

# 1

## Historical Background

### 1.1 Introduction

The purpose of this chapter is to explain how and why Planck introduced his famous quantum hypothesis and the constant  $h$ . I have added a few contributions from Einstein that are relevant for this book. We shall see that results based on the wave nature of light alternate with results based on its corpuscular nature. Eventually, it will be Planck's constant that will bridge the gap between these two viewpoints and lead to the foundation of quantum physics, unifying the two aspects of light, and much more.

But first a warning! This chapter is difficult to read because we are no longer used to thinking and reasoning along the same lines as our predecessors. Still, I think that it is of interest to follow the chain that started with Kirchhoff's second law and ended with Planck's hypothesis of quantized emission of radiation, using the tools available in their time. It gives a flavor of what physics was at that time. It also shows how much we have progressed since then.

### 1.2 Kirchhoff (1859)

#### 1.2.1 The Birth of Spectroscopy

The physicist Kirchhoff<sup>1</sup> was collaborating with the chemist Bunsen<sup>2</sup> (Fig. 1.1). Out of this collaboration emerged the science of spectroscopy. An early discovery was the phenomenon of spectral line inversion. The experiment is displayed schematically in Fig. 1.2.

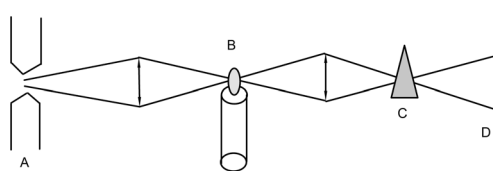
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<sup>1</sup>Gustav Robert Kirchhoff (*b.* Königsberg, 1824; *d.* Berlin, 1887).

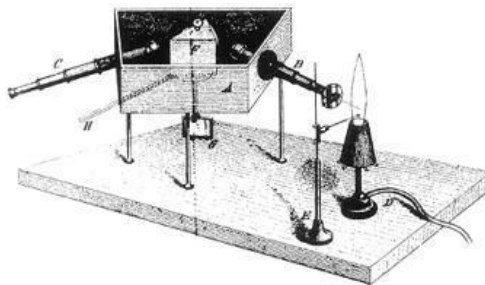
<sup>2</sup>Robert Wilhelm Bunsen (*b.* Göttingen, 1811; *d.* Heidelberg, 1899).



**Figure 1.1** Bunsen (standing) and Kirchhoff (sitting).



**Figure 1.2** Schematic representation of a spectroscopy experiment.



**Figure 1.3** Elements of the Bunsen–Kirchhoff set-up for spectroscopy.

The components of the experiment are:

- A an electric arc emitting a continuum of frequencies in a range containing the color yellow;
- B a bunsen (it is indeed the burner invented by R. W. Bunsen) burning NaCl;
- C a spectrum analyzer, *i.e.*, a dispersive device such as a prism; and
- D a display screen.

The elements B and C of their experiment are displayed in Fig. 1.3. The experiment revealed the following:

- If A is on and B is off, a continuous spectrum is observed at D.
- If A and B are both on, the continuous spectrum plus a few black lines are observed at D.
- If A is off but B is on, the continuous spectrum disappears and the Na yellow lines appear exactly where the black lines had been observed.

Hence, in the second case, the Na lines were emitted at A and absorbed at B; whereas, in the third case, the Na lines were emitted at B. Therefore, it can be concluded that, if a medium can emit light at a given frequency, it can also absorb light at the same frequency.

An immediate application of this observation was the analysis of the solar spectrum. The black lines of the solar spectrum (the so-called Fraunhofer lines) were attributed, in part, to absorption by water vapor in the Earth's atmosphere. The remaining lines were attributed to an element existing in the Sun. This was the first example of an extra-terrestrial chemical analysis. It led to the discovery of helium in the Sun (hence its name). Bunsen and Kirchhoff are also credited with the discovery of cesium and rubidium by means of spectroscopy.

### 1.2.2 The First Law

Kirchhoff decided to study theoretically the consequences of this experiment. He first introduced a number of definitions and assumptions:

1. He assumes that a medium, when heated, emits radiation that he calls thermal radiation.

2. A medium can interact with the radiation field either via absorption or via emission.
3. The radiation intensity is spread over a range of frequencies. Let  $\rho(\nu)$  be the radiation intensity at frequency  $\nu$  per unit volume, *i.e.*, the spectral density. The function  $\rho(\nu)$  also depends on temperature.
4. The medium is characterized by an absorption coefficient  $\alpha(\nu)$  and an emission coefficient  $e(\nu)$ . We assume for simplicity that the medium is homogeneous and isotropic, so that neither  $\alpha(\nu)$  nor  $e(\nu)$  are space-dependent. The absorption is necessarily non-negative. We assume that it is bounded, and we normalize  $\alpha$  such that its maximum equals unity. Hence  $0 \leq \alpha(\nu) \leq 1$ .
5. A fraction  $1 - \alpha(\nu)$  of the radiation is reflected without change of frequency and with the same angle as the incident radiation. Reflection occurring at a different angle is called “diffraction”. Hence it is assumed here that the radiation field is not diffracted by the medium.

Through the surface element  $d\sigma$ , during the time interval  $dt$ , the transfer of energy from the radiation field to the medium is  $\alpha(\nu)\rho(\nu)d\sigma dt$  and the transfer of energy from the medium to the radiation field is<sup>3</sup>  $e(\nu)d\sigma dt$ . If the combined system “medium + radiation field” is at thermodynamic equilibrium, there is an exact balance between emission and absorption:

$$[\alpha(\nu)\rho(\nu) - e(\nu)]d\sigma dt = 0 \quad (1.1)$$

But, at equilibrium, neither  $\alpha$  nor  $\rho$  nor  $e$  depend on space and time. Hence

$$\alpha(\nu)\rho(\nu) = e(\nu) \quad (1.2)$$

which is *Kirchhoff's first law*. It expresses quantitatively the observed fact that there is a relation between emission and absorption, and it introduces the function  $\rho(\nu)$  that will lead us to Planck's quantum hypothesis.

Let us define a black-body by

$$\alpha(\nu) = 1 \quad \text{for all } \nu \quad (1.3)$$

Thus a black-body is a medium that absorbs all radiation. Let us stress that this definition does not imply the absence of emission. Quite the contrary. A counter-intuitive example of a black-body is the Sun, which absorbs all the

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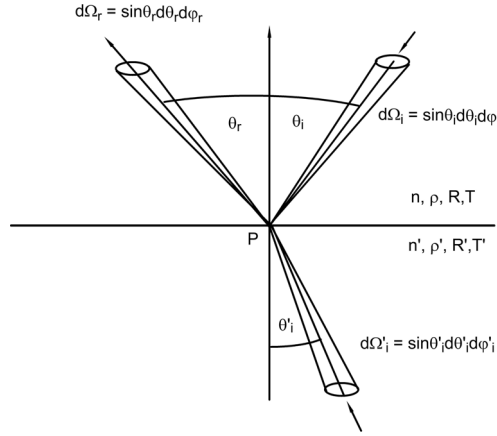
<sup>3</sup>This assumption is wrong: it only includes stimulated emission and neglects spontaneous emission (see the Quantum comment on page 7).

radiation reaching its surface. This does not prevent the Sun from emitting radiation via mechanisms other than reflection or diffraction.

It follows from the definition (1.3) that emission at any frequency is maximum for a black-body. In order to have the non-trivial solution  $e(\nu) \neq 0$ , we must have  $\alpha(\nu)\rho(\nu) \neq 0$ , which means that there is absorption at the same frequency and that the black-body must emit at the same frequency.

### 1.2.3 The Second Law

Let us now consider two media that are heated at arbitrary temperatures (Fig. 1.4). The radiation field intensity emitted in the solid angle  $d\Omega_r$  is the sum of the radiation field intensity reflected at P coming from the solid angle  $d\Omega_i$  and the radiation field intensity transmitted (refracted) at P from the solid angle  $d\Omega'_i$ .



**Figure 1.4** Radiation field emitted in the solid angle  $d\Omega_r$  as a function of the radiation field reflected from the solid angle  $d\Omega_i$  and the radiation field refracted through the interface at P from the solid angle  $d\Omega'_i$ . The two media are characterized by their refractive indices  $n$  and  $n'$ , radiation spectral densities  $\rho$  and  $\rho'$ , reflection coefficients  $R$  and  $R'$ , and temperatures  $T$  and  $T'$ .

At this point, Kirchhoff introduces two assumptions:

1. The radiation field frequency is not changed by either reflection or transmission.
2. The laws of light refraction are applicable to the radiation field:

- (i) the incident, reflected, and refracted fields are coplanar,  $\varphi_i = \varphi'_i = \varphi_r$ ;
- (ii)  $\theta_r = \theta_i$  and therefore  $d\Omega_r = d\Omega_i$ ;
- (iii)  $R' = R$  where  $R$  and  $R'$  are the reflection coefficients of the upper and lower media; and
- (iv)  $\sin \theta'_i / \sin \theta_r = n' / n$  where  $n$  and  $n'$  are, respectively, the refractive indices in the upper and lower media (Snell's law).

Let us consider the projection of the intensity balance on the surface normal to the interface at P:

$$\rho(\nu) \cos \theta_r d\Omega_r dt = R\rho(\nu) \cos \theta_i d\Omega_i dt + (1 - R')\rho'(\nu) \cos \theta'_i d\Omega'_i dt \quad (1.4)$$

and therefore

$$(1 - R)\rho(\nu) \cos \theta_r d\Omega_r dt = (1 - R')\rho'(\nu) \cos \theta'_i d\Omega'_i dt \quad (1.5)$$

Since

$$\begin{aligned} \cos \theta'_i d\Omega'_i &= \cos \theta'_i \sin \theta'_i d\theta'_i d\varphi'_i = \sin \theta'_i d(\sin \theta'_i) d\varphi'_i \\ &= \frac{n'}{n} d(\sin \theta'_i) d\varphi'_i \sin \theta_r = \left(\frac{n'}{n}\right)^2 \cos \theta_r d\Omega_r \end{aligned} \quad (1.6)$$

we have

$$\cos \theta_r (1 - R)[n^2 \rho(\nu) - n'^2 \rho'(\nu)] d\Omega_r dt = 0 \quad (1.7)$$

However, at thermodynamic equilibrium,  $\rho$  is independent of time and of solid angle. Hence the solution of equation (1.7) is

$$n^2 \rho(\nu) = n'^2 \rho'(\nu) \quad (1.8)$$

which is *Kirchhoff's second law*, sometimes called *Kirchhoff's theorem*. It states that the function  $n^2 \rho(\nu)$  is independent of the medium: it is a *universal function*. This universality will motivate physicists to determine  $\rho(\nu)$ . Eventually, it will be Planck who will solve the problem, climbing on the shoulders of giant forerunners.

**Note 1.** In the original paper, Kirchhoff used *reductio ad absurdum* to prove his theorem. Using thermodynamics, he proved that, if  $n^2 \rho(\nu) \neq n'^2 \rho'(\nu)$ , perpetual motion would be possible. Pringsheim<sup>4</sup> proposed the proof presented here.

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<sup>4</sup>Ernst Pringsheim (*b.* Breslau, Lower Silesia (today Wrocław, Poland), 1859; *d.* Breslau, 1917).

**Note 2.** The projection of the intensity balance on the surface parallel to the interface at P does not lead to any useful result. Indeed, we have

$$\rho(\nu) \sin \theta_r d\Omega_r dt = R\rho(\nu) \sin \theta_i d\Omega_i dt + (1 - R')\rho'(\nu) \sin \theta'_i d\Omega'_i dt \quad (1.9)$$

which leads, after simple manipulations, to the equation

$$(1 - R)n^2\rho(\nu) \left(1 - \frac{n' \cos \theta_r}{\sqrt{n^2 - n'^2 \sin^2 \theta_r}}\right) \sin \theta_r d\Omega_r dt = 0 \quad (1.10)$$

**Note 3.** Maxwell published his electromagnetic theory in 1865. Only later did physicists understand that light is an electromagnetic field. This property was unknown to Kirchhoff when he derived his two laws.

**Quantum comment.** The status of Kirchhoff's laws is quite extraordinary:

- On the one hand, Kirchhoff's second law was the motivation that drove physicists to seek the universal function  $n^2\rho(\nu)$ , a race that ended with Planck's hypothesis of quantized emission of radiation. Planck's constant  $h$  is universal because  $n^2\rho(\nu)$  is universal.
- On the other hand, we know with hindsight that Kirchhoff's first law is wrong – it was Einstein (see Section 1.6.3) who set this matter straight in 1916. Indeed, it only includes stimulated emission and neglects spontaneous emission! The lucky point is that the two laws are independent of each other: the mistake in the first law does not invalidate the second law.

## 1.3 Stefan (1879) and Boltzmann (1884)

### 1.3.1 Experimental Background

Stefan<sup>5</sup> (Fig. 1.5), who was a professor of theoretical physics in Vienna, is best known for an experimental law that bears his name. Making very approximate measurements, he showed that the total energy  $E$  radiated by a medium of volume  $V$  heated at temperature  $T$  varies with the fourth power of the temperature:

$$E = aVT^4 \quad \text{or} \quad E/V \equiv u = aT^4 \quad (1.11)$$

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<sup>5</sup>Josef Stefan (*b.* St. Peter (Austria), 1835; *d.* Vienna, 1893).

where  $a$  is a constant. Later Lummer,<sup>6</sup> Pringsheim, and Kurlbaum<sup>7</sup> succeeded in substantiating this result.



Figure 1.5 Josef Stefan.

### 1.3.2 Maxwell's Theory and Thermodynamics

Boltzmann<sup>8</sup> (Fig. 1.6), who obtained his PhD under Stefan on the kinetic theory of gases, in 1884 derived the Stefan law using for the very first time Maxwell's equations in thermodynamics.

The proof of Stefan's law by Boltzmann uses the radiation pressure law. The fact that electromagnetic radiation exerts a pressure upon any surface exposed to it was deduced theoretically by Maxwell<sup>9</sup> in 1871, and proven experimentally by Lebedev<sup>10</sup> in 1900 and independently by Nichols<sup>11</sup> and Hull<sup>12</sup> in 1901. According to Maxwell's theory, there is a very simple relation between the radiation field pressure  $p$  and the field energy  $E$  in a volume  $V$ :

$$pV = E/3 \quad \text{or} \quad p = u/3 \quad (1.12)$$

<sup>6</sup>Otto Lummer (*b.* Gera, 1860; *d.* Breslau, 1925).

<sup>7</sup>Ferdinand Kurlbaum (*b.* Burg bei Magdeburg, 1857; *d.* Berlin, 1927).

<sup>8</sup>Ludwig Eduard Boltzmann (*b.* Vienna, 1844; *d.* Duino (near Trieste), Italy, 1906).

<sup>9</sup>James Clerk Maxwell (*b.* Edinburgh, 1831; *d.* Cambridge, 1879).

<sup>10</sup>Pyotr Nikolaevich Lebedev (*b.* Moscow, 1866; *d.* Moscow, 1912). He graduated from Strasbourg University, where he also earned his PhD. The same is true for the founding father of theoretical physics in Russia, Leonid Isaakovich Mandelstam (*b.* Mogilev, Russian Empire (now Mahilyow, Belarus), 1879; *d.* Moscow, 1944).

<sup>11</sup>Ernest Fox Nichols (*b.* Leavenworth, Kansas, 1869; *d.* Washington, DC, 1924).

<sup>12</sup>Gordon Ferrie Hull (*b.* Garnet, Ontario, 1870; *d.* Hanover, NH, 1956).



**Figure 1.6** Ludwig Boltzmann.

Boltzmann used this theorem at thermodynamic equilibrium. Using the thermodynamic relation between the entropy  $S$ , the energy  $E$ , and the volume  $V$ , we have

$$TdS = dE + pdV = d(uV) + \frac{u}{3}dV = \frac{4}{3}udV + V\frac{du}{dT}dT \quad (1.13)$$

and therefore

$$dS = \frac{4u}{3T}dV + \frac{V}{T}\frac{du}{dT}dT \equiv \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \quad (1.14)$$

Since the left-hand side is a differential form, we must have

$$\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V \quad (1.15)$$

or equivalently

$$\frac{\partial}{\partial T}\left(\frac{4u}{3T}\right) = \frac{\partial}{\partial V}\left(\frac{V}{T}\frac{du}{dT}\right) \quad (1.16)$$

This equation is equivalent to

$$\frac{du}{dT} = 4\frac{u}{T} \quad (1.17)$$

which leads to the required result

$$u = aT^4 \quad (1.18)$$

This equation is referred to as the Stefan–Boltzmann law. It also follows from this result that

$$\frac{\partial S}{\partial T} = \frac{V}{T} \frac{du}{dT} = 4aVT^2 \quad (1.19)$$

and so

$$S(T) = \frac{4}{3}aVT^3 \quad (1.20)$$

For a reversible adiabatic change ( $\delta S = 0$ ), the result becomes that  $VT^3$  is a constant.

**Note 4.** It can be shown that Newton’s corpuscular theory of light yields exactly twice the radiation pressure obtained from Maxwell’s theory (see Planck, 1912, §60).

## 1.4 Wien (1893)

Wien<sup>13</sup> (Fig. 1.7) made the next significant contribution on the nature of the universal function  $n^2\rho(\nu)$ . He considered a reflecting plane (or piston) moving toward a source of heat radiation, as shown in Fig. 1.8. Heat radiation enters through B, is reflected by the mirror A, and escapes the system through C. Let us analyze this set-up.

1. The first step is to determine how the radiation field frequency varies as a function of the reflector velocity. At time  $t$  the number of waves between B and C is  $AB/\lambda + AC/\lambda'$ . At time  $t + \delta t$  the number of waves between B and C' is  $A'B/\lambda + A'C'/\lambda'$ . Thus, the wavenumber has decreased by

$$\delta n_w = (AB - A'B)/\lambda + (AC - A'C')/\lambda'$$

during the time interval  $\delta t$ . In the same interval, the number of waves having entered at B is  $\nu\delta t$  and the number of waves leaving through CC' is  $\nu'\delta t$ . Hence

$$\begin{aligned} (\nu' - \nu)\delta t &= \frac{AB - A'B}{\lambda} + \frac{AC - A'C'}{\lambda'} \\ &= \frac{AA'}{\lambda} + \frac{AA' \cos(\theta + \theta')}{\lambda'} \\ &= \left[ \frac{\nu}{c} + \frac{\nu'}{c} \cos(\theta + \theta') \right] \frac{v\delta t}{\cos \theta} \end{aligned} \quad (1.21)$$

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<sup>13</sup>Wilhelm Carl Werner Otto Fritz Franz Wien (*b.* Gaffken, East Prussia (now Poland), 1864; *d.* Munich, 1928). Nobel Prize in Physics 1911.



Figure 1.7 Wilhelm Wien.

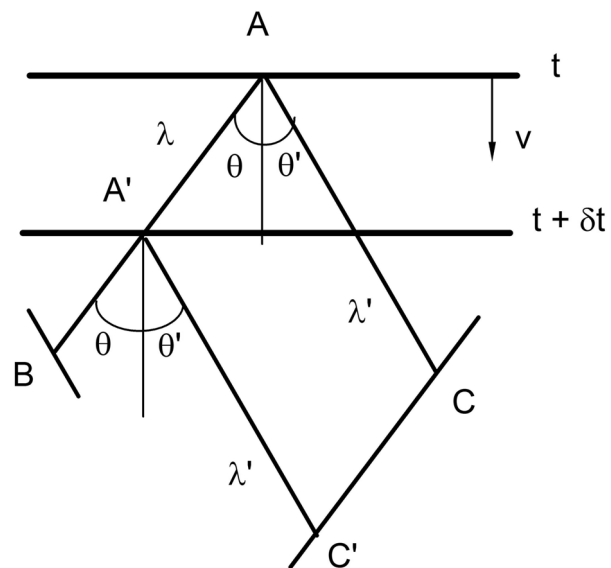


Figure 1.8 The set-up analyzed by Wien.

from which it follows that

$$\nu' = \nu \frac{v + c \cos \theta}{c \cos \theta - v \cos(\theta + \theta')} \quad (1.22)$$

However, in the *adiabatic limit*  $v \rightarrow 0$ , we have  $\theta' = \theta + \mathcal{O}(v)$ . Since the correction  $\mathcal{O}(v)$  must be dimensionless, the correct expansion must be  $\theta' = \theta + \mathcal{O}(v/c)$ . A deeper analysis would show that the series expansion is  $\theta' = \theta + \mathcal{O}(v^2/c^2)$ . This does not change the analysis made here. Hence

$$\begin{aligned} \nu' &= \nu \frac{1 + v/(c \cos \theta)}{1 - (v/c) \cos(\theta + \theta')/\cos \theta} \\ &\simeq \nu \frac{1 + v/(c \cos \theta)}{1 - (v/c)[\cos 2\theta/\cos \theta + \mathcal{O}(v/c)]} \\ &\approx \nu \left(1 + \frac{v}{c} \frac{1}{\cos \theta}\right) \left[1 + \frac{v \cos 2\theta}{c \cos \theta} + \mathcal{O}(v^2/c^2)\right] \\ &\approx \nu \left[1 + \frac{v}{c} \frac{1 + \cos 2\theta}{\cos \theta} + \mathcal{O}(v^2/c^2)\right] \\ &\approx \nu \left[1 + 2\frac{v}{c} \cos \theta + \mathcal{O}(v^2/c^2)\right] \end{aligned} \quad (1.23)$$

2. A second step is to derive a similar law for the radiation field energy. Suppose, for simplicity, that the reflecting surface is moving away from the radiation source. Let  $E_i dt$  be the radiation field hitting the receding mirror and  $E_r dt$  be the reflected radiation field energy, both in the time interval between  $t$  and  $t + dt$ . The pressure applied to the mirror is  $2(E_i/c) \cos \theta$  and hence the work is  $2(vE_i/c) \cos \theta dt$ . The energy balance is  $E_i dt = E_r dt + 2E_i(v/c) \cos \theta dt$ , which leads to the relation  $E_r = E_i[1 - 2(v/c) \cos \theta]$ . Therefore, for a mirror moving toward the source we have

$$E_r = E_i \left(1 + 2\frac{v}{c} \cos \theta\right) \quad (1.24)$$

3. The third step is to calculate the variation of the radiation field energy in a volume  $V$  closed by a perfectly reflecting piston that moves slowly toward the inside (thus reducing  $V$ ) with a velocity  $v \ll c$ . In the interval  $(\nu, \nu + d\nu)$  and  $(t, t + dt)$  the energy transferred to the piston in a solid angle  $d\Omega$  is

$$\begin{aligned} E_i(\nu) &= A\rho(\nu) \cos \theta d\nu dt d\Omega \\ &= \frac{c}{4\pi} A u(\nu) \cos \theta d\nu dt d\Omega \end{aligned} \quad (1.25)$$

where  $A$  is a constant. This energy is transferred in the interval  $(\nu', \nu' + d\nu')$  with  $\nu' = \nu[1 + 2(v/c)\cos\theta]$ . Hence, the energy transferred by reflection in the interval  $(\nu, \nu + d\nu)$  comes from

$$E_i(\bar{\nu}) = \frac{c}{4\pi} Au(\bar{\nu}) \cos\theta \, d\bar{\nu} dt d\Omega \quad (1.26)$$

where  $\nu = \bar{\nu}[1 + 2(v/c)\cos\theta]$  or equivalently  $\bar{\nu} \simeq \nu[1 - 2(v/c)\cos\theta]$ . The corresponding reflected energy is

$$\begin{aligned} E_r(\nu) &= \left(1 + 2\frac{v}{c}\cos\theta\right) E_i(\bar{\nu}) \\ &= \left(1 + 2\frac{v}{c}\cos\theta\right) \frac{c}{4\pi} Au(\bar{\nu}) \cos\theta \, d\bar{\nu} dt d\Omega \\ &= \frac{c}{4\pi} Au(\bar{\nu}) \cos\theta \, d\nu dt d\Omega \left(1 - 4\frac{v^2}{c^2}\cos\theta\right) \\ &= \frac{c}{4\pi} Au(\bar{\nu}) \cos\theta \, d\nu dt d\Omega + \mathcal{O}(v^2/c^2) \end{aligned} \quad (1.27)$$

where we have used  $\theta = \theta'$  and  $d\Omega = d\Omega'$  because the corrections are negligible. Since

$$u(\bar{\nu}) = u(\nu) - 2\frac{v}{c}\nu\cos\theta\frac{\partial u}{\partial\nu} + \dots \quad (1.28)$$

we find

$$\begin{aligned} E_r(\nu) &= \frac{c}{4\pi} A \left[ u(\nu) - 2\frac{v}{c}\nu\cos\theta\frac{\partial u}{\partial\nu} \right] d\nu dt \cos\theta \, d\Omega \\ &= E_i(\nu) - \frac{v\nu}{2\pi} A \cos^2\theta \frac{\partial u}{\partial\nu} d\nu dt d\Omega \end{aligned} \quad (1.29)$$

Integrating over a hemisphere yields

$$\begin{aligned} \Delta E d\nu dt &= -\frac{v\nu}{2\pi} A \frac{\partial u}{\partial\nu} d\nu dt \int_0^{2\pi} d\varphi \int_0^{\pi/2} \cos^2\theta \sin\theta \, d\theta \\ &= -\frac{v\nu}{3} A \frac{\partial u}{\partial\nu} d\nu dt \equiv \frac{\nu}{3} \frac{\partial u}{\partial\nu} d\nu dV \end{aligned} \quad (1.30)$$

because  $dV = -vAdt$ . But  $\Delta E d\nu dt \equiv dE d\nu = d(Vu)d\nu$ . Whence

$$d(Vu) = \frac{\nu}{3} \frac{\partial u}{\partial\nu} dV = u dV + V du$$

thus implying

$$\frac{\nu}{3} \frac{\partial u}{\partial\nu} = u + V \frac{\partial u}{\partial V}$$

and therefore

$$u(\nu, V) = \nu^3 \phi(\nu^3 V) \quad (1.31)$$

In this last expression,  $\phi$  is an arbitrary function.

4. The final step is simple. Let us assume that  $v \rightarrow 0$  and that the volume variation takes place adiabatically. This implies no heat exchange and therefore the entropy is constant, so that, from equation (1.20),  $VT^3$  is a constant. Thus  $u(\nu, V) = \nu^3 F(\nu/T)$  and, since  $u(\nu) = (4\pi/c)\rho(\nu)$ , we end up with Wien's law

$$\rho(\nu) = \nu^3 F(\nu/T) \quad (1.32)$$

or equivalently

$$u(\nu) = \frac{\nu^3}{c^3} \varphi(\nu/T) \quad (1.33)$$

where both  $F$  and  $\varphi$  are universal functions.

**Note 5.** Integrating  $u(\nu)$  over the whole frequency domain yields the Stefan–Boltzmann law:

$$\int_0^\infty u(\nu) d\nu = \int_0^\infty \nu^3 \frac{4\pi}{c} F(\nu/T) d\nu = T^4 \int_0^\infty \frac{4\pi}{c} x^3 F(x) dx \equiv AT^4 \quad (1.34)$$

**Note 6.** Wien's law (1.32) is usually referred to as Wien's displacement law. To understand why, let us consider how  $\rho$  varies with the wavelength. Let  $\rho(\nu)|d\nu| = \rho(\lambda)|d\lambda|$ . Given the dispersion relation  $\lambda\nu = c$ , we obtain

$$\rho(\lambda) = \frac{\nu^2}{c} \rho(\nu) = \frac{c^4}{\lambda^5} F\left(\frac{c}{\lambda T}\right) \quad (1.35)$$

From experiments, it is known that the function  $\rho(\lambda)$  has only one maximum. Let  $\lambda^*$  be the wavelength at which this maximum occurs. It is given by

$$\left. \frac{d\rho(\lambda)}{d\lambda} \right|_{\lambda=\lambda^*} = \frac{c^4}{\lambda^{*5}} \left[ -\frac{5}{\lambda^*} F\left(\frac{c}{\lambda^* T}\right) - \frac{c}{\lambda^{*2}} F'\left(\frac{c}{\lambda^* T}\right) \right] = 0 \quad (1.36)$$

where the prime denotes a derivative with respect to the argument. Thus

$$5F(x) + xF'(x) = 0 \quad (1.37)$$

and  $x = c/(\lambda^* T)$ . The existence of a solution  $x$  of equation (1.37) implies that

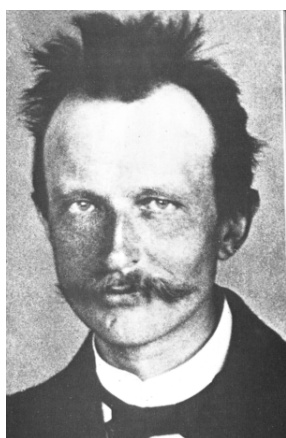
$$\lambda^* T = \text{constant} \quad (1.38)$$

which is the displacement law observed experimentally: the maximum of the spectral energy distribution  $\rho(\lambda, T)$  decreases as the temperature increases according to the law (1.38). It also follows from equation (1.37) that  $\rho(\lambda^*) \sim T^5$ .

## 1.5 Planck (1900)

### 1.5.1 Modeling Matter

The objective of Planck<sup>14</sup> (Fig. 1.9) was to find the function  $F$  that appears in Wien's law. It is clear from the previous analyses that thermodynamics alone cannot answer that question. Planck realized that he had to introduce a model describing the exchange of energy between the radiation field and matter. What was known at his time was that atoms contained electrons, negatively charged, though the atoms were neutral.



**Figure 1.9** Max Planck in 1901.

Another reason that was pressing Planck to solve the black-body radiation distribution riddle is that two colleagues, Lummer and Pringsheim, were developing refined techniques to build a black-body and to measure its spectral radiation distribution. Results were appearing and an explanation was still missing.

The first assumption introduced by Planck is that matter behaves as a collection of harmonic oscillators in its interaction with the radiation field. Each harmonic oscillator is an electric dipole, where two electric charges of opposite signs oscillate around the center of mass. The oscillator is characterized by a frequency  $\nu$  and a mass  $m$ . Using Maxwell's equations, Planck could at once derive two results:

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<sup>14</sup>Max Karl Ernst Ludwig Planck (*b.* Kiel, 1858; *d.* Göttingen, 1947). Nobel Prize in Physics 1918.

1. The energy emitted per unit time by each oscillator is

$$\delta E = \frac{2e^2}{3mc^3}(2\pi\nu)^2\langle\varepsilon\rangle \quad (1.39)$$

where  $\varepsilon$  is the oscillator energy and  $\langle\varepsilon\rangle$  is the time average of that energy:  $\langle\varepsilon\rangle = (1/T)\int_0^T \varepsilon(t)dt$ .

2. The work realized per unit time by a radiation field with a spectral distribution  $u(\nu)$  on the electric dipoles is

$$\delta W = \frac{\pi e^2}{3m}u(\nu) \quad (1.40)$$

Hence, at thermodynamic equilibrium, the two contributions must balance, and this leads to Planck's theorem:

$$u(\nu) = \frac{8\pi\nu^2}{c^3}\langle\varepsilon\rangle \quad (1.41)$$

This result is fundamental because it bridges the properties of the radiation field,  $u(\nu)$ , and of matter,  $\langle\varepsilon\rangle$ . It simply remains to calculate  $\langle\varepsilon\rangle$ . This is where classical physics received its death kiss.

### 1.5.2 The Quantum Hypothesis

Using equilibrium thermodynamics, Planck could easily show that

$$\langle\varepsilon\rangle = \frac{\int_0^\infty \varepsilon e^{-\beta\varepsilon}d\varepsilon}{\int_0^\infty e^{-\beta\varepsilon}d\varepsilon} = \frac{1}{\beta} = kT \quad (1.42)$$

which leads to the Rayleigh<sup>15</sup>–Jeans<sup>16</sup> law

$$u(\nu) = \frac{8\pi\nu^2}{c^3}kT \quad (1.43)$$

Tough luck for Planck! Not only was this result published earlier that year by a pair of British colleagues, but that law was only an approximation, valid in the low-frequency limit. Furthermore, it does not satisfy Wien's displacement law and, even worse, the total energy  $u = \int_0^\infty u(\nu)d\nu$  diverges.

Being a theoretical physicist with a solid background in mathematics, Planck realized that, if, instead of integrating over a continuous energy  $\varepsilon$

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<sup>15</sup>Lord Rayleigh, born John William Strutt (*b.* Langford Grove, Essex, 1842; *d.* Terling Place, Essex, 1919).

<sup>16</sup>Sir James Hopwood Jeans (*b.* Ormskirk, Lancashire, 1877; *d.* Dorking, Surrey, 1946).



to calculate  $\langle \varepsilon \rangle$ , he used discrete summations, a completely different result would emerge. This led him to formulate his famous quantum assumption: the oscillators that model matter can emit energy only by discrete quanta  $n\varepsilon_0$  with  $n = 1, 2, \dots$ . Now the average energy per oscillator becomes

$$\langle \varepsilon \rangle = \frac{\sum_{n=0}^{\infty} n\varepsilon_0 e^{-\beta n\varepsilon_0}}{\sum_{n=0}^{\infty} e^{-\beta n\varepsilon_0}} = \frac{\varepsilon_0}{e^{\beta\varepsilon_0} - 1} \quad (1.44)$$

and the spectral energy is

$$u(\nu) = \frac{8\pi\nu^2}{c^3} \frac{\varepsilon_0}{e^{\beta\varepsilon_0} - 1} \quad (1.45)$$

In order for the distribution (1.45) to be consistent with Wien's law (1.33), it is necessary and sufficient that  $\varepsilon_0/\nu$  be constant. Here is how Planck "proved" that this constant is universal. This constant has the dimensions of an action: energy  $\times$  time. Consider Wien's displacement law (1.38)

$$c^3 u(\nu)/\nu^3 = \varphi(\nu/T) \quad (1.46)$$

But  $uc^3/\nu^3$  and  $\nu/T$  do not have the same dimensions, and  $\varphi$  is a universal function. Therefore, there must be a constant, which we write as  $h$ , having the dimension of an action, that enables equation (1.46) to be expressed as  $x = \Phi(T/\nu)$  for the dimensionless variable  $x = uc^3/h\nu^3$ . Hence, the constant  $h$  must be universal!<sup>17</sup> This led Planck to write his fundamental result

$$\varepsilon_0 = h\nu \quad (1.47)$$

and therefore

$$u(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\beta h\nu} - 1} \quad (1.48)$$

For a medium with a refractive index  $n \neq 1$ , Planck's distribution becomes

$$u(\nu) = \frac{8\pi h\nu^3 n^3}{c^3} \frac{1}{e^{\beta h\nu} - 1} \quad (1.49)$$

With this result, Planck hit the jackpot. Not only was this spectral distribution in agreement with all previous theoretical results, but it fitted superbly the experimental curves obtained thus far for all frequencies and temperatures. An earthquake had taken place and quantum physics was born.

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<sup>17</sup>By the same argument, there must be a second universal constant that will make  $T/\nu$  dimensionless. This second universal constant is  $k/h$ , where  $k$  is Boltzmann's constant.

Two limiting cases can be considered:

1. in the low-frequency limit ( $\beta h\nu \ll 1$ ),

$$\begin{aligned} u(\nu) &= \frac{8\pi h\nu^3}{c^3} (1 + \beta h\nu - 1 + \dots)^{-1} \\ &\simeq \frac{8\pi h\nu^3}{\beta h\nu c^3} = \frac{8\pi\nu^2}{c^3} kT \end{aligned} \quad (1.50)$$

which is the Rayleigh–Jeans law derived that same year; and

2. in the high-frequency limit ( $\beta h\nu \gg 1$ ),

$$u(\nu) \simeq \frac{8\pi h\nu^3}{c^3} e^{-\beta h\nu} \quad (1.51)$$

which is a law proposed empirically by Wien in 1896.

**Note 7.** With the experimental results obtained by Pringsheim and Lummer for the black-body radiation, Planck obtained the value for  $h$  as  $h = 6.415 \times 10^{-27}$  erg s, a fairly good result if we compare it with the latest value given by the United States National Bureau of Standards (NBS):  $6.626\,068\,93(33) \times 10^{-27}$  erg s.

**Note 8.** The 1912 version of Planck’s lecture notes on the theory of heat radiation (Planck, 1912, §140) begins with the following statement:

While the oscillator is absorbing it must also be emitting, for otherwise a stationary state would be impossible. Now, since in the law of absorption just assumed the hypothesis of quanta has as yet found no room, it follows that it must come into play in some way or other in the emission of the oscillator, and this is provided for by the introduction of the hypothesis of emission of quanta.

This is quite incredible, but consistent with the fact that, in 1913, Planck recommended that Einstein be elected member of the Prussian Academy of Sciences:<sup>18</sup>

... despite the fact that sometimes he goes too far in his speculations, such as with his hypothesis of light quanta.

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<sup>18</sup>The full letter of recommendation can be found at <http://www.bbaw.de/akademie/kalender/biog-011-einstein.htm>

**Note 9.** Planck models matter in terms of harmonic oscillators, which we know to be completely wrong since the pioneering work of Bohr.<sup>19</sup> It is marvellous that a theory born under such bad auspices has such a formidable predictive power.

## 1.6 Einstein (1905, 1907, and 1916)

### 1.6.1 Quantization of Light Absorption (1905)

Although Planck had introduced the quantization of radiation emission by matter, he did not consider it a physical process, but rather as just a mere mathematical trick to derive the correct spectral energy density  $u(\nu)$ . During his *annus mirabilis*, Einstein<sup>20</sup> (Fig. 1.10) analyzed the recently discovered photoelectric effect. Being aware of Planck's analysis, he showed that the experimental results led to the conclusion that matter absorbs light in discrete quanta just as it does for emission. And the relation  $\varepsilon = n\varepsilon_0 = nh\nu$  was shown to be compatible with the experiments. This conclusion is important because it suggests that the quantization discovered by Planck may not be a simple mathematical artifact but, on the contrary, a fundamental property of matter.



**Figure 1.10** Albert Einstein in 1905.

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<sup>19</sup>Niels Henrik David Bohr (*b.* Copenhagen, 1885; *d.* Copenhagen, 1962). Nobel Prize in Physics 1922.

<sup>20</sup>Albert Einstein (*b.* Ulm, 1879; *d.* Princeton, 1955). Nobel Prize in Physics 1921.

### 1.6.2 Specific Heat of Solids (1907)

The expression (1.44) derived by Planck for the average energy

$$\langle \varepsilon \rangle = \frac{h\nu}{e^{\beta h\nu} - 1} \quad (1.52)$$

has a direct application to the properties of solids. As low temperatures were obtained experimentally, deviations from the classical laws began to appear. The classical result is the Dulong and Petit law for the specific heat of solids, which we can write as  $C_V = 3Nk$ , where  $N = 6.022\,1415(10) \times 10^{23} \text{ mol}^{-1}$  is the Avogadro<sup>21</sup> number. Einstein generalized this law in the following way:

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T} \frac{3Nh\nu}{e^{\beta h\nu} - 1} = 3Nk \left( \frac{\beta h\nu}{e^{\beta h\nu} - 1} \right)^2 e^{\beta h\nu} \quad (1.53)$$

Two limiting cases are:

1. at high temperature ( $\beta h\nu \rightarrow 0$ ),  $C_V = 3Nk + \mathcal{O}(\beta h\nu)$ , in agreement with the classical law; and
2. at low temperature ( $\beta h\nu \rightarrow \infty$ ),  $C_V = 3Nk(\beta h\nu)^2 e^{-\beta h\nu} \rightarrow 0$ , which explains the observed decrease of  $C_V$  at low temperature.

### 1.6.3 Spontaneous Emission (1916)

For the results derived in Sections 1.6.1 and 1.6.2, Einstein followed Planck in using the harmonic oscillator model for matter. Here, again, it is remarkable that good results could be derived from a wrong model.

In a series of three papers (the first two published in 1916, the third in 1917), Einstein analyzed the light–matter interaction on very general grounds, using the ideas of Kirchhoff but at the microscopic level. Einstein was aware of Bohr’s model for the atomic structure, which had been published in 1913. The question, then, was how to derive Planck’s law (1.48) using the Bohr model (Pais, 1982).

Consider an ensemble of atoms with a discrete energy spectrum interacting with a radiation field. Atoms can absorb or emit quanta of energy. The time variation of the number of atoms  $N_n$  of a given state  $n$  with energy  $E_n$  results from two processes: transitions from another state  $m$  (and

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<sup>21</sup>Lorenzo Romaco Amedeo Carlo Avogadro, Count of Quaregna Cerretto (*b.* Torino, 1776; *d.* Torino, 1856).

energy  $E_m$ ) to the state  $n$ , and transitions from the state  $n$  to another state  $m'$  (and energy  $E_{m'}$ ). Hence

$$\frac{dN_n(t)}{dt} = \sum_m P(m \rightarrow n)N_m(t) - \sum_{m'} P(n \rightarrow m')N_n(t) \quad (1.54)$$

At thermodynamic equilibrium,  $dN_n(t)/dt = 0$  so that

$$\sum_m P(m \rightarrow n)N_m(t) = \sum_{m'} P(n \rightarrow m')N_n(t) \quad (1.55)$$

However, thermodynamic equilibrium implies that:

$$\frac{N_m}{N_n} = e^{-\beta(E_m - E_n)} = e^{-\beta h \omega_{mn}} \quad (1.56)$$

Following the ideas of Kirchhoff, we assume that there are two processes:

- emission, for which  $P(n \rightarrow m) = A_{nm}$  with  $n > m$ ; and
- absorption, for which  $P(n \rightarrow m) = u(\omega_{mn})B_{nm}$  with  $n < m$ .

With these assumptions, equation (1.55) becomes

$$\begin{aligned} & \sum_{m>n} [A_{mn}N_n - u(\omega_{mn})B_{mn}N_m] \\ & + \sum_{m<n} [u(\omega_{mn})B_{mn}N_n - A_{nm}N_m] = 0 \end{aligned} \quad (1.57)$$

or

$$\begin{aligned} & \sum_{m>n} N_n [A_{mn} - u(\omega_{nm})B_{nm}e^{\beta(E_n - E_m)}] \\ & - \sum_{m<n} N_m [A_{nm} - u(\omega_{mn})B_{mn}e^{\beta(E_m - E_n)}] = 0 \end{aligned} \quad (1.58)$$

and therefore

$$A_{mn} - u(\omega_{nm})B_{nm}e^{\beta(E_n - E_m)} = 0 \quad (1.59)$$

Hence

$$u(\omega_{nm}) = \frac{A_{mn}}{B_{nm}} e^{-\beta h \omega_{nm}} \quad (1.60)$$

with  $E_n - E_m = h\omega_{nm}$ . This is not at all the expected result but rather the approximate law (1.51) derived by Wien. It was fairly easy for Einstein

to spot the weak point in his reasoning: the emission process is not adequately described. Thus, he made the following assumption: there are *two* types of emission processes, spontaneous and stimulated. Spontaneous emission is of the type previously introduced [ $P_{sp}(n \rightarrow m) = A_{nm}$ ], whereas stimulated emission is truly symmetric to the absorption process [ $P_{stim}(n \rightarrow m) = u(\omega_{nm})C_{nm}$ ]. The total probability of emission is

$$P(n \rightarrow m) = P_{sp}(n \rightarrow m) + P_{stim}(n \rightarrow m)$$

The balance equation (1.59) becomes

$$A_{mn} + u(\omega_{nm})[C_{mn} - B_{nm}e^{\beta(E_n - E_m)}] = 0 \quad (1.61)$$

or else

$$u(\omega_{nm}) = \frac{A_{mn}}{B_{nm}} \frac{1}{e^{\beta h \omega_{nm}} - C_{mn}/B_{nm}} \quad (1.62)$$

Consistency with Planck's law requires that

$$C_{mn} = B_{nm} \quad (1.63)$$

$$A_{mn} = \frac{8\pi h \nu^3}{c^3} B_{nm} \quad (1.64)$$

The microscopic processes of emission and absorption are defined only qualitatively: we know the ratio  $A_{mn}/B_{nm}$  but not yet  $A_{mn}$  and  $B_{nm}$  separately. It is quantum field theory that will fully answer this question.

# Part I

## Quantized Matter

