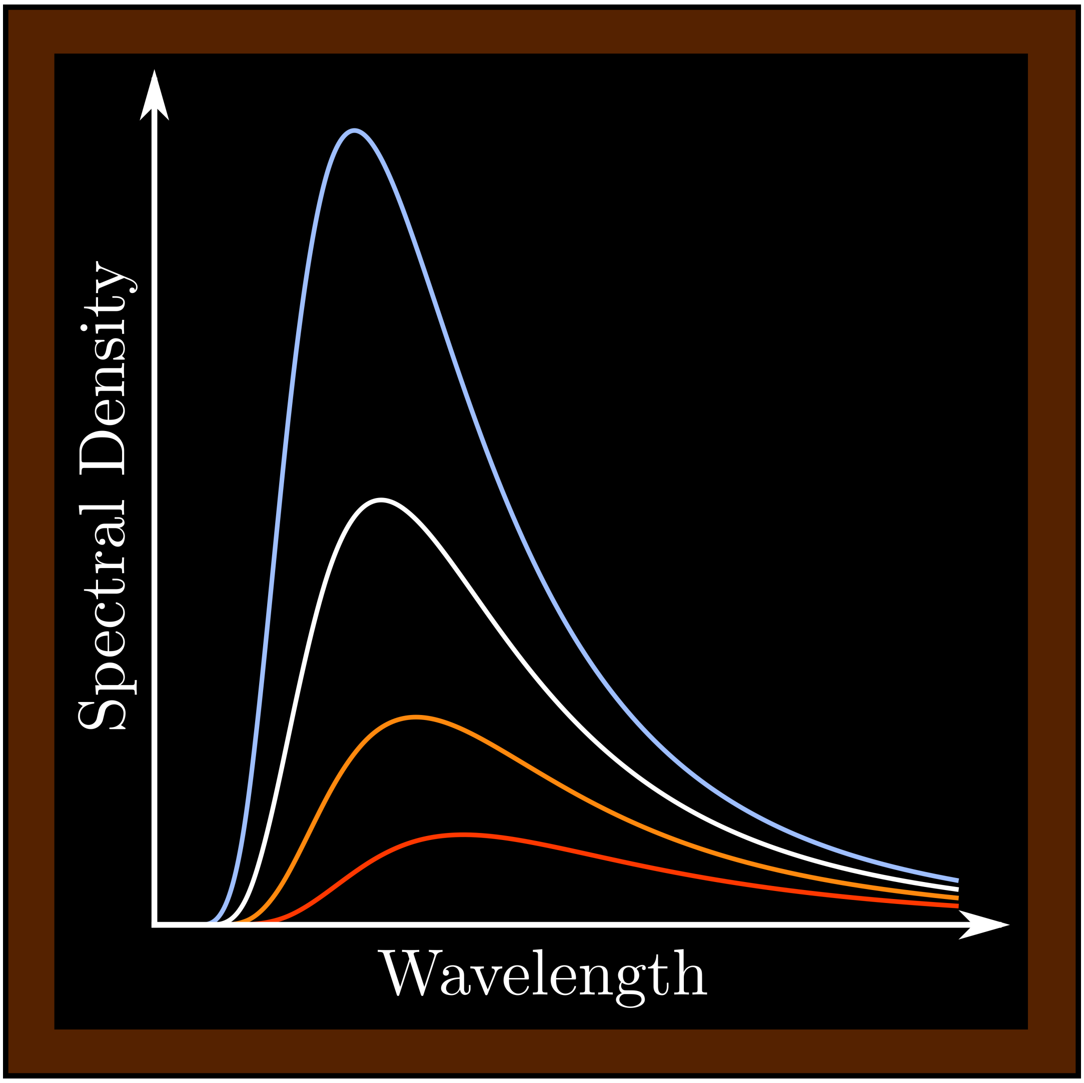
Thermal Radiation



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Introduction

In 1878, Professor Philipp von Jolly advised one of his students, a young Max Planck, not to dedicate his career to physics, remarking that "in this field, almost everything is already discovered, and all that remains is to fill a few unimportant holes." Planck would, as students tend to do, ignore the advice of his teacher and go on to spend his time filling in one such hole: the spectrum of light emitted from a heated body. He quickly ended up discovering that this particular problem it was less of a small hole and more of a gaping abyss. In order to find a satisfactory explanation for this phenomenon, Planck had to abandon the laws of classical mechanics, which had stood unchanged for over two centuries, kick starting the birth of quantum physics. It would not be an exaggeration to say that Max Planck's work on thermal radiation was the catalyst for the greatest advance in physics since Isaac Newton first proposed his laws of motion.

It has been known since antiquity that, if you heat an object up enough, it begins to emit light. Moreover, the colour and intensity of that light is dependent on the object's temperature. For example, when a blacksmith heats a piece of metal in a forge, it first begins to glow a dull, cherry red, then becomes brighter and brighter, changing colour to orange, then yellow, and eventually white, as it heats up. Throughout most of human history, understanding of what exactly heat and temperature are was too poor for an explanation of these observations to be within the realm of possibility. However, this all changed with the industrial revolution in the early nineteenth century. Motivated by trying to understand and design more efficient steam engines, physicists of the nineteenth century developed an entirely new field of study: thermodynamics. This provided a rigorous theoretical framework for analysing phenomena such as thermal radiation. Also in the nineteenth century, James Clerk Maxwell put forward his theory of electromagnetism, which identified light as propagating electromagnetic wave, providing the first description of how light interacts with material bodies.

With these building blocks securely in place, one could be forgiven for assuming that the task of describing thermal radiation would be a simple one. As it turned out, the reality was anything but. At first, thermodynamic and electromagnetic arguments were able to make some progress; most notably leading to the Stefan–Boltzmann law and Wien's displacement law, which explained effect of temperature on the brightness and colour respectively of thermal radiation. However, when it came to calculating the exact spectrum of thermal radiation, a problem soon emerged. According to the classical theories, any object at a temperature above absolute zero should radiate an essentially infinite amount of energy in high frequency electromagnetic waves. This so called ultraviolet catastrophe would only be satisfactorily resolved by the work of Max Planck and Albert Einstein with their hypothesis that the energy of electromagnetic radiation was not continuously distributed, but instead divided up into discrete quanta, which we now call photons.

These notes provide an overview of some of the important historical thoughts and results related to the study of thermal radiation. In the interest of brevity, some results will be stated without proof; however, we will always endeavour to provide some intuition about where those results come from.

1 Black Bodies

A perfect black body is defined to be an object which completely absorbs any and all electromagnetic radiation incident upon it. Just like the frictionless pulleys or massless springs one frequently encounters in mechanics classes, a true black body is an idealisation that does not really exist in nature. However, as far as we can tell, there is no law of nature that explicitly forbids the existence of black bodies, and the only restriction on how close we can get to one with a real object is how cleverly we can engineer its materials. As such, we can make physically meaningful statements about the properties of black bodies, so long as we keep in the back of our minds that we are really discussing the limiting behaviour of better and better approximations to a perfect black body.

An important property of black bodies is that the thermal radiation they emit depends only on their geometric shape and their temperature. We can see why this must be the case as follows. First, let us imagine that we have two black bodies which are the same shape (more specifically we want one to be the mirror image of the other). Let us arrange them on either side of a wall which has a single hole containing a prism, as shown in Figure 1. This ensures that only radiation of a specific wavelength, leaving the black bodies in a specific direction can pass between them. By symmetry, the fraction of the radiation emitted by one black body which falls on and is absorbed by the other will be the same in either direction. Thus, if one of the black bodies emits more strongly in the chosen wavelength and direction, then there will be a net flow of thermal energy between from one to the other. However, the second law of thermodynamics states that there can only be a net flow of heat from a hotter body to a colder one. As such, if the two black bodies are the same temperature, the net flow of heat between them must be zero for all possible arrangements of the wall and prism. Thus, the radiation emitted at any given wavelength and in any specified direction must be the same for both black bodies.

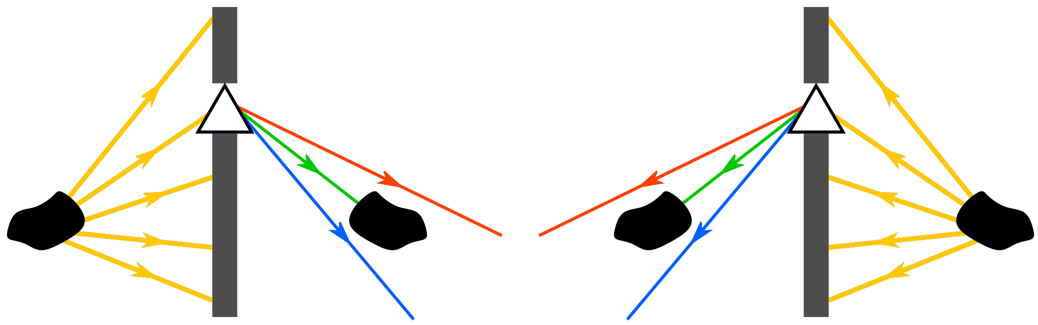

Figure 1. Two black bodies of the same shape that can only exchange energy via radiation emitted in a specific direction and with a specific wavelength. The thicker yellow rays indicate thermal light emitted by the black body, while the thinner red, blue, and green rays represent that same light after being split into is component wavelengths by the prism. The diagram on the left shows the radiation emitted by the left black body and vice versa.

The reason we are so interested in black bodies is that they provide a convenient reference point against which real objects can be compared. In particular, we do this by defining two properties of an object: its absorptivity

$$\alpha_\lambda = \left(\begin{array}{l}\text{the amount of light with wavelength } \lambda \text{ absorbed} \\ \text{by an object, divided by the amount absorbed} \\ \text{by an ideal black body of the same shape and} \\ \text{size}\end{array}\right) , \tag{1.1}$$

and its emissivity

$$\varepsilon_\lambda = \left(\begin{array}{l}\text{the amount of light with wavelength } \lambda \text{ radiated} \\ \text{by an object, divided by the amount that an ideal} \\ \text{black body of the same shape, size, and temper-} \\ \text{ature would radiate}\end{array}\right) . \tag{1.2}$$

We can repeat our thought experiment from before, but this time replace one of the black bodies with a real object of the same size and shape. The radiation transferred from the real object to the black body will be reduced by a factor of its emissivity, while the radiation transferred from the black body to the object will be reduced by a factor of its absorptivity. As such, the only way to maintain consistency with the second law of thermodynamics and have no net heat transfer when the two bodies are at the same temperature, is if

$$\alpha_{\lambda,\Omega} = \varepsilon_{\lambda,\Omega} , \tag{1.3}$$

a result known as Kirchhoff's law of thermal radiation. Equipped with this fact, all we need in order to predict the thermal radiation any chosen object will give off is its absorptivity, which is relatively easy to measure, and a description of the emission from a perfect black body. Following the discovery of his law in 1859, Kirchhoff announced that determining such a description was a problem of the highest importance, which turned out to be more true than he could have ever imagined.

2 Cavity Radiation

Suppose that we construct a sealed cavity with opaque walls; the exact material used does not matter, so long as they are capable of absorbing at least some radiation of any wavelength. If we now heat the walls up to some fixed temperature T, they will begin to emit thermal radiation of all wavelengths, which will then propagate through the cavity. After a short time, this radiation will encounter another wall, at which point some will be absorbed, while the rest is scattered at random directions back into the cavity. In this manner, radiation will steadily build up in the cavity until it reaches an equilibrium where all wavelengths are absorbed by the walls at the same rate they are emitted. It follows from Kirchhoff's law that this equilibrium will occur when the spectrum of radiation in the cavity is identical to that from a black body of temperature T, independently of the exact nature of the walls.

A nice way of understanding why this must be the case is to imagine boring a small hole in one of the cavity walls. Figure 2 shows the path of a light ray entering through the hole from outside. The light is scattered in random directions by the rough surfaces of the walls, with some of its energy being absorbed in every collision. If the hole is very small compared to the size of the box, it will take a large number of collisions before the incident light gets scattered back out of the hole, so the majority of the light's energy will be absorbed. In the limit of a box infinitely larger than the hole, the fraction of incident light that escapes the cavity will be infinitesimal, meaning that in this limit the hole behaves like a perfect black body. In this same limit the hole should have a negligible effect on the equilibrium distribution of radiation inside the cavity, except for the fact that it allows a small amount to leak out, which to an external observer would be perceived as thermal radiation from the black body that is the hole.

The radiation inside the cavity can be described by its spectral density u_λ, which is defined as

$$u_\lambda = \begin{pmatrix} \text{the energy of radiation contained within} \\ \text{a narrow band of wavelengths centred on} \\ \lambda\text{, per unit volume, per unit wavelength} \end{pmatrix} . \tag{2.1}$$

A nice way of thinking about the spectral density is as the function such that, in a small volume dV, the energy contained between the wavelengths λ and $\lambda + d\lambda$ is given by $u_\lambda dV d\lambda$. The total energy density of radiation can be calculated from the spectral density by integrating it over all wavelengths:

$$u = \int_0^\infty u_\lambda \, d\lambda \, . \tag{2.2}$$

Once it reaches equilibrium, the spectral density of the black body radiation inside the cavity must be uniform over the entire interior volume. If it were not, there would be a net diffusion of radiation from regions of higher density to regions of

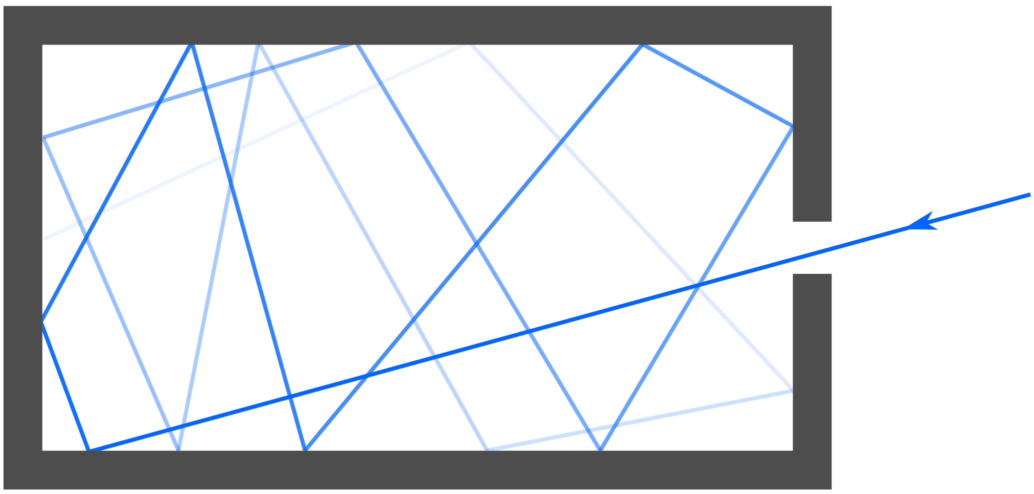

Figure 2. A light ray entering a hole in the wall of a cavity. Each time the ray is scattered by the walls, some fraction of the light's energy is absorbed, illustrated by the fading colour of the ray. Since the hole is small, the ray has to be scattered a great many times before it can re-emerge, and so it is essentially completely absorbed.

lower density, which, by definition, cannot happen in equilibrium. Furthermore, since the spectral density is determined by the local balance between emission and absorption at the walls, it must depend only on temperature, and not on any specifics of the cavity. Thus, we can say that in equilibrium

$$u_\lambda = \psi(\lambda, T)\,, \tag{2.3}$$

where ψ is a universal function of wavelength and temperature referred to as the black body spectral density. It follows therefore that, once it has reached equilibrium, the total energy density of the radiation within the cavity is given by

$$u = \Psi(T)\,, \tag{2.4}$$

where Ψ is a function of temperature only, referred to as the black body energy density, and given by

$$\Psi(T) = \int_0^\infty \psi(\lambda, T)\, dT\,. \tag{2.5}$$

For over forty years after Kirchhoff first discovered his law of thermal radiation, and hence realised the importance of the black body radiation that fills a cavity, physicists became preoccupied with determining the forms of these functions

3 The Stefan–Boltzmann Law

One of the first quantitative observations made about black body radiation was by Josef Stefan, who in 1877 used measurements made by John Tyndall, Pierre Louis Dulong, and Alexis Thérèse Petit to deduce that the energy density of black body radiation is given by

$$\Psi(T) = aT^4\,, \tag{3.1}$$

where T is its absolute temperature, and a is a constant, measured as being approximately $7.57 \times 10^{-16}\,\mathrm{J\,m^{-3}\,K^{-4}}$. Seven years later, Ludwig Boltzmann, a former student of Stefan, discovered a theoretical proof of the law by combining ideas from Maxwell's theory of electromagnetism with the fundamental principles of thermodynamics. In recognition of these contributions (3.1) is now referred to as the Stefan–Boltzmann law.

The centrepiece of Boltzmann's proof was an equation derived from the second law of thermodynamics that related the energy density of black body radiation to the pressure it exerts on the walls of a cavity. To start with, let us consider some arbitrary substance which contained within a volume V and heated to a temperature T. Classical thermodynamics requires that the total energy of the substance U and the pressure P that it exerts on the boundary of its container must obey the partial differential equation

$$\left(\frac{\partial U}{\partial V}\right)_T + P - T\left(\frac{\partial P}{\partial T}\right)_V = 0\,, \tag{3.2}$$

where the notation $(\partial X/\partial Y)_Z$ means the derivative of X with respect to Y when Z is constant. We shall not discuss the derivation of this equation in full detail. Instead, we simply note that, if a material disobeyed (3.2), it would be possible to use it in constructing a device that could transport heat from a cold body to a hotter one without any external input of energy, contradicting the second law of thermodynamics.

Boltzmann supplemented this general equation with two specific facts about black body radiation. Firstly, he noted that, since the total energy density is dependent only on temperature, we must have

$$U = \Psi(T)V \implies \left(\frac{\partial U}{\partial V}\right)_T = \Psi(T)\,. \tag{3.3}$$

In addition, Maxwell's equations of electromagnetism predict that, if electromagnetic radiation is confined within an opaque cavity, it will exert a pressure on the walls of that cavity equal to one third of the radiation's energy density; that is to say

$$P = \frac{\Psi(T)}{3} \implies \left(\frac{\partial P}{\partial T}\right)_V = \Psi'(T)\,, \tag{3.4}$$

where $\Psi'(T)$ denotes the first derivative of $\Psi(T)$. Substituting these facts into (3.2) and rearranging, we find that the energy density must satisfy the ordinary differential equation

$$\Psi'(T) = \frac{4\Psi(T)}{T}\,. \tag{3.5}$$

It is pretty straightforward to simply substitute in the Stefan–Boltzmann law (3.1) and note that it is indeed a solution to this equation; however, if we want to verify that this is the only possible solution, we need to expend a bit more effort. We can solve (3.5) using a method known as the separation of variables. First we divide both sides of the equation by u and then integrate with respect to T to obtain

$$\int \frac{\Psi'(T)}{\Psi(T)}\,dT = \int \frac{4}{T}\,dT\,. \tag{3.6}$$

These integrals are of a standard form and can be evaluated to yield

$$\ln\Psi(T) = 4\ln T + \ln a = \ln\left(aT^4\right)\,, \tag{3.7}$$

where $\ln a$ is introduced as an arbitrary constant of integration. As such, Boltzmann's derivation provided no explanation of why a takes the particular value it does. From here, it is a simple matter of exponentiating both sides of the equation to recover the Stefan–Boltzmann law.

4 Wien's Displacement Law

In order to make any progress on determining the black body spectral density it will be helpful for us to introduce a new concept: a cavity with perfectly white walls. When we say that the walls are perfectly white, we mean that they do not absorb, and hence to not emit, electromagnetic radiation of any wavelength, instead reflecting any light incident upon them in random directions. Since these reflections do not change the light's wavelength, it would be possible to store radiation with any desired distribution of spectral density in such a cavity without it being altered. This is useful because it allows us to consider the thermodynamic properties of radiation with spectra other than that of a black body.

In 1983, Wilhelm Wien had the key insight that, while the spectral density of radiation in a white walled cavity is constant if the walls remain stationary, it will change if the walls are moving. This is because the Doppler effect would cause light incident on a moving wall to change wavelength when it is reflected back into the cavity. Using the detailed description of the Doppler effect provided by Maxwell's theory of electromagnetism, Wien showed that, if you took radiation of spectral density u_λ contained in a volume V_1 and slowly expanded the cavity to a volume V_2, then the resulting spectral density $\tilde{u}_\lambda$ would be given by

$$\tilde{u}_\lambda = \frac{u_\lambda/\kappa}{\kappa^5} \quad \text{where} \quad \kappa = \left(\frac{V_2}{V_1}\right)^{1/3}. \tag{4.1}$$

This result is easiest to understand if we think about a cavity filled with monochromatic light, i.e radiation of a single wavelength. If we expand the cavity uniformly in all directions, then, since volume is proportional to length cubed, the side lengths of the cavity will all increase by a factor of κ. What equation (4.1) tells us is that during this expansion the radiation's wavelength will have increased by that same factor κ, such that its ratio to the side lengths remains unchanged. The factor of κ^5 in the denominator of (4.1) can be broken down as follows. There is a factor of κ^3

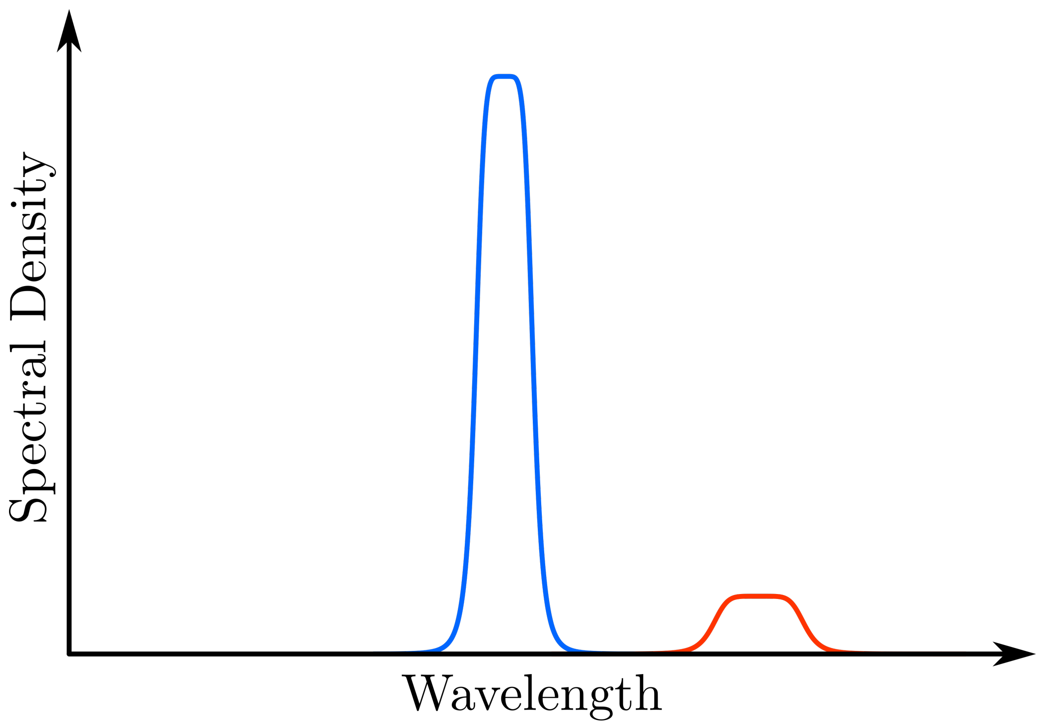

Figure 3. The blue curve shows the spectral density of a reasonably monochromatic sample of radiation. The red curve shows the spectral density of that same radiation after it has been slowly expanded.

due to the radiant energy is now spread over a larger volume, a factor of κ because the shifting wavelengths will have increased the bandwidth of the radiation, meaning its energy is spread over a greater range of wavelengths, and the final factor of κ represents energy lost due to the work performed by the radiation pressure on the moving walls. An example of this change in spectral density is shown in Figure 4.1.

Wien argued that, if you perform this process of slow expansion to a cavity filled with black body radiation, the final result should also be black body radiation, just of a different temperature. If this were not the case, then it would be possible to design a continuous cycle of compressing and expanding the radiation which could transport heat from a cold body to a hotter one without any input of energy, which would violate the second law of thermodynamics. As such, it follows that for initial temperature T_1 and expansion ratio κ there must be a final temperature T_2 such that

$$\psi(\lambda, T_2) = \frac{\psi(\lambda/\kappa, T_1)}{\kappa^5}\,. \tag{4.2}$$

If we want to know how the total energy density of the radiation has changed, we need to integrate the spectral densities over all wavelengths, which yields

$$\Psi(T_2) = \int_0^\infty \psi(\lambda, T_2)\,d\lambda = \int_0^\infty \frac{\psi(\lambda/\kappa, T_1)}{\kappa^5}\,d\lambda = \int_0^\infty \frac{\psi(\lambda/\kappa, T_1)}{\kappa^4}\,d(\lambda/\kappa) = \frac{\Psi(T_1)}{\kappa^4}\,. \tag{4.3}$$

Substituting in the Stefan–Boltzmann law (3.1) allows us to deduce that the initial and final temperatures are related by

$$aT_2^4 = \frac{aT_1^4}{\kappa^4} \implies T_2 = \frac{T_1}{\kappa}\,. \tag{4.4}$$

We can now eliminate the expansion ratio κ from (4.2), to obtain an expression connecting the black body spectral densities at temperatures T and T'

$$\psi(\lambda, T_2) = \frac{T_2^5\psi(T_2\lambda/T_1, T_1)}{T_1^5}\,. \tag{4.5}$$

The useful thing about this equation is that it means we only need to know the spectral density at one specific reference temperature, and then we can automatically deduce what the spectral density must be at any other temperature. An equivalent, but slightly more elegant, way of presenting this result is to say that the black body spectral density's dependence on wavelength and temperature must be expressible in the form

$$\psi(\lambda, T) = T^5\phi(\lambda T)\,, \tag{4.6}$$

where ϕ is some unknown function of a single variable, which can be thought of as the spectral density at unit temperature.

One of the more useful conclusions we can draw from equation (4.6) regards the peak wavelength in a black body's spectrum. For a given temperature, the wavelength $\lambda_{\max}$ at which the spectral density is a maximum will be the solution of the equation

$$\left(\frac{\partial\psi}{\partial\lambda}\right)_T = T^6\phi'(\lambda_{\max}T) = 0\,. \tag{4.7}$$

This implies that the peak wavelength is given by

$$\lambda_{\max} = \frac{b}{T}\,, \tag{4.8}$$

where b is a constant satisfying $\phi'(b) = 0$. The value of this constant can be determined experimentally, giving an approximate value of $2.90 \times 10^{-3}\,\mathrm{m\,K}$.

5 Wien's Formula

By the final decade of the nineteenth century, measurement techniques had advanced to the point that detailed measurements of black body spectra, such as those shown in Figure 4, were possible. This prompted a surge of interest in finding an analytic expression for the black body spectral density $\psi(\lambda, T)$. Over the years, a substantial number of different formulae were proposed, each motivated by its own set of ad hoc assumptions designed to fit a particular set of data. While all are interesting in their own right, the most historically significant was a formula proposed by Wilhelm Wien in 1896.

Wien arrived at his expression by imagining a hypothetical gas that was capable of absorbing some light at all wavelengths. If we had a large enough quantity of this gas, then any light travelling through it would be completely absorbed before it re-emerged, so the gas would behave like a black body. As such, all Wien needed to do in order to derive the spectrum of black body radiation was to develop a model of how the gas would emit radiation.

By that point in time it was fairly well accepted (at least among those scientists who actually believed in atoms) that, within a gas, the number of molecules moving with speed v was given by the Maxwell–Boltzmann distribution law

$$n(v) \propto v^2 e^{-3v^2/2v_{\mathrm{rms}}^2}\,, \tag{5.1}$$

where v_{rms} is the root mean square speed of the molecules. Moreover, it was known that v_{rms}^2 was proportional to the absolute temperature of the gas.

Alongside these results, Wien made the purely speculative hypothesis that each molecule of gas would radiate at a single wavelength with a specific intensity, both of which depended only on its velocity. It is important to note that Wien was not trying to claim that all gases, or indeed any real gas, behaved in this manner, but merely that such a gas was physically possible, and that since all black bodies emit the same radiation, they must radiate with the same spectrum as this hypothetical gas. From this hypothesis and (5.1), it follows that the black body spectral density must take the general form

$$\psi(\lambda, T) = F(\lambda) e^{-f(\lambda)/T}\,, \tag{5.2}$$

for some functions F and f whose specific expressions depend on the exact nature of the relationship between a molecule's velocity and the radiation it emits. Wien then

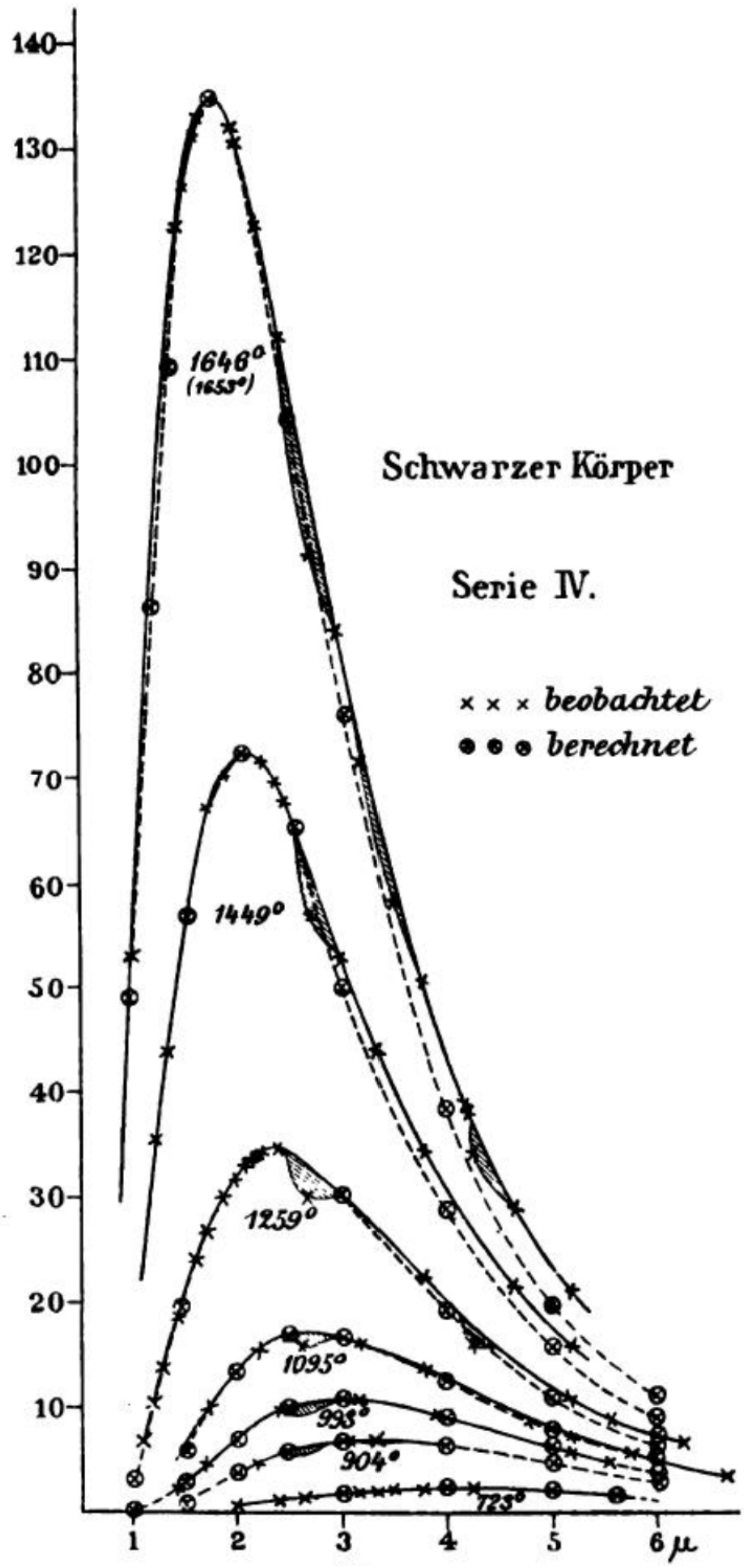

Figure 4. Experimental measurements of black body spectra from the end of the nineteenth century. The crosses joined by solid lines indicate observed data points, while the circles joined by dashed lines represent the best fit of Wien's proposed formula to the data.

Source: E. Lummer and E. Pringsheim, Verhandlungen der Deutschen Physikalischen Gesellschaft 1 (1899), 215-35, on 217 noted that the only possible function of this form consistent with the displacement law he derived from thermodynamic considerations is

$$\psi(\lambda, T) = \frac{C_1 e^{-C_2/\lambda T}}{\lambda^5}\,, \tag{5.3}$$

where C_1 and C_2 are constants. This corresponds to setting

$$\phi(\lambda T) = \frac{C_1 e^{-C_2/\lambda T}}{(\lambda T)^5} \tag{5.4}$$

in (4.6). With a little bit of work, it can be shown that, if this formula holds across all wavelengths, the Stefan–Boltzmann and Wien constants a and b are related to the constants C_1 and C_2 by

$$a = \frac{6C_1}{C_2^4} \quad \text{and} \quad b = \frac{C_2}{5}\,. \tag{5.5}$$

For several years, it was widely believed that Wien had found the correct description of black body radiation. As it happened, one of the strongest supporters of this position was Max Planck, who had become convinced after he re-obtained the result from a simple hypothesis about the entropy of an electromagnetic field. However, by the end of the century was becoming clear that, while Wien's approximation agreed with experiment for short wavelengths and low temperatures, it under-predicts the spectral density at long wavelengths and high temperatures. On a close inspection of Figure 4, we can see that the dashed lines representing Wien's formula do indeed fall beneath the observations at higher temperatures.

6 The Rayleigh–Jeans Law

In 1900, John William Strutt, 3rd Baron Rayleigh attempted to derive the black body spectral density using the principle of equipartition developed by James Clerk Maxwell and Ludwig Boltzmann. This principle states that, when a system is in thermal equilibrium, the average energy contained within each of its microscopic degrees of freedom is proportional to its temperature. For example, in a gas the microscopic degrees of freedom are the velocity components of the individual gas molecules, so equipartition ensures that the average molecular kinetic energy is proportional to the temperature of the gas.

If equipartition applies to an electromagnetic field inside a cavity, and as far as Rayleigh knew there was no reason why it should not, then the spectral density of black body radiation would have be expressible in the form

$$\psi(\lambda, T) = F(\lambda)T\,, \tag{6.1}$$

where F is some function proportional to the number of microscopic degrees of freedom per unit volume, per unit wavelength interval. The only expression of this form consistent with Wien's displacement law (4.6) is

$$\psi(\lambda, T) \propto \frac{T}{\lambda^4}\,. \tag{6.2}$$

A more complete calculation proceeds as follows. Together with James Jeans, Rayleigh realised that the microscopic degrees of freedom in a radiation field were directly connected to the standing waves that could form inside a cavity. In particular, each standing wave possesses four degrees of freedom: a displacement and velocity for each of the two possible polarisations of the electromagnetic wave. As such, he concluded that the spectral density of black body radiation could be expressed as

$$\psi(\lambda, T) = 4g(\lambda)\bar{\epsilon}_T \tag{6.3}$$

where $\bar{\epsilon}_T$ is the average energy per degree of freedom at temperature T, and $g(\lambda)$ is a function representing the number of standing waves per unit volume at wavelength λ.

It is easiest to determine the functional form of $g(\lambda)$ by considering the standing waves inside a cube of side length L. Rayleigh showed that the wavelengths of these standing waves must be given by

$$\lambda = \frac{2L}{\sqrt{n^2 + m^2 + l^2}}\,, \tag{6.4}$$

where n, m, and l are all positive integers. It follows The number of standing waves with wavelengths greater than λ will be equal to the number of points with integer coordinates within the positive octant of a sphere with radius

$$R_\lambda = \frac{2L}{\lambda}\,. \tag{6.5}$$

The volume of coordinate space per integer point is just equal to one, because each integer point sits in the centre of a cube with unit side length. Thus, the number of standing waves with wavelength greater than λ is equal to the volume of the octant

$$N_\lambda = \frac{\pi R_\lambda^3}{6} = \frac{4\pi L^3}{3\lambda^3}\,. \tag{6.6}$$

The number of standing waves per unit volume at a specific wavelength is then given by

$$g(\lambda) = -\frac{1}{L^3}\frac{dN_\lambda}{d\lambda} = \frac{4\pi}{\lambda^4}\,. \tag{6.7}$$

The average energy per degree of freedom is usually expressed as

$$\bar{\epsilon}_T = \frac{k_B T}{2}\,, \tag{6.8}$$

where k_B is known as Boltzmann's constant. An important thing to note here is that Boltzmann's constant can be measured independently of anything to do with thermal radiation. For example, in 1905 Albert Einstein proposed a method of determining its value by observing Brownian motion. As such, k_B is not an adjustable free parameter of our model in the same way that Wien's constants C_1 and C_2 were.

Putting this all together we find that, according to the principle of equipartition, the black body spectral density should be given by the Rayleigh–Jeans law

$$\psi(\lambda, T) = \frac{8\pi k_B T}{\lambda^4}\,. \tag{6.9}$$

Experiments confirmed this result to be accurate for long wavelengths, which were the problem area in Wien's formula, although it fails disastrously at shorter wavelengths, where the spectral density apparently diverges to infinity. Initially, Rayleigh was not too perturbed by this fact and simply assumed that there was some more complicated effect he was not aware of which prevented the shorter wavelengths from establishing equipartition. At this point in time, apparent violations of equipartition were already known to occur in the low temperature heat capacities of solids and gases, so Rayleigh's position was not particularly controversial. However, with the advantage of hindsight we can recognise that this so called ultraviolet catastrophe and the other observed violations of equipartition were the first signs that there was something deeply wrong with classical physics.

7 Planck's Law

In 1900, once it had been demonstrated beyond any doubt that the correct description of the black body radiation at long wavelengths was Rayleigh's instead of Wien's, the task facing theoretical physicists was to find a general law applicable at all wavelengths and temperatures. Within days of hearing the experimental results, Max Planck proposed that the spectral density might take the form

$$\psi(\lambda, T) = \frac{C_1/\lambda^5}{e^{C_2/\lambda T} - 1}\,, \tag{7.1}$$

for some values of the constants C_1 and C_2. The motivation behind this expression was simply that it provides a smooth interpolation between the two limiting formulae. When λ is small, $e^{C_2/\lambda T}$ will be large, and thus the -1 in the denominator will be negligible, so we can approximate

$$\frac{C_1/\lambda^5}{e^{C_2/\lambda T} - 1} \approx \frac{C_1/\lambda^5}{e^{C_2/\lambda T}} = \frac{C_1 e^{-C_2/\lambda T}}{\lambda^5}\,, \tag{7.2}$$

reproducing Wien's formula. On the other hand, when λ is large we can use the Taylor series approximation $e^x \approx 1 + x$ to say that

$$\frac{C_1/\lambda^5}{e^{C_2/\lambda T} - 1} \approx \frac{C_1/\lambda^5}{1 + C_2/\lambda T - 1} = \frac{C_1 T}{C_2 \lambda^4}\,, \tag{7.3}$$

which gives us the Rayleigh–Jeans law, provided $C_1/C_2 = 8\pi k_B$. The relationship between Planck's law and its two limits cases is shown graphically in Figure 5.

Just as for Wien's formula, it is possible to find relationships between the constants C_1 and C_2 in (7.1) and the Stefan–Boltzmann and Wien constants a and b. The calculations are rather involved so we will not go through them here, but the final results are

$$a = \frac{\pi^4}{15}\frac{C_1}{C_2^4} \quad \text{and} \quad b = 4.965114231744276303\cdots \times C_2\,. \tag{7.4}$$

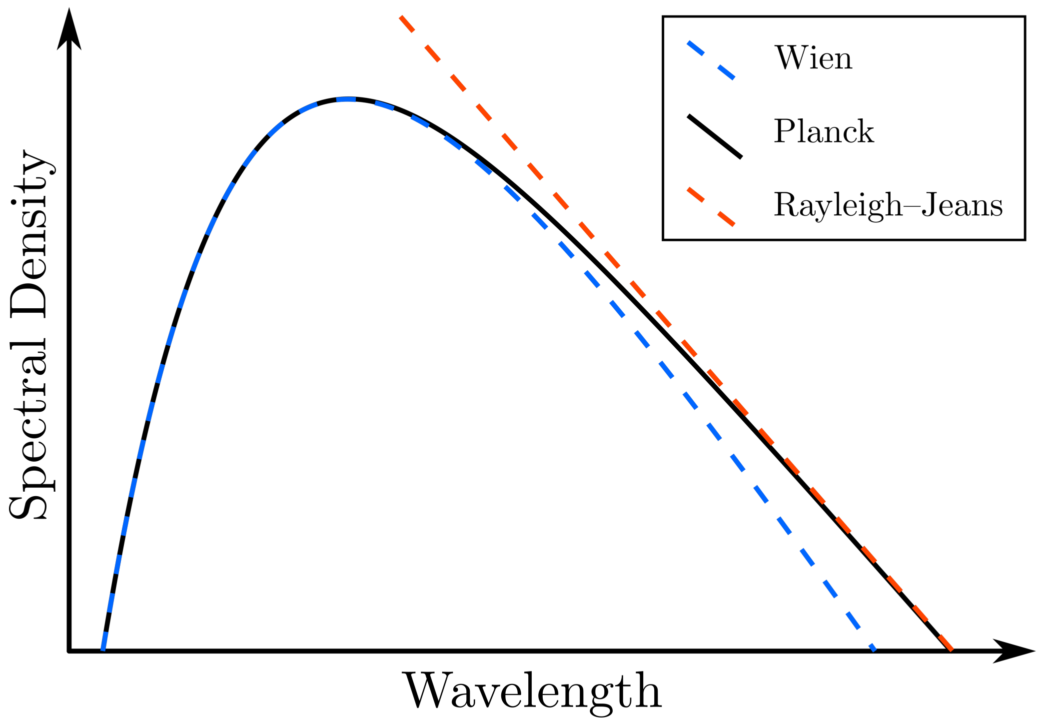

Figure 5. A plot of spectral density against wavelength at a specific temperature according to Planck's law, Wien's formula, and the Rayleigh–Jeans law. To aid with visibility both axes are plotted using logarithmic scales.

8 The Quantum Hypothesis

After it had been confirmed that his new formula was a good fit to experimental data, Planck devoted himself to finding derivation of the law from fundamental physical principles. He started by considering a specific model of a black body: a cavity containing a large number of harmonic oscillators with different natural frequencies. The idea being that each oscillator would resonate with electromagnetic radiation matching its natural frequency, and so with enough different oscillators they would be capable of absorbing all frequencies of radiation. Within this model Planck showed that the black body spectral density must be given by

$$\psi(\lambda, T) = \frac{8\pi\mathcal{E}(c/\lambda, T)}{\lambda^4}\,, \tag{8.1}$$

where c is the speed of light in vacuum, and $\mathcal{E}(\nu, T)$ is the average energy of a harmonic oscillator with natural frequency ν and temperature T. Since a harmonic oscillator has two degrees of freedom (one displacement and one velocity), we could apply the principle of equipartition to deduce that

$$\mathcal{E}(\nu, T) = 2\bar{\epsilon}_T = k_B T\,, \tag{8.2}$$

reproducing the Rayleigh–Jeans law. In order to replicate his formula, Planck had to make a radical new assumption. He supposed that, instead of being able to vary continuously, the energy of a harmonic oscillator was quantised to only take certain discrete values. Moreover he proposed that there was a universal constant h, now called Planck's constant, such that these discrete energy levels were integer multiples of $h\nu$.

In order to calculate the average energy of an oscillator, Planck made use of a result from Boltzmann that, when a system is in thermal equilibrium at temperature T, the probability of it being found in a particular state with energy E is proportional to e^{-E/k_BT}. Applying this idea to Planck's quantised oscillators, he found that the probability of having an energy $E = nh\nu$ is given by

$$p(E = nh\nu) = \left(1 - e^{-h\nu/k_BT}\right) e^{-nh\nu/k_BT}\,, \tag{8.3}$$

where the factor in the brackets is chosen so that the sum of all probabilities equals one. It then follows that the average energy of the oscillator is given by

$$\mathcal{E}(\nu, T) = h\nu p(E = h\nu) + 2h\nu p(E = 2h\nu) + 3h\nu p(E = 3h\nu) + \ldots\,. \tag{8.4}$$

Evaluating this infinite series yields the final result

$$\mathcal{E}(\nu, T) = \frac{h\nu}{e^{h\nu/k_BT} - 1}\,, \tag{8.5}$$

which leads to a black body spectral density of the form

$$\psi(\lambda, T) = \frac{8\pi hc/\lambda^5}{e^{hc/k_B\lambda T} - 1}\,. \tag{8.6}$$