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Microscopic reversibility demands lower open circuit voltage in multiple exciton generation solar cells

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ABSTRACT

Multiple exciton generation (MEG) increases the short circuit current of solar cells and is, therefore, often cited as a candidate scheme for surpassing the efficiency limit of single junction solar cells. Conventionally, limiting efficiencies for MEG solar cells have been calculated using quasi-equilibrium models that implicitly assume an effective separation of timescales between different processes. We show here that this separation of timescales is not possible for MEG solar cells, with Auger recombination, the inverse process to multi-exciton generation, needing to be considered explicitly in the efficiency limits of an MEG solar cell. We assess the impact of Auger recombination using a non-equilibrium model of a quantum dot solar cell that satisfies microscopic reversibility and can approximate experimental external quantum efficiency (EQE) curves of MEG solar cells. Recombination—both Auger and radiative—is treated in a quasi-equilibrium approach, which can be justified with a clear model for the separation of timescales. A key insight of this model is that the achievable voltage of the device, and hence the solar energy conversion efficiency, depends on the absolute values of the impact ionization rate and the rate at which electrons lose energy through phonon scattering. By contrast, the EQE profile at short circuit depends only on the ratio of these two rates. This shows that the potential of certain MEG solar cell approaches cannot be assessed from EQE improvements alone, which highlights the importance of considering non-equilibrium processes in models of solar energy conversion devices.

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Energy conversion devices exploit thermodynamic non-equilibrium to generate useful work; yet, they are typically analyzed using elements of equilibrium thermodynamics. Non-equilibrium in photovoltaic (PV) devices stems from the large temperature differential between the solar photons absorbed in the PV device and the PV device itself. Most PV device models use equilibrium thermodynamic quantities such as electro-chemical potentials and temperatures of charge carriers to describe current voltage characteristics.

These quasi-equilibrium models are accurate for solar cells because of the large separation of timescales between fast and slow processes. For example, the thermalization of carriers to a Fermi Dirac distribution within each band—with the temperature given by the lattice temperature—is extremely fast compared to radiative and non-radiative recombination, which is responsible for equilibration of electron densities between conduction and valence bands.[1] Electron-electron scattering and electron-phonon scattering that enable carrier thermalization do not have to be calculated explicitly; instead, their impact is accounted for by assuming two Fermi Dirac distributions for electrons and holes, respectively, thus eliminating the fast variables,[2] i.e., the energy-dependent occupation functions of electronic states. This leaves only electro-chemical potentials or quasi-Fermi levels, μ_c of electrons in the conduction band, and μ_v of the holes in the valence band, as slow variables that explicitly track carrier transport and recombination. In a single junction solar cell with good carrier mobility, the quasi-Fermi level separation (QFLS) between the electron population and the hole population is spatially uniform and given by the applied voltage. An I–V curve for a particular illumination condition of a conventional single junction solar cell can be readily calculated with knowledge of the external quantum efficiency (EQE)

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as a function of photon frequency and the saturation current of the device, assuming that the superposition principle is valid.

A solar cell exhibiting multiple exciton generation (MEG) is characterized by above-unity EQE for high photon energy. This occurs because electron hole pairs excited to highly energetic states may undergo an internal multiplication process due to Coulomb interaction between electronic states, e.g., impact ionization that competes with phonon relaxation on a similar timescale.[3–5] Nonetheless, calculations for the limiting efficiencies of MEG solar cells have used quasi-equilibrium models, assuming either a staircase model[6] for the external quantum efficiency (EQE) or a continuously increasing EQE.[7,8] The model by Werner *et al.*[6] was devised for a bulk material with impact ionization, while the model by Hanna *et al.*[8] is written with quantum dots (QDs) in mind. The physical differences in the impact ionization process between quantum confined systems and bulk systems, most notably the absence of momentum conservation in quantum dots, however, do not affect the efficiency limit considerations of those works. Real solar cells displaying above unity EQE show an EQE that increases continuously with energy,[9,10] and so at a first glance, the models assuming a continuously increasing EQE seem more relevant.

We show that the continuous model for the ideal I-V characteristics of such a cell does not correspond to any self-consistent set of limits that would allow for the separation of timescales that underlies any quasi-equilibrium model for carrier recombination. By developing a toy model for QD solar cells that satisfies microscopic reversibility and employs an internally consistent set of physical limits, we show that an increase in short circuit current due to MEG is necessarily linked to a decrease in open circuit voltage arising from Auger recombination. This insight has major implications when assessing potential efficiency increases due to the MEG process. In particular, predictions based solely on the increase in short circuit current would need to be revised down.

The MEG solar cell relies on impact ionization of high energy electrons that promote an additional electron from the valence to the conduction band, i.e., generate an additional electron-hole pair. This process can be repeated until the electron does not have sufficient excess energy. A model that obeys microscopic reversibility must also include Auger recombination, the inverse process of impact ionization. However, existing limiting efficiency models include only radiative recombination (the so-called radiative limit) and do not explicitly include Auger recombination. A purely radiative model can be justified, provided that the effect of impact ionization and Auger recombination can be accounted for using a relation between slow variables, describing quasi-equilibrium distributions.

To understand how this is achieved, we can analyze the related case of molecular singlet fission, for which a limiting efficiency has been calculated using a quasi-equilibrium model.[11] Here, a distinction is made between the timescale of cooling within the same subset of states, described by the same chemical potential, and the timescale of relaxation to a different subset of states. The physical motivation for this is given by the clear energetic gap, in combination with the necessity of spin flips, which dramatically slows inter-system crossing between singlet and triplet states. The hierarchy of timescales is such that cooling within a set of states is faster than singlet fission/triplet-triplet annihilation, which, in turn, is faster than relaxation between different sets of states.

A system attains quasi-equilibrium when a process and its reverse result in no change in free energy. In singlet fission, this occurs when the sum of the chemical potentials of the ground state and excited singlet state is equal to twice the chemical potential of the triplet state, i.e., $\mu_{S1} + \mu_{S0} = 2\mu_T$. Setting this quasi-equilibrium condition as the outcome of the fast singlet fission process, and assuming that the singlet has no other nonradiative relaxation pathway, allows for an elimination of Auger recombination from the limiting efficiency calculations.

Interestingly, the highest limiting efficiency occurs for endothermic fission where the singlet energy E_{S1} is smaller than twice the triplet energy $2E_T$[11] and energy conservation is fulfilled by drawing heat from the environment. Going beyond the purely radiative framework by introducing finite singlet fission rates shows that the competition between singlet fission and radiative recombination shifts the energy relation between ideal triplet and ideal singlet energy.[12] Finite rates introduce a benefit for exothermic fission, in which heat is released to the environment, because endothermic processes that draw heat from the environment are slowed exponentially with the amount of heat required and, therefore, become less favorable with slower singlet fission rates.

By contrast, in their staircase model, Werner *et al.*[6] assume that there exist MEG thresholds with discontinuous jumps at integer values of the bandgap energy. By not allowing for endothermic processes, it implicitly assumes that electron-phonon scattering cannot provide the required heat for an endothermic process. Therefore, to be consistent, electron-phonon scattering must be slower than, or on a similar timescale to, impact ionization. Radiative recombination is treated by summing generalized Planck equations for electron distributions, all at lattice temperature, with different quasi-Fermi levels determined by the energy in relation to the carrier multiplication thresholds. In this formalism, setting the QFLS to integer multiples of the applied voltage then effectively eliminates Auger recombination from limiting efficiency considerations. Auger recombination does not lead to a decrease in free energy, meaning that each Auger recombination event is compensated by a subsequent impact ionization event.

Assuming a common temperature equal to that of the lattice for each separate electron distribution is a consequence of efficient electron-phonon scattering terms with rates faster than radiative recombination. However, electron-phonon scattering between electronic states belonging to carrier distributions described by different quasi-Fermi levels must be much slower than impact ionization for the staircase model to hold. Such a behavior of electron-phonon scattering implies large energetic gaps between the states, i.e., an intermediate band model is implicitly assumed where multiple carrier populations exist in quasi-equilibrium in bands beyond the conventional valence and conduction bands.[7] So, while the staircase model for MEG can be mapped onto a physical model that is internally consistent, there are no known material systems that well approximate this model.

The continuous EQE model[8] was introduced as a refinement of the staircase model[6] to better describe the experimentally observed behavior of a gradual increase in internal (IQE) and, consequently, external quantum efficiencies in semiconductor materials, especially colloidal quantum dots (QDs).[3,10,13] Luque and Martí defined a model for the radiative recombination current that fulfills the minimal requirements of positive entropy production and zero current at zero voltage in the dark by accounting for radiative recombination alone,[14] implicitly eliminating Auger recombination from the model. In their model, the radiative recombination current I_{rad} is written as

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$$I_{rad} = \frac{2\pi}{h^3c^2}\int_0^\infty \frac{EQE(E)E^2}{e^{\frac{E-EQE(E)qV}{kT}} - 1} \quad (1)$$

in a manner that looks very similar to the opto-electronic reciprocity relation for single junction solar cells.[15] Here, V is the voltage of the device and T is the temperature of carriers, which is assumed to be equal to the temperature of the lattice.

The chemical potential of radiation is an imprint of the QFLS describing the occupancy of electrons and holes in the absorber material, which means that Eq. (1) reflects a system in which the QFLS of electrons and holes varies continuously with energy. Yet, quasi-equilibrium with regard to the impact ionization and Auger recombination processes requires multiples of QFLSs so that no free energy is generated in either process. Therefore, continuous QFLSs cannot be assumed and the continuous EQE model needs to be refined to be internally consistent and compatible with microscopic reversibility of impact ionization as well as absorption.

We use a simple non-equilibrium toy model for an MEG QD solar cell that is simultaneously capable of (i) approximating experimentally observed IQE and EQE curves, (ii) fulfills microscopic reversibility, and (iii) is capable of generating I–V characteristics that depend not only on the EQE curves but also on the absolute value of electron-phonon scattering and impact ionization rates. The radiative limit is recovered for simultaneously slow electron-phonon scattering and slow impact ionization. Similar to Spoor *et al.*,[5] we approximate the density of electronic states in the conduction band of the QDs by a series of discrete, equi-distant states with spin degeneracy 2, separated by an energy interval ΔE, as illustrated in Fig. 1. The valence band is simplified by assuming that all of the hole states are at a single energy, set to zero, for convenience, with a sufficient density of state, such that hole occupation probabilities remain small and the Boltzmann approximation is applicable. This simplifies the analysis and provides the ideal case for MEG in which the electrons carry all of the energy in excess of the bandgap.

Following photon excitation, an electron is excited from the ground state (GS) to an excitonic state X1 as shown in Fig. 1(a). In the event that the excitation energy $E_\gamma = \hbar\omega$ is $>2E_g$, impact ionization can create a bi-exciton X2 with probability p_{II}, shown in Fig. 1(b), or emit a phonon with probability $1 - p_{II}$, shown in Fig. 1(c). The

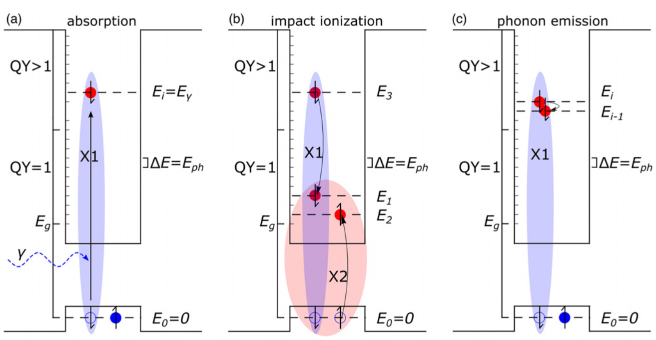

FIG. 1. The model QD with equi-distant conduction band states with a spin degeneracy of 2 and (a) an absorption event and [(b) and (c)] the two different processes that can occur to highly energetic electrons: (b) impact ionization and (c) emission of a phonon.

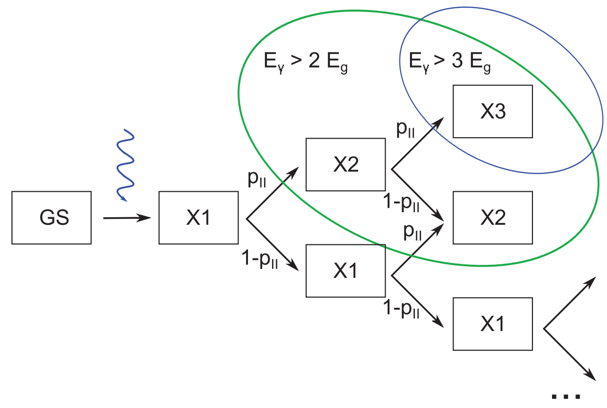

FIG. 2. A flowchart of the nonequilibrium dynamics of photo-excitation and relaxation. A single exciton (X1) in the QD is created upon excitation by a high energy photon, and with a certain probability p_{II}, impact ionization turns it into a bi-exciton (X2), while it loses energy to a phonon with probability $(1 - p_{II})$. This process is repeated until all the excitons in the QD do not have enough energy to undergo further impact ionization.

probability of impact ionization, p_{II}, increases with E_{ph} because there are more bi-exciton states to scatter into. A bi-exciton in which one of the excitons has energy above $2E_g$ could create a further exciton, resulting in an X3 state, which could split again, if one of the constituting excitons has energy above $2E_g$, etc. Figure 2 shows a flowchart of the model with the mathematical details of the model provided in the supplementary material.

The nonequilibrium part of the model traces highly excited excitons while they undergo a series of phonon emission and impact ionization events. The branching ratio between phonon emission and impact ionization is determined by the relative strength of the impact ionization matrix element and the phonon coupling matrix elements as well as the density of final (bi-excitonic) states for the impact ionization event. Both matrix elements are assumed to be constant with energy, while the density of bi-exciton states increases with energy. The frequency of net phonon emission (emission-absorption) ν_{ph} by an excited electron can be quantified by the electron energy loss rate (EELR),

$$EELR = \nu_{ph}E_{ph}, \quad (2)$$

which is the rate at which each highly excited electron loses energy to phonons.

Both Auger recombination and radiative recombination take place on much longer timescales and are driven by the free energy available from the QFLS, which, in the limit of infinite carrier mobility, is given by the applied voltage. Auger recombination that constitutes the inverse of exciton multiplication requires a bi-excitonic initial state. Therefore, the ideality factor of this recombination event is 1/2, stemming from the requirement of having four particles (two electrons and two holes). By contrast, Auger recombination or recombination from a charged QD state (a trion) requires only three particles and, therefore, has an ideality factor of 2/3. Since charged QD states (or trions) can, in principle, be avoided,[16] we separately consider a scenario with only bi-exciton recombination and a scenario with trion recombination.

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TABLE I. The parameters used in the toy model, bandgap E_g, phonon energy E_{ph}, equal to the energy spacing ΔE, ratio x_0 between impact ionization rate R_{II} and phonon scattering rate R_{ph}, thickness of the QD layer d_{QD}, and QD volume density n_{QD}.

E_g (meV)	E_{ph} (meV)	x_0	d_{QD} (nm)	n_{QD} (1/cm^3)
765	17	0.002	250	10^{18}

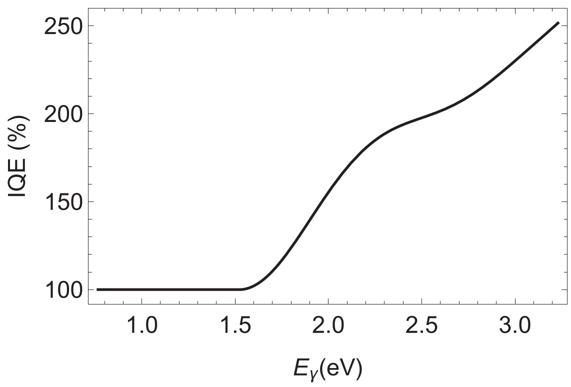

FIG. 3. The internal quantum efficiency for an MEG solar cell with parameters given in Table I. The curve is interpolated to obtain a continuous function from the discrete recursion relation given by Eq. S6 of the supplementary material.

Using the recursive model for the impact ionization probability with the parameter set defined in Table I, typical for PbSe QDs,[5] we calculate the *IQE* curve shown in Fig. 3(a). It well approximates the slope beyond the impact ionization threshold that is seen in experimental results from PbSe QD solar cells.[13] The threshold in our model is lower due to the approximation of giving all excess energy to the electrons.

While MEG enhances short-circuit current, the explicit inclusion of microscopic reversibility necessitates a decrease in open-circuit voltage. Figure 4 shows the *I*–*V* curves obtained by modeling the sun as a blackbody at 5800 K, with EELR in the QDs varying from 0.1 eV/ps to 10 eV/ps. The volume density of the QDs and the thickness of the QD layer (see Table I) follow those used in an experimental report of MEG.[10]

For bi-excitonic recombination, see Fig. 4(a), the open circuit voltage is reduced from the radiative limit voltage in the absence of MEG when the electron energy loss rate is 1 eV/ps. Yet, the maximum power point voltage is virtually unchanged. This is because the fill factor of the *I*–*V* curve increases dramatically for the device including MEG due to the lower ideality factor and, consequently, sharper onset of Auger recombination. At high levels of EELR (10 eV/ps)—and a correspondingly faster impact ionization rate to keep the ratio between phonon and impact ionization rate, x_0, and thereby the energy-dependent EQE, constant—a reduction in power conversion efficiency is observed.

If, however, Auger recombination from a negatively charged trion state (two electrons and one hole in the QD) is considered, the operating voltages and, thus, the efficiencies drop in all scenarios [see Fig. 4(b)]. This finding is in accordance with QD light emitting diodes,[16] where the exclusion of charged QD states enables a much higher efficiency.

Note that the voltages calculated here are much higher than the voltages found in experimental realizations of MEG QD solar cells.[9,10,17] This shows that these experimental realizations are not yet limited due to fundamental microscopic reversibility of the impact ionization process but rather due to other nonradiative recombination processes and large improvements upon these results are possible.

In conclusion, we have shown that consideration of the relative timescales of key energy conversion processes for solar cells is a critical consideration when formulating efficiency limit models. It was shown that two previous models developed for assessing the efficiency potential of solar cells displaying multiple exciton generation and impact ionization, respectively, violate the microscopic reversibility requirement and so overestimate the efficiency advantage on offer. The key missing element for both these models was identified as the lack of an inverse process for the MEG or impact ionization. We have presented a simple model, incorporating this insight, which improves not only understanding of how the MEG and impact ionization processes can

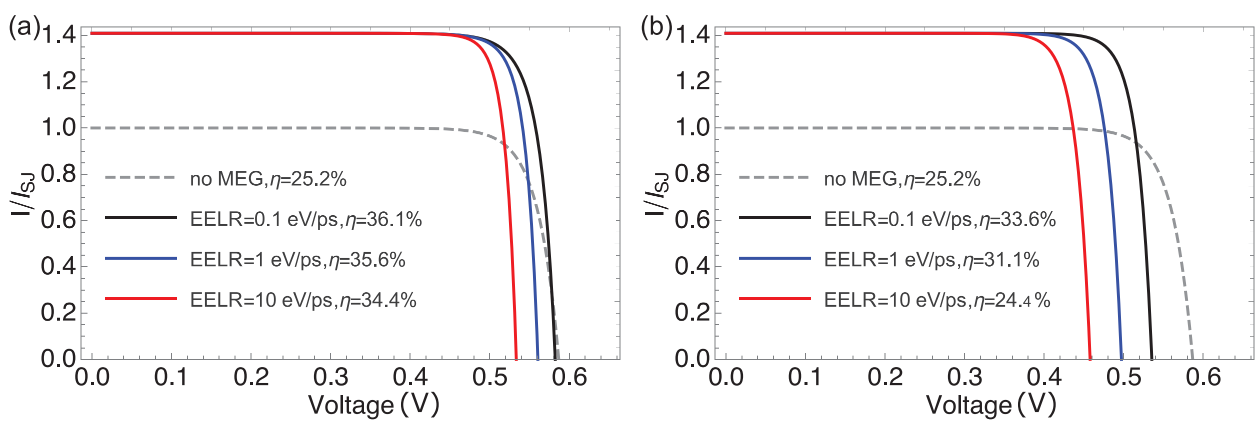

FIG. 4. *I*–*V* characteristics for MEG solar cells for several EELRs, normalized to a conventional single junction device of the same bandgap. The parameters used are given in Table I. A conventional solar cell with the same bandgap is shown for comparison. (a) shows the *I*–*V* curves assuming only bi-exciton Auger recombination, and (b) shows the *I*–*V* curves including trion Auger recombination. The dashed lines show the *I*–*V* curve of an ideal, conventional single junction device with the same bandgap for comparison.

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improve efficiency but also the factors that limit the improvements available. Our model looks at the non-equilibrium processes in QDs under excitation, taking into account the competition between impact ionization processes and phonon scattering. The model further treats much slower recombination processes in a consistent quasi-equilibrium manner that satisfies microscopic reversibility. Using this model, we show the impact of Auger recombination on the voltage and efficiency of MEG QD solar cells by tracing the whole *I–V* characteristics.

We found that the open circuit voltage is noticeably reduced from its radiative limit, but efficiency gains remain possible. However, we also show that preventing trion states from forming will be important to retain efficient operation. Critically, our analysis shows that knowledge of the EQE and, therefore, the short circuit current of MEG QD solar cells is insufficient to estimate possible efficiency improvements. This arises because the absolute magnitude of the beneficial impact ionization processes also places minimum requirements on the nonradiative recombination rates. Nonetheless, the efficiency of MEG QD solar cells could, in principle, significantly exceed the conventional single junction limit for the same bandgap if electron energy loss rates are relatively low and trion states are avoided.

See the supplementary material for a detailed description of the QD model employed to calculate EQE and Auger recombination.

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DATA AVAILABILITY

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

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