Overview

1) Simulating thin films

2) Electrical characterization of OPVs

3) Diffusion limited recombination in OPVs

4) The open circuit voltage

5) Conclusions

Diffusion limited recombination

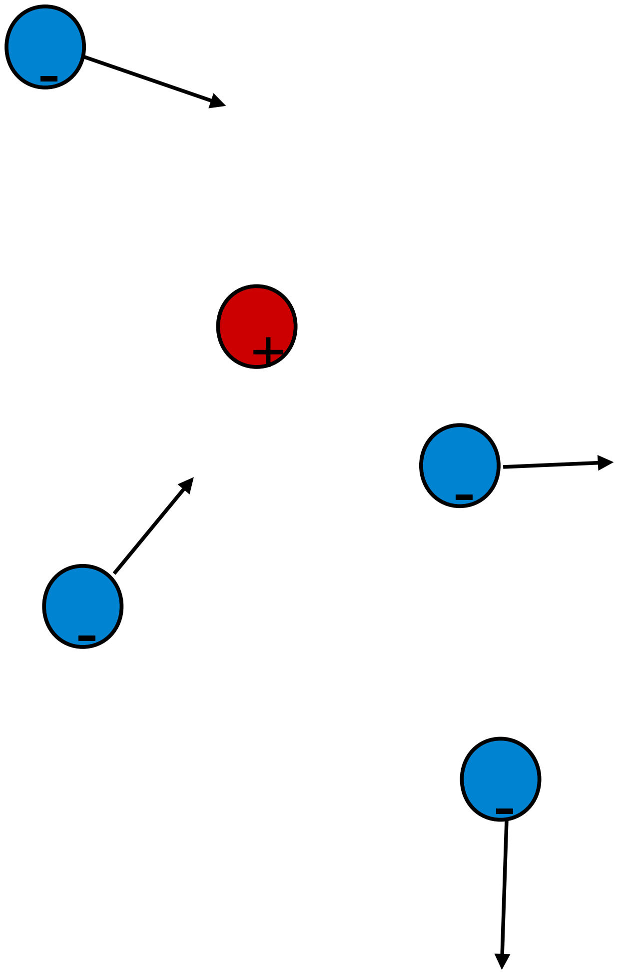
•Imagine you have a hole in the middle of a sea of electrons.

•Recombination will depend upon the probability of an electron meeting a hole.

•This probability will be proportional to the rate at which the electrons move around.

•And the density of electrons.

•A more formal expression for the rate at which carriers recombine is given by Langevin recombination.



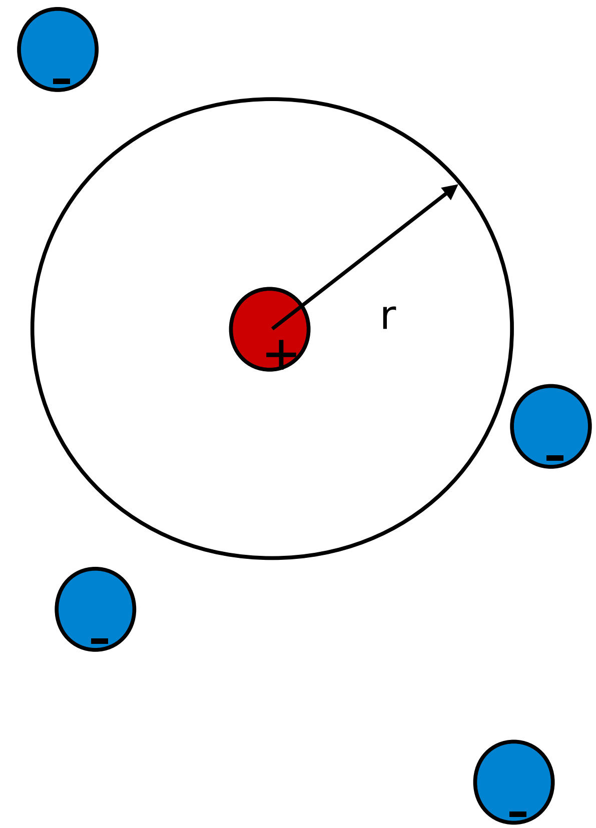
Langevin Recombination

•Recombination happens when an electron and hole get closer than the recombination radius r.

•This radius is defined as when the electrical potential and the thermal energy are equal.

$$E_{Coulomb} = E_{thermal}$$

$$\frac{q^2}{4\pi\epsilon r_c} = k_B T \longrightarrow r_c = \frac{q^2}{4\pi\epsilon k_B T}$$



Langevin 1903 (Ann. Chim. Phys. 28, 433)

Langevin recombination

The rate at which carriers drift across the boundary is given by.

$$j_{electron} = qn\mu E$$

The electric field is the first derivative of the potential.

$$j_{electron} = qn\mu \frac{q^2}{4\pi\epsilon r^2}$$

Multiply over the area of a sphere

$$I_{electron\ flux} = j_{electron} 4\pi r^2 = \frac{q^2 \mu n}{\epsilon}$$

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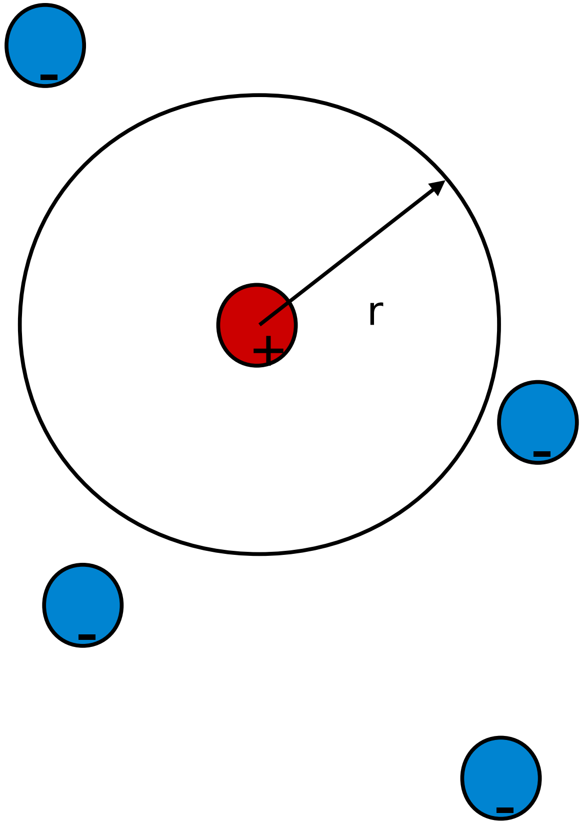
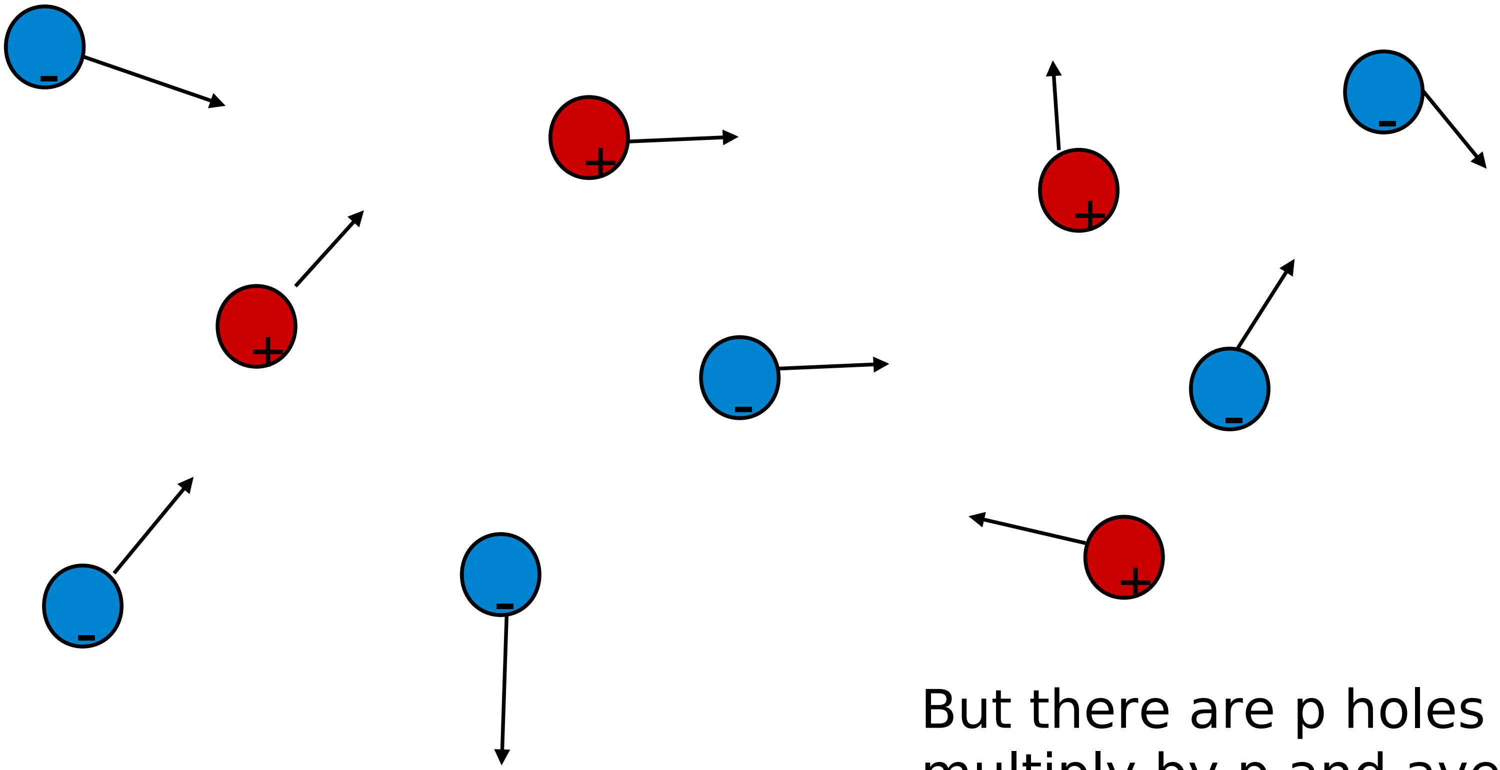


Langevin recombination for electrons and holes



But there are p holes therefore multiply by p and average over the electron and hole mobility.

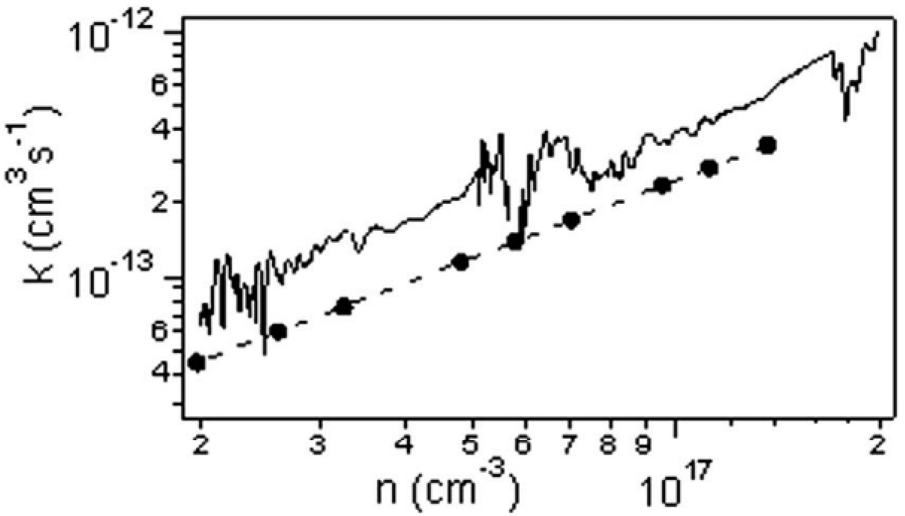
$$R = k\,n\,p \qquad k = \frac{q}{\epsilon}\left(\frac{\mu_n + \mu_p}{2}\right)$$

How good is Langevin recombination?

Langevin's theory predicts that the recombination prefactor is a constant:

$$k = \frac{q}{\epsilon}(\mu_n + \mu_p) \qquad R = k n p$$

However we observe a carrier density dependence of k.

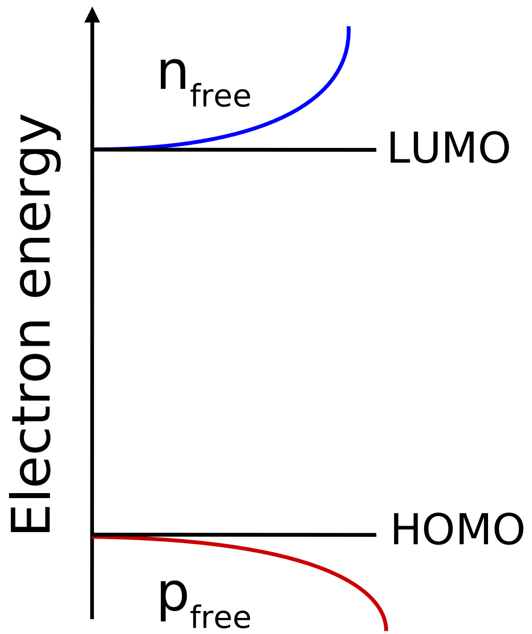


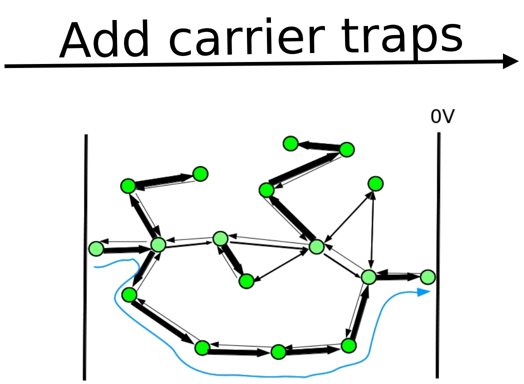
Shuttle et al. Phys. Rev. B 78, 113201 2008

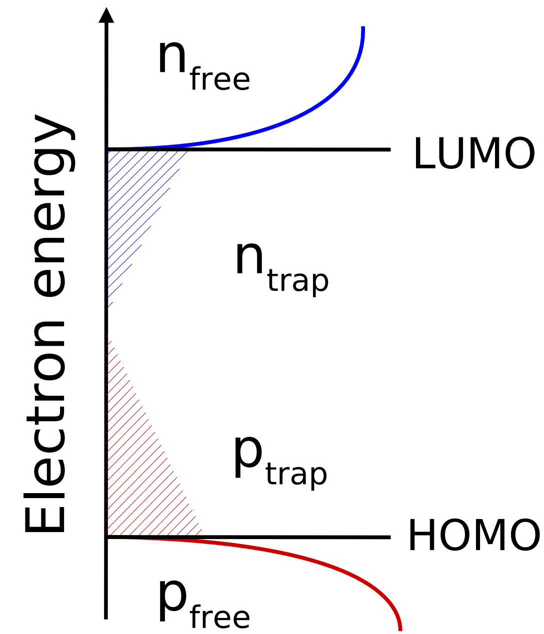
Our simple picture of recombination is too simple. When we try to model devices using pure Langevin theory we **can't reproduce the JV curves, charge extraction curves or TPV data** – can we improve the situation........

What's going wrong with Langevin recombination?

Well we assumed that all the carriers are free and thus trapping is neglected. However, we know from our molecular level simulations that there are a lot of traps.



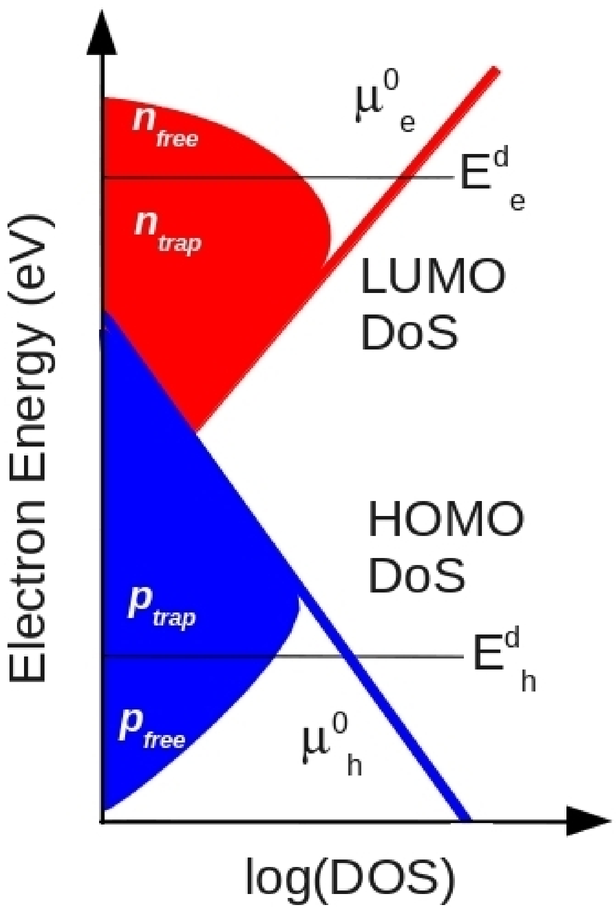




Parabolic band carriers move freely.

May be we need carrier traps?

How will this affect the mobility?



Carrier dependent mobility

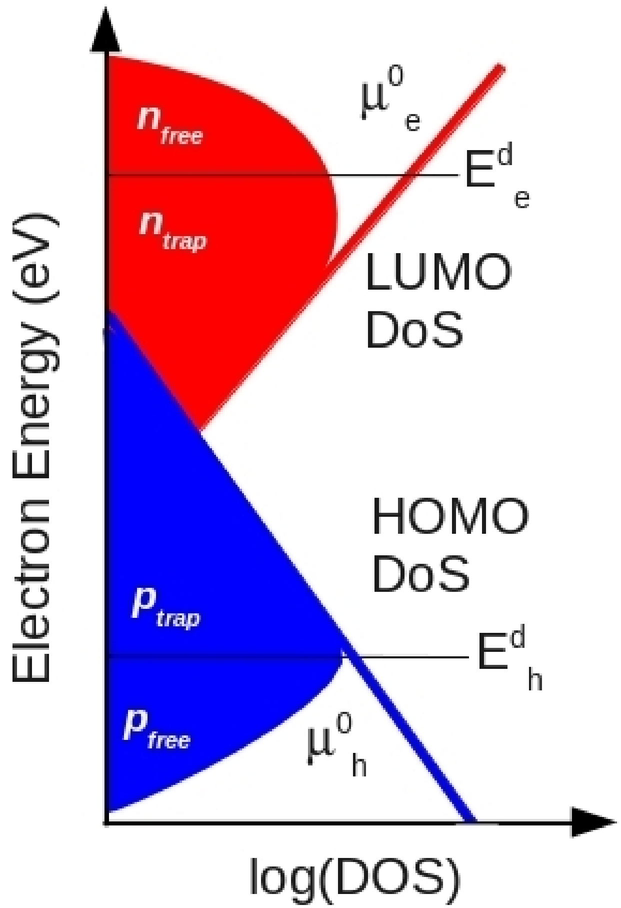
$$\mu_e(E_f)=\frac{\int_{E_e^d}^{\infty}\rho_{DOS}(E)f(E,E_f)\mu_e^0\,dE}{\int_{-\infty}^{\infty}\rho_{DOS}(E)f(E,E_f)\,dE}=\mu_e^0\frac{n_{free}}{n_{total}}$$

$$f(E,E_F)=\frac{1}{e^{\frac{(E-E_f)}{kT}}+1}$$

Analogous for the holes

Mobility now depend upon carrier density

How will this affect the mobility?



Carrier dependent mobility

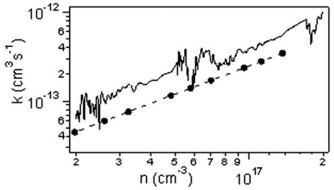
$$\mu_e(E_f)=\frac{\int_{E_e^d}^{\infty}\rho_{DOS}(E)f(E,E_f)\mu_e^0 dE}{\int_{-\infty}^{\infty}\rho_{DOS}(E)f(E,E_f)dE}=\mu_e^0\frac{n_{free}}{n_{total}}$$

Analogous for the holes

Trap limited Langevin recombination

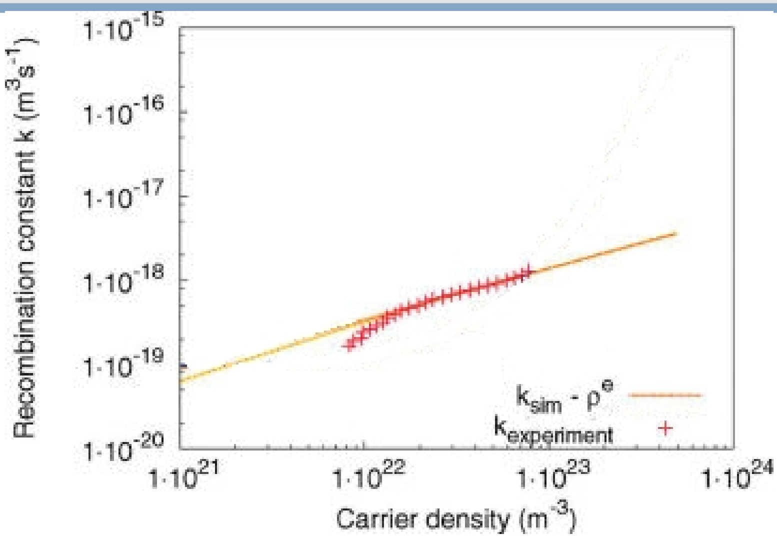
$$k(n,p)=\frac{q(\mu_e^0(n)+\mu_h^0(p))}{\epsilon_0\epsilon_r}$$

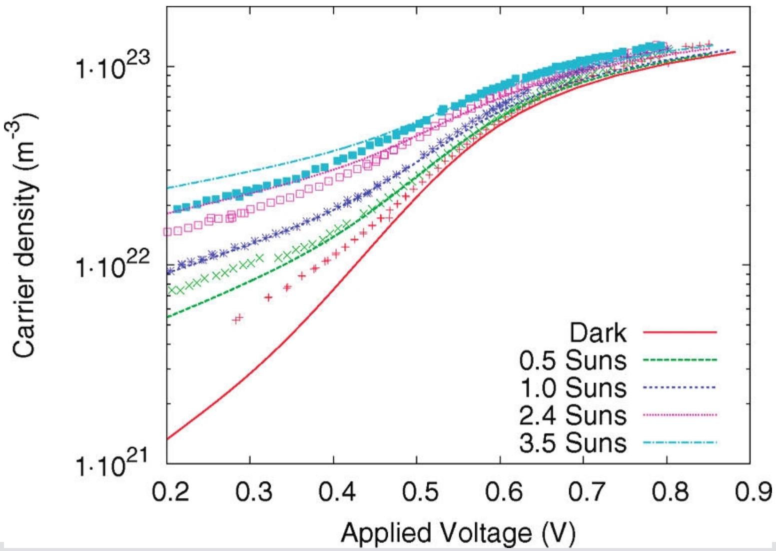
$$R=k(n,p)np$$

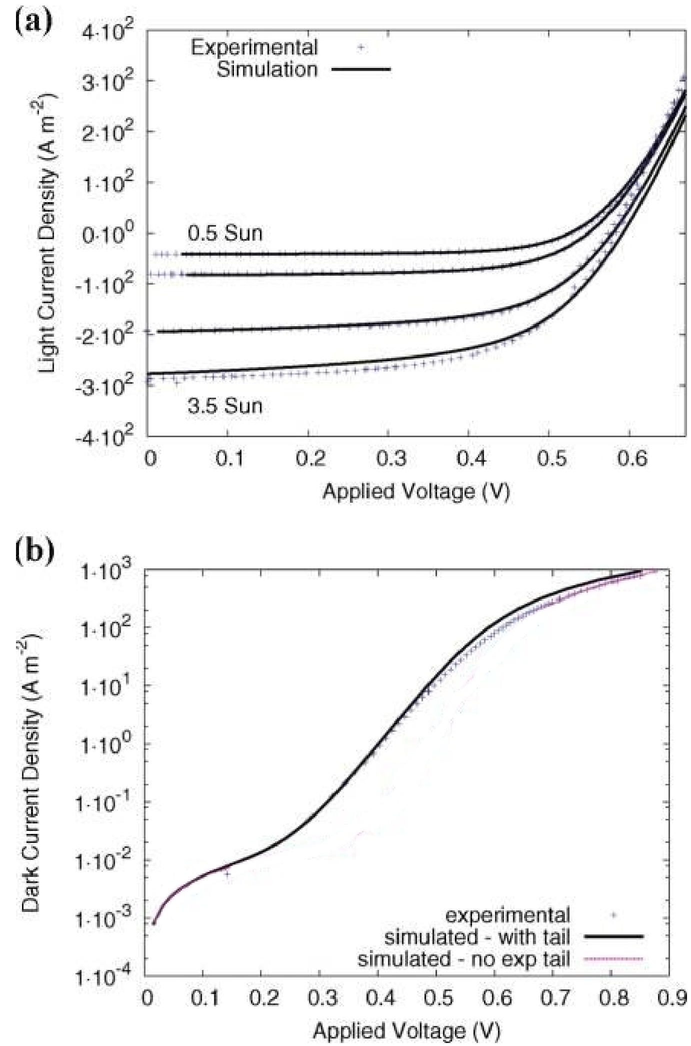


Mobility and recombination now depend upon carrier density

Comparison to experiment







MacKenzie et al. J. Phys. Chem. C, 10.1021/jp200234m

How realistic is this model?

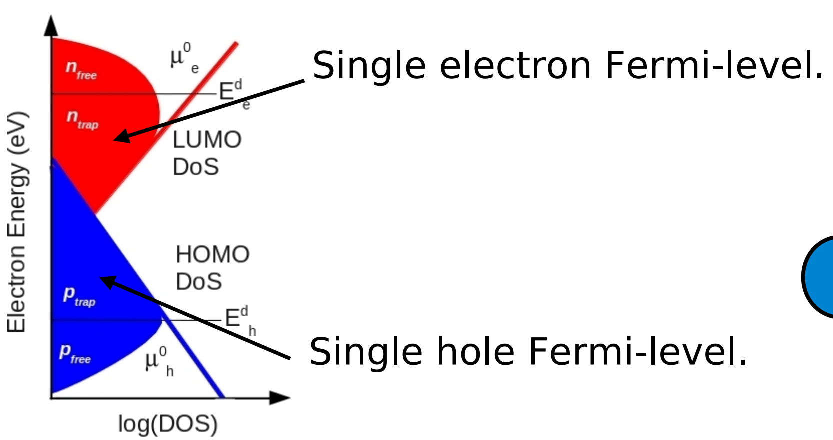
It works very well for steady state simulation.

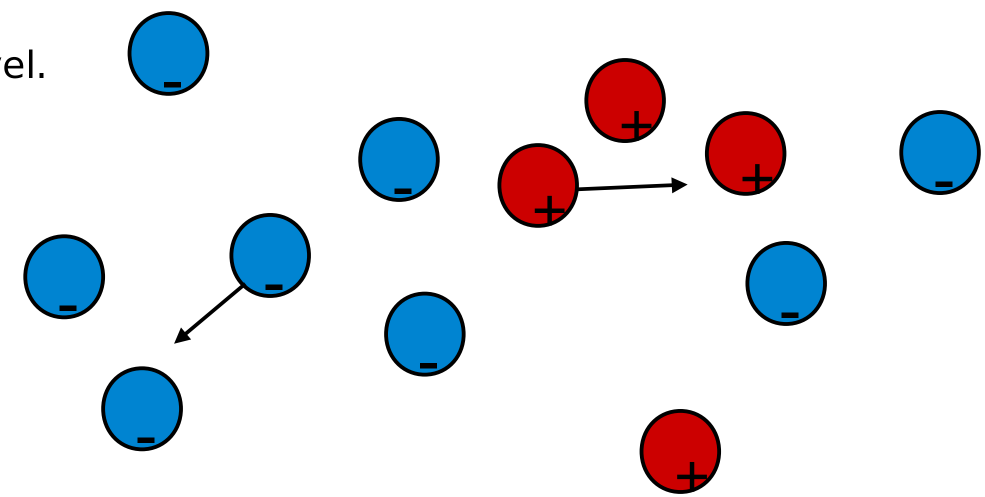
We assumed that all carriers have the same Fermi-level.

This means that all trapped and free electrons can interact instantaneously.

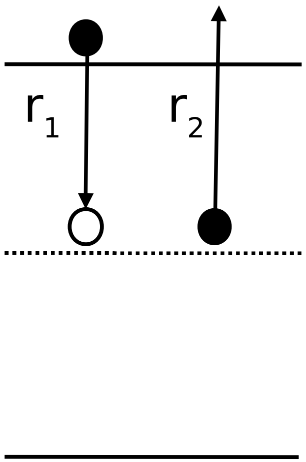
But should trapped carriers be able to interact with each other?

Would it not be more realistic to have only the free carriers interacting with the trapped carriers?





Shockley-Read-Hall recombination



E_c - LUMO

E_t - Trap

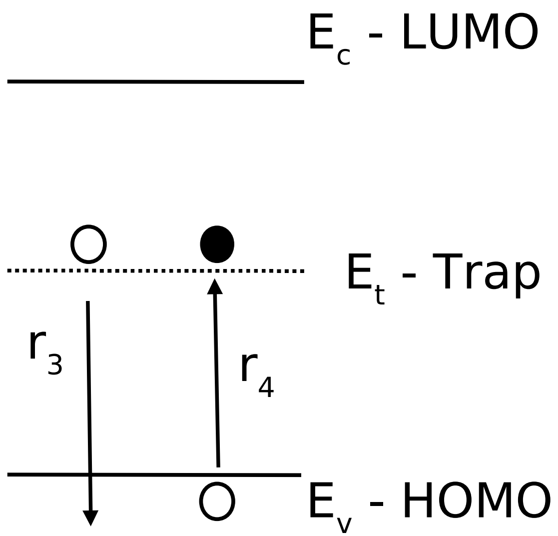
E_v - HOMO

Process	Rate	Description
electron capture	r_1	$n \cdot v_{th} \sigma_n N_t (1-f)$
electron emission	r_2	$e_n N_t f$

$$e_n = v_{th} \sigma_n N_c \exp\left(\frac{E_t - E_c}{kT}\right)$$

v_{th} = thermal velocity of carriers
σ = capture radious
N_t = trap density
f=Fermi-Dirac function describing occupation of the trap.

Shockley-Read-Hall recombination

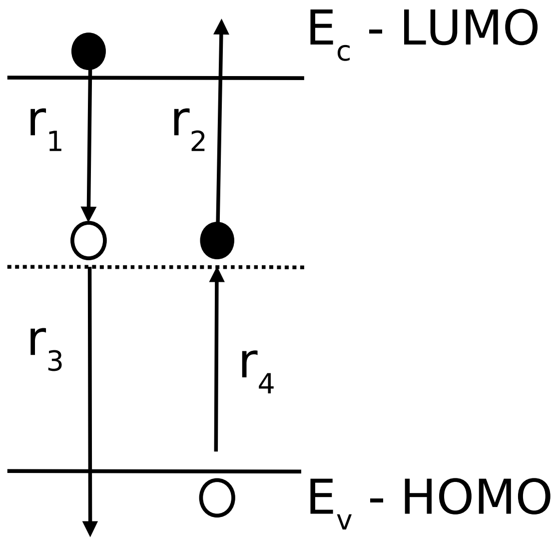


Process	Rate	
hole capture	r_3	$p\, v_{th} \sigma_p N_t f$
hole emission	r_4	$e_p N_t (1-f)$

$$e_p = v_{th} \sigma_p N_v \exp\left(\frac{E_v - E_t}{kT}\right)$$

v_{th} = thermal velocity of carriers
σ = capture radious
N_t = trap density
f= Fermi-Dirac function describing occupation of the trap.

Shockley-Read-Hall recombination



Electron density the trap:

$$\frac{\partial n_t}{\partial t} = r_1 - r_2 + r_3 - r_4$$

Loss of free electrons

$$R_n = r_1^e - r_2^e$$

Loss of free holes

$$R_n = r_4^e - r_3^e$$

Detailed balance is maintained. i.e. at equlibrium $r_1=r_2$ and $r_3=r_4$

Recombination is thus implicitly described.