COUNTING SUNRAYS: FROM OPTICS TO THE THERMODYNAMICS OF LIGHT

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ABSTRACT

This chapter considers quantum solar energy conversion from a thermodynamic point of view. Starting from geometrical optics, the concept of étendue is used to determine the number of photon states in a beam of light. This naturally leads to the definition of entropy, providing the foundation for the statistical mechanics of light beams. With emphasis on the thermodynamic functions per photon (in particular, the chemical potential), these concepts are illustrated first by comparing the thermodynamic limits of the geometric concentrators with the limits obtained by traditional arguments. The thermodynamic framework is then extended to novel applications. The fluorescent collector is modelled as an open thermodynamic system interacting with a room-temperature heat bath. A detailed thermodynamic description of the operation of a p-n junction solar cell then follows, starting from energy (voltage) rather than from the kinetic argument used by Shockley and Queisser. This provides a novel view of fundamental losses, each identified as a specific form of irreversible entropy generation. The chapter concludes with an analysis of a future photovoltaic device – a hot carrier solar cell where the voltage exceeds the Shockley-Queisser limit. The efficiency of this solar cell, obtained by thermodynamic arguments, is free from specific mechanisms or structures such as selective energy contacts. It is argued that this is the fundamental efficiency limit to the operation of single junction solar cells where thermalization of electron-hole pairs has been reduced or entirely eliminated.

1. INTRODUCTION

The application of thermodynamic principles to the conversion of solar energy into useful work has a distinguished history, stimulated by both the academic challenge and the immense technological potential. In the heart of the early quantitative works lies the balance between the incident and emitted energy – entropy flows. This methodology, leading to the celebrated Landsberg efficiency, was elaborated by Landsberg and Mallinson (1976), Petela (1964) and Press (1976). An application of Carnot efficiency to photothermal processes was given by Jeter (1981), with Badescu (2008) providing a unified thermodynamic view of the different conversion mechanisms.

An early insightful contribution by Rose (1960) showed how the photovoltaic effect can be derived from the Carnot cycle. Virtually in parallel, Shockley and Queisser (1961), in their celebrated detailed balance treatment, determined the limits of photovoltaic conversion (see, however, also Trivich and Flynn, 1955). Detailed balance here refers to the equality of the incident and emitted photon fluxes. Another, more traditional, meaning of this term will be introduced later in this chapter, following from the thermodynamic concept of the same name. A related thermodynamic discussion of photosynthetic conversion was given by Duysens (1964), Ross (1965), and Ross and Calvin (1967), with an elegant extension by Laverge and Joliot (1996). Yet another approach invokes endoreversibility, based on the operation of large scale conventional power stations (Curzon and Ahlborn, 1975; de Vos, 1992).

Closely linked to photovoltaics is the application of thermodynamic concepts to luminescence. Building on Einstein's ideas for a two level system (Einstein, 1917), Kennard (1918, 1926) and later Stepanov (1957) laid down the foundations and general principles that apply to the "thermodynamic" detailed balance of this process (see Sec. 4 of this Chapter). Other notable contributions to this field have been made by Landau (1946), Weinstein (1960), and Payen de la Garanderie (1965).

The thermodynamic analysis of solar energy conversion is usually considered to be synonymous with very high, even unrealistic, efficiencies, with little indication given of the associated loss mechanisms. This Chapter shows that this need not be the case. We shall show that a consistent and rigorous framework can be developed which can provide a realistic description of the present single-junction solar cells, pinpoint the thermodynamic nature of the fundamental losses in these devices, and suggest how these can be eliminated in future generations of solar energy conversion devices such as hot carrier solar cells.

Fundamental to this Chapter is the quantum nature of the conversion process. In the usual terminology, the word "quantum" usually refers to the presence of an energy gap, defining the characteristic energy of photons that play a role of "fuel" as well as "working medium" in the conversion device. We shall show that quantum considerations apply not only to the energy spectrum but also to the spatial coordinates of the light beam. To this end, Sec. 2 of this Chapter provides a link between the geometrical optics and the semi-classical limit of the wave theory of light. Key here is the concept of étendue: a geometric characteristic of the beam but also a measure of the phase space volume occupied by the transverse components of the photon field. Once the number of photon modes in a beam has been determined, it is a simple matter to define the entropy: the principal stepping stone towards thermodynamics (Sec. 3). Unlike the traditional thermodynamic analyses, the central element in this structure is not the entropy of the beam but the entropy *per photon*. This concept provides a powerful tool for the subsequent thermodynamic framework which unfolds with a brief illustration of the limits to the concentration of sunlight (still within the limits of geometrical optics). A more general illustration is also provided with the examination of the scattering and absorption of light in Sec. 4.

Applications to solar energy conversion then follow. Section 5 gives an overview of the fundamental efficiency limits of fluorescent collectors. Unlike concentrators based on geometrical optics where the frequency of light is conserved, fluorescent collectors represent an open thermodynamic system. Instead of entropy, their operation is therefore constrained by considerations based on free energy or, more precisely, the chemical potential - the free energy per photon.

The formalism that is developed in this Chapter covers not just monochromatic radiation but also realistic solar cells which absorb a broad spectrum of the incident sunlight. The mathematical tools that are needed for this purpose are developed in Sec. 6 where we show that, at moderate light intensities, the photon statistics bears a close resemblance to an ideal two-dimensional gas. Following a brief discussion of the energy-entropy balance in the absorption and emission of light (Sec. 7), a detailed thermodynamic description of the operation of a solar cell is presented in Sec. 8. It is shown that, when using arguments based on energy (voltage) rather than kinetics (current), the electrical characteristic of the solar cell follows directly from the ideal gas laws. This provides a novel view of the fundamental losses which can be identified as due to specific forms of irreversible entropy generation.

Section 9 considers a hypothetical photovoltaic device, the hot carrier solar cell. The efficiency of this device, which exceeds the Shockley-Queisser limit on account of a higher voltage, is obtained by thermodynamic arguments, independent of specific mechanisms or structures such as selective energy contacts. We therefore conclude that this is the thermodynamic limit to the operation of single junction solar cells where the thermalization of electron-hole pairs has been reduced or entirely eliminated.

2. COUNTING SUNRAYS

Viewed in a mathematical context, geometrical optics forms the limiting solution of the Maxwell wave equation when the wavelength of light is very short. In this limit, light propagates along lines (rays) defined by the shortest transit time between the source and the receiver, as embodied in Fermat's Principle of Least Time. Light rays, which are generally curved, become straight lines in the free space or in a medium where the refractive index is constant. The distribution of rays is generally assumed to be continuous, with no meaning assigned to the thickness of a ray.

A convenient characteristic of the beam in geometrical optics is the concept of étendue. For a narrow beam of angular spread $\delta\Omega$ passing through an area element δA, the element of étendue is defined as

$$\delta\mathcal{E} = n^2 \delta A \, \delta\Omega \cos\theta \tag{1}$$

where n is the refractive index of the medium and θ is the angle between the normal to δA and the direction of the wave vector $\boldsymbol{k}$ (Fig. 1a). For extended beams (where, for example, $\delta\Omega$ may depend on position), the total étendue can be obtained by an integration of (1). We may consider the simple case of direct (beam) sunlight which represents a narrow pencil of rays whose angular divergence presents a solid angle of $\Omega s = 6.85 \times 10^{-5}$ sterad. The étendue of such radiation passing through a planar surface of finite area A is easily obtained from (1), by replacing δA with A. For radiation with directions which extend over a complete hemisphere (for example, the diffuse sunlight), an integration of Eq. (1) over the angular variables gives

$$\mathcal{E} = \pi n^2 A \tag{2}$$

The traditional application of étendue to optical instruments derives primarily from the fact that the étendue of a beam propagating in a clear and transparent medium is conserved. In more recent times, this concept has proved also a convenient vehicle for the discussion of optical systems that concentrate sunlight (see, for example, Welford and Winston, 1978 where a proof of this theorem can be found). In other applications, however, this theorem appears in a range of different guises, associated with such distinguished names as Poincaré, Lagrange and Helmholtz (Born and Wolf, 1999)

For the purposes of this Chapter, geometrical optics provides a useful vantage point for the description of light but refinements will be needed to extend the scope to include rudiments of wavelike propagation. This will enable us to consider light as propagating in individual quantum states, rather than as a countless continuum. A useful analogy that we shall follow is the parallel between the diffraction limit of geometrical optics and Heisenberg's uncertainty principle.

Let us consider a narrow beam of light passing through a slit of width δx which defines its dimension in the coordinate space. The limit of geometrical optics, considered by the absence of diffraction, places a constraint on the spread of this beam in the k space, in the form

$$\delta x \, \delta k_x \geq 1 \tag{3}$$

The analogy with particle mechanics can now be established by recalling de Broglie relationship between wave vector and particle momentum: $\boldsymbol{p} = h\boldsymbol{k}$ (for a detailed development of the analogy between photons and particles described by classical mechanics see Joyce, 1974). Multiplying by the Planck constant h we find that (3) corresponds to the limit

$$\delta x \delta p_x \geq h \tag{4}$$

- in other words, the Heisenberg uncertainty principle. When applied to the six dimensional phase space of variables $x,y,z, p_x, p_y, p_z,$ condition (4) tells us that only one quantum state can occupy the volume $\delta x\ \delta y\ \delta z\ \delta p_x \delta p_y \delta p_z$.

A similar reasoning can be used to determine the volume of a quantum state in the phase space of rays in geometrical optics. It turns out that all we need to do is to transform the element of étendue into a suitable form where the result becomes immediately apparent. With a suitable choice of the coordinate system, the beam area δA becomes $\delta x \delta y,$ where δx and δy are small increments of the coordinates x and y. Similarly, the appropriate projection of the angular spread corresponds to increments δk_x and δk_y in the components of the wave vector transverse to the direction of propagation. A simple geometrical argument (Fig. 1b) then demonstrates that the étendue element (1) can be written as

$$\delta \mathscr{E} = \frac{n^2}{k^2} \delta x \delta y \delta k_x \delta k_y \tag{5}$$

The volume element $\delta x\ \delta y\ \delta k_x\ \delta k_y$ in the phase space of variables x,y,k_x, k_y is therefore equal to $k^2 \delta \mathscr{E} / n^2$, and cannot be smaller than unity. Thus, we can also say that $k^2 \delta \mathscr{E} / n^2$ contains a single quantum state, for occupation by photons in the beam. The term “mode” can also be used as the present discussion has a close parallel with the determination of the number of optical modes in a wave guide (see, for example, Brooker, 2002). The argument that we have used corresponds to the semi-classical limit and the number of modes is therefore likely to be large. It does not take much effort or imagination, however, to extend similar statistical concepts to waveguides or systems with a smaller number of modes.

We are now only a small step from being able to introduce statistical concepts to geometrical optics. Allowing for two directions of polarization, the above discussion shows that the integrated quantity

$$\frac{2k^2}{n^2}\mathscr{E} = \frac{2\nu^2}{c^2}\mathscr{E} \tag{6}$$

can be interpreted as the number of quantum states within a beam with frequency $\nu = ck/n$ and étendue $\mathscr{E}$. Since the wave vector is constant, the volume of a beam in the phase space of its transverse coordinates remains constant during the beam propagation in a clear, transparent medium. The conservation of étendue can therefore be interpreted as the Liouville theorem of classical mechanics, applied to photon propagation along rays in geometrical optics. Beam propagation in clear media where the number of quantum states is conserved then provides a firm foundation for the analysis of process that transform the beam and produce useful work. Based on the discussion above we may anticipate that such analysis will bear close similarities with statistical mechanics and thermodynamics.

3. STATISTICS OF MONOCHROMATIC RADIATION: LIMITS TO THE CONCENTRATION OF LIGHT

The equivalent of Liouville theorem for light beams that we have discussed in Sec. 2 make it an easy matter to lay down the foundations for a statistical treatment of light. Let us suppose that the $G = 2\mathscr{E} \nu^2 / c^2$ states in a beam of light [see Eq (6)] contain N photons. A standard argument shows that the number of ways that these photons (which are indistinguishable) can be distributed over the G states is equal to

$$W = \frac{(G+N)!}{G!N!} \approx \frac{(G+N)^{(G+N)}}{G^G N^N} \tag{7}$$

where the Stirling approximation has been used to obtain the second, approximate, equality. This leads to the following result for the entropy of the beam:

$$S = k_B \ln W = k_B \frac{2\nu^2}{c^2} \mathscr{E} \left\{ (1+\rho)\ln(1+\rho) - \rho \ln \rho \right\} \tag{8}$$

where k_B is the Boltzmann constant and $\rho = N/G$ is the mean number of photons per mode. Equation (8) has a familiar form. It can also be obtained by translating the number of photon states in a box into a number of states in a beam (Landau and Lifshitz, 1958). The new element that Eq. (8) brings in is the presence of étendue: an essential feature for the thermodynamic treatment that follows.

Let us now consider an optical system or instrument that accepts radiation of wavelength λ through an (entrance) aperture characterised by an étendue $\mathscr{E}_{in}$. Emitted radiation leaves the system through an (exit) aperture with étendue $\mathscr{E}_{exit}$. If there is no scattering or absorption of light in the system (an assumption we shall later relax) the étendue theorem tells us that $\mathscr{E}_{in} = \mathscr{E}_{exit}$. It is of interest to examine this result with the use of Eq. (8) from the view point of statistical mechanics.

To this end, let us consider the change in entropy when one photon of light passes through the system. Since the change of photons in each of the beams is equal to one this is, clearly

$$\Delta s = \frac{\partial S_{out}}{\partial N} - \frac{\partial S_{in}}{\partial N} \tag{9}$$

where S_{in} and S_{out} are the entropies (8) of the incident and emitted beams, and the number of photons N is equal in both beams. Denoting the entropy per photon by s, we have

$$s = \frac{\partial S}{\partial N} = k_B \ln\left(1 + \frac{2\nu^2}{c^2} \frac{\mathscr{E}}{N} \right) \tag{10}$$

and Eq. (9) gives

$$\Delta s = s_{out} - s_{in} = k_B \ln\left(1+\frac{2\nu^2}{c^2}\frac{\mathcal{E}_{out}}{N}\right) - k_B \ln\left(1+\frac{2\nu^2}{c^2}\frac{\mathcal{E}_{in}}{N}\right) \cong k_B \ln\left(\frac{\mathcal{E}_{out}}{\mathcal{E}_{in}}\right) \tag{11}$$

where the second equality holds if N is not too large – that is, for weak to moderate light intensities. We shall examine this approximation more closely in Sec. 6 of this Chapter.

Equation (11) gives a thermodynamic interpretation of étendue conservation. For the system in question, the étendue is conserved. Equation (11) then gives $\Delta s = 0$: in other words, light propagation in a clear and transparent medium can be considered as thermodynamically reversible. It is interesting to note that this result agrees with the optical meaning of reversibility as each photon can be brought back through the system to the initial state along the same ray (or within the same quantum state) that it has occupied during its propagation (Jones, 1953).

More generally, of course, the second law of thermodynamics tells us that entropy need not be conserved but it cannot decrease during the passage of photons through the system ($\Delta s \geq 0$). As long as the number of photons in the beam remains constant, this means that

$$\mathcal{E}_{in} \leq \mathcal{E}_{out} \tag{12}$$

In other words, the étendue may increase during light propagation but it never decreases. For example, photons in a beam can be scattered to enlarge the volume of phase space which they occupy but, at least in an isolated system, this volume can never decrease.

This argument can be used to re-visit, within the statistical framework, the well known limit that optics and statistical mechanics impose on the concentration of sunlight. Let us consider, for the moment, a pencil of direct sunlight with angular spread Ω_S incident onto the entrance aperture of area A_{ent} of the instrument in Fig. 2 so that $\mathcal{E}_{in} = \Omega_S A_{ent}$. The concentrated light is emitted from the exit aperture within the full hemisphere so that $\mathcal{E}_{exit} = \pi A_{exit}$, where A_{exit} is the area of the exit aperture. We assume that the incident and emitted light propagate in a medium with $n = 1$ and the number of photons is conserved. Introducing the concentration ratio $C = A_{exit} / A_{ent}$ and applying Eq. (12) then easily leads to the condition

$$C \leq \frac{\pi}{\Omega_S} \cong 46{,}000 \tag{13}$$

Equation (11) combined with second law of thermodynamics also tell us that, at least within the realm of geometrical optics, it is impossible to concentrate diffuse sunlight. Indeed, completely diffused sunlight is characterised by isotropic incidence where $\mathcal{E}_{in} = \pi A_{ent}$ and a similar argument as above gives $C \leq 1$: in other words, no concentration is possible. In the language of statistical mechanics, concentration of diffuse sunlight would entail the decrease of entropy by an amount equal to $\Delta S = k_B \ln C$. This is, of course, impossible in the present isolated optical system where photons do not interact with other photons nor with any material substance.

4. FROM OPTICS TO THERMODYNAMICS: THE SCATTERING AND ABSORPTION OF LIGHT

The statistical formalism that we have developed allows us to move outside the realm of geometrical optics and consider, for example, photon scattering which changes the direction of propagation in a statistical manner. More generally still, we may discuss photons which exchange energy with an absorbing and luminescent medium. In thermodynamics, such systems can no longer be considered as isolated but can be described as closed: the number of photons is conserved but energy is exchanged with an external heat reservoir. In a still more general setting, we shall later discuss photovoltaic or photochemical converters which produce useful work.

Initially, let us consider elastic scattering of radiation which does not change the wavelength of light. Suppose that a volume V which emits radiation is occupied by the scattering medium and contains N_{ph} photons. The scattering process ensures that photons are uniformly distributed, and makes the emitted radiation isotropic. Photon emission from the volume thus resembles the escape of particles in the classical kinetic theory of gases. Consider, for example, photons emitted in a time interval δt by a surface area δA, forming a thin pencil of rays within a solid angle $\delta\Omega$ which subtends an angle θ with the normal to the surface. These photons occupy a cylinder with base δA and height $(c/n)\delta t$, and the photon flux $\dot{N}$ emitted per unit time is thus

$$\dot{N} = \delta A\,\delta\Omega \cos\theta \frac{cN_{ph}}{4\pi V n} = \frac{c}{4\pi V n^3}\delta\mathscr{E}\, N_{ph} \qquad (14)$$

where we noted that the fraction of photons with the appropriate orientation is equal to $\delta\Omega/4\pi$ and we introduced the element of étendue $\delta\mathscr{E}$ from (1). Since $\delta\mathscr{E}$ is proportional to $\cos\,\theta$, Eq. (14) confirms that the emitted radiation complies with the Lambert law.

As an illustration let us suppose that such scattering medium occupies our familiar optical system shown by Fig. 2 in Sec. 3. According to (14), the photon flux emitted by each aperture is proportional to the étendue of the respective beam. The probability that a photon in the system escapes through the exit aperture is then equal to

$$Q_c = \frac{\mathscr{E}_{exit}}{\mathscr{E}_{ent} + \mathscr{E}_{exit}} \qquad (15)$$

where $\mathscr{E}_{ent}$ is the étendue of the beam emitted through the entrance aperture (which need not be the same as the étendue $\mathscr{E}_{in}$ of the incident beam !). Equation (15) may appear rather elementary but we shall see in Sec. 5 that, when generalised to light with different frequencies, it provides a convenient starting point for the discussion of the efficiency of fluorescent collectors.

The optical processes considered so far conserve photon frequency, and therefore also photon energy. We will now bring into the picture absorption and emission of radiation where photon energy need not be conserved. When the stimulated emission can be neglected, the rates which govern such absorption and emission processes comply with the Kennard-Stepanov relation (Kennard, 1918, 1926; Stepanov, 1957) which can be written in the form

$$\frac{1}{\tau}f(\nu)=\frac{8\pi n^2\nu^2}{c^2}\sigma_\nu e^{h(\nu_o-\nu)/k_BT} \tag{16}$$

where τ is the natural (radiative) lifetime, σ_ν is the absorption cross section, $f(\nu)$ is the fluorescence spectrum normalised to unity on the frequency scale, $h\nu_o$ is the energy of the electronic transition responsible for the absorption or fluorescence, and T is the temperature of the fluorescent medium. In semiconductors, a similar relation was discussed in some detail by van Roosbroek and Shockley (1954).

The Kennard-Stepanov relation (16) or its van Roosbroek-Shockley equivalent (we shall abbreviate the full family of these relations by KSvRS) is observed, to a certain degree of accuracy, in most molecular or semiconductor spectra. When it does accurately agree, it implies that photon emission occurs from a manifold of energy levels which are in thermal equilibrium with the surrounding medium. We shall see presently that KSvRS relations can be interpreted as a statement of microscopic reversibility or detailed balance, in the thermodynamic interpretation of this word.

In an idealised model, we shall assume that all photons that are absorbed by a certain volume of matter are also emitted - in other words, fluorescence occurs with a quantum yield of unity, and no photons are removed non-radiatively from the system. Absorption then does not remove photons from the system but only redistributes them between different frequency (or energy) states.

Let us consider the rate of photon transfer between two groups of states around frequencies ν and ν'. To be specific we consider a molecular system although this argument can easily be applied also to semiconductors. The rate of photon removal from states near frequency ν by absorption is,

$$\sigma_\nu N_o \, {}^{c}\!/_{n} N_{ph}(\nu)$$

where N_o is the number of molecules in the ground state. The fraction of these photons that will be re-emitted within a range of frequencies $\delta\nu'$ near ν' is simply $f(\nu')\,\delta\nu'$. The rate of photon transfer $\nu \rightarrow \nu'$ is equal to the product of these two factors:

$$\sigma_\nu N_o \, {}^{c}\!/_{n} N_{ph}(\nu)\, f(\nu')\,\delta\nu' \tag{17}$$

Within the limits of applicability of KSvRS relations we can approximate

$$N_{ph}(\nu)=\frac{8\pi n^3\nu^2}{c^3}e^{-h\nu/k_BT}\delta\nu \tag{18}$$

Substituting (16) and (19) into (17) we obtain the rate of photon transfer $\nu \rightarrow \nu'$ in the form

$$\sigma_{\nu} N_o \, {}^{c}\!/_{n} \, N_{ph}(\nu)\, \tau \frac{8\pi n^3 \nu^2}{c^3} \sigma_{\nu'} e^{h(\nu_o - \nu')/k_B T} \delta\nu' = \sigma_{\nu'} N_o \, {}^{c}\!/_{n} \, N_{ph}(\nu')\, f(\nu)\, \delta\nu \tag{19}$$

which is the same as the rate of transfer $\nu \rightarrow \nu'$, proving the detailed balance.

The combined features of unit quantum yield and detailed balance guarantee that the absorption/emission events bring radiation in a sufficiently thick volume of medium into thermal equilibrium, at the temperature of the absorbing substance. Since the photon number are conserved, such ‘photon gas’ will be described by the Bose-Einstein distribution

$$\rho_{\nu} = \frac{1}{e^{(h\nu - \mu)/k_B T} - 1} \tag{20}$$

where μ is the chemical potential which, in general, is not equal to zero.

Our treatment of the KSvRS relations implicitly assumes that the absorbing material is in complete thermal equilibrium at a single temperature T_o which characterises all the relevant degrees of freedom, including electronic and vibrational motion. Research show that this need not always be the case. Under some circumstances, electrons in the excited state can exist at a different (higher) temperature than the material itself. This temperature then also describes the emitted photons. We shall see in Sec. 9 that such “hot carrier” materials can also potentially increase the efficiency of photovoltaic conversion.

5. FLUORESCENT COLLECTORS

Fluorescent collectors, in the shape of a plate containing fluorescent dyes with solar cells attached at the edge, have recently re-emerged as a promising candidate for reducing the cost of solar energy conversion, cutting down on the size of the area of the solar cell. Unlike their geometric counterparts that were discussed in Sec. 3, fluorescent collectors are claimed to be able to concentrate diffuse sunlight. Based on the statistical theory that we have developed we shall show that this is indeed possible, and we will determine the limit to the efficiency of this process.

A schematic representation of a fluorescent collector is shown in Fig. 3. We denote by θ_c (where $\sin \theta_c = 1/n$) the critical angle with the normal to the front surface that defines the *escape cone* for total internal reflection (TIR). Light emitted within the escape cone will leave the collector directly or after a small number of internal reflections. Light emitted outside the escape cone remains trapped within the collector and is guided towards the solar cell at the edge of the collector. Light is therefore geometrically separated into two beams (one inside and one outside the escape cone) which are defined by the magnitude of the refractive index of the collector. If the refractive index is sufficiently large, a high proportion of the incident light (direct or diffuse) will be collected by the solar cell at the edge, with possibly a much smaller area than the front face of the collector.

A closer look at this argument, however, reveals a subtle paradox. A good collector has to absorb (and re-emit) a large fraction of the incident light. The absorption coefficient α of the collector material must therefore be substantially larger than the absorption length $1/d$, where d is the thickness of the collector. To reach the solar cell at the edge, the re-emitted light should not be re-absorbed again since each re-emission entails some of the light leaving the collector through the front surface. This requires that $\alpha < 1/L < 1/d$, where L is the linear dimension of the front face of the collector. Clearly, these two conditions are incompatible. We can therefore conclude that, if the collector is to operate efficiently, absorption of the incident light cannot take place at the same wavelength as the transport of the fluorescent photon flux. In effect, the operation of a good collector can be described in terms of two photon fluxes which propagate in separate “channels”, as follows:

- The absorption channel, extending over a large part of the solar spectrum where the absorption coefficient of the collector α_{abs} is large.

- The fluorescence / photon transport channel, formed by a narrow frequency interval at longer wavelengths, where the absorption coefficient α_{em} is small.

The apparent paradox concerning the size of the absorption coefficient is therefore resolved. The important point to note is that the two flux picture separates the beams by a mechanism based on different absorption coefficients at different wavelengths, rather than on the geometry of the collector.

Although fluorescent collectors which rely on this principle can be reasonably efficient (Kittidachachan *et al*, 2007), the presence of the escape cone represents a significant loss mechanism. We shall see presently that fluorescent collectors cannot reach their maximum potential unless this loss mechanism is eliminated. This can be done by means of relatively simple photonics (Markvart, 2006; Rau *et al,* 2005): with a photonic filter (or band stop) that reflects light within a specified spectral range. If such filter is placed at the top face of the collector (the entrance aperture) much of the escaping light can be blocked, and losses to the photon transport reduced to a minimum. We shall see, however, that these losses cannot be eliminated entirely as we need to leave a "window" open for the absorption of the incident photon flux. The ultimate efficiency limit is imposed by microscopic reversibility, and can be evaluated with the use of the thermodynamic tools that we have at our disposal.

To evaluate the limits on collector operation, is it convenient to picture the collector as a converter which transforms the incident beam, with frequency extending over the absorption channel with étendue $\mathscr{E}_{in}$, into the emitted beam with étendue $\mathscr{E}_{exit}$ and a different frequency range corresponding to the photon transport channel. The spectral range of each channel may be appreciable. This is particularly true for the absorption channel since the collector needs to absorb a broad spectrum of the incident light. Although a general treatment is possible (Markvart, 2006) we shall here confine ourselves to a simplified approach based on two monochromatic beams at frequencies ν_{abs} (absorption channel), and ν_{em} ($<\nu_{abs}$) (emission/transport channel). The frequency difference $\Delta\nu = \nu_{abs} - \nu_{em}$ corresponds to the Stokes shift of the fluorescent dye. In effect, the fluorescent collector has been replaced by a light concentrating instrument considered in Fig. 2 where the entrance and exit apertures have now acquired, alongside the étendue, also a frequency parameter.

Following Sec. 4, we define the collection efficiency Q_c of the collector as the probability that an incident photon, once absorbed, reaches the solar cell through the exit channel. In contrast with Sec. 4, however, the photon gas within the collector is no longer an isolated system, but exchange energy with a thermal reservoir through the absorption emission process. The thermal reservoir (or heat bath), represented by the fluorescent dye of the collector, supplies or absorbs the energy difference $h\Delta\nu$ between the absorbed and emitted photons. The equilibrium state is now characterised not by maximum entropy but maximum free energy: to be specific, it is a state with the maximum Helmholtz free energy F since the absorption and emission of light by the collector is assumed to take place at constant volume, neglecting any pressure dependence of the absorption or emission wavelengths.

The condition of equilibrium is equivalent to a statement that all photons in the collector have, in addition to the temperature, also an identical chemical potential. Since the chemical potential is equal to the free energy F per photon we have

$$\mu = u - Ts \tag{21}$$

where, for monochromatic photons, the energy per photon is $u = h\nu$ and s , the entropy per photon, is given by Eq. (10). Thus

$$\mu = h\nu - k_B T \ln\left(1 + \frac{2\nu^2}{c^2}\frac{\mathscr{E}}{N}\right) \cong h\nu - k_B T \ln\left(\frac{2\nu^2}{c^2}\frac{\mathscr{E}}{N}\right) \tag{22}$$

where the second, approximate, equality applies at moderate illumination intensities.

We retain the notation of Sec. 4 where the étendue of beam emitted from the transport (emission) channel is denoted by $\mathscr{E}_{exit}$ and the étendue of photons emitted from absorption channel (entrance aperture) by $\mathscr{E}_{ent}$. Substituting the relevant parameters into (22) and equating the chemical potentials then gives

$$h\nu_{abs} - k_B T_0 \ln\left(\frac{2\nu_{abs}^2}{c^2}\frac{\mathscr{E}_{ent}}{N_{ent}}\right) = h\nu_{em} - k_B T_0 \ln\left(\frac{2\nu_{em}^2}{c^2}\frac{\mathscr{E}_{exit}}{N_{exit}}\right) \tag{23}$$

where N_{exit} and N_{ent} are the numbers of photons in the beams emitted from the exit and entrance apertures, respectively, and T_o denotes the temperature of the collector. Since the number of photons in the collector is conserved, the sum $N_{exit} + N_{ent}$ is equal to the number of photons in the incident (absorbed) beam, and the collection efficiency is given by

$$Q_c = \frac{N_{exit}}{N_{ent} + N_{exit}} \tag{24}$$

Rearranging (23) then yields

$$Q_c = \frac{1}{1 + \frac{\mathscr{E}_{ent}\nu_{abs}^2}{\mathscr{E}_{exit}\nu_{em}^2} e^{-h\Delta\nu / k_B T_o}} \tag{25}$$

Equation (25) represents a generalization of the earlier result of Yablonovich (1980), and gives the ultimate collection efficiency of fluorescent collectors, as determined by the detailed balance.

The collection efficiency Q_c, of course, needs to be considered alongside the absorption efficiency to obtain the total optical efficiency of the collector. More detailed considerations (Markvart, 2006; Danos *et al*, 2005) based on a similar argument as (25) show that, even for appreciable gain (concentration) ratios, the total optical efficiency of fluorescent collectors can reach some 90% for the frequency range of interest for photovoltaic conversion. A similar conclusion was reached with the use of numerical modelling by Rau *et al* (2005).

6. A MATHEMATICAL INTERMEZZO: LIGHT BEAMS COVERING A BROAD FREQUENCY BAND

The reader may object that the theoretical analysis of fluorescent collectors in Sec. 5 has been based on monochromatic radiation. Since most cases of interest concern the absorption and emission of light over a range of wavelengths, a more general formalism is needed to deal with thermodynamic functions for beams extending over a broad frequency band.

For radiation in a cavity of some volume *V*, the appropriate entropy, energy and number of photons at equilibrium need no introduction. They are given by (see, for example, Landau and Lishitz, 1953):

$$S = k_B V \int_{(\nu)} \frac{8\pi n^3 \nu^2}{c^3} \left\{ (1+\rho_k)\ln(1+\rho_k) - \rho_k \ln \rho_k \right\} d\nu \tag{26}$$

$$U = V \int_{(\nu)} \frac{8\pi n^3 \nu^2}{c^3} h\nu \rho_\nu \, d\nu \tag{27}$$

$$N = V \int_{(\nu)} \frac{8\pi n^3 \nu^2}{c^3} \rho_\nu \, d\nu \tag{28}$$

where *(ν)* denotes the frequency interval in question and ρ_ν is the equilibrium photon occupation number (20). We shall now use Eq. (14), alongside the analogous relations for the energy and entropy flows, to translate the thermodynamic quantities per unit volume into the corresponding flows. More precisely, these are *convective* flows of energy, entropy and photon numbers that are carried by the beam and pass through a unit area per unit time:

$$\dot{S} = k_B \int_{(\nu)} \frac{2\nu^2}{c^2} \mathscr{E} \left\{ (1+\rho_k)\ln(1+\rho_k) - \rho_k \ln \rho_k \right\} d\nu \tag{29}$$

$$\dot{U} = \int_{(\nu)} \frac{2\nu^2}{c^2} \mathscr{E} \, h\nu \rho_\nu \, d\nu \tag{30}$$

$$\dot{N} = \int_{(\nu)} \frac{2\nu^2}{c^2} \mathscr{E} \, \rho_\nu \, d\nu \tag{31}$$

As in the discussion of the geometric and fluorescent concentrators, we shall consider the changes of these functions when a photon is added to or removed from a beam. We start with the energy and entropy change per photon removed from the volume *V*,

$$u = \left(\partial U / \partial N \right)_{V,T} \qquad s = \left(\partial S / \partial N \right)_{V,T} \tag{32}$$

As in Sec. 5, all processes are assumed to take place at constant volume. Using (14), the derivatives (32) can be re-written in terms of the derivatives of the flows (29) - (31):

$$u = \left(\partial \dot{U} / \partial \dot{N}\right)_{\mathcal{E},T} \qquad s = \left(\partial \dot{S} / \partial \dot{N}\right)_{\mathcal{E},T} \tag{33}$$

We note that the derivative at constant volume is now replaced by a derivative at constant étendue. The condition of absorption at constant volume therefore ensures that the absorbing substance interacts only with the transverse modes of the photon field, characterised by the étendue. Thus, for a broadband illumination, the energy and entropy per photon (33) replace the energy $h\nu$ and entropy (given by Eq. (10)) per photon in a monochromatic beam.

For a broad luminescence band, Eqs. (33) provide a simple but convenient formulae of calculating the energy and entropy change of a beam by the addition or a removal of a photon. They can be calculated without any difficulty numerically but become particularly simple for radiation of weak to moderate intensity when the occupation numbers ρ_ν are small. It can readily be shown that, for a semiconductor with bandgap $h\nu_g$, absorbing in the frequency range (ν_g, ∞) (Markvart, 2008),

$$\mu = E_g + k_B T \ln\left\{\frac{\dot{N}}{\mathcal{E}\gamma(T)}\right\} \tag{34}$$

$$s(\mathcal{E},T,\dot{N}) = k_B \ln\left\{\frac{\mathcal{E}\gamma(T)}{\dot{N}}\right\} + k_B T \frac{\gamma'(T)}{\gamma(T)} \cong k_B \left\{\ln\left[\frac{\mathcal{E}\gamma(T)}{\dot{N}}\right] + 1\right\} \tag{35}$$

$$u(\mathcal{E},T,\dot{N}) = h\nu_g + k_B T^2 \frac{\gamma'(T)}{\gamma(T)} \cong h\nu_g + k_B T \tag{36}$$

where

$$\gamma(T) = \int_{(\nu)} \frac{2\nu^2}{c^2} e^{h(\nu_g - \nu)/k_B T} d\nu = \frac{2\nu_g^2 k_B T}{hc^2}(1+\varepsilon) \tag{37}$$

and $\varepsilon = 2(k_B T/h\nu_g) + 2(k_B T/h\nu_g)^2$ is a small correction if $h\nu_g >> k_B T$. The approximate expressions (34) – (36) are accurate in what can be called the “non-degenerate limit”, when the Bose-Einstein statistics (20) reduces to the Maxwell-Boltzmann distribution. This is generally true if the difference $h\nu_g$ - μ is greater than about $3k_B T$.

Care needs to be exercised when applying Eqs. (34) – (36) to the conversion of solar radiation with T_S = 6000K. Dependig on the bandgap $h\nu_g$, the intensity of such radiation at maximum concentration may be too strong for Eqs. (34) – (36) to give reliable results. Notwithstanding, as a rule, these expressions hold well for concentration ratios of about 1000 or less and bandgaps of most interest for photovoltaic conversion.

It is interesting to note that if the correction ε is neglected, Eq. (34) and the approximate expressions in (35) and (36) coincide with the corresponding expressions for a two-dimensional ideal gas. Clearly, this is a consequence of the two degrees of freedom, resulting from the two angular variables that are needed to specify the directions (or co-ordinates) of a ray in space.

7. ENERGY-ENTROPY BALANCE FOR THE ABSORPTION AND EMISSION OF LIGHT

We now have our disposal the necessary tools to consider a beam of light from a thermodynamic viewpoint. Before turning to apply this formalism to the conversion of light into useful work, it is of interest to pause briefly to apply these concepts to the absorption and emission of light.

Suppose that the an incident beam of radiation is characterised by a certain thermodynamic parameters, for example, temperature, étendue, or chemical potential. The absorption of a photon from this beam increases the energy and entropy of the absorbing material by some amounts that we shall denote by u_{in} and s_{in}. For a monochromatic beam, for example, $u_{in}= h\nu$, and s_{in} is given by Eq. (10); for broad-band radiation, these quantities are determined by Eqs. (35) and (36).

Similarly, each emitted photon carries away some energy u_{out} and entropy s_{out}. For simplicity, we assume here that photons are absorbed and emitted through the same aperture although, of course, the étendues of the incident and emitted beams can be different. The temperature of the emitted beam is characteristic of the electronic degrees of freedom, and is usually assumed equal to a (single) temperature of the absorbing material T_o (see, for example, the discussion of KSvRS relations in Sec. 4). For the moment, however, we consider a more general situation for any temperature of the emitted beam.

In general, the energies of the incident and emitted photons are different ($u_{in} \neq u_{out}$), and each absorption/emission event rejects some heat (to be denoted by q_{ph}) which is absorbed by the low-temperature reservoir at temperature T_o . By virtue of energy conservation, we have

$$u_{in} = u_{out} + q_{ph} \tag{38}$$

Noting now that the entropy associated with transfer of heat q_{ph} to reservoir at T_o is equal to q_{ph} /T_o, we arrive at the following entropy balance in the absorption/ emission process

$$s_{in} = s_{out} + q_{ph} / T_o - \sigma_i \tag{39}$$

where σ_i is the entropy generated between the absorption and emission of a single photon (Fig. 4a).

Combining (38) and (39) we obtain the entropy generated per absorbed and re-emitted photon in the form

$$T_o \sigma_i = (u_{in} - u_{out}) - T_o (s_{in} - s_{out}) \tag{40}$$

The form of Eq. (40) is not coincidental. We shall see in Sec. 9 that, quite generally, the entropy generation per photon (40) represents a difference of *availabilities* (Pippard, 1964) of the absorbed and emitted photons.

Equation (40) will form a useful starting point for the discussion of photovoltaic conversion. To prepare the ground, we consider briefly the important limiting cases. If the emitted radiation is at equilibrium with the emitted substance at T_o (as is the case for the usual fluorescent media or solar cells), we can introduce the chemical potential μ_{out} of the emitted photons at temperature T_o, and write

$$T_o \sigma_i = (u_{in} - T_o s_{in}) - \mu_{out} \qquad (41)$$

If, furthermore, the incident light represents direct (beam) solar radiation which approximates well by a black body radiation with zero chemical potential we have, from (21), $s_{in} = u_{in}/T_S$, and

$$T_o \sigma_i = u_{in}(1 - T_o / T_S) - \mu_{out} \qquad (42)$$

The entropy generated per photon is thus given by the difference between the incident energy, multiplied by the Carnot efficiency, less the chemical potential of the emitted photons.

When the temperature and étendue of the emitted radiation are the same as for the incident beam, $u_{in} = u_{out}$, $s_{in} = s_{out}$ and no entropy is generated in the absorption/emission event ($\sigma_i = 0$). We shall see in Sec. 9 that this limit describes the operation of a hot carrier solar cell: an ideal device which produces the highest efficiency of a single-junction solar cell, as permitted by thermodynamics.

8. SOLAR CELL AS A HEAT ENGINE: THERMODYNAMIC ANALYSIS OF PHOTOVOLTAIC CONVERSION

A solar cell converts an incident photon into electrical energy or another form of useful work, to be denoted by w. As in the case of emission of radiation, some heat (to be denoted by q_w) is rejected into the low-temperature reservoir at temperature T_o; this is accompanied by the rejection of entropy equal to q_w/T_o . Since there is no entropy associated with the work w, the energy and entropy balance equations for the conversion process now become

$$\begin{aligned} u_{in} &= w + q_w \\ s_{in} &= q_w / T_o - \sigma_i \end{aligned} \tag{43}$$

For a solar cell, the work w is equal to qV, where V is the voltage generated by the solar cell and q is the electron charge. Combining the two equations (43) then gives this photogenerated voltage as

$$qV = u_{in} - T_o s_{in} - T_o \sigma_i \tag{44}$$

and if the incident photon originates from black body radiation (μ_{in} = 0),

$$qV = \left(1 - \frac{T_o}{T_s}\right) u_{in} - T_o \sigma_i \tag{45}$$

The thermodynamic expression for the solar cell voltage thus comes out in a standard form for the amount of work that can be produced between two reservoirs at temperatures T_S and T_o – in other words, the solar cell voltage can be calculated using a direct analogy with the operation of a heat engine (Fig. 4b). For each photon, the incident energy u_{in} which is extracted from the high temperature reservoir is converted with the Carnot efficiency. The voltage is then obtained by subtracting from this ideal value the losses due to entropy generation σ_i in the conversion process.

Substituting (40) into (44) we obtain

$$qV = u_{out} - T_o s_{out} \tag{46}$$

This expression will be discussed in a more general context in Sec. 9. Here and for the remainder of this section we restrict attention to the operation of standard solar cells where photons are emitted at temperature T_o. Since this is also the temperature to be used for the evaluation of u_{out} and s_{out} , we obtain the well known result

$$qV = \mu_{out} \tag{47}$$

In other words, the work carried out by the conversion of a photon into electrostatic or chemical energy is equal to the chemical potential of the emitted photons. This result is derived in many texts by invoking the theory of p-n junction solar cell but has been obtained here, quite generally, by an argument based solely on thermodynamics.

Let us now take a closer look at the losses which occur in the photovoltaic conversion process – in other words, those that contribute to the entropy generation σ_i . This discussion can be simplified considerably if we use the ideal-gas description of photon beams, as discussed in Sec. 6. The discussion so far has focused on photons that are converted into work. Depending on the applied load, however, the solar cell may act as both as a converter and as an emitter of radiation, to produce electrical current *I*, say, which is compatible with the electrical characteristics of the load. Accordingly, the incident and emitted photon fluxes (to be denoted henceforth by $\dot{N}_{in}$ and $\dot{N}_{out}$) need not be equal: for an ideal solar cell where all absorbed photons are either emitted or converted into electrical current

$$\dot{N}_{in} - \dot{N}_{out} = \dot{N}_{in}^{o} - \dot{N}_{out}^{o} + I/q \cong I/q \tag{48}$$

where $\dot{N}_{in}^{o}$ and $\dot{N}_{out}^{o}$ are the equilibrium photon fluxes at temperature T_o of the converter which occur if the étendue of the incident beam differs from the emitted beam. In the second part of (48) we have noted that the difference of the equilibrium fluxes can usually be safely neglected. Equation (48) represents the essence of the Shockley-Queisser detailed balance (Shockley and Queisser, 1961)

The expressions (35) and (36) for the energy *u* and entropy *s* per photon can therefore be written as

$$\begin{aligned} T_o\sigma_i = & \left\{u(T_S,\mathcal{E}_{in},\dot{N}_{in}) - u(T_o,\mathcal{E}_{out},\dot{N}_{out})\right\} - T_o\left\{s(T_S,\mathcal{E}_{in},\dot{N}_{in}) - s(T_o,\mathcal{E}_{out},\dot{N}_{out})\right\} = \\ & = \left[\left\{u(T_S) - u(T_o)\right\} - T_o\left\{s(T_S,\mathcal{E}_{in},\dot{N}_{in}) - s(T_o,\mathcal{E}_{in},\dot{N}_{in})\right\}\right] + \\ & \quad + \left[s(T_o,\mathcal{E}_{in},\dot{N}_{in}) - s(T_o,\mathcal{E}_{out},\dot{N}_{in})\right] + \left[s(T_o,\mathcal{E}_{out},\dot{N}_{in}) - s(T_o,\mathcal{E}_{out},\dot{N}_{out})\right] \end{aligned} \tag{49}$$

The three terms in square brackets in the last expression of (49) represent the three fundamental losses in the operation of an ideal solar cell.

Let us separate from (49) the last term, which we denote by σ_{kin}. This term corresponds to entropy generation due to finite current being extracted from the solar cell (a finite rate of turnover of the “heat engine”):

$$\sigma_{kin} = s(T_o,\mathcal{E}_{out},\dot{N}_{in}) - s(T_o,\mathcal{E}_{out},\dot{N}_{out}) = k_B \ln\left(\frac{\dot{N}_{in}}{\dot{N}_{out}}\right) \tag{50}$$

Thus

$$\sigma_{kin} = k_B \ln\left(\frac{I_\ell + I_o}{I_\ell + I_o - I}\right) \tag{51}$$

where $I_\ell = q\left(\dot{N}_{in} - \dot{N}_{in}^{o}\right)$ and $I_o = q\dot{N}_{out}^{o}$ correspond to the photogenerated and dark diode saturation current, respectively. By writing

$$qV = qV_{oc} - T_o\sigma_{kin} \tag{52}$$

it is not difficult to show that σ_{kin} (51) gives the usual I-V characteristic of the solar cell (Markvart, 2008b). This I-V characteristic is thus a direct consequence of the thermodynamic ideal-gas laws for the photon gas.

We now return to (49). The first and second terms on the right hand side of the last expression have been aired in some length (Markvart, 2007, 2008b) and only a brief discussion will be given here. The second term arises as a results of étendue expansion between the incident and emitted beams, with étendues $\mathcal{E}_{in}$ and $\mathcal{E}_{out}$:

$$\sigma_{\exp} = k_B \ln\left(\frac{\mathcal{E}_{out}}{\mathcal{E}_{in}}\right) \tag{53}$$

A related topic of angularly selective solar cells has recently been discussed by Badescu (2005) and by Peters *et al* in this volume. By microscopic reversibility (the quantum states that allow photons to enter the solar cell can also be used to emit them), $\mathcal{E}_{out} \geq \mathcal{E}_{in}$, and σ_{exp} is always greater than or equal to zero.

Finally, the first term on the right hand side of (49) is the entropy generation by "photon cooling" from temperature T_S to temperature T_o ,

$$\sigma_c = k_B\left(\frac{T_S}{T_o} - 1\right) - k_B \ln\left(\frac{T_S}{T_o}\right) \tag{54}$$

Since $T_S > T_o,$ $\sigma_i > 0$. This photon cooling term will be the subject of a more detailed examination in the next section where we discuss hot carrier conversion.

Thus, the open circuit voltage V_{oc} can be written as

$$qV_{oc} = \left(1 - \frac{T_o}{T_s}\right)u_{in} - T_o\left(\sigma_c + \sigma_{\exp}\right) \tag{55}$$

Substituting from (53) and (54) then gives

$$qV_{oc} = \left(1 - \frac{T_o}{T_s}\right)h\nu_g + k_B T_o \ln\left(\frac{T_S}{T_o}\right) - k_B T_o \ln\left(\frac{\mathcal{E}_{out}}{\mathcal{E}_{in}}\right) \tag{56}$$

Equation (56) is the thermodynamic analogue of the Shockley ideal solar cell equation to which it can be reduced by straightforward algebra. Various approximate forms of (56) have been obtained on a number of occasions in the past. In the more general form presented here, it shows that the maximum energy (voltage) produced in photovoltaic conversion is described completely by the temperatures of the two beams (considered here as thermal reservoirs) and their étendues. Similarly to an ideal heat engine, no specific details are needed for the engine (converter) nor the working medium.

9. HOT CARRIER SOLAR CELLS

Equation (56) gives the open circuit voltage of an ideal single-junction solar cell, in terms of the fundamental losses and their precise thermodynamic origins. Here we wish to consider in more detail one of these loss terms: the entropy generation σ_c which describes the irreversible cooling of the beam from solar temperature T_S to the ambient temperature T_o . This loss – which corresponds to the "thermalization" of electron-hole pairs in a semiconductor immediately after light absorption – is usually thought to be one of the two fundamental losses in the operation of an ideal solar cell. This question has been examined by Ross and Nozik (1982) who proposed a "hot carrier" solar cell where this loss is reduced or even eliminated. The formalism which we have developed allows us to consider this concept from a more fundamental point of view based on a thermodynamic argument, without resorting to specific conversion structures.

To prepare the ground for this more general analysis we note that the photon cooling loss and the associated entropy generation σ_c will be reduced if photons are emitted from the solar cell at a temperature T_a which is higher than the temperature T_o of the "cold" reservoir ($T_S \geq T_a > T_o$). Equations (38) – (46) then still hold since heat is rejected at the ambient temperature T_o and no assumption has been made about the temperature of the emitted photons. Highlighting explicitly the temperature argument in the energy and entropy of the emitted photons,

$$\begin{aligned} u_{out} &= u(T_a, \mathscr{E}_{out}, \dot{N}_{out}) \\ s_{out} &= s(T_a, \mathscr{E}_{out}, \dot{N}_{out}) \end{aligned} \tag{57}$$

and substituting into (46) we obtain the voltage in the form

$$qV = u(T_a, \mathscr{E}_{out}, \dot{N}_{out}) - T_o s(T_a, \mathscr{E}_{out}, \dot{N}_{out}) \tag{58}$$

Thus, the work qV is equal to the availability (or exergy) of the emitted photon, calculated for a process at constant volume (see, for example, Pippard, 1964).

Those familiar with classical thermodynamics will not be surprised at this result. Notwithstanding, it is instructive to digress for a moment and calculate directly the maximum amount of work that can be carried out by a photon, by using a standard thermodynamic argument based on availability. To this end, we consider a cavity or "box" filled with photons at temperature T_a which are to be converted into electricity. Denoting by p_o the equilibrium pressure and v the volume per photon we can define the availability per photon of radiation in the box as

$$a = u - T_o s + p_o \mathsf{v} \tag{59}$$

The maximum work w per photon is then equal to the difference of availability Δa between a photon in the box and a photon in thermal equilibrium at temperature T_o:

$$w = \Delta a = \Delta u - T_o \Delta s + p_o \Delta \mathsf{v} \tag{60}$$

Throughout this Chapter we have assumed that photovoltaic conversion takes place at constant volume, and therefore $\Delta V = 0$. Equation (60) provides a recipe how this analysis can be modified for a conversion process under different conditions, for example, at constant pressure (Markvart, to be published). Since the final product of the conversion process is equilibrium black body radiation at ambient temperature T_o (with energy and entropy u_o and s_o, respectively) which has a zero chemical potential ($\mu = u_o - T_o s_o = 0$), we have

$$w = \left(u - T_o s\right) - \left(u_o - T_o s_o\right) = u(T_a) - T_o s(T_a) \tag{61}$$

Noting the equality of the energy and entropy for “photons in a box” and “photons in a beam” (see Sec. 6), it is immediately observed that Eq. (61) is identical to Eq. (58). This argument shows that the voltage, generated by a hot carrier solar cell, is equal to the difference in availability of an emitted photon and a photon in thermal equilibrium at the temperature of the cold reservoir - in other words, it is equal to the maximum amount of work that can be produced by a photon at temperature T_a which reaches equilibrium at temperature T_o.

We note that, using the chemical potential $\mu_{out} = u_{out} - T_a s_{out}$, Eq. (58) can be re-written in the form

$$qV = u_{out}\left(1 - \frac{T_o}{T_a}\right) + \frac{T_o}{T_a}\mu_{out} \tag{62}$$

The first expression on the right hand side of (62) resembles the voltage of hot-carrier solar cells in the paper by Ross and Nozik (1982). Ross and Nozik have argued that carriers can be cooled without generating entropy if they are extracted from the hot reservoir at a single energy, through so-called selective energy contacts. The present approach is independent of a specific conversion mechanism, and the energy u and entropy s in (58) or (62) have been derived by a direct thermodynamic argument from the energy and entropy of the emitted photon beam. We are not aware of a detailed comparison between results obtained by the two theoretical approaches at the present time but work towards this aim is currently in progress (Markvart, to be published).

It is of interest to consider the important limiting cases. As expected, Eq. (58) or (62) reduce to (47) for $T_a = T_o$. For $T_a = T_S$ and $\mathcal{E}_{in} = \mathcal{E}_{out}$ when $\mu_{out} = \mu_{in} = 0$ and $u_{in} = u_{out}$, these equations become

$$qV = u_{out}\left(1 - \frac{T_o}{T_S}\right) \tag{63}$$

as discussed by Markvart (2007). In this case, only the entropy generation term σ_{kin} remains. No entropy is then generated near the open circuit when the conversion process becomes reversible.

Using the obtained results for the voltage, it is not difficult to determine the improvement in solar cell efficiency from hot carrier conversion. For simplicity, we restrict attention to the case of non-degenerate statistics, equivalent to the “ideal gas” approximation discussed at the end of Sec. 6. Figure 5 shows the I-V characteristic of a hot carrier solar cell with T_a = 3000K for a semiconductor with as bandagap of 1.4 (close to the bandgap of gallium arsenide). For one-sun illumination, the open circuit voltage in this case is equal to 1.39V, as compared with the maximum value of 1.15V for a standard solar cell operating at the ambient temperature of 300K. This can be contrasted with the thermodynamic energy of a photon absorbed at this bandgap of 2.22 eV, and the maximum open-circuit voltage for a hot-carrier solar cell operating at 6000K, equal to 2.11V.

The conversion efficiency as a function of the bandgap is shown in Fig. 6. The efficiency limit under one-sun illumination rises from about 31% for standard solar cell ($T_a = T_o$ = 300K) to 33 % for a hot carrier cell operating at T_a = 1,500K, 40% at T_a = 3,000K, and to 52% at T_a = 4,500K. Under fully concentrated sunlight, these efficiencies become 41% for a standard solar cell, 44 % at T_a = 1,500K, 53% at T_a = 3,000K, approaching 70% at T_a = 4,500K.

9. CONCLUSION

In this chapter we have shown how photovoltaic and photochemical conversion can be understood in thermodynamic terms. Starting from the concept of étendue within the realm of geometrical optics, we have moved into the parallel world of waves and quantum mechanics, and shown how the perception of a ray of light then coexists with the notion of mode, or photon state.

The discrete nature of light beams has then made it possible to develop statistical ideas in a similar fashion than in standard statistical mechanics. We have seen in Sec. 2 that photons in a beam behave similarly to particles of a two-dimensional ideal gas with étendue corresponding to the volume of the gas. The energy and entropy exchanged between the incident and emitted photon beams can then be rigorously defined, and used to determine the ultimate limits to the efficiency of quantum solar energy conversion devices such as fluorescent collectors and solar cells. The thermodynamic approach used in this Chapter justifies the conclusion that these limits depend solely on the parameters of the incident and emitted beams and not on the material parameters of the solar cell.

A detailed identification of the thermodynamic origins has allowed a full analysis of the fundamental losses in detail, and has made it possible to contemplate how the operation of these devices can be further improved. We were able to determine the ultimate limit to the efficiency which can be reached by the application of photonic structures to fluorescent collectors. We have also seen that the detailed balance limit of Shockley and Queisser is significantly lower than the maximum thermodynamic limit of a single junction solar cell. This limit can, in principle, be achieved with a hot-carrier solar cell. Such device converts the free-carrier heat acquired by electron-hole in the absorption of light into voltage at the terminals of the solar cell in a manner similar to the operation of a thermoelectric device. The practical demonstration of such a solar cell represents one of the exciting challenges to photovoltaics of the third millennium.

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Figure captions

Fig. 1. The definition of étendue. (a) The usual geometric definition in terms of a cross sectional area δA (not necessarily perpendicular to the beam) and the angular divergence $\delta\Omega$. (b) Étendue as an element of volume in the phase space of transverse coordinates of the beam. Note that the projection $\delta\Omega.\ cos\ \theta$ of the area on the unit sphere that corresponds to the solid angle $\delta\Omega$. onto the xy plane now becomes $\delta k_x \delta k_y / k^2$.

Fig. 2 Schematic diagram of an optical instrument for concentrating sunlight, considered as the transformation of étendue from $\mathcal{E}_{in}$ to $\mathcal{E}_{exit}$.

Fig. 3 The cross section of a fluorescent collector based on total internal reflection. Photons propagating along rays outside the escape cone are trapped and reach the solar cell at the edge, unless reabsorbed. Photons emitted within the escape cone leave through the front face of the collector and are lost from the system.

Fig. 4. A schematic diagram depicting the thermodynamic processes involved in the absorption/emission of light (a) and in photovoltaic conversion (b).

Fig. 5 The I-V characteristic of a hot-carrier solar cell with bandgap 1.4eV, at one sun illumination (denoted by V(3000K)). For clarity, this characteristic is plotted in the form of a function of current, normalised to the photogenerated current I_ℓ. For comparison, the graph also shows the thermodynamic energy per photon u_{in}, and losses by entropy generation through kinetic nature of this process (σ_{kin}), étendue expansion (σ_{exp}), and photon cooling from 6000K to 3000K. The *V-I* characteristic of an ideal conventional solar cell, denoted by V(300K), is also shown. The shaded region indicates the difference between the voltage of hot carrier and conventional solar cells.

Fig. 6 The efficiency of a hot carrier solar cell as a function of the bandgap, for three absorber temperatures, as well as the Shockley-Queisser efficiency limit at 300K, under one-sun illumination and fully concentrated sunlight.

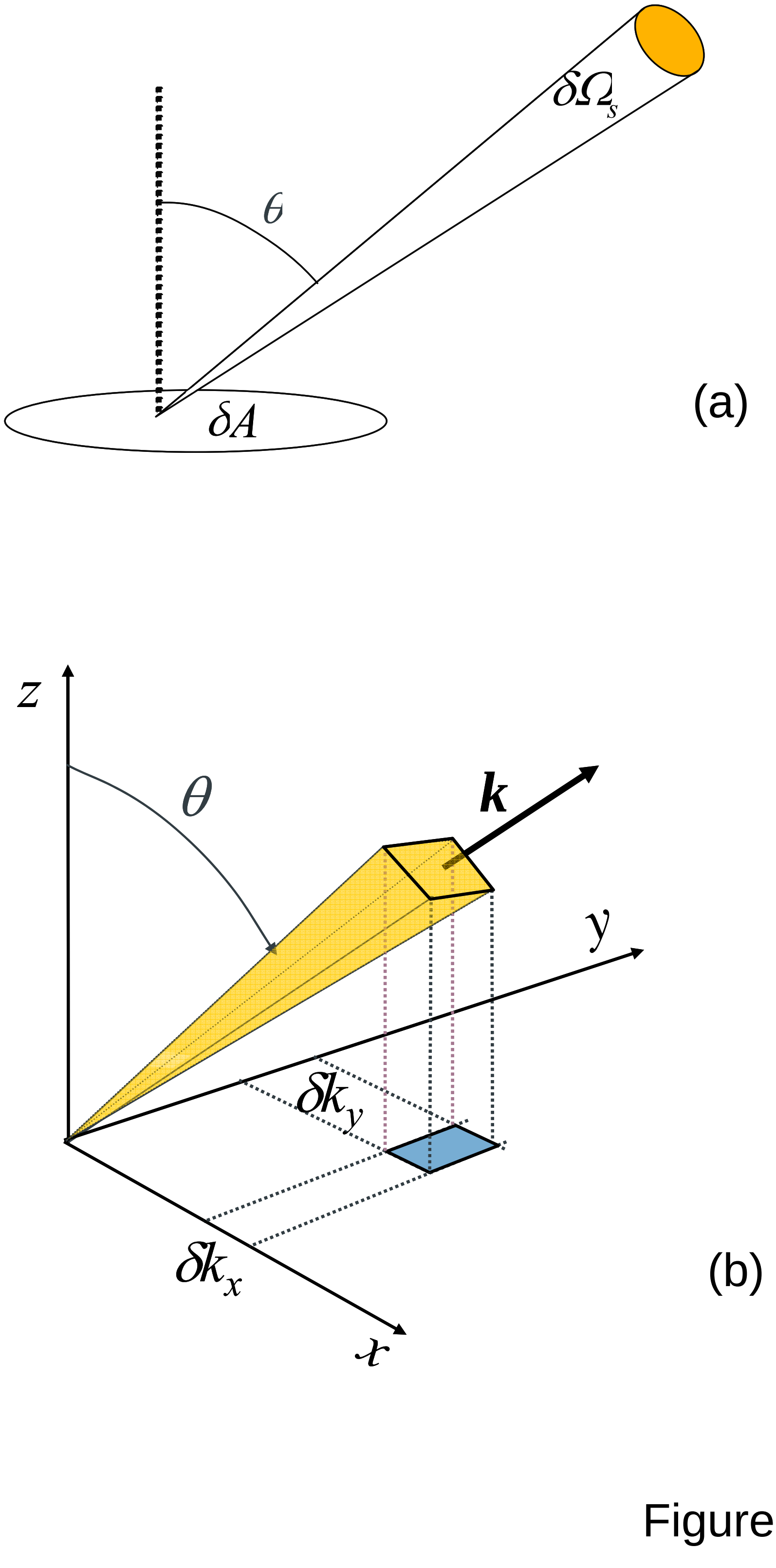

Figure 1

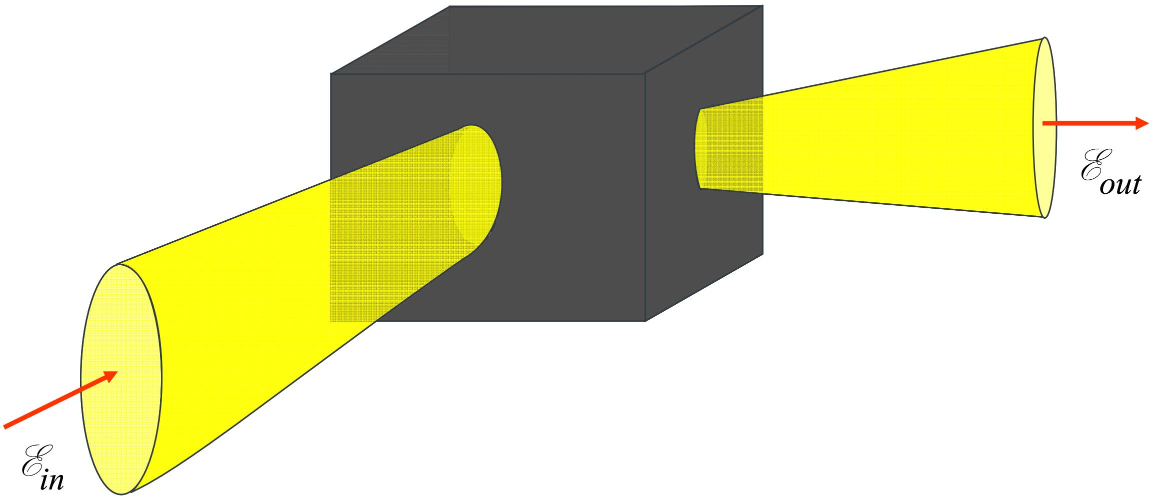

Figure 2

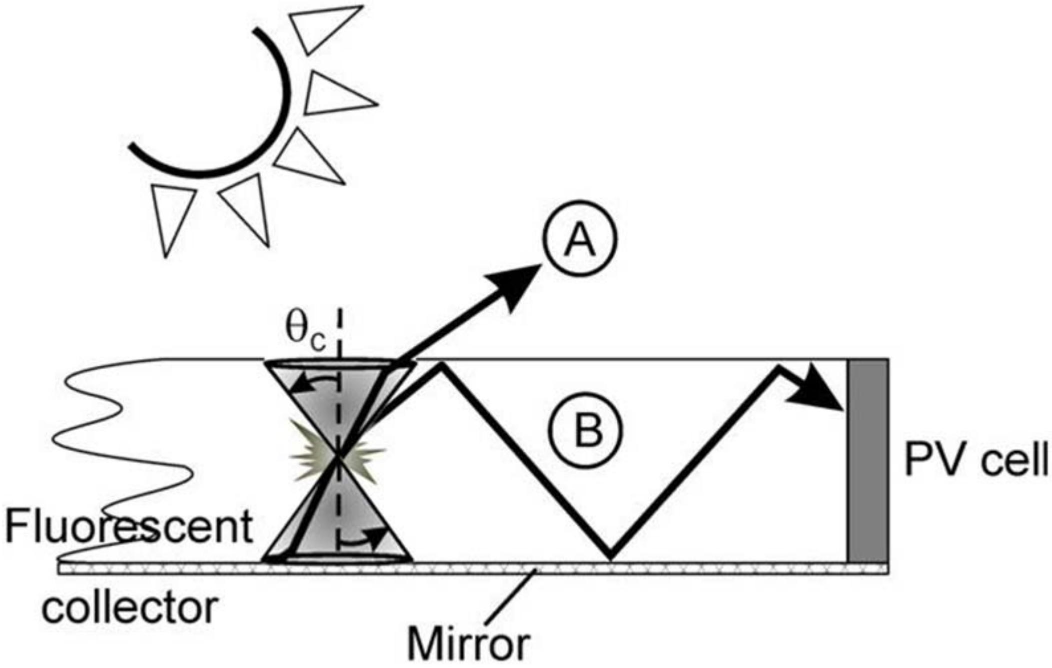

Figure 3

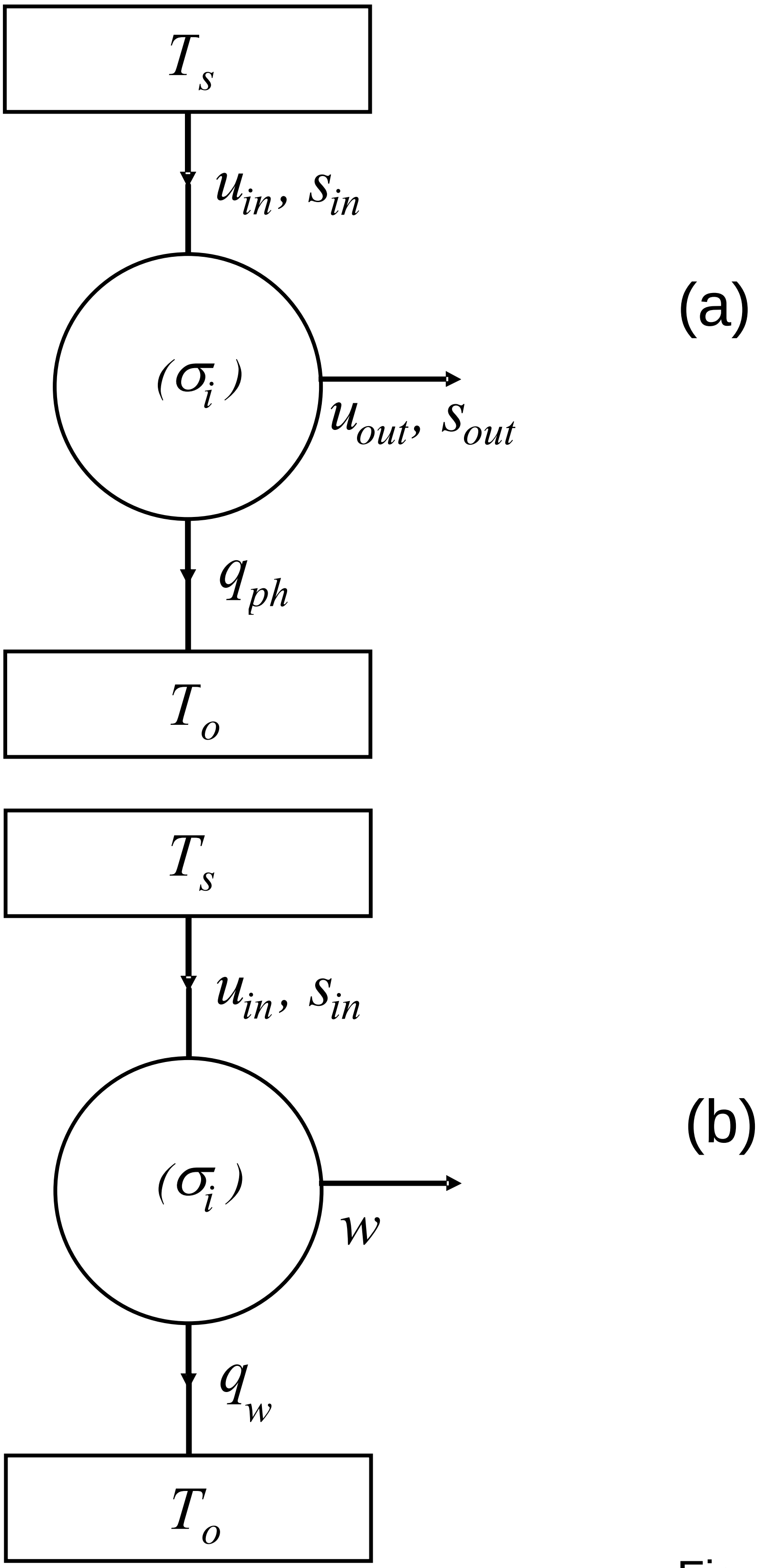

Figure 4

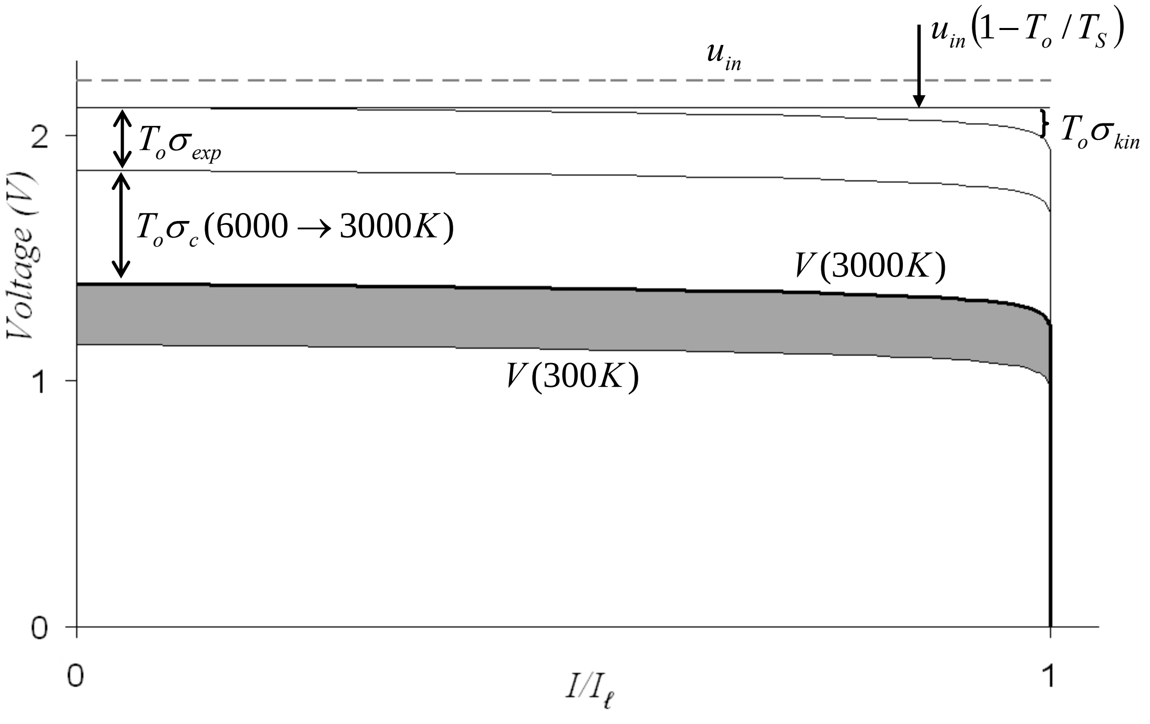
$u_{in}\left(1-T_o/T_S\right)$
u_{in}
$T_o\sigma_{exp}$
$T_o\sigma_{kin}$
$T_o\sigma_c(6000\rightarrow 3000K)$
$V(3000K)$
$V(300K)$
Voltage (V)
2
1
0
0
1
I/I_ℓ

Figure 5

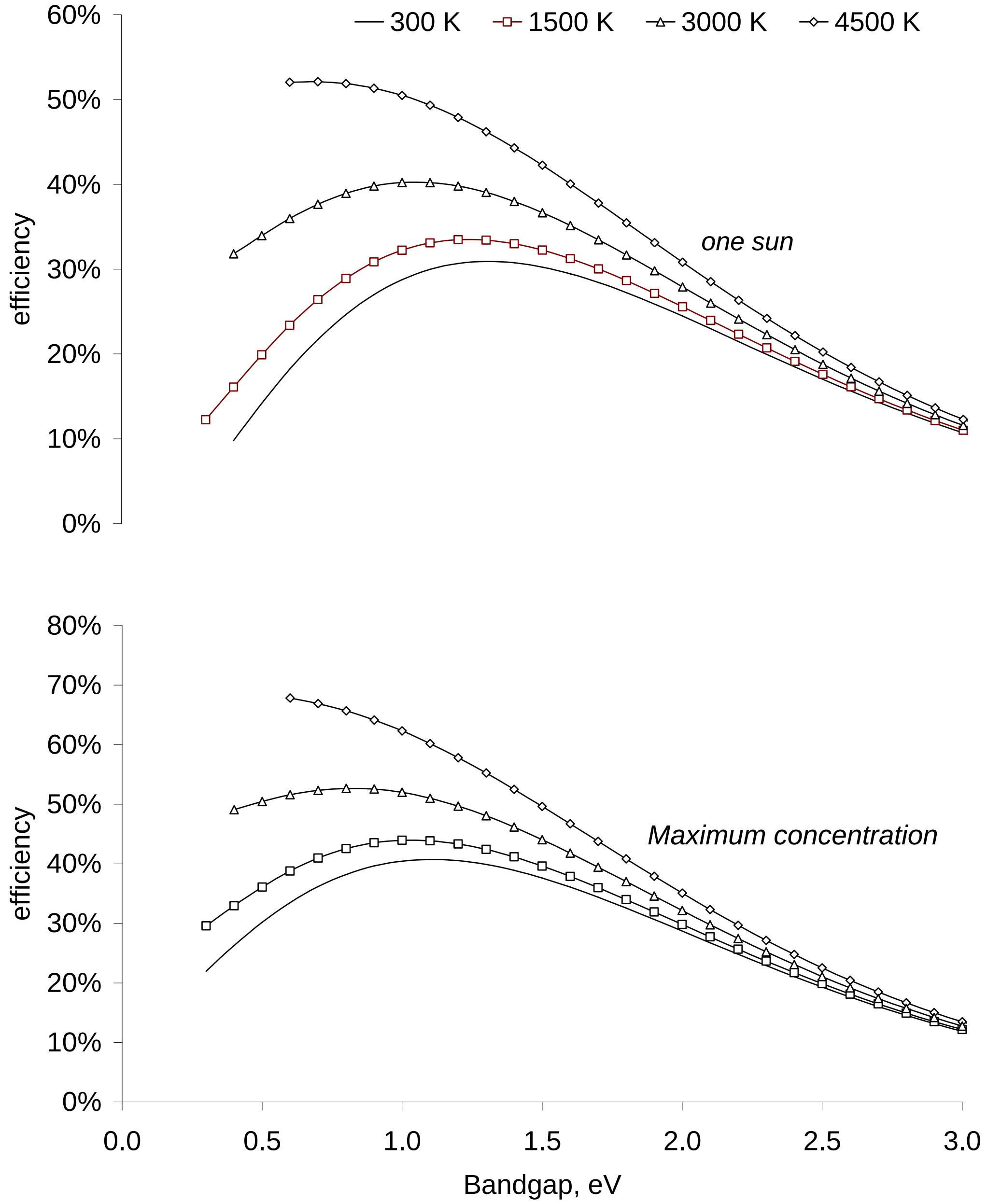
300 K
1500 K
3000 K
4500 K
one sun
Maximum concentration
efficiency
60%
50%
40%
30%
20%
10%
0%
80%
70%
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Bandgap, eV

Figure 6