

# A guide to blackbody physics

Daniel Suchet\*

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## Short summary

### Section 1 Radiometrics

This part is quite boring, but it is necessary to well define the quantities at stake : their definition are non-intuitive *at all* and lead to easy mistakes. Moreover, many authors have their own definition / notations of some quantities, making it even more confusing.

The following quantities are considered in this section: Radiant flux, Radiant exitance, Irradiance, Radiant intensity, Radiance, Optical étendue, Absorption coefficient, Absorptivity and Absorption rate

### Section 2 Thermodynamics of a (blackbody) radiation in a cavity

The photon density *inside* a blackbody (or gray-body) is derived, using several methods. Notably, the van Roosbroeck - Shockley equation, expressing the spontaneous emission rate inside the medium is obtained.

### Section 3 Thermodynamics of a blackbody radiation in free space

A discussion on the relation between the radiation inside the body and the radiation emitted by the body is offered and emitted flux of photon, energy and entropy are calculated. Several tricky questions are addressed: what is the entropy produced by emitting radiation ? What does a blackbody look like ? What is the validity range of classical approximations ? Should étendue or aperture be considered ?

### Section 4 Thermodynamics of graybodies

Kirchhoff law of radiation and the Shockley Queisser limit are presented in details, including a long discussion on chemical potentials in solar cells. The approach of Tom Markvart is also presented to give a thermodynamic interpretation on energy loss terms.

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\*daniel.suchet@polytechnique.org, Okada-lab, LIA Next PV, Research Center for Advanced Science and Technology, The University of Tokyo

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# 1 Radiometrics

This part is quite boring, but it is necessary to well define the quantities at stake : their definition are non-intuitive *at all* and lead to easy mistakes. Moreover, many authors have their own definition / notations of some quantities, making it even more confusing.

## 1.1 Radiometric quantities

- All quantity can be considered as *spectral* quantity, considering their derivative either with respect to the radiation frequency  $\nu$  or wavelength  $\lambda$ .
- Some quantities are tricky. Notably, the radiant intensity is *not* an intensity (ie a power per surface).
- There are many radiometric quantities, notably a whole bunch related to human eye sensitivity (luminous flux, luminous intensity (which is not an intensity, of course), illuminance...). These quantities are not relevant for energy consideration, and we will not use them in the following.

### Radiant flux $\Phi_E$ [W]

The radiant flux is the total amount of power carried by the radiation, either taken from the source or brought to the target. It is related to Poynting vector  $\mathbf{\Pi}$  :

$$\Phi_E = \int \langle \mathbf{\Pi} \rangle . d\mathbf{S} \tag{1}$$

### Radiant exitance $M$ [W.m<sup>-2</sup>]

The exitance is the power emitted by unit surface of the source (*exitance*). In any other field of physics, this would be called emitted intensity.

### Irradiance / *éclairage* $E$ [W.m<sup>-2</sup>]

The irradiance is the power received by unit surface of the target. In any other field of physics, this would be called received intensity.

## Radiant intensity $I_\Omega$ [W.str<sup>-1</sup>]

The radiant intensity is *not* an intensity. It is the amount of energy emitted per second by the whole surface of the emitter in a direction  $\Omega$ .

This quantity is used to define the Candela (one candela is the luminous intensity, in a given direction, of a source that emits monochromatic radiation of frequency  $540 \times 10^{12}$  Hz and that has a radiant intensity in that direction of  $1 / 683$  W per steradian.).

## Radiance / luminance énergétique $L_\Omega$ [W.str<sup>-1</sup>.m<sup>-2</sup>]

The radiance of a small surface  $dS$  in the direction  $\Omega$  is the amount of energy emitted or received per second, per surface and per steradian *divided by*  $\cos \theta$ . This quantity corresponds to the angular power as measured by an observer in the direction  $\Omega$ , where the *visible* surface is  $dS_{\text{vis}} = dS \cos \theta$ . This is very tricky, and has to be understood while keeping the definition of radiant intensity in mind. Let us try to illustrate the difference between both quantities :

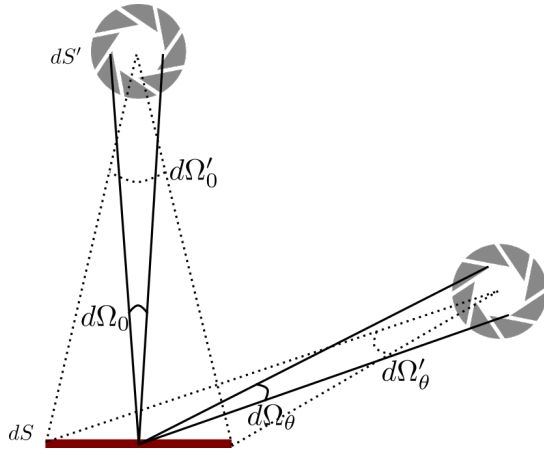


Figure 1: Radiance and radiant intensity

Consider a plate of surface  $dS$ , observed through an aperture  $dS'$  at a distance  $d$ .

Under normal incidence, the aperture receives a power  $d\phi_{E,0} \equiv I(0).d\Omega_0$ , where  $d\Omega_0 = \frac{dS'}{d^2}$  is the solid angle subtended by the aperture. Seen from the aperture, the plate occupies a solid angle  $d\Omega'_0 = \frac{dS}{d^2}$ , so the aperture perceives surface power per steradian of  $\frac{d\phi_{E,0}}{dS' d\Omega'_0} = \frac{I(0)}{dS} = L(0)$ .

From the side, the aperture receives a power  $d\phi_{E,\theta} = I(\theta).d\Omega_\theta$ , where  $d\Omega_\theta = \frac{dS'}{d^2} = d\Omega_0$ . But the surface seen from the aperture is now  $dS_{\text{vis}} = dS \cos \theta$ , and the solid angle subtended by the plate is therefore  $d\Omega'_\theta = \frac{dS \cos \theta}{d^2}$ . The aperture perceives now  $\frac{d\phi_{E,\theta}}{dS' d\Omega'_\theta} = \frac{I(\theta)}{\cos \theta} \cdot \frac{1}{dS} = L(\theta)$ .

If the radiant intensity is uniform  $L(\theta) = L(0)$ , then the radiance perceived by the observer increases with the angle as  $\cos^{-1} \theta$  : the aperture receives the same amount of power from the side as from the top, but the source seems smaller and therefore intense.

If the radiant intensity decreases with then angle as  $L(\theta) = L(0) \times \cos \theta$  (so called Lambertian emission, which is the case for a blackbody), then the radiance is uniform and the observer perceive the same intensity from all observation angles. The visual aspect of a blackbody is detailed in section 3.3.

The radiance is strongly related to the notion of *étendue*, which we present below.

## 1.2 Optical étendue

The optical étendue is a very powerful tool to describe the propagation of a radiation, or the influence of concentration for a solar panel. Consider a section  $dS$  of a beam ; the étendue is defined as

$$d\mathcal{E} = n^2 \cos \theta d\Omega dS \quad (2)$$

where  $d\Omega$  is the solid angle of the beam's direction,  $\theta$  is the angle between the section's normal and the beam's direction and  $n$  is the optical index of the medium. For a distant source under normal incidence, with  $\theta \leq \theta_c$  and a rotational symmetry along the axis<sup>1</sup>,

$$\mathcal{E} = 2\pi n^2 dS \int \cos \theta \sin \theta d\theta = n^2 \pi \sin^2 \theta_c dS \quad (3)$$

<sup>1</sup>By contrast, the solid angle subtended by the beam is  $\Omega = 2\pi \int \sin \theta d\theta = \pi \sin^2 \frac{\theta_c}{2}$

	$L_\Omega$	$I_\Omega$	$M$	$E$	$\phi_E$
$L_\Omega$	-	$\frac{1}{\cos\theta} \frac{\partial I_\Omega}{\partial S}$	$\frac{1}{\cos\theta} \frac{\partial M}{\partial \Omega}$		$n^2 \frac{\partial \phi_E}{\partial \mathcal{E}}$
$I_\Omega$	$(\int dS L_\Omega) \cos\theta$ $dI_\Omega = L_\Omega \cos\theta dS$	-			$\frac{\partial \phi_E}{\partial \Omega}$
$M$	$\int d\Omega L_\Omega \cos\theta$ $dM_E = L_\Omega \cos\theta d\Omega$		-		$\frac{\partial \phi_E}{\partial S}$
$E$	$\int d\Omega L_\Omega \cos\theta$			-	$\frac{\partial \phi_E}{\partial S}$
$\phi_E$	$\int dS d\Omega L_\Omega \cos\theta$	$\int d\Omega I_\Omega$	$\int dS M$	$\int dS E$	-

Table 1: Relations between radiometric quantities.

We present here some of the main properties of this quantity :

**Prop 1** The optical étendue of the emitter, as seen by the receiver, is the same as the optical étendue of the receiver, as seen by the emitter

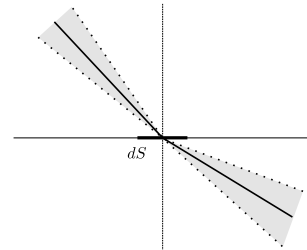
Let us consider a surface  $dS$  around  $M$  emitting radiation towards a surface  $dS'$  around  $M'$  on the receiver. We denote  $\theta$  (resp.  $\theta'$ ) the angle between  $dS$  (resp.  $dS'$ ) and  $MM'$ . The optical étendue of the beam takes the following form :

$$\begin{aligned}
d\mathcal{E}_{em \rightarrow rec} &= \cos\theta dS \times d\Omega' \\
&= \frac{\cos\theta dS \times \cos\theta' dS'}{MM'^2} \\
&= d\Omega \times \cos\theta' dS' = d\mathcal{E}_{rec \rightarrow em}
\end{aligned} \tag{4}$$

**Prop 2** The optical étendue is conserved over the propagation of a beam.

When the beam travels across a dioptr, Snell-Descartes laws imply  $n_2 \sin\theta_2 = n_1 \sin\theta_1$  (and therefore  $n_2 \cos\theta_2 d\theta_2 = n_1 \cos\theta_1 d\theta_1$ ) as well as  $\varphi_2 = \varphi_1$  (and therefore  $d\varphi_2 = d\varphi_1$ ). From there, the refraction laws give directly:

$$\begin{aligned}
d\mathcal{E}_1 &= n_1 \sin\theta_1 \times dS \times n_1 \cos\theta_1 \times d\theta_1 \times d\varphi_1 \\
&= n_2 \sin\theta_2 \times dS \times n_2 \cos\theta_2 \times d\theta_2 \times d\varphi_2 \\
&= d\mathcal{E}_2
\end{aligned}$$



**Corollary** In absence of absorption / emission, luminance divided by the optical index squared is a conserved quantity through the trajectory of the beam.

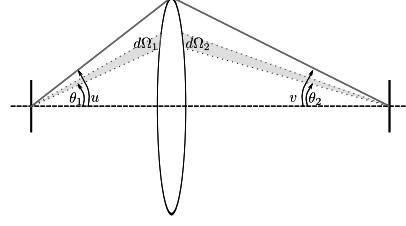
The power reaching / emitted from the surface  $dS$  can be expressed as  $d\phi_{in/out} = \frac{1}{n_{in/out}^2} L_{in/out} d\mathcal{E}_{in/out}$ . The previous equation together with energy conservation  $d\phi_{out} = d\phi_{in}$  leads to

$$\frac{L_{out}}{n_{out}^2} = \frac{L_{in}}{n_{in}^2} \tag{5}$$

**Corollary** Abbe sine law

Considering the lens as a stigmatic optical system, the conservation of the optical étendue can be written for each fragment of the incoming - outgoing beam, and integrated over the whole lens:

$$\begin{aligned}
 n_1^2 \cos \theta_1 \times dS_1 \times d\Omega_1 &= n_2^2 \cos \theta_2 \times dS_2 \times d\Omega_2 \\
 n_1^2 dS_1 \times \int d\Omega_1 \cos \theta_1 &= n_2^2 dS_2 \times \int d\Omega_2 \cos \theta_2 \\
 n_1^2 dS_1 \times \sin^2 u &= n_2^2 dS_2 \times \sin^2 v \quad (6)
 \end{aligned}$$



This means constrains the ability of an optical system to magnify an input beam. Consider an optical source of radiance  $L_\odot$ , far above the system, seen under a solid angle  $\Omega_\odot$ . Without optical concentration, a receiver (such as a solar panel) therefore would experience an irradiance  $E = L_\odot \Omega_\odot$ . Now imagine that a lens of radius  $r_l$  images the source on that covers the receiver, ie  $S_{\text{img}} = f^2 \Omega_\odot$ . From a naive geometric estimation, it seems that the image would collect all of the incident power reaching the lens  $L_\odot \Omega_\odot S_{\text{lens}}$  and with  $r_l = f \tan v$ , the irradiance would thus be increased by a factor  $\frac{\pi}{\Omega_\odot} \tan^2 v$ , which could be arbitrarily large.

Actually, this reasoning considers the radius of the lens and its focal distance as independent quantities, and assumes that regardless of  $r_l$ , an image of size  $S_{\text{img}}$  can be formed around the focal point. The conservation of étendue eq.(6) shows that this assumption is wrong. As  $v$  is increased, the size of the image  $S_{\text{img}}$  cannot be kept constant and the estimation  $S_{\text{img}} = f^2 \Omega_\odot$  is wrong.

This result appears explicitly in the following derivation

$$\begin{aligned}
 \phi E &= S_{\text{src}} \int_{\text{lens}} L_\odot \cos \theta d\Omega = L_\odot \pi S_{\text{src}} \sin^2 u \\
 &= L_\odot \pi S_{\text{img}} \sin^2 v \quad (7)
 \end{aligned}$$

where the last equality results from Abbe-Sine law. The irradiance perceived at the image position is therefore  $E_{\text{with lens}} = L_\odot \pi \sin^2 v$ . By contrast, in the absence of concentration optic, the irradiance is simply  $E_{\text{without lens}} = L_\odot \Omega_\odot$  as mentioned above. The concentration factor thus appears to be

$$C = \frac{E_{\text{with lens}}}{E_{\text{without lens}}} = \frac{\pi}{\Omega_\odot} \sin^2 v \leq 46\,500 \quad (8)$$

**Prop 3** The optical étendue accounts for the volume in phase space of a monochromatic beam

$$\begin{aligned}
 d^2 \mathbf{r} \cdot d^2 \mathbf{p} &= dx dy \times \cos \theta \times k^2 d\Omega \\
 &= \frac{\hbar^2 \omega^2}{c^2} \times d\mathcal{E} \quad (9)
 \end{aligned}$$

and Heisenberg uncertainty relation imposes  $\frac{\nu^2}{c^2} d\mathcal{E} \geq 1$ . Taking polarization into account, we can therefore interpret  $2 \frac{\nu^2}{c^2} \mathcal{E}$  as the number of quantum states within a beam of frequency  $\nu$  and optical étendue  $\mathcal{E}$ .

**Prop 4** The optical étendue accounts for the entropy of a monochromatic beam

Considering Boltzmann definition of the entropy

$$S_\lambda = k_B \log \Omega \quad (10)$$

where  $\Omega$  is the number of micro configuration of the system. Consider that the beam is composed of  $N$  photons distributed among  $2 \frac{\nu^2}{c^2} \mathcal{E}$  modes. There are

$$\Omega = \frac{\left(2 \frac{\nu^2}{c^2} \mathcal{E} + N\right)!}{\left(2 \frac{\nu^2}{c^2} \mathcal{E}\right)! N!} \quad (11)$$

number of ways to dispatch the photons, and the entropy is thus, using Stirling  $\log N! \simeq N \log(N/e)$  formula,

$$S_\lambda = k_B \log \left( 1 + 2 \frac{\mathcal{E}}{N\lambda^2} \right) \quad (12)$$

### 1.3 Absorption coefficient, absorptivity, absorption rate

**Absorption / emission rates**  $R(E)$ ,  $[L^{-3}.s^{-1}]$

Rates count the number of photons absorbed or emitted per unit of volume and of time. While the concept is pretty easy, several definition can actually be considered, rendering rates sometimes ambiguous:

- Sometimes, rates count the amount of *energy* absorbed or emitted per unit of volume and of time.
- Sometimes, rates count the total number of processes per second, or the number of processes per second and per atom. In the following, we will note such rates  $\Gamma$  instead of  $R$ .
- Three light-matter processes can be distinguished: absorption, spontaneous emission and stimulated emission. Each of them are associated to a rate, which we note  $R_\uparrow$ ,  $R_{sp}$  and  $R_\downarrow$  respectively. On top of that:

- Net absorption rate is often defined as the difference between absorption and stimulated emission

$$R_{abs} = R_\uparrow - R_\downarrow \quad (13)$$

- Total emission rate is often defined as the sum of spontaneous and stimulated contributions

$$R_{em} = R_{sp} + R_\downarrow \quad (14)$$

**Absorption coefficient** (or attenuation coefficient),  $a(E)$ ,  $[L^{-1}]$

The absorption coefficient expresses the amount of radiation energy absorbed by the medium per unit of traveled distance. The influence on the light intensity is given by the Beer-Lambert law, which basically expresses the conservation of energy.

The absorption coefficient is related to the *extinction coefficient*  $n''$ , which is the imaginary part of the medium optical index

$$a(E) = \frac{4\pi}{\lambda} n''(E) \quad (15)$$

where the factor 4 comes from the fact that intensities (rather than amplitudes) are considered.

The absorption coefficient is related to the net absorption rate

$$R_\uparrow - R_\downarrow = a(E) j_\gamma(E) = a(E) \frac{c}{n} n_\gamma(E) \quad (16)$$

Note that the absorption coefficient depends on the occupation of energy levels [1], even though this dependency is omitted most of the time.

**Absorptivity / emissivity**  $\alpha(E)$ ,  $\epsilon(E)$ , dimensionless,  $\leq 1$ .

It is customary to compare the ability of a non-black body to absorb or emit a radiation to that of a black body at the same temperature. The ratio between their exitance is given by the emissivity

$$\epsilon(E, T) = \frac{M_E(E, T)}{M_E^{BB}(E, T)} \quad (17)$$

The absorptivity is the fraction of incident power actually absorbed by the body (for a black body,  $\alpha(E, T) = 1$ ). As will be shown below, Kirchhoff's law of thermal radiation imposes  $\alpha(E) = \epsilon(E)$ .

The absorptivity can related to the absorption coefficient. Consider a slab of thickness  $d$ , in which the light can perform multiple reflections ; the fraction of absorbed power is

$$\alpha(E) = \frac{(1 - R(E)) (1 - e^{-a(E)d})}{1 - R(E) \times e^{-a(E)d}} \quad (18)$$

where  $R(E)$  is the reflection coefficient from the outside towards the slab. If multiple reflection are not considered, the denominator should be omitted.

## 2 Thermodynamics of a (blackbody) radiation in a cavity

As photons do not interact with themselves, the entropy of the whole distribution is conserved owing to the H-theorem and photons can not reach spontaneously a thermal equilibrium, in which the entropy is supposed to be maximal. To study a thermal ensemble of photons, we must therefore include in our description some matter, through which photons to interact [6].

### 2.1 Photon and energy density

There are several ways to recover the photon and energy distribution of the radiation trapped inside a blackbody, and each of them underline critical aspect of the underlying physics.

In this section, we first admit this expression and derive familiar results of blackbody physics. We will then consider four complementary ways to reach this expression.

#### 2.1.1 Final result : Particle and energy density within the cavity

Eventually, all approaches reach the same point, namely, the photon density at a given energy  $E$ , going in a give direction  $\Omega$

$$n_\gamma(E, \Omega) = \frac{E^2}{4\pi^3 \hbar^3 c^3} \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1} \quad (19)$$

and the energy spectrum is given by the distribution

$$u_E(E, \Omega) = E n_\gamma(E, \Omega) = \frac{E^3}{4\pi^3 \hbar^3 c^3} \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1} \quad (20)$$

Note that this expression is *not* Planck law. Planck law describes the spectrum of the radiation exiting the blackbody, while this expression describes the steady state of the radiation within the blackbody.

**Side remarks** changing units

$u_E(E, \Omega)$	$u_\omega(\omega, \Omega)$	$u_\nu(\nu, \Omega)$	$u_\lambda(\lambda, \Omega)$
$\frac{E^3}{4\pi^3 \hbar^3 c^3} \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1}$	$\frac{(\hbar\omega)^3}{4\pi^3 \hbar^2 c^3} \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$	$\frac{(h\nu)^3}{2\pi^2 \hbar^2 c^3} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}$	$\frac{2hc}{\lambda^5} \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1}$
$E_{\max} = 2.82 k_B T$	$\hbar\omega_{\max} = 2.82 k_B T$	$h\nu_{\max} = 2.82 k_B T$	$\lambda_{\max} = 0.2497 \frac{\text{m eV}}{k_B T}$

It is at first tricky to switch from frequency to wavelength description : it appears that  $\lambda_{\max} \neq \nu_{\max} c$  ! Keep in mind that we are here dealing with energy densities ; to get from one to the other, we need to consider the corresponding differential quantity

$$u(E)dE = u(\omega)d\omega = u(\lambda)d\lambda \quad (21)$$

Notably, the units these densities are different !

Integrated quantities can be easily obtained<sup>2</sup>. The total density of photons is given by

$$n_\gamma = \int dE d\Omega n_\gamma(E, \Omega) = \underbrace{2\zeta(3)}_{\sim 2.4} \times \frac{k_B^3 T^3}{\pi^2 \hbar^3 c^3} \quad (22)$$

<sup>2</sup>provided the integral  $\int_0^\infty du \frac{u^3}{e^u - 1} = \frac{\pi^4}{15}$  is given !

and the derivation of the energy density is

$$u = \int dE d\Omega u_E(E, \Omega) = \frac{4}{c} \sigma T^4 \quad (23)$$

Note that this expression is *not* the familiar  $\sigma T^4$  law, which accounts for the energy *leaving* the cavity. For the time being, the cavity is closed and we are calculating properties of the photon gas at equilibrium. We introduced the Stefan constant (memo hint :  $\sigma$  value is 5-6-7-8 in standard units)

$$\sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} \simeq 5.67 \times 10^{-8} \text{ W.m}^{-2}.\text{K}^{-4} \quad (24)$$

From there, we can easily estimate the average energy per photon :

$$\langle \hbar\omega \rangle = e/n_\gamma = 2.7 k_B T \quad (25)$$

### 2.1.2 Standard approach : Photon density of state and occupation number

The usual way to do this is to consider a cavity of typical size  $L$ , at a temperature  $T$ , in thermal equilibrium with a gas of photons trapped inside. As the size of the box does not matter, we will consider the gas spatially uniform and deal with volumic quantities.

We first calculate the density of states for photons. The energy carried by a photon of wave vector  $\mathbf{k}$  is

$$E = \hbar k \tilde{c} \quad (26)$$

where  $\tilde{c} = c/n$  is the average velocity of photons in the box<sup>3</sup>. Each state can be characterized by a wave vector  $\mathbf{k} = \frac{2\pi}{L} (n_x, n_y, n_z)$ , and the density of states is therefore given by

$$D_\gamma(\mathbf{k}) = 2 \left( \frac{L}{2\pi} \right)^3 \quad (27)$$

where the factor 2 accounts for the polarization of the photons. The density of states with a given modulus  $|k|$  is thus

$$D_\gamma(k) = \int d\mathbf{q} D_\gamma(\mathbf{q}) \delta(k - q) = 8\pi k^2 \left( \frac{L}{2\pi} \right)^3 \quad (28)$$

and considering  $D_\gamma(k)dk = D_\gamma(E)dE$ , we get the volumic density of state and the angular volumic density of state

$$D_\gamma(E) = D_\gamma(k) \frac{dk}{dE} = \frac{(\hbar\omega)^2}{\pi^2 \hbar^3 c^3} \quad D_{\gamma,\Omega}(E) = \frac{1}{4\pi} D_\gamma(E) \quad (29)$$

We admit that the occupancy of any energy state is given by the Bose-Einstein distribution

$$f_{BE}(E, \mu) = \frac{1}{\exp\left(\frac{1}{k_B T} (E - \mu)\right) - 1} \quad (30)$$

For a thermal radiation,  $\mu = 0$ . This will not be the case for the radiation of a semiconductor, as well be discussed later.

The volumic density of photons with a given energy  $E$  and direction  $\Omega$  is then

$$n_\gamma(E, \Omega) = D_{\gamma,\Omega}(E) f_{BE}(E) = \frac{E^2}{4\pi^3 \hbar^3 c^3} \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1} \quad (31)$$

#### Side remark Chemical potential

*Several arguments are generally given to show that the chemical potential of light is always zero. All of them are based on the fact, that photons are easily created and annihilated. The essence of the reasoning is that "...the absence of a conservation law for*

<sup>3</sup>In the following, we will assume  $n = 1$  for simplicity



photons leads to a zero value for the chemical potential.”

Non conservation of particle number by itself is not an argument for a zero chemical potential, because non conservation of particles is not restricted to photons. For example, consider a chemical reaction. Although the particle numbers are not conserved, the chemical potentials of the involved substances are nonzero. The chemical potentials of the products adjust to those of the reactants.

The same applies to photons. They are created or annihilated in “reactions” involving the excitations of matter, such as phonons and electron-hole pairs. The excitations of matter must be involved because although particle number is not conserved, the photon momentum and angular momentum are conserved, which does not allow an unrestricted variation of the photon number. This conservation leads to the well known selection rules for the interactions of photons with the excitations of matter. The photons derive their temperature and chemical potential from these interactions.

Würfel, [20] p181

### 2.1.3 Einstein coefficients approach - detail balance relation

In the previous approach, we considered that photons were only interacting with the walls of the cavity - which is sufficient to insure their thermalization. Let us now imagine that the cavity is actually filled with matter, in order to consider in more details the light-matter interaction responsible for this equilibration.

As a first model, we present the historical approach of Einstein coefficients [9], where matter is pictured by a very simple description.

#### Assumptions

1. We consider only two energy levels, labeled 1 and 2.
2. The population of each energy level is given by a Boltzmann distribution

$$N_i = \frac{g_i}{Z} e^{-\frac{E_i}{kT}} \quad (32)$$

where  $g_i$  is the degeneracy of the energy level and  $Z$  the partition function

3. The high and low energy behaviors of the blackbody distribution, as given by Wien law (eq (92)) and Rayleigh-Jeans law (eq (3.3.2)), are known from experimental measurements
4. Population dynamics are given by classical rate equations

$$\frac{dN_1}{dt} = +N_2 A_{21} + N_2 B_{21} u_\omega(T) - N_1 B_{12} u_\omega(T) \quad (33)$$

$$\frac{dN_2}{dt} = -N_2 A_{21} - N_2 B_{21} u_\omega(T) + N_1 B_{12} u_\omega(T) \quad (34)$$

where  $u_\omega(T)$  is the energy density of the radiation. The first term accounts for spontaneous emission  $2 \rightarrow 1$ , the second term corresponds to stimulated emission and the last one to absorption.

In steady state situation,

$$\frac{dN_2}{dt} = 0 \Rightarrow N_1 B_{12} u_\omega(T) = N_2 (A_{21} + B_{21} u_\omega(T)) \quad (35)$$

Considering Boltzmann distribution for the populations (assumption 2), and assuming that  $n_\gamma(\omega) \xrightarrow{T \rightarrow \infty} +\infty$ , the previous equality requires

$$B_{12} g_1 = B_{21} g_2 \quad (36)$$

and from there, the detailed balance leads to

$$u_\omega(T) = \frac{A_{21}/B_{21}}{\exp\left(\frac{E_2 - E_1}{k_B T}\right) - 1} \quad (37)$$

The comparison with Wien’s and Rayleigh-Jeans’ laws (assumption 3 and 4) gives Planck distribution:

$$\hbar\omega = E_2 - E_1 \quad \frac{A_{21}}{B_{21}} = \frac{\hbar}{\pi^2} \frac{\omega^3}{c^3} \quad (38)$$

and the emission and absorption rates per atom can be estimated as

$$\Gamma_{\uparrow} = \frac{R_{\uparrow}}{N_1} = A_{21} \frac{1}{\exp\left(\frac{E_2 - E_1}{k_B T}\right) - 1} \quad (39)$$

$$\Gamma_{\text{em}} = \frac{R_{\text{em}}}{N_2} = A_{21} \left( \frac{\exp\left(\frac{E_2 - E_1}{k_B T}\right)}{\exp\left(\frac{E_2 - E_1}{k_B T}\right) - 1} \right) \quad (40)$$

### Connection to detailed balance relation (inspired by Christophe Texier)

/!\ Might be a bit technical /!\

This simple model can be used to illustrate the detailed balance relation, which in its most generic form can be expressed as

$$\tilde{C}_{BA}(-\omega) = \tilde{C}_{AB}(\omega) e^{-\frac{\hbar\omega}{k_B T}} \quad (41)$$

where  $\tilde{C}_{AB}(\omega) = \int_{-\infty}^{+\infty} d\tau e^{i\omega\tau} \langle B(\tau)A \rangle$  is the Fourier transform of the correlation function of observables  $A$  and  $B$ .

To see this, consider a quantum description of the two levels system coupled to an electromagnetic radiation. The Hamiltonian of such a system is

$$\hat{H} = E_1 \underbrace{|g\rangle\langle g| + E_2 |e\rangle\langle e|}_{H_0} - \underbrace{X \cdot \sigma_x}_{H_{\text{int}}} \quad (42)$$

where  $\sigma_x$  couples together the excited and ground state, and  $X$  is an observable of the system driving the transition. In this example,  $X$  could be the electric field of the electromagnetic radiation.

Considering the time evolution of the system as given by Schrodinger equation, we can estimate the probability  $\mathcal{P}_{\uparrow}(t)$  that a system initially in the state  $|\psi(0)\rangle = |g\rangle \otimes |\phi_n\rangle$  (where  $|\phi_n\rangle$  is a state of the electromagnetic radiation) is transferred to the excited state at time  $t$

$$\mathcal{P}_{\uparrow}^{\phi_n}(t) = \frac{1}{\hbar^2} \int_0^t d\tau d\tau' e^{-i\omega_0(\tau-\tau')} \langle \phi_n | X(\tau)X(\tau') | \phi_n \rangle \quad (43)$$

where we introduced  $\hbar\omega_0 = E_2 - E_1$ . The total absorption probability is obtained summing over all possible states of the electromagnetic radiation, weighted by the probability  $p_{\phi_n}$  of realization:

$$\begin{aligned} \mathcal{P}_{\uparrow}(t) &= \sum_n p_{\phi_n} \mathcal{P}_{\uparrow}^{\phi_n}(t) = \frac{1}{\hbar^2} \int_0^t d\tau d\tau' e^{-i\omega_0(\tau-\tau')} \langle X(\tau)X(\tau') \rangle \\ &\simeq \frac{t}{\hbar^2} \tilde{C}_{XX}(-\omega) \end{aligned} \quad (44)$$

and the absorption rate per atom is thus related to the autocorrelation function as

$$\Gamma_{\uparrow} = \frac{d}{dt} \mathcal{P}_{\uparrow}(t) = \frac{1}{\hbar^2} \tilde{C}_{XX}(-\omega) \quad (45)$$

The same derivation can be performed for the total emission process (including spontaneous and stimulated emission), leading to

$$\Gamma_{\text{em}} = \frac{1}{\hbar^2} \tilde{C}_{XX}(\omega) \quad (46)$$

and the detailed balance relation eq.(41) can be re-written as a balance between absorption and emission processes

$$\Gamma_{\uparrow} = \Gamma_{\text{em}} e^{-\frac{\hbar\omega_0}{k_B T}} \quad (47)$$

## 2.1.4 Light-matter interaction approach - important for semiconductors results

/!\ Might be a bit technical /!\

We now turn to a more thorough description of the light matter interaction, based on Fermi Golden Rule. This approach is more general than the simple case of blackbody (where no chemical potential is considered) and serves as demonstration for the Van Roosbroeck - Shockley equation (eq. (60), [19]) that is of much use in solar cells physics.

### Absorption rate

Consider a quantum state  $\psi_1$  absorbing a photon of energy  $\hbar\omega$ . According to Fermi Golden Rule weighted by the occupancy of the excited state, the absorption rate can be estimated as

$$W_{1\uparrow}(\hbar\omega) = \frac{2\pi}{\hbar} \sum_{\psi_2} |M_{12}|^2 \delta(E_1 + \hbar\omega - E_2) \times (1 - f_2) \quad (48)$$

where  $\psi_2$  are all possible final states for this transition,  $f_2$  is the occupancy of this state,  $E_{1,2}$  is the energy of  $|\psi_{1,2}\rangle$  state and  $M_{12} = \langle\psi_2|V|\psi_1\rangle$  is the matrix element coupling the initial and final states through the interaction Hamiltonian  $V = -\mathbf{A}\cdot\mathbf{p}$ ,  $\mathbf{A}$  being the vector potential of the field<sup>4</sup> and  $\mathbf{p}$  the momentum operator. We

There are possibly several states  $\psi_1$  which can absorb a photon of energy  $\hbar\omega$ , and there are  $n_\gamma(\hbar\omega)$  photon with that energy per volume unit. The volumic absorption rate at this energy is thus

$$R_\uparrow(\hbar\omega) = n_\gamma(\hbar\omega) \sum_{\psi_1} W_{1\uparrow}(\hbar\omega) \times f_1 \quad (49)$$

$$= \frac{2\pi}{\hbar} n_\gamma(\hbar\omega) \int d\mathbf{k}_2 d\mathbf{k}_1 \rho_1(\mathbf{k}_1) \rho_2(\mathbf{k}_2) |M_{12}|^2 \delta(E_1 + \hbar\omega - E_2) \times f_1 (1 - f_2) \quad (50)$$

where we used the continuous expression of the sum  $\sum_{\psi_i} \rightarrow \int d\mathbf{k}_i \rho_i(\mathbf{k}_i)$ .

**Note** While this generic expression is somehow ugly, it reduces to familiar results in specific cases.

For instance, consider a direct transition in semiconductor. If the initial and final states are described by Bloch states ( $\psi_{1,2}(\mathbf{r}) = u_{1,2}(\mathbf{r})e^{i\mathbf{k}_{1,2}\cdot\mathbf{r}}$ ), then the matrix element imposes the selection rule  $\mathbf{k}_2 = \mathbf{k}_1$ . At low temperature ( $f_1 \simeq 1$ ,  $f_2 \simeq 0$ ) and considering the product  $\langle u_1 | \mathbf{p} | u_2 \rangle$  to be essentially the same for all states concerned by the transition,

$$R_\uparrow(\hbar\omega) = \frac{2\pi}{\hbar} n_\gamma(\hbar\omega) |M'_{12}|^2 \rho_{\text{JDOS}}(\hbar\omega) \quad (51)$$

where  $M'_{eg} = -\mathbf{A}\cdot\langle u_1 | \mathbf{p} | u_2 \rangle$  and the joint density of state is define

$$\begin{aligned} \rho_{\text{JDOS}}(\hbar\omega) &= \int d\mathbf{k} \rho_1(\mathbf{k}) \rho_2(\mathbf{k}) \delta(E_1 + \hbar\omega - E_2) \\ &\propto \sqrt{\hbar\omega - E_g} \end{aligned}$$

and we recover the well known square root dependence of the absorption coefficient.

Another option is to consider an indirect transition, where momentum is not conserved. In this case, we can consider that the matrix element  $M_{12}$  only depends the initial and final states' energy. If we assume this coupling to be the same for all allowed transitions, we find

$$R_\uparrow(\hbar\omega) = \frac{2\pi}{\hbar} n_\gamma(\hbar\omega) |M_{12}|^2 \int dE_1 \rho_1(E_1) \rho_2(E_1 + \hbar\omega) \quad (52)$$

$$\propto (\hbar\omega - E_g)^2 \quad (53)$$

and we recover the well known square dependence of the absorption coefficient.

### Emission rate

<sup>4</sup>Here, we consider a full quantum treatment where  $\mathbf{A}$  is an operator and does not include informations about the field state.

The rate for an excited state  $\psi_2$  to decay by stimulated emission can be expressed in the same way, by inverting the occupation factors (the upper state should be initially occupied, and the lower state free) :

$$R_{\downarrow}(\hbar\omega) = \frac{2\pi}{\hbar} n_{\gamma}(\hbar\omega) \int d\mathbf{k}_2 d\mathbf{k}_1 \rho_1(\mathbf{k}_1) \rho_2(\mathbf{k}_2) |M_{12}|^2 \delta(E_1 + \hbar\omega - E_2) \times f_2 (1 - f_1) \quad (54)$$

The spontaneous decay can also be expressed through the Fermi Golden Rule, considering that in the final state, the emitted photon can occupy any available mode  $D_{\gamma}$ :

$$R_{\text{sp}}(\hbar\omega) = \sum_{\psi_2} f_2 \left( \frac{2\pi}{\hbar} \sum_{\psi_1, E_{\gamma}} |M_{12}|^2 \delta(E_1 + E_{\gamma} - E_2) \delta(E_{\gamma} - \hbar\omega) \times (1 - f_1) \right) \quad (55)$$

$$= \frac{2\pi}{\hbar} D_{\gamma}(\hbar\omega) \int d\mathbf{k}_2 d\mathbf{k}_1 \rho_1(\mathbf{k}_1) \rho_2(\mathbf{k}_2) |M_{12}|^2 \delta(E_1 + \hbar\omega - E_2) \times f_2 (1 - f_1) \quad (56)$$

**Note** The proper way to estimate the emission rate depends on how the field is treated. In a full quantum picture, as above,  $\mathbf{A}$  can be expressed with creation and annihilation operators, and includes spontaneous emission. In a semi classic picture,  $\mathbf{A}$  is simply a vector whose module (squared) is related the photon density. Spontaneous emission is not included here, and has to be added by hand. This can be done by taking the quantum result (rate  $\propto n_{\gamma} + 1$ ), by taking the photon density as given by eq.19.

**Note** From the definition of the absorption rate and absorption coefficient, we can identify

$$a(\hbar\omega) = \frac{n}{c} \times \frac{2\pi}{\hbar} \int d\mathbf{k}_2 d\mathbf{k}_1 \rho_1(\mathbf{k}_1) \rho_2(\mathbf{k}_2) |M_{12}|^2 \delta(E_1 + \hbar\omega - E_2) \times (f_1 - f_2) \quad (57)$$

### Photon balance

In steady state, the absorption and emission processes must balance (this will not be the case when considering the radiation of a blackbody, see below)

$$0 = R_{\text{sp}}(\hbar\omega) + R_{\downarrow}(\hbar\omega) - R_{\uparrow}(\hbar\omega)$$

$$\Rightarrow n_{\gamma}(\hbar\omega) = D_{\gamma}(\hbar\omega) \frac{\int d\mathbf{k}_2 d\mathbf{k}_1 \rho_1(\mathbf{k}_1) \rho_2(\mathbf{k}_2) |M_{12}|^2 \delta(E_1 + \hbar\omega - E_2) \times (f_1 - f_2) \times \frac{f_2(1-f_1)}{(f_1-f_2)}}{\int d\mathbf{k}_2 d\mathbf{k}_1 \rho_1(\mathbf{k}_1) \rho_2(\mathbf{k}_2) |M_{12}|^2 \delta(E_1 + \hbar\omega - E_2) \times (f_1 - f_2)}$$

Considering that the occupation factor are given by  $f_i = \left( \exp\left(\frac{E_i - \mu_i}{k_B T}\right) + 1 \right)^{-1}$ , the last factor in the upper integrand can be rewritten as

$$\frac{f_2(1-f_1)}{(f_1-f_2)} = \frac{1}{\exp\left(\frac{E_2 - E_1 - (\mu_2 - \mu_1)}{k_B T}\right) - 1} \quad (58)$$

which remarkably does not depend on the integrated variables, since  $E_2 - E_1 = \hbar\omega$ . This factor can be taken out of the integral, and the ratio simplifies to 1. From there, the photon distribution can be calculated as:

$$n_{\gamma}(\hbar\omega) = D_{\gamma}(\hbar\omega) \frac{1}{\exp\left(\frac{\hbar\omega - \Delta\mu}{k_B T}\right) - 1} \quad (59)$$

where  $\Delta\mu = \mu_2 - \mu_1$  is the quasi Fermi levels splitting (see sec. 4.4), which is 0 for a thermal blackbody radiation.

**Note** From here, it is straight forward to reach the Van Roosbroeck–Shockley [19, 8, 3] equation<sup>5</sup>, which expresses the spontaneous emission rate:

$$R_{\text{sp}}(\hbar\omega) = R_{\uparrow}(\hbar\omega) - R_{\downarrow}(\hbar\omega)$$

$$= a(\hbar\omega) \frac{(\hbar\omega)^2}{\pi^2 \hbar^3 c^3} \frac{1}{\exp\left(\frac{\hbar\omega - \Delta\mu}{k_B T}\right) - 1} \quad (60)$$

<sup>5</sup>Properly speaking, Van Roosbroeck and Shockley considered a body with non-unit absorptivity. The idea of non-zero chemical potential was introduced by Lasher and Stern in 1964.

Note also that this relation is *not*, properly speaking, the generalized Planck law. The generalized Planck law expresses the radiation emitted from the blackbody towards the exterior ; while the Van Roosbroeck–Shockley relation accounts for the recombination rate *within* the blackbody cavity. This difference will be discussed in more details in section 3.1.

### 2.1.5 Density matrix approach - Important for entropy results

/!\ Might be a bit technical /!\

From a quantum perspective, the free electromagnetic field is described by the Hamiltonian

$$H = \sum_l \left( \hat{n}_l + \frac{1}{2} \right) \hbar \omega_l \quad (61)$$

where each mode  $l$  is defined by a frequency  $\omega_l$  and a polarization  $\mathbf{s}_l$ . The black body radiation corresponds to a thermal state

$$\rho = \frac{1}{Z} \exp \left( -\frac{1}{k_B T} \hat{H} \right) \quad (62)$$

$$Z = \text{Tr} \left( \exp \left( -\frac{1}{k_B T} \hat{H} \right) \right) \quad (63)$$

where we introduced the partition function  $Z$ . From there, using  $\text{Tr} \left( \exp \left( -\sum_l \frac{\hbar \omega_l}{k_B T} \hat{n}_l \right) \right) = \prod_l \frac{1}{1 - \exp \left( -\frac{\hbar \omega_l}{k_B T} \right)}$ , we get the diagonal terms of the density matrix, which give the probability for each occupation and for each mode

$$p(n_l) = \rho_{n_l, n_l} = \left( 1 - e^{-\frac{\hbar \omega_l}{k_B T}} \right) \exp \left( -\frac{\hbar \omega_l}{k_B T} n_l \right) \quad (64)$$

and the average photon number in any mode is given by

$$\langle \hat{n}_l \rangle = \sum_{n_l} n_l \rho_{n_l, n_l} = \frac{1}{e^{\frac{\hbar \omega_l}{k_B T}} - 1} \quad (65)$$

We can also express the probability to find  $n$  photon in the  $l$ -mode as a function of the average photon number in this mode

$$p_l(n) = \frac{1}{1 + \langle \hat{n}_l \rangle} \left( \frac{\langle \hat{n}_l \rangle}{1 + \langle \hat{n}_l \rangle} \right)^n \quad (66)$$

## 2.2 Thermodynamic quantities

### Heat capacity

The heat capacity accounts for the energy required to increase the temperature of the radiation inside the cavity. Its volumic expression is given by

$$c_V = \frac{\partial}{\partial T} u = 16 \frac{\sigma}{c} T^3 \quad (67)$$

### Pressure

To calculate the ambient pressure inside the cavity, we perform a momentum balance one one side of a fictitious surface  $d\mathbf{S}$ .

For each solid angle  $d\Omega$ , over the period  $dt$ , a number  $n_\gamma(E, \Omega) d\Omega dE \times c dt \times \cos \theta dS$  of photons with the energy  $E$  cross this surface, each of them carrying the momentum  $\hbar k \mathbf{u}_\Omega$ . When summing over all directions, only the normal component  $\hbar k \cos \theta$  contribute to the total momentum and we find

$$dP_{\text{tot}} = \underbrace{\left( \int dE d\Omega E \times n_\gamma(E, \Omega) \cos^2 \theta \right)}_{=u/3} \times dS \cdot dt \quad (68)$$

where we used  $\int \cos^2 \theta \sin \theta = \frac{1}{3}$ . From there, we identify the pressure inside the gas as

$$p = \frac{u}{3} = \frac{4\sigma}{3c} T^4 \quad (69)$$

## Entropy

The entropy is defined from the probability  $P(n_1, n_2, \dots)$  of finding exactly  $n_1$  photons in the mode 1,  $n_2$  photons in the mode 2 etc.

$$S = -k_B \sum_{n_1} \sum_{n_2} \dots P(n_1, n_2, \dots) \log P(n_1, n_2, \dots) \quad (70)$$

As all modes are independent,  $P(n_1, n_2, \dots) = p_1(n_1)p_2(n_2)\dots$ , where the probability  $p_l(n_l)$  of getting  $n_l$  photons in the  $l^{\text{th}}$  mode. Using the normalization of the probability law  $\sum_n p_l(n) = 1$ , we express the total entropy as the sum of the entropy of each mode:

$$S = \sum_{\text{mode}} \underbrace{-k_B \sum_n p_l(n_l) \log p_l(n_l)}_{S_l} \quad (71)$$

The single mode entropy  $S_l$  can be inferred from the expression eq.(66)<sup>6</sup>:

$$S_l = k_B [(1 + \langle \hat{n}_l \rangle) \log(1 + \langle \hat{n}_l \rangle) - \langle \hat{n}_l \rangle \log \langle \hat{n}_l \rangle] \quad (72)$$

To estimate the total entropy density, we consider the transition to continuum, with  $f_{\text{BE}}(E) = (e^{\beta E} - 1)^{-1}$ :

$$\begin{aligned} s_E(E, \Omega) &= D_\Omega(E) S_l \\ &= k_B \frac{E^2}{4\pi^3 \hbar^3 c^3} [(1 + f_{\text{BE}}(E)) \log(1 + f_{\text{BE}}(E)) - f_{\text{BE}}(E) \log(f_{\text{BE}}(E))] \end{aligned} \quad (73)$$

leading to

$$s = \int dV d\Omega s_E(E, \Omega) = \frac{16\sigma}{3c} T^3 \quad (74)$$

Derivation  $\backslash$  Might be a bit technical  $\backslash$

We first re-write the entropy density as

$$s_E(E, \Omega) = \frac{k_B}{4\pi^3 \hbar^3 c^3} \left[ \frac{1}{k_B T} \frac{E^3}{e^{\frac{E}{k_B T}} - 1} + \frac{1}{k_B T} E^3 + E^2 \log \left( \frac{1}{e^{\frac{E}{k_B T}} - 1} \right) \right]$$

The first term is  $u(E, \Omega)/T$  and its integration gives  $\frac{\sigma}{c} T^3$ . The second and third terms can be integrated by parts

$$\int dE E^2 \log \left( \frac{1}{e^{\frac{E}{k_B T}} - 1} \right) = \left[ \frac{E^3}{3} \log \left( \frac{1}{e^{\frac{E}{k_B T}} - 1} \right) \right]_0^\infty - \int dE \frac{E^3}{3} \left( 1 + \frac{1}{e^{\frac{E}{k_B T}} - 1} \right)$$

which gives an additional  $\frac{\sigma}{c} T^3/3$  contribution, hence the result.

## Side remark

Another approach would be to start from the fundamental thermodynamic relation at zero chemical potential

$$dU = TdS - pdV \quad (75)$$

and considering  $U = u \times V$  and  $S = s \times V$ , we obtain

$$ds = \left( \frac{16\sigma}{3c} T^3 - s \right) \frac{dV}{V} + 16 \frac{\sigma}{c} T^2 dT \quad (76)$$

---

<sup>6</sup>  $-\sum_n \left( \frac{1}{1+\langle \hat{n}_l \rangle} \left( \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \right)^n \log \left( \frac{1}{1+\langle \hat{n}_l \rangle} \left( \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \right)^n \right) \right) = \frac{1}{1+\langle \hat{n}_l \rangle} \log(1 + \langle \hat{n}_l \rangle) \sum_n \left( \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \right)^n + \frac{1}{1+\langle \hat{n}_l \rangle} \log \left( \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \right) \sum_n n \left( \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \right)^n$ , and  $\sum_n \left( \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \right)^n = \langle \hat{n}_l \rangle$  while  $\sum_n n \left( \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \right)^n = \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \sum_n n \left( \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \right)^{n-1} = \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \frac{\partial}{\partial \alpha} \left( \sum_n \left( \alpha \frac{\langle \hat{n}_l \rangle}{1+\langle \hat{n}_l \rangle} \right)^n \right) \Big|_{\alpha=1} = \langle \hat{n}_l \rangle (1 + \langle \hat{n}_l \rangle)$

Integrating this equation over the temperature at constant volume, and considering  $s(0\text{ K}) = 0$  leads to

$$s = \frac{16}{3} \frac{\sigma}{c} T^3 \quad (77)$$

### Partition function and thermodynamic potential

The previous results can also be obtained straightforwardly from the partition function  $Z$  introduced in eq.(63), which gives access to the thermodynamical potential

$$\begin{aligned} F &= -k_B T \times \log Z \\ &= -\frac{1}{3} u V = -\frac{4}{3} V \frac{\sigma}{c} T^4 \end{aligned} \quad (78)$$

Entropy, pressure and energy can be derived directly from the free energy  $F$ :

$$\begin{aligned} s &= -\frac{1}{V} \left( \frac{\partial F}{\partial T} \right) \Big|_{V, \mu} & p &= - \left( \frac{\partial F}{\partial V} \right) \Big|_{T, \mu} & u &= \frac{1}{V} (F + TS) \\ &= \frac{16}{3c} \sigma T^3 & &= \frac{4}{3} V \frac{\sigma}{c} T^4 = \frac{u}{3} & &= \frac{4}{c} \sigma T^4 \end{aligned}$$

### 2.3 Thermodynamic cycles

Just like any other fluid, a photon gas can undergo cycles of transformations and we have now all required tools to describe it. In this section, we consider for instance a Carnot cycle defined as follows

1. Reversible isothermal expansion  $V_A \rightarrow V_B$  of the gas at the "hot" temperature. During this step, the gas receives heat to produce work.

$$\begin{aligned} \Delta U_1 &= u(T_H) \Delta V = \frac{4}{c} \sigma T_H^4 (V_B - V_A) \\ \Delta S_1 &= s(T_H) \Delta V = \frac{16}{3c} \sigma T_H^3 (V_B - V_A) \end{aligned}$$

As the transformation is reversible, no entropy is created and  $\Delta S_1 = Q_1/T_H$ . We can thus estimate the heat and work provided to the photon gas during this step

$$\begin{aligned} Q_1 &= \frac{16}{3c} \sigma T_H^4 V_B \left( 1 - \frac{V_A}{V_B} \right) \geq 0 \\ W_1 &= \Delta U_1 - Q_1 = -\frac{4}{3c} \sigma T_H^4 V_B \left( 1 - \frac{V_A}{V_B} \right) \leq 0 \end{aligned}$$

Alternatively, the work can be calculated as  $W_1 = -p(T_H) \Delta V$ , reaching the same result.

2. Isentropic adiabatic expansion  $V_B \rightarrow V_C$  of the gas, such that the temperature reduces from  $T_H$  to  $T_C$ . During this step, the system cools down to produce work.

As the entropy is a state function, its variation during this step can be expressed as a function of the initial and final parameters only

$$\Delta S_2 = 0 = s(T_C) V_C - s(T_H) V_B$$

from where we estimate the relation

$$\frac{V_C}{V_B} = \frac{T_H^3}{T_C^3}$$

The energy change of the system is therefore

$$\Delta U_2 = W_2 = u(T_C) V_C - u(T_H) V_B = \frac{4}{c} \sigma T_H^4 V_B \left( \frac{T_C}{T_H} - 1 \right) \geq 0$$

3. Reversible isothermal compression  $V_C \rightarrow V_D$  of the gas at the "cold" temperature. During this step, the system receives work to produce heat.

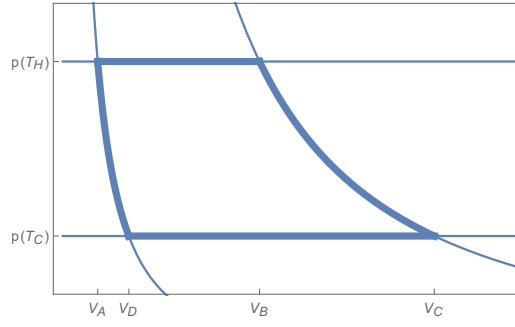


Figure 2: Carnot cycle for a photon gas. Note that the pressure of a photon gas depends solely on the temperature and isothermal transformations are therefore also isobar (horizontal line, unlike the parabolic  $p = \frac{nRT}{V}$  behavior of a classical gas). The isentropic evolution follows  $VT^3 = \text{cst} \Leftrightarrow pV^{3/4} = \text{cst}$  (unlike  $pV^\gamma = \text{cst}$  for a classical gas)

As in step one,

$$Q_3 = \frac{16}{3c}\sigma T_C^4 V_D \left(1 - \frac{V_C}{V_D}\right) \leq 0$$

$$W_3 = -\frac{4}{3c}\sigma T_C^4 V_D \left(1 - \frac{V_C}{V_D}\right) \geq 0$$

4. Isentropic adiabatic compression  $V_D \rightarrow V_A$  of the gas, such that the temperature rises from  $T_C$  to  $T_H$ . The system receives work to work to heat up.

As in step two,

$$W_4 = \frac{4}{c}\sigma T_C^4 V_D \left(\frac{T_H}{T_C} - 1\right)$$

and

$$\frac{V_D}{V_A} = \frac{T_H^3}{T_C^3} = \frac{V_C}{V_B}$$

The total work  $W_{\text{out}} = -\sum W_i$  performed by the system is therefore

$$W_{\text{out}} = \frac{4}{3c}\sigma T_H^4 V_B \left(1 - \frac{V_A}{V_B}\right) \left(1 - \frac{T_C}{T_H}\right)$$

$$= -(Q_1 + Q_2)$$

where the second equality simply results from the energy conservation over one cycle  $\Delta U_{\text{tot}} = 0$ . The efficiency is defined as the total work  $W = \sum W_i$  performed by the system divided by the heat  $Q_1$  provided during the cycle and takes the exact same form as for a classical gas

$$\eta = \frac{W}{Q_1} = \left(1 - \frac{T_C}{T_H}\right) \quad (79)$$

Carnot cycle is therefore the same for a classical or a photon gas.

### 3 Thermodynamics of a black body radiation in free space

So far, we only considered the properties of the radiation at equilibrium inside the cavity. What actually really interest us are the properties of the radiation emitted by the cavity towards free space. However, deriving emission properties from the previous study is not straightforward, and has to be done carefully. More generally, the connection between what is happening inside an absorber and what can be collected from its surface is a topic of broad interest, that notably inspired the reciprocity theorems by Rau [14, 5].

In this section, we will first discuss how to relate emission properties to the equilibrium properties of the radiation inside the cavity, then apply these results to the blackbody radiation studied before.



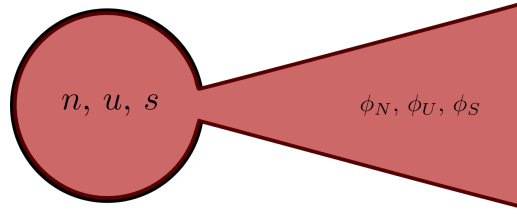


Figure 3: Blackbody properties (particle, energy and entropy densities) relate to a photon gas at equilibrium within the cavity. The blackbody *radiation* concern fluxes emitted from the cavity. As photons can not interact anymore once they escaped the blackbody, the radiation is fundamentally a non-equilibrium process.

### 3.1 Inside out

The main result in this part is that the output flux  $d\phi_N(E, \Omega)$  of photons at energy  $E$  emitted in the direction  $d\Omega$  can be related to the photon density inside the cavity as

$$d\phi_N(E, \Omega) = \alpha(E, \Omega) \times \frac{c}{4\pi} n_\gamma(E) \cdot \cos \theta d\Omega dE dA = \alpha(E, \Omega) \times \frac{c}{4\pi} n_\gamma(E) \frac{d\mathcal{E}}{n^2} dA \quad (80)$$

where  $0 \leq \alpha \leq 1$  is the body absorptivity. For a blackbody,  $\alpha = 1$ . This is not necessarily the case for a gray-body, as will be discussed in the following section.

The table below summarizes the expressions of the radiation inside the body, the emission rate inside the body, and the emission rate towards the exterior. These results are demonstrated in the next subsections.

	Blackbody $\mu = 0$	Gray-body $\mu \neq 0$
In the cavity eq. (20)	Bose Einstein $u_E(E, \Omega) = \frac{E^3}{4\pi^3 \hbar^3 c^3} \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1}$	Bose Einstein $u_E(E, \Omega) = \frac{E^3}{4\pi^3 \hbar^3 c^3} \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1}$
Emission rate eq. (60)	van Roosbroeck and Shockley $R_{\text{sp}} = \frac{(\hbar\omega)^2}{\pi^2 \hbar^3 c^3} \frac{1}{\exp\left(\frac{\hbar\omega - \Delta\mu}{k_B T}\right) - 1}$	van Roosbroeck and Shockley $R_{\text{sp}} = a(\hbar\omega) \frac{(\hbar\omega)^2}{\pi^2 \hbar^3 c^3} \frac{1}{\exp\left(\frac{\hbar\omega - \Delta\mu}{k_B T}\right) - 1}$
Radiation eq. (88)	Planck law $\phi_E(E, \Omega) = \frac{1}{4\pi^3 \hbar^3 c^2} \frac{\mathcal{E}}{n^2} \times \frac{E^3}{\exp\left(\frac{E}{k_B T}\right) - 1}$	Generalized Planck law $\phi_E(E, \Omega) = \frac{\alpha(E, \Omega)}{4\pi^3 \hbar^3 c^2} \frac{\mathcal{E}}{n^2} \times \frac{E^3}{\exp\left(\frac{E - \Delta\mu}{k_B T}\right) - 1}$

#### 3.1.1 Emission from an empty cavity

Let us first consider the standard empty-cavity model of a blackbody, as discussed before. As photons are not interacting within the cavity (but only with the cavity's walls), the output flux through a small opening  $dA$  in a direction  $\Omega$  can be estimated by a simple accounting over a period  $dt$  (cf Fig. 3)

All  $dn(E, \Omega)$  photons of energy  $E$  escaping the cavity through  $dA$  in a direction  $\Omega$  in the period  $dt$  occupy the volume

$$dV = c \cos \theta dt dA \quad (81)$$

and the corresponding output number of particles is thus  $(n_\gamma(E, \Omega) dE d\Omega) \times dV$ . The particle flux emitted in the direction  $\Omega$  is therefore given by

$$d\phi_N = \frac{c}{4\pi} n_\gamma(E) \cdot \cos \theta d\Omega dE dA = \frac{c}{4\pi} n_\gamma(E) \frac{d\mathcal{E}}{n^2} dA \quad (82)$$

#### 3.1.2 Emission from an filled cavity

If the (black or gray)body is filled with matter interacting with radiation, photons cannot be considered to follow ballistic trajectories anymore, and the previous accounting does not apply. Instead, a more detailed description of radiation propagation in the medium should be considered. This work was first done by Würfel, who related the spontaneous emission rate (as given by the van Roosbroeck-Shockley equation) to the output rate of the emitter [21]. To do so, let us consider a microscopic balance of photon in a small volume of matter in stationary regime:

$$\text{div } j_\gamma(x) = R_{\text{sp}} + R_\downarrow - R_\uparrow = R_{\text{sp}} - a(E) \times j_\gamma(x) \quad (83)$$

Assuming a uniform spontaneous emission rate, the photon flux reached after a slab of thickness  $d$  is thus  $j_\gamma(d) = (1 - e^{-a.d}) R_{\text{sp}}/a$ . The outgoing flux can then be expressed as

$$\phi_N(E, \Omega) = T j_\gamma(d) = \frac{\alpha(E, \Omega) \mathcal{E}}{4\pi^3 \hbar^3 c^2 n^2} \times \frac{E^2}{\exp\left(\frac{E-\Delta\mu}{k_B T}\right) - 1} \quad (84)$$

where  $T$  is the transmission coefficient at the interface.

### 3.2 Emitted number of photons

We will keep the most generic expression for the radiated flux of photons.

$$\phi_N(E, \Omega) = \frac{\alpha(E, \Omega) \mathcal{E}}{4\pi^3 \hbar^3 c^2 n^2} \times \frac{E^2}{\exp\left(\frac{E-\Delta\mu}{k_B T}\right) - 1} \quad (85)$$

For a blackbody,  $\alpha = 1$  and the total output flux of particles is given by integrating the angular part on all possible emission directions (usually,  $\theta \leq \theta_c \leq \frac{\pi}{2}$ ),

$$\phi_N = \frac{1}{4\pi^3 \hbar^3 c^2 n^2} \int dE \frac{E^2}{e^{\frac{E}{k_B T}} - 1} \quad (86)$$

$$= \frac{c\mathcal{E}}{4\pi} n = 2\mathcal{E}\zeta(3) \times \frac{k_B^3 T^3}{\pi^2 \hbar^3 c^3} \quad (87)$$

where  $\mathcal{E} = n^2 \int_{\text{app}} \cos\theta d\Omega \leq \pi$  is the radiation étendue.

### 3.3 Emitted power

The radiated power flux  $\phi_E(E, \Omega)$  (and radiant exitance  $dM_E = \phi_E(E, \Omega) d\mathcal{E}dA$ ) can be directly related to the photon flux

$$\phi_E(E, \Omega) = E \times \phi_N(E, \Omega) = \frac{\alpha(E, \Omega) \mathcal{E}}{4\pi^3 \hbar^3 c^2 n^2} \times \frac{E^3}{\exp\left(\frac{E-\Delta\mu}{k_B T}\right) - 1} \quad (88)$$

For a blackbody ( $\alpha = 1$  and  $\Delta\mu = 0$ ), this relation is the celebrated Planck law. In its most generic form, it was coined *generalized Planck law* by Würfel [21].

For a blackbody, the total output energy can be obtained by summing over all energies and directions:

$$\phi_E = \frac{c\mathcal{E}}{4\pi} u = \frac{\mathcal{E}}{\pi} \cdot \sigma T^4 \quad (89)$$

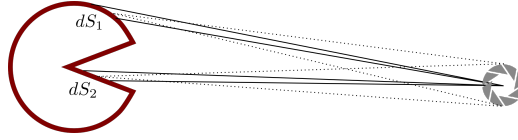
This last relation is the famous *Stefan's law*, which relates the total surfacic power to the temperature of the black body. However, this relation does not account for the spatial distribution of the emission, which is described by the related radiometric quantities:

$$I_\Omega = \int dE \frac{dM_E}{d\Omega} = \frac{\cos\theta}{\pi} \sigma T^4 \cdot dA \quad (90)$$

$$L_\Omega = \int dE \frac{dM_E}{\cos\theta d\Omega} = \frac{1}{\pi} \sigma T^4 \quad (91)$$

Remarkably, the radiant intensity is proportional to the cosine of the emission angle, and the radiance is consequently uniform, which is quite un-intuitive. This emission properties are defined as *Lambertian* emission.

### 3.3.1 What does a blackbody look like ?



Consider a blackbody with arbitrary shape, observed from an aperture of size  $S_{\text{app}}$  at distance  $d$ . The visual aspect of the blackbody depends on the intensity received by the observer, ie the energy flux per steradian in a given direction.

Imagine looking at the blackbody in a direction  $\theta_1$ , within a solid angle  $d\Omega$ . You are actually seeing the contribution of a surface  $dS_1 = d^2 \frac{d\Omega}{\cos\theta'_1}$  where  $\theta'_1$  is the angle between the line of sight and the normal to  $dS_1$ . This surface radiates a power  $d\phi_{E,1} = L_{BB} \cos\theta'_1 dS_1 \frac{S_{\text{app}}}{d^2}$ . From the aperture perspective, the radiant intensity is thus  $I(\theta_1) = L_{BB} S_{\text{app}}$ .

We now turn to look at in the direction  $\theta_2$ , within the same solid angle. The same derivation as above holds, and the radiant intensity takes the same value  $I(\theta_2) = I(\theta_1)$ .

*A blackbody does not radiate energy isotropically, but following a cosine law. For that reason, the blackbody seems to have the same brightness from all observation directions.*

It is therefore impossible to infer the surface shape of a blackbody from its emission : any black body will appear as a uniformly bright flat surface.

#### Note Solid angle or étendue ?

In many works, the spectral emission is given as a function of the solid angle  $\Omega$  subtended by the source

$$\phi_E(E) = \frac{\Omega}{4\pi^3 \hbar^3 c^2} \times \frac{E^3}{\exp\left(\frac{E}{k_B T}\right) - 1}$$

where the étendue  $\mathcal{E}$  is replaced by  $\Omega$  in the expression eq(88) derived above. It seems to me that this expression is only correct when the sun seen as small source at its zenith. It does not include the cosine term when the sun is close to the horizon, and overestimates the emission by a factor 2 under full concentration. To find the correct result, authors consider  $\Omega = \pi$  under full concentration, which doesn't make sense : if the source occupies the whole half-space,  $\Omega = 2\pi$  but  $\mathcal{E} = \pi$ .

### 3.3.2 Asymptotic expressions

Historically, high and low energy limits were derived as phenomenological models for the blackbody spectrum, but no approach could cover the whole energy spectrum. Planck law first came as an ad-hoc expression, and was correctly interpreted later on.

In this section, we will not oversee the historical derivation of Rayleigh-Jeans and Wien law, but recover them from Planck law, which is straightforward. The interesting part is to discuss the validity of the Wien law, which is often used in solar energy.

**Low energy limit : Rayleigh-Jeans law** For photons of low energy as compared to the blackbody temperature, the denominator of eq.(20) becomes  $\sim E/kT$ , leading to the Rayleigh-Jeans law:

$$u_\omega(T) \underset{T \rightarrow \infty}{\sim} \frac{k_B T \omega^2}{\pi^2 c^3} \quad (92)$$

**High energy limit : Wien law** It is often useful to approximate the Bose Einstein distribution by a Boltzmann distribution, neglecting the term  $-1$  in the denominator of eq.(20). This results in the so-called Wien distribution law:

$$n_\gamma(E) \sim \frac{E^2}{4\pi^3 \hbar^3 c^3} \exp\left(-\frac{E}{k_B T}\right) \quad u_E(E) \sim \frac{E^3}{4\pi^3 \hbar^3 c^3} \exp\left(-\frac{E}{k_B T}\right) \quad (93)$$

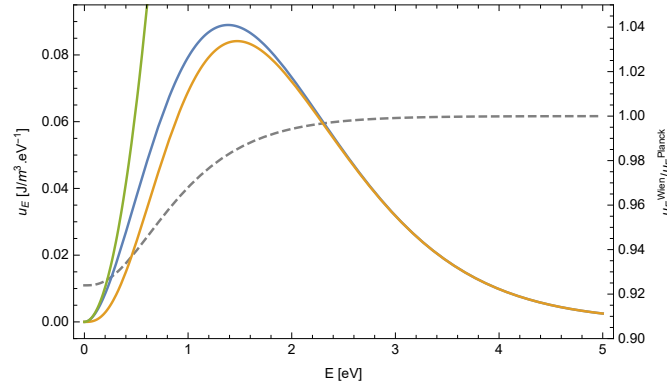


Figure 4: Energy spectrum of a blackbody at 5700 K, as given by Planck law (in blue), Rayleigh-Jeans law (in green) and Wien law (in yellow). The gray dashed curve indicates the ratio of the power above a given energy  $\int_E^\infty \phi_{BB}$  as given by Wien's and Planck's law.

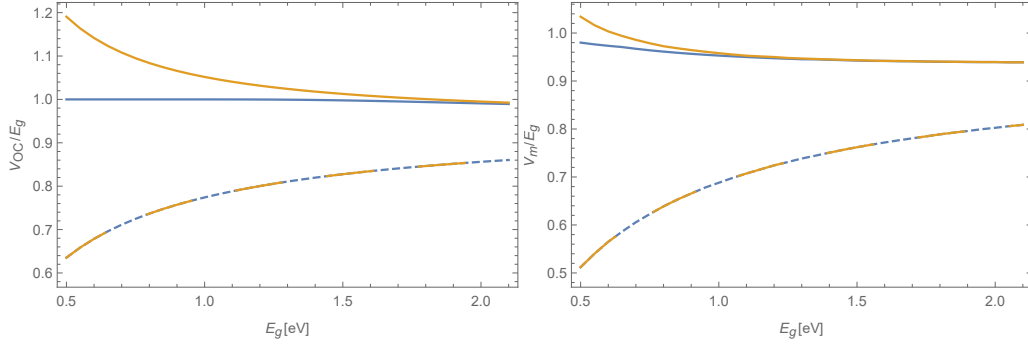


Figure 5: Open circuit voltage ( $V_{OC}$ ) and maximum power point ( $V_m$ ) in gap units as a function of the gap, calculated from the (generalized) Planck law (blue) and from Wien law (yellow) under concentration (plain curve) and under no concentration (dashed curve).

This approximation is valid for photons of energy  $\hbar\omega \gg k_B T$ . Numerically, the approximation for the power spectrum is better than 1% for  $\hbar\omega \gtrsim 4.5 k_B T$ . In solar cells, we are often interested in integrated quantities, rather than the spectrum itself. Figure 5 shows for instance the open circuit voltage and maximum power point of a single junction as estimated from both expressions.

### Take home message

1. Wien approximation is never correct for the sun at bandgaps considered in PV applications ( $4.5 k_B T_\odot \simeq 2.5$  eV), and the full Planck distribution should be used.
2. At ambient temperature, Wien approximation holds as long as the Fermi levels splitting does not get too close to the band gap. Notably,
  - (a) The maximal power point is well estimated for all concentrations for  $E_g > 1$  eV.
  - (b) The open voltage circuit is well estimated in the absence of concentration, but largely overestimated under full concentration.

### 3.4 Emitted entropy

In the same way, we can calculate the entropy flux carried away by photon escaping the cavity. We perform the calculation here in the case of a blackbody:

$$\phi_S(E) = k_B \frac{\mathcal{E}}{4\pi^3 n^2 \hbar^3 c^2} E^2 \left( \left( 1 + \frac{1}{e^{\frac{E}{kT}} - 1} \right) \log \left( 1 + \frac{1}{e^{\frac{E}{kT}} - 1} \right) - \frac{1}{e^{\frac{E}{kT}} - 1} \log \left( \frac{1}{e^{\frac{E}{kT}} - 1} \right) \right) \quad (94)$$

$$\phi_S = \frac{c\mathcal{E}}{4\pi} s = \frac{\mathcal{E}}{n^2 \pi} \cdot \frac{4}{3} \sigma T^3 \quad (95)$$

**Entropy creation** The question of the entropy creation is a tricky one.

Let's first assume the blackbody radiates in the vacuum. Over a period of time  $t$  (sufficiently short so that we assume the temperature of the blackbody is unchanged), the output energy is  $dE = \delta Q_{\text{out}} = M_E dA.t$  and the output entropy is  $dS = dS_{\text{out}} = M_S dA.t$ . Considering that the output entropy results from exchanged entropy  $\delta S_{\text{ex}} = \frac{\delta Q_{\text{out}}}{T}$  and created entropy  $\delta S_{\text{cr}}$ , we find an entropy creation rate due to the emission towards vacuum

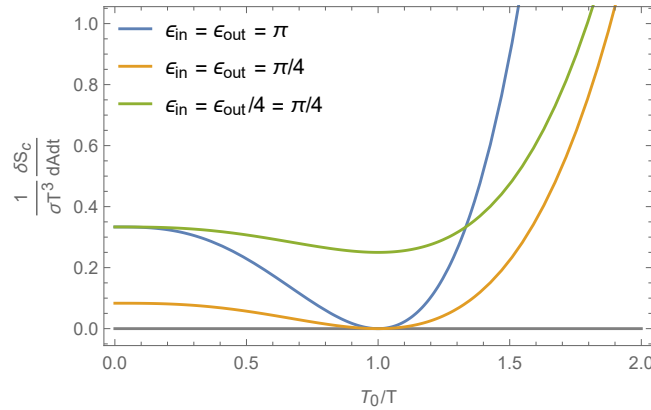
$$\frac{\delta S_{\text{cr}}}{dA dt} = \frac{dS - \delta S_{\text{ex}}}{dA dt} = \frac{\mathcal{E}_{\text{out}}}{n^2 \pi^3} \sigma T^3 \quad (96)$$

Now, in most cases, the blackbody is not alone in the vacuum, but can receive radiation from another blackbody. Let's assume this other blackbody, at temperature  $T_0$ , emits radiation with étendue  $\mathcal{E}_{\text{in}}$  towards the first blackbody. The net energy output is now  $dE = \delta Q_{\text{out}} - \delta Q_{\text{in}} = \frac{\mathcal{E}_{\text{out}}}{\pi} \sigma T^4 \left(1 - \frac{\mathcal{E}_{\text{in}} T_0^4}{\mathcal{E}_{\text{out}} T^4}\right)$  and the entropy output is  $dS = dS_{\text{out}} - dS_{\text{in}} = \frac{4}{3} \frac{\mathcal{E}_{\text{out}}}{\pi} \sigma T^3 \left(1 - \frac{\mathcal{E}_{\text{in}} T_0^3}{\mathcal{E}_{\text{out}} T^3}\right)$ , where we assumed the optical index is unity for the sake of simplicity. We can estimate the entropy creation rate as before

$$\begin{aligned} \frac{\delta S_{\text{cr}}}{dA dt} &= \frac{4}{3} \frac{\mathcal{E}_{\text{out}}}{\pi} \sigma T^3 \left(1 - \frac{\mathcal{E}_{\text{in}} T_0^3}{\mathcal{E}_{\text{out}} T^3}\right) - \frac{\mathcal{E}_{\text{out}}}{\pi} \sigma T^3 \left(1 - \frac{\mathcal{E}_{\text{in}} T_0^4}{\mathcal{E}_{\text{out}} T^4}\right) \\ &= \frac{\mathcal{E}_{\text{out}}}{\pi} \sigma T^3 \left(\frac{1}{3} - \frac{4}{3} \frac{\mathcal{E}_{\text{in}} T_0^3}{\mathcal{E}_{\text{out}} T^3} + \frac{\mathcal{E}_{\text{in}} T_0^4}{\mathcal{E}_{\text{out}} T^4}\right) \geq 0 \end{aligned} \quad (97)$$

As  $\mathcal{E}_{\text{out}} \geq \mathcal{E}_{\text{in}}$  due to Fermat's principle, the created entropy cannot be negative and its minimal value  $\frac{1}{3} \frac{\mathcal{E}_{\text{out}}}{\pi} \sigma T^3 (\mathcal{E}_{\text{out}} - \mathcal{E}_{\text{in}})$  is reached for  $T = T_0$ . If the étendue of emission matches that of absorption, then emission can be reversible.

It can be surprising that a simultaneous and independent absorption prevents emission from generating entropy. The trick here is that while the total entropy variation for the two processes  $dS = dS_{\text{abs}} + dS_{\text{em}}$  add directly, it is obviously not true for the entropy creation  $\delta S_{\text{cr}} \neq \delta S_{\text{cr,abs}} + \delta S_{\text{cr,em}}$ ; meaning that the entropy that was before created can now be exchanged instead.



This question of entropy production is not easy at all. In his 1982 paper on chemical potential of radiation [21], Würfel criticizes the familiar expression of entropy flux - leading to a strong backfire from Alexis De Vos [4]:

*Being among the authors suspected by Würfel for wrongly applying the notion of entropy currents in radiation, we would like to comment on his statements here. In the following section, the error in Würfel's thought experiment will be pointed out.*

Würfel further produce an article to fix the "paradox" raised in his previous work [22].

### 3.5 Energy conversion with a blackbody

#### 3.5.1 Muser efficiency

Let us consider a black body absorber at temperature  $T_{\text{abs}}$ , receiving energy from a thermal  $T_{\odot}$ ;

$$\phi_{E,\text{in}} = \frac{\mathcal{E}_{\text{in}}}{\pi} \sigma T_{\odot}^4 \times S_{\text{abs}} \quad (98)$$

Because of its finite temperature, the absorber also radiates and the corresponding energy loss is

$$\phi_{E,\text{rad}} = \frac{\mathcal{E}_{\text{out}}}{\pi} \sigma T_{\text{abs}}^4 \times S_{\text{abs}} \quad (99)$$

The remaining power is provided as heat to a heat engine, operating between the temperature of the absorber (hot source) and that of the ambient surroundings  $T_0$ . The efficiency of the heat engine is lower than that of Carnot cycle, and the maximal yield is thus

$$\eta_{\text{Muser}} = \frac{\dot{W}}{\phi_{E,\text{in}}} = \left(1 - \frac{\mathcal{E}_{\text{out}}}{\mathcal{E}_{\text{in}}} \frac{T_{\text{abs}}^4}{T_{\odot}^4}\right) \left(1 - \frac{T_0}{T_{\text{abs}}}\right) \quad (100)$$

Note that under one sun (without any concentration),  $\eta_{\text{Muser}} \leq 5.54\%$ , which is much lower than standard grade silicon solar panels ! This shows that a gapless material is quite inefficient for solar energy conversion.

#### 3.5.2 Lansberg efficiency

In the previous derivation, the absorber was used as a hot source, simply providing heat. We can also consider a situation where work is actually extracted directly from the absorber - provided that the entropy balance is respected.

Let's assume for now that no entropy is created during the absorption / emission process (we will see how below). Together with the absorption / radiation of energy, an entropy flux is to be considered

$$\phi_{S,\text{in}/\text{rad}} = \frac{4}{3} \frac{\mathcal{E}_{\text{in/out}}}{\pi} \sigma T_{\odot/\text{abs}}^3 \times S_{\text{abs}} \quad (101)$$

The entropy flux difference has to be evacuated as heat provided by the absorber to the outside

$$\frac{\dot{Q}_1}{T_{\text{abs}}} = \phi_{S,\text{in}} - \phi_{S,\text{rad}} \quad (102)$$

and can be used by a Carnot engine to produce a work rate  $\dot{W}_1 = \dot{Q}_1 \left(1 - \frac{T_0}{T_{\text{abs}}}\right)$ . The remaining power  $\phi_{E,\text{in}} - \phi_{E,\text{rad}} - \dot{Q}_1 = \dot{W}_2$  can be extracted as work. The total efficiency of the Lansberg machine is given by

$$\eta_{\text{Lansberg}} = \frac{\dot{W}_1 + \dot{W}_2}{\phi_{E,\text{in}}} = \left(1 - \frac{\mathcal{E}_{\text{out}}}{\mathcal{E}_{\text{in}}} \frac{T_{\text{abs}}^4}{T_{\odot}^4} - \frac{4}{3} \frac{T_0}{T_{\text{abs}}} \left(\frac{T_{\text{abs}}}{T_{\odot}} - \frac{\mathcal{E}_{\text{out}}}{\mathcal{E}_{\text{in}}} \frac{T_{\text{abs}}^4}{T_{\odot}^4}\right)\right) \quad (103)$$

**Note** We saw in the previous paragraph that reversible emission / absorption of radiation could only take place when  $\mathcal{E}_{\text{out}} = \mathcal{E}_{\text{in}}$  and  $T_{\text{abs}} = T_{\odot}$ , in which case the output power is trivially zero. It therefore requires some trick to find a situation where Lansberg efficiency is actually relevant.

One option is to resort to optical insulator [16, 2] such that the light emitted by the absorber is directed not in the direction of the source, but rather towards a second absorber slightly colder, which emit itself towards a third one and so on.

Doing so allows to consider that at each step, the temperature  $T$  of the absorber is very close to that of the radiation  $T + dT$ . The corresponding efficiency is thus<sup>7</sup>

$$d\eta = \sigma(T + dT)^4 \left(1 - \frac{\mathcal{E}_{\text{out}}}{\mathcal{E}_{\text{in}}} \frac{T^4}{(T + dT)^4} - \frac{4}{3} \frac{T_0}{T} \left(\frac{T}{(T + dT)^4} - \frac{\mathcal{E}_{\text{out}}}{\mathcal{E}_{\text{in}}} \frac{T^4}{(T + dT)^4}\right)\right) \simeq 4\sigma T^3 \left(1 - \frac{T_A}{T}\right) dT$$

<sup>7</sup>Up to the first order, the infinitesimal efficiency  $d\eta$  is the same considering Muser or Clausius expression.

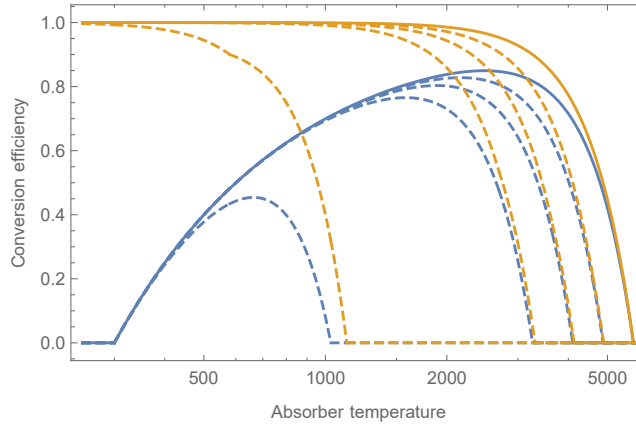


Figure 6: Conversion efficiency for a Muzer engine (blue) and a Lansberg engine (yellow) under sunlight with  $\mathcal{E}_{\text{out}}/\mathcal{E}_{\text{in}} = 1, 2, 4, 10$  and  $1000$ .

and the expression of Lansberg efficiency is recovered when adding all contributions from  $T_{\odot}$  to  $T_0$  :

$$\eta = \int_{T_0}^{T_{\odot}} d\eta = \sigma T_{\odot}^4 \left( 1 + \frac{1}{3} \frac{\mathcal{E}_{\text{out}}}{\mathcal{E}_{\text{in}}} \frac{T_0^4}{T_{\odot}^4} - \frac{4}{3} \frac{T_0}{T_{\odot}} \right)$$

## 4 Thermodynamics of graybodies

We considered so far the behavior of a blackbody, able to absorb and emit all frequencies. In many applications, it is however necessary to take into account the absorption profile of the system under scrutiny. In its simplest form, the absorptivity of a semi conductor should for instance be accounted by a step function

$$\alpha(E) = \theta(E - E_g) \quad (104)$$

where  $E_g$  is the energy gap. Introducing an additional energy scale complexifies severely the model developed so far, as the photon gas is now allowed to feature a non-zero chemical potential.

### 4.1 Kirchhoff law of radiation - non perfect absorption

While a blackbody is defined as the best possible absorber (and emitter), it is necessary to also consider *gray* bodies, with non unit absorptivity. Kirchhoff law of radiation relates the ability of a body to absorb any wavelength in any direction to the ability of that body to emit the same wavelength in the same direction:

$$\alpha(E, \Omega) = \epsilon(E, \Omega) \quad (105)$$

The proof of this theorem is actually not straightforward, and the angular part requires additional assumptions on the problem [18].

#### Proof

The direction averaged Kirchhoff law of radiation  $\alpha(E) = \epsilon(E)$  can be obtained from a careful energy balance. Let's consider a body with emissivity  $\epsilon_1(E)$  and absorptivity  $\alpha_1(E)$ . The energy balance for the body exposed to a thermal radiation of radiance  $L_T(\lambda)$  imposes

$$\int dE M_E^{BB}(E) \epsilon_1(E) = \int dE M_E^{BB}(E) \alpha_1(E) \quad (106)$$

which is not enough to conclude on the identity between emissivity and absorptivity at all wavelength.

Let's now put the body inside a cavity, the radiative behavior of which is characterized by  $\epsilon_2, \alpha_2$ . We assume thermal equilibrium at temperature  $T$  between the body and the cavity.

The spectral irradiance arriving on the body is  $\phi_{\text{in}}(E) = M_E^{\text{BB}}(E)\epsilon_2(E) + (1 - \alpha_2(E))\phi_{\text{out}}(E)$  where the spectral irradiance reaching the cavity is expressed as  $\phi_{\text{out}}(E) = M_E^{\text{BB}}(E)\epsilon_1(E) + (1 - \alpha_1(E))\phi_{\text{in}}(E)$ .

Solving this simple system leads to

$$\begin{aligned}\phi_{\text{in}}(E) &= M_E^{\text{BB}} \frac{\epsilon_2 - \epsilon_1(1 - \alpha_2)}{1 - (1 - \alpha_1)(1 - \alpha_2)} \\ \phi_{\text{out}}(E) &= M_E^{\text{BB}} \frac{\epsilon_1 - \epsilon_2(1 - \alpha_1)}{1 - (1 - \alpha_1)(1 - \alpha_2)}\end{aligned}$$

and the energy balance requires

$$\int dE \phi_{\text{in}}(E) = \int dE \phi_{\text{out}}(E) \Rightarrow \int dE M_E^{\text{BB}} \frac{\alpha_1 \alpha_2}{1 - (1 - \alpha_1)(1 - \alpha_2)} \left( \frac{\epsilon_1}{\alpha_1} - \frac{\epsilon_2}{\alpha_2} \right) = 0 \quad (107)$$

The trick is that this relation holds for whatever cavity material, ie whatever  $\epsilon_2, \alpha_2$ . This is possible if and only if  $\epsilon \propto \alpha$ , and the first equation imposes  $\epsilon(E) = \alpha(E)$  for each energy, hence the direction-averaged Kirchhoff law of radiation.

## 4.2 Energy conversion with a gray-body: Shockley-Queisser limit

The most celebrated estimation of the single junction maximal efficiency was derived by Shockley and Queisser in 1961 [17]. The key ingredients to their model are:

1. Perfect absorption: every photon from the sun with energy over the absorber bandgap generates an electron-hole pair

$$\dot{N}_{\text{in}, \odot} = \frac{\mathcal{E}_{\text{in}}}{4\pi^3 \hbar^3 c^2} \int_{E_g}^{\infty} dE \frac{E^2}{\exp\left(\frac{E}{kT_{\odot}}\right) - 1} \quad (108)$$

In addition, the cell gathers the blackbody radiation from its environment

$$\dot{N}_{\text{in}, \text{env}} = \frac{\mathcal{E}_{\text{out}} - \mathcal{E}_{\text{in}}}{4\pi^3 \hbar^3 c^2} \int_{E_g}^{\infty} dE \frac{E^2}{\exp\left(\frac{E}{kT}\right) - 1} \quad (109)$$

2. Thermalization: the photo-generated populations relax towards two quasi Fermi distributions at the lattice temperature  $T$ , with chemical potential  $\mu_n$  and  $\mu_p$  for electrons and holes respectively.
3. Radiative limit: Only radiative recombination are taken into account. Owing to the generalized Planck law eq. (85), the corresponding recombination takes place at a rate

$$\dot{N}_{\text{out}} = \frac{\mathcal{E}_{\text{out}}}{4\pi^3 \hbar^3 c^2} \int_{E_g}^{\infty} dE \frac{E^2}{\exp\left(\frac{E - \Delta\mu}{kT}\right) - 1} \quad (110)$$

where  $\Delta\mu = \mu_n - \mu_p$  is the quasi Fermi levels splitting.

4. Perfect collection: all non-recombined carriers are extracted from the absorber. The resulting electrical current is thus

$$I = q (\dot{N}_{\text{in}, \odot} + \dot{N}_{\text{in}, \text{env}} - \dot{N}_{\text{out}}) \quad (111)$$

and each electron is extracted at a voltage  $V$  such that (see annex 4.4 for a derivation of this result)

$$\Delta\mu = qV \quad (112)$$

The output power can thus be estimated as

$$P(E_g, V) = I \times V = \frac{qV}{4\pi^3 \hbar^3 c^2} \int_{E_g}^{\infty} dE \left( \frac{\mathcal{E}_{\text{in}} E^2}{\exp\left(\frac{E}{kT_{\odot}}\right) - 1} + \frac{(\mathcal{E}_{\text{out}} - \mathcal{E}_{\text{in}}) E^2}{\exp\left(\frac{E}{kT}\right) - 1} - \frac{\mathcal{E}_{\text{out}} E^2}{\exp\left(\frac{E - qV}{kT}\right) - 1} \right) \quad (113)$$



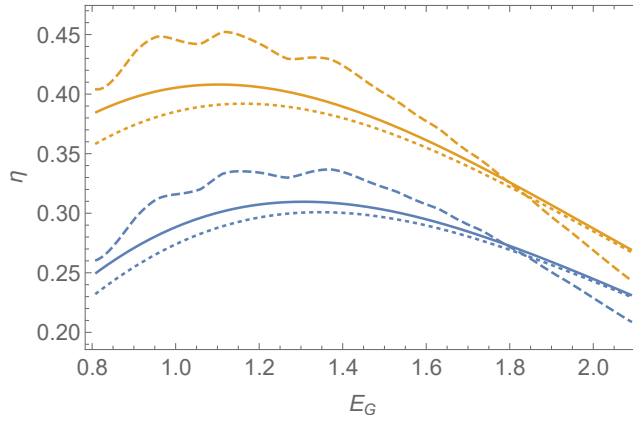


Figure 7: Efficiency in SQ model as a function of the gap, as estimated from generalized Planck law (plain), Wien law for both sun and cell emissions (dotted) and the actual AM1.5 spectra (dashed). If Wien law is applied to cell emission only, and the sun radiation is described by the full Planck law, plain curves are obtained. Blue : no concentration. Yellow : full concentration.

and the conversion efficiency is defined as

$$\eta(E_g) = \frac{\max_V [P(E_g, V)]}{P_{\text{in}, \odot}(E_g)} \quad (114)$$

### Large gap approximation

If the gap is large enough for a Boltzmann approximation to hold (cf section 3.3.2),

$$P(E_g, V) \simeq qV \left( I_{\text{sc}} - \left( e^{\frac{qV}{kT}} - 1 \right) + \frac{\mathcal{E}_{\text{in}}}{\mathcal{E}_{\text{out}}} \right) I_{\text{dark}} \quad (115)$$

$$\rightarrow \begin{cases} qV \left( I_{\text{sc}} - e^{\frac{qV}{kT}} I_{\text{dark}} \right) & \text{under full concentration} \\ \sim qV \left( I_{\text{sc}} - \left( e^{\frac{qV}{kT}} - 1 \right) I_{\text{dark}} \right) & \text{under zero concentration} \end{cases} \quad (116)$$

where we introduced the short circuit and dark currents, defined respectively as

$$I_{\text{sc}} = \frac{\mathcal{E}_{\text{in}}}{4\pi^3 \hbar^3 c^2} \int_{E_g}^{\infty} dE \frac{E^2}{\exp\left(\frac{E}{kT_{\odot}}\right) - 1} \quad (117)$$

$$I_{\text{dark}} \simeq \frac{\mathcal{E}_{\text{out}}}{4\pi^3 \hbar^3 c^2} \int_{E_g}^{\infty} dE E^2 \exp\left(\frac{E}{kT}\right) \quad (118)$$

$$= \frac{\mathcal{E}_{\text{out}}}{4\pi^3 \hbar^3 c^2} e^{-\frac{E_g}{kT}} \times kT \left( 2k^2 T^2 + 2kT E_g + E_g^2 \right) \quad (119)$$

### Efficiency versus gap

The efficiency of a single junction of gap  $E_g$ , as estimated from the Shockley-Queisser model, considering generalized Planck law at 6000K, Wien law (ie Boltzmann approximation) and the actual AM1.5 solar spectrum reach the ground.

**Note** While this simple model leads very insightful results concerning solar conversion efficiency, it should be noted that it is *not physical* properly speaking. Notably, the step-like absorptivity  $\alpha(E) = \theta(E - E_g)$  should be smoothed, which can lead to significant reduction of the efficiency [15, 7]. Furthermore, just like radiative recombination, Auger interactions cannot be avoided and should be taken into account for a more accurate description.

### 4.3 Energy and entropy per photon: Markvart's approach.

/!\ Might be a bit technical /!\

In the previous sections, we essentially considered *volumic* quantities to describe the photon gas. As the chemical potential  $\mu$  for the photons appears now as a relevant quantity, we should rather analyze the distribution in terms of quantity *per photon*  $u_n, s_n$ . This approach has been developed by Tom Markvart [12, 11, 13], and leads to interesting interpretation of previous results.

As mentioned before, it is difficult to derive quantities for the radiation beam, as it is not a system at thermal equilibrium itself. The trick is to perform calculations considering the emitting blackbody cavity, and to estimate the properties of the beam from there using the simple accounting presented in section 3.1

$$u_n = \left( \frac{\partial U}{\partial N} \right)_{V,T} = \left( \frac{\partial \phi_E}{\partial \phi_N} \right)_{\mathcal{E},T} \quad s_n = \left( \frac{\partial S}{\partial N} \right)_{V,T} = \left( \frac{\partial \phi_S}{\partial \phi_N} \right)_{\mathcal{E},T} \quad (120)$$

and the expressions can be deduced from the chain rule.

We will now derive them for a semiconductor with a wide gap. From eq.(85), it is possible to express the chemical potential of the radiation from the photon flux

$$\exp\left(\frac{\mu}{k_B T}\right) = \frac{\phi_N}{\mathcal{E} \gamma(T)} \exp\left(\frac{E_g}{k_B T}\right) \quad (121)$$

where the gamma is defined as

$$\gamma(T) = \frac{E_g^2 k_B T}{4\pi^3 \hbar^3 c^2} \left( 1 + 2 \frac{k_B T}{E_g} + 2 \left( \frac{k_B T}{E_g} \right)^2 \right) \text{ for } \alpha = \theta (E - E_g) \quad (122)$$

Using this expression of  $\mu$  in the Boltzmann limit (Wien law) of eq.(88), we can express the energy flux of the beam as a function of the photon flux

$$\phi_E = \phi_N \times E_G \frac{1 + 3x_g^{-1} + 3x_g^{-2} + 6x_g^{-3}}{1 + 2x_g^{-1} + 2x_g^{-2}} \quad (123)$$

and we can deduce the expression of the energy per photon<sup>8</sup>

$$u_n(\mathcal{E}, T) = E_g + k_B T \frac{1 + 4x_g^{-1} + 6x_g^{-2}}{1 + 2x_g^{-1} + 2x_g^{-2}} \simeq E_g + k_B T \quad (124)$$

which depends only on the photon gas temperature. In the same way, we can derive the expression of entropy per photon

$$s_n(\mathcal{E}, T) = k_B \log \frac{\mathcal{E} \gamma(T)}{N} + k_B T \frac{\gamma'}{\gamma} \simeq k_B \left( \log \frac{\mathcal{E} \gamma(T)}{N} + 1 \right) \quad (125)$$

which depends not only on the temperature, but also on the étendue and photon flux.

### 4.3.1 A detailed analysis of entropy production

Consider an absorber at temperature  $T_{\text{abs}}$ , illuminated by a radiation characterized by a photon flux  $\phi_{N,\text{in}}$ , a temperature  $T_{\text{in}}$ , an étendue  $\mathcal{E}_{\text{in}}$  and a chemical potential  $\mu_{\text{in}}$  (which is zero for a thermal radiation). Each photon with energy  $u_{\text{in}}$  and entropy  $s_{\text{in}}$  absorbed by the converter generates an electron-hole pair, which can be extracted to provide useful energy as work  $w_{\text{out}}$ , dissipate heat  $q_{\text{out}}$  in the absorber or recombine to re-emit a photon with energy  $u_{\text{out}}$  and entropy  $s_{\text{out}}$ . The outgoing radiation is defined by  $\phi_{N,\text{out}}$ ,  $T_{\text{abs}}$ ,  $\mathcal{E}_{\text{out}}$  and  $\tau_{\text{out}}$ , and is emitted in an environment at temperature  $T_{\text{env}}$  (the distinction between absorber and environment temperature is useful when dealing with hot carriers solar cells).

I'm still not sure how, but Markvart shows from there that the entropy generation per photon takes the following form:

$$\begin{aligned} T_{\text{env}} s_{\text{crea}} &= [u_{\text{in}} - u_{\text{out}}] - T_{\text{env}} [s_{\text{in}} - s_{\text{out}}] \\ &= T_{\text{env}} (s_{\text{cool}} + s_{\text{rad}} + s_{\text{kin}}) \end{aligned}$$

<sup>8</sup>This expression is different from the one presented by Markvart (factor  $4x_g^{-1}$  instead of  $x_g^{-1}$ , in which case the second term takes the form  $k_B T^2 \gamma' / \gamma$ )

- The first term accounts for the irreversible cooling of photons from the source temperature to the absorber temperature - or equivalently for the thermalization of photo-excited carriers

$$s_{\text{cool}} = \frac{1}{T_{\text{env}}} [u_n(T_{\text{in}}) - u_n(T_{\text{abs}})] - (s_n(\mathcal{E}_{\text{in}}, T_{\text{in}}, \dot{N}_{\text{in}}) - s_n(\mathcal{E}_{\text{in}}, T_{\text{abs}}, \dot{N}_{\text{in}})) \quad (126)$$

$$= k_B \left[ \frac{T_{\text{in}}}{T_{\text{env}}} \left( 1 - \frac{T_{\text{abs}}}{T_{\text{in}}} \right) - \log \frac{T_{\text{in}}}{T_{\text{abs}}} \right] \quad (127)$$

- The outgoing beam can be radiated in more directions than the incident one, leading to increase of the disorder. This appears as a entropy production term related to the optical étendue mismatch

$$s_{\text{rad}} = s_n(\mathcal{E}_{\text{in}}, T_{\text{abs}}, \dot{N}_{\text{in}}) - s_n(\mathcal{E}_{\text{out}}, T_{\text{abs}}, \dot{N}_{\text{in}}) = k_B \log \left( \frac{\mathcal{E}_{\text{out}}}{\mathcal{E}_{\text{in}}} \right) \quad (128)$$

The argument in the log term is related to the concentration and this term can be made arbitrarily small when the outgoing étendue approaches the incoming one.

- As electrical current is extracted from the system, the conversion of heat into usable energy is performed at a finite rate. This results in an entropy production

$$s_{\text{kin}} = s_n(\mathcal{E}_{\text{out}}, T_{\text{abs}}, \dot{N}_{\text{in}}) - s_n(\mathcal{E}_{\text{out}}, T_{\text{abs}}, \dot{N}_{\text{out}}) = k_B \log \frac{\dot{N}_{\text{in}}}{\dot{N}_{\text{out}}} \quad (129)$$

which can be related to the extracted current. Taking into account non-radiative losses  $\dot{N}_{\text{nr}}$ , particle conservation leads to

$$\dot{N}_{\text{in}} - \dot{N}_{\text{out}} = \dot{N}_{\text{in}}^0 - \dot{N}_{\text{out}}^0 - I/q - \dot{N}_{\text{nr}} \quad (130)$$

where the emission value  $\dot{N}_{\text{out}}^0$  in absence of illumination result in a dark current  $I_0 = q\dot{N}_{\text{out}}^0$  and the photo generated current takes the form  $I_L = q(\dot{N}_{\text{in}} - \dot{N}_{\text{in}}^0)$ , leading to

$$s_{\text{kin}} = k_B \log \left( \frac{I_L + I_0}{I_L + I_0 - I} \right) + k_B \log \left( 1 + \frac{\dot{N}_{\text{nr}}}{\dot{N}_{\text{out}}} \right) \quad (131)$$

#### 4.3.2 Influence on the conversion efficiency

Owing to energy conservation, a solar cell outputs a power

$$\phi_{\text{out}} = \phi_{E,\text{in}} - \phi_{E,\text{out}} \quad (132)$$

where  $\phi_{E,\text{in}}$  is the power received from the sun and  $\phi_{E,\text{out}}$  is the power radiated by the absorber. Obviously, not all this output power is actually useful and one should distinguish the heat rate  $\dot{Q}_{\text{out}}$  (which is wasted) from the electrical work rate  $\dot{W}_{\text{out}} = I \times V$ ,  $V$  being the photo-voltage produced by the cell.

As discussed in section 4.4, the work output results is accounted by the free energy of the particles

$$qV = u_{\text{out}} - T_{\text{env}}s_{\text{out}} = \left( 1 - \frac{T_{\text{env}}}{T_{\text{abs}}} \right) u_{\text{out}} + \frac{T_{\text{env}}}{T_{\text{abs}}} \mu_{\text{out}} \quad (133)$$

Any loss or defect will result in a decrease of the output current, or of the free energy of extracted particles, or both. The entropy generation terms introduced before appear as loss in the output voltage (or equivalently in

the free energy) :

$$\begin{aligned}
 qV &= \left(1 - \frac{T_{\text{env}}}{T_{\text{in}}}\right) u_{\text{in}} - T_{\text{env}} s_{\text{crea}} & (134) \\
 &= \underbrace{\left(1 - \frac{T_{\text{env}}}{T_{\text{in}}}\right) E_g}_{\text{Gap}} - \underbrace{k_B \log\left(\frac{\mathcal{E}_{\text{out}}}{\mathcal{E}_{\text{in}}}\right)}_{\text{Concentration}} - \underbrace{k_B \log\left(1 + \frac{N_{\text{nr}}}{N_{\text{out}}}\right)}_{\text{Non-rad. losses}} \\
 &\quad + \underbrace{k_B T_{\text{env}} \log\left(\frac{T_{\text{in}}}{T_{\text{abs}}}\right)}_{\text{Cooling}} + \underbrace{\left(\frac{T_{\text{abs}} - T_{\text{env}}}{T_{\text{in}}}\right) k_B T_{\text{in}}}_{\text{hot carriers}} \\
 &\quad - \underbrace{k_B \log\left(\frac{I_L + I_0}{I_L + I_0 - I}\right)}_{\text{kinetic}} & (135)
 \end{aligned}$$

#### 4.4 Annex to section 4: Chemical potentials, electro chemical potentials and Fermi levels

Chemical potential can be a confusing concept, all the more as the same word can be used with different meanings depending on who is talking... In this section, we review basic properties of the chemical potential (tribute to Steven Byrnes).

Concept	Notation	Definition	For semiconductor physicists	For electrochemists
Total chemical potential	$\mu$	The total energy it takes to add an electron to the system.	Fermi energy, chemical potential	Electrochemical potential
Total chemical potential of conduction-band electrons	$\mu_n$	The total energy given by removing an electron from the conduction band.	"Electron quasi Fermi level" or "Electron imref"	Total chemical potential of conduction-band electrons
Total chemical potential of valence-band electrons	$\mu_p$	The total energy it takes to add an electron to the valence band.	"Hole quasi fermi level" or "Hole imref"	Total chemical potential of valence-band electrons
Electric potential	$\phi$	The energy it takes to bring an electron from infinity to vacuum level.	"Electric potential", "Voltage", "Band-bending"	Galvani potential
Internal Chemical potential	$\mu^0$	The energy it takes to bring an electron from vacuum level to the system.	"Fermi level relative to vacuum" (not really used)	Chemical potential
Fermi energy	$\epsilon_F$	Chemical potential at 0K.	not really used	not really used

1. Generally speaking, the chemical potential is the conjugated variable to particle number (just like pressure and volume or temperature and entropy). For a more complete derivation of the chemical potential, see the corresponding document.
2. The rigorous definition of the Fermi energy (ie the internal chemical potential at  $T \rightarrow 0$  K) is not used in solar cell physics, and the internal chemical potential is seldom used.
3. Rigorously speaking, chemical potential is defined at equilibrium - ie *not* under illumination or extraction, when particles are actively transferred from one band to the other. Yet, it is usually considered that, among each band, populations manage to equilibrate. This leads to consider a chemical potential *for each band*. Note however that, properly speaking, the system does not have *a* chemical potential at all - just like a temperature can not be defined for an ice cube in a cup of hot water.

4. The electrochemical potential (which we will inappropriately call “Fermi energy” and note  $\mu$  from now on) is related to the electric potential and internal chemical potential through

$$\mu = \mu^0 - q\varphi \quad (136)$$

where  $q = 1.6 \times 10^{-19}$  C is the elementary charge.

5. Most important is the relationship between the voltage delivered by the cell and the splitting of the quasi-Fermi levels

$$qV = \Delta\mu = \mu_n - \mu_p \quad (137)$$

To demonstrate this identity, consider the n-contact injecting electrons in an electrical circuit. When  $dN < 0$  electrons are extracted from this contact, the energy provided by the system is  $-dU = -\bar{\epsilon}dN$ , where  $\bar{\epsilon}$  is the average energy per electron. This energy is provided as both heat  $\delta Q$  and work  $\delta W$  to the environment, and of course it is the work part that we care about. The maximum amount of work that can be recovered can be inferred from the variation of the free energy.

#### Reminder Free energy

During any transformation, the entropy variation is larger the exchanged quantity

$$dS \geq \frac{\delta Q}{T} \quad (138)$$

Consequently, for an isothermal transformation, the work produced by the system can be majorated by the variation of Helmholtz free energy  $F$

$$-\delta W \leq -(dU - TdS) = -dF \quad (139)$$

where  $F = U - TS$  is Helmholtz free energy.

Using the thermodynamic identity  $dF = SdT - pdV + \phi dQ + \mu_n^0 dN$ , we can estimate the free energy variation in the contact

$$dF_n = \left( \underbrace{-q\phi_n + \mu_n^0}_{\mu_n} \right) dN \quad (140)$$

In the same way, injecting the same number of particles from the environment into the p-contact modifies its free energy by

$$dF_p = \left( \underbrace{-q\phi_p + \mu_p^0}_{\mu_p} \right) (-dN) \quad (141)$$

and the maximal work produced by the transfer of  $dN$  from the n-contact to the p-contact is then

$$-qVdN \equiv \delta W_{\max} = -dF_n - dF_p \quad (142)$$

$$\Rightarrow qV = \mu_n - \mu_p \quad (143)$$

*The voltage delivered by the solar cell is set by the difference in quasi Fermi levels between the two contacts of the cell.*

#### Note voltage in Hot carriers solar cells

In the ideal case, the difference in quasi Fermi levels between the two contacts of the cell is given by the quasi Fermi levels splitting in the absorber. The situation is a bit more tricky in hot carriers solar cells (HCSC) and deserve some additional precautions. In HCSC, the temperature of electrons in the absorber is not the same that of electrons in the contact. To relate the difference in Fermi levels of the contact to the quasi Fermi levels splitting in the absorber, we can detail the energy variation in the absorber when  $-dN > 0$  are extracted from the through an energy selective contact  $E_{\text{ext},n}$ .

We can also express the energy variation in the contact which collects these particles.

$$dU_{\text{abs},n} = E_{\text{ext},n}dN = T_{\text{abs}}dS_{\text{abs},n} + \mu_{\text{abs},n}dN \quad (144)$$

$$dU_{\text{con},n} = -E_{\text{ext},n}dN = T_{\text{con}}dS_{\text{con},n} - \mu_{\text{con},n}dN \quad (145)$$

In the mean time, the same amount of carriers are injected in the other side of the junction at energy  $E_{\text{ext},p}$ , and identical expressions can be formulated. From there, we can estimate the total entropy variation both for the absorber and for the contacts:

$$dS_{\text{abs}} = dS_{\text{abs},n} + dS_{\text{abs},p} = \frac{E_{\text{ext}} - \Delta\mu_{\text{abs}}}{T_{\text{abs}}}dN \quad (146)$$

$$dS_{\text{con}} = dS_{\text{con},n} + dS_{\text{con},p} = -\frac{E_{\text{ext}} - \Delta\mu_{\text{con}}}{T_{\text{con}}}dN \quad (147)$$

In the best case scenario, this extraction process is reversible and does not produce entropy<sup>9</sup>, ie  $dS_{\text{abs}} + dS_{\text{con}} = 0$ . This allows to relate the HCSC voltage to the quasi Fermi levels splitting in the cell and to the extraction level:

$$qV = \Delta\mu_{\text{con}} = \left(1 - \frac{T_{\text{con}}}{T_{\text{abs}}}\right) E_{\text{ext}} + \frac{T_{\text{con}}}{T_{\text{abs}}}\Delta\mu_{\text{abs}} \quad (148)$$

Note that for a standard solar cell,  $T_{\text{abs}} = T_{\text{con}}$  and the extraction energy plays no role.

## 5 Orders of magnitude

To be completed

### Solar parameters

**Solid angle**  $\Omega_{\odot} = 6.8 \times 10^{-5}$ ,  $\alpha = 32'$

**Photon flux**  $\phi_N = 6 \cdot 10^{21}$  photon/s/m<sup>2</sup>  $\Leftrightarrow$  977 A/m<sup>2</sup>

**Energy flux**  $\phi_E = 1300$  W/m<sup>2</sup>

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<sup>9</sup>While this reversible situation can be considered at vanishingly small current, it provides an unreachable upper bound out of open circuit conditions [10].

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