



From steam engine to solar cells: can thermodynamics guide the development of future generations of photovoltaics?

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Thermodynamics has played a singular role in the development of virtually all energy technologies to-date. This review argues that it also has a role to play in the understanding and design of solar cell operation, particularly looking toward the future, high-efficiency solar cells. After a historical overview of the key developments in the ‘thermodynamics of light,’ the conversion of a monochromatic light beam is used as a starting point to analyze the conversion process, examine the fundamental losses in terms of irreversible entropy generation, and consider in detail one of the key applications: the Shockley–Queisser detailed balance. We review and compare the principal suggestions for the highest theoretical efficiency of solar energy conversion, and analyze one possible embodiment of such a third-generation structure: the hot-carrier solar cell. A somewhat different application of the statistical approach—light trapping—is reviewed at a fundamental level, and the future potential is considered for devices which combine such a ‘thermodynamic squeezing’ of light with latest developments in photonics, leading to a photonic bandgap solar cell. We argue that the widespread use of thermodynamic tools in the current photovoltaics research, especially when combined with the potential benefits to future devices, already indicates that our thinking should not be about *if* but *how* thermodynamics can guide us to make better solar cells. © 2016 The Authors. *WIREs Energy and Environment* published by John Wiley & Sons, Ltd.

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INTRODUCTION

Most of the energy forms we use today have their roots in thermodynamics. With origins dating back to the peak of the industrial revolution, classical thermodynamics has expanded beyond the immediate energy sector into a branch of science that pervades many scientific disciplines today. It is

therefore no surprise that thermodynamics has been called upon to furnish the theoretical tools needed to support even one of the most recent forms of energy conversion: photovoltaics.

An early mention of thermodynamics with reference to the operation of a solar cell was the ‘Shockley paradox.’^{1,a} However, we shall show that many ideas behind the thermodynamic fundamentals of solar cell operation date even to a much earlier time. Perhaps it is only a coincidence that Carnot’s classical paper on the efficiency of conversion into mechanical work² appeared some 15 years before what is now considered to be the first observation of the photovoltaic effect.³ Carnot’s work provided the

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first impetus that grew into a quantitative framework now called thermodynamics. And it was the application of thermodynamic to electromagnetic radiation that gave rise to quantum mechanics at the turn of the 20th century laying down, as we shall see, the foundation stones for the understanding of modern photovoltaics in thermodynamic terms.

Our review starts with a brief historical perspective in the section *The Foundation Pillars* of several key concepts that underpin what is now sometimes called the ‘thermodynamics of light.’ Building on this foundation, we shall chart the progress toward the current understanding by using examples of ideas, concepts, strategies, and views that contributed to the field. We shall not aim to provide a complete list of efficiencies^{4,b} but, in section *Light, Heat, and Work*, we shall take a look at a range of classical theories aiming to determine the limits to solar energy conversion and the related process of light emission. The following sections then introduce the quantum nature of light into the conversion process. In section *Quantum Solar Energy Conversion*, we examine the kinetics and current considerations of the celebrated detailed balance theory of Shockley and Queisser. *Thermodynamics of Photovoltaic Conversion* section then revisits this subject on the basis of thermodynamics, bringing in new perspectives on the conversion process and fundamental energy losses.

A key objective of this review is to consider new avenues and opportunities for research. Two examples have been chosen in the section *Future Directions: Beyond the Shockley-Queisser Limit* to illustrate the potential of thermodynamics to achieve very high conversion efficiencies: the maximum limit to the efficiency of solar energy conversion and the hot-carrier solar cells. *Light Trapping* section examines a somewhat different application of statistical techniques to the capture of solar radiation, without reference to temperature or heat.

THE FOUNDATION PILLARS

Current photovoltaic technologies—the principal focus of this paper—are the product of modern materials science, underpinned by the quantum theory. They have emerged from developments in solid state electronics and have close relationships with other solid state devices such as microelectronic circuits. However, we shall see that the roots of their operation have deeper and more ancient origins, and the understanding of the theoretical foundations will bring us to the early days of quantum theory and

thermodynamics. Not surprisingly, what many consider to be the first paper which kick-started the quantum theory combined thermodynamics with electromagnetism, in the concept of black-body radiation. Here, we review briefly four areas that can be considered as the foundation stones for a satisfactory understanding of solar energy conversion in thermodynamic terms.

The Size of a Beam of Light

Thermodynamics deals with the energy attributes of substance confined in a well-defined volume. Our aim here is to find corresponding characteristics for a beam of light. In contrast with geometrical optics which describes light propagation in terms of light rays, energy conversion requires to define bundles of rays (*light beams*) that have finite dimensions and are able to carry macroscopic amounts of energy. This distinction first became apparent in the analysis of concentration of light⁵ which requires optimum illumination of the receiver (a solar cell or heated fluid), without necessitating image formation. The new field of nonimaging optics therefore defined a new characteristics of the light beam: the *étendue*.^{6,c,d} A key feature of the *étendue* which underpins its importance in optics to its invariance: the *étendue* of a beam propagating in a clear and transparent medium is conserved (see for e.g., Ref 5 where a proof of this theorem can be found).

The element of *étendue* of a narrow beam of angular spread $\delta\omega$ passing through an area δA is defined as

$$\delta\mathcal{E} = n^2 \delta A \delta\omega \cos \theta \quad (1)$$

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 \mathbf{k} . For an extended beam, the total *étendue* is obtained by an integration of Eq. (1) giving the *étendue* of diffuse sunlight propagating in vacuum or air with directions extending over a complete hemisphere as $\mathcal{E} = \pi A$.

The *étendue* has yet another facet of fundamental significance for the thermodynamics of light: it is proportional to a volume element in the phase space of coordinate variables x , y and wave vector components k_x , and k_y .^{5,7,e} By analogy with the early quantum mechanics, the *étendue* \mathcal{E} can thus be considered as a measure of the number of quantum states in the beam available for photon occupation.⁸ The conservation of *étendue* in a clear medium can then be interpreted as the invariance of the volume of a beam in the phase space of its transverse coordinates

(an equivalent of the Liouville theorem of classical mechanics), and the conservation of the number of quantum states. This provides a firm foundation for the analysis of processes that transform the beam, in close similarity to the volume variable in statistical mechanics and thermodynamics.

Black-Body Radiation

Radiation emitted by heated objects—the subject of an intense research activity in the second half of the 19th century—gradually evolved into a universal concept which we now call black-body radiation: electromagnetic energy in thermal equilibrium with matter, characterized by the usual thermodynamic quantities such as temperature, pressure, and volume. The key formula that eventually emerged is the Planck's distribution law, usually written in terms the energy density of black-body radiation at a certain temperature T . Planck never fully accepted the implication of his theory and the existence of light quanta that we now call photons.⁹ Having photovoltaics in mind, however, it will be more convenient to work with quantities relating to photons rather than with the energy of electromagnetic radiation, and we shall write Planck's law in the form

$$n_{ph} = \frac{8\pi n^3 \nu^2}{c^3} \rho_\nu(T) \quad (2)$$

where n_{ph} is the number of photons per unit frequency per unit volume, ν is the frequency, c is the speed of light, h is the Planck constant, k_B is the Boltzmann constant, n is the refractive index of the medium, and $\rho_\nu(T)$ —what we now call the occupation probability of a quantum state—is given by

$$\rho_\nu(T) = \frac{1}{e^{h\nu/k_B T} - 1} \quad (3)$$

When examined in a modern context, several features of Planck's formulae (2), (3) deserve a special attention. The occupation probability (3) can be viewed as a special case of Bose–Einstein distribution with the chemical potential equal to zero. In thermodynamic terms this means that photons which form black-body radiation represent pure heat, and have no capacity to perform work in an isothermal process. This point will be taken up again in the sections *Quantum Solar Energy Conversion*, *Thermodynamics of Photovoltaic Conversion*, and *Future Directions*.

A further point of note is that the formula for photon density Eq. (2) implies the existence of not one but two forms of equilibria: an equilibrium between levels at different energy, as expressed by the occupation probability (3), and an equilibrium between different directions of propagation, as expressed by the multiplicity factor for each energy level. This latter aspect of Planck's statistics will be discussed in more detail in the section *Light Trapping*.

The statistical nature of Eq. (2), with origins close to the kinetic theory of gases, required Planck to build bridges between the work of Maxwell, Kirchhoff, and particularly Boltzmann^{10,11,f} by bringing into play a relation linking n_{ph} with the photon flux density ϕ_ν —the number of photons passing through a unit perpendicular area per unit solid angle per unit time:

$$\phi_\nu(T) = \frac{c n_{ph}(T)}{n} = 2 \left(\frac{n\nu}{c} \right)^2 \rho_\nu(T) \quad (4)$$

The existence of the universal function of temperature $\phi_\nu(T)$ was already stipulated by Kirchhoff but it was determined, in the form (4), only later by Planck, as part of his theory of black-body radiation. The number of photons that propagate in a quasi-monochromatic beam of frequency width $\delta\nu$ with étendue \mathcal{E} emitted by a black body at temperature T and passing through area A per unit time is then, by (1)

$$\Phi = \mathcal{E} \frac{\phi_\nu(T)}{n^2} \delta\nu = \frac{\mathcal{E}}{\pi A} \Phi_o(T) \quad (5)$$

where $\Phi_o(T)$ refers to the photon flux emitted by a black body into a full hemisphere in vacuum. As the photon flux and the étendue are both conserved, so must be the ratio ϕ_ν/n^2 , as already evident from the second equation (4). This is the photon flux analogue of the brightness theorem.¹²

The concept of black body, as a perfect absorber and emitter of radiation, is of a special significance for solar energy conversion as it represents a good approximation for the radiation emitted by the Sun. This similarity provides a powerful basis for a theoretical understanding: representing the Sun's radiation as a black body affords a valuable tool that has been developed over many years, and is available in a standard form in most textbooks on thermodynamics and statistical physics (see e.g., Refs 13 and 14).

Heat and Work

Bringing together the words ‘work’ and ‘thermodynamics’ immediately evokes the notion of Carnot efficiency. Carnot’s result, although resting firmly on the ‘caloric’ concept, marked the birth of a new field: thermodynamics. With a remarkable insight, Carnot predicted that a quantity Q_h of heat, extracted from a high-temperature reservoir can be converted to work with an efficiency at most

$$\eta_C = 1 - \frac{T_o}{T_S} \quad (6)$$

whilst heat Q_ℓ must be rejected into a low-temperature reservoir (Figure 2(a)). Anticipating the application to solar radiation, the temperatures of the high- and low-temperature reservoirs have (6) been set equal at the solar temperature T_S and the ambient temperature T_o . Carnot’s efficiency proved to be an inspired foundation for what was to become the second law of thermodynamics. Since an ideal heat engine operates in a cyclical manner, the working medium returns to the same point at the beginning of the cycle. Neither the properties of the working medium nor the properties of the surroundings thus enter the argument.

We shall see that—perhaps surprisingly—Carnot efficiency appears profusely in the numerous formulae that have been suggested for solar energy conversion and that will be discussed in the sections that follow. Equally important, however, is to examine the subtle but important differences between the operation of a solar energy converter and the Carnot engine which—as we shall see—cause the efficiencies achievable in solar energy conversion to be lower than the value (6). The analysis of different models and reasons to explain this difference are among the key objectives of this paper.

Detailed Balance between Absorption and Emission of Radiation

The relationship between the absorption and emission of radiation is a key characteristic of the energy exchange between matter and the radiation field. The intense research effort in this field has brought about several different expressions of what we may now call detailed balance between absorption and emission of radiation. Indeed, some of this work paved the way to the discovery of Planck’s radiation formula.²⁰

The three different relations between absorption and emission of radiation by matter are summarized in Figure 1. The first general relationship between absorption and emission was formulated by

Kirchhoff for radiation emitted by the surface of a heated body.²¹ Paraphrased in terms of photons rather than energies, Kirchhoff surmised that the ratio of the rate at which photons are emitted by a unit area to the absorbing power a is equal to a universal function of only the temperature of the substance and the wavelength or frequency of emission²¹—our photon flux density (Eq. (4), Figure 1(a)).

Planck elaborated on Kirchhoff’s ideas by noting that radiation can only be absorbed or generated in a volume element of a body rather than on the surface.²² He expressed this balance in terms of the absorption coefficient α_V and the coefficient of emission ε_V (emission rate by a small interior volume into a unit solid angle, per unit volume and unit frequency interval, Figure 1(b); see also Ref 23^g). A further historic contribution was made by Einstein who, in his theory of radiation paper,²⁴ extended Planck’s photon balance to describe transitions between the quantum states of matter and showed that a consistency with the Planck radiation law required the existence of stimulated emission (Figure 1(c)). Einstein’s detailed balance, initially developed for atomic lines, was later generalized to molecules by Kennard^{25,26} and Stepanov.^{27,28}

Although discussed for more than 100 years, the thermodynamic issues highlighted in this section and the underpinning assumptions continue to come under scrutiny to this day. Questions relating to entropy associated with absorption and emission of radiation^{29,30} and the associated assumption of reciprocity³¹ retain the attention of the research community, and will only be resolved with further research. Other relations between absorption and emission of light, including a geometrical interpretation, will be examined when we investigate the foundations of light trapping.

LIGHT, HEAT, AND WORK.

The Foundation Pillars section has set the scene by an outline of several scientific disciplines which connect light with thermodynamics. However, little has been said how these tools can be applied to the actual conversion processes, and what constraints apply when light is transformed into other useful energy forms such as mechanical work, electricity, or chemical energy. This section takes the first step in this direction with a snapshot of several early theories which use thermodynamics to describe solar energy conversion. The conversion process is usually considered without making any significant assumptions about the conversion device. The ideas in this

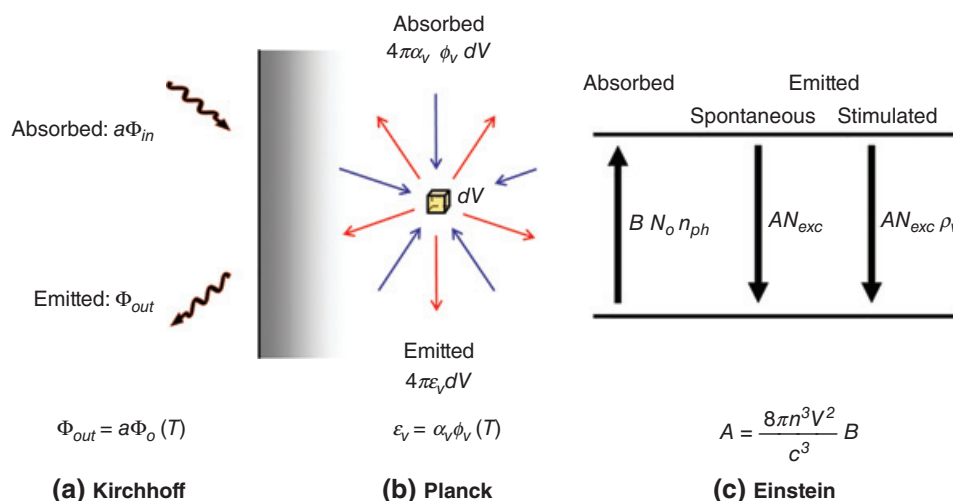


FIGURE 1 | Different facets of the balance and reversibility between absorption and emission of radiation. (a) Kirchhoff's law relating the photon emission rate Φ_{out} to the absorptivity a and the photon emission rate $\Phi_o(T)$ of a black body. Kirchhoff's law holds for the total emission as well as for its spectral components. (b) Planck's relation between the emission (ϵ_v) and absorption (α_v) coefficients at frequency ν for a small volume element in the interior of a body. (c) Einstein's relation, linking the photon absorption and emission rates to transitions between quantum levels of the medium. N_o and N_{exc} denote the numbers of atoms in the ground and excited states, respectively.

section can also be described as emerging from classical (rather than quantum) physics, to be contrasted with the discussion in later sections where emphasis is placed on quantum converters.

Based on the Sun as a source of black-body radiation at a temperature T_S of 6000 K and taking the low-temperature reservoir as the surroundings at an ambient temperature of $T_o = 300$ K (these numbers will be used throughout this review), a ready estimate for the maximum efficiency of a solar energy converter using the Carnot efficiency (6) gives a limit of 95%. It soon becomes apparent, however, that this limit is too generous and cannot be reached even by an ideal theoretical device. Clearly, a number of features and facets of the conversion processes should be taken into account if the efficiency limit is to have at least a semblance of reality.

Energy and Power. The Photothermal and Endoreversible Engines

The first concern that comes to mind is of the Carnot efficiency as an *energy efficiency*: a ratio of two numbers, each with the dimension of energy. The efficiency of a useful solar energy converter is invariably understood to mean the power output divided by power incident on the device: it is therefore a *power efficiency*. As the argument behind Carnot efficiency rests on equilibrium thermodynamics, it is clear that the power efficiency of the Carnot engine is zero. A similar problem in a more general setting has been the subject of research for many years and is often

grouped under a heading of 'finite time thermodynamics'.^{32,33} This section takes a brief look at two examples in application to solar energy conversion.

An early model based on the conversion of solar power was proposed by Castaños and colleagues^{33,34} and by Jeter³⁵ for what is now referred to as photothermal efficiency. The heat input to the engine is taken as the difference between the black-body energy flux received from the Sun at temperature T_S and the black-body flux emitted by the converter at a temperature T_c . This heat is then converted with the Carnot efficiency for a converter operating between the temperatures T_c and the ambient temperature T_o . The resulting power efficiency can then be written as

$$\eta_{PT} = \left\{ 1 - \left(\frac{T_c}{T_S} \right)^4 \right\} \left(1 - \frac{T_o}{T_c} \right) \quad (7)$$

The value of η_{PT} usually quoted represents the maximum with respect to the converter temperature T_c ; for $T_S = 6000$ K and $T_o = 300$ K, the optimum T_c is equal to 2544 K.

A different approach to model the dynamic (rather than static) operation of the engine is to ascribe the resulting losses to the heat flow which supplies and takes away energy to and from the engine (Figure 2(b)). As these losses (which are proportional to the difference of temperatures of the reservoirs and the inlet and output to the heat engine) occur outside the ideal heat engine/converter, this

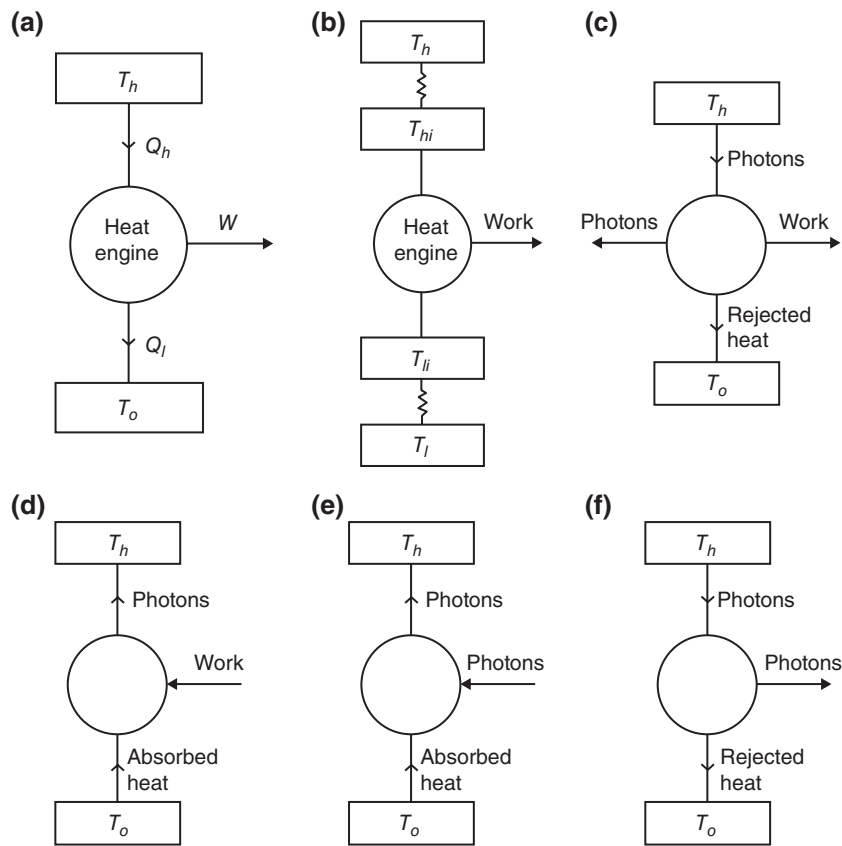


FIGURE 2 | Different heat engines that have, at various times, been considered in the context of solar energy conversion. (a) A schematic diagram of Carnot cycle which will form the starting point for our discussions. The engine absorbs heat Q_h from a high-temperature reservoir at temperature T_h and rejects heat Q_l into a low-temperature reservoir, assumed throughout this paper to be at the temperature of the surroundings T_o . (b) A schematic representation of the endoreversible engine (after Ref 15). The jagged lines show the heat supply by conduction to and from the Carnot engine, operating between two reservoirs at temperatures T_{hi} and T_{li} . (c) The general scheme of a solar energy converter¹⁶ where photons are absorbed as high-temperature heat at temperature T_h , rejecting heat at temperature T_o while emitting photons in a separate channel and performing work. (d) An optical heat pump proposed by Weinstein¹⁷ as a model for electroluminescence. Electrical input (viewed as work) supplemented by the low-grade heat at temperature T_o is converted into photon emission, equivalent to high-temperature heat at temperature T_h . (e) An optical heat pump considered by Chukova as a thermodynamic model for a photoluminescence device.¹⁸ (f) Scheme of a light emitting device, serving as a thermodynamic model for a solar cell.¹⁹

type of engine is usually called *endoreversible*. The resulting *energy* efficiency at the maximum power output then comes out as^{15,36–38}

$$\eta_{CA} = 1 - \left(\frac{T_o}{T_h} \right)^{1/2} \quad (8)$$

The efficiency (8), sometimes known as the Curzon–Ahlborn efficiency, has had some success in modeling the efficiency of conventional power plants but has also been used as the starting point in a discussion aiming to compare and contrast the power and energy efficiencies in more general terms.³² For $T_h = 6000$ K and $T_o = 300$ K, the efficiency of the endoreversible engine is equal to 77.7%.

The power and energy efficiencies of the photothermal and Curzon–Ahlborn engines are compared in Figure 3, highlighting the losses due to a finite rate of turnover of the engine. A notable feature of these graphs is the existence of a maximum turnover rate Q_{max} for each engine where the dynamic losses match the work produced by the engine, and the net output of both energy and power is zero.

The Available Work. Landsberg Efficiency

At the fundamental level, the nature of energy supply to the engine is at the heart of a different model for solar energy conversion. The photothermal and

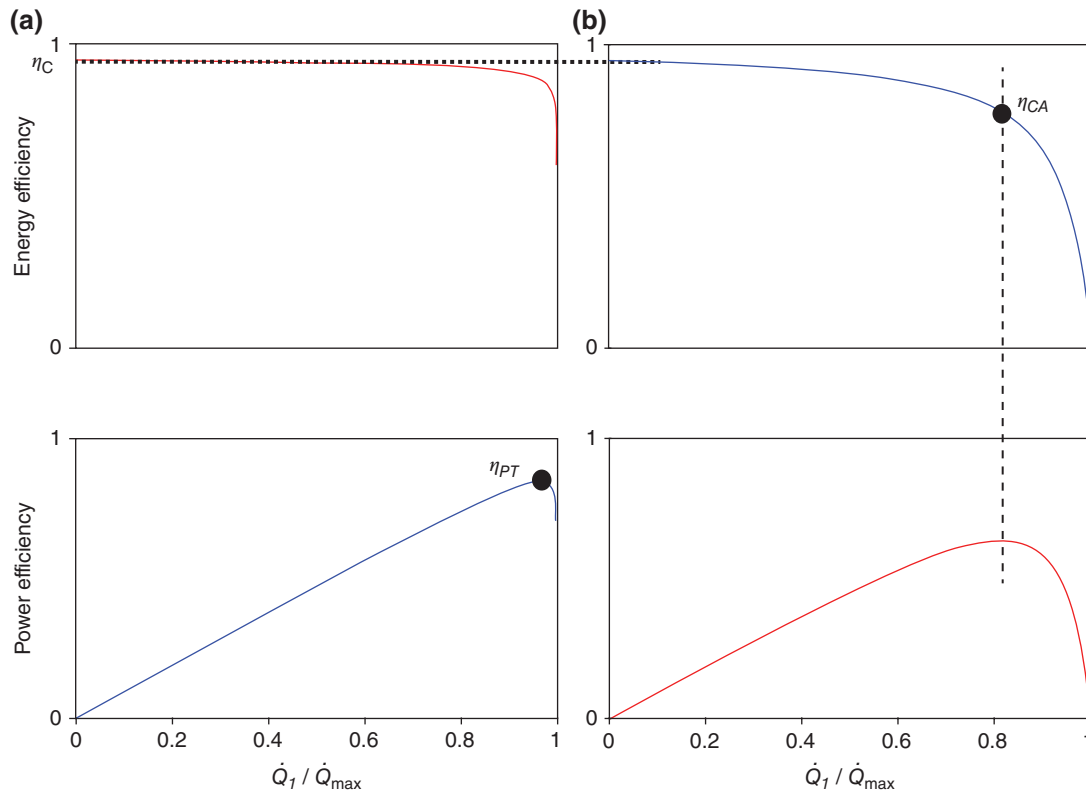


FIGURE 3 | The energy and power efficiencies of the photothermal (a) and endoreversible (b) engines: η_{CA} denotes the *energy efficiency* of the Curzon–Ahlborn (endoreversible) engine and η_{PT} the photothermal *power efficiency*. Both efficiencies are determined at the point where the engine delivers maximum power. \dot{Q}_1 denotes the rate of heat supply to the Carnot engine, with the maximum value \dot{Q}_{\max} .

endoreversible engines consider the energy delivery as a continuous process. One can consider an alternative picture where solar radiation arrives in the form of finite energy packets which are consumed when converted to useful work. Photons are transported to Earth from the Sun as light beams, in a process akin to convection or ballistic transport, which could be compared to particle motion as described by classical mechanics,³⁹ without the need to employ the laws of thermodynamics. It can therefore be argued that statistical concepts such as entropy play no part in photon transport in a clear medium, and that the absorption of light differs from the absorption of heat by a heat engine which is associated with a change in entropy.

A model can thus be perceived where, instead of absorbing heat, a hot working medium in the form of solar radiation at temperature T_S , is injected into the engine. Work can then be carried out by cooling the medium inside the engine to a state of equilibrium with its surroundings at temperature T_o and pressure p_o . The maximum amount of available work

W_{\max} can be determined by the method of thermodynamics in terms of the *availability* or *exergy*:^{39,i}

$$W_{\max} = U_S - T_o S_S + p_o V_S = \left(1 - \frac{T_o}{T_S}\right) U_S - \left(\frac{p_S}{T_S} - \frac{p_o}{T_o}\right) T_o V_S \quad (9)$$

where U_S and S_S are the internal energy and entropy of a radiant energy packet at temperature T_S with volume V_S . Equation (9) has been adapted for equilibrium black-body radiation with chemical potential equal to zero.

It is instructive to consider the different processes leading to the Carnot and Landsberg efficiencies in more detail. The Carnot engine receives heat from a high temperature source (the Sun, at temperature T_S) and rejects heat into the surroundings at temperature T_o . Unlike the Carnot cycle, however, the availability process is not cyclical, and the work done by and on the engine must include the work on or by the surroundings at pressure p_o .⁴⁰ We note that the input energy to the Carnot engine is *heat*

exchanged at temperature T_S (equal to $T_S\Delta S = T_S S_S$) but the initial energy for the conversion process described by availability (9) is the *internal energy* U_S at temperature T_S and volume V_S . Accordingly, the conversion efficiency is thus defined as W_{\max}/UT_S . In mathematical terms, the efficiencies of the two processes differ in the second term of the second equation (9). This term (which is always negative) will be the subject of discussion in several parts of this review; for brevity, it will be denoted by $-\Delta_p$ and referred to simply as the pressure correction.

The notion of solar energy conversion leading to available work was followed by Petela,⁴¹ Press,⁴² and Landsberg and Mallinson⁴³ who determined the maximum work that can be carried out by a volume of black-body radiation at temperature T_S if cooled to temperature T_o , leading to what is now usually called the Landsberg efficiency

$$\eta_L = \frac{W_{\max}}{U_S} = 1 - \frac{4T_o}{3T_S} + \frac{1}{3} \left(\frac{T_o}{T_S} \right)^4 \quad (10)$$

The use of Carnot and Landsberg efficiencies has been discussed in detail in Refs 44–46. All three efficiencies discussed above as functions of the ratio T_o/T_S are compared in Figure 8.

As presented in this review, Eq. (10) is considered as energy efficiency. In the literature, in contrast, the Landsberg efficiency is usually portrayed as power efficiency—either as a result of a derivation based on energy flows (see the section *Energy and Entropy Flows*) or simply by changing the work W_{\max} into power or energy flow. Notwithstanding, the emphasis placed in this review on the distinction between energy and power efficiency requires that a more rigorous argument is sought to justify the notion of Landsberg efficiency as power efficiency. Indeed, we shall show in the section *The Maximum Efficiency of Solar Energy Conversion* on fundamental grounds that this notion may require a reappraisal.

Energy and Entropy Flows

One can simply brush aside the difficult process to justify the difference between power and conversion efficiencies (which bears many similarities to the differences between the transition from classical to irreversible thermodynamics) and apply the laws of equilibrium thermodynamics directly to energy rates rather than to energy quantities themselves. This was the approach taken by Landsberg and Tonge⁴⁷ who used rate equations for a system not dissimilar to the Carnot heat engine, to describe the balance between

incident and emitted photon fluxes as well as the production of useful work (Figure 2(c)) by an incident energy (solar) flux \dot{U}_{in} :

$$\begin{aligned} \dot{U}_{in} &= \dot{U}_{out} + \dot{Q} + \dot{W} \\ \dot{S}_{in} &= \dot{S}_{out} + \dot{Q}/T_o - \dot{S}_i \end{aligned} \quad (11)$$

where \dot{U}_{out} and \dot{S}_{out} denote the energy and entropy fluxes of the emitted photons, \dot{Q} is the heat flux rejected into a low-temperature reservoir at temperature T_o , \dot{W} is the rate of work (electrical energy) done by the converter, and \dot{S}_i is the rate of irreversible entropy generation. Interestingly, the application of Eq. (11) to the conversion of black-body radiation at temperature T_S by a converter at T_o under reversible operation with $\dot{S}_i = 0$, leads again to the Landsberg efficiency (10). As already noted at the end of the previous section, however, the energy input is now the energy flux \dot{U} rather than the energy U of a volume V of black-body radiation.

Landsberg and Tonge⁴⁷ showed that the determination of an upper bound on the efficiencies or coefficients of performance reduces to the determination of the appropriate temperatures T_{out} and T_{exc} of the emitted and exciting radiation. This is a simple matter for monochromatic radiation where a suitable definition had already been provided previously by Landau.⁴⁸ For broadband radiation, the situation is more complex as it is impossible to correctly match the spectrum as well as the total radiance/energy flux by using a single temperature. We shall see in *Quantum Solar Energy Conversion* section that a satisfactory resolution of this issue had to await a later development: the introduction of a finite chemical potential of radiation.

The definition of a satisfactory effective temperature becomes particularly acute for solar radiation on the ground where the spectrum resembles the black-body spectrum but the total energy flux is, of course, much lower. This led Landsberg and Tonge to introduce the concept of diluted black-body radiation¹⁶ where the energy flux is reduced by a factor of

$$\varepsilon = \mathcal{E}_{in}/\mathcal{E}_{out} = C\omega_S/\pi \quad (12)$$

with respect to the full black-body flux, where \mathcal{E}_{in} and \mathcal{E}_{out} are the étendues of the incident and emitted beams and C is the concentration ratio. Landsberg and Tonge show that the formalism allows the determination of the appropriate entropy, and hence, gives an effective temperature of the diluted black-body radiation which can be used to obtain an upper

bound on the conversion efficiency with the use of (10).

The model of Landsberg and Tonge built on the previous work by Weinstein¹⁷ who used rate equations to study the conversion of work into optical emission excited by the injection of electrical current where the energy of the emitted photon can exceed the electrostatic energy of the applied bias,⁴⁹ in a model based on a heat engine (Figure 2(d)). Chukova¹⁸ later extended Weinstein's result to photoluminescence (Figure 2(e)). More recently, a similar line of work has been pursued in connection with laser cooling.⁵⁰

QUANTUM SOLAR ENERGY CONVERSION. KINETIC ASPECTS

The focus of our review so far has been what could be called the classical approach to the thermodynamics of solar energy conversion: the conversion of the incident energy flux in terms of equilibrium thermodynamics, with no attempt to describe the quantum nature of solar radiation as a stream of photons. The theoretical foundations of modern photovoltaics, accompanied by an improved understanding of photochemical energy conversion in photosynthesis, are underpinned by the quantum nature of solar energy conversion where photons play a primary role.

A brief glance at the output of a solar cell along the current voltage characteristic will illustrate the main features of the conversion process. The energy generated by a photon is directly related to the voltage at the solar cell terminals, or to energy content of the molecular product. Near the open circuit, the solar cell is an energy converter where each photon produces energy qV , under conditions similar to classical thermodynamics because the 'turnover rate' I/q (represented here by the extraction of charge carriers) is low. Near the short circuit, on the other hand, the solar cell resembles a kinetic device, converting photons into electrons in an electrical circuit, at a rate given by the turnover rate I/q . When extended to produce the complete current-voltage characteristic both viewpoints are, of course, equivalent. As we shall see in the next sections, each aspect provides a different aspect on the device operation and a different description of losses in conversion. We begin our discussion with a review of the more traditional approach, the kinetics, based on currents and photon flows. We will return to consider the energy aspects and thermodynamics in the section *Thermodynamics of Photovoltaic Conversion*.

The Shockley—Queisser Model of Detailed Balance

We have already noted that the origins of modern photovoltaics are anchored in semiconductor technology. A satisfactory understanding of the fundamental limits on solar cell operation, however, relies on an insight from a different branch of science. This came with a description of the solar cell solely in terms of the characteristics of the incident and emitted energy beams of light, in a breakthrough paper by William Shockley and Hans-Joachim Queisser⁵¹ in the early 1960's.

Based on what might now seem a simple strategy, Shockley and Queisser called their method 'detailed balance'. Indeed, certain similarities will be recognized with the balance between absorption and emission as summarized in Kirchhoff's law in the *Foundation Pillars* section. What Shockley and Queisser had in mind was to equate the incident (and completely absorbed) flux Φ_{in} of photons with energy above the bandgap E_g at temperature T_s to the flux Φ_{out} in the same energy range at temperature T_o emitted by the cell, allowing for a fraction of photons which are used for conversion to electrical current I :

$$\Phi_{in} = \Phi_{out} + I/q \quad (13)$$

A model for the incident flux was at hand in the form of black-body radiation emitted by the Sun (see the *Foundation Pillars* section) but no universally accepted view was available to describe the photon flux emitted by a semiconductor under electrical excitation. Shockley and Queisser made an approximation which turned out to be surprisingly accurate: to multiply the equilibrium photon flux at the ambient temperature by a factor equal to the rate of increase of radiative recombination at a semiconductor junction under applied voltage V :

$$\begin{aligned} \Phi_{in} &= C \frac{\omega_S}{\pi} \Phi_o(T_s) \\ \Phi_{out} &= e^{qV/k_B T_o} \Phi_o(T_o) \end{aligned} \quad (14)$$

where ω_S is the solid angle subtended by the Sun, C is the concentration ratio ($C = 1$ for one sun illumination and $C = \pi/\omega_S$ for maximum concentration), and the photon fluxes refer to the range of photon energies $h\nu > E_g$, where E_g is the bandgap of the semiconductor. Combining Eqs. (13) and (14) gives the current voltage characteristic of an ideal solar cell:

$$I = I_l - I_o \left(e^{qV/k_B T_o} - 1 \right) \quad (15)$$

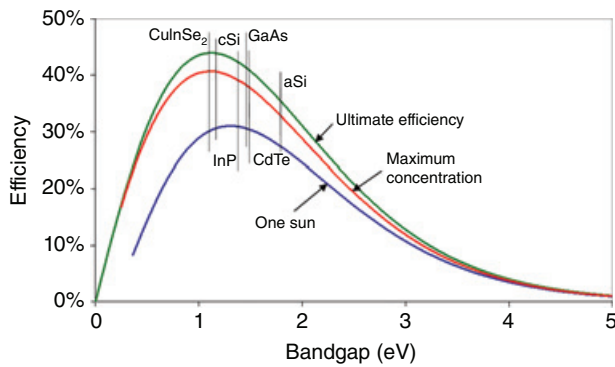


FIGURE 4 | The Shockley–Queisser ideal efficiency of a single-junction solar cell as a function of the semiconductor bandgap, together with the bandgaps of a number semiconductor with photovoltaic applications. The incident and emitted light beams have the black-body spectrum at temperatures 6000 and 300 K, respectively.

where I_l and I_o are the photogenerated and dark saturation currents,

$$\begin{aligned} I_o &= q\Phi_o(T_o) \\ I_l + I_o &= qC\frac{\omega_S}{\pi}\Phi_o(T_S) \end{aligned} \quad (16)$$

Figure 4 shows the ideal efficiencies as functions of the bandgap E_g under one-sun illumination, under maximum concentration of sunlight, and what Shockley and Queisser called the ‘ultimate efficiency’—a result obtained earlier by Trivich and Flinn⁵² and Müser⁵³ who approximated the open-circuit voltage by the voltage E_g/q corresponding to the bandgap of the semiconductor.

A key element of the Shockley–Queisser result was to show that efficiency limit for solar cell operation is described completely by the characteristics of the incident and emitted light beams. Equations (14) and (15) describe the well-known current voltage characteristic of an ideal solar cell which has enjoyed much success since the early days of photovoltaics. From a more fundamental point of view, however, a correction is required to put the emitted photon flux on a more rigorous footing. This correction became apparent from the photoluminescence studies which indicated that the photon fluxes emitted as fluorescence or phosphorescence are described well by the Bose–Einstein distribution with a non-zero chemical potential.^{54,55} The emitted photon flux Φ_{out} then takes the form of a ‘generalized Planck’s law,’ where the occupation probability (3) is replaced by a value

which follows from the full Bose–Einstein statistics⁵⁶

$$\rho_\nu(T, \mu) = \frac{1}{e^{(h\nu - \mu)/k_B T} - 1} \quad (17)$$

The chemical potential μ in (17) is set equal to the electrostatic energy qV corresponding to the voltage produced by the solar cell. Numerically, the difference between the original and ‘corrected’ I–V characteristics has little significance except under a very high concentration of incident sunlight. The basic structure, however, completes the foundation of photovoltaics, and could be later built on to describe solar cell operation in terms of an ‘engine’ operating between two equilibrium reservoirs of the photon gas.

Although the open-circuit voltage cannot be calculated analytically, a useful approximation exists for weak to moderate illumination intensities:⁵⁷

$$qV_{oc} = \left(1 - \frac{T_o}{T_S}\right)E_g + k_B T_o \ln\left(\frac{T_S}{T_o}\right) - k_B T_o \ln\left(\frac{\mathcal{E}_{out}}{\mathcal{E}_{in}}\right) \quad (18)$$

Additional corrections can be applied to improve the accuracy of this formula to bring it to a useful form for practical applications.⁸ Equation (18) will form the starting point for the discussion of solar cell voltage in thermodynamic terms in the section *Thermodynamics of Photovoltaic Conversion*, where we will identify the origin of each term in this equation.

Photochemical Energy Conversion in Photosynthesis

An early application of thermodynamics to quantum solar energy conversion was to describe one of the most ancient energy conversion processes on Earth: photosynthesis. Photosynthesis usually evokes the picture of a complex set of chemical reactions where sunlight converts water and carbon dioxide into carbohydrates and oxygen. The energy producing part of the photosynthetic reaction, however, bears a remarkable similarity to solid state photovoltaics. The key feature that underlines this similarity is that the primary reaction consists of a sequence of oxidation–reduction reactions: in other words, electron transfer. Energy is collected in a light-harvesting unit and transferred to the photochemical reaction center (trap) by exciton transport (Figure 5). The complex of energy conversion reactions (sometimes called storage) then follows, initiated by charge

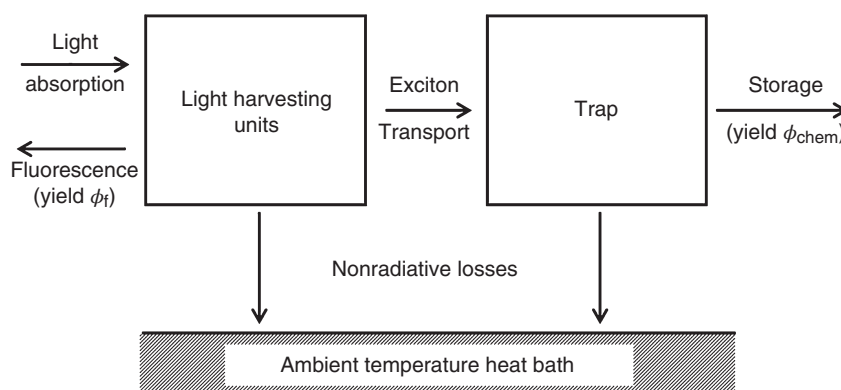


FIGURE 5 | A schematic diagram of the primary photosynthetic energy conversion process (after Refs 58 and 59).

separation across the photosynthetic membrane. Research into the primary steps in photosynthesis has contributed much to the understanding of thermodynamic concepts by linking energy production with luminescence.

A discussion of the photosynthetic primary energy conversion in thermodynamic terms was initiated by Duysens⁶⁰ who proposed, on an intuitive basis, that the efficiency of the conversion process could be described by the Carnot efficiency (6). Similarly to the discussion in the section *Light, Heat, And Work*, the dilution of solar radiation was allowed by using an effective temperature T_{eff} instead of the true black-body temperature of solar radiation T_s . This effective temperature was determined by equating the observed photoexcitation rate to the rate of photon absorption from a black-body radiation at temperature T_{eff} . A more detailed description on molecular basis was provided by Ross and Calvin⁶¹ (see also Ross,^{62,63} Bolton,⁶⁴ and Lavergne and Joliot⁶⁵) who introduced the chemical potential of the reaction products, linked to the concentration P^* of the excited state of the primary electron donor P :

$$\Delta\mu = k_B T_o \ln \left(\frac{P^*}{P_o} \right) \quad (19)$$

where P_o^* is the concentration of P^* in thermal equilibrium in the dark at ambient temperature T_o .

The field was reviewed, in a particularly clear form, by Knox^{58,59} who showed that

$$\Delta\mu = \left(1 - \frac{T_o}{T_{eff}} \right) \Delta E + k_B T_o \ln(\varphi_f) + k_B T_o \ln(\varphi_{chem}) \quad (20)$$

Equation (20) generalizes Duysen's result which is represented by the first term on the right-hand side.

Since $T_{eff} \leq T_s$, this term expresses both the second law of thermodynamics and the reduction in efficiency due to 'dilution' of solar radiation on Earth. The second term represents a correction for nonradiative transitions when the fluorescence yield φ_f is less than unity. The last term which includes the probability of chemical reaction (the 'chemical yield' φ_{chem}) links the energy production per electron (as expressed by $\Delta\mu$) to the 'power' production discussed already in the *Light, Heat, and Work* section, and indicates that if energy is to be produced at a finite rate, $\Delta\mu$ must decrease from its maximum value at 'open circuit' (or 'static head'⁶⁶) where the overall rate of chemical reaction is zero.

THERMODYNAMICS OF PHOTOVOLTAIC CONVERSION. SOLAR CELL AS A HEAT ENGINE.

An alternative view to the detailed balance method discussed in *The Shockley–Queisser Model* can be obtained by combining the energy aspects of the conversion process with the quantum nature of sunlight and of the energy produced. The key parameter is then the useful work per photon—in thermodynamics terms, the free energy, or chemical potential:

$$\mu = u - Ts \quad (21)$$

where u and s are the energy and entropy per photon.^{67,j} The thermodynamic approach with focus on energy parameters bears the promise of shedding a new light on the fundamental losses in the conversion process, and providing a theoretical basis for novel devices and structures aiming to exceed the Shockley–Queisser limit^{68–72} or constructing a thermodynamic cycle for a solar cell.^{45,73}

Since a solar cell emits light as well as produces power in the external circuit, the analysis may be simplified by considering the solar cell simply as a light emitting device (Figure 2(f)).^k Since, under optimum operation, the emitted photons are in equilibrium with the electron-hole system which performs work, the energy produced by the solar cell can be determined by equating the work to the chemical potential of the emitted beam.¹⁹ We can then follow a similar philosophy as in *Light, Heat, and Work* section to write down the required energy–entropy balance, but this time *per incident photon*:

$$\begin{aligned} u_{in} &= u_{out} + Q \\ s_{in} &= s_{out} + Q/T_o - \sigma_i \end{aligned} \quad (22)$$

where the subscripts in and out refer to incident and emitted beams with étendues \mathcal{E}_{in} and \mathcal{E}_{out} at temperature T_s and T_o , respectively, Q is the heat rejected into a low-temperature reservoir at temperature T_o and σ_i is the irreversible entropy generated in the conversion process. A simple transformation of Eq (22) now yields:

$$qV = \mu_{out} = \left(1 - \frac{T_o}{T_s}\right) u_{in} - T_o \sigma_i \quad (23)$$

giving the energy efficiency of conversion in the form (see Table 1)

$$\eta_e = qV/u_{in} = \eta_C - T_o \sigma_i / u_{in} \quad (24)$$

Equations (23) and (24) express the work produced by a quantum of solar radiation in terms which are familiar from classical thermodynamics. Sometimes referred to as the Guy–Stodola theorem,^{74,75} the work that can be carried out by a thermal source is equal to the input energy (in this instance, radiation originating from a black-body source with $\mu_{in} = 0$) converted with the Carnot efficiency, less losses due to irreversible entropy

generation σ_i . Since the entropy-generation term σ_i depends on the current produced by the solar cell, Eq. (24) demonstrate a close link between the energy efficiency of a solar cell and its current–voltage characteristic, expressed in the form of voltage as a function of current.

To be of practical use, Eq. (23) has to be supplemented by a formula for the entropy balance

$$T_o \sigma_i = \Delta u - T_o \Delta s \quad (25)$$

where the Δ denotes a difference between quantities pertaining to the incident and emitted beam. Equation (25) provides a recipe for how the irreversible losses can be determined using, for example, standard results from the statistical mechanics of radiation.^{13,22} In keeping with an earlier remark concerning Eq. (21), we note that the expression on the right-hand side of (25) resembles the availability/exergy of one photon, without the pressure correction—in other words, describing a process at constant volume. We shall return to this point in the section *The Maximum Efficiency of Solar Energy Conversion*.

The use of Eqs. (23) and (25) will now be illustrated on the examples of two specific conversion devices: a monochromatic, or two-level, converter and a single-junction solar cell, providing a parallel to the Shockley–Queisser treatment in the section *Quantum Solar Energy Conversion*.

Monochromatic Photon Gas

The analysis of a two-level converter which converts photons in a monochromatic beam (more precisely, quasi-monochromatic radiation with frequencies $\nu \rightarrow \nu + \delta\nu$) into useful work or electricity has been of interest as a prototype model for a solar cell since the early days of photovoltaics. It provides a clear link to thermodynamics and the Carnot efficiency, by effectively generalizing the Einstein's balance between absorption and emission by introducing photon

TABLE 1 | Different Photovoltaic Efficiencies, Which Are Used in This Review

Efficiency	Definition	Remarks
η_e	$\eta_e = qV/u_{in}$	Energy (voltage) efficiency
η_P	$\eta_P = \frac{1}{\Phi_m} \eta_e = i\eta_e$	Power efficiency, within the spectral range of the converter
η	$\eta = scf \eta_P = scf i\eta_e$	Usual solar cell conversion efficiency

u_{in} is the average incident photon energy and Φ_m is the incident photon flux, both within the absorption range of the converter / solar cell. The spectral coverage factor is given by $scf = \dot{U}_0^{(h\nu > E_g)} / \dot{U}_0$, where the energy fluxes in the numerator and denominator refer to the spectral range absorbed by the semiconductor and the full spectrum, respectively.

fluxes at different temperatures^{76,77} (see also Ref 78). The key relation which underpins the thermodynamic analysis is the expression for the monochromatic photon entropy:¹³

$$s_\nu = k_B \ln \left(1 + \mathcal{E} \frac{G_\nu}{\Phi_\nu} \right) \quad (26)$$

where $G_\nu = 2\nu^2 \delta\nu / c^2$ and Φ_ν is the photon flux in a small frequency range $\delta\nu$ at frequency ν . We note that entropy per photon increases with increasing étendue \mathcal{E} and decreases with increasing photon flux.

For monochromatic radiation $u_{in} = u_{out} = h\nu$. The conversion process therefore proceeds with no photon energy losses between absorption and emission, the first term on the right-hand side of (25) vanishes and the irreversible entropy generation σ_i is determined solely by the entropy balance between the incident and emitted photons of monochromatic light at frequency ν .

We shall consider first the conversion process under maximum concentration of sunlight. The Landsberg–Tonge dilution factor ϵ (12) is then equal to unity and the open-circuit voltage corresponds to the photon energy converted with the Carnot efficiency:

$$qV_{oc} = \left(1 - \frac{T_o}{T_s} \right) h\nu \quad (27)$$

Comparison with (23) shows that entropy generation σ_i vanishes at open circuit indicating a reversible energy transformation as implied, of course, by the thermodynamic nature of the Carnot engine.

As finite current is extracted from the converter, the irreversible entropy generation σ_i becomes non-zero—in fact, as a consequence of the second law of

thermodynamics, σ_i can only be positive. This also follows from the application of the detailed balance (13) to the monochromatic converter. Use of the generalized Planck law (15) then shows that, for $I > 0$, the chemical potential μ must be smaller than at open circuit. Since the energy $h\nu$ is constant, (21) implies an increase of entropy on account of irreversible nature of the conversion process. The voltage produced by the two-level converter $qV = qV_{oc} - T_o\sigma_i$ must therefore decrease from the open-circuit value as current is extracted from the converter. We can draw a parallel between entropy generation resulting from non-zero current (to be denoted by σ_{kin}) and the losses in photothermal and endoreversible engines due to a finite rate of turnover of the heat engine. For the two-level converter, the entropy generation can be written down in a closed form by using Eq. (26)

$$\sigma_i = s_{out} - s_{in} = k_B \ln \left(\frac{1 - ie^{-x_s}}{1 - i} \right) \quad (28)$$

where $i = I/(q\Phi_{in})$, with Φ_{in} the incident black-body photon flux in the frequency range $\delta\nu$, denotes the normalized current produced by the converter, and $x_s = h\nu/k_B T_s$.

The energy efficiency η_e is a useful characteristic of a heat engine but, as in the analysis of thermodynamic engines in the section *Light, Heat, and Work*, the key parameter of solar cells is the power efficiency η_P (see Table 1) which takes into account the kinetic nature of the conversion process. As defined here, the power efficiency η_P refers only to the monochromatic radiation which is absorbed by the solar cell. In comparison with the energy efficiency η_e , the power efficiency η_P contains an additional loss $(1 - i)\eta_e$ due to the (free) energy carried away by

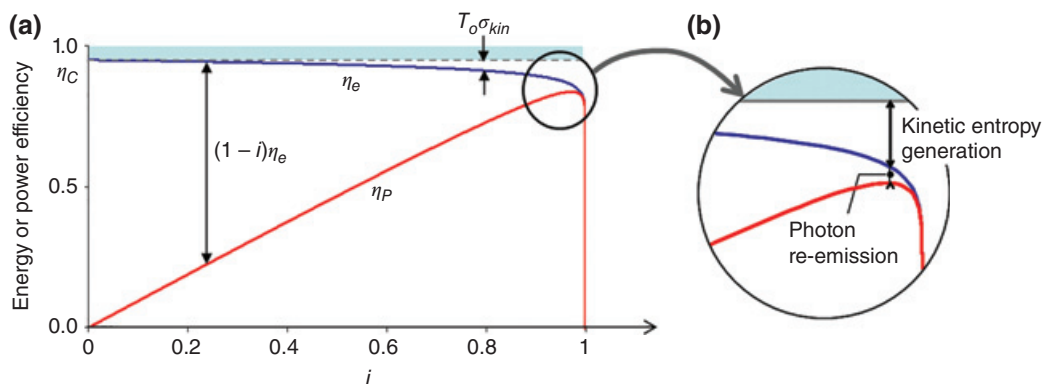


FIGURE 6 | The I-V characteristic of a two-level converter as energy efficiency. (a) The energy efficiency (blue line) showing the Carnot energy not available for conversion (shaded by blue) and the loss on account of irreversible entropy generation on account of current extraction. The power efficiency (red line) includes additionally the power loss by photon emission $(1 - i)\eta_e$. The inset in (b) shows losses at the maximum power point.

photons emitted by the solar cell. It highlights the fact that, while the principal loss channel for power at short circuit is the irreversible entropy generation σ_i contained in η_e , losses near the open circuit are dominated by photon emission (Figure 6).

The interplay between the thermodynamic and kinetic losses is usually summarized by the fill factor: ratio of the maximum power divided by the product of open-circuit voltage and short-circuit current. The fill factor provides a ‘conversion factor’ between the power efficiency and the energy efficiency at short circuit, including losses by both kinetic entropy generation and photon re-emission:¹

$$\eta_P = ff \eta_e(oc) \quad (29)$$

For the ideal monochromatic converter under maximum concentration $\eta_e(oc)$ is equal to the Carnot efficiency. We note that (29) can be written in a form familiar from standard solar cell theory:

$$P_v = ff I_{sc} V_{oc} \quad (30)$$

where P_v is the power produced by the monochromatic converter at the maximum power point.

We are now in position to analyze the conversion process under one-sun illumination. The Landsberg–Tonge dilution factor then becomes $\varepsilon = \pi/\omega_S < 1$. The concomitant étendue expansion results in entropy generation (to be denoted by σ_{exp}), in a process analogous to the expansion of gas into vacuum, resulting in an additional further voltage loss $T_o \sigma_{exp}/q$. This has a further consequence that a monochromatic converter can only meaningfully convert a part of the solar spectrum under one-sun illumination as low energy photons cannot produce a positive chemical potential, or voltage. At frequencies above this threshold, the entropy generation can be written as

$$\sigma_i = \sigma_{exp} + \sigma_{kin} \quad (31)$$

where σ_{kin} is the entropy (28) and

$$\sigma_{exp} = k_B \ln \left\{ e^{-x_S} - \frac{\pi}{\omega_S} (1 - e^{-x_S}) \right\} \cong k_B \ln \left(\frac{\pi}{\omega_S} \right) \quad (32)$$

where the approximate expression holds at sufficiently high-photon frequencies.

The Single-junction Solar Cell

No discussion of the thermodynamics of photovoltaic conversion would be complete without at least a brief

look at the ideal single-junction solar cell. As already indicated, this analysis parallels the Shockley–Queisser treatment but focuses on voltage rather than current as the principal variable. In the present terminology, we consider a converter that absorbs all radiation with photon energy above a certain threshold defined by the semiconductor bandgap E_g , and converts an incident beam with photon flux Φ_{in} , étendue \mathcal{E}_{in} at temperature T_S , into a beam with parameters Φ_{out} , \mathcal{E}_{out} , and T_o , while producing useful work $w = \mu_{out} = qV$ per photon.

The voltage of such a converter can again be obtained from Eq. (23). In comparison with the monochromatic converter, the conversion of broadband solar radiation results in an additional loss through entropy generation and heat rejection into the low-temperature reservoir. The new entropy-generation term σ_{cool} describes ‘photon cooling’ due to the thermalization of photogenerated electron-hole pairs (and thus also of the emitted photons with which they are in equilibrium) by the interaction with lattice vibrations. σ_{cool} can be determined from Eq. (25), allowing for the fact that photons emitted at the ambient temperature T_o now have a lower energy than the incident photons at temperature T_S . The analysis is particularly simple in the limit of weak to moderate illumination^m when the photon statistics resembles an ideal two-dimensional gas:

$$\sigma_{cool} \cong k_B \left\{ \left(\frac{T_S}{T_o} - 1 \right) - \ln \left(\frac{T_S}{T_o} \right) \right\} \quad (33)$$

Although present in all current-generation solar cells, the thermalization loss expressed by σ_{cool} is not, in principle, unavoidable. A hypothetical device where this loss is avoided—a hot-carrier solar cell—is discussed further in the section *The Model of Ross and Nozik*.

Combining all three irreversible losses gives the total entropy generation $\sigma_i = \sigma_{exp} + \sigma_{kin} + \sigma_{cool}$ and evaluating the resulting expression for voltage (23) confirms the result (18), obtained by the Shockley–Queisser detailed balance. The present treatment, however, distinguishes the different contributions to the fundamental losses, as shown by the different processes that make up the energy efficiency (24) in Figure 7(a).

We can now approach the key attribute of solar cell operation: power conversion. The power efficiency η_P (29) was defined for monochromatic radiation. In a similar fashion, we can consider the power efficiency for a broadband converter for radiation which is actually absorbed by an ideal solar cell—in

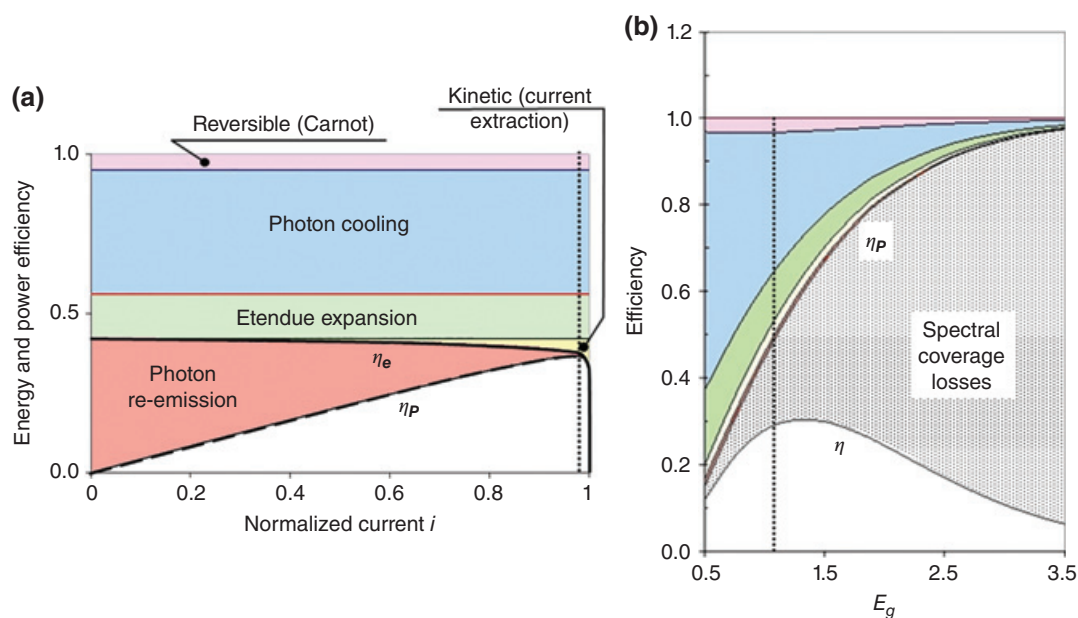


FIGURE 7 | The fundamental losses in an ideal single-junction solar cell. (a) The energy (η_e) and power (η_p) efficiencies (heavy full and dashed lines, respectively) plotted against the normalized current $i = I/(q\Phi_{in})$. The dotted vertical dashed line shows the maximum power point. The graph corresponds to the room temperature bandgap 1.12 eV of crystalline silicon. (b) The solar cell conversion efficiency under one-sun illumination and losses at the maximum power point, plotted against the bandgap E_g of the solar cell material. The colors indicating thermodynamic losses correspond to those in part (a). Spectral coverage losses are equal to $1 - scf$. The dotted line shows the bandgap used in the graph of energy and power efficiencies in part (a).

other words, by considering only the spectral region with photon energy in excess of the semiconductor bandgap E_g . Similarly to the two-level converter, η_p is obtained from the energy (or voltage) efficiency by including an additional loss due to photon re-emission, giving rise to the fill factor as discussed in the section *The Single-Junction Solar Cell* (see Figure 7(a)).

The power efficiency η_p is not the usual conversion efficiency used in the textbooks on photovoltaics. This efficiency—which we shall simply denote by η —includes, as a loss, photons with energies below the bandgap E_g which cannot be absorbed by the cell. From the thermodynamic viewpoint, this loss is clearly of a different nature than losses considered so far and should be considered on a different footing. We shall include this loss in terms of a spectral coverage factor scf which describes the fraction of below-bandgap light in the black-body spectrum (see Table 1).

The expression for solar cell efficiency as a product of the spectral coverage factor, the normalized rate of energy extraction i , and the energy efficiency summarizes the thermodynamic view of fundamental losses in solar cells. The solar cell efficiency η as a function of the bandgap E_g is plotted in Figure 7(b) which extends, corrects and refines a

similar plot of Ref 79 to include a full classification of losses in thermodynamic terms.

FUTURE DIRECTIONS: BEYOND THE SHOCKLEY–QUEISSER LIMIT.

Thermodynamics is particularly useful in mapping out the potential of new conversion devices and schemes. It has also proved to be a valuable tool in identifying ideas which violate the fundamental physics—usually the second law of thermodynamics (see, e.g., the suggestion⁷⁰ and the arguments^{71,72,80} which demonstrated the internal inconsistency of the proposed device).

The number of ideas and proposed structures that employ a reasoning based at least in part on thermodynamics is now too large to cover in a review of this size. We shall focus here on two well-known areas of photovoltaics research where thermodynamics plays an indispensable role.

The Maximum Efficiency of Solar Energy Conversion

Arguably, the quest to determine the maximum attainable efficiency for any solar energy converter has provided one of the grand challenges to

theoreticians since the early days of research in this field. Two limits that have been prominent in this discussion include the Landsberg efficiency and the efficiency of the so-called infinite tandem,^{81,82} identical to a combination of an infinite set of monochromatic converters discussed in the section *Monochromatic Photon Gas* and to be discussed below, which would cover the full solar spectrum. Below, we review a recent unified framework⁸⁵ which elucidates the link between these two limits and proposes a new limit that combines the two.

To this end, we note that the argument used to obtain the Landsberg efficiency was based on the maximum work determined in terms of availability. An identical result can be obtained from the maximum work (w_ν , say) *per photon* at a frequency ν , and the results weighted by the number of photons and integrated over the full spectrum:

$$W_{\max} = \int_0^\infty w_\nu n_\nu(T_S) d\nu = \eta_L U(T_S) \quad (34)$$

where $w_\nu = h\nu(1 - T_o/T_S) - \delta_p$, and δ_p is the pressure correction per photon. When integrated, (34) gives

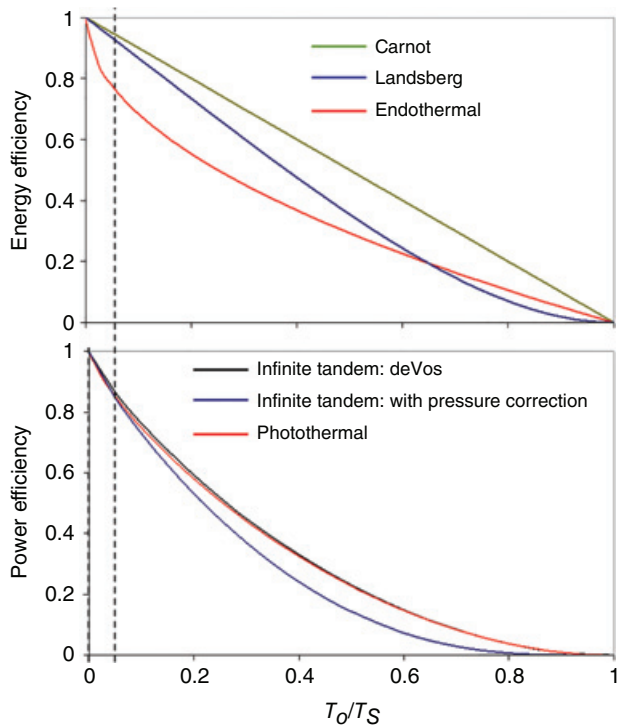


FIGURE 8 | The various energy (a) and power (b) efficiencies considered in this paper as functions of the ratio of the temperatures of the cold and hot reservoirs. The dashed line corresponds to the temperatures $T_S = 6000$ K and $T_o = 300$ K.

the total pressure correction Δ_p in (9)—in other words, w_ν/q and the open-circuit voltage (27) for the monochromatic converter are linked in an analogous manner as the Landsberg and Carnot efficiencies (10) and (6) for the full spectrum of solar radiation.

To complete the parallel with a solar cell, we use the Planck relation (4) between photon density and hemispherical flux which corresponds to the photogenerated current $(qc/4)n_\nu \rightarrow J_\nu^l$. Finally, we set $(c/4)W_{\max} \rightarrow P_L$, where P_L is the power produced by a converter obtained by combining all the spectral contributions to obtain

$$P_L = \int_0^\infty V_\nu^{oc} J_\nu^l d\nu = \eta_L \dot{U}(T_S) \quad (35)$$

A comparison of Eq. (35) and the result based on standard solar cell theory (30) now reveals the difference between work obtained the energy and power efficiencies obtained using the availability argument: the power P_L (35) obtained using the availability argument does not contain the fill factor—in other words, it does not include losses described by the kinetic entropy generation σ_{kin} . We have argued in this review that this loss is unavoidable by virtue of the second law of thermodynamics: as the entropy is a decreasing function of the number of photons in the beam and the number of emitted photons is less than the number of incident and absorbed photons, the extraction of current from each elemental solar must necessarily leads to entropy generation (see also *Monochromatic Photon Gas* section). This argument shows that the suggestion in Ref 31 that σ_{kin} can be made to vanish with the use of nonreciprocal structures would violate the second law of thermodynamics.

We can now progress to obtain the maximum conversion efficiency allowed by thermodynamics. The elementary work w_ν , and hence V_ν^{oc} , can be determined without difficulty by methods of statistical mechanics, giving also σ_{kin} and the fill factor.⁸⁵ Inserting the fill factor into (35), we obtain the maximum efficiency η_{\max} attainable by any solar energy converter, which makes allowance for pressure correction as expressed in the Landsberg efficiency:

$$P_{\max} = \int_0^\infty V_\nu^{oc} J_\nu^l ff_\nu d\nu = \eta_{\max} \dot{U}(T_S) \quad (36)$$

The efficiency η_{\max} as a function of the ratio T_o/T_S is shown in Figure 8; for $T_S = 6000$ K, $\eta_{\max} = 85.0\%$.⁸

A previous widely used result for the maximum overall efficiency was obtained by deVos^{81,82} by a detailed balance argument for the efficiency of an infinite stack of tandem solar cells which, for $T_S = 6000$ K, comes out as 86.8%. A thermodynamic argument⁸⁷ later showed that that the resulting efficiency is equivalent to the method of *Monochromatic Photon Gas*—in other words, setting the open circuit voltage of each elemental converter equal to the energy $h\nu$ converted with the Carnot efficiency $(1 - T_o/T_S)$ but neglecting the pressure correction of the Landsberg efficiency. The deVos efficiency is plotted as a function of the ratio T_o/T_S in Figure 8. Interestingly, this graph is very close to the graph of the photothermal efficiency, as noted already in Ref 31 (see also Ref 88). The relationship between different efficiencies that have been suggested as representing the maximum achievable efficiency of solar energy conversion discussed in this review are shown in Figure 9.

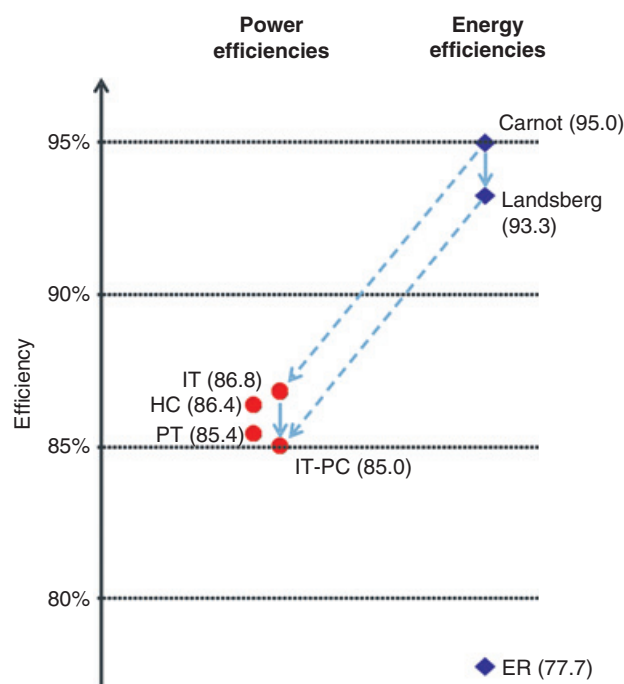


FIGURE 9 | The efficiencies discussed under the maximum concentration of sunlight in this paper for $T_S = 6000$ K and $T_o = 300$ K. PT, Photothermal; ER, Endoreversible (both discussed in the *Light Heat and Work* section); IT, Infinite tandem; IT-PC, Infinite tandem with pressure correction; HC, Hot-carrier (the last three discussed in the *Future Directions* section). The four efficiencies in the Carnot—Landsberg scheme are linked by dashed gray arrows to indicate the insertion of the fill factor/kinetic entropy generation and by full arrows to show the pressure correction.

Hot-Carrier Solar Cell. The Model of Ross and Nozik

In an attempt to increase the solar cell efficiency above the Shockley–Queisser limit, Ross and Nozik⁸⁹ proposed a model which aims to eliminate the thermalization loss due to entropy generation (33) on photon cooling. In such a hot-carrier solar cell, photogenerated electron-hole pairs created by light come to a mutual thermal equilibrium by electron–electron interaction alone, without interaction with lattice vibrations, and do not therefore incur the associated energy loss. In their model, the interaction of carriers in the absorber/hot reservoir with carriers at contacts at ambient temperature occurs via ‘selective energy contacts’: only and holes in a very narrow energy range are extracted in the charge separation process (Figure 10). The optimum energy ΔE_{use} which was transferred between the two reservoirs was to be determined by an optimization of the overall conversion process. Ross and Nozik assumed that this limited interaction between the two reservoirs does not disrupt the thermal equilibrium, and that work in the form of electrochemical potential is thus carried reversibly, without any entropy generation.

On further analysis, Würfel et al.⁸⁶ concluded that the Ross and Nozik model contained serious inconsistencies. The extraction of electron-hole pairs at a single energy other than the average energy would make it impossible for the system to achieve steady-state operation upon illumination. A further objection can be raised with respect to the elective energy contacts which remove carriers within a very narrow energy range from the hot reservoir and inject a monoenergetic jet of hot carriers into the ambient temperature reservoir. It is far from obvious, on the grounds of equilibrium thermodynamics, how this mechanism provides a thermodynamically reversible pathway for the exchange of electron-hole pairs between two reservoirs at different temperatures while carrying out the maximum amount of work.

Notwithstanding, a consistent model of hot-carrier converter can be reconstructed based on elements of the Ross and Nozik scheme, in search of the maximum efficiency which can be attained by eliminating the entropy generation by photon cooling. To this end, we assume, in keeping with Ross and Nozik, that electron-hole pairs reach an equilibrium without energy loss to phonons. The hot carriers are then cooled to ambient temperature and perform work in a Carnot engine, details of which we leave unspecified.

The model to be consider here, summarized in Figure 11, considers incident photons in a beam with

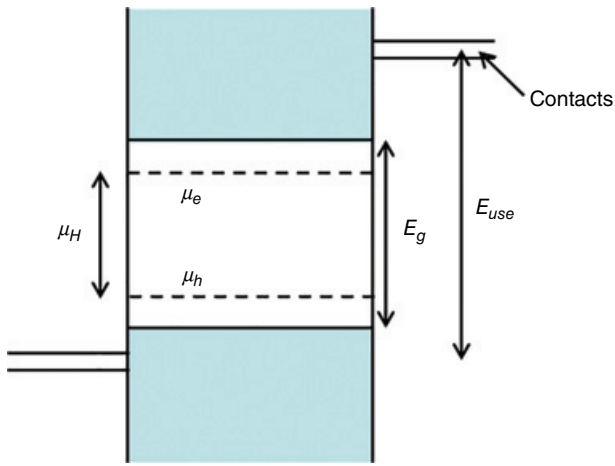


FIGURE 10 | A schematic representations of the band structure and relevant energies in a hot-carrier solar cell. In an optimum structure, the bandgap E_g would be close to zero.

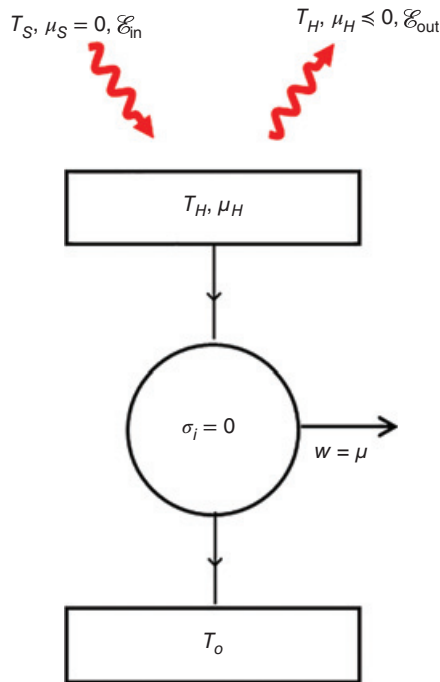


FIGURE 11 | A schematic representation of the modified Ross and Nozik model. Photons absorbed in a hot absorber acquire temperature T_H and chemical potential μ_H . Some photons are emitted and some are converted to electricity in a Carnot engine, with maximum efficiency. Entropy is generated only in the absorption/emission process.

étendue \mathcal{E}_{in} that are absorbed in an absorber. Photons which are not converted into electrical current are emitted, in a beam with étendue \mathcal{E}_{out} , in such a way that the energy per photon is conserved. The entropy of photons in the emitted beam will be higher than in the incident beam since $\mathcal{E}_{out} \geq \mathcal{E}_{in}$. The chemical

potential of photons in the emitted beam (denoted by μ_H) will therefore be lower than in the incident beam of black-body radiation, and must be therefore negative. In general, the étendue expansion will also result in a lower absorber temperature (to be denoted by T_H) since the full-spectrum black-body radiation is not an ideal gas, unlike the moderate-intensity radiation with an energy threshold considered in *Quantum Solar Energy Conversion* section. The emitted photons are in equilibrium with the hot electron-hole pairs, at temperature T_H and chemical potential μ_H which are now cooled to the ambient temperature whilst carrying out reversible work (Figure 11)

The model can be readily analyzed for an ideal hot-carrier converter operating under one-sun illumination.⁹⁰ The analysis is similar to the single-junction solar cell although differences arise in detail as an optimum hot-carrier solar cell absorbs the full solar spectrum which implies that, unlike in conventional solar cells, the ideal bandgap is close to zero. The first steps in the conversion process—photon absorption and subsequent equilibration of the hot-carrier reservoir at temperature T_H and chemical potential μ_H are conveniently considered together. Under one-sun operation, the étendue expansion results in a chemical potential which is negative and large in magnitude. The analysis can be carried out analytically with the results, at open circuit,

$$T_H = \frac{\pi^4}{90\zeta(3)} T_S = 5402 \text{ K}$$

$$\mu_H = k_B T_H \ln \left\{ \zeta(3) \frac{\omega_S}{\pi} \left(\frac{T_S}{T_H} \right)^3 \right\} = -4.76 \text{ eV} \quad (37)$$

where $\zeta(3) = 1.202$ is the Riemann zeta function. A similar model was considered by Parrott⁹¹ as a representation of solar radiation by black-body spectrum. When finite current is extracted from the cell and fewer photons are emitted by the cell, the temperature T_H remains constant along the current-voltage characteristic but chemical potential μ_H decreases (Figure 12(a) and (b)).

The work carried out by the hot electron-hole pairs is now set equal to the chemical potential at $T = T_o$, and can be found from the energy/entropy balance equations (22) by setting $u_{in} \rightarrow u_H$, $s_{in} \rightarrow s_H = (u_H - \mu_H)/T_H$ and $\mu_{out} \rightarrow u_{out} - T_o s_{out}$, giving

$$\mu = u_H - T_o s_H = \left(1 - \frac{T_o}{T_H} \right) u_H + \frac{T_o}{T_H} \mu_H \quad (38)$$

analogous to the Ross and Nozik result with the replacement $\Delta E_{use} \rightarrow u_H = u_S$. The final output from

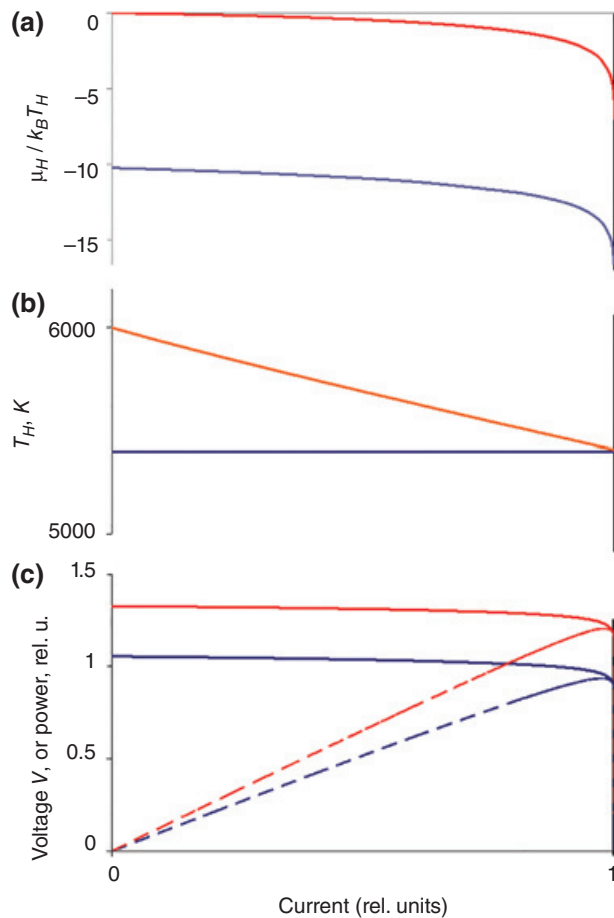


FIGURE 12 | The thermodynamic parameters of the hot-carrier solar cell. Red lines correspond to maximum concentration; blue lines to one-sun illumination. (a) The ratio $\mu_H / k_B T_H$ of the chemical to thermal energy for the absorber. (b) The temperature T_H of the hot absorber. (c) The current–voltage and power characteristics (full and dashed lines, respectively).

the hot-carrier solar cell can be described by a conventional current–voltage characteristic of an ideal single-junction solar cell with $V_{oc} = 1.055$ V, $J_e = 1147$ A/m² and a fill factor of 0.887 (Figure 12 (c)). The resulting conversion efficiency of 67.0% can be compared with the Ross and Nozik result 65.7% (obtained, however, under a different spectrum) and the efficiency 68.2% for an infinite tandem under one-sun illumination.

The operation of a hot-carrier solar cell under maximum concentration is similar in principle. At open circuit, the temperature of emitted photons and excited electron-hole pairs is equal to the temperature of the solar radiation $T_S = 6000$ K, and the chemical potential is zero. The open-circuit voltage corresponds to the average photon energy u_S in the full solar spectrum equal to 1.397 eV, converted with the Carnot efficiency: $qV_{oc} = u_S^*(1 - T_o/T_S) = 1.327$ eV. As finite current is extracted from the cell, the temperature T_H , and chemical potential μ_H both decrease (Figure 12(a) and (b)). At short circuit, the photogenerated current corresponds to the full photon flux of 52.6×10^6 A/m².

LIGHT TRAPPING

Not all energy aspects of radiation with relevance to photovoltaics involve temperature or heat, or are directly concerned with energy conversion. One such area is the capture of solar radiation and the phenomenon of light trapping.

The fundamental nature of this concept can be understood by considering the balance of energy and photon flow near the interface between two media with different refractive indices (Figure 13(a) and (b)). As the photon density per unit volume in a

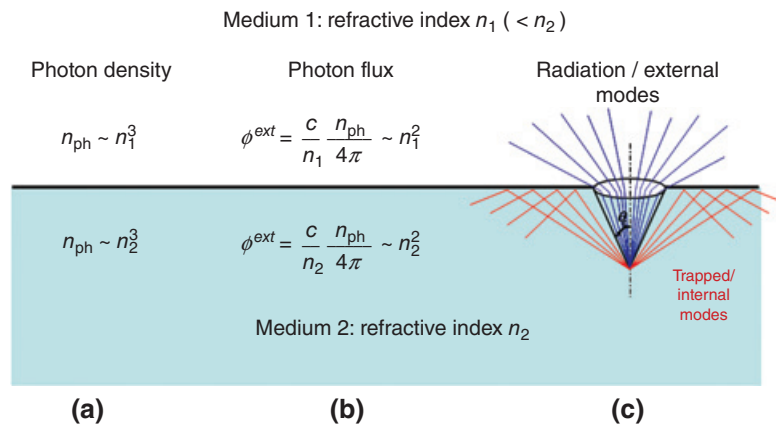


FIGURE 13 | The energy densities (a) and photon fluxes (b) at the interface between two media with different refractive indices. (c) The radiation and trapped modes in a medium with a higher refractive index, separated by the 'escape cone' with critical angle θ_c defined by the Snell's law.

dielectric with a refractive index n is n^3 times higher than in vacuum, Planck's relation (4) predicts different photon fluxes directed from opposite sides toward an interface between two media of different optical density. The equilibrium balance of flows across the interface is established by virtue of geometry and Snell's law: only photons within the 'escape cone' are allowed to escape, creating a directional barrier for photon flow from the optically denser medium (Figure 13(c)). This constraint makes it more difficult for photons to escape, trapping photons in the optically denser medium.

An range of ingenious ways have been proposed how this situation can be exploited to improve the capture of solar radiation (see Ref 92 for a recent comprehensive review of this field). In this chapter, we confine ourselves to statistical techniques that have proved most successful in practical applications.

The key feature of statistical light trapping is that the photon gas achieves completely random orientations. We may recall that such concept was already considered by Kirchhoff and Planck (see *Black Body Radiation* section). The randomness in orientations in black-body radiation occurs by virtue of strong absorption and re-emission. In contrast, light trapping is considered for weakly absorbing media where random orientations of photon directions are caused by scattering. The maximum permitted occupation of the trapped photon states is then reached under a full directional equilibrium, resulting in the highest enhancement of absorption.

Let us consider a volume V of such optically random medium with a refractive index n , in equilibrium with a surrounding medium with a refractive index of unity (Figure 14). The requirement that the absorption and emission of external radiation be balanced by photon creation and annihilation in the bulk then gives the fundamental condition for statistical light trapping. This is expressed in mathematical terms by linking the Kirchhoff's law for emission from the surface of the medium with the total

emission rate within the volume described by Planck's law:

$$e_\nu \mathcal{E} = (1 - r_\nu) \epsilon'_\nu V \quad (39)$$

where e_ν and ϵ'_ν are the Kirchhoff's surface emissivity and Planck's volume emission coefficient (see *Balance between Absorption and Emission of Radiation* section). For full generality, we have assumed that photon emission or absorption from the volume is constrained to a beam with any étendue \mathcal{E} . By virtue of equilibrium, we could assume the photon density per unit volume in the medium to be constant both with respect to position and orientation.

Equation (39) expresses the fact that all photons emitted inside a volume will be emitted to the exterior unless reabsorbed. It introduces a new quantity r_ν :^{93,94} the average probability that a photon, created in the interior of the medium, is reabsorbed before being emitted from the volume. From an alternative viewpoint, r_ν complements Kirchhoff's absorptivity a_ν for photons arriving from the interior of the medium.

Equation (39) can be transformed into an absorption balance with the use of the relevant Kirchhoff's and Planck's laws, relating, at the same time, photon fluxes inside and outside the medium with the use of the brightness theorem (*Balance between Absorption and Emission of Radiation* section):

$$a_\nu \mathcal{E} = 4\pi(1 - r_\nu)\alpha_\nu n^2 V \quad (40)$$

Equation (40) can easily be solved for strongly scattering media where the stochastic nature of photon paths ensures that the probability of photon absorption is the same, regardless whether photons originate inside or outside the medium. This makes it possible to set $a_\nu = r_\nu$, giving:

$$r_\nu = \frac{\ell_{opt}\alpha}{1 + \ell_{opt}\alpha} \quad (41)$$

where

$$\ell_{opt} = \frac{4\pi n^2 V}{\mathcal{E}} \quad (42)$$

denotes the mean path length that photons traverse before escape. Result (42) can also be obtained directly based on the stochastic nature of radiation by using an argument analogous to the escape of gas through a hole⁹⁴ if augmented by a factor due to the directional barrier to photon escape.

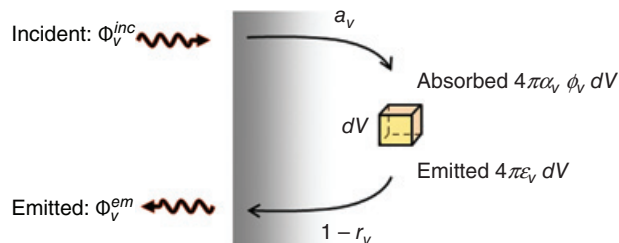


FIGURE 14 | The Kirchhoff and Planck relations between the absorption and emission of radiation by a volume dV (to be compared with Figure 1).

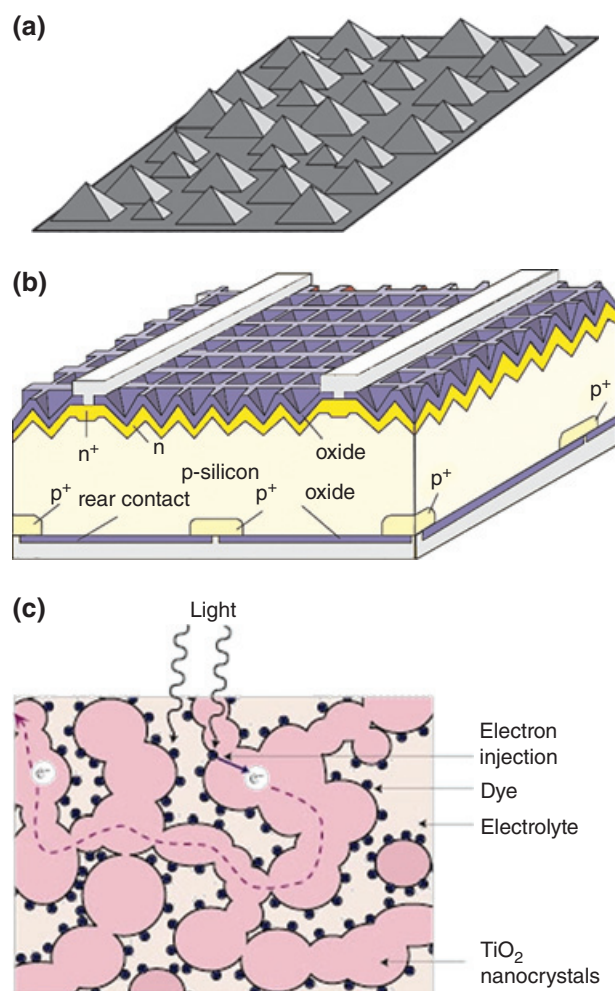


FIGURE 15 | Examples of light trapping schemes in several current types of solar cells. (a) Light trapping in the form of small pyramids etched in the top surface as implemented in, for example, the COMSAT ‘black’ solar cell.⁹⁷ (b) A more sophisticated form of surface texturing in the form of inverted pyramids on the UNSW PERL cell.⁹⁸ (c) Structure of the dye-sensitized (Grätzel) cell with light trapping by scattering from titanium oxide nanoparticles.⁹⁶

Equation (42) can be written in a number of modified but similar forms, and has been used to discuss light trapping in a wide variety of solar cell structures^{95–98} (Figure 15). Applied to a thin layer of thickness d , Eq. (42), simplifies to

$$\ell_{opt} = 4n^2d \quad (43)$$

known as the Yablonovitch limit.^{99,100}

Light trapping has been successful in improving the operation of commercial devices, particularly crystalline silicon solar cells. Equation (43) predicts a theoretical enhancement in path length by a factor of about 50 in comparison with a single passage

through a layer of semiconductor. In practical situations, this has made it possible to manufacture commercial or near-commercial crystalline silicon solar cell of thickness 20–30 μm —a significant saving in material over traditional solar cells several 100 μm thick. The ultimate objective, however, must be to achieve a good efficiency with a cell thickness of the order of a micrometer or less, comparable with thin film or organic-based devices.

Understandably, there is currently much research in this direction. A considerable effort is devoted, in particular, to studies of light trapping in ultra-thin layers where scattering is generated by plasmon modes at metallic nanoparticles deposited on the surface.¹⁰¹ The trapped modes then form a discrete set, and a full understanding is needed of the relationship between the optical path length (42) and the density of trapped modes in the thin layer or waveguide (see, e.g., Refs 102 and 103). The gains through increased absorption in specific spectral regions may be offset against dissipative losses in the metal particles and a reduced entropic advantage of fewer trapped modes.¹⁰⁴ The use of molecular dipoles for a similar purpose has also been suggested.¹⁰⁵ Whatever the final outcome, ideas based on thermodynamics are already being used to advantage. An example of recent developments can serve the recent clarification¹⁰⁶ based on the reciprocity between absorption and emission, that the increase in short-circuit current due to light trapping is mitigated by an increase in the dark saturation current, lowering the open-circuit voltage. Whatever the enhancement, light trapping by itself cannot therefore be used to surpass the Shockley–Quisser limit, as has recently been suggested.¹⁰⁷

Other suggestion to enhance light trapping is based on expanding the thermodynamic analysis into the frequency domain. This is easily achieved by the management of photon directions as well as frequency using photon absorption and re-emission as fluorescence (Figure 16). In thermodynamic terms, the fluorescent medium then effectively exchanges energy with the photon field which no longer represents as an isolated system. This energy loss can then be traded for an extension of the path length through solar cell beyond the monochromatic limit (42), or for an étendue reduction in a device that emits light.¹⁰⁸ These two applications are briefly discussed below.

A device which transforms the entropy change on photon cooling into an étendue reduction is called a fluorescent concentrator/collector. It usually represents a fluorescent plate that absorbs light from the large face and emits the fluorescent light through the edge, making it possible to employ significantly smaller solar cells. Studied since the late 1970s,^{109–112} the

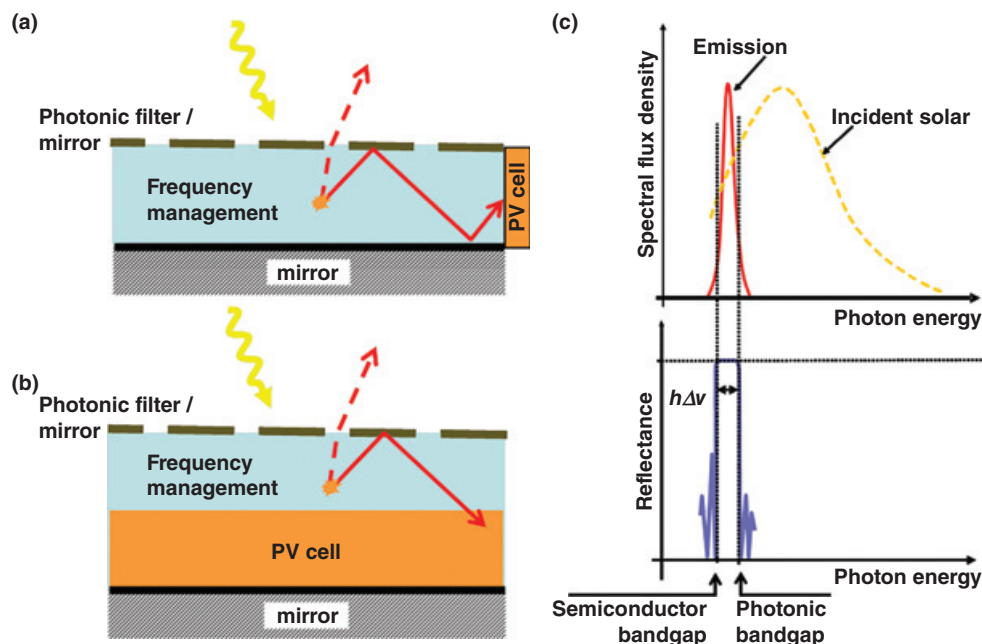


FIGURE 16 | Principles of photonic frequency management based on thermodynamics. (a) The fluorescent concentrator/collector, where a photonic bandstop helps to guide emitted light toward a solar cell at the edge. (b) The photonic bandgap solar cell where a photonic bandstop traps assists the trapping of light emitted by the highly absorbing photon management layer inside a poorly absorbing solar cell. (c) The reflectance of the photonic bandstop in (a) and (b) compared with the spectrum of the incident and fluorescent radiation.

interest in fluorescent collectors has recently been revived due to the availability of a wider range of dyes and the developments in photonics. There is much optimism for a substantial increase over the current overall efficiencies (solar cell plus collector) of 7–8%^{113,114}. Particularly, fruitful direction appears to be the application of photonic structures to trap the narrow-band fluorescent light while allowing most of the incident broadband solar flux to be absorbed by the collector (Figure 16(c)). Such structures can limit photon losses to less than about 10% of the incident light, leading to overall efficiencies of 18–20% with a good crystalline silicon solar cell.¹¹⁵

This ‘thermodynamic squeezing’ of light which lies in the heart of operation of the fluorescent collectors can also be used to advantage to improve the capture of weakly absorbed light. The use of a photonic filter in combination with frequency management extends the photon path length by a factor equal to an inverse of the Boltzmann factor appropriate to the frequency bandwidth of the trapped light:¹¹⁵

$$\ell_{opt} \cong 4n^2 d e^{h\Delta\nu/k_B T_o} \quad (44)$$

If the width of the frequency band stop $\Delta\nu$ is large, the photonic structure would block a large part of

the spectrum but for an optimum value which transmits a sufficient part of the solar spectrum while ensuring a substantial enhancement in light trapping, as illustrated on the example of a predicted quantum efficiency that can be reached by a solar cells¹¹⁶ (Figure 17).

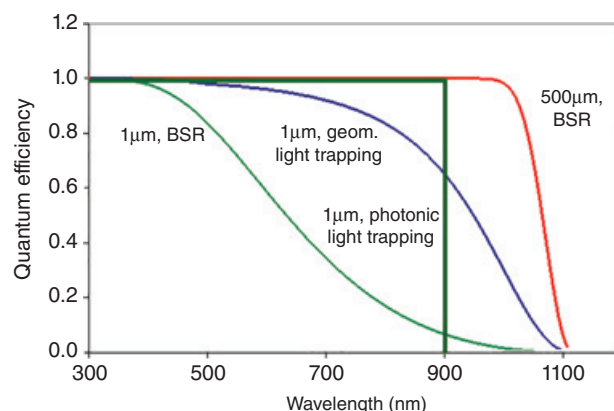


FIGURE 17 | The internal quantum efficiencies of solar cells with geometric and photonic light trapping, compared with a conventional (thickness 500 μm) and thin (1 μm) crystalline silicon solar cells. BSR indicates Back Surface Reflector (after Ref 116).

TABLE 2 | Efficiencies of Solar Cells with Quantum Efficiencies Shown in Figure 17

500 μm c-Si cell	30.3%
1 μm cell (BSR only)	15.6%
1 μm cell (geometric light trapping)	26.0%
1 μm cell (photonic light trapping)	30.7%

The predicted power conversion efficiencies are shown in Table 2. Remarkably, the cell efficiency of a cell with thickness merely 1 μm is now comparable with (and even slightly exceeds!) the efficiency of the 500 μm cell.

CONCLUSION AND OUTLOOK

Solar radiation can be represented as high-temperature heat and its conversion into useful work or electricity is described well by the laws of thermodynamics. It is therefore not surprising that thermodynamics now forms a routine part of the modeling toolset for both the current and future generations of solar cells, and our thinking should not be about *if* but *how* thermodynamics can guide us to make better solar cells.

The theoretical framework of thermodynamic applications to solar energy conversion has witnessed steady development but a number of theoretical questions and problem areas remain. How can thermodynamics be used to increase the solar cell efficiency? Several ideas have been discussed (for example, hot-carrier solar cells, reviewed in the *Model of Ross and Nozik* section) but the theory still requires development to reach a satisfactory level of understanding. Questions remain about the relationship between the application of classical thermodynamics to kinetic processes and the issues of reciprocity or microscopic reversibility. Can nonreciprocal structures lead to higher efficiencies than those that were discussed in this review?

What clues can thermodynamics provide as to new mechanisms and materials? With increasing use of nanotechnology and a drive toward ever thinner devices, effective capture of sunlight is key to the efficient new solar cells. A classical approach to light trapping was reviewed in the Light Trapping section, but there is a need to extend the theory to ultrathin solar cells in the form of wave guides or photonic structures that trap or concentrate sunlight. Quantum heat engines have been proposed based on the thermodynamic description of masers and lasers^{117,118} involving coherent transitions between quantum levels coupled to heat baths. These engines

can operate as quantum amplifiers or refrigerators¹¹⁹—can a similar approach (possibly based on rectifying antennas)^{120,121} be exploited to benefit solar energy conversion?

These are just a few, almost random thoughts. Few persons alive during the age of the steam engine would have predicted the success of thermodynamics in the design of modern aircraft, rockets, automobiles, and energy equipment that we enjoy today. It is likely that the ‘thermodynamics of light’ will see many years of further development, with application to new devices that are yet to be discovered. Its true moment of success may well be ahead of us.

NOTES

^a The possibility to excite photons with energy higher than the corresponding applied voltage. See Ref 1.

^b A comprehensive review of efficiencies that have been considered for solar energy conversion can be found in Ref 4.

^c Although the name appears to be fairly recent, similar concepts have been associated much earlier with such distinguished names as Poincaré, Lagrange, and Helmholtz.

^d A clear exposition of the optical ideas behind the concept of étendue can be found in Ref 6.

^e The first paper that appears to have drawn attention to the link between étendue and a volume on the phase space appears to be in Ref 7.

^f A particularly clear discussion of this point can be found in Ref 11.

^g In photon terminology that will be used throughout this paper, the balance between absorption and emission was formulated for semiconductors (but can be easily generalized).²³

^h This subject is reviewed in a particularly clear form in Ref 32.

ⁱ See, for example, Section 20 in Ref 13 or Chapter 7 in Ref 14.

^j More rigorously, the internal energy u , entropy s as well as the chemical potential μ refer to adding or removing a photon at constant volume rather than at constant pressure, as in the usual analysis of chemical reactions. We shall return to this assumption later in *Thermodynamics of Photovoltaic Conversion* section.

^k A full treatment in terms of rate of photon emission and work (as depicted in Figure 2(c)) is described in Ref 67, leading to identical results.

^l In our analysis, the fill factor contains the current corresponding to the full photon flux $q\Phi_m$ rather than the more usual photogenerated current I_L . In practical applications, the difference between the two—equal to the dark saturation current I_o —is very small and can be safely neglected.

^m In practical terms, this implies a concentration ratio of less than about a hundred for a silicon solar cell.

ⁿ This value was obtained by a more accurate numerical procedure than in Ref 85, and is slightly lower than the result 85.2% reported there.

^o Detailed discussions of reabsorption (also called photon recycling) with application to solar cells can be found in Refs 83, 84 and 93.

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