Lecture 2

Photon in, Electron out: Basic Principle of PV

References:
Black Body Radiation

**Photon** -- *quanta of the electromagnetic field*. They are *massless bosons of spin 1* (in units $\hbar$) and move with the speed of light. The linearity of Maxwell equations implies that *the photons do not interact with each other*. The mechanism of establishing equilibrium in a photon gas is *absorption and emission* of photons by matter. In equilibrium, the *chemical potential* for a photon gas is zero.

$$E = \frac{hc}{\lambda}$$

$h$ is Planck's constant and $c$ is the speed of light in vacuum. A convenient rule for converting between photon energies, in electron-Volts, and wavelengths, in nm:

$$E = \frac{1240 \ nm}{\lambda} (eV)$$

**Black Body** - any object that is a perfect emitter (as it is hot) and a perfect absorber (as it is cold) of radiation. A black body emits quanta of radiation-photons-with a distribution of energies determined by its *characteristic temperature*, $T_s$. 
Black Body Radiation

Planck's law of black body radiation

\[
I(E,T) = \frac{2F_s}{h^3c^2} \cdot \frac{E^3}{\exp\left(\frac{E}{k_B T}\right) - 1}
\]

\(F_s\) is geometric factor. \(F_s = \pi \sin^2 \theta_s\)

\(\theta_s\) is the half angle subtended by the sun to the point where the flux is measured. For the sun as seen from the earth, \(\theta_s = 0.26^\circ\), \(F_s = 2.16 \times 10^{-5} \pi\).

\[
I(\lambda,T) = \frac{2hc^2}{\lambda^5} \cdot \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1}
\]

per unit solid angle.

\[
I(E,T) = E b_s(E,T)
\]

photon flux density
Wien's Displacement Law

- Most objects emit radiation at many wavelengths.
- However, there is one wavelength where an object emits the largest amount of radiation.
- This wavelength is found with Wein’s Law:

\[ \lambda_{\text{max}} = \frac{2898 \text{ mm} \ K}{T} \]

Wien's displacement law states that the hotter an object is, the shorter the wavelength at which it will emit most of its radiation.

Q: At what wavelength does the sun emit most of its radiation?
Q: At what wavelength does the earth emit most of its radiation?
Black Body Radiation

The **Stefan-Boltzmann law** relates the total amount of radiation emitted by an object to its temperature:

\[ E = \sigma T^4 \]

**E:** total amount of radiation emitted by an object per square meter (Watts m\(^{-2}\)).

**\( \sigma \):** a constant called the **Stefan-Boltzmann constant** \((5.67 \times 10^{-8} \text{ Watts m}^{-2} \text{ K}^{-4})\).

**T:** the thermodynamic temperature of the object.

\[
\sigma = \frac{2\pi^5 k_B^4}{15c^2h^3} = 5.6704 \times 10^{-8} \text{ Js}^{-1} \text{ m}^{-2} \text{ K}^{-4}
\]

Consider the earth and sun:

Sun: \( T = 6000 \text{ K} \)

Q: is this a lot of radiation??? Compare to a 100 Watt light bulb.....

Earth: \( T = 288 \text{ K} \)

Q: If you double the temperature of an object, how much more radiation will it emit?
Visible Spectrum

<table>
<thead>
<tr>
<th>Color</th>
<th>Wavelength Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>red</td>
<td>~ 700–630 nm</td>
</tr>
<tr>
<td>orange</td>
<td>~ 630–590 nm</td>
</tr>
<tr>
<td>yellow</td>
<td>~ 590–560 nm</td>
</tr>
<tr>
<td>green</td>
<td>~ 560–490 nm</td>
</tr>
<tr>
<td>blue</td>
<td>~ 490–450 nm</td>
</tr>
<tr>
<td>violet</td>
<td>~ 450–400 nm</td>
</tr>
</tbody>
</table>
Color of Objects

The color of an object depends on both the physics of the object in its environment and the characteristics of the perceiving eye and brain. Physically, objects can be said to have the **color of the light leaving their surfaces**.

- Light arriving at an opaque surface is either reflected "specularly", scattered, or absorbed – or some combination of these.
- Opaque objects that do not reflect specularly have their color determined by which **wavelengths of light they scatter more**. If objects scatter all wavelengths, they appear white. If they absorb all wavelengths, they appear black.
- Objects that transmit light are either **translucent** or **transparent**.
- Objects may emit light that they generate themselves, rather than merely reflecting or transmitting light. e.g. **chemoluminescent**, **electroluminescent**.
- Objects may absorb light and then as a consequence emit light that has different properties. e.g. **fluorescent** or **phosphorescent**.
reflection, illusion, scattering, electroluminescence, illusion, fluorescence
The extraterrestrial spectrum of solar irradiance resembles the spectrum of a **black body** at 5760 K. The extraterrestrial solar irradiance, as a function of wavelength, is greatest at visible wavelengths, **300-800 nm**, peaking in the blue-green.
The Terrestrial Solar Irradiance

Light is absorbed and scattered by various atmospheric constituents. The spectrum reaching the earth’s surface is both attenuated and changed in shape.

Attenuation of solar irradiance by the atmosphere is quantified by the “Air Mass” factor:

\[ n_{\text{AirMass}} = \frac{\text{optical path length to Sun}}{\text{optical path length if Sun directly overhead}} = \text{cos} \, e \gamma_S \]

For convenience, the standard terrestrial solar spectrum is defined as the Air Mass 1.5 (AM1.5, corresponding to an angle of elevation of 41.81° or solar zenith angle of 48.19°) spectrum normalized so that the integrated irradiance is 1000 W/m².
Actual irradiances vary on account of seasonal and daily variations in the position of the sun and orientation of the earth and condition of sky. Average global irradiances vary from <100 W/m$^2$ at high latitudes to >300 W/m$^2$.  

Source: NASA 2008

http://cleantechlawandbusiness.com/
Solar Cell in Dark and under Illumination

Ambient radiation  Solar cell  Spontaneous emission

Solar radiation  Spontaneous emission

Energy Conservation
Equilibrium of Solar Cell in Dark

Consider a cell in dark, in thermal equilibrium with the ambient...

Assuming the ambient radiates like a black body at $T_a$ and is received over a hemisphere ($F_a=\pi$), incident flux of thermal photons from the ambient normal to the surface of solar cell:
Equilibrium of Solar Cell in Dark

The electron current density equivalent to the absorbed photon flux if each photon of energy $E$ generates one electron, is

$$j_{abs}(E) = q(1 - R(E))a(E)b_a(E)$$

$a(E)$ is the probability of absorption of a photon of energy $E$ (absorbance or absorptivity), $R(E)$ is the probability of photon reflection.

Here we assume the rear surface of the cell is a perfect reflector. The equivalent current for absorbed thermal photons is

$$qA(1 - R(E))a(E)b_a(E)$$
Equilibrium of Solar Cell in Dark

Consider a cell in dark, in thermal equilibrium with the ambient \((T_a)\)...
Equilibrium of Solar Cell in Dark

If $\varepsilon$ is the probability of emission of a photon of energy $E$ (emissivity), the equivalent current density for photon emission through the surface of the cell is

$$j_{rad}(E) = q(1 - R(E))\varepsilon(E)b_a(E)$$

$$b_a(E) = b_e(E,0)$$

In order to maintain a steady state, $j_{abs}$ and $j_{rad}$ must balance and therefore

$$\varepsilon(E) = a(E)$$

In quantum mechanical terms, it is a result of detailed balance that matrix element for optical transition from ground to excited state and from excited to ground state must be identical.
Under illumination by a solar photon flux $b_s(E)$, the cell absorbs solar photons of energy $E$ at a rate

$$\left(1 - R(E)\right)a(E)b_s(E)$$

The equivalent current density for photon absorption includes a contribution of thermal photons from both sun and ambient, and

$$j_{abs}(E) = q\left(1 - R(E)\right)a(E)\left[b_s(E) + \left(1 - \frac{F_s}{F_a}\right)b_a(E)\right]$$
Solar Cell Under Illumination

As a result of illumination, part of the electron population has raised electrochemical potential energy, and the system develops a chemical potential $\Delta \mu > 0$. According to Planck’s radiation law, the photon flux emitted normal to the surface (surrounding media is air):

$$b_e(E, \Delta \mu) = \frac{2\pi}{h^3 c^2} \cdot \frac{E^2}{\exp\left(\frac{E - \Delta \mu}{k_B T_a}\right) - 1}$$

If $\varepsilon$ is the probability of photon emission, the equivalent current density for photon emission is

$$j_{rad}(E) = q(1 - R(E))\varepsilon(E)b_e(E, \Delta \mu)$$

The net equivalent current density is

$$j_{abs}(E) - j_{rad}(E)$$
Solar Cell Under Illumination

Generalized detailed balance argument shows that \( e(E) = a(E) \) if \( \Delta \mu \) is constant through the device. So

\[
j_{\text{abs}}(E) - j_{\text{rad}}(E) = q(1 - R(E))a(E)\left[b_s(E) + \left(1 - \frac{F_s}{F_a}\right)b_a(E) - b_e(E, \Delta \mu)\right]
\]

This can be divided into contributions from net absorption (in excess to that at equilibrium) and net emission (radiative recombination) current density

\[
j_{\text{abs(net)}}(E) = q(1 - R(E))a(E)\left[b_s(E) - \frac{F_s}{F_a}b_a(E)\right] \quad b_a(E) = b_e(E, 0)
\]

\[
j_{\text{rad(net)}}(E) = q(1 - R(E))a(E)\left[b_e(E, \Delta \mu) - b_e(E, 0)\right]
\]

The radiative recombination is an unavoidable loss. It means that the absorbed solar radiant energy can never be fully utilized by the solar cell.
Work Available from a Solar Cell

\[ P = JV \]

Short Circuit Photocurrent
Consider a two band system for which the ground state is initially full and the excited state empty. The bands are separated by a band gap, \( E_g \). Since the angular range of the sun is so small compared to the ambient,

\[ j_{abs(\text{net})}(E) = q \left( 1 - R(E) \right) a(E) b_s(E) \]

If each electron has a probability, \( \eta_c(E) \), of being collected, the photocurrent density at short circuit,

\[ J_{sc} = q \int_0^\infty \eta_c(E)(1 - R(E))a(E)b_s(E)dE \]

This is identical to that obtained with the quantum efficiency \( QE(E) \),

\[ J_{sc} = q \int_0^\infty QE(E)b_s(E)dE \]
Work Available from a Solar Cell

Short Circuit Photocurrent

For the most efficient solar cell, we assume it has:

- Perfectly absorbing, non-reflecting material. All incident photons of energy \( E > E_g \) are absorbed to promote exactly one electron to the upper band;
- Perfect charge separation. All electrons surviving radiative recombination are collected and delivered to the external circuit. \( \eta_c(E) = 1 \)

This gives the maximum photocurrent for that band gap.

\[
Q(E) = a(E) = \begin{cases} 
1 & E \geq E_g \\
0 & E \leq E_g 
\end{cases}
\]

So

\[
J_{sc} = q \int_{E_g}^{\infty} b_s(E) dE
\]

Photocurrent is a function only of the band gap and the incident spectrum.
Work Available from a Solar Cell

Dark Current

Dark current is the current that flows through the photovoltaic device in the opposite direction to the photocurrent when a bias is applied.

Assume that in an ideal cell material no carriers are lost through non-radiative recombination. The only loss process is the unavoidable radiative relaxation of electrons through spontaneous emission. For a flat plate cell with perfect rear reflector, the dark current density is

\[ J_{\text{rad}}(\Delta \mu) = q \int (1 - R(E))a(E)[b_e(E,\Delta \mu) - b_e(E,0)]dE \]

The above assumes that \( \Delta \mu \) is constant over the surface of the cell and using the detailed balance result, \( a(E) = \varepsilon(E) \)

In an ideal material with lossless carrier transport, \( \Delta \mu \) can be further assumed constant everywhere and

\[ \Delta \mu = qV \]
Work Available from a Solar Cell

Photocurrent
Assuming that dark current and photocurrent can be added,

\[ J(V) = J_{sc} - J_{dark}(V) \]

The net cell current density,

\[ J(V) = q \int_{0}^{\infty} (1 - R(E)) a(E) \left\{ b_s(E) - \left[ b_e(E,qV) - b_e(E,0) \right] \right\} dE \]

Apply with the step-like absorption function,

\[ J(V) = q \int_{E_g}^{\infty} \left\{ b_s(E) - \left[ b_e(E,qV) - b_e(E,0) \right] \right\} dE \]

Integration shows \( J(V) \) is strongly bias dependent and has the approximate form,

\[ J(V) = J_{sc} - J_0 \left[ \exp\left( \frac{qV}{k_B T} \right) - 1 \right] \]

\( J_0 \) is a temperature dependent constant for a particular material. The above equation just resembles the ideal diode equation.
Work Available from a Solar Cell

The net current is the difference between the two photon flux densities: the *absorbed flux* and the *emitted flux*.

- As $V$ increases, the emitted flux increases and the net current decreases;
- At $V_{oc}$ the total emitted flux exactly balances the total absorbed flux and the net current is zero;
- If $V$ increases further, the emitted flux exceeds the absorbed and the cell begins to act like a LED.

$$V_{oc} < \frac{E_g}{q}$$
Work Available from a Solar Cell

Limiting Efficiency

*Incident and extracted power* from the photon fluxes are needed to calculate the power conversion efficiency. The incident power density is obtained by integrating the incident irradiance over photon energy,

\[
P_s = \int_0^\infty E_b_s(E_s) dE
\]

For an ideal photoconverter, it is assumed that no potential loss through the circuit. All collected electrons have \( \Delta \mu \) of electrical potential energy and deliver \( \Delta \mu \) of work to the external circuit. Since

\[
\Delta \mu = qV
\]

We have for the extracted power density,

\[
P = VJ(V)
\]

Where

\[
J(V) = J_{sc} - J_0 \left[ \exp \left( \frac{qV}{k_BT} \right) - 1 \right]
\]
Work Available from a Solar Cell

Limiting Efficiency

The power conversion efficiency is

\[ \eta = \frac{VJ(V)}{Ps} \]

Maximum efficiency is achieved as

\[ \frac{d}{dV} (VJ(V)) = 0 \]

The bias at which the above extremum condition occurs is the maximum power bias - \( V_m \).

Q: How to achieve maximum power output of solar cells in practice?

Principle of optimizing the power output of solar cells: \( R = -dV/dI \)
Factors Affecting Work Available from a Solar Cell

Effect of Band Gap

The power conversion efficiency of the ideal two band photoconverter is a function only of $E_g$ and the incident spectrum.

If the incident spectrum is fixed, $\eta$ depends only on $E_g$. For any spectrum there is an optimum band gap where $\eta$ has a maximum.

For solar irradiation, maximum efficiency of $\sim 33\%$ at a $E_g$ of $\sim 1.4$ eV.
Effect of Band Gap

No photons with energy less than $E_g$ contribute to the available power. Photons of $E > E_g$ are absorbed but deliver only $\Delta \mu$ ($= qV_m$) of electrical energy to the load. The fraction of power available is $\Delta \mu / E$. 

Factors Affecting Work Available from a Solar Cell

[Graph showing the relationship between photon energy and irradiance]
Factors Affecting Work Available from a Solar Cell

Effect of Spectrum

• The spectrum of a 5760 K black body with the angular width of the sun is a good model of the extra-terrestrial (AM0) spectrum. The efficiency is ~31% at a band gap of 1.3 eV.
• Red shift of the spectrum by reducing the temperature of source gives rise to reduced optimum band gap and the limiting efficiency. \( T_s = T_a \)
• Increasing the temperature of the source increases the photo-conversion efficiency. \( T_a \rightarrow 0 \)
• As \( T_a \rightarrow 0 \), no radiative current, the optimum operating bias is \( V = E_g / q \). If all carriers are collected with \( \Delta \mu = qV \), the maximum efficiency is

\[
\eta = \frac{E_g \int_{E_g}^{\infty} b_s(E) dE}{\int_0^{\infty} E b_s(E) dE}
\]

Max. efficiency of ~44% at a \( E_g \) of ~2.2 eV for a 6000K black body sun. In practice, the cooling of the cell below the ambient requires an input of energy which reduces the net efficiency.
Factors Affecting Work Available from a Solar Cell

Effect of Spectrum

The Shockley-Queisser limit or detailed balance limit refers to the maximum theoretical efficiency of a solar cell using a p-n junction to collect power from the cell.

**Factors Affecting Work Available from a Solar Cell**

**Effect of Spectrum**

Another way of improving the efficiency through the spectrum is to alter the angular width of the sun.

\[
I(E,T) = \frac{2F_s}{\hbar^2 c^2} \cdot \frac{E^3}{\exp\left(\frac{E}{k_B T_s}\right) - 1}
\]

The solid angle subtended by the sun can be increased by concentrating the light.

E.g. for light concentrated by a factor 1000, a limiting \( \eta \) of \( \sim 37\% \) at \( E_g=1.1 \) eV is predicted.

The cell emits radiation in all directions while it absorbs sunlight only from a small angular range. Increasing the angular range improves the balance, and the absorbed flux will increase relative to the emitted flux. So the net photocurrent will increase.

\[
J(V) = q \int_{E_g}^{\infty} \left\{b_s(E) - \left[b_s(E,qV) - b_e(E,0)\right]\right\} dE
\]
Requirements for the Ideal Photoconverter

**Assumptions** have been made:

- The photovoltaic material has an **energy gap** which separates states which are normally full from states which are normally empty;
- All incident light with $E > E_g$ is **absorbed**;
- Each absorbed photon **generates** exactly one electron-hole pair;
- Excited charges do not **recombine** except radiatively as required by the detailed balance;
- Excited charges are completely **separated**;
- Separated charges are **transported** to the external circuit without loss.

(1) **Energy Gap**: Semiconductors with band gap in the range 0.5-3 eV absorb visible light to excite electrons across the band gap. At 300K

- III-V compound semiconductors GaAs (1.42 eV), InP (1.35 eV)
- Si (1.1 eV) most popular.
- CdTe (1.56 eV), CuIn$_x$Ga$_{1-x}$Se$_2$ (CIGS, 1.02-1.65 eV), thin film PV
- Organic semiconductors (semiconducting molecular materials).
Requirements for the Ideal Photoconverter

(2) **Light Absorption**: incident photon with $E > E_g$ is required.

- Absorbing layer should be thick enough (to increase its optical depth);
- A few tens or hundreds of microns thickness is enough for most semiconductors to achieve perfect absorption;
- Requirements of high optical depth and good charge collection make very high demand of material quality.

(3) **Charge Separation**:

- **Spatial asymmetry** at the contact of materials is required to drive the charges (electron/hole) away from the point of promotion;
- The driving force can be an electric field or a gradient in electron density;
- The asymmetry is generally provided by a junction (an interface between two electronically different materials or between layers of the same material treated in different ways). Semiconductor p-n junction is the classical model of a solar cell;
- The quality of junction is of central importance for efficient photovoltaic conversion.
Requirements for the Ideal Photoconverter

(4) **Lossless Transport:**
- The material should be a good electrical conductor;
- No resistive loss (no series/parallel resistances). Materials around the junction should be highly conducting and make good Ohmic contact to the external circuit.

(5) **Optimum Load Resistance:** The load resistance should be matched with the maximum power point of the module/array, rather than the cell.

**Reasons for the non-ideal performance:**
- Incomplete absorption of the incident light. Photons are reflected or pass through the cell without being absorbed, which reduces the photocurrent.
- Non-radiative recombination of photogenerated carriers. Excited charges are trapped and recombined before being collected, which reduces both photocurrent and photovoltage.
- Voltage drop due to series resistance between the point of photogeneration and the external circuit, which reduces the available power.
Summary

• Black body radiation.
• Solar cell in dark and under illumination.
• Factors affecting the limiting efficiency: Band gap and spectrum.
• Requirements for an ideal solar cell.