
How Solar Cells Work

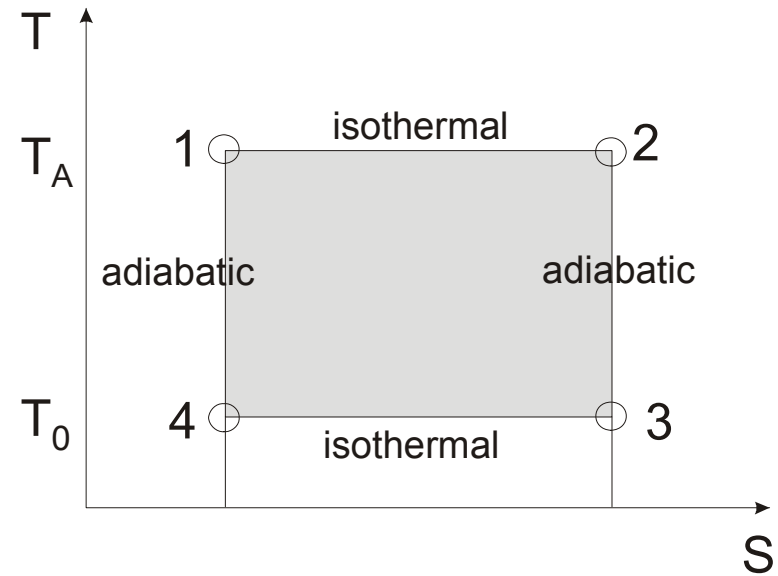
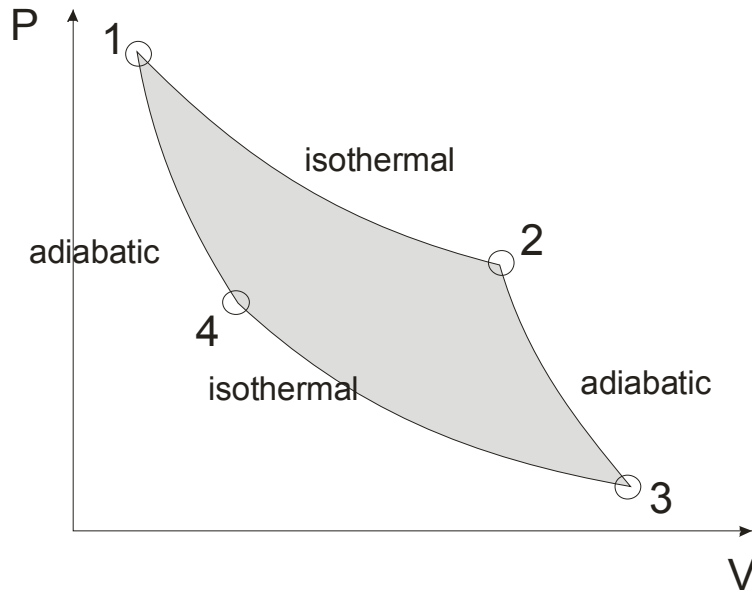
Basic theory of photovoltaic energy conversion

Peter Würfel
University of Karlsruhe, Germany

Three Messages

- Sun is a heat source, solar cells must be heat engines
 - Important conversion step
solar heat \Rightarrow chemical energy of electron-hole pairs
limited by thermodynamics
 - Conversion of chemical energy \Rightarrow electrical energy
can be 100% efficient and needs more than a pn-
junction
-

Carnot process

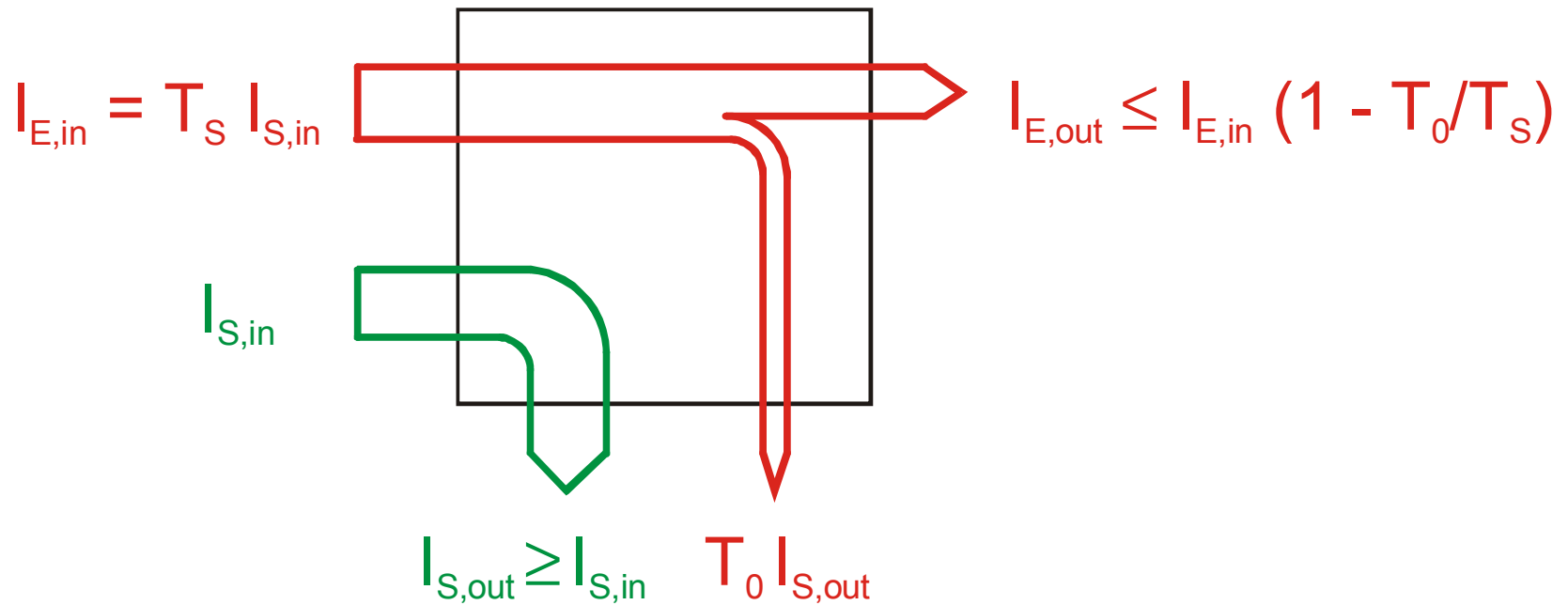


Important: generation of (entropy-) Free Energy by cooling

$$F = E - TS$$

Solar cells are heat engines

- Principle



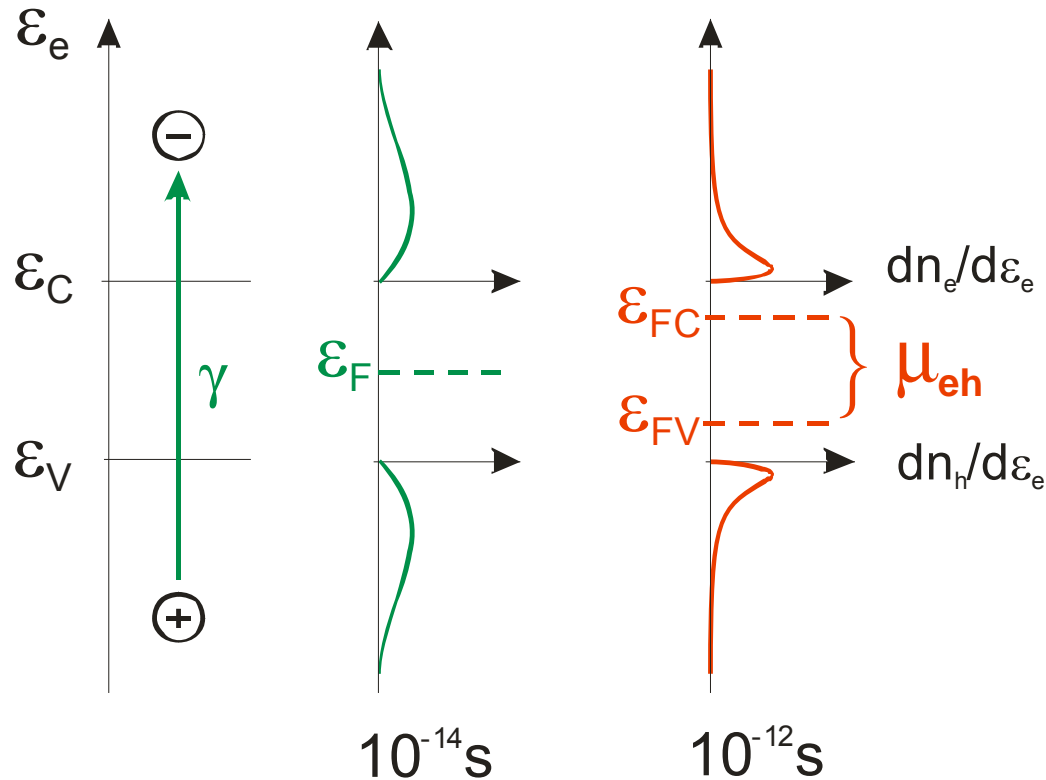
The solar cell as a heat engine?

Questions:

What is the working medium (the gas)?

What kind of free energy is produced?

Conversion of solar heat into chemical energy of electrons and holes



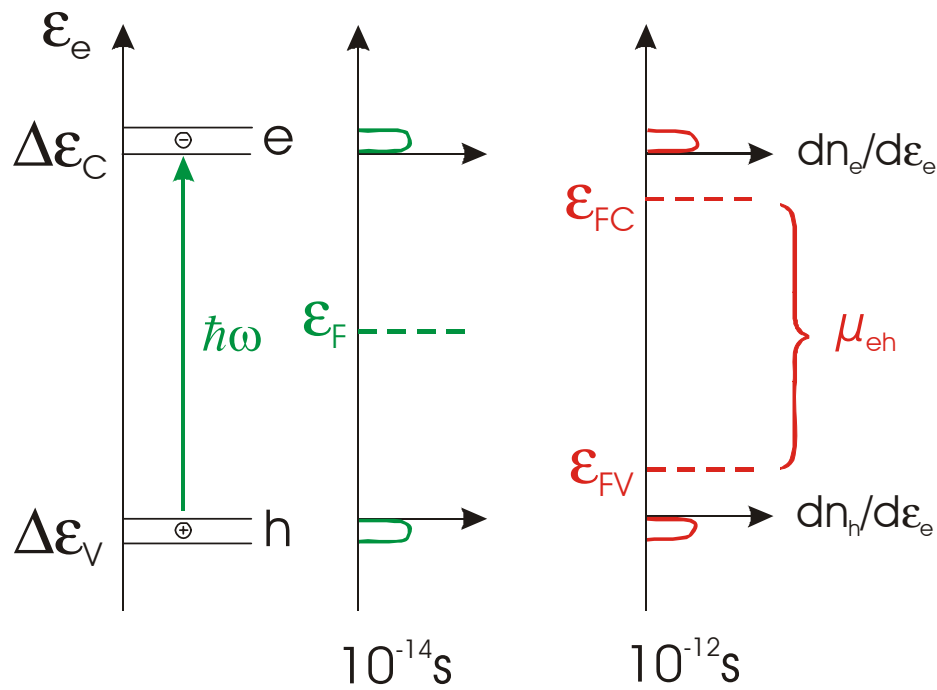
Energy per photon $\hbar\omega \rightarrow$ chemical energy μ_{eh} per e-h pair by thermalisation

energy gap is necessary

Maximum chemical energy

Reduce entropy generation during thermalisation by
reducing the energy range, for which Fermi-distribution is established

ideal: isoenergetic thermalisation in narrow energy ranges is isentropic



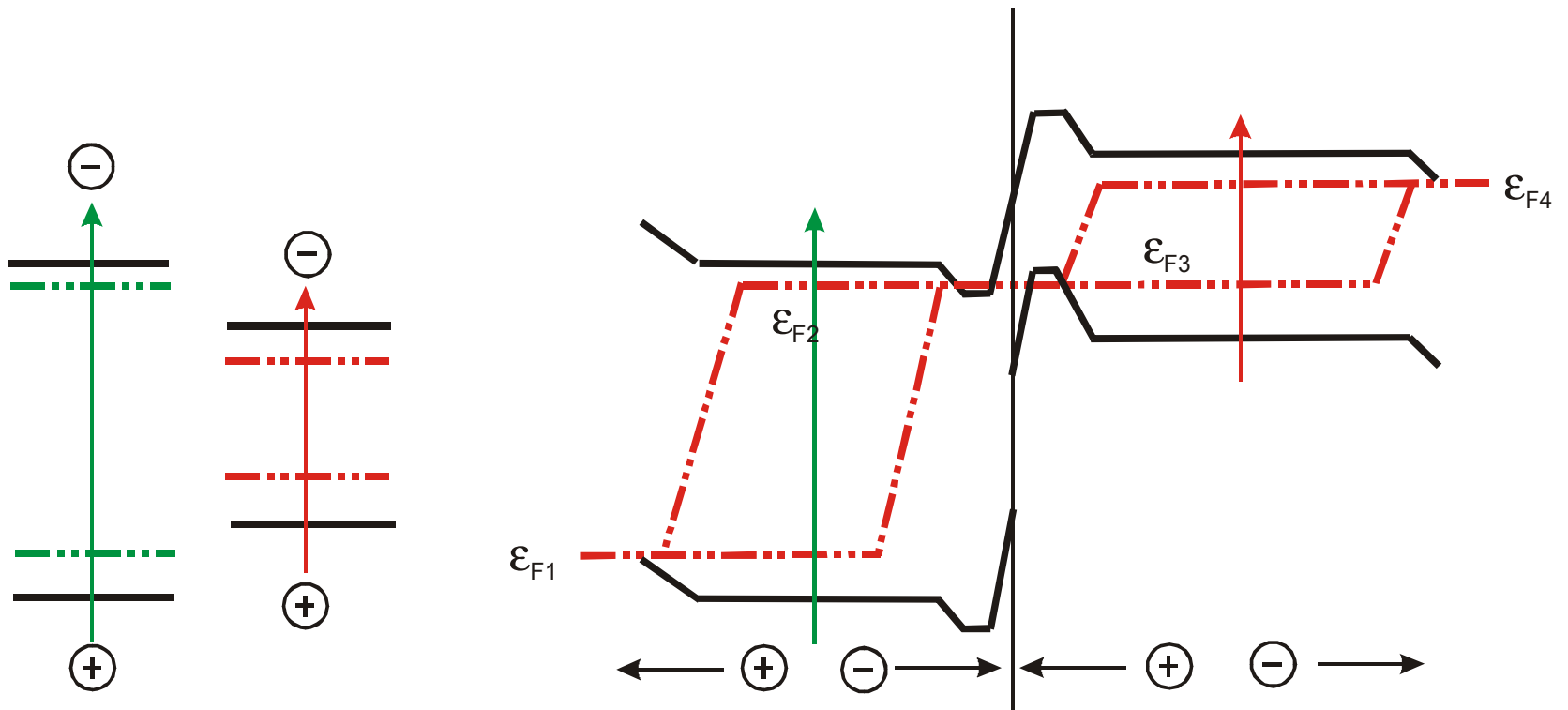
→ tandem cells

Tandem cells

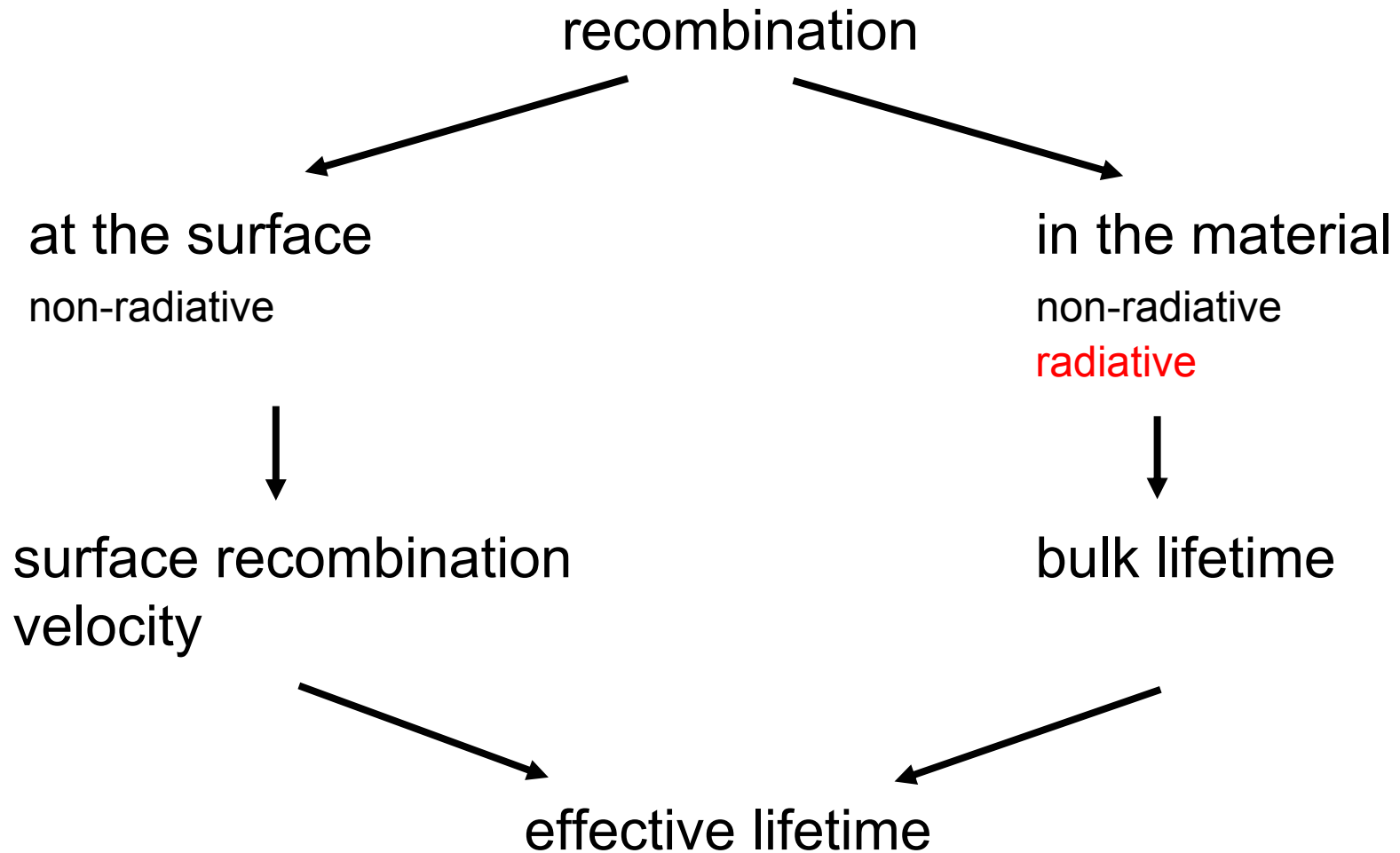
2 cells \rightarrow 4 Fermi-energies for 4 energy ranges

4-level system

3 Fermi-energies for connection in series



Recombination



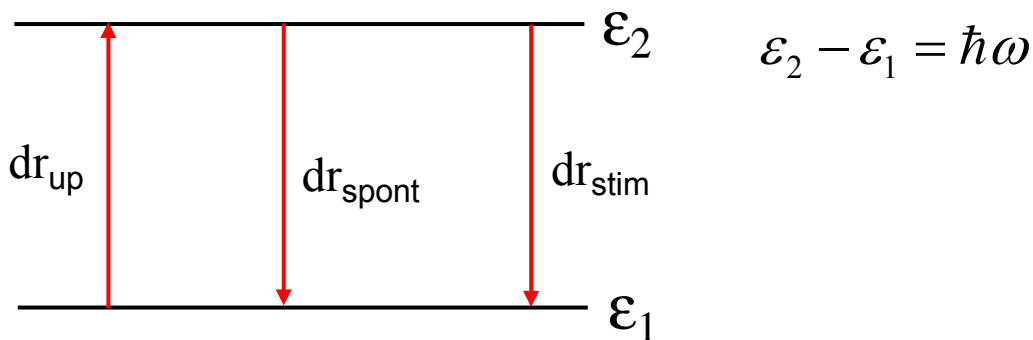
Recombination

Direct optical transitions in 2-level system

$$dr_{up}(\hbar\omega) = |M|^2 D_{12} f(\varepsilon_1) [1 - f(\varepsilon_2)] \frac{dj_\gamma(\hbar\omega)}{d(\hbar\omega)} d(\hbar\omega) \quad \text{upwards}$$

$$dr_{stim}(\hbar\omega) = |M|^2 D_{12} f(\varepsilon_2) [1 - f(\varepsilon_1)] \frac{dj_\gamma(\hbar\omega)}{d(\hbar\omega)} d(\hbar\omega) \quad \left. \vphantom{dr_{stim}(\hbar\omega)} \right\} \text{downwards}$$

$$dr_{spont}(\hbar\omega) = |M|^2 \frac{c_0}{n} D_\gamma(\hbar\omega) D_{12} f(\varepsilon_2) [1 - f(\varepsilon_1)] d(\hbar\omega) \quad \left. \vphantom{dr_{spont}(\hbar\omega)} \right\}$$



density of states for photons

$$D_\gamma(\hbar\omega) = \frac{\Omega n^3}{4\pi^3 \hbar^3 c_0^3} (\hbar\omega)^2$$

Absorption coefficient

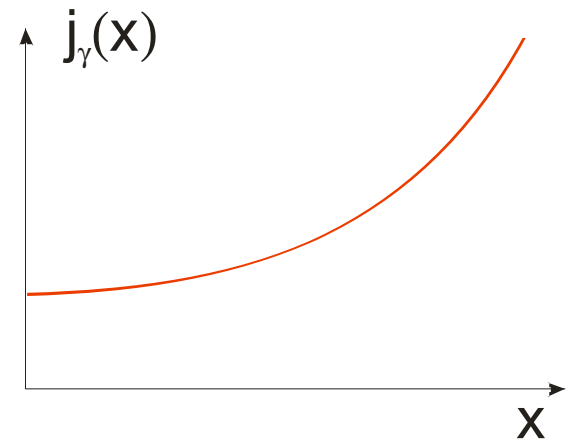
$$\begin{aligned} dr_{abs}(\hbar\omega) &= dr_{up}(\hbar\omega) - dr_{stim}(\hbar\omega) \\ &= |M|^2 D_{12} [f(\varepsilon_1) - f(\varepsilon_2)] dj_\gamma(\hbar\omega) \\ &= \alpha_{12}(\hbar\omega) dj_\gamma(\hbar\omega) \end{aligned}$$

absorption coefficient $\alpha_{12}(\hbar\omega) = |M|^2 D_{12} [f(\varepsilon_1) - f(\varepsilon_2)]$

$$\alpha_{12}(\hbar\omega) < 0 \quad \text{for} \quad f(\varepsilon_2) > f(\varepsilon_1)$$

amplification

$$j_\gamma(\hbar\omega, x) = j_\gamma(\hbar\omega, 0) (1 - r(\hbar\omega)) \exp(-\alpha_{12}(\hbar\omega)x)$$



Spontaneous emission

replace $|M|^2 D_{12} = \frac{\alpha_{12}(\hbar\omega)}{[f(\varepsilon_1) - f(\varepsilon_2)]}$ in spontaneous emission rate

$$dr_{spont}(\hbar\omega) = \alpha_{12}(\hbar\omega) \frac{c_0}{n} D_\gamma(\hbar\omega) \frac{[1 - f(\varepsilon_1)] f(\varepsilon_2)}{[f(\varepsilon_1) - f(\varepsilon_2)]} d\hbar\omega$$

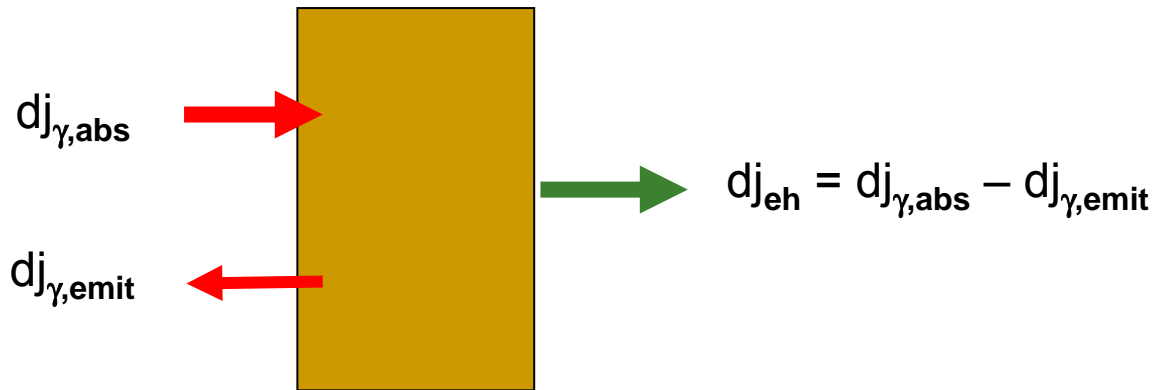
with $f(\varepsilon_1) = \frac{1}{\exp\left(\frac{\varepsilon_1 - \varepsilon_{FV}}{kT}\right) + 1}$ and $f(\varepsilon_2) = \frac{1}{\exp\left(\frac{\varepsilon_2 - \varepsilon_{FC}}{kT}\right) + 1}$ and $\varepsilon_2 - \varepsilon_1 = \hbar\omega$

$$dr_{spont}(\hbar\omega) = \alpha(\hbar\omega) \frac{c_0}{n} D_\gamma(\hbar\omega) \frac{d(\hbar\omega)}{\exp\left(\frac{\hbar\omega - (\varepsilon_{FC} - \varepsilon_{FV})}{kT}\right) - 1}$$

Production of chemical energy

$$dj_{eh} = dg_{eh} - dr_{eh}$$

only radiative recombination, monochromatic



generalized Planck law

$$dj_{\gamma}(\hbar\omega) = a(\hbar\omega) \frac{\Omega}{4\pi^3 \hbar^3 c^2} \frac{(\hbar\omega)^2}{\exp\left[\frac{\hbar\omega - (\varepsilon_{FC} - \varepsilon_{FV})}{kT}\right] - 1} d\hbar\omega$$

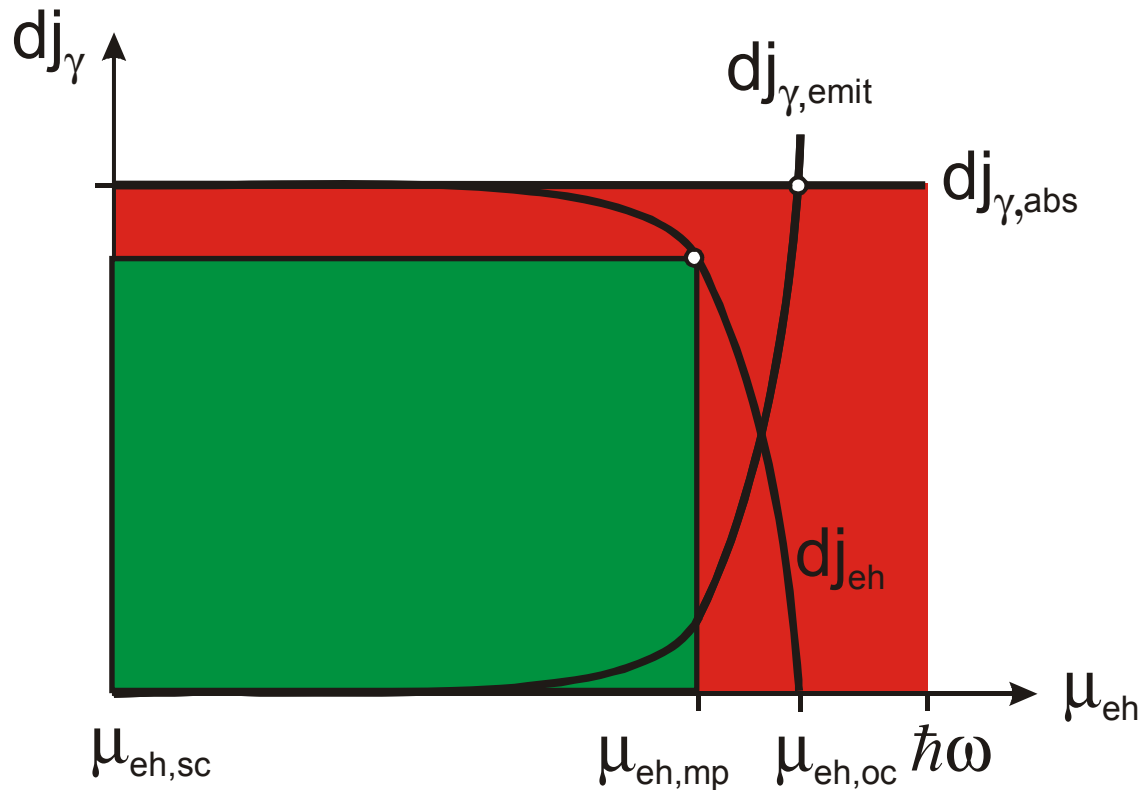
absorptance

$$a(\hbar\omega) = (1 - R(\hbar\omega)) \{1 - \exp(-\alpha(\hbar\omega)d)\}$$

Sun:	$T = T_S$	$\varepsilon_{FC} - \varepsilon_{FV} = 0$	$\varepsilon_{FC} - \varepsilon_{FV} = \mu_{eh}$
Semiconductor:	$T = T_0$	$\varepsilon_{FC} - \varepsilon_{FV} \neq 0$	

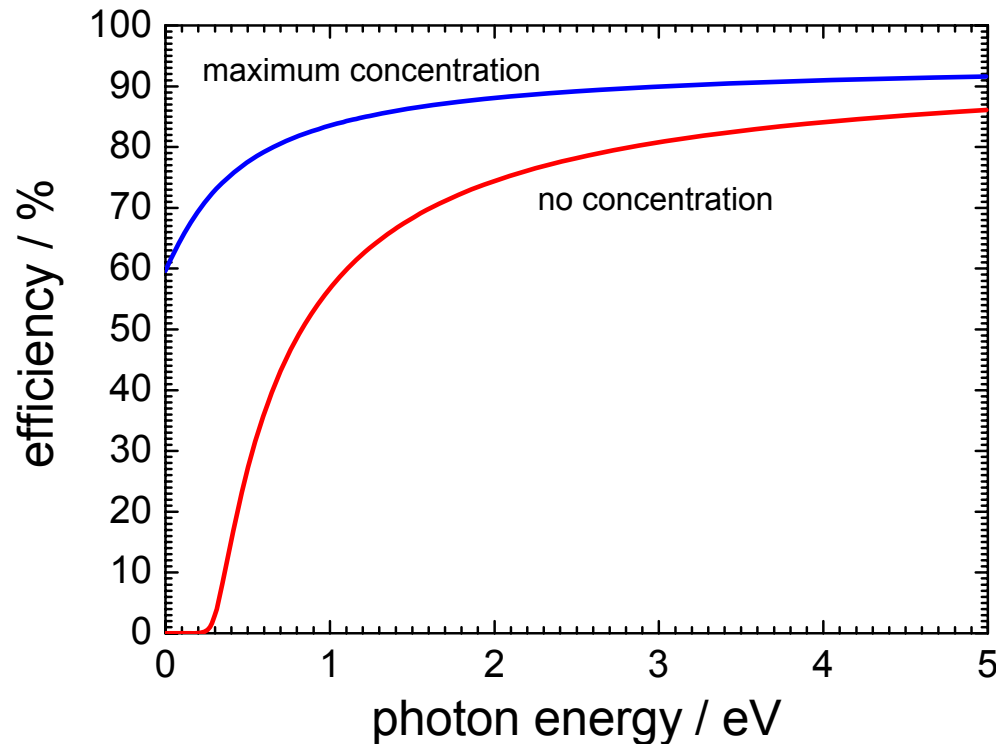
Characteristic for production of chemical energy by monochromatic light

$$dj_{eh}(\mu_{eh}) = dj_{\gamma,abs} - dj_{\gamma,emit}(\mu_{eh})$$



$$\eta = \frac{\text{green}}{\text{red}}$$

Production of chemical energy from monochromatic radiation



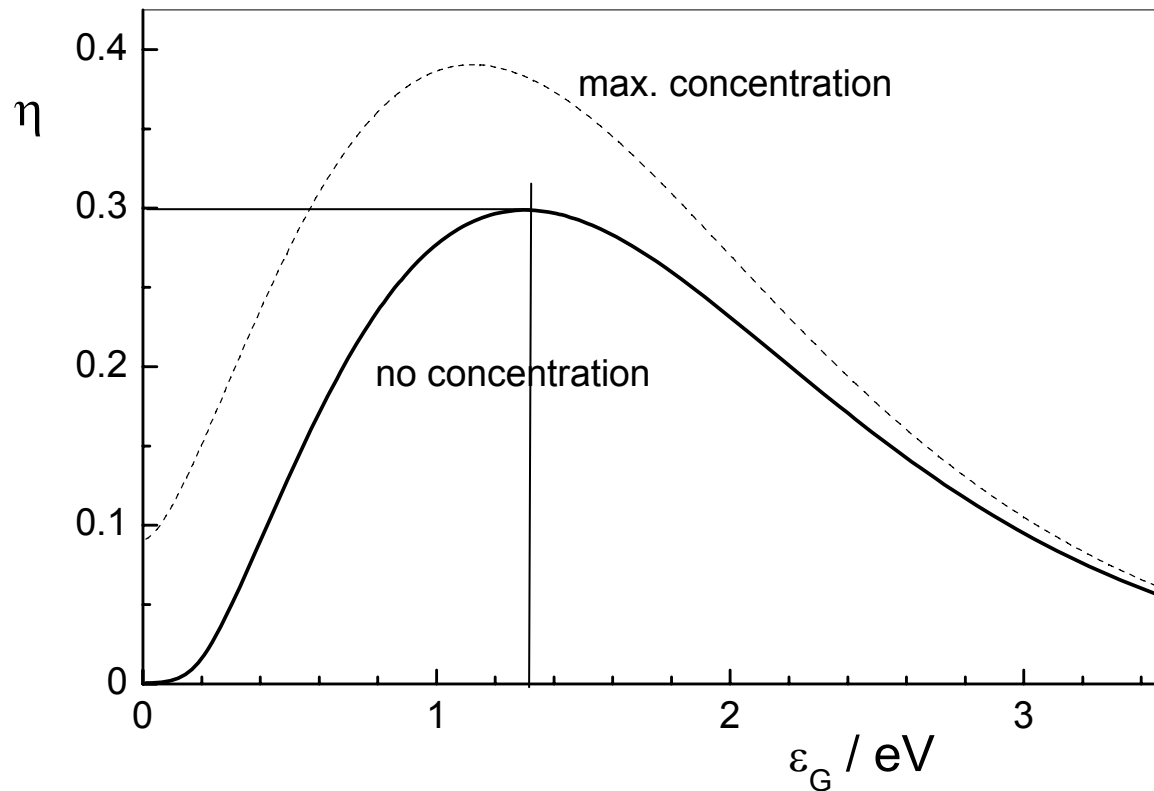
Infinite tandem: $\eta = 86\%$ max. concentration

Production of chemical energy

in wide band semiconductor with total solar spectrum

(Shockley-Queisser)

AM0 spectrum



Optimal materials

full absorption above energy threshold (in a thin film)

minimum recombination for given difference of Fermi-energies:

radiative recombination

good materials for solar cells should be luminescing

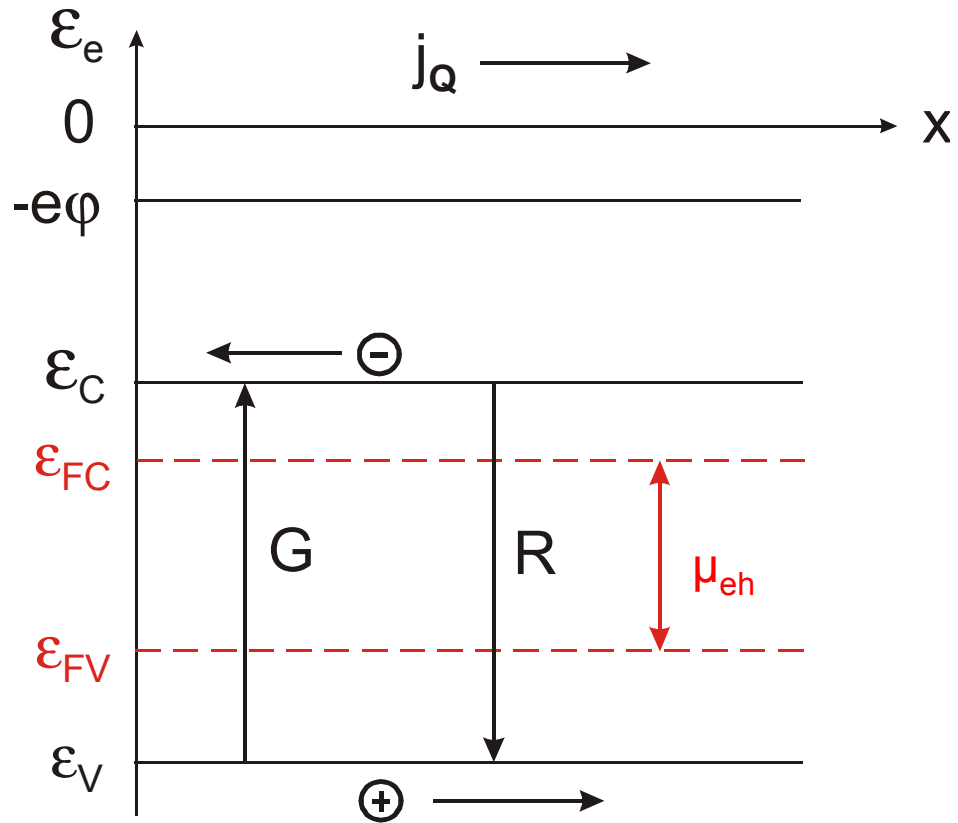
advantage for organic materials?

difference of the Fermi-energies (chemical energy per eh-pair) is obtained from luminescence intensity

Chemical energy \rightarrow electrical energy

Charge current

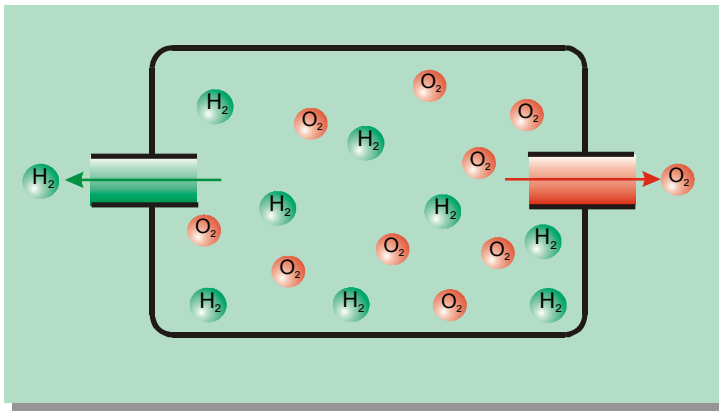
$$j_Q = -e (G - R)$$



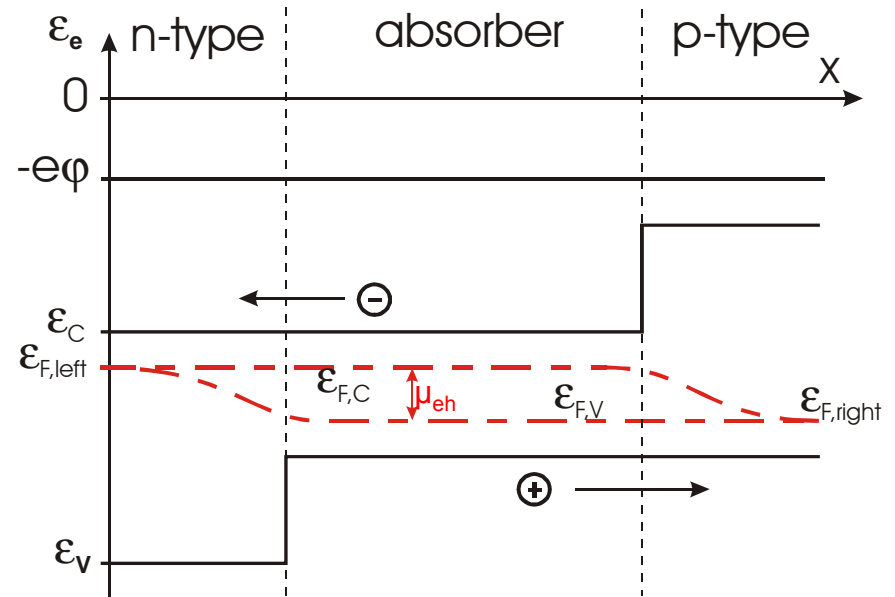
Separation of electrons and holes with semi-permeable membranes

■ $\leftarrow \text{H}_2, \text{O}_2 \rightarrow$

■ $\leftarrow e, h \rightarrow$



Voltage: $eV = \epsilon_{F,\text{right}} - \epsilon_{F,\text{left}} = \mu_{eh}$



Transport properties, drift current

acceleration $a_i = \frac{z_i e E}{m_i^*}$

$$\langle v_i \rangle = \int_0^\infty a_i \exp(-t/\tau_{c,i}) dt = a_i \tau_{c,i}$$

$$\langle v_i \rangle = z_i \frac{e}{m_i^*} \tau_{c,i} E .$$

mobility $b_i = \frac{e \tau_{c,i}}{m_i^*}$

drift current

$$j_{Q,f,i} = z_i^2 e n_i b_i E = \sigma_i E$$

$$j_{Q,f,i} = -\frac{\sigma_i}{z_i e} \text{grad}(z_i e \varphi)$$

Diffusion current

diffusion current

$$\mu_i = \mu_{i,0} + kT \ln \left(\frac{n_i}{N_i} \right) \quad \text{chemical potential of particles } i$$

$$j_{Q,d,i} = z_i e (-D_i \text{grad } n_i) \quad \text{Fick's law of diffusion}$$

$$j_{Q,d,i} = z_i e n_i D_i \frac{\text{grad } n_i}{n_i} = - \frac{z_i e n_i D_i}{kT} \text{grad } \mu_i$$

$$\text{Einstein relation} \quad \frac{b_i}{D_i} = \frac{e}{kT}$$

$$j_{Q,d,i} = - \frac{z_i e n_i b_i}{e} \text{grad } \mu_i = - \frac{\sigma_i}{z_i e} \text{grad } \mu_i$$

total charge current

$$j_{Q,i} = -\frac{\sigma_i}{z_i e} \{ \text{grad} \mu_i + \text{grad}(z_i e \varphi) \}$$

$$j_{Q,i} = -\frac{\sigma_i}{z_i e} \text{grad}(\mu_i + z_i e \varphi) = -\frac{\sigma_i}{z_i e} \text{grad} \eta_i$$

electrochemical potential

$$\eta_i = \mu_i + z_i e \varphi$$

for electrons ($z_i = -1$) and holes ($z_i = +1$)

$$j_Q = \frac{\sigma_e}{e} \text{grad} \eta_e - \frac{\sigma_h}{e} \text{grad} \eta_h$$

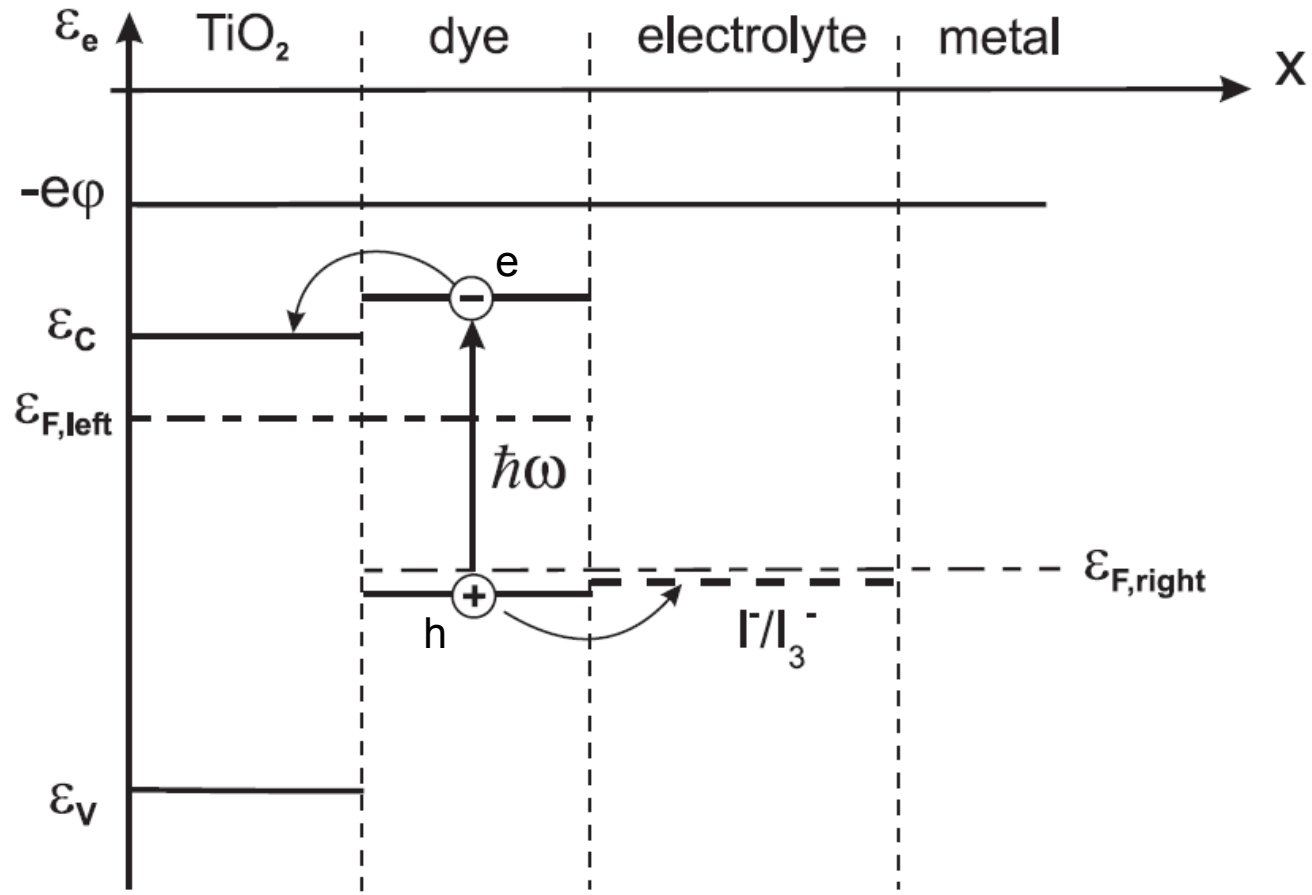
$$\eta_e = \mu_e - e \varphi = \varepsilon_{FC}$$

$$\eta_h = \mu_h + e \varphi = -\varepsilon_{FV}$$

$$j_Q = \frac{\sigma_e}{e} \text{grad} \varepsilon_{FC} + \frac{\sigma_h}{e} \text{grad} \varepsilon_{FV}$$

field and diffusion currents do not exist

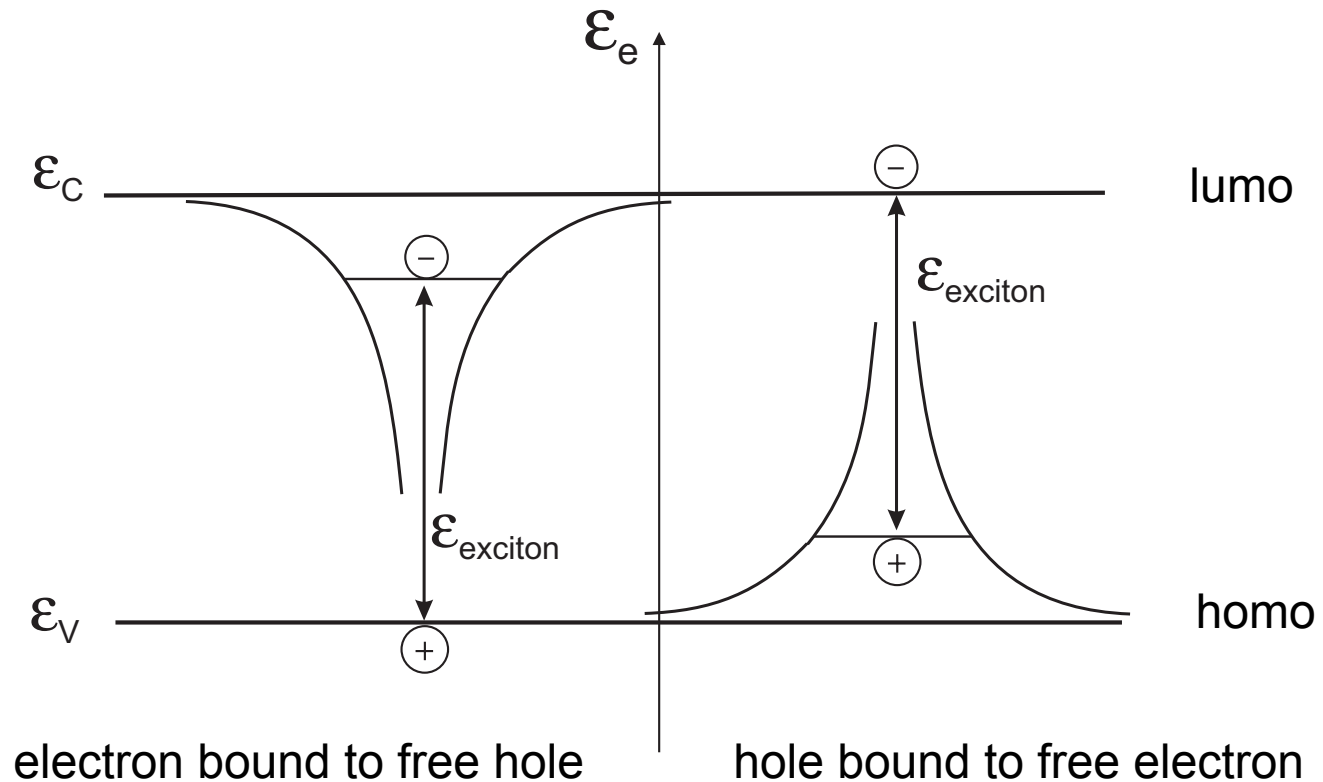
Dye Solar Cell



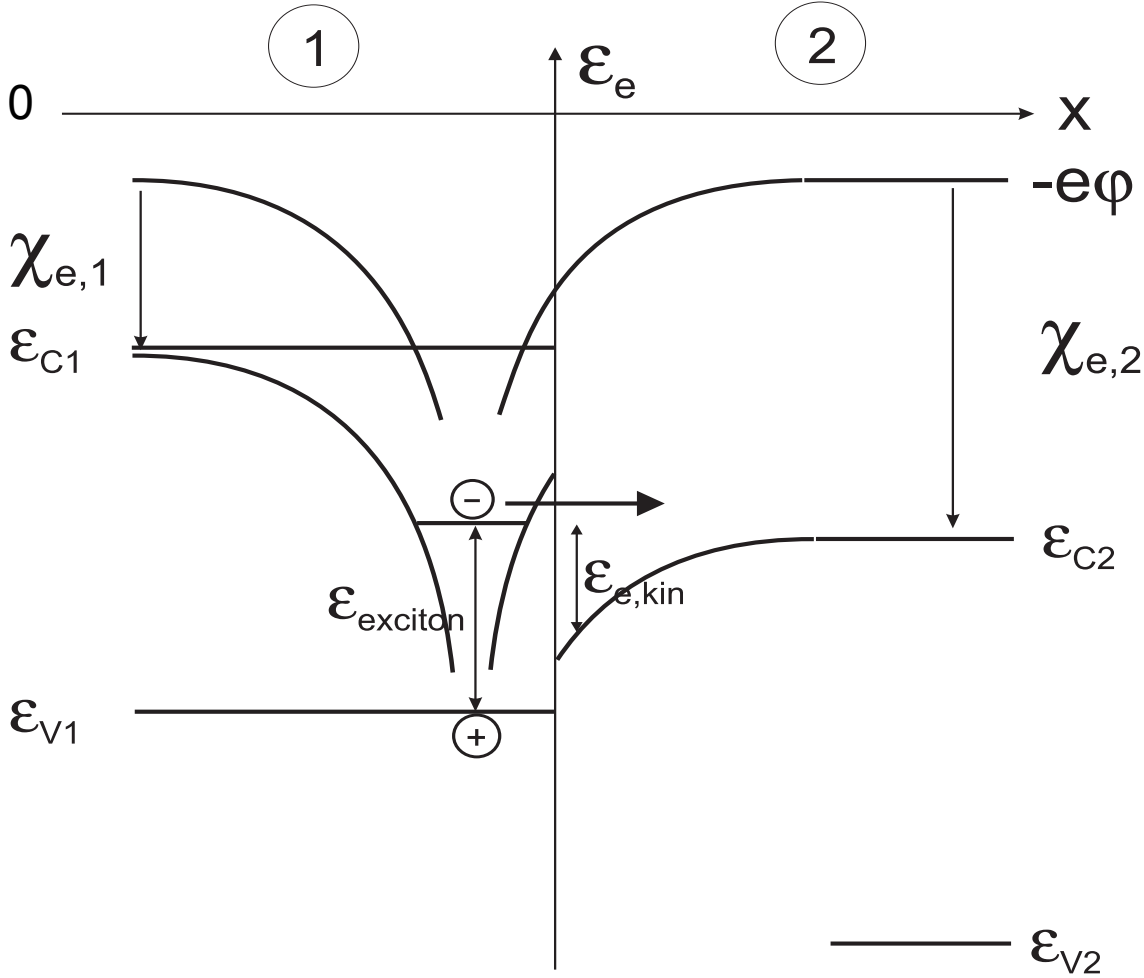
Problem: e and h bound in exciton

Problems with excitons in organic semiconductors

large exciton binding energy



exciton dissociation



Requirements for solar cell structures

Conditions for optical and electrical properties of absorbers

splitting of Fermi-energies

selective transport

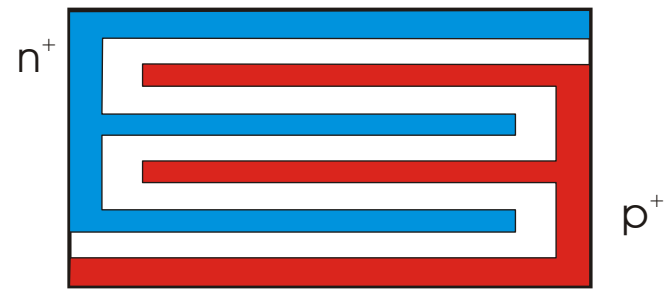
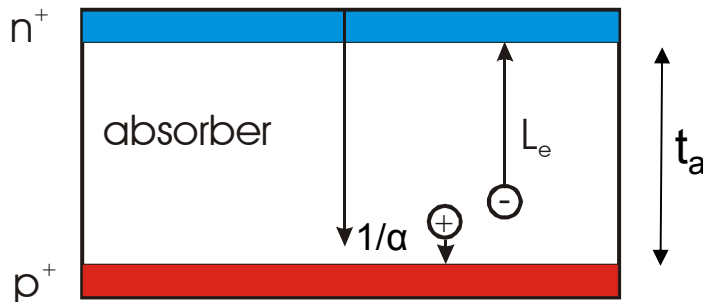
Sufficient condition:

$$L_e, L_h \gg t_a \gg 1/\alpha$$

Necessary condition:

$L_e, L_h \gg$ distance between membranes

rules out low mobility absorbers



$$t_a \gg 1/\alpha$$

bulk heterojunction

Advantage of nano-structures in conventional solar cells

- distance between membranes on nm-scale
 - absorbers can have poor transport properties
 - Problem: large interface area may increase recombination
-

luminescence as a tool to prove energy conversion efficiency

spectral intensity of luminescence

$$dR_{eh}(x) = \alpha(\hbar\omega) \frac{\Omega_{emission}}{4\pi^3 \hbar^3 c^2} \frac{(\hbar\omega)^2}{\exp\left(\frac{\hbar\omega - [\varepsilon_{FC}(x) - \varepsilon_{FV}(x)]}{kT_0}\right) - 1} d\hbar\omega$$

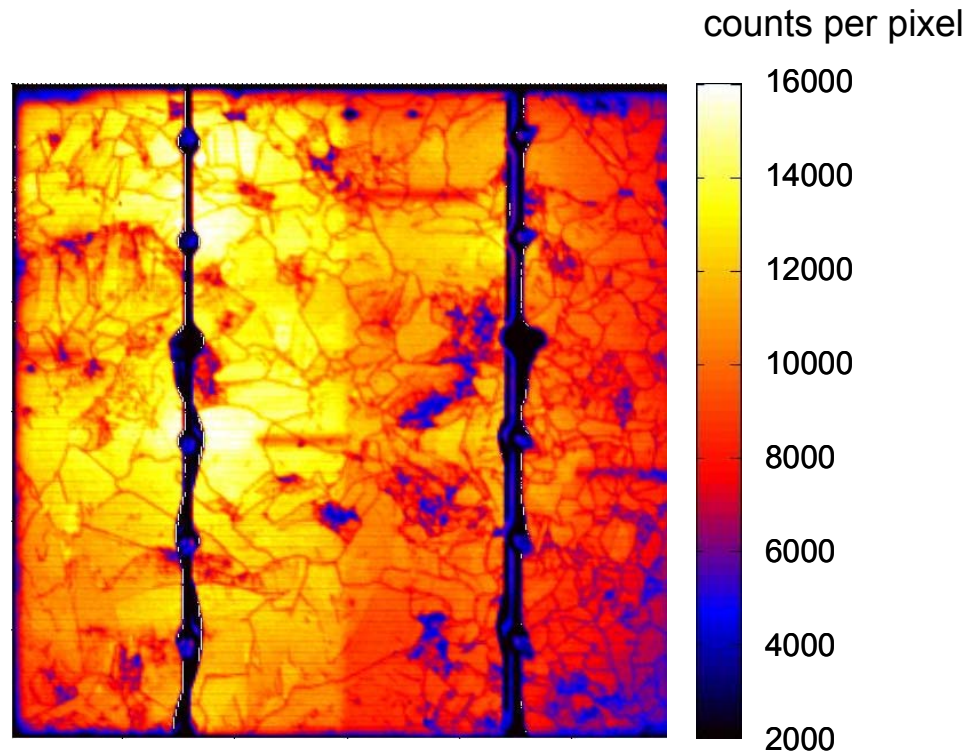
spectral emission of photons through surface of homogeneous system

$$dj_{\gamma,emit} = a(\hbar\omega) \frac{\Omega_{emission}}{4\pi^3 \hbar^3 c^2} \frac{(\hbar\omega)^2}{\exp\left(\frac{\hbar\omega - (\varepsilon_{FC} - \varepsilon_{FV})}{kT_0}\right) - 1} d\hbar\omega$$

$$a(\hbar\omega) = [1 - R(\hbar\omega)][1 - \exp(\alpha(\hbar\omega)L_e)]$$

Luminescence as a characterization tool

Electroluminescence $\lambda < 1000$ nm



Physics of Solar Cells

