Thermomechanical model of solar cells

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Abstract The paper considers a model for the solar cell as a mechanical open-cycle thermodynamic engine where chemical potential is produced in an isochoric process corresponding to the thermalization of electron-hole pairs. Expansion of the beam under one-sun illumination and current generation are described as isothermal lost work. More generally, voltage produced in an open cycle process corresponds to availability, leading to a correction to the Shockley-Queisser detailed balance limit.

I. INTRODUCTION

Thermodynamics provides an alternative view of photovoltaic conversion, adding fundamental aspects to the traditional electronic model.[1,2,3] Perceiving, in the Shockley Queisser detailed balance,[4] photon fluxes as heat, thermodynamics allows the energy – in other words, voltage - to be determined in terms of photon entropy.

In this paper, a thermodynamic model of the solar cell is developed by a direct analogy with the classical thermodynamics of mechanical heat engines. This theoretical angle becomes possible by employing a relationship between the number of photons N in a volume V representing the solar cell which emits photons in a beam with étendue $\mathscr{E}$ and photon flux Ψ:[5]

$$\Psi = \frac{c}{4\pi} \mathscr{E} \frac{N}{V} \qquad (1)$$

Equation (1) establishes a correspondence, between the photon number N and photon flux density Ψ on the one hand, and between the volume V and the étendue on the other. In particular, it permits the definition of a volume v of a "thermodynamic photon" in terms of the beam parameters $\mathscr{E}$ and Ψ:

$$v = \frac{V}{N} = \frac{c}{4\pi} \frac{\mathscr{E}}{\Psi} \qquad (2)$$

The thermodynamic photons that mean here are thermal photons, similar to a photons of blackbody radiation but restricted to the spectral interval which can be absorbed by the solar cell – in other words, radiation with photon energy in excess of the semiconductor bandgap E_g . We shall call this radiation quasi-blackbody radiation. The volume per photon in a solar cell at temperature T emitting with unit emissivity / absorptivity into a full hemisphere (étendue πA, where A is the cell area) is then

$$v = \frac{c}{4\Phi_{E_g}(T)} \qquad (3)$$

where

$$\Phi_{E_g}(T) = \frac{\Psi}{A} = \frac{2\pi}{h^3 c^2} \int\limits_{E_g}^{\infty} \frac{E^2}{e^{E/k_B T} - 1} dE \qquad (4)$$

is the photon flux density.

II. CHEMICAL WORK FROM PHOTONS

We start by writing down the equivalent of the first law of thermodynamics for a photon in the form

$$du = Tds - pdv \qquad (5)$$

where T and p are the temperature and pressure, and u and s are the energy and entropy per photon. Equation (5) will be supplemented by an equation for the free energy per photon – the chemical potential μ :

$$\mu = u - Ts \qquad (6)$$

Equation (6) divides photon energy u into a part - the chemical potential - which can be extracted to carry out useful work or generate voltage. The second term on the right hand side – proportional to the entropy – is the heat that needs to be exchanged with a reservoir at the same temperature as the source of photons when a photon is emitted or absorbed.

The chemical potential replaces mechanical work of classical thermodynamics as the key parameter in a thermodynamic treatment of photovoltaics. To represent this different slant, we replace photon energy u in (5) by the chemical potential (6):

$$d\mu = -sdT - pdv \qquad (7)$$

With the relevant formalism in place, we can now picture a thermodynamic process to mimic photovoltaic conversion, as the conversion of a solar photon at temperature T_S into a photon at ambient temperature T_o whilst producing work. The initial (solar) photon has a chemical potential of zero, corresponding to blackbody radiation. The final (ambient temperature) photon has a chemical potential equal to the voltage in energy units at the contact of the solar cell.

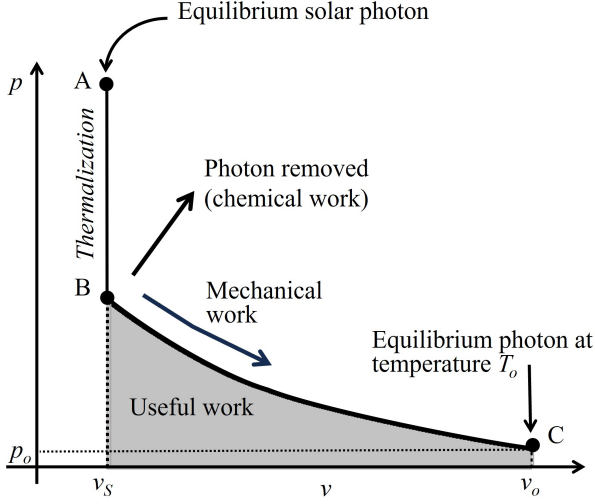[a)]Also at the School of Engineering Sciences, University of Southampton, UK

FIG. 1. Chemical work produced by photon cooling (thermalization) from temperature T_S to temperature T_o, compared with mechanical work along the isotherm BC.

As is customary, we will picture this process in a $p-v$ diagram for one photon - one photon of quasi-blackbody radiation with an optical bandgap E_g.[6] The first part of the conversion process is thermalization of the electron-hole pairs, accompanied by cooling the photon gas to temperature T_o.

We consider here, for the moment, conversion at open circuit when the emitted photon flux is equal to the incident (and fully absorbed) photon flux. Let us also assume that the conversion takes place under maximum concentration of sunlight. This means that the emitted and incident beams cover the full hemisphere, and have the same étendue πA.

Equation (2) then tells us that the beam transformation takes place at constant volume, and can be represented by line AB in Fig. 1, where the volume v_S is given by Eq. (3) with $T=T_S$. In mechanical terminology, thermalization is therefore an isochoric process. Constant volume means that no mechanical work is carried out during thermalization. But the photon produces chemical work by increasing its chemical potential from zero at point A to some finite value μ_{max} at point B. This chemical potential is equal to the chemical potential of electron-hole pairs with which the photons are in equilibrium.

Following thermalization at point B, the photon gas reaches the final temperature T_o but its density $n^{ph}=1/v_S$ is high. There are now two options: photons can be removed by absorption to produce current. Alternatively, the photon gas can perform mechanical work w by isothermal expansion BC to reach complete equilibrium at density $1/v_o$, ambient temperature T_o, and chemical potential zero.

We can represent the two processes – thermalization leading to chemical potential μ_{max}, and the mechanical w work done by expansion BC – quantitatively by integrating Eq. (7). We observe that each of the two steps AB and BC corresponds integration over one variable T or v, giving

$$\mu_o - \mu_S = 0 = -\int_{T_S}^{T_o} s\,dT - \int_{v_S}^{v_o} p\,dv \qquad (8)$$

since the chemical potential of the equilibrium photons at the beginning and end of the process is zero. The second term on the right hand side of (8) is the mechanical work w. The first term gives the chemical potential μ_{max} produced by thermalization:

$$\mu_{max} = \int_{T_o}^{T_S} s(v_s,T)\,dT \qquad (9)$$

Equation (8) therefore expresses the equivalence of the chemical and mechanical work. Let us first interpret the meaning of μ_{max} in the language of photovoltaics. To this end we assume that photon density is sufficiently low and photons form an ideal gas law which, for one photon, reads

$$pv = k_B T \qquad (10)$$

Evaluating the second integral in Eq. (8) then gives

$$\mu_{max} = w = k_B T_o \int_{v_S}^{v_o} \frac{dv}{v} = k_B T_o \ln\left(\frac{v_o}{v_S}\right) \qquad (11)$$

where the volume v_o is given by (3) with $T=T_o$. In terms of photon flux densities,

$$\mu_{max} = k_B T_o \ln\left\{\frac{\Phi_{E_g}(T_S)}{\Phi_{E_g}(T_o)}\right\} = qV_{oc}^{max} \qquad (12)$$

in other words, the Shockley-Queisser open circuit voltage in energy units, under maximum concentration of sunlight.

Equation (12) was obtained by direct means in[7] discussing also its relationship with the Trivich and Flinn[8] approximation for the voltage, and the voltage generated by hot carrier solar cells.

III. ISOTHERMAL LOSSES

We can pursue the mechanical analogy further to model the conversion process more generally, under one-sun illumination, away from open circuit. At one sun intensity, the solar cell converts an incident beam with étendue $\mathscr{E}_{in} = \omega_S A$, where ω_S is the solid angle subtended by the Sun. As the solar cell emits a beam into the full hemisphere (étendue $\mathscr{E}_{out} = \pi A$), the photon gas expands from the volume v_S under maximum concentration to a volume $v_1 = v_S(\pi/\omega_S)$.

The chemical potential of the emitted light is again obtained by integrating (7), this time along the path ABD in the $p-v$ diagram (Fig. 2). The temperature integration produces again the chemical potential μ_{max} but there is now a further contribution, from the volume integral. This contribution is negative, and represents a "lost work" of magnitude

$$w_{loss}^{(1)} = \int_{v_S}^{v_1} p\,dv \qquad (13)$$
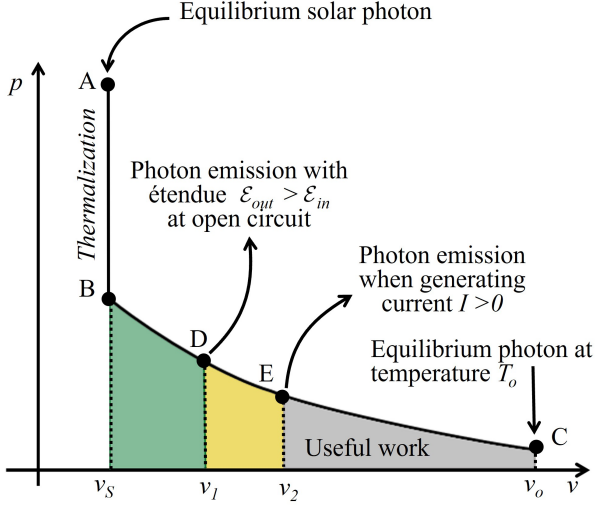
FIG. 2. Isothermal losses pictures in the $p - v$ plane.

Using (10), the integral (13) is easily evaluated to give

$$w_{loss}^{(1)} = k_B T_o \ln \left(\frac{\pi}{\omega_S} \right) \tag{14}$$

We observe that the conversion of one-sun radiation incurs a loss (14) due to the expansion of the light beam in the conversion process. Using our mechanical analogy, this is similar to the lost work in an expansion of gas into vacuum.

We can now consider current generation. Generation of current (with density J, say) reduces the emitted photon flux density by an amount J/q. The emitted photon flux density at point D, $(\omega_S/\pi)\Phi_{Eg}(T_S)$, will therefore be reduced to $(\omega_S/\pi)\Phi_{Eg}(T_S) - J/q$, moving the emission to point E where the volume per photon is increased by

$$\frac{v_2}{v_1} = \frac{(\omega_S/\pi)\Phi_{Eg}(T_S)}{(\omega_S/\pi)\Phi_{Eg}(T_S) - J/q} \tag{15}$$

with respect to point D. The corresponding lost work is given by

$$w_{loss}^{(2)} = \int_{v_1}^{v_2} p\,dv = k_B T_o \ln \left(\frac{v_2}{v_1} \right) \tag{16}$$

We can relate the loss (16) to solar cell parameters since

$$J_\ell = (\omega_S/\pi)\Phi_{Eg}(T_S) - \Phi_{Eg}(T_o)$$
$$J_o = \Phi_{Eg}(T_o) \tag{17}$$

where J_ℓ and J_o are the photogenerated and dark saturation current densities. The lost work (or loss in chemical potential) (16) then becomes

$$w_{loss}^{(2)} = k_B T_o \ln \left(\frac{J_\ell + J_o}{J_\ell + J_o - J} \right) \tag{18}$$

Collecting together (12), (14) and (18) we obtain

$$qV_{oc} = qV_{oc}^{max} - k_B T_o \ln \left(\frac{\pi}{\omega_S} \right)$$
$$qV = qV_{oc} - k_B T_o \ln \left(\frac{J_\ell + J_o}{J_\ell + J_o - J} \right) \tag{19}$$

which transforms, using (17), into

$$J = J_\ell - J_o \left(e^{qV/k_B T_o} - 1 \right) \tag{20}$$

in other words, the usual solar cell equation with parameters (17). In thermodynamic terms, the isothermal losses (14) and (18) are due to irreversible entropy generation.[2]

IV. DISCUSSION

We have shown that the thermomechanical model of the solar cell is equivalent to the Shockley-Queisser detailed balance model. This is not surprising as what we have done is to replace the incident and emitted light beams, modelled as quasi-blackbody radiation, by heat. As the chemical potential of this radiation is zero, the equivalence with heat is evident.

Notwithstanding, it is of interest to compare the present model with heat engines of classical thermodynamics. These engines, in contrast with the present model, operate in a cyclical manner. Let us consider such a heat engine on the example of a steam turbine (Fig. 3). A steam turbine converts steam at high temperature and pressure into low temperature steam at the exit from the turbine. The steam then has to be returned to the high temperature inlet of the turbine by heating in a boiler. This closes the cycle and permits a description of the steam turbine as a standard heat engine.

If high-temperature steam were to be available free of charge, we can dispense with the boiler and consider only the open cycle consisting of work produced by cooling the high temperature steam to ambient temperature. The steam – or, in our case, photons – acts as both fuel and working medium.[9]

A further difference with classical closed cycle engines appears if we examine the medium which surround the engine.
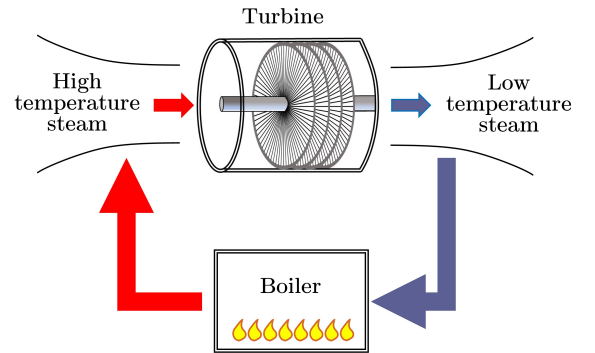

FIG. 3. Open and closed cycle conversion, illustrated on the example of a steam turbine.

In a closed cycle operation, the work carried out by the equilibrium pressure p_o of this medium does not appear by virtue of the fact that the elements of work $p_o \delta V$ cancel in the compression and expansion parts of the cycle.

This is not the case for an open-cycle converter where the work carried out by the external medium, equal to $p_o(v_o - v_S)$ in Fig. 1, should be subtracted from the useful work. This is a well known result of classical thermodynamics which gives the useful work as availability[10]; it is also the reason why the limiting efficiency for the conversion of full blackbody radiation is the Landsberg efficiency, rather than the Carnot efficiency[11,12] (see also[13]).

The "availability correction" to the Shockley-Queisser voltage can easily be estimated to be about $k_B T_o / q \simeq 26$ mV - not large but noticeable, lowering the Shockley-Queisser efficiency limit by about 1% absolute.

V.   ACKNOWLEDGEMENT

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[6] We should emphasize that the $p - v$ diagrams considered in this paper are not to scale as the actual volume and pressure change by many orders of magnitude.

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[9] Interestingly, such open cycle operation is characteristic also for other renewable energy applications such as wind, tidal or geothermal energy.

[10] See, for example, A.B. Pippard, The Elements of Classical Thermodynamics. Cambridge, Cambridge University Press, 1964.

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