III

Thermodynamics of Radiation

11. Electromagnetic waves & photons

We will consider here a system of photons, i.e. of the massless particles which are the quanta associated with the electro-magnetic field. The behaviour of such photon “gases” in thermal equilibrium can be analysed experimentally by measuring the thermodynamical properties of the electro-magnetic radiation.

R • This is a very intuitive process: everybody knows that when you heat e.g. steel to make a sword, the metal radiates in the visible part of the electro-magnetic spectrum ... it glows red!
• As we will see, photons are special bosons: their number is not conserved, which gives them a very peculiar statistical behaviour: their chemical potential is nil.

Definition 11.0.1 We call *blackbody* a closed cavity which contains a photon gas in thermal equilibrium with a thermostat.

R • It is easy to make a blackbody in practice. All one needs to do is to take a container of volume V and keep it at constant temperature T. A system of electro-magnetic waves is spontaneously created within the container, i.e. in Quantum Mechanical parlance, a system of photons. The physical quantities associated with this system can be measured by poking a hole of negligible size in one of the container walls and observe the characteristics of the radiation emitted through it*.
• The characteristics of this radiation have been well known since the end of the 19$^{\text{th}}$ century, and their analysis led Planck in 1900 to formulate the “quantum hypothesis”, starting point of the scientific revolution which led to the discovery of Quantum Mechanics†.

*Also called blackbody radiation or thermal radiation.

†This is sometimes referred to as the ”ultra-violet” catastrophe because as we will see, in the classical formulation of Maxwell’s, each electro-magnetic wave behaves like an independent harmonic oscillator, and so an infinite number of them implies infinite energy, which is contributed mostly from short wavelengths, hence the ultra-violet name. This issue is resolved in Quantum Mechanics because quantum harmonic oscillators *cannot* take any continuous energy value.

11.1 Electro-magnetic eigenmodes of a container

Our starting point will be the classical theory of electro-magnetism, with the goal to use it to determine the individual quantum states that the system of photons can occupy. In other words we will follow in Planck's footsteps.

Let us consider, without loss of generality, an empty cubic container of size L. From a classical point of view, the most general electro-magnetic field that can exist inside this container is given by Maxwell's equations. Since these equations are linear, their general solution is a linear superposition of monochromatic elementary solutions that fulfil the boundary conditions imposed by the container walls. These monochromatic solutions are called the *eigenmodes* of the cavity.

Let us derive them. Consider the case were the walls of the cavity are perfectly reflecting[‡]: this enforces strict boundary conditions, in the sense that both the tangential component of the electric field, $\vec{E}$, and the normal component of the magnetic field, $\vec{B}$, must vanish at the walls[§]. Such boundary conditions allow to use simple progressive monochromatic plane waves to describe the spatial and temporal and dependence of all $\vec{E}$ and $\vec{B}$ field components, i.e. these two fields will be a sum of terms of the form $\exp\big(i(\vec{k}\cdot\vec{r}-\omega t)\big)$, where $\vec{k}$ is the wave vector, $\vec{r}$ is the position vector and ω is the angular frequency. Maxwell's equations in vacuum enforce $\|\vec{k}\| \equiv k = \omega/c$ with c the speed of light. The boundary conditions restrict the values of $\vec{k}$ to $k_x = n_x\, 2\pi/L$, $k_y = n_y\, 2\pi/L$, $k_z = n_z\, 2\pi/L$, where n_x, n_y and $n_z \in \mathbb{Z}$[¶]. Maxwell's equations also imply that for each $\vec{k}$, the $\vec{E}$ and $\vec{B}$ fields of that wave are perpendicular to $\vec{k}$ and perpendicular to one another: this allows two independent polarization states in the plane perpendicular to $\vec{k}$.

In summary, an electro-magnetic eigenmode of our cubic cavity is characterized by an eigenvector $\vec{k}$ such that its components obey $k_x = n_x\, 2\pi/L$, $k_y = n_y\, 2\pi/L$, $k_z = n_z\, 2\pi/L$ and a polarization state. Its angular frequency is given by $k = \omega/c$ and the most general electro-magnetic field that can exist in the cavity is a linear combination of eigenmodes thus defined. For macroscopic applications we want to know the number of eigenmodes, $g(\omega)\,\mathrm{d}\omega$, whose angular frequencies are comprised in the interval $[\omega, \omega + \mathrm{d}\omega]$. We can calculate this number by counting the number of eigenmodes whose wave vector $\vec{k}$ has a modulus between $[k, k + \mathrm{d}k]$. This number is $2 \times \big(L/(2\pi)\big)^3 \times 4\pi k^2\,\mathrm{d}k$, where the three multiplicative factors represent the number of polarization states, the inverse volume of an elementary cell and the volume of a spherical shell in $k-$space respectively. Replacing k by ω/c and $\mathrm{d}k$ by $\mathrm{d}\omega/c$, we obtain the *classical* spectral density of eigenmodes:

$$g(\omega) = \frac{L^3\omega^2}{\pi^2 c^3} = \frac{V\omega^2}{\pi^2 c^3} \tag{11.1}$$

11.2 Quantification of eigenmodes: photons

If we remained in the classical world, the amplitude of each eigenmode (i.e. of the corresponding $\vec{E}$ and $\vec{B}$ fields) and consequently its energy, could take any continuous value

[‡] This is the case where the container is made of a perfect conductor.

[§] As usual, real life boundary conditions are more complex than that, but it is not necessary to know them perfectly to determine the macroscopic behaviour of the system. In other words, we can choose "perfect" boundary conditions, as long as the size of the box L is much larger than the particle de Broglie wavelength, $\lambda_B \equiv h/p$, where p is the momentum of the particles, they will not affect the behaviour of the system.

[¶] This calculation is very similar to the one you have already seen for the wave function of an ideal gas in a box. Note that the eigenmode $n_x = n_y = n_z = 0$, i.e. $\vec{k} = \vec{0}$ and $\omega = 0$ must, in general, be set aside. It exists whatever the size of the cavity and corresponds to a constant electro-magnetic field, but given our specific choice of boundary conditions its amplitude is equal to zero.

in $[0, +\infty]$. In reality, the energy of the electro-magnetic field, as that of a material system is quantified.

More precisely, to an electro-magnetic wave with wave vector $\vec{k}$ and angular frequency ω, we can associate particles called photons whose momentum $\vec{p}$ and energy ϵ are given by the Planck-Einstein relations $\vec{p} = \hbar\vec{k}$ and $\epsilon = \hbar\omega$[‖]. From $k = \omega/c$, we thus get that $\epsilon = \|\vec{p}\|c \equiv pc$ for photons. If one compares this relation between energy and momentum to that of a particle of mass m given by special relativity, $\epsilon = \sqrt{p^2c^2 + m^2c^4}$, one deduces that photons must be massless particles. The two possible polarization states of the electro-magnetic wave with wave vector $\vec{k}$ translate into two independent spin states[**] for the corresponding photons with momentum $\vec{p} = \hbar\vec{k}$. So a classical eigenmode characterized by $\vec{k}$ and a polarization state appears as a possible individual state for photons trapped in the cavity[††].

From the classical spectral density of eigenmodes (11.1) (and using $\omega = \epsilon/\hbar$ and $\mathrm{d}\omega = \mathrm{d}\epsilon/\hbar$), we therefore deduce the following individual density of state for photons:

$$g(\epsilon) = \frac{V\epsilon^2}{\pi^2\hbar^3c^3} \tag{11.2}$$

11.3 Statistical properties of photons

11.3.1 Peculiarities of photons

• As their spin is an integer, they are bosons.

• They do not interact with one another, but only with the cavity walls which is how the system reaches thermal equilibrium, so they constitute an ideal gas.

R Truly speaking, this last statement is not correct, as you will see when you study Quantum Electro Dynamics (the theory of quantification of the electro-magnetic field which accounts for its coupling to charged particles). Pairs of photons can interact to momentarily produce an e^-e^+ pair for instance. However this effect scales like α^2 times the coupling between matter and radiation which thermalises, where $\alpha \equiv 1/137$ is the fine structure constant, so it is negligible for our blackbody study.

• Their number is *not* conserved. This is a new situation. To better understand what it means, let us look more closely at how the electro-magnetic field, i.e. the photon gas, arises in the cavity and reaches thermal equilibrium. As the walls are kept at constant temperature T, thermal agitation sets the charged particles they contain (essentially the e^-) in motion. These random motions create (classically) random electro-magnetic fields which propagate freely inside the cavity and in turn induce motions of the charged particles in its walls. So a (quite) weak coupling (for a macroscopic cavity) exists between the photon gas and the matter that makes the walls. This drives the system to thermal equilibrium.

R One could think that since walls are made of atoms, emission lines specific to these atoms would preferentially appear in the blackbody radiation spectrum, which would

[‖]This means that the energy of the wave with angular frequency ω is $N_\omega\,\hbar\omega$ where N_ω is the number of photons the wave is made of.

[**]This does not mean, however that the photon is a fermion with spin $s = 1/2$. A more careful study shows that photons are bosons with spin $s = 1$, and the reason why the spin can only be ±1 and not 0 is that for massless particles, the momentum $\vec{p}$ can never be $\vec{0}$ since their speed must remain equal to c no matter the reference frame chosen. Choosing $\vec{p}$ as the quantification axis, the only two possible states are therefore $\pm\, s\hbar$ for the projected value of the spin along this axis. These correspond to the left and right circular polarization of the corresponding electro-magnetic wave.

[††]Note that we naturally excluded the classical mode $\vec{k} = \vec{0}$ in this quantification.

then be expected to depend on the nature of the walls. However, this does not happen: the structure of the walls is sufficiently rich that *all* frequencies are coupled to the thermostat (vibration of atoms, impurities, defects, etc ...). So at equilibrium, the number of photons of a given frequency solely depends on the temperature T of the thermostat.

The coupling thus described looks similar to what happens with paramagnets or molecules: the photons exchange energy with the thermostat to reach thermal equilibrium and the total energy is conserved in these exchanges. However, the fundamental difference with these other systems is that the interaction between matter and radiation occurs through the absorption or emission of photons, so that their total number does not remain constant. This is *not* a situation where the number of particles can fluctuate by exchanging some with a reservoir, so that the total number of particles (gas + reservoir) remains constant either. This is a *completely* different physical problem in which the total number of particles is *not* conserved.

11.3.2 Photon distribution function

So how do we resolve this issue? In the same way you derived the Bose-Einstein statistics, but realizing that the constraint of fixed mean number of particles does not apply, so that the Lagrange multiplier $-\beta\mu$, or equivalently the chemical potential of the photons, μ (since $-\beta = -1/(k_B T)$ is fixed), must be *nil* ‡‡. This immediately yields the following mean occupation number of a single-particle state i for photons:

$$\bar{n}_i = \frac{1}{\exp\big(\epsilon_i/(k_B T)\big) - 1} \tag{11.3}$$

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• $\epsilon_i = 0$ is naturally excluded as it corresponds to $\vec{k} = \vec{0}$, which, as we have seen, is impossible for photons. So the divergence of $\bar{n}_i$ when $\epsilon_i \to 0$ is irrelevant.
• Bose-Einstein condensation *cannot* happen for photons: one cannot fix the total number of particles, it is μ which stays constant instead!

‡‡In other words, the grand canonical ensemble is the natural choice here as the number of particles varies, but the mean number of particles, $\bar{N}$, is *not* constrained, so its associated Lagrange multiplier must be nil.

12. Blackbody radiation laws

12.1 Planck's law

This is the fundamental law from which one can deduce all the others. It concerns the spectral electro-magnetic energy density $u(\omega, T)$ of the blackbody. Max Planck discovered it empirically before demonstrating it from the notion of quantification*.

Within a cavity of macroscopic volume V as defined in the previous chapter, individual possible energies for photons can practically be considered as continuous, and when thermal equilibrium with the thermostat at temperature T is reached, the mean occupation number $\bar{n}$ of an individual state with energy $\epsilon^\dagger$ thus reads:

$$\bar{n}(\epsilon, T) = \frac{1}{\exp\big(\epsilon/(k_B T)\big) - 1} \tag{12.1}$$

Assume that the system considered is sufficiently large so that one can neglect fluctuations (i.e. we are in the thermodynamical limit). The number of photons $\mathrm{d}N(\epsilon, T)$ which have individual energy in the range $[\epsilon, \epsilon + \mathrm{d}\epsilon]$ at temperature T is obtained by multiplying the number of photons occupying each of the individual states (12.1) by the number of such states, $g(\epsilon)\,\mathrm{d}\epsilon$:

$$\mathrm{d}N(\epsilon, T) = \bar{n}(\epsilon, T) g(\epsilon)\,\mathrm{d}\epsilon \tag{12.2}$$

As each of them has energy ϵ (with error $\mathrm{d}\epsilon$), plugging in equation (11.2) for $g(\epsilon)$, the total energy $\mathrm{d}U(\epsilon, T)$ of this system of photons is:

$$\mathrm{d}U(\epsilon, T) = \epsilon\,\mathrm{d}N(\epsilon, T) = \frac{\epsilon}{\exp\big(\epsilon/(k_B T)\big) - 1}\left(\frac{V\epsilon^2}{\pi^2\hbar^3 c^3}\right)\mathrm{d}\epsilon \tag{12.3}$$

and since $\epsilon = \hbar\omega$ for a photon, we get $\mathrm{d}U(\epsilon, T) = V u(\omega, T)\,\mathrm{d}\omega$, with

*We will discuss more in detail later in this chapter why the mathematical form of u for the blackbody contradicts the classical theory of electromagnetism.

†Note that we have dropped the subscripts i for $\bar{n}$ and ϵ in equation (11.3) in order to simplify notation.

Law 8 — Planck's law.

$$u(\omega,T)=\frac{\hbar\omega^3}{\pi^2c^3}\,\frac{1}{\exp\big(\hbar\omega/(k_BT)\big)-1} \tag{12.4}$$

R The Planck law is *only* valid in the case where the radiation is in thermal equilibrium with a thermostat. This constitute an important restriction, as in practice most emission/absorption of photons takes place *out of* equilibrium. Arguably the most common example is lighting by an electric lamp which *irreversibly* transforms electric energy into radiation.

12.2 How does it look like?

Let us draw u as a function of ω for a fixed T. As usual, we identify the function main features (asymptotic behaviour, extrema) to do so:

- At low frequencies, when $\hbar\omega \ll k_BT$, we can expand the exponential term to obtain $u(\omega,T)\simeq k_BT\omega^2/(\pi^2c^3)$, which is called the *Rayleigh-Jeans formula*. So the spectral energy density is a parabola when $\omega\to 0$.
- At high frequencies, when $\hbar\omega \gg k_BT$, we get $u(\omega,T)\simeq \hbar\omega^3\exp\big(-\hbar\omega/(k_BT)\big)/(\pi^2c^3)$, which is the so-called *Wien's law*. So the spectral energy density decreases exponentially when $\omega\to+\infty$.
- The maximum of u, $\omega_{\max}$, can be derived from the calculation of the logarithmic derivative $u^{-1}(\partial u/\partial\omega)_T$, which yields a simple transcendental equation which one can easily solve numerically. We leave it as an exercise to show that this procedure yields to *Wien's displacement law* $\omega_{\max}=2.821\,k_BT/\hbar$, where the maximum angular frequency is proportional to the temperature, T.

These considerations lead to the graph below (Fig. 12.1).

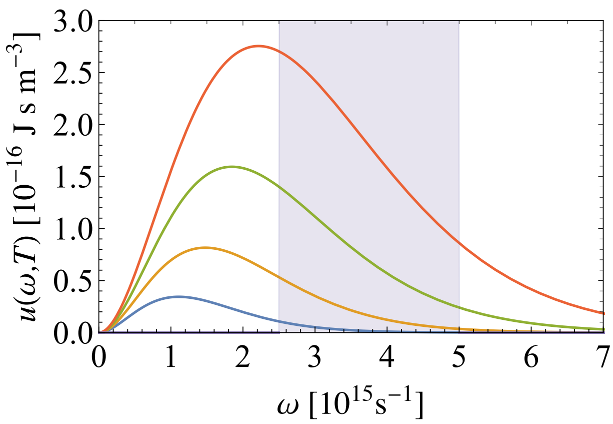

Figure 12.1: Planck's law (equation (12.4)) plot for several temperatures: 3000K in blue, 4000K in orange, 5000K in green and 6000K (approximate temperature of the Sun surface) in red. The band shaded in light purple indicates the visible light frequency range.

R • While the peak in frequency, $\omega_{\max}$ shifts to higher frequencies proportionally to T as T increases, the total energy (area under the u curve in Fig. 12.1) grows like T^4.
• Also note that the number of photons $N(\omega,T)$ has a similar shape to $u(\omega,T)$ with

only the power law index of ω reduced by one. This means that the photon number increases dramatically with T!

12.3 Why classical theory fails

In the classical wave theory of electro-magnetism, each of the eigenmodes of the cavity behaves like a simple harmonic oscillator with the same angular frequency. Indeed, taking the curl of Maxwell's curl equations for the electric and magnetic fields and eliminating $\vec{B}$ from the equation for $\vec{E}$ yields the standard wave equation:

$$\nabla^2\vec{E}(\vec{r},t) - \frac{1}{c^2}\frac{\partial^2\vec{E}(\vec{r},t)}{\partial t^2} = \vec{0} \tag{12.5}$$

As previously discussed, we can write the electric field as a linear combination of all the eigenmodes of the cavity, which upon explicitly separating the time and spatial dependence of the progressive monochromatic plane waves reads[‡]:

$$\vec{E}(\vec{r},t) = \sum_{\vec{k},\sigma} A_{\vec{k},\sigma}(t)\,\vec{\mathcal{E}}_{\vec{k},\sigma}(\vec{r})$$

Injecting this in the wave equation (12.5) gives:

$$\sum_{\vec{k},\sigma}\left(\frac{\mathrm{d}^2A_{\vec{k},\sigma}(t)}{\mathrm{d}t^2} + c^2k^2A_{\vec{k},\sigma}(t)\right)\vec{\mathcal{E}}_{\vec{k},\sigma}(\vec{r}) = \vec{0} \tag{12.6}$$

where the term in between brackets must vanish for each combination of $(\vec{k},\sigma)$ in order for a non-nil $\vec{E}$ to obey Maxwell's equations. This term has the well-known form of a sum of one dimensional simple harmonic oscillators, and we know from the classical equipartition of energy theorem (see 9.1.1) that when they are in contact with a thermostat at temperature T, the mean energy of each one of these is k_BT. So classical theory predicts a spectral energy density, using the spectral density of eigenmodes (11.1):

$$u_{\text{class}}(\omega,T) = k_BTg(\omega)/V = k_BT\omega^2/(\pi^2c^3) \tag{12.7}$$

which dramatically fails to reproduce Wien's experimental results (high frequency exponential decrease and maximum which shifts linearly with temperature). Furthermore, upon integrating $u_{\text{class}}(\omega,T)$ over the whole range of frequency $\omega \in [0,+\infty[$, one finds that the total energy density $u_{\text{class}}(T)$ diverges! This is the so-called "ultra-violet" catastrophe as the energy divergence comes from short wavelengths, i.e. large ω.

12.4 Thermodynamical quantities

12.4.1 Total energy: towards Stefan-Boltzmann's law

On the other hand, integrating equation (12.4) over the entire range of possible frequencies $\omega \in [0,+\infty[$ and multiplying by the volume, V, one obtains the total energy

$$U(T,V) = \frac{V\hbar}{\pi^2c^3}\int_0^{+\infty}\frac{\omega^3}{\exp\big(\hbar\omega/(k_BT)\big)-1}\,\mathrm{d}\omega \tag{12.8}$$

[‡]The summation over σ includes the possible different polarization states.

which, contrary to the classical result, does converge[§]! Let us calculate it. A change of variable $x = \hbar\omega/(k_B T)$ gives

$$\begin{aligned} U(T,V) &= \frac{V\hbar}{\pi^2 c^3}\left(\frac{k_B T}{\hbar}\right)^4 \underbrace{\int_0^{+\infty} \frac{x^3}{\exp(x)-1}\,\mathrm{d}x} \\ &= \frac{V\hbar}{\pi^2 c^3}\left(\frac{k_B T}{\hbar}\right)^4 \qquad \frac{\pi^4}{15} \end{aligned} \tag{12.9}$$

as the integral in the first equality is a known combination of Gamma functions which equals to $\pi^4/15$. So we finally get:

$$U(T,V) = V u(T) = V\frac{\pi^2\, k_B^4}{15\,\hbar^3 c^3} T^4 \equiv aVT^4 \tag{12.10}$$

where the constant $a = \pi^2 k_B^4/(15\,\hbar^3 c^3)$ is *not* the Stefan-Boltzmann constant, σ, which appears in front of the power emitted per unit surface rather than the energy. We will derive it in the next chapter. However, the scaling of the total energy in T^4 is identical to that of the power emitted per unit surface, which hints that Stefan-Boltzmann's law, as we will see later, is a consequence of Planck's.

12.4.2 Grand potential, pressure and entropy

The grand potential of the photon system, by definition is:

$$\begin{aligned} \Phi &= -k_B T \sum_i \ln(1+\bar{n}_i) \\ &= -k_B T \int_0^{+\infty} g(\epsilon)\ln(1+\bar{n}(\epsilon,T))\,\mathrm{d}\epsilon \\ &= -k_B T \frac{V}{\pi^2\hbar^3 c^3}\int_0^{+\infty} \epsilon^2 \ln\left(1+\frac{1}{\exp\left(\epsilon/(k_B T)\right)-1}\right)\mathrm{d}\epsilon \\ &= -\frac{V}{\pi^2\hbar^3 c^3}\int_0^{+\infty} \frac{\epsilon^3}{3}\,\frac{1}{\exp\left(\epsilon/(k_B T)\right)-1}\,\mathrm{d}\epsilon \\ &= -\frac{1}{3}U(T,V) \end{aligned} \tag{12.11}$$

where the intermediate step of calculating the integral over the logarithm function is performed using an integration by parts. This naturally yields the equation of state of the

[§]Strictly speaking, we are faced with a consistency problem: we should be able to derive the total energy of the photon gas from a purely quantised point of view, rather than the semi-classical approach we have followed in these notes. In other words, we should be able to use the average energy of a simple quantum harmonic oscillator (equation (9.8) divided by N and with $U_0^{(1D)} = 0$), representing a particular field eigenmode, to write:

$$U(T,V) = \int_0^{+\infty} g(\omega)\left(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp\left(\hbar\omega/(k_B T)\right)-1}\right)\mathrm{d}\omega = \frac{V}{\pi^2 c^3}\int_0^{+\infty}\left(\frac{\hbar\omega^3}{2} + \frac{\hbar\omega^3}{\exp\left(\hbar\omega/(k_B T)\right)-1}\right)\mathrm{d}\omega$$

However, whilst the second term in the integral does yield the same result as equation (12.8) there also appears a first term $\hbar\omega^3/2$ which diverges when integrated over the whole range of possible ω values. This term arises because the energy of the fundamental level of a quantum harmonic oscillator is not zero (as can be seen by setting the quantum number n, interpreted here as the number of photons in the field eigenmode (earlier defined as N_ω), to $n = 0$ in equation (9.4)). This energy of the quantised electro-magnetic field which is present even in the absence of photons is referred to as *vacuum energy* or zero-point energy and (more or less) happily renormalised away, but this is another (long and very involved) story!

photon gas by calculating the pressure:

$$\boxed{p = -\left(\frac{\partial \Phi}{\partial V}\right)_T = \frac{1}{3}\,u(T)} \tag{12.12}$$

which is the classical radiation pressure traditionally derived for isotropic radiation.

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• As $\mu = 0$ for the photon gas, there are only two variables, T & V.
• As the number of photons N is not fixed, the equation of state cannot be a function of the volume because V is the only extensive variable left! So this "extensiveness" cannot be compensated to make the pressure intensive, as is the case for an ideal gas where one can multiply by N to get the intensive factor N/V in front of the temperature dependence. As a consequence, the photon gas pressure is a function of temperature *alone*.

As for the entropy, we have

$$S = -\left(\frac{\partial \Phi}{\partial T}\right)_V = \frac{4}{3}\,\frac{U(T,V)}{T} \tag{12.13}$$

which goes to zero when $T \to 0$ in the same way that fermions and massive bosons do.

13. Absorption & emission of radiation

Experiment shows that a sufficiently heated body emits light, e.g. the filament of a lamp, hot iron etc ... This thermal radiation emission is the subject of this section and we will show that it is intrinsically linked to the ability of the body to absorb radiation externally emitted.

13.1 Definitions

Let the power radiated by an infinitesimal surface element $\mathrm{d}S$, centred on point M of a body $\mathcal{B}$, in an infinitesimal solid angle $\mathrm{d}\Omega$ around the direction defined by unit vector $\hat{k}$ and in an infinitesimal band of angular frequency $[\omega, \omega + \mathrm{d}\omega]$ be:

$$\mathrm{d}P \equiv \eta(\omega, \hat{k}, M, T)\, \mathrm{d}\omega\, \mathrm{d}\Omega\, \mathrm{d}S \tag{13.1}$$

This relation defines the *emissivity*, η, of the body $\mathcal{B}$. It has the dimension of an energy per unit surface [J m^{-2}] and depends on the nature of the body $\mathcal{B}$, the point M chosen on its surface, the temperature T at which the body is heated, the angular frequency ω at which the emitted radiation is observed as well as the direction $\hat{k}$ along which this latter propagates*. If we call ϑ and φ $(0 \leq \vartheta \leq \pi\,;\ 0 \leq \varphi \leq 2\pi)$ the angles which mark the direction of $\hat{k}$ with respect to the normal to $\mathrm{d}S$ in M and an axis perpendicular to this normal which serves as origin for φ, we then have, as usual for a spherical coordinate system, $\mathrm{d}\Omega = \sin\vartheta\, \mathrm{d}\vartheta\, \mathrm{d}\varphi$.

Suppose now that $\mathcal{B}$ receives electro-magnetic radiation emitted by external sources. By analogy with what we just did for emission, let us write the power received at the same point M by the same surface element $\mathrm{d}S$, but in the angular frequency range $[\omega', \omega' + \mathrm{d}\omega']$ and which arrives within the solid angle $\mathrm{d}\Omega'$ around the direction defined by the unit vector $\hat{k}'$ as:

$$\mathrm{d}P \equiv \varpi(\omega', \hat{k}', M)\, \mathrm{d}\omega'\, \mathrm{d}\Omega'\, \mathrm{d}S \tag{13.2}$$

*To be complete, in some cases it also depends on the polarization state of the emitted radiation, but we will neglect this in these lectures.

Quite clearly, the quantity ϖ has the same dimension as the emissivity η. In the most general case, part of this power $\mathrm{d}P$ is absorbed by $\mathcal{B}$, and the rest is sent back, whether by reflection or diffusion[†]. We then define the *absorptivity*, α of the body $\mathcal{B}$ at point M as the fraction of the received power that is absorbed. This is a *dimensionless* number that depends on the nature of the body $\mathcal{B}$, the point M chosen on its surface, the temperature T at which the body is heated, but also on the angular frequency ω' and the direction $\hat{k}'$ of the incident radiation. In other words, $\alpha = \alpha(\omega', \hat{k}', M, T)$.

13.2 The case of the blackbody

We (would like to) call "blackbody" , a body $\mathcal{B}$ whose absorptivity verifies:

$$\alpha(\omega', \hat{k}', M, T) = 1\,, \quad \forall(\omega', \hat{k}')$$

That is to say, a *blackbody* is a body which absorbs *all* the power of the incident radiation it receives at point M, regardless of its wavelength and direction. It is called that way because if you illuminate it with any radiation, it does not reflect or diffuse any component of this radiation, which makes it look black.

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- It is possible for a body to be a blackbody only in a certain range of temperature.
- As we have already seen, a black body emits radiation, so it will only appear black to the eye if its temperature is not too high, because in that case its emission at visible wavelengths is negligible. If you shine visible light on it, it will absorb it entirely and therefore does not send back any colour!

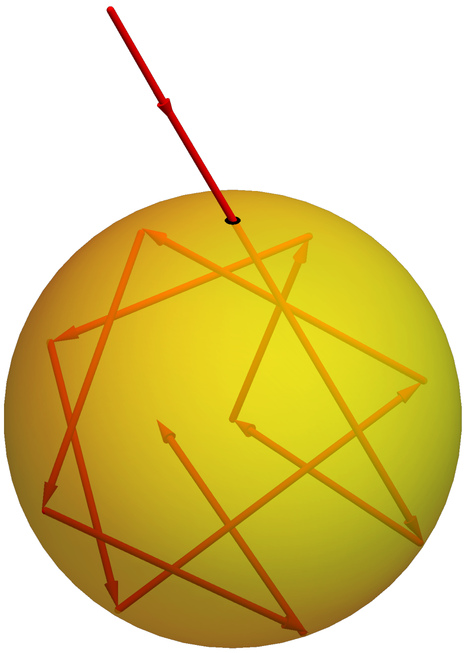

Figure 13.1: Schematics of the closest practical realisation of a true blackbody. A light ray (red line with arrows) is trapped inside a spherical cavity.

A surface plastered with soot is an approximative blackbody (at least for radiation at visible and near-visible wavelengths), but the practical realisation that is closest to a true

[†]We assume that $\mathcal{B}$ is sufficiently thick and opaque that no radiation can go through it.

blackbody consists in poking a small hole in a closed container (see Fig. 13.1). Indeed, any radiation directed towards this hole under any angle will be trapped in the cavity with almost no chance of coming out of it. It is because we always refer to this prototype that we say *the* blackbody.

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• The link with the previous chapter definition of the blackbody as a gas of photons in thermal equilibrium in a cavity should be straightforward: if you poke a hole in the said cavity, you find yourself in the same situation as in Fig. 13.1!
• Sometimes you will hear people talk about "white body" for a body with $\alpha = 0$, or "grey body" for intermediate cases.

13.3 Kirschoff's law

13.3.1 Statistical equilibrium

Let us put a body $\mathcal{B}$ in thermal equilibrium with a photon gas at temperature T, i.e. let us place $\mathcal{B}$ in a closed container in contact with a thermostat at temperature T and wait for the equilibrium to be established. In such an equilibrium situation, the total power emitted and absorbed by $\mathcal{B}$ are equal.

Having picked a unit vector $\hat{k}$, we consider the radiation emitted in that direction and the radiation received in the same direction, i.e. along a unit vector $-\hat{k}$, to mathematically write this equilibrium condition as:

$$\int \Big[\eta(\omega, \hat{k}, M, T) - \alpha(\omega, -\hat{k}, M, T)\, \varpi(\omega, -\hat{k}, M, T)\Big]\, \mathrm{d}\omega\, \mathrm{d}\Omega\, \mathrm{d}S = 0 \tag{13.3}$$

However, this cancellation is not only global, it must also happen locally at each point of $\mathcal{B}$ and for each ω and $\hat{k}$. Indeed, should there exist a contribution $(\eta - \alpha\varpi) > 0$ over a small domain $\delta_1(\omega, \vartheta, \varphi, M)$ of the body $\mathcal{B}$, it should then be compensated by a negative contribution on another domain $\delta_2(\omega', \vartheta', \varphi', M')$ since the integral must vanish. As we can change η and α for δ_2 without altering δ_1, by e.g. sticking a piece of opaque screen on the surface element $\mathrm{d}S_2$ to prevent exchanges between this surface element and the gas of photons in the container, this would destroy the global cancellation without affecting the equilibrium between $\mathcal{B}$ and the radiation. We must therefore conclude that:

$$\eta(\omega, \hat{k}, M, T) = \alpha(\omega, -\hat{k}, M, T)\, \varpi(\omega, -\hat{k}, M, T) \tag{13.4}$$

Now we can calculate $\varpi(\omega, -\hat{k}, M, T)$ in this situation, because we know that the photon gas at equilibrium must follow the Planck law derived in the previous chapter! The number of photons $\mathrm{d}N(\vec{k}', T)$ with wave vectors in the range $[\vec{k}', \vec{k}' + \mathrm{d}\vec{k}']$ at temperature T therefore is:

$$\mathrm{d}N(\vec{k}', T) = 2\frac{V}{(2\pi)^3}\frac{\mathrm{d}^3k'}{\exp\big(\hbar\omega'/(k_B T)\big) - 1} \tag{13.5}$$

All these photons have a speed c in the direction $\vec{k}'$ and an energy $\hbar\omega' = \hbar c k'$. Those which hit the surface element, $\mathrm{d}S$, of $\mathcal{B}$, centred at M, during the time interval $[t, t + \mathrm{d}t]$, are contained in a cylinder of base $\mathrm{d}S$ and axis of length $c\,\mathrm{d}t$ parallel to $\vec{k}'$. This allows us to write the energy received by $\mathrm{d}S$ during $\mathrm{d}t$ as:

$$\varpi(\omega', \hat{k}', M, T)\, \mathrm{d}t\, \mathrm{d}S\, \mathrm{d}\Omega'\, \mathrm{d}\omega' = \hbar\omega'\, \mathrm{d}N(\vec{k}', T)\frac{c\cos\vartheta\, \mathrm{d}t\, \mathrm{d}S}{V} \tag{13.6}$$

where ϑ is the angle between $-\vec{k}'$ and the normal to $\mathrm{d}S$ at M (see Fig. 13.2).

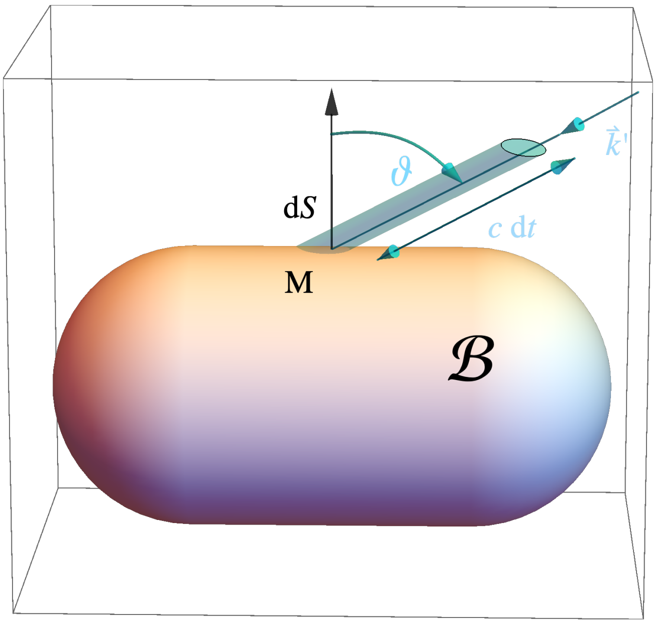

Figure 13.2: Geometrical view of photons in the cavity hitting the body $\mathcal{B}$.

Given that $\mathrm{d}^3k' = k'^2 \mathrm{d}k'\,\mathrm{d}\Omega' = \omega'^2/c^3 \mathrm{d}\omega'\,\mathrm{d}\Omega'$, we can inject equation (13.5) into (13.6) to get:

$$\varpi(\omega', \hat{k}', M, T) = \frac{\hbar\omega'^3}{4\pi^3 c^2} \frac{\cos\vartheta}{\exp\left(\hbar\omega'/(k_B T)\right) - 1} = \frac{c}{4\pi} u(\omega', T)\cos\vartheta \tag{13.7}$$

where, as expected, the spectral energy density of Planck's law, $u(\omega', T)$, given by equation (12.4), appears. Going back to our cancellation equation (13.4), we are thus able to derive:

Law 9 — Kirschoff's law.

$$\frac{\eta(\omega, \hat{k}, M, T)}{\alpha(\omega, -\hat{k}, M, T)} = \frac{c}{4\pi} u(\omega, T)\cos\vartheta \tag{13.8}$$

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- The left hand side term in Kirschoff's law only involves *intrinsic* properties of the body studied, i.e., both η and α are independent of the conditions in which $\mathcal{B}$ is placed: they remain the same even when the body emits/absorbs radiation in a *non*-equilibrium situation!
- The right hand side term, on the contrary, is a *universal* function of T, ω and direction *only*.

In other words, Kirschoff's law states that the ratio between emissivity and absorptivity is *independent* of the body considered and of the point chosen on its surface. Another way to state this is that "good absorbers are good emitters" and vice-versa.

13.3.2 Application to the blackbody: Stefan-Boltzmann's law

In the case of the blackbody, as we have seen, the absorptivity is by definition $\alpha_B(\omega, -\hat{k}, M, T) = 1$ and so its emissivity, $\eta_B(\omega, \hat{k}, M, T) = c/(4\pi)\, u(\omega, T)\cos\vartheta$, is *independent of its nature*.

It thus serves as a reference, as it is simply proportional to $\cos\vartheta$, where ϑ is the angle between the direction of observation and the normal to the surface of the blackbody. This dependence on direction is referred to as *Lambert's law.* Integrating over all directions we obtain the power emitted in the angular frequency band $[\omega, \omega + \mathrm{d}\omega]$ by the surface element $\mathrm{d}S$:

$$\begin{aligned} P_B(\omega, T)\,\mathrm{d}\omega\,\mathrm{d}S &= \mathrm{d}\omega\,\mathrm{d}S \int \eta_B(\omega, \hat{k}, M, T)\,\mathrm{d}\Omega \\ &= \mathrm{d}\omega\,\mathrm{d}S\,\frac{c}{4\pi} u(\omega, T) \int_0^{2\pi} \mathrm{d}\varphi \int_0^{\pi/2} \cos\vartheta \sin\vartheta\,\mathrm{d}\vartheta \end{aligned} \tag{13.9}$$

where the last integral over ϑ only goes to $\pi/2$ because radiation is only emitted outside of the body. We thus deduce that $P_B(\omega, T) = cu(\omega, T)/4$. That is to say, a measure of the power emitted per unit surface of the blackbody directly yields the energy density of a photon gas in thermal equilibrium! This explains why Planck's law, initially destined to describe blackbody radiation, was deduced from the properties of the photon gas.

Finally, the total power per unit surface of the blackbody obeys:

Law 10 — Stefan-Boltzmann's law.

$$P_B(T) = \int_0^{+\infty} P_B(\omega, T)\,\mathrm{d}\omega = \frac{\pi^2 k^4}{60 c^2 \hbar^3} T^4 \equiv \sigma T^4 \tag{13.10}$$

where σ is called *Stefan-Boltzmann's constant.*