Magneto-Hydrodynamic (MHD) Flow in Electrolyte Solutions around Cylinders with Application in Liquid Chromatography (LC)

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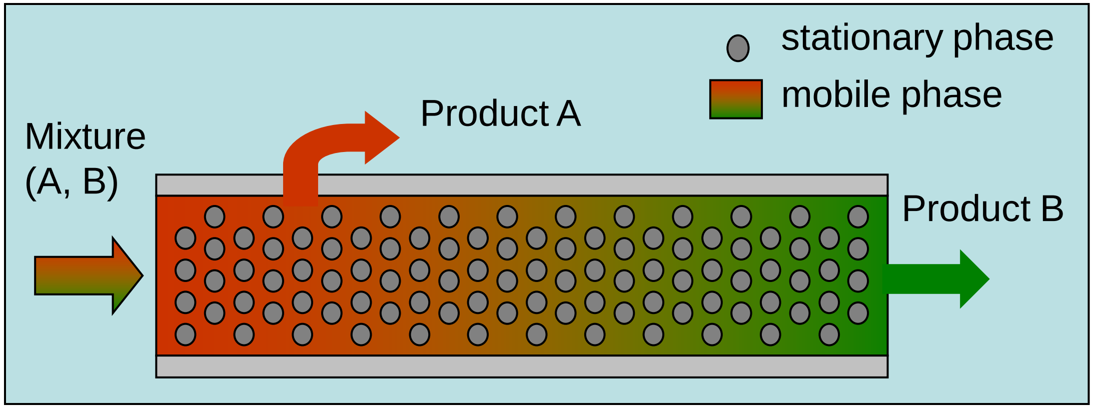
Introduction to Liquid Chromatography



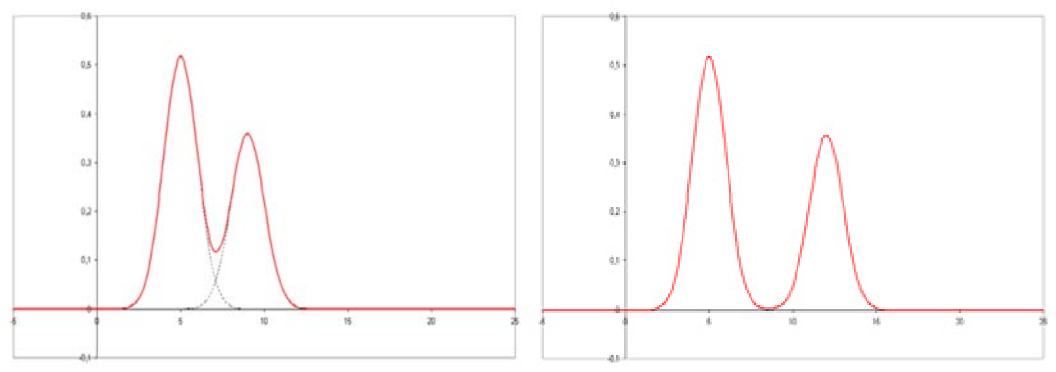
● stationary phase

▨ mobile phase

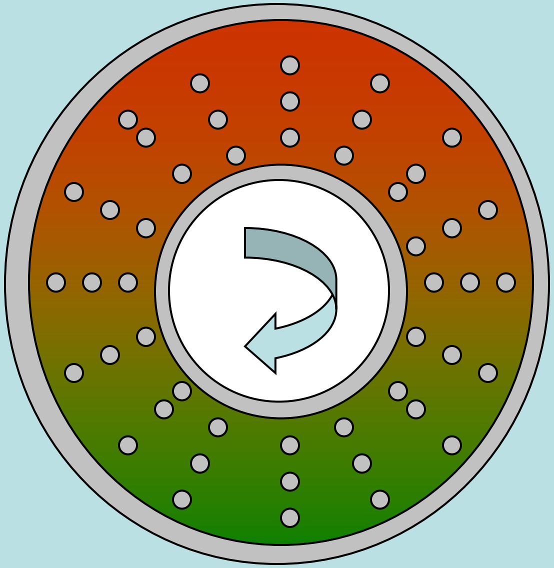
Mixture
(A, B)

Product A

Product B



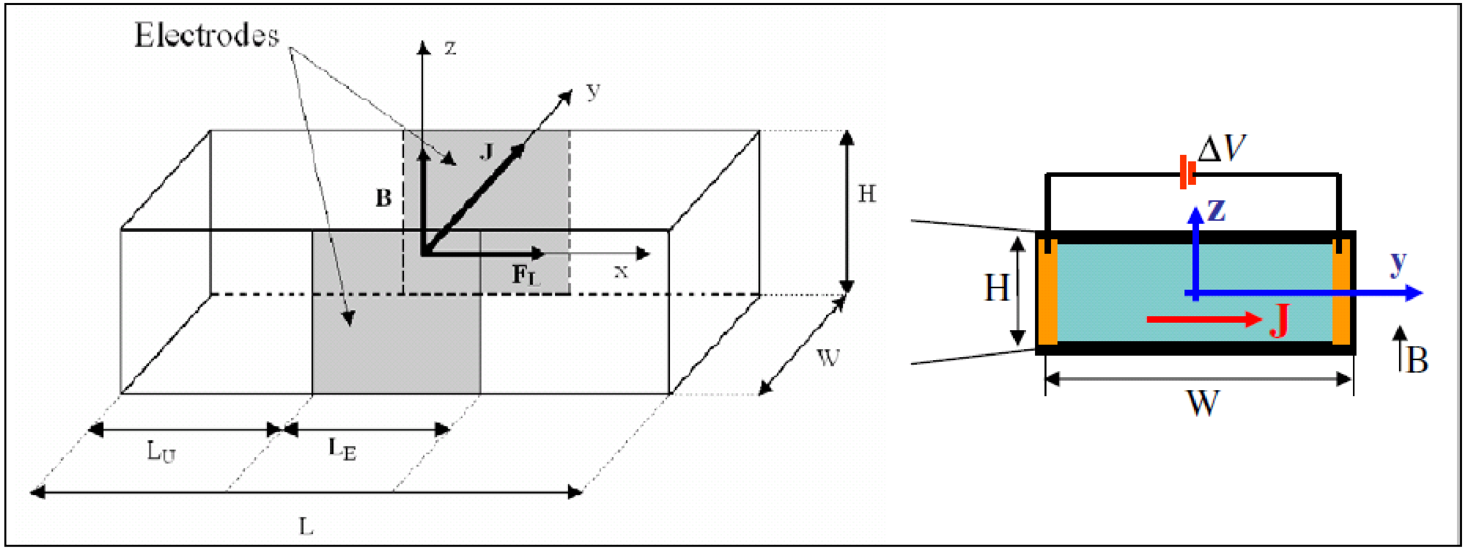
Chromatogram of two overlapping / separate peaks



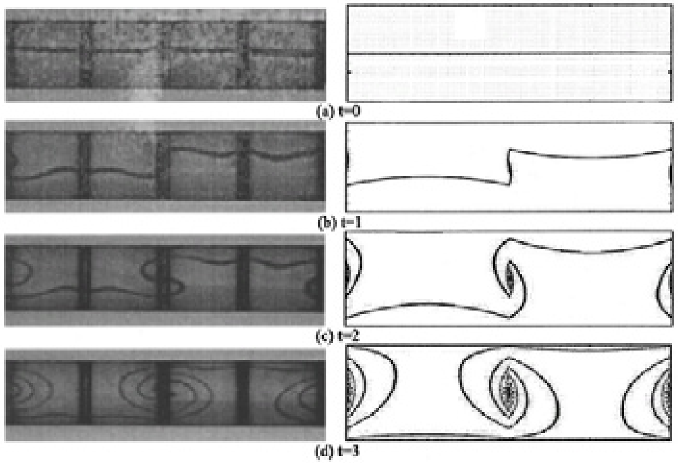
Cyclic liquid chromatography provides infinite column length

Chromatography is a physical method of separation. It involves passing a mixture dissolved in a "mobile phase" through a stationary phase, which separates the analyte to be measured from other molecules in the mixture based on differential partitioning between the mobile and stationary phases.

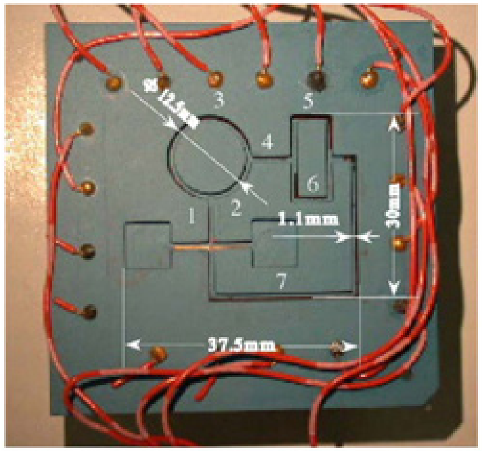
Magnetohydrodynamic Driven Fluidic Device



MHD Pumping, Qian & Bau 2009

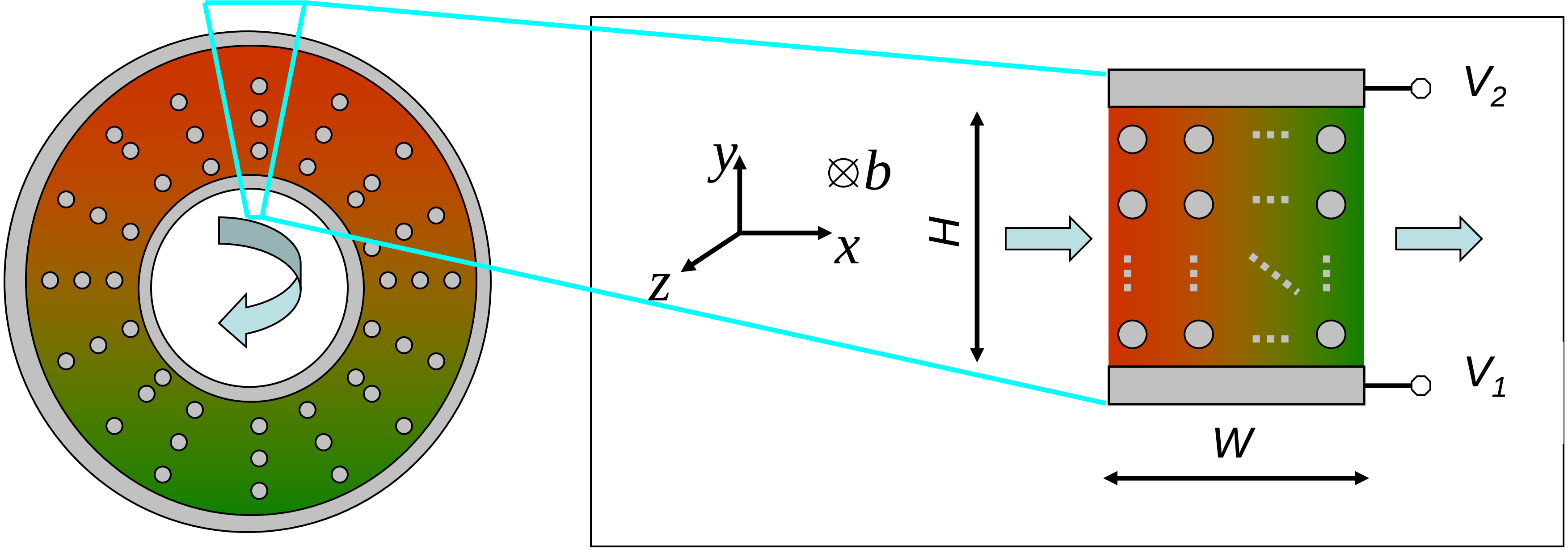


MHD Mixing, Xiang & Bau 2003



MHD Network, Zhong, Yi & Bau 2002

MHD Driven Cyclic LC



Advantages:

1. Handle small sample volumes on microfluidic devices
2. Continuous flow chromatography
3. Infinite column length
4. No moving parts for pumping
5. Controllable flow rate/ separation time

Theory for Ion Transfer

- Nernst-planck

$$\vec{N}_i = \vec{u}c_i - D_i \nabla c_i - z_i \mu_i F c_i \nabla \phi \qquad \vec{j} = -F \sum_{i=1}^{k} z_i \vec{N}_i$$

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \vec{N} = 0$$

- Poisson

$$\nabla^2 \phi = \frac{\rho}{\varepsilon^2} \qquad \rho = \sum_i z_i c_i$$

- Butler-Volmer

$$\vec{n} \cdot \vec{j} = j_0 \left\{ c_1 e^{(1-\alpha)\Delta z[\phi - V_1]/RT} - c_2 e^{-\alpha \Delta z[\phi - V_1]/RT} \right\}, y = -H/2$$

$$n \cdot \vec{j} = j_0 \left\{ c_2 e^{-\alpha \Delta z[\phi - V_2]/RT} - c_1 e^{(1-\alpha)\Delta z[\phi - V_2]/RT} \right\}, y = H/2$$

- Mass Conserv.

$$\int_A c_i dA = c_{i0}$$

- Electro-neutral

$$\sum_{i=1}^{k} z_i c_i = 0$$

Theory for Fluid Motion

- Navier-Stokes

$$\rho\left(\frac{\partial\vec{u}}{\partial t}+\vec{u}\cdot\nabla\vec{u}\right)=-\nabla p+\mu\nabla^{2}\vec{u}+f_{mag}$$

$$f_{mag}=f_{L}+f_{\nabla B}+f_{E}+f_{M}$$

$$f_{L}=\boxed{\vec{j}}\times\vec{b}$$

$$f_{\nabla B}=\frac{\chi_{m}c_{m}b}{\mu_{0}}\nabla b$$

$$f_{E}=F\nabla\phi\cdot\Sigma z_{i}c_{i}$$

$$f_{M}=\sigma\left(\vec{u}\times\vec{b}\right)\times\vec{b}$$

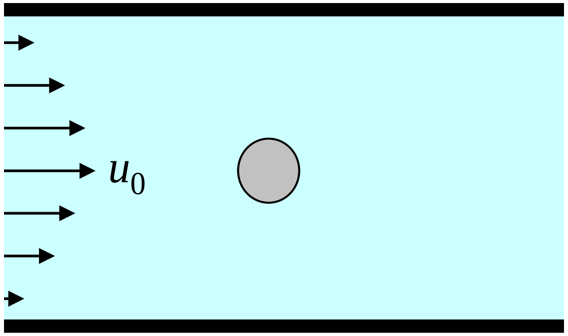
Assumptions:
1. Uniform magnetic field
2. Low magnetic Reynolds number

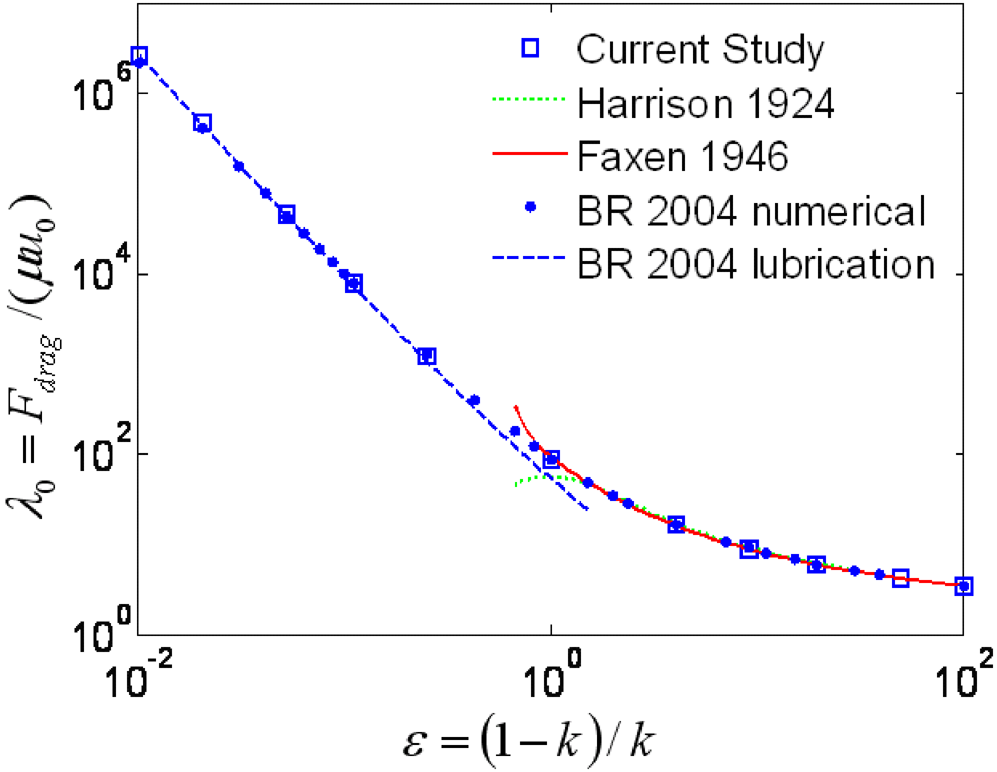
Full Problem: Strongly Coupled NP + NS

Code Verification I – Pressure Driven Flow

$$F_{drag} = F_p + F_\mu = \oint_S \left\{ -n_x p + \mu \left[2n_x u_x + n_y (u_y + v_x) \right] \right\} dS$$

$$\lambda_0 = F_{drag} / (\mu u_0) \qquad \varepsilon = (1-k)/k \qquad k = d/H$$



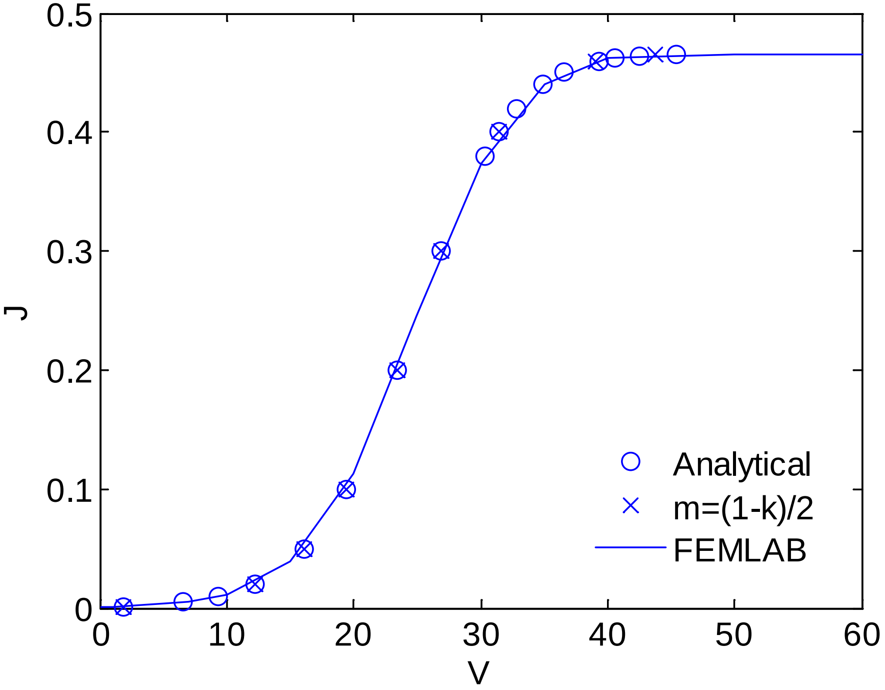


Code Verification II – Electrochemistry of RedOx

$$A^{z_1+}, B^{z_2+}, C^{z_3-} \qquad A^{z_1+} + (z_2 - z_1)e^- \Leftrightarrow B^{z_2+}$$

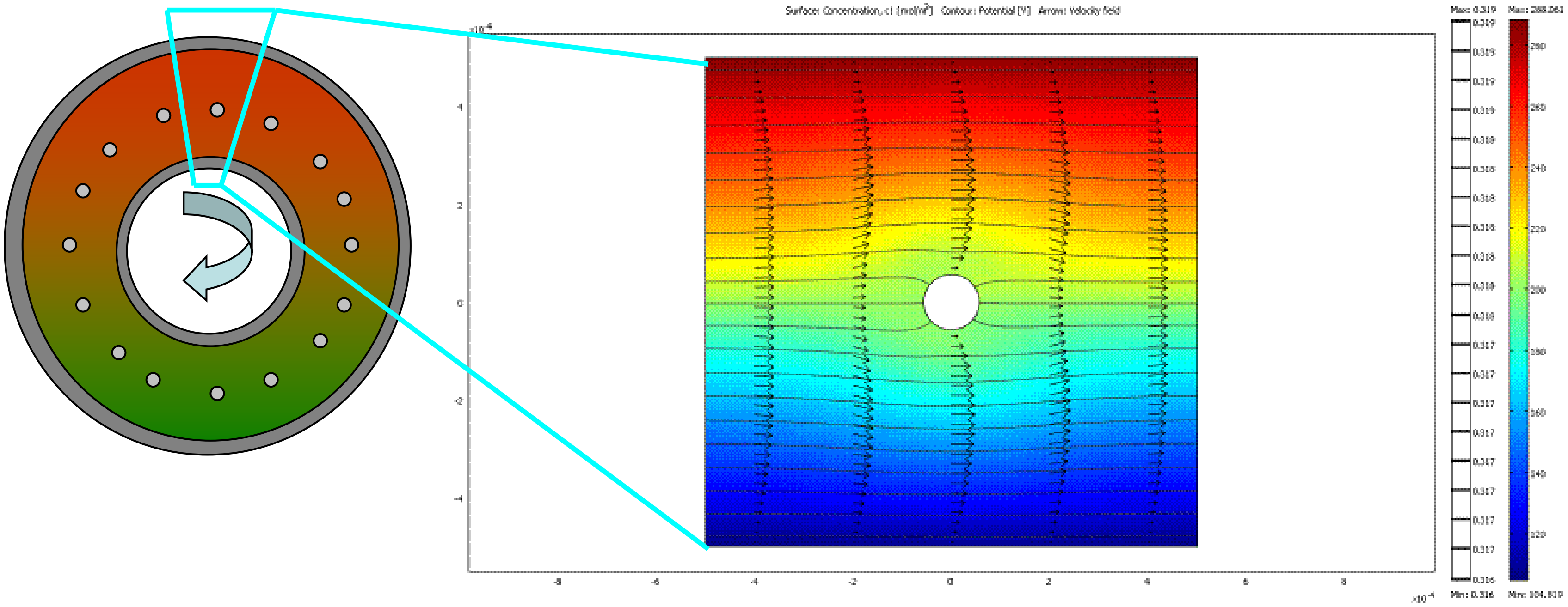
$$Y = \frac{y}{H}, \quad C_i = \frac{c_i}{\overline{c}_3}, \quad \Phi = \frac{\phi}{RT/F}, \quad J = \frac{j}{D_1 F \overline{c}_3 / H}$$

$$\alpha = 0.5, k = 0.2, J_0 = 0.001$$



Current-voltage relation, comparison between FEMLAB simulation and analytical results

2-D Full Model for MHD Flow around Cylinders

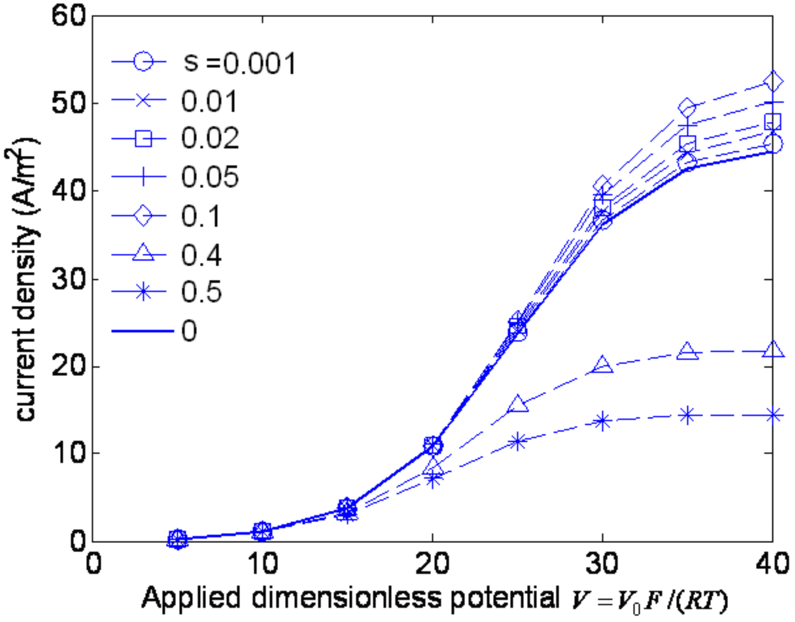


$$H = 1mm \quad W = 1mm \quad d = 0.11mm \quad s = \pi d^2 / 4HW = 0.01$$

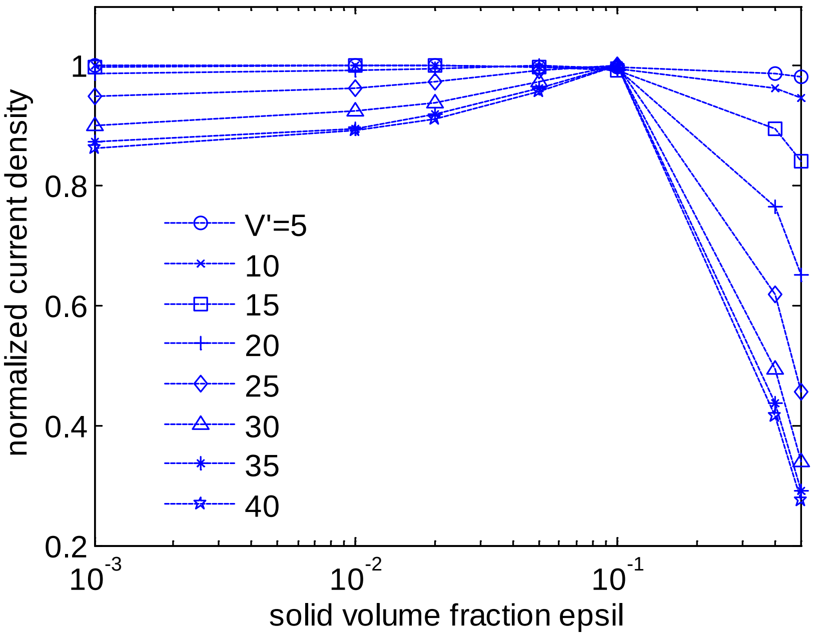
$$j_0 = 10^{-6} A/m^2 \quad \alpha = 0.5 \quad \overline{c_i} = (0.2, 0.2, 1)M \quad z_i = (3, 2, -1)$$

$$D_i = (1, 4/3, 1) \times 10^{-9} m^2/s \quad V_0 = 25RT/F \quad B = 0.4T$$

2-D Full Model for MHD Flow around Cylinders

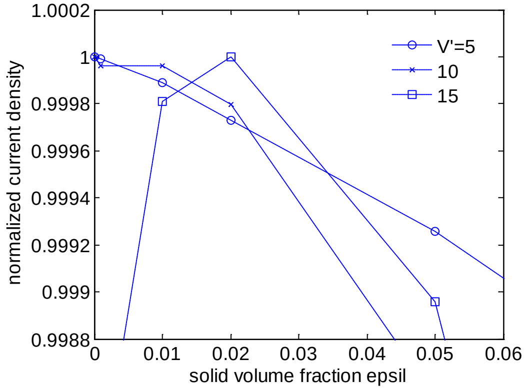


j~V curve at different s values



j~s curve at different V values

- Limiting current depends on solid volume fraction
- s for maximum current depends on applied potential
- y-velocity & x-velocity gradient causes current change
- Total number of mobile ions different with s



Ionic & Equivalent Conductivity

- Ionic conductivity

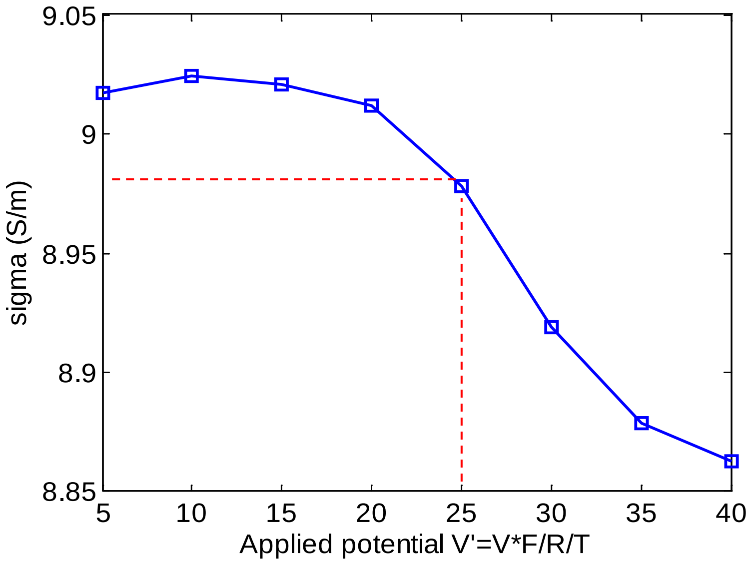
$$\vec{N}_i = \vec{u}c_i - D_i\nabla c_i - z_i\mu_i F c_i \nabla\phi$$

$$\vec{j} = -F\sum_{i=1}^{k} z_i \vec{N}_i$$

$$= \cancelto{0}{-D_iF\nabla\left(\sum z_ic_i\right)} - \left(\sum F^2 z_i^2 \nu_i c_i\right)\nabla\phi$$

$$= -\sigma\nabla\phi$$

$$\boxed{\sigma_{ionic} = \frac{F^2}{RT}\sum z_i^2 D_i c_i}$$



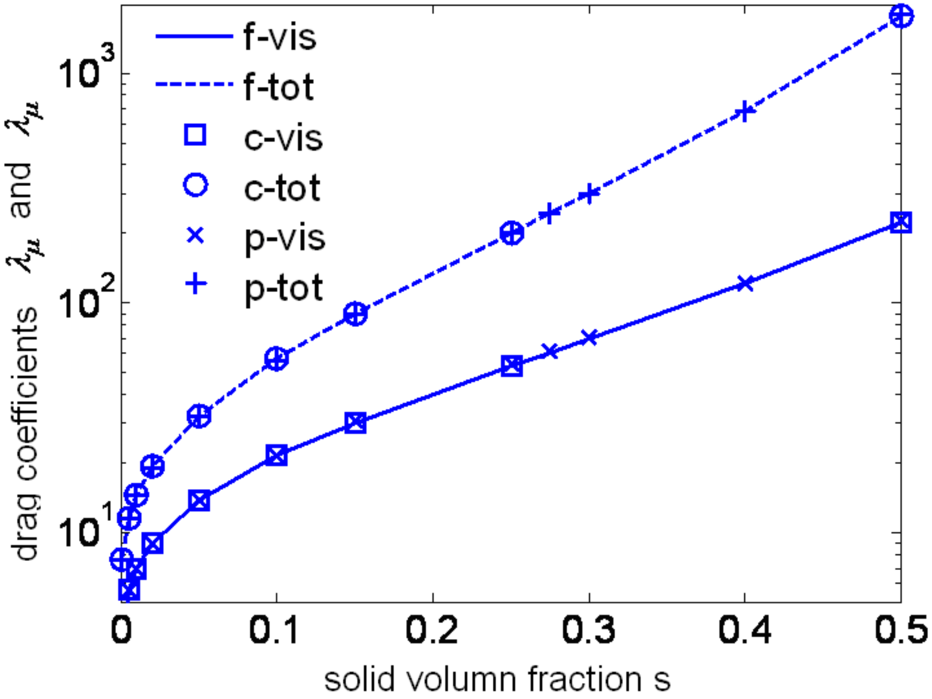
- Equivalent conductivity

$$\boxed{\sigma_{eff} = \frac{jL}{\phi(H)-\phi(0)}}$$

$$\boxed{\begin{aligned}&\nabla\cdot\vec{j} = 0\\ &\nabla\cdot\left(\sigma_{eff}\nabla\phi\right) = 0\end{aligned}}$$

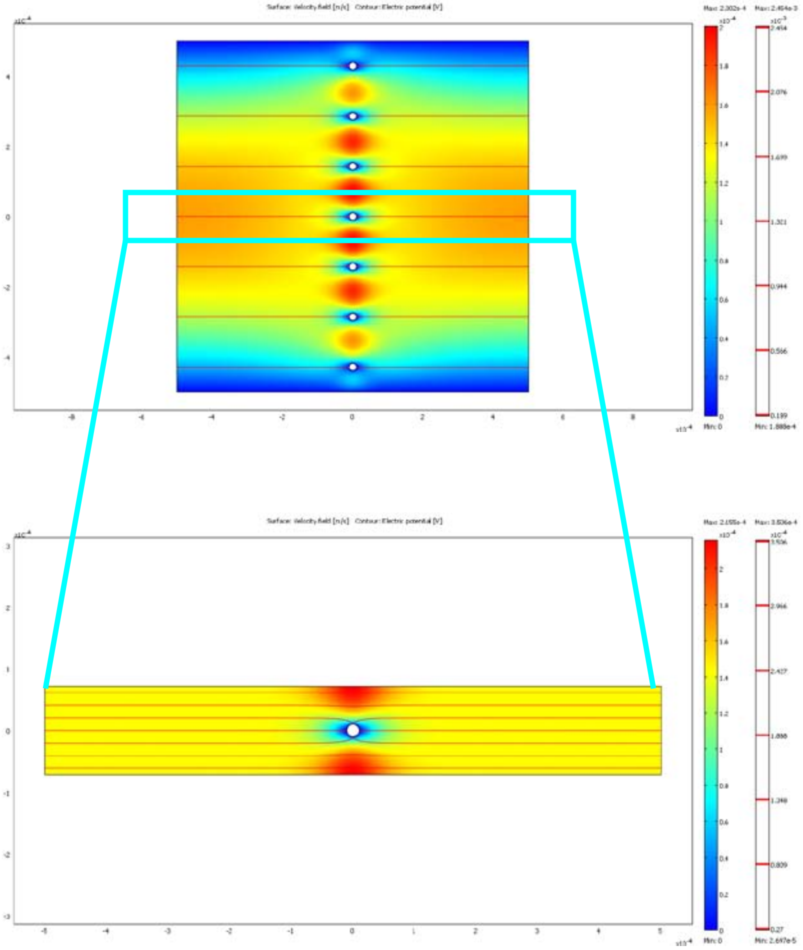
$$\boxed{\begin{aligned}V &= 25RT/F\\ \sigma_{eff} &= 8.98\Omega^{-1}m^{-1}\\ \Delta\phi &= 2.64mV\end{aligned}}$$

Comparison of Different Models for 2D MHD

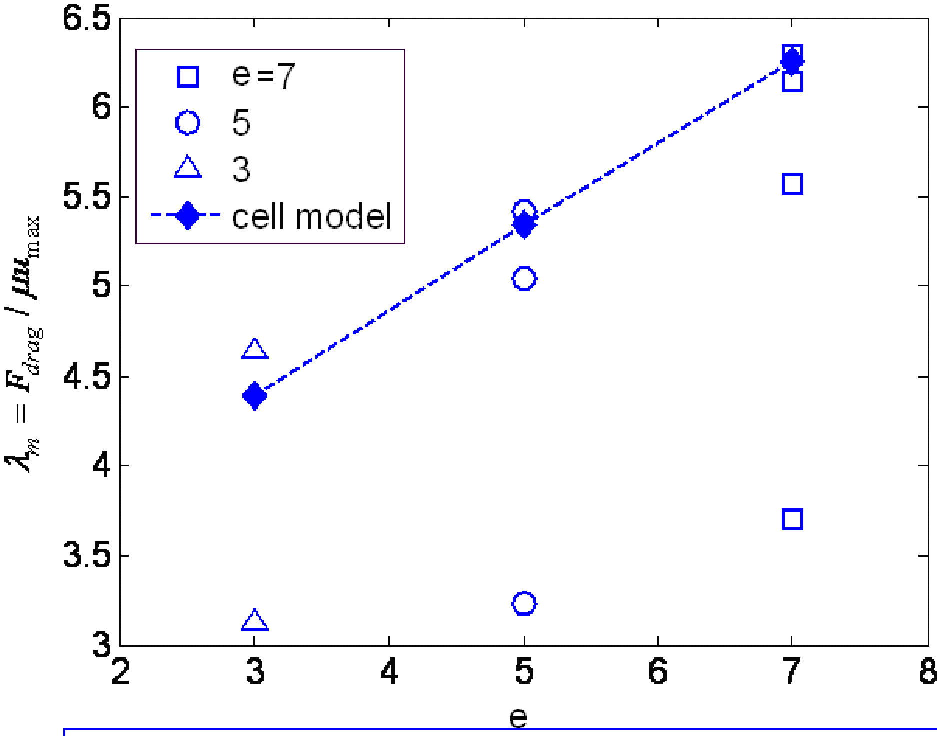


f	–	full model
c	–	conductivity model
p	–	pressure driven flow
vis	–	viscous drag coefficient $\lambda_\mu = F_\mu / \mu\bar{u}$
tot	–	total drag coefficient $\lambda = F_{drag} / \mu\bar{u}$

Multiple Rows – Conductivity Model



$$\lambda_m = F_{drag} / \mu u_{\max}$$



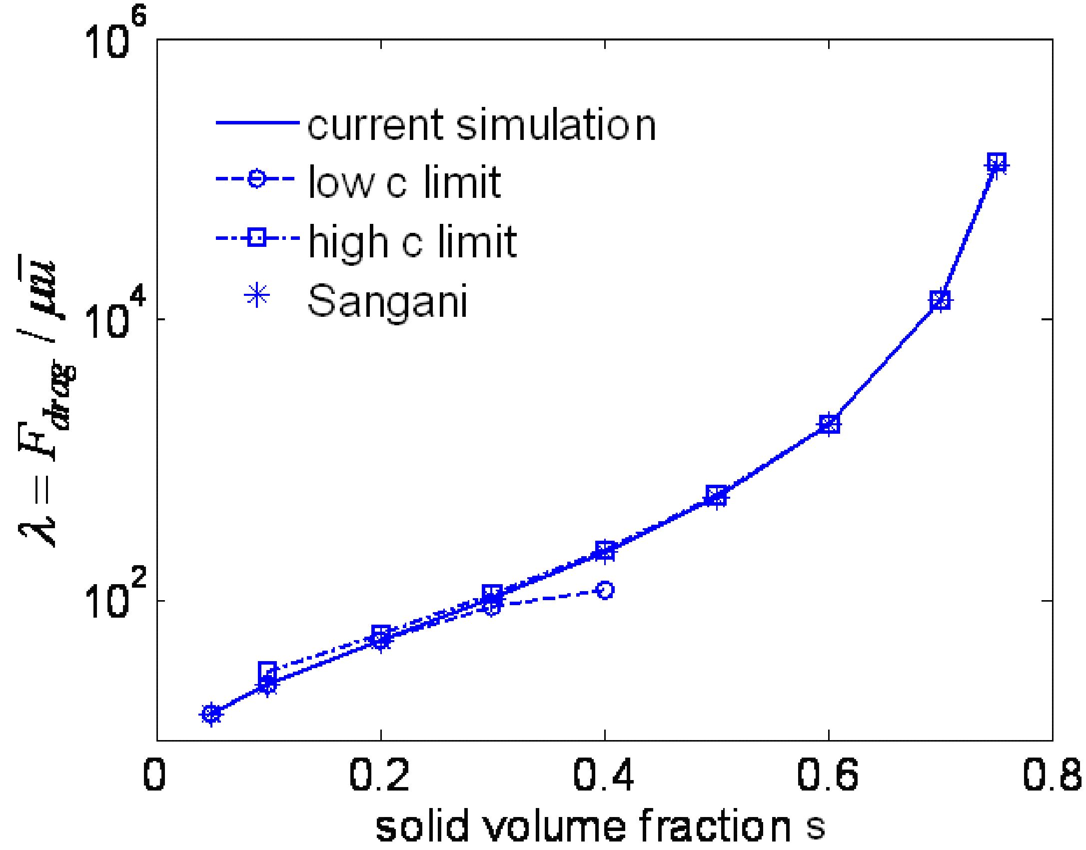
Comparison of results from:

Symbols – columns of e cylinders

Dashed line – a representative cell with a single cylinder

Pillar Array – Conductivity Model

$$H = W = 1mm$$



Comparison of drag coefficients for square array:

Solid line – conductivity model MHD flow

Symbols – pressure driven flow

Porous Media – Darcy Brinkman Model

$$\left\{\nabla\cdot\frac{\gamma}{\varepsilon_p}\left[\nabla\vec{u}+\left(\nabla\vec{u}\right)^T\right]\right\}+\left(\frac{\mu}{\kappa}\vec{u}+\vec{f}_L+\nabla p\right)=0$$

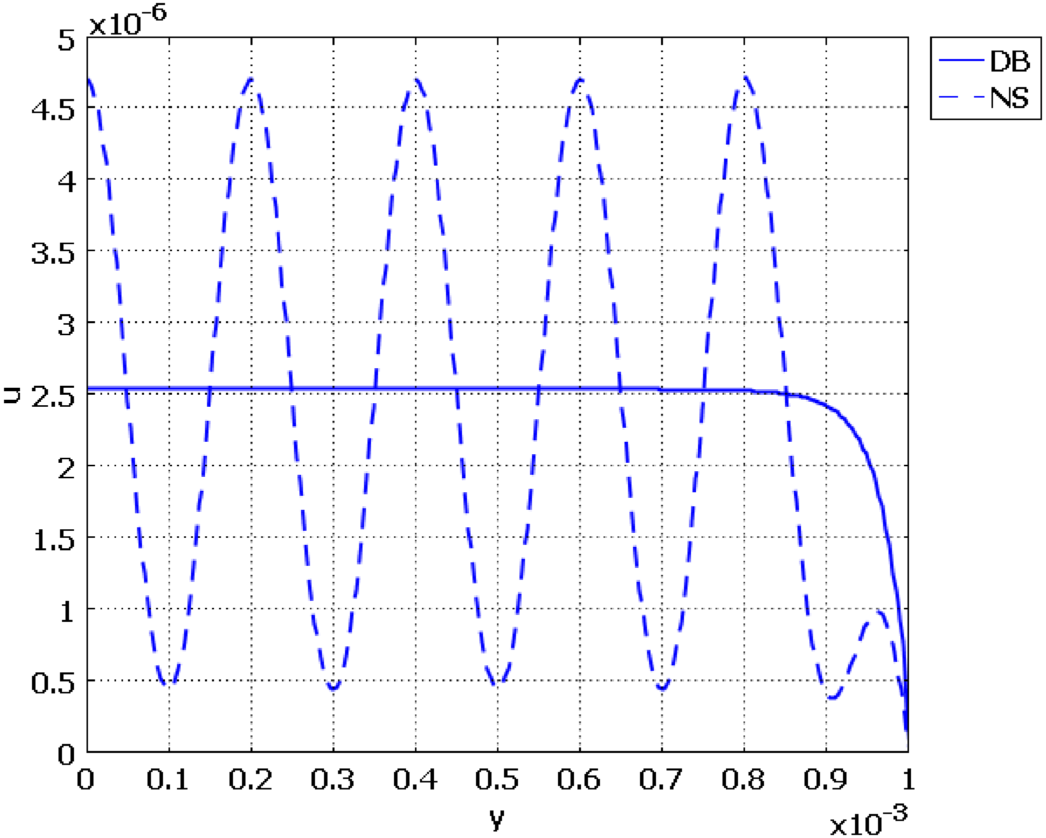
$$\nabla\cdot\vec{u}=0$$

$$H=W=0.2mm$$

$$d=0.1mm$$

$$\left.\begin{array}{l}\kappa=7.96\times10^{-10}m^2\\ \overline{f}_L=3.19N/m^3\end{array}\right\}\varepsilon_p=0.8$$

$$\Delta\phi=0.264mV$$



Conclusions

1. The drag coefficient of the MHD flow agrees with that predicted for pressure-driven flow around single and multiple pillars.

2. A simpler Ohmic model was able to properly describe the MHD flow.

3. MHD flow in the pillar array can be simulated using computational unit cells with periodic/ symmetry boundary conditions.

4. The presence of pillars in the MHD conduit does not necessarily reduce the current transmitted between the electrodes.

- **Thank You !**
- **Questions ?**

1-D J~V relation for RedOx Electrolyte I

$A^{z_1+}, B^{z_2+}, C^{z_3-}$ $\quad$ $A^{z_1+} + (z_2 - z_1)e^- \Leftrightarrow B^{z_2+}$ $\quad$ V

$$\frac{y}{H}, \quad \frac{c_i}{\overline{c}_3}, \quad \frac{\phi}{RT/F}, \quad \frac{j}{D_1 F \overline{c}_3 / H}$$

$$\boxed{\begin{aligned}
&\frac{dC_1}{dY} + z_1 C_1 \frac{d\Phi}{dY} = -\frac{J}{z_1 - z_2} \\
&\frac{dC_2}{dY} + z_2 C_2 \frac{d\Phi}{dY} = \frac{D_1}{D_2} \cdot \frac{J}{z_1 - z_2} \\
&\frac{dC_3}{dY} - z_3 C_3 \frac{d\Phi}{dY} = 0 \\
&z_1 C_1 + z_2 C_2 = z_3 C_3
\end{aligned}}$$

$$z_1 = 3, z_2 = 2, z_3 = 1$$

$$C_1 + C_2 = J\left(1 - \frac{D_1}{D_2}\right) \cdot \left(\frac{1}{2} - X\right) + \frac{3-k}{2} - C_3$$

$$C_3{}^2 - \left[\frac{J}{4} \cdot \left(\frac{1}{2} - X\right) + \frac{3-k}{2}\right] C_3 + m = 0$$

$$C_3 = \frac{b + \sqrt{b^2 - 4m}}{2} \qquad b = \frac{J}{4} \cdot \left(\frac{1}{2} - X\right) + \frac{3-k}{2}$$

$$C_1 = 3C_3 - 2b \quad C_2 = 3b - 4C_3 \qquad C_3 = \frac{b + \sqrt{b^2 - (1-k)^2}}{2}$$

$$\boxed{J = J_0 \left\{ \frac{C_1(0)}{k} e^{(1-\alpha)[\Phi(0) - V_1]} - \frac{C_2(0)}{(1-3k)/2} e^{-\alpha[\Phi(0) - V_1]} \right\} \; at \;\; Y = 0}$$

$$J = J_0 \left\{ \frac{C_2(1)}{(1-3k)/2} e^{-\alpha[\Phi(1) - V_2]} - \frac{C_1(1)}{k} e^{(1-\alpha)[\Phi(1) - V_2]} \right\} \; at \;\; Y = 1$$

$$\left[12 \frac{D_1}{D_2} C_1 + \left(6 + 2\frac{D_1}{D_2}\right) C_2\right] dC_1 + \left[\left(3 + 6\frac{D_1}{D_2}\right) C_1 + 6C_2\right] dC_2 = 0$$

$$\boxed{e^{\Phi(0)} = \frac{2k}{1-3k} \cdot \frac{C_2(0) + C_2(1) \exp^{\alpha(V_2 - \Delta\Phi)}}{C_1(0) + C_1(1) \exp^{(\alpha-1)(V_2 - \Delta\Phi)}}}$$

$$\frac{D_1}{D_2} = \frac{3}{4} \qquad (C_1 + C_2)(3C_1 + 2C_2) = m$$

$$m = \frac{1-k}{2} \qquad \boxed{\frac{d\Phi}{dX} = \frac{1}{C_3} \frac{dC_3}{dX}}$$

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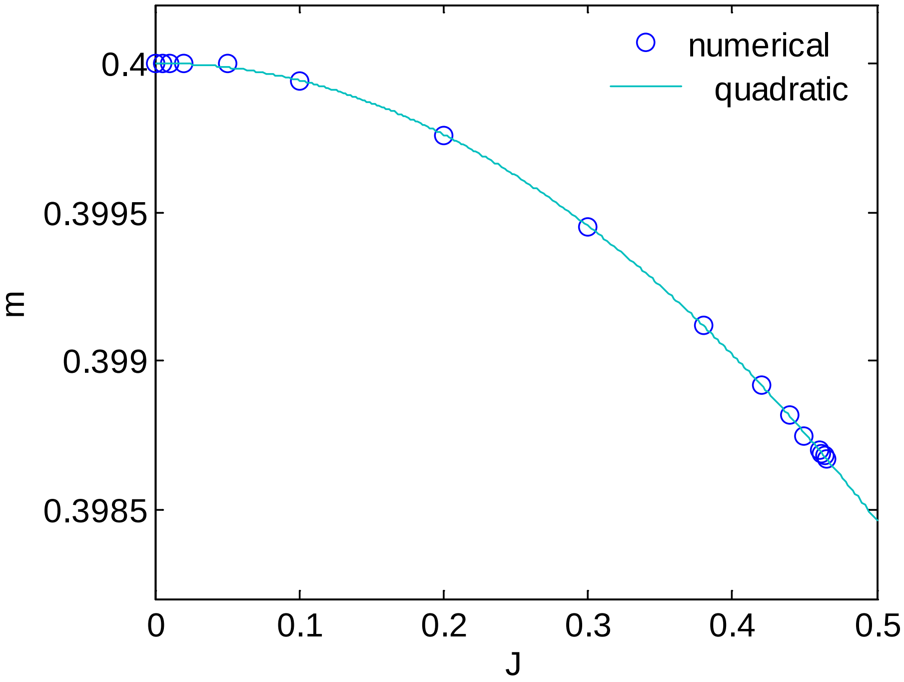
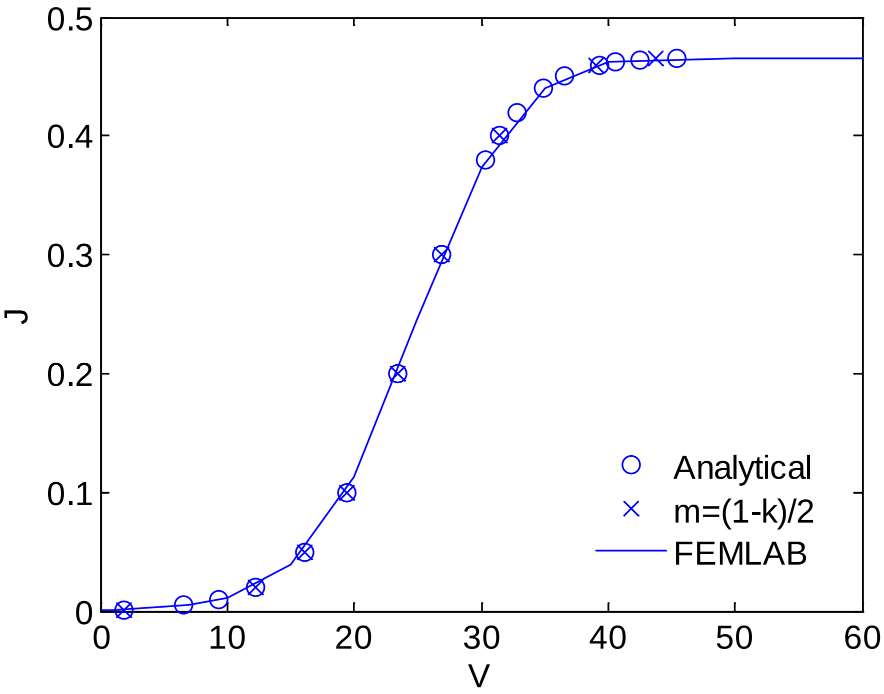
$$Y = \frac{y}{H}, \quad C_i = \frac{c_i}{\bar{c}_3}, \quad \Phi = \frac{\phi}{RT/F}, \quad J = \frac{j}{D_1 F \bar{c}_3 / H}$$

$$(C_1 + C_2)(3C_1 + 2C_2) = m$$



Determine the integration constant as a function of injection current

$$\alpha = 0.5, k = 0.2, J_0 = 0.001$$



Current-voltage relation, comparison between different methods

Slip Velocity Effect

$$u_{//} = -\frac{\varepsilon_0 \varepsilon_r \zeta E_{//}}{\mu}$$