1. **Depletion region**

The right stratagy to find the width of the depletion region is to ask oneself what one can know about a pn-junction. There is the band structure of the used materials which gives the potential drop across the depletion region. Another quantity which is known is the doping concentration. As a conclusion one can say, that it is needed to find a relation between the potential (voltage) and the doping concentrations. The voltage is defined as:

$$V(x) = -\int E(x)dx$$

The respective E-field is defined by Poisson's equation:

$$\frac{dE}{dx} = \frac{1}{\epsilon\epsilon_0}\rho(x)$$

The charge density is defined by the doping concentrations:

$$\rho(x) = \begin{cases} -qN_A, & -x_p \leq x \leq 0 \\ qN_D, & 0 \leq x \leq x_n \end{cases}$$

So that:

$$E(x) = \begin{cases} -q\dfrac{N_A}{\epsilon\epsilon_0}x + C_1, & -x_p \leq x \leq 0 \\ q\dfrac{N_D}{\epsilon\epsilon_0}x + C_2, & 0 \leq x \leq x_n \end{cases}$$

In those steps we're assuming that the depletion region is restricted between x_p and x_n. Out of this assumption it follows that outside the depletion region there is no field.

$$E(-x_p) = E(x_n) = 0$$

$$\Rightarrow C_1 = -\frac{qN_A}{\epsilon\epsilon_0}x_p, C_2 = -\frac{qN_D}{\epsilon\epsilon_0}x_n$$

Another restriction is that the electrical field must be continuous, everywhere. This leads to the following charge balance condition:

$$N_A x_p = N_D x_n$$

This means nothing else as that the charge amount on the positive side is the same as on the negative side. The last step is to derive the voltage:

$$V(x) = -\int E(x)dx = \begin{cases} \dfrac{qN_A}{\epsilon\epsilon_0}\left(\dfrac{x}{2} + x_p\right)x + C_3 \\ \dfrac{qN_A}{\epsilon\epsilon_0}\left(x_n - \dfrac{x}{2}\right)x + C_4 \end{cases}$$

We are allowed to define:

$$V(-x_p) = 0 \Rightarrow C_3 = \frac{qN_A}{\epsilon\epsilon_0}x_p^2$$

C_4 can be found by

$$V_n(x = 0) = V_p(x = 0) \Rightarrow C_4 = \frac{qN_A}{\epsilon\epsilon_0}x_p^2$$

The end result is:

$$V(x) = -\int E(x)dx = \begin{cases} \dfrac{qN_A}{2\epsilon\epsilon_0}\left(x + x_p\right)^2 \\ \dfrac{qN_A}{\epsilon\epsilon_0}\left(x_n - \dfrac{x}{2}\right)x + \dfrac{qN_A}{\epsilon\epsilon_0}x_p^2 \end{cases}$$

Voltage across the pn-junction corresponds to the Fermi-Level difference of both materials:

$$V_0 = \frac{q}{2\epsilon\epsilon_0}\left(N_D x_n^2 + N_A x_p^2\right)$$

For $N_D x_n = N_A x_p$ it follows:

$$W = x_p + x_n = \sqrt{\frac{2\epsilon\epsilon_0}{q} V_0 \left(\frac{1}{N_A} + \frac{1}{N_D}\right)}$$

b)

$$C = qN_D A \frac{dx_n}{dV_0}, \qquad x_n = \sqrt{\frac{2\epsilon\epsilon_0}{q}\frac{N_A}{N_D}\frac{1}{N_A + N_D}V_0}$$

$$C = \sqrt{\frac{q\epsilon\epsilon_0}{2V_0}\frac{N_A N_D}{N_A + N_D}}A = \frac{\epsilon\epsilon_0}{x_n}A$$

This can be reexpressed to:

$$C^2 = \frac{q\epsilon\epsilon_0}{2V_0}\frac{N_A N_D}{N_A + N_D}A^2$$

$$\frac{1}{C^2} = \frac{2}{q\epsilon\epsilon_0}\frac{N_A + N_D}{N_A N_D}\frac{1}{A^2}V_0$$

$$\frac{\partial}{\partial V_0}\left(\frac{1}{C^2}\right) = \frac{2}{q\epsilon\epsilon_0}\frac{N_A + N_D}{N_A N_D}\frac{1}{A^2}$$

2. Rate equation formalism

Decay of the excited state:

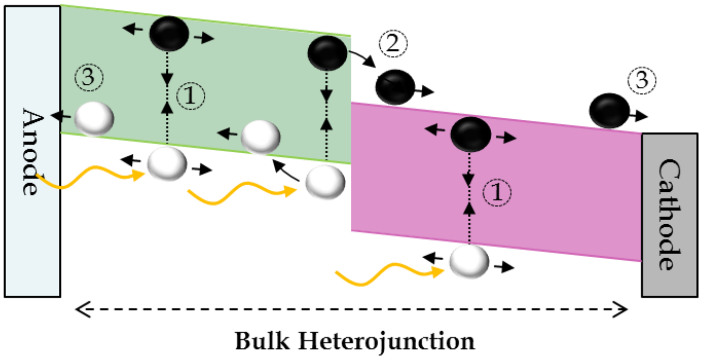
$$\frac{dn_e}{dt} = -(k_1 + k_2)n_e$$

Decay of charge transfer state:

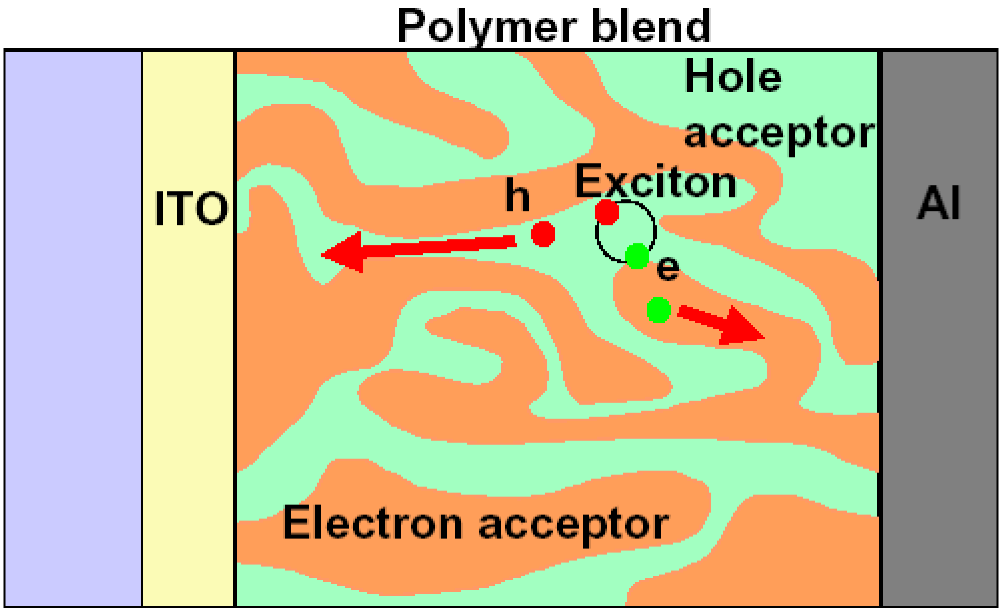
$$\frac{dn_{CT}}{dt} = k_2 n_e - (k_3 + k_4)n_{CT}$$

3. Excitonic diffusion length

a) HOMO and LUMO level:



b) Diffusion length



The important length scale is the "thickness" of the hole acceptor or electron acceptor channels. If the produced exciton needs to travel a longer time then his life time to the phase separation surface it will recombine and won't contribute to the current. To find an upper threshold for the lengthscale one needs to calculate the diffusion length:

$$\begin{aligned} L &= \sqrt{D\tau} \\ &= \sqrt{2 \cdot 10^{-3}\frac{cm^2}{s} \cdot 10^{-9}s} \\ &\approx 14.1 \cdot nm \end{aligned}$$

c) Charge extraction rate

The time for traveling through the bulk heterojunction is:

$$t = \frac{d}{v}, \qquad v = \mu E$$

$$t = \frac{d^2}{\mu V} = 2\mu s = \frac{1}{k}$$

k is the rate with which charge carriers are effectively contributing to the current.

d) Langevin Recombination

The Langevin recombination describes the recombination rate under the assumption that a charge carrier gets attracted by a charge carrier with the opposite sign. This can be describe by the drift current:

$$j = qn\mu E$$

$$= qn\mu \frac{Q}{4\pi\epsilon\epsilon_0 r^2}$$

Now we integrate over the area surrounding the charge carrier:

$$q\frac{dn}{dt} = \frac{qQn\mu}{\epsilon\epsilon_0}$$

$$q\frac{dn}{dt} = q^2 np\frac{\mu}{\epsilon\epsilon_0}, \beta = q^2\frac{\mu}{\epsilon\epsilon_0}$$

For a certain charge carrier density there is an equilibrium state between recombination and charge extraction:

$$\beta n^2 = kn$$

$$n = \frac{k}{\beta}$$

e) Quantum efficiency

Now we can formulate a model in which everything can be taken into account. Let us assume that the charge generation rate is constant:

$$\frac{dn}{dt} = G_0 - \beta n^2 - kn$$

In the steady-state case the decaying rates are in balance with the generating rate

$$0 = -\beta n^2 - kn + G_0$$

This is the case for a certain density:

$$n_{1/2} = -\frac{k}{2\beta} \pm \sqrt{\frac{k^2}{4\beta^2} - \frac{G_0}{\beta}}$$

Quantum efficiency:

$$EQE = \frac{k}{\beta n}$$