ASYMPTOTICALLY PRESERVING NUMERICAL METHODS FOR LARGE REACTION DIFFUSION SYSTEMS WITH APPLICATIONS TO SOLAR CELL DESIGN

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[2]: California State San Jose, [3]: First Solar Inc.

SOLAR CELLS

Function

$$\partial_t n = \mathfrak{T}_n n + G(n,p), \ \partial_t p = \mathfrak{T}_p p - G(n,p)$$

$n(x,t)$: density of electrons;
$p(x,t)$: density of holes;
$\mathfrak{T}_{n,p}$: transport operator;
G: generation / recombination term.

Function: External photons generate free electrons through G. They get transported by $\mathfrak{T}_n$ to a terminal and 'harvested'.

SOLAR CELL EFFICIENCY

- Energy efficiency: $\dfrac{\text{electric energy output}}{\text{photon energy input}}$.
  Theorem: Limited to $\approx 30\%$ in standard solar cells.
- Cost efficiency: Cost = production cost + replacement cost (lifetime).
  - Production Cost:
    Standard ('thick') solar cells; made of crystalline Si.
    Thin film solar cells: made of poly-crystalline materials (c.f. CaTe, CIGS) (require less raw material).
  - Lifetime:
    Pollutants ('Defects') diffuse into the cell, become ionized and ruin (in the long run) the functionality of the cell.
    Pollutants: $Cl^{\pm}, O^{\pm}, S^{\pm}, As^{\pm}, \ldots$

Goal: Simulate the impact of design parameters during the production process on the structure and simulate the deterioration process.

THE MODEL$_{04}$

Transport of free electrons and holes:

$$\partial_t n = \nabla \cdot (\nabla \mathrm{n} - \mathrm{n}\nabla\phi) + G,\ \partial_t p = \nabla \cdot (\nabla \mathrm{p} + \mathrm{p}\nabla\phi) - G$$

Poisson equation:

$$\boxed{\nabla \cdot \varepsilon \nabla\phi = \mathrm{n} - \mathrm{p} + dop(\vec{u}),\ dop(u) = \sum_{m=1}^{M} z_m u_m}$$

Defect transport and reaction

$$\boxed{\partial_t u_m = \nabla \cdot D_m(\nabla u_m + z_m u_m \nabla\phi) + r_m(n, \vec{u}),\ m = 1 : M}$$

$\vec{u} = (u_1, .., u_M)$ defect densities, z_m : charge of species m.

$\vec{r}(n, \vec{u}) = (r_1, .., r_M)$ (binary) reaction among defects (chemical) or between defects and electrons (c.f. $Cl^0 + n \to Cl^-$).

$$r_n(\vec{u}) = \vec{u}^T A_n \vec{u} + B_n \vec{u}$$

CHALLENGES$_{06}$

Evolution of defects coupled to free electrons via reactions $\vec{r}$.
Evolution of free electrons coupled to defects via the doping dop and the potential ϕ.

Remark: For given defects and given dop, the numerical treatment of electron and hole transport is well developed.

Challenge 1: Couple large diffusion reaction system for the defects $\vec{u}$ to the (well understood) carrier transport model.

Challenge 2

Poly-crystalline material $\Rightarrow$ Different transport properties (diffusion matrices) within the overlap of different crystals $\Rightarrow$ Grain boundaries.

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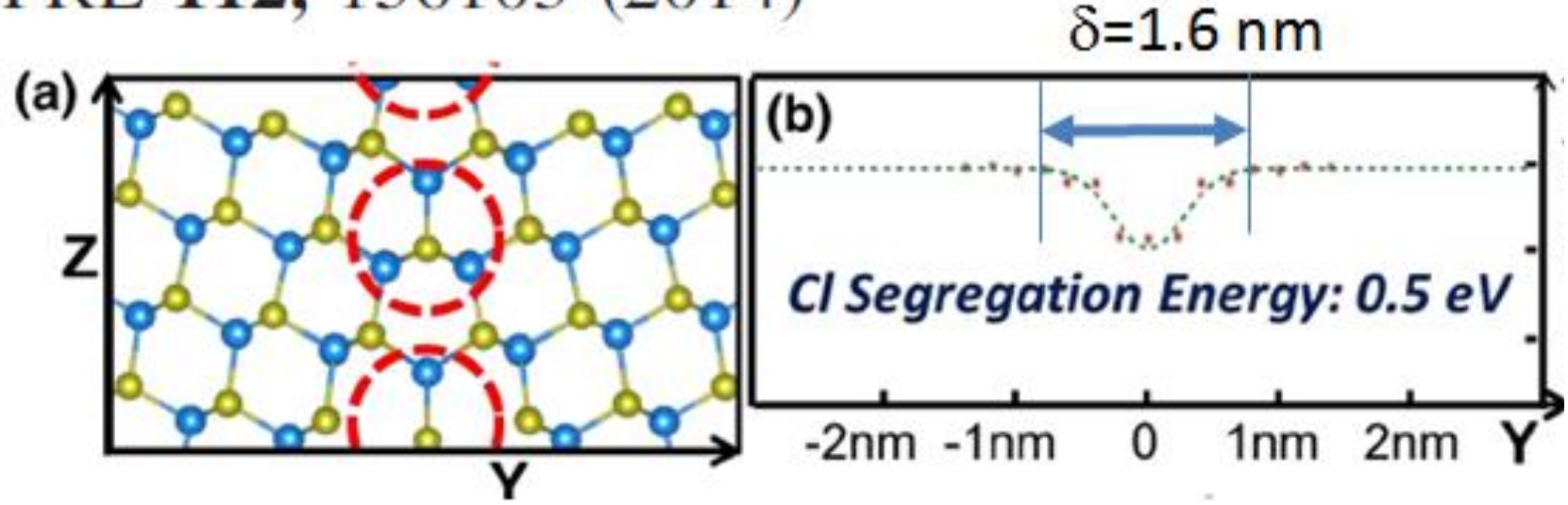
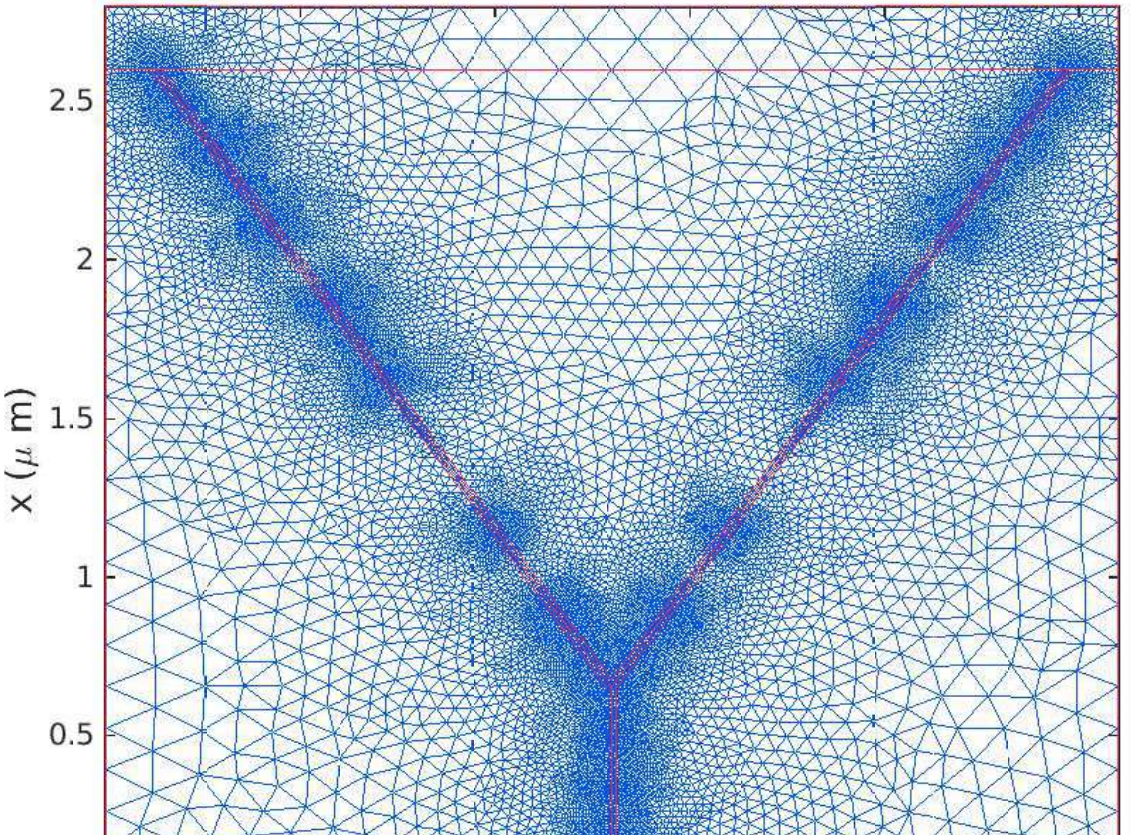


Requires locally fine mesh resolution

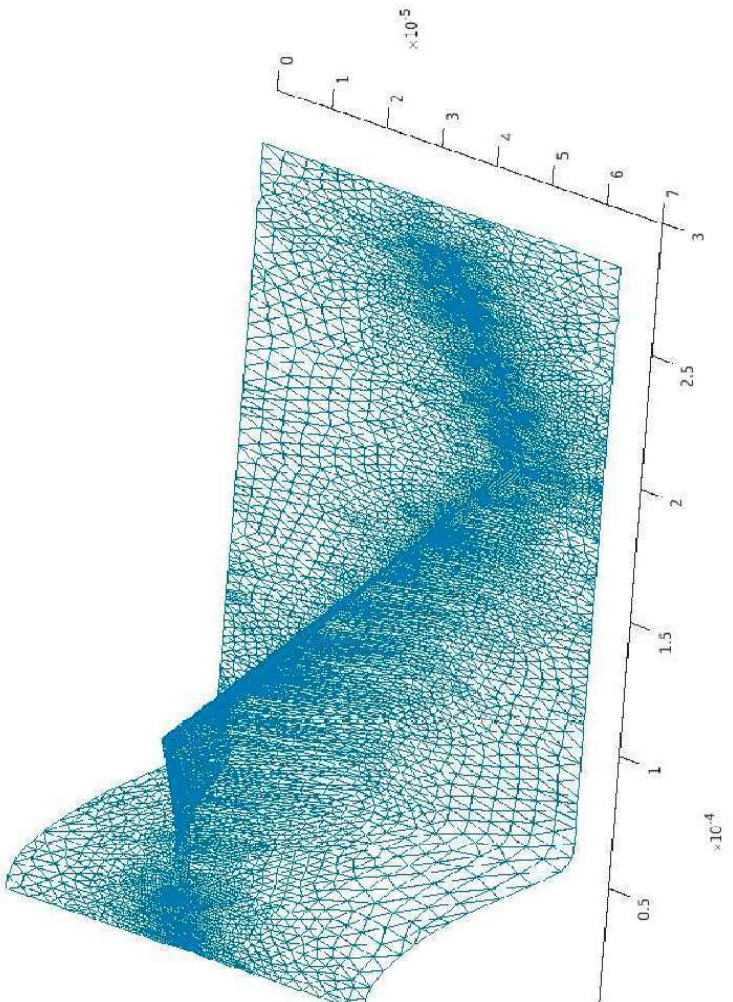
Comparing Branch Results



Enhanced transport coefficients within grain boundaries

Chlorine density

Zig-Zag Results



SUMMARY$_{08}$

- Large diffusion reaction system for charged defects on a complicated (structured) medium.
- Coupled to well developed methodology for electrodynamic equations

ISSUES

1. Size: Up to 50-60 species (defects, Cl, As, O, S.....) in various charged states. Complicated geometry (even in 2-D) $\Rightarrow$ $O(10^6)$ variables.
2. Multiscale in space: grain boundaries.
3. Multiple time scales: Electronic scale ($10^{-7} sec$, Defect reaction scale $minutes - hours$, Diffusion time scale ($years$).
   - Implicit methods in time (after discretization, linearization etc.) need the inversion of block - penta-diagonal matrices of size $N_{grid} * N_{spec}^2$. Direct Sparse solution would need $O(N_{grid}^2 * N_{spec}^3)$ operations per time step.

To be a useful engineering tool this has to run on a 'reasonable' work station.

OUTLINE

1. Practical numerical issues $\Rightarrow$ operator splitting methods.
2. Operator splitting methods for multi-scale problems.
   - Time scale resolution problem for 'standard' operator splitting.
   - Asymptotic analysis and relation to kinetic theory.
3. Asymptotically preserving (AP) operator splitting methods.
4. Results
5. Conclusions

OPERATOR SPLITTING METHODS 12

$$\partial_t u_n(x,t) = \mathfrak{D}_{\mathfrak{n}} u_n(x,t) + r_n(\vec{u}(x,t)),\ n = 1 : N_{spec}$$

Operator splitting: split transport and reactions
Given $\vec{u}(x,t_k)$, compute $\vec{u}(x,t_k+\Delta t)$ via

- Step 1: Given $\vec{u}(x,t_k)$, compute $\vec{u}^{(1)}(x,t_k+\Delta t)$ by

$$\partial_t u_n^{(1)}(x,t) = \mathfrak{D}_{\mathfrak{n}} u_n^{(1)},\ for\ t_k \le t \le t_k+\Delta t,$$

$$\text{IC: } u^{(1)}(t_k) = u(t_k),\ \text{compute } \vec{u}^{(1)}(x,t_k+\Delta t),\ n = 1 : N_{spec}$$

- Step 2: Given $\vec{u}^{(1)}(x,t_k+\Delta t)$, compute $\vec{u}^{(2)}(x,t_k+\Delta t)$ by

$$\partial_t \vec{u}^{(2)}(x,t) = \vec{r}(\vec{u}^{(2)}(x,t)),\ for\ t_k \le t \le t_k+\Delta t,$$

$$\text{IC: } \vec{u}^{(2)}(x,t_k) = \vec{u}^{(1)}(x,t_k+\Delta t),\ \forall x$$

set $\vec{u}(t_k+\Delta t) = \vec{u}^{(2)}(t_k+\Delta t)$

Step 1: N_{spec} decoupled linear diffusion equations. $O(N_{grid}^2 * N_{spec})$ operations.
Step 2: N_{grid} decoupled nonlinear reaction equations. $O(N_{grid} * N_{spec}^2)$ operations.
Compare to fully implicit method:

$$\frac{\text{fully implicit}}{\text{operator splitting}} = \frac{N_{grid}^2 * N_{spec}^3}{N_{grid}^2 * N_{spec} + N_{grid} * N_{spec}^2}$$

Operator splitting yields computational savings of $O(1000)$ for practical problems.

THE MULTI-SCALE PROBLEM 14

Observation: The operator splitting method above produces the wrong transport dynamics if the fast reaction scale is not resolved ($\Delta t\vec{r} > 1$).

Basic mechanism:
–Assume two species s_1 and s_2 with diffusion coefficients D_1 and D_2 with $D_1 >> D_2$.
–Assume a reaction $s_1 \rightarrow s_2$ much faster than both diffusion scales.
so, we have $\approx \frac{D_2}{|\Omega|^2} << \frac{D_1}{|\Omega|^2} << r$.

- Using operator splitting, in a time interval Δt, a particle of type s_1 travels on average a distance $\Delta x = \sqrt{\Delta t D_1}$. Then it gets converted into s_2.
- In reality, it should almost immediately be converted into s_2 and travel only a distance $\Delta x = \sqrt{\Delta t D_2} << \sqrt{\Delta t D_1}$.
- This means we compute the wrong wave speeds for the diffusion - convection - reaction wave, unless we resolve the reaction time scale $\Delta t r << 1$.

Given the scales, $T_{end} \approx years$ $r \approx \frac{1}{minutes}$, this is unacceptable!

A TOY EXAMPLE[15]

Three (uncharged) species: S_1: mobile defect; S_2: vacancy (empty lattice site); S_3: defect on lattice site.

Reaction: $S_1 + S_2 \rightarrow S_3$

$$\begin{pmatrix} \partial_t u_1 \\ \partial_t u_2 \\ \partial_t u_3 \end{pmatrix} = \begin{pmatrix} \nabla \cdot \nabla u_1 & -\frac{1}{\varepsilon} u_1 u_2 \\ & -\frac{1}{\varepsilon} u_1 u_2 \\ & \frac{1}{\varepsilon} u_1 u_2 \end{pmatrix}$$

$\varepsilon << 1$ ratio of diffusion to reaction time scale.

- Consider an isolated system (von Neumann b.c.)
- Monitor $u_1(x,t)$ at the right collector as a measure of the wave speeds.

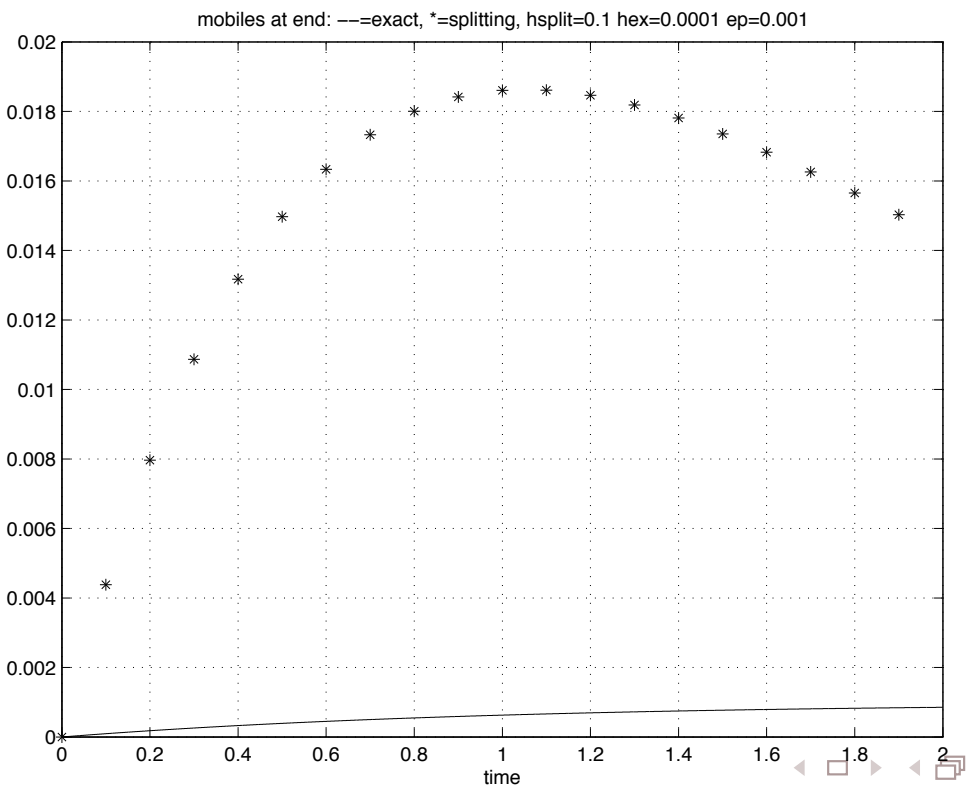
1

[1] B. Sportisse, J. Comp. Phys. (2000)

Mobile defect at right endpoint as function of time.

'*': operator splitting solution with $\Delta t = 100\varepsilon$.

'-': operator splitting solution with $\Delta t = 0.1\varepsilon$



PARALLEL TO KINETIC MODELS 17

Kinetic models for binary interactions

$$\partial_t u(x,y,t) + \mathfrak{T}u = \mathfrak{Q}(u,u)$$

x: 'space',
$\mathfrak{T}$: linear transport operator in x.
y: attribute (velocity),

$\mathfrak{Q}$: quadratic operator, modeling random binary collisions under the IID assumption.

$$\mathfrak{Q}(u,u)(x,y) = \int K(y,y_1,y',y_1')u(x,y')u(x,y_1')\,dy'y_1'y_1 -$$

$$\int K(y',y_1',y,y_1)u(x,y)u(x,y_1)\,dy'y_1'y_1$$

$K(y,y_1,y',y_1')$: probability $(y',y_1') \to (y,y_1)$

Usual approach for $\mathfrak{Q} >> \mathfrak{T}$: Asymptotics , moment closures, etc.

- Find conserved quantities $\kappa\mathfrak{Q}(u,u) = 0 \; \forall u$
- Parameterize the local equilibrium $\mathfrak{Q}(\phi(z), \phi(z)) = 0 \; \forall z$.
- Moment closure gives large time asymptotics:

$$\boxed{\partial_t \kappa\phi(z) + \kappa\mathfrak{T}\phi(z) = 0}$$

Replace $y \to n \in \{1, .., N_{spec}\} \Rightarrow$ same structure as discrete velocity model for the Boltzmann equation.

Problems:

1. No topology in the discrete attribute space $\{1, .., N_{spec}\}$.
2. No microscopically conserved quantities $\Rightarrow$ no H- theorem.
3. Local equilibrium given by a system of N_{spec} quadratic equations. [2]

[2] Conradi, C., Flockerzi, D., Raisch, J., Stelling, J.: P. Natl. Acad. Sci. 104(49), (2007)

BASIC IDEA$_{20}$

Replace finding local equilibria and conservation laws by numerical linear algebra.

$$\partial_t \vec{u}(x,t) = \mathfrak{D}\vec{u} + \frac{1}{\varepsilon}\vec{r}(\vec{u})$$

$\varepsilon << 1$: ratio of reaction to diffusion time scale.
Introduce the product of reactions as independent variable: $\vec{v} = \frac{1}{\varepsilon}\vec{r}(\vec{u})$.
Gives the system

$$\boxed{\partial_t \vec{u}(x,t) = \mathfrak{D}\vec{u} + \vec{v},\ \partial_t \vec{v} = \frac{1}{\varepsilon}R(\vec{u})(\mathfrak{D}\vec{u} + \vec{v})}$$

with $R(\vec{u}) = \frac{\partial \vec{r}(\vec{u})}{\partial \vec{u}}$.
$R(\vec{u})$ will be in general rank deficient $\Rightarrow$ For a given $\vec{u}$, the fast dynamics will happen on the orthogonal complement of the left nullspace of $R(\vec{u})$.

Example: reaction: $s_1 + s_2 \rightarrow s_3$

$$\vec{r}(\vec{u}) = \begin{pmatrix} -u_1 u_2 \\ -u_1 u_2 \\ u_1 u_2 \end{pmatrix}, \; R(\vec{u}) = \begin{pmatrix} -u_2 & -u_1 & 0 \\ -u_2 & -u_1 & 0 \\ u_2 & u_1 & 0 \end{pmatrix}$$

rank =1, dim(null(R))=2

ASYMPTOTICS 24

For given $\vec{u}$ the problem is linear! Given $\vec{u}$ and $R(\vec{u})$, compute projection $P(\vec{u})$ with

$$\boxed{P(\vec{u})R(\vec{u}) = R(\vec{u})P(\vec{u}) = 0}$$

Split $\vec{v} = \frac{1}{\varepsilon}\vec{r}(\vec{u})$ into nullspace component and orthogonal complement.

$$\boxed{\vec{v} = \tilde{v} + \hat{v}, \tilde{v} = P(\vec{u})\vec{v},\ \hat{v} = (id - P)\vec{v}}$$

$$\partial_t \tilde{v} = \frac{dP(\vec{u})}{dt}(\tilde{v} + \hat{v}),\ \partial_t \hat{v} = \frac{1}{\varepsilon}R(\mathfrak{D}\vec{u} + \hat{v}) - \frac{dP(\vec{u})}{dt}(\tilde{v} + \hat{v})$$

- $P(\vec{u}(t))$ will evolve on the slow time scale.
- For $\varepsilon \to 0$ the fast time scale component $\hat{v}$ converges to $R(\mathfrak{D}u + \hat{v} = 0 \Rightarrow \hat{v} = -(id - P)\mathfrak{D}\vec{u}$.

THE REDUCED PROBLEM

This gives the reduced problem

$$\partial_t \vec{u}(x,t) = P\mathfrak{D}\vec{u} + \tilde{v},\ \partial_t \tilde{v}(x,t) = \frac{dP(\vec{u})}{dt}(\tilde{v} - (id - P)\mathfrak{D}\vec{u})$$

Step 1: For given $u(x,t)$, compute
$P(x,t) = G_R G_L,\ G_L^T G_R(u) = id,\ G_L R(u) = 0,\ RG_R = 0$ (analytically for small problems, numerically in general, The left nullspace G_L corresponds to the nullspace of the Stochiometry matrix).

Step 2: Solve

$$\partial_t \vec{u}(x,t) = P\mathfrak{D}\vec{u} + \tilde{v},\ \partial_t \tilde{v}(x,t) = \frac{dP(\vec{u})}{dt}(\tilde{v} - (id - P)\mathfrak{D}\vec{u})$$

Remark: Step 1 quite computationally expensive since different nullspace bases have to be computed for every gridpoint. [3]

[3] Craciun, G., Feinberg, SIAM J. Appl. Math. (2006)

TOY PROBLEM (REDUCED)$_{27}$

Reaction: $s_1 + s_2 \rightarrow s_3$

$$\vec{r}(\vec{u}) = \begin{pmatrix} -u_1 u_2 \\ -u_1 u_2 \\ u_1 u_2 \end{pmatrix}, \; R(\vec{u}) = \begin{pmatrix} -u_2 & -u_1 & 0 \\ -u_2 & -u_1 & 0 \\ u_2 & u_1 & 0 \end{pmatrix}$$

rank =1, dim(null(R))=2

$$G_L = \begin{pmatrix} -1 & 1 \\ 1 & 0 \\ 0 & 1 \end{pmatrix}, \; G_R = \frac{1}{u_1 + u_2} \begin{pmatrix} -u_1 & 0 \\ u_2 & 0 \\ u_1 & u_1 + u_2 \end{pmatrix}, \; P = G_R G_U^T$$

AP (Asymptotically Preserving) Schemes [28]

General idea: $\boxed{\partial_t u_\varepsilon = \mathfrak{F}^\varepsilon(u_\varepsilon) \to (\varepsilon \to 0) \to u_\varepsilon \to u_0}$

Discretization:

$$u_h^\varepsilon(t+h) = \mathcal{F}_h^\varepsilon(u_h^\varepsilon(t)) \to_{(h\to 0)} \to u_h^\varepsilon \to u_0^\varepsilon = u^\varepsilon$$

$$\lim_{\varepsilon\to 0}\lim_{h\to 0} u_h^\varepsilon = \lim_{\varepsilon\to 0} u^\varepsilon = u^0$$

$$u_h^\varepsilon(t+h) = \mathcal{F}_h^\varepsilon(u_h^\varepsilon(t)) \to_{(\ \varepsilon\to 0)} \to u_h^\varepsilon \to u_h^0$$

$$\lim_{\eta\to 0}\lim_{\varepsilon\to 0} u_h^\varepsilon = \lim_{h\to 0} u_h^0 = u^0$$

$$\begin{array}{ccccc} u_h^\varepsilon & & \to_{(h\to 0)} & \to & u_0^\varepsilon \\ \downarrow & & & & \downarrow \\ (\varepsilon\to 0) & & & & (\varepsilon\to 0) \\ \downarrow & & & & \downarrow \\ u_h^0 & & \to_{(h\to 0)} & \to & u_0^0 \end{array}$$

In practice: For $h << 1$, $\varepsilon << 1$ we obtain the same result for ~~$h << \varepsilon$ and $\varepsilon << h$~~ ! [4]

[4] S. Jin, L. Pareschi: in Hyperbolic Problems: Theory, Numerics, Applications, Ed. H. Freistuhler and G. Warnecke, Birkhauser-Verlag, Berlin, (2001).

AN AP- OPERATOR SPLITTING SCHEME 31

Given $\vec{u}(x, t_k)$
Set $u^0(x) = u(x, t_k)$ and $v^0(x) = \frac{1}{\varepsilon}\vec{r}(\vec{u}(x, t_k))$

Step 1: Compute the Jacobian $R(x) = \frac{\partial \vec{r}}{\partial \vec{u}}(x, t_k)\ \forall x$

Step 2: Solve for the reaction product

$$\partial_t \vec{v}^1 = \frac{1}{\varepsilon} R(\vec{u}^0)(\mathfrak{D}\vec{u}^0 + \vec{v}^1),\ t_k \le t \le t_k + \Delta t,\ v^1(\vec{x}, t) = \vec{v}^0$$

via an L- stable method (backward Euler) without projection.

Step 3: Transport Solve

$$\partial_t u^1 = \mathfrak{D}u^1 + v^1(x, t + \Delta t),\ t_k \le t \le t_k + \Delta t,\ u^1(x, t) = u^0$$

Set $u(x, t_k + \Delta t) = u^1(x, t_k + \Delta t)$

Remark:
Step 2 is local in x

$$\partial_t \vec{v}^1(x,t) = R(\vec{u}^0(x))(\mathfrak{D}\vec{u}^0(x) + \vec{v}^1(x,t)) \ \forall x$$

Step 3 is local in the index n

$$\partial_t u_n^1(x,t) = \mathfrak{D}_n u_n^1(x,t) + v_n^1(x,t+\Delta t), \ n = 1 : N_{spec}$$

$\Rightarrow$ The computational work is twice the work of the original splitting method.

Theorem

If the numerical method used in the reaction step is $L-$ stable, then this scheme is AP, i.e. for $\varepsilon \to 0$ and Δt fixed we obtain a discretization of the reduced analytical problem.

Reason: Solving the equation

$$\partial_t \vec{v}^1(x,t) = \frac{1}{\varepsilon} R(\vec{u}^0(x))(\mathfrak{D}\vec{u}^0(x) + \vec{v}^1(x,t)) \ \forall x$$

for $\vec{v}^1$ by an $L-$ stable scheme projects the term $\mathfrak{D}\vec{u}^0(x) + \vec{v}^1(x,t)$ into the nullspace of R for $\Delta t >> \varepsilon$ [5]

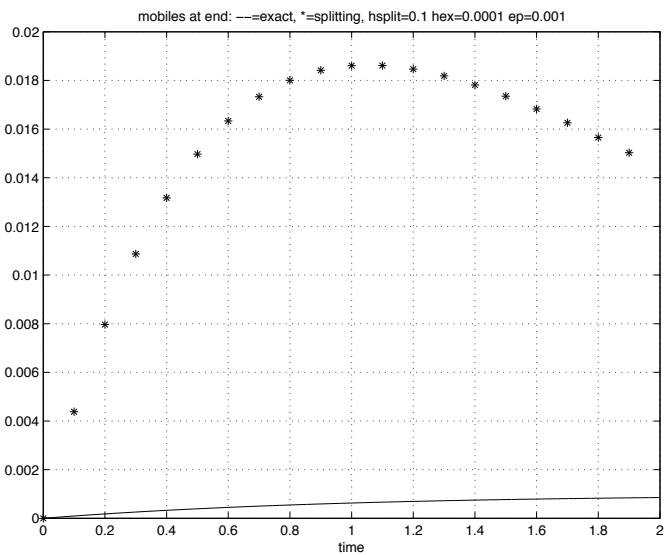
[5] D. Brinkman, D. Guo, C. Ringhofer, J. Applied. Phys. (2017) (to appear)

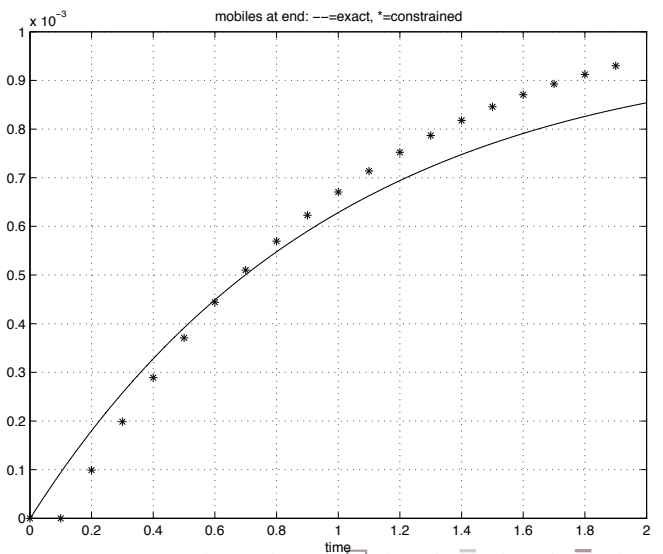
RESULTS OF THE AP OPERATOR SPLITTING SCHEME FOR THE TOY PROBLEM[34]

Reaction: $S_1 + S_2 \rightarrow S_3$ Mobile defect at right endpoint as function of time. Left: standard splitting, Right: AP - splitting

'*': operator splitting solution with $\Delta t = 100\varepsilon$.

'-': operator splitting solution with $\Delta t = 0.1\varepsilon$





LARGE TIME RESULTS OF THE AP OPERATOR SPLITTING SCHEME FOR THE TOY PROBLEM

Reaction: $S_1 + S_2 \rightarrow S_3$ Mobile defect at right endpoint as function of time. Left: standard splitting, Right: AP - splitting

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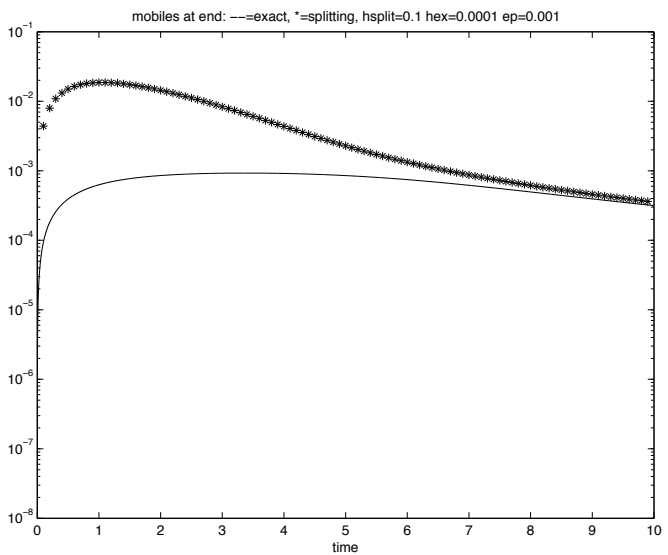
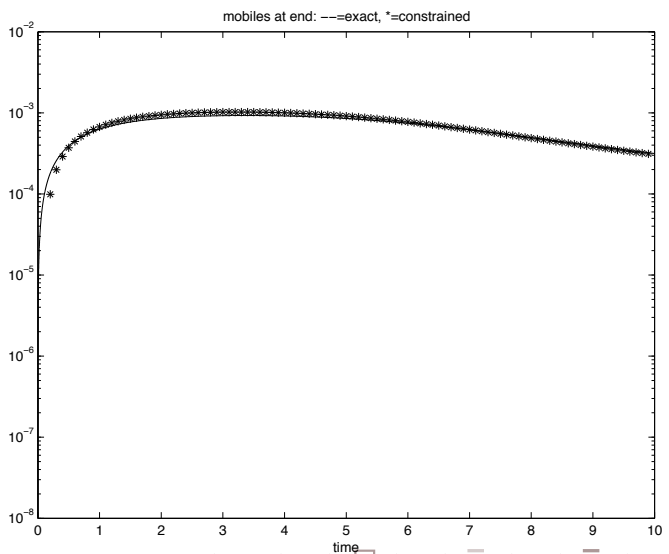




A MORE REALISTIC PROBLEM

Stochiometric Matrix

S is a 20x16 matrix

Each row is a reaction

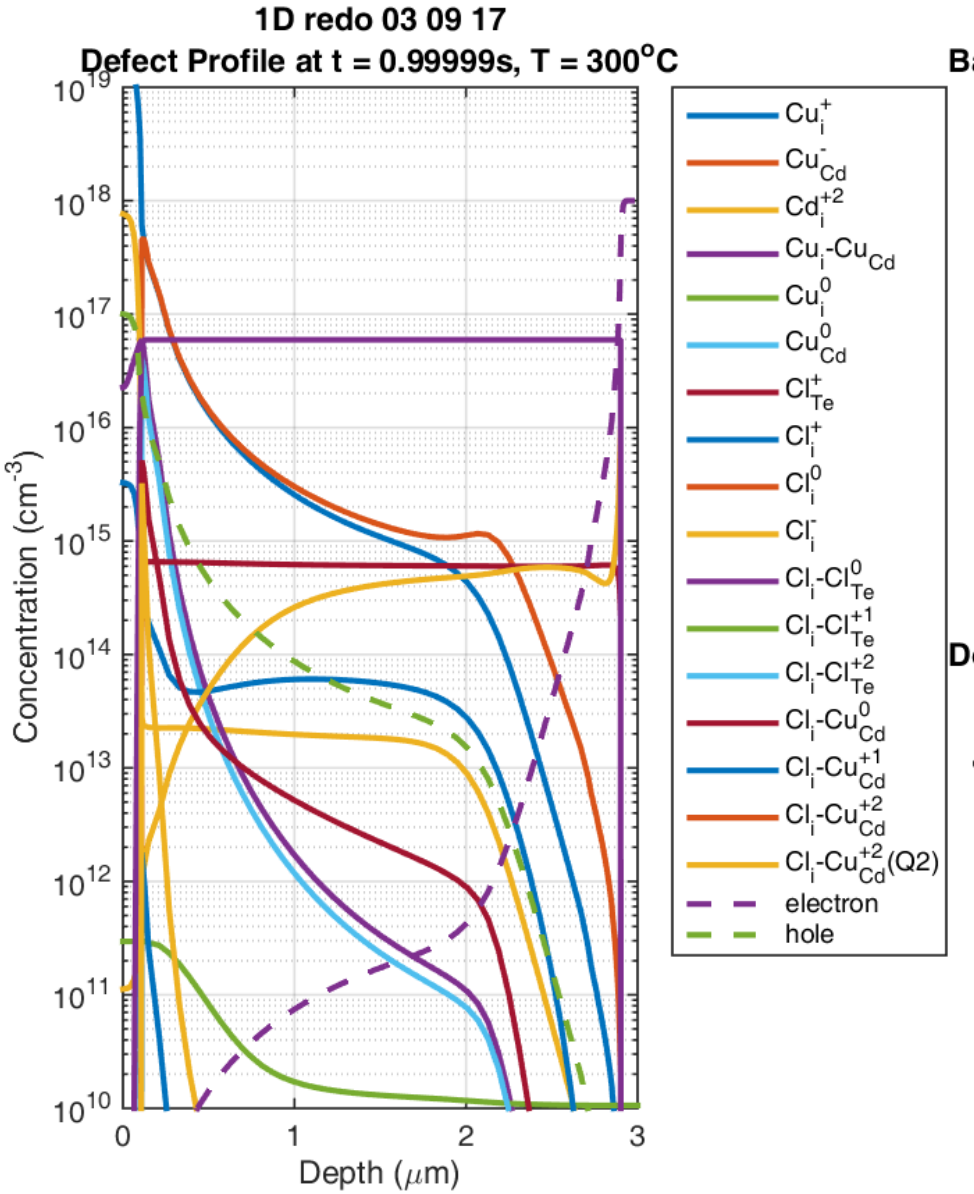
Rank[S] = 13

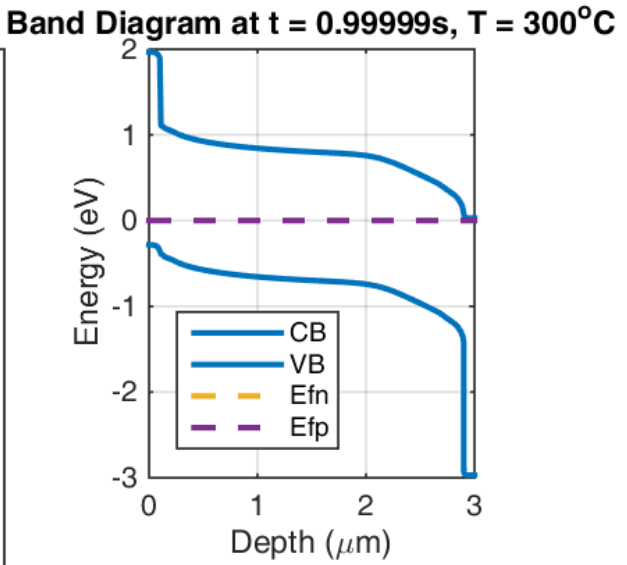
Rank[null(S)]=3

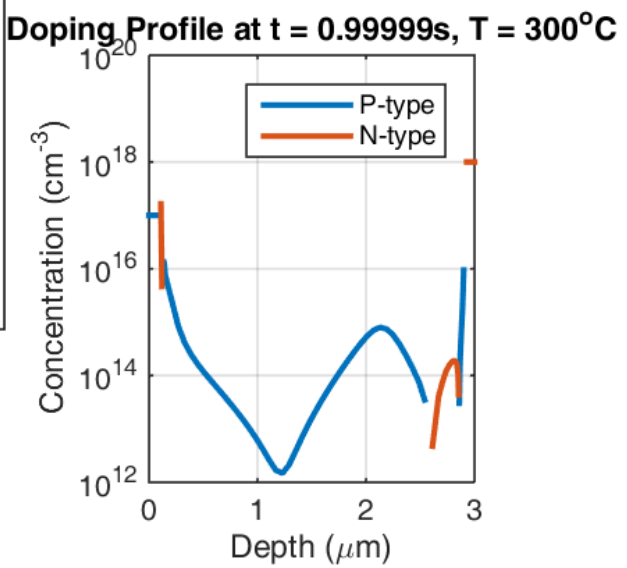
$$
\begin{pmatrix}
1 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 2 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 1 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 2 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & -1 & 0 \\
1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1
\end{pmatrix}
$$

A MORE REALISTIC PROBLEM

Snapshot: 16 defects, 20 reactions







CONCLUSIONS

1. Methodology for large reaction diffusion systems with different time scales, using asymptotic analysis.
2. - Compute local reaction equilibria by imbedding the system, using additional variables and local linear algebra.
   - Derive asymptotically preserving schemes, which do not need to resolve the fast reaction time scale.
3. Methodology developed for thin film solar cells, but applicable to many problems.