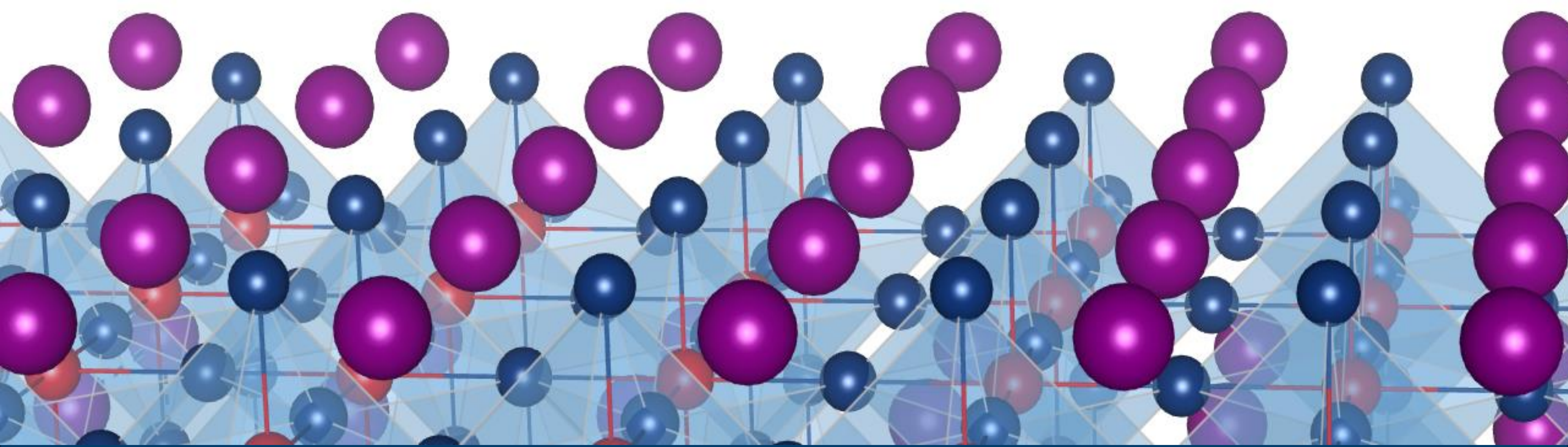


DEVICE PHYSICS OF PEROVSKITE SOLAR CELLS

- AN INTRODUCTION

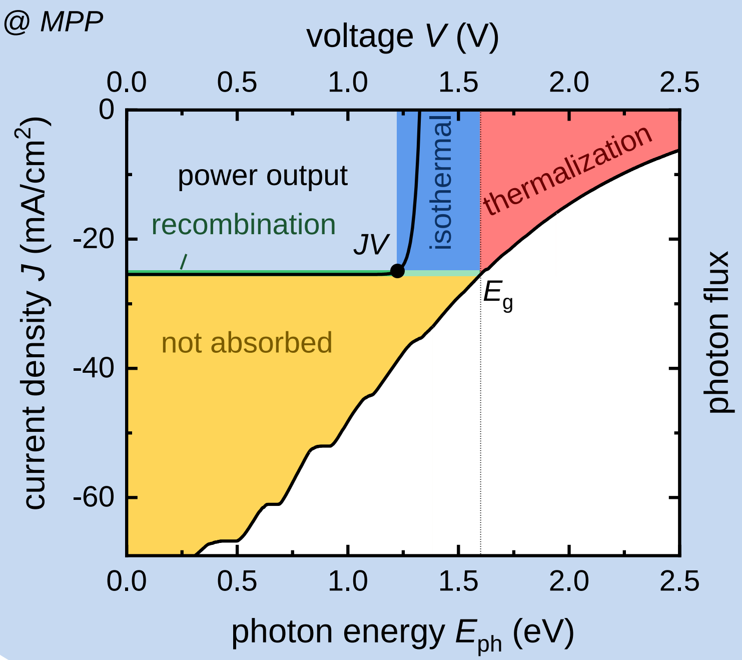
Thomas Kirchartz

IEK-5 Photovoltaik, Forschungszentrum Jülich

Outline

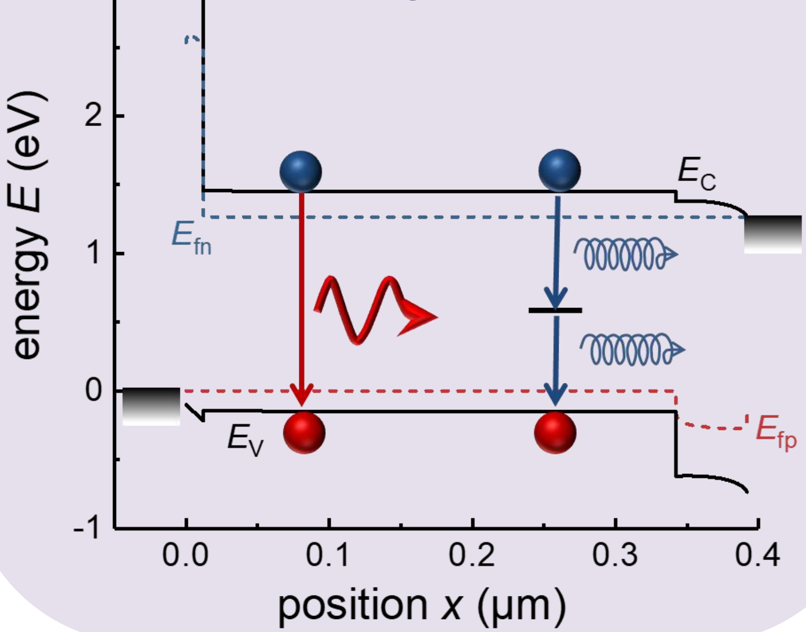
Ideal Solar Cell

Detailed Balance Model

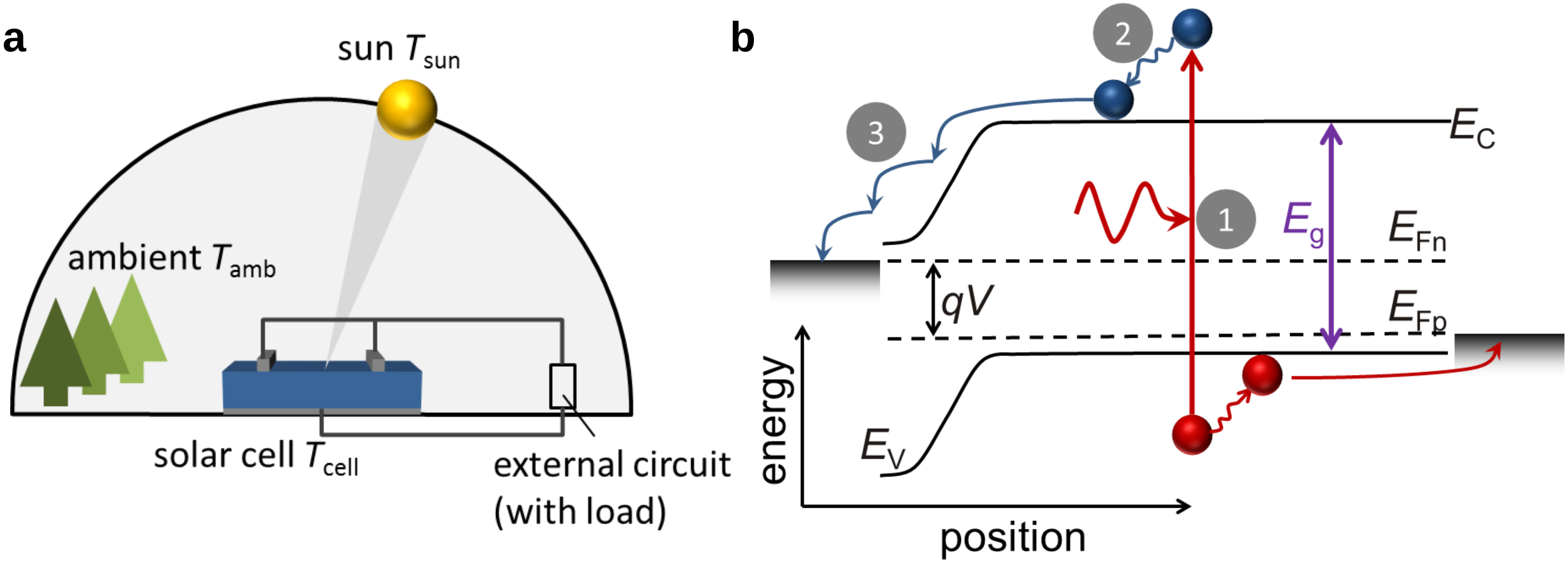


Device Physics Basics

Recombination, Transport and the Band Diagram



Photovoltaic Mechanism

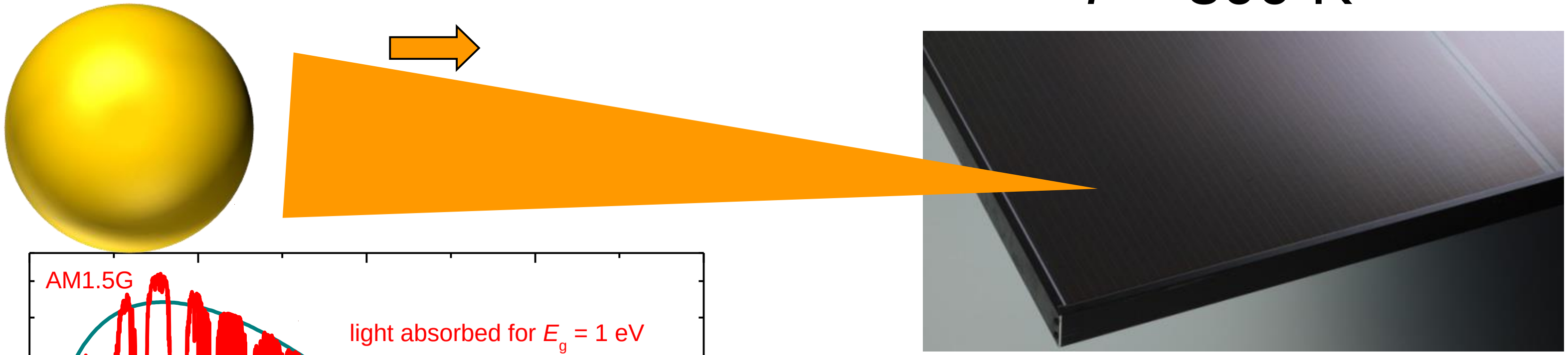


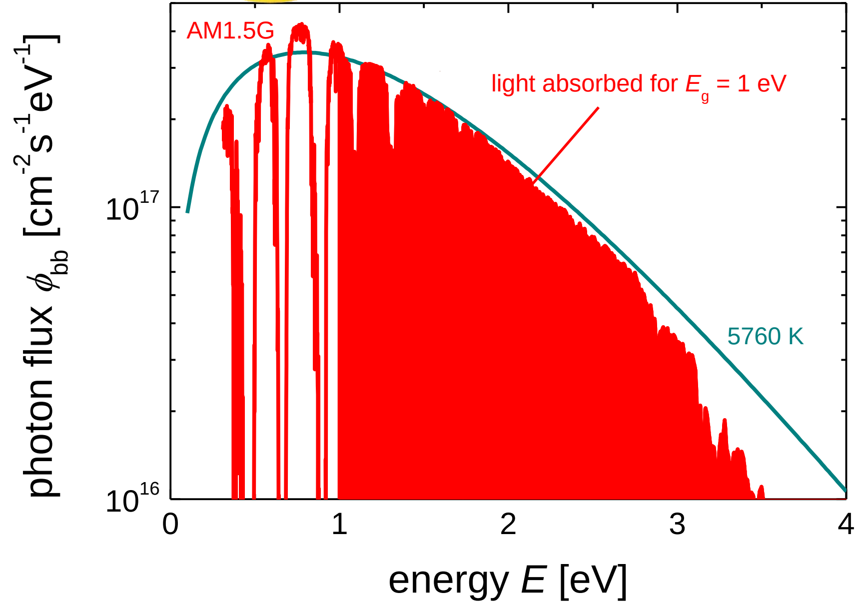
Guillemoles et al. Nat. Photonics (2019)

Shockley-Queisser model - J_{sc}

T = 5760 K

T = 300 K



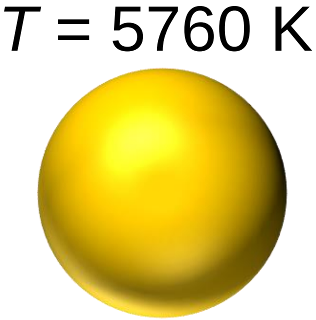


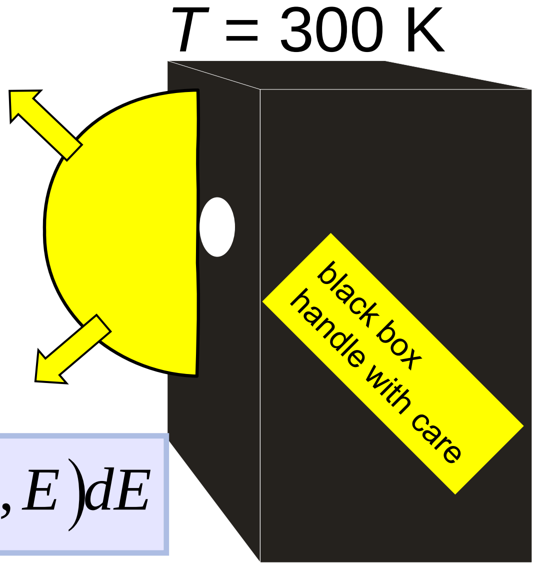
$$J_{sc} = q\int a(E)\phi_{sun}(E)dE$$

solar spectrum $\phi_{sun}(E)$

absorptance $a(E)$

Solar cell → Sun





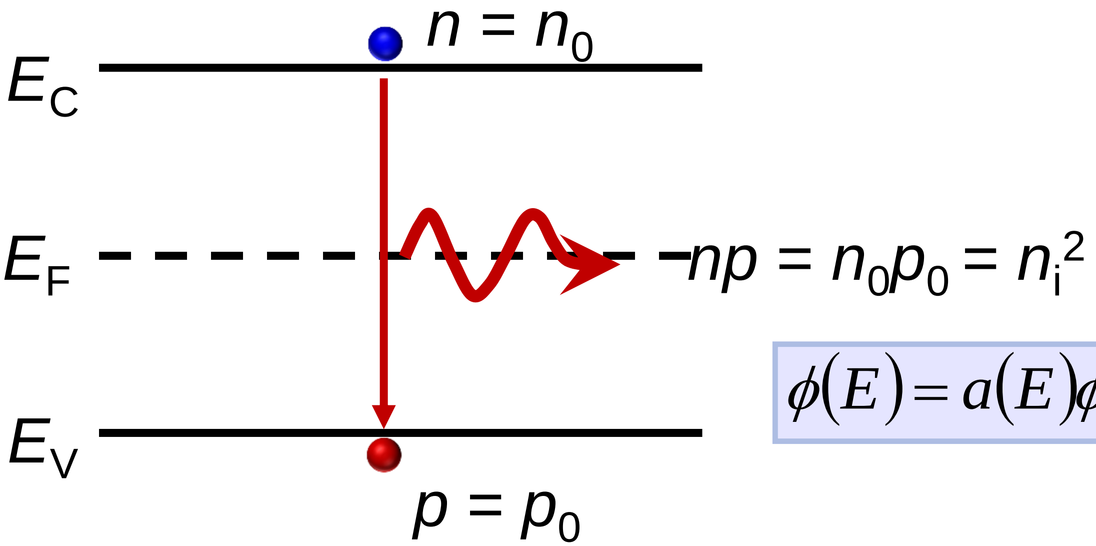
$$J_{0,\mathrm{em}} = q\int a(E)\,\phi_{\mathrm{bb}}(T_{\mathrm{sc}},E)\,dE$$

Elementary charge q

Black body spectrum $\phi_{\mathrm{bb}}(E)$

absorptance $a(E)$ = emissivity $e(E)$

Radiative Recombination

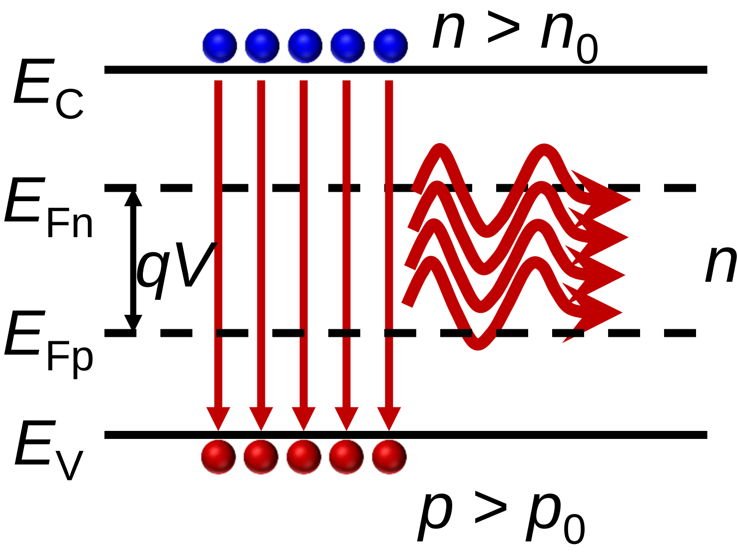


$np = n_0 p_0 = n_i^2$

$$\phi(E) = a(E)\phi_{bb}(E)$$

equilibrium

Radiative Recombination

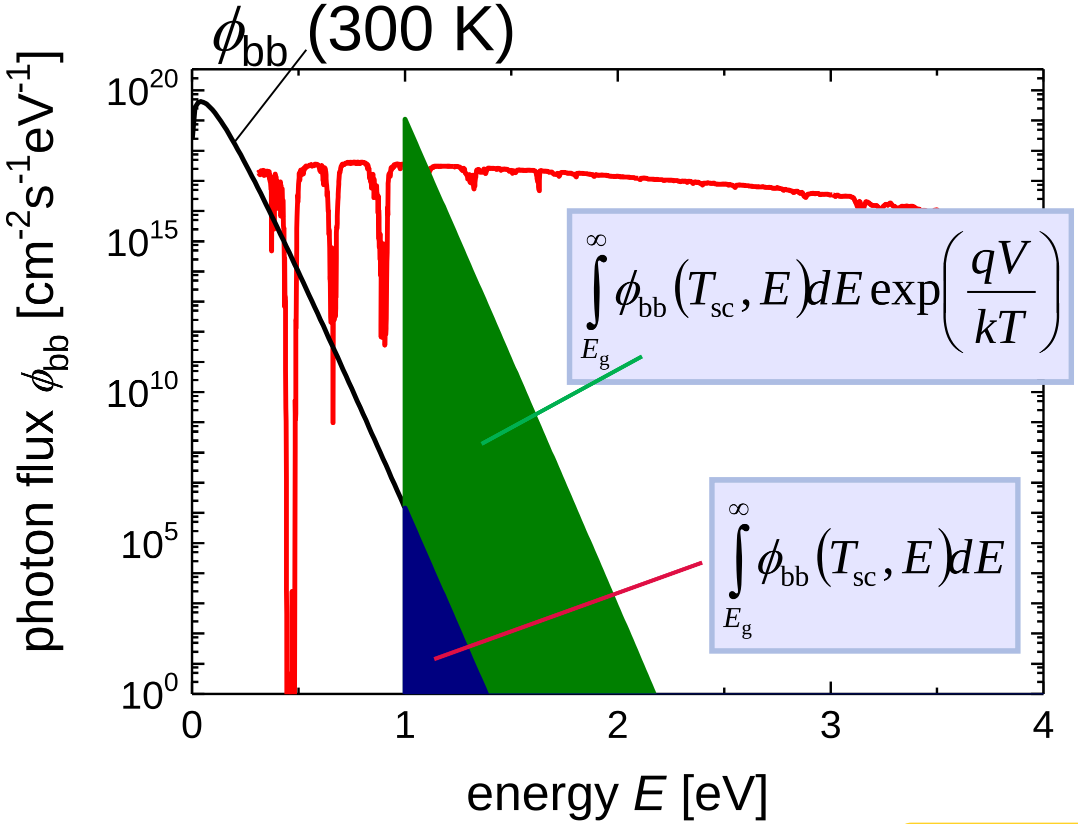


$$np = n_i^2 \exp(qV/kT)$$

$$\phi(E) = a(E)\phi_{bb}(E)e^{qV/kT}$$

Non-equilibrium

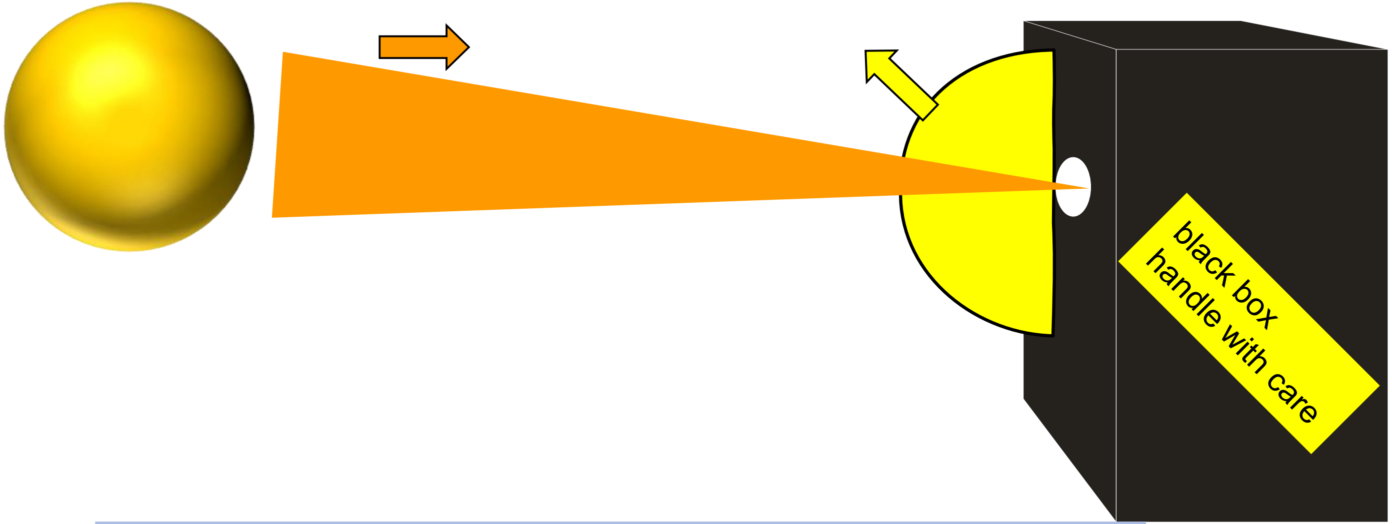
Balance Between Generation and Recombination



$$\int_{E_g}^{\infty} \phi_{bb}(T_{sc}, E)\, dE \exp\left(\frac{qV}{kT}\right)$$

$$\int_{E_g}^{\infty} \phi_{bb}(T_{sc}, E)\, dE$$

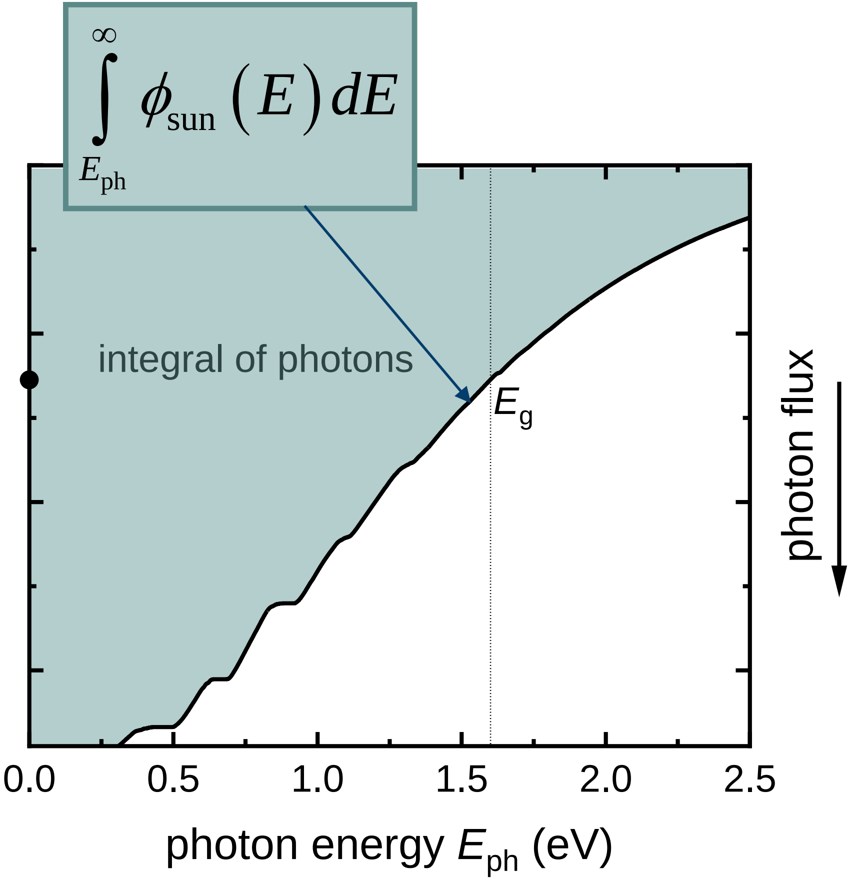
The Current-Voltage Curve



$$J = J_{\mathrm{d}} - J_{\mathrm{sc}}$$

$$= q\int a(E)\phi_{\mathrm{bb}}(T_{\mathrm{sc}},E)\,dE\left[\exp\left(\frac{qV}{kT}\right)-1\right]-J_{\mathrm{sc}}$$

Available photon flux



$$\int_{E_{ph}}^{\infty} \phi_{sun}(E)\,dE$$

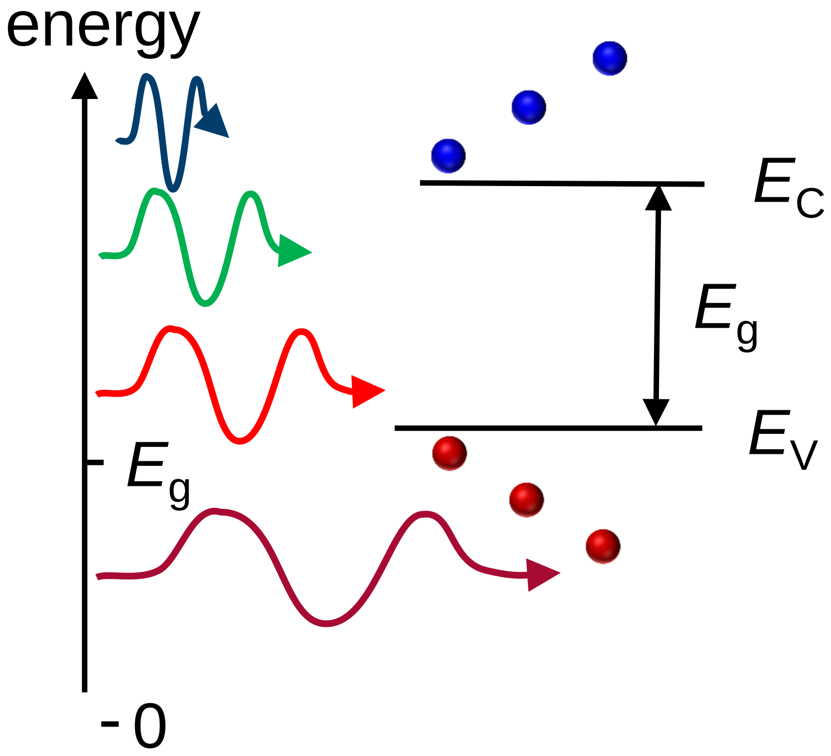
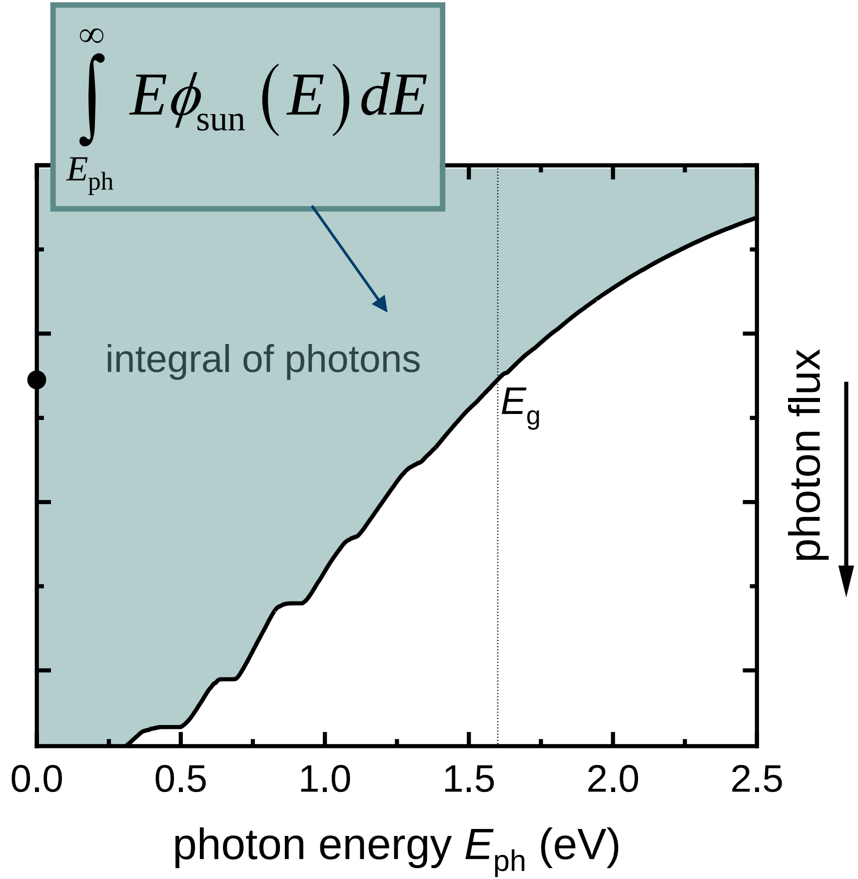


Figure credits: L. Krückemeier, U. Rau

Available photon flux



$$\int_{E_{\mathrm{ph}}}^{\infty} E\phi_{\mathrm{sun}}\left(E\right)dE$$

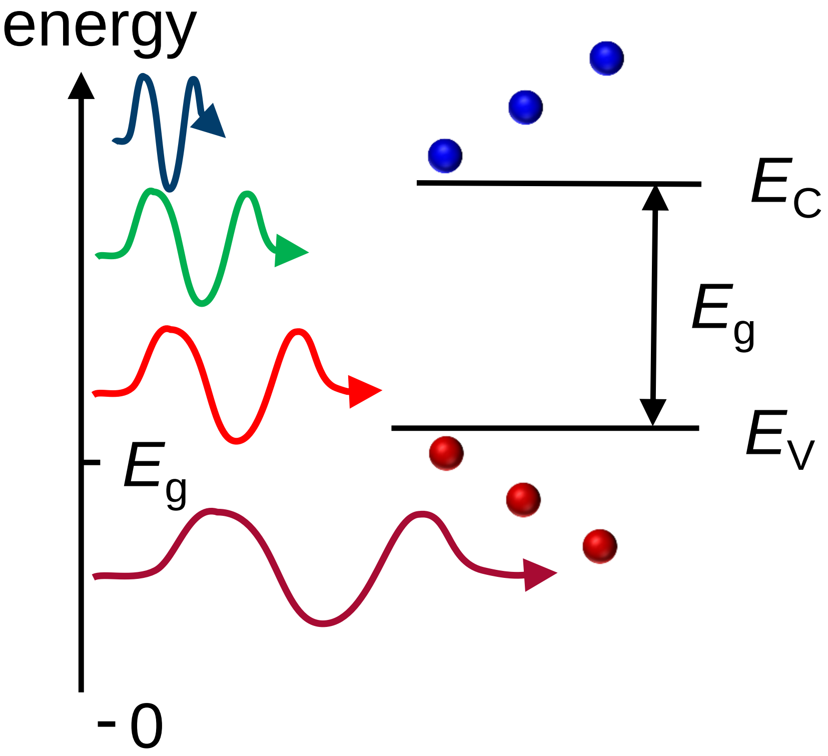
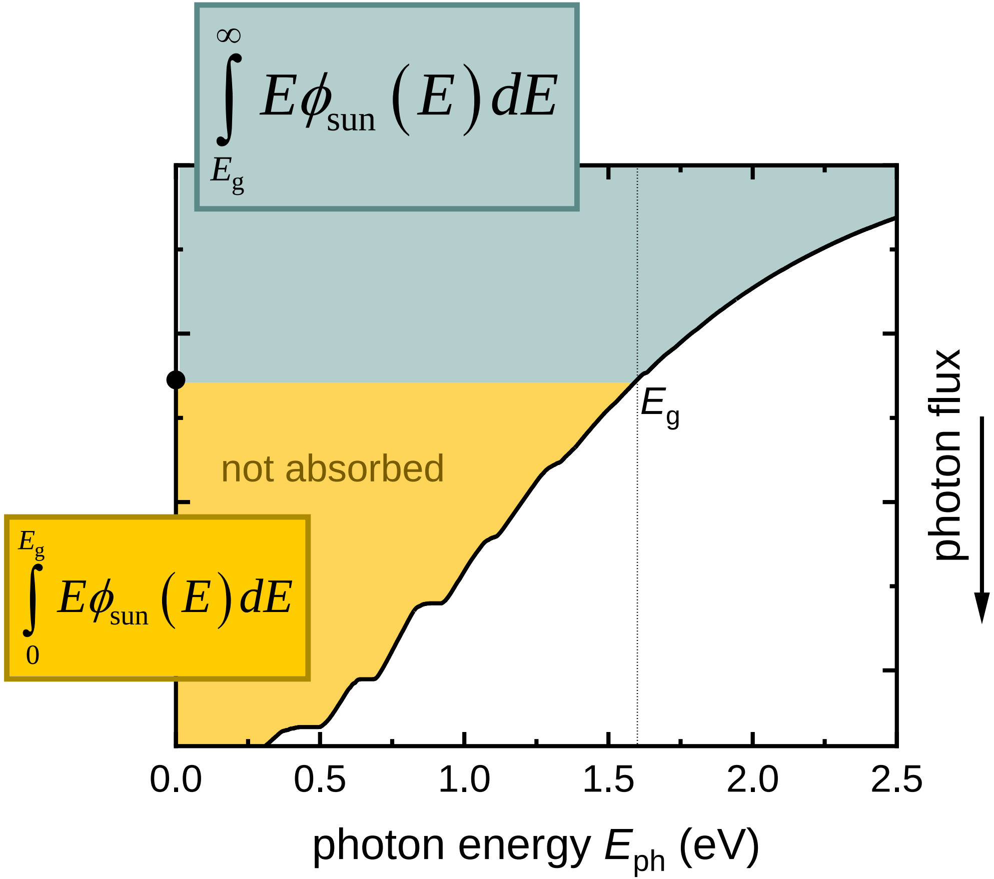


Figure credits: L. Krückemeier, U. Rau

Absorbed photon flux



$$\int_{E_g}^{\infty} E\phi_{\text{sun}}(E)\,dE$$

$$\int_{0}^{E_g} E\phi_{\text{sun}}(E)\,dE$$

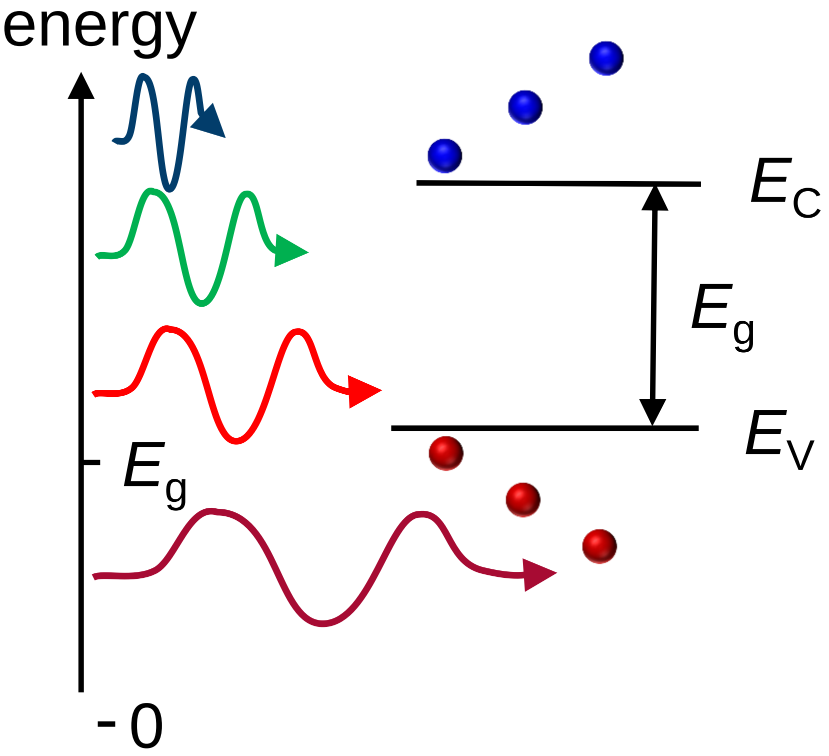
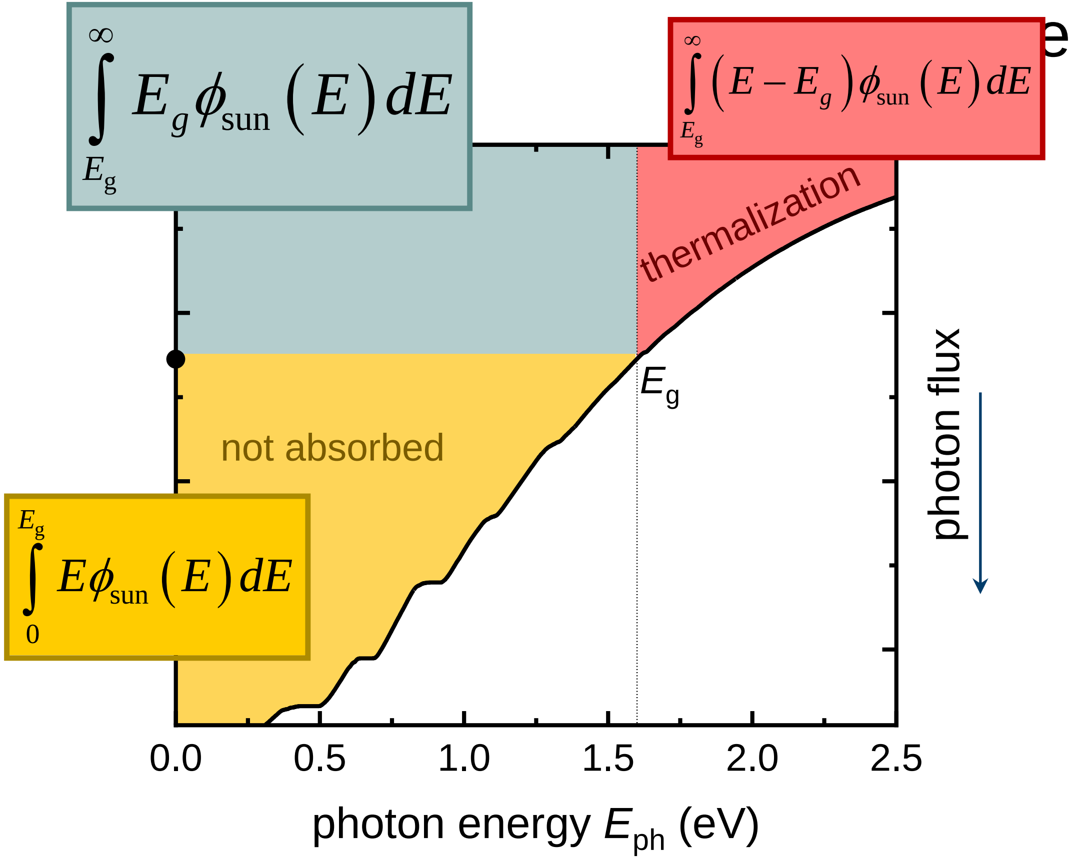


Figure credits: L. Krückemeier, U. Rau

Energy loss due to thermalization



$$\int_{E_g}^{\infty} E_g \phi_{\text{sun}}(E)\,dE$$

$$\int_{E_g}^{\infty} (E - E_g)\,\phi_{\text{sun}}(E)\,dE$$

$$\int_{0}^{E_g} E\,\phi_{\text{sun}}(E)\,dE$$

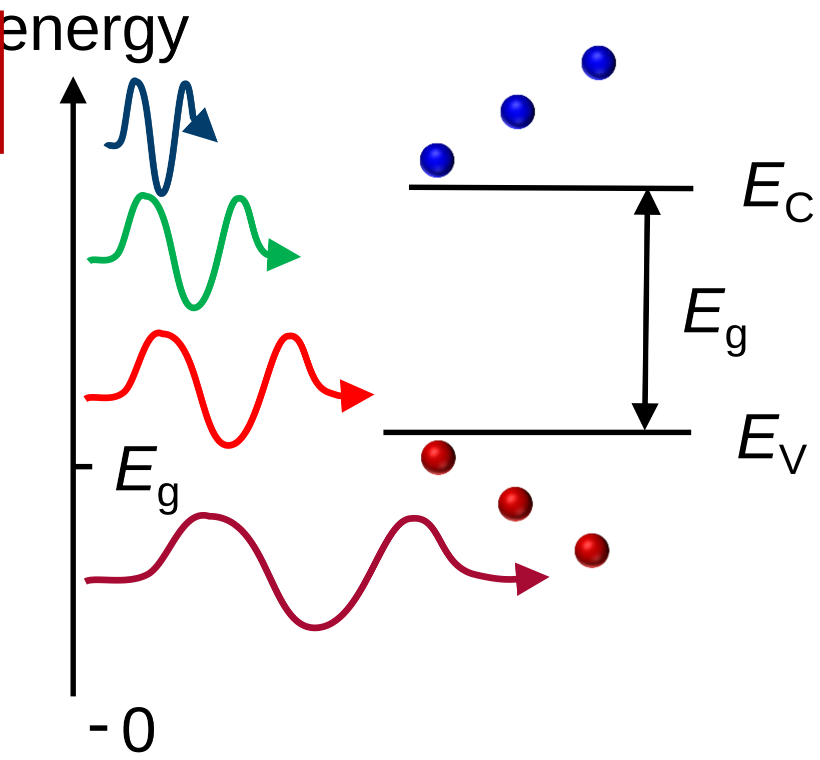
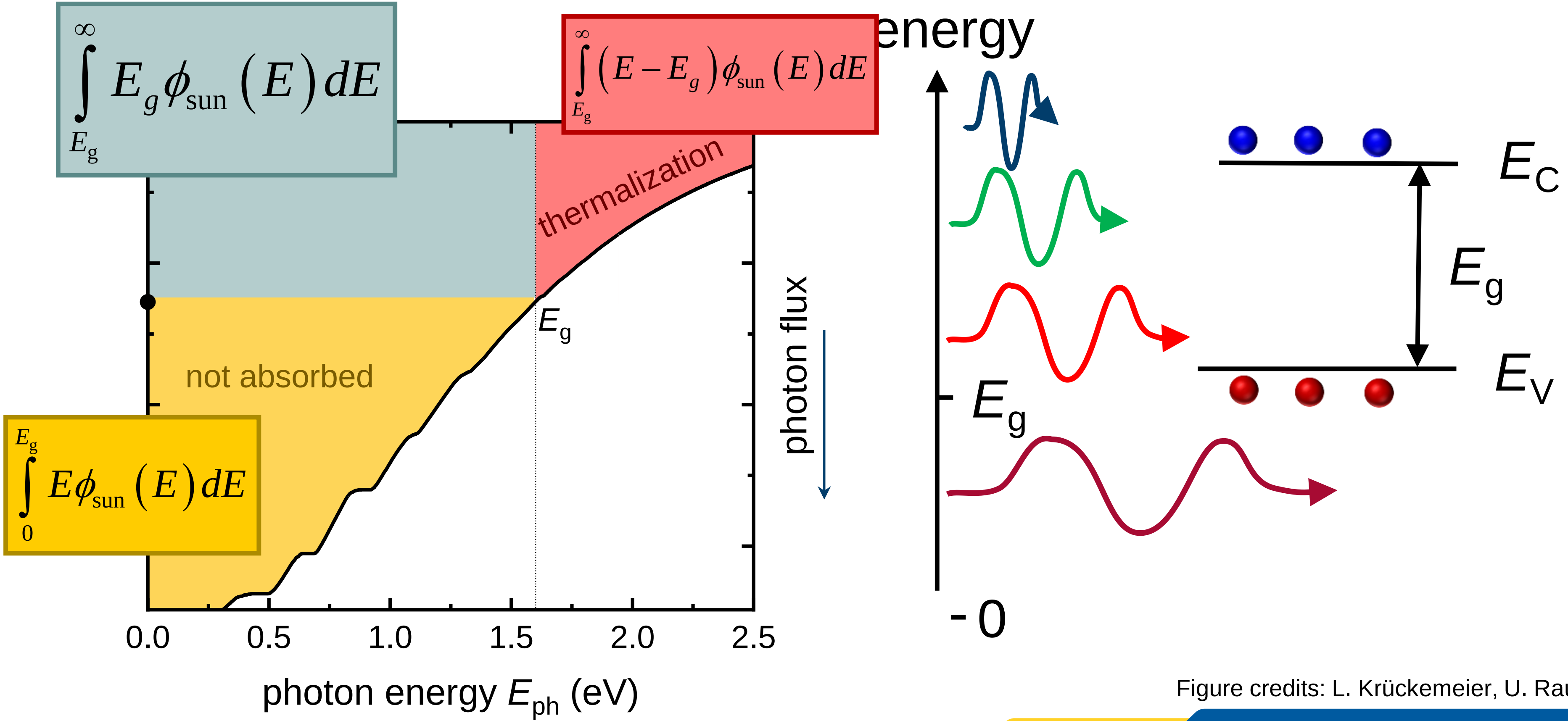


Figure credits: L. Krückemeier, U. Rau

Energy loss due to thermalization



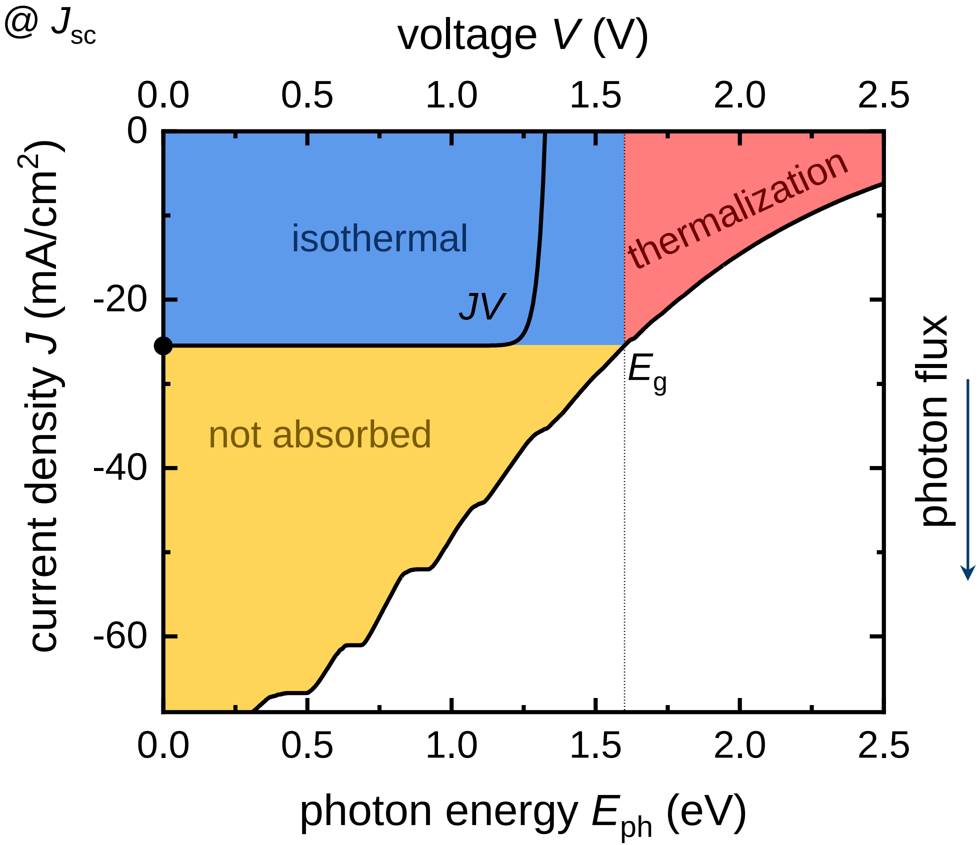
$$\int_{E_g}^{\infty} E_g \phi_{\text{sun}}(E)\,dE$$

$$\int_{E_g}^{\infty} (E-E_g)\,\phi_{\text{sun}}(E)\,dE$$

$$\int_{0}^{E_g} E\phi_{\text{sun}}(E)\,dE$$

Figure credits: L. Krückemeier, U. Rau

Losses at short circuit (thermalization in the contacts)



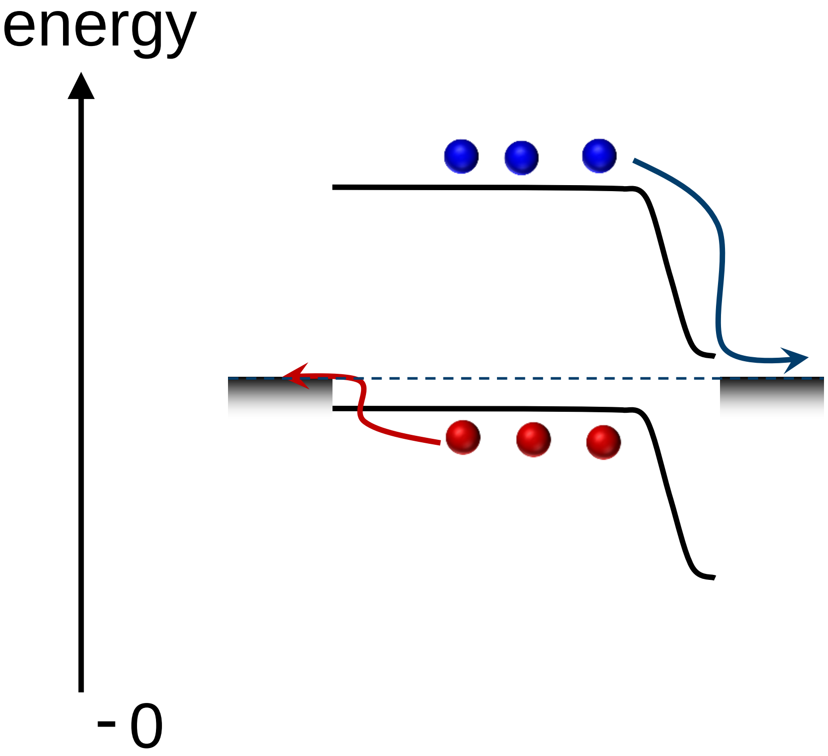
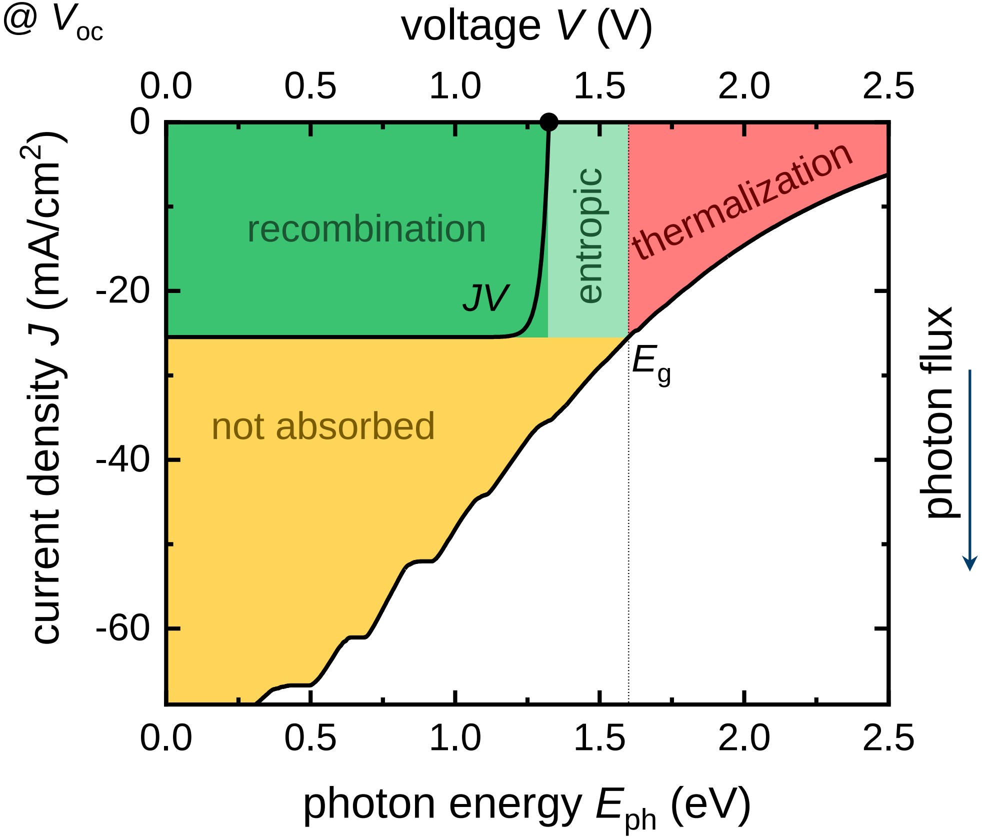


Figure credits: L. Krückemeier

Losses at open circuit (recombination)

@ V_{oc}



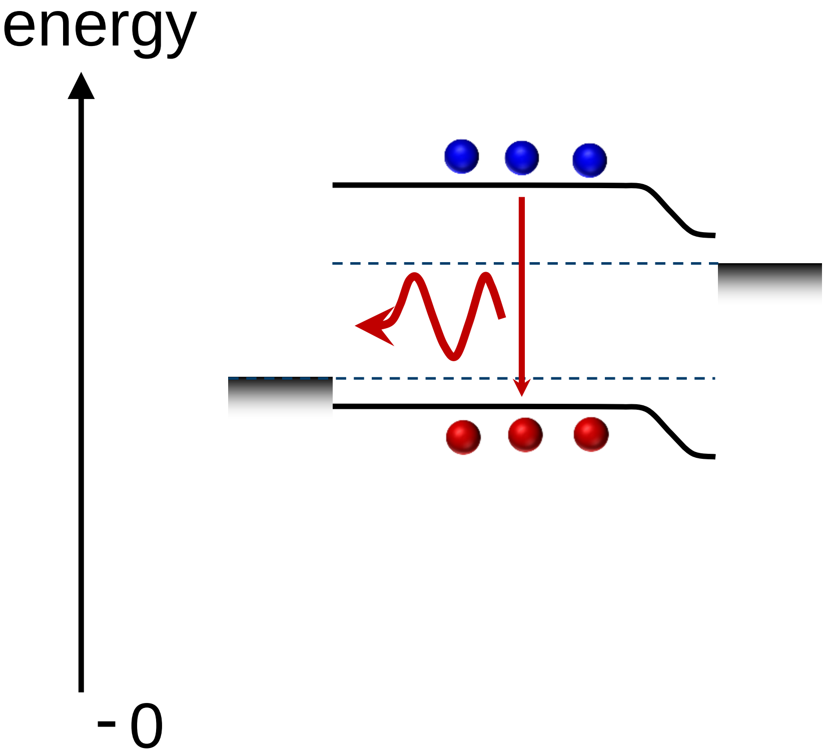
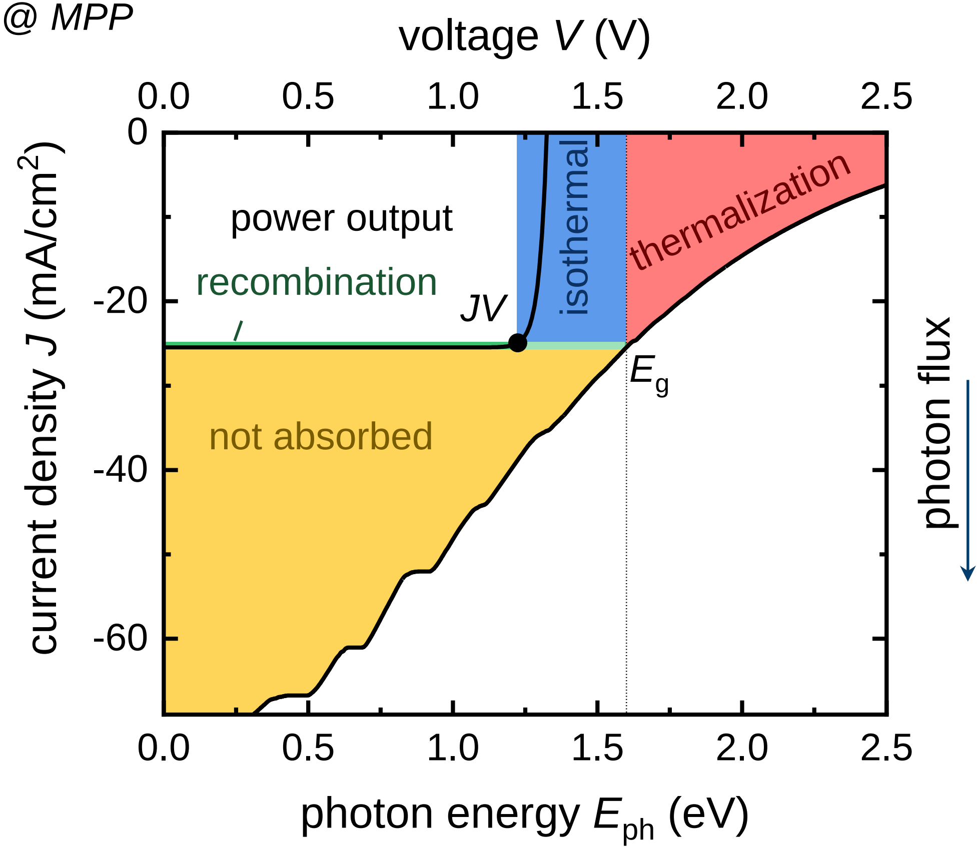


Figure credits: L. Krückemeier

Losses at the maximum power point

@ MPP



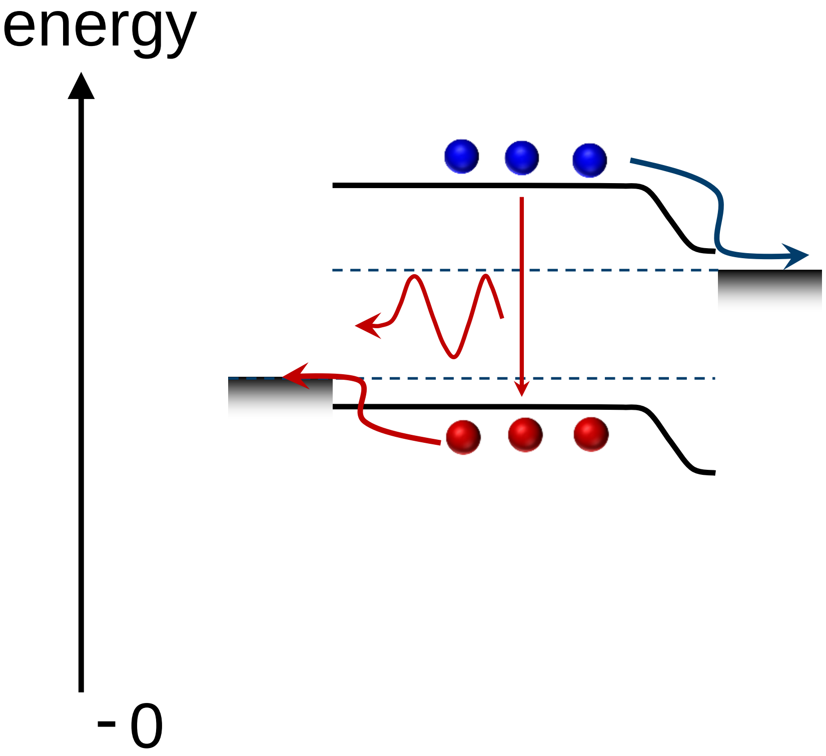
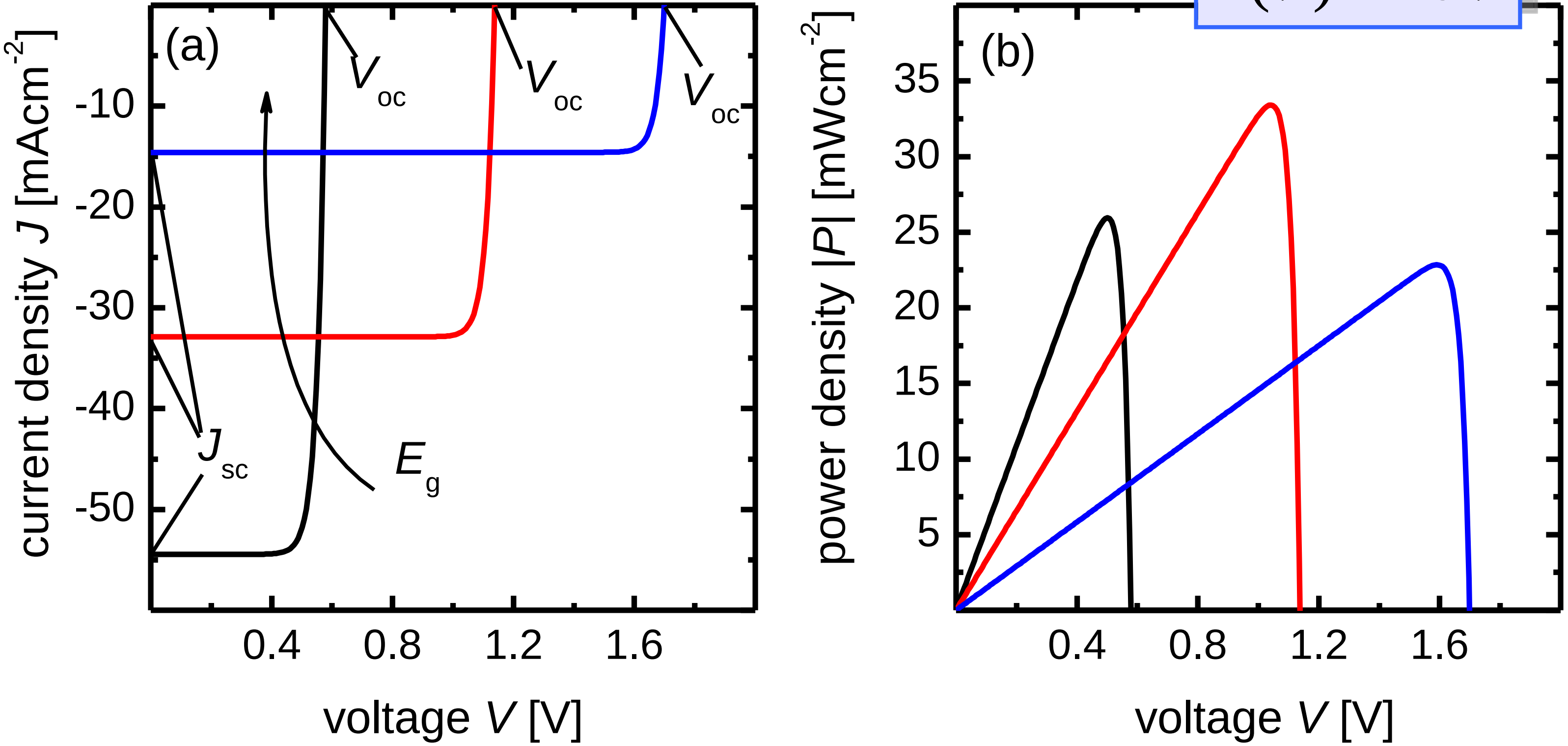


Figure credits: L. Krückemeier

Current Density and Power Density

vs. Voltage

$$P(V) = -JV$$



Losses as a function of voltage

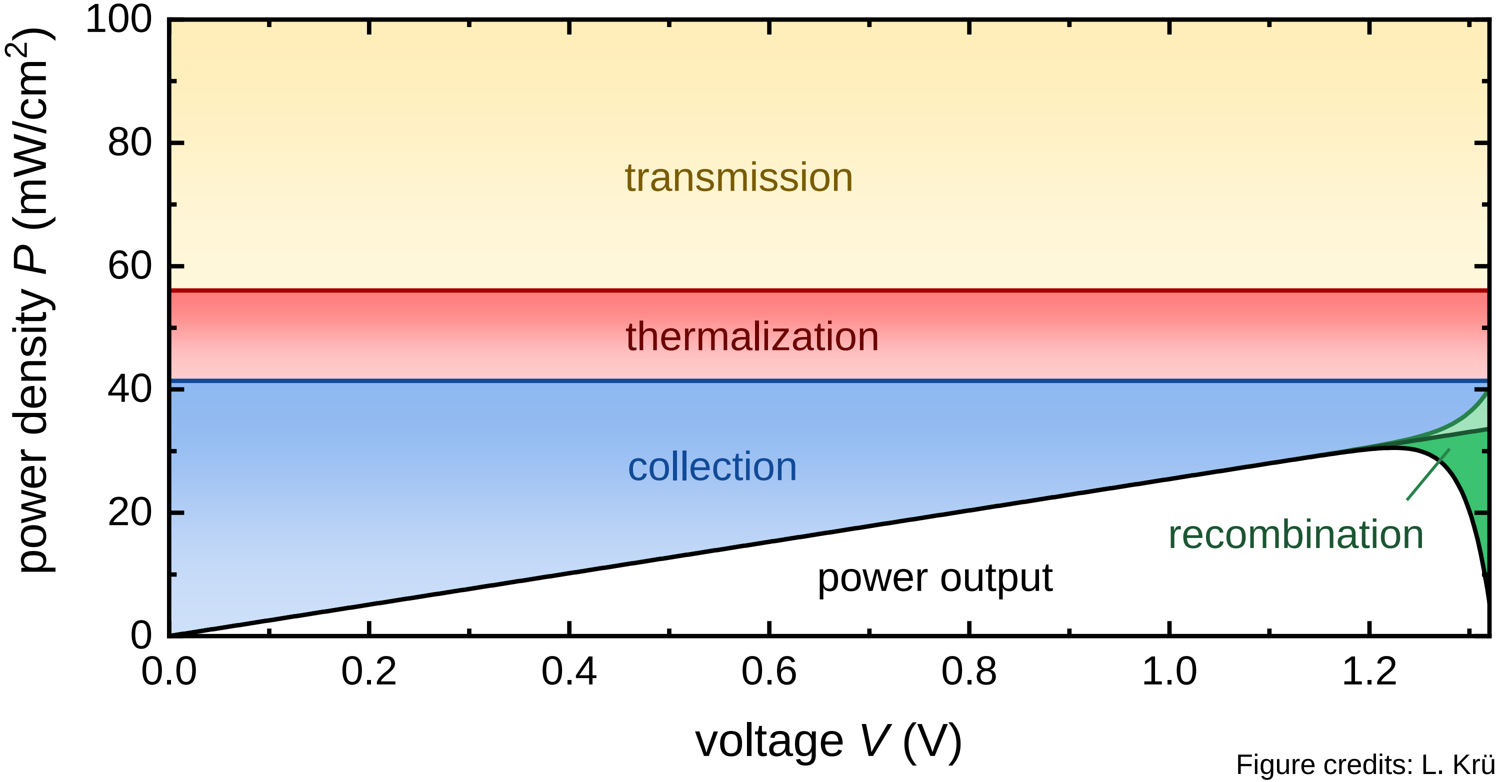
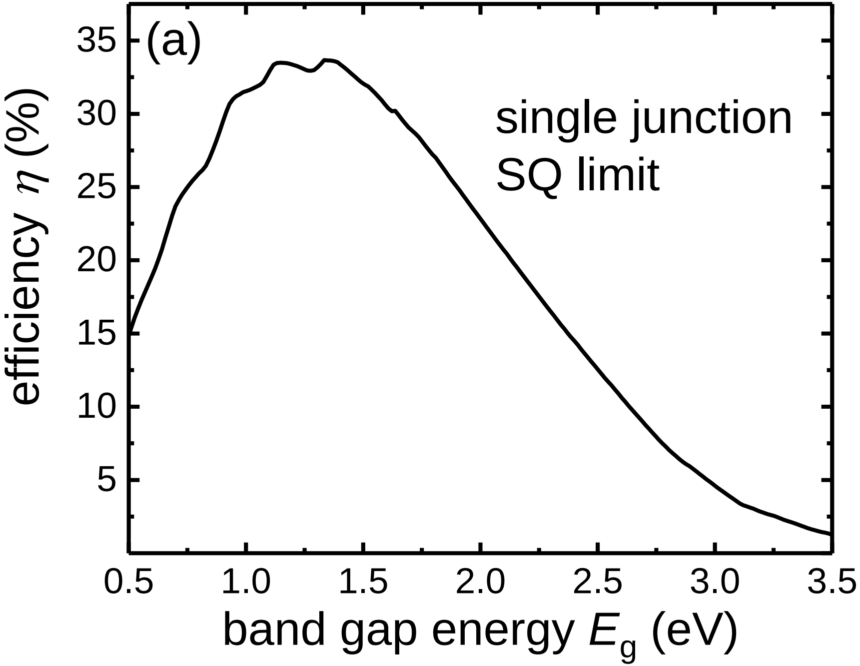


Figure credits: L. Krückemeier

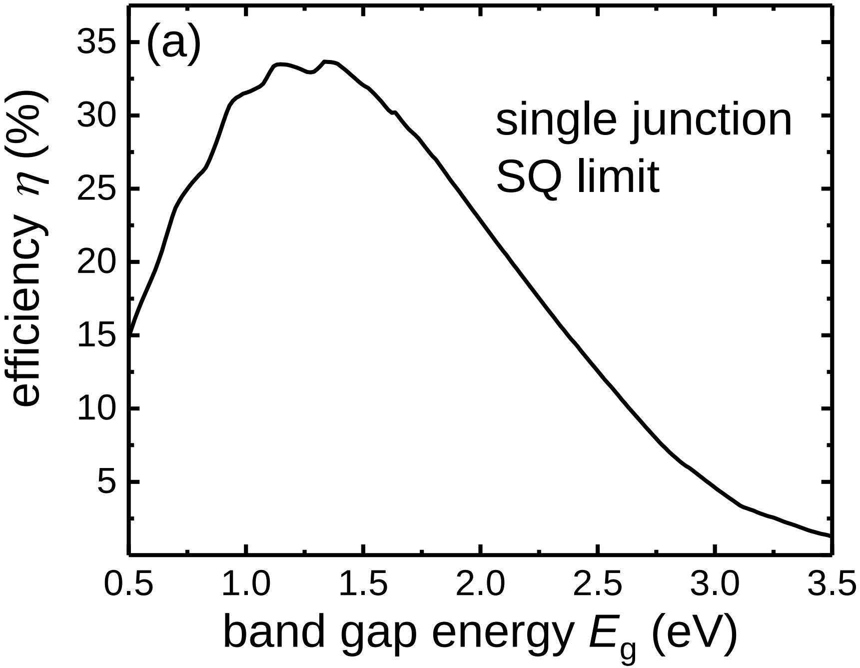
Shockley-Queisser Limit

Shockley and Queisser, J. Appl. Phys. (1961)



Shockley-Queisser Limit

Shockley and Queisser, J. Appl. Phys. (1961)



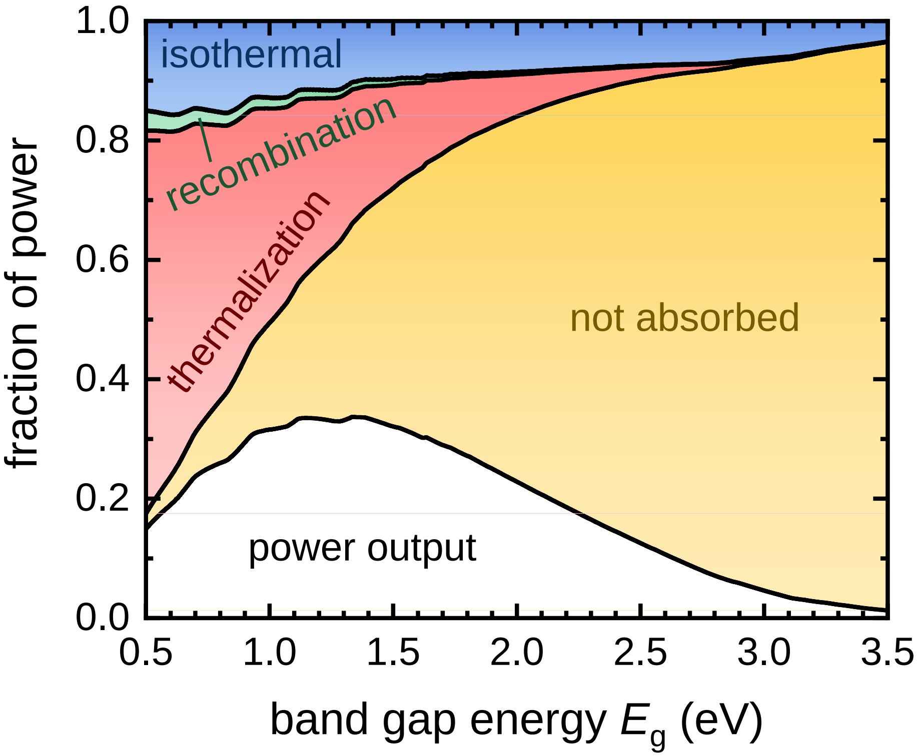
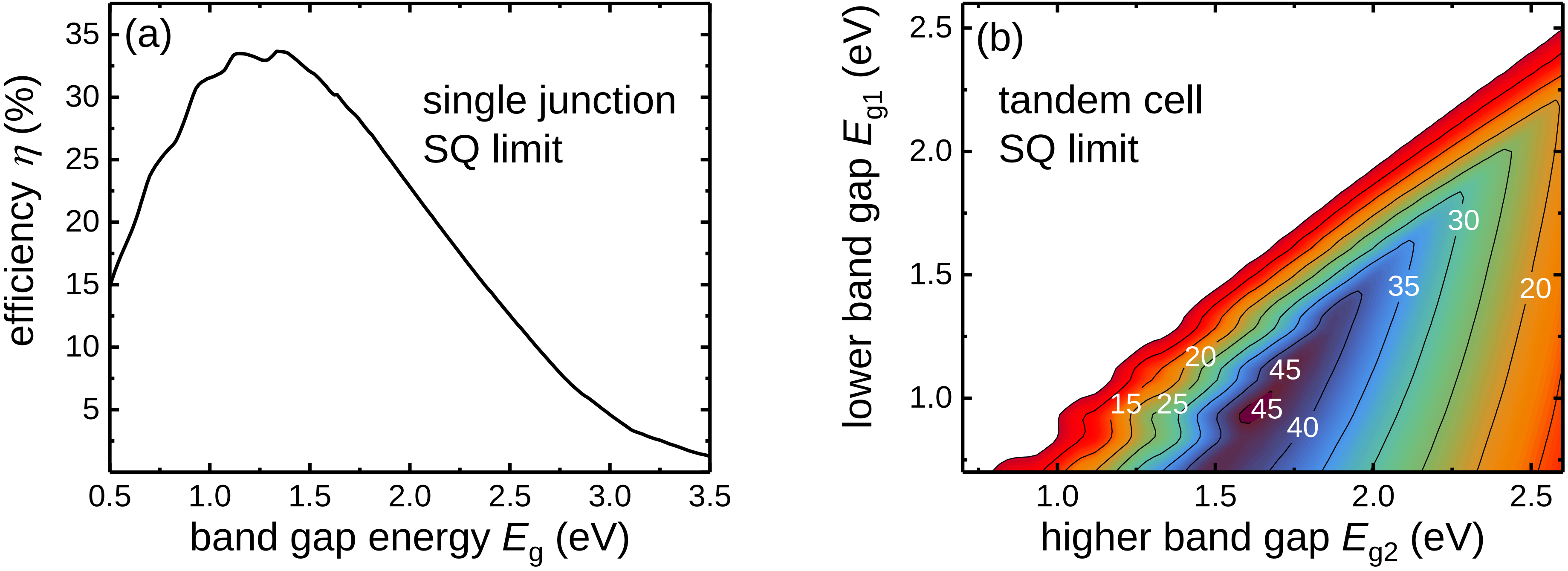


Figure credits: L. Krückemeier

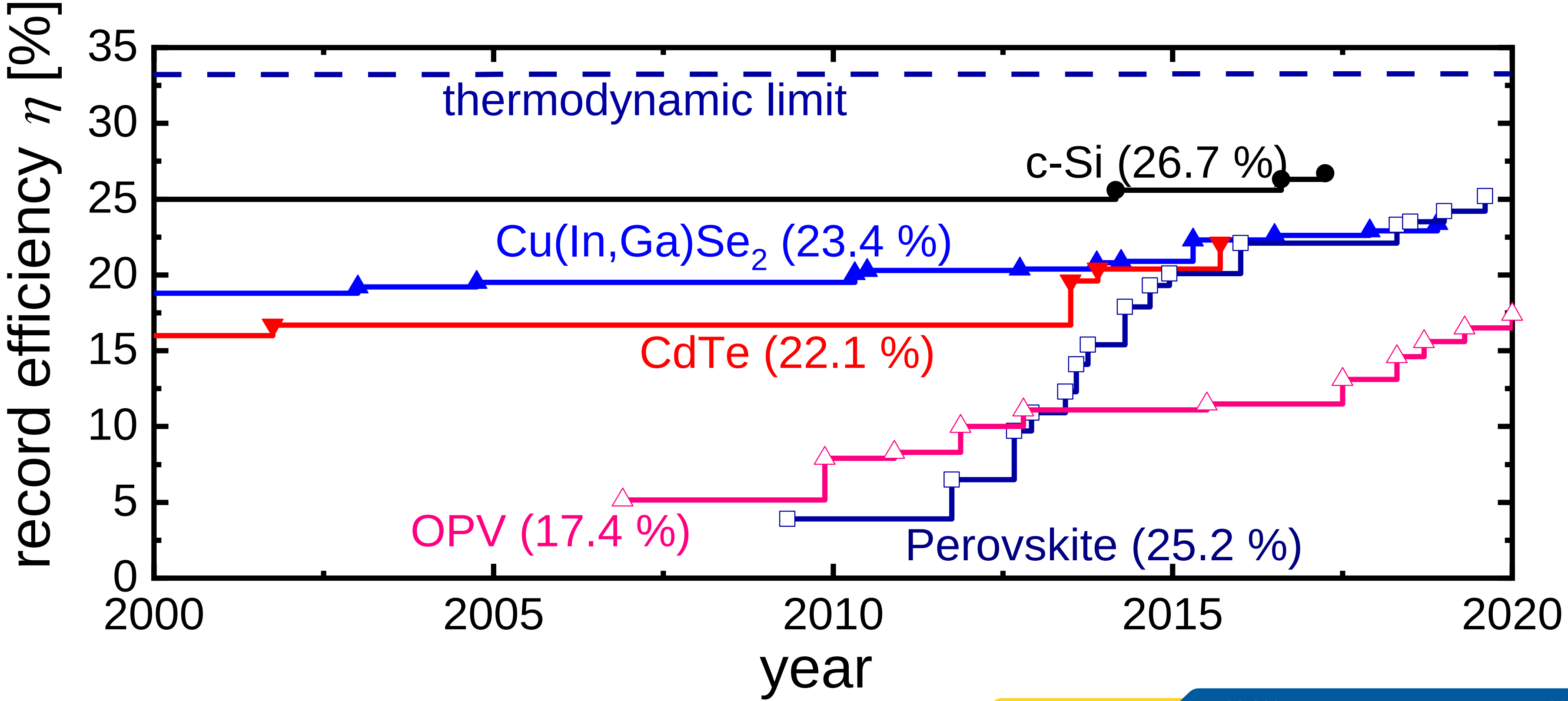
Shockley-Queisser Limit

Shockley and Queisser, J. Appl. Phys. (1961)

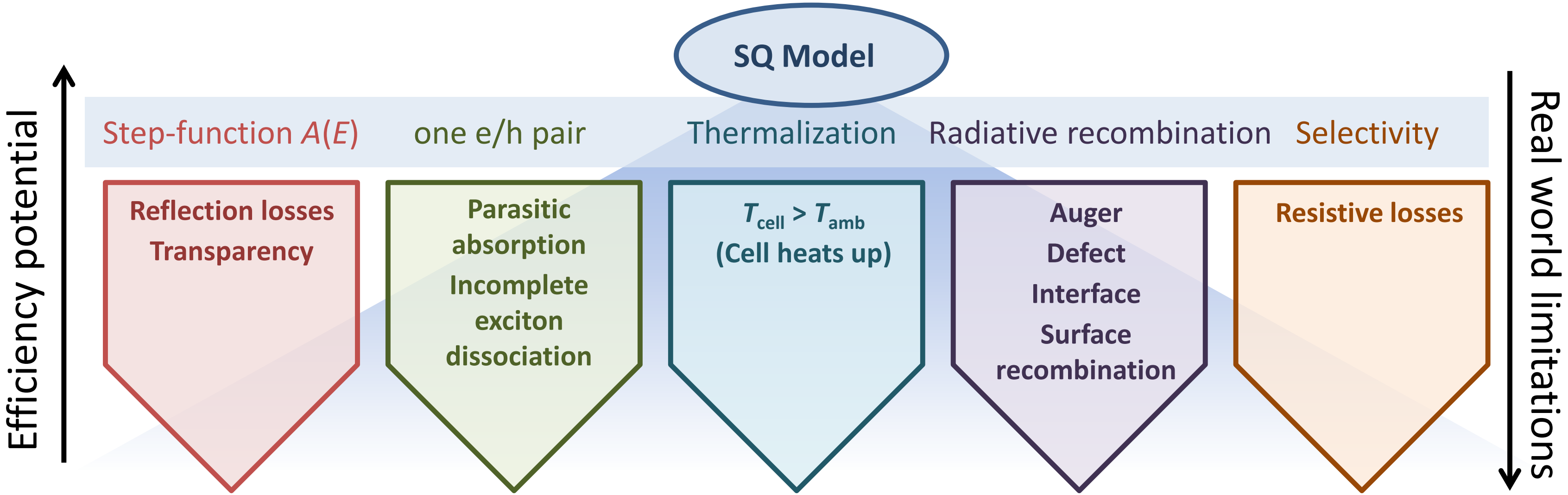


Kirchartz and Rau, Adv. Energy Mat. (2018)

Efficiency trends for different PV technologies



Ideal solar cell vs. Real world losses



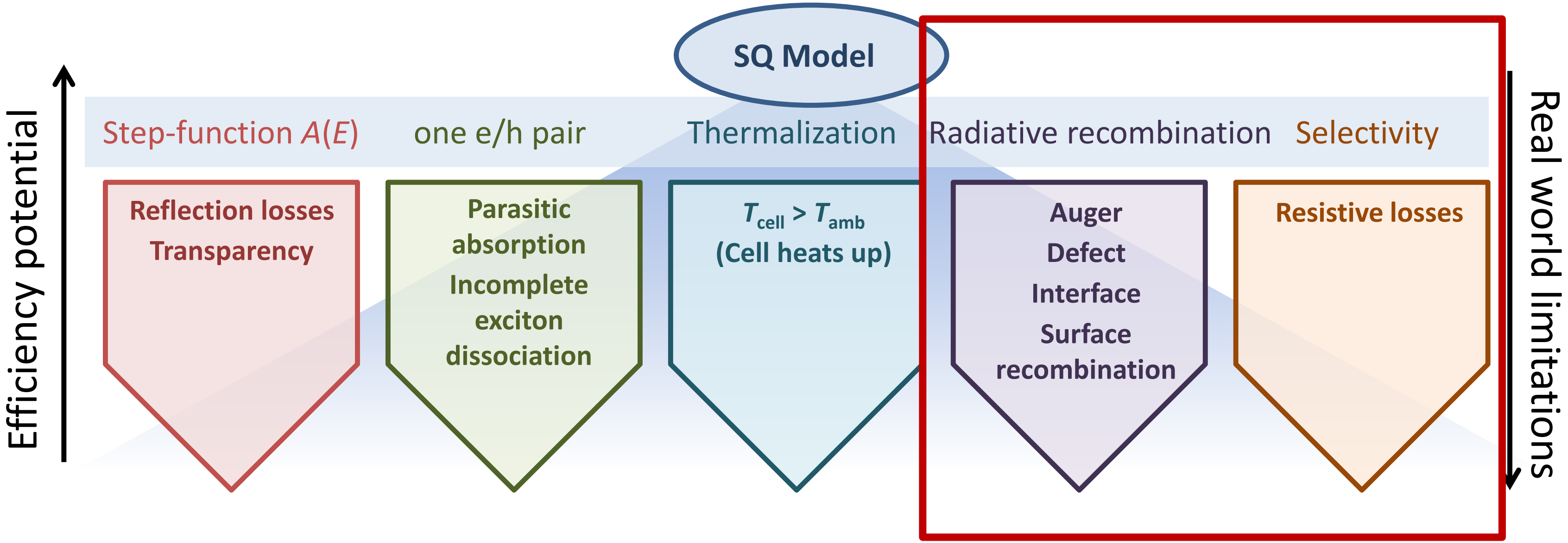
SQ Model

Efficiency potential

Real world limitations

Step-function *A*(*E*)	one e/h pair	Thermalization	Radiative recombination	Selectivity
Reflection losses **Transparency**	**Parasitic absorption** **Incomplete exciton dissociation**	**$T_{cell} > T_{amb}$** **(Cell heats up)**	**Auger** **Defect** **Interface** **Surface recombination**	**Resistive losses**

Ideal solar cell vs. Real world losses



Efficiency potential

SQ Model

Step-function $A(E)$

one e/h pair

Thermalization

Radiative recombination

Selectivity

Reflection losses

Transparency

Parasitic absorption

Incomplete exciton dissociation

$T_{cell} > T_{amb}$

(Cell heats up)

Auger

Defect

Interface

Surface recombination

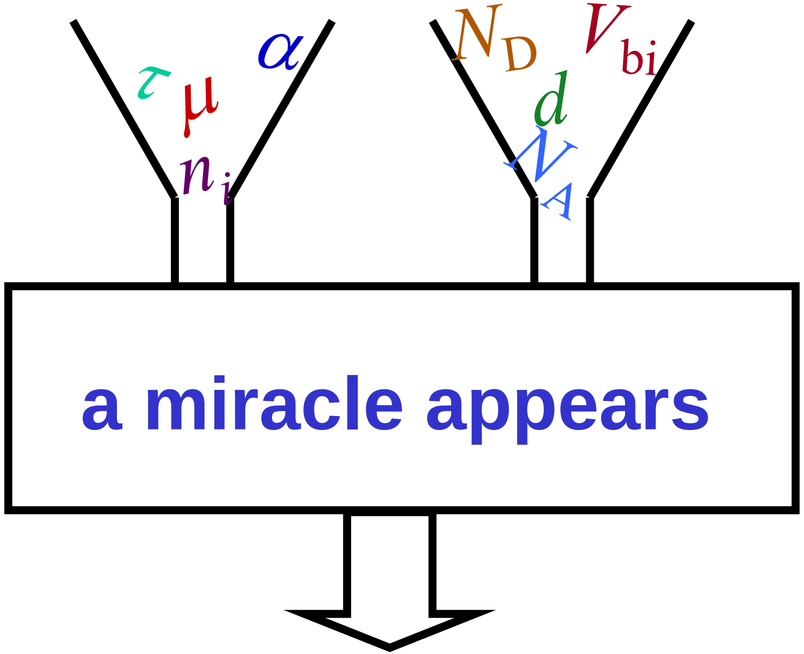
Resistive losses

Real world limitations

Electric or electronic losses

Device physics of solar cells

From material parameters to device performance

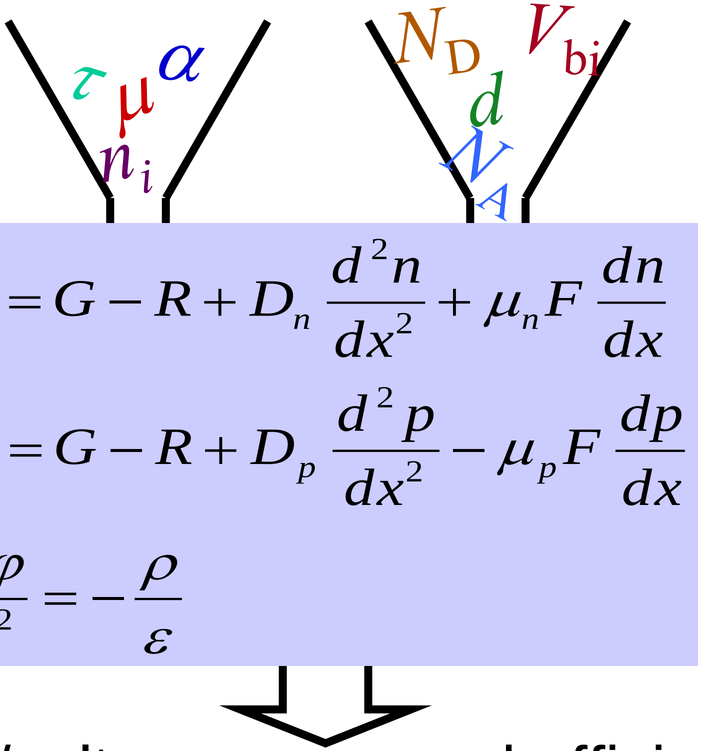


a miracle appears

current/voltage curve and efficiency η

Device physics of solar cells

From material parameters to device performance



$$\frac{dn}{dt} = G - R + D_n \frac{d^2 n}{dx^2} + \mu_n F \frac{dn}{dx}$$

Continuity equation for electrons

$$\frac{dp}{dt} = G - R + D_p \frac{d^2 p}{dx^2} - \mu_p F \frac{dp}{dx}$$

Continuity equation for holes

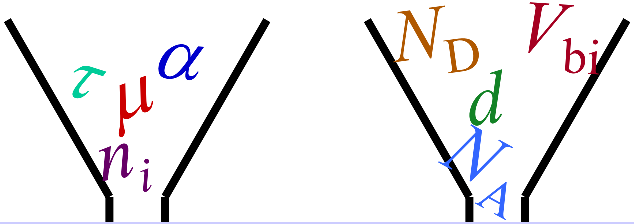
$$\frac{d^2 \varphi}{dx^2} = -\frac{\rho}{\varepsilon}$$

Poisson equation

current/voltage curve and efficiency η

Device physics of solar cells

From material parameters to device performance



$$\frac{dn}{dt} = G - R + D_n \frac{d^2 n}{dx^2} + \mu_n F \frac{dn}{dx}$$

$$\frac{dp}{dt} = G - R + D_p \frac{d^2 p}{dx^2} - \mu_p F \frac{dp}{dx}$$

$$\frac{d^2 \varphi}{dx^2} = -\frac{\rho}{\varepsilon}$$

current/voltage curve and efficiency η

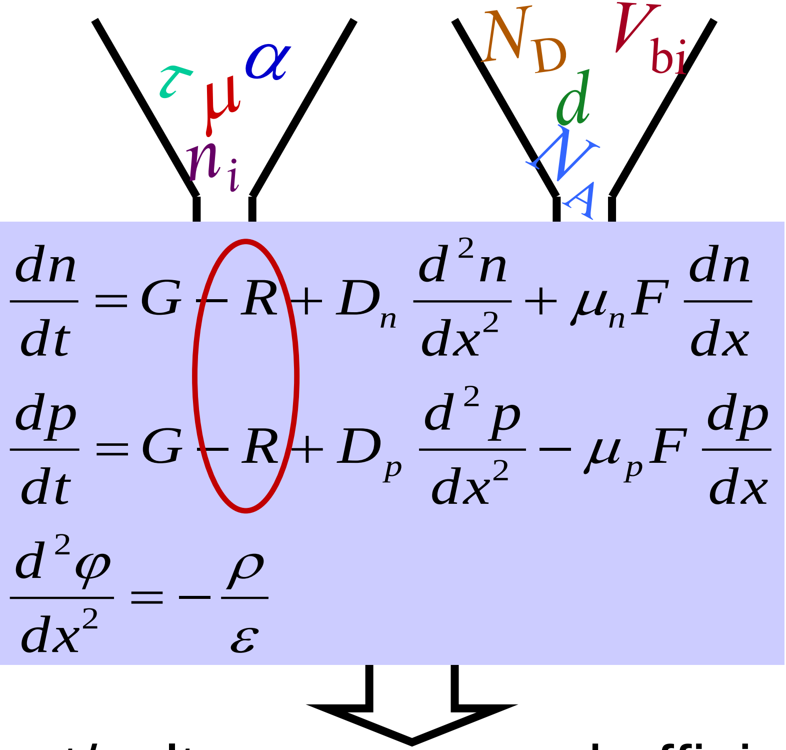
Definition: Generation rate of electron-hole pairs

Topic: optics

Depends on absorption coefficient α, thickness *d* and aspects such as light trapping or the presence of anti-reflective coatings

Device physics of solar cells

From material parameters to device performance



$$\frac{dn}{dt} = G \boxed{-R} + D_n \frac{d^2 n}{dx^2} + \mu_n F \frac{dn}{dx}$$

$$\frac{dp}{dt} = G \boxed{-R} + D_p \frac{d^2 p}{dx^2} - \mu_p F \frac{dp}{dx}$$

$$\frac{d^2 \varphi}{dx^2} = -\frac{\rho}{\varepsilon}$$

current/voltage curve and efficiency η

Definition: Recombination rate of electron-hole pairs

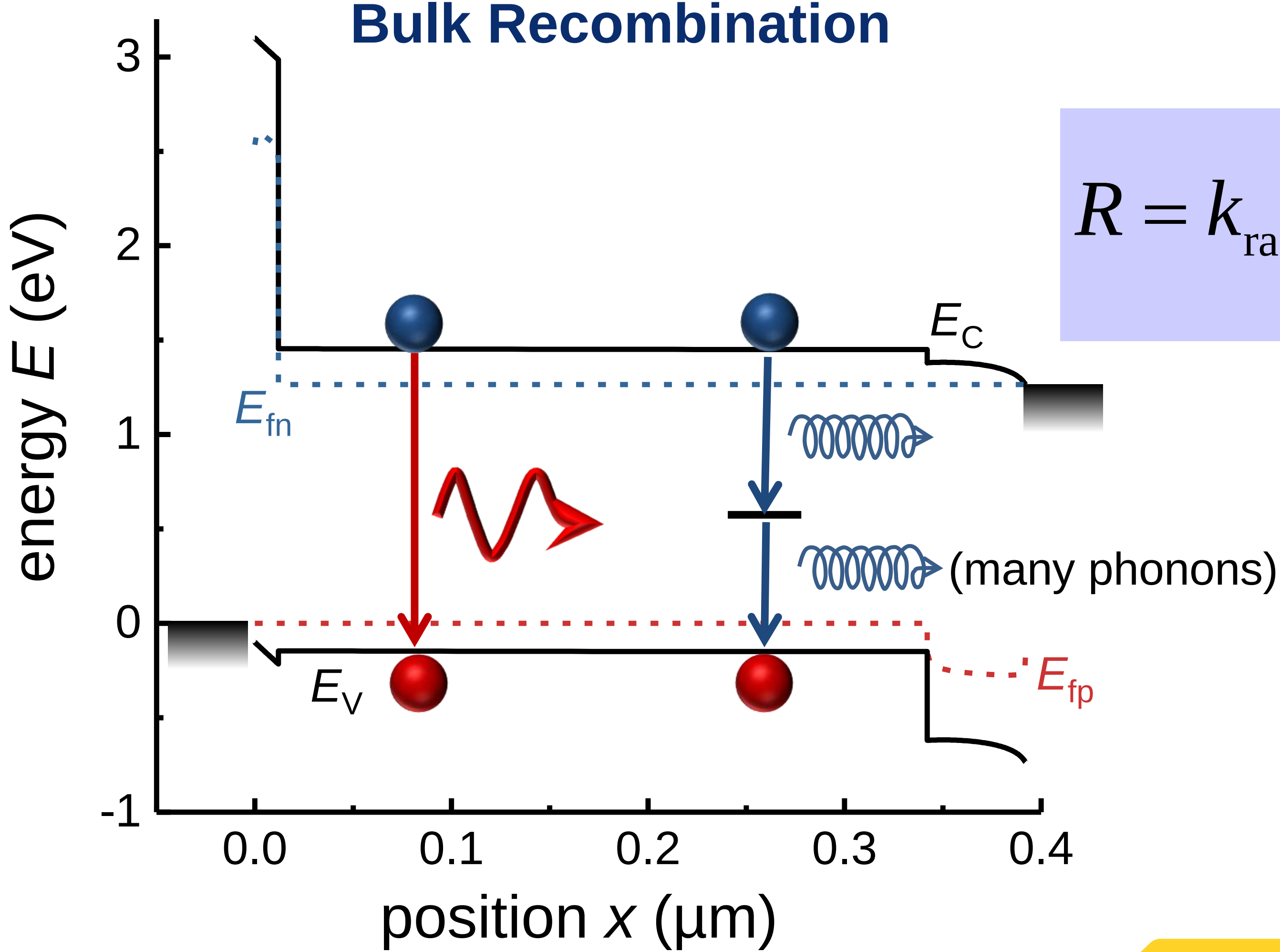
Topic: electronic properties

Depends on defect densities and positions, capture coefficients, carrier densities. Example:

$$R = k_\mathrm{rad} np + \frac{np}{\tau_\mathrm{p} n + \tau_\mathrm{n} p}$$

(rad. SRH)

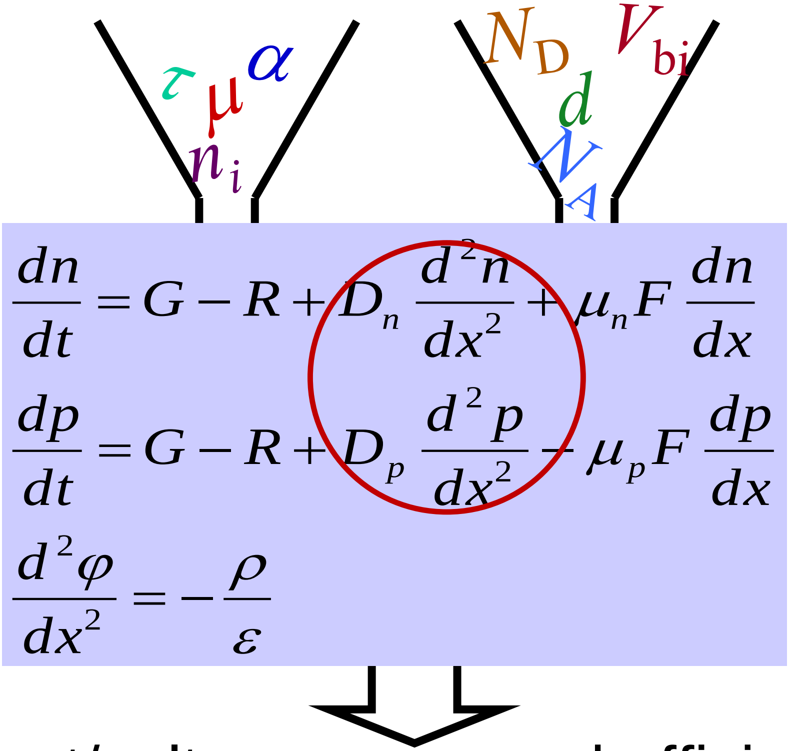
Bulk Recombination



$$R = k_{\mathrm{rad}} np + \frac{np}{\tau_{\mathrm{p}} n + \tau_{\mathrm{n}} p}$$

Device physics of solar cells

From material parameters to device performance



$$\frac{dn}{dt} = G - R + \boxed{D_n \frac{d^2 n}{dx^2}} + \mu_n F \frac{dn}{dx}$$

$$\frac{dp}{dt} = G - R + \boxed{D_p \frac{d^2 p}{dx^2}} - \mu_p F \frac{dp}{dx}$$

$$\frac{d^2 \varphi}{dx^2} = -\frac{\rho}{\varepsilon}$$

current/voltage curve and efficiency η

Definition: Spatial derivative of the diffusion current

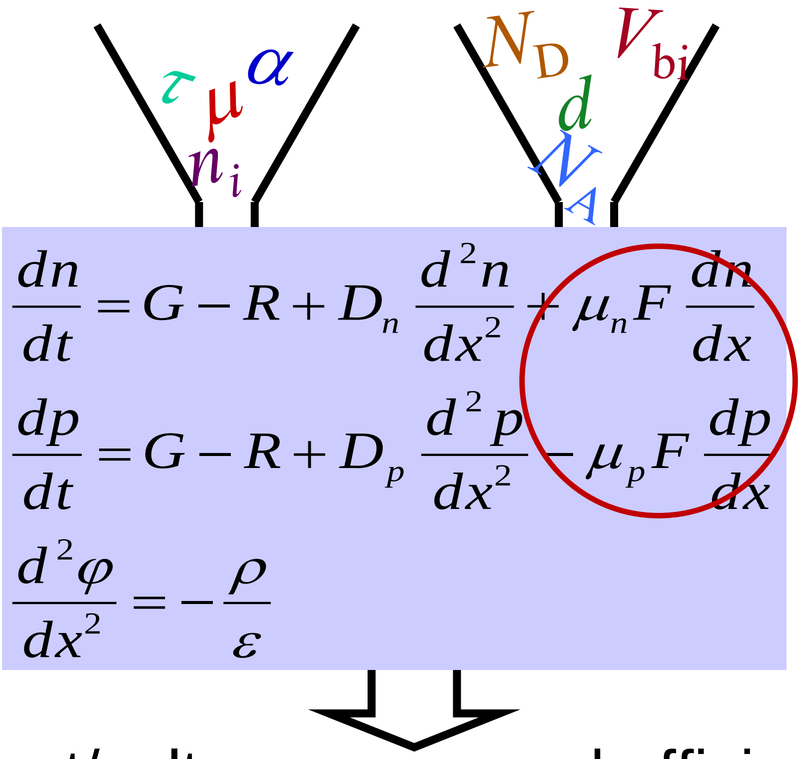
Topic: charge transport

Depends on mobility and carrier density gradients. Note:

$$D = \mu \frac{kT}{q}$$

Device physics of solar cells

From material parameters to device performance



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$$\frac{dp}{dt} = G - R + D_p \frac{d^2 p}{dx^2} - \mu_p F \frac{dp}{dx}$$

$$\frac{d^2 \varphi}{dx^2} = -\frac{\rho}{\varepsilon}$$

current/voltage curve and efficiency η

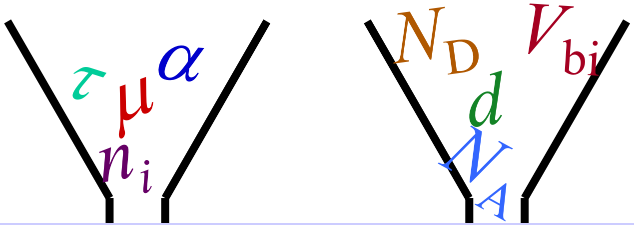
Definition: Spatial derivative of the drift current

Topic: charge transport

Depends on mobility μ, carrier density *n*,*p* and electric field *F*.

Device physics of solar cells

From material parameters to device performance



$$\frac{dn}{dt} = G - R + D_n \frac{d^2 n}{dx^2} + \mu_n F \frac{dn}{dx}$$

$$\frac{dp}{dt} = G - R + D_p \frac{d^2 p}{dx^2} - \mu_p F \frac{dp}{dx}$$

$$\frac{d^2 \varphi}{dx^2} = -\frac{\rho}{\varepsilon}$$

current/voltage curve and efficiency η

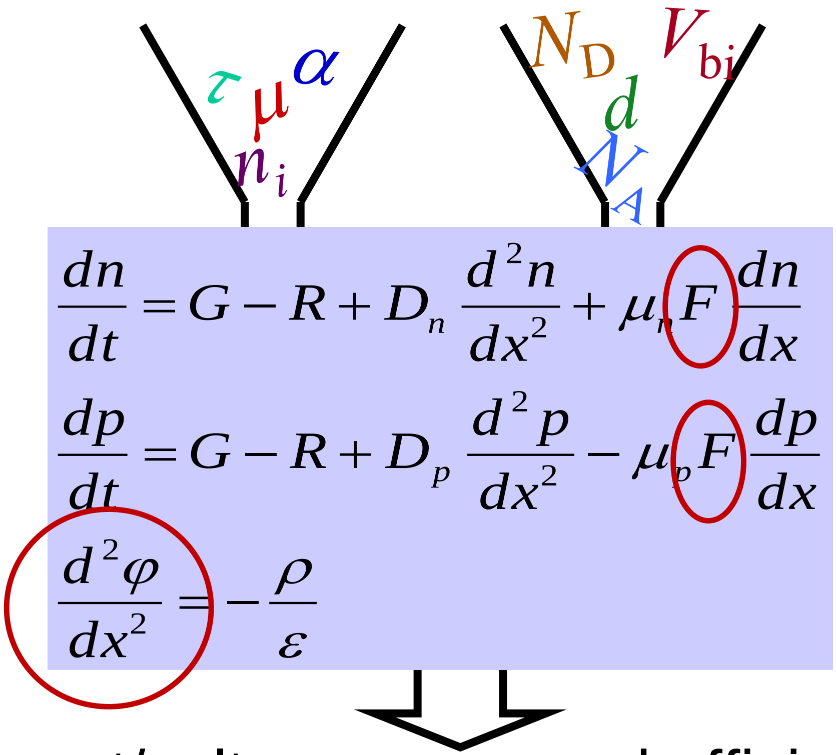
Definition: Second derivative of the electrostatic potential

Topic: electrostatics

Depends on space charge ρ and permittivity ε. Affected strongly by doping. Note:

$$\rho = q(p - n + N_\mathrm{D} - N_\mathrm{A})$$

Coupled differential equations



$$\frac{dn}{dt} = G - R + D_n \frac{d^2 n}{dx^2} + \mu_n F \frac{dn}{dx}$$

$$\frac{dp}{dt} = G - R + D_p \frac{d^2 p}{dx^2} - \mu_p F \frac{dp}{dx}$$

$$\frac{d^2\varphi}{dx^2} = -\frac{\rho}{\varepsilon}$$

current/voltage curve and efficiency η

Shape of the band diagram?

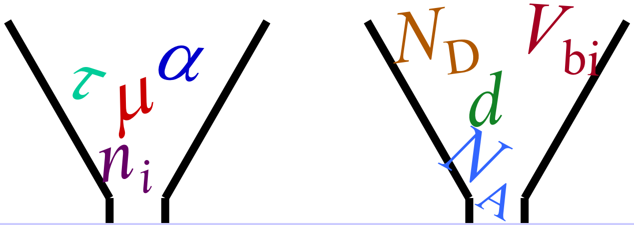
$$R = k_\mathrm{rad} np + \frac{np}{\tau_\mathrm{p} n + \tau_\mathrm{n} p}$$

$$-\frac{d\varphi}{dx} = F$$

Electric field

$$\rho = q(p - n + N_\mathrm{D} - N_\mathrm{A})$$

Coupled differential equations



$$\frac{dn}{dt} = G - R + D_n \frac{d^2 n}{dx^2} + \mu_n F \frac{dn}{dx}$$

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$$\frac{d^2\varphi}{dx^2} = -\frac{\rho}{\varepsilon}$$

current/voltage curve and efficiency η

Recombination?

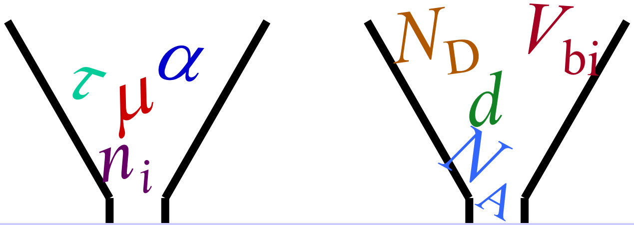
$$R = k_{\mathrm{rad}} np + \frac{np}{\tau_{\mathrm{p}} n + \tau_{\mathrm{n}} p}$$

$$-\frac{d\varphi}{dx} = F$$

Electric field

$$\rho = q(p - n + N_{\mathrm{D}} - N_{\mathrm{A}})$$

Coupled differential equations



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$$\frac{dp}{dt} = G - R + D_p \frac{d^2 p}{dx^2} - \mu_p F \frac{dp}{dx}$$

$$\frac{d^2 \varphi}{dx^2} = -\frac{\rho}{\varepsilon}$$

current/voltage curve and efficiency η

Effect of free carriers on space charge?

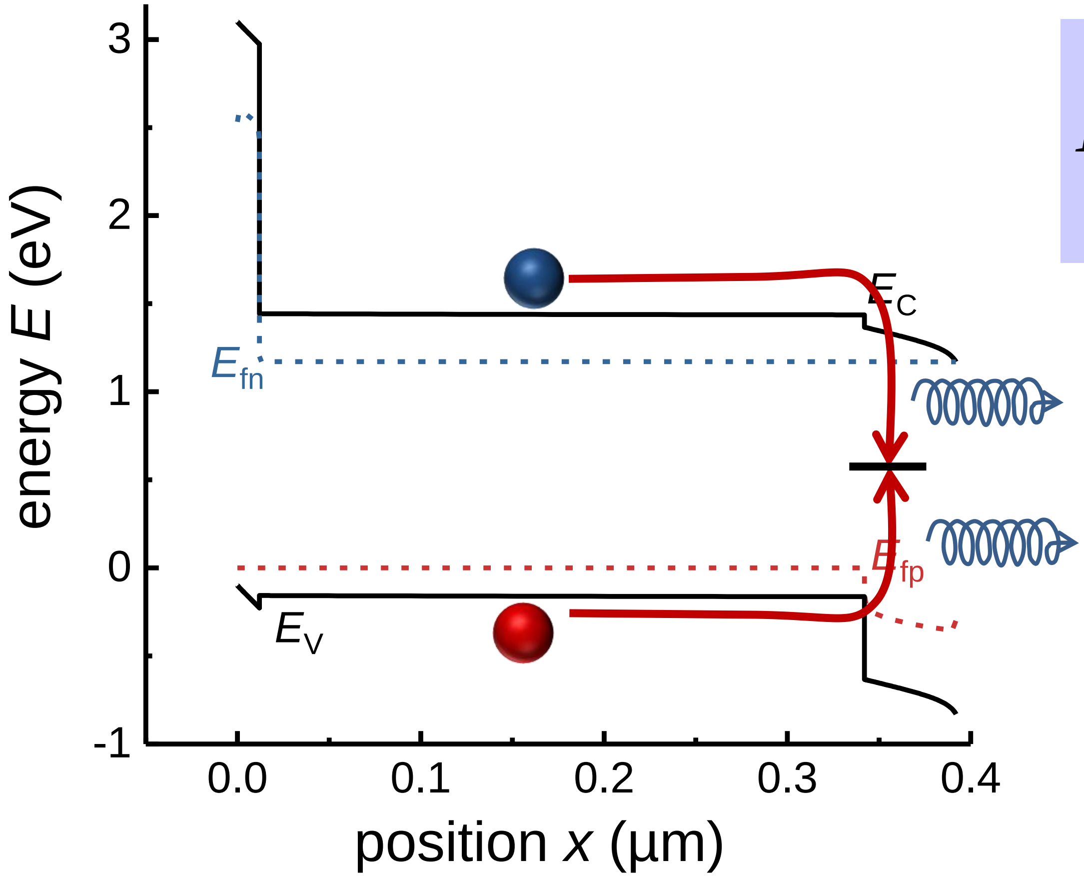
$$R = k_{\mathrm{rad}} np + \frac{np}{\tau_{\mathrm{p}} n + \tau_{\mathrm{n}} p}$$

$$-\frac{d\varphi}{dx} = F$$

Electric field

$$\rho = q(p - n + N_{\mathrm{D}} - N_{\mathrm{A}})$$

Interface recombination



$$R = \frac{np}{n/S_p + p/S_n}$$

R: Recombination rate per unit area.

$S_{n/p}$: surface recombination velocity in cm/s.

Banddiagrams and Fermi levels

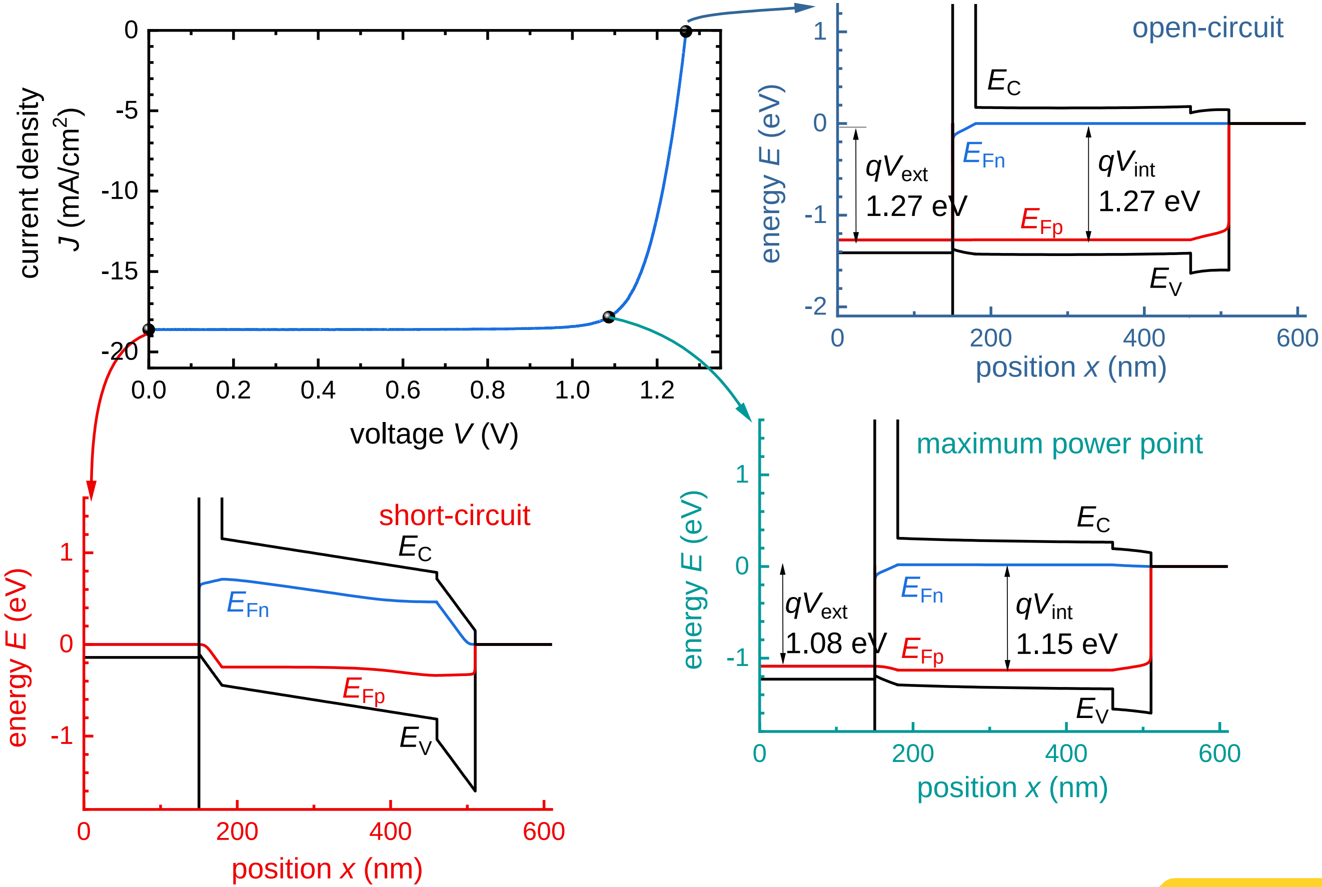
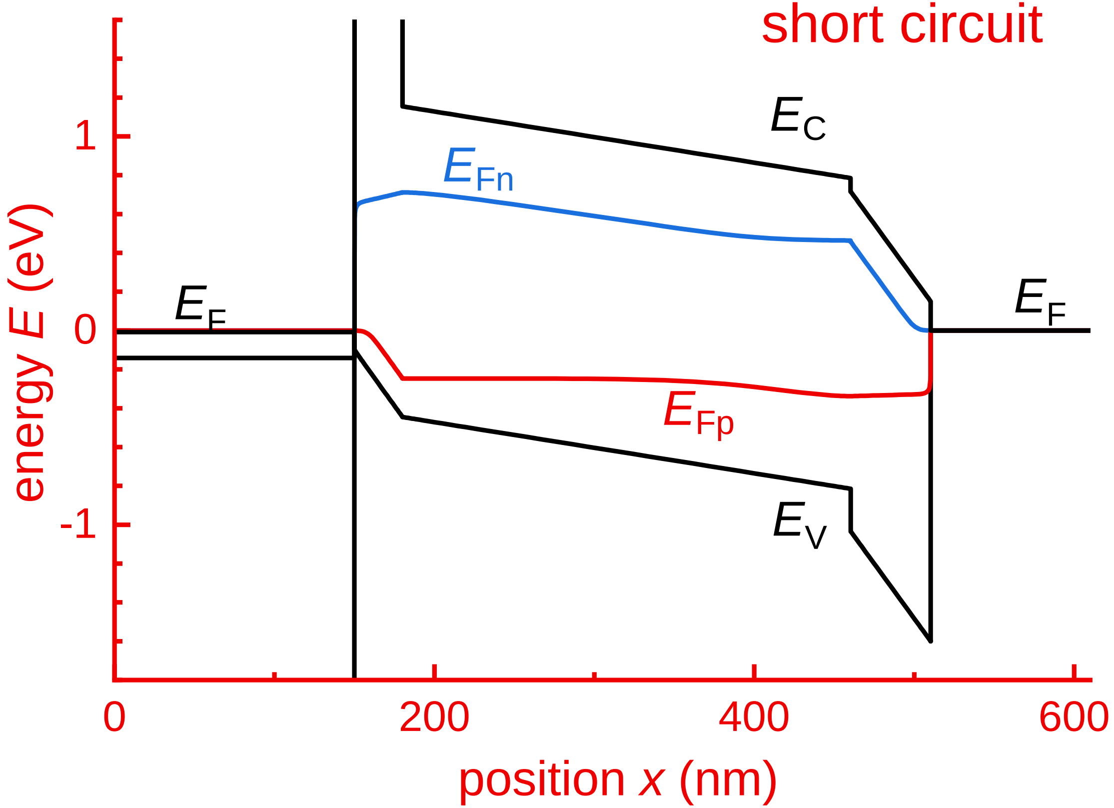


Figure credits: adapted from L. Krückemeier

Gradient of the quasi-Fermi level

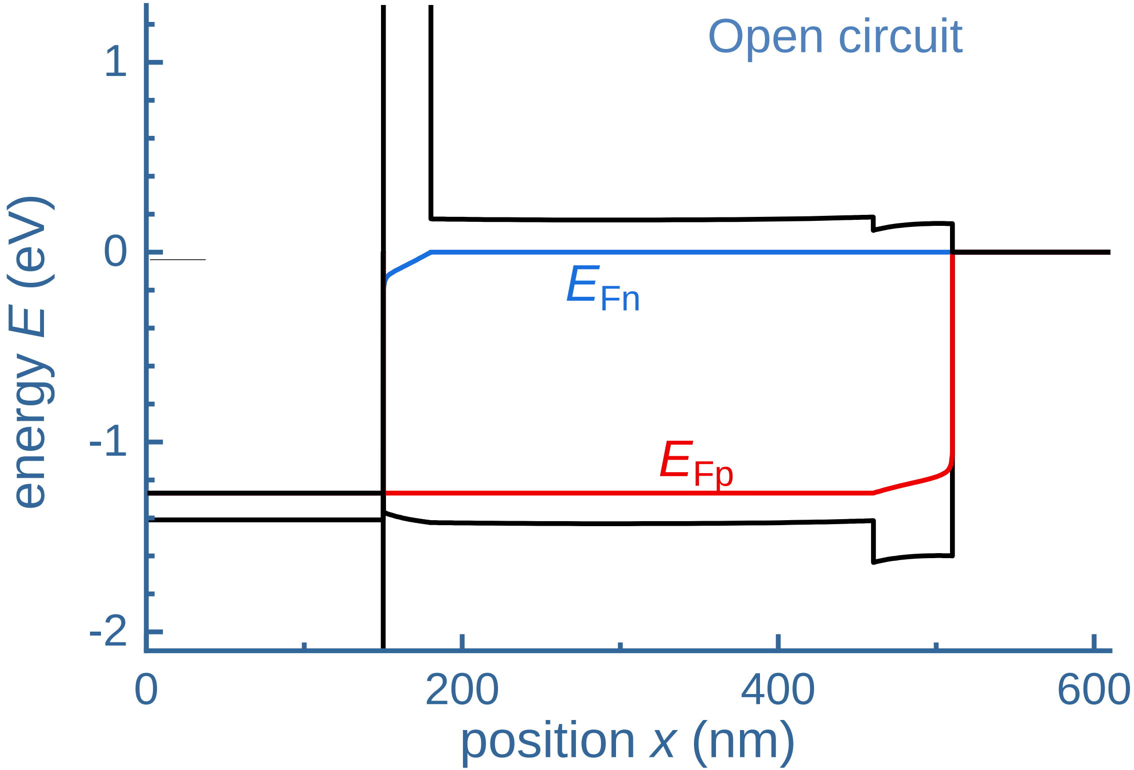


$$J_n = n\mu_n \frac{dE_{Fn}}{dx}$$

$$J_p = p\mu_p \frac{dE_{Fp}}{dx}$$

Figure credits: adapted from L. Krückemeier

Gradient of the quasi-Fermi level

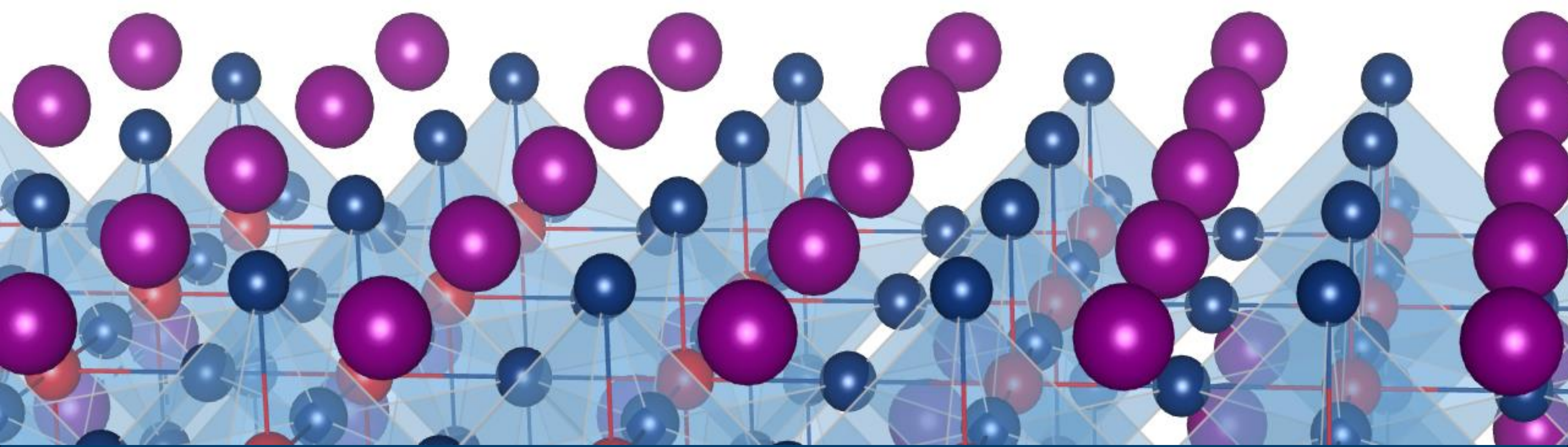


$$J_n = n\mu_n \frac{dE_{Fn}}{dx}$$

$$J_p = p\mu_p \frac{dE_{Fp}}{dx}$$

No current flow, no gradient

Figure credits: adapted from L. Krückemeier



INTRODUCING THE SPEAKERS

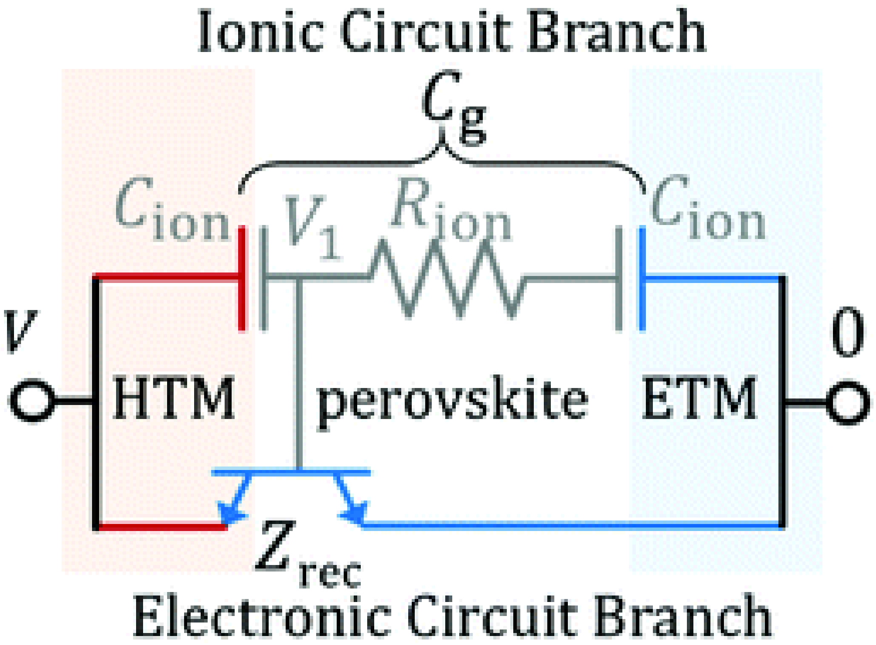
HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

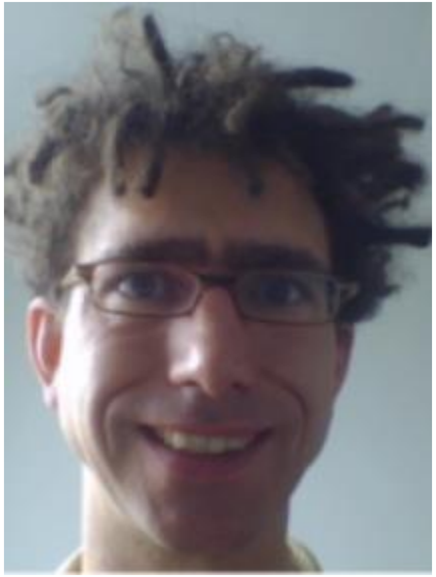
JÜLICH Forschungszentrum

Piers Barnes, Imperial College

Imperial College London

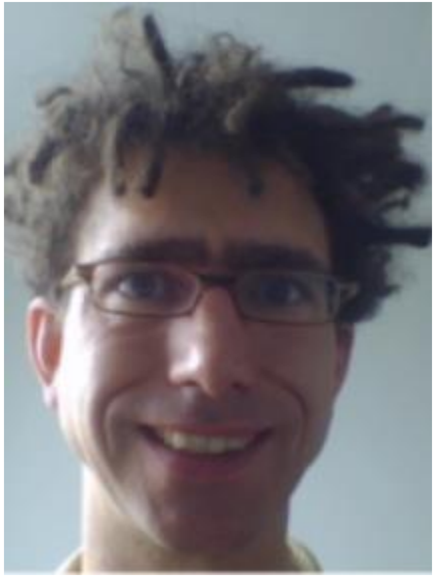
An Equivalent Circuit Model to Interpret Transient and Frequency Domain Behaviour of Perovskite Solar Cell Operation





Piers Barnes, Imperial College

An Equivalent Circuit Model to Interpret Transient and Frequency Domain Behaviour of Perovskite Solar Cell Operation



A positive voltage is applied to the the hole transporting material (HTM) electrode of a perovskite solar cell. We might expect this to gradually reduce the amount positive ionic charge to accumulated at this interface.

How would you expect the electronic current through the cell in the dark to change in response to the change ionic charge redistribution if recombination of electrons at the HTM/perovskite interface interface limits the cell current?

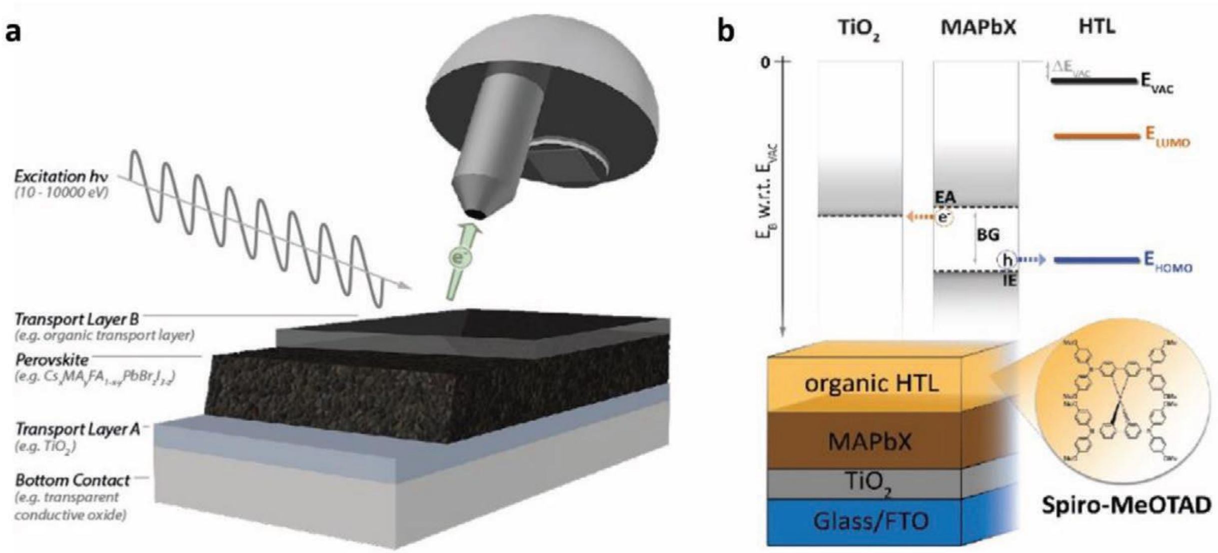
- *Current increases/decreases with time?*

How would you expect the electronic current through the cell in the dark to change as the ionic charge redistributes if injection of electrons at the opposite interface limits the cell current?

- *Current increases/decreases with time?*

Philip Schulz

Surface and Interface Analysis of Perovskite Solar Cells



Bechu et al. Adv. Energy Mater. 2020

Philip Schulz

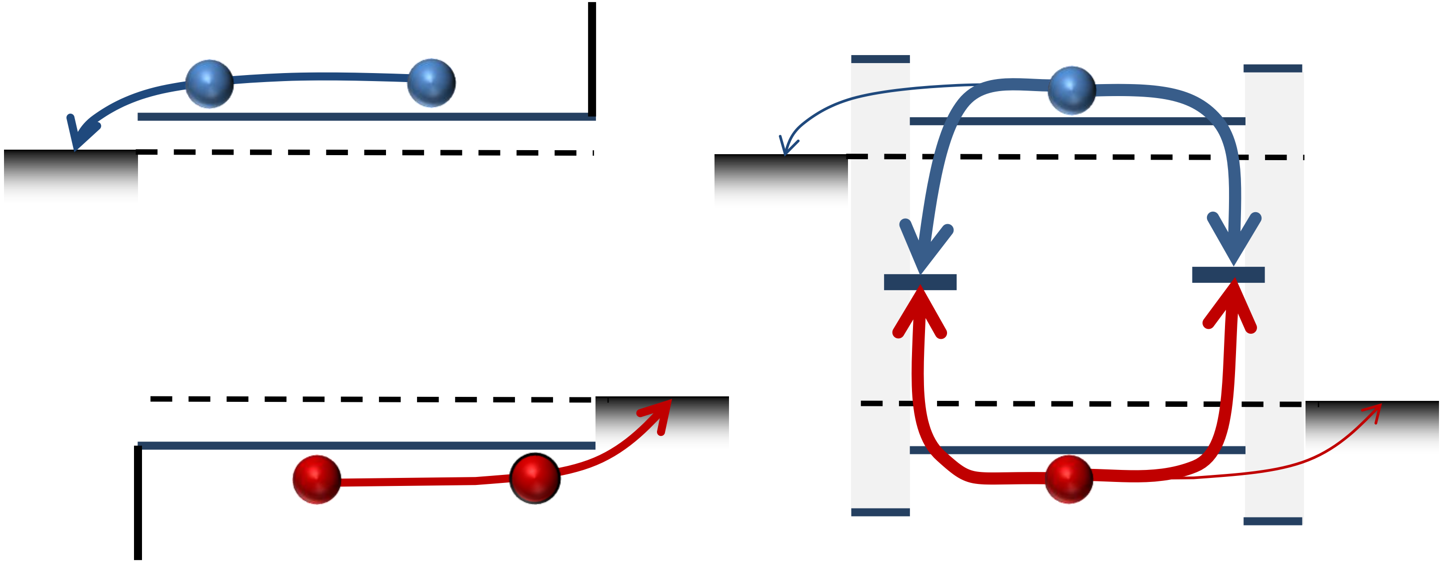
Surface and Interface Analysis of Perovskite Solar Cells

Which of the following semiconductor properties, among others, can be probed by ultraviolet and X-ray photoemission spectroscopy (UPS/XPS): The position of the conduction band minimum and valence band maximum, the effective mass of electrons and holes, or the ionization energy?

- *All of the above.*
- *The band positions and ionization energy.*
- *The effective mass of electrons and holes, but requires an angle-resolved spectrometer.*
- *The position of the valence band maximum, the effective mass of holes and the ionization energy.*
- *Only the band positions and effective mass of electrons and holes.*
- *Only the valence band onset and the ionization energy.*

Uwe Rau, Forschungszentrum Jülich

The Transformation of Chemical into Electrical Potential in Solar Cells: a Contact Issue



Selective vs. not so selective contacts.
See e.g. Rau et al. Adv. Mater. Interf. 2019

Uwe Rau, Forschungszentrum Jülich

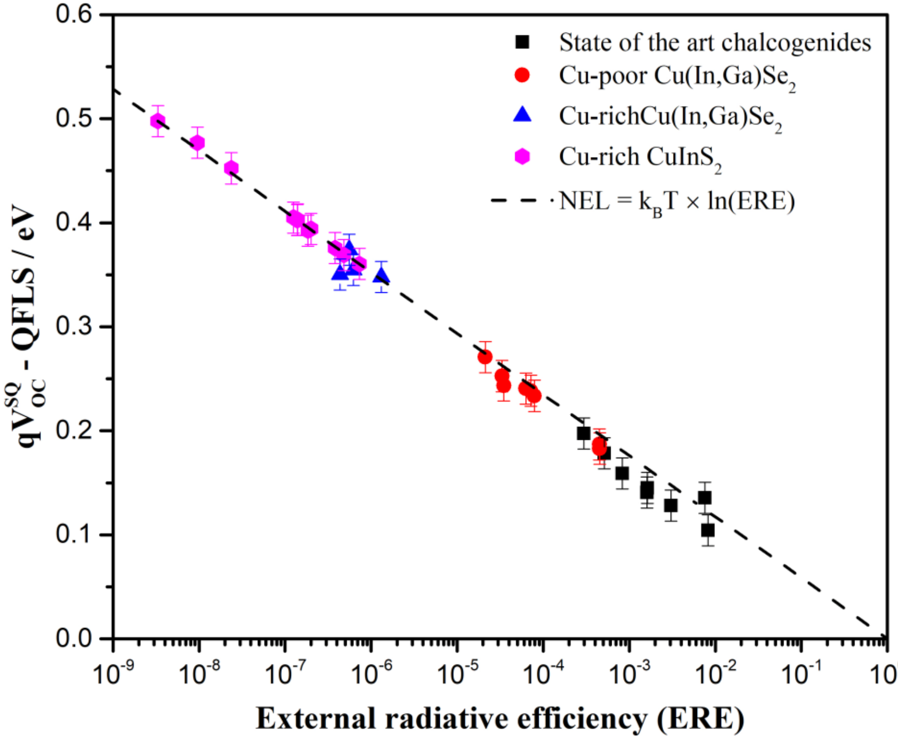
The Transformation of Chemical into Electrical Potential in Solar Cells: a Contact Issue

Which of the following statements on the use of equivalent circuit models for solar cells are correct?

- *Because the diode equation is non-linear we cannot use an equivalent circuit model. However we can always make a linear expansion to derive an equivalent circuit for the case of small deviations from a working point.*
- *Because the series resistance is dependent on the external voltage, the problem gets inherently non-linear. A linear expansion at a given working point is still possible, and therefore we can always have a correct equivalent circuit for the small signal analysis.*
- *The series resistance is dependent on the external voltage and the problem gets non-linear. A linear expansion at a given working point is not generally possible because we cannot express the interaction between the external voltage and the internal voltage (i.e. the chemical potential of charge carriers) by a difference of a single potential. However, at a working point where both potentials are equal an equivalent circuit model works for the small signal analysis.*
- *One of the equations describing the solar cell contains two different potentials (electrostatic and chemical). An equivalent circuit model can only deal with a single potential. However, an equivalent circuit model works for the small signal analysis at open circuit condition.*
- *One of the equations describing the solar cell contains two different potentials (electrostatic and chemical). An equivalent circuit model can only deal with a single potential. However, an equivalent circuit model works for the small signal analysis at short circuit condition.*
- *Equivalent circuits are generally unphysical because they do not account for the quantum nature of the photovoltaic effect.*

Susanne Siebentritt, Université du Luxembourg

Solar Cell Characterisation by Photoluminescence



Susanne Siebentritt, Université du Luxembourg

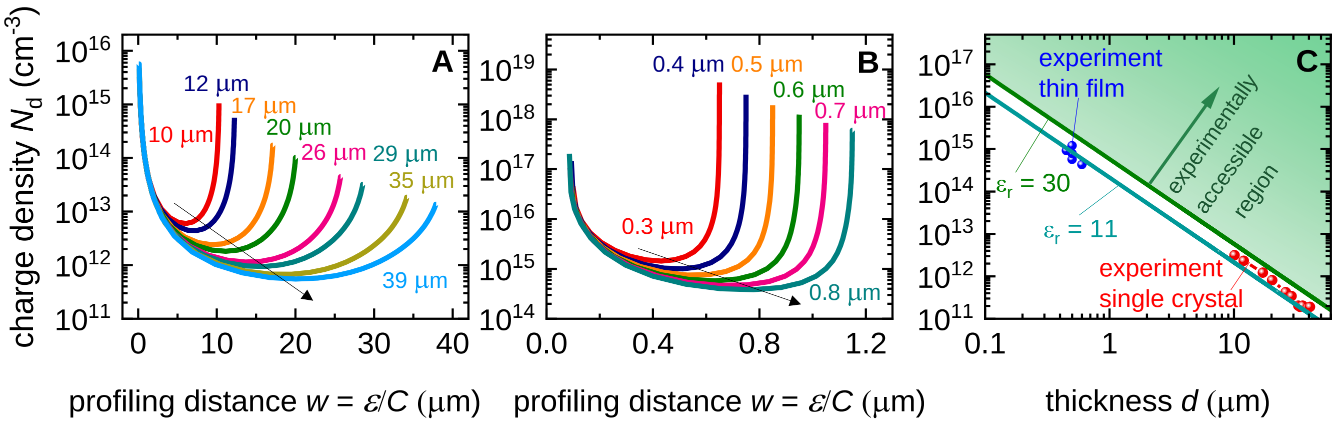
Solar Cell Characterisation by Photoluminescence

To achieve high quasi-Fermi level splitting (and high open circuit voltage) at a given excitation it helps to have:
(choose as many as apply)

- high doping
- low deep defect concentration
- high mobilty
- long charge-carrier lifetime
- good band alignment at the contacts

Thomas Unold, Helmholtz Zentrum Berlin

Characterization of PV materials and cells – basic checks for consistency



Experimentally accessible regions for defect density determination from *C*(*V*)
Ravishankar et al. arXiv:2008.02892

Thomas Unold, Helmholtz Zentrum Berlin

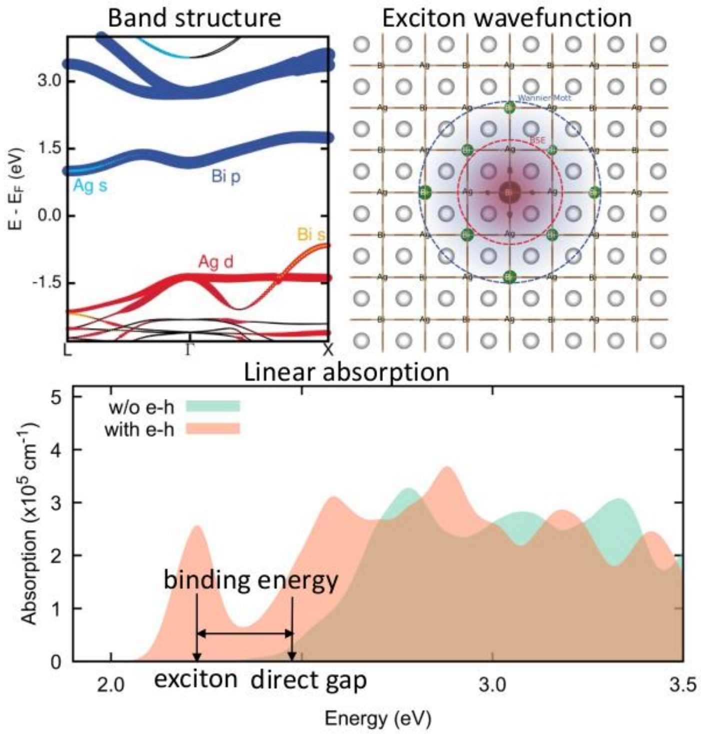
Characterization of PV materials and cells – basic checks for consistency

Which of these statements are correct?

- *From capacitance-voltage profiling of a 400nm thick halide perovskite solar cell (dielectric constant = 33), a doping density in the absorber layer of 10^{14} cm^{-3} can be deduced.*
- *To measure a carrier density of $10^{12}cm^{-3}$ in a pn-junction or p-i-n junction with capacitance-voltage profiling (or Mott-Schottky analysis) the absorber layer (epsilon=12) has to be larger than 15 µm.*
- *The photoluminescence quantum efficiency (PLQY) of a solar cell is always smaller than the PLQY of an absorber layer without contacts, since in the case of the solar cell there is charge separation.*
- *The ideal photoluminescence transient of a photovoltaic material should be a monoexponential independent of the excitation density.*
- *For the case of strong interface recombination at the contacting layers, increasing the carrier lifetime of the carriers in the absorbing semiconductor material will not improve the open-circuit voltage.*

Linn Leppert, University of Twente

Optoelectronic properties of halide perovskites from first principles numerical modeling



Linn Leppert, University of Twente

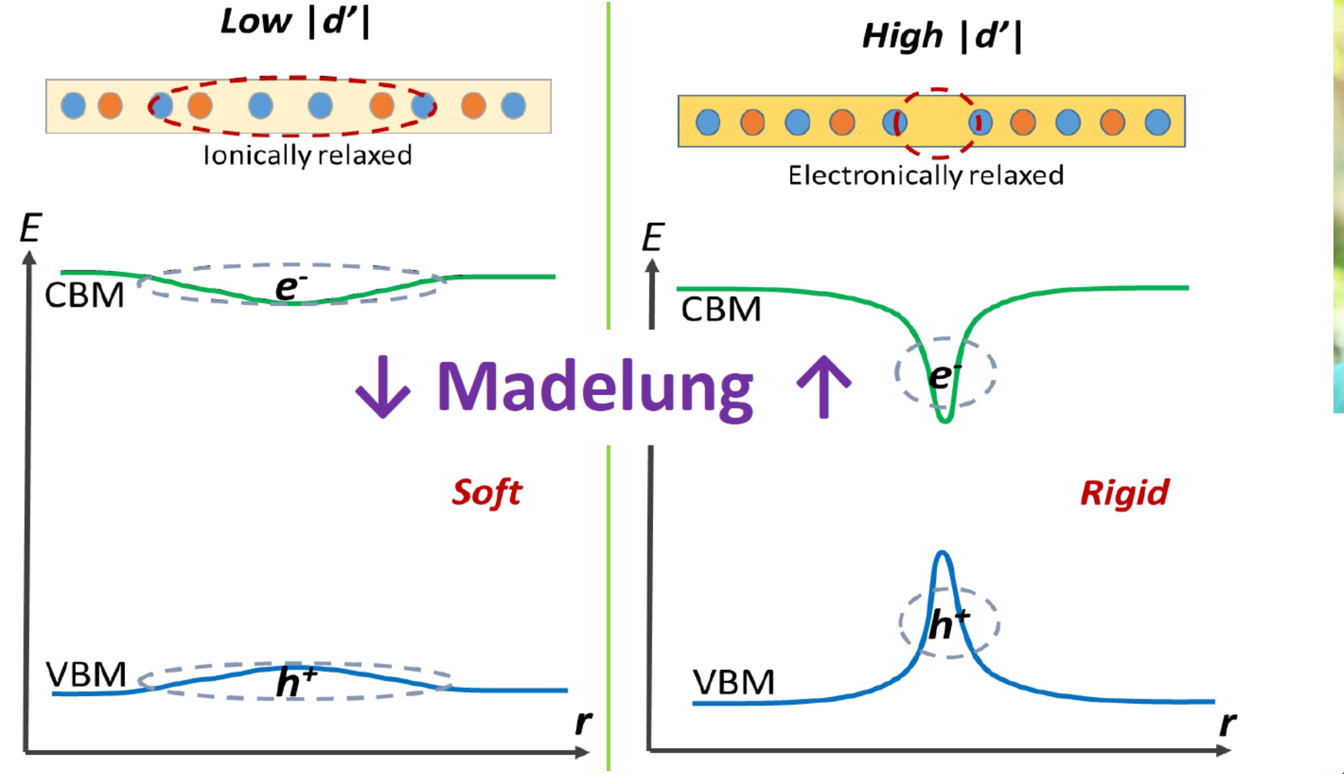
Optoelectronic properties of halide perovskites from first principles numerical modeling

You have performed one standard density functional theory (DFT) calculation of MAPI on your desktop computer. Can you extract the ionization potential from this calculation?

- *Yes, I just need to find out what the energy of the highest occupied electronic state is.*
- *No, DFT is a ground state theory, therefore I would need to perform a second calculation in which I remove an electron from the system, and then calculate the ionization potential as the difference in total energies of the neutral and ionized system.*
- *Yes, but I need to define what the zero of the energy scale is by constructing a surface slab and aligning the eigenvalues to the potential far away from the slab.*
- *No, I cannot run a DFT calculation of MAPI on my desktop computer. More computing cores and memory are needed for doing such a calculation.*

David Cahen, Weizmann Institute and Bar-Ilan

Defects & Halide Perovskites: Tautology, Oxymoron or What?



David Cahen, Weizmann Institute and Bar-Ilan

Defects & Halide Perovskites: Tautology, Oxymoron or What?

Which of the following assumptions or “laws” are valid / used in Defect Chemical descriptions of crystalline ordered solids at STP conditions; the densities of defects in which can be viewed as dilute (including the densities of any defect complexes):

- **B**oltzmann statistics
- **C**harge conservation
- **C**harge neutrality
- **C**onservation of matter
- **F***or semiconducting (and metal) solids:* only electrons (holes) are mobile
- **M**ass Action (Guldberg-Waage) law
- **H**armonic approximation
- **L**ong- and short-range order
- **T**hree rules of accounting

Thank you for your attention

and have fun during the conference!

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

JÜLICH Forschungszentrum