

11 Case Study V

The origins of the concept of quanta

Quanta and relativity are phenomena of physics which are quite outside our everyday experience – they are also perhaps the greatest discoveries of twentieth-century physics. In the debate between those supporting the Copernican and geocentric models of the Universe, discussed in Chapter 3, one of the issues raised by opponents of the Copernican picture concerned ‘the deception of the senses’: if these phenomena are of such fundamental importance, why are we not aware of them in our everyday lives? Quanta and relativity were both discovered by very careful experiment, the results of which could not be accounted for within the context of Newtonian physics. Indeed, these phenomena are arguably ‘non-intuitive’, and yet they lie at the foundations of the whole of modern physics.

In this case study, we will study in some detail the origins of the concept of quanta. For me, this is one of the most dramatic stories in intellectual history. It is also very exciting and catches the flavour of an epoch when, within 25 years, physicists’ view of nature changed totally and completely new perspectives were opened up. The story illustrates many important points about how physics and theoretical physics work in practice. We find the greatest physicists making mistakes, individuals having to struggle against the accepted views of virtually all physicists, and, most of all, a level of inspiration and scientific creativity which I find dazzling. If only everyone, and not only those who have had a number of years training as physicists or mathematicians, could appreciate the intellectual beauty of this story.

In addition to telling a fascinating and compelling story, I want to prove everything essential to it using the physics and mathematics available at the time. This provides a splendid opportunity for reviewing a number of important areas of basic physics in their historical context. We will find a striking contrast between those phenomena which can be explained classically and those which necessarily involve quantum ideas. The story will cover the years from about 1890 to the 1920s, by which date all physicists had to come to terms with a new view of physics in which all the fundamental entities are quantised.

The story will centre upon the work of two very great physicists – Planck and Einstein. Planck is properly given credit for the discovery of quantisation and we will trace how this came about. Einstein’s contribution was even greater in that, long before anyone else, he inferred that all natural phenomena are quantum in nature, and he was the first to put the subject on a firm theoretical basis.

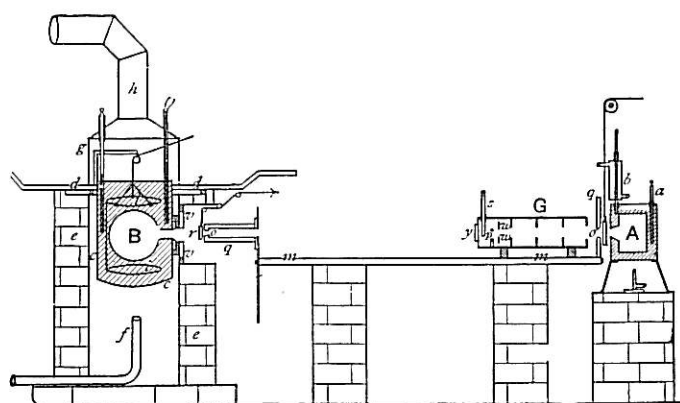


Figure V.1: Lummer and Pringsheim's apparatus of 1897 for determining experimentally the Stefan-Boltzmann law with high precision. The relative intensities of radiation from the enclosure B and the reference black body A could be found by moving the detector G along the table between them until the illumination from each source was equal. (From H.S. Allen and R.S. Maxwell, 1952, *A Text-book of Heat*, Vol. II, p. 746, London: Macmillan and Co.)

I based my original version of this story upon a set of lectures by Martin J. Klein entitled *The Beginnings of the Quantum Theory*¹ and published in the proceedings of the fifty-seventh Varenna Summer School. When I first read them, I found these lectures a revelation and felt cheated that I had not known this story before. I acknowledge fully my indebtedness to Professor Klein in inspiring what I consider in many ways to be the core of the present volume. Kindly, he sent me further materials after the publication of the first edition of this book. I have found his article 'Einstein and the wave-particle duality'² particularly valuable.

To my regret, having delivered lectures on these topics from 1978 to 1980, I was unaware of the important volume by Thomas S. Kuhn *Black-Body Theory and the Quantum Discontinuity 1894–1912* (1978)³ when I sent the first edition of this book to press. Kuhn's book is in my view a masterpiece and he digs deeply into much of the material discussed in this case study. Kuhn's profound insights have changed some of my perceptions as recorded in the first edition of the present text. For those who wish to pursue these topics in more detail, his book is essential reading.

V.1 References

- 1 Klein, M.J. (1977). *History of twentieth century physics*, Proc. International School of Physics 'Enrico Fermi', Course 57, p. 1. New York and London: Academic Press.
- 2 Klein, M.J. (1964). Einstein and the wave-particle duality, *The New Philosopher*, 3, 1–49.
- 3 Kuhn, T.S. (1978). *Black-Body Theory and the Quantum Discontinuity 1894–1912*. Oxford: Clarendon Press.

11 Black-body radiation up to 1895

11.1 The state of physics in 1890

In the course of the case studies treated so far, we have been building up a picture of the state of physics and theoretical physics towards the end of the nineteenth century. The achievement had been immense. In mechanics and dynamics, the Lagrangian and Hamiltonian dynamics described briefly in Chapter 7, were well understood. In thermodynamics, the first and second laws were firmly established, largely through the efforts of Clausius and Lord Kelvin, and the full ramifications of the concept of entropy in classical thermodynamics were being elaborated. In Chapters 5 and 6, we described how Maxwell derived the equations of electromagnetism. Hertz's experiments of 1887–9 demonstrated beyond any shadow of doubt that, as predicted by Maxwell, light is a form of electromagnetic wave. This discovery provided a firm theoretical foundation for the wave theory of light, which could account for virtually all the known phenomena of optics.

The impression is sometimes given that most physicists of the 1890s believed that the combination of thermodynamics, electromagnetism and classical mechanics could account for all known physical phenomena and that all that remained to be done was to work out the consequences of these hard-won achievements. In fact, it was a period of ferment when there were still many fundamental unresolved problems which exercised the greatest minds of the period.

We have discussed the ambiguous status of the kinetic theory of gases and the equipartition theorem as expounded by Clausius, Maxwell and Boltzmann. The fact that these could not account satisfactorily for all the known properties of gases was a major barrier to their acceptance. The status of atomic and molecular theories of the structure of matter came under attack both for the technical reasons outlined above and also because of a movement away from mechanistic atomic models for physical phenomena in favour of empirical or phenomenological theories. The origin of the 'resonances' within molecules, which were presumed to be the origin of spectral lines, had no clear interpretation and was an embarrassment to supporters of the kinetic theory. Boltzmann had discovered the statistical basis of thermodynamics, but the theory had won little support, particularly in the face of a movement which denied that kinetic theories had any value, even as hypotheses. The negative result of the Michelson–Morley experiment was announced in 1887 – we will take up that story in Case Study VI on special relativity. A useful portrait of the state of physics in the last decades of the nineteenth century is provided by David Lindley in his book *Boltzmann's Atom*.¹

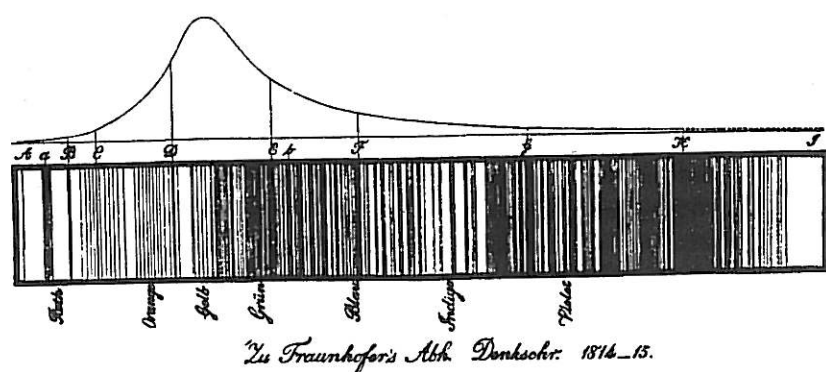


Figure 11.1: Fraunhofer's solar spectrum of 1814 showing the vast number of absorption lines. The colours of the various regions of the spectrum are shown, as well as the labels of the prominent absorption lines.

Among these unresolved problems was the origin of the spectrum of *black-body radiation*, the answer to which was to prove to be the key not only to the discovery of quantisation but also to the resolution of many other problems listed above. The discovery of quantisation and quanta was the precursor of the modern quantum theory of matter and radiation.

11.2 Kirchhoff's law of emission and absorption of radiation

The first step along the path to the understanding of the spectrum of black-body radiation was the discovery of spectral lines. In 1802, spectroscopic measurements of the solar spectrum were made by William Wollaston, who observed five strong dark lines. This observation was followed up in much greater detail by Joseph Fraunhofer, the son of a glazier and an experimenter of genius. Early in his career, Fraunhofer became one of the directors of the Benediktbreuern Glass Factory in Bavaria, one of its main functions being the production of high-quality glass components for surveying and military purposes. His objective was to improve the quality of the glasses and lenses used in these instruments and for this he needed much improved wavelength standards. The breakthrough came in 1814 with his discovery of the vast array of dark absorption features in the solar spectrum (Fig. 11.1). The ten prominent lines were labelled A, a, B, C, D, E, b, F, G, H and, in addition, there were 574 fainter lines between B and H. One of his great contributions was the invention of an instrument with which he could measure precisely the deflection of light passing through the prism. To achieve this, he placed a theodolite on its side and observed the spectrum through a telescope mounted on the theodolite's rotating ring – this device was the first high-precision *spectrograph*. Fraunhofer also measured the wavelengths of the sun's spectral lines precisely using a diffraction grating, a device invented by Thomas Young just over a decade earlier.

Fraunhofer noted that the strong absorption feature which he labelled D consisted of two lines of the same wavelengths as the strong double emission line components observed in lamp-light. Foucault was able to reproduce the D-lines in the laboratory by passing the

radiation from a carbon arc through a sodium flame in front of the slit of the spectrograph. It was realised that absorption lines are the characteristic signatures of different elements; the most important experiments were carried out by Robert Bunsen and Gustav Kirchhoff. The Bunsen burner, as it came to be called, had the great advantage of enabling the spectral lines of various elements to be determined without contamination by the burning gas. In Kirchhoff's monumental series of papers of 1861–3, entitled 'Investigations of the solar spectrum and the spectra of the chemical elements',² the solar spectrum was compared with the spectra of 30 elements using a four-prism arrangement, designed so that the spectrum of the element and the solar spectrum could be observed simultaneously. He concluded that the cool, outer regions of the solar atmosphere contained iron, calcium, magnesium, sodium, nickel and chromium and probably cobalt, barium, copper and zinc as well.³

In the course of these studies, in 1859 Kirchhoff formulated his law concerning the relation between the coefficients of emission and absorption of radiation and how these can be related to the spectrum of thermal equilibrium radiation, what came to be known as *black-body radiation*. Let us begin by clarifying the definitions we will use throughout this case study.

11.2.1 Radiation intensity and energy density

Consider a region of space in which a small element of area dA is exposed to a radiation field. In a time dt , the total amount of energy passing through dA is $dE = S dA dt$, where S is the *total flux density* of radiation and has units W m^{-2} . We will be concerned with understanding the *spectral energy distribution* of the radiation, and so let us work in terms of the power arriving per unit area per unit frequency interval, S_ν , so that $S = \int S_\nu d\nu$. We will refer to S_ν as the *flux density*; its units are $\text{W m}^{-2} \text{Hz}^{-1}$. In the case of an isotropic point source of radiation of luminosity L_ν , at distance r , placing the elementary area normal to the direction of the source, the flux density of radiation is, by the conservation of energy,

$$S_\nu = \frac{L_\nu}{4\pi r^2}. \quad (11.1)$$

The units of luminosity are W Hz^{-1} .

The flux density depends upon the orientation of the area dA in the radiation field. It is meaningless to think of the radiation approaching the area along a particular ray. Rather, as in Chapter 10 for a flux of molecules, we should consider the flux of radiation dS_ν arriving within an element of solid angle $d\Omega$ in the direction of the unit vector \mathbf{i}_θ , which lies at some angle θ to the vector dA (see Fig. 11.2(a)). This leads to one of the key quantities needed in our study, the intensity of radiation. If we now orient the area dA normal to the direction \mathbf{i}_θ of the incoming rays (Fig. 11.2(b)), then the *intensity*, or *brightness*, of the radiation, I_ν , is defined to be the quotient of the flux density dS_ν and the solid angle $d\Omega$ within which this flux density originates:

$$I_\nu = \frac{dS_\nu}{d\Omega}. \quad (11.2)$$

Thus, the intensity is the flux density per unit solid angle – its units are $\text{W m}^{-2} \text{Hz}^{-1} \text{sr}^{-1}$.

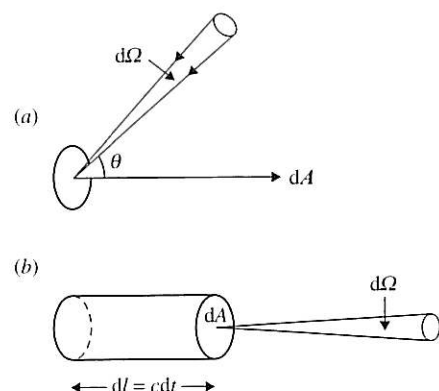


Figure 11.2: (a) The contribution of the flux density of radiation dS_ν arriving within $d\Omega$ to the total energy flux through the area dA . Note that the flux density dS_ν is defined as the power per unit frequency interval, arriving per unit area within the solid angle $d\Omega$, when the area vector dA is parallel to the direction of propagation. Then, the intensity of radiation is defined to be $I_\nu = dS_\nu/d\Omega$. (b) Illustrating how to relate intensity I_ν to the energy density u_ν of radiation.

Just as in the case of fluid flow, we can write the energy flux through the area dA from the solid angle $d\Omega$ at angle θ as $i_\theta \cdot dA dS_\nu$. Thus the energy per unit frequency interval at frequency ν flowing through dA in time dt is

$$dE_\nu = \int_{\Omega} I_\nu i_\theta \cdot dA dt d\Omega. \quad (11.3)$$

In the case of an isotropic radiation field, I_ν is independent of direction and so $I_\nu(\theta) = I_0 = \text{constant}$. Then

$$dE_\nu = I_0 dt \int_{\Omega} i_\theta \cdot dA d\Omega = I_0 dt |dA| \int_0^\pi \cos \theta \times 2\pi \sin \theta d\theta = 0. \quad (11.4)$$

As expected, there is no net energy flux through any elementary area placed in an isotropic radiation field.

Let us now relate the intensity I_ν to the spectral energy density of radiation u_ν within an elementary volume dV . Consider the power per unit area arriving normal to the elementary area dA within the element of solid angle $d\Omega$, which we can make as small as we like (Fig. 11.2(b)). Then, the radiation which passes through this area in this direction in time dt is contained in the volume of a cylinder of cross-sectional area dA and length $c dt$ (Fig. 11.2(b)). By conservation of energy, as much energy flows into the near end of the cylinder at the speed of light as flows out of the other end. Therefore, the energy $dU_\nu(\theta)$ contained in the volume at any time is found from

$$dU_\nu(\theta) d\Omega = I_\nu dA dt d\Omega. \quad (11.5)$$

The energy density of radiation $u_\nu(\theta) d\Omega$ is found by dividing by the volume of the cylinder $dV = dA c dt$, that is

$$u_\nu(\theta) d\Omega = \frac{dU_\nu(\theta)}{dV} d\Omega = \frac{I_\nu d\Omega}{c}. \quad (11.6)$$

To find u_ν , the energy density of radiation per unit frequency interval at frequency ν , now integrate over solid angle:

$$u_\nu = \int_{\Omega} u_\nu(\theta) d\Omega = \frac{1}{c} \int_{\Omega} I_\nu d\Omega. \quad (11.7)$$

Thus

$$u_\nu = \frac{4\pi}{c} J_\nu, \quad (11.8)$$

where we have defined the *mean intensity* J_ν to be

$$J_\nu = \frac{1}{4\pi} \int_{\Omega} I_\nu d\Omega. \quad (11.9)$$

The total energy density is found by integrating over all frequencies:

$$u = \int u_\nu d\nu = \frac{4\pi}{c} \int J_\nu d\nu. \quad (11.10)$$

There is an important feature of the intensity of radiation from a source. Suppose the source is a sphere of luminosity L_ν and radius a at distance r . Then, the intensity of radiation measured by an observer at distance r is

$$I_\nu = \frac{S_\nu}{\Omega} = \frac{L_\nu/(4\pi r^2)}{\pi a^2/r^2} = \frac{L_\nu/(4\pi)}{\pi a^2}, \quad (11.11)$$

which is independent of the distance of the source. The intensity is just the luminosity of the source per steradian divided by its projected surface area, that is, πa^2 for a spherical source.

11.2.2 Kirchhoff's law of emission and absorption

Radiation in thermodynamic equilibrium with its surroundings was first described theoretically by Gustav Kirchhoff in 1859, while he was conducting the experiments described at the beginning of this section. His arguments are fundamental to the understanding of the physics of radiation processes.⁴

When radiation propagates through a medium, its intensity can decrease because of absorption by the material of the medium or increase because of its radiative properties. To simplify the argument leading to Kirchhoff's law, we assume that the emission from the material within the cylinder shown in Fig. 11.2(b) is *isotropic* and that we can neglect scattering of the radiation. We can then define a *monochromatic emission coefficient* j_ν such that the power radiated into the solid angle $d\Omega$ from the cylindrical volume is

$$dI_\nu dA d\Omega = j_\nu dV d\Omega, \quad (11.12)$$

where dI_ν is the intensity of the radiation from the path length dl of the material; j_ν has units $\text{W m}^{-3} \text{ Hz}^{-1} \text{ sr}^{-1}$ and is the intensity radiated per unit solid angle per unit path length. Since the emission is assumed to be isotropic, the *volume emissivity* of the medium is $\epsilon_\nu = 4\pi j_\nu$. We can write the volume of the cylinder dV as $dA dl$ and so

$$dI_\nu = j_\nu dl. \quad (11.13)$$

We now define the *monochromatic absorption coefficient* α_ν , which measures the loss of intensity from the beam in the material, by the relation

$$dI_\nu dA d\Omega \equiv -\alpha_\nu I_\nu dA d\Omega dl. \quad (11.14)$$

This can be regarded as a phenomenological relation based upon experiment. It can be interpreted in terms of the absorption cross-section of the atoms or molecules of the medium, but this was not necessary for Kirchhoff's argument. Equation (11.14) simplifies to

$$dI_\nu = -\alpha_\nu I_\nu dl. \quad (11.15)$$

Therefore, the *transfer equation* for radiation can be written, including both emission and absorption,

$$\frac{dI_\nu}{dl} = -\alpha_\nu I_\nu + j_\nu. \quad (11.16)$$

This equation enabled Kirchhoff to understand the relation between the emission and absorption properties of the lines observed in the laboratory and in solar spectroscopy. If there is no absorption then $\alpha_\nu = 0$ and the solution of the transfer equation is

$$I_\nu(l) = I_\nu(l_0) + \int_{l_0}^l j_\nu(l') dl', \quad (11.17)$$

the first term representing the background emission intensity and the second emission from the medium located between l_0 and l . If there is absorption and no emission, $j_\nu = 0$, the solution of (11.16) is

$$I_\nu(l) = I_\nu(l_0) \exp \left[- \int_{l_0}^l \alpha_\nu(l') dl' \right], \quad (11.18)$$

where the exponential term describes the absorption of radiation by the medium. The term in brackets is often written in terms of the *optical depth* of the medium, τ_ν , where

$$\tau_\nu = \int_{l_0}^l \alpha_\nu(l') dl', \quad \text{and so} \quad I_\nu(l) = I_\nu(l_0) e^{-\tau_\nu}. \quad (11.19)$$

Kirchhoff went further and determined the relation between the coefficients of emission and absorption by considering what happens when the processes of emission and absorption take place within an enclosure which has reached thermodynamic equilibrium. The first part of the argument concerns the general properties of the equilibrium spectrum. That such a unique spectrum must exist can be deduced from the second law of thermodynamics, as follows. Suppose we have two enclosures of arbitrary shape, both containing electromagnetic radiation in thermal equilibrium at temperature T , and a filter is placed between them which allows only radiation in the frequency interval ν to $\nu + d\nu$ to pass between them. Then, if $I_\nu(1) d\nu \neq I_\nu(2) d\nu$, energy could flow spontaneously between them, violating the second law. The same type of argument can be used to show that the radiation must be isotropic. Therefore, the intensity spectrum of equilibrium radiation must be a unique function of only

temperature and frequency, which can be written

$$I_\nu = B_\nu(T) \quad (11.20)$$

where $B_\nu(T)$ is a universal function of T and ν .

Now, suppose a volume of an emitting medium is maintained at temperature T . The emission and absorption coefficients will have some dependence upon temperature, which we do not know. Suppose we now place the emitting volume in an enclosure containing electromagnetic radiation in thermal equilibrium at temperature T . Then, after a very long time, the emission and absorption processes must be in balance, so that there is no change in the intensity of the radiation throughout the volume. In other words, in the transfer equation (11.16) $dI_\nu/dl = 0$, so that $\alpha_\nu I_\nu = j_\nu$ and the intensity spectrum is the universal equilibrium spectrum $B_\nu(T)$,

$$\alpha_\nu B_\nu(T) = j_\nu. \quad (11.21)$$

This is *Kirchhoff's law of emission and absorption*, which showed that the emission and absorption coefficients for any physical process are related by the as yet unknown spectrum of equilibrium radiation. This expression enabled Kirchhoff to understand the relation between the emission and absorption properties of flames, arcs, sparks and the solar atmosphere. In 1859, however, very little was known about the form of $B_\nu(T)$. As Kirchhoff remarked, 'It is a highly important task to find this function.'⁵ This was one of the great experimental challenges for the remaining decades of the nineteenth century.

11.3 The Stefan-Boltzmann law

In 1879, Josef Stefan, Director of the Institute of Experimental Physics in Vienna, deduced the law which bears his name, primarily from experiments carried out by Tyndall at the Royal Institution of Great Britain on the radiation from platinum strip heated to different known temperatures, but also by reanalysing cooling experiments carried out by Dulong and Petit in the early years of the 19th century.⁶ He found that the rate of energy emission over all wavelengths (or frequencies) is proportional to the fourth power of the absolute temperature T ,

$$-\frac{dE}{dt} = \text{total radiant energy per second} \propto T^4. \quad (11.22)$$

In 1884, his former pupil, Ludwig Boltzmann, by then a professor at Graz, deduced this law from classical thermodynamics.⁷ It is important that his analysis was entirely classical. Let us demonstrate how this can be done without taking any short cuts.

Consider a volume filled only with electromagnetic radiation in equilibrium with the walls of the container and suppose that the volume is closed by a piston so that the 'gas' of radiation can be compressed or expanded. Now add some heat dQ to the 'gas' reversibly. As a result, the total internal energy increases by dU and work is done on the piston, so that the volume increases by dV . Then, according to the first law of thermodynamics,

$$dQ = dU + p dV. \quad (11.23)$$

Now introduce the increase in entropy $dS = \delta Q/T$, so that

$$T dS = dU + p dV, \quad (11.24)$$

as was derived in Section 9.8. We convert (11.24) into a partial differential equation by dividing through by dV at constant T :

$$T \left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial U}{\partial V} \right)_T + p. \quad (11.25)$$

We now use one of Maxwell's relations (A9.12), which was derived in appendix section A9.2,

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

to recast relation (11.25). Therefore,

$$T \left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial U}{\partial V} \right)_T + p. \quad (11.26)$$

This is the relation we were seeking, because we can now find the relation between U and T if an equation of state for the gas, that is, a relation between p , V and U , can be determined.

The equation of state can be derived from Maxwell's electromagnetic theory and was proved by Maxwell in his great work *A Treatise on Electricity and Magnetism*⁸ published in 1873. Let us derive the radiation pressure of a 'gas' of electromagnetic radiation by essentially the same route followed by Maxwell. If you already know the answer, $p = \frac{1}{3}u$ where u is the energy density of radiation, and you can prove it classically then you may wish to advance to subsection 11.3.3.

11.3.1 The reflection of electromagnetic waves by a conducting plane

The expression for radiation pressure can be derived from the fact that when electromagnetic waves are reflected by a conductor they exert a force at the interface. To understand the nature and magnitude of this force according to classical electrodynamics, we need to work out the currents which flow in a conductor under the influence of incident electromagnetic waves. Let us consider the case in which waves are normally incident on a sheet of large but finite conductivity (Fig. 11.3). This will provide excellent revision of the use of some of the tools developed in our study of electromagnetism (Chapters 5 and 6).

Figure 11.3 shows on the left a vacuum and on the right a medium with conductivity σ . The incident and reflected waves and the transmitted waves are shown by arrows. From our studies in Chapters 3 and 4, we can write down the *dispersion relations* for waves propagating in the vacuum and in the conducting medium:

$$\text{in the vacuum,} \quad k^2 = \omega^2/c^2; \quad (11.27)$$

$$\begin{aligned} \text{in the conductor,} \quad \nabla \times \mathbf{H} &= \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J}, & \nabla \times \mathbf{E} &= -\frac{\partial \mathbf{B}}{\partial t}, \\ \mathbf{J} &= \sigma \mathbf{E}, & \mathbf{D} &= \epsilon \epsilon_0 \mathbf{E}, & \mathbf{B} &= \mu \mu_0 \mathbf{H}. \end{aligned} \quad (11.28)$$

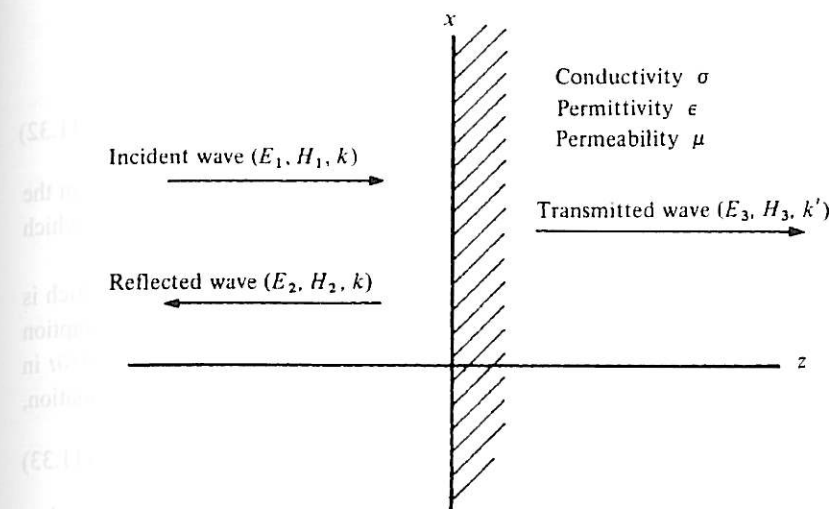


Figure 11.3: An electromagnetic wave incident at an interface between a vacuum and a highly conducting medium.

Using the relations developed in appendix section A5.6 for a travelling wave of form $\exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$,

$$\nabla \times \rightarrow i\mathbf{k} \times \quad \text{and} \quad \frac{\partial}{\partial t} \rightarrow -i\omega,$$

we find that

$$\begin{aligned} \mathbf{k} \times \mathbf{H} &= -(\omega \epsilon \epsilon_0 + i\sigma) \mathbf{E}, \\ \mathbf{k} \times \mathbf{E} &= \omega \mathbf{B}. \end{aligned} \quad (11.29)$$

Thus, in the conductor we obtain a dispersion relation similar to (11.27) but with $\omega \epsilon \epsilon_0$ replaced by $\omega \epsilon \epsilon_0 + i\sigma$, that is,

$$k^2 = \epsilon \mu \frac{\omega^2}{c^2} \left(1 + \frac{i\sigma}{\omega \epsilon \epsilon_0} \right). \quad (11.30)$$

Let us consider the case in which the conductivity is very high, $\sigma/(\omega \epsilon \epsilon_0) \gg 1$. Then

$$k^2 = i \frac{\mu \omega \sigma}{\epsilon_0 c^2}.$$

Since $i^{1/2} = 2^{-1/2}(1+i)$, the solution for k is

$$k = \pm \left(\frac{\mu \omega \sigma}{2 \epsilon_0 c^2} \right)^{1/2} (1+i), \quad \text{that is,} \quad k = \pm \left(\frac{\mu \omega \sigma}{2 \epsilon_0 c^2} \right)^{1/2} e^{i\pi/4}. \quad (11.31)$$

The phase relations between \mathbf{E} and \mathbf{B} in the wave can now be found from the second relation of (11.29), $\mathbf{k} \times \mathbf{E} = \omega \mathbf{B}$.

In *free space*, k is real and \mathbf{E} and \mathbf{B} oscillate in phase and with constant amplitude. In the conductor, however, (11.31) shows that there is a difference of $\pi/4$ between the phases

of E and B and both fields decrease exponentially into the conductor, that is,

$$\begin{aligned} E &\propto \exp[i(kz - \omega t)], \\ &= \exp\left(-\frac{z}{l}\right) \exp\left[i\left(\frac{z}{l} - \omega t\right)\right], \end{aligned} \quad (11.32)$$

where $l = [2\epsilon_0 c^2 / (\mu \omega \sigma)]^{1/2}$. The amplitude of the wave decreases by a factor $1/e$ in the length l , which is called the *skin depth* of the conductor. It is the typical depth to which electromagnetic fields can penetrate into the conductor.

There is an important general feature of the solution represented by (11.32), which is worth noting. If we trace back the steps involved in arriving at this solution, the assumption that the conductivity is high corresponds to neglecting the displacement current $\partial \mathbf{D} / \partial t$ in comparison with \mathbf{J} . Then, the equation we have solved has the form of a diffusion equation,

$$\nabla^2 \mathbf{H} = \sigma \epsilon_0 \frac{\partial \mathbf{H}}{\partial t}. \quad (11.33)$$

In general, wave solutions of diffusion equations have dispersion relations of the form $k = A(1 + i)$; that is, the real and imaginary parts of the wave vector are equal, corresponding to waves which decay in amplitude by $e^{-2\pi}$ in each complete cycle. This is true for equations such as:

(i) the heat conduction equation,

$$\kappa \nabla^2 T - \frac{\partial T}{\partial t} = 0, \quad \kappa = \frac{K}{\rho C}, \quad (11.34)$$

where K is the thermal conductivity of the medium, ρ its density, C the specific heat and T the temperature;

(ii) the diffusion equation,

$$D \nabla^2 N - \frac{\partial N}{\partial t} = 0, \quad (11.35)$$

where D is the diffusion coefficient and N the number density of particles;

(iii) the equation for viscous waves,

$$\frac{\mu}{\rho} \nabla^2 \mathbf{u} - \frac{\partial \mathbf{u}}{\partial t} = 0, \quad (11.36)$$

where μ is the viscosity, ρ the density of the fluid and \mathbf{u} the fluid velocity. This equation is derived from the Navier–Stokes equation for fluid flow in a viscous medium (see the appendix to Chapter 7).

Returning to our story (Fig. 11.3), we now match the E and H vectors of the waves at the interface between the two media. Taking z to be the direction normal to the interface, we introduce the following:

for the incident wave,

$$\begin{aligned} E_x &= E_1 \exp[i(kz - \omega t)], \\ H_y &= \frac{E_1}{Z_0} \exp[i(kz - \omega t)], \end{aligned} \quad (11.37)$$

where $Z_0 = (\mu_0 / \epsilon_0)^{1/2}$ is the impedance of free space;

for the reflected wave,

$$\begin{aligned} E_x &= E_2 \exp[-i(kz + \omega t)], \\ H_y &= -\frac{E_2}{Z_0} \exp[-i(kz + \omega t)]; \end{aligned} \quad (11.38)$$

for the transmitted wave,

$$\begin{aligned} E_x &= E_3 \exp[i(k'z - \omega t)], \\ H_y &= E_3 \frac{(\mu \omega \sigma / 2 \epsilon_0 c^2)^{1/2}}{\omega \mu \mu_0} (1 + i) \exp[i(k'z - \omega t)], \end{aligned} \quad (11.39)$$

where k' is given by the value of k in the relation (11.31). The expression for H_y has been found by substituting for k in the relation between E and B , $\mathbf{k} \times \mathbf{E} = \omega \mathbf{B}$.

For simplicity, let us write $q = [(\mu \omega \sigma / 2 \epsilon_0 c^2)^{1/2} (\omega \mu \mu_0)^{-1}] (1 + i)$. Then

$$H_y = q E_3 \exp[i(k'z - \omega t)]. \quad (11.40)$$

The boundary conditions require E_x and H_y to be continuous at the interface (see Section 6.5), that is, at $z = 0$,

$$\begin{aligned} E_1 + E_2 &= E_3, \\ \frac{E_1}{Z_0} - \frac{E_2}{Z_0} &= q E_3. \end{aligned} \quad (11.41)$$

Therefore

$$\frac{E_1}{1 + q Z_0} = \frac{E_2}{1 - q Z_0} = \frac{E_3}{2}. \quad (11.42)$$

In general, q is a complex number and hence there are phase differences between E_1 , E_2 and E_3 . We are, however, interested in the case in which the conductivity is very large, $|q| Z_0 \gg 1$, and hence

$$\frac{E_1}{q Z_0} = -\frac{E_2}{q Z_0} = \frac{E_3}{2}, \quad (11.43)$$

that is,

$$E_1 = -E_2 \quad \text{and} \quad E_3 = 0.$$

Therefore, at the interface, the total electric field strength $E_1 + E_2$ is zero and the magnetic field strength $H_1 + H_2 = 2H_1$.

It may seem as though we have strayed rather far from the thermodynamics of radiation, but we are now able to work out the pressure exerted by the incident wave upon the surface.

11.3.2 The formula for radiation pressure

Suppose that the radiation is confined in a box with rectangular sides and the waves bounce back and forth between the walls at $z = \pm z_1$ (Fig. 11.3). Assuming that the walls of the box

are highly conducting, as in the preceding subsection, we now know the values of the electric and magnetic field strengths in the vicinity of the walls for normal incidence.

Part of the origin of the phenomenon of radiation pressure may be understood as follows. The electric field in the conductor E_x causes a current density to flow in the $+x$ direction,

$$J_x = \sigma E_x. \quad (11.44)$$

But the force per unit volume acting on this electric current in the presence of a magnetic field is

$$\mathbf{F} = N_q q (\mathbf{v} \times \mathbf{B}) = \mathbf{J} \times \mathbf{B}, \quad (11.45)$$

where N_q is the number of conduction electrons per unit volume and q is the electronic charge. Since \mathbf{B} is in the $+y$ direction, this force acts in the $\mathbf{i}_x \times \mathbf{i}_y$ -direction; this is the k -direction, that of the incident wave. Therefore, the pressure acting on a layer of thickness dz in the conductor is

$$dp = J_x B_y dz. \quad (11.46)$$

However, we also know that in the conductor $\text{curl } \mathbf{H} = \mathbf{J}$, because the conductivity is very high, and hence we can relate J_x and B_y by

$$\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} = J_x.$$

Since $H_z = 0$, $-\partial H_y / \partial z = J_x$. Substituting into (11.46),

$$dp = -B_y \frac{\partial H_y}{\partial z} dz. \quad (11.47)$$

Therefore,

$$p = - \int_0^\infty B_y \frac{\partial H_y}{\partial z} dz = \int_0^{H_0} B_y dH_y,$$

where H_0 is the value of the magnetic field strength at the interface and, according to the analysis of subsection 11.3.1, $H \rightarrow 0$ as $z \rightarrow \infty$. For a linear medium, $B_0 = \mu\mu_0 H_0$ and hence

$$p = \frac{1}{2} \mu\mu_0 H_0^2. \quad (11.48)$$

Notice that this pressure is associated with induced currents flowing in the conducting medium.

Now we have to ask what other forces act at the vacuum-conductor interface. These are associated with the stresses in the electromagnetic fields themselves and are given by the appropriate components of the Maxwell stress tensor. In our simple case, we can derive the magnitude of these stresses by an argument based on Faraday's concept of lines of force. Suppose a uniform longitudinal magnetic field is confined within a long rectangular perfectly conducting tube (Fig. 11.4). If the medium is linear, so that $B = \mu\mu_0 H$, the energy per unit length of tube is

$$E = \frac{1}{2} B H l,$$

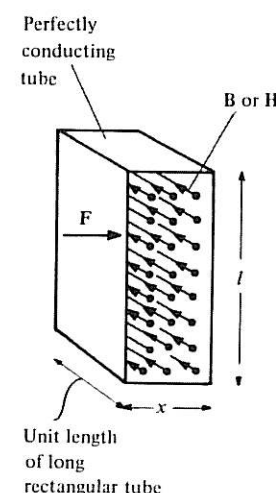


Figure 11.4: A long perfectly conducting rectangular tube enclosing a longitudinal magnetic field. When the tube is compressed by a force F in the z -direction, the magnetic flux enclosed by the tube is conserved. For more details of magnetic flux freezing, see, for example, M.S. Longair (1992), *High Energy Astrophysics*, Vol. 2, 307–12, Cambridge: Cambridge University Press.

where z is the width and l the height of the tube. Now squash the width of the tube by dz whilst maintaining the same number of lines of force through it. Then the magnetic flux density increases to $Bz/(z - dz)$ because of conservation of lines of force and correspondingly, because the field is linear, H becomes $H z / (z - dz)$. Thus, the energy in the volume becomes

$$\begin{aligned} E + dE &= \frac{1}{2} B H l z^2 \frac{1}{(z - dz)}, \\ dE &= \frac{1}{2} B H l z \left(1 + \frac{dz}{z} \right) - \frac{1}{2} B H l z, \\ &= \frac{1}{2} B H l dz. \end{aligned}$$

But this increase in energy must be the result of external work done against the magnetic field,

$$F dz = dE = \frac{1}{2} B H l dz.$$

Thus, the force per unit area p_m is $F/l = \frac{1}{2} B H$; it acts *perpendicularly* to the field direction. We can write

$$p_m = \frac{1}{2} \mu\mu_0 H^2. \quad (11.49)$$

We can apply exactly the same argument to the electrostatic field, in which case the total force per unit area associated with the electric and magnetic fields is*

$$p = \frac{1}{2} \epsilon\epsilon_0 E^2 + \frac{1}{2} \mu\mu_0 H^2. \quad (11.50)$$

* Here E refers to the magnitude of the electric field.

This argument applies to the fields in both regions but, because the value of μ is different on either side of the interface, there is a pressure difference across it associated with the presence of the magnetic fields.

We have shown that, at the interface, $E_x = 0$ and $H_y = H_0 = 2H_1$. Hence in the vacuum adjacent to the interface $p = \frac{1}{2}\mu_0 H_0^2$. Inside the conductor the stress is $\frac{1}{2}\mu\mu_0 H_0^2$. Therefore, from (11.48), the total pressure on the conductor is

$$p = \underbrace{\frac{1}{2}\mu_0 H_0^2}_{\text{stress in vacuum}} - \underbrace{\frac{1}{2}\mu\mu_0 H_0^2}_{\text{stress in conductor}} + \underbrace{\frac{1}{2}\mu\mu_0 H_0^2}_{\text{force on conduction current}},$$

so that

$$p = \frac{1}{2}\mu_0 H_0^2. \quad (11.51)$$

The energy density in the wave propagating in the positive z -direction in the vacuum is $\frac{1}{2}(\epsilon_0 E_1^2 + \mu_0 H_1^2) = \mu_0 H_1^2$. Therefore, since $H_0 = 2H_1$,

$$p = \frac{1}{2}\mu_0 H_0^2 = 2\mu_0 H_1^2 = 2\epsilon_1 = \epsilon_0, \quad (11.52)$$

where ϵ_0 is the total energy density of radiation in the vacuum, being the sum of the energy densities in the incident and reflected waves.

Equation (11.52) is the relation between the pressure and energy density for a 'one-dimensional' gas of electromagnetic radiation, confined between two reflecting walls. In an isotropic-three dimensional volume, there are equal energy densities associated with radiation propagating in the three orthogonal directions, that is,

$$\epsilon_x = \epsilon_y = \epsilon_z = \epsilon_0,$$

and hence the radiation pressure p is

$$p = \frac{1}{3}\epsilon, \quad (11.53)$$

where ϵ is the total energy density of radiation.

This somewhat lengthy demonstration shows how it is possible to derive the pressure of a gas of electromagnetic radiation entirely by classical arguments. I have purposely given this simple treatment because I prefer to use these physical arguments rather than the more mathematical treatment starting from Maxwell's equations and involving the use of the Maxwell stress tensor for the electromagnetic field. This is how Maxwell derived the expression for radiation pressure in Section 793 of the second volume of his *Treatise on Electricity and Magnetism* of 1873.⁸ In his argument, the pressure of a 'gas' of electromagnetic radiation in free space was derived directly from (11.50). On averaging this expression over the period of the electromagnetic waves, the relation $p = \epsilon_0$ for a one-dimensional gas is found directly.

11.3.3 The derivation of the Stefan-Boltzmann law

The relation (11.53) between p and ϵ for a gas of electromagnetic radiation leads to the Stefan-Boltzmann law. From (11.26), writing $U = \epsilon V$

$$\begin{aligned} \frac{T}{3} \left(\frac{\partial \epsilon}{\partial T} \right)_V &= \left(\frac{\partial(\epsilon V)}{\partial V} \right)_T + \frac{\epsilon}{3}, \\ \frac{T}{3} \left(\frac{\partial \epsilon}{\partial T} \right)_V &= \epsilon + \frac{\epsilon}{3} = \frac{4\epsilon}{3}. \end{aligned}$$

This relation between ϵ and T can be integrated immediately:

$$\frac{d\epsilon}{\epsilon} = 4 \frac{dT}{T}, \quad \ln \epsilon = 4 \ln T, \quad \epsilon = aT^4. \quad (11.54)$$

This is the calculation which Boltzmann carried out in 1884 and his name is justly associated with the *Stefan-Boltzmann law*. The constant a is given by

$$a = \frac{8\pi^5 k^4}{15c^3 h^3} = 7.566 \times 10^{-16} \text{ J m}^{-3} \text{ K}^{-4}. \quad (11.55)$$

We will derive this expression in Section 13.3.

The expression (11.54) for the energy density of radiation can be related to the energy emitted per unit area per second from the surface of a black body at temperature T . Suppose that the black body is placed in an enclosure maintained in thermal equilibrium at temperature T and that $N(E)$ is the number density of radiation modes of energy E in the enclosure. If the energy of a mode is E then the rate at which energy arrives at the wall per unit area per second, and consequently the rate I at which the energy must be reradiated from it, is from (10.13) $\frac{1}{4}N(E)Ec = \frac{1}{4}N\bar{E}c = \frac{1}{4}\epsilon c$. Therefore,

$$I = \frac{\epsilon c}{4} = \frac{ac}{4} T^4 = \sigma T^4 = 5.67 \times 10^{-8} T^4 \text{ W m}^{-2} \quad (11.56)$$

where σ is the Stefan-Boltzmann constant. The experimental evidence for the Stefan-Boltzmann law was not particularly convincing in 1884 and it was not until 1897 that Lummer and Pringsheim undertook very careful experiments which showed that the law was indeed correct to high precision (see Fig. V.1 at the start of this case study).

11.4 Wien's displacement law and the spectrum of black-body radiation

The spectrum of black-body radiation was not particularly well known in 1895, but there had already been important theoretical work carried out by Wilhelm Wien on the form which the radiation law should have. *Wien's displacement law*⁹ was derived using a combination of electromagnetism and thermodynamics, as well as dimensional analysis. Let us show exactly what Wien did in this work, published in 1893, which was to be of central importance in the subsequent story.

First of all, Wien worked out how the properties of a 'gas' of radiation change when it undergoes a reversible adiabatic expansion. The analysis starts with the basic thermodynamic

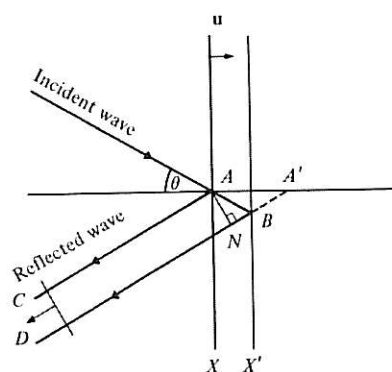


Figure 11.5: Illustrating the change in wavelength of an electromagnetic wave reflected from a perfectly conducting plane moving to the right at speed u .

relation

$$\delta Q = dU + p dV.$$

In an adiabatic expansion $\delta Q = 0$ and, for a 'gas' of radiation, $U = \varepsilon V$ and $p = \frac{1}{3}\varepsilon$. Therefore

$$\begin{aligned} d(\varepsilon V) + \frac{1}{3}\varepsilon dV &= 0, \\ V d\varepsilon + \varepsilon dV + \frac{1}{3}\varepsilon dV &= 0, \end{aligned}$$

so that

$$\frac{d\varepsilon}{\varepsilon} = -\frac{4}{3} \frac{dV}{V}.$$

Integrating,

$$\varepsilon = \text{constant} \times V^{-4/3}. \quad (11.57)$$

But $\varepsilon = aT^4$ and hence

$$TV^{1/3} = \text{constant}. \quad (11.58)$$

Since V is proportional to the cube of the radius r of a spherical volume,

$$T \propto r^{-1}. \quad (11.59)$$

The next step in deriving Wien's displacement law is to work out the relation between the wavelength of the radiation and the volume of the enclosure in a reversible adiabatic expansion. Let us carry out two simple calculations which demonstrate the answer. First of all, we determine the change in wavelength if a wave is reflected from a slowly moving mirror (Fig. 11.5). The initial position of the mirror is at X and we suppose that at that time one of the maxima of the incident waves is at A . It is then reflected along the path AC . Now suppose that by the time the next wavecrest arrives at the mirror, the latter has moved to X' and hence the maximum has to travel an extra distance ABN as compared with the first

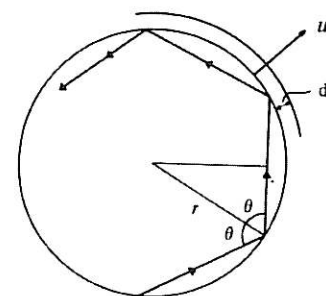


Figure 11.6: Illustrating the differential change in wavelength of an electromagnetic wave as it is reflected inside a spherical volume expanding at speed u .

maximum, that is, the distance between maxima, the wavelength, is increased by an amount $d\lambda = AB + BN$. By symmetry,

$$AB + BN = A'N = AA' \cos \theta.$$

But

$$AA' = 2 \times \text{distance moved by mirror} = 2XX' = 2uT,$$

where u is the velocity of the mirror and T is the period of the wave. Hence,

$$\begin{aligned} d\lambda &= 2uT \cos \theta, \\ &= 2\lambda \frac{u}{c} \cos \theta, \quad \text{since } d\lambda \ll \lambda. \end{aligned} \quad (11.60)$$

Notice that this result is correct only to first order in small quantities, but that is all we need since we are interested in differential changes.

Now suppose the wave is confined within a spherical reflecting cavity, which is expanding slowly, and that its angle of incidence with respect to the normal to the sphere is θ (Fig. 11.6). We can work out the number of reflections which the wave makes with the sphere, and hence the total change in wavelength, as the cavity expands from r to $r + dr$ at speed u , assuming $u \ll c$.

If the velocity of expansion is small, θ remains the same for all reflections as the sphere expands by an infinitesimal distance dr . The time it takes for the sphere to expand a distance dr is $dt = dr/u$ and, from the geometry of Fig. 11.6, the time between reflections for a wave propagating at velocity c is $2r \cos \theta / c$. The number of reflections in time dt is therefore $c dt / (2r \cos \theta)$ and the change in wavelength $d\lambda$ is

$$d\lambda = \left(\frac{2u\lambda}{c} \cos \theta \right) \left(\frac{c dt}{2r \cos \theta} \right),$$

that is,

$$\frac{d\lambda}{\lambda} = \frac{u dt}{r} = \frac{dr}{r}.$$

Integrating, we find

$$\lambda \propto r. \quad (11.61)$$

Thus, the wavelength of the radiation increases linearly in proportion to the radius of the spherical volume.

We can now combine this result with (11.59), $T \propto r^{-1}$, and find that

$$T \propto \lambda^{-1}. \quad (11.62)$$

This is one aspect of *Wien's displacement law*. If radiation undergoes a reversible adiabatic expansion, the wavelength of a particular set of waves changes inversely with temperature. In other words, the wavelength of the radiation is 'displaced' as the temperature changes. In particular, if we follow the maximum of the radiation spectrum, it should follow the law $\lambda_{\max} \propto T^{-1}$. This was found to be in good agreement with experiment.

Now Wien went significantly further than this and combined the two laws, the Stefan-Boltzmann law and the law $T \propto \lambda^{-1}$, to set constraints upon the form of the equilibrium radiation spectrum. His first step was to note that if any system of bodies is enclosed in a perfectly reflecting enclosure then eventually all of them come to thermal equilibrium through the emission and absorption of radiation – in this state, as much energy is radiated as is absorbed by the bodies per unit time. Thus, if we wait long enough, the radiation in the enclosure attains a black-body radiation spectrum at a certain temperature T . According to the arguments presented in subsection 11.2.2, first enunciated by Kirchhoff, the radiation must be isotropic, and the only parameter which can characterise the radiation spectrum is the temperature, T .

The next step is to note that if the black-body radiation is initially at temperature T_1 and the enclosure undergoes a reversible adiabatic expansion then by definition the expansion proceeds infinitely slowly, so that the radiation takes up an equilibrium spectrum at all stages in the expansion to a lower temperature T_2 . The crucial point is that the radiation spectrum is of equilibrium black-body form, at the beginning and end of the expansion. The unknown radiation law must therefore scale appropriately with temperature.

Consider the radiation in the wavelength interval λ_1 to $\lambda_1 + d\lambda_1$ and let its energy density be $\varepsilon = u(\lambda_1) d\lambda_1$, that is, $u(\lambda)$ is the energy density per unit wavelength interval or per unit bandwidth. Then, according to Boltzmann's analysis given in subsection 11.3.3, the energy associated with any particular wavelength range $d\lambda$ changes as T^4 and hence

$$\frac{u(\lambda_1) d\lambda_1}{u(\lambda_2) d\lambda_2} = \left(\frac{T_1}{T_2}\right)^4, \quad (11.63)$$

where λ_2 is the wavelength after the expansion. But from (11.62) $\lambda_1 T_1 = \lambda_2 T_2$, and hence $d\lambda_1 = (T_2/T_1) d\lambda_2$. Therefore,

$$\frac{u(\lambda_1)}{T_1^5} = \frac{u(\lambda_2)}{T_2^5}, \quad \text{that is,} \quad \frac{u(\lambda)}{T^5} = \text{constant}. \quad (11.64)$$

Since $\lambda T = \text{constant}$, (11.64) can be rewritten

$$u(\lambda) \lambda^5 = \text{constant}. \quad (11.65)$$

Now, the only combination of T and λ which is constant during the expansion is the product λT , and hence we can conclude that, in general, the constant in (11.65) can only be

constructed out of functions involving λT . Therefore, the radiation law must have the form

$$u(\lambda) \lambda^5 = f(\lambda T) \quad (11.66)$$

or

$$u(\lambda) d\lambda = \lambda^{-5} f(\lambda T) d\lambda. \quad (11.67)$$

This is the complete form of *Wien's displacement law* and it sets important constraints upon the form of the black-body radiation spectrum.

We will find it more convenient to work in terms of frequencies rather than wavelengths, and so let us convert Wien's displacement law into frequency form:*

$$u(\lambda) d\lambda = u(\nu) d\nu,$$

and use

$$\lambda = c/\nu, \quad d\lambda = -\frac{c}{\nu^2} d\nu.$$

Hence from (11.67)

$$u(\nu) d\nu = \left(\frac{c}{\nu}\right)^{-5} f\left(\frac{\nu}{T}\right) \left(-\frac{c}{\nu^2} d\nu\right), \quad (11.68)$$

that is,

$$u(\nu) d\nu = \nu^3 f\left(\frac{\nu}{T}\right) d\nu. \quad (11.69)$$

This is really rather clever. Notice how much Wien was able to deduce using only rather general thermodynamic arguments. We will see in a moment how crucial this argument proved to be in establishing the correct formula for black-body radiation.

This was all new when Planck first became interested in the problem of the spectrum of equilibrium radiation in 1895. Let us now turn to Planck's huge contributions to the understanding of the spectrum of black-body radiation.

11.5 References

- 1 Lindley, D. (2001). *Boltzmann's Atom*. New York: The Free Press.
- 2 Kirchhoff, G. (1861–3). Part 1, *Abhandl. der Berliner Akad.* (1861), p. 62, (1862), p. 227; part 2 (1863), p. 225.
- 3 An excellent description of these early spectroscopic studies is given by J.B. Hearnshaw in *The Analysis of Starlight* (1986), Cambridge: Cambridge University Press.
- 4 I particularly like the careful discussion of the fundamentals of radiative processes by G.B. Rybicki and A.P. Lightman, *Radiative Processes in Astrophysics* (1979), New York: John Wiley and Sons.
- 5 Kirchhoff, G. (1859). *Ber. der Berliner Akad.*, p. 662. (*Trans. Phil. Mag.*, 19, 193, 1860.)

* Here $u(\lambda)$ and $u(\nu)$ are different, though closely related, functions, the forms of which are defined by their respective arguments, likewise $f(\lambda T)$ and $f(\nu/T)$.