

## SHORT COMMUNICATION OPEN ACCESS

## Thermodynamic Limit on the Open Circuit Voltage of Solar Cells

Tom Markvart<sup>1,2</sup> <sup>1</sup>Engineering Sciences, University of Southampton, Southampton, UK | <sup>2</sup>Centre for Advanced Photovoltaics, Czech Technical University, Prague, Czech Republic**Correspondence:** Tom Markvart (tm3@soton.ac.uk)**Received:** 23 August 2024 | **Revised:** 3 February 2025 | **Accepted:** 17 February 2025**Funding:** This work was supported by Ministry of Education, Youth and Physical Education (in Czech Republic), funding a project Energy Conversion and Storage (grant no. CZ.02.01.01/00/22\_008/0004617) within the programme Johannes Amos Comenius, Excellent Research.**Keywords:** photovoltaics | thermodynamics | thermoelectricity

## ABSTRACT

A new thermodynamic limit for the open circuit voltage of solar cells that includes thermalization is obtained in terms of photon entropy. A simple graphical construction makes it possible to link this limit to the existing limits for single junction cells due to Trivich and Flinn, Shockley and Queisser, Würfel, and the thermodynamic Carnot-type limit for hot-carrier solar cell. At the fundamental level, this limit points to similarity between photovoltaic and thermoelectric energy conversion.

With solar cell efficiencies approaching limits to their performance, a careful discussion of these limits becomes increasingly important. As the maximum short circuit current is set by the incident photon flux, the focus is on the open-circuit voltage.

The first simple limit of this type

$$qV_{oc}^{TF} = E_g \quad (1)$$

where  $E_g$  is the semiconductor bandgap, was suggested by Trivich and Flinn in 1955 [1]. A more rigorous limit, proposed by Shockley and Queisser in 1961 [2], is given by the balance between incident and emitted radiation

$$qV_{oc}^{SQ} = k_B T_o \ln \left\{ \frac{\Phi(T_s)}{\Phi(T_o)} \right\} \quad (2)$$

with the photon flux density

$$\Phi(T) = 2\pi \int_{\nu_g}^{\infty} \left( \frac{\nu}{c} \right)^2 \frac{d\nu}{e^{h\nu/k_B T} - 1} \quad (3)$$

where  $T = T_s = 6000\text{ K}$  for solar radiation and  $T = T_o = 300\text{ K}$  for radiation at ambient temperature,  $\nu_g = E_g/h$ ,  $h$  is the Planck constant,  $k_B$  is the Stefan–Boltzmann constant, and  $c$  is the speed of light. Equations (2) and (3) are for maximum concentration of sunlight.

Equation (2) is satisfactory for most purposes but a more general version, valid also for highly concentrated radiation, follows from equating Würfel's expression for radiation flux with a finite chemical potential to the incident solar flux density: [3]

$$\Phi(T_s) = 2\pi \int_{\nu_g}^{\infty} \left( \frac{\nu}{c} \right)^2 \frac{d\nu}{e^{(h\nu - qV_{oc}^W)/k_B T_o} - 1} \quad (4)$$

since, in an ideal solar cell, the electrostatic energy of the carriers separated at contacts is equal to the chemical potential of photons. In contrast with the Shockley–Queisser voltage (2) that can be obtained directly using Equation (3) for both the solar photons and the photons emitted from the cell, the determination of  $V_{oc}^W$  from Equation (4) requires solving numerically the balance equation (4).

These limits—valid for a single-junction cell—should be contrasted with the maximum thermodynamic limit which would be obtained if solar photons with average energy  $u_s$  in thermal radiation with frequencies above  $\nu_g$  were to be converted with Carnot efficiency (see Section A (or Data A) in [Supporting Information](#) for a rigorous definition of  $u_s$ ):

$$qV_{oc}^C = \left(1 - \frac{T_o}{T_s}\right) u_s \quad (5)$$

Equation (5) applies to a hypothetical device where electron-hole pairs do not lose energy by thermalization—in other words, the hot carrier solar cell [4–6].

With a view towards next generation photovoltaics, it is of interest to obtain a thermodynamic limit which would include thermalization, and link expressions (1), (2), (4) and (5). Such limit can be obtained by invoking photon entropy and its relationship to the chemical potential.

First, the photon flux density  $\Phi(T)$  in a beam is transformed into number of photons  $N$  in a cavity of volume  $V$  that emits this beam. To this end, we can apply an expression for effusion through a hole to radiation gas [7],

$$\Phi(T) = \frac{c}{4} \frac{N}{V} \quad (6)$$

We can now define the entropy per photon by

$$s = \left( \frac{\partial S}{\partial N} \right)_{V,T} \quad (7)$$

where  $S$  is the total entropy of radiation in the cavity: blackbody radiation with frequencies extending from  $\nu_g$  to  $\infty$  (see Section B (or Data B) in [Supporting Information](#). Then, using a Maxwell-type relation [8],

$$\left( \frac{\partial S}{\partial N} \right)_{V,T} = - \left( \frac{\partial \mu}{\partial T} \right)_{V,N} \quad (8)$$

we integrate (8) with (7) to obtain

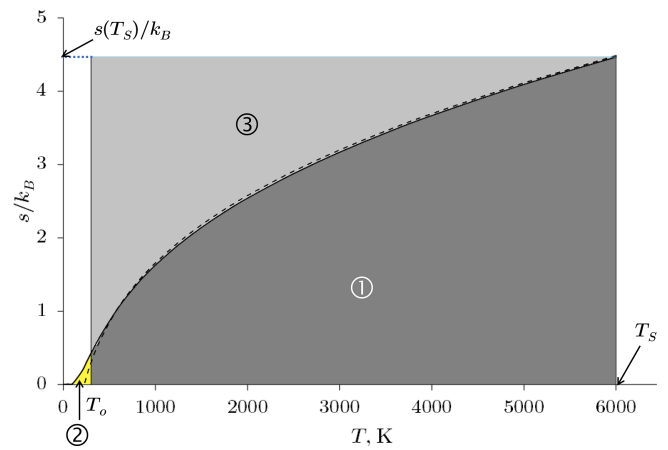
$$\mu(T_s) - \mu(T_o) = \int_{T_o}^{T_s} \left( \frac{\partial \mu}{\partial T} \right)_{V,N} dT = - \int_{T_o}^{T_s} s(n_s, T) dT \quad (9)$$

where the photon density  $n_s$  in the argument of the entropy  $s$  is kept constant at the density corresponding to the solar beam. Noting that the chemical potential  $\mu(T_s)$  of solar photons is zero

$$qV_{oc} = \mu(T_o) = \int_{T_o}^{T_s} s(n_s, T) dT \quad (10)$$

Equation (10) is the required general thermodynamic expression that can be used to link the different facets of the open circuit voltage.

Figure 1 shows the integration of the photon entropy  $s$  over temperature  $T$  as given by Equation (10). The solid line represents the numerically obtained solution for the Würfel case (radiation



**FIGURE 1** | The entropy  $s$  per photon as a function of temperature for radiation with photon energies  $h\nu > 1.5$  eV. Area ① corresponds to the voltage determined according to the Shockley-Queisser detailed balance (Equation (2), dashed line) or Würfel's equation (Equation (4), full line); the sum of areas ① and ② gives the Trivich and Flinn limit (1). Area ③ represents the losses by thermalization, making the rectangle obtained by combining areas ① and ③ equal to the voltage (5) resulting from the conversion of photons with energy  $u_s$ , with Carnot efficiency.

flux given by Equation (4)) and the dashed line corresponds to the SQ case with Equation (3). The dark grey area (1) under the solid line corresponds then to the integral given by Equation (10), that is, the open circuit voltage.

Viewed in more detail, there are two areas as there are two curves: one corresponding to the rigorous representation of entropy (full line, see [Equation S11](#)) which gives the open circuit voltage according to Equation (4). The dashed line is photon entropy in a low-density approximation [7]

$$s(n_s, T) = k_B \left\{ \ln \left( \frac{\gamma(T)}{n_s} \right) + T \frac{\gamma'(T)}{\gamma(T)} \right\} \quad (11)$$

where  $\gamma(T)$  is the photon density of states (see Section B in [Supporting Information](#) or Ref. [7]). Equation (11) is analogous to the Sackur-Tetrode equation for the entropy per atom in an ideal monatomic gas (see, e.g., ref. [9]), and leads to the Shockley-Queisser value of the open circuit voltage (2).

To proceed further we express the chemical potential of photons emitted from the cell in terms of their average energy  $u$  and the entropy (7) (see [Data S1A](#)):

$$\mu = u - T_o s \quad (12)$$

As the temperature  $T_o$  tends to zero,  $u \rightarrow E_g$ , the second term on the right hand side of (12) tends to zero, and the chemical potential tends to the bandgap  $E_g$ . Hence,

$$\int_0^{T_s} s(n_s, T) dT = E_g = qV_{oc}^{TF} \quad (13)$$

The integral

$$qV_{oc}^{TF} - qV_{oc}^W = \int_0^{T_o} s(n_s, T) dT \quad (14)$$

represented by the area ② therefore gives the difference between the Trivich–Flinn open-circuit voltage (1) and the Würfel limit given by (4).

A further analysis is possible by integrating Equation (10) by parts:

$$qV_{oc} = [s(T)T]_{T_o}^{T_s} - \int_{T_o}^{T_s} T ds = s(T_s)T_s \left(1 - \frac{T_o}{T_s}\right) - \left\{ \int_{s(T_o)}^{s(T_s)} T ds - [s(T_s) - s(T_o)]T_o \right\} \quad (15)$$

The first term of the right hand side of (15)—represented by the area of the rectangle ① + ② in Figure 1—corresponds to the Carnot-type voltage (5). This is because the heat  $s(T_s)T_s$  is equal to the mean solar photon energy  $u_s$  using the fact that the chemical potential of the solar radiation is zero. The light grey area ③ in Figure 1 then corresponds to the term in braces in Equation (15), that is, to the energy that is lost through thermalization. As discussed in Ref. [6], this energy loss represents the irreversible entropy generation.

In thermodynamics terms, the integral (10) and Figure 1 give the open circuit voltage whilst keeping the photon density constant and equal to the solar photon density. This is an isochoric process, corresponding to equal étendues of the incident beam and the beam emitted by the solar cell, and therefore maximum concentration of sunlight [7, 10].

The fundamental relationship between voltage and entropy extends beyond photovoltaics. Indeed, the voltage generated in a thermoelectric between temperatures  $T_c$  and  $T_h$  is given by

$$V = \int_{T_c}^{T_h} S dT \quad (16)$$

where  $S$  is the Seebeck coefficient or thermopower (see, e.g., Ref. [8]). As  $S$  is the charge-carrier entropy  $s$  divided by its charge,  $S = \pm s/q$ , Equation (16) is just Equation (10) written for electrons or holes. Vice versa, we could call the photon entropy  $s$  divided by the fundamental charge photon thermopower.

## Acknowledgements

This work was supported by project ‘Energy Conversion and Storage’, grant no. CZ.02.01.01/00/22\_008/0004617, programme Johannes Amos Comenius, Excellent Research. Open access publishing facilitated by Ceske vysoke uceni technicke v Praze, as part of the Wiley - CzechELib agreement.

## Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

## References

1. D. Trivich and P. Flinn, “Maximum Efficiency of Solar Energy Conversion by Quantum Processes,” in *Solar Energy Research*, eds. F. Daniels and J. Duffie (London: Thames and Hudson, 1955): 143.
2. W. Shockley and H. J. Queisser, “Detailed Balance Limit of Efficiency of p-n Junction Solar Cells,” *Journal of Applied Physics* 32 (1961): 510.
3. P. Würfel, “The Chemical Potential of Radiation,” *Journal of Physics C: Solid State Physics* 15 (1982): 3967.
4. R. T. Ross and A. Nozik, “Efficiency of Hot-Carrier Solar Energy Converters,” *Journal of Applied Physics* 53 (1982): 3813.
5. T. Markvart, “Hot Carrier Solar Cells by Adiabatic Cooling,” *Applied Physics Letters* 125 (2024): 203503.
6. T. Markvart, “From Steam Engine to Solar Cells: Can Thermodynamics Guide the Development of Future Generations of Photovoltaics?,” *Wiley Interdisciplinary Reviews: Energy and Environment* 5 (2016): 543–569.
7. T. Markvart, “The Thermodynamics of Optical Étendue,” *Journal of Optics A: Pure and Applied Optics* 10 (2008): 015008.
8. H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, (2nd ed) ed. (New York: John Wiley & Sons, 1985).
9. C. Kittel and H. Kroemer, *Thermal Physics*, 2nd ed. (New York: W.H. Freeman and Co., 1980).
10. T. Markvart, “Solar Cell as a Heat Engine: Energy-Entropy Analysis of Photovoltaic Conversion,” *Physica Status Solidi A* 205 (2008): 2752.

## Supporting Information

Additional supporting information can be found online in the Supporting Information section.