

## 13 Black-body radiation and Planck's formula

This concluding Lecture contains a lighter load of mathematics than most of the other Lectures. From the mathematical perspective, we will see some applications of improper integrals and infinite series, usually studied in a second semester of Calculus. At the same time, this Lecture will also attempt to describe the historical background of the emergence of **Quantum Mechanics** — the area of physics on which most modern technology (and much of science) is based.

In Section 1, we begin by providing such a historical background. We will only glance over related mathematical details, but focus on what prompted Max Planck to derive his famous formula that revolutionized physics. In subsequent sections, we will more carefully examine his and his scientific opponents' derivations of that formula and then analyze some of its elementary consequences. Finally, in the last section, we will mention a curious modification of Planck's formula (made by Planck himself), which was confirmed much later in Quantum Electrodynamics.

### 13.1 Historical background of Planck's formula

#### 13.1.1 The historical stage before Planck

In the middle of the 19th century, physicists actively studied absorption and emission of radiation by heated objects, or **thermal radiation**. An object whose temperature is higher than the ambient temperature was known to emit more radiation than it absorbs from its surroundings. Conversely, a cooler object absorbs more radiation than it emits. Thus, thermal radiation is the main mechanism by which an object comes into thermal, or **thermodynamic, equilibrium** with its surroundings and hence, in this sense, it is related to Newton's cooling law mentioned in Lecture 9.

What is thermal radiation made of? It is now a well established scientific fact that all macroscopic objects consist of atoms, and atoms themselves consist of charged particles. At temperatures above absolute zero (which includes all practical cases around us), the atoms are in a state of constant and chaotic motion. It is also well known now that moving charged particles emit electromagnetic waves, and frequencies of those emitted waves depend on the particles' accelerations. Thus, thermal radiation consists of electromagnetic waves of various frequencies or, equivalently, wavelengths. We will refer to the wavelength in this section but will convert to the frequency "picture" later on, in Section 2. The notation for the wavelength is  $\lambda$ .

Note that the above description has been based on a number of modern concepts, which were not known or accepted in the middle of the 19th century. For example, the theory of electromagnetic waves (and the emission of such waves by accelerating charged particles) was developed in early 1870's by James Clerk Maxwell and experimentally confirmed in late 1880's by Heinrich Hertz, while the first active studies of thermal radiation laws occurred in 1850's (see below). So it may be an interesting project in physics history to understand how radiation was viewed back then. We, however, will not consider this topic here.

By late 1850's, it has been known that objects made of different materials and kept at different temperatures emit different amounts of radiation. Let  $E_\lambda d\lambda$  denote the amount of radiation energy emitted by an element of the object's surface within a small solid angle and into a wavelength interval  $[\lambda, \lambda + d\lambda]$ . Also, suppose that the object's surface is irradiated by, say, light, which is a form of radiation. Part of this radiation is reflected, and part absorbed.

Let  $A_\lambda$  denote the *percentage* of the radiation absorbed. It has been known by late 1850's that  $E_\lambda$  and  $A_\lambda$  are related in such a way that poor absorbers (i.e., good reflectors) are also poor emitters.

Then, in 1859, the great German physicist Gustav Kirchhoff stated a **law of thermal radiation** named after him:

*For an object that is in thermal equilibrium with its surroundings<sup>14</sup>, one has*

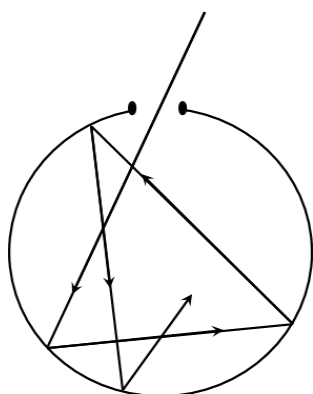
$$\frac{E_\lambda}{A_\lambda} = K_\lambda(T), \quad (13.1)$$

where  $K_\lambda(T)$  is a constant that depends only on the object's temperature  $T$  (and also on the wavelength), but is independent of the material and shape of the object.

Thus, while objects made of different materials emit and absorb radiation differently, their ratio of the emission and absorption coefficients as defined by (13.1) is independent of the material.

For an absolutely absorbing (i.e., "black") body, which absorbs all the incident radiation,  $A_\lambda = 1$  for all wavelengths. Then from Eq. (13.1) it follows that

$$K_\lambda(T) = E_\lambda |_{\text{black body}}.$$



Thus, the meaning of the universal (i.e., material- and shape-independent) constant  $K_\lambda(T)$  is that it is the *density of radiation* (per wavelength interval) emitted by a black body. Incidentally, since the absorption by a black body is the maximum and the ratio of the emitted to absorbed amounts of radiation is the same for all materials, then the emittance of the black body is also the maximum among all objects. This observation is consistent with a previously noted fact, known before Kirchhoff, that poor absorbers are also poor emitters and, conversely, good absorbers are also good emitters.

At this point it is instructive to ask a question: *What is, then, a black body?* A good physical approximation to a black body is a tiny hole made in a cavity with no other openings, as schematically shown in the figure above. Any ray of radiation entering the hole will be reflected by the cavity's walls and eventually absorbed by them. On the other hand, due to thermal chaotic motion, the molecules of the walls emit some radiation, in addition to also absorbing it. After a "sufficiently long time", *equilibrium between the walls and the radiation* inside the cavity is reached. In the equilibrium, a *detailed balance* takes place: at any given time, the amount of the emitted radiation of a given wavelength, polarization, and direction equals, on *average*, the amount of absorbed radiation with the same properties. In other words, importantly for a later discussion, *there is a thermodynamic equilibrium between the walls and the radiation.*

Thus, in practice, radiation from any cavity with a tiny hole very closely approximates the radiation of a black body. A familiar example of a cavity with a hole is a building with

<sup>14</sup>e.g., any object in a classroom where a constant temperature has been maintained sufficiently long, or a star in outer space

windows. The windows appear darker than the outside walls. One can say that they appear approximately black, as most light that gets into a window never reflects back to the observer; in other words, it is absorbed, regardless of its wavelength.

The above description makes no reference to the material of the inner walls of the cavity. That is, it implies that no matter what this material may be, a tiny hole in a cavity will radiate approximately as an ideal black body. You may want to know that while this statement is widely accepted in modern physics, it is still not entirely undisputed. For example, the paper by P.-M. Robitaille posted alongside this Lecture defends an alternative point of view, namely that the radiation of an actual cavity depends both on the material of the cavity's inner walls and also on the angle at which this radiation is measured. (However, the quantitative measure of this dependence has remained unclear to me.)

Returning now to the Kirchhoff's radiation law, it is evident that the *total energy* of radiation emitted by the black body into *all* wavelengths is the function of only the temperature  $T$  but not of the material the body is made of:

$$\int_0^{\infty} K_{\lambda}(T) d\lambda = u(T). \quad (13.2)$$

In 1879, a Slovene physicist, mathematician, and poet Jožef Stefan, who lived and worked in Vienna, Austria, formulated the **Stefan–Boltzmann** law for the total radiated energy<sup>15</sup>:

$$u(T) = \text{const} \cdot T^4. \quad (13.3)$$

By the *mid-1890's*, some experimental data for the spectral density  $K_{\lambda}(T)$  of the emitted radiation were collected for short (see below) wavelengths. Data for longer wavelengths were not available at that time due to experimental limitations. A number of researchers proposed several different analytical forms for  $K_{\lambda}(T)$ , basing their considerations on two criteria: (i) provide a fit for the available data; and (ii) satisfy the Stefan–Boltzmann law (13.3).

In 1895, a German physicist, an experimentalist Friedrich Paschen proposed an expression

$$K_{\lambda}(T) = b \cdot \lambda^{-\gamma} \cdot e^{-a/(\lambda T)} \quad (13.4)$$

with some constants  $a, b$  and with  $\gamma \approx 5.7$  to fit his own latest experiments. To this, another German physicist, a theoretician Wilhelm Wien pointed out that one must have  $\gamma = 5$  to satisfy the Stefan–Boltzmann law. Indeed, the integration of (13.4) using  $u$ -substitution yields:

$$\begin{aligned} \int_0^{\infty} K_{\lambda}(T) d\lambda &= \int_0^{\infty} b \cdot \lambda^{-\gamma} \cdot e^{-a/(\lambda T)} d\lambda && \left| \begin{array}{l} x = \lambda T \\ d\lambda = \frac{dx}{T} \end{array} \right. \\ &= b \int_0^{\infty} \left(\frac{x}{T}\right)^{-\gamma} e^{-\frac{a}{x}} \cdot \frac{dx}{T} \\ &= b \cdot \int_0^{\infty} x^{-\gamma} e^{-\frac{a}{x}} dx \cdot T^{\gamma-1} = \text{const} \cdot T^{\gamma-1}, \end{aligned} \quad (13.5)$$

which coincides with (13.3) and (13.2) for  $\gamma = 5$ . In an attempt to obtain a better agreement with the theory, Paschen redid his experiments and fit the data to expression (13.4) with  $\gamma \approx 5.2$ .

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<sup>15</sup>Stefan deduced this law from experimental measurements made by an Irish physicist John Tyndall. Ludwig Boltzmann, who was a former student of Stefan and by the 1880's had become one of the greatest physicists of his time, used a thermodynamics framework to derive this law theoretically in 1884. We will encounter other contributions by Boltzmann later in this Lecture.

In 1899, a German physicist Max Planck rederived Wien's formula (i.e., (13.4) with  $\gamma = 5$ ) from phenomenological thermodynamical considerations. However, later in that year, two German physicists Otto Lummer and Ernst Pringsheim obtained new experimental data for longer wavelengths ( $\lambda = 12 \div 18 \mu\text{m}$ ) showing that there was a *systematic deviation* from the Wien–Planck's formula. In 1900, Planck gave two different derivations of another, new formula that matched the latest experimental data.

### 13.1.2 Planck's discovery

In 1900, Max Planck was 42 years old and had an established name in thermodynamics. In particular, it was he who stated the Second Law of Thermodynamics in the for well-known today: “If a system evolves in thermal and mechanical isolation from the ambient environment, then its entropy increases.” (Entropy is a measure of disorder of the system. Originally, the Second Law was formulated in different forms by the mathematical physicists Rudolph Clausius, of Germany, and William Thompson (Lord Kelvin), of Ireland, in the 1850's). A corollary of Planck's formulation of the Second Law is this: Since a system in thermal and mechanical isolation is known to evolve toward thermodynamic equilibrium, then in this equilibrium, the system's entropy must be a maximum. It is this connection between a thermodynamic equilibrium and the entropy that motivated Planck's interest in the black-body radiation theory. We explain this in some detail now.

At the end of the 19th century, there was much criticism of Thermodynamics, based on a simple question: How can the *time-reversible* laws of Mechanics lead to *time-irreversible* laws of Thermodynamics? (For example, the evolution of any system towards a thermodynamic equilibrium is a time-irreversible process.) The main figure in Statistical Thermodynamics was the great Austrian physicist Ludwig Boltzmann, who advocated the irreversibility of Thermodynamics, but could not explain the irreversibility satisfactorily. (This was *not* Boltzmann's fault; a satisfactory argument for such an explanation was developed only in the second half of the 20th century — this is the theory of dynamical chaos.)

Planck wanted to resolve the above Mechanics-versus-Thermodynamics paradox. He turned to the black-body radiation problem for two reasons. First, the black-body radiation is in thermodynamic equilibrium with its source (see the paragraph after the figure in Section 13.1.1), so its entropy should be at a maximum (according to the Second Law of Thermodynamics). Second, radiation was perceived as a continuous substance, as opposed to gases, that consist of discrete molecules. So Planck hoped to find the cause for the irreversibility in the fact that a system can be viewed as continuous rather than discrete. What happened instead was that at the end, Planck had to assume that radiation was also discrete!

Thus, as we said earlier, in 1900 Planck first retrieved the Wien's law (Eq.(13.4) with  $\gamma = 5$ ), but after Lummer and Pringsheim pointed out its deviation from their experimental data, he modified his derivation to arrive at

$$K_\lambda(T) = \frac{b \cdot \lambda^{-5}}{e^{a/\lambda T} - 1} \quad (13.6)$$

(for some other constants  $a$  and  $b$  than in (13.4)). His first derivation of this formula, done in October 1900, was based solely on phenomenological Thermodynamics and required no assumptions about microscopic properties of radiation. Remarkably, the agreement between his new formula (13.6) and the most recent experimental data was very good.

Next, Planck attempted to rederive this “good” formula using microscopic considerations of Statistical Mechanics developed by Boltzmann. He succeeded and reobtained such a formula

in December 1900. He assumed that the radiation could be subdivided into discrete chunks (*quanta*) of energy  $\varepsilon$ . This was a common trick of continuum mechanics: assume discreteness and then pass to the continuous limit. Probably, this was also Planck's intention. But he found that his formula (13.6) could be obtained *only if*  $\varepsilon$  was taken to be a *specific function* of the radiation's frequency  $\nu$ :

$$\varepsilon = h\nu, \quad (13.7)$$

where he found a value for the constant  $h$  to be close to its value

$$h = 6.626 \cdot 10^{-27} \text{ erg} \cdot \text{s}$$

that we accept today. (1 erg =  $1\text{g} \cdot \frac{\text{cm}^2}{\text{s}^2}$ .) This constant  $h$  is the famous Planck constant.

### 13.1.3 Subsequent historical development

In 1906, Planck wrote "Lectures on the Theory of Thermal Radiation", where, among other things, he gave a detailed derivation of his formula. It is often said that since the time Planck derived that formula in 1900 using the assumption of discrete nature of radiation, he was trying (unsuccessfully) to get rid of that assumption. However, according to a comprehensive account of Planck's discovery in [T.S. Kuhn, "Black-body theory and quantum discontinuity 1894-1912," Clarendon Press, Oxford/Oxford University Press, New York, 1978; p. 126], this was *not* the case. Overcoming the discreteness assumption was *not* a central theme of Planck's research. While in his original microscopic derivation in December 1900 he assumed that the molecules of the walls emitted quanta of energies  $n\varepsilon = nh\nu$ , when he first published that derivation in 1901, he wrote that the molecules could emit radiation with energies *lying between*  $nh\nu$  and  $(n+1)h\nu$ . Both derivations gave an almost identical result, as we will show in the last section of this Lecture. Thus, Planck did *not* consider the radiation being *intrinsically* discrete, although he had to introduce discreteness into his derivations.

The realization that Planck's derivation *did mean* that the radiation *actually consists* of discrete quanta, appeared gradually as a result of contributions to this issue by a number of notable scientists, including: Hendrik A. Lorentz (of Holland), Paul Ehrenfest (of Austria), Max von Laue (of Germany), and Albert Einstein (at that time, Einstein was young and little-known). In particular, Lorentz gave a new derivation of Planck's formula in 1910, and Einstein gave yet another, totally different derivation of it in 1916 when he wrote a ground-laying paper on induced and spontaneous radiation.

On the other side of the barricades in 1900–1905 were two prominent opponents of Planck's formula: Lord Rayleigh<sup>16</sup> and an English physicist James Jeans<sup>17</sup>. In 1900, Rayleigh proposed a formula

$$K_\lambda(T) = b\lambda^{-4} \cdot T \cdot e^{-a/(\lambda T)}, \quad (13.8)$$

where the pre-exponential factor had some phenomenological explanation, while the  $e^{-a/(\lambda T)}$  was brought in "by brute force" to provide agreement with the experiment. In 1905, Jeans used Maxwell's electrodynamic equations to rigorously derive that

$$K_\lambda(T) = b\lambda^{-4} \cdot T, \quad (13.9)$$

<sup>16</sup>John William Strutt, 3rd Baron Rayleigh, was the great English physicist who, with William Ramsay, discovered the element argon, an achievement for which he earned the Nobel Prize for Physics in 1904. He also made fundamental contributions to the theories of wave propagation, optics, acoustics, and fluid dynamics, where many phenomena now bear his name. Rayleigh was a doctoral advisor of J.J. Thompson and G.P. Thompson, who will be mentioned later in this Lecture. Lord Rayleigh was one of the very few members of higher nobility who won fame as an outstanding scientist.

<sup>17</sup>Jeans was knighted in 1928 for his contributions in Astronomy.

where he also derived a value for constant  $b$ . He argued that for small  $\lambda$ , for which his formula was in blatant contradiction with both the experiments and common sense (as we will show in a later section), Maxwell's equations were not applicable for some unknown reason. It may be interesting to note that later Jeans not only converted to the Quantum theory, but also became one of its first proponents in England.

After 1911, the black-body radiation theory was overshadowed by a newly emerged topic of specific heat calculation and measurement for solid-state substances. Planck's formula, however, found experimental confirmation there as well.

A critical development that eventually propelled Planck's discovery into its prominent place occurred in 1913. In that year, a young (and later, the great) Danish physicist Niels Bohr related Planck's hypothesis of discreteness of radiation with two then-unexplainable phenomena inside the atom: the atom's stability and radiation spectra emitted by atoms. A couple years before that, in 1911, Ernst Rutherford, based on the results of his experiments carried out at the University of Manchester, proposed the *planetary model* of an atom. (An earlier model, proposed by J.J. Thompson<sup>18</sup> in 1904<sup>19</sup>, considered an atom as a pudding, with electrons being included there as raisins.) There was a problem with Rutherford's planetary model, however. An electron rotating about the nucleus has centripetal acceleration. According to Maxwell's electromagnetic theory, any accelerating charged particle must emit radiation. Therefore, a rotating electron would constantly emit radiation and hence lose energy, so that eventually it would fall into the nucleus. Rutherford was well aware of this problem, but insisted that in spite of it, an atom still had to look like the Solar System. Niels Bohr, who was a young researcher in Rutherford's lab, came up with a geniously simple solution: An electron cannot emit continuously, but only by quanta. Therefore, when it orbits the nucleus, the electron does not emit at all (because it cannot emit part of a quantum), and hence the atom is stable. The only possibility for an electron to emit a quantum is when it goes (for whatever reason) from one stationary orbit to another. Calculations that Bohr did using this principle yielded the first-ever theoretical explanation of experimentally observed atomic radiation spectra. Thus, Bohr's ingenious idea of the connection between Planck's quantum hypothesis and atomic physics paved the way to the creation of Quantum Mechanics.

## 13.2 Density of states of the radiation

In this and the next Sections, we will set the stage for the derivation of Planck's formula (13.6), which will follow in Section 13.4.

In Section 13.1 we referred to the wavelength of radiation, as it was done in the actual development of this theory in the 19th century. In this and the following Sections we will "change the variable" from the wavelength  $\lambda$  to the angular frequency  $\omega$  of the radiation.

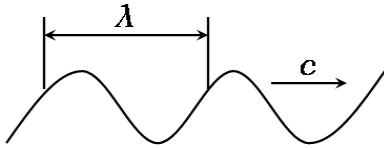
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<sup>18</sup>Joseph John Thompson, the great British physicist, made fundamental contributions to the theory of electrical conductance in gases and discovered the electron in 1897. His numerous awards included the Nobel Prize, the Knighthood, and the Order of Merit. He was a mentor to seven future Nobel laureates, one of whom was Rutherford. J.J.'s son, Sir G.P. Thompson, also won the Nobel Prize in 1937 for proving the wavelike properties of electrons.

<sup>19</sup>In the same year, a Japanese physicist Hantaro Nagaoka proposed the first, although incorrect, planetary model of the atom. It was based around the analogy of the theory of the stability of the Saturnian rings, proposed by Sir James Clerk Maxwell in 1859.

Any wave can be characterized by: the wavelength  $\lambda$ , the speed  $c$ , the period  $\tau = \lambda/c$ , the frequency  $\nu = 1/\tau = c/\lambda$ , or, equivalently, by the angular frequency

$$\omega = 2\pi\nu = \frac{2\pi c}{\lambda}. \quad (13.10)$$



In what follows we will refer to both the frequency  $\nu$  and the angular frequency  $\omega$  as simply the frequency, since this will not lead to a confusion of the two.

Let us recall that our final goal is to derive Eq. (13.6) for the radiation spectral density  $K_\lambda(T)$ . Since we now are using the frequency instead of the wavelength in our description, we need to relate  $K_\omega(T)$  with  $K_\lambda(T)$ . This is done as follows. The energy of radiation emitted within a wavelength interval  $[\lambda, \lambda + \Delta\lambda]$  can be written in two ways:

$$K_\lambda(T)d\lambda = K_\omega(T)d\omega. \quad (13.11)$$

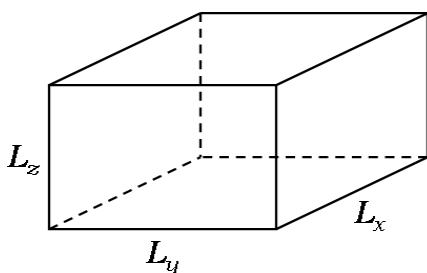
The l.h.s. of this equation is merely the definition of the spectral density  $K_\lambda(T)$ . The r.h.s. expresses the fact that  $\lambda$  and  $\omega$  are related by a one-to-one function (13.10). Then, Eqs. (13.11) and (13.10) provide a relation between  $K_\lambda(T)$  and  $K_\omega(T)$ :

$$K_\lambda(T) = K_\omega(T) \left| \frac{d\omega}{d\lambda} \right| = K_\omega(T) \cdot \frac{2\pi c}{\lambda^2}. \quad (13.12)$$

(Note that this change of variables is analogous to those we did in Lecture 4.)

To begin the derivation of  $K_\omega(T)$ , consider a large box with some dimensions  $L_x, L_y, L_z$ , as shown below. The density of the radiated energy then equals:

$$\underbrace{K_\omega(T)}_{\substack{\text{average energy} \\ \text{per } \omega\text{-interval} \\ \text{per volume}}} d\omega = \left( \frac{\text{number of frequencies in the interval } [\omega, \omega + d\omega] \text{ in the box}}{\text{volume of the box}} \right) \cdot \left( \begin{array}{c} \text{average energy of one radiation} \\ \text{mode of frequency } \omega \end{array} \right). \quad (13.13)$$



The qualifier “average” above is used because the radiation is in equilibrium with its source *on average* over some macroscopic interval of time. In this Section we will estimate the *first term* on the r.h.s. of (13.13). (It is possible to compute this term exactly using the Maxwell equations for the radiation, but this will not be required for our purposes.)

First we note that

$$\left( \begin{array}{c} \text{number of frequencies in the} \\ \text{interval } [\omega, \omega + d\omega] \text{ in the box} \end{array} \right) = \frac{dZ}{d\omega} d\omega, \quad (13.14)$$

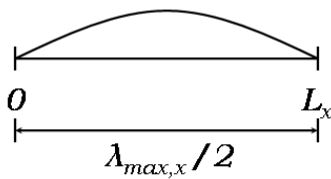
where  $Z(\omega)$  is the number of frequencies *up to*  $\omega$  that can exist in this box. From Maxwell's equations describing the electromagnetic radiation in vacuum (and our box is assumed to contain vacuum, i.e., no matter), it can be shown that allowed frequencies of the radiation propagating in any one direction are spaced *evenly* (see an explanation after Eq. (13.17) below). Then,

$$Z(\omega) = \text{const} \cdot \underbrace{\left( \frac{\omega}{\omega_{\min,x}} \right)}_{\substack{\text{number of waves} \\ \text{in } x\text{-direction}}} \cdot \underbrace{\left( \frac{\omega}{\omega_{\min,y}} \right)}_{\substack{\text{number of waves} \\ \text{in } y\text{-direction}}} \cdot \underbrace{\left( \frac{\omega}{\omega_{\min,z}} \right)}_{\substack{\text{number of waves} \\ \text{in } z\text{-direction}}}, \quad (13.15)$$

where  $\omega_{\min,x}$  is the minimum frequency of radiation that can propagate in the box in the  $x$ -direction; and similarly for  $\omega_{\min,y}$  and  $\omega_{\min,z}$ .

This minimum frequency exists because there is the maximum wavelength,

$$\lambda_{\max,x} = 2L_x \quad (13.16)$$



that can exist between the walls located  $L_x$  units apart. (The illustrating figure on the left assumes that the wave is zero at the walls, but a similar result can also be obtained for other boundary conditions.)

Now, from (13.16) and (13.10),

$$\omega_{\min,j} = \frac{2\pi c}{2L_j} = \frac{\pi c}{L_j}, \quad j = \{x, y, z\}. \quad (13.17)$$

From the Figure above one can conclude that the next two largest wavelengths are  $2L_x/2$  and  $2L_x/3$ , where, respectively, two and three semi-periods of the wave fit between the walls. The corresponding frequencies, in analogy with (13.17), are  $2\omega_{\min,x}$  and  $3\omega_{\min,x}$ . This illustrates the statement, made before Eq. (13.15), that the frequencies of the radiation in a box are spaced evenly.

Next, from (13.15) and (13.17) one has:

$$\begin{aligned} Z(\omega) &= \text{const} \cdot \frac{\omega^3}{(\pi c)^3 / (L_x L_y L_z)} \\ &= \text{const} \cdot \frac{\omega^3}{(\pi c)^3} \cdot L_x L_y L_z. \end{aligned} \quad (13.18)$$

An exact solution of Maxwell's equations for the radiation's electromagnetic field with two transverse polarizations yields the value of the constant in (13.18) to be:

$$\text{const} = \frac{\pi}{3}. \quad (13.19)$$



Then, according to (13.14) and (13.18), (13.19):

$$\left( \begin{array}{c} \text{number of frequencies in} \\ [\omega, \omega + d\omega] \text{ in the box} \end{array} \right) = \frac{\omega^2 d\omega}{\pi^2 c^3} \cdot L_x L_y L_z, \quad (13.20)$$

and finally,

$$\frac{\left( \begin{array}{c} \text{number of frequencies in} \\ [\omega, \omega + d\omega] \text{ in the box} \end{array} \right)}{\text{volume of the box}} = \frac{\omega^2 d\omega}{\pi^2 c^3}. \quad (13.21)$$

We have derived the first term on the r.h.s. of (13.13). To proceed with the derivation of the second term, we need some elementary background in the statistical mechanics of gases. This is given in the next Section.

### 13.3 Elementary background from the Maxwell–Boltzmann kinetic theory of gases

In gases, molecules move chaotically, and so different molecules usually have different velocities, both in their direction and in magnitude. Therefore, one can speak about the *probability* to find a molecule within a given interval of velocities at a certain location in space. Let

$$p(v_x, v_y, v_z) dv_x dv_y dv_z \quad (13.22)$$

be the probability to find a molecule with the  $x$ -,  $y$ -, and  $z$ -components of its velocity being within the intervals  $[v_x, v_x + dv_x]$ ,  $[v_y, v_y + dv_y]$ ,  $[v_z, v_z + dv_z]$ .

A fundamental law derived by James Clerk Maxwell and Ludwig Boltzmann at the end of the 19th century states that for gases, or for any other systems of particles, in thermodynamic equilibrium,

$$p(v_x, v_y, v_z) = \text{const} \cdot e^{-E/(kT)}, \quad (13.23)$$

where  $T$  is the temperature,  $k$  is the *Boltzmann constant*, and  $E$  is the energy of the particle. For example, if one neglects the potential energy of the particles (such as the gravitational potential energy of the molecules in a gas), then

$$E = E_{\text{kinetic}} = \frac{m}{2}(v_x^2 + v_y^2 + v_z^2). \quad (13.24)$$

A corollary of the Maxwell–Boltzmann law that is important for us is the so-called ***energy equipartition theorem***:

*In thermodynamic equilibrium, the average energy corresponding to each “degree of freedom” of a particle is  $\frac{1}{2}kT$ .*

This fact is derived in courses on thermodynamics and statistical physics.<sup>20</sup> The “degrees of freedom” in this theorem are closely related to the *coordinates*  $q$  introduced in Lecture 7 in connection with the Lagrangian, and their time derivatives,  $\dot{q}$ . An example important for further development of our theory is that of a *harmonic oscillator*, considered in Lecture 6 – 8. The energy of such an oscillator, which equals the sum of its kinetic and potential energies, is

$$E_{\text{oscillator}} = \frac{m\dot{q}^2}{2} + \frac{\beta q^2}{2},$$

<sup>20</sup>A more precise statement of this theorem requires that the energy depend on the “degrees of freedom” quadratically.

where  $\beta$  is some proportionality constant. Thus, an oscillator has *two* “degrees of freedom”,  $q$  and  $\dot{q}$ . If an oscillator comes, e.g., by means of collisions with surrounding particles, into thermodynamic equilibrium with the ambient matter, then, according to the equipartition theorem, its average energy is

$$\langle E_{\text{oscillator}} \rangle = 2 \cdot \frac{1}{2} kT = kT, \quad (13.25)$$

where the factor ‘2’ occurs because the oscillator has *two* “degrees of freedom”. The result expressed by Eq. (13.25) was widely accepted by physicists in the late 19th century.

We are now prepared to derive an expression for the second term on the r.h.s. of Eq. (13.13) and thereby obtain Planck’s formula.

### 13.4 Rayleigh–Jeans and Planck’s formulae

First, however, we will obtain the Rayleigh–Jeans Eq. (13.9) (even though this formula both is incorrect and, historically, was derived *after* the correct Planck’s formula). We will do so to highlight the key difference between the two formulae.

Recall that to complete the derivation of the spectral density  $K_\omega(T)$  in Eq. (13.13), we need to find the average energy of one radiation mode of frequency  $\omega$ . By the end of the 19th century it was well-known to physicists that a mode of radiation of a given frequency is *mathematically equivalent* to an oscillating string, or, in other words, to an oscillator. This follows directly from Maxwell’s equations of the electromagnetic theory. Therefore, in 1905, Jeans made the following connection: (i) a radiation mode is analogous to an oscillator; (ii) the average energy of an oscillator that is in thermodynamic equilibrium with its surroundings is  $kT$  (see Eq. (13.25)); (iii) hence the average energy of one frequency mode of the black-body radiation, which is known to be in thermodynamic equilibrium with its source (see Section 13.1.1), equals  $kT$ , *independently* of the mode’s frequency! Substituting this result into (13.13) and also using our earlier result (13.21), one obtains the **Rayleigh–Jeans formula**:

$$K_\omega(T) = \frac{\omega^2}{\pi^2 c^3} \cdot kT. \quad (13.26)$$

To verify that Eqs. (13.26) and (13.9) are equivalent, we utilize the relation between  $K_\lambda(T)$  and  $K_\omega(T)$  given by Eq. (13.12) (see also (13.10)):

$$\begin{aligned} K_\lambda(T) &= \left( \frac{\omega^2}{\pi^2 c^3} \cdot kT \right) \cdot \frac{2\pi c}{\lambda^2} \\ &= \left( \frac{\left(\frac{2\pi c}{\lambda}\right)^2}{\pi^2 c^3} \cdot kT \right) \cdot \frac{2\pi c}{\lambda^2} = \frac{8\pi}{\lambda^4} kT. \end{aligned} \quad (13.27)$$

This is the Rayleigh–Jeans formula in the form equivalent to (13.9).

We will now give a derivation of Planck’s formula, Eq. (13.6). It should be noted that the way we will do it is *not* how Planck originally derived his formula in 1900 or even re-derived it in 1906 (see Section 13.1.2).

Let us *assume* that a radiation mode consists of *discrete quanta*, with the energy of each quantum being (see (13.7)):

$$\varepsilon = h\nu \equiv \hbar\omega, \quad \hbar \equiv \frac{h}{2\pi}, \quad (13.28)$$

where  $\omega$  is the frequency of the mode. A mode can have several quanta in it. If it contains  $n$  quanta, then the energy of such a mode is  $n\varepsilon = n\hbar\omega$ . Then the problem of finding the average energy of a mode with frequency  $\omega$  is mathematically equivalent to that of finding the average number of quanta in such a mode. A key and nontrivial step is to realize that *the probability* of having a *discrete* black-body radiation mode with energy  $E$  is:

$$P(E) = \text{const} \cdot e^{-E/(kT)}, \quad (13.29)$$

where the constant in (13.29) is chosen so as to have:

$$\sum_{\text{all discrete } E} P(E) = 1. \quad (13.30)$$

At first glance, Eq. (13.29) may look just like the *Boltzmann law* (13.23). However, the nontrivial part of the connection between these two formulae is that while (13.29) defines a *probability* (i.e. a *finite* number), Eq. (13.23) defines the *probability density*, so that the corresponding *probability* (13.22) is an infinitesimally small number. More importantly, note that the integration variables in (13.22) are  $v_x, v_y, v_z$ , and *not*  $E$ . Therefore, if we were to compute the probability density  $p(E)$  from

$$p(E)dE = p(v_x, v_y, v_z)dv_xdv_ydv_z,$$

which is a counterpart of Eq. (13.11), then the proportionality constant between  $p(E)$  and  $p(v_x, v_y, v_z)$  would depend on  $E$  (similarly to how the proportionality constant between  $K_\lambda(T)$  and  $K_\omega(T)$  in (13.12) depends on  $\lambda$ ). Consequently, the *probability density* of having a radiation mode with a *continuously changing* energy  $E$  would *not* be

$$p(E) \propto e^{-E/(kT)}.$$

Nevertheless, for the *probability* (as opposed to a probability density) of having a radiation mode with *discrete* values of  $E$ , the Boltzmann law (13.29) holds.

Returning to the problem of finding the *average* energy of a black-body radiation mode, we write this average energy,  $\langle E \rangle$ , using the standard formula of the probability theory for average values:

$$\langle E \rangle = \sum_{\text{all discrete } E} E \cdot P(E), \quad (13.31)$$

where  $E = n\hbar\omega$ . We now need to determine the constant in the formula (13.29) for  $P(E)$ . This follows from the normalization equation (13.30):

$$\text{const}_{(13.29)} \cdot \sum_{n=0}^{\infty} e^{-n\hbar\omega/(kT)} = 1,$$

whence

$$\text{const}_{(13.29)} = \frac{1}{\sum_{n=0}^{\infty} e^{-n\hbar\omega/(kT)}}. \quad (13.32)$$

Note that the inclusion of the term with  $n = 0$  into the sum in (13.32) means, physically, that one has to allow for a nonzero probability for the mode to contain no quanta. In other words,

there is a nonzero probability to have *no radiation* with a given frequency at any instance of time.

Substituting (13.28), (13.29), and (13.32) into (13.31), one has:

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} (n\hbar\omega)e^{-n\hbar\omega/(kT)}}{\sum_{n=0}^{\infty} e^{-n\hbar\omega/(kT)}}. \quad (13.33)$$

Such an expression is calculated using the following trick. Denote

$$-\frac{\hbar\omega}{kT} \equiv x;$$

then (13.33) becomes:

$$\begin{aligned} \langle E \rangle &= \hbar\omega \frac{\sum_{n=0}^{\infty} n e^{nx}}{\sum_{n=0}^{\infty} e^{nx}} = \hbar\omega \frac{\frac{d}{dx} \sum_{n=0}^{\infty} e^{nx}}{\sum_{n=0}^{\infty} e^{nx}} \\ &= \hbar\omega \frac{d}{dx} \ln \left( \sum_{n=0}^{\infty} e^{nx} \right) = \hbar\omega \frac{d}{dx} \ln \left( \sum_{n=0}^{\infty} (e^x)^n \right) \Big|_{\text{geometric series}} \\ &= \hbar\omega \frac{d}{dx} \ln \left( \frac{1}{1 - e^x} \right) = \hbar\omega \frac{e^x}{1 - e^x} = \frac{\hbar\omega}{e^{-x} - 1}. \end{aligned}$$

Finally,

$$\langle E \rangle = \frac{\hbar\omega}{e^{\hbar\omega/(kT)} - 1}. \quad (13.34)$$

Substituting this expression, along with (13.21), into (13.13), one obtains **Planck's formula**:

$$K_{\omega}(T) = \frac{\omega^2}{\pi^2 c^3} \cdot \frac{\hbar\omega}{e^{\hbar\omega/(kT)} - 1}. \quad (13.35)$$

The equivalence of (13.35) and (13.6) is established following the lines of the calculations in Eq. (13.27).

The above derivation of Planck's formula is attributed to H.A. Lorentz (1910). The original Planck's derivations of this formula, that used the concept of entropy, may be found in the book by T.S. Kuhn, "Black-body theory and the quantum discontinuity 1894–1912," which we have referenced in Section 13.1.3.

### 13.5 Corollaries of Rayleigh–Jeans and Planck's formulae

As we mentioned in Section 13.1.3, the Rayleigh–Jeans formula (13.26) is in blatant contradiction with common sense. Indeed, let us use that formula to compute the total amount of energy radiated by a black body into all frequencies:

$$u = \int_0^{\infty} K_{\omega}(T) d\omega = \frac{kT}{\pi^2 c^3} \int_0^{\infty} \omega^2 d\omega = \infty. \quad (13.36)$$

Paul Ehrenfest called this problem of the Rayleigh–Jeans formula *the ultraviolet catastrophe*. (A connection here is the following. The divergence of the integral in (13.36) occurs for large  $\omega$ ; large frequencies  $\omega$  correspond to small wavelengths  $\lambda$  (see (13.10)); and finally, the color of light changes from red to violet as the light’s wavelength decreases.) Jeans, of course, was well aware of this problem, and so before he eventually converted to the Quantum theory, he had been insisting that Maxwell’s electromagnetic equations, on which the derivation of the term  $\omega^2/(\pi^2 c^3)$  in (13.21) was based, were not applicable for very short wavelengths for some unknown reason.

We will now show that Planck’s formula (13.35): (i) predicts a *finite* value for the total radiated energy and (ii) for small frequencies reduces to the Rayleigh–Jeans formula (so, in that region, both formulae are consistent with the experiment). We will begin with item (ii).

Let  $\hbar\omega \ll kT$ . Then, using the first two terms of the Maclaurin series for  $e^{\hbar\omega/(kT)}$  in Eq. (13.34), one has:

$$\langle E \rangle |_{\hbar\omega \ll kT} \approx \frac{\hbar\omega}{\left(1 + \frac{\hbar\omega}{kT}\right) - 1} = kT; \quad (13.37)$$

this is precisely the value for the average energy of a radiation mode that Jeans used in deriving (13.26).

Now let us compute the total amount of radiated energy using Planck’s formula:

$$u(T) = \int_0^\infty K_\omega(T) d\omega = \int_0^\infty \frac{\omega^2}{\pi^2 c^3} \cdot \frac{\hbar\omega d\omega}{e^{\hbar\omega/(kT)} - 1}.$$

Following the approach used in Eq. (13.5), we make a variable substitution

$$y = \frac{\hbar\omega}{kT}, \quad \omega = y \frac{kT}{\hbar}, \quad d\omega = dy \cdot \frac{kT}{\hbar}$$

in the above integral to obtain:

$$u = \frac{(kT)^4}{\hbar^3 \pi^2 c^3} \int_0^\infty \frac{y^3 dy}{e^y - 1}. \quad (13.38)$$

It remains to show that the improper integral in (13.38) converges. First, we check that there is no divergence at  $\underline{y \approx 0}$ :

$$\left. \frac{y^3}{e^y - 1} \right|_{y \ll 1} \approx \frac{y^3}{(1 + y) - 1} = y^2;$$

this shows that the integrand is a continuous, and hence, integrable, function at  $y = 0$ . At the other end of the integration interval, i.e. for  $\underline{y \rightarrow \infty}$ , one has

$$\frac{y^3}{e^y - 1} \approx y^3 e^{-y},$$

which decays faster than any power of  $y$ . Hence, the integral converges at that limit also. Finally, the exact value of the integral can be found with Mathematica<sup>21</sup> to be  $(\pi^4/15)$ . Substituting this in (13.38) yields the total radiated energy being in agreement with the Stefan–Boltzmann law (13.3):

$$u(T) = \frac{k^4 \pi^2}{15 \hbar^3 c^3} \cdot T^4. \quad (13.39)$$

<sup>21</sup>An analytical technique to compute this integral is considered in the homework.

It is interesting to point out that the constant in the Stefan–Boltzmann law is expressed via three physical fundamental constants: the Boltzmann constant  $k$ , the Planck constant  $\hbar$ , and the speed of light  $c$ .

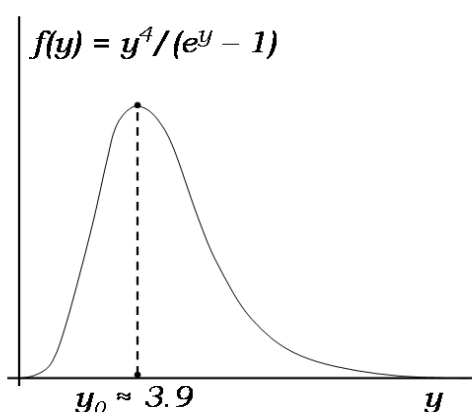
To conclude this Section, we will point out a corollary of Planck’s formula which is encountered in everyday life. Recall that  $K_\lambda(T)d\lambda$  is the energy emitted by a black body into the wavelength interval  $d\lambda$ . The human eye, however, reacts *not to the energy but to the number of photons* which the eye detects per unit time. The number of photons (per wavelength interval) is related to the radiation energy density in a simple manner:

$$N_\lambda(T) = \frac{\left( \begin{array}{c} \text{density of} \\ \text{radiation energy} \end{array} \right)}{\left( \begin{array}{c} \text{energy of} \\ \text{one photon} \end{array} \right)} \Bigg|_{(13.28), (13.10)} \equiv \frac{K_\lambda(T)}{hc/\lambda} \Bigg|_{(13.35), (13.6)} = \frac{\text{const} \cdot \lambda^{-4}}{e^{hc/(\lambda kT)} - 1}. \quad (13.40)$$

Using the  $y$ -substitution equivalent to the one we used before Eq. (13.38), we have:

$$N_\lambda(T) = \frac{\text{const} \cdot \left(\frac{hc}{\lambda kT}\right)^4 \cdot \left(\frac{kT}{hc}\right)^4}{e^{hc/(\lambda kT)} - 1} = \text{const}' \cdot T^4 \cdot \left(\frac{y^4}{e^y - 1}\right), \quad (13.41)$$

where  $\text{const}' = \text{const} \cdot (k/(hc))^4$ .



Equation (13.41) and the figure on the left show that the maximum number of radiated photons occurs for the value of  $y$  which maximizes the last fraction in (13.41), whence

$$\lambda_{\text{max}} \approx \left(\frac{ch}{3.9k}\right) / T. \quad (13.42)$$

This is called the **Wien’s displacement law**, which Wilhelm Wien derived from his formula (13.4) in 1894.

This law says that the wavelength of the maximal observed emittance decreases (“is displaced”) in inverse proportion to the temperature. Thus, as the body is heated, it glows first in infrared (very long wavelengths, over 1  $\mu\text{m}$ ), then in red, then in blue, and then in ultraviolet. For example, the approximate temperatures of (the surfaces of the) three well-known stars are: Betelgeuse — 3400°K, our Sun — 5800°K, and Sirius — 9500°K. Betelgeuse and Sirius are known as the Red and Blue stars, respectively, while our Sun’s color is yellow. You will be asked to use Eq. (13.42) to verify these color assignments in a homework problem. Moreover, four cautionary notes regarding a correspondence between star temperatures and their observed radiation spectrum are in order.

First, while star temperatures can be approximately deduced from Wien’s law, they are not deduced from the location of the peak of the spectral density (i.e., from (13.41) or (13.42)). A detailed discussion of this can be found in [D. Cenadelli, M. Potenza, M. Zeni, “Stellar temperatures by Wiens law: Not so simple,” *Am. J. Phys.* **80**, 391 (2012); doi: 10.1119/1.3699958]. There are also other methods to measure a star’s temperature, e.g., by measuring the strengths of absorption lines corresponding to various atoms (e.g., hydrogen) in the star’s radiation spectrum.

Second, radiation originates at various layers of the star, and the temperature of each layer usually depends on the depth of the layer beneath the surface. Thus, the radiation spectrum of a star is a superposition of several Planckian functions (13.41) each corresponding to a different temperature. If these temperatures are not too far apart, the overall spectrum can be thought of a Planckian function corresponding to some average temperature.

Third, even if the star emits a Planckian spectrum, the observer on Earth will detect it with distortions, due to the fact that different wavelengths are absorbed and scattered by the atmosphere differently. Generally, shorter wavelengths are absorbed or scattered more, which shifts the peak of the *observed* spectral density towards longer wavelengths.

The above three reasons, and how they may affect the observed radiation spectrum, are relatively straightforward to understand, at least conceptually. Our last note will be about an issue whose resolution is not known to this instructor. Notice that if one expresses the photon density (13.41) in terms of frequency rather than wavelength, one obtains from (13.40) and (13.12) a different function than (13.41):

$$N_{\omega}(T) \propto \omega^2 / (e^{\hbar\omega/(kT)} - 1) \propto y^2 / (e^y - 1).$$

If we maximize this function instead of (13.41), that we would have obtained a different numerical coefficient in Wien's law: instead of "3.9" in (13.42), one would obtain the maximum at  $y \approx 1.6$ . This appears to imply that the star colors depend on relative to which variable, wavelength or frequency, we maximize the number of photons. This, of course, cannot be true. While I am not aware of a concrete resolution of this paradox, I suspect that it should be sought in a detailed mechanism of how the eye perceives different colors. Some references that may contain relevant information are listed on the course website.

## 13.6 Planck's formula and Quantum Electrodynamics

We conclude this Lecture with a curious historical fact. In 1913, Planck published the second edition of his Lectures on the Theory of Thermal Radiation (see Section 13.1.3), where he gave a new derivation of his formula. Conceptually, that derivation was similar to the one presented in Section 4, but he made a modification that slightly changed the final result. Namely, back in 1900, he assumed that the radiation's energy could be subdivided into discrete values (which later turned out to be the true quanta of light):  $0, \varepsilon, 2\varepsilon, 3\varepsilon$ , etc. In 1913, he said that the energy of the mode *could lie in the intervals*  $[0, \varepsilon), [\varepsilon, 2\varepsilon), [2\varepsilon, 3\varepsilon)$ , etc, and that the equilibrium state of the radiation was reached by transitions among those intervals. Note that this is almost like having no discreteness at all! With this modification, Planck's earlier derivation goes through with only a little change: the average energy of the radiation in the interval  $[0, \varepsilon)$  is  $\frac{1}{2}\varepsilon$ ; in  $[\varepsilon, 2\varepsilon) - \varepsilon + \frac{1}{2}\varepsilon$ ; in  $[2\varepsilon, 3\varepsilon) - 2\varepsilon + \frac{1}{2}\varepsilon$ , etc. All this does<sup>22</sup> is shift the average energy of the radiation mode by  $\frac{1}{2}\varepsilon$ :

$$\langle E \rangle = \frac{\hbar\omega}{e^{\hbar\omega/(kT)} - 1} + \frac{1}{2}\hbar\omega. \quad (13.43)$$

However small this added term on the r.h.s. is, it turned out to have observable implications in the theory of specific heats of solids. And, remarkably, it was detected by experiments of that time that the  $\frac{1}{2}\hbar\omega$ -term indeed needed to be there!

<sup>22</sup>You will show this in a homework problem.

Equation (13.43) has another highly nontrivial implication. The average number of photons (i.e. the quanta of light) *per mode* is:

$$\begin{aligned} n_\omega &= \frac{\text{average energy per mode}}{\text{energy of one photon}} = \frac{\langle E \rangle}{\hbar\omega} \\ &= \frac{1}{e^{\hbar\omega/(kT)} - 1} + \frac{1}{2}. \end{aligned} \tag{13.44}$$

In absolute vacuum, the temperature is zero (since there are no particles in vacuum, there is no thermal motion and hence, by definition, the temperature must vanish). Then, since

$$\lim_{T \rightarrow 0} e^{\hbar\omega/(kT)} = e^\infty = \infty$$

for all  $\omega \neq 0$ , then in (13.44),

$$n_\omega|_{T=0} = 0 + \frac{1}{2} = \frac{1}{2}. \tag{13.45}$$

This says that in vacuum, there is, *on average*,  $\frac{1}{2}$  photon for each possible frequency of radiation, and hence vacuum is not really empty! This result was proved several decades later in Quantum Electrodynamics. Thus, Planck's *incorrect* derivation of (13.43) predicted a correct result.