A Kinetic Theory Derivation of Planck's Law for Black Body Radiation

$$\epsilon = h\nu$$

$$\frac{dE}{dt} = -\frac{q^2 a^2}{6\pi\varepsilon_0 c^3}$$

$$\frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT}-1}$$

$$PV = NkT$$

$$\bar{E}_\nu = \frac{c^3\,\rho\nu}{8\pi\nu^2}$$

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1   Black Body Radiation

Imagine a large cavity with reflective walls containing a radiation field with a spatially uniform spectral density ρ_ν. Inside the cavity are a large number of electromagnetic resonators with a variety of different resonant frequencies, each of which consists of a small charged particle connected to a fixed point in space by a harmonic potential. These resonators can absorb and emit radiation at their specific resonant frequency. In addition, let us suppose that the cavity is filled with a diffuse, neutral gas. The molecules of this gas do not interact directly with the electromagnetic field, but can collide and exchange energy with the resonators. Since energy can be transferred between all the different degrees of freedom in this system, if we wait long enough it should settle into thermal equilibrium at some temperature T. Once this has happened, the spectral density will be, by definition, that of black body radiation at temperature T.

2   Spectral Density

The state of the radiation field inside a cavity can be characterised by its spectral density ρ_ν. This is a measure of the radiation energy density per unit frequency interval. That is to say

$$\rho_\nu d\nu = \left(\begin{array}{c} \text{energy density of the radiation} \\ \text{contained within a frequency} \\ \text{band of width } d\nu \text{ centred on } \nu \end{array} \right). \tag{2.1}$$

In order to meaningfully determine the frequency of a wave, we would have to observe it for several periods of its oscillation. So when we discuss the energy contained within a frequency band, we are implicitly assuming that this energy has been somehow averaged over time scales longer than the characteristic period of the radiation.

Let us consider a single component of the electric field $X(t)$ at a particular point inside the cavity, and at the time t. Over some time interval between $t = 0$ and $t = \tau$ we can represent $X(t)$ as the Fourier series

$$X(t) = \sum_{n=1}^{\infty} A_n \sin \left(\frac{2n\pi t}{\tau} - \phi_n \right), \tag{2.2}$$

for some set of amplitudes A_n and phases ϕ_n. If we imagine performing this same expansion for a number of different intervals, each of length τ but with randomly chosen starting times, then we would obtain a range of different values for the A_n and ϕ_n, characterised by some probability distribution.

Since the frequencies of the oscillations in the Fourier expansion increase in increments of $1/\tau$, we can associate the nth term with the frequency band

$$\nu = \frac{n}{\tau}, \quad d\nu = \frac{1}{\tau}. \tag{2.3}$$

Since there are three components of the electric field, and three components of the magnetic field, each of which will carry on average the same energy, the single component we are considering here will represent one sixth of the spectral density in this frequency band. The energy density of a single component of the electric field is given by $\varepsilon_0 X^2/2$, and the average value of a sinusoid squared is half its amplitude, so it follows that

$$\frac{\rho_{n/\tau}}{6\tau} = \frac{\varepsilon_0 \overline{A_n^2}}{4} \implies \overline{A_n^2} = \frac{2\rho_{n/\tau}}{3\varepsilon_0 \tau} \,, \tag{2.4}$$

where the bar indicates the averaging over the probability distribution of different values for the amplitude.

3 Planck's Condition for Radiative Equilibrium

Let us consider a single resonator of natural frequency ν inside the cavity. If we ignore its interactions with the electromagnetic field and the free gas molecules, then its motion will be described by the simple differential equation

$$m\frac{d^2x}{dt^2} + 4\pi^2 m\nu^2 x = 0 \,, \tag{3.1}$$

where m is the mass of the charged particle, and x is its displacement from its equilibrium position. The total energy of this oscillator is given by the sum of its potential and kinetic energies

$$E_\nu = 2\pi^2 m\nu^2 \, x^2 + \frac{m}{2}\left(\frac{dx}{dt}\right)^2 . \tag{3.2}$$

The solution to this equation is well known to take the form of a sinusoidal oscillation

$$x(t) = \sqrt{\frac{E_\nu}{2\pi^2 m\nu^2}} \sin(2\pi\nu t - \phi) \,. \tag{3.3}$$

These free oscillations are not particularly useful to us on their own, since we are really concerned about the interactions between the resonators and everything else inside the cavity. There are three key effects in play here. Firstly, at random time intervals a gas molecule will collide with a resonator, transferring some amount of energy and momentum. Secondly, as it oscillates the resonator will give off energy in the form of electromagnetic radiation. Finally, the electromagnetic field in the cavity will exert a driving force on the charged particle which could either transfer energy to or from the oscillator.

Collisions between a gas molecule and a resonator only last for a very short time. Moreover, if the gas in the cavity is sufficiently diffuse, the typical time between those collisions will be very long. This difference in time scales allows us to break down the behaviour of the resonators into long periods where they interact only electromagnetically, interspersed with short periods of collision with gas molecules during which the electromagnetic interactions are negligible. For now, we shall focus

on the former, investigating how energy is transferred between the resonators and the radiation field inside the cavity.

A complete description of the interactions of an oscillating charge with the electromagnetic fields is rather complicated. However, if we restrict our attention to weakly charged particles, then we can make some approximations to simplify matters significantly. Provided we wait long enough, the electromagnetic fields inside the cavity will reach thermal equilibrium no matter how small the charges of the resonators are. As such, we are free to make this approximation without compromising the accuracy of our final result.

To begin with, let us consider the case when the radiation field is zero, and so there are no external electromagnetic forces acting on the resonator. As the charged particle oscillates back and forth, it will give off electromagnetic radiation at a rate described by Larmor's formula

$$\frac{dE_\nu}{dt} = -\frac{q^2 a^2}{6\pi\varepsilon_0 c^3} \,, \tag{3.4}$$

where q is the charge of the charged particle and a is its acceleration. Let us suppose that the time between two collisions with gas molecules is τ. The total energy lost by the resonator during this period will be given by

$$\Delta E_\nu = -\frac{q^2 \langle a^2 \rangle \tau}{6\pi\varepsilon_0 c^3} \,, \tag{3.5}$$

where the notation $\langle \ldots \rangle$ implies a time average. Since we are assuming that q is very small, the total energy radiated by the resonator will be a very small fraction of its total energy. This means that, to a very good approximation, we can neglect the radiative corrections to the motion of the charged particle. In other words, we can use (3.3) to evaluate the time averaged acceleration, giving

$$\langle a^2 \rangle = \frac{4\pi^2 \nu^2 E_\nu}{m} \implies \Delta E_\nu = -\frac{2\pi q^2 \nu^2 E_\nu \tau}{3\varepsilon_0 m c^3} \,. \tag{3.6}$$

If the radiation field is non-zero, then there will also be a transfer of energy to the resonator as a result of work being done by the driving force acting on the charged particle. If we let $X(t)$ represent the component of the electric field aligned with the resonator at time t, then the driving force will be given by $qX(t)$, which we can add into equation (3.1) to obtain the driven oscillator equation

$$m\frac{d^2 x}{dt^2} + 4\pi^2 m\nu^2 x = qX(t) \,. \tag{3.7}$$

In order to find the energy transferred to the resonator between collisions we only need to consider the interval between $t = 0$ and $t = \tau$. As such, we can take a Fourier series decomposition of $X(t)$ in the manner of (2.2) to obtain the equation

$$m\frac{d^2 x}{dt^2} + 4\pi^2 m\nu^2 x = \sum_{n=1}^{\infty} qA_n \sin\left(\frac{2n\pi t}{\tau} - \phi_n\right) \,. \tag{3.8}$$

For simplicity, we will assume that τ is an integer multiple of $1/\nu$, the natural period of the resonator. This will introduce errors on the order of $1/\nu\tau$, which is

very small, so our conclusions should still be applicable to the general case. Under this assumption, the only term in the Fourier expansion which provides a net transfer of energy to the resonator is $n = \nu\tau$, that is to say the term whose frequency exactly matches that of the resonator. Thus, we can drop the other terms and consider the equation

$$m\frac{d^2x}{dt^2} + 4\pi^2 m\nu^2 x = qA_{\nu\tau}\sin(2\pi\nu t - \phi_{\nu\tau})\,. \tag{3.9}$$

This is the equation for a harmonic oscillator being driven at its resonant frequency, and has the solution

$$x(t) = \sqrt{\frac{E_\nu}{2\pi^2 m\nu^2}}\sin(2\pi\nu t - \phi)$$
$$- \frac{qA_{\nu\tau}}{4\pi\nu m}\left(t\cos(2\pi\nu t - \phi_{\nu\tau}) - \frac{\cos\phi_{\nu\tau}}{2\pi\nu}\sin(2\pi\nu t)\right)\,, \tag{3.10}$$

where the constant E_ν is energy of the resonator at $t = 0$. We can use (3.2) to determine the energy at $t = \tau$, and hence the energy transferred to the resonator

$$\Delta E_\nu = \frac{q^2 A_{\nu\tau}^2 \tau^2}{8m} + \sqrt{\frac{q^2 E_\nu A_{\nu\tau}^2 \tau^2}{2m}}\sin(\phi - \phi_{\nu\tau})\,. \tag{3.11}$$

Combining this with our expression (3.6) for the energy radiated by the resonator, which will be unchanged by the external driving field to leading order in the small charge q, we can say that the total energy transferred to the resonator between two collisions is

$$\Delta E_\nu = \frac{q^2 A_{\nu\tau}^2 \tau^2}{8m} + \sqrt{\frac{q^2 E_\nu A_{\nu\tau}^2 \tau^2}{2m}}\sin(\phi - \phi_{\nu\tau}) - \frac{2\pi q^2 \nu^2 E_\nu \tau}{3\varepsilon_0 mc^3}\,. \tag{3.12}$$

The parameters $A_{\nu\tau}$, E_ν, ϕ, and ϕ_ν will all vary in an essentially random manner between different intervals of time. As such, what we are really interested in is the average value of this expression, since this will tell us the net flow of energy from the radiation field into the resonator over long time scales. The phase difference $\phi - \phi_{\nu\tau}$ will fluctuate randomly over all possible values so the sine term will average to zero and the average value of $A_{\nu\tau}^2$ can be related to the spectral density by (2.4), allowing us to say that

$$\overline{\Delta E_\nu} = \frac{q^2 \rho_\nu \tau}{12m\varepsilon_0} - \frac{2\pi q^2 \nu^2 \bar{E}_\nu \tau}{3\varepsilon_0 mc^3} = \frac{2\pi q^2 \nu^2}{3\varepsilon_0 mc^3}\left(\frac{\rho_\nu c^3}{8\pi\nu^2} - \bar{E}_\nu\right)\,. \tag{3.13}$$

If the resonators are in thermal equilibrium with the radiation field, then there should be no net transfer of energy between them. In other words, the expression above must be equal to zero, which implies that the spectral density and average resonator energy are related by

$$\bar{E}_\nu = \frac{\rho_\nu c^3}{8\pi\nu^2}\,. \tag{3.14}$$

This is Planck's condition for radiative equilibrium. All we need now to determine the temperature dependence of the black body spectral density is to know the how the average energy of a resonator changes with temperature.

4 The Maxwell–Boltzmann Distribution

We shall now turn our attention to the thermal equilibrium of the gas molecules within the cavity. The state of the gas is most efficiently characterised by its distribution function $f(\boldsymbol{p})$, which is defined such that

$$f(\boldsymbol{p})\,d^3\boldsymbol{p} = \left(\begin{array}{c} \text{number density of gas molecules} \\ \text{with their momenta in a small} \\ \text{region } d^3\boldsymbol{p} \text{ centred on } \boldsymbol{p} \end{array} \right). \qquad (4.1)$$

For simplicity, we shall suppose that the gas is ideal, meaning that there are no long range interactions between the molecules, and thus they can only exchange energy and momentum via instantaneous collisions. We can define the collision rate $\Gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \to \boldsymbol{p}_3, \boldsymbol{p}_4)$ as

$$\Gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \to \boldsymbol{p}_3, \boldsymbol{p}_4)\,d^3\boldsymbol{p}_1\,d^3\boldsymbol{p}_2\,d^3\boldsymbol{p}_3\,d^3\boldsymbol{p}_4 = \left(\begin{array}{c} \text{rate of collisions per unit} \\ \text{volume between molecules} \\ \text{with initial momenta in the} \\ \text{small regions } d^3\boldsymbol{p}_1, d^3\boldsymbol{p}_2 \text{ and} \\ \text{final momenta in the small} \\ \text{regions } d^3\boldsymbol{p}_3, d^3\boldsymbol{p}_4 \end{array} \right). \qquad (4.2)$$

The collision rate depends on the value of the distribution function; if there are more molecules of a particular momentum, then naturally collisions between molecules with that momentum will occur more frequently. As such, we can express it as

$$\Gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \to \boldsymbol{p}_3, \boldsymbol{p}_4) = f(\boldsymbol{p}_1)f(\boldsymbol{p}_2)\gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \to \boldsymbol{p}_3, \boldsymbol{p}_4), \qquad (4.3)$$

where the normalised collision rate $\gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \to \boldsymbol{p}_3, \boldsymbol{p}_4)$ depends only the identity of the gas molecules in question. For example, if the molecules are hard spheres with mass m and radius R, then we will find that

$$\gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \to \boldsymbol{p}_3, \boldsymbol{p}_4) = \frac{16R^2}{m}\delta^{(3)}(\boldsymbol{p}_1 + \boldsymbol{p}_2 - \boldsymbol{p}_3 - \boldsymbol{p}_4)\delta(|\boldsymbol{p}_1 - \boldsymbol{p}_2|^2 - |\boldsymbol{p}_3 - \boldsymbol{p}_4|^2), \qquad (4.4)$$

The Dirac delta functions in this expression ensure that the collision rate is only non-zero if the total momentum and kinetic energy are the same in the initial and final states. Since energy and momentum are always conserved, this fact will hold true independently of the details of the molecular interactions in our specific gas.

Another important property of (4.4) is its symmetry under an interchange of the initial and final states. This is also a fairly general property of collision rates, and follows from two fundamental facts. Firstly, the underlying physics of the molecular collisions is invariant under time reversal, which means that if we were to watch a video recording of a collision we would have no way of telling if it was playing in reverse or not. Since momenta would have their directions inverted by a time reversal, this implies that we must have

$$\gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \to \boldsymbol{p}_3, \boldsymbol{p}_4) = \gamma(-\boldsymbol{p}_3, -\boldsymbol{p}_4 \to -\boldsymbol{p}_1, -\boldsymbol{p}_2). \qquad (4.5)$$

In addition, the collisions are invariant under parity transformations, meaning that if we were to watch a collision occur we would have to way of telling if we were seeing a mirror image or not. This tells us that

$$\gamma(-\boldsymbol{p}_3, -\boldsymbol{p}_4 \to -\boldsymbol{p}_1, -\boldsymbol{p}_2) \to \gamma(\boldsymbol{p}_3, \boldsymbol{p}_4 \to \boldsymbol{p}_1, \boldsymbol{p}_2), \qquad (4.6)$$

and hence that the normalised collision rate is invariant under the interchange of the initial and final states.

The principle of detailed balance states that, when a system is in thermal equilibrium, every process within that system occurs at the same rate as its reverse process. Applied to an ideal gas this means that, at equilibrium, we must have

$$\Gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \rightarrow \boldsymbol{p}_3, \boldsymbol{p}_4) = \Gamma(\boldsymbol{p}_3, \boldsymbol{p}_4 \rightarrow \boldsymbol{p}_1, \boldsymbol{p}_2) \,, \tag{4.7}$$

for all values of the $\boldsymbol{p}_1, \boldsymbol{p}_2, \boldsymbol{p}_3, \boldsymbol{p}_4$. Expanding this expression out in terms of the normalised collision rate and invoking the symmetry between initial and final states lets us rewrite this condition as

$$f(\boldsymbol{p}_1) f(\boldsymbol{p}_2) \gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \rightarrow \boldsymbol{p}_3, \boldsymbol{p}_4) = f(\boldsymbol{p}_3) f(\boldsymbol{p}_4) \gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \rightarrow \boldsymbol{p}_3, \boldsymbol{p}_4) \,. \tag{4.8}$$

For collisions which do not conserve energy and momentum this constraint is trivially satisfied since $\gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \rightarrow \boldsymbol{p}_3, \boldsymbol{p}_4)$ will be equal to zero, meaning no collisions occur in either direction. However, when the conservation laws are obeyed, $\gamma(\boldsymbol{p}_1, \boldsymbol{p}_2 \rightarrow \boldsymbol{p}_3, \boldsymbol{p}_4)$ will be non-zero and we must have

$$f(\boldsymbol{p}_1) f(\boldsymbol{p}_2) = f(\boldsymbol{p}_3) f(\boldsymbol{p}_4) \,. \tag{4.9}$$

Taking logarithms of both sides, we can thus conclude that, for any momenta where a collision is possible, it must be the case that

$$\ln f(\boldsymbol{p}_1) + \ln f(\boldsymbol{p}_2) = \ln f(\boldsymbol{p}_3) + \ln f(\boldsymbol{p}_4) \,. \tag{4.10}$$

In other words, the logarithm of the distribution function is an additive conserved quantity.

There are only three independent quantities that are conserved in all collisions: the number of molecules, energy, and momentum. As such, (4.10) can only hold if the logarithm of the distribution is a linear combination of these three quantities. Assuming that the gas is cold enough that relativistic contributions to the kinetic energy are negligible, we can therefore say that

$$-\ln f(\boldsymbol{p}) = \alpha + \frac{\beta \boldsymbol{p}^2}{2} + \boldsymbol{\gamma} \cdot \boldsymbol{p} \,, \tag{4.11}$$

where the α, β, and $\boldsymbol{\gamma}$ are constant coefficients. The minus sign in front of the logarithm is purely conventional, and is included so that the coefficients have a more natural physical interpretation.

If the cavity containing the gas is at rest, then the average momentum of the gas molecules will be zero, and so we can conclude that $\boldsymbol{\gamma} = 0$. Furthermore, we can determine the value of α by noting that when we integrate the distribution function over all momenta we must obtain

$$\int f(\boldsymbol{p}) \, d^3\boldsymbol{p} = \frac{N}{V} \,, \tag{4.12}$$

where N is the total number of gas molecules and V is the volume of the cavity. Putting this all together, we can deduce that the distribution function of the gas has only one free parameter, β, and is given by

$$f(\boldsymbol{p}) = \frac{N}{V} \left(\frac{\beta}{2\pi m} \right)^{3/2} e^{-\beta \boldsymbol{p}^2 / 2m} \,. \tag{4.13}$$

We can use the distribution function to calculate macroscopic properties of the gas. For example, let us suppose that we want to know the pressure P exerted by the gas on the walls of its container. In this case, we can invoke the virial theorem of classical mechanics to deduce that

$$P = \int \frac{\boldsymbol{p}^2}{3m} f(\boldsymbol{p}) \, d^3\boldsymbol{p} = \frac{N}{V\beta} \, . \tag{4.14}$$

By comparing this to the ideal gas law

$$PV = NkT \, , \tag{4.15}$$

where k is Boltzmann's constant and T is the absolute temperature of the gas, we can deduce that the parameter β is given by

$$\beta = \frac{1}{kT} \, . \tag{4.16}$$

Substituting this result back into (4.13) yields the well known Maxwell–Boltzmann distribution

$$f(\boldsymbol{p}) = \frac{N}{V} \frac{e^{-\boldsymbol{p}^2/2mkT}}{(2\pi mkT)^{3/2}} \, . \tag{4.17}$$

5 Kinetic Equilibrium

We now wish to consider the thermal equilibrium between the gas molecules and the resonators. We can describe the resonators in a very similar way to the gas molecules by introducing the distribution function $p_\nu(E)$, defined by

$$p_\nu(E) \, dE = \begin{pmatrix} \text{proportion of the resonators with natural} \\ \text{frequency } \nu \text{ which have energies in a} \\ \text{small range } dE \text{ centred on } E \end{pmatrix} . \tag{5.1}$$

Just as we did for the gas particles, we can define a collision rate between gas molecules and resonators as

$$\Gamma_\nu(\boldsymbol{p}_1, E_1 \to \boldsymbol{p}_2, E_2) \, d^3\boldsymbol{p}_1 \, dE_1 \, d^3\boldsymbol{p}_2 \, dE_2 = \begin{pmatrix} \text{rate of collisions per} \\ \text{resonator where the gas} \\ \text{molecule's initial and final} \\ \text{momenta are in the regions} \\ d^3\boldsymbol{p}_1 \text{ and } d^3\boldsymbol{p}_2 \text{ and the} \\ \text{resonators initial and final} \\ \text{energies are in } dE_1 \text{ and} \\ dE_2 \end{pmatrix} . \tag{5.2}$$

We can also define a normalised collision rate which depends only on the nature of the interactions between the resonators and gas molecules

$$\Gamma_\nu(\boldsymbol{p}_1, E_1 \to \boldsymbol{p}_2, E_2) = f(\boldsymbol{p}_1) p_\nu(E_1) \gamma_\nu(\boldsymbol{p}_1, E_1 \to \boldsymbol{p}_2, E_2) \, . \tag{5.3}$$

Following essentially the same argument which we used to obtain (4.10), we can argue that the normalised collision rate will be symmetric under the interchange of initial and final states, and thus that the principle of detailed balance implies that

$$f(\boldsymbol{p}_1) p_\nu(E_1) = f(\boldsymbol{p}_2) p_\nu(E_2) \, . \tag{5.4}$$

Substituting in the Maxwell–Boltzmann distribution for $f(\boldsymbol{p})$, and applying conservation of energy

$$E_1 + \frac{\boldsymbol{p}_1^2}{2m} = E_2 + \frac{\boldsymbol{p}_2^2}{2m}\,, \tag{5.5}$$

we can deduce that for any two allowed values of the resonator energy

$$p_\nu(E_1) = p_\nu(E_2)e^{(E_2 - E_1)/kT}\,.$$

If we treat the resonators as classical objects capable of having any energy within a continuous spectrum, we would then conclude that

$$p_\nu(E) = \frac{1}{kT}e^{-E/kT} \implies \bar{E}_\nu = \int_0^\infty E p_\nu(E)\, dE = kT\,. \tag{5.6}$$

Substituting this result into Planck's condition for radiative equilibrium yields the famous, ultravioletly divergent Rayleigh–Jeans law

$$\bar{E}_\nu = \frac{\rho_\nu c^3}{8\pi\nu^2} \implies \rho_\nu = \frac{8\pi\nu^2 kT}{c^3}\,. \tag{5.7}$$

The way to avoid this is to assert that the resonators cannot have any energy they like, and that their energies are instead quantised to certain discrete levels. If we suppose that a resonator can only possess integer multiples of some value ϵ, we can instead write the distribution function as

$$p_\nu(E) = \left(1 - e^{-\epsilon/kT}\right)\sum_{n=0}^\infty e^{-n\epsilon/kT}\delta(E - n\epsilon)\,. \tag{5.8}$$

In this case, the average energy can be calculated as

$$\bar{E}_\nu = \int_0^\infty E p_\nu(E)\, dE = \left(1 - e^{-\epsilon/kT}\right)\sum_{n=0}^\infty n\epsilon e^{-n\epsilon/kT}\,. \tag{5.9}$$

The infinite sum can be evaluated to yield

$$\bar{E}_\nu = \frac{\epsilon}{e^{\epsilon/kT} - 1} \implies \rho_\nu = \frac{8\pi\epsilon\nu^2}{c^3\left(e^{\epsilon/kT} - 1\right)}\,. \tag{5.10}$$

Planck found that in order to match the observed properties of black body spectra, the energy ϵ needed to be proportional to the frequency of the resonator. Thus, he concluded that

$$\epsilon = h\nu \implies \rho_\nu = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{h\nu/kT} - 1}\,, \tag{5.11}$$

a result known as Planck's law.