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Does non-reciprocity break the Shockley–Queisser limit in single-junction solar cells?

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ABSTRACT

The efficiency of single-junction solar cells is bounded by the Shockley–Queisser limit of 41%. However, standard derivation for this limit constrains the system to be reciprocal, and what non-reciprocity can bring for single-junction solar cells remains yet to be clarified. Here, we prove that even with non-reciprocity, the ultimate efficiency of single-junction solar cells is still subject to the Shockley–Queisser limit. We show that the Shockley–Queisser limit does not rely on the detailed balance, but rather is a consequence of the integrated balance between the absorption and emission processes, as required by the second law of thermodynamics.

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The efficiency of single-junction solar cells is known to be upper bounded by the Shockley–Queisser limit. The standard derivation of the Shockley–Queisser limit makes extensive use of the concept of detailed balance.[1] In fact, this limit was referred to as the detailed balance limit in the title of the original Shockley–Queisser paper.[1] Detailed balance concerns the balance between the light absorption and emission processes and is the same as Kirchhoff's law, which states that the directional spectral absorptivity and emissivity must be equal.[2] Kirchhoff's law is a result of the Lorentz reciprocity that applies to almost all standard materials, including typical metals and semiconductors used in solar cell structures.

In recent years, it has been shown that Kirchhoff's law and, hence, the detailed balance can be strongly violated with the use of non-reciprocal photonic structures consisting of magneto-optical materials.[3–14] Moreover, Park *et al.* recently showed that non-reciprocal multi-junction cells can outperform the theoretical efficiency limits for reciprocal multi-junction cells.[15] Therefore, a natural question arises: Does the Shockley–Queisser limit still hold if one constructs a non-reciprocal single-junction solar cell?

In this paper, we prove that the Shockley–Queisser limit still holds for a single-junction solar cell even if the reciprocity and, hence, the detailed balance are broken. Our proof makes use of an "integrated balance" relation between the absorption and emission processes that is directly related to the second law of thermodynamics. Our results indicate that the Shockley–Queisser limit is a stronger theoretical result as compared with what the original derivation implied.

We consider the system of Fig. 1, where a single-junction solar cell at room temperature $T_C = 300\,\mathrm{K}$ exchanges radiation with the Sun at the temperature $T_S = 6000\,\mathrm{K}$ and the rest of the sky at temperature T_C. We assume the Sun and the sky to behave as blackbodies, and they are represented in the figure as fractions of a spherical shell. A small solar cell is located in the middle of this shell. For the sake of simplicity, we place a reflector below the cell, which allows us to only consider the radiative processes occurring over the upper hemisphere as shown in the figure. We note that the same conclusion as our paper also applies to bifacial solar cells where light is incident from both sides of the cell.[16] The solid angle of the spherical cap occupied by the Sun is Ω_S, and that of the entire hemisphere is Ω_H. Therefore, we write the solid angle of the fraction of the shell occupied by the sky excluding the Sun as $\Omega_H - \Omega_S$.

We set the cell's directional spectral emissivity as $\epsilon(\theta, \phi, E)$ and absorptivity as $a(\theta, \phi, E)$, which are functions of polar angle θ, azimuthal angle ϕ, and energy of the emitted/absorbed photon E. Note that in this paper, unlike the original Shockley–Queisser paper, we do not assume Kirchhoff's law to hold, that is, we do not assume that

$$\epsilon(\theta, \phi, E) = a(\theta, \phi, E). \tag{1}$$

We first analyze the case in which the Sun is absent, and the cell is in thermal equilibrium with the surrounding hemisphere at the temperature T_C. In addition, we assume a filter placed between the cell and the hemisphere that only passes radiation of certain energy E with a narrow bandwidth ΔE.[2,17] We assume E to be higher than the solar

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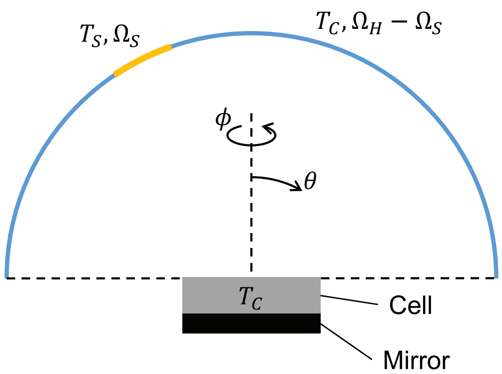

FIG. 1. Illustration of a single-junction solar cell and surrounding sky. The sky is represented as a spherical shell, where the yellow region shows the fraction occupied by the Sun, and the blue region shows the rest of the sky.

cell's bandgap E_G, and incident photons are absorbed by the cell with 100% efficiency. We also assume that the recombination taking place in the cell is purely radiative. In this case, the emitted photon flux $n_{\epsilon 0}(E)$ can be expressed as

$$n_{\epsilon 0}(E) = \frac{2}{h^3c^2}\frac{E^2}{\exp\left(\frac{E}{kT_C}\right)-1}\Delta E\int_{\Omega_H}\epsilon(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi, \tag{2}$$

and the absorbed photon flux $n_{a0}(E)$ as

$$n_{a0}(E) = \frac{2}{h^3c^2}\frac{E^2}{\exp\left(\frac{E}{kT_C}\right)-1}\Delta E\int_{\Omega_H}a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi, \tag{3}$$

where h, c, and k are the Planck constant, the speed of light in vacuum, and the Boltzmann constant, respectively. Because we are considering the equilibrium state, $n_{\epsilon 0}(E) = n_{a0}(E)$, and the following equation holds for arbitrary E:

$$\int_{\Omega_H}\epsilon(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi = \int_{\Omega_H}a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi. \tag{4}$$

A relation equivalent to Eq. (4), but expressed in systems with a discrete set of ports, was proposed in Ref. 18. We refer to Eq. (4) as integrated balance, to be contrasted to the detailed balance or Kirchhoff's law of Eq. (1). The integrated balance arises because the total absorption and emission for an object must equal if the object is in thermal equilibrium with its environment, as required by the second law of thermodynamics. This integrated balance between the emissivity and absorptivity is the basis of our following derivation. In fact, in the end, it turns out that the Shockley–Queisser limit can be proved with the relation of integrated balance only, without resorting to the use of detailed balance.

We now analyze the case where the Sun is present. We consider first the contributions from the photons with energy centered at E with a narrow bandwidth of ΔE. We express the operating voltage across the cell as V. Throughout our study, we follow the sign convention in which the positive values of the current and voltage correspond to the cell acting as a power source. Then, emitted photon flux $n_\epsilon(E)$ can be expressed as

$$n_{\epsilon}(E) = \frac{2}{h^3c^2}\frac{E^2}{\exp\left(\frac{E-qV}{kT_C}\right)-1}\Delta E\int_{\Omega_H}\epsilon(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi, \tag{5}$$

where the voltage V enters as a chemical potential of photons qV.[19–21] Using the integrated balance relation of Eq. (4), $n_\epsilon(E)$ becomes

$$n_{\epsilon}(E) = \frac{2}{h^3c^2}\frac{E^2}{\exp\left(\frac{E-qV}{kT_C}\right)-1}\Delta E\int_{\Omega_H}a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi. \tag{6}$$

We note that the condition of integrated balance allows us to express the total emitted photon flux in terms of the absorptivity of the cell.

For the absorbed photon flux, the portion originating from the Sun can be expressed as

$$n_{aS}(E) = \frac{2}{h^3c^2}\frac{E^2}{\exp\left(\frac{E}{kT_S}\right)-1}\Delta E\int_{\Omega_S}a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi, \tag{7}$$

and the portion originating from the rest of the sky is

$$n_{aC}(E) = \frac{2}{h^3c^2}\frac{E^2}{\exp\left(\frac{E}{kT_C}\right)-1}\Delta E\int_{\Omega_H-\Omega_S}a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi. \tag{8}$$

Using Eqs. (6)–(8), the density of the current $J(E)$ collected from the cell, due to the absorption and emission of photons in the narrow band of energy around E, is

$$\begin{aligned} J(E) &= q(n_{aS}(E)+n_{aC}(E)-n_\epsilon(E)) \\ &= \frac{2q}{h^3c^2}\frac{E^2}{\exp\left(\frac{E}{kT_S}\right)-1}\Delta E\int_{\Omega_S}a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi \\ &\quad+\frac{2q}{h^3c^2}\frac{E^2}{\exp\left(\frac{E}{kT_C}\right)-1}\Delta E\int_{\Omega_H-\Omega_S}a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi \\ &\quad-\frac{2q}{h^3c^2}\frac{E^2}{\exp\left(\frac{E-qV}{kT_C}\right)-1}\Delta E\int_{\Omega_H}a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi, \end{aligned} \tag{9}$$

where q is the elementary charge. By dividing the last term of Eq. (9), which describes the emission process of the cell, into two separate integrals, one over Ω_S and the other over $\Omega_H - \Omega_S$, we obtain

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$$J(E) = \frac{2q}{h^3c^2}\left[\frac{E^2}{\exp\left(\frac{E}{kT_S}\right)-1} - \frac{E^2}{\exp\left(\frac{E-qV}{kT_C}\right)-1}\right] \times \Delta E \int_{\Omega_S} a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi + \frac{2q}{h^3c^2}\left[\frac{E^2}{\exp\left(\frac{E}{kT_C}\right)-1} - \frac{E^2}{\exp\left(\frac{E-qV}{kT_C}\right)-1}\right] \times \Delta E \int_{\Omega_H-\Omega_S} a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi. \quad (10)$$

From the perspective of conventional derivation,[1,22] where Kirchhoff's law of Eq. (1) holds, dividing the emission part of Eq. (9) as above can be physically understood as treating the emission back to the Sun and that to the rest of the sky separately, so that the first term of Eq. (10) corresponds to the contributions to the current from photon exchange in the Sun's direction, while the second term corresponds to the contributions from photon exchange in the directions of other parts of the sky. In contrast, in this work, without the constraint of detailed balance, dividing the emission term into two separate parts is simply a mathematical trick and does not necessarily entail physical interpretation.

Then, power generated from the cell per unit area is $P(E) = J(E) \times V$, which can be expressed as

$$P(E) = \frac{2qV}{h^3c^2}\left[\frac{E^2}{\exp\left(\frac{E}{kT_S}\right)-1} - \frac{E^2}{\exp\left(\frac{E-qV}{kT_C}\right)-1}\right] \times \Delta E \int_{\Omega_S} a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi + \frac{2qV}{h^3c^2}\left[\frac{E^2}{\exp\left(\frac{E}{kT_C}\right)-1} - \frac{E^2}{\exp\left(\frac{E-qV}{kT_C}\right)-1}\right] \times \Delta E \int_{\Omega_H-\Omega_S} a(\theta,\phi,E)\cos\theta\sin\theta d\theta d\phi. \quad (11)$$

For the cell to generate power, V must be positive. In Eq. (11), the part in the bracket of the second term is always negative when V is positive. Therefore, in order to maximize the power, it is advantageous to have $a(\theta,\phi,E) = 0$ in the directions away from the Sun. Moreover, the part in the bracket of the first term should be positive for power generation, which makes it advantageous to have $a(\theta,\phi,E) = 1$ in the direction of the Sun. Under this condition, the maximum power density that can be achieved due to photon exchange in the narrow bandwidth around E is

$$P_{\max}(E) = f_S\frac{2\pi qV}{h^3c^2}\left[\frac{E^2}{\exp\left(\frac{E}{kT_S}\right)-1} - \frac{E^2}{\exp\left(\frac{E-qV}{kT_C}\right)-1}\right]\Delta E, \quad (12)$$

where $f_S = \int_{\Omega_S}\cos\theta\sin\theta d\theta d\phi/\pi$ represents the fraction of the hemisphere occupied by the Sun. Summing up Eq. (12) for all energy above the cell's bandgap E_G leads to the total generated power per unit area of

$$P_m = f_S\frac{2\pi qV}{h^3c^2}\int_{E_G}^{\infty}\left[\frac{E^2}{\exp\left(\frac{E}{kT_S}\right)-1} - \frac{E^2}{\exp\left(\frac{E-qV}{kT_C}\right)-1}\right]dE. \quad (13)$$

The efficiency of the cell is

$$\eta = \frac{P_m}{P_S}, \quad (14)$$

where

$$P_S = \frac{2}{h^3c^2}\int_0^{\infty}\frac{E^3}{\exp\left(\frac{E}{kT_S}\right)-1}dE\int_{\Omega_S}\cos\theta\sin\theta d\theta d\phi = f_S\sigma T_S^4 \quad (15)$$

is the total power flux of sunlight as seen by the cell. In Eq. (15), σ is the Stefan–Boltzmann constant.

For a solar cell with a given bandgap, the efficiency is maximized by choosing the optimal voltage V. This optimization process is standard as described in Ref. 1 and yields the maximum efficiency of 41% with the bandgap at $E_G = 1.1$ eV. Thus, our analysis, without assuming reciprocity, obtains results that are identical to the standard analysis where reciprocity and, hence, detailed balance are assumed. Our result indicates that breaking reciprocity does not improve the efficiency limit for single-junction solar cells.

We note that in deriving the efficiency limit of Eq. (14), the factor f_S, which describes the fraction of the hemisphere occupied by the sun, cancels. Therefore, the efficiency limit is independent of f_S. The efficiency limit for single-junction cell is the same for the case of maximum concentration, where the incident solar radiation occupies the entire hemisphere and hence $f_S = 1$, and for the case of direct sunlight where there is no solar concentration and $f_S = 2.2 \times 10^{-5}$. This result is known in the standard solar cell analysis.[22–25] Here, we generalize it for non-reciprocal systems. Our analysis indicates that, in the cases where $f_S < 1$ and, hence, part of the hemisphere is not occupied by the Sun, the requirement to reach the efficiency limit is to have unity absorptivity in the direction of the Sun and zero absorptivity everywhere else. There is no constraint on the direction of the emissivity of the cell.

In a recent paper, it was noted that non-reciprocal multi-junction solar cells can have efficiency reaching the Landsberg limit, which exceeds the efficiency limit of reciprocal multi-junction cells.[15] Reference 15 is related to earlier works that showed attaining the Landsberg limit is possible with the use of non-reciprocal structures.[26,27] The designs of Refs. 15 and 27 exploit the fact that the angular absorptivity and emissivity of a solar cell layer can be different in a non-reciprocal system. Therefore, the emission from a given solar cell layer needs not go back to the Sun, but rather can be directed toward another cell layer for the opportunity of additional power generation. Such an opportunity does not occur for single-junction cells.

Our conclusion is that non-reciprocity cannot be used to improve the efficiency of single-junction cells over the Shockley–Queisser limit. Previously, it was shown that a multi-junction cell can be constructed using a single material having a single bandgap, with efficiency exceeding the Shockley–Queisser limit.[28] Such a single-material multi-junction cell can benefit from the use of non-reciprocity as was noted in Ref. 29. Our conclusion is compatible with these results.

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The conclusion of our work differs from that of a recent paper by Sergeev and Sablon, who claimed that non-reciprocity can be used to improve the efficiency of a single-junction solar cell.[30] We note that the maximum efficiency that they showed is at 41%, which is the Shockley–Queisser limit (see Fig. 4 of Ref. 30). Moreover, their design of a solar cell (Fig. 2 of Ref. 30) assumed that a cell can reabsorb all the photons that it emits. We believe such an assumption violates the second law of thermodynamics.

In summary, we demonstrate that power efficiency maximization of a single-junction solar cell without the assumption of Kirchhoff's radiation law still leads to the Shockley–Queisser limit of 41%. The only constraint imposed on the relation between directional absorptivity and emissivity is the relation of integrated balance, which is a direct consequence of the second law of thermodynamics. Therefore, in order for non-reciprocity to play a role in enhancing solar cell efficiency via photon management, multi-junction structure is required. Our results indicate that the Shockley–Queisser limit is not the consequence of detailed balance, which is in contrast with the title of the seminal paper of Ref. 1. Rather, the Shockley–Queisser limit is a requirement of the second law of thermodynamics on single-junction solar cells and, therefore, is a far stronger result.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Yubin Park: Conceptualization (equal); Formal analysis (lead); Investigation (lead); Methodology (lead); Validation (equal); Writing – original draft (lead); Writing – review & editing (equal). **Shanhui Fan:** Conceptualization (equal); Funding acquisition (lead); Project administration (lead); Supervision (lead); Validation (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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