Ben-Gurion University of the Negev

Thermodynamic considerations in the photovoltaic systems detailed balance law

23rd Sede Boqer Symposium on Solar Electricity Production

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Outline

1. Thermodynamic approach (thermo)
2. Photovoltaics approach (PV)
3. Inconsistency of the two approaches
4. Possible solution: The unified approach
5. The unified approach at open circuit
6. The unified approach doing work
7. Conclusions

Thermodynamics

Thermodynamics of power production

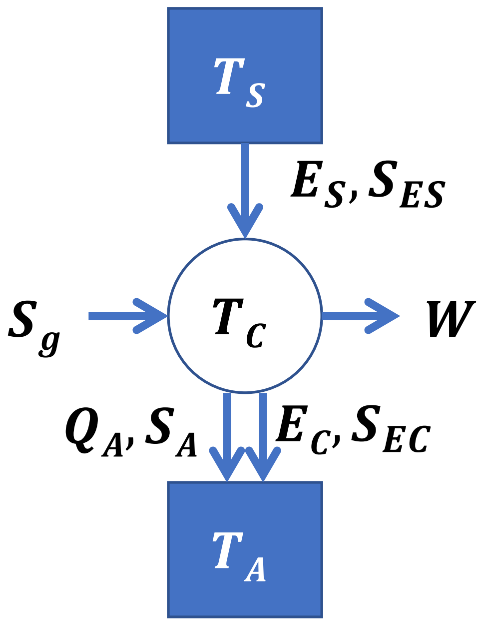
- **The 1st law (Conservation of the energy flux):** $E_{in} = E_{out}$
- **The 2nd law (Positive entropy production):** $S_{gen} = S_{out} - S_{in} \geq 0$

1. The thermodynamic available work is found by balancing the energy and entropy fluxes between the hot and the cold reservoirs.

2. Since the entropy law does not establishes a unique connection, so is available work.

3. The thermodynamic limit of for the available work is found by looking for the set of parameters that maximizes it.

Example: The available work from the sun's radiative heat flux – The Landsberg's Efficiency



- First (Energy) law: $E_S = E_C + Q_A + W$
- Second (Entropy) law: $S_{ES} + S_{gen} = S_{EC} + S_A$

  For the conductive heat: $S_A = \frac{Q_A}{T_A}$

- Now, the entropy law become: $Q_A = (S_{ES} + S_{gen} - S_{EC})T_A$
- And the work: $W = E_S - E_C - (S_{ES} + S_{gen} - S_{EC})T_A$
- The efficiency: $\eta \triangleq \frac{W}{E_S} = \left(1 - \frac{T_A S_{ES}}{E_S}\right) - \left(1 - \frac{T_A S_{EC}}{E_S}\right)\frac{E_C}{E_S} - \frac{T_A S_{gen}}{E_S}$

  For a black body:

$$E = \sigma T^4 \qquad\qquad S = \frac{4E}{3T}$$

We find:

$$\eta = 1 - \frac{4T_A}{3T_S} + \frac{4T_A T_C^3}{3T_S^4} - \frac{T_C^4}{T_S^4} - \frac{T_A S_{gen}}{E_S}$$

Maximal efficiency:

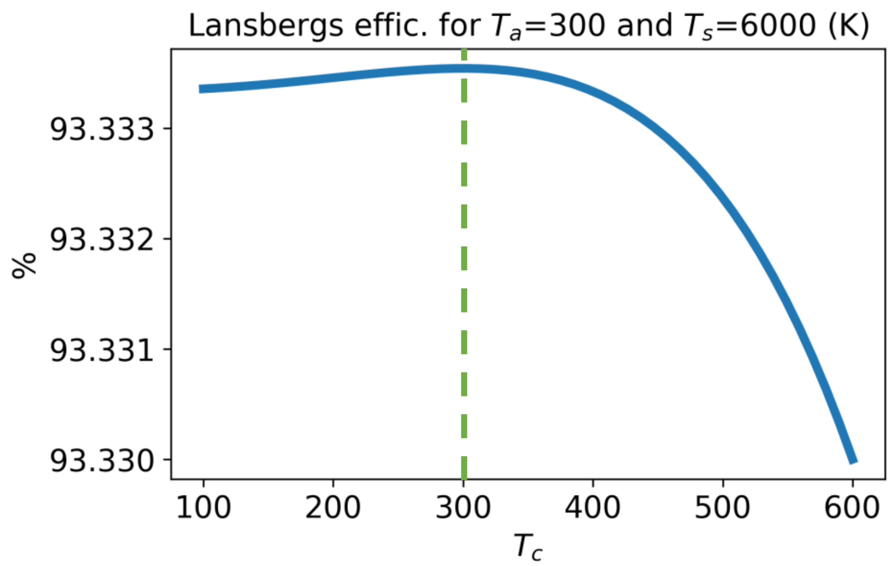
$$S_{gen} = 0$$

$$T_C = T_A$$

Whereupon:

$$\eta = 1 - \frac{4T_A}{3T_S} + \frac{T_A^4}{3T_S^4}$$

Which is the “Landsberg efficiency”



- For $T_s = 6000K$ and $T_A = 300$: η_L =0.933
- Landsberg analysis, therefore, does not carry much “improvement” over Carnot’s 0.95 efficiency.
- The lack of additional constraints allows $S_{gen} = 0$.

Photovoltaics

The Photovoltaic (PV) effect

- The photovoltaic effect is governed by *detailed balance* (DB), which is also a conservation law but for the number of particles, not their energy or entropy:

Number of generated particles = Number of depleted particles

- For an equilibrium between photons and charge-carriers, the particle number (rate) is:

$$N(V,T) = \frac{2\Omega Ae}{c^2h^3}\int_g^\infty \frac{E^2dE}{\exp\left(\frac{E-V}{kT}\right)-1}$$

- The number of particles is a function of the following parameters:
  - g is the semiconducting material bandgap
  - Ω is a geometric radiation factor (solid angle of beam)
  - A is the area
  - V is the chemical potential (free energy of particle)
  - T is the temperature

The photovoltaic efficiency: The Shockley & Queisser approach

- The DB including the current, I:

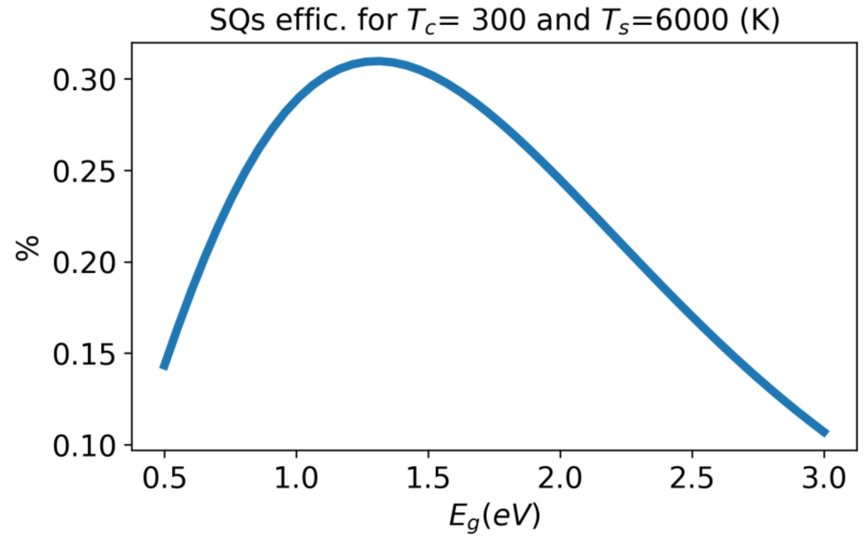
$$N(0,T_s) = N(V,T_c) + I(V)$$

$T_{s,c}$ are the sun and cell temperatures, respectively (with corresponding $\Omega_{s,c}$ factors).

- This single constraint is solved for $I(\mathrm{V})$ at a given T_c, and the efficiency is:

$$\eta = \frac{VI}{P_{sun}}$$

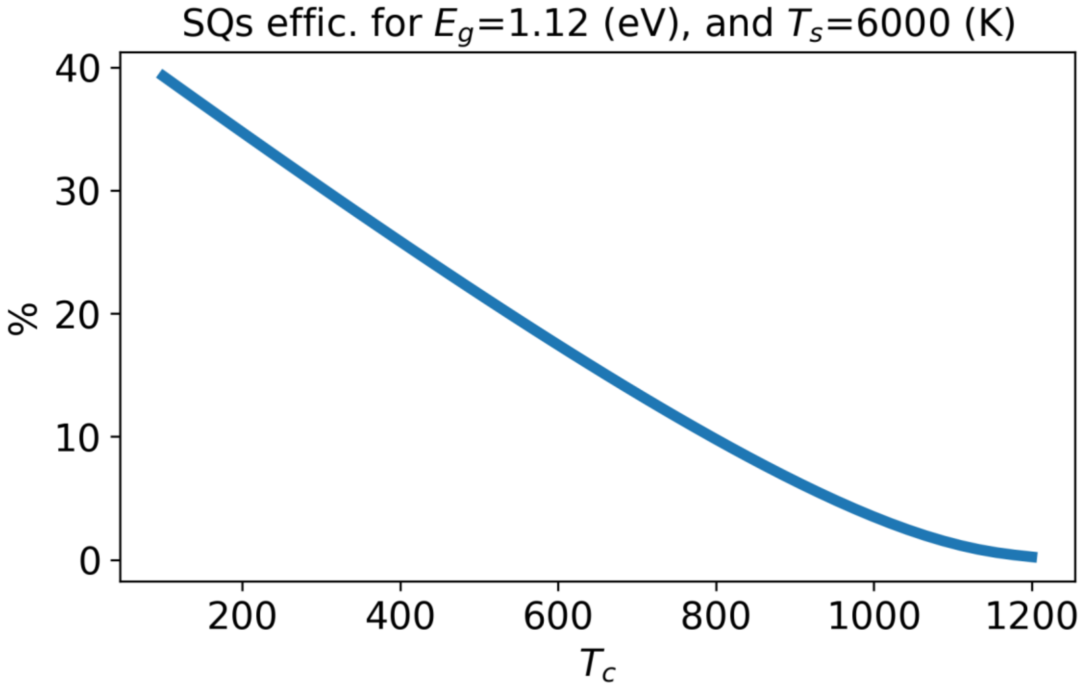
P_{sun} is the insolation power (power carried by sun's radiation).




```
# Sys params
Ts = 6000*k/e     # suns temp
Tc = 300*k/e      # cell's temp
Os = 6.87e-5      # sun's viewing solid angle
Oc = pi           # cell's viewing solid angle
```

SQ limit as a function of the cell's temp

- We can also calculate the SQ effic. as a function of the cell's temp for a fixed bandgap.
- In this case, we find that the efficiency drops with increasing temperature:



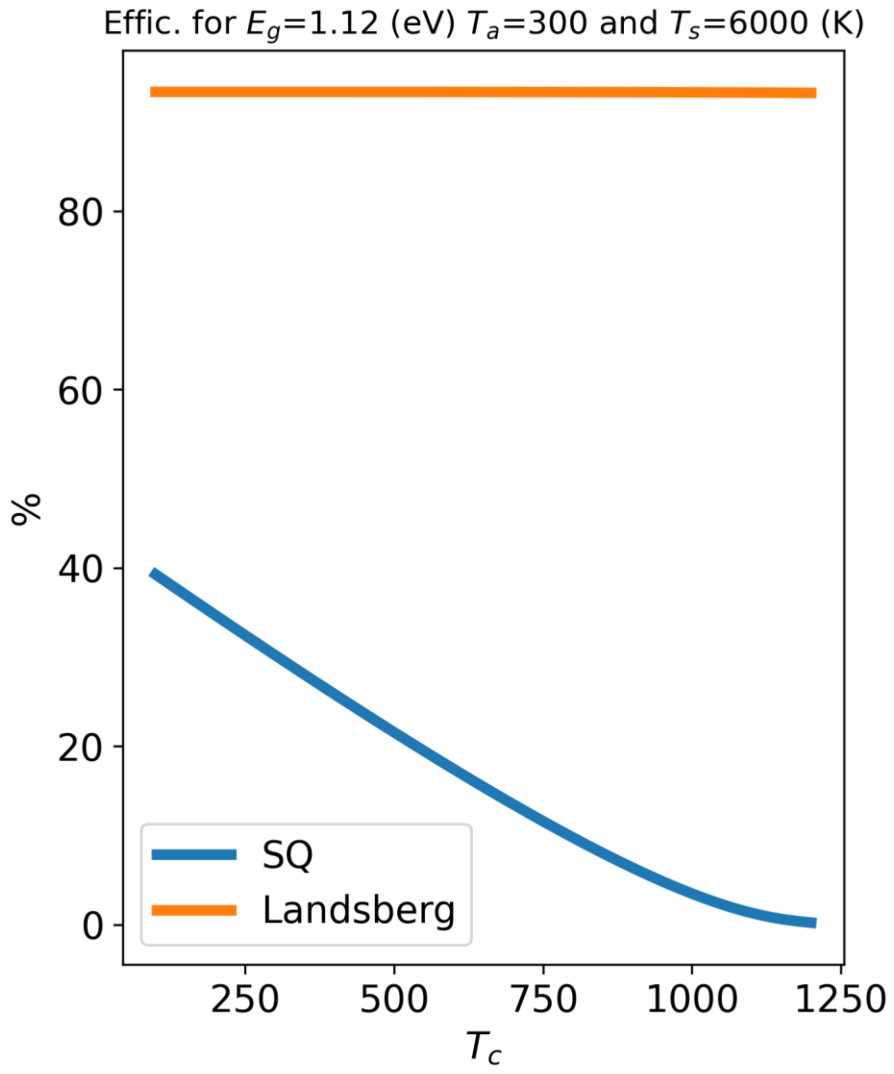
Inconsistency of Thermodynamics and the detailed balance approach

Let us compare the two approaches

The two approaches yields radically different results for a similar scenario

- Landsberg follows from thermodynamics 1st and 2nd laws:
  - ➢ No account of a bandgap.

- SQ follows from the DB law:
  - ➢ The existence of bandgap substantially reduces the efficiency
  - ➢ No explicit account is made of thermodynamics' laws



(Classical) Thermodynamics interpretation of the DB law

There is a substantial body of literature (Ross 1967, Wurfel 1980, Markvart 2008, and more) that shows that at open circuit conditions ($I = 0$) the following holds:

$$N(0, T_s) = N(V, T_c) \Rightarrow V_{oc} \simeq \left(1 - \frac{T_c}{T_s}\right) E_g + kT_c \log(\phi)$$

where ϕ is the quantum efficiency of the process and kT_c is in eV units

The above is not satisfying from the following reasons:

- This is an approximation for $E_g > kT_c$.
- No work is done at open circuit, whereas the primer objective of thermodynamics (in the spirit of Carnot, Landsberg, etc.) is to find the maximal available work.

Where is the power production thermodynamics in the DB approach?

- The DB law is based on the cell temp., T_c, and its potential, V:

$$N(0, T_s) = N(V, T_c) + I$$

Seemingly, we have one equation with two unknowns, V and T_c.

SQ solved this by assuming that the cells temp., T_c, is known (and equal to that of its immediate surroundings).

One can say that there is a corresponding (un-written) energy balance:

$$\mathrm{Q} = E(0, T_s) - E(V, T_c) - \tilde{E}I$$

Namely, the surplus of energy is conducted as heat (Q).

Here, $N(V,T)$ and $E(V,T)$ are the following integrals:

- The rate integral:

$$N(V,T) = \frac{2\Omega Ae}{c^2h^3}\int_g^\infty \frac{E^2 dE}{\exp\left(\frac{E-V}{kT}\right)-1}$$

- The energy integral:

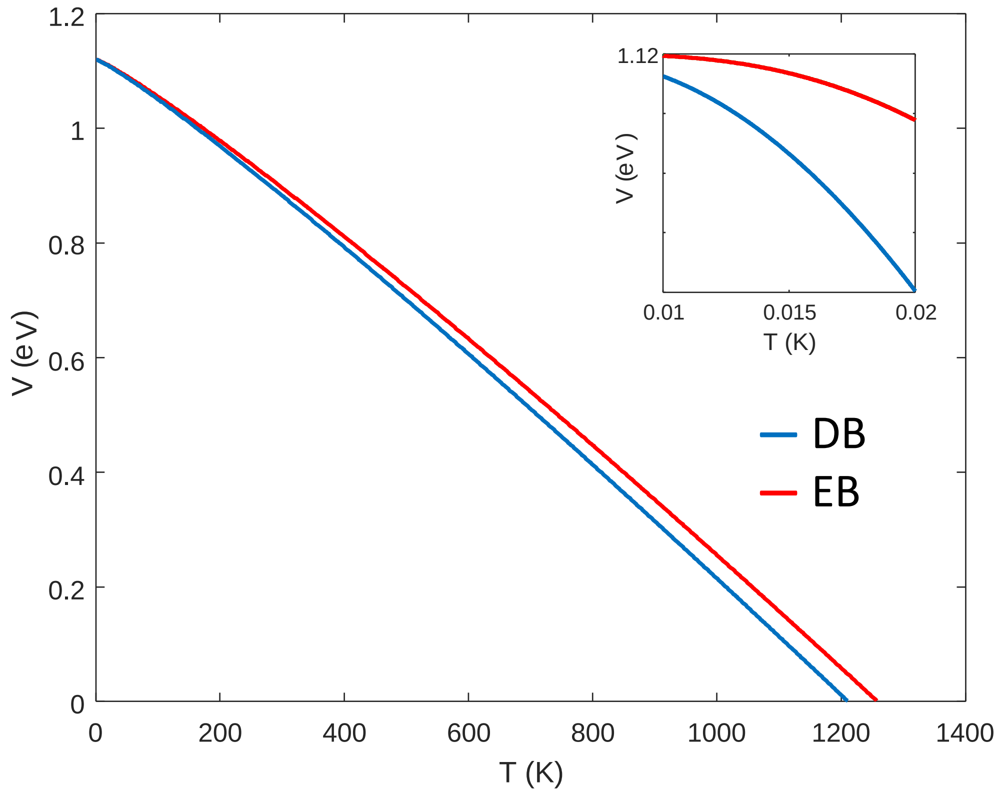
$$E(V,T) = \frac{2\Omega Ae}{c^2h^3}\int_g^\infty \frac{E^3 dE}{\exp\left(\frac{E-V}{kT}\right)-1}$$

What if there is no environment?

- Let us imagine a piece of a silicon wafer floating freely in outer space.
- If there is no environment, then $Q = 0$.
- Let us further assume that this wafer is facing the sun while its back is prevented from radiating (by being pained white, for example).
- What would be the solution of the pertaining detailed and energy balances:

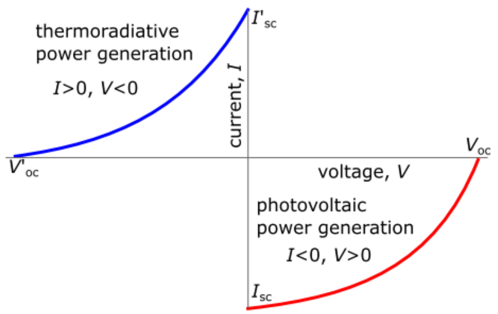
$$N(0, T_s) - N(V, T_c) = 0$$
$$E(0, T_s) - E(V, T_c) = 0$$

- Seemingly, we have two equations with two unknows.
- Unfortunately, however, the two cannot be mutually solved.
    - The energy balance (EB) and the detailed balance (DB) do not admit a simultaneous solution over a thermodynamic acceptable range of parameters ($T > 0$ and $0 < V < g$).

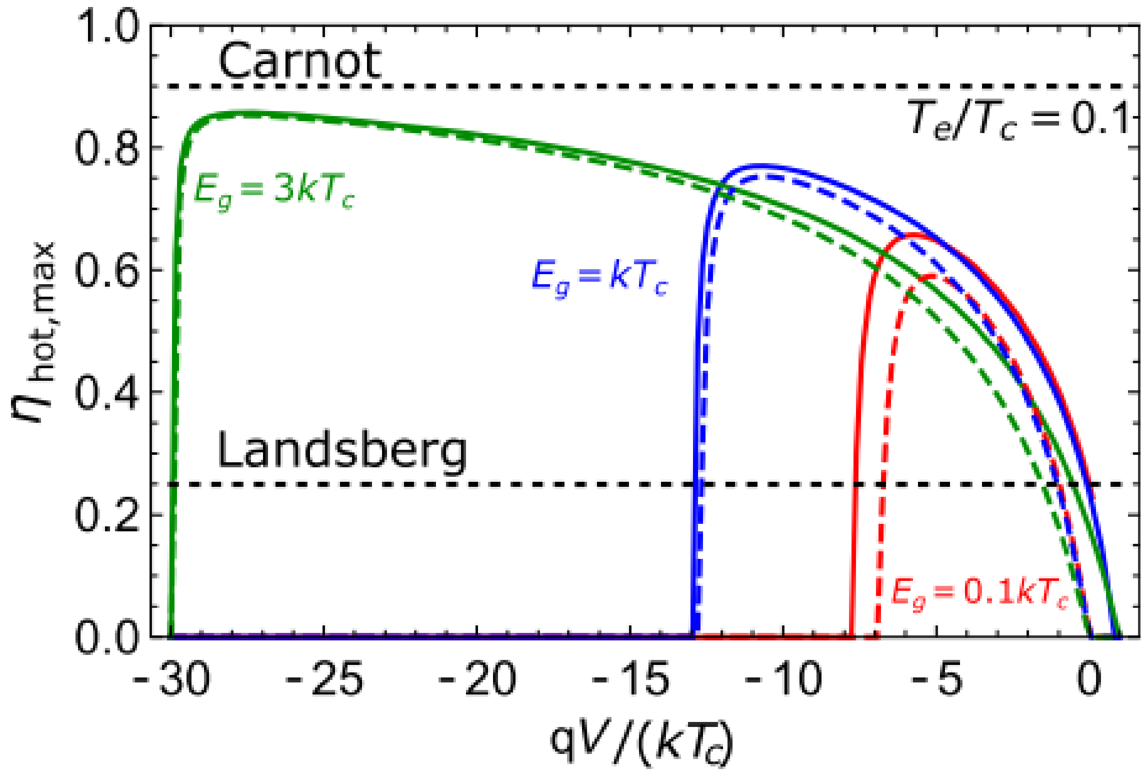


Parameters are chosen to resemble a Si cell on an earth-like orbit: $\Omega_s = 6.87 \times 10^{-5} sr$, $\Omega_c = \pi\ sr$, $g = 1.12\ eV$, $T_s = 5778\ K$.

Similarly for a thermo-radiative process



Phys. Rev. Appl. 12, 064018 (2019)



- **Solid line: Thermodynamics of power generation**
- **Dashed line: The DB approach**

Conclusion: DB and thermodynamics 1st law are not always in agreement!

Similar conclusions:

1. It is not always true that the DB law is agreement with the thermodynamics of power generation.
2. The SQ approach is for zero heat resistivity to a material environment.
3. There is a fundamental shortcoming in our present understanding of the PV effect.

Possible solution

What can possibly resolve this issue

1. Non-equilibrium
2. No DB an open circuit cell with $Q = 0$

➢ Cons: It is expected that a single-junction cell in outer space would have a well-defined temperature and potential at open circuit.

We are inclined to look for a quasi-equilibrium solution.

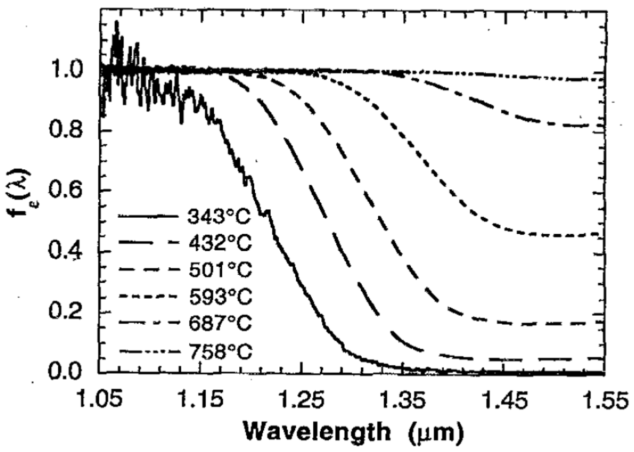
➢ Energy and detailed balance integrals are valid and retains their present form.

➢ Kirchhoff's radiation law is maintained.

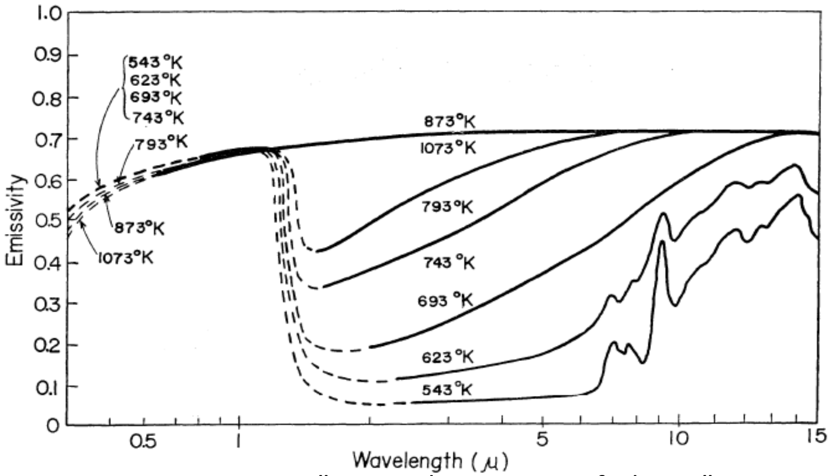
➢ We expect that removing heat conduction would elevate the cell’s temperature.

The SC emissivity at elevated temperatures

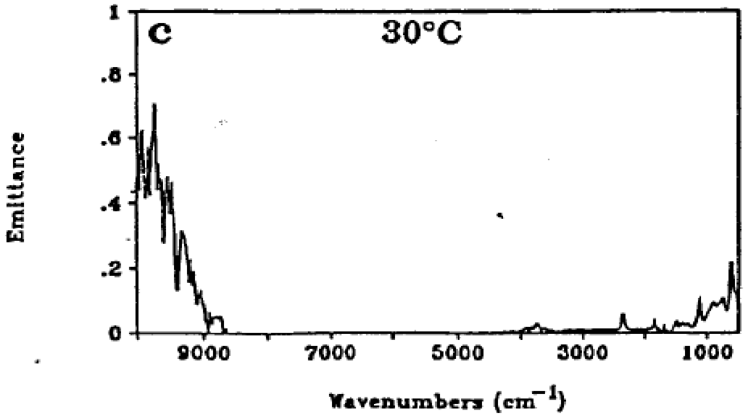
- Experiments shows that the sub-bandgap emissivity gradually rises with temperature.
- This trends continues until such temperature that the semiconductor becomes a black-body.

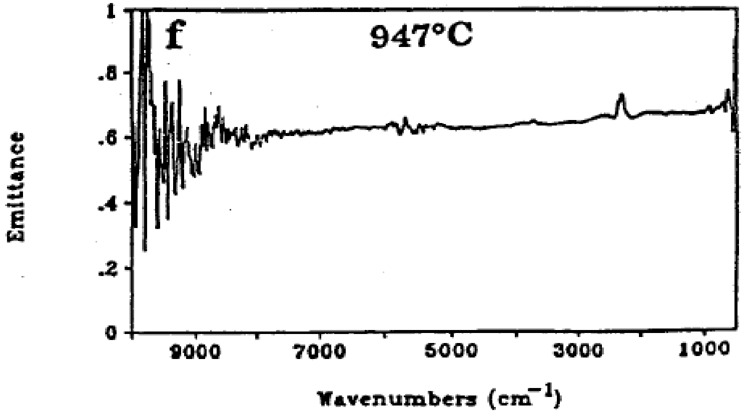


Timans, P. J. "Emissivity of silicon at elevated temperatures." *Journal of Applied Physics* 74.10 (1993): 6353-6364.



Satō, Tsutomu. "Spectral emissivity of silicon." *Japanese Journal of Applied Physics* 6.3 (1967): 339.



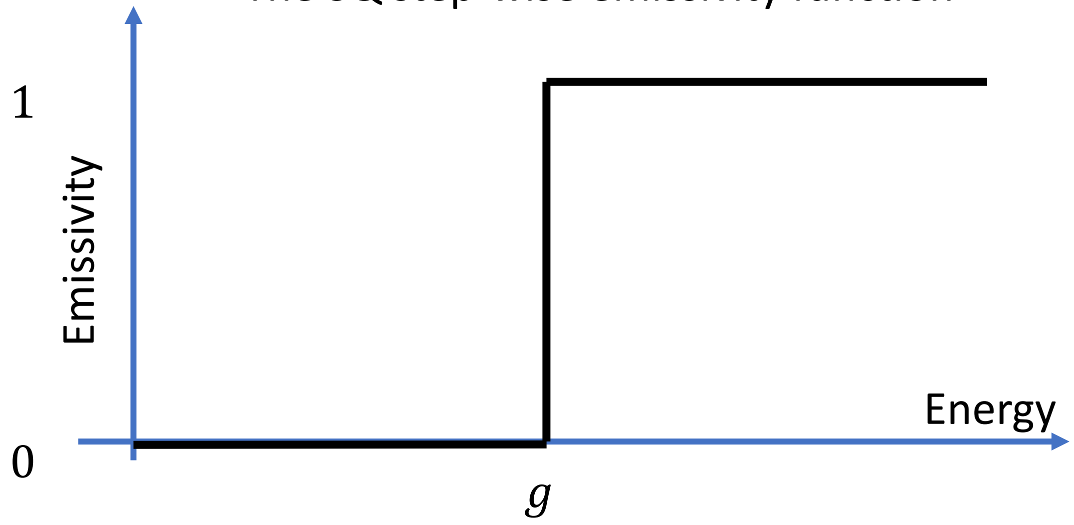


Ravindra, Nuggehalli M., et al. "Temperature-dependent emissivity of silicon-related materials and structures." *IEEE Transactions on semiconductor manufacturing* 11.1 (1998): 30-39.

SQ step emissivity hypothesis

- The SQ analysis considers a step emissivity for the SC.
- This emissivity gives maximum efficiency.
- Is it possible that the step emissivity case is an over-simplification from a thermodynamic perspective?
- Is it possible that a system must retain some nonzero sub-bandgap emissivity?

The SQ step-wise emissivity function



Step-wise emissivity function

$$\varepsilon = \begin{cases} 0 & E < g \\ 1 & E \geq g \end{cases}$$

Balance equations + sub-bandgap thermal emission

- DB an EB with sub-bandgap thermal emission:

$$N_g^{\infty}(0, T_s) = N_g^{\infty}(V, T_c)$$

$$\varepsilon_{sb} E_0^{g}(0, T_s) + E_g^{\infty}(0, T_s) = \varepsilon_{sb} E_0^{g}(0, T_c) + E_g^{\infty}(V, T_c)$$

  - We have added sub-bandgap emission proportionality factor ε_{sb}.
  - Sub-bandgap emission is thermal ($V = 0$).
  - This addition is not in violation of Kirchhoff's radiation law.

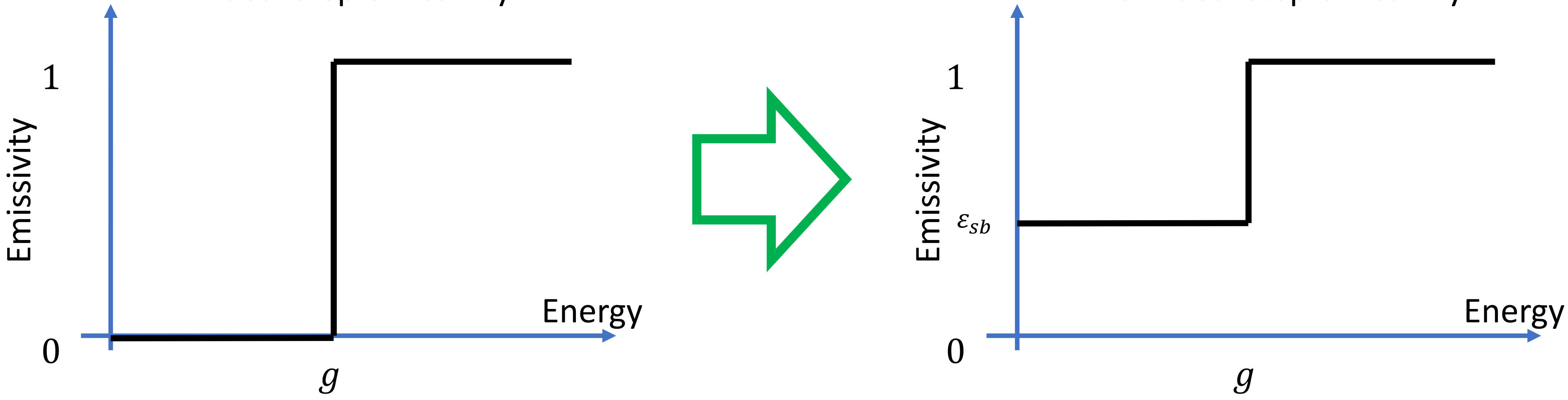
We propose to replace the ideal step-emissivity with somewhat less restrictive from of it

$$\varepsilon = \begin{cases} 0 & E < g \\ 1 & E \geq g \end{cases}$$

$$\varepsilon = \begin{cases} 0 \leq \varepsilon_{sb} \leq 1 & E < g \\ 1 & E \geq g \end{cases}$$

Ideal step emissivity

Non-ideal step emissivity

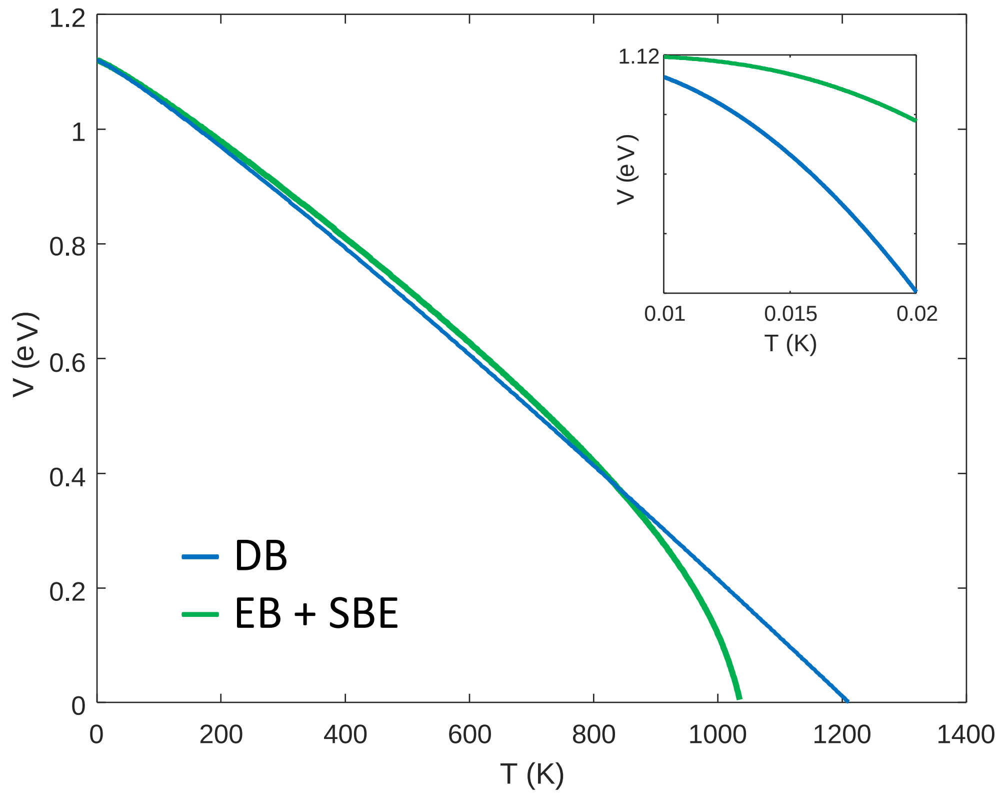


The effect of ε_{sb}

Intersection between DB and EB emerges.

- DB and EB are simultaneously solved for a given T and V
- Different ε_{sb} yields different solution (T and V).
- Each solution has a different work associated with it.
- We are interested in the maximal work.
- Maximal work corresponds to minimal entropy generation.

$\varepsilon_{sb} = 0.015$



The unified approach at open circuit

- DB:

$$N_g^\infty(0,T_s) = N_g^\infty(V,T_c)$$

- EB:

$$\varepsilon_{sb} E_0^g(0,T_s) + E_g^\infty(0,T_s) = \varepsilon_{sb} E_0^g(0,T_c) + E_g^\infty(V,T_c) + Q$$

- SB:

$$\varepsilon_{sb} S_0^g(0,T_s) + S_g^\infty(0,T_s) + S_g = \varepsilon_{sb} S_0^g(0,T_c) + S_g^\infty(V,T_c) + \frac{Q}{T_c}$$

  - Q is the heat conduction from the semiconductor to its environment
  - $\tilde{E}$ and $\tilde{S}$ are the charge-carrier energy and entropy removed from the system by the current I.

$N(V,T)$ and $E(V,T)$ are the following integrals:

Rate integral:

$$N_a^b(V,T) = \frac{2\Omega Ae}{c^2h^3}\int_a^b E^2\phi dE$$

Energy integral:

$$E_a^b(V,T) = \frac{2\Omega Ae}{c^2h^3}\int_a^b E^3\phi dE$$

Entropy integral:

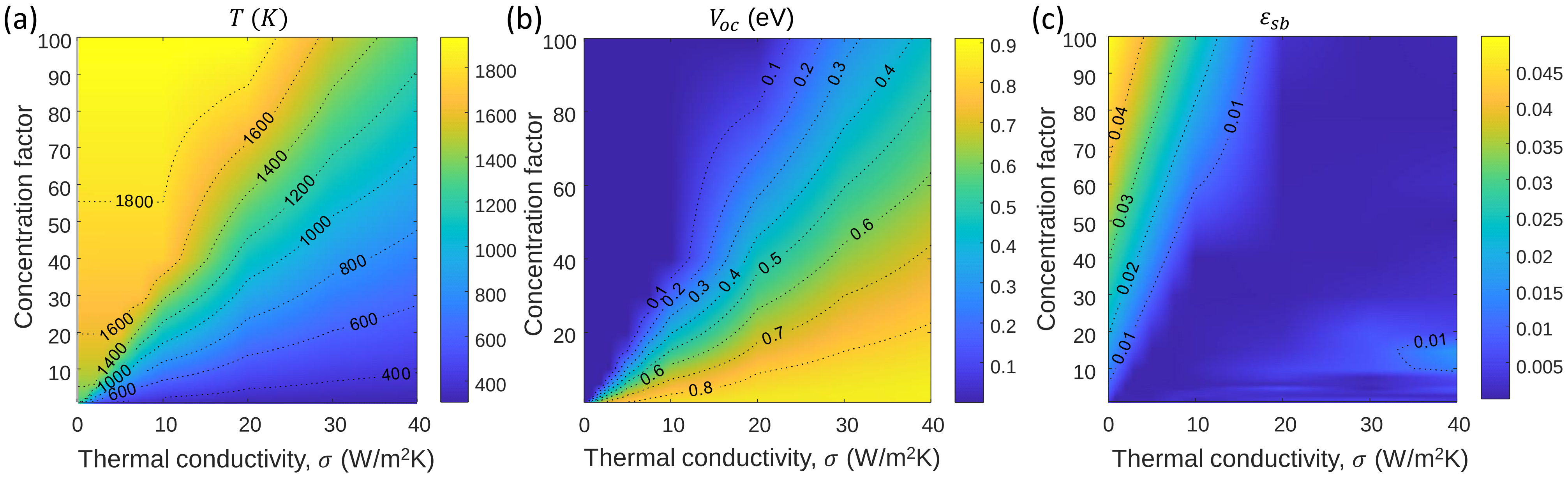
$$S(T,V) = \frac{2\Omega e}{c^2h^3}\int_g^\infty E^2[(\phi+1)\ln(\phi+1) - \phi\ln(\phi)]dE$$

Bosons per energy state (generalized Plank law / BE statistics): $\phi = \frac{1}{\exp\left(\frac{E-V}{kT}\right)-1}$

The open circuit of the unified approach

Open circuit as a function of the heat conduction and the solar concentration

- Heat conduction: $Q = \sigma(T_c - 300)$
- Concentration factor: $C = \frac{\Omega_s}{6.87\times10^{-5}}$



- Reasonable dependencies of T, V_{oc}, and ε_{sb} on the thermal conductivity and the solar concentration.
- Due to the minimization of S_g, there is non-zero ε_{sb} only once $V_{oc} = 0$.

Work production from the unified approach

The unified DB, EB, and SB approach with heat conduction and current

- DB:

$$N_g^{\infty}(0,T_s) = N_g^{\infty}(V,T_c) + I$$

- EB:

$$\varepsilon_{sb}E_0^g(0,T_s) + E_g^{\infty}(0,T_s) = \varepsilon_{sb}E_0^g(0,T_c) + E_g^{\infty}(V,T_c) + \tilde{E}I + Q$$

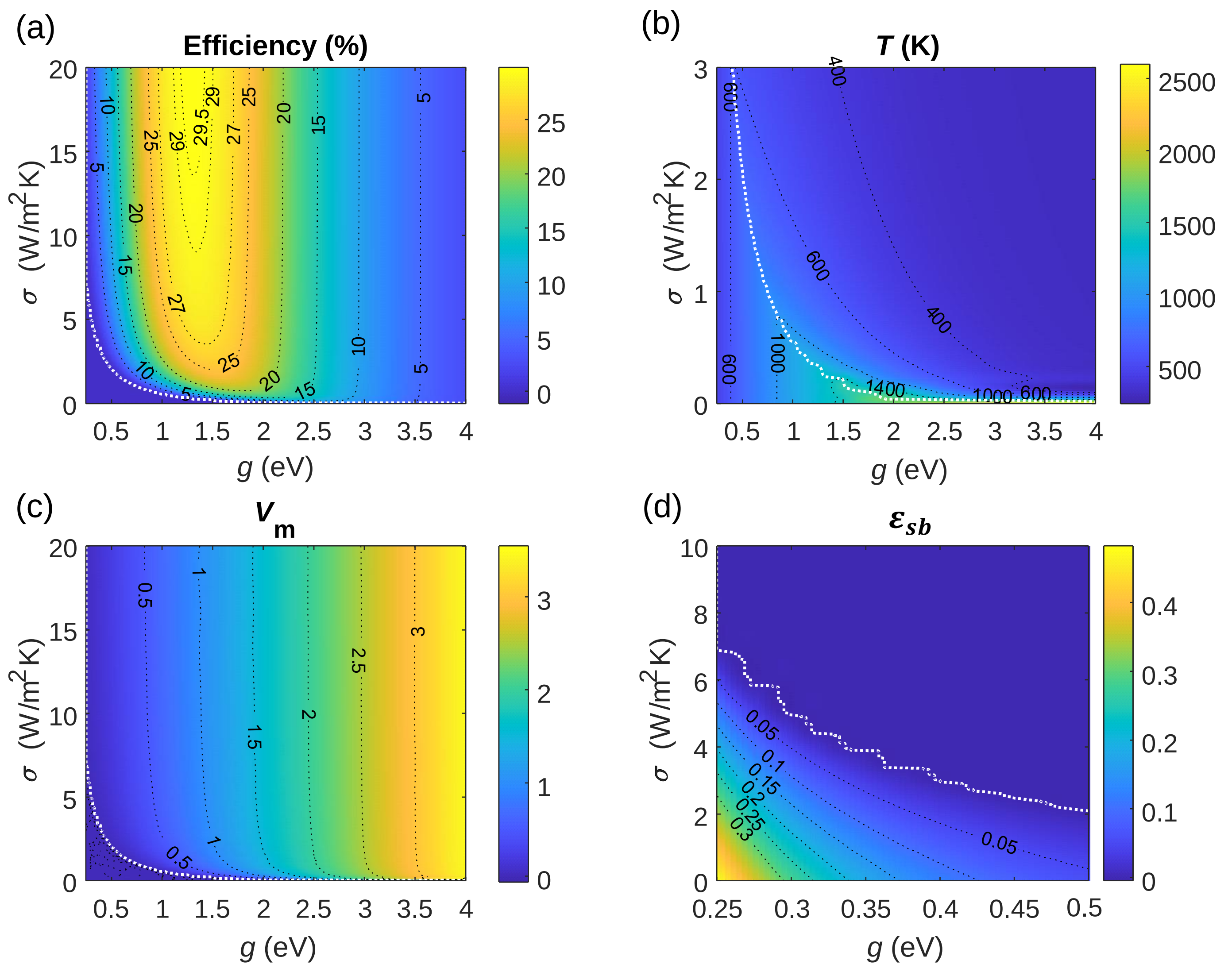
- SB:

$$\varepsilon_{sb}S_0^g(0,T_s) + S_g^{\infty}(0,T_s) + S_g = \varepsilon_{sb}S_0^g(0,T_c) + S_g^{\infty}(V,T_c) + \tilde{S}I + \frac{Q}{T_c}$$

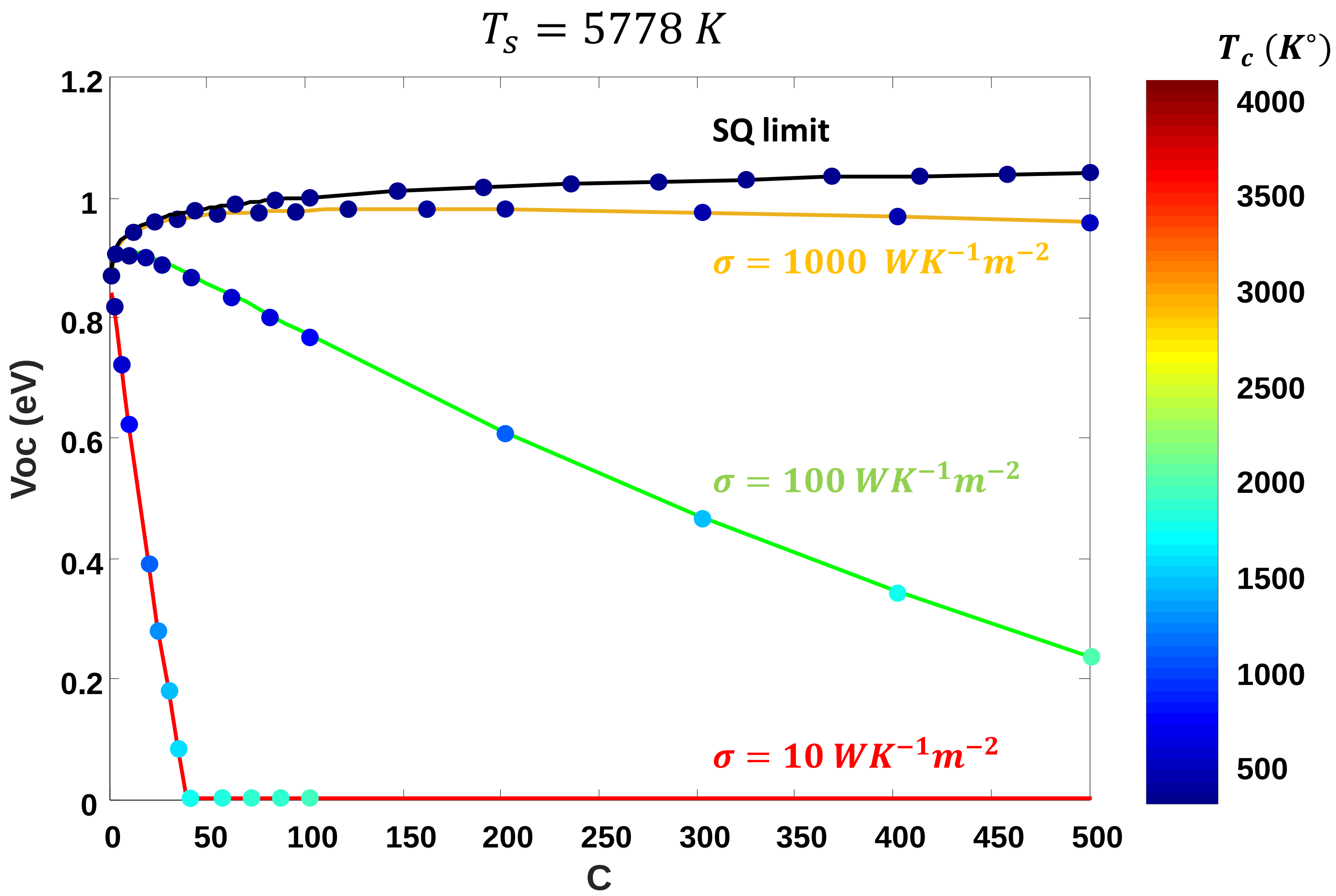
  - Q is the heat conduction from the semiconductor to its environment
  - $\tilde{E}$ and $\tilde{S}$ are the average energy and entropy of a single charge carrier:

$$\tilde{E} = \frac{E_g^{\infty}(V,T_c)}{N_g^{\infty}(V,T_c)} \qquad \tilde{S} = \frac{S_g^{\infty}(V,T_c)}{N_g^{\infty}(V,T_c)}$$

- Two regime appear:
  - Work producing one with $\varepsilon_{sb} = 0$
  - Thermal one with $V = 0$
- White dotted line indicates $V = \varepsilon_{sb} = 0$
- Temperature maxes on this line.
- Heat conduction is important at the optimal bandgap, less so for non-ideal ones.
- V_m is the potential for maximal work production.
- Scales are different among panels.

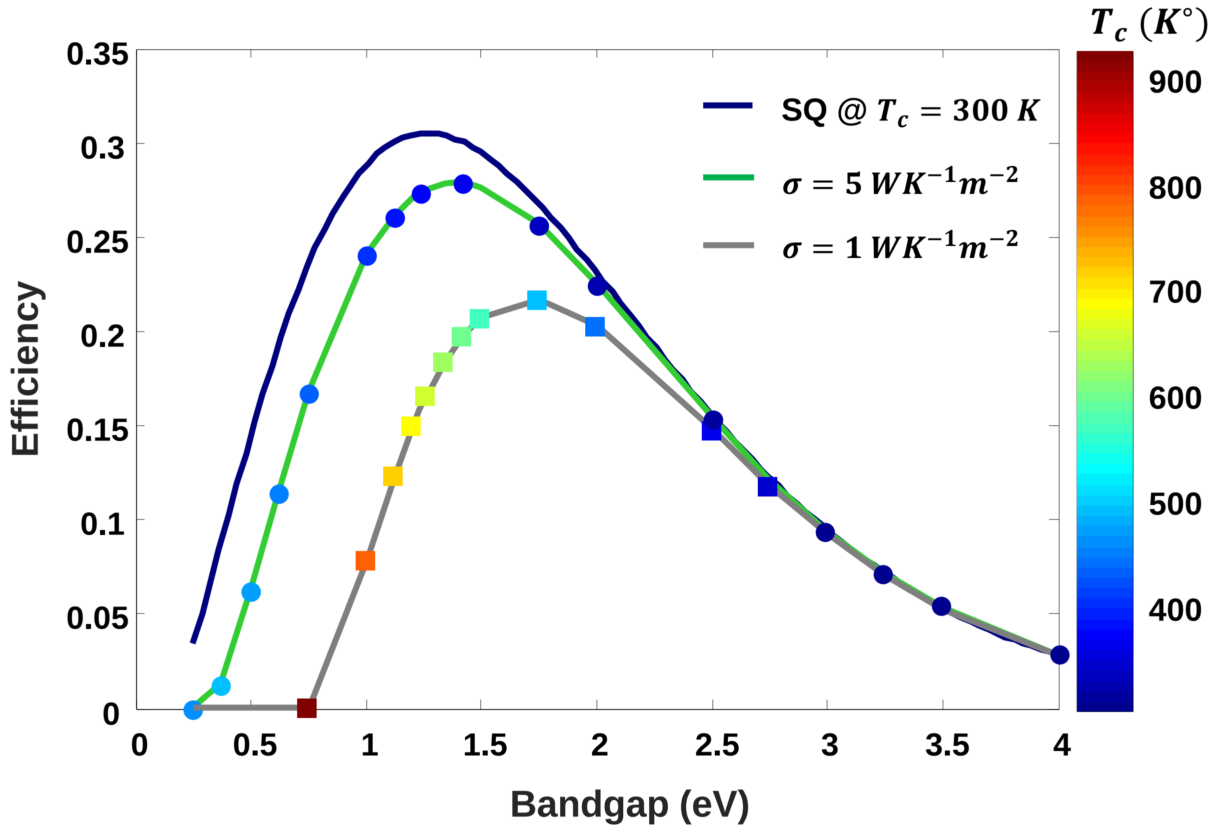


Another view on the Interplay between concentration (C) and heat conduction



Compared to the SQ efficiency plot

- The fixed temperature SQ calculations are replaced with a fixed heat conduction coefficient σ.
- Efficiency and optimal bandgap are affected by the ability to conduct heat.



* Calculations are for a 5800K black-body source

What could be the source of ε_{sb}?

- Carrier-carrier and carrier-phonon scattering are known intra-band dissipation mechanisms.
- Dissipation inevitably leads to charge oscillations (the fluctuation-dissipation theorem).
- Charge oscillation leads to radiation.
- Therefore, intra-band scattering causes ε_{sb}.
- Our model brings a thermodynamic justification for intra-band scattering.

Conclusions

- Detailed balance is not necessarily in agreement with thermodynamics 1st and 2nd laws in their present flux balance formulation.
- We propose that non-zero sub-bandgap emissivity should be included in the thermodynamic balance laws to resolve this issue.
- This proposition refines what should be considered an “ideal cell” in the Shockley and Queisser sense.
- The model foresees that the luminescence from a semi-conducting material would collapse to that of a black-body at elevated temperatures, which agrees with previous observations.
- The models foresees two operation regimes for a semi-conductor, a work producing one and a thermal one.
- The model brings forth the importance of heat conduction to solar cell efficiency calculations.
- Non-radiative recombinations can readily be incorporated to the model.
- At this stage, the model is a proposition pending experimental proof.

Thank you very much

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