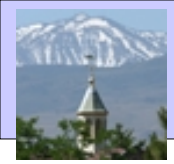




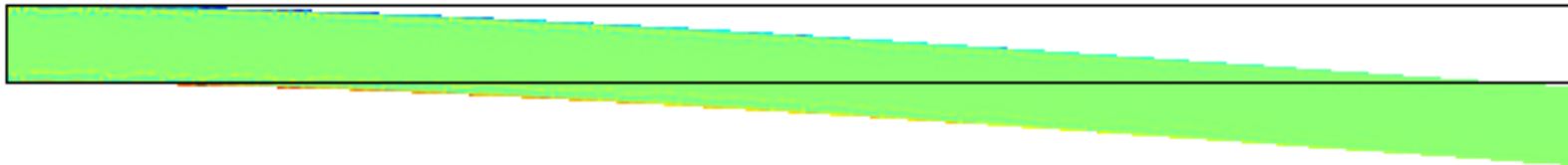
Research review

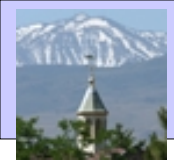
My research at the moment (01/04/07)
Deivid Pugal



Previously completed tasks

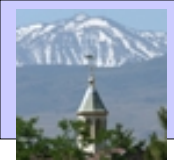
- Model of movement of the cations.
 - $\frac{\partial C}{\partial t} + \nabla \cdot (-D \nabla C - z u C \nabla V) = 0$
- Model of electric field change due to the ion movement
 - $\nabla^2 \phi = -\rho$





Bending model

- Assumption is that internal forces are due to charge imbalance
- No Euler beam theory
- Plane strain module, in Comsol, instead:
 - More suitable for finite element analysis
 - Dynamic instead of static solution.



Bending model - overview

- Body forces in are defined as

$$-\nabla \cdot \sigma = \vec{F}$$

- Where σ is symmetric stress tensor and it is related to strain in the following way: $\sigma = D \varepsilon$

- Where again

$$\varepsilon = \begin{bmatrix} \epsilon_x & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{xy} & \epsilon_y & \epsilon_{yz} \\ \epsilon_{xz} & \epsilon_{yz} & \epsilon_z \end{bmatrix} \quad \epsilon_i = \frac{\partial u_i}{\partial x_i} \quad \epsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

- And D is elacticity matrix (inverse D is flexibility matrix).
Includes variables such as *Poisson's ratio* and *Young's modulus*



Bending model – Rayleigh damping

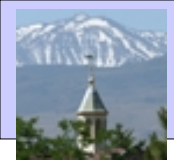
- For transient analysis, we also have to consider damping!
- Comsol uses Rayleigh damping. Motion of the system:

$$m \frac{d^2 u}{dt^2} + \xi \frac{du}{dt} + ku = f(t)$$

$$\xi = \alpha m + \beta k$$

- So the damping parameter ξ is expressed in terms of mass m and stiffness k

- In my model: $\alpha = 1 \left[\frac{1}{s} \right], \beta = 0.05 [s]$

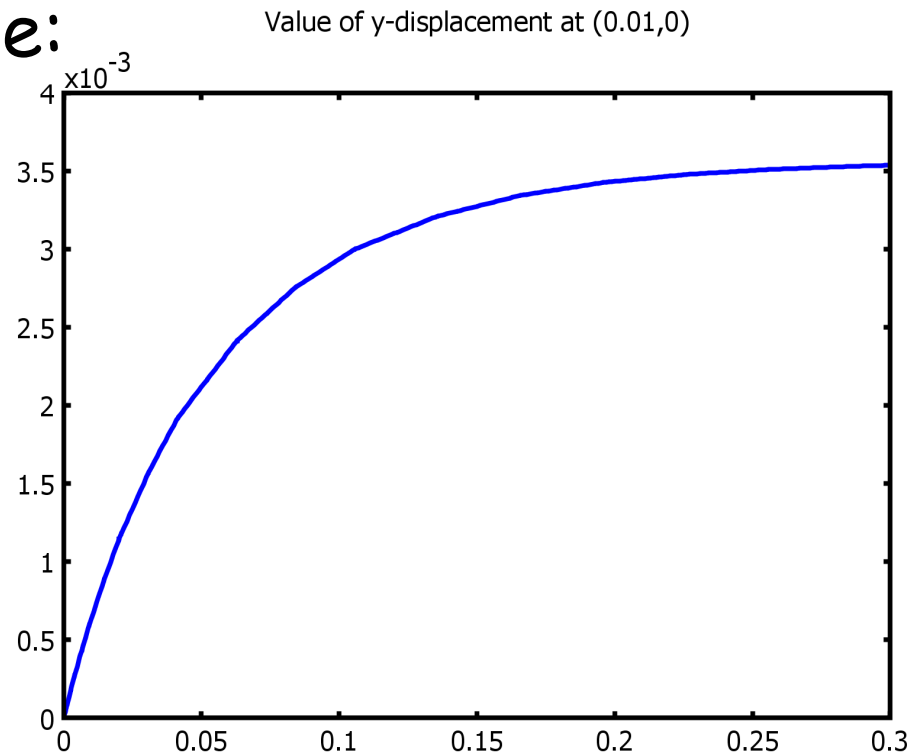


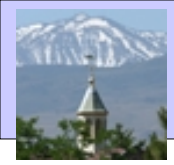
Bending model - forces

- Force in each point of IPMC is defined as:

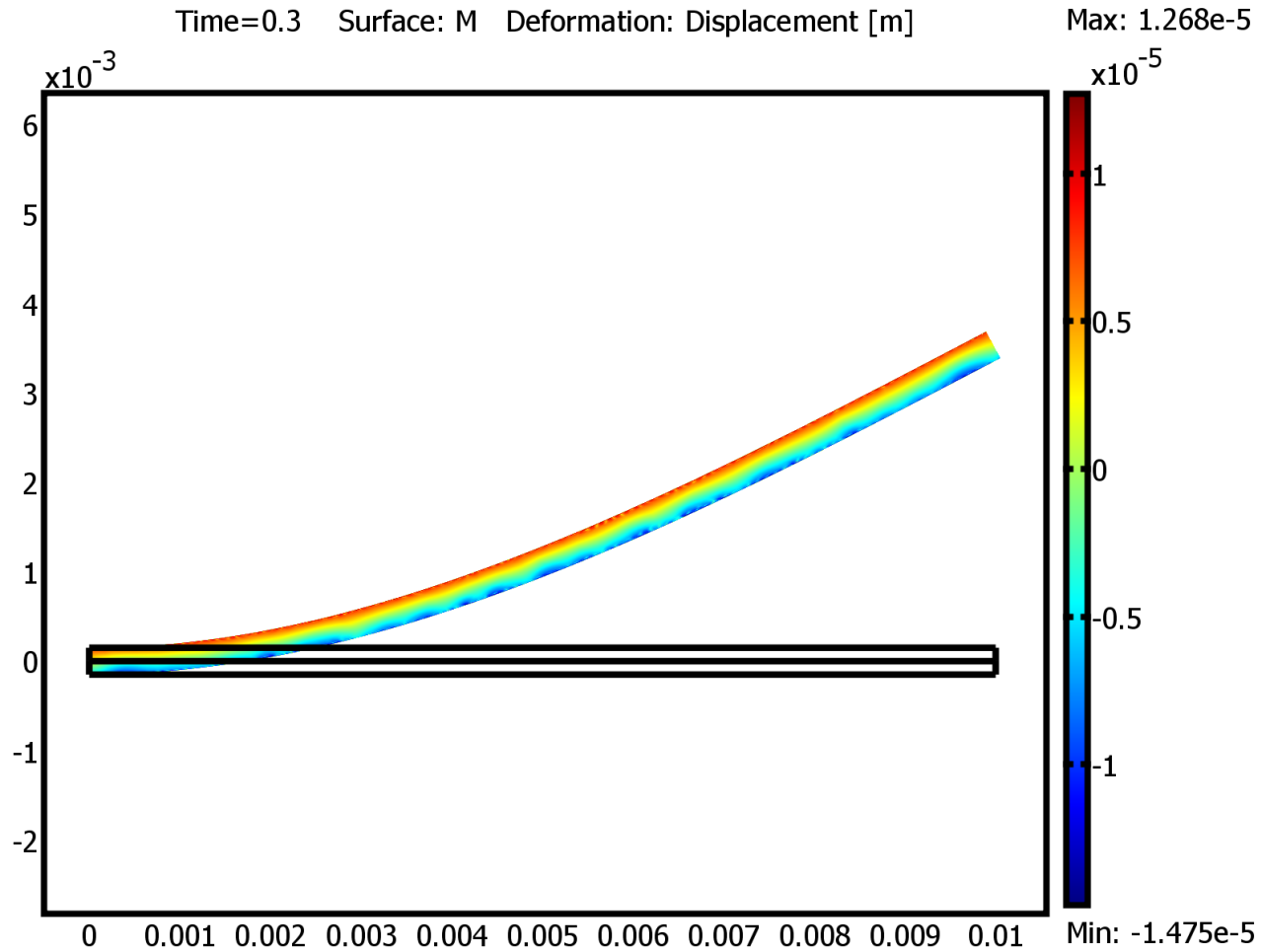
$$A \cdot (C_{Na} - C_{SO})$$

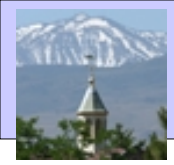
- Displacement in time:





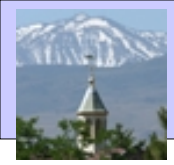
Bending model - an illustration





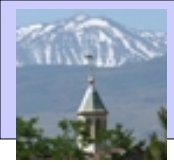
Electrochemical oscillations

- Background
 - Oscillations occur due to electrochemical reactions on platinum sites in acidic environment.
 - Reactions oscillate due to changing double layer potential.
 - Reactions cause periodic contamination of platinum sites → conductivity change...

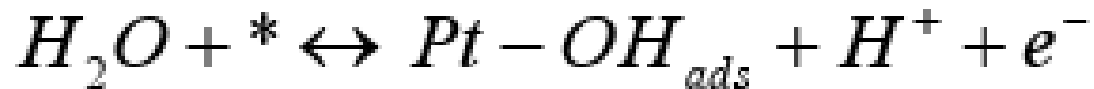
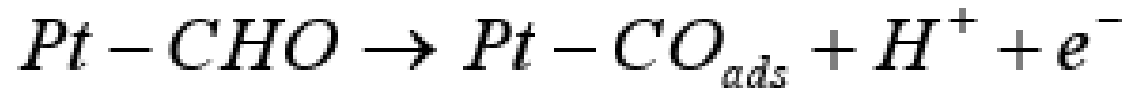
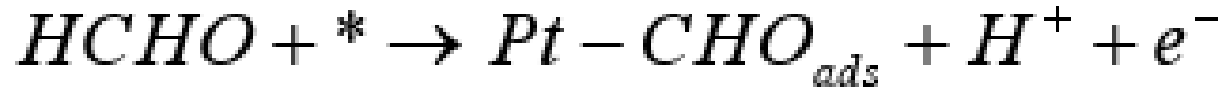


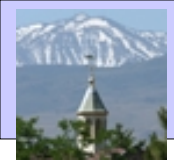
Electrochemical oscillations

- Reaction mechanisms
 - CO adsorbs to active platinum sites (from HCHO) – does not quite depend on DL potential -> however, causes increase of the potential.
 - Higher potential causes rapid OH adsorption.
 - CO and OH react and desorb as CO₂ -> causes change of the potential also

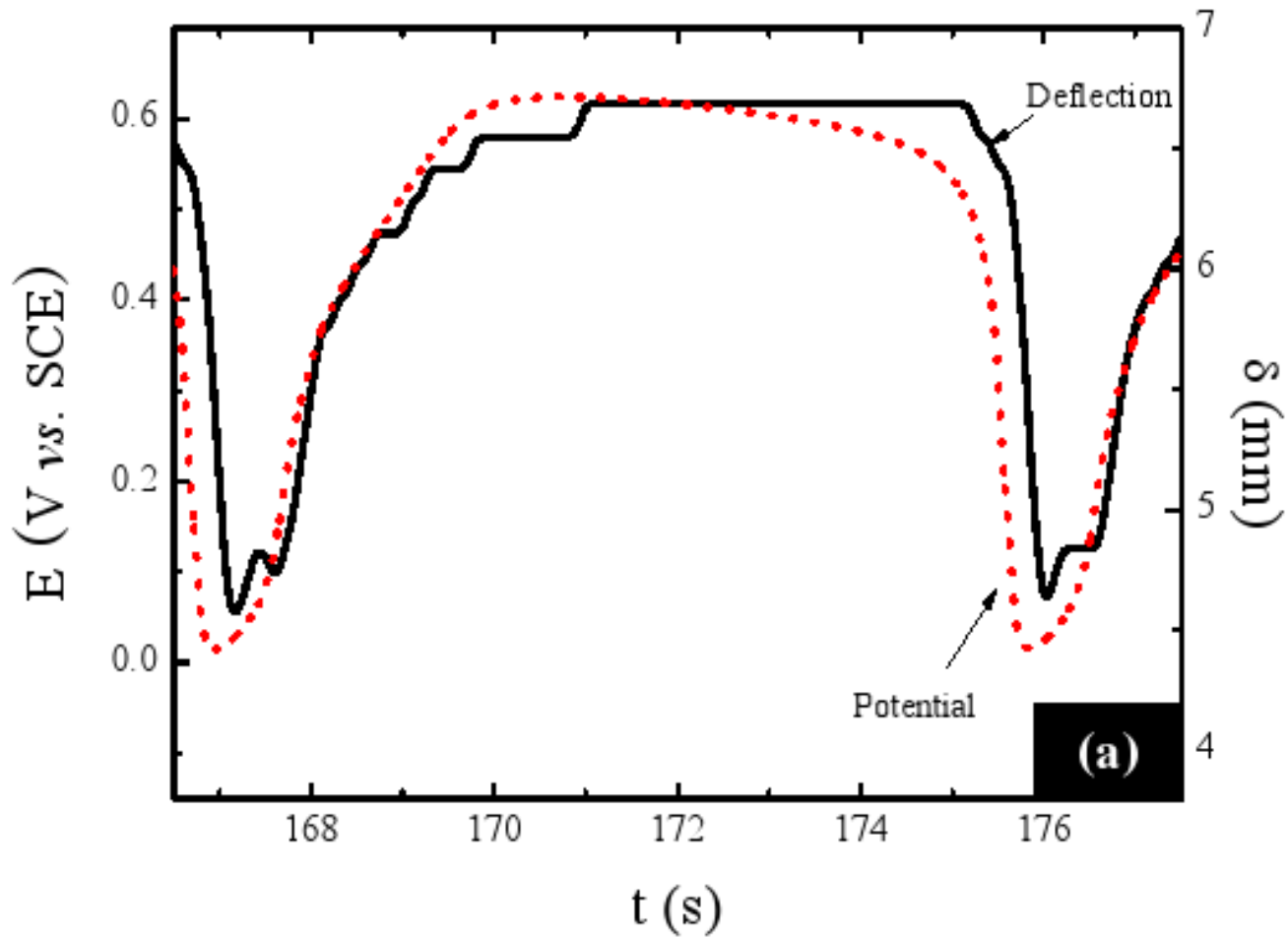


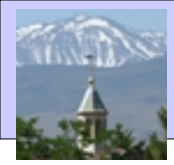
Electrochemical oscillations





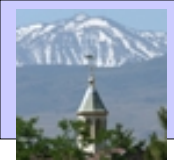
Electrochemical oscillations





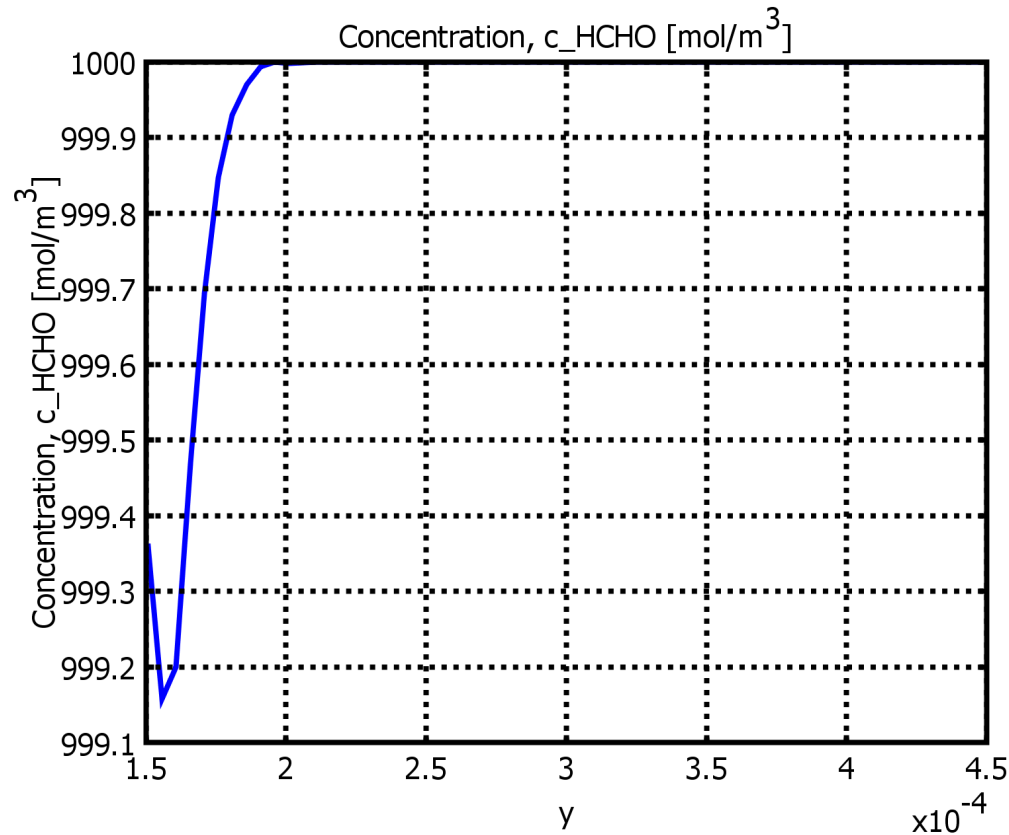
Electrochemical oscillation

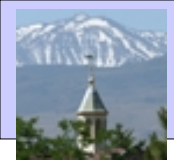
- Electrochemical oscillations occur due to poisoning of Pt surface with CO , OH
- So the Modelling:
- First, introducing the diffusion layer (for $HCHO$ diffusion)
 - An article suggested thickness of the diffusion layer about 0.3mm
 - It means that if chemical reactions occur at the one end of the layer, then there is still const. concentration of reacting species at the other end.



Electrochemical oscillation - conc. change

- Concentration change near platinum surface due to electrochemical reactions - must be considered in model!





Equations - on surface of platinum electrode

- Basically, I use slight modification of equations from Doyeon's PhD thesis.

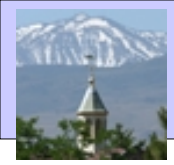
$$\dot{\theta}_{CO} = R \cdot k_2 \cdot (1 - \theta_{CO} - \theta_{OH}) - k_4 \cdot \theta_{CO} \cdot \theta_{OH}$$

$$\dot{\theta}_{OH} = k_3 \cdot (1 - \theta_{CO} - \theta_{OH}) - k_3 \cdot \theta_{OH} - k_4 \cdot \theta_{CO} \cdot \theta_{OH}$$

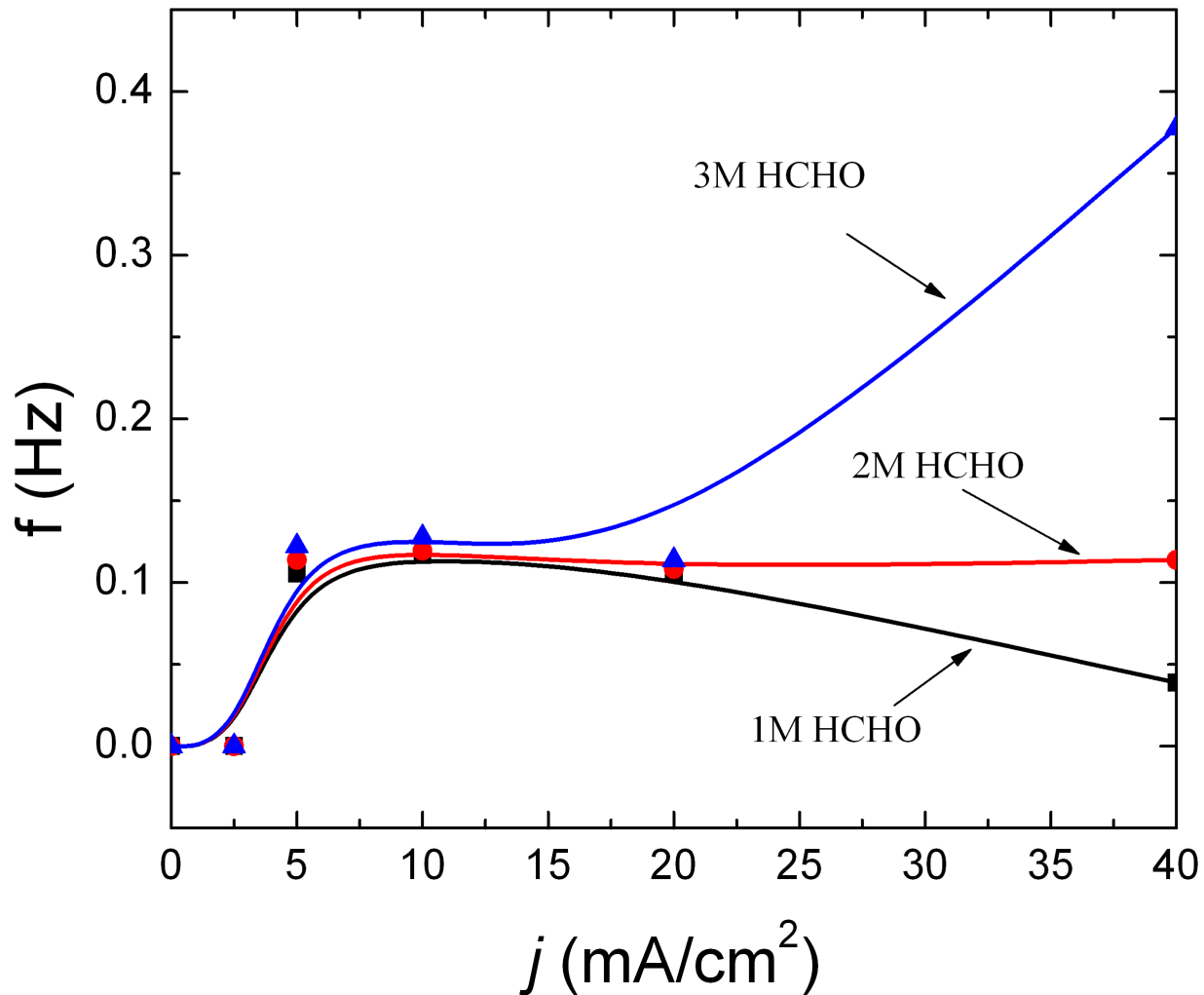
$$\dot{E} = I_{th} + \frac{(I - I_{th}) \cdot R \cdot \text{sgn}(c_{HCHO} - c_{HCHO2M})}{j \cdot (k_1 \cdot (1 - \theta_{OH} - \theta_{CO}) + k_4 \cdot \theta_{CO} \cdot \theta_{OH})}$$

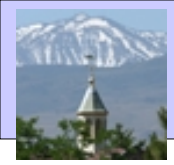
$$R = \frac{c_{HCHO}}{c_{HCHO2M}}$$

- Doyeon's model worked for 2M solution of HCHO
- This model also takes account concentration and applied constant current in range 10mA to 30mA



Electrochemical oscillations



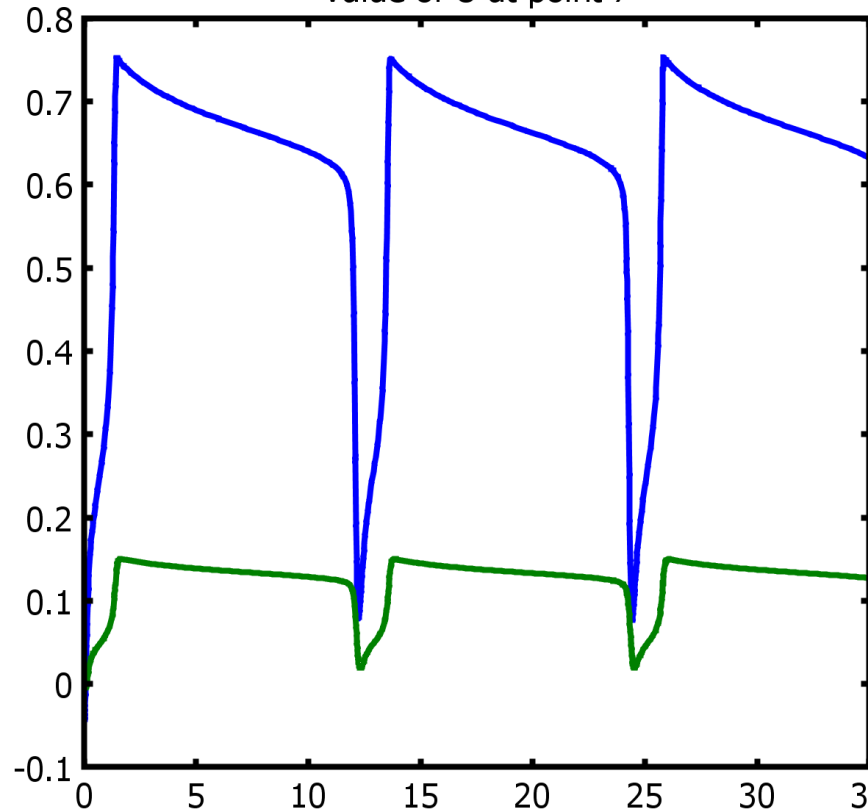


Displacement and voltage oscillations

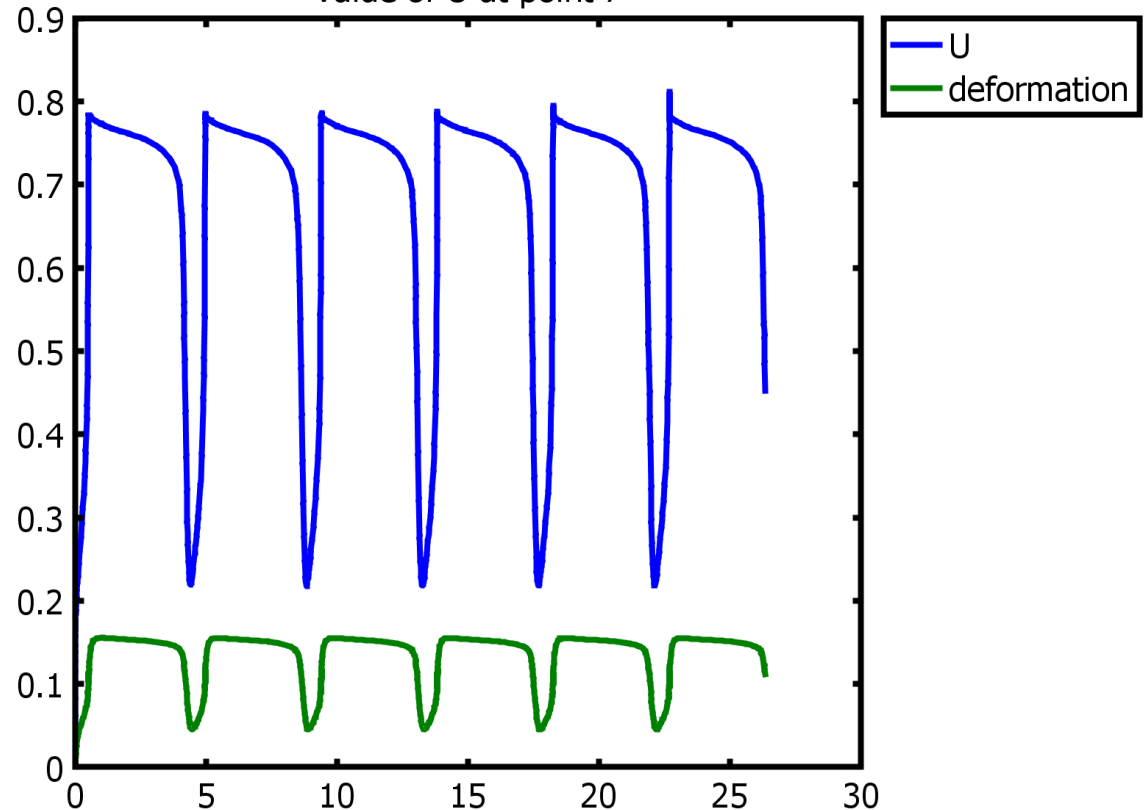
1M HCHO, 25mA/cm²

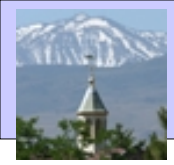
3M HCHO, 25mA/cm²

Value of U at point 7



Value of U at point 7





Further goals

- Check all units and numbers. Specially everything related to diffusion layer.
- Better physical justification for addons to Doyeon's equations
- Write an article.