943

The law was verified by Lummer and Pringsheim in 1899. The numbers for $\lambda_{\max}$ for a given temperature T, read from *Figure* 3, and the product $\lambda_{\max}T$ are given in *Table* 1.

It is clear from *Table* 1 that the black-body spectrum indeed follows Wien's displacement law. We must point out that if some other feature were chosen as an identifier of the wavelength, the value of λT would be different for that feature but remains unchanged as the temperature of the black body changes. The reader may verify this for the wavelengths where the emitted power is half of the maximum; for the left of $\lambda_{\max}$ this value is about 1825 micron-K and for the right the value is about 5500 micron-K at all temperatures.

Obtaining the displacement law was only the first step in Wien's analysis. He wanted to understand the shape of the black-body spectrum. For this, he applied Stefan's law for energy contained in the spectrum between wavelengths λ_1 and $\lambda_1 + \mathrm{d}\lambda_1$. Accordingly,

$$\frac{u(\lambda_1)\mathrm{d}\lambda_1}{u(\lambda_2)\mathrm{d}\lambda_2} = \left(\frac{T_1}{T_2}\right)^4 . \tag{18}$$

This combined with equation (16) gives

$$\frac{u(\lambda_1)}{T_1^5} = \frac{u(\lambda_2)}{T_2^5} = \text{constant}. \tag{19}$$

Temp K	E_{max}	$E_{max} T^{-5} \times 10^{17}$
1646	135.5	1121
1449	73.3	1147
1259	34.3	1084
1095	17.7	1124
995	11.1	1138
904	6.7	1110
725	2.2	1098

Table 2. Experimental verification of equation (20).

As discussed in *Appendix* 2, the radiation coming out of a cavity is directly proportional to the radiation density inside it. Thus the emissivity defined by equation (5) should also satisfy

$$\frac{e_{\lambda 1}}{T_1^5} = \frac{e_{\lambda 2}}{T_2^5} = \text{constant}. \qquad (20)$$

As noted earlier, the constant above would be different for different wavelengths. Equation (20) was also verified by Lummer and Pringsheim. Radiated emission from a black body as a function of the wavelength for different temperatures as obtained by them is shown in *Figure* 3. If we now read the emitted radiation $E_{\max}$ at $\lambda_{\max}$ for different temperatures and divide it by the fifth power of the temperature, we should get a constant according to equation (20). This is done in *Table* 2 with the numbers taken from the plot of *Figure* 3.

As is clearly seen from *Table* 2, equation (20) is satisfied to a high degree of accuracy by experimental numbers for the black-body spectrum. It is thus established that for a point in the black-body spectrum, specified by a wavelength at a given temperature, the ratio given by equation (19) or (20) remains unchanged as one looks at another temperature and the corresponding wavelength given by equation (15) or (16). Thus this ratio must be a function $f(\lambda T)$ of the product λT of the wavelength and temperature. This makes the ratio of equation (19) dependent on the wavelength at a given temperature and at the same time keep it unchanged for points related by equation (15) as the temperature of the body changes. Thus in general

$$\frac{u(\lambda)}{T^5} = f(\lambda T). \tag{21}$$

Using equation (15), this can also be written as

$$u(\lambda) = \frac{F(\lambda T)}{\lambda^5}. \tag{22}$$

Since $u(\lambda)\,\mathrm{d}\lambda$ is the energy contained in the range $\mathrm{d}\lambda$, the formula above is transformed to a function of the frequency $\nu = \frac{c}{\lambda}$ by writing $\mathrm{d}\lambda = -\frac{c}{\nu^2}\mathrm{d}\nu$ and is given as

$$u(\nu) = \nu^3 \phi\left(\frac{\nu}{T}\right), \tag{23}$$

where ϕ is an unknown function.

We pause here for a moment to marvel at Wien's clever use of thermodynamics to provide insights into the nature of black-body spectrum.

Next, Wien took one more step and assumed that the frequency of radiation emitted by molecules should be proportional to their kinetic energy, i.e., $\frac{1}{2}mv^2 = a\nu$, and the intensity of radiation at that frequency would depend on the number of molecules at that kinetic energy, i.e., it is proportional to $e^{-\frac{1}{2}mv^2/kT}$, where k is Boltzmann's constant. Based on this, he proposed the following formula for the density of black-body radiation

$$u = \frac{A}{\lambda^5}e^{-b/\lambda T} \quad \text{or} \quad u(\nu) = \frac{A\nu^3}{c^4}e^{-b\nu/cT}. \tag{24}$$

This formula gave a very good fit to the black-body spectrum as a shown in *Figure* (3). Notice that the constant b can be related to $\lambda_{\max}$ for temperature T by maximizing u above with respect to λ and gives $b = 5\lambda_{\max}T$. Although there appears to be some deviation from the experimental curve for large wavelengths, the match near the maximum is nearly perfect. In any case, experimental numbers are more accurate near the maximum so the formula provided by Wien was really a satisfactory one. For his pathbreaking work, Wien was awarded the Nobel Prize in 1911. The importance of his work is clearly reflected by the Nobel Prize presentation speech. Some excerpts from the speech are given below:

The work done by Wien really set the stage for Max Planck to enter the scene.

"In 1893 Wien published a theoretical paper which was destined to acquire the utmost importance in the development of radiation theory".

"Wien's displacement law provides half the answer to the problem".

"The importance of Wien's displacement law extends in various directions".

"The method has successfully been applied to the determination of the temperature of our light sources, of the sun and of some of the fixed stars, and has yielded extremely interesting results".

"In 1894 he deduced a black-body radiation law. This law has the virtue that, at short wavelengths, it agrees with the above mentioned experimental investigations by Lummer and Pringsheim".

Towards the end of the speech it is mentioned that "It was Planck who solved this problem and his formula provides the long sought-after connecting link between radiation energy, wavelength and black body temperature". Thus the work done by Wien really set the stage for Max Planck to enter the scene.

Planck's Work: The Birth of Quanta

Max Planck had studied physics under Helmholtz and Kirchhoff at Berlin. He was highly fascinated by the second law of thermodynamics and had self-studied Clausius' papers. As a researcher he had been investigat-

Planck started by analyzing the energy equilibrium between a radiating dipole and a radiation field.

ing how the second law could be applied to different physics problems. In 1894 he turned his attention to the problem of black-body radiation. Please recall that the analysis of Wien discussed above had come out in that year. In the following account of Planck's introduction of the concept of quanta, note the dates to appreciate the pace at which Planck must have worked.

Planck started by analyzing the energy equilibrium between a radiating dipole and a radiation field. By equating the energy absorbed by an oscillator to the energy radiated by it – so that equilibrium exists between the radiation in a cavity and the oscillators on its walls absorbing and radiating energy – he found that the energy density $u(\nu)$ in a cavity is related to the average energy $E(\nu)$ of a radiating oscillator by the following formula:

$$u(\nu) = \frac{8\,\pi\,\nu^2}{c^3} E(\nu). \qquad (25)$$

Thus if we could calculate the average energy per oscillator, the results for spectral density could also be obtained through equation (25). This is what Planck had to say about it in his Nobel Lecture:

"The noteworthy result was found that this connection was in no way dependent upon the nature of the resonator, particularly its attenuation constant – a circumstance which I welcomed happily since the whole problem thus became simpler, for instead of the energy of radiation, the energy of the resonator could be taken and, thereby, a complex system, composed of many degrees of freedom, could be replaced by a simple system of one degree of freedom."

It must be pointed out that taking $E(\nu) = kT$ in equation (25) leads to the Rayleigh–Jeans formula,

$$u(\nu) = \frac{8\,\pi\,\nu^2}{c^3} kT \qquad (26)$$

for black-body radiation, and it is found to fit the spectrum well at large wavelengths and high temperatures. Having obtained the result above, Planck now started attacking the problem of black-body spectrum and failed in his initial attempts. Planck then started applying second law of thermodynamics for further investigations. According to him (Nobel Lecture):

Planck was concerned with the irreversibility of the energy exchange between resonator (oscillator) and radiation.

"So there was nothing left for me but to tackle the problem from the opposite side, that of thermodynamics, in which field I felt, moreover, more confident. In fact my earlier studies of the Second Law of Heat Theory stood me in good stead, so that from the start I tried to get a connection, not between the temperature but rather the entropy of the resonator and its energy, and in fact, not its entropy exactly but the second derivative with respect to the energy since this has a direct physical meaning for the irreversibility of the energy exchange between resonator and radiation."

As is clear from the quote above, Planck was concerned with the irreversibility of the energy exchange between resonator (oscillator) and radiation. In particular, if resonator was away from equilibrium then its entropy must increase as it moved towards equilibrium. What does it mean it terms of its second derivative with respect to the energy?

Suppose a system is away from the equilibrium energy by an amount ΔE. As it moves towards equilibrium, its energy changes by an amount $\mathrm{d}E$. Then Planck first showed that the change in its entropy is proportional to $\Delta E \times \mathrm{d}E \times \frac{\partial^2 S}{\partial E^2}$. Thus for entropy to increase as the resonator energy approached its equilibrium value, the second derivative $\frac{\partial^2 S}{\partial E^2}$ must be negative since ΔE and $\mathrm{d}E$ will have opposite signs in such a process. He therefore defined the entropy of an oscillator to be

$$S = -\frac{E}{\beta\nu} \ln\left(\frac{E}{\alpha\nu\, e}\right), \qquad (27)$$

where e is the base of natural logarithm. The formula can be derived from Wien's law as is easily seen. Combine equation (25) with Wien's formula of equation (24) to write the energy of an oscillator as

$$E(\nu) = \alpha\nu\, \mathrm{e}^{-\beta\nu/T} \; (\alpha > 0 \text{ and } \beta > 0). \qquad (28)$$

Invert this equation and use $\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$ to get

$$\left(\frac{\partial S}{\partial E}\right)_V = -\frac{1}{\beta\nu}\ln\left(\frac{E}{\alpha\nu}\right), \qquad (29)$$

which is integrated to get equation (27). What is important, however, is that the second derivative of the entropy comes out to be negative thereby satisfying Planck's requirement. The second derivative simply is

$$\frac{\partial^2 S}{\partial E^2} = -\frac{1}{\beta\nu}\frac{1}{E} \qquad (30)$$

showing the consistency of the Wien's law with the principle of increase of entropy. After this things started moving really fast. Planck presented these results in June 1900, but soon after, in October 1900, Rubens and Kurlbaum (Rubens and Kurlbaum, *Berliner Berichte*, pp.929-941, 1900) showed convincingly that Wien's law deviated from experimental numbers at large wavelengths and high temperatures. The results of their investigations are shown in *Figure* 6 where the energy emitted at wavelength of 24μ is plotted against temperature. Recall that such a deviation for large wavelengths was also noticed in *Figure* 3 but Rubens and Kurlbaum worked at a wavelength well beyond the upper limit of the results of Lummer and Pringsheim displayed in *Figure* 3. Thus from their work it became absolutely clear that for large wavelengths (small frequencies) Wien's formula underestimates the experimental results at high temperatures, whereas the Rayleigh–Jeans formula (equation 26) is very close to the experimental numbers. Rubens and

From the work of Rubens and Kurlbaum, it became absolutely clear that for large wavelengths Wien's formula underestimates the experimental results at high temperatures.

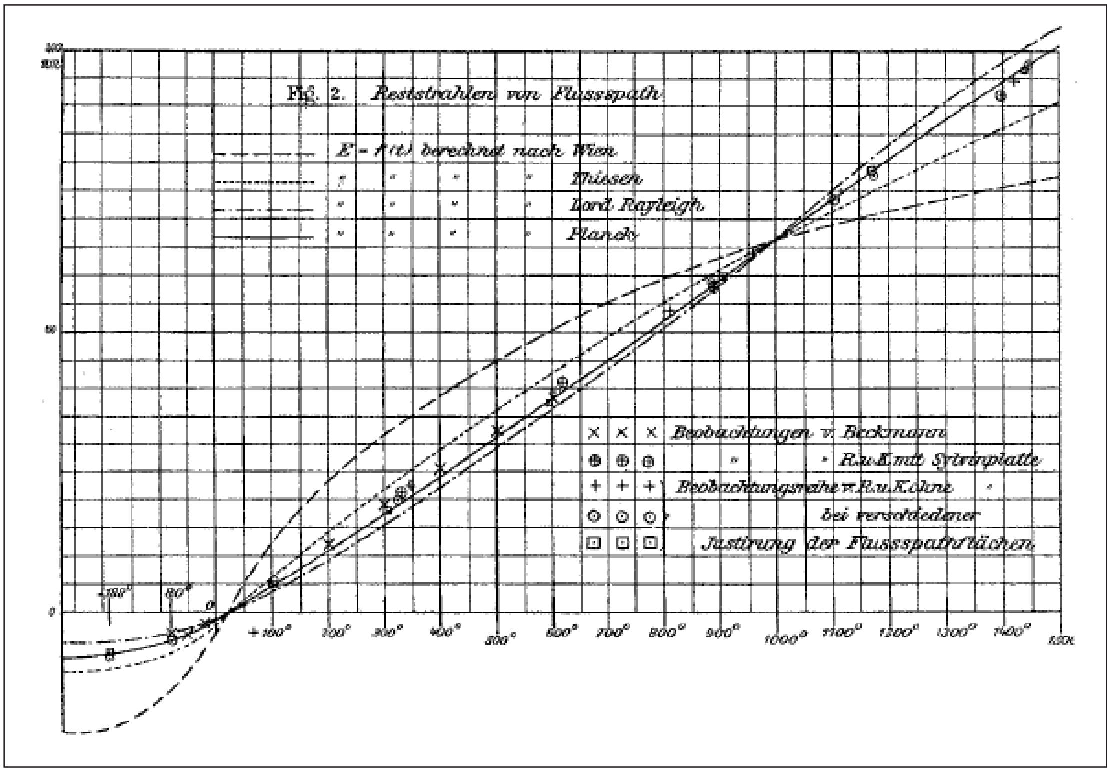


Figure 6. Experimental results of Rubens and Kurlbaum compared to different theories of black body radiation (Rubens and Kurlbaum, Annalen der Physik, Vol.4, p.649,1901).

Kurlbaum had told Planck about their results before publishing them. So Planck got back to work to modify Wien's formula and got a new expression for the black-body spectrum that fitted well with experimental data at all temperatures and wavelengths. Rubens and Kurlbaum also compared Planck's formula with their experimental results and showed beyond any doubt that his formula matched perfectly with the experiments (*Figure* 6). We now describe how Planck obtained his formula.

From experiments of Rubens and Kurlbaum, it was clear that at small frequencies and high temperatures Rayleigh–Jeans formula was close to the experimental results. Thus the entropy expression (equation 27) and its second derivative (equation 30) could not be correct in this range. Since the Rayleigh–Jeans formula is based on the energy E of the resonator being proportional to the temperature T, the first derivative of the entropy S

of an oscillator, $\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T}$, would be inversely proportional to its energy. This implies that $\frac{\partial^2 S}{\partial E^2} \propto \frac{1}{E^2}$. On the other hand, Wien's formula gave the second derivative to be inversely proportional to E. The correct expression for the second derivative should go from $\frac{1}{E}$ to $\frac{1}{E^2}$ as the temperature increased. Planck therefore interpolated between these two limits and wrote

$$\frac{\partial^2 S}{\partial E^2} = -\frac{a}{E(b+E)} \quad (a > 0,\ b > 0). \tag{31}$$

Integrating this gives

$$\frac{\partial S}{\partial E} = -\frac{a}{b} \ln\left(\frac{E}{E+b}\right). \tag{32}$$

Equating this to $\frac{1}{T}$ and inverting the equation gives

$$E = \frac{b}{\mathrm{e}^{b/aT} - 1}, \tag{33}$$

when combined with equation (25) this leads to

$$u(\nu) = \frac{8\pi\nu^2}{c^3} \frac{b}{\mathrm{e}^{b/aT} - 1}. \tag{34}$$

Since by Wien's analysis, $u(\nu)$ has the form given by equation (23), b in the equation above must be proportional to the frequency ν. Taking $b = \beta\nu$, we get

$$u(\nu) = \frac{8\pi\nu^3}{c^3} \frac{\beta}{\mathrm{e}^{\beta\nu/aT} - 1}. \tag{35}$$

This is Planck's formula in its primitive form. The constants β and a could be calculated by comparing with Wien's formula and matching with the coefficients employed there. The numbers could also be obtained from Stefan's constant and the value of $\lambda_{\max} T$. As mentioned above, it fitted the data of Rubens and Kurlbaum perfectly. From the formula above, Planck also obtained the entropy of an oscillator to be

$$S = a\left[\left(1 + \frac{E}{\beta\nu}\right) \ln\left(1 + \frac{E}{\beta\nu}\right) - \frac{E}{\beta\nu} \ln \frac{E}{\beta\nu}\right]. \tag{36}$$

So far what Planck had presented was only an interpolation formula that fitted with the experimental data well. However, it was not clear what it meant. Planck was conscious of this fact. He says in his Nobel Lecture:

"...However, even if the radiation formula should prove itself to be absolutely accurate, it would still only have, within the significance of a happily chosen interpolation formula, a strictly limited value. For this reason, I busied myself, from then on, that is, from the day of its establishment, with the task of elucidating a true physical character for the formula, and this problem led me automatically to a consideration of the connection between entropy and probability, that is, Boltzmann's trend of ideas; until after some weeks of the most strenuous work of my life, light came into the darkness, and a new undreamed-of perspective opened up before me."

As is evident from above, Planck now worked very hard to get a physical interpretation of his formula. For this he employed Boltzmann's approach to obtain entropy of an oscillator. According to Boltzmann, entropy S of a system is related to the number of ways Ω that a system could have a given energy E as follows:

$$S = k \ln \Omega. \tag{37}$$

Further when a system is in equilibrium, the corresponding entropy achieves its maximum value. Maximizing entropy of a system gives probability $P(E)$, that a system at temperature T has energy E, to be

$$P(E) \propto \mathrm{e}^{-E/kT}. \tag{38}$$

Planck calculated the entropy of an oscillator in the following way: He assumed that given total energy E_N was divided among N oscillators so that the average energy is E. Further for purposes of counting, let the energy E_N be made up of small elements of energy ε so that

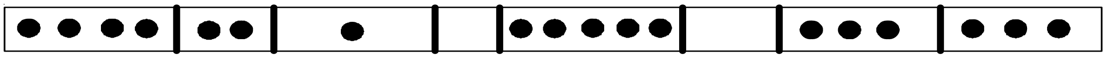


Figure 7. Distribution of P elements (●) among N oscillators (separated by ▌).

the total number of such elements is P. Thus

$$N = \frac{E_N}{E} \quad and \quad P = \frac{E_N}{\varepsilon}. \tag{39}$$

The number of ways that this system could have energy E_N is equal to the number of ways the P elements could be distributed among the N oscillators. This is shown in *Figure* 7 where elements are denoted by filled circles and oscillators by rectangular boxes separated by a vertical bar which are $(N-1)$ in number.

To count the number of ways the filled circles in the figure above could be distributed in the N boxes, we can count the number of ways the circles and the bars together can be arranged. Each one of these arrangements would create N boxes and certain number of circles in them. This gives $(N+P-1)!$ arrangements. However since all the elements are equivalent and so are the bars, their permutation among each other does not create any new arrangement. Thus the number obtained above is larger by this factor. Therefore the correct number of distinguishable ways that P elements can be distributed among N oscillators is given as

$$\Omega = \frac{(N+P-1)!}{(N-1)!P!}. \tag{40}$$

Using Stirling's formula for large numbers of N and P, this can be approximated as

$$\Omega = \frac{(N+P)^{(N+P)}}{N^N P^P}. \tag{41}$$

Thus entropy per oscillator is given as

$$S = \frac{1}{N} k \ln \Omega = k \left[\left(1 + \frac{E}{\varepsilon}\right) \ln \left(1 + \frac{E}{\varepsilon}\right) - \frac{E}{\varepsilon} \ln \frac{E}{\varepsilon} \right] \tag{42}$$

This has exactly the same form as equation (36). It is therefore tempting here to compare the two expressions and conclude that each energy element ε cannot be taken to be arbitrarily small but must equal $\beta\nu$. Similarly a in equation (36) should be equal to the Boltzmann constant k. However, Planck applied a different argument. Combining equations (23) and (25), he first writes

For proper accounting of black-body radiation, the energy element is not just a convenient counting tool but has a definite value, a quantum of energy, for a given frequency.

$$E(\nu) = \nu\phi\left(\frac{\nu}{T}\right), \tag{43}$$

which is then inverted to get

$$\frac{\nu}{T} = f\left(\frac{E}{\nu}\right) \quad \text{or} \quad \frac{1}{T} = \frac{1}{\nu} f\left(\frac{E}{\nu}\right). \tag{44}$$

However, $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$. Thus using equation (44) above gives

$$dS = \mathrm{d}\left(\frac{E}{\nu}\right) f\left(\frac{E}{\nu}\right) \Rightarrow S = F\left(\frac{E}{\nu}\right). \tag{45}$$

Thus entropy of an oscillator is a function of the ratio $\frac{E}{\nu}$ of its average energy E and its frequency ν. This immediately implies that $\varepsilon = h\nu$, where h is a constant. As pointed out above, this means that for proper accounting of black-body radiation, the energy element is not just a convenient counting tool but has a definite value, a quantum of energy, for a given frequency. One can now work backwards from this expression of the entropy to get the average energy $E(\nu)$ of the oscillator. It comes out to be

$$E(\nu) = \frac{h\nu}{\mathrm{e}^{h\nu/kT} - 1} \tag{46}$$

When combined with equation (25) it gives

$$u(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{\mathrm{e}^{h\nu/kT} - 1} \tag{47}$$

Using Stefan–Boltzmann constant σ and the Wien's constant b (equation 24), Planck obtained the values of h

At the time when Planck obtained the value of Boltzmann's constant from the radiation formula, there was no other way that it could be obtained.

and k to be

$$h = 6.55 \times 10^{-27} \text{ erg.sec and } k = 1.346 \times 10^{-16} \text{ erg/deg.} \quad (48)$$

Planck presented this work in a paper titled 'On energy distribution law in the normal spectrum' at a meeting of the German Physical Society on December 14, 1900, which is now regarded as the birthday of Quantum Theory.

At the time when Planck obtained the value of Boltzmann's constant from the radiation formula, there was no other way that it could be obtained. In fact after getting the value of k, Planck calculated the Avogadro's number N_{A} from the gas constant R and electronic charge e from the Faraday constant F as given below:

$$N_{\mathrm{A}} = \frac{R}{k} = 6.175 \times 10^{23} \text{ per mole and}$$
$$e = \frac{F}{N_{\mathrm{A}}} = 4.69 \times 10^{-10} \text{ esu.} \quad (49)$$

The following is an excerpt from Planck's Nobel Lecture on the calculation of e:

"At the time when I carried out the corresponding calculation from the radiation law, an exact proof of the number obtained was quite impossible, and not much more could be done than to determine the order of magnitude which was admissible. It was shortly afterward that E Rutherford and H Geiger succeeded in determining, by direct counting of the alpha particles, the value of the electrical elementary charge, which they found to be 4.65×10^{-10} *esu; and the agreement of this figure with the number calculated by me, 4.69×10*$^{-10}$ *esu, could be taken as a decisive confirmation of the usefulness of my theory."*

This concludes our description of Planck's work. We end it by quoting from the Nobel Prize presentation speech that sums up Planck's contribution nicely:

"Planck's radiation theory is, in truth, the most significant lodestar for modern physical research, and it seems that it will be a long time before the treasures will be exhausted which have been unearthed as a result of Planck's genius".

After Planck introduced the concept of quantum of energy as discussed above, it was examined critically for its logical consistency and for the method of calculating entropy that Planck applied. Einstein in particular questioned these aspects of Planck's theory and in his attempt to find answers to these questions, he made revolutionary contributions to the theory of quanta and provided a solid footing to this new concept. In the following section, we discuss his contributions.

Planck had introduced the entropy of an oscillator by taking the logarithm of the number of possible states.

Einstein and the Theory of Quanta: Are Quanta Real?

As pointed out above, Planck had introduced the entropy of an oscillator by taking the logarithm of the number of possible states. On the other hand Boltzmann's procedure really meant that when in equilibrium, the number of oscillators and their average energy be calculated by maximizing the entropy. When Einstein studied Planck's work he had precisely this objection to Planck's analysis. In hindsight, we can say that Planck got the correct answer because he counted the number of states (equation 40) for indistinguishable particles properly to match the expression for entropy (equation 36) of an oscillator that he already had. Using the same counting procedure S N Bose later showed how the radiation density formula indeed follows when entropy is maximized.

Einstein had another objection to Planck's analysis: According to him a logical inconsistency of Planck's theory was that whereas the oscillators are assumed to have quantized energy levels (a new concept), classical results

Planck concluded from his investigations that oscillators must have energy in units of energy elements $\varepsilon = h\nu$.

are used to work out their rate of radiation. We now discuss how Einstein resolved these.

To find the average energy of an oscillator by applying Boltzmann's procedure, we first need the probability that the system has certain energy. If an oscillator can have energy only in units of $h\nu$, then the possible energies that it can have are $nh\nu$ $(n = 0, 1, 2, \cdots)$. The probability that it has energy $nh\nu$ is given by Boltzmann to be proportional to $\mathrm{e}^{-nh\nu/kT}$. Thus the average energy of an oscillator will be

$$E(\nu) = \frac{\sum\limits_n nh\nu\, \mathrm{e}^{-nh\nu/kT}}{\sum\limits_n \mathrm{e}^{-nh\nu/kT}} = \frac{h\nu}{e^{h\nu/kT} - 1} \qquad (50)$$

This is the same expression (equation 46) that is obtained by Planck. The difference is that whereas Planck concluded from his investigations that oscillators must have energy in units of energy elements $\varepsilon = h\nu$, here at the outset, it is assumed that oscillators can take energies only in certain quanta and then, Boltzmann's procedure is applied to find the average energy.

On the logical inconsistency Einstein had the following to say (A Einstein, *Annalen der Physik*, **Vol.17**, p.132, 1905), English translation A B Arons and M B Peppard, *Am. J. Phys.*, **Vol.33**, p.367, 1965):

A logical inconsistency of Planck's theory was that whereas the oscillators are assumed to have quantized energy levels (a new concept), classical results are used to work out their rate of radiation.

"It should be kept in mind that optical observations refer to values averaged over time and not to instantaneous values. Despite the complete experimental verification of the theory of diffraction, reflection, refraction, dispersion and so on, it is conceivable that a theory of light operating with continuous three-dimensional functions will lead to conflicts with experience if it is applied to the phenomena of light generation and conversion".

He then goes on to show that light with low energy density can be thought of as a collection of particles each with energy proportional to the frequency of light ν. He does this by showing that if the volume of radiation is changed without changing its energy, the associated entropy change is similar to that of an ideal gas. As such the radiation can then be thought of as a collection of particles of light. The restriction to low density comes from the use of Wien's formula, which is exact for low density radiation, in the analysis. We now present Einstein's analysis.

Consider the spectral density $\phi(\nu)$ (per unit volume) of the entropy S of radiation in volume V_0 so that

$$S = V_0 \int \phi(\nu)\mathrm{d}\nu. \tag{51}$$

Now

$$\frac{dS}{\mathrm{d}E} = \frac{1}{T} \;\Rightarrow\; \frac{\partial\phi}{\partial u} = \frac{1}{T}. \tag{52}$$

Next write Wien's formula (equation 24) as $u(\nu) = \frac{8\pi h}{c^3}\frac{\nu^3}{e^{h\nu/kT}}$, invert it to get $\frac{1}{T}$ and use equation (48) to write

$$\frac{\partial\phi}{\partial u} = \frac{k}{h\nu}\ln\frac{8\pi\, h\nu^3}{c^3 u}. \tag{53}$$

This is easily integrated to get

$$\phi = -\frac{k\,u}{h\nu}\left(\ln\frac{uc^3}{8\pi h\,\nu^3} - 1\right), \tag{54}$$

Consider now the total radiation in the spectral range $\Delta\nu$ contained in volume V_0. Its energy E will be given as $E = V_0 u(\nu)\Delta\nu$. Thus using equation (51) the total entropy of this radiation is

$$S_0 = V_0\phi(\nu)\Delta\nu = -\frac{kE}{h\nu}\left(\ln\frac{Ec^3}{8\pi\, h\,\nu^3\, V_0\,\Delta\nu} - 1\right). \tag{55}$$

Now suppose that the volume of radiation is changed (say cavity expanded) to V keeping its total energy E the same, and in the process the entropy of radiation between frequencies ν and $\nu + \Delta\nu$ changes to S. Then the change $(S - S_0)$ can be easily calculated from equation (51) and comes out to be

$$S - S_0 = \frac{kE}{h\nu} \ln \frac{V}{V_0}. \qquad (56)$$

Change in the entropy of low density radiation of constant total energy upon change of it's volume is similar to the change in the entropy of an ideal gas.

Compare this with the change in entropy of N ideal gas molecules undergoing exactly the same process. The change in their entropy is given as

$$S - S_0 = kN \ln \frac{V}{V_0}. \qquad (57)$$

A comparison of equations (56) and (57) shows that the radiation contained between frequencies ν and $\nu + \Delta\nu$ can be considered as a collection of $\frac{E}{h\nu}$ number of particles. Since the total energy is E, this implies that energy of each particle is $h\nu$. This analysis shows that radiation of frequency ν can be considered as consisting of particles of energy $h\nu$ each. Thus according to Einstein (A Einstein, *Annalen der Physik* **Vol.17**, p.132, 1905).

"In accordance with the assumption to be considered here, the energy of light ray spreading out from a point source is not continuously distributed over an increasing space but consists of a finite number of energy quanta which are localized at points in space, which move without dividing, and which can only be produced and absorbed as complete units".

Having shown theoretically that light could be considered as a collection of quanta of energy $h\nu$ each, Einstein next considered three phenomena, namely,

(i) Stokes' Rule: Frequency of photoluminescent emission is less than that of the incident light,

Einstein showed that light could be considered as a collection of quanta of energy $h\nu$ each.

(ii) The Photoelectric Effect: Energies of photoelectrons are independent of the intensity of the incident light, and

(iii) Photoionization of Gases: A minimum frequency of light is required to ionize a gas, which could not be explained using classical theory of radiation. He applied the new idea of energy quanta of radiation to successfully explain all three of them. The explanation gave solid experimental support to the concept of quanta of radiation.

Einstein's contribution to the concept of quantization does not end here. He further generalized it to state that not only electromagnetic oscillators but mechanical ones also have energy in units of $h\nu$.

The story of Einstein's contribution to the concept of quantization does not end here. He further generalized it to state that not only electromagnetic oscillators but mechanical ones also have energy in units of $h\nu$. He used this to explain the fact that specific heat of solids goes to zero with temperature going to zero. The experimental situation in 1900 in connection with the specific heat of solids was as follows. Dulong–Petit law stated that specific heat of solids is $3R$, where R is the gas constant, per mole. However, it was seen experimentally that some materials, particularly light elements, did not obey Dulong–Petit law and their heat capacities were smaller than $3R$. For some other elements, as the temperature was increased, the specific heat rose rapidly and attained the value of $3R$ at high temperatures. Einstein asked (A Einstein, *Annalen der Physik*, **Vol.22**, p.180, 1907):

"...for the following question forces itself upon us. If the elementary oscillators that are used in the theory of the energy exchange between radiation and matter cannot be interpreted in the sense of the present kinetic molecular theory, must we not also modify the theory for the other oscillators that are used in the molecular theory of heat?"

Thus Einstein proposed that even the energy of an atom in a solid, vibrating with frequency ν will be given by equation (46) for each degree of freedom. Thus the energy of N such atoms will be

$$U = 3N \frac{h\nu}{e^{h\nu/kT} - 1}, \qquad (58)$$

"... This remarkable theory, for which Planck received the Nobel Prize for Physics in 1918, suffered from a variety of drawbacks and about the middle of the first decade of this century it reached a kind of impasse."
From the presentation speech of the Nobel Prize to Einstein

and the corresponding specific heat

$$\frac{\mathrm{d}U}{\mathrm{d}T} = 3R\left(\frac{h\nu}{kT}\right)^2 \frac{\mathrm{e}^{h\nu/kT}}{\left(\mathrm{e}^{h\nu/kT}-1\right)^2}. \tag{59}$$

This expression explains that for light elements, which have relatively larger frequencies, the specific heat should be smaller than $3R$. As the temperature becomes higher, the specific heat should attain the value $3R$ given by Dulong and Petit law. Interestingly, the expression above predicted that the specific heat would vanish as $T \to 0$. This was confirmed experimentally by Nernst.

We end this section with a quote from the presentation speech of the Nobel Prize to Einstein:

"A third group of studies, for which in particular Einstein has received the Nobel Prize, falls within the domain of the quantum theory founded by Planck in 1900. This theory asserts that radiant energy consists of individual particles, termed "quanta", approximately in the same way as matter is made up of particles, i.e. atoms. This remarkable theory, for which Planck received the Nobel Prize for Physics in 1918, suffered from a variety of drawbacks and about the middle of the first decade of this century it reached a kind of impasse. Then Einstein came forward with his work on specific heat and the photoelectric effect".

Concluding Remarks

In this article we have covered a period in the development of modern physics that gave us an absolutely new concept that the energy is not exchanged in a continuous manner but in quantized form. We started with an introduction to black body and its spectrum and discussed the pathbreaking work of Wien. This work really laid foundations of further exploration by Planck. Taking an approach based on the second law of thermodynamics, Planck came up with an interpolation formula that fitted the experimental results for the black-body spectrum perfectly. However, Planck did not stop there but tried to get a meaning of his formula. In this process he was led to introduce the concept of quantum of energy. This was a tremendous insight and a bold departure from the set theories at that time. The theory was put on a solid footing by Einstein who critically examined Planck's theory and in the process contributed significantly to establish the principal of quanta. Planck's thoughts about his work are reflected from a letter he wrote on October 7, 1931 to an American colleague R W Wood. Parts of this letter are quoted below (taken from suggested reading [3]):

"Briefly summarized, what I did can be described as simply an act of desperation.... I had been wrestling unsuccessfully for six years (since 1894) with the problem of equilibrium between radiation and matter and I knew this problem was of fundamental importance to physics; I also knew the formula that expresses the energy distribution in the normal spectrum. A theoretical interpretation therefore had to be found at any cost, no matter how high.... This approach was opened to me by maintaining the two laws of thermodynamics. For the rest, I was ready to sacrifice every one of my previous conviction about physical laws".

Suggested Reading

[1] M Jammer, ***The conceptual development of quantum mechanics***, **McGraw Hill, New York, 1966.**

[2] **M N Saha and B N Srivastava,** ***Treatise on heat,*** **The Indian Press Pvt.Ltd., Kolkata, III edition, 1950.**

[3] **M S Longair,** ***Theoretical concepts in physics,*** **Cambridge University Press, London 1984.**

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"A new scientific truth does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die, and a new generation grows up that is familiar with it."

"For it is work which is the favourable wind that makes the ship of human life sail the high seas, and as for the evaluation of the worth of this work, there is an infallible, time-honoured measure, a phrase which pronounces the final authoritative judgement of all times: By their fruits ye shall know them".

– Max Planck

Appendix 1. Kirchhoff's Law

An argument for $\frac{e_\lambda}{a_\lambda} = E_\lambda$ is given here on the basis of isotropy of radiation inside a cavity. Since the surface of a body in a hollow cavity and the walls of the cavity form a cavity themselves, the radiation inside the new cavity is also isotropic. Let the cavity be made of a material with emissive power e_λ and let its absorption and reflection coefficients be r_λ and a_λ, respectively. Similarly let the corresponding quantities for the material of the body be e'_λ, r'_λ and a'_λ. Now any radiation inside the cavity can be thought of as the sum of radiation reflected from the surface of the cavity and that being emitted from it. Since radiation is isotropic, the intensity of radiation incident from any direction is the same as the intensity of radiation reflected in any direction. Therefore if the radiation inside the cavity corresponds to that of a body with emissive power E_λ, radiation incident on a small area $\mathrm{d}A$ of the cavity wall (or the surface of the body inside) per unit cross-section per unit solid angle per unit time from any direction is proportional to $E_\lambda \,\mathrm{d}\lambda$ in the range $\mathrm{d}\lambda$. Radiation reflected per unit cross-section per unit solid angle per unit time is going to be proportional to $r_\lambda E_\lambda \,\mathrm{d}\lambda$ for the cavity wall and $r'_\lambda E_\lambda \,\mathrm{d}\lambda$ for the body surface (the constant of proportionality for both the incident and the reflected radiation is the same and depends on the angle of incidence or reflection, see Appendix 2). In particular let us look at the direction perpendicular to $\mathrm{d}A$. The total radiation going out from the wall in that direction is the sum $(e_\lambda \,\mathrm{d}\lambda + r_\lambda E_\lambda \,\mathrm{d}\lambda)$ of the reflected and the emitted radiation per unit cross-section per unit solid angle per unit time. But this is precisely the radiation existing inside the cavity. Therefore

$$e_\lambda + r_\lambda E_\lambda = E_\lambda,$$

which in turn gives

$$e_\lambda = E_\lambda(1 - r_\lambda) = E_\lambda a_\lambda \quad \{a_\lambda + r_\lambda = 1\}$$
$$\Rightarrow \frac{e_\lambda}{a_\lambda} = E_\lambda$$

Exactly the same arguments apply for radiation coming from the surface of the body. Thus, $\frac{e'_\lambda}{a'_\lambda} = E_\lambda$.

This implies that $\frac{e'_\lambda}{a'_\lambda} = \frac{e_\lambda}{a_\lambda} = E_\lambda$.

E_λ must therefore be a universal constant. Now following the arguments in the main text, it can be shown to be independent of the geometry of a cavity and equal to the emissive power of a black body.

Appendix 2. Energy Density and Pressure of Electromagnetic Radiation in a Cavity

Consider a plane electromagnetic wave traveling in the x-direction as shown in *Figure* A2.1.

The electric field of the wave is in y-direction and is given as $E(x,t) = E_0 e^{i(kx-\omega t)}$. The electromagnetic wave contains energy and it also transports it in the direction of travel. The wave also carries momentum in the same direction. If the average energy content of the wave is u, the energy carried by it across a unit area in unit time S, and the momentum it carries across a unit area in unit time p, then these quantities are given in terms of E_0 as (here c is the speed of light)

$$u = \frac{1}{2}\varepsilon_0 E_0^2,$$

$$S = cu, \qquad \text{(A2.1)}$$

$$p = \frac{S}{c} = u.$$

The energy carried across a unit area in unit time is known as the intensity of radiation. Further, because of the momentum carried by the wave, if a plane wave falls on a perfectly absorbing plate of area A, it will apply a force on it and its value would be equal to uA, i.e., the total energy passing through the area. To visualize these concepts, imagine a fluid of density ρ flowing with speed v in the x-direction. The fluid then has energy and carries energy and momentum across a given area. The kinetic energy per unit volume of the fluid is $u = \frac{1}{2}\rho\, v^2$, the energy and momentum carried across a unit area per unit time are $S = \frac{1}{2}\rho\, v^3$ and $p = \rho\, v^2$, respectively.

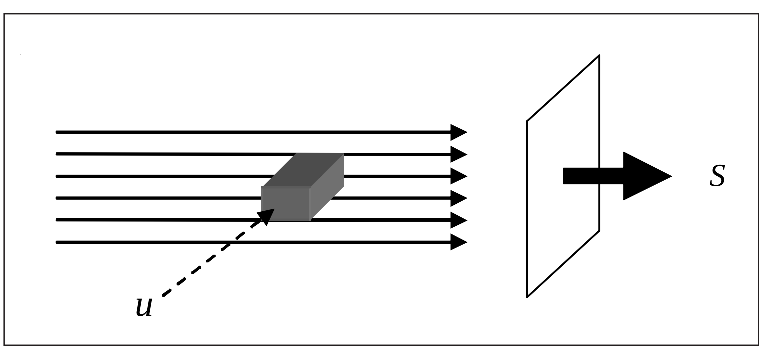


Figure A2.1. A plane wave traveling in the positive x-direction. The energy content per unit volume is u and energy passing per unit area unit time is S.

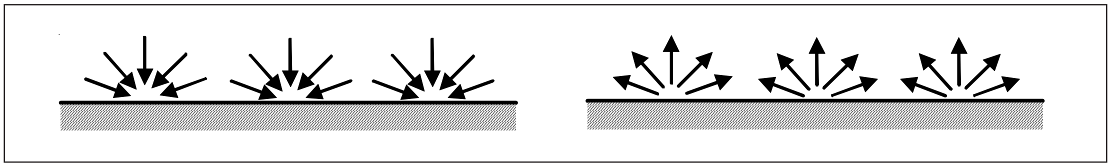


Figure A2.2. Because of the isotropic nature of radiation inside a cavity, the energy incident on the surface or radiating out of it looks exactly the same at any point on the surface.

Now in a cavity the radiation is isotropic. Thus at any point in it the energy density is the same and the intensity of radiation is identical in all directions. We now wish to find the average energy per unit area coming out of a small hole made on the walls of the cavity. We also want to derive the pressure on the walls of the cavity that the radiation applies. These quantities are important in the study of black-body radiation.

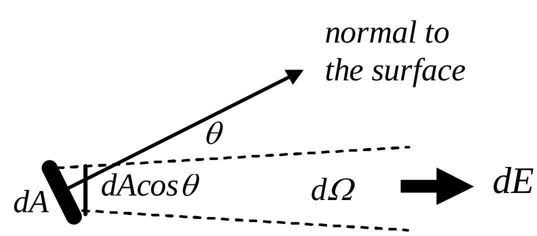
Consider a small part of the wall of a black body cavity as shown in *Figure* A2.2.

Because of the isotropy of radiation inside the cavity, the intensity of radiation looks exactly the same from any point on the wall. Similarly intensity of radiation coming out of the surface has the same value in all directions. This is made mathematically more precise as follows: Let the total energy, radiating in the full solid angle of 2π, coming out of a small portion $\mathrm{d}A$ be P Joules per unit area per unit time. Then the energy $\mathrm{d}E$ going into solid angle $\mathrm{d}\Omega$ at an angle θ from the normal to the surface (*Figure* A2.3) is given by the relation

$$\mathrm{d}E = \frac{P}{2\pi}\cos\theta\,\mathrm{d}A\,\mathrm{d}\Omega \tag{A2.2}$$

In the equation above, the factor of $\cos\theta$ arises because the intensity of radiation in all directions is the same and is given by the energy divided by the area normal to the direction; the latter is $\mathrm{d}A\cos\theta$ (see *Figure* A2.3).

Figure A2.3. Radiation energy being emitted from a small area dA of a body in solid angle dΩ at an angle θ from the normal to the surface. The projection of area dA in perpendicular to the direction of emission is dAcosθ.



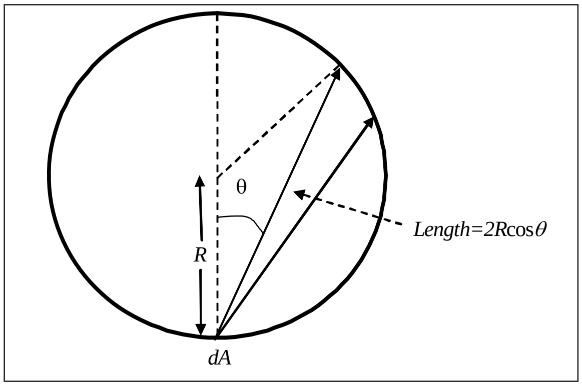


Figure A2.4. A large spherical cavity of radius R.

In a cavity, P would depend on the temperature of the cavity. We are now ready to find the energy density of radiation inside the cavity and also the pressure due to it on the walls of the cavity. We will also find the relation between the energy density and the energy that comes out of a hole made in the cavity.

Take a large cavity of radius R shown in *Figure* A2.4. Let its walls continuously emit energy P per unit area per unit time. When the radiation hits the surface, it gets totally absorbed so that the total energy in the cavity remains the same. We calculate the energy contained in the cavity and divide it by its volume to find the energy density.

For this take a small area dA on its surface. The radiation that comes out of it into the solid angle dΩ at an angle θ reaches the wall of the cavity in time $\Delta t = \frac{2R\cos\theta}{c}$, where c is the speed of light. Since energy going into this solid angle per unit time is given by equation A2.2, the total energy filling the small volume between two rays, shown in *Figure* A2.4, is given by

$$\mathrm{d}E\,\Delta t = \frac{P}{2\pi}\cos\theta\,\mathrm{d}A\,\mathrm{d}\Omega\,\frac{2R\,\cos\theta}{c}. \tag{A2.3}$$

Thus the energy ΔE that fills the entire cavity due to radiation from the area dA is given by integrating the expression above over $\theta = 0$ to $\theta = \frac{\pi}{2}$ and comes out to be

$$\Delta E = \frac{2PR}{3c}\mathrm{d}A. \tag{A2.4}$$

Since the total surface area of the cavity that is emitting radiation is $4\pi R^2$, the total energy E filling the cavity due to radiation from all around is given by

$$E = \frac{8\pi\,P\,R^3}{3c}, \tag{A2.5}$$

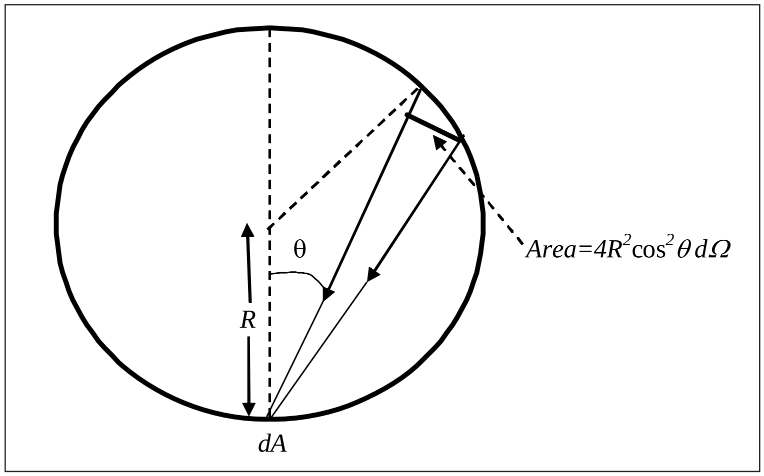


Figure A2.5. Radiation incident on small area element dA from a portion of the wall of a cavity.

which then gives the energy density to be

$$u = \frac{2P}{c}. \tag{A2.6}$$

We now calculate the pressure due to this radiation. For this, we again consider the cavity above and let the radiation from all over the cavity fall on the small area at its bottom and calculate the radiation force on this area (*Figure* A2.5). Dividing this force by the area gives the pressure. The calculation is slightly more involved than the previous calculation of the energy density.

As shown in the figure the area from which we consider the incident radiation is equal to $\frac{4R^2\cos^2\theta\,\mathrm{d}\Omega}{\cos\theta} = 4R^2\cos\theta\,\mathrm{d}\Omega$ and it makes a solid angle $\frac{\mathrm{d}A\cos\theta}{4R^2\cos^2\theta} = \frac{\mathrm{d}A}{4R^2\cos\theta}$ on the area dA. Thus the radiation energy dE going to area element dA is

$$\begin{aligned}\mathrm{d}E &= 4R^2\cos\theta\,\mathrm{d}\Omega \times \frac{P}{2\pi}\cos\theta \times \frac{\mathrm{d}A}{4R^2\cos\theta}\\ &= \frac{P}{2\pi}\cos\theta\,\mathrm{d}\Omega\,\mathrm{d}A.\end{aligned} \tag{A2.7}$$

The corresponding intensity dS is

$$\mathrm{d}S = \frac{\mathrm{d}E}{\mathrm{d}A\ \cos\ \theta} = \frac{P}{2\pi}\mathrm{d}\Omega. \tag{A2.8}$$

This intensity causes a momentum transfer of amount $\frac{S}{c}$ per unit area across the projection d$A\cos\theta$ of the area element dA normal to the direction of radiation. Thus the total momentum transfer to the area dA per unit time is $\frac{P}{2\pi\,c}\mathrm{d}\Omega\,\mathrm{d}A\ \cos\theta$.

Its component normal to the area dA gives the force $\frac{P\cos^2\theta}{2\pi\, c}\mathrm{d}\Omega\,\mathrm{d}A$ on this area. Thus the pressure due to the incident radiation is

$$p_1 = \frac{1}{\mathrm{d}A}\int\limits_{\theta=0}^{\theta=\pi/2}\frac{P\cos^2\theta}{2\pi\, c}\mathrm{d}\Omega\,\mathrm{d}A$$

$$= \frac{P}{3\,c}. \tag{A2.9}$$

This is pressure only due to the incident radiation. The radiation leaving the area dA also adds to this pressure by Newton's third law. Let us now calculate this pressure p_2 and get the total pressure by adding p_1 and p_2. The total energy leaving dA per unit time into a solid angle dΩ at angle θ is

$$\mathrm{d}E = \frac{P}{2\pi}\cos\theta\,\mathrm{d}A\,\mathrm{d}\Omega, \tag{A2.10}$$

and it carries with it a total momentum of $\frac{\mathrm{d}E}{c}$ per unit time. By momentum conservation the same amount of momentum is transferred to the area element dA in the direction making an angle θ normal to this area. The pressure p_2 due to radiation emitted from dA is therefore

$$p_2 = \frac{1}{\mathrm{d}A}\int\frac{\mathrm{d}E}{c}\cos\theta = \frac{P}{2\pi\, c}\int\limits_{\theta=0}^{\theta=\pi/2}\cos^2\theta\,\mathrm{d}\Omega$$

$$= \frac{P}{3\,c}. \tag{A2.11}$$

Thus the total pressure due to radiation inside the cavity is $p_1 + p_2 = \frac{2P}{3\,c}$ and is written in terms of the energy density u as

$$p = \frac{u}{3} \tag{A2.12}$$

In a similar manner the total radiation coming out of the area element dA per unit time is obtained by integrating expression in equation (A2.10) and gives the result $\frac{P}{2}\mathrm{d}A$. Thus radiation R coming out the hole per unit time per unit area can be written in terms of the energy density inside as

$$R = \frac{c}{4}u. \tag{A2.13}$$