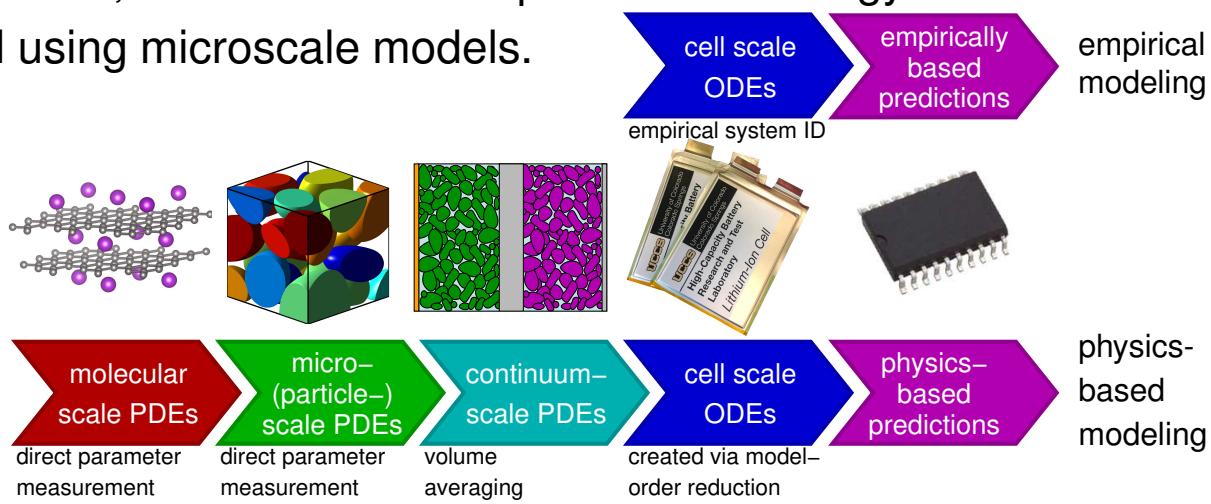


Continuum (Porous Electrode) Cell Models

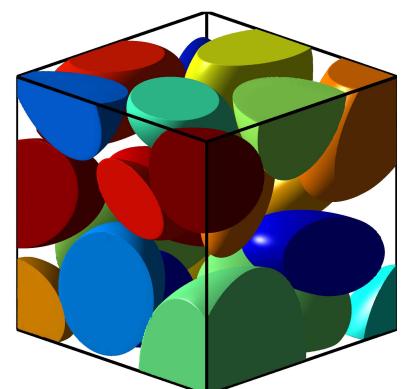
4.1: Chapter goals

- Mathematical models of physical phenomena are expressed most readily at the microscopic scale, for homogeneous materials.
- Accordingly, we have just finished developing microscale models of mechanisms inside lithium-ion cells.
- These described, in three dimensions, the charge and mass balance within the solid particles and within the electrolyte, separately.
- These models can be used to simulate small volumes inside electrodes, comprising small clusters of particles, in order to get ideas of how particle sizes and mixtures of geometries, etc, interact.
- However, it is infeasible with present technology to simulate an entire cell using microscale models.

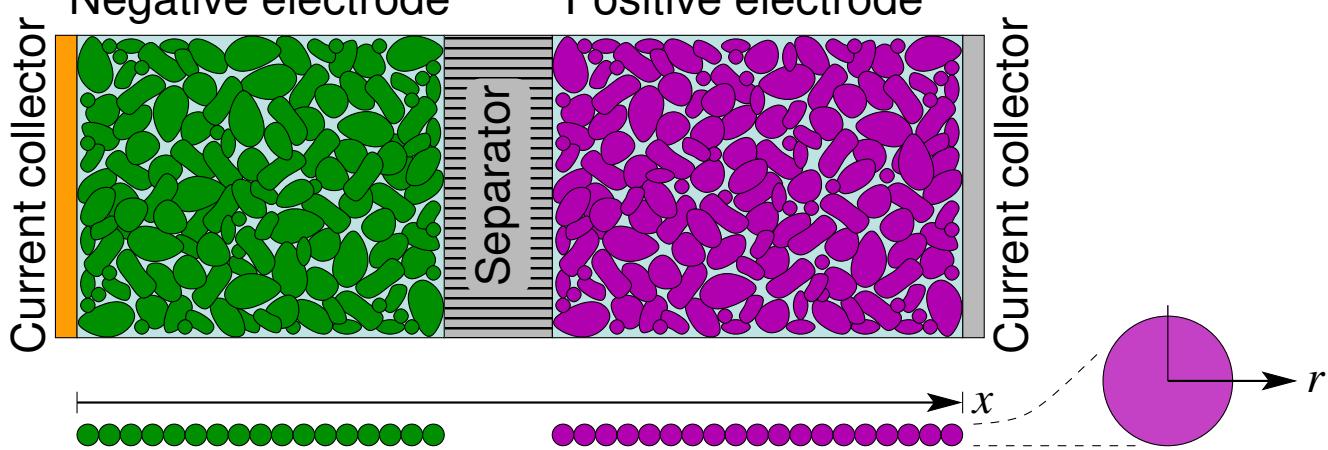


- For cell-level models, we require reduced-complexity macro-scale models that capture the dominant physics of the micro-scale.

- One approach to creating a macro-scale model is by volume-averaging microscopic quantities over a finite but small unit of volume.
- The resultant model is called a “continuum” model.
- Modeling an object as a continuum assumes that the substance of the object completely fills the space it occupies.
 - Modeling an electrode in this way ignores the fact that it is made of particles, and so is not continuous;
 - Modeling the electrolyte this way ignores the fact that it is filled with particles, so is not continuous;
 - However, on length scales much greater than that of a particle’s radius, such models are highly accurate.
- Instead of predicting values of variables at a specific point in a cell, continuum models tell you the average behavior inside the solid and electrolyte in the neighborhood of a specific point.
- Solid and electrolyte “phases” are still considered separately, but their interactions within the volume must be factored in. Microscale geometries need not be known—an average geometry is assumed.
- To make continuum models, we use a volume-averaging approach.
- When volume averaging, we are no longer dealing with homogeneous materials.
- The sample volume is assumed to contain multiple “phases” of matter.
- The figure shows a matrix of solid particles where the voids are filled with electrolyte.



- When we compute volume-average equations, we need to take the multi-phase nature of the sample volume into account.
- The continuum models that we develop can be used in 3-D, but we specialize to a 1-D description of cell dynamics, with an added “pseudo-dimension” that describes activity inside the solid.



- The diagram shows, roughly to (typical) scale, the actual geometry of a lithium-ion cell cross section, the model x dimension, and the model r pseudo dimension.

Goals: Volume-averaging theorems and continuum cell model

- Our first goal is to prove the following three theorems:¹

- Volume-averaging theorem 1 for scalar field ψ :

$$\langle \nabla \psi_\alpha \rangle = \nabla \langle \psi_\alpha \rangle + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \hat{\mathbf{n}}_\alpha dA.$$

- Volume-averaging theorem 2 for vector field ψ :

$$\langle \nabla \cdot \psi_\alpha \rangle = \nabla \cdot \langle \psi_\alpha \rangle + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \cdot \hat{\mathbf{n}}_\alpha dA.$$

¹ The derivations rely heavily on: W.G. Gray and P.C.Y. Lee, “On the theorems for local volume averaging of multiphase systems,” *Int. J. Multiphase Flow*, Vol. 3, pp. 333–40.

3. Volume-averaging theorem 3 for scalar field ψ :

$$\left\langle \frac{\partial \psi_\alpha}{\partial t} \right\rangle = \frac{\partial \langle \psi_\alpha \rangle}{\partial t} - \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \mathbf{v}_{\alpha\beta} \cdot \hat{\mathbf{n}}_\alpha dA.$$

- Then, we will apply these volume-averaging theorems to the microscale models from the prior chapter of notes to derive:
 1. The volume-average approximation for charge conservation in the solid phase of the porous electrode, which is

$$\nabla \cdot (\sigma_{\text{eff}} \nabla \bar{\phi}_s) = a_s F \bar{j}.$$
 2. The solid-phase mass-conservation equation,

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_s r^2 \frac{\partial c_s}{\partial r} \right).$$
 3. The volume-average approximation for charge conservation in the electrolyte phase of the porous electrode, which is

$$\nabla \cdot (\kappa_{\text{eff}} \nabla \bar{\phi}_e + \kappa_{D,\text{eff}} \nabla \ln \bar{c}_e) + a_s F \bar{j} = 0.$$
 4. The volume-average approximation for mass conservation in the electrolyte phase of the porous electrode, which is

$$\frac{\partial (\varepsilon_e \bar{c}_e)}{\partial t} = \nabla \cdot (D_{e,\text{eff}} \nabla \bar{c}_e) + a_s (1 - t_+^0) \bar{j}.$$
 5. The volume-average approximation to the microscopic Butler–Volmer kinetics relationship, $\bar{j} = j(\bar{c}_{s,e}, \bar{c}_e, \bar{\phi}_s, \bar{\phi}_e)$.

4.2: Indicator and Dirac delta functions

- We begin by deriving the volume-averaging theorems.
- The sample volume is divided into two phases: the phase of interest is denoted α ; all other phase(s) are lumped into β .
- Our goal is to find the average value of some variable in phase α .
- To help with notation, we define an indicator function for phase α as

$$\gamma_\alpha(x, y, z, t) = \begin{cases} 1, & \text{if point } (x, y, z) \text{ is in phase } \alpha \text{ at time } t; \\ 0, & \text{otherwise.} \end{cases}$$

- We will need to take derivatives of γ_α , which are zero everywhere except at the $\alpha-\beta$ phase boundaries.
- But, how do we evaluate the derivative right on the boundary?

The Dirac delta function

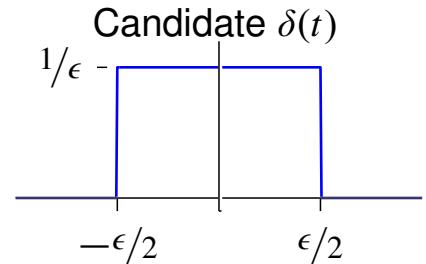
- To explore this, we introduce the Dirac delta function $\delta(x, y, z, t)$.
- This function is unusual—it is defined in terms of its *properties* rather than by stating exactly its *value*. These properties are:

$$\delta(x, y, z, t) = 0, \quad (x, y, z) \neq 0.$$

$$\iiint_V \delta(x, y, z, t) dV = 1.$$

- This is not an ordinary kind of function. It is a *generalized* function, which can have *many* different but equivalent equations describing it.
- In one dimension, an example definition is

$$\delta(x) = \lim_{\epsilon \rightarrow 0} \begin{cases} \frac{1}{\epsilon}, & |x| \leq \epsilon/2; \\ 0, & \text{otherwise.} \end{cases}$$



- This has area 1 for all values of ϵ , and as $\epsilon \rightarrow 0$ it has zero width.
- We can compact notation if we define the “pulse function”

$$\Pi(x) = \begin{cases} 1, & |x| < 1/2; \\ 0, & \text{otherwise.} \end{cases}$$

- Then, we can write

$$\delta(x) = \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} \Pi\left(\frac{x}{\epsilon}\right).$$

Sifting property of the Dirac delta function

- The Dirac delta function has several important properties.
- The *sifting property* states that in one dimension

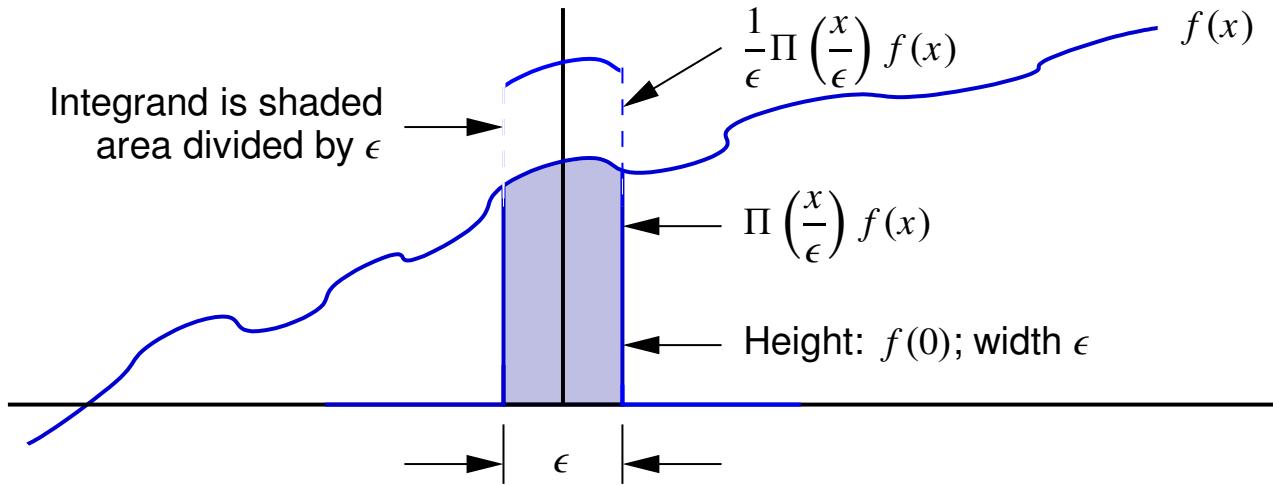
$$\int_{-\infty}^{\infty} f(x, t) \delta(x - x_0, t) dx = f(x_0, t).$$

- The value of the function at the location of the Dirac delta is “sifted out,” and the integral of a function is replaced by the value of that function at a specific point.
- In three dimensions, using vector form, if $\mathbf{x} = (x, y, z)$, and $\mathbf{x}_0 = (x_0, y_0, z_0)$ we can write

$$\iiint_V f(\mathbf{x}, t) \delta(\mathbf{x} - \mathbf{x}_0, t) dV = \begin{cases} f(\mathbf{x}_0, t), & \text{if } \mathbf{x}_0 \text{ is inside } V; \\ 0, & \text{otherwise.} \end{cases}$$

- We will sketch a proof of this relationship in one dimension for $x_0 = 0$.
- Consider using a pulse shape as our candidate Dirac delta function. We write

$$\int_{-\infty}^{\infty} f(x) \delta(x) dx = \lim_{\epsilon \rightarrow 0} \int_{-\infty}^{\infty} \frac{1}{\epsilon} \Pi\left(\frac{x}{\epsilon}\right) f(x) dx.$$



- We see that $f(x)$ is multiplied by zero at nearly every point in the integral.
- But, in the ϵ neighborhood of $x = 0$, it is being multiplied by $1/\epsilon$.
- If $f(x)$ is continuous around $x_0 = 0$, then it will approach the constant value $f(0)$ over the interval $-\epsilon/2$ to $\epsilon/2$.
- So, the integral becomes $f(0)$ times the ϵ width of the Dirac delta multiplied by the $1/\epsilon$ height of the Dirac delta. That is,

$$\int_{-\infty}^{\infty} f(x)\delta(x) dx = \frac{1}{\epsilon} \epsilon f(0) = f(0).$$

- This proof sketch can be generalized to $x_0 \neq 0$ and higher dimensions quite readily.
- The bottom line is that an integral involving a Dirac delta drops one dimension and sifts out the value of the function in the integrand at the location of the Dirac delta.
- For example,

$$\iiint_V f(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}_{\alpha\beta}) dV = \iint_{A_{\alpha\beta}} f(\mathbf{x}) dA,$$

where $\mathbf{x}_{\alpha\beta}$ is the set of points on the surface $A_{\alpha\beta}$ of the $\alpha-\beta$ interface.

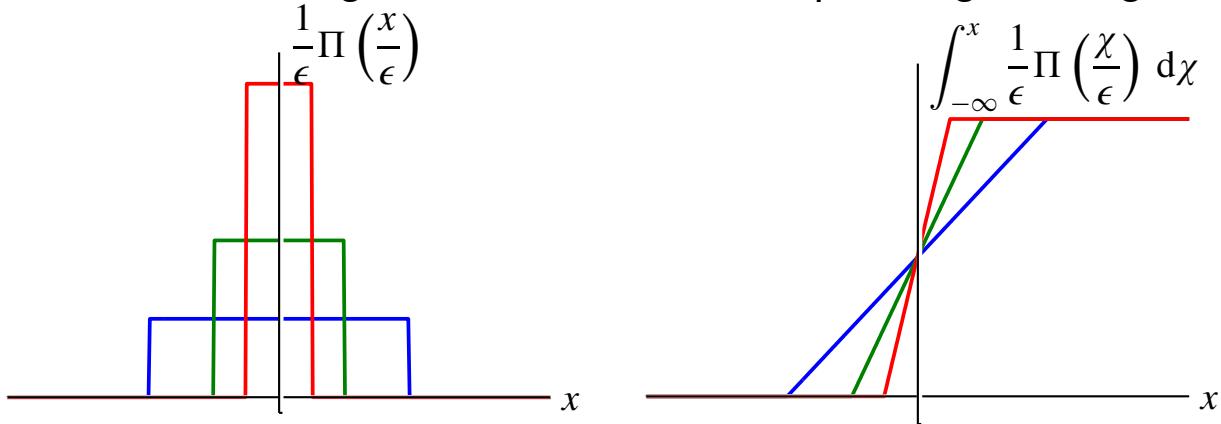
4.3: Gradient of an indicator function

Running integral of a Dirac delta function

- Now, consider integrating a 1-D Dirac delta from $-\infty$ to x .
- That is, we wish to compute

$$\int_{-\infty}^x \delta(\chi) d\chi.$$

- In the figure below, the left frame shows three candidate Dirac delta functions; the right frame shows corresponding running integrals.



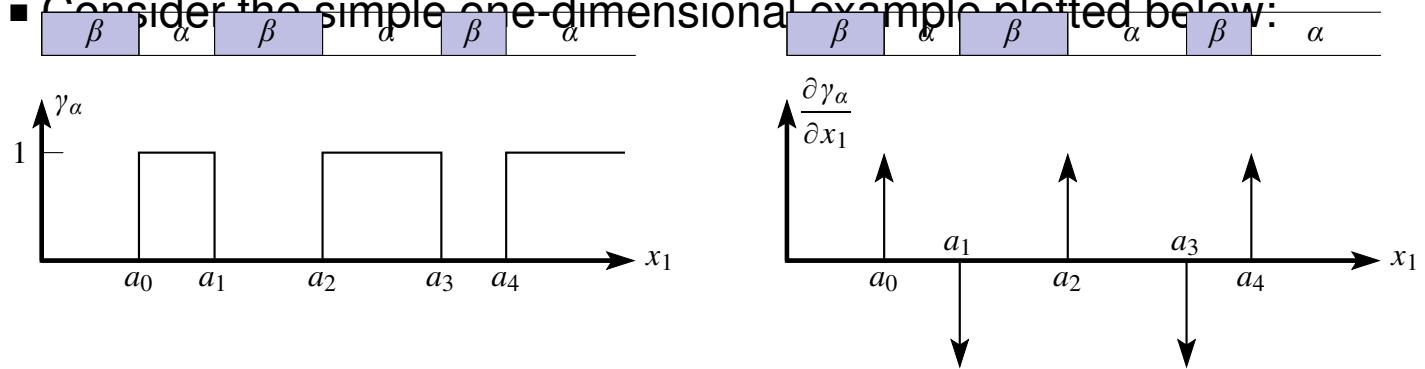
- In the integral, if point x is to the left of the rectangle, the integral sums up a lot of zero values, and the result is zero.
- If point x is to the right of the rectangle, the integral contains the entire Dirac delta function within its limits, so the result must be one.
- If point x falls in the middle of the delta function, the result is finite but undefined (as different candidate delta functions could be used).
- The more closely the approximate Dirac delta function approaches the true Dirac delta, the more closely the integral approaches a step function. In the limit,

$$\int_{-\infty}^x \delta(\chi) d\chi = \begin{cases} 0, & x < 0 \\ 1, & x > 0. \end{cases}$$

- That is, the running integral of a Dirac delta function is a step function.
- Also, the derivative of a step function is the Dirac delta function.

Gradient of the indicator function

- Now, we get to the reason for introducing the Dirac delta function: We need to be able to represent the gradient of the indicator function.
- Consider the simple one-dimensional example plotted below:



- The indicator function $\gamma_\alpha = 1$ for values of x_1 in phase α ; else it is zero.
- Its derivative, $\partial \gamma_\alpha / \partial x_1$, comprises Dirac delta functions.

$$\begin{aligned} \frac{\partial \gamma_\alpha(x_1, t)}{\partial x_1} &= \delta(x_1 - a_0(t)) - \delta(x_1 - a_1(t)) + \delta(x_1 - a_2(t)) \\ &\quad - \delta(x_1 - a_3(t)) + \delta(x_1 - a_4(t)). \end{aligned}$$

- If we define a unit normal vector $\hat{\mathbf{n}}_\alpha$ that points *outward* from the α -phase toward the β -phase at all $\alpha-\beta$ interfaces, we have

$$\frac{\partial \gamma_\alpha(x_1, t)}{\partial x_1} = - \sum_{k=0}^4 \hat{\mathbf{n}}_\alpha \cdot \hat{\mathbf{i}} \delta(x_1 - a_k(t)),$$

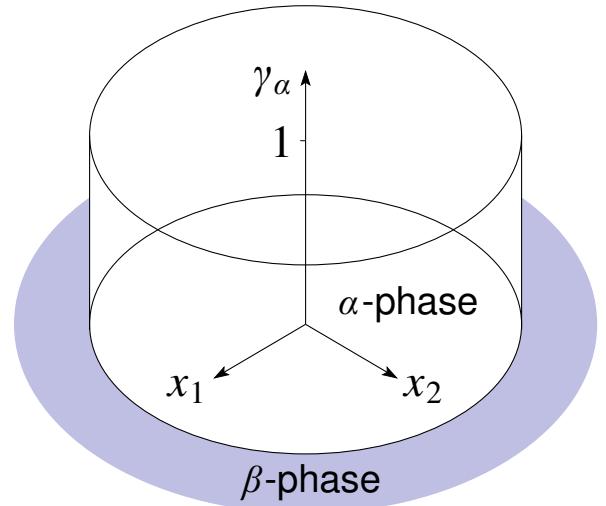
where $\hat{\mathbf{i}}$ is a unit vector in the positive x_1 direction.

- Now, consider a two-dimensional example. In this instance,

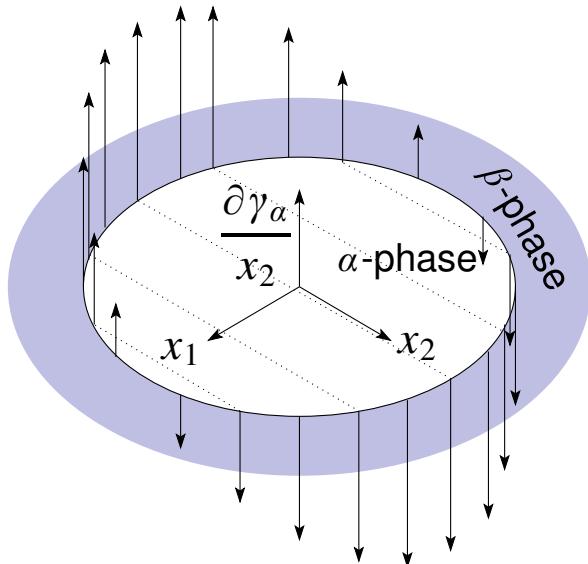
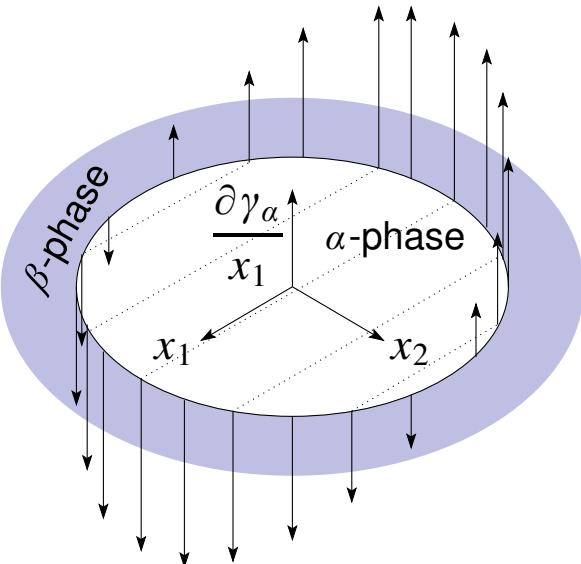
$$\frac{\partial \gamma_\alpha(x_1, x_2, t)}{\partial x_1} = -\hat{\mathbf{n}}_\alpha \cdot \hat{\mathbf{i}} \delta(\mathbf{x} - \mathbf{x}_{\alpha\beta}, t)$$

$$\frac{\partial \gamma_\alpha(x_1, x_2, t)}{\partial x_2} = -\hat{\mathbf{n}}_\alpha \cdot \hat{\mathbf{j}} \delta(\mathbf{x} - \mathbf{x}_{\alpha\beta}, t),$$

where \mathbf{x} is a position vector, $\hat{\mathbf{j}}$ is a unit vector in the positive x_2 direction, and $\mathbf{x}_{\alpha\beta}$ is the position vector of the $\alpha-\beta$ interface.



- x_1 and x_2 partials shown below:



- We generalize to three dimensions by defining the gradient operator over some scalar field $\psi(x, y, z, t)$ as

$$\nabla \psi(x, y, z, t) \triangleq \frac{\partial \psi}{\partial x} \hat{\mathbf{i}} + \frac{\partial \psi}{\partial y} \hat{\mathbf{j}} + \frac{\partial \psi}{\partial z} \hat{\mathbf{k}}$$

- Then, $\nabla \gamma_\alpha(\mathbf{x}, t) = -\hat{\mathbf{n}}_\alpha \delta(\mathbf{x} - \mathbf{x}_{\alpha\beta}, t)$.

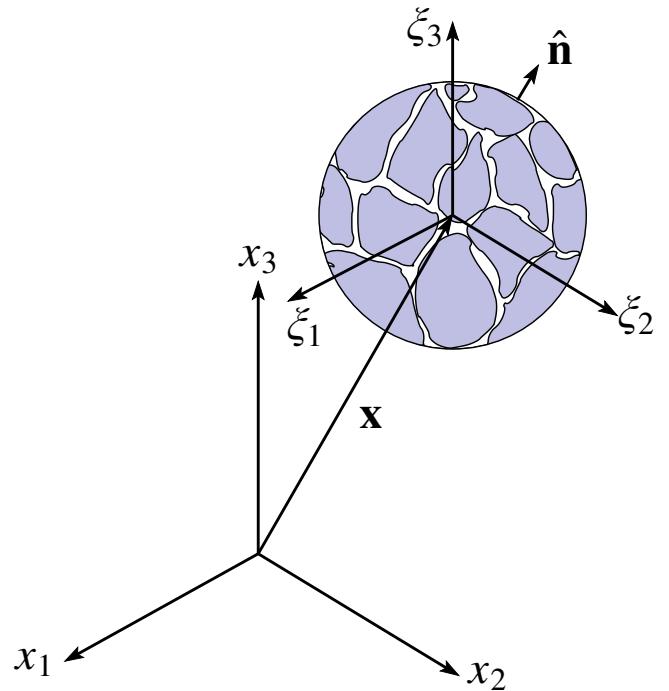
4.4: Phase and intrinsic averages

- When applying averaging techniques to obtain continuum equations, it is necessary to select an averaging volume that will result in meaningful averages.
- This can be met when the characteristic length of the averaging volume is much greater than the pore openings (between particles), but much less than the electrode length.
- Additionally, the orientation, shape, and size of the averaging volume will be independent of space and time.
- We define a local coordinate system ξ_1, ξ_2, ξ_3 , which has axes parallel with the x_1, x_2, x_3 system, but whose origin is located at position \mathbf{x} .
- The location of the averaging volume with respect to the ξ coordinate system is independent of \mathbf{x} .
- For example, we may set the centroid of the averaging volume to the origin of the ξ system.
- The phase average $\langle \psi_\alpha \rangle$ of a property ψ over phase α is defined as

$$\langle \psi_\alpha(\mathbf{x}, t) \rangle = \frac{1}{V} \iiint_V \psi(\mathbf{x} + \boldsymbol{\xi}, t) \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) dV_\xi,$$

where volume $V = V_\alpha + V_\beta$ is independent of space and time.

- However, V_α and V_β themselves will depend on \mathbf{x} and will also depend on t if the medium is deformable (*i.e.*, the phase boundary moves).



- Physically, the phase average is a property of the α -phase only averaged over the entire volume occupied by both the α - and β -phases in the averaging volume.
- Note that we could also write this integral as

$$\langle \psi_\alpha(\mathbf{x}, t) \rangle = \frac{1}{V} \iiint_{V_\alpha(\mathbf{x}, t)} \psi(\mathbf{x} + \boldsymbol{\xi}, t) dV_\xi,$$

but this is less useful since the limits of integration depend on spatial location and on time if the medium deforms.

- The intrinsic phase average $\bar{\psi}_\alpha$ of a property ψ over phase α is

$$\bar{\psi}_\alpha(\mathbf{x}, t) = \frac{1}{V_\alpha(\mathbf{x}, t)} \iiint_{V_\alpha(\mathbf{x}, t)} \psi(\mathbf{x} + \boldsymbol{\xi}, t) dV_\xi.$$

- It describes a property of the α -phase averaged over that phase only.
- Comparing the two types of phase average, we see

$$\langle \psi_\alpha(\mathbf{x}, t) \rangle = \varepsilon_\alpha(\mathbf{x}, t) \bar{\psi}_\alpha(\mathbf{x}, t), \quad \text{or} \quad \bar{\psi}_\alpha(\mathbf{x}, t) = \frac{1}{\varepsilon_\alpha(\mathbf{x}, t)} \langle \psi_\alpha(\mathbf{x}, t) \rangle,$$

where the volume fraction of the α -phase is defined as

$$\varepsilon_\alpha(\mathbf{x}, t) = \frac{V_\alpha(\mathbf{x}, t)}{V} = \frac{1}{V} \iiint_V \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) dV_\xi.$$

EXAMPLE: Consider a rock-filled beaker, where $\varepsilon_s = 0.5$, and a second electrolyte-filled beaker having salt concentration 1000 mol m^{-3} . We pour electrolyte into the first beaker until it is full, so $\varepsilon_e = 0.5$.

- Taking a phase average of salt concentration in the porous media,

$$\langle c_e \rangle = \frac{1}{V} \iiint_{V_e} c_e(\mathbf{x} + \boldsymbol{\xi}, t) dV_\xi = c_e \frac{V_e}{V} = 0.5c_e = 500 \text{ mol m}^{-3}.$$

- Taking an intrinsic phase average of the salt concentration instead

$$\bar{c}_e = \frac{1}{V_e} \iiint_{V_e} c_e(\mathbf{x} + \boldsymbol{\xi}, t) dV_\xi = c_e \frac{V_e}{V_e} = c_e = 1000 \text{ mol m}^{-3}.$$

- The phase average tells us, from the perspective of the entire volume, what is the concentration of salt in the volume.
- The intrinsic phase average tells us, from the perspective of the solution within the volume, the concentration of salt in the solution.
- Intrinsic phase average is directly related to micro-scale models where physical measurements are made, so is the one we will use.
- But, we will derive our equations in terms of the phase average (easier), and convert to intrinsic phase averages when finished.
- Before proceeding with the averaging theorems, we examine a useful identity involving the gradient operator.
 - Define ∇_x to refer to the gradient taken with respect to the \mathbf{x} coordinates, holding ξ_1 , ξ_2 , and ξ_3 constant;
 - Define ∇_ξ to refer to the gradient taken with respect to the ξ coordinates, holding x_1 , x_2 , and x_3 constant;
 - Define ∇ to refer to either ∇_x or ∇_ξ .
- If a function is symmetrically dependent on \mathbf{x} and ξ (*i.e.*, it depends on $\mathbf{x} + \xi$ rather than on \mathbf{x} and ξ) the gradient in the \mathbf{x} -coordinate system is equal to the gradient in the ξ -coordinate system:

$$\nabla_x \psi(\mathbf{x} + \xi, t) = \nabla_\xi \psi(\mathbf{x} + \xi, t) = \nabla \psi(\mathbf{x} + \xi, t)$$

$$\nabla_x \gamma_\alpha(\mathbf{x} + \xi, t) = \nabla_\xi \gamma_\alpha(\mathbf{x} + \xi, t) = \nabla \gamma_\alpha(\mathbf{x} + \xi, t).$$

PROOF: Consider

$$\begin{aligned} \nabla_x \psi(\mathbf{x} + \xi, t) &= \nabla_x \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t) \\ &= \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial x_1} \hat{\mathbf{i}} \end{aligned}$$

$$\begin{aligned}
& + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial x_2} \hat{\mathbf{j}} \\
& + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial x_3} \hat{\mathbf{k}} \\
= & \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_1 + \xi_1)} \underbrace{\frac{\partial(x_1 + \xi_1)}{\partial x_1}}_1 \hat{\mathbf{i}} \\
& + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_2 + \xi_2)} \underbrace{\frac{\partial(x_2 + \xi_2)}{\partial x_2}}_1 \hat{\mathbf{j}} \\
& + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_3 + \xi_3)} \underbrace{\frac{\partial(x_3 + \xi_3)}{\partial x_3}}_1 \hat{\mathbf{k}} \\
= & \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_1 + \xi_1)} \hat{\mathbf{i}} \\
& + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_2 + \xi_2)} \hat{\mathbf{j}} \\
& + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_3 + \xi_3)} \hat{\mathbf{k}}.
\end{aligned}$$

■ Similarly,

$$\begin{aligned}
\nabla_{\xi} \psi(\mathbf{x} + \boldsymbol{\xi}, t) &= \nabla_{\xi} \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t) \\
&= \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial \xi_1} \hat{\mathbf{i}} \\
&\quad + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial \xi_2} \hat{\mathbf{j}} \\
&\quad + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial \xi_3} \hat{\mathbf{k}}
\end{aligned}$$

$$\begin{aligned}
&= \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_1 + \xi_1)} \underbrace{\frac{\partial(x_1 + \xi_1)}{\partial\xi_1}}_1 \hat{\mathbf{i}} \\
&\quad + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_2 + \xi_2)} \underbrace{\frac{\partial(x_2 + \xi_2)}{\partial\xi_2}}_1 \hat{\mathbf{j}} \\
&\quad + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_3 + \xi_3)} \underbrace{\frac{\partial(x_3 + \xi_3)}{\partial\xi_3}}_1 \hat{\mathbf{k}} \\
&= \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_1 + \xi_1)} \hat{\mathbf{i}} \\
&\quad + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_2 + \xi_2)} \hat{\mathbf{j}} \\
&\quad + \frac{\partial \psi(x_1 + \xi_1, x_2 + \xi_2, x_3 + \xi_3, t)}{\partial(x_3 + \xi_3)} \hat{\mathbf{k}}.
\end{aligned}$$

- By comparing the final forms for $\nabla_x \psi(\mathbf{x} + \boldsymbol{\xi}, t)$ and $\nabla_{\xi} \psi(\mathbf{x} + \boldsymbol{\xi}, t)$, we see that the two are equal.
- By the same argument, $\nabla_x \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) = \nabla_{\xi} \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t)$.
- Also, by the same argument,

$$\nabla_x \cdot \boldsymbol{\psi}(\mathbf{x} + \boldsymbol{\xi}, t) = \nabla_{\xi} \cdot \boldsymbol{\psi}(\mathbf{x} + \boldsymbol{\xi}, t) = \nabla \cdot \boldsymbol{\psi}(\mathbf{x} + \boldsymbol{\xi}, t).$$

4.5: Volume-averaging theorems 1 and 2

Volume-averaging theorem 1

- We wish to show for scalar field ψ , if ψ is continuous in the α phase,

$$\langle \nabla \psi_\alpha \rangle = \nabla \langle \psi_\alpha \rangle + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \hat{\mathbf{n}}_\alpha dA.$$

- We start with the definition of phase average for generic quantity θ :

$$\langle \theta_\alpha(\mathbf{x}, t) \rangle = \frac{1}{V} \iiint_V \theta(\mathbf{x} + \boldsymbol{\xi}, t) \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) dV_\xi.$$

- Then, letting $\theta = \nabla \psi$,

$$\langle \nabla \psi_\alpha(\mathbf{x}, t) \rangle = \frac{1}{V} \iiint_V [\nabla \psi(\mathbf{x} + \boldsymbol{\xi}, t)] \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) dV_\xi.$$

- Recall the product rule from calculus: $\nabla(AB) = (\nabla A)B + A(\nabla B)$, and let $A = \psi(\mathbf{x} + \boldsymbol{\xi}, t)$ and $B = \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t)$.

- Noticing that the integrand is of the form $(\nabla A)B$, we can then write

$$\begin{aligned} \langle \nabla \psi_\alpha(\mathbf{x}, t) \rangle &= \frac{1}{V} \iiint_V \nabla[\psi(\mathbf{x} + \boldsymbol{\xi}, t) \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t)] dV_\xi \\ &\quad - \frac{1}{V} \iiint_V \psi(\mathbf{x} + \boldsymbol{\xi}, t) [\nabla \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t)] dV_\xi. \end{aligned}$$

- Substituting the known gradient of the indicator function gives

$$\begin{aligned} \langle \nabla \psi_\alpha(\mathbf{x}, t) \rangle &= \frac{1}{V} \iiint_V \nabla[\psi(\mathbf{x} + \boldsymbol{\xi}, t) \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t)] dV_\xi \\ &\quad + \frac{1}{V} \iiint_V \psi(\mathbf{x} + \boldsymbol{\xi}, t) \hat{\mathbf{n}}_\alpha \delta(\mathbf{x} + \boldsymbol{\xi} - \mathbf{x}_{\alpha\beta}, t) dV_\xi. \end{aligned}$$

- By the properties of the delta function, the second volume integral drops to a surface integral over the $\alpha-\beta$ phase interface

$$\frac{1}{V} \iiint_V \psi(\mathbf{x} + \boldsymbol{\xi}, t) \hat{\mathbf{n}}_\alpha \delta(\mathbf{x} + \boldsymbol{\xi} - \mathbf{x}_{\alpha\beta}, t) dV_\xi = \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \hat{\mathbf{n}}_\alpha dA,$$

and we get

$$\begin{aligned} \langle \nabla \psi_\alpha(\mathbf{x}, t) \rangle &= \frac{1}{V} \iiint_V \nabla [\psi(\mathbf{x} + \boldsymbol{\xi}, t) \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t)] dV_\xi \\ &\quad + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \hat{\mathbf{n}}_\alpha dA. \end{aligned}$$

- We consider $\nabla = \nabla_x$ on the RHS, so it may be removed from the integral because V is independent of \mathbf{x} . Thus, we obtain

$$\begin{aligned} \langle \nabla \psi_\alpha \rangle &= \nabla \left[\frac{1}{V} \iiint_V \psi(\mathbf{x} + \boldsymbol{\xi}, t) \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) dV_\xi \right] \\ &\quad + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \hat{\mathbf{n}}_\alpha dA \\ \langle \nabla \psi_\alpha \rangle &= \nabla \langle \psi_\alpha \rangle + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \hat{\mathbf{n}}_\alpha dA, \end{aligned}$$

which proves volume averaging theorem 1.

INTERPRETATION: Volume average of gradient = gradient of volume average plus correction term.

- Correction sums up scaled vectors pointing away from the $\alpha-\beta$ interface. Result points in the direction of largest surface field.
- By extension, we can find the intrinsic phase average

$$\begin{aligned} \overline{\nabla \psi_\alpha} &= \frac{1}{\varepsilon_\alpha} \langle \nabla \psi_\alpha \rangle = \frac{1}{\varepsilon_\alpha} \left[\nabla \langle \psi_\alpha \rangle + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \hat{\mathbf{n}}_\alpha dA \right] \\ &= \frac{1}{\varepsilon_\alpha} \left[\nabla (\varepsilon_\alpha \bar{\psi}_\alpha) + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \hat{\mathbf{n}}_\alpha dA \right]. \end{aligned}$$

- Rearranging this expression gives

$$\varepsilon_\alpha \nabla \overline{\psi_\alpha} = \nabla (\varepsilon_\alpha \bar{\psi}_\alpha) + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \hat{\mathbf{n}}_\alpha dA.$$

- Be careful to note that ε_α is *inside* the gradient operator on the RHS, which is important if ε_α is a function of \mathbf{x} .

Volume-averaging theorem 2

- We wish to show for vector field ψ , if ψ is continuous in the α phase,

$$\langle \nabla \cdot \psi_\alpha \rangle = \nabla \cdot \langle \psi_\alpha \rangle + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \cdot \hat{\mathbf{n}}_\alpha dA.$$

- We start with the definition of phase average for generic quantity θ

$$\langle \theta_\alpha(\mathbf{x}, t) \rangle = \frac{1}{V} \iiint_V \theta(\mathbf{x} + \xi, t) \gamma_\alpha(\mathbf{x} + \xi, t) dV_\xi.$$

- Then, if $\theta = \nabla \cdot \psi$,

$$\langle \nabla \cdot \psi_\alpha(\mathbf{x}, t) \rangle = \frac{1}{V} \iiint_V [\nabla \cdot \psi(\mathbf{x} + \xi, t)] \gamma_\alpha(\mathbf{x} + \xi, t) dV_\xi.$$

- The divergence operator also satisfies a product rule

$$\nabla \cdot (\gamma \mathbf{F}) = (\nabla \gamma) \cdot \mathbf{F} + \gamma (\nabla \cdot \mathbf{F}). \text{ Let } \mathbf{F} = \psi(\mathbf{x} + \xi, t) \text{ and } \gamma = \gamma_\alpha(\mathbf{x} + \xi, t).$$

- Noticing that the integrand is of the form $\gamma (\nabla \cdot \mathbf{F})$, we can write

$$\begin{aligned} \langle \nabla \cdot \psi_\alpha(\mathbf{x}, t) \rangle &= \frac{1}{V} \iiint_V \nabla \cdot [\psi(\mathbf{x} + \xi, t) \gamma_\alpha(\mathbf{x} + \xi, t)] dV_\xi \\ &\quad - \frac{1}{V} \iiint_V \psi(\mathbf{x} + \xi, t) \cdot [\nabla \gamma_\alpha(\mathbf{x} + \xi, t)] dV_\xi. \end{aligned}$$

- Substituting the known gradient of the indicator function gives

$$\begin{aligned} \langle \nabla \cdot \psi_\alpha(\mathbf{x}, t) \rangle &= \frac{1}{V} \iiint_V \nabla \cdot [\psi(\mathbf{x} + \xi, t) \gamma_\alpha(\mathbf{x} + \xi, t)] dV_\xi \\ &\quad + \frac{1}{V} \iiint_V \psi(\mathbf{x} + \xi, t) \cdot \hat{\mathbf{n}}_\alpha \delta(\mathbf{x} + \xi - \mathbf{x}_{\alpha\beta}, t) dV_\xi. \end{aligned}$$

- As before, the second volume integral drops to a surface integral over the $\alpha-\beta$ phase interface

$$\frac{1}{V} \iiint_V \psi(\mathbf{x} + \boldsymbol{\xi}, t) \cdot \hat{\mathbf{n}}_\alpha \delta(\mathbf{x} + \boldsymbol{\xi} - \mathbf{x}_{\alpha\beta}, t) dV_\xi = \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \cdot \hat{\mathbf{n}}_\alpha dA,$$

and we get

$$\begin{aligned} \langle \nabla \cdot \psi_\alpha(\mathbf{x}, t) \rangle &= \frac{1}{V} \iiint_V \nabla \cdot [\psi(\mathbf{x} + \boldsymbol{\xi}, t) \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t)] dV_\xi \\ &\quad + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \cdot \hat{\mathbf{n}}_\alpha dA. \end{aligned}$$

- We consider $\nabla \cdot = \nabla_x \cdot$ on the RHS, so it may be removed from the integral because V is independent of \mathbf{x} . Thus, we obtain

$$\begin{aligned} \langle \nabla \cdot \psi_\alpha \rangle &= \nabla \cdot \left[\frac{1}{V} \iiint_V \psi(\mathbf{x} + \boldsymbol{\xi}, t) \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) dV_\xi \right] \\ &\quad + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \cdot \hat{\mathbf{n}}_\alpha dA \\ \langle \nabla \cdot \psi_\alpha \rangle &= \nabla \cdot \langle \psi_\alpha \rangle + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \cdot \hat{\mathbf{n}}_\alpha dA, \end{aligned}$$

which proves volume averaging theorem 2.

INTERPRETATION: Volume average of divergence = divergence of volume average plus correction term.

- Correction sums flux out of surface across $\alpha-\beta$ interface.
- By extension, the intrinsic phase average is

$$\varepsilon_\alpha \overline{\nabla \cdot \psi_\alpha} = \nabla \cdot (\varepsilon_\alpha \bar{\psi}_\alpha) + \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \cdot \hat{\mathbf{n}}_\alpha dA.$$

4.6: Volume-averaging theorem 3

- We wish to show for scalar field ψ , if ψ is continuous in the α phase,

$$\left\langle \frac{\partial \psi_\alpha}{\partial t} \right\rangle = \frac{\partial \langle \psi_\alpha \rangle}{\partial t} - \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \mathbf{v}_{\alpha\beta} \cdot \hat{\mathbf{n}}_\alpha \, dA,$$

where $\mathbf{v}_{\alpha\beta}$ is the velocity of displacement of the interface.

- We start with the definition of phase average for generic quantity θ

$$\langle \theta_\alpha(\mathbf{x}, t) \rangle = \frac{1}{V} \iiint_V \theta(\mathbf{x} + \boldsymbol{\xi}, t) \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \, dV_\xi.$$

- Then if we let $\theta = \partial \psi / \partial t$,

$$\left\langle \frac{\partial \psi_\alpha}{\partial t} \right\rangle = \frac{1}{V} \iiint_V [\partial \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) / \partial t] \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \, dV_\xi.$$

- By calculus product rule, $\partial(AB)/\partial t = (\partial A/\partial t)B + A(\partial B/\partial t)$. Let $A = \psi(\mathbf{x} + \boldsymbol{\xi}, t)$ and $B = \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t)$.
- Noticing that the integrand is of the form $(\partial A/\partial t)B$, we can write

$$\begin{aligned} \left\langle \frac{\partial \psi_\alpha}{\partial t} \right\rangle &= \frac{1}{V} \iiint_V \partial[\psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t)] / \partial t \, dV_\xi \\ &\quad - \frac{1}{V} \iiint_V \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) [\partial \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) / \partial t] \, dV_\xi. \end{aligned}$$

- Because V is independent of time, the order of differentiation or integration in the first term may be reversed, and we obtain

$$\left\langle \frac{\partial \psi_\alpha}{\partial t} \right\rangle = \frac{\partial \langle \psi_\alpha \rangle}{\partial t} - \frac{1}{V} \iiint_V \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) [\partial \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) / \partial t] \, dV_\xi.$$

- First note that if the α phase is *not* deforming, the partial derivative will be zero, and the integral term goes away.
 - This is the case we are concerned about.

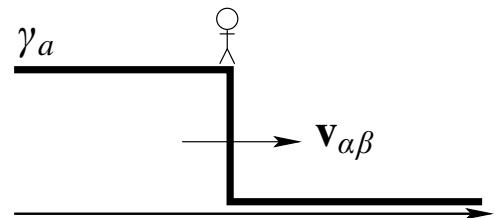
- It is more complex if the α phase *is* deforming. Then, γ_α will be a function of time, and the second term will be nonzero in general.
- We will use the fact that the total derivative of γ_α with respect to time is

$$\begin{aligned}\frac{d\gamma_\alpha}{dt} &= \frac{\partial\gamma_\alpha}{\partial t} + \frac{dx_1}{dt}\frac{\partial\gamma_\alpha}{\partial x_1} + \frac{dx_2}{dt}\frac{\partial\gamma_\alpha}{\partial x_2} + \frac{dx_3}{dt}\frac{\partial\gamma_\alpha}{\partial x_3} \\ &= \frac{\partial\gamma_\alpha}{\partial t} + \frac{d\mathbf{x}}{dt} \cdot \nabla\gamma_\alpha.\end{aligned}$$

- Note: $\partial\gamma_\alpha/\partial t$ states how γ_α changes as a function of time only. $d\gamma_\alpha/dt$ instead states how an observer's measurement of γ_α changes as a function of all variables, including observer's own velocity $d\mathbf{x}/dt$.
- To understand this, first suppose that $\partial\gamma_\alpha/\partial t = 0$. This means that the γ_α function itself is not changing.
- If we are located at some stationary (x_1, x_2, x_3) point, our velocity $d\mathbf{x}/dt = 0$, and we will look around and see that nothing is changing, so the (total) derivative will also be zero.
- However, if we are moving around the function at some nonzero velocity $d\mathbf{x}/dt$, then we will experience a change in the value of γ_α that we measure, even though the function itself isn't changing, simply because we are evaluating it at different points.
 - Thus, $d\gamma_\alpha/dt \neq 0$ in general, even when $\partial\gamma_\alpha/\partial t = 0$.
 - Further, we will get different values for $d\gamma_\alpha/dt$ when we move around the space at different velocities $d\mathbf{x}/dt$.
- This simplifies when the observation point moves at the same speed as the $\alpha-\beta$ phase boundary, $d\mathbf{x}/dt = \mathbf{v}_{\alpha\beta}$:

$$\frac{\partial\gamma_\alpha}{\partial t} = \frac{d\gamma_\alpha}{dt} - \mathbf{v}_{\alpha\beta} \cdot \nabla\gamma_\alpha.$$

- For this choice of $d\mathbf{x}/dt$, the total derivative becomes what is known as a substantial derivative that moves with the interface.
- An observer “surfing on” the moving interfacial boundary will notice no change in γ_α versus time.
- It remains a step function that shifts with the moving boundary.
- The value of the function measured by the observer moving at velocity $\mathbf{v}_{\alpha\beta}$ doesn’t vary with time.
- So, the total derivative is zero when $d\mathbf{x}/dt = \mathbf{v}_{\alpha\beta}$, and we can write



- This yields

$$\begin{aligned} \left\langle \frac{\partial \psi_\alpha}{\partial t} \right\rangle &= \frac{\partial \langle \psi_\alpha \rangle}{\partial t} + \frac{1}{V} \iiint_V \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \mathbf{v}_{\alpha\beta}(\mathbf{x} + \boldsymbol{\xi}, t) \cdot \nabla \gamma_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) dV_{\boldsymbol{\xi}} \\ &= \frac{\partial \langle \psi_\alpha \rangle}{\partial t} + \frac{1}{V} \iiint_V \psi_\alpha(\mathbf{x} + \boldsymbol{\xi}, t) \mathbf{v}_{\alpha\beta}(\mathbf{x} + \boldsymbol{\xi}, t) \cdot (-\hat{\mathbf{n}}_\alpha \delta(\mathbf{x} + \boldsymbol{\xi} - \mathbf{x}_{\alpha\beta})) dV_{\boldsymbol{\xi}} \\ \left\langle \frac{\partial \psi_\alpha}{\partial t} \right\rangle &= \frac{\partial \langle \psi_\alpha \rangle}{\partial t} - \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \mathbf{v}_{\alpha\beta} \cdot \hat{\mathbf{n}}_\alpha dA. \end{aligned}$$

INTERPRETATION: Volume average of time derivative = time derivative of volume average plus correction term.

- Correction accounts for a net dilution of field ψ_α if V_α is growing, or a concentration of the field ψ_α if the V_α is shrinking.
- By extension

$$\varepsilon_\alpha \left[\frac{\partial \psi_\alpha}{\partial t} \right] = \frac{\partial (\varepsilon_\alpha \bar{\psi}_\alpha)}{\partial t} - \frac{1}{V} \iint_{A_{\alpha\beta}} \psi_\alpha \mathbf{v}_{\alpha\beta} \cdot \hat{\mathbf{n}}_\alpha dA.$$

4.7: Continuum models: Charge conservation in the solid

- We now apply the volume-averaging theorems to develop continuum model equivalents of the five microscale model equations.
- Start with the microscale model of charge conservation in the solid,

$$\nabla \cdot (\mathbf{i}_s) = \nabla \cdot (-\sigma \nabla \phi_s) = 0.$$

- Using intrinsic averages and volume-averaging theorem 2

$$\begin{aligned} \varepsilon_s \overline{\nabla \cdot (-\sigma \nabla \phi_s)} &= \nabla \cdot \left(\varepsilon_s \overline{(-\sigma \nabla \phi_s)} \right) + \frac{1}{V} \iint_{A_{se}} (-\sigma \nabla \phi_s) \cdot \hat{\mathbf{n}}_s \, dA \\ 0 &= \nabla \cdot \left(\varepsilon_s \overline{(-\sigma \nabla \phi_s)} \right) + \frac{1}{V} \iint_{A_{se}} (-\sigma \nabla \phi_s) \cdot \hat{\mathbf{n}}_s \, dA. \end{aligned}$$

- Let's look at the integral term first. Note that we are integrating over the solid-electrolyte boundary.
- Last chapter, we noted the boundary condition for the charge conservation equation; namely,

$$\hat{\mathbf{n}}_s \cdot \sigma \nabla \phi_s = -Fj.$$

ASSUME: That j is homogeneous, and that we can model j using volume-averaged inputs.

$$\begin{aligned} \frac{1}{V} \iint_{A_{se}} (-\sigma \nabla \phi_s) \cdot \hat{\mathbf{n}}_s \, dA &= \frac{1}{V} \iint_{A_{se}} Fj(c_s, c_e, \phi_s, \phi_e) \, dA \\ &\approx \frac{A_{se}}{V} Fj(\bar{c}_{s,e}, \bar{c}_e, \bar{\phi}_s, \bar{\phi}_e) \\ &\approx a_s Fj(\bar{c}_{s,e}, \bar{c}_e, \bar{\phi}_s, \bar{\phi}_e) = a_s F \bar{j}. \end{aligned}$$

ASSUME: To calculate a_s , we typically assume spherical particles with radius R_s and volume fraction ε_s :

$$a_s = \frac{\text{total surface area of spheres in volume}}{\text{total volume of a sphere}}$$

$$= \varepsilon_s \frac{4\pi R_s^2}{\frac{4}{3}\pi R_s^3} = \frac{3\varepsilon_s}{R_s}.$$

- So, we now have the result

$$0 = \nabla \cdot \left(\varepsilon_s \overline{(-\sigma \nabla \phi_s)} \right) + a_s F \bar{j}$$

$$\nabla \cdot \left(\varepsilon_s \overline{(-\sigma \nabla \phi_s)} \right) = -a_s F \bar{j}.$$

- What to do with the $\overline{(-\sigma \nabla \phi_s)}$ term? We might consider using volume-averaging theorem 1, but note that we don't know what $\phi_s \hat{n}_s$ is at the boundary, so are unable to evaluate this term.

ASSUME: Instead, it's common to model $\varepsilon_s \overline{(-\sigma \nabla \phi_s)} \approx -\sigma_{\text{eff}} \nabla \bar{\phi}_s$.

- The effective conductivity $\sigma_{\text{eff}} = \frac{\varepsilon_s \sigma \delta}{\tau}$, where $\delta < 1$ is the constrictivity of the and $\tau \geq 1$ is the tortuosity of the media.
- That is, σ is the *bulk* conductivity of homogeneous materials, and σ_{eff} is the *effective* conductivity of the solid in the porous media.
- Note that $\sigma_{\text{eff}} < \sigma$ since there are restrictions to flow of current.
- It is frequently assumed that $\sigma_{\text{eff}} = \sigma \varepsilon_s^{\text{brug}}$, where “brug” is Bruggeman’s coefficient, and is normally assumed to take on the value of 1.5, although other values may work better.
- To get better value for σ_{eff} , we could do microscale simulations with realistic particle geometries, or measure directly via experiment.
- Collecting the above results, we now have the final continuum model of charge conservation in the solid,

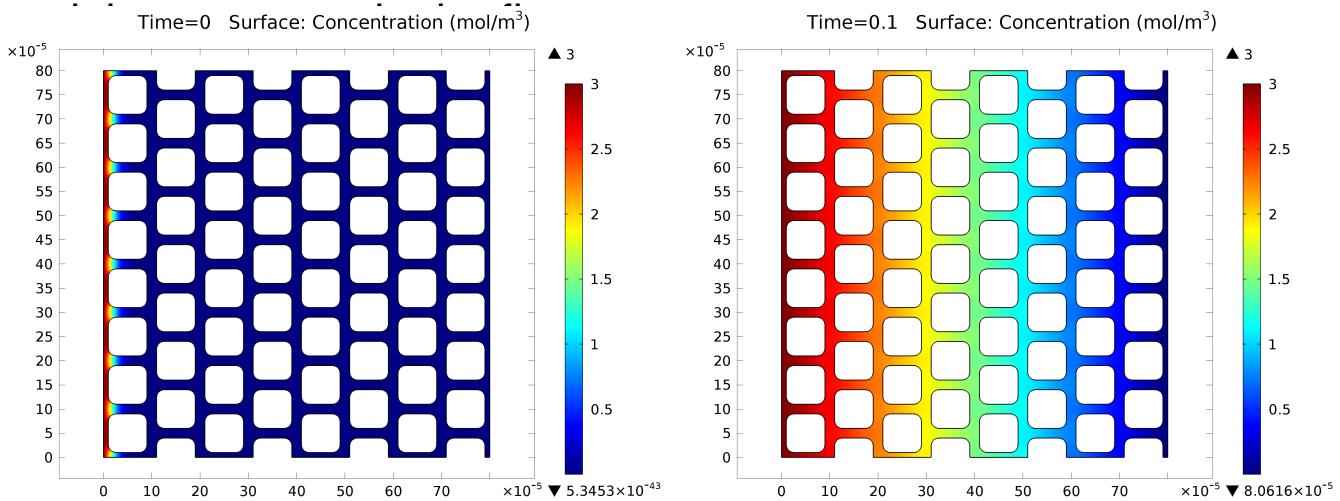
$$\nabla \cdot (-\sigma_{\text{eff}} \nabla \bar{\phi}_s) = -a_s F \bar{j}.$$

- Also note that $\varepsilon_s \bar{\mathbf{i}}_s = \varepsilon_s (\overline{-\sigma \nabla \phi_s}) = -\sigma_{\text{eff}} \nabla \bar{\phi}_s$.

How well does the Bruggeman relationship work?

- We now illustrate, by example, how well an effective property in a volume-average equation can represent the effect of an intrinsic property in a microscale equation.
- We use the PDE simulation system COMSOL to help find results (example is adapted from COMSOL documentation).
- Consider the simplified microscale electrolyte concentration equation

$$\frac{\partial c}{\partial t} + \nabla \cdot (-D \nabla c) = 0,$$



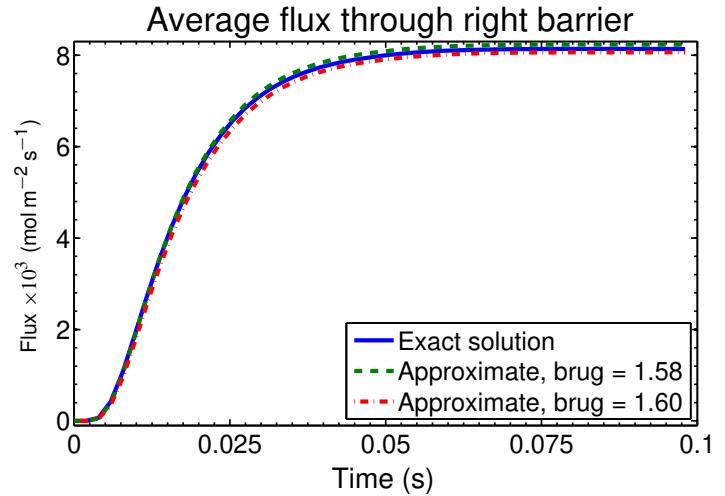
- The rectangular objects are obstacles, which are similar in a sense to the solid particles in an electrode.
- The voids between the rectangular objects are open, much like pores in an electrode through which electrolyte can move.
- At $t = 0$ (left frame), there is a high concentration of material at the left boundary, and zero concentration elsewhere.

- By time 0.1 s (right frame), there is a uniform concentration gradient established through the porous structure, as indicated by the shading.
- We're interested in modeling the flux of material out the right edge. It is zero at time $t = 0$, and increases to a steady-state value over time.
- We simulate the high-fidelity PDE model over the complex geometry; we also make a one-dimensional continuum model via

$$\varepsilon \frac{\partial \bar{c}}{\partial t} + \nabla \cdot (-D_{\text{eff}} \nabla \bar{c}) = 0,$$

where $D_{\text{eff}} = D_{\varepsilon^{\text{brug}}}$.

- The microscale solution is drawn as the solid blue line.
- Continuum-model solutions are drawn for $\text{brug} = 1.58$ and $\text{brug} = 1.60$.



- With the correct choice of “brug,” the continuum model gives predictions that are very close to the exact solution.
 - Results are nearly indistinguishable when $\text{brug} = 1.59$.
- So, this example shows us that representing an effective property as a constant times the intrinsic property can be very accurate.
- However, the Bruggeman constant may need to be different from the commonly used value of 1.5 to achieve the best match.

4.8: Mass conservation in the solid and electrolyte

Mass conservation in the solid

- As mentioned earlier, our continuum model has spatial dimension(s) *plus* a pseudo dimension.
- This pseudo dimension represents what is happening at some point inside a particle that resides at some spatial location.
 - We could make a continuum model with three spatial dimensions plus an additional pseudo dimension, resulting in a pseudo-four-dimensional model. The math we develop here is general enough to encompass this case, but
 - We ultimately specialize to a model with one spatial dimension plus the additional pseudo dimension, resulting in a pseudo-two-dimensional model.
- We assume that there is a particle centered at any spatial location, that the particle is spherical, and that the concentration of lithium within the particle is spherically symmetric.
- So, to create the continuum equation for mass conservation within the solid, we don't need to use any volume-averaging theorems, because we are not volume averaging! Instead, we're specializing the microscale equation to these assumptions.
- Recall the microscale model, $\frac{\partial c_s}{\partial t} = \nabla \cdot (D_s \nabla c_s)$.
- Recall further that the divergence of a vector field can be written in spherical coordinates as

$$\nabla \cdot \mathbf{F} = \frac{1}{r^2} \frac{\partial(r^2 F_r)}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial(\sin \theta F_\theta)}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial F_\phi}{\partial \phi}.$$

ASSUME: Spherical particles, with symmetry in both the θ and ϕ axes.

This gives

$$\nabla \cdot \mathbf{F} = \frac{1}{r^2} \frac{\partial(r^2 F_r)}{\partial r}.$$

- Applying this to the RHS of the microscopic model gives

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_s r^2 \frac{\partial c_s}{\partial r} \right).$$

Mass conservation in the electrolyte

- Recall the microscale equation for mass conservation in the electrolyte,

$$\frac{\partial c_e}{\partial t} = \nabla \cdot (D_e \nabla c_e) - \frac{\mathbf{i}_e \cdot \nabla t_+^0}{F} - \nabla \cdot (c_e \mathbf{v}_0),$$

where, for simplicity, we have chosen to write

$$D_e = D \left(1 - \frac{d \ln c_0}{d \ln c_e} \right).$$

ASSUME: We're going to immediately specialize to the case where we assume that $\nabla t_+^0 = 0$ and $\mathbf{v}_0 = 0$. We also assume that the phases do not deform, so $\mathbf{v}_{se} = 0$.

- Taking the intrinsic volume average of the LHS using volume-averaging theorem 3 gives

$$\overline{\left[\frac{\partial c_e}{\partial t} \right]} = \frac{1}{\varepsilon_e} \left(\frac{\partial(\varepsilon_e \bar{c}_e)}{\partial t} \right).$$

- Taking intrinsic volume average of the RHS using volume-averaging theorem 2 gives

$$\overline{\nabla \cdot (D_e \nabla c_e)} = \frac{1}{\varepsilon_e} \left(\nabla \cdot (\varepsilon_e \overline{D_e \nabla c_e}) + \frac{1}{V} \iint_{A_{se}} D_e \nabla c_e \cdot \hat{\mathbf{n}}_e dA \right).$$

- We address the integral in the RHS: where we recall from the boundary conditions in the prior chapter that $\hat{\mathbf{n}}_e \cdot (D_e \nabla c_e) = (1 - t_+^0) j$.
- Using the same approach as before, we assume uniform flux over the interface and write

$$\begin{aligned} \frac{1}{V} \iint_{A_{se}} D_e \nabla c_e \cdot \hat{\mathbf{n}}_e \, dA &= \frac{1}{V} \iint_{A_{se}} (1 - t_+^0) j(c_s, c_e, \phi_s, \phi_e) \, dA \\ &= \frac{A_{se}}{V} (1 - t_+^0) \bar{j} = a_s (1 - t_+^0) \bar{j}. \end{aligned}$$

- Therefore, the RHS becomes

$$\overline{\nabla \cdot (D_e \nabla c_e)} = \frac{1}{\varepsilon_e} (\nabla \cdot (\varepsilon_e \overline{D_e \nabla c_e}) + a_s (1 - t_+^0) \bar{j}).$$

- We now address the $\nabla \cdot (\varepsilon_e \overline{D_e \nabla c_e})$ term. Following the same kind of reasoning as before, we write this as

$$\nabla \cdot (\varepsilon_e \overline{D_e \nabla c_e}) \approx \nabla \cdot (D_{e,\text{eff}} \nabla \bar{c}_e),$$

where $D_{e,\text{eff}} = \frac{\varepsilon_e D_e \delta}{\tau}$ and we often assume $D_{e,\text{eff}} = D_e \varepsilon_e^{\text{brug}}$ where “brug” is generally taken to be 1.5.

- So, combining all results

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

- Rewriting this gives our mass balance equation for the electrolyte,

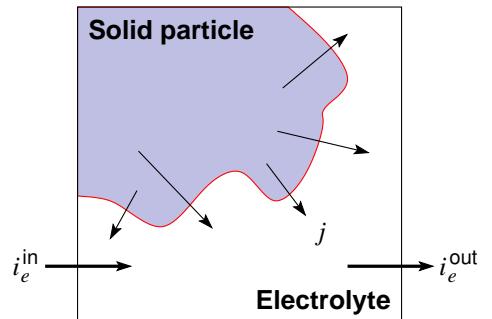
$$\frac{\partial(\varepsilon_e \bar{c}_e)}{\partial t} = \nabla \cdot (D_{e,\text{eff}} \nabla \bar{c}_e) + a_s (1 - t_+^0) \bar{j}.$$

Commenting on the $(1 - t_+^0)$ term,

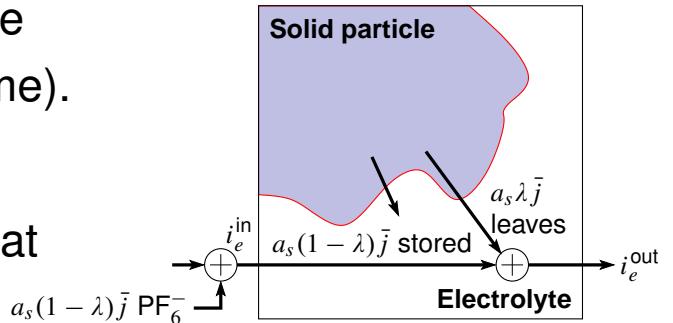
- If you have been paying close attention, the $(1 - t_+^0)$ term in the above equation might strike you as odd—none of the other closure terms include this factor.

- Let's quickly look at an intuitive explanation of what is happening.
- Consider a volume element having an interface between a solid particle and the electrolyte.
- Lithium flux is out of the particle, across the red boundary.
- Per our earlier assumptions, the volume-averaged lithium flux is

$$a_s \bar{j} = \frac{1}{V} \iint_{A_{se}} j(c_s, c_e, \phi_s, \phi_e) dA.$$



- Not all of the pore-wall flux remains in the volume (increasing c_e).
- Neither does all of the flux escape the volume (which would keep c_e the same).
- Let λ be the fraction of the flux that escapes, and $1 - \lambda$ be the fraction that is stored.
- To maintain macroscopic charge neutrality, $a_s(1 - \lambda)\bar{j}$ negatively charged PF_6^- ions must be stolen from the neighboring volume.
- So the fraction of the added current that is carried by the Li^+ ion is $\lambda\bar{j}$ and the fraction of the added current that is carried by the PF_6^- ion is $(1 - \lambda)\bar{j}$.
- By definition of t_+^0 , then, we must have $\lambda = t_+^0$.
- Therefore, the amount of lithium that stays in the local volume and contributes to changing the local concentration is $a_s(1 - t_+^0)\bar{j}$.



4.9: Charge conservation in electrolyte; Butler–Volmer; BCs

Charge conservation in electrolyte

- Recall the microscale electrolyte charge-conservation equation,

$$\nabla \cdot \mathbf{i}_e = \nabla \cdot \left(-\kappa \nabla \phi_e - \frac{2\kappa RT}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) (t_+^0 - 1) \nabla \ln c_e \right) = 0.$$

- For simplicity, we re-write this as

$$\nabla \cdot \mathbf{i}_e = \nabla \cdot (-\kappa \nabla \phi_e - \kappa_D \nabla \ln c_e) = 0,$$

where we have defined

$$\kappa_D = \frac{2\kappa RT}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_e} \right) (t_+^0 - 1).$$

- Using volume-averaging theorem 2 gives

$$\overline{\nabla \cdot \mathbf{i}_e} = \frac{1}{\varepsilon_e} \left(\nabla \cdot (\varepsilon_e \bar{\mathbf{i}}_e) + \frac{1}{V} \iint_{A_{se}} \mathbf{i}_e \cdot \hat{\mathbf{n}}_e dA \right).$$

- We can compute the value of the integral by recalling that $\mathbf{i}_e \cdot \hat{\mathbf{n}}_e = -jF$ on the interface. Therefore, we approximate the integral by $-a_s F \bar{j}$.

$$\overline{\nabla \cdot \mathbf{i}_e} = \frac{1}{\varepsilon_e} \left(\nabla \cdot (\varepsilon_e \bar{\mathbf{i}}_e) - a_s F \bar{j} \right) = 0$$

$$0 = \nabla \cdot (\varepsilon_e \bar{\mathbf{i}}_e) - a_s F \bar{j}.$$

- Note that

$$\varepsilon_e \bar{\mathbf{i}}_e = \varepsilon_e \left(-\kappa \overline{\nabla \phi_e} + -\kappa_D \overline{\nabla \ln c_e} \right).$$

- As before, we approximate

$$-\varepsilon_e \overline{\kappa \nabla \phi_e} \approx -\kappa_{\text{eff}} \nabla \bar{\phi}_e$$

$$-\varepsilon_e \overline{\kappa_D \nabla \ln c_e} \approx -\kappa_{D,\text{eff}} \nabla \ln \bar{c}_e,$$

where $\kappa_{\text{eff}} = \kappa \varepsilon_e^{\text{brug}}$ and $\kappa_{D,\text{eff}} = \kappa_D \varepsilon_e^{\text{brug}}$.

- Mathematically, it might be better to approximate $\overline{\nabla \ln c_e} \approx \varepsilon_e \nabla \ln \bar{c}_e$ by doing a Taylor-series expansion of $\ln c_e$ around \bar{c}_e and keeping the lower two terms in a volume-average integral.
- This would contribute an extra ε_e to the result. However this is not generally done (probably because we can set $\kappa_{D,\text{eff}}$ to any value we want, which might have the extra ε_e built in already, and probably because the $\ln \bar{c}_e$ term tends not to be as large as the $\bar{\phi}_e$ term).
- Combining, we get two results:

$$\varepsilon_e \bar{\mathbf{i}}_e = -\kappa_{\text{eff}} \nabla \bar{\phi}_e - \kappa_{D,\text{eff}} \nabla \ln \bar{c}_e,$$

and

$$\nabla \cdot (\kappa_{\text{eff}} \nabla \bar{\phi}_e + \kappa_{D,\text{eff}} \nabla \ln \bar{c}_e) + a_s \bar{j} F = 0.$$

Lithium movement between the solid and electrolyte phases

- We have already used this result, but for completeness we recall that

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

- This shows up in models as:

$$\begin{aligned} \frac{1}{V} \iint_{A_{se}} j(c_s, c_e, \phi_s, \phi_e) dA &\approx \frac{A_{se}}{V} j(\bar{c}_{s,e}, \bar{c}_e, \bar{\phi}_s, \bar{\phi}_e) \\ &\approx a_s j(\bar{c}_{s,e}, \bar{c}_e, \bar{\phi}_s, \bar{\phi}_e) = a_s \bar{j}. \end{aligned}$$

Boundary conditions for pseudo 2-D model

Charge conservation of the solid

- The electrical current through the solid *at the current collector* must equal the total current entering/exiting the cell. That is,

$$\varepsilon_s \bar{\mathbf{i}}_s = -\sigma_{\text{eff}} \nabla \bar{\phi}_s = \frac{I_{\text{app}}}{A},$$

where I_{app} is the total cell applied current in [A], and A is the current-collector plate area in [m^2].

- Similarly, the electrical current through the solid at the separator interface must be zero.
- For the positive electrode,

$$\left. \frac{\partial \bar{\phi}_s}{\partial x} \right|_{x=L^{\text{neg}}+L^{\text{sep}}} = 0, \quad \text{and} \quad \left. \frac{\partial \bar{\phi}_s}{\partial x} \right|_{x=L^{\text{tot}}} = \frac{-I_{\text{app}}}{A\sigma_{\text{eff}}}.$$

- For the negative electrode,

$$\left. \bar{\phi}_s \right|_{x=0} = 0, \quad \text{and} \quad \left. \frac{\partial \bar{\phi}_s}{\partial x} \right|_{x=L^{\text{neg}}} = 0.$$

- It is also true, for the anode, that $\left. \frac{\partial \bar{\phi}_s}{\partial x} \right|_{x=0} = \frac{-I_{\text{app}}}{A\sigma_{\text{eff}}}$, but when all PDEs of the battery model are integrated together, this condition is redundant and is not implemented.

Mass conservation of the solid

- Boundary conditions on the mass conservation equation are:

$$\left. \frac{\partial c_s}{\partial r} \right|_{r=0} = 0, \quad \text{and} \quad D_s \left. \frac{\partial c_s}{\partial r} \right|_{r=R_s} = -\bar{j},$$

where positive \bar{j} indicates lithium flowing out of the particle.

Mass conservation of the electrolyte

- There must be no electrolyte flux at the cell boundaries

$$\left. \frac{\partial \bar{c}_e}{\partial x} \right|_{x=0} = \left. \frac{\partial \bar{c}_e}{\partial x} \right|_{x=L^{\text{tot}}} = 0.$$

Charge conservation of the electrolyte

- The ionic current must be zero at the current collectors. At the separator boundaries, the ionic current must equal the total current entering/exiting the cell:

$$\varepsilon_e \bar{\mathbf{i}}_e = -\kappa_{\text{eff}} \nabla \bar{\phi}_e - \kappa_{D,\text{eff}} \nabla \ln \bar{c}_e = \frac{I_{\text{app}}}{A}.$$

- So, at the current collector boundaries, we have:

$$\kappa_{\text{eff}} \frac{\partial \bar{\phi}_e}{\partial x} + \kappa_{D,\text{eff}} \frac{\partial \ln \bar{c}_e}{\partial x} \Big|_{x=0} = \kappa_{\text{eff}} \frac{\partial \bar{\phi}_e}{\partial x} + \kappa_{D,\text{eff}} \frac{\partial \ln \bar{c}_e}{\partial x} \Big|_{x=L^{\text{tot}}} = 0.$$

- As before, we have boundary conditions at the separator interfaces, but these are redundant and not implemented:

$$-\kappa_{\text{eff}} \frac{\partial \bar{\phi}_e}{\partial x} - \kappa_{D,\text{eff}} \frac{\partial \ln \bar{c}_e}{\partial x} \Big|_{x=L^{\text{neg}}} = -\kappa_{\text{eff}} \frac{\partial \bar{\phi}_e}{\partial x} - \kappa_{D,\text{eff}} \frac{\partial \ln \bar{c}_e}{\partial x} \Big|_{x=L^{\text{neg}}+L^{\text{sep}}} = \frac{I_{\text{app}}}{A}.$$

4.10: Cell-level quantities; PDE simulation methods

Cell voltage

- Cell voltage is equal to the positive current-collector's potential minus the negative current-collector's potential.
- Since the solid phase is in direct electrical contact with the current collector, we then compute the cell voltage as

$$v(t) = \bar{\phi}_s(L^{\text{tot}}, t) - \bar{\phi}_s(0, t).$$

- And, since we have defined $\bar{\phi}_s(0, t) = 0$, we can further simplify to

$$v(t) = \bar{\phi}_s(L^{\text{tot}}, t).$$

Cell total capacity

- Cell total capacity is determined in the same manner as in Chap. 3:

$$Q^{\text{neg}} = AFL^{\text{neg}} \varepsilon_s^{\text{neg}} c_{s,\max}^{\text{neg}} |x_{100\%} - x_{0\%}| / 3600 \text{Ah}$$

$$Q^{\text{pos}} = AFL^{\text{pos}} \varepsilon_s^{\text{pos}} c_{s,\max}^{\text{pos}} |y_{100\%} - y_{0\%}| / 3600 \text{Ah},$$

and

$$Q = \min(Q^{\text{neg}}, Q^{\text{pos}}) \text{ Ah.}$$

Cell state of charge

- Similarly, cell state of charge is determined in the same manner as in Chap. 3:

$$\begin{aligned} z &= \frac{c_{s,\text{avg}}^{\text{neg}} / c_{s,\max}^{\text{neg}} - x_{0\%}}{x_{100\%} - x_{0\%}} \\ &= \frac{c_{s,\text{avg}}^{\text{pos}} / c_{s,\max}^{\text{pos}} - y_{0\%}}{y_{100\%} - y_{0\%}}. \end{aligned}$$

Model simulations

- We have the full set of equations for the continuous scale, which is great, but useless unless we can do something with them.
- One very important application of the model is to use it in simulation to help understand how a cell works, and then use that to inform how a cell should be built, and/or how a cell should be operated.
- Digital simulation of continuous phenomena require discretizing the problem in time and space.

FINITE DIFFERENCE: Divide space and time into small segments.

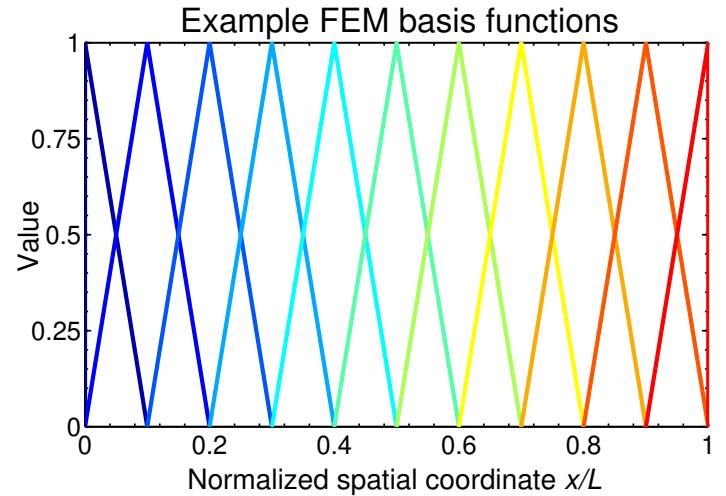
- Discretize the derivatives in the equations using Euler's rule or similar over these segments.
- Write the resulting system of equations, and solve using a linear algebra solver at each time step.
- The linear diffusion example in Chap. 3 introduced this method.

FINITE VOLUME: Divide time into small segments, space into volumes.

- Flux terms at volume boundaries are evaluated, and concentrations are updated to reflect the material fluxes.
- This method enforces mass balance: because the flux entering a given volume is identical to that leaving the adjacent volume, these methods are conservative.
- Another advantage of the finite volume method is that it is easily formulated to allow for unstructured meshes.
- The method is used in many CFD packages.
- The spherical diffusion example in Chap. 3 introduced this method.

FINITE ELEMENT: Time is discretized as with the other two methods.

- Space, however, is formulated as a summation over N quadratic or linear basis or *finite-element* functions $\psi_m(x)$ for $1 \leq m \leq N$.
- One example is shown below.
- Each color represents a linear (triangular-shaped) basis function such that the summation of these $N = 11$ functions is equal to 1 at every x location.



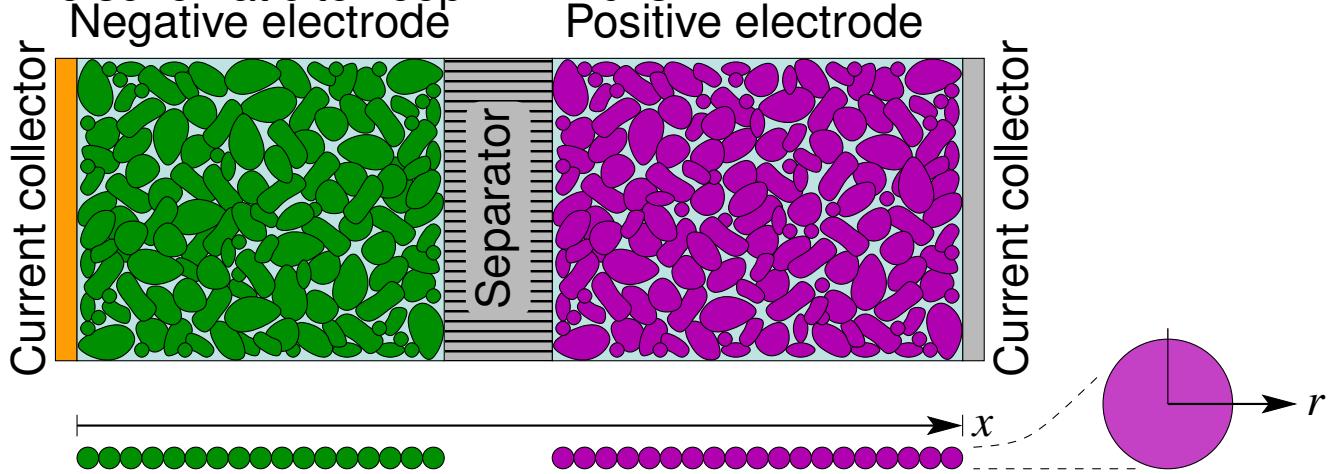
- Then, the variable being studied is written as a weighted sum.
- For example, if we are interested in some variable $\theta(x, t)$, we write it as

$$\theta(x, t) = \sum_{m=1}^N \theta_m(t) \psi_m(x).$$

- This simplifies the problem since the $\psi_m(x)$ are fixed:
 - We convert a two-dimensional problem $\theta(x, t)$ into N one-dimensional problems $\theta_m(t)$.
 - These are then evaluated by rewriting the PDEs in vector form for these one-dimensional variables, and solving.
 - The shape and spacing of the elements can be varied to improve accuracy in specific areas, as long as they always sum to 1.

4.11: Implementation in COMSOL

- Each PDE-evaluation method has advantages and disadvantages, and each has been used to simulate models of battery cells.
- Here, we introduce COMSOL, a commercial FEM solver code, primarily because it is driven by a GUI that makes it relatively straightforward to implement and modify model equations.
- The schematic to keep in mind is



- Most equations work in one dimension, x , but one works in a second radial pseudo dimension, as we will see later on.

Charge conservation in the solid

- The first thing we need to do is to rewrite the PDEs in a manner most easily digested by COMSOL.
- The first equation we desire to implement is:

$$\nabla \cdot (\sigma_{\text{eff}} \nabla \bar{\phi}_s) = a_s F \bar{j}.$$

- First, we note that the COMSOL implementation normalizes the lengths of each cell region to 1.

- We will use symbol \bar{x} to represent position with respect to normalized length, and x to denote actual position.
- In the negative electrode, $\bar{x} = x/L^{\text{neg}}$; in the positive electrode, $\bar{x} = (x - L^{\text{neg}} - L^{\text{sep}})/L^{\text{pos}}$. Generically $\bar{x} = x/L + \text{cst.}$
- Therefore, also,

$$\frac{\partial(\cdot)}{\partial\bar{x}} = \frac{\partial(\cdot)}{\partial x} \frac{\partial x}{\partial\bar{x}} = L \frac{\partial(\cdot)}{\partial x}$$

$$\frac{\partial(\cdot)}{\partial x} = \frac{\partial(\cdot)}{\partial\bar{x}} \frac{\partial\bar{x}}{\partial x} = \frac{1}{L} \frac{\partial(\cdot)}{\partial\bar{x}}.$$

- This changes the equation we wish to implement to:

$$\frac{1}{L} \nabla \cdot \left(\frac{\sigma_{\text{eff}}}{L} \nabla \bar{\phi}_s \right) = a_s F \bar{j}.$$

- The COMSOL implementation multiplies both sides by L (better convergence)

$$\nabla \cdot (\sigma_{\text{eff}}/L * \phi_{sx}) = L * a_s * F * j,$$

where the following variables are defined

σ_{eff}	a_s	\bar{j}	L	$\bar{\phi}_s$	F
σ_{eff}	a_s	j	L	ϕ_s	F

- Note that in COMSOL syntax,

$$\phi_{sx} = \frac{d}{dx} \phi_s,$$

and COMSOL's “ x ” is our normalized dimension “ \bar{x} ”.

Mass conservation in the solid

- We desire to implement

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_s r^2 \frac{\partial c_s}{\partial r} \right).$$

- Note that this equation operates in the “pseudo” dimension, r , instead of the linear dimension x .
- That is, at every “ x ” location, a copy of this radial equation is operating, representing the radially symmetric concentration profile of lithium in a representative spherical particle sitting at that “ x ” location.
- We also normalize the radial dimension: Let $\bar{r} = r/R_s$.
- Then, $r^2 = R_s^2 \bar{r}^2$ and $\frac{\partial(\cdot)}{\partial r} = \frac{1}{R_s} \frac{\partial(\cdot)}{\partial \bar{r}}$. This allows us to re-write our PDE as

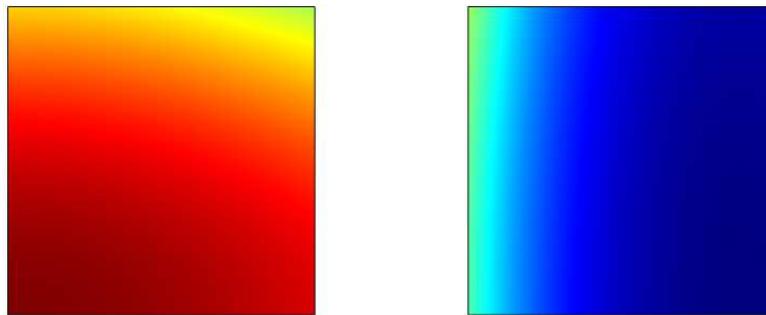
$$\frac{\partial c_s}{\partial t} = \left(\frac{1}{R_s^2 \bar{r}^2} \right) \frac{1}{R_s} \frac{\partial}{\partial \bar{r}} \left(D_s (R_s^2 \bar{r}^2) \frac{1}{R_s} \frac{\partial c_s}{\partial \bar{r}} \right).$$

- Multiply both sides of the equation by $\bar{r}^2 R_s$ and rearrange to get what COMSOL implements

$$\bar{r}^2 R_s \frac{\partial}{\partial t} c_s + \frac{\partial}{\partial \bar{r}} \left(-D_s \frac{\bar{r}^2}{R_s} \frac{\partial c_s}{\partial \bar{r}} \right) = 0,$$

except that COMSOL uses y instead of \bar{r} .

- Note that COMSOL implements the all of the spatially adjacent particles as blocks:



- In this figure,
 - The horizontal dimension is the cell “ x ” spatial dimension;

- The vertical dimension is the radial “ r ” pseudo-dimension (particle surface is at top, $r = R_s$; particle center is at bottom, $r = 0$);
 - The left block represents the anode and the right is the cathode;
 - Dark red is high concentration; dark blue is low concentration;
 - This is a cell at a high SOC that is presently discharging.
- There is no diffusion of lithium in the horizontal dimension, but there is diffusion in the “vertical” or radial dimension.
- This is represented in COMSOL using the equation:

$$\hat{y}^2 * R_s * \frac{\partial c_s}{\partial t} + \nabla \cdot \left(- \begin{bmatrix} 0, & 0 \\ 0, & \hat{y}^2 * D_s / R_s \end{bmatrix} * \nabla c_s \right) = 0,$$

where $\nabla = \left[\frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right]$ and where the following variables are defined:

$$\begin{array}{c|c} R_s & D_s \\ \hline & \\ R_s & D_s \end{array}$$

Charge conservation in the electrolyte

- We desire to implement

$$\nabla \cdot (\kappa_{\text{eff}} \nabla \bar{\phi}_e + \kappa_{D,\text{eff}} \nabla \ln \bar{c}_e) + a_s F \bar{j} = 0.$$

- Once again, COMSOL normalizes lengths, which converts the equation to

$$\frac{1}{L} \nabla \cdot \left(\frac{\kappa_{\text{eff}}}{L} \nabla \bar{\phi}_e + \frac{\kappa_{D,\text{eff}}}{L} \nabla \ln \bar{c}_e \right) = -a_s F \bar{j}.$$

- COMSOL implements $\nabla \ln \bar{c}_e$ as $\frac{1}{\bar{c}_e} \nabla \bar{c}_e$. It also multiplies both sides of the equation by L (better convergence), so the equation that is

actually implemented is:

$$\nabla \cdot (\kappa_{\text{eff}}/L * (\phi_{\text{ex}} + \kappa_{D,\text{fact}} * 1/c_e * c_{\text{ex}})) = -L * a_s * F * j.$$

where the following variables are defined

κ_{eff}	$\kappa_{D,\text{eff}}/\kappa_{\text{eff}}$	a_s	j	L	ϕ_e	c_e	F
<code>kappa_eff</code>	<code>kappa_D_fact</code>	<code>as</code>	<code>j</code>	<code>L</code>	<code>phi_e</code>	<code>c_e</code>	<code>F</code>

- Note again that in COMSOL syntax,

$$\phi_{\text{ex}} = \frac{d}{dx} \phi_e \quad \text{and} \quad c_{\text{ex}} = \frac{d}{dx} c_e,$$

and COMSOL's “ x ” is our normalized dimension “ \bar{x} ”.

Mass conservation in the electrolyte

- We desire to implement

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

- Once again, COMSOL normalizes lengths, which converts the equation to

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

- What is actually implemented is

$$\text{eps_e} * L * \frac{\partial c_e}{\partial t} + \nabla \cdot (-D_{e,\text{eff}}/L * \nabla c_e) = L * a_s * (1 - t_{\text{plus}}) * j,$$

where the following variables are defined

$D_{e,\text{eff}}$	t_+^0	a_s	j	L	ε_e
<code>D_e_eff</code>	<code>t_plus</code>	<code>as</code>	<code>j</code>	<code>L</code>	<code>eps_e</code>

Butler–Volmer equation

- Notice that the units of k_0 are rather awkward.
 - The exponential terms of the Butler–Volmer equation are unitless, and j has units $\text{mol m}^{-2} \text{s}^{-1}$.
 - Therefore, k_0 must have units of $\text{mol}^{\alpha-1} \text{m}^{4-3\alpha} \text{s}^{-1}$.
 - COMSOL struggles with units having non-integer powers, so this poses a problem.
- A solution is to define a normalized exchange current density

$$\begin{aligned} i_0 &= F k_0 c_e^{1-\alpha} (c_{s,\max} - c_{s,e})^{1-\alpha} c_{s,e}^\alpha \\ &= F \underbrace{k_0 c_{e,0}^{1-\alpha} c_{s,\max}}_{k_0^{\text{norm}}} \left(\frac{c_e}{c_{e,0}} \right)^{1-\alpha} \left(\frac{c_{s,\max} - c_{s,e}}{c_{s,\max}} \right)^{1-\alpha} \left(\frac{c_{s,e}}{c_{s,\max}} \right)^\alpha, \end{aligned}$$

where $c_{e,0}$ is the at-rest concentration of lithium in the electrolyte.

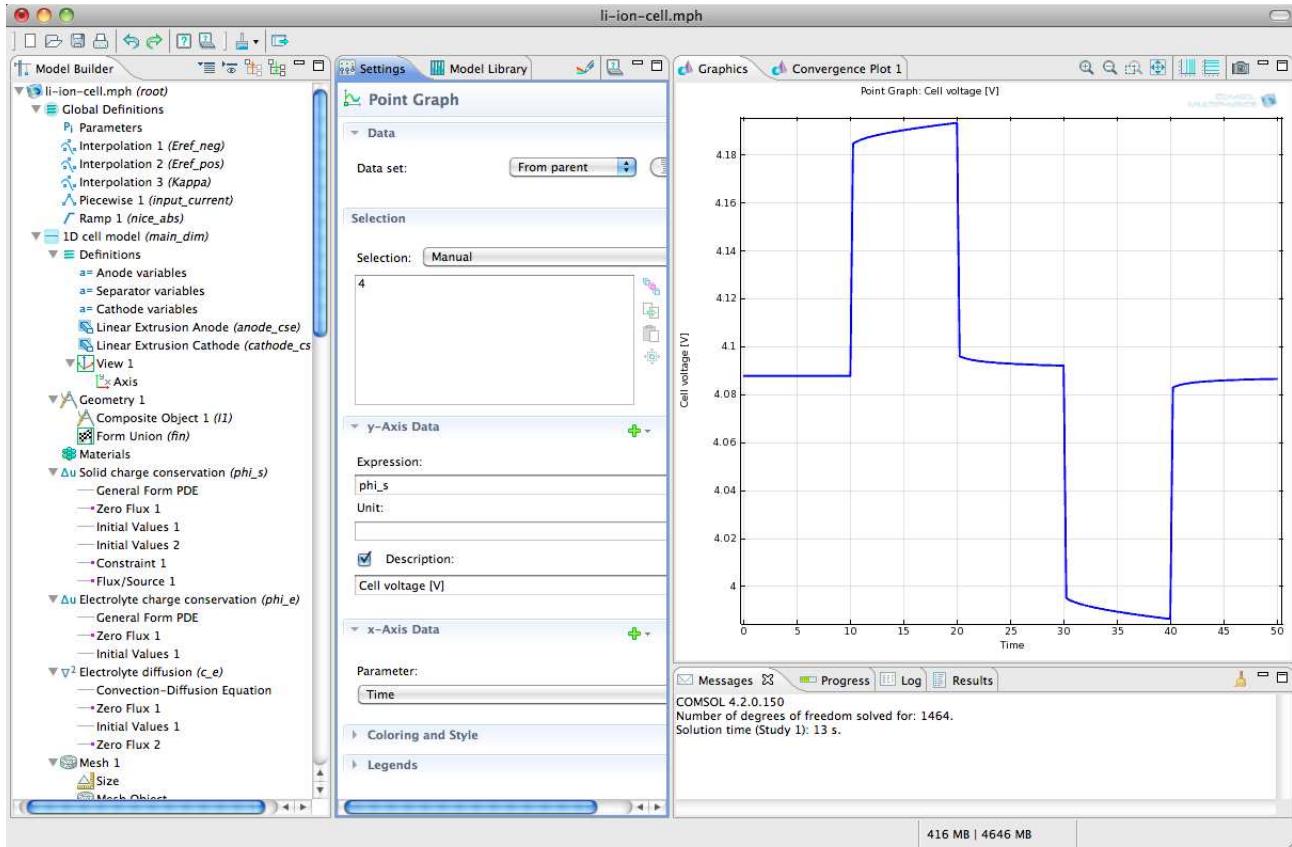
- Re-arranging the exchange current density in this form makes the terms raised to non-integer powers themselves unitless, and gives k_0^{norm} units of $\text{mol m}^{-2} \text{s}^{-1}$, which is much easier to work with.
- We can rewrite the Butler–Volmer equation as

$$\begin{aligned} j &= k_0^{\text{norm}} \left(\left(\frac{c_e}{c_{e,0}} \right) \left(\frac{c_{s,\max} - c_{s,e}}{c_{s,\max}} \right) \right)^{1-\alpha} \left(\frac{c_{s,e}}{c_{s,\max}} \right)^\alpha \\ &\quad \times \left\{ \exp \left(\frac{(1-\alpha)F}{RT} \eta \right) - \exp \left(-\frac{\alpha F}{RT} \eta \right) \right\}. \end{aligned}$$

- Also note: most articles that discuss simulation of lithium-ion cells do not give values for k_0 . Instead, they give values of i_0 that apply at the beginning of the simulation, from which you must derive k_0 or k_0^{norm} .

Running COMSOL

- Here's a screenshot taken when running COMSOL.



- It is simulating a rest followed by a charge pulse, followed by a rest, followed by a discharge pulse, followed by a rest.

Where from here?

- We're making excellent progress. We're now at a point where we can fairly readily simulate cell performance and behavior.
- But, the equations are still far too complicated to implement in a real-time embedded system, as needed for battery controls.
- So, our next step is to look at ways to reduce the complexity of the model equations, while still retaining the physics behind them.

Glossary

- $a_s(x, y, z, t)$ [$\text{m}^2 \text{m}^{-3}$] is the *specific interfacial area*: the area of the boundary between solid and electrolyte per unit volume.
- $\bar{c}_e(x, y, z, t)$ [mol m^{-3}] is the intrinsic volume average concentration of lithium in the electrolyte in the vicinity of a particular location.
- $\bar{c}_{s,e}(x, y, z, t)$ [mol m^{-3}] is the intrinsic volume average concentration of lithium at the interface between solid and electrolyte in the vicinity of a particular location.
- $\delta(x, y, z, t)$ [unitless] is the constrictivity of a porous media in the vicinity of a point. $\delta < 1$.
- $D_{e,\text{eff}}(x, y, z, t)$ [$\text{m}^2 \text{s}^{-1}$] is a short form for $D_{e,\text{eff}} \approx D_e \varepsilon_e^{\text{brug}} = D_e \varepsilon_e^{1.5}$.
- $\varepsilon_e(x, y, z, t)$ [unitless] is the *porosity* or *volume fraction* of the electrolyte phase in an electrode (other phases include the solid phase and inert-materials phase).
- $\varepsilon_s(x, y, z, t)$ [unitless] is the *volume fraction* of the solid phase in an electrode (other phases include the electrolyte phase and inert-materials phase).
- $\phi(x, y, z, t)$ [V] is the scalar field representing the electric potential at a given point.
- $\bar{\phi}_e(x, y, z, t)$ [V] is the intrinsic volume averaged scalar field representing the electric potential in the electrolyte in the vicinity of a given point.
- $\bar{\phi}_s(x, y, z, t)$ [V] is the intrinsic volume averaged scalar field representing the electric potential in the solid in the vicinity of a given point.

- $j(x, y, z, t)$ [$\text{mol m}^{-2} \text{s}^{-1}$] is the rate of positive charge flowing *out of* a particle across a boundary between the solid and the electrolyte.
- $\bar{j}(x, y, z, t)$ [$\text{mol m}^{-2} \text{s}^{-1}$] is the volume-averaged rate of positive charge flowing *out of* a particle across a boundary between the solid and the electrolyte.
- $\kappa(x, y, z, t)$ [S m^{-1}] is a material-dependent parameter of the electrolyte called the *bulk conductivity* of homogenous materials without inclusions in the vicinity of a given point.
- $\kappa_{\text{eff}}(x, y, z, t)$ [S m^{-1}] is the *effective conductivity* of the electrolyte, representing a volume averaged conductivity of the electrolyte phase in a porous media in the vicinity of a given point. We often model $\kappa_{\text{eff}} \approx \kappa \varepsilon_e^{\text{brug}} = \kappa \varepsilon_e^{1.5}$.
- $\kappa_{D,\text{eff}}(x, y, z, t)$ [A m^{-1}] is a short form for $\kappa_{D,\text{eff}} \approx \kappa_D \varepsilon_e^{\text{brug}} = \kappa_D \varepsilon_e^{1.5}$.
- $\sigma(x, y, z, t)$ [S m^{-1}] is a material-dependent parameter of the solid electrode particles called the *bulk conductivity* of homogenous materials without inclusions in the vicinity of a given point.
- $\sigma_{\text{eff}}(x, y, z, t)$ [S m^{-1}] is an electrode-dependent parameter called the *effective conductivity*, representing a volume averaged conductivity of the solid matrix in a porous media in the vicinity of a given point. We often model $\sigma_{\text{eff}} \approx \sigma \varepsilon_s^{\text{brug}} = \sigma \varepsilon_s^{1.5}$.
- $\tau(x, y, z, t)$ [unitless] is the tortuosity of the porous media in the vicinity of a point. $\tau \geq 1$.