Variational method for the minimization of entropy generation in solar cells

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Variational method for the minimization of entropy generation in solar cells

Sjoerd Smit and W. M. M. Kessels

Articles you may be interested in

Communication: Maximum caliber is a general variational principle for nonequilibrium statistical mechanics
J. Chem. Phys. **143**, 051104 (2015); 10.1063/1.4928193

Statistical mechanical theory for steady state systems. VI. Variational principles
J. Chem. Phys. **125**, 214502 (2006); 10.1063/1.2400859

Publisher's Note: "Optimizing the driving function for nonequilibrium free-energy calculations in the linear regime: A variational approach" [J. Chem. Phys.122, 104106 (2005)]
J. Chem. Phys. **123**, 039901 (2005); 10.1063/1.2006669

Optimizing the driving function for nonequilibrium free-energy calculations in the linear regime: A variational approach
J. Chem. Phys. **122**, 104106 (2005); 10.1063/1.1860556

Entropy production and thermodynamics of nonequilibrium stationary states: A point of view
Chaos **14**, 680 (2004); 10.1063/1.1781911

Variational method for the minimization of entropy generation in solar cells

Sjoerd Smit and W. M. M. Kessels[a)]
*Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven,
The Netherlands*

In this work, a method is presented to extend traditional solar cell simulation tools to make it possible to calculate the most efficient design of practical solar cells. The method is based on the theory of nonequilibrium thermodynamics, which is used to derive an expression for the local entropy generation rate in the solar cell, making it possible to quantify all free energy losses on the same scale. The framework of non-equilibrium thermodynamics can therefore be combined with the calculus of variations and existing solar cell models to minimize the total entropy generation rate in the cell to find the most optimal design. The variational method is illustrated by applying it to a homojunction solar cell. The optimization results in a set of differential algebraic equations, which determine the optimal shape of the doping profile for given recombination and transport models. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4916787]

I. INTRODUCTION

Following the analysis of the efficiency potential of single-junction solar cells by Shockley and Queisser,[1] the upper limit on the efficiency of solar cells has been determined in literature under various idealized assumptions (see, e.g., Refs. 2–4). For many practical types of solar cells, however, it is still unclear how to realize the highest possible efficiency because of the presence of specific (non-ideal) loss mechanisms that limit the efficiency potential of the cell. For example, in solar cells based on crystalline silicon (*c*-Si), Auger recombination and surface recombination at the metal contacts limit the attainable efficiency considerably, whereas in an ideal solar cell only radiative recombination would occur. Furthermore, these non-ideal loss mechanisms often have complex interactions in the cell design, making it difficult to find the optimal trade-off between them. In homojunction cells, for example, the high doping densities in the emitter and back surface field (BSF) function to limit the recombination at the metal contact, but simultaneously give rise to increased Auger recombination.

To aid in the practical design of these kinds of non-ideal solar cells, detailed models have been developed to predict their efficiency. Programs like PC1D,[5] AFORS-HET,[6] and ASA[7] are all *efficiency-predictive* in this sense. Efficiency-predictive simulations are commonly used in parametric optimization studies where the simulation results of the solar cell design are used to improve the design iteratively and provide a cost efficient alternative for experimental trials. However, the parameter space for such optimization problems can become very large if many different parameters are optimized simultaneously. For example, to optimize the doping profile $\rho(x)$ of a homojunction cell in complete generality, it is in principle possible to parameterize the function $\rho(x)$ using a spline function with a high density of control nodes, but this will lead to an unfeasibly large parameter space.

The goal of this work is to introduce the *design-predictive* method of Variational Entropy Generation Minimization (VEGM), which aims to circumvent iterative optimization altogether. The VEGM method extends the scope of current efficiency-predictive methods by making it possible to directly predict the optimal solar cell design for a given set of physical constraints and non-ideal loss mechanisms that depend on the materials used. The main difference with efficiency-predictive methods is in the figure of merit used to optimize the solar cell. Iterative methods based on efficiency-predictive models optimize the solar cell based on figures of merit such as the output power P, open circuit voltage V_{OC}, and short circuit current J_{SC}. These figures of merit are determined on the boundary of the solar cell, and it is therefore often non-trivial to understand how changes to the design in the *bulk* of the cell will affect P, V_{OC}, and J_{SC} on the *boundary*. The key point of the new approach is to de-emphasize the importance the usual boundary figures of merit and instead focus on the total rate of entropy production Q_S as a new bulk figure of merit. Unlike P, V_{OC}, and J_{SC}, the total rate of entropy production Q_S is an integral over the bulk of the cell and thus combines local information from the whole cell. Therefore, Q_S can be optimized using variational methods to immediately predict the most efficient cell given a set of geometrical and physical constraints. In this work, the Euler-Lagrange (EL) method will be used to minimize Q_S, but in principle any variational optimization method can be used.

The type of solar cell considered here is a device that converts blackbody radiation from the sun into electrochemical energy (in the form of electron-hole pairs) and then into work (in the form of an electric current).[8] Like any other device that converts heat into work, the solar cell produces entropy under operation and the more entropy it produces, the more energy is lost in the form of low-grade heat. Therefore, the problem of maximizing P is equivalent to that of minimizing Q_S, which is an integral of the local entropy production rate q_s over the domain of the cell Ω

$$Q_S = \int_\Omega q_s \, dV. \tag{1}$$

It is important to note that Q_S should be minimized under the constraints that the solar cell is operating at maximum power

[a)]Electronic mail: w.m.m.kessels@tue.nl

     117, 134504-1

conditions under illumination, since the absolute minimum entropy generation rate is trivially $Q_S = 0$ in the dark at thermodynamic equilibrium.

Equation (1) shows that q_s is the central quantity that is required for the variational optimization of a solar cell. The expression for q_s will be derived in the following paragraphs using nonequilibrium thermodynamics, which is a field that has not found widespread use in the solar cell community. For this reason, the method of De Groot and Mazur[9] is used, which is conceptually simple and can be related to traditional semiconductor physics (as commonly practiced in the field of photovoltaics) with relatively little effort. A general background of this method for nonequilibrium thermodynamics can also be found in the books of, e.g., Kuiken,[10] Le Bellac et al.,[11] or Kjelstrup and Bedeaux.[12] General thermodynamic treatments of semiconductors physics can be found in the works of, e.g., Lindefelt[13] and Parrott.[14]

II. ENTROPY PRODUCTION IN SOLAR CELLS

To derive q_s, three components from the theory of nonequilibrium thermodynamics are required; the assumption of local thermodynamic equilibrium (LTE); and the continuity equations for the extensive variables. The derivation for q_s presented below is based on the aforementioned literature sources and has been reduced to the essentials as much as possible for the sake of accessibility.

For a solar cell in global equilibrium, the relevant thermodynamic quantities are: entropy S; internal energy U; temperature T; volume V; the electron/hole electrochemical potentials $\eta_{n,p}$; and finally the total number of electrons and holes $N_{n,p}$. The electrochemical potentials are defined as

$$\eta_n = \mu_n^c - e\phi, \quad \eta_p = \mu_p^c + e\phi, \quad (2)$$

with $\mu_{n,p}^c$ being the chemical potentials for the electrons and holes, e being the elementary charge, and ϕ being the electrostatic potential. Because of the fundamental coupling between charge and particle, η_n and η_p are the relevant thermodynamic potentials for the electrons and holes and there is no need to consider ϕ and $\mu_{n,p}^c$ separately.[8] Related to $\eta_{n,p}$ are the more commonly used quasi-Fermi energies $E_{Fn,p}$, given by $\eta_n = E_{Fn}$ and $\eta_p = -E_{Fp}$. It is assumed that pressure is not an important thermodynamic quantity for a solar cell because the kinetic energy and momentum of the electrons/holes do not play a significant role in the operation of the device.

It should be noted that there is also entropy associated with the angular distribution of the radiation field and the consideration of this distribution can therefore also help to improve solar cells[15] and in principle it is possible to minimize the entropy generation rate of the total system consisting of the solar cell and the radiation field taken together. For this work, however, only the entropy balance of the solar cell itself will be considered and the radiation field will be regarded as a source term for the processes in the semiconductor. This simplifying approximation is well-suited for material systems where radiative recombination is not the main loss mechanism, such as c-Si.[13]

With the quantities identified in the previous paragraph, the first law of thermodynamics for a solar cell in global equilibrium can be stated in terms of S

$$dS = \frac{1}{T}\,dU + \frac{-E_{Fn}}{T}\,dN_n + \frac{E_{Fp}}{T}\,dN_p. \quad (3)$$

Observe that in this formulation, U, N_n, and N_p are considered to be the independent thermodynamic variables and S is the fundamental potential, so $S = S(U, N_n, N_p)$. To generalize Eq. (3) to (nonequilibrium) operating conditions, LTE is assumed. Under this assumption, the system is divided into finite volumes that are small enough to reach equilibrium with their surroundings on a macroscopic timescale, yet microscopically large so that they can be accurately described by thermodynamic variables. It is furthermore assumed that the functional form of Eq. (3) remains valid locally. The local form of Eq. (3) is stated using volumetric densities of the extensive variables, which are indicated by a lower case letter: entropy density s, internal energy density u, and the electron/hole densities n, p. These quantities are all dependent on time t and position $\boldsymbol{x}$, but these dependencies will not be stated explicitly in equations unless confusion can arise. The local form of Eq. (3) is, therefore,

$$ds = \frac{1}{T}\,du + \frac{-E_{Fn}}{T}\,dn + \frac{E_{Fp}}{T}\,dp. \quad (4)$$

The densities s, u, n, and p satisfy local continuity equations. Let $q_{s,u,n,p}$ and $\boldsymbol{J}_{s,u,n,p}$ denote the local sources and currents of s, u, n, and p, respectively. Then

$$\frac{\partial s}{\partial t} + \nabla \cdot \boldsymbol{J}_s = q_s, \quad (5a)$$

$$\frac{\partial u}{\partial t} + \nabla \cdot \boldsymbol{J}_u = q_u, \quad (5b)$$

$$\frac{\partial n}{\partial t} + \nabla \cdot \boldsymbol{J}_n = q_n = G - R, \quad (5c)$$

$$\frac{\partial p}{\partial t} + \nabla \cdot \boldsymbol{J}_p = q_p = G - R. \quad (5d)$$

Here, G is the generation rate and R is the recombination rate of electron-hole pairs. Note that $\boldsymbol{J}_{n,p}$ are defined as particle currents (unit: $\text{cm}^{-2}\,\text{s}^{-1}$) and that the currents $\boldsymbol{J}_{s,u,n,p}$ are considered in the barycentric frame of the cell (so $\boldsymbol{J}_{s,u,n,p} = 0$ under global equilibrium conditions). To find q_s, first the t derivative of Eq. (4) is taken

$$\frac{\partial s}{\partial t} = \frac{1}{T}\frac{\partial u}{\partial t} + \frac{-E_{Fn}}{T}\frac{\partial n}{\partial t} + \frac{E_{Fp}}{T}\frac{\partial p}{\partial t}. \quad (6)$$

From Eqs. (5) and (6), the time derivatives can be eliminated. The entropy current $\boldsymbol{J}_s$ can then be eliminated by using the following relation for the currents:[16]

$$\boldsymbol{J}_s = \frac{1}{T}\boldsymbol{J}_u + \frac{-E_{Fn}}{T}\boldsymbol{J}_n + \frac{E_{Fp}}{T}\boldsymbol{J}_p. \quad (7)$$

After rearranging, q_s is then obtained

$$q_s = \frac{1}{T} q_u + \frac{E_{Fn} - E_{Fp}}{T}(R - G) + \boldsymbol{F}_u \cdot \boldsymbol{J}_u + \boldsymbol{F}_n \cdot \boldsymbol{J}_n + \boldsymbol{F}_p \cdot \boldsymbol{J}_p.$$

$$(8)$$

In Eq. (8), the forces $\boldsymbol{F}_{u,n,p}$ are defined by $\boldsymbol{F}_u = \nabla(1/T)$, $\boldsymbol{F}_n = \nabla(-E_{Fn}/T)$, and $\boldsymbol{F}_p = \nabla(E_{Fp}/T)$. The expression for q_s derived here agrees with expressions for power loss in solar cells derived in the literature previously,[17,18] but also includes thermal effects through the term $\boldsymbol{F}_u \cdot \boldsymbol{J}_u$, which includes entropy production due to transport of heat. The heat flux $\boldsymbol{J}_Q$ is given by

$$\boldsymbol{J}_u = \boldsymbol{J}_Q + E_{Fn}\boldsymbol{J}_n - E_{Fp}\boldsymbol{J}_p \qquad (9)$$

and can be used to rewrite Eq. (8) as

$$Tq_s = q_u + (E_{Fn} - E_{Fp})(R - G)$$
$$- \frac{\nabla T}{T} \cdot \boldsymbol{J}_Q - \nabla E_{Fn} \cdot \boldsymbol{J}_n + \nabla E_{Fp} \cdot \boldsymbol{J}_p. \qquad (10)$$

Equation (10) gives the source term for the entropy balance in the solar cell. The first two terms correspond to the transfer of entropy from the radiation field to the solar cell; electron-hole recombination; and the creation of entropy due to the non-radiative relaxation of electron-hole pairs immediately after the absorption of a photon. The last three terms in Eq. (10) are entropy production terms that correspond to irreversible transport phenomena. An overview of the physical meaning of the terms in Eq. (10) is given in Fig. 1.

The $\boldsymbol{F}_{u,n,p}$ introduced in Eq. (8) are referred to as forces because they drive the currents $\boldsymbol{J}_{u,n,p}$. According to Onsager theory,[19] the most general relation (for an isotropic medium and linear transport phenomena) between the currents and forces takes the form

$$\begin{pmatrix} \boldsymbol{J}_u \\ \boldsymbol{J}_n \\ \boldsymbol{J}_p \end{pmatrix} = \begin{pmatrix} L_{uu} & L_{un} & L_{up} \\ L_{nu} & L_{nn} & L_{np} \\ L_{pu} & L_{pn} & L_{pp} \end{pmatrix} \begin{pmatrix} \boldsymbol{F}_u \\ \boldsymbol{F}_n \\ \boldsymbol{F}_p \end{pmatrix}. \qquad (11)$$

The L_{ij} in Eq. (11) are the transport coefficients for the solar cell. Onsager theory states that the matrix L is symmetric (due to microscopic reversibility) and positive-definite (due
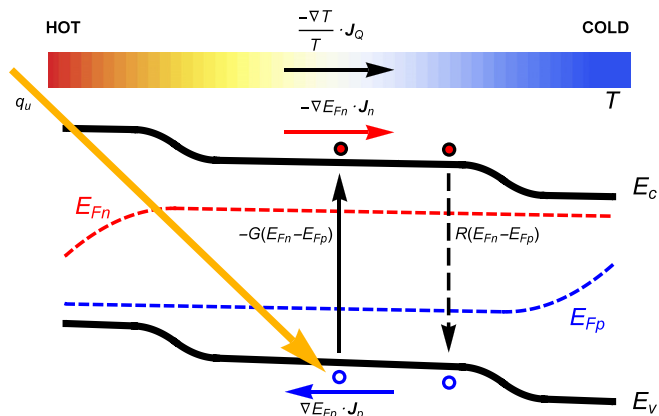

FIG. 1. Schematic band diagram of an illuminated solar cell that illustrates the physical processes corresponding to the terms in the entropy generation rate as given by Eq. (10). It is assumed that the temperature in the cell is higher on the side facing the light, as indicated by the color gradient.

to the fact entropy cannot spontaneously decrease). In traditional solar cell modeling, only the transport coefficients L_{nn} and L_{pp} (which are proportional to the electron and hole conductivities) are commonly used, while the remaining transport coefficients are implicitly assumed to be negligible.

In most solar cells, recombination of electron-hole pairs at the boundary $\partial\Omega$ of the cell will also contribute to the total rate of entropy generation. The surface entropy production rate $Q_{S,surf}$ should be added to the bulk contribution and can be calculated by

$$Q_{S,surf} = \int_{\partial\Omega} \frac{E_{Fn} - E_{Fp}}{T} R_{surf} \, dA. \qquad (12)$$

In Eq. (12), R_{surf} is the surface recombination rate (in $\text{cm}^{-2}\,\text{s}^{-1}$).

Equations (8) and (10) can be used directly to gain additional insight into simulation results from common solar cell simulation tools such as AFORS-HET. In order to plot power losses due to recombination and Ohmic dissipation in a solar cell, it is useful to define the dissipative part of q_s, which will be denoted by q_{diss}

$$Tq_{diss} = (E_{Fn} - E_{Fp})R - \frac{\nabla T}{T} \cdot \boldsymbol{J}_Q - \nabla E_{Fn} \cdot \boldsymbol{J}_n + \nabla E_{Fp} \cdot \boldsymbol{J}_p.$$

$$(13)$$

Because q_{diss} is always positive, it can be conveniently plotted as a color map on top of a band diagram calculation to show where the greatest losses of free energy are occurring. This is illustrated in Fig. 2. However, it is important to remark that in order to optimize the solar cell completely, it is necessary to not only minimize the total dissipation but to also make sure that the generation of electron-hole pairs takes place in regions of the cell where the Fermi level splitting is greatest, as can be seen from the term $-(E_{Fn} - E_{Fp})G$ in Eq. (10).

It is interesting to note that for a one-dimensional solar cell at constant temperature and under steady-state operation, the relation between the total entropy generation rate Q_S and output power P can be obtained by direct integration. It is assumed that the electrons are extracted at $x = 0$ and the holes at $x = d$. Let $e\Phi = (E_{Fn}(0) - E_{Fp}(d))$ be the voltage over the cell and $J_0 = e(J_p - J_n)$ be the total charge current (which is constant throughout the cell). Then $P = \Phi J_0$. The total solar energy absorption in the solar cell will be denoted by $Q_U = \int_0^d q_u \, dx$. The recombination rate at the electron contact equals $R_{surf}(0) = -J_p(0)$ and that at the hole contact $R_{surf}(d) = J_n(d)$. Using Eqs. (5), (8), and (12), Q_S is then given by

$$TQ_S = \int_0^d Tq_s \, dx + TQ_{S,surf}$$
$$= \int_0^d (q_u - E_{Fn}J'_n + E_{Fp}J'_p - E'_{Fn}J_n + E'_{Fp}J_p)dx$$
$$+ \sum_{x=\{0,d\}} [E_{Fn}(x) - E_{Fp}(x)]R_{surf}(x)$$
$$= Q_U - \Phi J_0 = Q_U - P. \qquad (14)$$
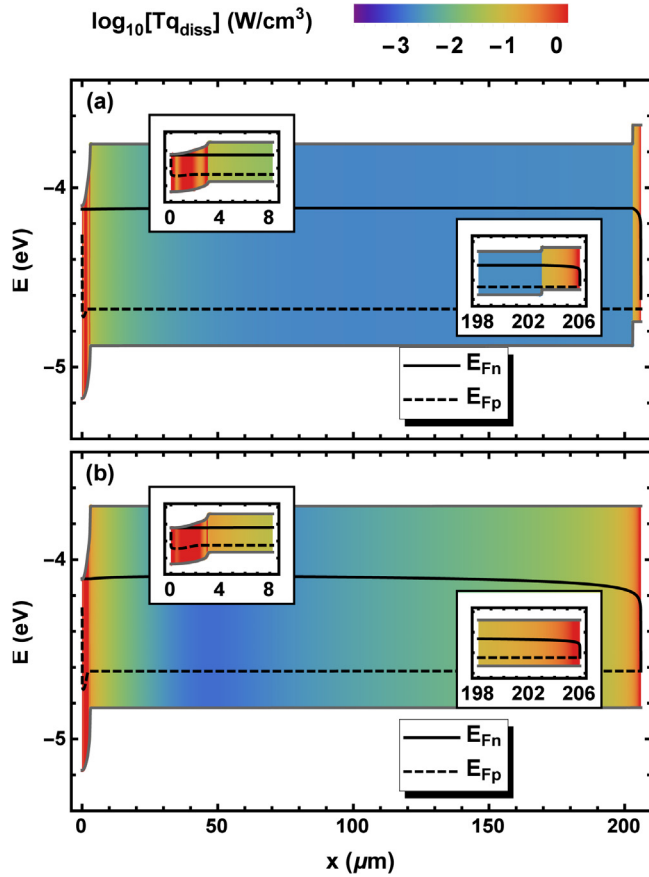
log$_{10}$[Tq$_{diss}$] (W/cm^3)

FIG. 2. Band diagram calculations (performed in AFORS-HET) of a *p*-type *c*-Si homojunction solar cell (a) with backside diffusion (BSF) and (b) without BSF. The entropy production rate is shown using a color map. The insets show magnifications near the surface of the cell. The BC $E_{Fn} = E_{Fp}$ was realized by choosing a sufficiently high surface recombination velocity.

Equation (14) demonstrates that the minimization of Q_S indeed leads to the maximization of P, provided that Q_U has been given (e.g., from optical modeling) or fixed in some other fashion. This again demonstrates that some care should be taken when minimizing entropy production, since a cell in equilibrium in the dark trivially produces no entropy.

III. VARIATIONAL SOLAR CELL OPTIMIZATION

With Eqs. (8) and (11), the total entropy generation rate Q_S can now be considered as a functional that depends on all relevant solar cell variables such as n, p, and ϕ: $Q_S = Q_S[n(\mathbf{x}), p(\mathbf{x}), \phi(\mathbf{x}), ...]$. This makes it possible to minimize Q_S using variational methods such as the EL method. There are, however, physical laws that need to be satisfied by the solution, so these laws need to be added as constraints to the optimization procedure. In addition, other practical constraints can be imposed as well. Hence, the VEGM method consists of four steps:

(1) The relevant unknowns are identified as well as the physical equations that need to be satisfied.
(2) The Lagrange multiplier method is used to construct a functional Λ which, when minimized, will lead to a solution that simultaneously minimizes Q_S and

satisfies all physical equations and additional constraints.
(3) The EL method is used to find the set of differential equations for the stationarity of Λ.
(4) The obtained set of equations is solved using a numerical method.

In the next paragraphs, the first three steps of the VEGM method will be illustrated by applying it to a homojunction solar cell to optimize the doping profile $\rho(\mathbf{x})$ (expressed in cm^{-3}). The solar cell will be modeled under assumptions commonly used in literature. This means that the device is considered at constant temperature T (so $\mathbf{F}_u = 0$) and under steady-state operation. It is assumed that the boundary of the cell $\partial\Omega$ consists of perfectly passivated surface (meaning that $R_{surf} = 0$) and metal contacts. At the metal contacts the boundary condition (BC) $E_{Fn} = E_{Fp}$ is assumed since Fermi level splitting is not possible in a metal. With these BCs, $Q_{S,surf} = 0$ in Eq. (12) and only bulk contributions to Q_S need to be considered. This does, however, not mean that recombination at the metal contacts does not generate entropy, but only that the entropy is generated in the bulk rather than at the contact (as can be seen in Fig. 2).

To obtain a transport model equivalent to ordinary semiconductor physics, the off-diagonal transport coefficients in Eq. (11) $L_{un} = L_{nu} = 0$, $L_{up} = L_{pu} = 0$ and $L_{np} = L_{pn} = 0$ are assumed negligible. Taken together, these assumptions amount to neglecting the Seebeck and Peltier effects as well as off-diagonal transport effects between electrons and holes. From a microscopic point of view, the assumption $L_{np} = 0$ means that electron-hole collisions are neglected.[13] The diagonal coefficients for charge transport are $L_{nn} = Tn\mu_n/e$ and $L_{pp} = Tp\mu_p/e$ (with $\mu_{n,p}$ being the electron/hole mobilities). The mobilities $\mu_{n,p} = \mu_{n,p}[\rho(\mathbf{x})]$ are assumed to depend on the doping density ρ. The local absorption of solar heat q_u is assumed known from optical modeling, as well as the generation rate $G = G(\mathbf{x})$. For recombination model R, the general form

$$R = R(\mathbf{x}, n, p, \rho) \qquad (15)$$

is used, indicating that R depends on n, p, and ρ as well as on $\mathbf{x}$ explicitly (due to, e.g., a position-dependent defect density). Furthermore, Boltzmann statistics will be assumed, so $E_{Fn,p}$ are related to n, p, and ϕ by

$$n = N_C \exp\left(\frac{E_{Fn} + \chi + \phi}{kT}\right), \qquad (16)$$

$$p = N_V \exp\left(-\frac{E_{Fp} + \chi + E_G + \phi}{kT}\right), \qquad (17)$$

with $N_{C,V}$ being the effective densities of states for the conduction and valence bands, χ and E_G the electron affinity and band gap (all assumed to be constant), and k the Boltzmann constant.

Next, the set of physical functions Y and transport equations Ξ that describe the solar cell are specified. The set of functions Y that will be used is given by: $Y = \{n, p, \phi, \rho\}$. If

the equations are stated as $\xi_i = 0$, the set of equations $\Xi = \{\xi_i\}$ is

$$\xi_1 = \nabla \cdot \left(-\frac{\mu_n n}{e}\nabla E_{Fn}\right) - (G - R),$$

$$\xi_2 = \nabla \cdot \left(\frac{\mu_p p}{e}\nabla E_{Fp}\right) - (G - R),$$

$$\xi_3 = \nabla^2 \phi + \frac{e^2}{\epsilon}(p - n + \rho).$$

Here, $\xi_{1,2}$ are the drift-diffusion equations and ξ_3 is the Poisson equation. Because ρ is considered to be an unknown, the set Ξ consists of three equations in the four unknowns Y and is therefore underdetermined. However, the requirement that the solution minimizes Q_S is used to make the problem well-posed.

To minimize Q_S subject to the constraints set by Eqs. Ξ, the following functional Λ is minimized:

$$\Lambda[Y, \{\lambda_i\}] = \int \left(Tq_s + \sum_{i=1}^{3}\lambda_i(\boldsymbol{x})\xi_i\right)\mathrm{d}V$$

$$= \int \Big(q_u - (E_{Fn} - E_{Fp})(G - R) - \nabla E_{Fn} \cdot \boldsymbol{J}_n \cdot$$

$$+ \nabla E_{Fp} \cdot \boldsymbol{J}_p + \sum_{i=1}^{3}\lambda_i(\boldsymbol{x})\xi_i\Big)\mathrm{d}V.$$

$$(18)$$

The functional Λ depends on the four functions Y as well as the three scalar Lagrange multiplier functions $\lambda_i(\boldsymbol{x})$, which ensure that Eqs. Ξ are satisfied for all $\boldsymbol{x} \in \Omega$.

Because Λ depends on seven scalar functions, there are also seven EL equations that correspond to the stationarity requirement $\delta\Lambda = 0$. The three EL equations for the λ_i reproduce the three Eqs. Ξ, while the EL equations for the four functions Y generate four new equations. The latter set of four equations can be simplified by making the substitutions $\lambda_1 = \hat{\lambda}_1 - E_{Fn}$ and $\lambda_2 = \hat{\lambda}_2 + E_{Fp}$. The resulting four differential algebraic equations (DAEs) are

$$\nabla \cdot \left(\frac{\mu_n n}{e}\nabla\hat{\lambda}_1\right) = n\frac{\partial R}{\partial n}\frac{\hat{\lambda}_1 + \hat{\lambda}_2}{kT} - \frac{\boldsymbol{J}_n \cdot \nabla\hat{\lambda}_1}{kT} - \frac{e^2 n \lambda_3}{\epsilon kT}, \quad (19a)$$

$$\nabla \cdot \left(\frac{\mu_p p}{e}\nabla\hat{\lambda}_2\right) = p\frac{\partial R}{\partial p}\frac{\hat{\lambda}_1 + \hat{\lambda}_2}{kT} - \frac{\boldsymbol{J}_p \cdot \nabla\hat{\lambda}_2}{kT} + \frac{e^2 p \lambda_3}{\epsilon kT}, \quad (19b)$$

$$\nabla \cdot (\mu_n n\nabla\hat{\lambda}_1 - \mu_p p\nabla\hat{\lambda}_2 + e\nabla\lambda_3) = 0, \quad (19c)$$

$$\frac{e^2}{\epsilon}\lambda_3 + \frac{\partial R}{\partial \rho}(\hat{\lambda}_1 + \hat{\lambda}_2) = \frac{\boldsymbol{J}_n \cdot \nabla\hat{\lambda}_1}{\mu_n}\frac{\partial \mu_n}{\partial \rho} + \frac{\boldsymbol{J}_p \cdot \nabla\hat{\lambda}_2}{\mu_p}\frac{\partial \mu_p}{\partial \rho}. \quad (19d)$$

The BCs for the $\lambda_{1,2,3}$ are obtained by considering the natural BCs that make Λ stationary (see, e.g., Wan[20] and the Appendix). The natural BCs depend on the BCs that have been imposed on the variables Y as well as on $Q_{S,surf}$. For example, if n and p are fixed at the boundaries (i.e., Dirichlet BCs) and $Q_{S,surf} = 0$ (as has been assumed here), the natural BCs require that $\lambda_1 = \lambda_2 = 0$ on $\partial\Omega$ (note that these BCs are

stated in terms of $\lambda_{1,2}$ rather than $\hat{\lambda}_{1,2}$). The BCs for λ_3 depend on those of ϕ: on boundaries with a Dirichlet BC for ϕ the BC $\lambda_3 = 0$ applies, while on boundaries with a Neumann BC on ϕ the BC $\hat{\boldsymbol{n}} \cdot \nabla\lambda_3 = \hat{\boldsymbol{n}} \cdot [2(\boldsymbol{J}_n - \boldsymbol{J}_p) + (\mu_p p/e)\nabla\lambda_2 - (\mu_n n/e)\nabla\lambda_1]$ applies (with $\hat{\boldsymbol{n}}$ the outward unit normal vector on $\partial\Omega$).

There are seven EL equations in seven the functions Y and $\lambda_{1,2,3}$, so the system of DAEs can be solved by a numerical method to obtain the optimal shape for ρ. This illustrates the trade-off between parametric optimization and the variational method: in the VEGM method the set of differential equations is larger and has to be derived for each particular optimization problem, but the numerical solution has to be computed only once and the shape functions such as ρ are optimized in complete generality rather than parametrically.

In conclusion, the framework of nonequilibrium thermodynamics offers a useful perspective for the analysis of local power losses in photovoltaic devices. By considering the entropy generation rate, it becomes possible to take into account electrical, optical and thermal losses and compare them on a uniform scale. The total entropy generation rate can be regarded as a functional, making it possible to optimize solar cells by taking advantage of the power of the calculus of variations. The design-predictive method of Variational Entropy Generation Minimization can take advantage of detailed models for, e.g., charge carrier recombination and mobility reduction due to semiconductor doping and use these models to predict, e.g., the optimal doping profile for a homojunction solar cell. In short, the VEGM method should be considered as an extension of the field of numerical solar cell modeling that makes it possible to find the optimal trade-off between the many complex loss mechanisms that occur in real solar cells.

ACKNOWLEDGMENTS

APPENDIX: BOUNDARY CONDITIONS FOR THE VEGM METHOD

Consider the homojunction solar cell in one-dimensional (1D) at constant T for simplicity. The domain of the cell is the interval $\Omega = [0, d]$ and the boundary of the cell consists of the two points $\partial\Omega = \{0, d\}$. The cell is described by the set of physical functions $Y = \{n, p, \phi, \rho\}$ and transport equations $\Xi = \{\xi_i\}$. This time the effect of the surface entropy generation will be accounted for in generality, so $Q_{S,surf} \neq 0$. The functional Λ then becomes

$$\Lambda[Y, \{\lambda_i\}] = \int_0^d \left(Tq_s + \sum_{i=1}^3 \lambda_i(x)\xi_i \right) dx + TQ_{S,surf}$$

$$= \int_0^d \left(q_u - (E_{Fn} - E_{Fp})(G - R) \right.$$

$$\left. - E'_{Fn}J_n + E'_{Fp}J_p + \sum_{i=1}^3 \lambda_i(x)\xi_i \right) dx$$

$$+ \sum_{x \in \partial\Omega} [E_{Fn}(x) - E_{Fp}(x)]R_{surf}(x)$$

$$= \int_0^d L(x)\, dx + \sum_{x \in \partial\Omega} L_B(x). \qquad (A1)$$

In Eq. (A1), the symbols L and L_B have been introduced. The part inside of the integral L is often referred to as the Lagrangian of the problem. The boundary term L_B will be called the boundary Lagrangian here, but sometimes it is also referred to as *salvage value* or *terminal payoff* (these terms are more common in variational problems in economics).

To obtain the proper BCs for the variational problem $\delta\Lambda = 0$, it is necessary to consider both the first order variation of L as well as that of L_B. Calculating this variation gives

$$\delta\Lambda = \int_0^d \left(\sum_y \frac{\partial L}{\partial y} \delta y + \frac{\partial L}{\partial y'} \delta y' + \frac{\partial L}{\partial y''} \delta y'' + \dots \right) dx$$

$$+ \sum_{x \in \partial\Omega} \sum_y \left(\frac{\partial L_B}{\partial y} \delta y + \frac{\partial L_B}{\partial y'} \delta y' + \frac{\partial L_B}{\partial y''} \delta y'' + \dots \right).$$

$$(A2)$$

The sum over y runs over all functions Y as well as the λ_i. Note that $\delta(y') = (\delta y)' = \delta y'$ since the functional differential δ commutes with ordinary derivatives such as d/dx. The EL equations are obtained by repeated application of partial integration on the integral in Eq. (A2) until no derivatives of the first order variations (i.e., $\delta y'$, $\delta y''$, etc.) appear under the integral anymore

$$\delta\Lambda = \int_0^d \sum_y \left(\frac{\partial L}{\partial y} - \left(\frac{\partial L}{\partial y'}\right)' + \left(\frac{\partial L}{\partial y''}\right)'' - \dots \right) \delta y\, dx$$

$$+ \sum_{x \in \partial\Omega} \sum_y \left\{ \left[\hat{\boldsymbol{n}}\left(\frac{\partial L}{\partial y'} - \left(\frac{\partial L}{\partial y''}\right)' \right) + \frac{\partial L_B}{\partial y} \right] \delta y \right.$$

$$\left. + \left[\hat{\boldsymbol{n}}\frac{\partial L}{\partial y''} + \frac{\partial L_B}{\partial y'} \right] \delta y' + \dots \right\}. \qquad (A3)$$

Here, $\hat{\boldsymbol{n}}$ is the 1D unit outward normal vector defined by $\hat{\boldsymbol{n}}(0) = -1$, $\hat{\boldsymbol{n}}(d) = 1$. Note that no assumptions have been made on the boundary values of δy and its derivatives yet. The requirement $\delta\Lambda = 0$ has consequence for both the part under the integral and for the boundary terms. Under the integral, the first order variation δy can be any infinitesimal function, so in order for the integral to be zero, the prefactor of δy has to be zero for every point x. Assuming that L does not depend on higher derivatives than y'', the EL equations are

$$\frac{d^2}{dx^2}\left(\frac{\partial L}{\partial y''} \right) - \frac{d}{dx}\left(\frac{\partial L}{\partial y'} \right) + \frac{\partial L}{\partial y} = 0. \qquad (A4)$$

The EL Eq. (A4) is a necessary condition for the stationarity of Λ, but it is not sufficient since the boundary terms in Eq. (A3) must be zero as well. On $\partial\Omega$, all variations δy and $\delta y'$ are independent of each other. This means that for every term one has to choose between setting the variation equal to zero (i.e., picking a BC for y or y') or setting the prefactor of that variation to zero. The latter choice results in a so-called natural BC.

To illustrate this, consider the boundary terms involving δn and $\delta n'$ on the boundary $x = d$. It is assumed that this is the hole-collecting boundary and therefore $R_{surf}(d) = \hat{\boldsymbol{n}}J_n(d)$. Because the variations in n and n' are independent, each of the terms involving $\delta n(d)$ and $\delta n'(d)$ have to be zero, so

$$\left(E'_{Fn} + \lambda'_1 + \frac{(\lambda_1 + E_{Fn} - E_{Fp})\phi'}{kT} \right)\delta n(d) = 0, \qquad (A5a)$$

$$(\lambda_1 + E_{Fn} - E_{Fp})\delta n'(d) = 0. \qquad (A5b)$$

Both Eqs. (A5a) and (A5b) have to be satisfied, but $\delta n(d)$ and $\delta n'(d)$ cannot be zero simultaneously since the transport equation for n is second order. This means that a choice has to be made between imposing either a Dirichlet BC for n (so $\delta n(d) = 0$) or a Neumann BC ($\delta n'(d) = 0$). A Dirichlet BC for n leads to a natural BC for λ_1 specified by Eq. (A5b) while a Neumann BC leads to a natural BC for λ_1 specified by Eq. (A5a). The BCs for λ_3 are similarly obtained by considering the boundary terms involving $\delta\phi$ and $\delta\phi'$.

In solar cell modeling, it is often desirable to consider more general types of BC than just Dirichlet and Neumann BCs. Such general BCs can be employed in the VEGM method by the use of Lagrange multipliers. For example, the recombination at the metal contact can be described by an effective surface recombination velocity S_{eff}: $R_{surf} = S_{eff}\Delta n$. Here, Δn is the injection level, which is approximately n at the hole-collecting contact. The desired BC for electron transport is therefore: $J_n(d) = \hat{\boldsymbol{n}}S_{eff}\, n(d)$. This mixed BC cannot be used directly in the variational approach since it makes the variations in $\delta n(d)$ and $\delta n'(d)$ interdependent. To remedy this, the BC is enforced with a (scalar) Lagrange multiplier λ_n by adding the term $\lambda_n[J_n(d) - \hat{\boldsymbol{n}}S_{eff}\, n(d)]$ to the boundary Lagrangian L_B. After that, Λ is minimized with respect to λ_n in addition to all the other variables, thus ensuring that the BC $J_n(d) = \hat{\boldsymbol{n}}S_{eff}\, n(d)$ is satisfied by the solution. The boundary terms for $\delta n(d)$, $\delta n'(d)$ and $\delta\lambda_n$ are then

$$\left(\left[\frac{\phi'}{kT} - \hat{\boldsymbol{n}}\frac{eS_{eff}}{kT\mu_n} \right]\lambda_n + E'_{Fn} + \lambda'_1 \right.$$

$$\left. + \frac{(\lambda_1 + E_{Fn} - E_{Fp})\phi'}{kT} \right)\delta n(d) = 0 \qquad (A6)$$

$$(\lambda_1 + \lambda_n + E_{Fn} - E_{Fp})\delta n'(d) = 0, \qquad (A7)$$

$$(J_n - \hat{\boldsymbol{n}}S_{eff}\, n)\delta\lambda_n = 0. \qquad (A8)$$

In this case, natural BCs have to be used to satisfy Eqs. (A6–A8), since $\delta n(d)$, $\delta n'(d)$, and $\delta \lambda_n$ are all nonzero. From Eqs. (A6) and (A7), the multiplier λ_n can be eliminated to obtain the (mixed) BC for λ_1.

[1] W. Shockley and H. J. Queisser, J. Appl. Phys. **32**, 510 (1961).

[2] C. H. Henry, J. Appl. Phys. **51**, 4494 (1980).

[3] A. De Vos and H. Pauwels, Appl. Phys. **25**, 119 (1981).

[4] A. Richter, M. Hermle, and S. W. Glunz, IEEE J. Photovolt. **3**, 1184 (2013).

[5] D. Clugston and P. Basore, in *Conference Record of the Twenty Sixth IEEE Photovoltaic Specialists Conference-1997* (IEEE, 1997), pp. 207–210.

[6] R. Stangl, C. Leendertz, and J. Haschke, in *Solar Energy*, edited by R. D. Rugescu (InTech, 2010), pp. 319–352.

[7] B. Pieters, J. Krc, and M. Zeman, in *2006 IEEE 4th World Conference on Photovoltaic Energy Conference* (IEEE, 2006), pp. 1513–1516.

[8] P. Würfel, *Physics of Solar Cells* (Wiley-VCH Verlag GmbH & Co, 2005).

[9] S. de Groot and P. Mazur, *Non-equilibrium Thermodynamics* (Dover Publications, 1984).

[10] G. D. Kuiken, *Thermodynamics of Irreversible Processes* (Wiley, 1994).

[11] M. L. Bellac, F. Mortessagne, and G. G. Batrouni, *Equilibrium and Non-Equilibrium Statistical Thermodynamics* (Cambridge University Press, 2004).

[12] S. Kjelstrup and D. Bedeaux, *Non-Equilibrium Thermodynamics of Heterogeneous Systems* (World Scientific Publishing Co. Pte. Ltd., 2008).

[13] U. Lindefelt, J. Appl. Phys. **75**, 942 (1994).

[14] J. Parrott, IEEE Trans. Electron Devices **43**, 809 (1996).

[15] A. Polman and H. A. Atwater, Nat. Mater. **11**, 174 (2012).

[16] It should be noted that different arguments to obtain this expression for J_s can be found in literature. We adopt the view that the First Law in the form of Eq. (4) determines the relationship between the currents given in Eq. (7).

[17] R. Brendel, S. Dreissigacker, N.-P. Harder, and P. P. Altermatt, Appl. Phys. Lett. **93**, 173503 (2008).

[18] J. Greulich, H. Höffler, U. Würfel, and S. Rein, J. Appl. Phys. **114**, 204504 (2013).

[19] L. Onsager, Phys. Rev. **37**, 405 (1931).

[20] F. Y. Wan, *Introduction to the Calculus of Variations and its Applications* (Chapman and Hall, 1995).