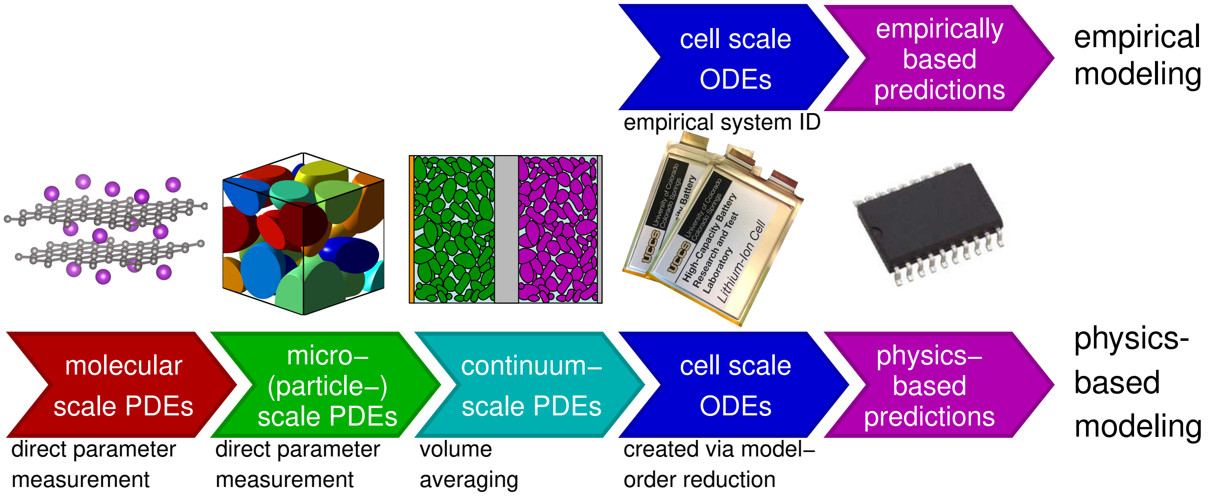
Reduced Order Models of Cell Dynamics

6.1: Approach and first steps, leading to R_{ct} and $R_{s,e}$

- We have now seen the approach to convert a continuum-scale PDE to a discrete-time ODE via finding transfer functions and the DRA.
- We now find all cell transfer functions, run the DRA, verify results.



cell scale ODEs

empirically based predictions

empirical modeling

empirical system ID

molecular scale PDEs

micro–(particle–) scale PDEs

continuum–scale PDEs

cell scale ODEs

physics–based predictions

physics-based modeling

direct parameter measurement

direct parameter measurement

volume averaging

created via model–order reduction

- Specifically, we have now implemented $\widetilde{C}_{s,e}(s)/J(s)$, which allows us to compute lithium surface concentration for a single particle at a single x location if we know the lithium flux at that point, $j(x,t)$.
- We have reduced the infinite-order radial pseudo dimension to a small finite order ODE. However, we still need an infinite set of these ODEs if we are to solve for what is happening at every x coordinate!
- We specialize to a 1D cell model, following the approach of Smith *et al.* allowing us to solve for any desired set of cell variables at any desired set of x locations, with a single small finite-order ODE.[1]

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[1] Smith, K., Rahn, C.D., and Wang, C-Y, "Control oriented 1D electrochemical model of lithium ion battery," *Energy Conversion and Management*, 48, 2007, pp. 2565–78.

- We initially focus on modeling negative-electrode variables. We'll see later that it is simple to generalize to the positive electrode.
- We make two fundamental assumptions when creating the reduced-order models:

  1. We assume linear behavior: We linearize nonlinear equations using Taylor series;
  2. We assume that the reaction flux $j(x,s)$ is decoupled from (not a function of) the electrolyte concentration $c_e(x,s)$.

- Begin by linearizing the Butler–Volmer kinetic relationship. Recall:

$$j = k_0 {c_e}^{1-\alpha}(c_{s,\max} - c_{s,e})^{1-\alpha}{c_{s,e}}^{\alpha}\left\{\exp\left(\frac{(1-\alpha)F}{RT}\eta\right) - \exp\left(-\frac{\alpha F}{RT}\eta\right)\right\},$$

where $\eta = \phi_s - \phi_e - U_{\text{ocp}} - FR_{\text{film}}j$.

  - Note the new term, $FR_{\text{film}}j$, which models the voltage drop due to flux through the ionic resistance of the electrode's surface film.

- We write, where we define $\phi_{s\text{-}e} = \phi_s - \phi_e$,

$$\frac{j}{k_0 {c_e}^{1-\alpha}(c_{s,\max} - c_{s,e})^{1-\alpha}{c_{s,e}}^{\alpha}} = \exp\left(\frac{(1-\alpha)F}{RT}\left(\phi_{s\text{-}e} - U_{\text{ocp}} - FR_{\text{film}}j\right)\right) - \exp\left(-\frac{\alpha F}{RT}\left(\phi_{s\text{-}e} - U_{\text{ocp}} - FR_{\text{film}}j\right)\right).$$

- Note that j appears on both sides of this expression, and because of the nonlinear nature of the RHS, we cannot solve for j in general.
- Our approach is to use Taylor series on both sides of the equation separately to make a linear approximation.
- The linearization set-point p^* is defined as: $p^* = \{c_{s,e} = c_{s,0},\ c_e = c_{e,0},\ \phi_{s\text{-}e} = U_{\text{ocp}}(c_{s,0}),\ j = 0\}$.

- Then, linearizing the LHS, we get:

$$\begin{aligned}\text{LHS} &\approx \text{LHS}(p^*) + \left.\frac{\partial\text{LHS}}{\partial c_{s,e}}\right|_{p^*}(c_{s,e}-c_{s,0}) + \left.\frac{\partial\text{LHS}}{\partial c_e}\right|_{p^*}(c_e-c_{e,0}) + \left.\frac{\partial\text{LHS}}{\partial j}\right|_{p^*} j\\ &= 0 + 0\times(c_{s,e}-c_{s,0}) + 0\times(c_e-c_{e,0})\\ &\qquad + \frac{1}{k_0 {c_{e,0}}^{1-\alpha}(c_{s,\max}-c_{s,0})^{1-\alpha}{c_{s,0}}^{\alpha}} j\\ &= j/j_0.\end{aligned}$$

- Linearizing the RHS, we get:

$$\begin{aligned}\text{RHS} &\approx \text{RHS}(p^*) + \left.\frac{\partial\text{RHS}}{\partial \phi_{s\text{-}e}}\right|_{p^*}(\phi_{s\text{-}e} - U_{\text{ocp}}(c_{s,0})) + \left.\frac{\partial\text{RHS}}{\partial c_{s,e}}\right|_{p^*}(c_{s,e}-c_{s,0})\\ &\qquad + \left.\frac{\partial\text{RHS}}{\partial j}\right|_{p^*} j\\ &= 0 + \frac{F}{RT}\big(\phi_{s\text{-}e} - U_{\text{ocp}}(c_{s,0})\big) - \frac{F}{RT}\left[\left.\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\right|_{c_{s,0}}\right](c_{s,e}-c_{s,0})\\ &\qquad - \frac{F^2 R_{\text{film}}}{RT} j.\end{aligned}$$

- Equating the linearized LHS $=$ RHS, and defining $\tilde{c}_{s,e} = c_{s,e} - c_{s,0}$ and $\tilde{\phi}_{s\text{-}e} = \phi_{s\text{-}e} - U_{\text{ocp}}(c_{s,0})$, we get

$$\begin{aligned}\frac{j}{j_0} &= \frac{F}{RT}\tilde{\phi}_{s\text{-}e} - \frac{F}{RT}\left[\left.\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\right|_{c_{s,0}}\right]\tilde{c}_{s,e} - \frac{F^2 R_{\text{film}}}{RT} j\\ \tilde{\phi}_{s\text{-}e} &= \left(\frac{RT}{j_0 F} + F R_{\text{film}}\right) j + \left[\left.\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\right|_{c_{s,0}}\right]\tilde{c}_{s,e}\\ &= F(R_{\text{ct}} + R_{\text{film}}) j + \left[\left.\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\right|_{c_{s,0}}\right]\tilde{c}_{s,e},\end{aligned}$$

if we define the "charge transfer resistance" $R_{\text{ct}} = \dfrac{RT}{j_0 F^2}$.

- Before proceeding we take a brief diversion to make a transfer function for η. Rearranging the prior result gives

$$jF(R_{\text{ct}} + R_{\text{film}}) = \phi_s - \phi_e - U_{\text{ocp}}(c_{s,0}) - \left[\left. \frac{\partial U_{\text{ocp}}}{\partial c_{s,e}} \right|_{c_{s,0}} \right] \tilde{c}_{s,e}.$$

- Notice that the last two terms are a Taylor-series linearization of $U_{\text{ocp}}(c_{s,e})$, so we re-write as

$$\begin{aligned} jF(R_{\text{ct}} + R_{\text{film}}) &= \phi_s - \phi_e - U_{\text{ocp}}(c_{s,e}) \\ jFR_{\text{ct}} &= \phi_s - \phi_e - U_{\text{ocp}}(c_{s,e}) - FR_{\text{film}} j = \eta. \end{aligned}$$

- So, we have that $\eta(x,t) = FR_{\text{ct}} j(x,t)$,
  - This helps explain the "charge transfer resistance" terminology—it's the "resistance" of the "activation polarization" of the Butler–Volmer equation, or the voltage drop beyond OCP over the interface between solid and electrolyte.
- We define a solid–electrolyte surface resistance $R_{s,e} = R_{\text{ct}} + R_{\text{film}}$. Then,

$$jFR_{s,e} = \phi_{s\text{-}e} - U_{\text{ocp}}(c_{s,0}) - \left[\left. \frac{\partial U_{\text{ocp}}}{\partial c_{s,e}} \right|_{c_{s,0}} \right] \tilde{c}_{s,e}.$$

- We'll keep these results in our back pocket for now, and proceed to look at the cell potentials ϕ_s and ϕ_e.

6.2: Next steps, leading to impedance ratio $\nu^2(s)$

- Our first step is to define a dimensionless spatial variable $z = x/L$, where L is the electrode thickness.
  - The location $z = 0$ represents the current collector interface;
  - The location $z = 1$ represents the separator interface.
- Recall the solid-phase charge conservation equation, with normalized variable z,
$$\frac{\sigma_{\text{eff}}}{L^2}\frac{\partial^2}{\partial z^2}\phi_s = a_s F j,$$
with boundary conditions $\left.\frac{\sigma_{\text{eff}}}{L}\frac{\partial \phi_s}{\partial z}\right|_{z=0} = \frac{-i_{\text{app}}}{A}$ and $\left.\frac{\partial \phi_s}{\partial z}\right|_{z=1} = 0$.
- Also recall the electrolyte-phase charge conservation equation, also normalized
$$\frac{\kappa_{\text{eff}}}{L^2}\frac{\partial^2}{\partial z^2}\phi_e + \frac{\kappa_{D,\text{eff}}}{L^2}\frac{\partial^2}{\partial z^2}\ln c_e = -a_s F j,$$
with boundary conditions
$$\left.\kappa_{\text{eff}}\frac{\partial \phi_e}{\partial z} + \kappa_{D,\text{eff}}\frac{\partial \ln c_e}{\partial z}\right|_{z=0} = 0$$
$$\left.\frac{\kappa_{\text{eff}}}{L}\frac{\partial \phi_e}{\partial z} + \frac{\kappa_{D,\text{eff}}}{L}\frac{\partial \ln c_e}{\partial z}\right|_{z=1} = \frac{-i_{\text{app}}}{A}.$$
- By assumption 2, we ignore the electrolyte concentration, giving
$$\frac{\kappa_{\text{eff}}}{L^2}\frac{\partial^2}{\partial z^2}\phi_e = -a_s F j,$$
with boundary conditions $\left.\frac{\partial \phi_e}{\partial z}\right|_{z=0} = 0$ and $\left.\frac{\kappa_{\text{eff}}}{L}\frac{\partial \phi_e}{\partial z}\right|_{z=1} = \frac{-i_{\text{app}}}{A}$.
- We subtract these two PDEs to arrive at a single static PDE for phase potential difference $\phi_{s\text{-}e} = \phi_s - \phi_e$,

$$\frac{\partial^2}{\partial z^2}\phi_{s\text{-}e} = a_s F L^2 \left(\frac{1}{\sigma_{\text{eff}}} + \frac{1}{\kappa_{\text{eff}}}\right) j$$

with boundary conditions $\dfrac{\sigma_{\text{eff}}}{L}\dfrac{\partial \phi_{s\text{-}e}}{\partial z}\bigg|_{z=0} = \dfrac{-\kappa_{\text{eff}}}{L}\dfrac{\partial \phi_{s\text{-}e}}{\partial z}\bigg|_{z=1} = \dfrac{-i_{\text{app}}}{A}$.

- We would like to be able to write a homogeneous PDE in terms of $\phi_{s\text{-}e}$ by eliminating j.
- Recall our earlier result: $\tilde{\phi}_{s\text{-}e} = FR_{s,e}j + \left[\dfrac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\bigg|_{c_{s,0}}\right]\tilde{c}_{s,e}$.
- Proceeding by taking Laplace transforms (and noticing that all signals are functions of both time and space),

$$\widetilde{\Phi}_{s\text{-}e}(z,s) = FR_{s,e}J(z,s) + \left[\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\bigg|_{c_{s,0}}\right]\widetilde{C}_{s,e}(z,s).$$

- To treat the rightmost term, write

$$\widetilde{C}_{s,e}(z,s) = \frac{\widetilde{C}_{s,e}(z,s)}{J(z,s)}J(z,s).$$

- We have already determined the transfer function $\widetilde{C}_{s,e}(s)/J(s)$ for a single spatial location from the Jacobsen–West paper.
- But, in the solid, we are assuming that diffusion happens only along the r dimension (not the z dimension), so transfer functions at every location $z = z_0$ has the same form as every other, and we can write $\widetilde{C}_{s,e}(z,s)/J(z,s) = \widetilde{C}_{s,e}(s)/J(s)$.
- This gives (remembering that $\beta = R_s\sqrt{s/D_s}$)

$$\begin{aligned}\widetilde{\Phi}_{s\text{-}e}(z,s) &= \left(FR_{s,e} + \left[\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\bigg|_{c_{s,0}}\right]\frac{\widetilde{C}_{s,e}(s)}{J(s)}\right)J(z,s)\\ &= F\left(R_{s,e} + \left[\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\bigg|_{c_{s,0}}\right]\frac{R_s}{FD_s}\left[\frac{1}{1-\beta\coth(\beta)}\right]\right)J(z,s).\end{aligned}$$

- Note that since $\tilde{\phi}_{s\text{-}e} = \phi_{s\text{-}e} - U_{\text{ocp}}(c_{s,0})$, we also have $\dfrac{\partial^2 \tilde{\phi}_{s\text{-}e}}{\partial z^2} = \dfrac{\partial^2 \phi_{s\text{-}e}}{\partial z^2}$, so we can write

$$\begin{aligned}
\frac{\partial^2 \tilde{\phi}_{s\text{-}e}(z,t)}{\partial z^2} &= a_s F L^2 \left(\frac{1}{\sigma_{\text{eff}}} + \frac{1}{\kappa_{\text{eff}}}\right) j(z,t) \\
\frac{\partial^2 \widetilde{\Phi}_{s\text{-}e}(z,s)}{\partial z^2} &= a_s F L^2 \left(\frac{1}{\sigma_{\text{eff}}} + \frac{1}{\kappa_{\text{eff}}}\right) J(z,s) \\
&= a_s L^2 \left(\frac{1}{\sigma_{\text{eff}}} + \frac{1}{\kappa_{\text{eff}}}\right) \times \\
&\qquad \left(R_{s,e} + \left[\left.\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\right|_{c_{s,0}}\right] \frac{R_s}{F D_s} \left[\frac{1}{1 - \beta \coth(\beta)}\right]\right)^{-1} \widetilde{\Phi}_{s\text{-}e}(z,s)
\end{aligned}$$

with boundary conditions

$$\frac{\sigma_{\text{eff}}}{L} \left.\frac{\partial \widetilde{\Phi}_{s\text{-}e}(z,s)}{\partial z}\right|_{z=0} = \frac{-\kappa_{\text{eff}}}{L} \left.\frac{\partial \widetilde{\Phi}_{s\text{-}e}(z,s)}{\partial z}\right|_{z=1} = \frac{-I_{\text{app}}(s)}{A}.$$

- For convenience of notation, we define dimensionless variable $\nu(s)$ as

$$\boxed{\nu(s) = L\sqrt{\frac{a_s}{\sigma_{\text{eff}}} + \frac{a_s}{\kappa_{\text{eff}}}} \Bigg/ \sqrt{R_{s,e} + \left[\left.\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\right|_{c_{s,0}}\right] \frac{R_s}{F D_s} \left[\frac{1}{1-\beta \coth(\beta)}\right]}.}$$

- Note that $\nu^2(s)$ is a (unitless) ratio of impedances:
  - Numerator is parallel impedance to electronic and ionic current of solid and electrolyte in x dimension
  - Denominator is impedance across solid–electrolyte boundary and due to diffusion in r dimension.

6.3: Negative-electrode transfer functions

- Substituting $\nu(s)$ gives us the homogeneous PDE

$$\frac{\partial^2 \widetilde{\Phi}_{s\text{-}e}(z,s)}{\partial z^2} - \nu^2(s)\widetilde{\Phi}_{s\text{-}e}(z,s) = 0.$$

- The generic solution to this PDE is

$$\widetilde{\Phi}_{s\text{-}e}(z,s) = k_1 \cosh(\nu(s)z) + k_2 \sinh(\nu(s)z),$$

where k_1 and k_2 are chosen to satisfy the boundary conditions.

- As our boundary conditions are written as gradients, we differentiate

$$\frac{\partial \widetilde{\Phi}_{s\text{-}e}(z,s)}{\partial z} = k_1\nu(s)\sinh(\nu(s)z) + k_2\nu(s)\cosh(\nu(s)z).$$

- From the first boundary condition, we have

$$\frac{\sigma_{\text{eff}}}{L}\frac{\partial \widetilde{\Phi}_{s\text{-}e}(z,s)}{\partial z}\bigg|_{z=0} = \frac{\sigma_{\text{eff}}}{L}k_2\nu(s) = \frac{-I_{\text{app}}(s)}{A}$$

$$k_2 = \frac{-I_{\text{app}}(s)L}{A\sigma_{\text{eff}}\nu(s)}.$$

- From the second boundary condition, we have

$$\frac{-\kappa_{\text{eff}}}{L}\frac{\partial \widetilde{\Phi}_{s\text{-}e}(z,s)}{\partial z}\bigg|_{z=1} = \frac{-\kappa_{\text{eff}}}{L}\left[k_1\nu(s)\sinh(\nu(s)) + \frac{-I_{\text{app}}(s)L}{A\sigma_{\text{eff}}}\cosh(\nu(s))\right]$$

$$\frac{-I_{\text{app}}(s)}{A} = \frac{-\kappa_{\text{eff}}}{L}\left[k_1\nu(s)\sinh(\nu(s)) + \frac{-I_{\text{app}}(s)L}{A\sigma_{\text{eff}}}\cosh(\nu(s))\right]$$

$$k_1\nu(s)\sinh(\nu(s)) = \frac{I_{\text{app}}(s)L}{A\kappa_{\text{eff}}}\left[1 + \frac{\kappa_{\text{eff}}}{\sigma_{\text{eff}}}\cosh(\nu(s))\right]$$

$$k_1 = \frac{I_{\text{app}}(s)L}{A\nu(s)\sinh(\nu(s))}\left[\frac{1}{\kappa_{\text{eff}}} + \frac{1}{\sigma_{\text{eff}}}\cosh(\nu(s))\right].$$

- Substituting these values of k_1 and k_2 into $\widetilde{\Phi}_{s\text{-}e}(z,s)$ gives

$$\begin{aligned}\widetilde{\Phi}_{s\text{-}e}(z,s) &= \frac{I_{\text{app}}(s)L}{A\nu(s)\sinh(\nu(s))}\left[\frac{1}{\kappa_{\text{eff}}}+\frac{1}{\sigma_{\text{eff}}}\cosh(\nu(s))\right]\cosh(\nu(s)z)\\ &\quad+\frac{-I_{\text{app}}(s)L}{A\sigma_{\text{eff}}\nu(s)}\sinh(\nu(s)z)\end{aligned}$$

$$\begin{aligned}\frac{\widetilde{\Phi}_{s\text{-}e}(z,s)}{I_{\text{app}}(s)} &= \frac{L}{A\nu(s)\sinh(\nu(s))}\left[\frac{1}{\kappa_{\text{eff}}}\cosh(\nu(s)z)+\frac{1}{\sigma_{\text{eff}}}\cosh(\nu(s))\cosh(\nu(s)z)\right.\\ &\quad\left.-\frac{1}{\sigma_{\text{eff}}}\sinh(\nu(s))\sinh(\nu(s)z)\right].\end{aligned}$$

- Some trigonometric manipulations give us the following final form

$$\boxed{\frac{\widetilde{\Phi}^{\text{neg}}_{s\text{-}e}(z,s)}{I_{\text{app}}(s)} = \frac{L^{\text{neg}}\left[\sigma^{\text{neg}}_{\text{eff}}\cosh(\nu^{\text{neg}}(s)z)+\kappa^{\text{neg}}_{\text{eff}}\cosh(\nu^{\text{neg}}(s)(z-1))\right]}{A\sigma^{\text{neg}}_{\text{eff}}\kappa^{\text{neg}}_{\text{eff}}\nu^{\text{neg}}(s)\sinh(\nu^{\text{neg}}(s))}.}$$

- Finding $\widetilde{\Phi}_{s\text{-}e}(z,s)/I_{\text{app}}(s)$ is key to unlocking all other transfer functions.
- We now proceed to find all other negative-electrode transfer functions very quickly.
- We can now write

$$\frac{J(z,s)}{I_{\text{app}}(s)} = \frac{J(z,s)}{\widetilde{\Phi}_{s\text{-}e}(z,s)}\frac{\widetilde{\Phi}_{s\text{-}e}(z,s)}{I_{\text{app}}(s)} = \frac{\nu^2(s)}{a_sFL^2\left(\frac{1}{\kappa_{\text{eff}}}+\frac{1}{\sigma_{\text{eff}}}\right)}\frac{\widetilde{\Phi}_{s\text{-}e}(z,s)}{I_{\text{app}}(s)}.$$

- Expanding gives,

$$\boxed{\frac{J^{\text{neg}}(z,s)}{I_{\text{app}}(s)} = \nu^{\text{neg}}(s)\frac{\sigma^{\text{neg}}_{\text{eff}}\cosh(\nu^{\text{neg}}(s)z)+\kappa^{\text{neg}}_{\text{eff}}\cosh(\nu^{\text{neg}}(s)(z-1))}{a^{\text{neg}}_sFL^{\text{neg}}A(\kappa^{\text{neg}}_{\text{eff}}+\sigma^{\text{neg}}_{\text{eff}})\sinh(\nu^{\text{neg}}(s))}.}$$

- Using this result, we can also write

$$\frac{\widetilde{C}_{s,e}(z,s)}{I_{\text{app}}(s)} = \frac{\widetilde{C}_{s,e}(z,s)}{J(z,s)}\frac{J(z,s)}{I_{\text{app}}(s)} = \frac{R_s}{D_s}\left[\frac{1}{1-R_s\sqrt{s/D_s}\coth(R_s\sqrt{s/D_s})}\right]\frac{J(z,s)}{I_{\text{app}}(s)}.$$

- Expanding, we get our final form:

$$\boxed{\begin{aligned}\frac{\widetilde{C}_{s,e}^{\text{neg}}(z,s)}{I_{\text{app}}(s)} &= \left[\frac{\sigma_{\text{eff}}^{\text{neg}}\cosh(\nu^{\text{neg}}(s)z) + \kappa_{\text{eff}}^{\text{neg}}\cosh(\nu^{\text{neg}}(s)(z-1))}{a_s^{\text{neg}} F L^{\text{neg}} A D_s^{\text{neg}}(\kappa_{\text{eff}}^{\text{neg}} + \sigma_{\text{eff}}^{\text{neg}})\sinh(\nu^{\text{neg}}(s))}\right] \times \\ &\qquad \left[\frac{R_s^{\text{neg}}\nu^{\text{neg}}(s)}{1 - R_s^{\text{neg}}\sqrt{s/D_s^{\text{neg}}}\coth(R_s^{\text{neg}}\sqrt{s/D_s^{\text{neg}}})}\right].\end{aligned}}$$

- Finally, we wish to develop a transfer function for $\phi_s(z,t)$.
- Recall the differential equation that governs ϕ_s:

$$\frac{\sigma_{\text{eff}}}{L^2}\frac{\partial^2}{\partial z^2}\phi_s = a_s F j.$$

  - Taking Laplace transforms, we expect to have to perform a double integral of $J(z,s)$ to arrive at the transfer function we want.
  - We must also add back in any constants that may have disappeared from the original relationship via differentiation.

- We begin by defining $i_s(z,t)$ [A m^{-2}] to be the electronic current that flows through the solid at any z location.
  - The PDE for $i_s(z,t)$ is: $-\dfrac{1}{L}\dfrac{\varepsilon_s \partial i_s(z,t)}{\partial z} = a_s F j(z,t)$.
  - We have limiting cases $\varepsilon_s i_s(0,t) = i_{\text{app}}(t)/A$ and $i_s(1,t) = 0$.

- The transfer function for $I_s(z,s)$ with respect to the input current can then be found as:

$$\varepsilon_s \frac{I_s(z,s)}{I_{\text{app}}(s)} = \frac{1}{A} - a_s F L \int_0^z \frac{J(z',s)}{I_{\text{app}}(s)}\,\mathrm{d}z'$$

$$= \frac{\sigma_{\text{eff}}\left(\sinh(\nu(s)) - \sinh(z\nu(s))\right) - \kappa_{\text{eff}}\sinh((z-1)\nu(s))}{A(\kappa_{\text{eff}} + \sigma_{\text{eff}})\sinh(\nu(s))},$$

where we have solved the integral using Mathematica.

- As a test, note that $\varepsilon_s \dfrac{I_s(0,s)}{I_{\text{app}}(s)} = \dfrac{1}{A}$ and $\dfrac{I_s(1,s)}{I_{\text{app}}(s)} = 0$, as we expect.
- We now wish to find $\phi_s(z,t)$ from $i_s(z,t)$.
  - The differential equation we wish to use annihilates the value of $\phi_s(0,t)$ which cannot be solved by directly integrating $i_s(z,t)$.
  - So, we define $\tilde{\phi}_s(z,t) = \phi_s(z,t) - \phi_s(0,t)$ and proceed.
- We compute $\tilde{\phi}_s(z,t)$ by integrating $i_s(z,t)$:

$$\frac{\widetilde{\Phi}_s(z,s)}{I_{\text{app}}(s)} = -\frac{L\varepsilon_s}{\sigma_{\text{eff}}}\int_0^z \frac{I_s(\zeta,s)}{I_{\text{app}}(s)}\,\mathrm{d}\zeta.$$

- We again lean very heavily on Mathematica to find

$$\boxed{\begin{aligned}\frac{\widetilde{\Phi}_s^{\text{neg}}(z,s)}{I_{\text{app}}(s)} = -L^{\text{neg}}\Bigg[&\frac{\kappa_{\text{eff}}^{\text{neg}}\left(\cosh(\nu^{\text{neg}}(s)) - \cosh((z-1)\nu^{\text{neg}}(s))\right)}{A\sigma_{\text{eff}}^{\text{neg}}(\kappa_{\text{eff}}^{\text{neg}} + \sigma_{\text{eff}}^{\text{neg}})\nu^{\text{neg}}(s)\sinh(\nu^{\text{neg}}(s))}\\ &+ \frac{\sigma_{\text{eff}}^{\text{neg}}\left(1 - \cosh(z\nu^{\text{neg}}(s)) + z\nu^{\text{neg}}(s)\sinh(\nu^{\text{neg}}(s))\right)}{A\sigma_{\text{eff}}^{\text{neg}}(\kappa_{\text{eff}}^{\text{neg}} + \sigma_{\text{eff}}^{\text{neg}})\nu^{\text{neg}}(s)\sinh(\nu^{\text{neg}}(s))}\Bigg].\end{aligned}}$$

- As a test, note that $\dfrac{\widetilde{\Phi}_s(0,s)}{I_{\text{app}}(s)} = 0$, as we expect.
- Because, for a cell, we define $\phi_s(x,t)|_{x=0} = 0$, $\tilde{\phi}_s(z,t) = \phi_s(z,t)$ for the negative electrode.
- It's slightly more complicated for the positive electrode, as we will see.

6.4: Positive-electrode transfer functions

- So far, we have focused on negative-electrode variables.
- We now derive transfer functions for the positive-electrode variables.
- Starting with $\widetilde{\Phi}_{s\text{-}e}(z,s)$, the derivation for the positive electrode remains unchanged up until the point where we find that

$$\frac{\partial^2\widetilde{\Phi}_{s\text{-}e}(z,s)}{\partial z^2} - \nu^2(s)\widetilde{\Phi}_{s\text{-}e}(z,s) = 0.$$

- However, the boundary conditions are different. To be careful, we write them in terms of x rather than z:

$$\sigma_{\text{eff}}\left.\frac{\partial\widetilde{\Phi}_{s\text{-}e}(x,s)}{\partial x}\right|_{x=L^{\text{tot}}} = -\kappa_{\text{eff}}\left.\frac{\partial\widetilde{\Phi}_{s\text{-}e}(x,s)}{\partial x}\right|_{x=L^{\text{tot}}-L^{\text{pos}}} = \frac{-I_{\text{app}}(s)}{A}.$$

- As with the negative electrode, we define $z=0$ at current-collector boundary and $z=1$ at the separator boundary. That gives

$$x = L^{\text{tot}} - zL^{\text{pos}}.$$

- To re-write these boundary conditions in terms of z, note that

$$\frac{\partial\widetilde{\Phi}_{s\text{-}e}}{\partial z} = \frac{\partial\widetilde{\Phi}_{s\text{-}e}}{\partial x}\frac{\partial x}{\partial z} = -L^{\text{pos}}\frac{\partial\widetilde{\Phi}_{s\text{-}e}}{\partial x}.$$

- This allows us to write

$$\frac{\sigma_{\text{eff}}}{L^{\text{pos}}}\left.\frac{\partial\widetilde{\Phi}_{s\text{-}e}(z,s)}{\partial z}\right|_{z=0} = \frac{-\kappa_{\text{eff}}}{L^{\text{pos}}}\left.\frac{\partial\widetilde{\Phi}_{s\text{-}e}(z,s)}{\partial z}\right|_{z=1} = \frac{+I_{\text{app}}(s)}{A}.$$

- Sign changes cause k_1 and k_2 to have equal magnitude but opposite sign from previous result.
- Therefore, for the positive electrode,

$$\boxed{\frac{\widetilde{\Phi}^{\text{pos}}_{s\text{-}e}(z,s)}{I_{\text{app}}(s)} = \frac{-L^{\text{pos}}\left[\sigma^{\text{pos}}_{\text{eff}}\cosh(\nu^{\text{pos}}(s)z) + \kappa^{\text{pos}}_{\text{eff}}\cosh(\nu^{\text{pos}}(s)(z-1))\right]}{A\sigma^{\text{pos}}_{\text{eff}}\kappa^{\text{pos}}_{\text{eff}}\nu^{\text{pos}}(s)\sinh(\nu^{\text{pos}}(s))},}$$

- We can compute $\Phi_{s\text{-}e}^{\text{pos}}(z,s) = \widetilde{\Phi}_{s\text{-}e}^{\text{pos}}(z,s) + U_{\text{ocp}}^{\text{pos}}(c_{s,0}^{\text{pos}})$.

- Likewise, since everything depends on $\widetilde{\Phi}_{s\text{-}e}(z,s)$,

$$\boxed{\frac{J^{\text{pos}}(z,s)}{I_{\text{app}}(s)} = -\nu^{\text{pos}}(s)\frac{\sigma_{\text{eff}}^{\text{pos}}\cosh(\nu^{\text{pos}}(s)z) + \kappa_{\text{eff}}^{\text{pos}}\cosh(\nu^{\text{pos}}(s)(z-1))}{a_s^{\text{pos}}FL^{\text{pos}}A(\kappa_{\text{eff}}^{\text{pos}} + \sigma_{\text{eff}}^{\text{pos}})\sinh(\nu^{\text{pos}}(s))}.}$$

and

$$\boxed{\begin{aligned}\frac{\widetilde{C}_{s,e}^{\text{pos}}(z,s)}{I_{\text{app}}(s)} = -&\left[\frac{\sigma_{\text{eff}}^{\text{pos}}\cosh(\nu^{\text{pos}}(s)z) + \kappa_{\text{eff}}^{\text{pos}}\cosh(\nu^{\text{pos}}(s)(z-1))}{a_s^{\text{pos}}FL^{\text{pos}}AD_s^{\text{pos}}(\kappa_{\text{eff}}^{\text{pos}} + \sigma_{\text{eff}}^{\text{pos}})\sinh(\nu^{\text{pos}}(s))}\right]\times\\ &\left[\frac{R_s^{\text{pos}}\nu^{\text{pos}}(s)}{1 - R_s^{\text{pos}}\sqrt{s/D_s^{\text{pos}}})\coth(R_s^{\text{pos}}\sqrt{s/D_s^{\text{pos}}})}\right].\end{aligned}}$$

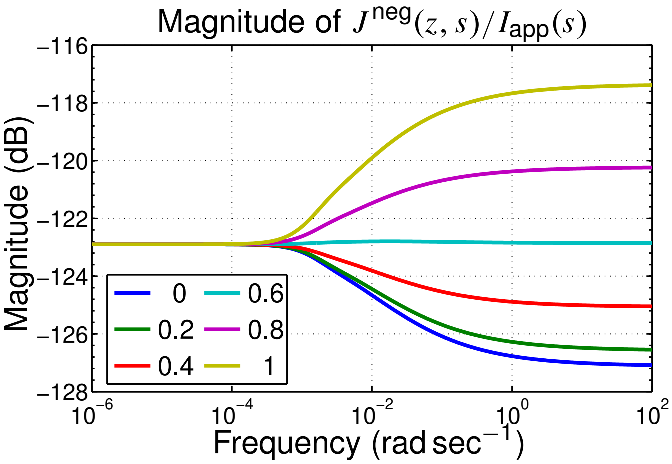
- We can compute $C_{s,e}(z,s) = \widetilde{C}_{s,e}(z,s) + c_{s,0}$, where $c_{s,0}$ is the linearization set-point value for the positive electrode.

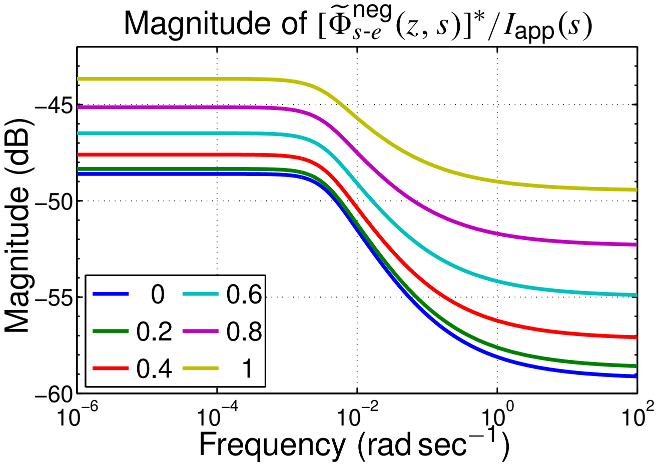
- Finally,

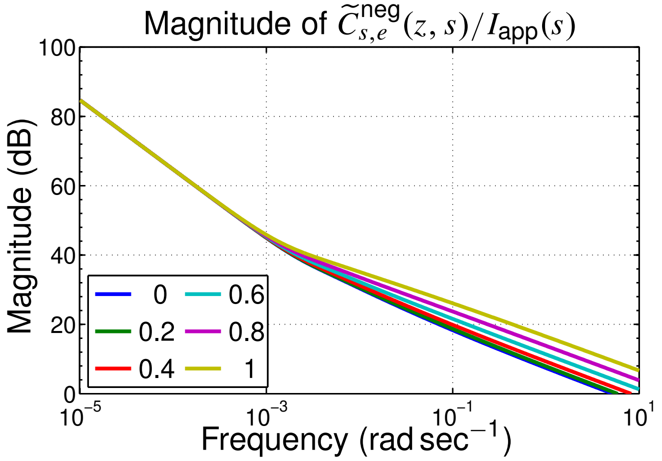
$$\boxed{\begin{aligned}\frac{\widetilde{\Phi}_s^{\text{pos}}(z,s)}{I_{\text{app}}(s)} = L^{\text{pos}}&\left[\frac{\kappa_{\text{eff}}^{\text{pos}}\left(\cosh(\nu^{\text{pos}}(s)) - \cosh((z-1)\nu^{\text{pos}}(s))\right)}{A\sigma_{\text{eff}}^{\text{pos}}(\kappa_{\text{eff}}^{\text{pos}} + \sigma_{\text{eff}}^{\text{pos}})\nu^{\text{pos}}(s)\sinh(\nu^{\text{pos}}(s))}\right.\\ &\left.+\frac{\sigma_{\text{eff}}^{\text{pos}}\left(1 - \cosh(z\nu^{\text{pos}}(s)) + z\nu^{\text{pos}}(s)\sinh(\nu^{\text{pos}}(s))\right)}{A\sigma_{\text{eff}}^{\text{pos}}(\kappa_{\text{eff}}^{\text{pos}} + \sigma_{\text{eff}}^{\text{pos}})\nu^{\text{pos}}(s)\sinh(\nu^{\text{pos}}(s))}\right].\end{aligned}}$$

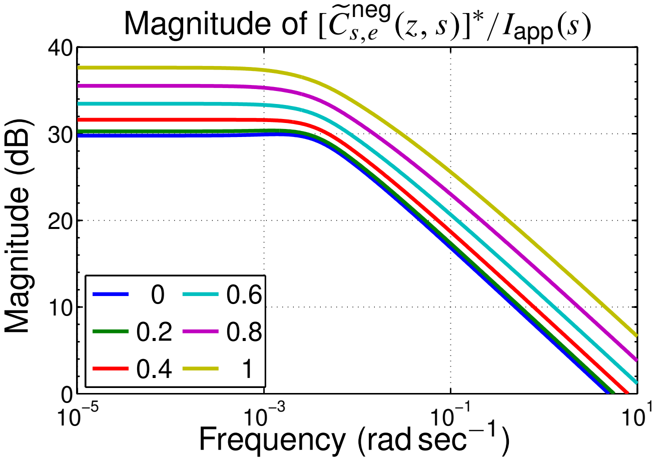
- We could compute $\Phi_s(z,s) = \widetilde{\Phi}_s(z,s) + \Phi_s(0,s)$ if we knew what $\Phi_s(0,s)$ was. Unfortunately, we do not, at least so far.
- We do know that it is the overall cell voltage, which we shall learn how to compute later on.

- These transfer functions are mathematically very messy and have an infinite number of poles and zeros (and we're just getting started!).
- But, a small state-space model can very closely approximate them.
- As a clue that we may be able to do this, we first see some Bode magnitude plots, which look pretty normal, for the most part.

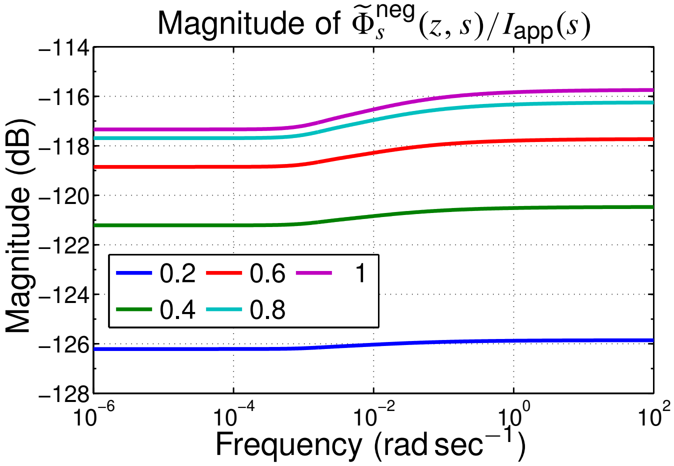








- The DRA from notes Ch. 5 is able to convert these transfer functions into a low-order state-space model that works very well.



6.5: A one-dimensional model of $c_e(x,t)$: first steps

- The goal of the next sections is to provide an ODE solution to the PDE equation of lithium concentration in the electrolyte:

$$\frac{\partial \varepsilon_e(x)c_e(x,t)}{\partial t} = \nabla \cdot (D_{e,\text{eff}}(x)\nabla c_e(x,t)) + a_s(x)(1-t_+^0)j$$

where the boundary conditions are,

$$\frac{\partial c_e(0,t)}{\partial x} = 0 \qquad \text{and} \qquad \frac{\partial c_e(L^{\text{tot}},t)}{\partial x} = 0,$$

and the initial distribution is $c_e(x,0) = c_{e,0}$.

ASSUME: We assume that $D_{e,\text{eff}}$ and ε_e are uniform (constant) over each region of the cell, but may have different values in the negative electrode, separator, and positive electrode.

- We also define $\tilde{c}_e(x,t) = c_e(x,t) - c_{e,0}$. This converts the PDE into one that can be solved via transfer functions

$$\frac{\partial \varepsilon_e(x)\tilde{c}_e(x,t)}{\partial t} = \nabla \cdot (D_{e,\text{eff}}(x)\nabla \tilde{c}_e(x,t)) + a_s(x)(1-t_+^0)j$$

where the boundary conditions are,

$$\frac{\partial \tilde{c}_e(0,t)}{\partial x} = 0 \qquad \text{and} \qquad \frac{\partial \tilde{c}_e(L^{\text{tot}},t)}{\partial x} = 0,$$

and the initial distribution is $\tilde{c}_e(x,0) = 0$.

- We desire to show that the reduced-order solution involves first-order ordinary-differential-equation "modes," each having the form:

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{c}_{e,n} = -\lambda_n \tilde{c}_{e,n}(t) + j_n(t),$$

where the electrolyte concentration is the weighted summation:

$$\tilde{c}_e(x,t) = \sum_{n=0}^{\infty} \tilde{c}_{e,n}(t)\Psi(x;\lambda_n).$$

- We then derive a transfer-function $\widetilde{C}_e(x,s)/I_{\text{app}}(s)$ based on $\tilde{c}_e(x,t)$.

Sturm–Liouville problem and Green's identity

- In the course of solving for the transfer function, we'll find that we can write the PDE in terms of a Sturm–Liouville problem, which is an ordinary differential equation having the general form

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[p(x)\frac{\mathrm{d}\Psi(x)}{\mathrm{d}x}\right] + q(x)\Psi(x) + \lambda w(x)\Psi(x) = 0,$$

over the finite closed interval $[a, b]$.

  - We don't prove it here, but it is important to note that the solutions to the Sturm–Liouville problem give real eigenvalues λ_n that can be ordered such that $\lambda_1 < \lambda_2 < \lambda_3 < \cdots < \lambda_n < \cdots \to \infty$.
  - Corresponding to each eigenvalue λ_n is a unique (up to a normalization constant) eigenfunction $\Psi(x; \lambda_n)$ that has exactly $n - 1$ zero crossings in (a, b).
  - The eigenfunction $\Psi(x; \lambda_n)$ is called the nth fundamental solution satisfying the regular Sturm–Liouville problem.
  - The normalized eigenfunctions form an orthonormal basis with respect to the weighting function $w(x)$

$$\int_a^b \Psi(x; \lambda_n)\Psi(x; \lambda_m)w(x)\,\mathrm{d}x = \delta_{mn},$$

where $\delta_{mn} = 0$ if $m \neq n$ and $\delta_{mn} = 1$ if $m = n$.

- Solving Sturm–Liouville problems requires Green's identity, which can be proven as follows: Define a linear operator, L,

$$L \equiv \frac{\mathrm{d}}{\mathrm{d}x}\left[p(x)\frac{\mathrm{d}}{\mathrm{d}x}\right] + q(x).$$

- The Sturm–Liouville can then be rewritten as,

$$L(\Psi) + \lambda w(x)\Psi = 0.$$

- For *any* two functions, v and u, we can write

$$L(v) = \frac{\mathrm{d}}{\mathrm{d}x}\left[p(x)\frac{\mathrm{d}v}{\mathrm{d}x}\right] + q(x)v$$

$$L(u) = \frac{\mathrm{d}}{\mathrm{d}x}\left[p(x)\frac{\mathrm{d}u}{\mathrm{d}x}\right] + q(x)u.$$

- Multiplying the first equation by u, the second equation by v, and subtracting gives,

$$\begin{aligned} uL(v) - vL(u) &= u\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}v}{\mathrm{d}x}\right) + uqv - v\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}u}{\mathrm{d}x}\right) - vqu \\ &= u\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}v}{\mathrm{d}x}\right) - v\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}u}{\mathrm{d}x}\right). \end{aligned}$$

- We integrate by parts to get

$$\begin{aligned} &\int_a^b \left[u\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}v}{\mathrm{d}x}\right) - v\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}u}{\mathrm{d}x}\right)\right]\,\mathrm{d}x \\ &\qquad = \int_a^b u\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}v}{\mathrm{d}x}\right)\,\mathrm{d}x - \int_a^b v\frac{\mathrm{d}}{\mathrm{d}x}\left(p\frac{\mathrm{d}u}{\mathrm{d}x}\right)\,\mathrm{d}x \\ &\qquad = \left[p\frac{\mathrm{d}v}{\mathrm{d}x}u\bigg|_a^b - \int_a^b p\left(\frac{\mathrm{d}u}{\mathrm{d}x}\right)\left(\frac{\mathrm{d}v}{\mathrm{d}x}\right)\,\mathrm{d}x\right] \\ &\qquad\qquad - \left[p\frac{\mathrm{d}u}{\mathrm{d}x}v\bigg|_a^b - \int_a^b p\left(\frac{\mathrm{d}u}{\mathrm{d}x}\right)\left(\frac{\mathrm{d}v}{\mathrm{d}x}\right)\,\mathrm{d}x\right]. \end{aligned}$$

- The integrals in the RHS cancel, yielding Green's identity,

$$\int_a^b [uL(v) - vL(u)]\,\mathrm{d}x = p\left(u\frac{\mathrm{d}v}{\mathrm{d}x} - v\frac{\mathrm{d}u}{\mathrm{d}x}\right)\bigg|_a^b.$$

Setting up the solution

- We use the "separation-of-variables" approach to "solve" the PDE.

  - We first find an infinite series of eigenfunctions and eigenvalues.
  - We then use only the first few terms of the expansion.

- We begin by solving the homogeneous PDE (with $j = 0$).
  - Solving the homogeneous boundary value problem gives the eigenvalues λ_n and the eigenfunctions $\Psi(x; \lambda_n)$ that are used for both the homogeneous and inhomogeneous solutions.
  - We then generalize this solution to find the forced PDE solution.

- The homogeneous problem is given by,

$$\frac{\partial \tilde{c}_e(x,t)}{\partial t} = \frac{1}{\varepsilon_e(x)} \frac{\partial}{\partial x} D_{e,\text{eff}}(x) \frac{\partial \tilde{c}_e(x,t)}{\partial x},$$

with the same boundary conditions and initial conditions as before.

- There are also internal boundary conditions where the three regions of the cell join. First, we assume continuity:

$$\tilde{c}_e((L^{\text{neg}})^-, t) = \tilde{c}_e((L^{\text{neg}})^+, t)$$

$$\tilde{c}_e((L^{\text{neg}} + L^{\text{sep}})^-, t) = \tilde{c}_e((L^{\text{neg}} + L^{\text{sep}})^+, t).$$

- We also need to say something about the slope of the concentration function on either side of an internal boundary.
- Notice what happens when we use the product rule on the RHS of the PDE:

$$\frac{\partial}{\partial x} D_{e,\text{eff}}(x) \frac{\partial \tilde{c}_e(x,t)}{\partial x} = D_{e,\text{eff}}(x) \frac{\partial^2 \tilde{c}_e(x,t)}{\partial x^2} + \left(\frac{\partial \tilde{c}_e(x,t)}{\partial x}\right)\left(\frac{\partial D_{e,\text{eff}}(x)}{\partial x}\right).$$

- There is no physical problem with the first term in this expression, but the second term has Dirac delta functions at region boundaries in general because of the discontinuity in $D_{e,\text{eff}}(x)$.

- This doesn't make physical sense, so we constrain the solution to zero out these delta functions

$$\frac{\partial}{\partial x} D_{e,\text{eff}}(x) \frac{\partial \tilde{c}_e(x,t)}{\partial x} = \lim_{x^+ - x^- \to 0} \frac{D_{e,\text{eff}}(x^+)\frac{\partial \tilde{c}_e(x^+,t)}{\partial x} - D_{e,\text{eff}}(x^-)\frac{\partial \tilde{c}_e(x^-,t)}{\partial x}}{x^+ - x^-} = 0$$

at the boundaries where $x = L^{\text{neg}}$ or $x = L^{\text{neg}} + L^{\text{sep}}$. This gives:

$$D_{e,\text{eff}}^{\text{neg}} \frac{\partial \tilde{c}_e((L^{\text{neg}})^-,t)}{\partial x} = D_{e,\text{eff}}^{\text{sep}} \frac{\partial \tilde{c}_e((L^{\text{neg}})^+,t)}{\partial x}$$

$$D_{e,\text{eff}}^{\text{sep}} \frac{\partial \tilde{c}_e((L^{\text{neg}} + L^{\text{sep}})^-,t)}{\partial x} = D_{e,\text{eff}}^{\text{pos}} \frac{\partial \tilde{c}_e((L^{\text{neg}} + L^{\text{sep}})^+,t)}{\partial x}.$$

6.6: Solution to the homogeneous PDE

- The separation-of-variables method assumes that the the solution can be broken up into the product of a function of time only, $h(t)$, and a function of position only, $\Psi(x)$:

$$\tilde{c}_e(x,t) = h(t)\Psi(x).$$

- Substituting the assumed form into the original PDE gives

$$\frac{\mathrm{d}h(t)}{\mathrm{d}t}\Psi(x) = \frac{1}{\varepsilon_e(x)}\frac{\partial}{\partial x}D_{e,\text{eff}}(x)h(t)\frac{\partial \Psi(x)}{\partial x}.$$

- We separate time-dependent variables on one side, and position dependent variables on the other,

$$\frac{1}{h(t)}\frac{\mathrm{d}h(t)}{\mathrm{d}t} = \frac{1}{\varepsilon_e(x)\Psi(x)}\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \Psi(x)}{\partial x}.$$

- Since the LHS is a function of time only, and the RHS is a function of position only, and they are equal for all time and all position, they must both be equal to a constant.

$$\frac{\mathrm{d}h(t)}{\mathrm{d}t} = -\lambda h(t)$$

$$\frac{\partial}{\partial x}D_{e,\text{eff}}\frac{\partial \Psi(x)}{\partial x} = -\lambda\varepsilon_e(x)\Psi(x).$$

- Note that there are an infinite number of λ that solve these equations.

- So, we rethink the notation and change $h(t) \mapsto h(t;\lambda)$ and change $\Psi(t) \mapsto \Psi(t;\lambda)$. Rewriting,

$$\frac{\mathrm{d}h(t;\lambda)}{\mathrm{d}t} = -\lambda h(t;\lambda)$$

$$\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \Psi(x;\lambda)}{\partial x} = -\lambda\varepsilon_e(x)\Psi(x;\lambda).$$

- The solution to the first equation has the form,

$$h(t;\lambda)=h(0;\lambda)e^{-\lambda t}.$$

- Each of the eigenfunctions $\Psi(x;\lambda)$ is divided into three parts: one for each cell region.
- For the negative electrode, we have (where k_1 and k_2 are (possibly) functions of λ, but this dependence has been omitted for brevity),

$$\Psi^{\text{neg}}(x;\lambda)=k_1\cos(\sqrt{\lambda\varepsilon_e^{\text{neg}}/D_{e,\text{eff}}^{\text{neg}}}x)+k_2\sin(\sqrt{\lambda\varepsilon_e^{\text{neg}}/D_{e,\text{eff}}^{\text{neg}}}x).$$

- The boundary condition at $x=0$ eliminates the $\sin(\cdot)$ term:

$$\Psi^{\text{neg}}(x;\lambda)=k_1\cos\left(\sqrt{\lambda\varepsilon_e^{\text{neg}}/D_{e,\text{eff}}^{\text{neg}}}x\right).$$

- For the separator, we have

$$\Psi^{\text{sep}}(x;\lambda)=k_3\cos\left(\sqrt{\lambda\varepsilon_e^{\text{sep}}/D_{e,\text{eff}}^{\text{sep}}}x\right)+k_4\sin\left(\sqrt{\lambda\varepsilon_e^{\text{sep}}/D_{e,\text{eff}}^{\text{sep}}}x\right).$$

- For this region, the $\sin(\cdot)$ term is not automatically eliminated, and the two functions must scaled so that the interior boundary conditions are met automatically.
  - For continuity, letting

    $$\omega_1=L^{\text{neg}}\sqrt{\lambda\varepsilon_e^{\text{neg}}/D_{e,\text{eff}}^{\text{neg}}}\qquad\text{and}\qquad\omega_2=L^{\text{neg}}\sqrt{\lambda\varepsilon_e^{\text{sep}}/D_{e,\text{eff}}^{\text{sep}}},$$

    we have

    $$k_1\cos(\omega_1)=k_3\cos(\omega_2)+k_4\sin(\omega_2).$$

  - For the first derivative criterion:

$$D_{e,\text{eff}}^{\text{neg}}\left[-k_1\frac{\omega_1}{L^{\text{neg}}}\sin(\omega_1)\right]=D_{e,\text{eff}}^{\text{sep}}\left[-k_3\frac{\omega_2}{L^{\text{neg}}}\sin(\omega_2)+k_4\frac{\omega_2}{L^{\text{neg}}}\cos(\omega_2)\right].$$

- We have two equations and two unknowns (k_3 and k_4), which can be solved in terms of k_1

$$\begin{bmatrix} \cos(\omega_2) & \sin(\omega_2) \\ -D_{e,\text{eff}}^{\text{sep}}\omega_2\sin(\omega_2) & D_{e,\text{eff}}^{\text{sep}}\omega_2\cos(\omega_2) \end{bmatrix} \begin{bmatrix} k_3 \\ k_4 \end{bmatrix} = k_1 \begin{bmatrix} \cos(\omega_1) \\ -D_{e,\text{eff}}^{\text{neg}}\omega_1\sin(\omega_1) \end{bmatrix}.$$

- Finally, for the positive electrode, we have

$$\Psi^{\text{pos}}(x;\lambda) = k_5\cos\left(\sqrt{\lambda\varepsilon_e^{\text{pos}}/D_{e,\text{eff}}^{\text{pos}}}x\right) + k_6\sin\left(\sqrt{\lambda\varepsilon_e^{\text{pos}}/D_{e,\text{eff}}^{\text{pos}}}x\right).$$

- For continuity, letting

$$\omega_3 = (L^{\text{neg}} + L^{\text{sep}})\sqrt{\frac{\lambda\varepsilon_e^{\text{sep}}}{D_{e,\text{eff}}^{\text{sep}}}} \quad \text{and} \quad \omega_4 = (L^{\text{neg}} + L^{\text{sep}})\sqrt{\frac{\lambda\varepsilon_e^{\text{pos}}}{D_{e,\text{eff}}^{\text{pos}}}},$$

we have

$$k_3\cos(\omega_3) + k_4\sin(\omega_3) = k_5\cos(\omega_4) + k_6\sin(\omega_4).$$

- For the first derivative criterion:

$$D_{e,\text{eff}}^{\text{sep}}\left[-k_3\frac{\omega_3}{L^{\text{neg}}+L^{\text{sep}}}\sin(\omega_3) + k_4\frac{\omega_3}{L^{\text{neg}}+L^{\text{sep}}}\cos(\omega_3)\right]$$
$$= D_{e,\text{eff}}^{\text{pos}}\left[-k_5\frac{\omega_4}{L^{\text{neg}}+L^{\text{sep}}}\sin(\omega_4) + k_6\frac{\omega_4}{L^{\text{neg}}+L^{\text{sep}}}\cos(\omega_4)\right].$$

- We have two equations and two unknowns (k_5 and k_6), which can be solved in terms of k_3 and k_4

$$\begin{bmatrix} \cos(\omega_4) & \sin(\omega_4) \\ -D_{e,\text{eff}}^{\text{pos}}\omega_4\sin(\omega_4) & D_{e,\text{eff}}^{\text{pos}}\omega_4\cos(\omega_4) \end{bmatrix} \begin{bmatrix} k_5 \\ k_6 \end{bmatrix}$$
$$= \begin{bmatrix} \cos(\omega_3) & \sin(\omega_3) \\ -D_{e,\text{eff}}^{\text{sep}}\omega_3\sin(\omega_3) & D_{e,\text{eff}}^{\text{sep}}\omega_3\cos(\omega_3) \end{bmatrix} \begin{bmatrix} k_3 \\ k_4 \end{bmatrix}.$$

- So, overall we have

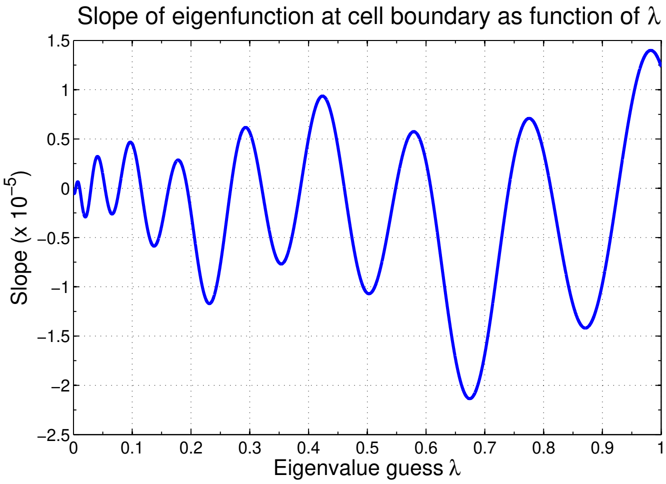
$$\Psi(x;\lambda) = \begin{cases} \Psi^{\text{neg}}(x;\lambda), & 0 \le x < L^{\text{neg}}; \\ \Psi^{\text{sep}}(x;\lambda), & L^{\text{neg}} \le x < L^{\text{neg}} + L^{\text{sep}}; \\ \Psi^{\text{pos}}(x;\lambda), & L^{\text{neg}} + L^{\text{sep}} \le x \le L^{\text{tot}}. \end{cases}$$

- By Sturm–Liouville theory, we know that we can choose the different eigenfunctions to be orthonormal with respect to the weighting function $\varepsilon_e(x)$ by selecting k_1 such that

$$\int_0^{L^{\text{tot}}} \Psi^2(x;\lambda)\varepsilon_e(x)\,\mathrm{d}x = 1.$$

- The final boundary condition $\partial\Psi(L^{\text{tot}};\lambda)/\partial x = 0$ imposes the condition that allows us to solve for λ_n.

- Generally, this cannot be done in closed form. So, we use numeric methods to search an interval for zero crossings of $\mathrm{d}\Psi(L^{\text{tot}};\lambda)/\mathrm{d}x$ as a function of λ. An example is shown.



- We denote the ordered set of eigenvalues as $\{\lambda_n\}$. Then, the solution to the homogeneous problem is the superposition,

$$\boxed{\tilde{c}_e(x,t) = \sum_{n=0}^{\infty} h(0;\lambda_n)\Psi\,(x;\lambda_n)\,e^{-\lambda_n t}.}$$

6.7: Solution to the forced PDE

- We now generalize the solution to the inhomogeneous case to solve

$$\frac{\partial \tilde{c}_e(x,t)}{\partial t} = \frac{1}{\varepsilon_e(x)}\frac{\partial}{\partial x} D_{e,\text{eff}}(x)\frac{\partial \tilde{c}_e(x,t)}{\partial x} + \frac{a_s(x)(1-t_+^0)}{\varepsilon_e(x)} j(x,t).$$

- Our approach is to transform $\tilde{c}_e(x,t)$ into a series expansion using the eigenfunctions of the homogeneous solution, $\Psi(x;\lambda_n)$ as a basis set.

- Any piecewise smooth function can be expanded in terms of the eigenfunctions.

$$\tilde{c}_e(x,t) = \sum_{n=0}^{\infty} \tilde{c}_{e,n}(t)\Psi(x;\lambda_n),$$

  where $\tilde{c}_{e,n}(t)$ are the generalized Fourier coefficients of $\tilde{c}_e(x,t)$.

- Taking the partial derivative of this equation with respect to time gives,

$$\frac{\partial \tilde{c}_e(x,t)}{\partial t} = \sum_{n=0}^{\infty} \frac{\mathrm{d}\tilde{c}_{e,n}(t)}{\mathrm{d}t}\Psi(x;\lambda_n).$$

- Substituting into the original PDE gives:

$$\sum_{n=0}^{\infty} \frac{\mathrm{d}\tilde{c}_{e,n}(t)}{\mathrm{d}t}\Psi(x;\lambda_n) = \frac{1}{\varepsilon_e(x)}\frac{\partial}{\partial x} D_{e,\text{eff}}(x)\frac{\partial \tilde{c}_e(x,t)}{\partial x} + \frac{a_s(x)(1-t_+^0)}{\varepsilon_e(x)} j(x,t).$$

- Therefore, to reduce the LHS of the above equation, we now multiply both sides by $\Psi(x;\lambda_m)\varepsilon_e(x)$ and integrate from 0 to L^{tot}.

$$\int_0^{L^{\text{tot}}} \sum_{n=0}^{\infty} \frac{\mathrm{d}\tilde{c}_{e,n}(t)}{\mathrm{d}t}\Psi(x;\lambda_n)\Psi(x;\lambda_m)\varepsilon_e(x)\,\mathrm{d}x$$

$$= \int_0^{L^{\text{tot}}} \Psi(x;\lambda_m)\frac{\partial}{\partial x} D_{e,\text{eff}}(x)\frac{\partial \tilde{c}_e(x,t)}{\partial x}\,\mathrm{d}x$$

$$+ \int_0^{L^{\text{tot}}} a_s(x)(1-t_+^0) j(x,t)\Psi(x;\lambda_m)\,\mathrm{d}x.$$

- Because $\int_0^{L^{\text{tot}}} \Psi(x;\lambda_n)\Psi(x;\lambda_m)\varepsilon_e(x)\,\mathrm{d}x = \delta_{mn}$, the integral on the left is non-zero only when $m = n$. Therefore,

$$\frac{\mathrm{d}\tilde{c}_{e,n}(t)}{\mathrm{d}t} = \int_0^{L^{\text{tot}}} \Psi(x;\lambda_n)\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \tilde{c}_e(x,t)}{\partial x}\,\mathrm{d}x + \int_0^{L^{\text{tot}}} a_s(x)(1-t_+^0)j(x,t)\Psi(x;\lambda_n)\,\mathrm{d}x. \qquad (6.1)$$

- We want to simplify the first term on the right hand side, and we do this by using Green's identity.
- Note that $\Psi(x;\lambda)$ are the solutions to a Sturm–Liouville problem with $p(x) = 1$, $q(x) = 0$, and $w(x) = \varepsilon_e(x)$.
- We focus again on the first term:

$$\int_0^{L^{\text{tot}}} \Psi(x;\lambda_n)\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \tilde{c}_e(x,t)}{\partial x}\,\mathrm{d}x.$$

- We use Green's identity with $v = \Psi(x)$ and let $u = \tilde{c}_e(x,t)$ and let $p = D_{e,\text{eff}}(x)$:

$$\int_0^{L^{\text{tot}}} \left[\tilde{c}_e(x,t)\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \Psi(x)}{\partial x} - \Psi(x;\lambda_n)\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \tilde{c}_e(x,t)}{\partial x}\right]\mathrm{d}x$$
$$= D_{e,\text{eff}}(x)\left(\tilde{c}_e(x,t)\frac{\partial \Psi(x;\lambda_n)}{\partial x} - \Psi(x;\lambda_n)\frac{\partial \tilde{c}_e(x,t)}{\partial x}\right)\Bigg|_0^{L^{\text{tot}}}.$$

- In our problem, the RHS goes to 0 because of boundary conditions

$$\left.\frac{\partial \Psi(x;\lambda_n)}{\partial x}\right|_{x\in\{0,L^{\text{tot}}\}} = \left.\frac{\partial \tilde{c}_e(x,t)}{\partial x}\right|_{x\in\{0,L^{\text{tot}}\}} = 0.$$

- Therefore,

$$\int_0^{L^{\text{tot}}} \tilde{c}_e(x,t)\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \Psi(x)}{\partial x}\mathrm{d}x = \int_0^{L^{\text{tot}}} \Psi(x;\lambda_n)\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \tilde{c}_e(x,t)}{\partial x}\mathrm{d}x.$$

- The LHS can be written as:

$$\int_0^{L^{\text{tot}}} \tilde{c}_e(x,t)\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \Psi(x)}{\partial x}\,\mathrm{d}x = -\lambda_n \int_0^{L^{\text{tot}}} \tilde{c}_e(x,t)\Psi(x;\lambda_n)\varepsilon_e(x)\,\mathrm{d}x,$$

because Ψ satisfies the homogeneous case:

$$\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \Psi(x)}{\partial x} + \lambda_n\varepsilon_e(x)\Psi_n = 0.$$

- Substituting, we get

$$\int_0^{L^{\text{tot}}} \Psi(x)\frac{\partial}{\partial x}D_{e,\text{eff}}(x)\frac{\partial \tilde{c}_e(x,t)}{\partial x}\,\mathrm{d}x = -\lambda_n \int_0^{L^{\text{tot}}} \tilde{c}_e(x,t)\Psi(x;\lambda_n)\varepsilon_e(x)\,\mathrm{d}x.$$

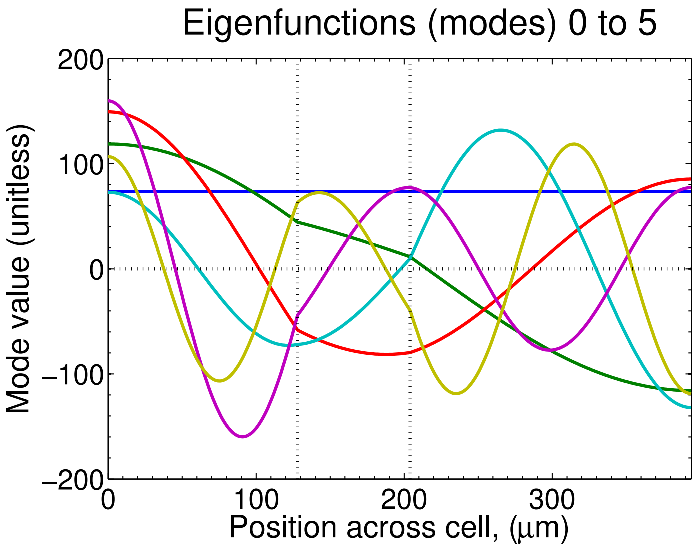
- Using this in Eq. (6.1),

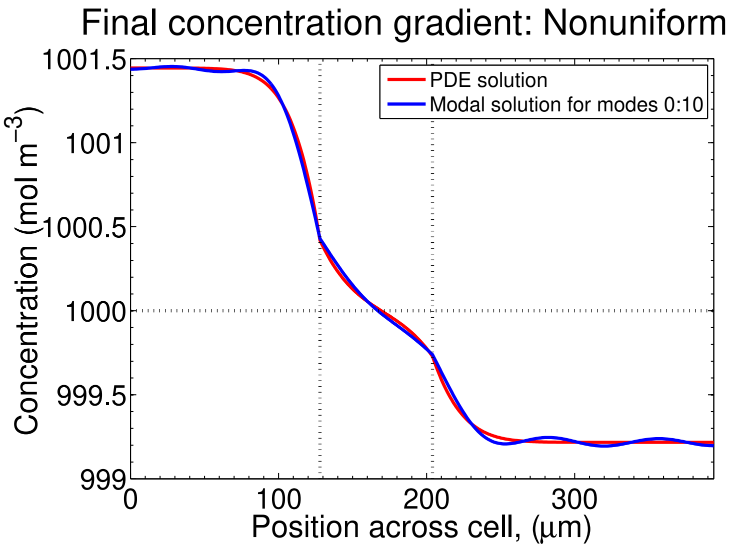
$$\begin{aligned}\frac{\mathrm{d}\tilde{c}_{e,n}(t)}{\mathrm{d}t} &= -\lambda_n \int_0^{L^{\text{tot}}} \tilde{c}_e(x,t)\Psi(x;\lambda_n)\varepsilon_e(x)\,\mathrm{d}x \\ &\qquad + \int_0^{L^{\text{tot}}} a_s(x)(1-t_+^0)j(x,t)\Psi_n(x)\,\mathrm{d}x \\ &= -\lambda_n\tilde{c}_{e,n}(t) + \underbrace{\int_0^{L^{\text{tot}}} a_s(x)(1-t_+^0)j(x,t)\Psi_n(x)\,\mathrm{d}x}_{j_n(t)}.\end{aligned}$$

Example of $c_e(x,t)$

- Consider a cell with the following properties, and apply a step current to the cell.

$$\begin{array}{lll} L^{\text{neg}} = 128\,\mu\text{m} & \varepsilon_e^{\text{neg}} = 0.357 & D_{e,\text{eff}}^{\text{neg}} = 1.60\times 10^{-11}\,\text{m}^2\,\text{s}^{-1} \\ L^{\text{sep}} = 76\,\mu\text{m} & \varepsilon_e^{\text{sep}} = 0.724 & D_{e,\text{eff}}^{\text{sep}} = 4.62\times 10^{-11}\,\text{m}^2\,\text{s}^{-1} \\ L^{\text{pos}} = 190\,\mu\text{m} & \varepsilon_e^{\text{pos}} = 0.444 & D_{e,\text{eff}}^{\text{pos}} = 2.22\times 10^{-11}\,\text{m}^2\,\text{s}^{-1} \end{array}$$





A transfer-function model for $\tilde{c}_e(x,t)$

- To compute $\tilde{c}_e(x,t)$ via transfer-function methods, we note that it is formed from a summation of $\tilde{c}_{e,n}(t)$ terms.
- We can compute $\tilde{c}_e(x,t)$ if we know $\tilde{c}_{e,n}(t)$, so we proceed by finding a transfer function for $\tilde{c}_{e,n}(t)$:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\tilde{c}_{e,n}(t) &= -\lambda_n \tilde{c}_{e,n}(t) + j_n(t)\\ s\widetilde{C}_{e,n}(s) &= -\lambda_n \widetilde{C}_{e,n}(s) + J_n(s)\\ \frac{\widetilde{C}_{e,n}(s)}{I_{\text{app}}(s)} &= \frac{1}{s+\lambda_n}\frac{J_n(s)}{I_{\text{app}}(s)},\end{aligned}$$

so we are going to need to find a transfer function for $j_n(t)$ first.

- We begin by writing,

$$\begin{aligned}j_n(t) &= \int_0^{L^{\text{tot}}} a_s(x)(1-t_+^0)\, j(x,t)\Psi(x;\lambda_n)\,\mathrm{d}x\\ &= \int_0^{L^{\text{neg}}} a_s^{\text{neg}}(1-t_+^0)\, j(x,t)\Psi(x;\lambda_n)\,\mathrm{d}x\end{aligned}$$

$$+\int_{L^{\text{neg}}+L^{\text{sep}}}^{L^{\text{tot}}} a_s^{\text{pos}}(1-t_+^0)j(x,t)\Psi(x;\lambda_n)\,\mathrm{d}x$$
$$= j_n^{\text{neg}}(t)+j_n^{\text{pos}}(t).$$

- Looking at the negative electrode first:

$$j_n^{\text{neg}}(t) = a_s^{\text{neg}}(1-t_+^0)\int_0^{L^{\text{neg}}} j(x,t)\Psi(x;\lambda_n)\,\mathrm{d}x$$
$$\frac{J_n^{\text{neg}}(s)}{I_{\text{app}}(s)} = a_s^{\text{neg}}(1-t_+^0)\int_0^{L^{\text{neg}}} \frac{J^{\text{neg}}(x/L^{\text{neg}},s)}{I_{\text{app}}(s)}\Psi(x;\lambda_n)\,\mathrm{d}x,$$

where
$$\frac{J^{\text{neg}}(z,s)}{I_{\text{app}}(s)}=\nu^{\text{neg}}(s)\left[\frac{\sigma_{\text{eff}}^{\text{neg}}\cosh(\nu^{\text{neg}}(s)z)+\kappa_{\text{eff}}^{\text{neg}}\cosh(\nu^{\text{neg}}(s)(z-1))}{a_s^{\text{neg}}FL^{\text{neg}}A(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})\sinh(\nu^{\text{neg}}(s))}\right].$$

- The transfer function is (computed in Mathematica)

$$\frac{J_n^{\text{neg}}(s)}{I_{\text{app}}(s)} = \frac{k_1(1-t_+^0)\omega_n^{\text{neg}}\sin(\omega_n^{\text{neg}})\left(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}}\cosh(\nu^{\text{neg}}(s))\right)\nu^{\text{neg}}(s)}{AF(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})\left((\omega_n^{\text{neg}})^2+(\nu^{\text{neg}}(s))^2\right)\sinh(\nu^{\text{neg}}(s))}$$
$$+\frac{k_1(1-t_+^0)\left(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}}\cos(\omega_n^{\text{neg}})\right)(\nu^{\text{neg}}(s))^2}{AF(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})\left((\omega_n^{\text{neg}})^2+(\nu^{\text{neg}}(s))\right)},$$

where $\omega_n^{\text{neg}} = L^{\text{neg}}\sqrt{\lambda_n\varepsilon_e^{\text{neg}}/D_{e,\text{eff}}^{\text{neg}}}$.

- Looking at the positive electrode now,

$$j_n^{\text{pos}}(t) = a_s^{\text{pos}}(1-t_+^0)\int_{L^{\text{tot}}-L^{\text{pos}}}^{L^{\text{tot}}} j(x,t)\Psi(x;\lambda_n)\,\mathrm{d}x$$
$$\frac{J_n^{\text{pos}}(s)}{I_{\text{app}}(s)} = a_s^{\text{pos}}(1-t_+^0)\int_{L^{\text{tot}}-L^{\text{pos}}}^{L^{\text{tot}}} \frac{J^{\text{pos}}((L^{\text{tot}}-x)/L^{\text{pos}},s)}{I_{\text{app}}(s)}\Psi(x;\lambda_n)\,\mathrm{d}x$$

where (noting negative sign because of positive electrode)
$$\frac{J^{\text{pos}}(z,s)}{I_{\text{app}}(s)}=-\nu^{\text{pos}}(s)\left[\frac{\sigma_{\text{eff}}^{\text{pos}}\cosh(\nu^{\text{pos}}(s)z)+\kappa_{\text{eff}}^{\text{pos}}\cosh(\nu^{\text{pos}}(s)(z-1))}{a_s^{\text{pos}}FL^{\text{pos}}A(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}})\sinh(\nu^{\text{pos}}(s))}\right].$$

- The transfer function is (computed in Mathematica)

$$\begin{aligned}
\frac{J_n^{\text{pos}}(s)}{I_{\text{app}}(s)} = {} & \frac{k_5(1-t_+^0)\omega_n^{\text{pos}}\sin(\omega_n^{\text{sep}})\left(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}}\cosh(\nu^{\text{pos}}(s))\right)\nu^{\text{pos}}(s)}{AF(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}})\left((\omega_n^{\text{pos}})^2+(\nu^{\text{pos}}(s))^2\right)\sinh(\nu^{\text{pos}}(s))} \\
& - \frac{k_5(1-t_+^0)\omega_n^{\text{pos}}\sin(\omega_n^{\text{tot}})\left(\sigma_{\text{eff}}^{\text{pos}}+\kappa_{\text{eff}}^{\text{pos}}\cosh(\nu^{\text{pos}}(s))\right)\nu^{\text{pos}}(s)}{AF(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}})\left((\omega_n^{\text{pos}})^2+(\nu^{\text{pos}}(s))^2\right)\sinh(\nu^{\text{pos}}(s))} \\
& - \frac{k_5(1-t_+^0)\left(\sigma_{\text{eff}}^{\text{pos}}\cos(\omega_n^{\text{sep}})+\kappa_{\text{eff}}^{\text{pos}}\cos(\omega_n^{\text{tot}})\right)(\nu^{\text{pos}}(s))^2}{AF(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}})\left((\omega_n^{\text{pos}})^2+(\nu^{\text{pos}}(s))^2\right)} \\
& + \frac{k_6(1-t_+^0)\omega_n^{\text{pos}}\cos(\omega_n^{\text{tot}})\left(\sigma_{\text{eff}}^{\text{pos}}+\kappa_{\text{eff}}^{\text{pos}}\cosh(\nu^{\text{pos}}(s))\right)\nu^{\text{pos}}(s)}{AF(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}})\left((\omega_n^{\text{pos}})^2+(\nu^{\text{pos}}(s))^2\right)\sinh(\nu^{\text{pos}}(s))} \\
& - \frac{k_6(1-t_+^0)\omega_n^{\text{pos}}\cos(\omega_n^{\text{sep}})\left(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}}\cosh(\nu^{\text{pos}}(s))\right)\nu^{\text{pos}}(s)}{AF(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}})\left((\omega_n^{\text{pos}})^2+(\nu^{\text{pos}}(s))^2\right)\sinh(\nu^{\text{pos}}(s))} \\
& - \frac{k_6(1-t_+^0)\left(\sigma_{\text{eff}}^{\text{pos}}\sin(\omega_n^{\text{sep}})+\kappa_{\text{eff}}^{\text{pos}}\sin(\omega_n^{\text{tot}})\right)(\nu^{\text{pos}}(s))^2}{AF(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}})\left((\omega_n^{\text{pos}})^2+(\nu^{\text{pos}}(s))^2\right)},
\end{aligned}$$

where $\omega_n^{\text{pos}} = L^{\text{pos}}\sqrt{\lambda_n\varepsilon_e^{\text{pos}}/D_{e,\text{eff},}^{\text{pos}}}$, $\omega_n^{\text{tot}} = L^{\text{tot}}\sqrt{\lambda_n\varepsilon_e^{\text{pos}}/D_{e,\text{eff},}^{\text{pos}}}$, and $\omega_n^{\text{sep}} = \omega_n^{\text{tot}} - \omega_n^{\text{pos}}$.

- Overall, we have

$$\frac{\widetilde{C}_{e,n}(s)}{I_{\text{app}}(s)} = \frac{1}{s+\lambda_n}\left[\frac{J_n^{\text{neg}}(s)}{I_{\text{app}}(s)} + \frac{J_n^{\text{pos}}(s)}{I_{\text{app}}(s)}\right].$$

- Yes, this is a mess. The good news is that we'll develop tools that deal with the mess quite nicely.

6.8: A one-dimensional model of $\phi_e(x,t)$

- We now wish to develop an independent transfer function for $\phi_e(x,t)$.
- We start with the differential equation

$$\frac{\partial \phi_e(x,t)}{\partial x} = \frac{-\varepsilon_e i_e(x,t)}{\kappa_{\text{eff}}} + \frac{2RT}{F}(1-t_+^0)\frac{\partial \ln c_e(x,t)}{\partial x}.$$

- We will deal with the two terms of this equation separately.
- First, we can write an expression for $\varepsilon_e i_e(x,t)$,

$$i_e(x,t) = \begin{cases} \displaystyle\int_0^x \frac{a_s^{\text{neg}} F j^{\text{neg}}(\xi,t)}{\varepsilon_e^{\text{neg}}}\,\mathrm{d}\xi, & 0 \le x \le L^{\text{neg}}; \\ \dfrac{i_{\text{app}}(t)}{\varepsilon_e^{\text{sep}} A}, & L^{\text{neg}} \le x \le L^{\text{neg}} + L^{\text{sep}}; \\ \dfrac{i_{\text{app}}(t)}{\varepsilon_e^{\text{pos}} A} - \displaystyle\int_{L^{\text{neg}}+L^{\text{sep}}}^x \frac{a_s^{\text{pos}} F j^{\text{pos}}(\xi,t)}{\varepsilon_e^{\text{pos}}}\,\mathrm{d}\xi\,, & L^{\text{neg}} + L^{\text{sep}} \le x \le L^{\text{tot}}. \end{cases}$$

- A transfer function for $i_e(x,t)$ in the negative electrode is

$$\begin{aligned} \frac{I_e(x,s)}{I_{\text{app}}(s)} &= \frac{a_s^{\text{neg}} F}{\varepsilon_e^{\text{neg}}} \int_0^x \frac{J^{\text{neg}}(\xi/L^{\text{neg}},s)}{I_{\text{app}}(s)}\,\mathrm{d}\xi, \\ &= \frac{\kappa_{\text{eff}}^{\text{neg}}\left(\sinh(\nu^{\text{neg}}(s)) - \sinh\left(\frac{(L^{\text{neg}}-x)\nu^{\text{neg}}(s)}{L^{\text{neg}}}\right)\right)}{\varepsilon_e^{\text{neg}} A(\kappa_{\text{eff}}^{\text{neg}} + \sigma_{\text{eff}}^{\text{neg}})\sinh(\nu^{\text{neg}}(s))} \\ &\quad + \frac{\sigma_{\text{eff}}^{\text{neg}} \sinh\left(\frac{x\nu^{\text{neg}}(s)}{L^{\text{neg}}}\right)}{\varepsilon_e^{\text{neg}} A(\kappa_{\text{eff}}^{\text{neg}} + \sigma_{\text{eff}}^{\text{neg}})\sinh(\nu^{\text{neg}}(s))}. \end{aligned}$$

- A transfer function for $i_e(x,t)$ in the separator is $\dfrac{I_e(x,s)}{I_{\text{app}}(s)} = \dfrac{1}{\varepsilon_e^{\text{sep}} A}$.
- A transfer function for $i_e(x,t)$ in the positive electrode is

$$\frac{I_e(x,s)}{I_{\text{app}}(s)} = \frac{1}{\varepsilon_e^{\text{pos}} A} - \frac{a_s^{\text{pos}} F}{\varepsilon_e^{\text{pos}}} \int_{L^{\text{neg}}+L^{\text{sep}}}^x \frac{J^{\text{pos}}((L^{\text{tot}}-\xi)/L^{\text{pos}},s)}{I_{\text{app}}(s)}\,\mathrm{d}\xi,$$

$$= \frac{\kappa_{\text{eff}}^{\text{pos}}\left(\sinh(\nu^{\text{pos}}(s)) - \sinh\left(\frac{(x-L^{\text{neg}}-L^{\text{sep}})\nu^{\text{pos}}(s)}{L^{\text{pos}}}\right)\right)}{\varepsilon_e^{\text{pos}} A(\kappa_{\text{eff}}^{\text{pos}} + \sigma_{\text{eff}}^{\text{pos}}) \sinh(\nu^{\text{pos}}(s))}$$

$$+ \frac{\sigma_{\text{eff}} \sinh\left(\frac{(L^{\text{tot}}-x)\nu^{\text{pos}}(s)}{L^{\text{pos}}}\right)}{\varepsilon_e^{\text{pos}} A(\kappa_{\text{eff}}^{\text{pos}} + \sigma_{\text{eff}}^{\text{pos}}) \sinh(\nu^{\text{pos}}(s))}.$$

- We now integrate the PDE for ϕ_e

$$\phi_e(x,t) - \phi_e(0,t) = \int_0^x \frac{-\varepsilon_e i_e(\xi,t)}{\kappa_{\text{eff}}} + \frac{2RT}{F}(1-t_+^0)\frac{\partial \ln c_e(\xi,t)}{\partial \xi}\,\mathrm{d}\xi.$$

- Define $\tilde{\phi}_e(x,t) = \phi_e(x,t) - \phi_e(0,t)$.
- Then, $\tilde{\phi}_e(x,t)$ comprises two parts:
  - The first part, $\left[\tilde{\phi}_e(x,t)\right]_1$, can be determined via transfer functions
  - The second part, $\left[\tilde{\phi}_e(x,t)\right]_2$, can be determined via known $c_e(x,t)$.
- Let's continue to look at the first part. In the negative electrode,

$$\frac{[\widetilde{\Phi}_e(x,s)]_1}{I_{\text{app}}(s)} = \int_0^x \frac{-\varepsilon_e^{\text{neg}} I_e(\xi,s)}{\kappa_{\text{eff}}^{\text{neg}} I_{\text{app}}(s)}\,\mathrm{d}\xi$$

$$= -\frac{L^{\text{neg}}\sigma_{\text{eff}}^{\text{neg}}\left(\cosh\left(\frac{x}{L^{\text{neg}}}\nu^{\text{neg}}(s)\right) - 1\right)}{A\kappa_{\text{eff}}^{\text{neg}}(\kappa_{\text{eff}}^{\text{neg}} + \sigma_{\text{eff}}^{\text{neg}})\nu^{\text{neg}}(s)\sinh(\nu^{\text{neg}}(s))} - \frac{x}{A(\kappa_{\text{eff}}^{\text{neg}} + \sigma_{\text{eff}}^{\text{neg}})}$$

$$- \frac{L^{\text{neg}}\kappa_{\text{eff}}^{\text{neg}}\left(\cosh\left(\frac{(L^{\text{neg}}-x)}{L^{\text{neg}}}\nu^{\text{neg}}(s)\right) - \cosh(\nu^{\text{neg}}(s))\right)}{A\kappa_{\text{eff}}^{\text{neg}}(\kappa_{\text{eff}}^{\text{neg}} + \sigma_{\text{eff}}^{\text{neg}})\nu^{\text{neg}}(s)\sinh(\nu^{\text{neg}}(s))}.$$

- At the negative-electrode/separator boundary we have

$$\frac{[\widetilde{\Phi}_e(L^{\text{neg}},s)]_1}{I_{\text{app}}(s)} = -\frac{L^{\text{neg}}\left((\sigma_{\text{eff}}^{\text{neg}} - \kappa_{\text{eff}}^{\text{neg}})\tanh\left(\frac{\nu^{\text{neg}}(s)}{2}\right)\right)}{A\kappa_{\text{eff}}^{\text{neg}}(\kappa_{\text{eff}}^{\text{neg}} + \sigma_{\text{eff}}^{\text{neg}})\nu^{\text{neg}}(s)} - \frac{L_{\text{neg}}}{A(\kappa_{\text{eff}}^{\text{neg}} + \sigma_{\text{eff}}^{\text{neg}})}.$$

- In the separator, we then have

$$\frac{[\widetilde{\Phi}_e(x,s)]_1}{I_{\text{app}}(s)} = -\frac{L^{\text{neg}}\left((\sigma_{\text{eff}}^{\text{neg}}-\kappa_{\text{eff}}^{\text{neg}})\tanh\left(\frac{\nu^{\text{neg}}(s)}{2}\right)\right)}{A\kappa_{\text{eff}}^{\text{neg}}(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})\nu^{\text{neg}}(s)} - \frac{L_{\text{neg}}}{A(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})} - \frac{x-L^{\text{neg}}}{A\kappa_{\text{eff}}^{\text{sep}}}.$$

- At the separator/positive-electrode boundary we have

$$\frac{[\widetilde{\Phi}_e(L^{\text{neg}}+L^{\text{sep}},s)]_1}{I_{\text{app}}(s)} = -\frac{L^{\text{neg}}\left((\sigma_{\text{eff}}^{\text{neg}}-\kappa_{\text{eff}}^{\text{neg}})\tanh\left(\frac{\nu^{\text{neg}}(s)}{2}\right)\right)}{A\kappa_{\text{eff}}^{\text{neg}}(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})\nu^{\text{neg}}(s)} - \frac{L_{\text{neg}}}{A(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})} - \frac{L^{\text{sep}}}{A\kappa_{\text{eff}}^{\text{sep}}}.$$

- In the positive electrode, we then have

$$\begin{aligned}\frac{[\widetilde{\Phi}_e(x,s)]_1}{I_{\text{app}}(s)} = &-\frac{L^{\text{neg}}\left((\sigma_{\text{eff}}^{\text{neg}}-\kappa_{\text{eff}}^{\text{neg}})\tanh\left(\frac{\nu^{\text{neg}}(s)}{2}\right)\right)}{A\kappa_{\text{eff}}^{\text{neg}}(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})\nu^{\text{neg}}(s)} - \frac{L_{\text{neg}}}{A(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})}\\ &- \frac{L^{\text{sep}}}{A\kappa_{\text{eff}}^{\text{sep}}} - \frac{L^{\text{pos}}\left(1-\cosh\left(\frac{(L^{\text{neg}}+L^{\text{sep}}-x)}{L^{\text{pos}}}\nu^{\text{pos}}(s)\right)\right)}{A(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}})\sinh(\nu^{\text{pos}}(s))\nu^{\text{pos}}(s)}\\ &- \frac{L^{\text{pos}}\sigma_{\text{eff}}^{\text{pos}}\left(\cosh\left(\nu^{\text{pos}}(s)\right)-\cosh\left(\frac{(L^{\text{tot}}-x)}{L^{\text{pos}}}\nu^{\text{pos}}(s)\right)\right)}{A\kappa_{\text{eff}}^{\text{pos}}(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}})\sinh(\nu^{\text{pos}}(s))\nu^{\text{pos}}(s)}\\ &- \frac{(x-L^{\text{neg}}-L^{\text{sep}})}{A(\kappa_{\text{eff}}^{\text{pos}}+\sigma_{\text{eff}}^{\text{pos}})}.\end{aligned}$$

- At the cell boundary we have

$$\frac{[\widetilde{\Phi}_e(L^{\text{tot}},s)]_1}{I_{\text{app}}(s)} = -\frac{L^{\text{neg}}\left((\sigma_{\text{eff}}^{\text{neg}}-\kappa_{\text{eff}}^{\text{neg}})\tanh\left(\frac{\nu^{\text{neg}}(s)}{2}\right)\right)}{A\kappa_{\text{eff}}^{\text{neg}}(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})\nu^{\text{neg}}(s)} - \frac{L_{\text{neg}}}{A(\kappa_{\text{eff}}^{\text{neg}}+\sigma_{\text{eff}}^{\text{neg}})}$$

$$
- \frac{L^{\text{sep}}}{A\kappa_{\text{eff}}^{\text{sep}}} - \frac{L^{\text{pos}}\left((\sigma_{\text{eff}}^{\text{pos}} - \kappa_{\text{eff}}^{\text{pos}})\tanh\left(\frac{\nu^{\text{pos}}(s)}{2}\right)\right)}{A\kappa_{\text{eff}}^{\text{pos}}(\kappa_{\text{eff}}^{\text{pos}} + \sigma_{\text{eff}}^{\text{pos}})\nu^{\text{pos}}(s)}
$$
$$
- \frac{L_{\text{pos}}}{A(\kappa_{\text{eff}}^{\text{pos}} + \sigma_{\text{eff}}^{\text{pos}})}.
$$

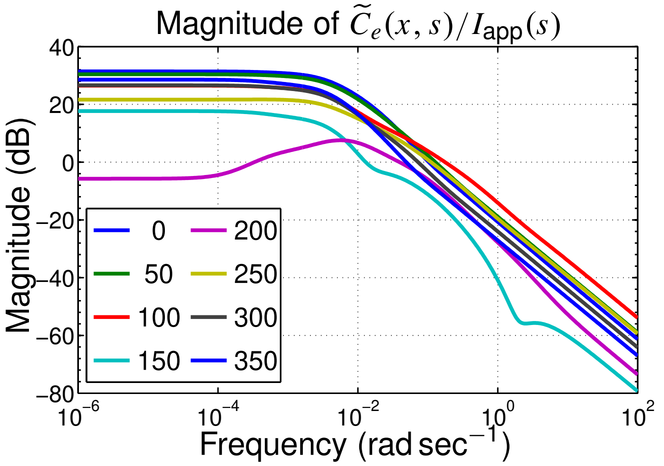
- Now, we focus on the second term of $\tilde{\phi}_e(x,t)$.

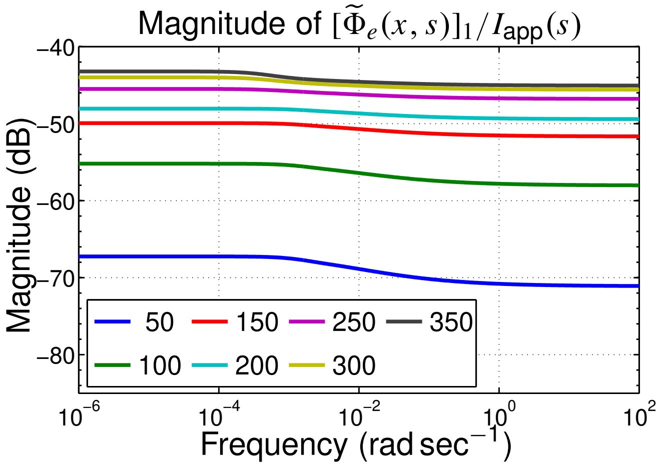
$$
\begin{aligned}
\left[\tilde{\phi}_e(x,t)\right]_2 &= \frac{2RT(1-t_+^0)}{F}\int_0^x \frac{\partial \ln c_e(\xi,t)}{\partial \xi}\,\mathrm{d}\xi \\
&= \frac{2RT(1-t_+^0)}{F}\left[\ln c_e(x,t) - \ln c_e(0,t)\right].
\end{aligned}
$$

- To compute $\tilde{\phi}_e(x,t)$, we must compute its two parts and add them.
- To recover $\phi_e(x,t)$ from $\tilde{\phi}_e(x,t)$, we must compute $\phi_e(0,t)$:

$$
\begin{aligned}
\phi_e(0,t) &= \phi_s(0,t) - \phi_{s\text{-}e}(0,t) \\
&= 0 - (\tilde{\phi}_{s\text{-}e}(0,t) + U_{\text{ocp}}^{\text{neg}}(c_{s,0})) \\
\phi_e(x,t) &= \tilde{\phi}_e(x,t) - \tilde{\phi}_{s\text{-}e}(0,t) - U_{\text{ocp}}^{\text{neg}}(c_{s,0}).
\end{aligned}
$$

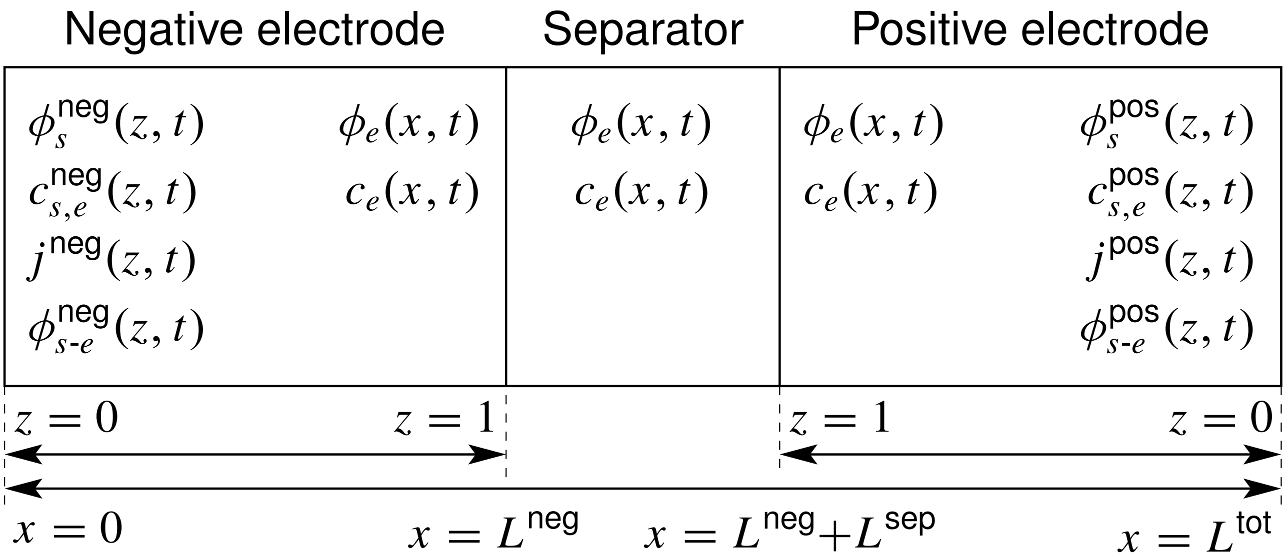
- Some final Bode magnitude plots, for now:





6.9: Summary of transfer functions

- The ROM produced by the DRA algorithm can be requested to produce any arbitrary set of the (linearized) cell electrochemical variables at any feasible location across the cell.
- Electrode-only quantities use a normalized spatial variable z, which varies from 0 at the current collector to 1 at the separator boundary.
- Electrolyte quantities use the spatial variable x, which varies from 0 at the negative-electrode current collector to L^{tot} at the positive-electrode current collector.



- The ROM produced by the DRA comprises $\widehat{\boldsymbol{A}}$, $\widehat{\boldsymbol{B}}$, $\widehat{\boldsymbol{C}}$, and $\widehat{\boldsymbol{D}}$ matrices such that

$$\boldsymbol{x}[k+1] = \widehat{\boldsymbol{A}}\boldsymbol{x}[k] + \widehat{\boldsymbol{B}}i_{\text{app}}[k]$$

$$\tilde{\boldsymbol{y}}[k] = \widehat{\boldsymbol{C}}\boldsymbol{x}[k] + \widehat{\boldsymbol{D}}i_{\text{app}}[k],$$

where $\boldsymbol{x}[k]$ is a state vector with no known retained physical significance, and $\tilde{\boldsymbol{y}}[k]$ comprises the linearized outputs that were requested by the user when creating the ROM.

- Nonlinear corrections are added to the linear outputs to arrive at the desired electrochemical state variables.

Solid surface concentration: The DRA produces a debiased estimator $\tilde{c}_{s,e}(z,t)$ of the solid surface concentration variable.

- The nonlinear estimate of $c_{s,e}(z,t)$ is found by adding the equilibrium concentration to $\tilde{c}_{s,e}(z,t)$:

$$c_{s,e}(z,t) = \tilde{c}_{s,e}(z,t) + c_{s,0}.$$

Potential in solid: The DRA produces a debiased estimator $\tilde{\phi}_s(z,t)$ of the solid potential variable.

- In the negative electrode, the nonlinear estimate of $\phi_s(z,t)$ is equal to the debiased estimate: $\phi_s(z,t) = \tilde{\phi}_s(z,t)$.
- In the positive electrode, $\phi_s(z,t) = \tilde{\phi}_s(z,t) + v(t)$, where the calculation of $v(t)$ is discussed shortly.

Concentration in electrolyte: The DRA produces a debiased estimator $\tilde{c}_e(x,t)$ of the electrolyte concentration.

- The nonlinear estimate of $c_e(x,t)$ is found by adding the equilibrium concentration to $\tilde{c}_e(x,t)$

$$c_e(x,t) = \tilde{c}_e(x,t) + c_{e,0}.$$

Solid–electrolyte potential difference: The DRA produces a debiased integrator-removed estimator $\tilde{\phi}^*_{s\text{-}e}(z,t)$ of the solid–electrolyte potential difference.

- Note that the transfer function $\widetilde{\Phi}^{\text{neg}}_{s\text{-}e}(z,s)/I_{\text{app}}(s)$ has a pole at the origin, which is removed prior to using the DRA to give the $[\widetilde{\Phi}^{\text{neg}}_{s\text{-}e}(z,s)]^*/I_{\text{app}}(s)$ transfer function.

- The integrator response could be added back manually, as in $\tilde{\phi}_{s\text{-}e}(t) = \tilde{\phi}^*_{s\text{-}e}(t) + \left(\tilde{\phi}^{\text{res0}}_{s\text{-}e}\right) x_i(t)$, where $x_i(t)$ is the integrator state of the DRA model, but better performance is obtained by looking deeper at what is actually happening.
- Recall that

$$c_{s,\text{avg}}(t) = \left(\tilde{c}^{\text{res0}}_{s,e}\right) x_i(t) + c_{s,0}$$

and note that

$$\tilde{\phi}^{\text{res}_0}_{s\text{-}e} = \left.\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\right|_{c_{s,0}} \times \tilde{c}^{\text{res}_0}_{s,e}$$

because

$$\tilde{\phi}_{s\text{-}e}(t) = \tilde{\phi}^*_{s\text{-}e}(t) + \left[\left.\frac{\partial U_{\text{ocp}}}{\partial c_{s,e}}\right|_{c_{s,0}} \cdot \tilde{c}^{\text{res}_0}_{s,e}\right] x_i(t).$$

- Therefore, since $\phi_{s\text{-}e} = \tilde{\phi}_{s\text{-}e} + U_{\text{ocp}}(c_{s,0})$, we can write

$$\phi^{\text{neg}}_{s\text{-}e} = [\tilde{\phi}^{\text{neg}}_{s\text{-}e}]^* + \left(U^{\text{neg}}_{\text{ocp}}(c^{\text{neg}}_{s,0}) + \left[\left.\frac{\partial U^{\text{neg}}_{\text{ocp}}}{\partial c^{\text{neg}}_{s,e}}\right|_{c^{\text{neg}}_{s,0}}\right]\left(c^{\text{neg}}_{s,\text{avg}} - c^{\text{neg}}_{s,0}\right)\right),$$

where the second term on the right-hand side is equal to the first two terms of the Taylor series expansion of $U^{\text{neg}}_{\text{ocp}}(c^{\text{neg}}_{s,\text{avg}})$ around the starting average concentration $c^{\text{neg}}_{s,0}$.

- Therefore, we find that we achieve more accurate results if we implement $[\widetilde{\Phi}^{\text{neg}}_{s\text{-}e}(z,s)]^*/I_{\text{app}}(s)$ and then compute

$$\phi^{\text{neg}}_{s\text{-}e}(0,t) = [\tilde{\phi}^{\text{neg}}_{s\text{-}e}(0,t)]^* + U^{\text{neg}}_{\text{ocp}}(c^{\text{neg}}_{\text{s,avg}}(t)).$$

Potential in electrolyte: The electrolyte potential $\phi_e(x,t)$ uses two DRA terms: $\left[\tilde{\phi}_e(x,t)\right]_1$, and $c_e(x,t)$ as computed above:

$$\phi_e(x,t) = \left[\tilde{\phi}_e(x,t)\right]_1 - \phi_{s\text{-}e}(0,t) + \underbrace{\frac{2RT(1-t_+^0)}{F}\ln\left(\frac{c_e(x,t)}{c_e(0,t)}\right)}_{\left[\tilde{\phi}_e(x,t)\right]_2}.$$

Reaction flux: Outputs $j(z,t)$ from the DRA are a linearized approximation to the true $j(z,t)$. There is no additional correction to this variable.

Overpotential: If we assume that the charge-transfer coefficient $\alpha = 0.5$, as is often the case, we can then write

$$j = 2k_0\sqrt{c_e(c_{s,\max} - c_{s,e})c_{s,e}}\,\sinh\left(\frac{F}{2RT}\eta\right).$$

- This can be inverted to solve for the overpotential

$$\eta^{\text{pos}}(z,t) = \frac{2RT}{F}\text{asinh}\left(\frac{j^{\text{pos}}(z,t)}{2k_0^{\text{pos}}\sqrt{c_e(z,t)(c_{s,\max}^{\text{pos}} - c_{s,e}^{\text{pos}}(z,t))c_{s,e}^{\text{pos}}(z,t)}}\right)$$

$$\eta^{\text{neg}}(z,t) = \frac{2RT}{F}\text{asinh}\left(\frac{j^{\text{neg}}(z,t)}{2k_0^{\text{neg}}\sqrt{c_e(z,t)(c_{s,\max}^{\text{neg}} - c_{s,e}^{\text{neg}}(z,t))c_{s,e}^{\text{neg}}(z,t)}}\right).$$

6.10: Cell voltage

- We wish to be able to use our prior results to compute the terminal voltage of the cell, $v(t) = \phi_s(L^{\text{tot}}, t) - \phi_s(0, t)$.
- Recall that $\eta = \phi_s - \phi_e - U_{\text{ocp}} - FR_{\text{film}}j$, so we can write

$$\begin{aligned} v(t) = {} & \eta^{\text{pos}}(0,t) + \phi_e(L^{\text{tot}},t) + U_{\text{ocp}}^{\text{pos}}(c_{s,e}^{\text{pos}}(0,t)) + FR_{\text{film}}^{\text{pos}} j^{\text{pos}}(0,t) \\ & - \eta^{\text{neg}}(0,t) - \phi_e(0,t) - U_{\text{ocp}}^{\text{neg}}(c_{s,e}^{\text{neg}}(0,t)) - FR_{\text{film}}^{\text{neg}} j^{\text{neg}}(0,t). \end{aligned}$$

  - Note that some like-looking parameter values have been separated as a reminder that R_{ct} and R_{film}, for example, might have different values in the negative and positive electrodes.
  - We have seen how to compute the linear terms via transfer functions, and how to compute the nonlinear terms from the linear terms.
- Combining like terms:

$$\begin{aligned} v(t) = {} & F\left(R_{\text{film}}^{\text{pos}} j^{\text{pos}}(0,t) - R_{\text{film}}^{\text{neg}} j(0,t)\right) + \left[\tilde{\phi}_e(L^{\text{tot}},t)\right]_1 \\ & + \left(\eta^{\text{pos}}(0,t) - \eta^{\text{neg}}(0,t)\right) + \left[\tilde{\phi}_e(L^{\text{tot}},t)\right]_2 \\ & + \left(U_{\text{ocp}}^{\text{pos}}(c_{s,e}^{\text{pos}}(0,t)) - U_{\text{ocp}}^{\text{neg}}(c_{s,e}^{\text{neg}}(0,t))\right). \end{aligned}$$

- The linear transfer functions can be grouped together. Define

$$\frac{V_{\text{lin}}(s)}{I_{\text{app}}(s)} = F\left(R_{\text{film}}^{\text{pos}} \frac{J^{\text{pos}}(0,s)}{I_{\text{app}}(s)} - R_{\text{film}}^{\text{neg}} \frac{J^{\text{neg}}(0,s)}{I_{\text{app}}(s)}\right) + \frac{\left[\tilde{\phi}_e(L^{\text{tot}},s)\right]_1}{I_{\text{app}}(s)}.$$

- If this transfer function is implemented in the DRA to produce a single output $v_{\text{lin}}(t)$, then we can write

$$v(t) = v_{\text{lin}}(t) + \eta^{\text{pos}}(0,t) - \eta^{\text{neg}}(0,t)$$

$$+\left[\tilde{\phi}_e(L^{\text{tot}},t)\right]_2 + \left(U_{\text{ocp}}^{\text{pos}}(c_{s,e}^{\text{pos}}(0,t)) - U_{\text{ocp}}^{\text{neg}}(c_{s,e}^{\text{neg}}(0,t))\right).$$

- This output equation requires implementing a minimum number of seven transfer functions to be able to compute cell voltage: $v_{\text{lin}}(t)$, $j(0,t)$, $j(L^{\text{tot}},t)$, $c_e(L^{\text{tot}},t)$, $c_e(0,t)$, $c_{s,e}^{\text{pos}}(0,t)$, and $c_{s,e}^{\text{neg}}(0,t)$.

Frequency response and cell impedance

- The voltage equation can also be manipulated to form the linearized small-signal frequency response of the cell, which is the negative of the impedance spectrum.
- We linearize the overpotential via $\eta(z,t) \approx FR_{\text{ct}}j(z,t)$.
- The remaining nonlinear terms in the voltage equation are

$$\left[\tilde{\phi}_e(L^{\text{tot}},t)\right]_2 \quad \text{and} \quad \left[U_{\text{ocp}}^{\text{pos}}(c_{s,e}^{\text{pos}}(0,t)) - U_{\text{ocp}}^{\text{neg}}(c_{s,e}^{\text{neg}}(0,t))\right].$$

- Writing out the first term, we have

$$\left[\tilde{\phi}_e(L^{\text{tot}},t)\right]_2 = \frac{2RT(1-t_+^0)}{F}\left[\ln(c_e(L^{\text{tot}},t) - \ln(c_e(0,t))\right].$$

- Linearizing the logarithm via Taylor-series expansion gives

$$\begin{aligned}\ln(c_e) &\approx \ln(c_{e,0}) + \left[\left.\frac{\partial \ln c_e}{\partial c_e}\right|_{c_{e,0}}\right.(c_e - c_{e,0}) \\ &= \ln(c_{e,0}) + \left(\frac{c_e - c_{e,0}}{c_{e,0}}\right) = \ln(c_{e,0}) + \frac{\tilde{c}_e}{c_{e,0}}.\end{aligned}$$

- So,

$$\left[\tilde{\phi}_e(L^{\text{tot}},t)\right]_2 \approx \frac{2RT(1-t_+^0)}{F}\left[\frac{\tilde{c}_e(L^{\text{tot}},t) - \tilde{c}_e(0,t)}{c_{e,0}}\right].$$

- Using a similar means, the open-circuit-potential relationships can be linearized

$$\begin{aligned}U_{\text{ocp}}(c_{s,e}) &\approx U_{\text{ocp}}(c_{s,0}) + \left[\frac{\partial U_{\text{ocp}}(c_{s,e})}{\partial c_{s,e}}\right|_{c_{s,0}}(c_{s,e}-c_{s,0})\\ &= U_{\text{ocp}}(c_{s,0}) + \left[\frac{\partial U_{\text{ocp}}(c_{s,e})}{\partial c_{s,e}}\right|_{c_{s,0}}\tilde{c}_{s,e}.\end{aligned}$$

- So, a linearized model of cell voltage is then

$$\begin{aligned}v(t) \approx\; & FR_{s,e}^{\text{pos}}j^{\text{pos}}(0,t) - FR_{s,e}^{\text{neg}}j^{\text{neg}}(0,t) + \left[\tilde{\phi}_e(L^{\text{tot}},t)\right]_1\\ &+ \frac{2RT(1-t_+^0)}{F}\left[\frac{\tilde{c}_e(L^{\text{tot}},t)-\tilde{c}_e(0,t)}{c_{e,0}}\right]\\ &+ \left[U_{\text{ocp}}^{\text{pos}}(c_{s,0}^{\text{pos}}) - U_{\text{ocp}}^{\text{neg}}(c_{s,0}^{\text{neg}})\right]\\ &+ \left[\frac{\partial U_{\text{ocp}}^{\text{pos}}(c_{s,e}^{\text{pos}})}{\partial c_{s,e}^{\text{pos}}}\right|_{c_{s,0}^{\text{pos}}}\tilde{c}_{s,e}^{\text{pos}}(0,t) - \left[\frac{\partial U_{\text{ocp}}^{\text{neg}}(c_{s,e}^{\text{neg}})}{\partial c_{s,e}^{\text{neg}}}\right|_{c_{s,0}^{\text{neg}}}\tilde{c}_{s,e}^{\text{neg}}(0,t).\end{aligned}$$

- We define a debiased voltage

$$\tilde{v}(t) = v(t) - \left[U_{\text{ocp}}^{\text{pos}}(c_{s,0}^{\text{pos}}) - U_{\text{ocp}}^{\text{neg}}(c_{s,0}^{\text{neg}})\right].$$

- Then, the transfer function from applied current to variations in cell voltage around its equilibrium setpoint (with the open-circuit voltage offset removed) is

$$\begin{aligned}\frac{\widetilde{V}(s)}{I_{\text{app}}(s)} =\; & FR_{s,e}^{\text{pos}}\frac{J^{\text{pos}}(0,s)}{I_{\text{app}}(s)} - FR_{s,e}^{\text{neg}}\frac{J^{\text{neg}}(0,s)}{I_{\text{app}}(s)} + \frac{[\widetilde{\Phi}_e(L^{\text{tot}},s)]_1}{I_{\text{app}}(s)}\\ &+ \frac{2RT(1-t_+^0)}{Fc_{e,0}}\left[\frac{\widetilde{C}_e(L^{\text{tot}},s)}{I_{\text{app}}(s)} - \frac{\widetilde{C}_e(0,s)}{I_{\text{app}}(s)}\right]\\ &+ \left[\frac{\partial U_{\text{ocp}}^{\text{pos}}(c_{s,e}^{\text{pos}})}{\partial c_{s,e}^{\text{pos}}}\right|_{c_{s,0}^{\text{pos}}}\frac{\widetilde{C}_{s,e}^{\text{pos}}(0,s)}{I_{\text{app}}(s)} - \left[\frac{\partial U_{\text{ocp}}^{\text{neg}}(c_{s,e}^{\text{neg}})}{\partial c_{s,e}^{\text{neg}}}\right|_{c_{s,0}^{\text{neg}}}\frac{\widetilde{C}_{s,e}^{\text{neg}}(0,t)}{I_{\text{app}}(s)},\end{aligned}$$

where the individual transfer functions are as defined earlier in this chapter.

- Note that since cell voltage is equal to open-circuit voltage minus current times generalized impedance,

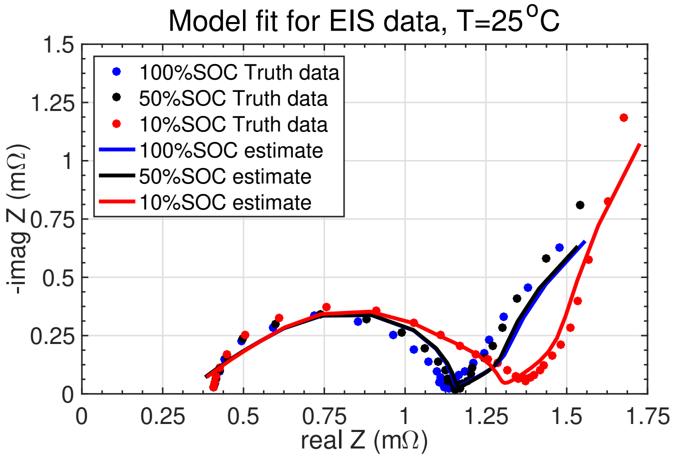
$$v(t) = \mathrm{OCV}(z(t)) - Zi_{\text{app}}(t),$$

we have $\tilde{v}(t) = -Zi_{\text{app}}(t)$, and

$$Z(s) = -\frac{\widetilde{V}(s)}{I_{\text{app}}(s)}.$$

- This relationship produces the impedance spectrum, which can be compared with results from laboratory electrochemical impedance spectroscopy (EIS) tests.

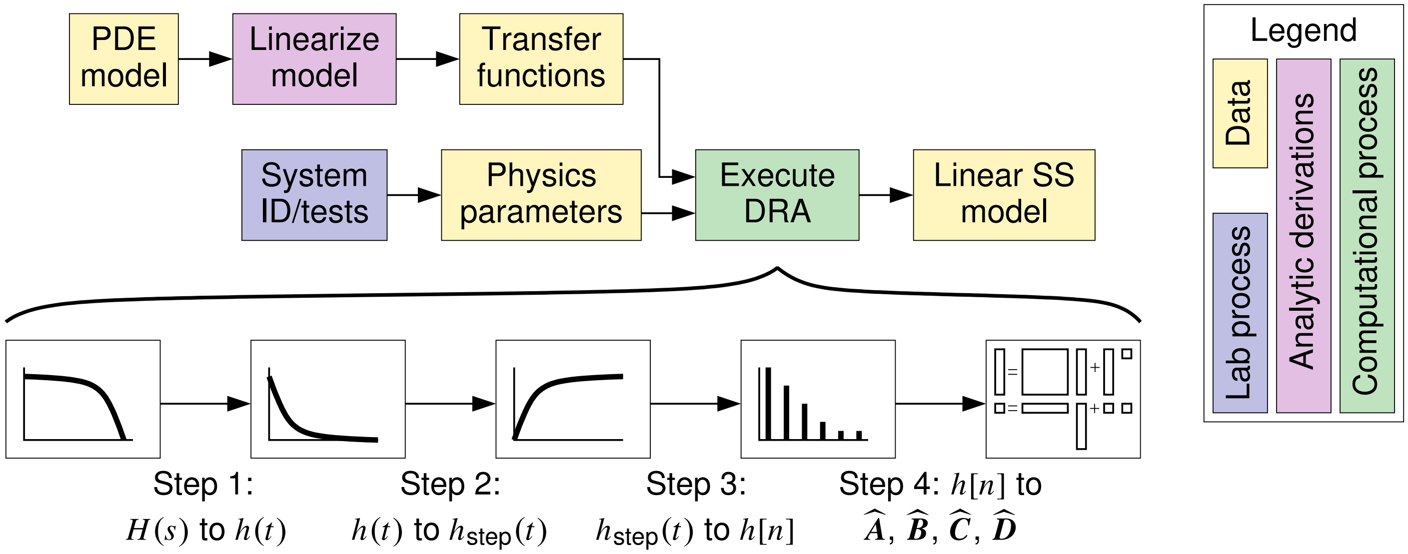
- Figure shows representative result comparing physics-based-model frequency-response fit with measured data.



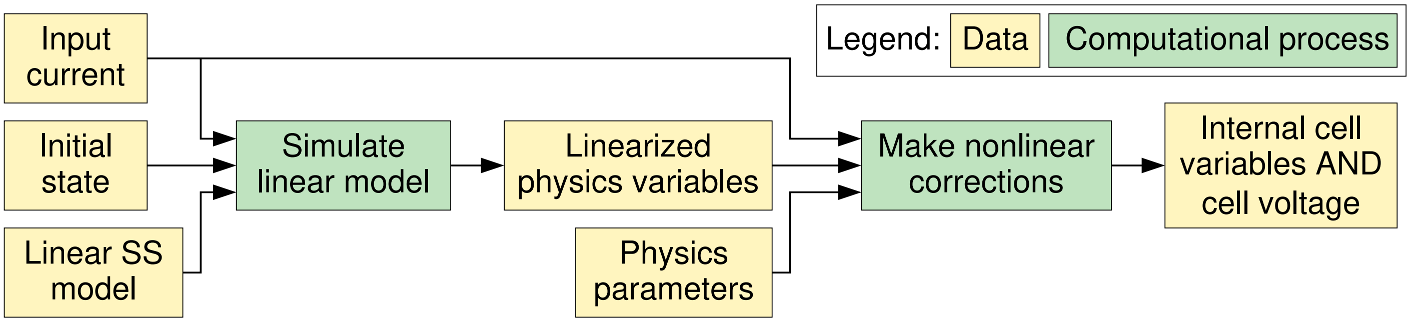
- We see a “bump” in the plot that is not explained by the model developed to date; it is from a “double-layer capacitor” effect, and modeling its behavior is beyond the scope of this course.

6.11: Full cell model

- It is straightforward to apply the DRA to the full cell model.
  - Select which transfer functions you want to implement, at which z or x locations across the cell;
  - Perform DRA steps 1 through 3 on each transfer function to get discrete-time unit-pulse responses of all variables of interest;
  - Stack all unit-pulse responses on top of each other, forming a set of single-input multi-output Markov parameters;
  - Run DRA step 4 to get the state-space system realization. Diagonalize if desired.
- We find that we can achieve very good results using only four model states, plus one integrator state.
- First, a pictorial overview; then, some specifics.
  - Finding the model:



  - Simulating the model:


Legend: Data Computational process

Input current

Initial state

Linear SS model

Simulate linear model

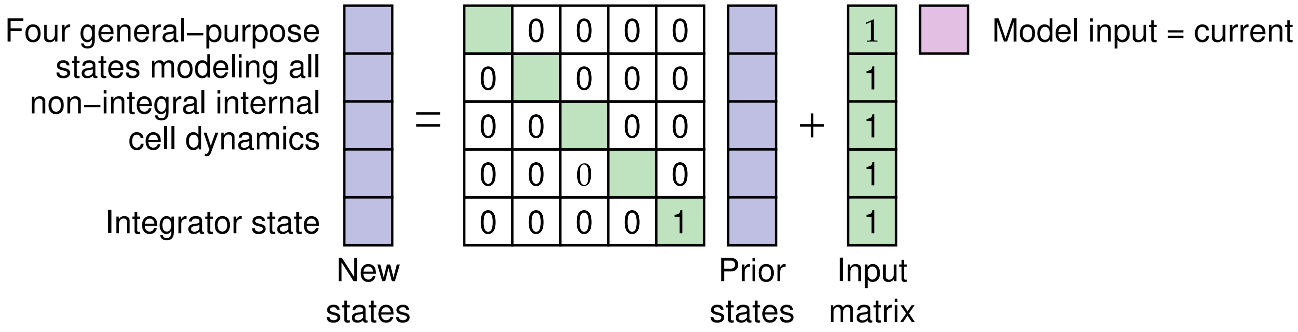
Linearized physics variables

Physics parameters

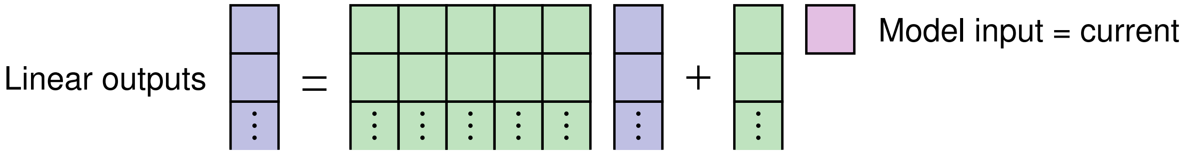
Make nonlinear corrections

Internal cell variables AND cell voltage

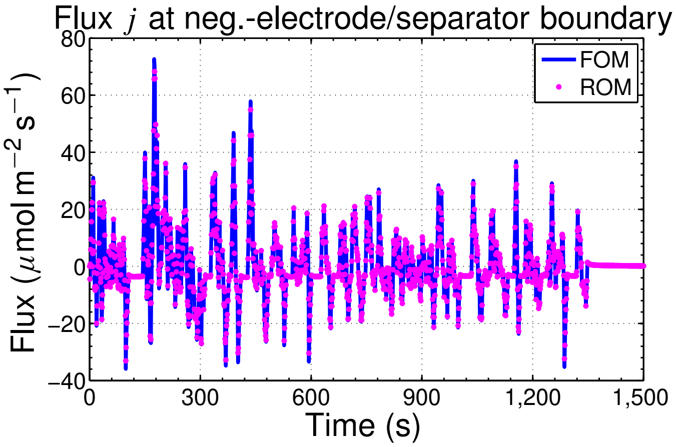
- The state equation can be visualized as

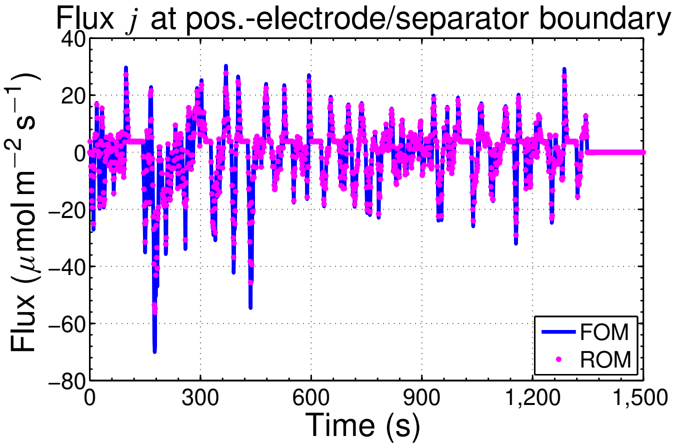


- The linear output equation can be visualized as

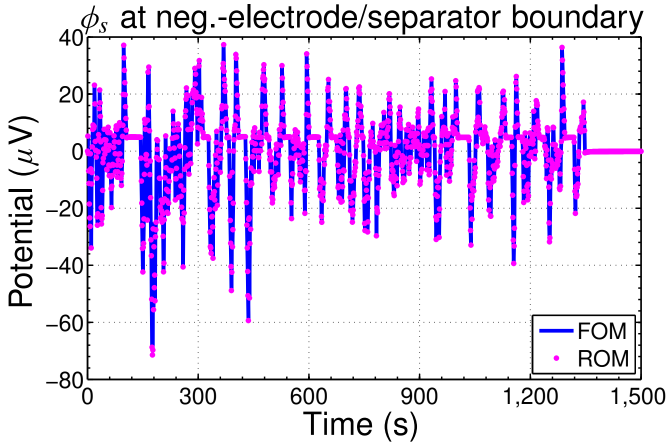


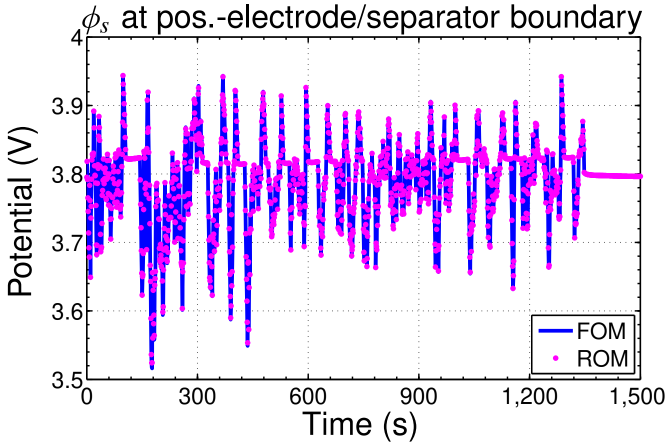
- Cell voltage is a nonlinear combination of the linear outputs.
- The following plots show comparisons between the continuum-scale cell model predictions and the ROM predictions for a cell excited by an urban dynamometer driving schedule (UDDS) test.
- First, we see the Butler–Volmer current density

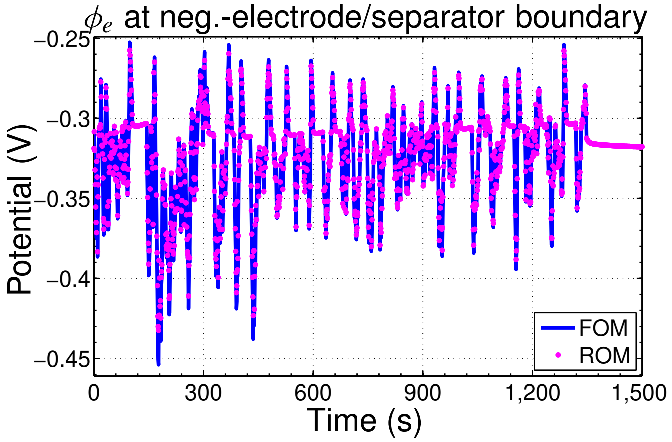

Flux j at neg.-electrode/separator boundary

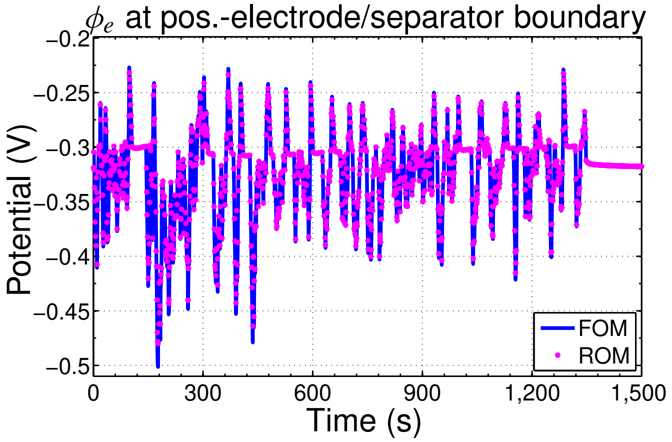

Flux j at pos.-electrode/separator boundary

- Next, we see solid and electrolyte phase potential:

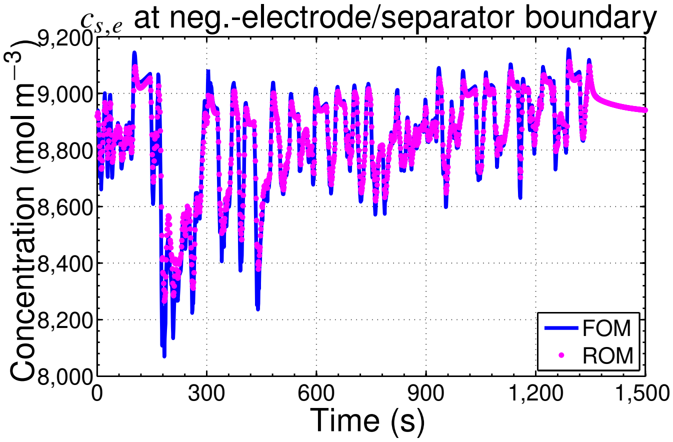

ϕ_s at neg.-electrode/separator boundary

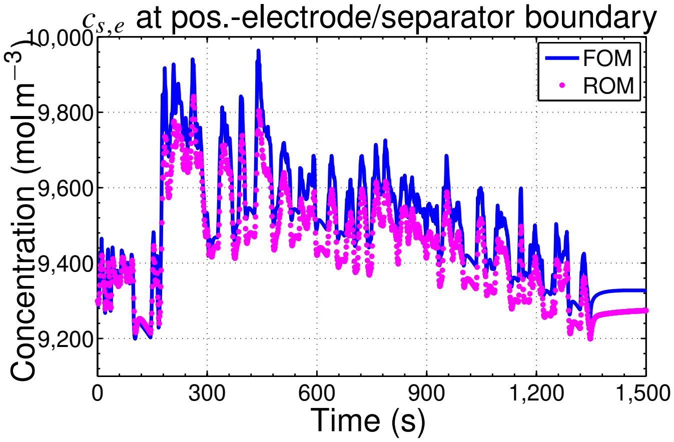

ϕ_s at pos.-electrode/separator boundary

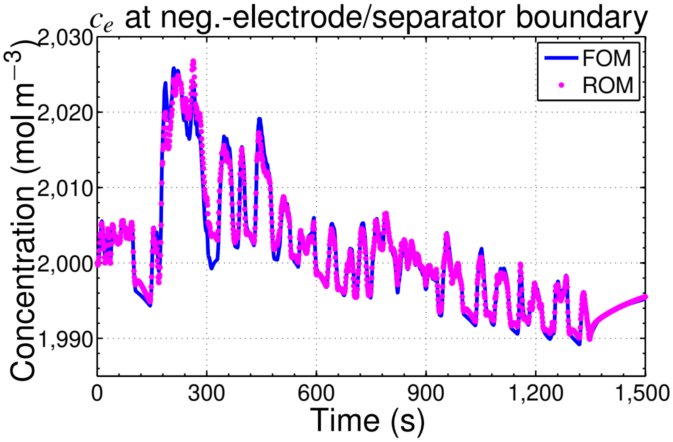

ϕ_e at neg.-electrode/separator boundary

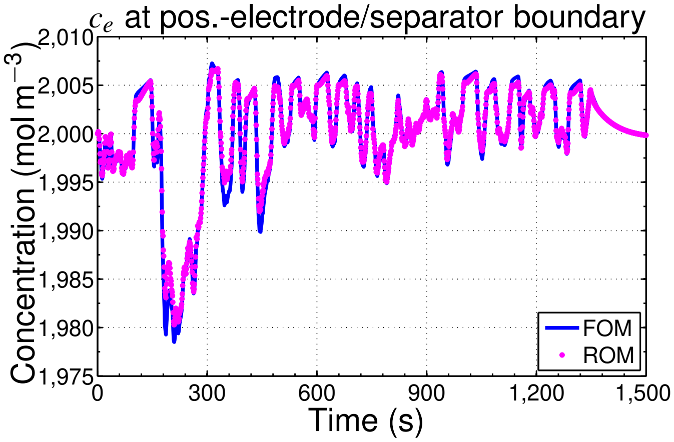

ϕ_e at pos.-electrode/separator boundary

- Next, we see solid surface concentration and electrolyte concentration of lithium

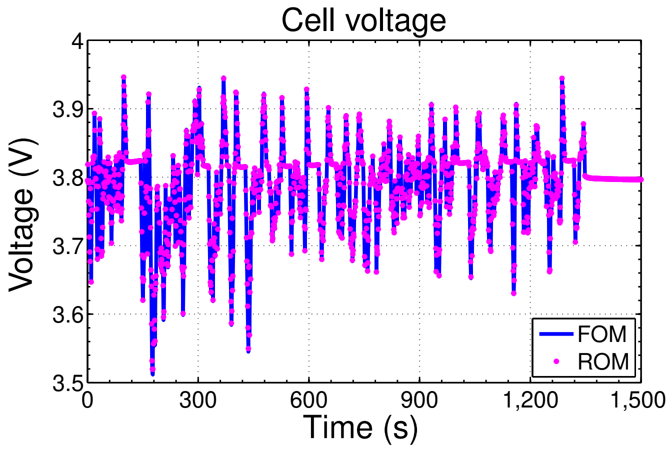


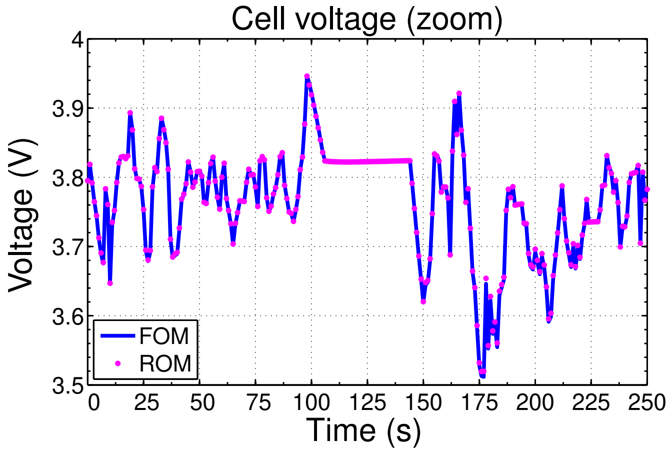






- Finally, we see v_{cell} comparisons. RMS error of around 1 mV.





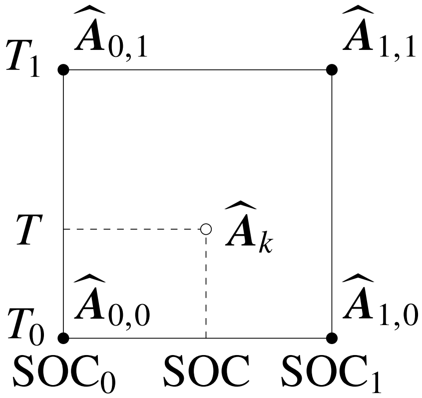
6.12: Model blending

- The ROM we've developed to this point was derived by linearizing the PDE model around a specific operational setpoint.
- However, as model dynamics can vary with temperature and SOC, we find that a single model is often not sufficient.
- In order to model the cell over a wide range of both temperature and SOC, we use a model-blending approach.

IDEA: Precompute ROMs at multiple temperature and SOC setpoints. Then, during operation, use them to generate a best "average" ROM specialized for the present instantaneous temperature and SOC.

Blending the models

- Individual reduced-order models are generated *a priori* using the DRA over the expected operating range of temperatures and SOCs.
- For simplicity, we assume that the setpoints fall on a rectangular (z,T) grid.
- These precomputed models are blended in real time using bilinear interpolation to generate a time-varying state-space model, as illustrated in the figure.



- We define $\text{SOC}_0 \le \text{SOC} < \text{SOC}_1$, where SOC_0 and SOC_1 are the nearest SOC setpoint values among the precomputed models.
- Similarly, we define $T_0 \le T < T_1$ to be the nearest temperature setpoint values bracketing the cell's present operating temperature.

- We then define blending factors θ_z and θ_T as

$$\theta_z = \frac{\text{SOC} - \text{SOC}_0}{\text{SOC}_1 - \text{SOC}_0} \quad \text{and} \quad \theta_T = \frac{T - T_0}{T_1 - T_0}.$$

- The value of the time-varying blended $\widehat{\boldsymbol{A}}_k$ matrix is found from

$$\widehat{\boldsymbol{A}}_k = (1-\theta_T)\left((1-\theta_z)\widehat{\boldsymbol{A}}_{0,0} + \theta_z\widehat{\boldsymbol{A}}_{1,0}\right) + \theta_T\left((1-\theta_z)\widehat{\boldsymbol{A}}_{0,1} + \theta_z\widehat{\boldsymbol{A}}_{1,1}\right),$$

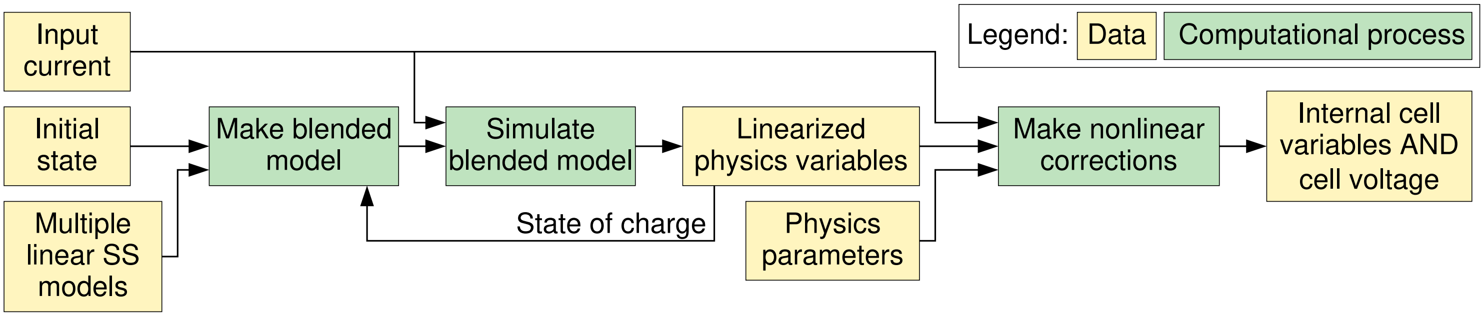
  where $\widehat{\boldsymbol{A}}_{0,0}$ is the $\widehat{\boldsymbol{A}}$ matrix of the precomputed model at SOC_0 and T_0, $\widehat{\boldsymbol{A}}_{0,1}$ at SOC_0 and T_1, $\widehat{\boldsymbol{A}}_{1,0}$ at SOC_1 and T_0, and $\widehat{\boldsymbol{A}}_{1,1}$ at SOC_1 and T_1.

- The time-varying blended $\widehat{\boldsymbol{B}}_k$, $\widehat{\boldsymbol{C}}_k$, and $\widehat{\boldsymbol{D}}_k$ matrices can be found in the same manner (although we see some simplifications in the next section, which make it unnecessary to blend $\widehat{\boldsymbol{B}}_k$).

- The state-space equations are then modified with these time-varying blended matrices to become

$$\begin{aligned} \boldsymbol{x}[k+1] &= \widehat{\boldsymbol{A}}_k\boldsymbol{x}[k] + \widehat{\boldsymbol{B}}_k i_{\text{app}}[k] \\ \tilde{\boldsymbol{y}}[k] &= \widehat{\boldsymbol{C}}_k\boldsymbol{x}[k] + \widehat{\boldsymbol{D}}_k i_{\text{app}}[k]. \end{aligned}$$

- The figure illustrates the real-time aspect of the overall model-blending approach.



Legend: Data Computational process
Input current
Initial state
Multiple linear SS models
Make blended model
Simulate blended model
Linearized physics variables
State of charge
Physics parameters
Make nonlinear corrections
Internal cell variables AND cell voltage

- During operation, the present cell SOC and temperature are used to generate blended state-space matrices.

- State vector $\boldsymbol{x}[k]$ is updated using these time-varying matrices, and linearized outputs $\tilde{\boldsymbol{y}}[k]$ are computed from the updated state vector. The SOC calculated at each time step from the internal states is fed back into the linear model as an input to blending process.

Sorting the model

- One complication when implementing the model-blending scheme arises from the fact that state-space models are not unique.
- An infinite number of different state descriptions with corresponding $\{\widehat{\boldsymbol{A}}, \widehat{\boldsymbol{B}}, \widehat{\boldsymbol{C}}, \widehat{\boldsymbol{D}}\}$ represent the same input–output relationship.
- This fact poses a potential problem when model blending because for the method to work all elements of the matrix $\widehat{\boldsymbol{A}}_{0,0}$ must be consistent in meaning with the corresponding elements of the matrices $\widehat{\boldsymbol{A}}_{1,0}$, $\widehat{\boldsymbol{A}}_{0,1}$, and $\widehat{\boldsymbol{A}}_{1,1}$.
- If not, unrelated elements will be averaged together, producing a meaningless result.
- The DRA algorithm itself does not guarantee that models generated at different temperature and SOC setpoints will exhibit a consistent state-space description.
- There is a simple remedy, however, which is to transform all precomputed models into a common framework.
- We do so as follows. We begin by supposing that a linear discrete-time state-space model produced by the DRA is of the form

$$\begin{aligned}\boldsymbol{x}^{(0)}[k+1] &= \widehat{\boldsymbol{A}}^{(0)}\boldsymbol{x}^{(0)}[k] + \widehat{\boldsymbol{B}}^{(0)} i_{\text{app}}[k]\\ \tilde{\boldsymbol{y}}[k] &= \widehat{\boldsymbol{C}}^{(0)}\boldsymbol{x}^{(0)}[k] + \widehat{\boldsymbol{D}} i_{\text{app}}[k].\end{aligned}$$

- The superscript “(0)” on several of the model terms indicates that these matrices and signals arise from the untransformed model produced directly from the DRA. We will use superscripts “(1),” “(2),” and “(3)” in the following to indicate different stages of model transformation.
- For the first transformation, we define a new state vector $\boldsymbol{x}^{(1)}[k]$, such that $\boldsymbol{x}^{(0)}[k] = \boldsymbol{T}^{(1)}\boldsymbol{x}^{(1)}[k]$, where $\boldsymbol{T}^{(1)}$ is some square invertible matrix.
- We have an equivalent input–output relationship between $i_{\text{app}}[k]$ and $\boldsymbol{y}[k]$ if we write

$$\boldsymbol{x}^{(1)}[k+1] = \underbrace{(\boldsymbol{T}^{(1)})^{-1}\widehat{\boldsymbol{A}}^{(0)}\boldsymbol{T}^{(1)}}_{\widehat{\boldsymbol{A}}^{(1)}}\boldsymbol{x}^{(1)}[k] + \underbrace{(\boldsymbol{T}^{(1)})^{-1}\widehat{\boldsymbol{B}}^{(0)}}_{\widehat{\boldsymbol{B}}^{(1)}} i_{\text{app}}[k]$$

$$\tilde{\boldsymbol{y}}[k] = \underbrace{\widehat{\boldsymbol{C}}^{(0)}\boldsymbol{T}^{(1)}}_{\widehat{\boldsymbol{C}}^{(1)}}\boldsymbol{x}^{(1)}[k] + \widehat{\boldsymbol{D}} i_{\text{app}}[k].$$

- We have great freedom in choosing the transformation matrix $\boldsymbol{T}^{(1)}$, so long as it is invertible.
- Consider first choosing $\boldsymbol{T}^{(1)} = \boldsymbol{V}$, where $\boldsymbol{V}$ is a matrix whose columns are the eigenvectors of $\widehat{\boldsymbol{A}}^{(0)}$.
- The resulting $\widehat{\boldsymbol{A}}^{(1)}$ matrix will be diagonal.[2] The diagonal elements of $\widehat{\boldsymbol{A}}^{(1)}$ are called the *poles* of the system, and represent the dynamic time constants.

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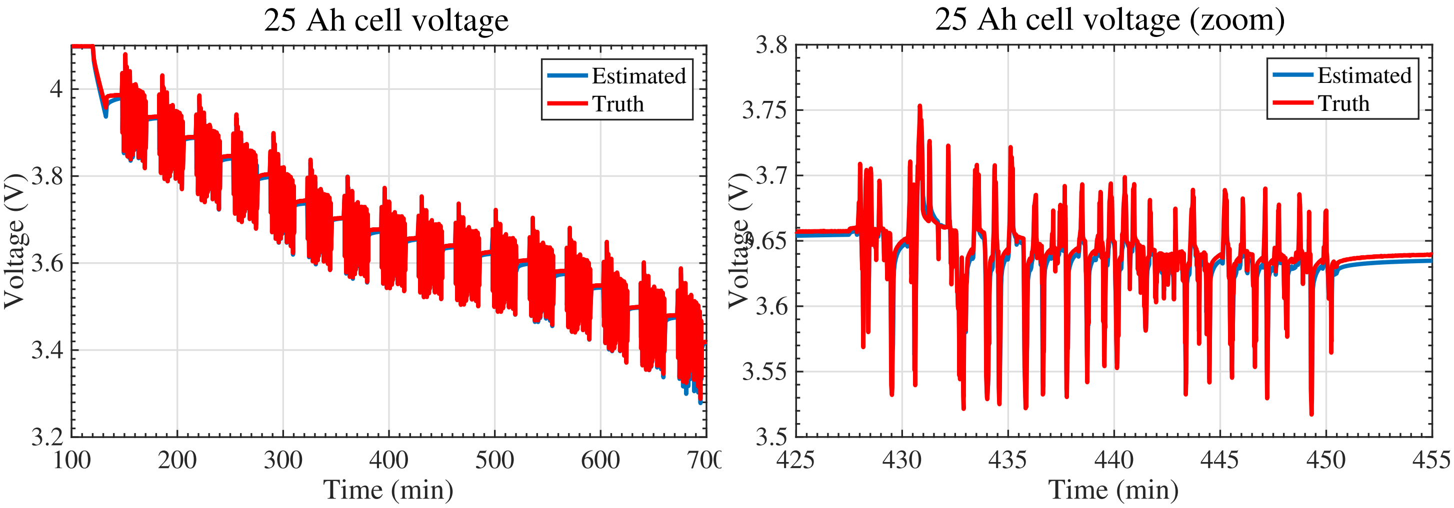
[2] For this to be possible, the $\widehat{\boldsymbol{A}}^{(0)}$ matrix must be diagonalizable, requiring that the eigenvectors in $\boldsymbol{V}$ be linearly independent. In our experience, the output of the DRA has always resulted in a diagonalizable $\widehat{\boldsymbol{A}}^{(0)}$ matrix; however, we know of no guarantee of this. In cases where the eigenvectors are linearly dependent, it is always possible to choose a transformation to put the $\widehat{\boldsymbol{A}}^{(1)}$ matrix into a Jordan form, which is what should be done instead.

- Already, this first transformation has uncovered some physical meaning in the model. Also,
  - Storage requirements of transformed model are reduced, as $n \times n$ matrix $\widehat{\boldsymbol{A}}^{(1)}$ contains only n non-zero values (on its diagonal),
  - Computation requirements are reduced, since only the diagonal elements of the $\widehat{\boldsymbol{A}}$ matrices need to be blended and fewer multiplies are needed to implement $\widehat{\boldsymbol{A}}^{(1)}\boldsymbol{x}^{(1)}[k]$ than $\widehat{\boldsymbol{A}}^{(0)}\boldsymbol{x}^{(0)}[k]$.
- Since eigenvectors are unique only up to a scaling factor, we utilize this remaining degree of freedom to simplify our matrices further.
- Here, we elect to normalize the $\widehat{\boldsymbol{B}}$ matrix to have units value elements.
- This, of course, presupposes that there are no zero elements in $\widehat{\boldsymbol{B}}$, which is guaranteed if the system is completely controllable.
- The Ho–Kalman algorithm used in the DRA always produces a minimal state-space description, so we have this guarantee.
- Thus, we then apply a second transformation, choosing $\boldsymbol{T}^{(2)} = \text{diag}(\widehat{\boldsymbol{B}}^{(1)})$.
- In the resulting transformed model, $\widehat{\boldsymbol{B}}^{(2)}$ contains only ones, and $\widehat{\boldsymbol{A}}^{(2)}$ will be unchanged from $\widehat{\boldsymbol{A}}^{(1)}$.
- This transformation has resulted in $\widehat{\boldsymbol{B}}^{(2)}$ and $\widehat{\boldsymbol{C}}^{(2)}$ matrices that are all scaled in a consistent way.
- It also reduces storage requirements, as $\widehat{\boldsymbol{B}}^{(2)}$ is known to always contain only ones, which do not need to be stored.
- Computation has also been reduced, as $\widehat{\boldsymbol{B}}$ matrices don't need to be blended (they are all the same), and because multiplication $\widehat{\boldsymbol{B}}_k i_{\text{app}}[k]$ is simply a repetition of the elements of $i_{\text{app}}[k]$.

- Finally, we choose a third transformation $\boldsymbol{T}^{(3)}$ to permute the elements of $\widehat{\boldsymbol{A}}^{(2)}$ such that $\widehat{\boldsymbol{A}}^{(3)}$ remains diagonal, but its elements appear in order of ascending magnitude. The $\widehat{\boldsymbol{B}}^{(3)}$ matrix remains all ones.
- For any particular temperature and SOC setpoint, we define the final scaled and sorted precomputed model as having $\widehat{\boldsymbol{A}} = \widehat{\boldsymbol{A}}^{(3)}$, $\widehat{\boldsymbol{B}} = \widehat{\boldsymbol{B}}^{(3)} = \mathbf{1}_{n\times 1}$, and $\widehat{\boldsymbol{C}} = \widehat{\boldsymbol{C}}^{(3)}$. The model $\widehat{\boldsymbol{D}}$ matrix is unchanged from the one produced by the DRA.

Where from here?

- We now have a reduced-order physics-based model of cell dynamics that agrees very closely with the continuum-scale predictions.
- When physics-based model parameter values are well tuned, model matches physical cell performance very well.
- Results below for Panasonic 25 Ah NMC//graphite cell:



- This model executes in very reasonable time, having only five states.
- What's missing?
  - A thermal model: How does temperature affect dynamics? How do dynamics affect temperature?

  - How to identify parameters of physics-based models?
  - How to model cell degradation?
  - How to use these models in an application?

- We'll look at the thermal model next; others are topics of follow-on course(s).