Mathematical models for Semiconductors: Special case: Solar Cells

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Motivation

Mathematical Modelling of solar cells(semiconductor)

Reference: Semiconductor equations, P. Markowich, C. Ringhofer, C. Schmeiser, Springer 1990

Introduction: What/How do we model?

- Basic transport equations which model the flow of charge carriers in semiconductors
- They describe evolution of the phase space (position-momentum space) density function of electrons and/or holes
- Kinetic equations :
  - Quantum mechanical models : quantum Liouville equation (many body Schrödinger equation)
  - Classical models : motion of particles based on Newton's second law(classical Liouville equation)
  - Semi-Classical models : modification of the classical Liouville equation to incorporate quantum effects
- Kinetic equations starting point for deriving the Drift-Diffusion semiconductor model(fluid mechanical model)
- Kinetic models : computationally very costly due to high dimensions
- Dimension reduction : depends on the properties of the interaction force field
  - Long range Columb force : Vlasov equation (Liouville + Field equation)
  - Long and short range forces : Boltzmann equation

The Liouville equation - setup

- Basic equation which governs the motion of charged particles under a force (assume classical mechanics)
- Motion of single electron in vacum under the action of an electric field E: let $x,\ v \in \mathbb{R}^3$ position and velocity, q is the electron charge and m its mass

$$\text{Force on the electron: } \mathcal{F} = -qE,$$
$$\text{Newton's second law: } \mathcal{F} = m\dot{v}$$

we obtain the initial value problem

$$\dot{x} = v, \qquad x(t=0) = x_0$$
$$\dot{v} = -\frac{q}{m}E, \qquad v(t=0) = v_0$$

trajectories in the position-velocity space $w(t; x_0, v_0) = (x(t), v(t))$

The Liouville transport equation - single electron

- Instead of a given (x_0, v_0) we consider the joint probability density $f_I = f_I(x, v)$ of the initial position and velocity with

$$f_I(x, v) \geq 0, \quad \iint f_I(x, v) dx dv = 1$$

- Goal: derive a continum equation for the probability density $f = f(x, v, t)$ which evolves from $f_I = f(x, v, t = 0)$
- Reasonable to assume that f does not change along the trajectories: $f(w(t; x, v), t) = f_I(x, v), \ \forall x, v, \ t \geq 0$
- Differentiating with respect to t we get

$$\partial_t f + \dot{x} \cdot \text{grad}_x f + \dot{v} \cdot \text{grad}_v f = 0$$

and replacing $\dot{x}, \ \dot{v}$ we obtain the famous Liouville equation

Liouville–transport equation

$$\partial_t f + v \cdot \text{grad}_x f - \frac{q}{m} E \cdot \text{grad}_v f = 0$$

The Liouville transport equation - ensemble of particles

- Assume we have M particles: $x = (x_1, \ldots, x_M) \in \mathbb{R}^{3M}$
  $v = (v_1, \ldots, v_M) \in \mathbb{R}^{3M}$, $\mathcal{F} = (\mathcal{F}_1, \ldots, \mathcal{F}_M) \in \mathbb{R}^{3M}$

Liouville–transport equation

$$\partial_t f + v \cdot \text{grad}_x f + \frac{1}{m} \mathcal{F} \cdot \text{grad}_v f = 0$$

- The probability of the ensemble to be in the subset B of the $6M-$dimensional position-velocity space at time t is given by

$$P_M(B, t) = \iint_B f(x, v, t) dx dv$$

- The Liouville equation is linear hyperbolic and its characteristics are the trajectories of the particles

$$\dot{x}_i = v_i, \quad \dot{v}_i = \frac{1}{m} \mathcal{F}_i, \quad i = 1, \ldots, M$$

The Liouville equation - Moments

- Conservation property We assume in the sequel that the force field $\mathcal{F}$ is divergence free :

$$\mathrm{div}_v \mathcal{F} = 0, \quad x \in \mathbb{R}^{3M}, \ v \in \mathbb{R}^{3M}, \ t \geq 0$$

then by assuming the solution decays as $|x| \to \infty, \ |v| \to \infty$ then it can shown

$$\frac{d}{dt} \int_{\mathbb{R}_x^{3M}} \int_{\mathbb{R}_v^{3M}} f(x,v,t) dv dx = 0 \Rightarrow$$

$$\int_{\mathbb{R}_x^{3M}} \int_{\mathbb{R}_v^{3M}} f(x,v,t) dv dx = \int_{\mathbb{R}_x^{3M}} \int_{\mathbb{R}_v^{3M}} f_I(x,v) dv dx = 1, \ t \geq 0$$

- Moments: $n(x,t)$-position density, $J(x,t)$-current density

$$n(x,t) = \int_{\mathbb{R}_v^{3M}} f(x,v,t) dv$$

$$J(x,t) = -q \int_{\mathbb{R}_v^{3M}} v f(x,v,t) dv$$

The Liouville equation - Moments

- The conservation property :

$$\int_{\mathbb{R}_x^{3M}} n(x,t)dx = \int_{\mathbb{R}_x^{3M}} n_I(x)dx, \;\; t \geq 0$$

- Integrating formally the Liouville equation w.r.t v we obtain the macroscopic particle continuity equation

$$\partial_t n(x,t) - \frac{1}{q}\mathrm{div}_x J(x,t) = 0$$

- Solvability: If the maps

$$w(t;\cdot,\cdot) : \mathbb{R}_x^{3M} \times \mathbb{R}_v^{3M} \to \mathbb{R}_x^{3M} \times \mathbb{R}_v^{3M}$$

are sufficiently smooth and $1-1$ and if $f_I(x,v)$ is sufficiently differentiable then there is a unique solution to the Liouville equation and it is given

$$f(x,v,t) = f_I(w^{-1}(t;x,v)), \quad x \in \mathbb{R}_x^{3M}, \; v \in \mathbb{R}_v^{3M}, \; t \geq 0$$

The Liouville equation - Dimension reduction

- Two fundamental difficulties with the Liouville equation
  - There are no models for short range and long range interactions
  - The dimension of $M-$particle ensemble is $6M$ in phase space which prohibitively large in practical applications
- Dimension Reduction
  - Derive the BBGKY-hierarchy(Bogoliubov, Born, Green, Kirkwood, Yvon): system of equations for the position velocity densities of sub-ensembles consisting of $d-$electrons, $d = 1, \ldots, M$. To do so, we assume a certain structure of the interaction field i.e. weak two particle interactions, integrating the Liouville eqn w.r.t. position-velocity of $M - d$ particles, and take the formal limit $M \to \infty$. A particular solution of the hierarchy is obtained determined by a single function of three positions and three velocity coordinates and time.
  - This is the solution of the Vlasov equation, which can be considered as an "aggregated" one-particle Liouville eqn.
  - In semiconductors the short range interactions of the particles with the lattice are more important than short range forces between particles. To account for these one needs to extend the Vlasov equation to obtain the Boltzmann equation

The Vlasov equation

The Vlasov eqn is given by

$$\partial_t F + v \cdot \mathrm{grad}_x F - \frac{q}{m} E_{eff} \cdot \mathrm{grad}_v F = 0, \quad x \in \mathbb{R}^3_x, \ v \in \mathbb{R}^3_v, \ t > 0$$

$$E_{eff}(x,t) = E_{ext}(x,t) + \int_{\mathbb{R}^3_{x*}} n(x_*,t) E_{int}(x,x_*) dx_*, \ x \in \mathbb{R}^3_x, \ t > 0$$

$$F(x,v,t) = MP(x,v,t), \ \text{P one particle density}$$

$$n(x,t) = \int_{\mathbb{R}^3_v} F(x,v,t) dv$$

$$J(x,t) = -q \int_{\mathbb{R}^3_v} vF(x,v,t) dv$$

Many body physics through the nonlocal term involving particle interactions $E_{int}(x,x_*)$

The Vlasov-Poisson system

A very important long range force acting between two electrons is the Coulomb force

$$E_{int}(x,y) = -\frac{q}{4\pi\epsilon_s}\frac{x-y}{|x-y|^3},\ x,y \in \mathbb{R}^3,\ x \neq y$$

Then we easily get

$$\text{div } E_{eff} = \text{div } E_{ext} - \frac{q}{\epsilon_s} n \quad \nabla \times E_{eff} = \nabla \times E_{ext}$$

so if $\nabla \times E_{ext} = 0$ then $\nabla \times E_{eff} = 0$ so there potential functions $V_{eff},\ V_{ext}$ such that

$$E_{eff} = -\text{grad}\, V_{eff} \quad \text{and} \quad E_{ext} = -\text{grad}\, V_{ext} \implies$$
$$-\Delta V_{eff} = -\Delta V_{ext} - \frac{q}{\epsilon_s} n$$

The Vlasov-Poisson system

Assuming that the external field is produced by ions of charge $+q$(holes) then by Coulomb's law

$$E_{ext}(x,t) = \frac{q}{4\pi\epsilon_s}\int_{\mathbb{R}^3_y} C(y,t)\frac{x-y}{|x-y|^3}dy$$

where $C(x,t)$ is the number density of the background ions. Then

$$\text{div } E_{ext} = \frac{q}{\epsilon_s}C \implies \Delta V_{ext} = -\frac{q}{\epsilon_s}C \implies$$

$$-\epsilon_s \Delta V_{eff} = \rho, \quad \rho = q(C-n)$$

ρ is the charge density of the system consisting of conduction electrons and positively charged background ions(holes).

Vlason-Poisson system

$$\partial_t F + v\cdot \text{grad}_x F + \frac{q}{m}\text{grad}V_{eff}\cdot \text{grad}_v F = 0$$

$$-\epsilon_s \Delta V_{eff} = \rho$$

The Boltzmann equation - Collisions

- The Vlasov eqn. neglects short range interactions(collisions) of particles with other particles in the ensemble or the lattice.
- Collisions : particles are scattered from one state to another with their velocity changing very fast, while their position change slowly
- Extension of Vlasov to include a statistical account for the scattering events, besides the long range interactions.
- The Boltzmann equation

$$\partial_t F + v \cdot \mathrm{grad}_x F - \frac{q}{m} E_{eff} \cdot \mathrm{grad}_v F = Q(F),\ x \in \mathbb{R}^3_x,\ v \in \mathbb{R}^3_v, t > 0$$

$$Q(F)(x, v, t) = \int_{\mathbb{R}^3_v} (s(x, v^*, v) F^* (1 - F) - s(x, v, v^*) F (1 - F^*))\, dv^*$$

F density, Q collision operator, $s(x, v^*, v)$ is the transition rate for an electron at x to change v^* to v, E_{eff} as in Vlasov.

Fluid Dynamical Models

- A compromise between physical accuracy and computational efficiency: instead of $3+3+1$ we have $3+1$
- Dependent variables are moments(averages) of the phase space density w.r.t. velocity
- Derived from Boltzmann using two techniques
  - Perturbation argument(asymptotic expansion): Exploits the smallness of the mean free path and expands the phase space density function in powers of this parameter(Hilbert expansion). For semiconductors done by (F. Poupaud)
  - Moments methods:
    - ⋆ An ansatz is assumed for the phase space density function in Boltzmann eqn
    - ⋆ The ansatz describes the dependence on the velocity containing parameters depending on position and time
    - ⋆ Inserting this ansatz the Boltzmann eqn is multiplied by linearly independent functions of velocity and integrated of the velocity space
    - ⋆ We get a hierarchy of p.d.e's depending on space and time only. Moments represent macroscopic quantities(mass, momentum, energy, etc)

Drift-Diffusion equations

- Derived by a two species system of Boltzmann equations (Bi-polar model)
- ...using either the asymptotics of mean free path or moments
- This is the basic model used for semiconductor modelling, for two species : electrons n and holes p forming a $p-n$ *junction*

$$
\begin{aligned}
q\partial_t n - \text{div}\ J_n &= -qR \\
q\partial_t p + \text{div}\ J_p &= -qR \\
J_n &= q\mu_n(V_T \text{grad} n + nE) \\
J_p &= -q\mu_p(V_T \text{grad} p + pE) \\
R &= A(x)(np - n_i^2) \\
D_n = \mu_n V_T,\ D_p &= \mu_p V_T,\ V_T = \frac{\kappa T}{q} \\
E &= -\text{grad} V
\end{aligned}
$$

Mathematical Modelling of Solar Cells

Solar Cells

- Commercial PV systems are based on Silicon(crystalline) made solar cells.
- Solar cells have certain architectures: *Al-BSF, PERC, Heterojunction, Perovskite, Organic, Tandem*(Silicon+organic)
- Most commercial PV systems are based on *Al-BSF, PERC, Heterojunction* solar cells. Efficiency around 15-20%.
- *Perovskite, Organic* solar cells are not commercially available yet. Manufactured, studied and tested only at laboratories. High efficiencies 22-28%
- Each architecture requires different mathematical model.
- For *Al-BSF, PERC* we can assume that we are in the low injection regime: Diffusion is the dominating force, rather transport. In this case one of the species can be neglected depending on the type of solar cell
- Mathematical modelling for *Perovskite* solar cells is recent.

Basic Principles

Working principle of a solar cell :

- Photovoltaic effect: Generation of a potential difference at the junction of two different materials in response to electromagnetic radiation.
- Photoelectric effect: electrons are emitted from a material that has absorbed light with a frequency above a material dependent threshold frequency.

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Photovoltaic effect:

1. Generation of charge carries due to absorptions of photons in the materials that form a junction
2. Separation of the photo-generated charge carriers in the junction
3. Collection of the photo-generated charge carriers at the terminals of the junction

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Loss mechanisms:

1. inability to convert photons to electricity
2. thermal effects

These two losses amount about half the incident solar energy

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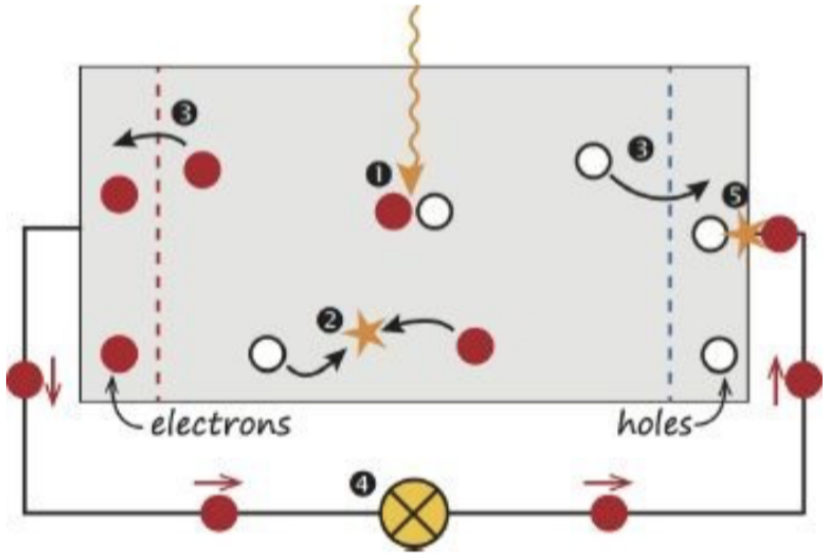
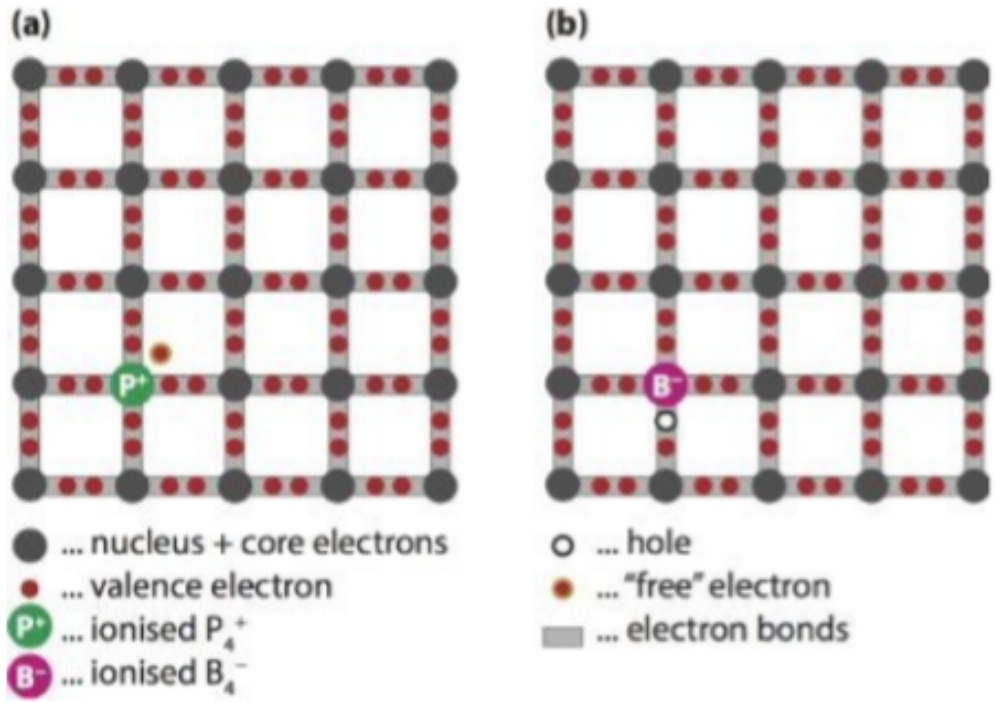


Silicon junction, Doping

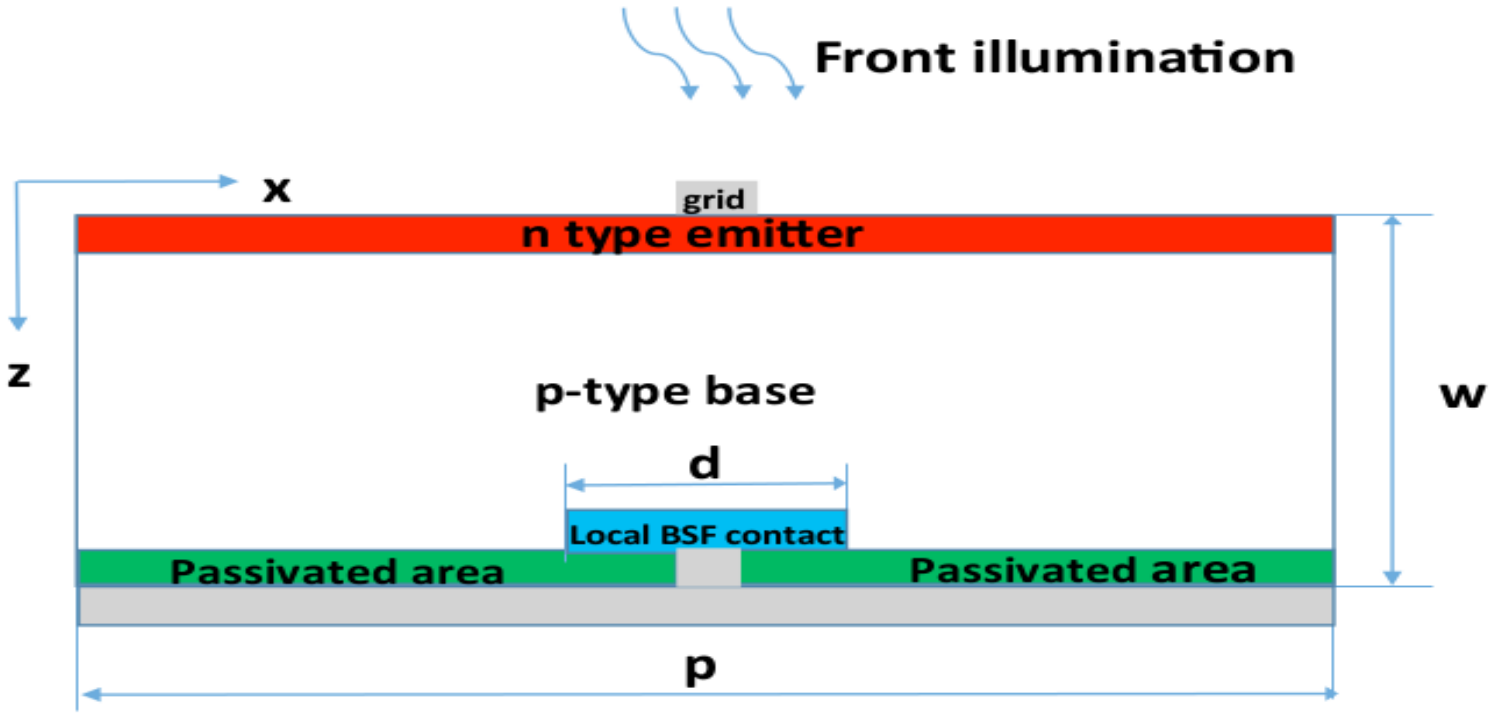
Silicon(14) is the basic material for solar cells. A junction is created by two layers of silicon which are doped by two different elements namely Boron(5) and Phosphorus(15).



- Phosphorus(donor) donates a free electron. Boron(acceptor) creates a hole.
- p-type semiconductor : holes dominate its electrical conductivity
- n-type semiconductor : electrons dominate its electrical conductivity
- Doping concentration(cm^{-3}) range : $10^{12} - 10^{20}$

Typical configuration

Geometry of a p-type solar cell : $p = 1200\mu m, w = 180\mu m, d = \%p$



Basic Mathematical Model

Two basic effects : Drift and Diffusion of carriers : n(electron), p(holes) densities

Drift of carriers

Drift is the motion of a charged particle in response to an electric field.

Diffusion of carriers

Diffusion is the motion of charged particles from regions of high particle concentration into to regions of low particle concentration due to random thermal motion

Basic Mathematical Model

Drift - Diffusion system of equations of semiconductors :

$$\frac{\partial n}{\partial t} = \nabla \cdot J_n + G - R, \quad J_n = \mu_n\, n\, E + D_n\, \nabla n$$
$$\frac{\partial p}{\partial t} = -\nabla \cdot J_p + G - R, \quad J_p = \mu_p\, p\, E - D_p\, \nabla p$$
$$\epsilon \nabla \cdot E = q(p - n + N), \quad E = -\nabla V$$
$$G(z) = \int_\lambda \alpha(\lambda) I_0(\lambda) \frac{\lambda}{h\, c} e^{-\alpha(\lambda) z}, \quad R = \frac{n\, p - n_i^2}{\tau_n (p + p_t) + \tau_p (n + n_t)}$$

$h, c, q, \mu_n, \mu_p, D_n, D_p, \epsilon, n_i, \tau_n, \tau_p, n_t, p_t, N$, constants : $10^{-34} - 10^{16}$ posing serious computational challenges

Non-equilibrium Boltzmann approximation

$$n = n_i \exp\left[\frac{V - \phi_n}{V_T}\right], \; p = n_i \exp\left[\frac{\phi_p - V}{V_T}\right] \implies n\, p = n_i^2 \exp\left[\frac{\phi_p - \phi_n}{V_T}\right]$$

ϕ_n, ϕ_p : quasi-Fermi potentials, $V_T = \frac{kT}{q}$ thermal voltage

Mathematical Model for *Al-BSF, PERC* cells

We introduce a new model based on two simplifying assumptions

- Solar cell operates at steady state : no transient phenomena
- Low injection regime : Current transport is dominated by diffusion($n << p, p \cong N_A >> n_i^2$). System decouples and 2nd equation can be neglected. (Most commercial Silicon based solar cells are in this regime).

To handle the variate of scales we introduce a new change of variables

$$\xi = \frac{x}{L_n},\ L_n = \sqrt{D_n \tau_n},\ n = N_A \exp\left[\frac{V - \phi_n}{V_T}\right],\ \eta = \frac{n}{N_A}$$

$$u = \frac{V}{V_C},\ v = \frac{\phi_n}{V_C} \implies \eta = \exp\left(\frac{V_C}{V_T}(u - v)\right)$$

$$V_C = \frac{D_n - D_p}{\mu_p} = V_T\left(\frac{\mu_n}{\mu_p} - 1\right),\ g_n(z) = G(z)\frac{L_n^2}{N_A D_n},\ j_{0,np} = J_0 \frac{L_n}{qD_p N_A}\frac{V_T}{V_C}$$

Mathematical Model for *Al-BSF, PERC* cells

The mathematical model is

$$-\Delta\eta + \eta = g_n(z)$$
$$-\Delta u + \eta = g_n(z)$$

- Vertical sides: $x = 0, L,\ z \in (0, w) :\ \nabla\eta \cdot \zeta = 0, \quad \nabla u \cdot \zeta = 0.$
- Top side: $z = 0,\ x \in (0, L)$,

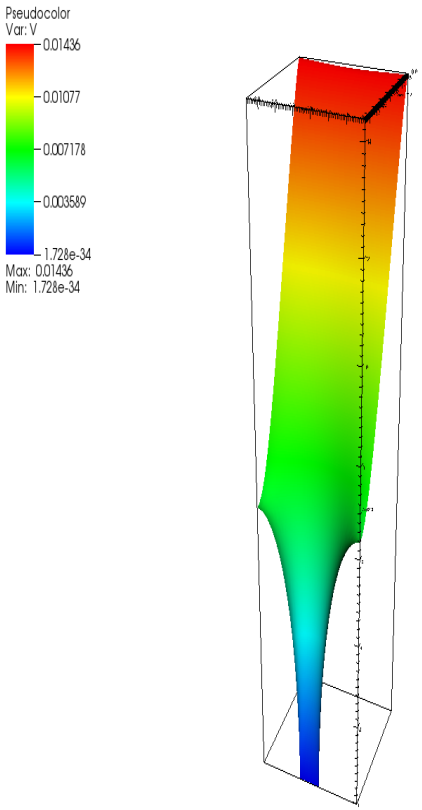
$$\nu_A^2\, \eta = \exp\left(\frac{V_C}{V_T}(V_b + u)\right) - 1,$$
$$\nabla u \cdot \zeta = \nu_A^2\, j_0 \left(1 - \exp\left(-\frac{V_C}{V_T}(V_b + u)\right)\right).$$

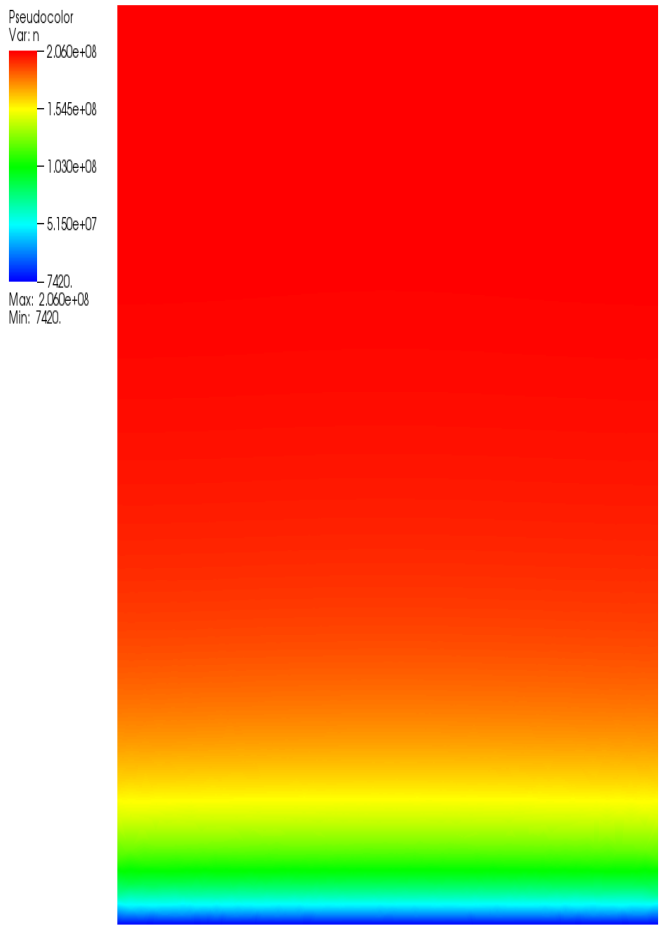
- Bottom side : $z = w,\ x \in (0, L)$,

$$\nabla\eta \cdot \zeta = -s_n\, \eta,$$
$$\text{outside contact} : \nabla u \cdot \zeta = -s_n\, \eta,$$
$$\text{inside contact} : u = 0,$$

where $V_b = \frac{V_{bias}}{V_C}$, $\nu_A = \frac{n_i}{N_A}$, $j_0 = J_0 \frac{L_n}{qD_pN_A}\frac{V_T}{V_C}$ and $s_n = S\frac{L_n}{D_n}$. are known. ζ outward normal to the surface.

Numerical results : 2D simulations

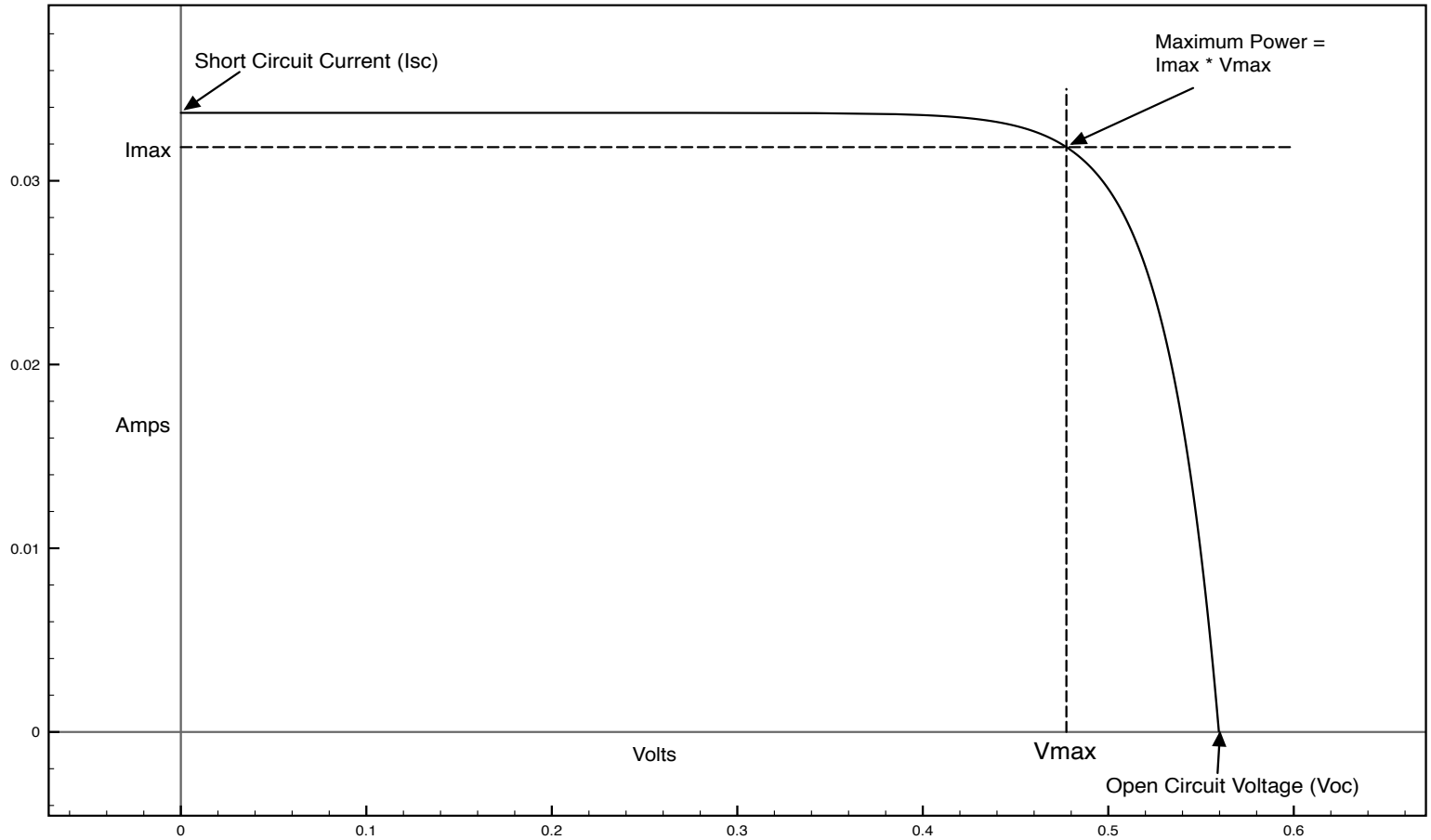




Numerical Results : Engineering point of view

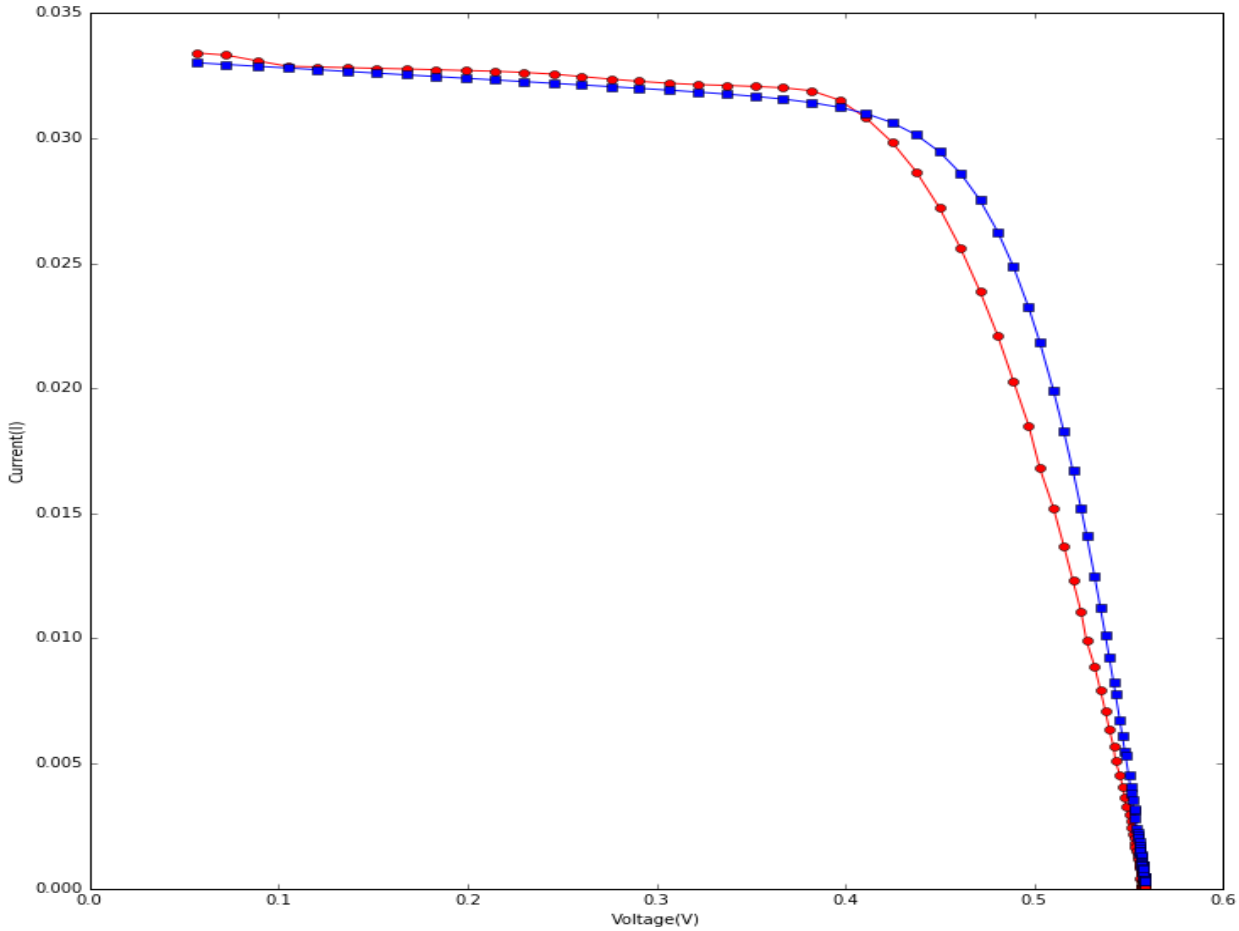
IV-Curve

A current-voltage characteristic or IV-curve is a relationship between the electric current through a circuit or device, and the corresponding voltage.



Numerical Results : Comparison with experiments

Experiments : red line, Simulations : blue line



Effects not included in the model : Resistance, Temperature losses

Recap

Very challenging field: Modelling, Analysis, Computations, Data Science

- Open problems
  - Mathematical Modelling, especially for Perovskite solar cells
  - Numerical solution of the models, very challenging, parallelization,
  - Parameters: many operating parameters are unknown eg. temperature, resistances
- Machine & Statistical learning
  - Parameter estimation
  - Local weather, Solar effects, Soiling effects
  - Energy yield prediction from Solar Irradiance and other factors

Thank You