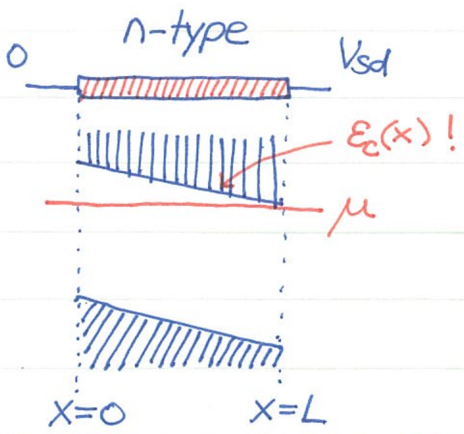
HH0043 Nonequilibrium Semiconductors

Consider a piece of n-type semiconducting wire with a voltage difference V_{sd} across the ends. If we ASSUME the system is in equilibrium, there would be just one universal chemical potential μ. The band bending is linear,

$$\boxed{\varepsilon_c(x) = \varepsilon_c(0) - \frac{eV_{sd}}{L}\cdot x}$$



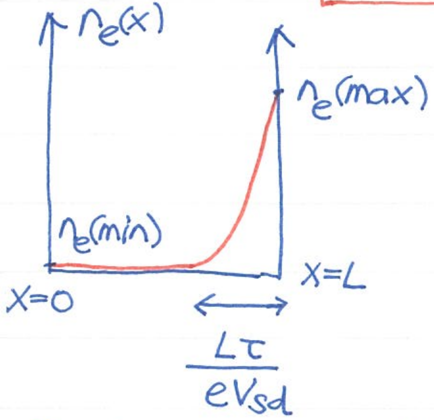
One can estimate the charge distribution,

$$n_e(x) = n_c\, e^{-[\varepsilon_c(x)-\mu]/\tau} = n_c\, e^{-[\varepsilon_c(0)-\mu]/\tau}\cdot \underbrace{e^{eV_{sd}x/L\tau}}$$

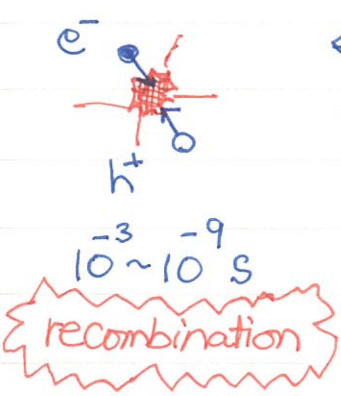
exponetial growth.

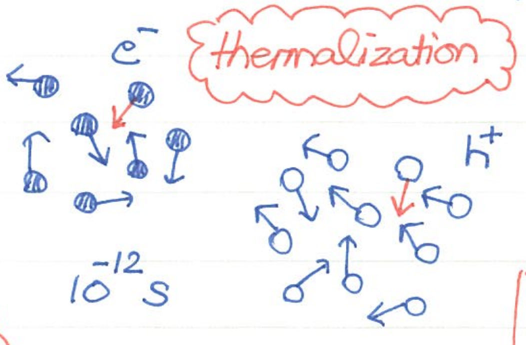
$$\longrightarrow \quad \boxed{n_e(x) = n_e(0)\, e^{eV_{sd}x/L\tau}}$$

most electrons accumulate near $x=L$ within a length scale $L\tau/eV_{sd}$. Although holes are minority in the n-type S.C., one can repeat the same calculation, leading to a similar profile. Does this make sense to you? What happens to the Ohm's law $V_{sd} = IR$?



⊘ Quasi-Fermi levels: In semiconductors, there are different time scales for different relaxation processes. Because thermalization occurs within much shorter time scale, it is possible for e^- and h^+ having diff. Fermi levels μ_c and μ_v

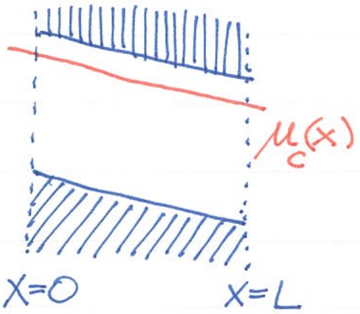




$$\boxed{\begin{aligned} f_c(\varepsilon,\tau) &= \frac{1}{e^{(\varepsilon-\mu_c)/\tau}+1} \\ f_v(\varepsilon,\tau) &= \frac{1}{e^{(\varepsilon-\mu_v)/\tau}+1} \end{aligned}}$$

μ_c and μ_v are not the chemical potential, referred as quasi-Fermi levels.

Now we can generalize the notion of quasi-Fermi level further. Going back to our semiconducting wire, our common sense tells us that there should be a current flowing and the electron density should be more or less constant.



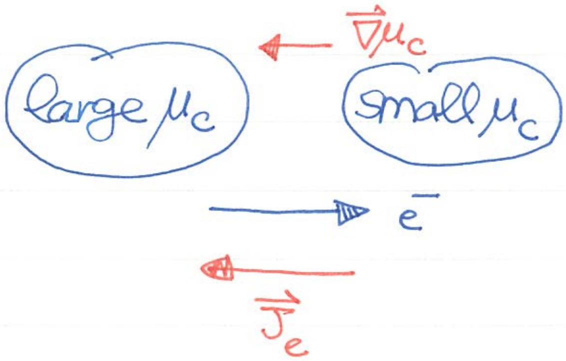
The quasi-Fermi level is $\boxed{\mu_c(x) = \mu_c(0) - \frac{eV_{sd}}{L}x}$

The electron density can be estimated,

$$n_e(x) = n_c\, e^{-[\varepsilon_c(x)-\mu_c(x)]/\tau} = n_c\, e^{-[\varepsilon_c(0)-\mu(0)]/\tau}$$

$$\longrightarrow \boxed{n_e(x) = n_e(0) = \text{const!!}}$$ ← no charge accumulation

But! There should be a flowing current. Electrons tend to flow from large μ_c to small μ_c.



$$\boxed{\vec{J}_e \propto \vec{\nabla}\mu_c}$$ ← watch out for directions.

It is also reasonable to guess that $\vec{J}_e \propto n_e$ — more electrons, more current flowing. Combine both n_e and $\vec{\nabla}\mu_c$ together, we introduce the mobility of conduction electrons $\tilde{\mu}_e$ (sorry for the confusing notation....)

$$\boxed{\vec{J}_e = n_e \tilde{\mu}_e \vec{\nabla}\mu_c}$$

$\mu_c = \varepsilon_c + \tau \log\left(\frac{n_e}{n_c}\right)$ It becomes clear later that $\vec{J}_e$ contains TWO parts.

$\vec{\nabla}\mu_c = \vec{\nabla}\varepsilon_c + \frac{\tau}{n_e}\vec{\nabla}n_e$ Substitute into the expression for current:

$$\boxed{\vec{J}_e = \underbrace{e n_e \tilde{\mu}_e \vec{E}}_{\text{drift}} + \underbrace{e D_e \vec{\nabla}n_e}_{\text{diffusion}}}$$

Here I have used:

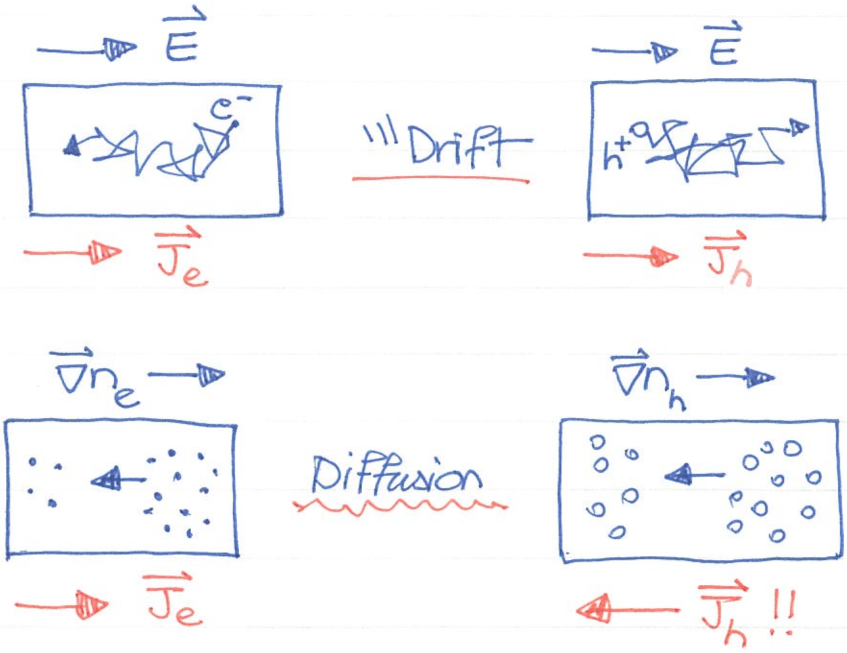
(1) $\vec{\nabla}\varepsilon_c = -e\vec{\nabla}\varphi = e\vec{E}$

(2) $D_e = \tilde{\mu}_e \tau / e$ ← diffusion constant

Similarly, one can derive the electric current $\vec{J}_h$ due to hole propagation.

$$\boxed{\vec{J}_h = e n_h \tilde{\mu}_h \vec{E} - e D_h \vec{\nabla} n_h}$$

minus sign for the 2^{nd} term.



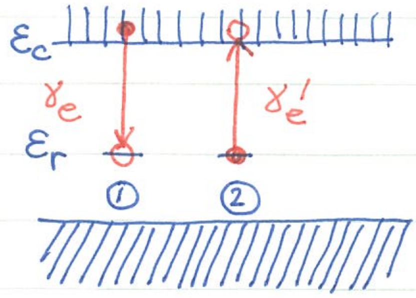
"Drift" is caused by external electric field. Both $\vec{J}_e$ and $\vec{J}_h$ have the same direction as that of $\vec{E}$.

Diffusion is caused by collisions. But!

$(\vec{J}_e, \vec{\nabla} n_e)$ same.
$(\vec{J}_h, \vec{\nabla} n_h)$ opposite.

⑦ Electron-hole recombination: Consider e^--h^+ recombination rate through impurity level @ $\varepsilon = \varepsilon_r$

For electrons decay to the impurity level,



$$\boxed{R_{c\to r} = (1-f_r)\cdot n_e \cdot \gamma_e} \quad ①$$

empty level — occupied conduction orbitals

The inverse process is described by a similar formula

$$\boxed{\begin{aligned} R_{r\to c} &= f_r (n_c - n_e)\gamma_e' \\ &\approx f_r n_c \gamma_e' \end{aligned}} \quad ②$$

OK, some explanations are in order.... $n_e = n_c e^{-(\varepsilon_c-\mu)/\tau}$

can be viewed as n_c orbitals at $\varepsilon = \varepsilon_c$ with occupation prob. p_0.

Thus, $n_e = n_c \cdot p$. On the other hand, the effectively "empty" orbitals can be estimated as $n_{empty} = n_c(1-p) = n_c - n_e \simeq n_c$!!

The net electron recombination rate is

$$\boxed{R_e = R_{c\to r} - R_{r\to c} = \gamma_e \left[(1-f_r)\, n_e - f_r\, n_c \left(\frac{\gamma_e'}{\gamma_e}\right) \right]}$$

The ratio can be computed by detail balance in equilibrium.

① $$(f_r)_{eq} = \frac{1}{e^{(\varepsilon_r-\mu)/\tau}+1} \longrightarrow \left(\frac{1-f_r}{f_r}\right)_{eq} = e^{(\varepsilon_r-\mu)/\tau}$$

② $$(n_e)_{eq} = n_c\, e^{-(\varepsilon_c-\mu)/\tau}$$

③ In addition, $R_e = 0$ in equilibrium.

④ assume γ_e', γ_e' are robust, independent of equilibrium conditions

Collecting all pieces of information together,

$$(1-f_r)_{eq}(n_e)_{eq} - (f_r)_{eq}\, n_c \left(\frac{\gamma_e'}{\gamma_e}\right) = 0 \longrightarrow \frac{\gamma_e'}{\gamma_e} = \left[\frac{n_e(1-f_r)}{n_c f_r}\right]_{eq}$$

$$\boxed{\frac{\gamma_e'}{\gamma_e} = e^{-(\varepsilon_c-\mu)/\tau}\, e^{(\varepsilon_r-\mu)/\tau} = e^{-(\varepsilon_c-\varepsilon_r)/\tau}}$$

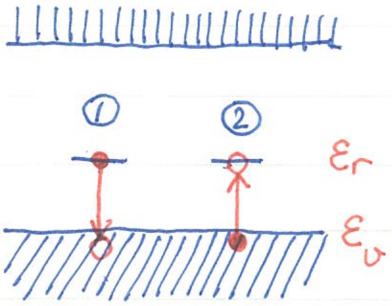
note that $\gamma_e' < \gamma_e$.
Why ?

Introduce the parameter $n_e^* \equiv n_c\, e^{-(\varepsilon_c-\varepsilon_r)/\tau}$ (electron concentration IF $\mu = \varepsilon_r$), the electron recombination rate is

$$\boxed{R_e = \gamma_e \left[(1-f_r)\, n_e - f_r\, n_e^* \right]}$$

← in general, the rate is not necessarily zero!

Now we turn to the second step: hole recombination



① $R_{r\to v} = f_r\, n_h\, \gamma_h$

② $R_{v\to r} = (1-f_r)(n_v - n_h)\,\gamma_h' \approx (1-f_r)\, n_v\, \gamma_h'$

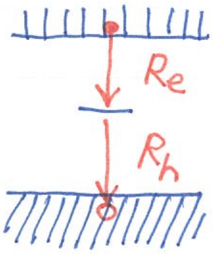
The rate for hole recombination is

$$R_h = R_{r\to v} - R_{v\to r} = \gamma_h \left[f_r\, n_h - (1-f_r)\, n_v \left(\frac{\gamma_h'}{\gamma_h}\right) \right]$$

Again, the ratio γ_h'/γ_h can be found by detail balance in equilibrium. $\left(\frac{\gamma_h'}{\gamma_h}\right) = e^{-(\varepsilon_r-\varepsilon_v)/\tau}$ again, $\gamma_h' < \gamma_h$

The recombination rate for holes can thus be written as

$$\boxed{R_h = \gamma_h \left[f_r n_h - (1-f_r) n_h^* \right]}$$ where $n_h^* = n_v e^{-(\varepsilon_r-\varepsilon_v)/\tau}$



In steady state, $df_r/dt = 0$, i.e. f_r is independent of time. In consequence, $\boxed{R_e = R_h \equiv R}$

① $R = \gamma_e \left[(1-f_r) n_e - f_r n_e^* \right]$

② $R = \gamma_h \left[f_r n_h - (1-f_r) n_h^* \right]$

Combine ①, ② to eliminate f_r.

$$\longrightarrow \boxed{R = \frac{\gamma_e \gamma_h}{(n_e+n_e^*)\gamma_e + (n_h+n_h^*)\gamma_h} (n_e n_h - n_i^2)}$$

I've used the relation: $n_e^* n_h^* = n_i^2$

The above result is the recombination rate for $e^- - h^+$ in steady state (nonequilibrium!). In thermal equilibrium, $n_e n_h = n_i^2$.
$\longrightarrow R = 0$ in equilibrium as expected.

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