Supporting Information for

Relating Band Edge DOS Occupancy Statistics Associated Excited State Electrons Entropy Generation to Free Energy Loss and Intrinsic V_{oc} Deficit of Solar Cells

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Appendix

1. Another derivation based on Sackur-Tetrode entropy equation

Another understanding of this point of view can start with the Sackur-Tetrode equation for the entropy of monatomic ideal gases.

Now consider the occupation of electrons over the density of states of semiconductor absorber of a solar cell. For solar cell under dark, the valence band of absorber would be completely occupied and the conduction band would be empty for any temperature *T*. Under this condition, the entropy *S* of the electrons would be zero, as there is only one possibility of producing a fully occupied valence band and an empty conduction band. While, promoting electrons from the valence band to the conduction band by light excitation would then lead to not only an increase in the energy, but also an increase in the entropy as well. This is because there are now many possibilities for removing an electron from any of about 10^{22} states/cm^3 of the valence band and exciting it to any of 10^{22} states/cm^3 of the conduction band.

In 1912, Sackur and Tetrode independently put forward an equation for the absolute entropy of a monoatomic classical ideal gas, which is known as the Sackur-Tetrode equation. This is a pioneering investigation about 100 years ago which incorporates quantum considerations. This entropy *S* at temperature *T* can be written as[1]:

$$\frac{S}{N} = k_{\mathrm{B}}\left\{\frac{5}{2} + \ln\left[\frac{V}{N}\left(\frac{2\pi m k_{\mathrm{B}} T}{h^2}\right)^{3/2}\right]\right\} = \sigma \qquad \text{(s1)}$$

where *N* is the number of particles in the gas, k_{B} is Boltzmann's constant, *V* is the volume of the gas, *m* is the mass of a gas particle and *h* is Planck's constant. Obviously, σ represents the (average) entropy of a single particle in the gas.

In solar cell, light excitation produces electrons in conduction band (CB) and holes in valence band (VB), which relax almost instantaneously (on the submillisecond time scale) to the conduction band minimum (CBM) and the valence band maximum (VBM) and to reach thermal equilibrium with the lattice semiconductor. A large number of such excited electrons form electron gas, which can be seen as ideal monoatomic gas.

Appling the Sackur-Tetrode equation to the electron gas and accounting for the fact that electrons (and holes) have two spin orientations, which doubles the number of possible states, for electrons/holes in a semiconductor, the equation is modified to:

$$\sigma_{\mathrm{e/h}} = k_{\mathrm{B}}\left\{\frac{5}{2}+\ln\left[\frac{2}{n}\left(\frac{2\pi m * k_{\mathrm{B}}T}{h^{2}}\right)^{3/2}\right]\right\} \qquad \text{(s2)}$$

where $n = N/V$ is the spatial density of electron and m is replaced be m^* of a semiconductor.

According to the equation 6, equation 31 can be re-written as:

$$\sigma_{\mathrm{e/h}} = k_{\mathrm{B}}\left(\frac{5}{2}+\ln\frac{N_{\mathrm{C}}(N_{\mathrm{V}})}{n(p)}\right) \qquad \text{(s3)}$$

Obviously, the only difference ($5/2k_{\mathrm{B}}$) of the equation s3 and 19 is the terms on the right. Note that the Boltzmann constant $k_{\mathrm{B}} \approx 1.38\times10^{-23}$ J/K, while the calculated average entropy of a single carrier as given in Figure 3c is on the order of 10^{-20} J/K, almost a thousand times that of k_{B}. Therefore, in equation s3, compared with the second term on the right, the first term can be ignored. This leads to:

$$\boldsymbol{\sigma}_{\mathbf{e/h}} = k_{\mathbf{B}}\left(\frac{5}{2}+\ln\frac{N_{\mathrm{C}}(N_{\mathrm{V}})}{n(p)}\right) \approx k_{\mathbf{B}}\ln\frac{N_{\mathrm{C}}(N_{\mathrm{V}})}{n(p)} = \Delta s_{\mathrm{e/h}} \qquad \text{(s4)}$$

This means that, the Sackur-Tetrode entropy of equation s2 and s3 is in fact the average entropy of a single carrier that we derived above, equation 19.

It has been proved that each conduction band electron (hole) in this gas has a mean kinetic energy of $3/2k_{\mathrm{B}}T$ and volume energy $k_{\mathrm{B}}T$ ($= pv$) with the potential energy E_{C} ($-E_{\mathrm{V}}$) as well as an entropy $\sigma_{\mathrm{e/h}}$. The free energy or electrochemical potential $\mu_{\mathrm{e/h}}$ of an excited state electron (hole) is the sum of these terms minus the entropy $\sigma_{\mathrm{e/h}}$ per charge carrier:

$$\left.\begin{aligned}
\mu_{\mathrm{e}} &= E_{\mathrm{C}}+\frac{5}{2}k_{\mathrm{B}}T - T\sigma_{\mathrm{e}} = E_{\mathrm{C}}+\frac{5}{2}k_{\mathrm{B}}T - k_{\mathrm{B}}T\left\{\frac{5}{2}+\ln\left[\frac{2}{n}\left(\frac{2\pi m_{\mathrm{e}}^{*}k_{\mathrm{B}}T}{h^{2}}\right)^{3/2}\right]\right\} && \text{(s5-1)}\\
\mu_{\mathrm{h}} &= -E_{\mathrm{V}}+\frac{5}{2}k_{\mathrm{B}}T - T\sigma_{\mathrm{h}} = -E_{\mathrm{V}}+\frac{5}{2}k_{\mathrm{B}}T - k_{\mathrm{B}}T\left\{\frac{5}{2}+\ln\left[\frac{2}{p}\left(\frac{2\pi m_{\mathrm{h}}^{*}k_{\mathrm{B}}T}{h^{2}}\right)^{3/2}\right]\right\} && \text{(s5-2)}
\end{aligned}\right\}$$

Substituting the effective mass m^* of the electrons (holes) and effective density of states of the energy band from equation 16 for m we find:

$$\left.\begin{aligned}
\mu_{\mathrm{e}} &= E_{\mathrm{C}}+\frac{5}{2}k_{\mathrm{B}}T - k_{\mathrm{B}}T\left(\frac{5}{2}+\ln\frac{N_{\mathrm{C}}}{n}\right) && \text{(s6-1)}\\
\mu_{\mathrm{h}} &= -E_{\mathrm{V}}+\frac{5}{2}k_{\mathrm{B}}T - k_{\mathrm{B}}T\left(\frac{5}{2}+\ln\frac{N_{\mathrm{V}}}{p}\right) && \text{(s6-2)}
\end{aligned}\right\}$$

Thus, we have:

$$\Delta\mu = E_{\mathrm{Fn}} - E_{\mathrm{Fp}} = \mu_{\mathrm{C}} - \mu_{\mathrm{V}} = \mu_{\mathrm{e}} + \mu_{\mathrm{h}} = E_{\mathrm{g}} - k_{\mathrm{B}}T\ln\frac{N_{\mathrm{C}}N_{\mathrm{V}}}{np} \qquad \text{(s7)}$$

This result, obtained directly from entropy analysis of electron gas, is consistent with equation 5.

2. On the derivation of equation 15

In the main text, for equation 15

$$\begin{aligned}
&\Delta S = k_{\mathrm{B}}\ln\frac{N!}{(N-\mathrm{n})!\times n!} = k_{\mathrm{B}}\{\ln(N!) - \ln[(N-n)!] - \ln(n!)\} \\
&\approx k_{\mathrm{B}}\{(N\ln N - N) - [(N-n)\ln(N-n) - (N-n)] - (n\ln n - n)\} \qquad (15) \\
&= k_{\mathrm{B}}\left[N\ln\frac{N}{N-n} + n\ln\frac{N-n}{n}\right]
\end{aligned}$$

we simply make the following treatment:

the term $N\ln\frac{N}{N-n}$ is approximately equal to 0, as $N >> n$ and then $N - n \approx N$.

Considering that when $x \to 0$, ln (1+x) should approach x: ln (1+x) → x. Thus, a more accurate process of the above equation should be:

$$N\ln\frac{N}{N-n} = N\ln\frac{(N-\mathrm{n})+n}{N-n} = N\ln\left(1+\frac{n}{N-n}\right) \approx N\ln\left(1+\frac{n}{N}\right) \qquad \text{(s8)}$$

Considering ln (1+x) → x, when $x \to 0$, we should have:

$$N\ln\frac{N}{N-n} = N\ln\frac{(N-\mathrm{n})+n}{N-n} = N\ln\left(1+\frac{n}{N-n}\right) \approx N\ln\left(1+\frac{n}{N}\right) \approx N\frac{n}{N} = n \qquad \text{(s9)}$$

Then equation s9 should be:

$$\Delta S \approx k_{\mathrm{B}}\left(n + n\ln\frac{N}{n}\right) = nk_{\mathrm{B}}\left(1+\ln\frac{N}{n}\right) \qquad \text{(s9')}$$

And thus the entropy changes of excited n electrons and p holes are:

$$\left.\begin{aligned}
\Delta S_{\mathrm{e}} &\approx k_{\mathrm{B}}\left(n+n\ln\frac{N_{\mathrm{C}}}{n}\right)=nk_{\mathrm{B}}\left(1+\ln\frac{N_{\mathrm{C}}}{n}\right) && \text{(s10-1)}\\
\Delta S_{\mathrm{h}} &\approx k_{\mathrm{B}}\left(p+p\ln\frac{N_{\mathrm{V}}}{p}\right)=nk_{\mathrm{B}}\left(1+\ln\frac{N_{\mathrm{V}}}{p}\right) && \text{(s10-2)}
\end{aligned}\right\}$$

Accordingly, the average entropy per electron/hole becomes:

$$\left.\begin{aligned}
\Delta s_{\mathrm{e}} &= \frac{\Delta S_{\mathrm{e}}}{n}=k_{\mathrm{B}}+k_{\mathrm{B}}\ln\frac{N_{\mathrm{C}}}{n} && \text{(s11-1)}\\
\Delta s_{\mathrm{h}} &= \frac{\Delta S_{\mathrm{h}}}{p}=k_{\mathrm{B}}+k_{\mathrm{B}}\ln\frac{N_{\mathrm{V}}}{p} && \text{(s11-2)}
\end{aligned}\right\}$$

However, careful examination shows that n/N does not approaches 0, as n and N are both finite (n is about 10^{14} - 10^{16} cm^{-3} and N is about 10^{17} - 10^{22} cm^{-3}). Therefore, although the treatment of equation s9 seems more accurate than that of equation 16, it is not strictly true in mathematics and is also an approximate treatment just as what we have done in the main text.

In order to further quantitatively demonstrate under what conditions our approximate treatment is more accurate and how reliable our approximate treatment is, we have calculated the specific values of $N\ln\frac{N}{N-n}$ and $n\ln\frac{N-n}{n}$ with different DOS (N) and under varying excitation intensity (n). The specific results are presented in **Table S1**.

Table S1. Values for $N\ln\frac{N}{N-n}$ and $n\ln\frac{N-n}{n}$ with different DOS (N) and under varying excitation intensity (n).

n N	10^{18}	10^{20}	10^{22}
10^{16}	~10^{16} ~$3\times2.3\times10^{16}$	~10^{16} ~$4\times2.3\times10^{16}$	~10^{16} ~$6\times2.3\times10^{16}$
10^{14}	~10^{14} ~$4\times2.3\times10^{14}$	~10^{14} ~$6\times2.3\times10^{14}$	~10^{14} ~$8\times2.3\times10^{14}$
10^{12}	~10^{12} ~$6\times2.3\times10^{12}$	~10^{12} ~$8\times2.3\times10^{12}$	~10^{12} ~$10\times2.3\times10^{12}$
10^{10}	~10^{10} ~$8\times2.3\times10^{10}$	~10^{10} ~$10\times2.3\times10^{10}$	~10^{10} ~$12\times2.3\times10^{10}$

Note: Values in green stands for $N\ln\frac{N}{N-n}$ and values in red stands for $n\ln\frac{N-n}{n}$. They all represent the number of possible microscopic states (Ω) of the thermodynamic system of photogenerated carriers in solar cells.

From Table S1, we can see that $N\ln\frac{N}{N-n}$ are always smaller than $n\ln\frac{N-n}{n}$ with different DOS (N) and under varying excitation intensity (n). Moreover, $N\ln\frac{N}{N-n}$ can be neglected (this is what we have done in this work) in contrast to $n\ln\frac{N-n}{n}$ when N is as large and n is as small as possible (lower right corner of the table). This implies that when calculating the total number of possible microscopic states (Ω) of the thermodynamic system of photogenerated carriers in solar cells, $N\ln\frac{N}{N-n}$ can be neglected compared with $n\ln\frac{N-n}{n}$.

Above discussions suggest that our theory is more accurate for solar cell based on semiconductor with large DOS under weak illumination (lower right corner of the table). While, as a simple approximation, our theory in the present work is fairly reliable.

Reference

1.Nagata S. An alternative expression to the Sackur-Tetrode entropy formula for an ideal gas. **Chemical Physics 2018**, 504: 8-12.