Self-consistent model of charge-carrier injection: extension to the case of a degenerate organic semiconductor

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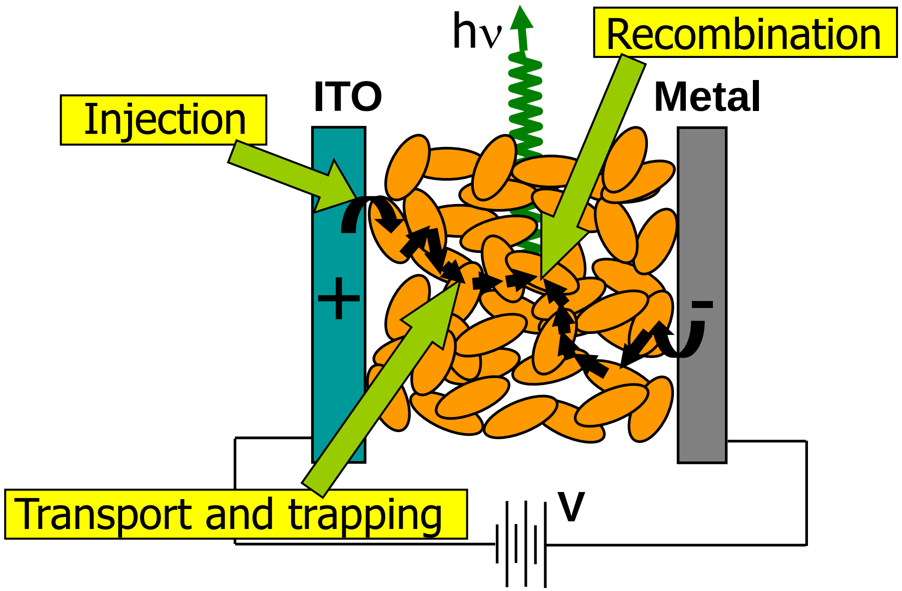
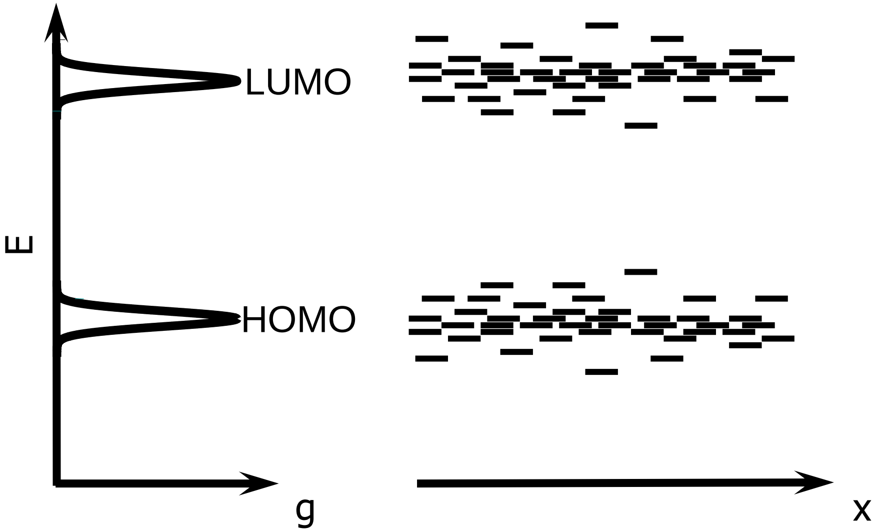
Outline

- Outline of the previous self-consistent model of charge-carrier injection and transport accounting for discrete nature of charge carriers (MMF approach)
- Approximations for the charge-carrier density in the case of Gaussian DOS
- Extension of the MMF model to the case of degenerate semiconductor: voltage-barrier chart, current-voltage characteristics for unipolar devices
- Conclusion

Important factors of electronic processes in organic semiconductors and our aims

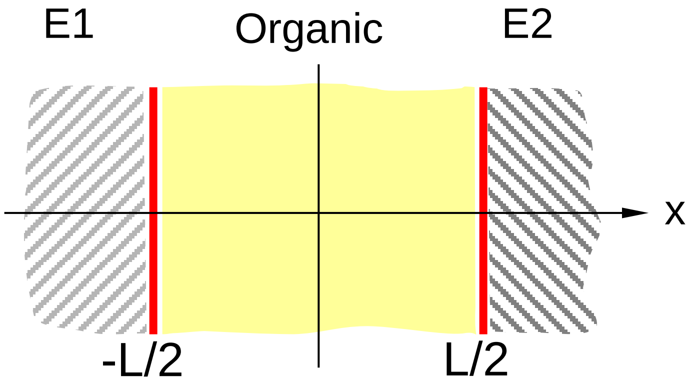




- We need in a self-consistent model of charge injection and transport in organic semiconductors allowing to extract from experiments important device parameters (carrier concentrations, mobilities, injection barriers, field distribution) and to evaluate the fatigue stability of specific devices

Self-consistent 1D mean-field model of charge-carrier injection and unipolar transport in a single-layer device

Keypoints of the model



A. Organic semiconductor:

$$kT\mu_i \frac{dp_i(x)}{dx} - e\mu_i p_i(x) F_i(x) = -j$$

$$\frac{dF_i(x)}{dx} = \frac{e}{\varepsilon_i \varepsilon_0} p_c(x)$$

narrow DOS: $g(E) = P_c \delta(E - E_c)$

Boltzmann statistics of the carriers: $p_i(x) = P_c \exp\left[\frac{E_c - \kappa_i(x) - e\varphi(x)}{kT}\right]$

B. Electrodes: Thomas-Fermi approximation

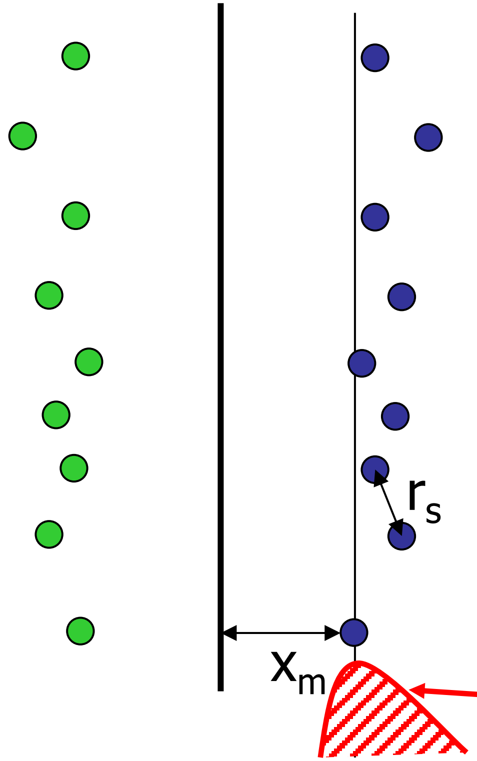
C. Self-consistent boundary conditions at the electrode/OSC interfaces:

a) electric displacement and electrochemical potential are continuous

b) electrostatic potential is continuous (mean-field (MF) approach) or has a jump $\Delta\varphi_e = \delta\varphi_{Sch}$ (modified mean-field (MMF) model)

Neumann et al. JAP **100**, 084511 (2006); Genenko et al., PRB **81**, 125310(2010)

Charge-carrier injection: many-particle vs single-particle (SP) mechanism

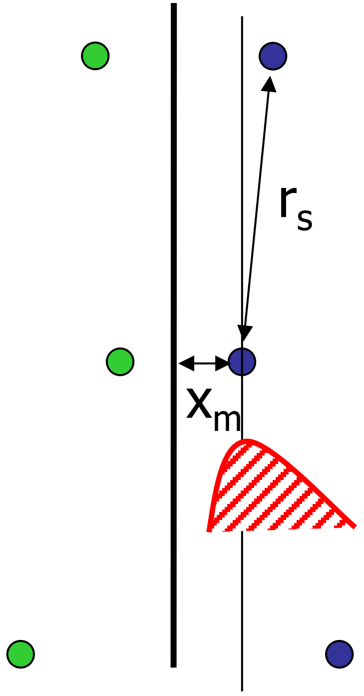


SP/MF criterion

Individual image force = mean-force from other particles

$$\boxed{x_m \cong 0.2 r_s} = 0.2\, p_i^{-1/3}$$

SP Schottky barrier

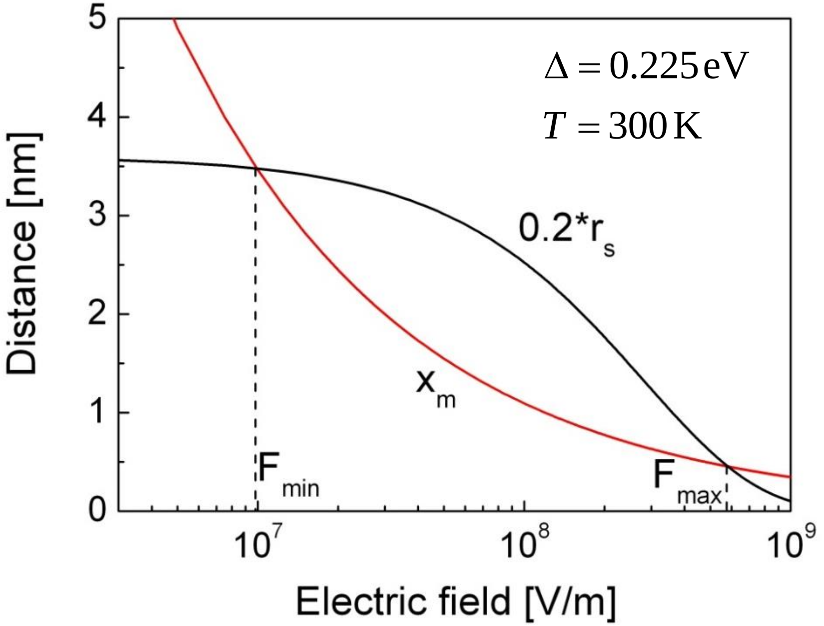


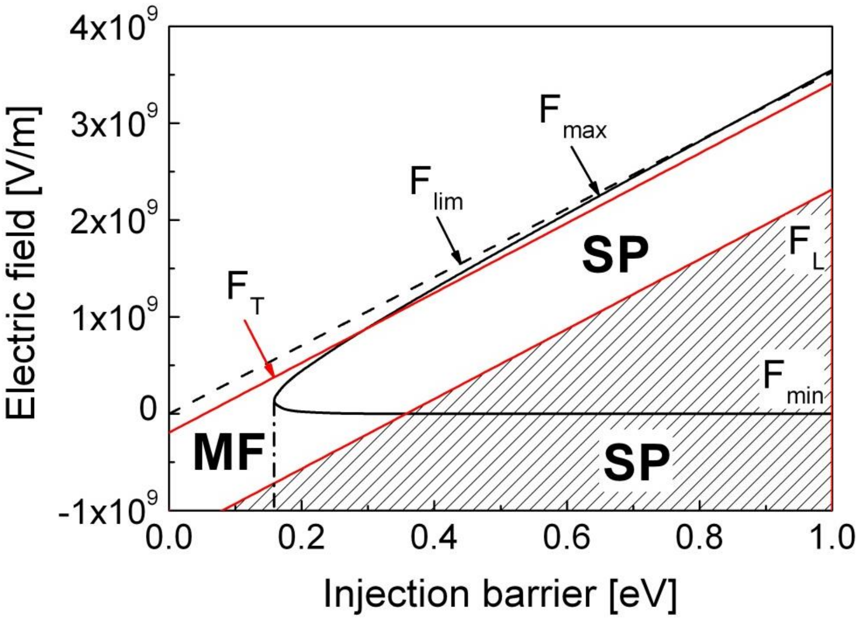
$$x_m^{\pm} = \sqrt{\frac{e}{16\pi\varepsilon_0\varepsilon_i \left|F_i(\pm L/2)\right|}}$$

$$p_i(\pm L/2) = P_c \exp\left\{-\frac{\Delta^{\pm}}{kT} \mp \frac{e l_{TF}^{\pm}}{kT}\left[\frac{\varepsilon_i}{\varepsilon_e^{\pm}} F_i(\pm L/2) - \cancel{\frac{j}{\gamma_e^{\pm}}}\right]\right\}$$

Genenko et al., PRB **81**, 125310(2010)

Validity of SP and MF approximations: field region





ITO	Organic
$n^-_\infty = 10^{20}\,\text{cm}^{-3}$	$P = 10^{21}\,\text{cm}^{-3}$
$\varepsilon^-_e = 9.3$	$\varepsilon_i = 3$
$\mu^-_e = 30\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$	$\mu_p = 10^{-4}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$
$\kappa^-_\infty = 0.225\,\text{eV}$	

Additionally:

$$r_s = L \Rightarrow F_L$$

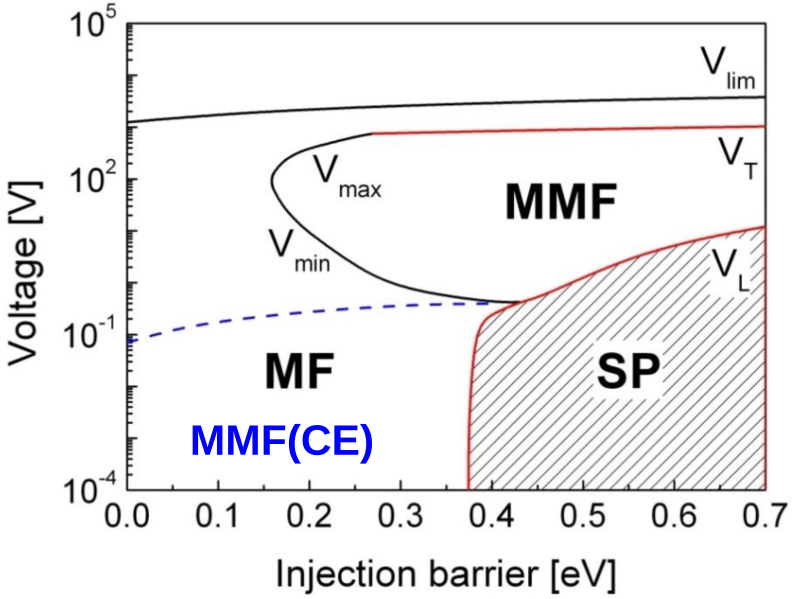
$$r_s = l_{Coulomb} = e^2 / 32\pi\varepsilon_0\varepsilon_i kT \Rightarrow F_T$$

Account of charge-carrier discreteness in the MF approach

Boundary conditions:

$$p_i(\pm L/2) = P_c \exp\left[-\frac{\Delta^{\pm}}{kT} \mathrm{m} \frac{eF_i(\pm L/2) l_{TF}^{\pm}}{kT} \frac{\varepsilon_i}{\varepsilon_e^{\pm}} + \left(1 - \frac{x_m^{\pm}}{0.2 r_s^{\pm}}\right) \frac{e\delta\varphi_{sch}^{\pm}}{kT} \theta\left(0.2 r_s^{\pm} - x_m^{\pm}\right) \right]$$

ITO/Organic/Al



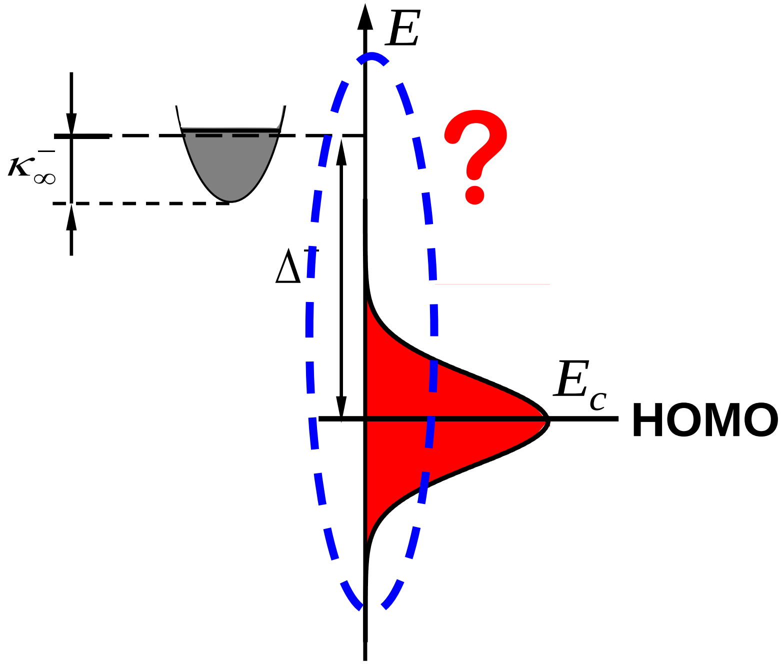
$$V = \int_{-\infty}^{\infty} dx\, F(x) - V_{\mathrm{BI}}$$

$$V_{\mathrm{BI}} = \int_{-\infty}^{\infty} dx\, F(x) \Big|_{j=0}$$

Genenko et al., PRB **81**, 125310(2010)

What changes for the Gaussian DOS?

ITO/OSC interface



$$p_i(x) = \int_{-\infty}^{\infty} dE\, g(E)\, f\left(E, \kappa_i(x)\right)$$

$$= \frac{P_c}{\sqrt{2\pi}\sigma_c} \int_{-\infty}^{\infty} dE \frac{\exp\left(-\frac{(E-E_c)^2}{2\sigma_c^2}\right)}{\exp\left(\frac{\kappa_i(x)+e\varphi(x)-E}{kT}\right)+1}$$

In the „Boltzmann regime“:

$$\boxed{\Delta^{\pm} \to \Delta^{\pm} - \frac{\sigma_c^2}{2kT}}$$

- Whether the Boltzmann statistics of carriers is still relevant in the case of realistic Gaussian DOS of OSC, especially for calculation of the carrier density at the electrode/OSC interfaces?

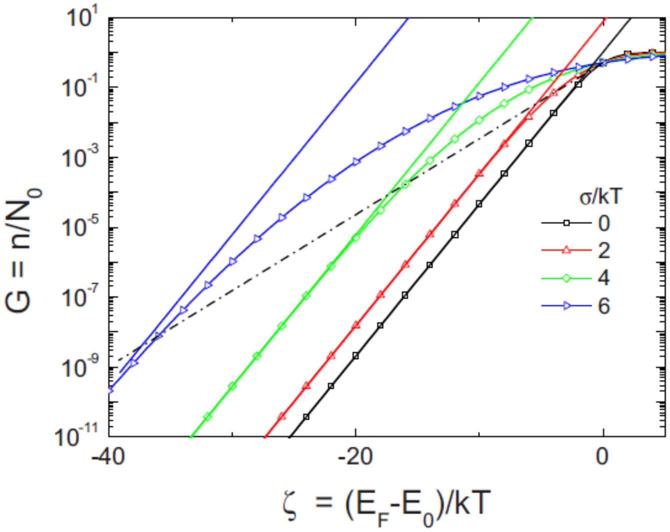
Charge-carrier density as Gauss-Fermi integral

Paasch & Scheinert, JAP **107**, 104501 (2010)

$$n = \int dE\, g(E)\, f(E, E_F) = \frac{N_0}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} dE' \exp\left(-\frac{E'^2}{2\sigma^2}\right) \left[\exp\left(\frac{E' - E_F + E_0}{kT}\right) + 1\right]^{-1}$$

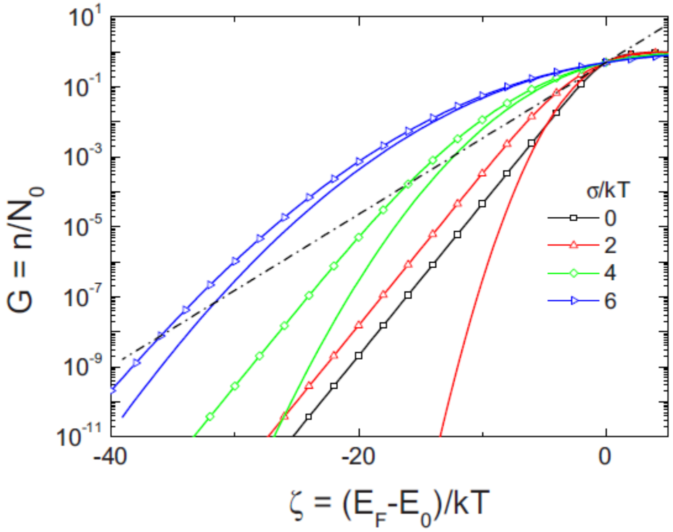
Nondegenerate limit: $f(E, E_F) \rightarrow \exp\left(\frac{E_F - E}{kT}\right)$

$$n = N_0 \exp\left(\frac{E_F - E_0}{kT} + \frac{\sigma^2}{2(kT)^2}\right)$$



Degenerate limit: $f(E, E_F) \rightarrow \theta(E_F - E)$

$$n = \frac{N_0}{2} \operatorname{erfc}\left(-\frac{E_F - E_0}{\sigma\sqrt{2}}\right)$$



Crossover at $\zeta = -\frac{\sigma^2}{2(kT)^2}$: $n_{cr} = \frac{N_0}{2} \exp\left(-\frac{\sigma^2}{2(kT)^2}\right)$

For σ(300K) = 0.1 eV $n_{cr} \sim 10^{-4} N_0$

PS analytical approximation for GF integral

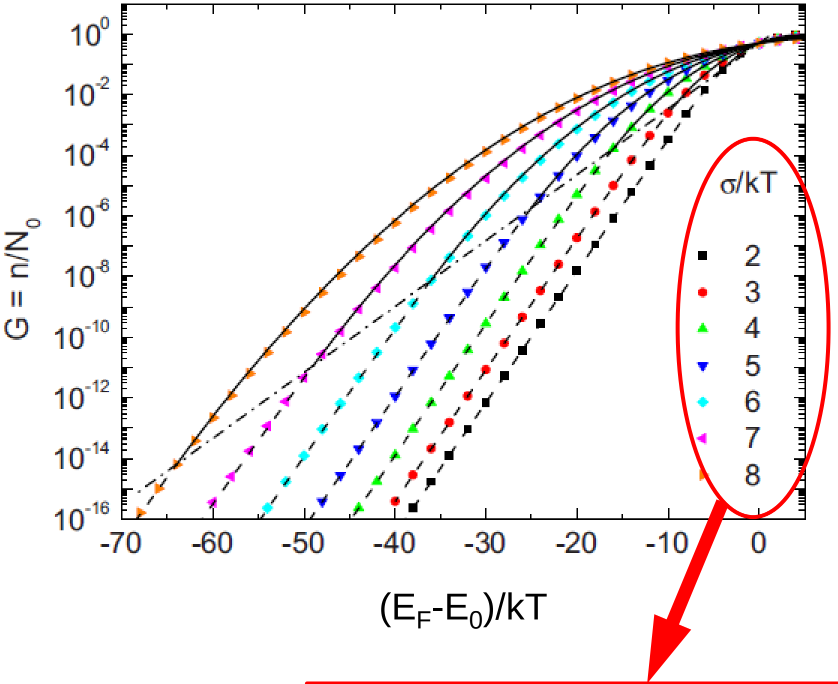
Paasch & Scheinert, JAP **107**, 104501 (2010)

$$\zeta = \frac{E_F - E_0}{kT}, \quad s = \frac{\sigma}{kT}$$

$$\frac{n}{N_0} = \begin{cases} \exp\left(\zeta + \frac{s^2}{2}\right)\left[\exp\left(K(s)\left(\zeta + s^2\right)\right) + 1\right]^{-1}, & \zeta \le -s^2 \\ \frac{1}{2}\operatorname{erfc}\left(-\frac{\zeta}{s\sqrt{2}} H(s)\right), & \zeta \ge -s^2 \end{cases}$$

$$H(s) = \frac{\sqrt{2}}{s}\operatorname{erfc}^{-1}\left[\exp\left(-\frac{s^2}{2}\right)\right]$$

$$K(s) = 2\left\{1 - \frac{H}{s}\sqrt{\frac{2}{\pi}}\exp\left[\frac{s^2}{2}\left(1 - H^2\right)\right]\right\}$$



σ_c(300K) = 0.05 - 0.2 eV

- After appropriate modifications this approximation can be applied to the MMF boundary conditions

MMF boundary conditions in the case of Gaussian DOS

Self-consistent boundary conditions at the electrode/OSC interfaces are:

$$p_i\left(\pm\frac{L}{2}\right)=\frac{P_c}{\sqrt{2\pi}\sigma_c}\int_{-\infty}^{\infty}dE\exp\left(-\frac{E^2}{2\sigma_c^2}\right)\left[\exp\left(\frac{\Delta_{eff}^{\pm}-E}{kT}\right)+1\right]^{-1}$$

$$\Delta_{eff}^{\pm}=\Delta^{\pm}\pm el_{TF}^{\pm}\left(\frac{\varepsilon_i}{\varepsilon_e^{\pm}}F(\pm L/2)-\frac{j}{\gamma_e^{\pm}}\right)-\left(1-\frac{x_m^{\pm}}{0.2r_s^{\pm}}\right)e\delta\varphi_{sch}^{\pm}\theta\left(0.2r_s^{\pm}-x_m^{\pm}\right)$$

With substitutions $\zeta\left(\pm\frac{L}{2}\right)=\frac{\Delta_{eff}^{\pm}}{kT},\quad s=\frac{\sigma_c}{kT}$:

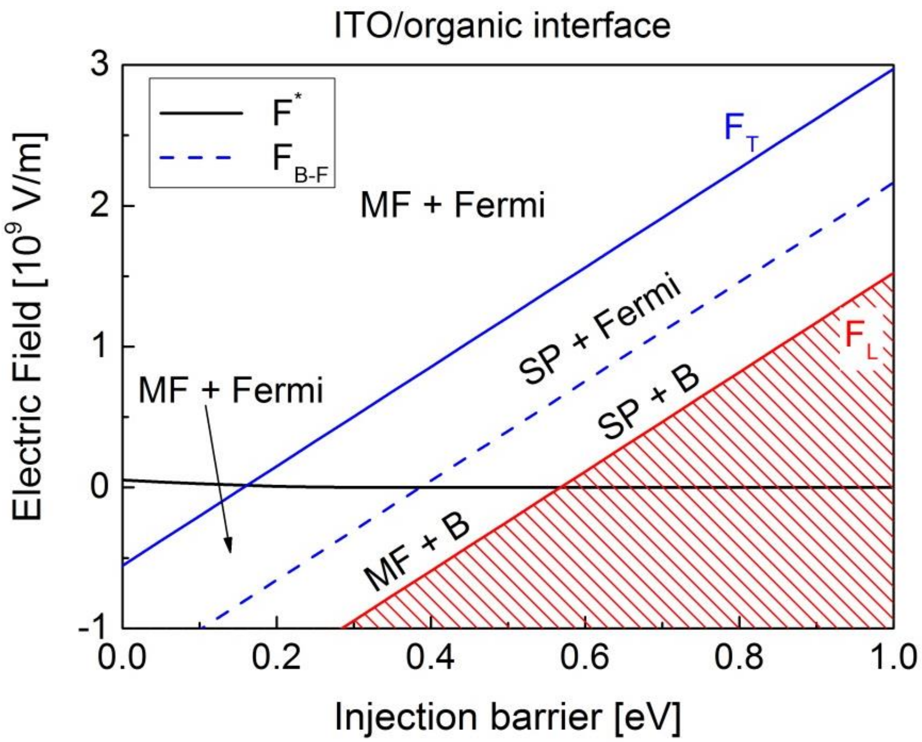
$$\frac{p_i(\pm L/2)}{P_c}=\begin{cases}\exp\left(\zeta\left(\pm\frac{L}{2}\right)+\frac{s^2}{2}\right)\left[\exp\left(K(s)\left(\zeta\left(\pm\frac{L}{2}\right)+s^2\right)\right)+1\right]^{-1}, & \zeta\left(\pm\frac{L}{2}\right)\geq s^2\\ \frac{1}{2}\operatorname{erfc}\left(-\frac{\zeta(\pm L/2)}{s\sqrt{2}}H(s)\right), & \zeta\left(\pm\frac{L}{2}\right)\leq s^2\end{cases}$$

Field-injection barrier chart

$$x_m = 0.2\,p_i^{-1/3} \Rightarrow F^*$$

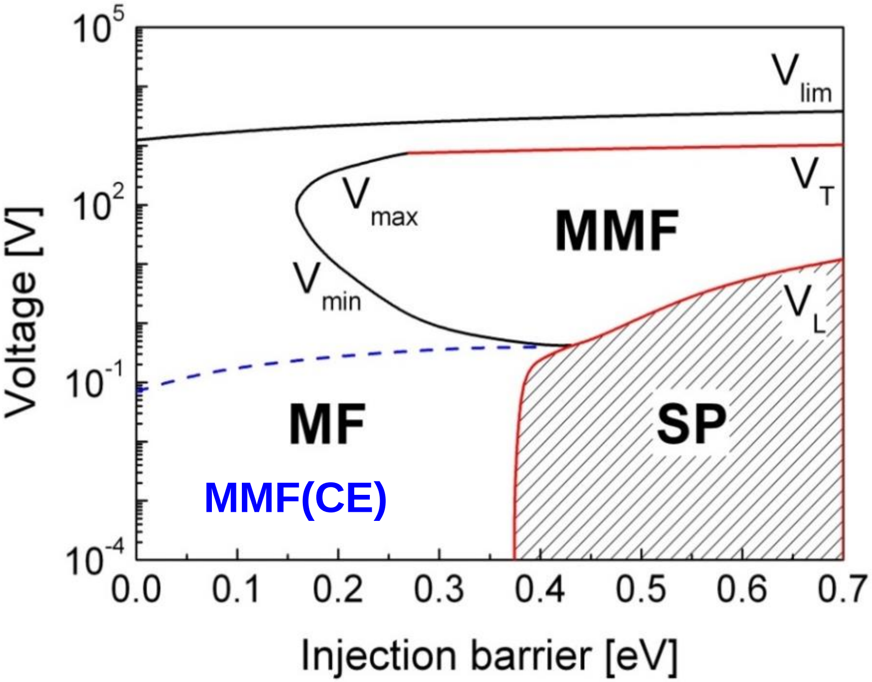
$$\boxed{\Delta^- - e l_{TF}^- \left(\frac{\varepsilon_i}{\varepsilon_e^-} F(-L/2) - \frac{j}{\gamma_e^-} \right) = \frac{\sigma_c^2}{kT} \Rightarrow F_{B-F}}$$

ITO	Organic
$n_\infty^- = 10^{20}\,\mathrm{cm}^{-3};\quad \varepsilon_e^- = 9.3$ $\mu_e^- = 30\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ $\kappa_\infty^- = 0.225\,\mathrm{eV}$	$P_c = 10^{21}\,\mathrm{cm}^{-3};\quad \varepsilon_i = 3$ $\mu_p = 10^{-6}\,\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ $\sigma_c = 0.1\,\mathrm{eV}$

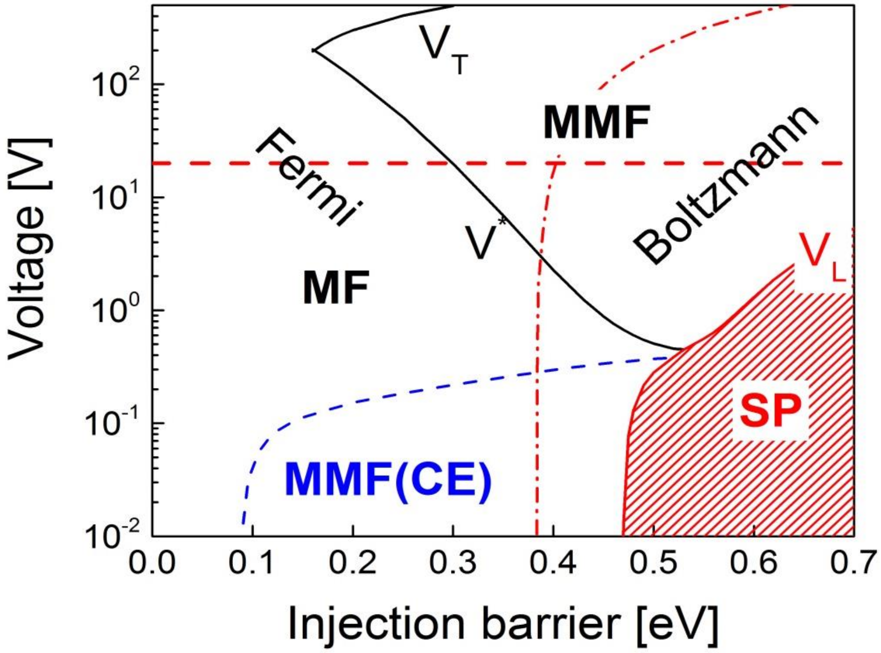


Voltage-barrier chart for injecting electrode

ITO/Organic/Al



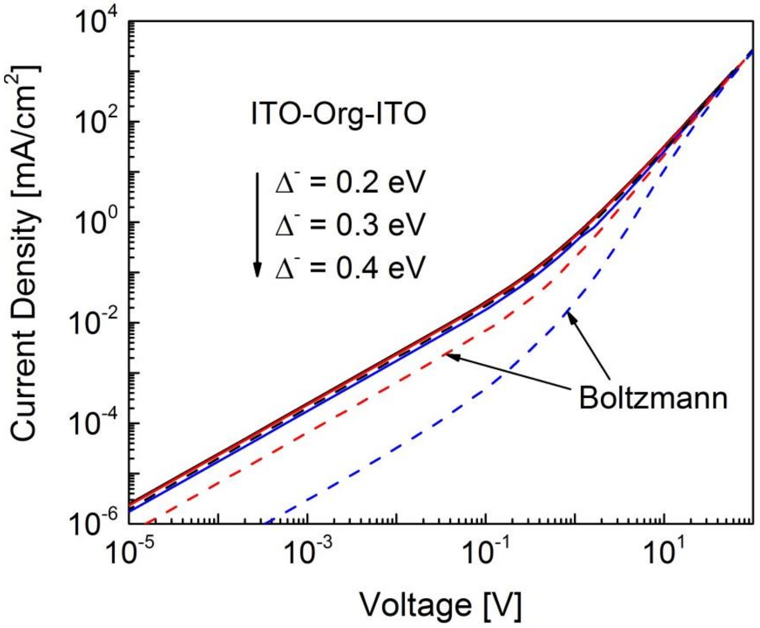
Boltzmann statistics only



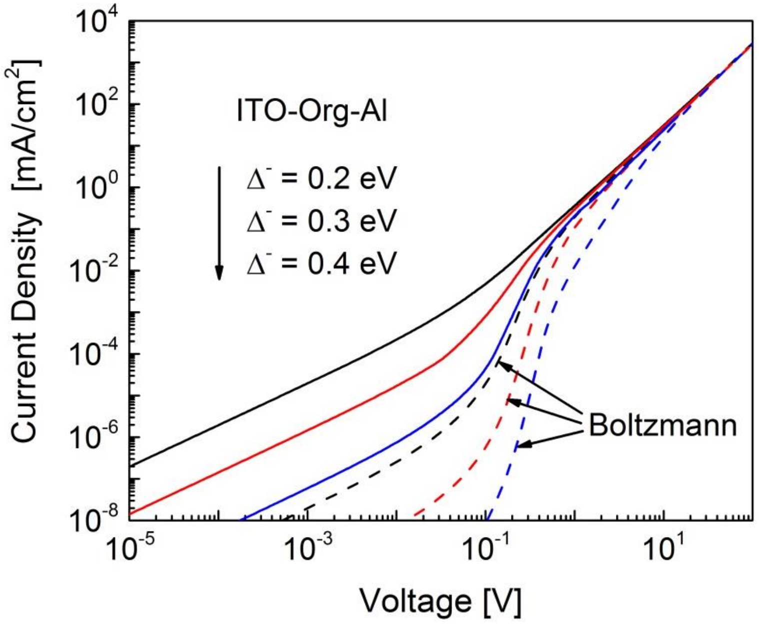
extended approach

Simulated current-voltage characteristics

ITO/OSC(100nm)ITO



ITO/OSC(100nm)Al



- ❑ Assumption of the „Boltzmann regime“ for injected carriers results in sufficient undervalueing of calculated current density, especially at low voltages

Conclusions

- The mean-field, self-consistent model of charge-carrier injection and transport in organic semiconductors accounting for discrete nature of charge carriers is extended to the case of degenerate OSC with the Gaussian shape of DOS
- The extended approach is applicable now for arbitrary values of injected carrier densities in the wide range of DOS parameters
- It is expected to improve the fitting of measured current-voltage characteristics, particularly at applied voltages near and well below the built-in potential value

(Also, for fitting of fatigued bipolar IV characteristics –
the challenge unresolved yet...)