The detailed balance limit for photovoltaics

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1 Density of solar photons

The scope of these notes is to write a few remarks about the Shockley-Queisser limit [1], also implemented also in a MATLAB® code, and using realistic data for solar spectra. Indeed, in [1], the Sun is modeled as a blackbody at 6000 K. Instead, in this work we are going to use data from the National Renewable Energy Laboratory (NREL). In particular, let's focus on the AM1.5G spectrum[1], as shown in Fig. 1. Let $s_{\mathrm{AM1.5}}$ be an example of solar spectrum in the NREL format. It is useful to know that it reported versus the wavelength λ and that it has units

$$[s_{\mathrm{AM1.5}}] = \frac{\mathrm{W}}{\mathrm{m}^2}\frac{1}{\mathrm{nm}}. \tag{1}$$

In order to make this more treatable by our expressions, we are going to convert $s_{\mathrm{AM1.5}}$ in the corresponding number of photons generated per unit time (p.u.t.), per unit area (p.u.a.), per unit energy (p.u.e.): φ:

$$\varphi = \frac{\mathrm{d}\{\text{phot. numb. p.u.a., p.u.t.}\}}{\mathrm{d}E} = \underbrace{\frac{\text{phot. numb. p.u.a. p.u.t.}}{\frac{\mathrm{d}\{\text{phot. power p.u.a.}\}}{\mathrm{d}\lambda}}}_{s_{\mathrm{AM1.5}}} \left|\frac{\mathrm{d}\lambda}{\mathrm{d}E}\right| \underbrace{\frac{\text{phot. numb. p.u.a. p.u.t.}}{\text{phot. power p.u.a}}}_{E}. \tag{2}$$

[1] the notation for spectra, in this example AM1.5G, is used to indicate "air mass 1.5", *i.e.,* assume that the thickness of the atmosphere is 1.5 times that of the zenith (that corresponds to a 48.2° zenith angle)

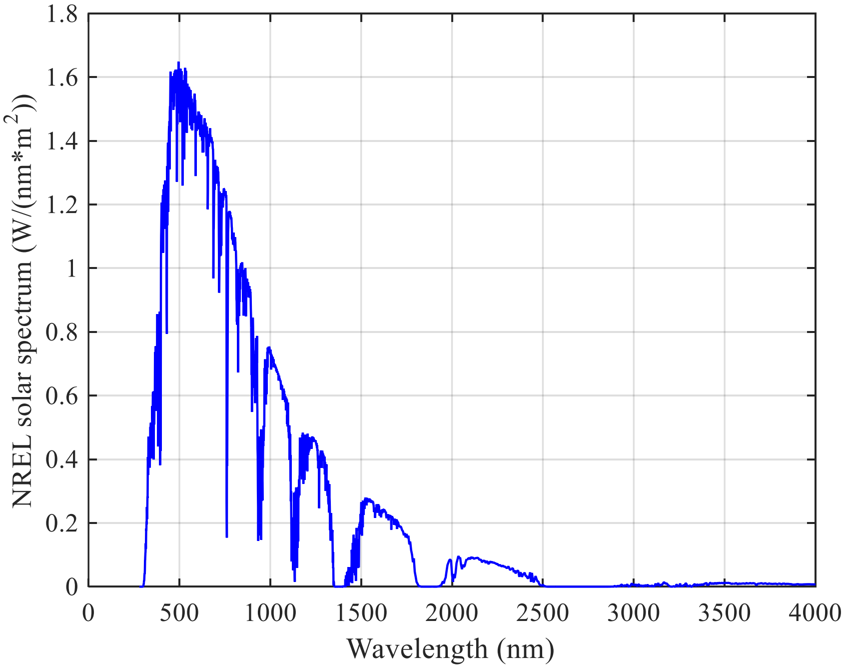


Figure 1: Plot of the NREL solar spectrum data versus photon wavelength.

Having identified two of the three terms in (2) as $s_{\mathrm{AM1.5}}$ and the energy of each single photon, E, which is related to its wavelength λ by the de Broglie relation

$$E = \hbar\omega = hf = \frac{hc}{\lambda}, \tag{3}$$

it is possible to compute the central term as

$$\left|\frac{\mathrm{d}\lambda}{\mathrm{d}E}\right| = \left|\frac{\mathrm{d}}{\mathrm{d}E}\left[\frac{hc}{E}\right]\right| = \left|hc\frac{\mathrm{d}}{\mathrm{d}E}\left[\frac{1}{E}\right]\right| = \frac{hc}{E^2}. \tag{4}$$

It is worth to spend few words about the need of the absolute value. Because λ and E are inversely proportional, rigorously, we should have $\mathrm{d}\lambda \propto -\mathrm{d}E$: this indicates that, for growing E, we have decreasing λ (and viceversa). The reason why we can avoid to introduce this sign is related to numerical implementation aspects: these differentials are used within integrals, but the change of variables causes also the integration bounds to start from the higher to the lower. If our implementation uses always integration bounds defined from the lower to the higher (because, *e.g.,* the vectors containing the values of λ and E are always sorted), then this sign should be removed by the absolute value. However, by plugging (4) in (2), we can finally obtain

$$\varphi = s_{\mathrm{AM1.5}}\frac{hc}{E^3}. \tag{5}$$

The physical meaning of (5) is: φ is the number of photons hitting a $1\,\mathrm{m}^2$ area in $1\,\mathrm{s}$ and having an energy included from E to $E + \mathrm{d}E$.

The first relevant quantity that can be computed from the solar spectrum is the total power per unit area received from the Sun, P_{tot}. To this aim,

$$P_{\mathrm{tot}} = \int_{E_{\mathrm{min}}}^{E_{\mathrm{max}}} \varphi(E) E \,\mathrm{d}E, \tag{6}$$

where E_{min}, E_{max} are the minimum and maximum energies provided, in terms of wavelength, from NREL, evaluated with (3) from λ_{max} and λ_{min}, respectively. Because φ is per unit energy, the $\mathrm{d}E$ removes the energy dependence and ultimately multiplying times the photon energy E inside the integral returns a power per unit area, which is further remarked to have units:

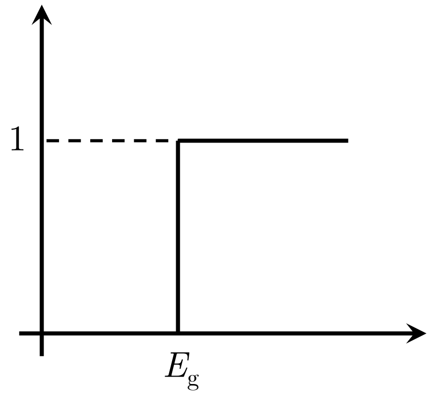


Figure 2: Sketch of the absorptivity model adopted in the Shockley-Queisser formulation.

$$[P_{\text{tot}}] = \frac{\text{W}}{\text{m}^2}.$$

2 Ultimate efficiency

Starting from φ as defined in the previous section, Shockley and Queisser suggest[2] that it is already possible to compute an *ultimate efficiency*, η_{ult}, of a photovoltaic system. This is defined assuming that all the photons having energy greater than the semiconductor bandgap, E_{g}, produce *precisely the same effect as photons having bandgap* E_{g}. In this view, the following power density p.u.a. can be defined as:

$$P_{\text{ult}} = \int_{E_{\min}}^{E_{\max}} \alpha(E, E_{\text{g}})\varphi(E)E_{\text{g}} \,\mathrm{d}E, \tag{7}$$

which is very similar to (6), but with two differences: the first is the presence of the absorptivity $\alpha(E, E_{\text{g}})$, which depends on the chosen material, and the fact that E_{g} is present in place of E, to indicate that such an *ultimate power* is only related to radiative processes, *i.e.,* having energies equal to the gap, therefore ignoring what happens during thermalizations. In this work, we are going to assume, for the absorptivity $\alpha(E, E_{\text{g}})$, a step profile as the one shown in Fig. 2, described by the piece-wise defined expression

$$\alpha(E, E_{\text{g}}) = \begin{cases} 1, & E > E_{\text{g}} \\ 0, & E < E_{\text{g}}. \end{cases} \tag{8}$$

In this view, it is possible to re-write (7) as

$$P_{\text{ult}} = \int_{E_{\min}}^{E_{\max}} \alpha(E, E_{\text{g}})\varphi(E)E_{\text{g}} \,\mathrm{d}E = E_{\text{g}} \int_{E_{\text{g}}}^{E_{\max}} \varphi(E) \,\mathrm{d}E = E_{\text{g}}\Phi^{>}(E_{\text{g}}), \tag{9}$$

where we have extracted E_{g} from the integral, and defined $\Phi^{>}(E_{\text{g}})$ as the photon density p.u.a. p.u.t. having energy greater than the energy gap E_{g}:

$$\Phi^{>}(E_{\text{g}}) = \int_{E_{\min}}^{E_{\max}} \alpha(E, E_{\text{g}})\varphi(E) \,\mathrm{d}E = \int_{E_{\text{g}}}^{E_{\max}} \varphi(E) \,\mathrm{d}E. \tag{10}$$

It is now possible to compute the ultimate efficiency as

$$\eta_{\text{ult}} = \frac{P_{\text{ult}}}{P_{\text{tot}}} = \frac{P_{\text{ult}}(E_{\text{g}})}{P_{\text{tot}}} = \frac{E_{\text{g}}\Phi^{>}(E_{\text{g}})}{P_{\text{tot}}}, \tag{11}$$

[2]The exact quote is: "Each photon with energy greater than E_{g} produces one electronic charge q at a voltage $V_{\text{g}} = E_{\text{g}}/\text{q}$.

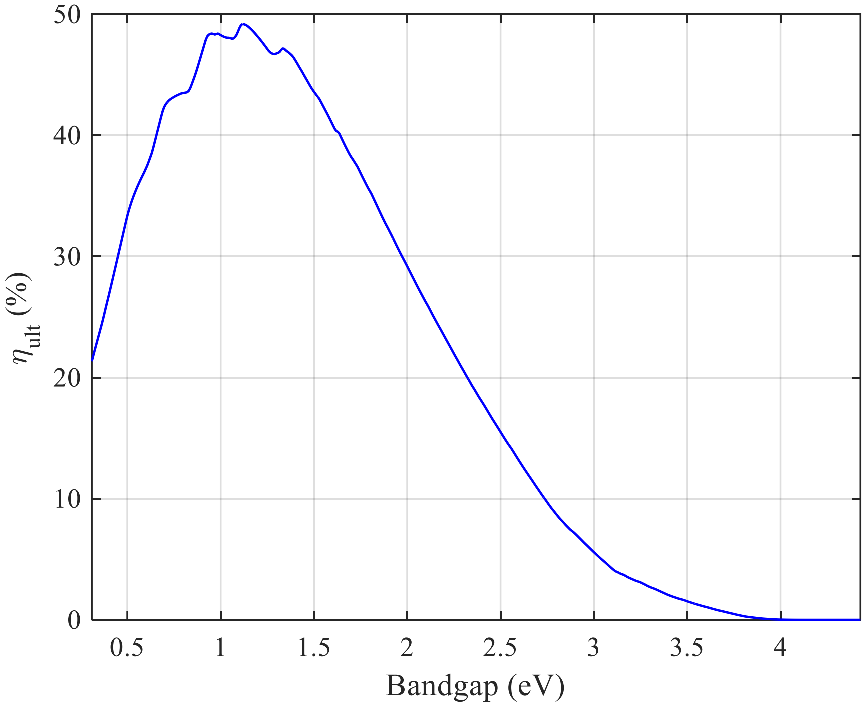


Figure 3: Ultimate efficiency vs. bandgap

where it is further remarked that P_{ult} (which depends on the bandgap and, therefore, on the semiconductor used to realize the solar cell) and P_{tot} are power densities per unit area. As an example, Fig. 3 shows the ultimate efficiency computed with (11) and the AM1.5G spectrum chosen as a reference case study for these notes.

One should avoid overinterpretating this plot: the ultimate efficiency indicates an **upper bound** of the photovoltaic efficiency, but it does not mean that it is possible to achieve, for bandgaps close to 1.1 eV (Si, for example), solar cells with 50% efficiency. The correct interpretation is that **it is not possible to have efficiencies above 50%**. However, the major question, at this point, should be: **is this a good upper bound** ? In other words, is it possible to find upper bounds which are lower, and therefore more indicative of the maximum efficiencies achievable by a solar cell?

3 Current-voltage characteristics of a solar cell

In order to answer to the last question of the previous section, when Shockley and Queisser presented the ultimate efficiency, in addition to the approximated model of the Sun as a blackbody, they interpreted it as the efficiency of a solar cell forced to work at $T = 0\,\text{K}$. In this view, it is like neglecting every information about the cell being a semiconductor with a current flowing through it. In this view, a better upper bound could be achieved by including these effects in the model.

Tracing JV characteristics only on the basis of *first principles* is going to be the toughest task of our to-do list. This, because we have to choose carefully *which first principle* we should use to formulate our model. In [1, Sect. III], Shockley and Queisser state that the JV results from balancing:

1. generation of e-h pairs by the incident solar radiation;
2. radiative recombination of e-h pairs (and consequent generation of photons);
3. nonradiative recombination processes;
4. extraction of holes from the p-region and electrons from the n-region in the form of a current density J_{ext} (or, given a device with cross section area A, $I = AJ_{\text{ext}}$), which withdraws e-h pairs at a rate AJ_{ext}/q;

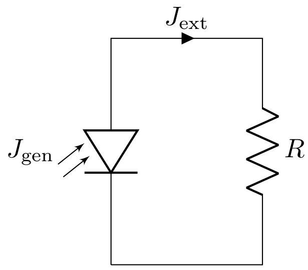


Figure 4: Set-up of a solar panel for realistic operation: the diode is illuminated, leading to an optical generation current J_{gen}, part of which is converted, net of internal microscopic processes, into an external current J_{ext}, useful to feed a load resistance R.

this current can be interpreted as the current which can be extracted by the solar cell when it is connected to an external circuit (*e.g.,* a load resistance).

These four statements can be synthesized by the following equation:

$$J_{gen} - J_{rec} - J_{ext} = 0, \tag{12}$$

where J_{gen} indicates the current contribution generated by the solar light incident on the cell, and J_{rec} the recombination current. Remarkably, one could establish an analogy of (12) with a carrier continuity equation, where J_{ext} is the *total device current*[3]. This equation could be conveniently re-written as

$$J_{ext} = J_{gen} - J_{rec}. \tag{13}$$

From the last expression, one could understand a major difference compared to the *usual convention.* In fact, in (13), the sign of J_{ext} has been changed, *i.e.,* J_{ext} is expressed with the **circuit generator convention**[4]. This is clear if we recall that, considering for example a photodiode, optical generation causes an increase of the inverse saturation current, which in the usual convention is negative; here, it appears that the total current has the same sign of the generation current. To further clarify this idea, let's consider the following circuit representation:

It is to be remarked that J_{ext} is the only observable electrical current in the device.

Given the fundamental equation (13), the scope of the following sections is computing the two main ingredients, namely J_{gen} and J_{rec}, in such a way to being able to trace the JV characteristics of a solar cell.

3.1 Solar generation

The solar generation term J_{gen} can be computed quite easily from (10), since the generation current is simply equal to the density of photons p.u.a., p.u.t., having energy greater than the bandgap, multiplied times the elementary charge q:

$$J_{gen}(E_g) = \mathrm{q} \int_{E_{min}}^{E_{max}} \alpha(E, E_g)\varphi(E)\, \mathrm{d}E = \mathrm{q}\Phi^{>}(E_g). \tag{14}$$

3.2 Recombination processes

Recombination is the hard point, because we have to describe it from *first principles*, *i.e.,* trying to neglect possible technological issues. Technology problems are related to defects, which give rise to nonradiative recombinations through intermediate (in the forbidden region) energy levels: basically, Shockley-Read-Hall (SRH)

[3] Even though this equation resembles a carrier continuity equation, neither drift nor diffusion are included. Shockley and Queisser indicate this hypothesis by assuming *infinite mobility*: this allows the collection of carrier, regardless of where (in the device) they have been generated. It is like having both drift and diffusion tending to ∞, and compensate each other, disappearing and reducing the carrier continuity equation to (12), *i.e.,* a balance between generation, recombination and extraction

[4] this means, having voltage and current with the same direction, so, have a **generated power** as a positive quantity for the cell.

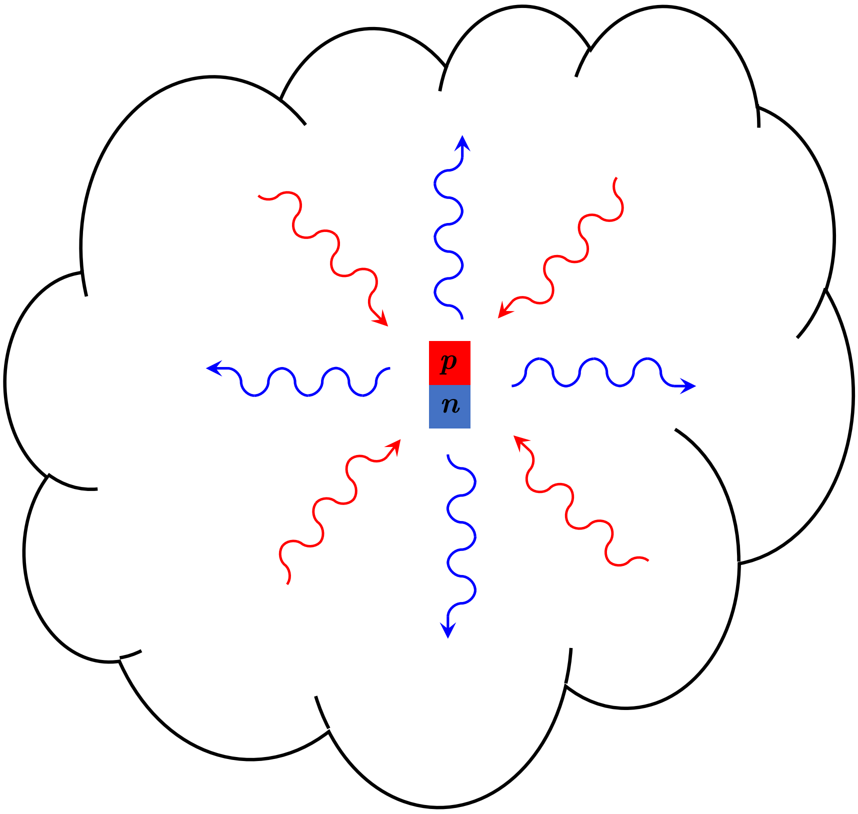


Figure 5: Pictorial representation of the interaction of the solar cell (*pn junction*) with the surrounding blackbody (represented as a cloud). Being the two at thermodynamic equilibrium, the solar cell emits the same number of photons that absorbes from the blackbody, and *viceversa*.

theory [2]. This is **neglected** in this work, because it is technology-dependent, **not fundamental**, and therefore cannot be considered to formulate an efficiency upper bound: as technology improves, this limitation disappears! Another recombination process is Auger, which is actually fundamental, but it occurs at high injections, which is quite unlikely to regard the operation of a solar cell. Joule heating does not really exist, because we consider the mobility to be infinite, therefore the device has no internal resistance; free-carrier absorption is neglected as well.

Having removed all these recombinations, the only fundamental mechanism which can limit the efficiency is **radiative recombination**. Radiative recombination occurs also at operation regimes comparable to SRH (if the material quality is sufficiently high), and, if the solar cell temperature T is non-zero, it means that the cell is not only absorbing photons, but also **emitting** them.

Shockley and Queisser quantified the radiation on the basis of the following concept experiment [3, 1]. Imagine to have a solar cell (a *pn* junction) at a temperature T, with neither contacts nor current flowing through it (electrical/circuit current equal to 0), surrounded by a blackbody at the same temperature. If $T \neq 0$, the outer blackbody emits a radiation, *i.e.,* a number of photons p.u.a., p.u.t, determined by Planck's law:

$$N_{\mathrm{C0}} = \frac{2\pi}{\mathrm{c}^2 h^2} \frac{E^2}{\exp\left(\dfrac{E}{k_{\mathrm{B}}T}\right) - 1} \,\mathrm{d}E. \tag{15}$$

Take a moment to appreciate that this is the first time that the solar cell temperature T enters in our equations! So: the outer blackbody and the *pn* junction are at the same temperature, no current is flowing, so they are **at thermodynamic equilibrium**, as it is sketched in Fig. 5. The cell reacts to the emission of the blackbody (therefore absorption, from the cell's perspective) by emitting photons. And, because the two are at equilibrium, the number of photons absorbed from the blackbody coincides with the number of emitted photons by the cell.

Finally: because in this device it is pretty unlikely to have stimulated emission, it is possible to assume that **spontaneous emission** is the dominant radiative mechanism. To summarize these ideas:

- We enclosed the pn junction in a blackbody with its same temperature, T.
- Because $T \neq 0$, the blackbody emits photons, and the pn junction must absorb them.
- Because no current flows through the junction and the temperature of the cell is the same, the cell and the blackbody are at equilibrium, so the cell emits the same number of photons that it absorbs from the blackbody.
- Because only spontaneous emission makes sense to exist, we can compute the spontaneous emission rate at equilibrium as the blackbody emission. The is the genial idea of the Shockley-Queisser paper [1]: instead of focusing the analysis on the cell, the concept experiment allows to evaluate radiation on the basis of thermodynamic considerations!

So, at equilibrium, we have that the current contribution related to radiative recombination is:

$$J_{\mathrm{rec},0}(E_{\mathrm{g}}) = \mathrm{q}\int_{E_{\mathrm{min}}}^{E_{\mathrm{max}}} \alpha(E, E_{\mathrm{g}}) N_{\mathrm{C0}}(E)\,\mathrm{d}E = \mathrm{q}\int_{E_{\mathrm{g}}}^{E_{\mathrm{max}}} N_{\mathrm{C0}}(E)\,\mathrm{d}E, \tag{16}$$

which has dimensions of a current density.

3.3 Tracing JV characteristics

We can take advantage of the fact that the dominant radiative mechanism is spontaneous emission to formulate our model out of equilibrium, to achieve $J_{\mathrm{rec}}(E_{\mathrm{g}}, V)$. In fact, it is well known that spontaneous emission depends on the product of electron and hole densities, np. as a consequence that it is required to have an electron-hole recombination process to generate a photon. Therefore, it is understood that (16) can be generalized out of equilibrium as [3][5]

$$J_{\mathrm{rec}}(E_{\mathrm{g}}, V) = J_{\mathrm{rec},0}\left(\frac{np}{n_{\mathrm{i}}^2} - 1\right). \tag{17}$$

At equilibrium, $np = n_{\mathrm{i}}^2$ and therefore this current goes to 0. In this view, (17) is a **net** recombination current, whereas (16) is a recombination –but not generation– current. Then, for increasing n and p, J_{rec} grows as well.

Achieving (17) has been a bit tough, but worth. Indeed, it contains all the ingredients required to compute, together with (13) and (14), the JV characteristics of the solar cell. Indeed, exploiting Shockley's relations, here recalled

$$\begin{aligned} n &= n_{\mathrm{i}}\exp\left(\frac{E_{\mathrm{Fn}} - E_{\mathrm{Fi}}}{k_{\mathrm{B}}T}\right) \\ p &= n_{\mathrm{i}}\exp\left(\frac{E_{\mathrm{Fi}} - E_{\mathrm{Fp}}}{k_{\mathrm{B}}T}\right), \end{aligned} \tag{18}$$

one can write

$$np = n_{\mathrm{i}}^2\exp\left(\frac{E_{\mathrm{Fn}} - E_{\mathrm{Fi}} + E_{\mathrm{Fi}} - E_{\mathrm{Fp}}}{k_{\mathrm{B}}T}\right) = n_{\mathrm{i}}^2\exp\left(\frac{E_{\mathrm{Fn}} - E_{\mathrm{Fp}}}{k_{\mathrm{B}}T}\right) = n_{\mathrm{i}}^2\exp\left(\frac{\mathrm{q}V}{k_{\mathrm{B}}T}\right). \tag{19}$$

This last expression requires some mediation. First, let's think about an ordinary diode, *biased*: it is known that, in it, $E_{\mathrm{Fn}} - E_{\mathrm{Fp}}$ is equal to $\mathrm{q}V$, *i.e.,* to the voltage applied to the diode; this is the motivation of the last step of (19). However, here the scenario is different: what happens in a solar cell is that it is illuminated, and e-h pairs are generated. Then, spontaneous emission tries to eliminate them. In other words, in a solar cell the voltage V is something that restores the balance between optical generation and spontaneous emission. This is

[5] for drift-diffusion experts, (17) is basically equivalent to

$$\mathrm{q}\int_{\mathrm{device}} B(np - n_{\mathrm{i}}^2)\,\mathrm{d}z$$

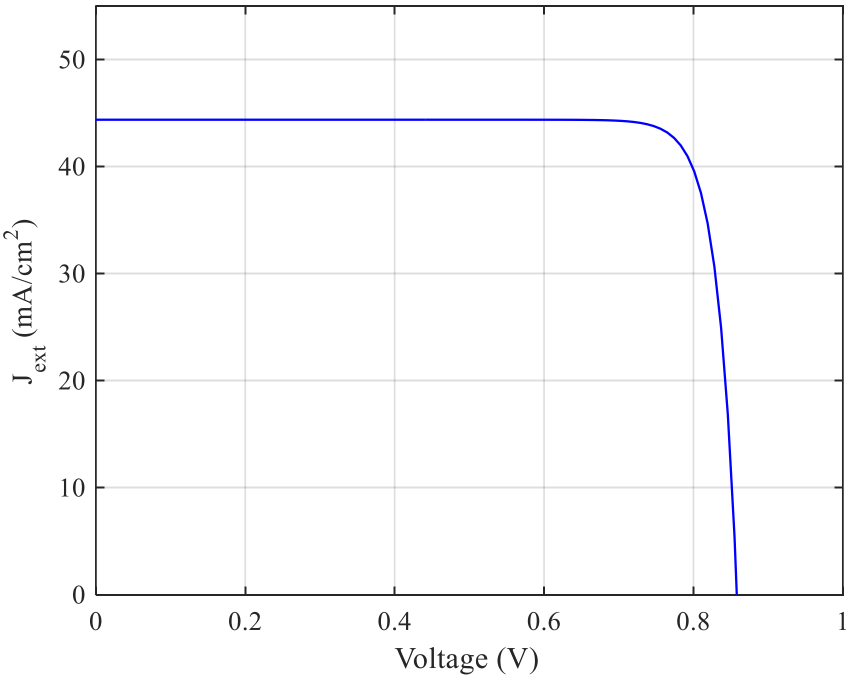


Figure 6: Example of JV characteristics traced with the Shockley-Queisser model, at $T = 300\,\mathrm{K}$ and for $E_g = 1.1\,\mathrm{eV}$.

why a solar cell should be thought as a *battery*, rather than a *diode*. And this motivates the choice of writing J_{ext} in (13) with the **generator convention**.

Putting everything together, we are finally in shape to write J_{ext} as:

$$J_{ext}(E_g, V) = J_{gen}(E_g) - J_{rec}(E_g, V) = J_{gen}(E_g) - J_{rec,0}\left[\exp\left(\frac{V}{V_T}\right) - 1\right], \tag{20}$$

where we exploited

$$V_T = \frac{k_B T}{q}.$$

Figure 6 shows an example of JV characteristics traced with (20), for $E_g = 1.1\,\mathrm{eV}$ and $T = 300\,\mathrm{K}$. To this aim, V has been treated as an independent variable. From a circuit standpoint, this could be seen as using as boundary condition a voltage source, rather than a resistance[6].

4 Solar cells: figures of merit

4.1 Short-circuit current, open-circuit voltage

From the JV characteristics shown in Fig. 6, it is possible to appreciate two quite peculiar **non**-operation points:

- the short-circuit current J_{SC}, *i.e.,* the current flowing through the device for $V = 0$;
- the open-circuit voltage V_{OC}, *i.e.,* the voltage measurable on the device with $J = 0$.

These are **non**-operation points because we must think to the solar cell as a **generator**, not as a **diode**: Because the generated power is:

[6] Notice that this is the same procedure carried out when tracing the JV characteristics of a solar cell with a drift-diffusion simulator: we force the circuit voltage as a boundary condition, allowing to draw $J_{ext}(V)$.

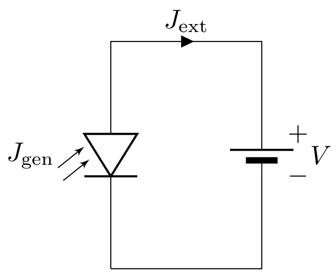


Figure 7: Circuit for the experimental and/or drift-diffusion characterization of a solar panel. Compared to that of Fig. 3, which indicates the real-world operation, in this circuit V is enforced externally through a voltage generator, and J_{ext} is measured.

$$P = IV = AJV, \tag{21}$$

if $J = 0$ or $V = 0$, the power produced by the solar cell is 0.

The final scope of a generator is to generate power and to provide it to a **load**, therefore to a **resistor**, R. In this view, the short circuit and open circuit are the two *extreme* loads, for $R \to 0$ and $R \to \infty$. Nevertheless, J_{SC} and V_{OC} are quite interesting figures of merit, as they provide some intuitive indication of the solar cell performance.

As far as J_{SC} is concerned, its calculation is pretty straightforward:

$$J_{\text{SC}} = J_{\text{ext}}|_{V=0} = J_{\text{gen}}, \tag{22}$$

i.e., the short-circuit current is simply equal to the generation term from (14).

For what concerns the open-circuit voltage V_{OC}, it is defined for $J_{\text{ext}} = 0$, so, by enforcing this condition on (20), we have:

$$0 = J_{\text{gen}}(E_{\text{g}}) - J_{\text{rec},0}\left[\exp\left(\frac{V_{\text{OC}}}{V_{\text{T}}}\right) - 1\right] \simeq J_{\text{gen}}(E_{\text{g}}) - J_{\text{rec},0}\exp\left(\frac{V_{\text{OC}}}{V_{\text{T}}}\right), \tag{23}$$

where we exploited the fact that, at $V = V_{\text{OC}}$, it is pretty likely that the exponential is much larger than 1. After manipulating as

$$\exp\left(\frac{V_{\text{OC}}}{V_{\text{T}}}\right) = \frac{J_{\text{gen}}(E_{\text{g}})}{J_{\text{rec},0}(E_{\text{g}})},$$

one obtains

$$V_{\text{OC}}(E_{\text{g}}) = V_{\text{T}} \ln\left(\frac{J_{\text{gen}}(E_{\text{g}})}{J_{\text{rec},0}(E_{\text{g}})}\right). \tag{24}$$

An important point about V_{OC} is that its maximum value is the bandgap voltage[7], $V_{\text{g}} = E_{\text{g}}/\text{q}$. Indeed, recalling the derivation (19), the exponent V arises from a difference of quasi-Fermi levels, which is lower than the bandgap[8]. To close this discussion, Fig. 8 shows two curves versus the bandgap E_{g}: one is the bandgap itself (dashed red curve), one is $V_{\text{OC}}(E_{\text{g}})$, which is clearly following E_{g}, but is always lower than it.

[7] It is possible to find several proofs and arguments about this point, which are based on expressions of $J_{\text{rec},0}$ recalling the I_0 of a diode (inverse saturation current), or something similar, but be very careful about them: these proofs often rely on lifetimes, diffusion lengths, and implicitly these quantities pertain Shockley-Read-Hall theory and/or go against the *infinite mobility* hypothesis. Instead, Shockley and Queisser in [1, eq.(3.21)] rely on a different argument, about the fact that the integral of (15) gives *linear* and *logarithmic* contributions; the latter, for $V_{\text{T}} \to 0$, are negligible. In order to simplify this very complex integral, one could approximate the denominator with the exponential (neglect the additional 1).

[8] unless we consider the unrealistic case of degenerate semiconductors

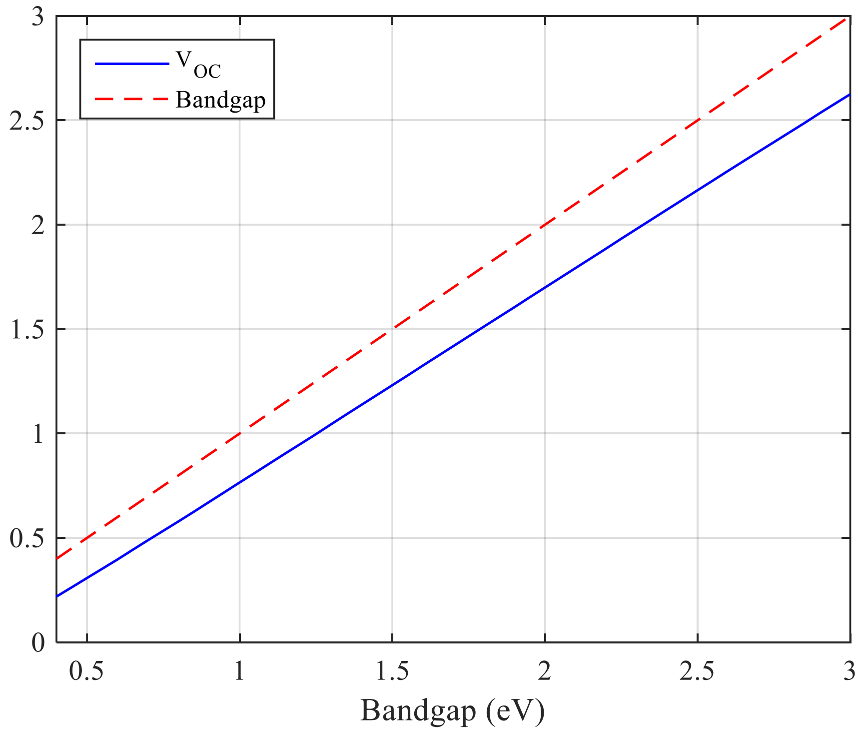


Figure 8: Comparison of the short-circuit voltage with the corresponding bandgap.

4.2 Maximum power point, fill factor, detailed balance limit

The solar cell must be used as a **generator**, *i.e.*, something that provides power to a load connected to it. In other words, we should tailor, as circuit boundary condition for the circuit in Fig. 3, a resistance R forcing the solar cell to operate in the maximum power point (MPP), R_{MPP}:

$$R_{\mathrm{MPP}} = \frac{V_{\mathrm{MPP}}}{AJ_{\mathrm{MPP}}}. \tag{25}$$

This means that, in order to design the optimal load for the solar cell, we need to find the maximum power point voltage, then compute the J_{MPP} from (20), and use (25). Recalling that the power density p.u.a. P can be written as

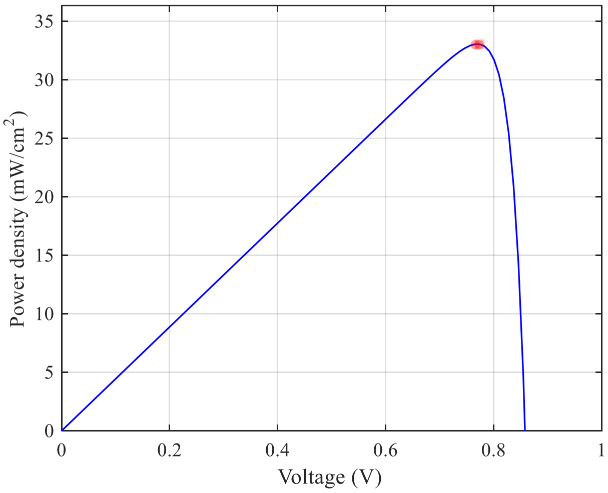
$$P = J_{\mathrm{ext}}V. \tag{26}$$

Figure 9 shows an interpretation of the maximum power point on the basis of this definition. The left figure shows the product JV versus V. In addition to the obvious observation that the open-circuit and short-circuit conditions are not providing any power, it can be seen that this curve has a maximum at about 0.775 V. Then, the right figure is the same of 6, where also the straight line JR_{MPP} is shown, emphasizing how this resistance acts as a boundary condition for the solar cell, forcing its bias point.

The figure contains another interesting pictorial representation, which is the shaded rectangle defined by the J and V axes, and by the $V = V_{\mathrm{OC}}$ and $J = J_{\mathrm{SC}}$ straight lines. Imagine that, ideally, the solar cell characteristics would be equal to such rectangle: in this case, the maximum power would be the highest possible. In this view, one could define the *fill factor*, η_{FF}, as

$$\eta_{\mathrm{FF}} = \frac{P_{\mathrm{MPP}}}{V_{\mathrm{OC}}J_{\mathrm{SC}}} = \frac{V_{\mathrm{MPP}}J_{\mathrm{MPP}}}{V_{\mathrm{OC}}J_{\mathrm{SC}}}. \tag{27}$$

The fill factor is an interesting figure of merit for the solar cell. Indeed, V_{OC} and J_{SC} provide indications about the solar cell performance in *extreme* conditions, but without giving any information of what happens *in the middle*, where it is most likely that the cell is going to operate. This is quantified by the fill factor. Referring



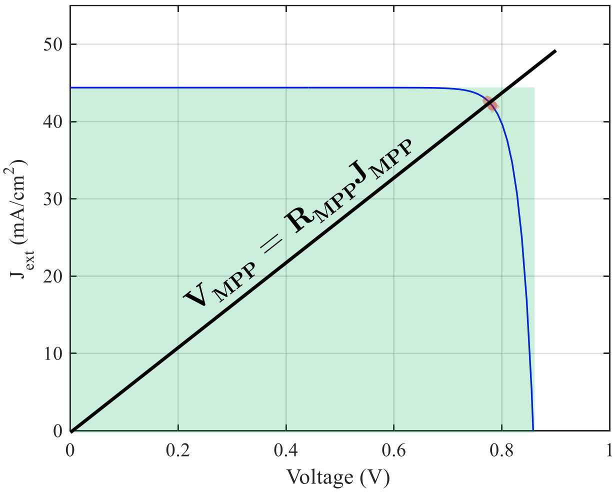


Figure 9: Left: power density p.u.a. vs voltage; the maximum power point is indicated in red. Right: JV characteristics, with a superimposed green rectangle built intersecting the $V = V_{OC}$ and $J = J_{SC}$ axes; this is useful to introduce the idea of fill factor.

to Fig. 9(right), the fill factor can be interpreted as the ratio of the areas closed by the JV characteristics and that of the green shaded rectangle: if the areas are coincident (ratio equal to 1), then the power at the MPP is the highest possible, given V_{OC} and J_{SC}.

Now, let's try to propose some expression to evaluate V_{MPP}. First, it could be useful to re-write J_{ext} in a handier way. Based on the definition of V_{OC} (see (23)), we can state that

$$J_{gen} = J_{rec,0} \exp\left(\frac{V_{OC}}{V_T}\right).$$

Seen from another perspective, V_{OC} is the voltage for which radiative recombination becomes so strong that it fully compensates $J_{gen} = J_{SC}$. Of course, for $V > V_{OC}$, we have $J_{ext} < 0$, so the solar cell behaves as a traditional diode, no longer as a generator: we are out of the *photovoltaic region* $0 < V < V_{OC}$. Therefore, we are sure that $V_{MPP} < V_{OC}$. Substituting the last expression in (20), we obtain

$$J_{ext} \simeq J_{rec,0}\left[\exp\left(\frac{V_{OC}}{V_T}\right) - \exp\left(\frac{V}{V_T}\right)\right], \tag{28}$$

where the approximation is related to neglecting the -1, because it is pretty likely that V_{MPP} is quite close to V_{OC}. Then, we can plug this expression in (26), leading to

$$P = J_{ext}V = J_{rec,0}\left[V\exp\left(\frac{V_{OC}}{V_T}\right) - V\exp\left(\frac{V}{V_T}\right)\right].$$

Because our aim is to find the voltage at which P is maximum, then we can look for the zero of the derivative of the last expression. The derivative is:

$$\frac{\partial P}{\partial V} = J_{rec,0}\left[\exp\left(\frac{V_{OC}}{V_T}\right) - \exp\left(\frac{V}{V_T}\right) - \frac{V}{V_T}\exp\left(\frac{V}{V_T}\right)\right].$$

If we set this expression to 0, we find easily

$$\exp\left(\frac{V}{V_T}\right)\left[1 + \frac{V}{V_T}\right] = \exp\left(\frac{V_{OC}}{V_T}\right).$$

By applying the logarithm to both sides, and the property $\log(xy) = \log(x) + \log(y)$, we have:

$$\frac{V_{MPP}}{V_T} + \ln\left(1 + \frac{V_{MPP}}{V_T}\right) = \frac{V_{OC}}{V_T}, \tag{29}$$

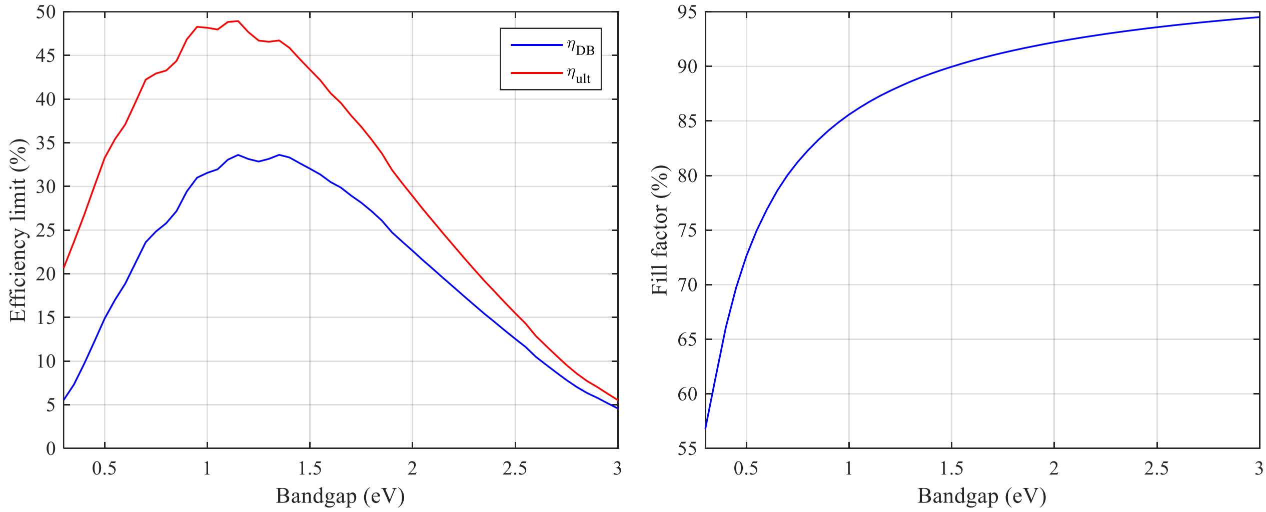


Figure 10: Left: comparison of the ultimate (red) and detailed balance (blue) efficiency limits versus bandgap. Right: fill factor vs bandgap.

which relates V_{OC} to V_{MPP}. Unfortunately, being this relation nonlinear, it requires an interative solver to be solved. As an example, we can formulate a Newton's method by trying to minimize the function f defined as:

$$f = \frac{V_{\text{MPP}}}{V_{\text{T}}} + \ln\left(1 + \frac{V_{\text{MPP}}}{V_{\text{T}}}\right) - \frac{V_{\text{OC}}}{V_{\text{T}}}, \tag{30}$$

whose derivative is

$$\frac{\mathrm{d}f}{\mathrm{d}V_{\text{MPP}}} = \frac{1}{V_{\text{T}}} + \frac{1}{1 + \frac{V_{\text{MPP}}}{V_{\text{T}}}}\frac{1}{V_{\text{T}}} = \frac{1}{V_{\text{T}}} + \frac{1}{V_{\text{T}} + V_{\text{MPP}}}. \tag{31}$$

Then, this can be used to formulate a Newton's method, to refine V_{MPP} as

$$V_{\text{MPP}}^{(k+1)} = V_{\text{MPP}}^{(k)} - \frac{f^{(k)}}{\frac{\mathrm{d}f^{(k)}}{\mathrm{d}V_{\text{MPP}}}} \tag{32}$$

where k indicates the Newton's iteration. A good guess for V_{MPP} is $0.9V_{\text{OC}}$, to start the iterations.

An alternative, more *optimization-oriented* solution, is to compute directly P, and try to minimize the quantity $1/P$ instead[9].

Once V_{MPP} is known, then J_{MPP} can be computed with (20), and P_{MPP} with (26). Finally, it is possible to define the detailed balance efficiency limit, η_{DB}, as:

$$\eta_{\text{DB}} = \frac{P_{\text{MPP}}}{P_{\text{tot}}}. \tag{33}$$

Figure 10(left) shows the detailed balance efficiency limit η_{DB} (blue curve), and compares it with the ultimate efficiency (red curve), which is apparently higher: this means that the detailed balance efficiency limit is a much more sensible upper bound, being lower of the ultimate one! For completeness, also the fill factor is reported (right), versus the bandgap energy, showing how it increases with it.

[9]usually, solvers work well in minimizing problems, not in maximizing, so we can try to minimize the reciprocal of the quantity that we want to maximize.

5 Loss mechanisms in solar cells

We have computed the efficiency limit of a solar cell. Now, we are going to compute its *complements*, *i.e.,* all those terms that act as *losses* wasting part of the total solar power P_{tot}. This is pretty interesting because it could suggest strategies aimed at *overcoming* such limit.

5.1 Limitations to the ultimate efficiency

Great limitations appear considering even just the ultimate efficiency η_{ult}. In fact, when formulating it, we already accept two loss sources.

5.1.1 Sub-bandgap photons

Photons with energy lower than the bandgap are lost, since they cannot induce the creation of a e-h pair. In this view, one could define the power density p.u.a. of photons having $E < E_{\mathrm{g}}$, $P^{<}$, as

$$P^{<} = \int_{E_{\min}}^{E_{\mathrm{g}}} E\phi(E)\,\mathrm{d}E, \tag{34}$$

so that the loss contribution caused by these photons is:

$$\ell^{<} = \frac{P^{<}}{P_{\mathrm{tot}}}. \tag{35}$$

5.1.2 Thermalization

Thermalization concerns the fact that, if a photon has $E > E_{\mathrm{g}}$, then not all of this energy helps creating e-h pairs: 1 photon corresponds just to 1 pair, regardless of the energy of the photon. In other words, the excess of energy is lost due to thermalization: energetic carriers thermalize immediately and an energy equal to $E - E_{\mathrm{g}}$ is lost

$$P_{\mathrm{th}} = \int_{E_{\mathrm{g}}}^{E_{\max}} (E - E_{\mathrm{g}})\phi(E)\,\mathrm{d}E, \tag{36}$$

so that the loss contribution caused by thermalization is:

$$\ell_{\mathrm{th}} = \frac{P_{\mathrm{th}}}{P_{\mathrm{tot}}}. \tag{37}$$

For what concerns the ultimate efficiency, this is all we need, since

$$\eta_{\mathrm{ult}} + \ell^{<} + \ell_{\mathrm{th}} = 1,$$

as it is also shown in Fig. 11, where the ultimate efficiency is compared to the other two contributions.

5.2 Limitations to the detailed balance efficiency

As demonstrated by Fig. 10, η_{ult} is a worst lower bound with respect to η_{DB}, meaning that it is possible to identify other loss mechanisms missing in the formulation of η_{ult}. The *useful power* is just

$$\eta_{\mathrm{DB}} P_{\mathrm{tot}} = V_{\mathrm{MPP}} J_{\mathrm{MPP}}.$$

Therefore, we have to look for what we are still missing.

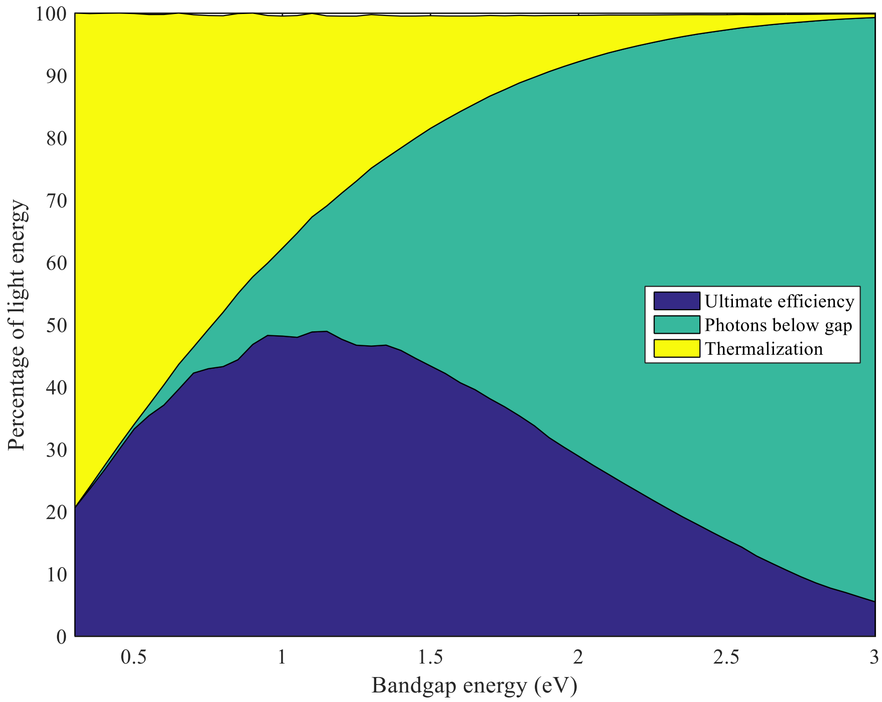


Figure 11: Decomposition of solar power into ultimate efficiency and remaining loss contributions.

5.2.1 Recombination losses

The first additional loss which we can imagine is radiative recombination: most of the detailed balance formulation is based on it, therefore it is pretty reasonable that it takes away some of our power. Inverting (20) and considering to work in the MPP, we can find

$$J_{\text{rec}} = J_{\text{gen}} - J_{\text{MPP}}.$$

Radiative recombination (the only mechanism in our model) involves energy transitions with energy E_{g}, so we could evaluate the radiated power P_{rec} to be

$$P_{\text{rec}} = E_{\text{g}}\frac{J_{\text{rec}}}{\text{q}} = E_{\text{g}}\left[\frac{J_{\text{gen}}}{\text{q}} - \frac{J_{\text{MPP}}}{\text{q}}\right] = E_{\text{g}}\left[\Phi^{>} - \frac{J_{\text{MPP}}}{\text{q}}\right], \tag{38}$$

from which it is possible to evaluate the loss contribution of radiative recombination,

$$\ell_{\text{rec}} = \frac{P_{\text{rec}}}{P_{\text{tot}}}. \tag{39}$$

5.2.2 Bandgap loss

We could verify that (39) and (33) do not add up to (11), showing that there is a missing term. In order to find it, we could simply proceed by subtraction:

$$\begin{aligned} P_{\text{ult}} - P_{\text{MPP}} - P_{\text{rad}} &= E_{\text{g}}\Phi^{>} - J_{\text{MPP}}V_{\text{MPP}} - E_{\text{g}}\left[\Phi^{>} - \frac{J_{\text{MPP}}}{\text{q}}\right] = \\ &= J_{\text{MPP}}\left(\frac{E_{\text{g}}}{\text{q}} - V_{\text{MPP}}\right) \triangleq P_{\text{g}}. \end{aligned} \tag{40}$$

We have defined this power density as P_{g} because of the interpretation we could attempt: by looking at it, we could imagine that are losses pertaining the fact that $V_{\text{MPP}} < V_{\text{g}}$. In fact, the quasi-Fermi level splitting would

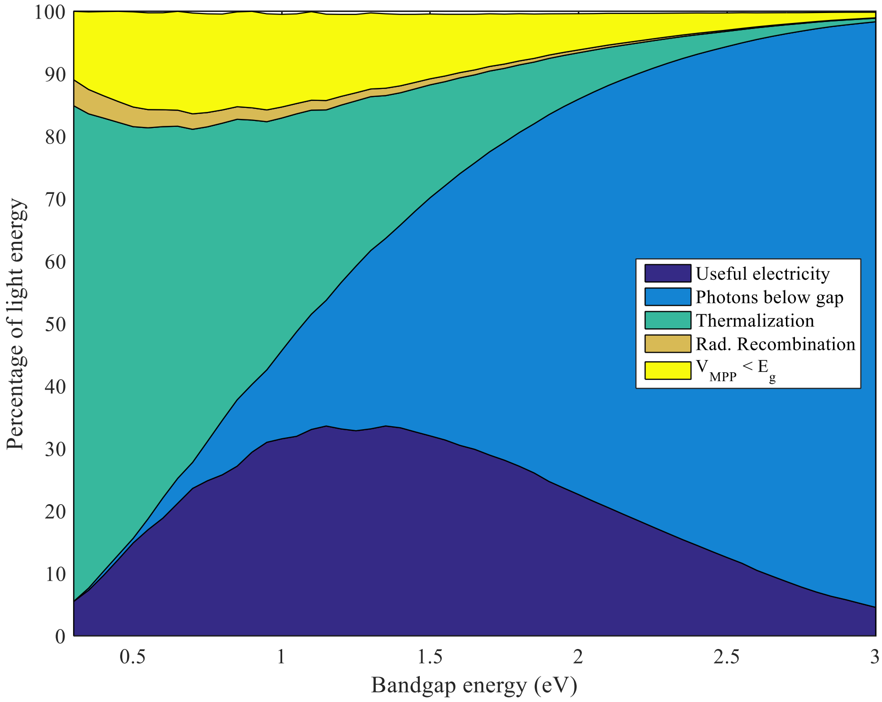


Figure 12: Decomposition of solar power into potentially-useful electricity (detailed balance limit) and remaining loss contributions.

have *more room* before their upper bound (the bandgap), but the MPP is not compatible with it. Then, just like with the previous terms, it is possible to calculate the corresponding loss contribution as

$$L_{\mathrm{g}} = \frac{P_{\mathrm{g}}}{P_{\mathrm{tot}}} \tag{41}$$

As a final result, Fig. 12 shows the various loss contributions, compared to the useful energy, computed with (34)–(41).

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