

# Reactive Transport in Porous Electrodes: From Pore-scale to Macroscale Descriptions

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## Abstract

Macroscopic homogenized descriptions of reactive electrolyte transport through porous electrodes capture important sub-scale effects by the use of effective parameters, such as the dispersion tensor or the effective reaction rate.

We apply the volume averaging method (VAM) [2] to upscale the transport of electrolyte through periodic unit cells and evaluate the dependency and sensitivity of macroscopic effective parameters on pore-scale properties.

The effective parameters can be applied in macroscopic cell models of redox flow batteries to study the effect of different pore-scale geometries within porous electrodes on the mass transfer rate or homogeneity of the electric current density.

## Pore-scale Geometry

The porous medium is assumed to be spatially periodic. Within each periodic unit cell, the electrode geometry is modelled as a collection of straight fibers:

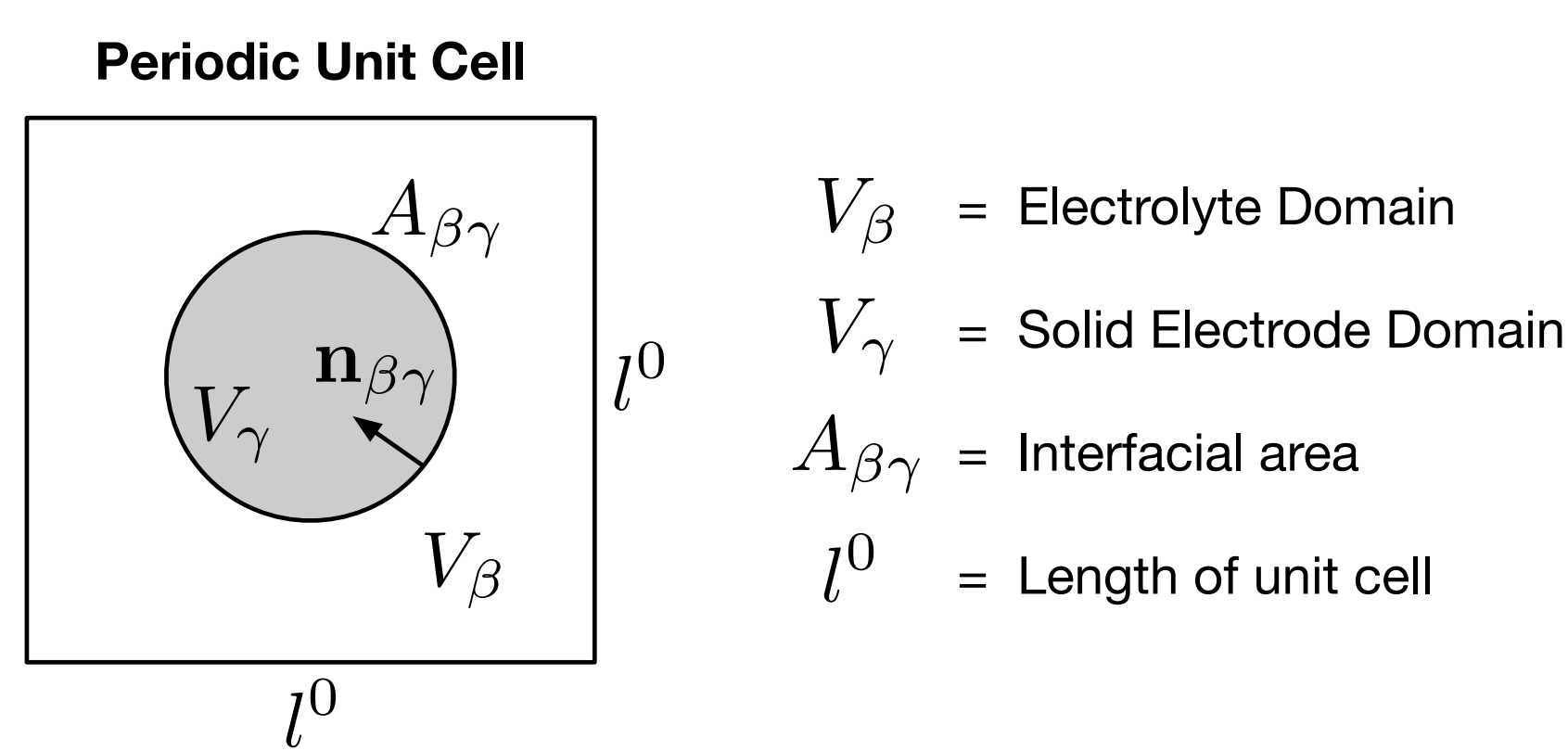
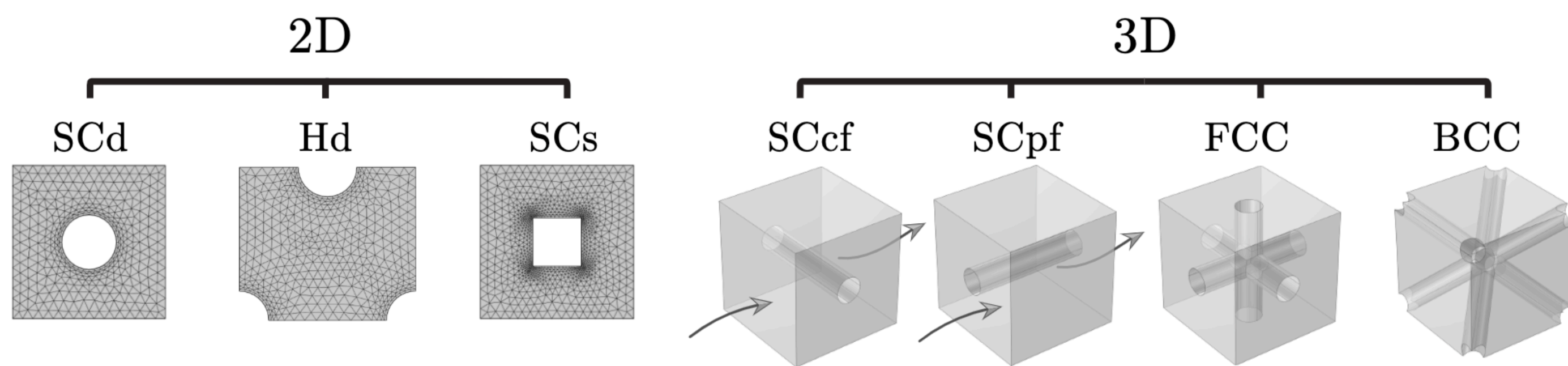


Illustration of a periodic unit cell.

In this work we consider various simplified periodic fiber arrangements:



## Pore-scale Transport Equations

The pore-scale electrolyte transport is assumed to fulfill the simplifying assumptions:

- steady-state
- negligible ohmic resistivity
- creeping flow conditions
- local electroneutrality
- dilute electrolyte concentrations
- isothermal conditions
- equal and constant diffusion coefficients
- heterogeneous Butler-Volmer type reactions

The transport of the electro-active species in oxidized and reduced form is governed by the dimensionless advection-diffusion equation

$$Pe_l^* \cdot \bar{\mathbf{v}} \cdot \bar{\nabla} \bar{c}_i = \bar{\nabla}^2 \bar{c}_i, \quad i = \{\text{ox, red}\},$$

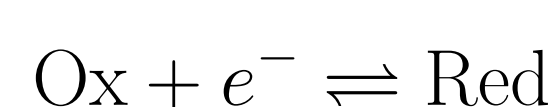
where  $Pe_l^* = l^0 v^0 / D$  is a Peclet number with  $D = D_{\text{ox}} = D_{\text{red}} = \text{const.}$  and

$$\bar{x} = \frac{x}{l^0}, \quad \bar{c}_i = \frac{c_i}{c^0}, \quad \bar{\mathbf{v}} = \frac{\mathbf{v}}{(l^0)^2 \mu^{-1} \|\nabla \langle p \rangle^\beta\|}, \quad \bar{\nabla} = l^0 \nabla,$$

where  $l^0$  is the unit cell size and  $\langle p \rangle^\beta$  denotes the intrinsic volume average of the pressure.

## Electrochemical Reactions

We consider the heterogeneous one-electron transfer redox reaction



at the electrode surface, which is modelled with the Butler-Volmer type reaction equation

$$-\bar{\nabla} \bar{c}_{\text{ox}} \cdot \mathbf{n}_{\beta\gamma} \Big|_{\bar{A}_{\beta\gamma}} = Ki_l^a \bar{c}_T - (Ki_l^a + Ki_l^c) \cdot \bar{c}_{\text{ox}},$$

where  $\bar{c}_T = \bar{c}_{\text{red}} + \bar{c}_{\text{ox}} = \text{const.}$  is the total constant electrolyte concentration and

$$Ki_l^a = Ki_l e^{(1-\beta_s)\bar{\eta}}, \quad Ki_l^c = Ki_l e^{-\beta_s\bar{\eta}},$$

where  $Ki_l = k_0 l^0 / D$  is a dimensionless kinetic number,  $k_0$  is a reaction constant,  $\beta_s$  is the symmetry factor and  $\bar{\eta} = (E - E_f^0) / V^0$  with  $V^0 = RT/F$  is a spatially constant overpotential.

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## Volume-averaged Macroscopic Model

The macroscopic species transport is governed by

$$Pe_l^* \bar{\nabla} \cdot (\langle \bar{c}_{\text{ox}} \rangle^\beta \langle \bar{\mathbf{v}} \rangle^\beta) = \bar{\nabla} \cdot (\bar{\mathbf{D}}^{\text{eff}} \cdot \bar{\nabla} \langle \bar{c}_{\text{ox}} \rangle^\beta) - Ki_l^{\text{eff}} \frac{\bar{a}_v}{\epsilon} (\langle \bar{c}_{\text{ox}} \rangle^\beta - \langle \bar{c}_{\text{ox}}^{\text{eq}} \rangle^\beta),$$

where  $\epsilon$  is the porosity and  $\bar{a}_v$  denotes a dimensionless specific surface area.

The effective dispersion tensor and kinetic number are given by

$$\bar{\mathbf{D}}^{\text{eff}} = \mathbf{I} + \langle \mathbf{n}_{\beta\gamma} \mathbf{f} \rangle_{\beta\gamma}^\beta - Pe_l^* \langle \mathbf{f} \tilde{\mathbf{v}} \rangle^\beta, \quad Ki_l^{\text{eff}} = Ki_l \left( e^{(1-\beta_s)\bar{\eta}} + e^{-\beta_s\bar{\eta}} \right) \left( 1 + \frac{\epsilon \langle s \rangle_{\beta\gamma}^\beta}{\bar{a}_v} \right)$$

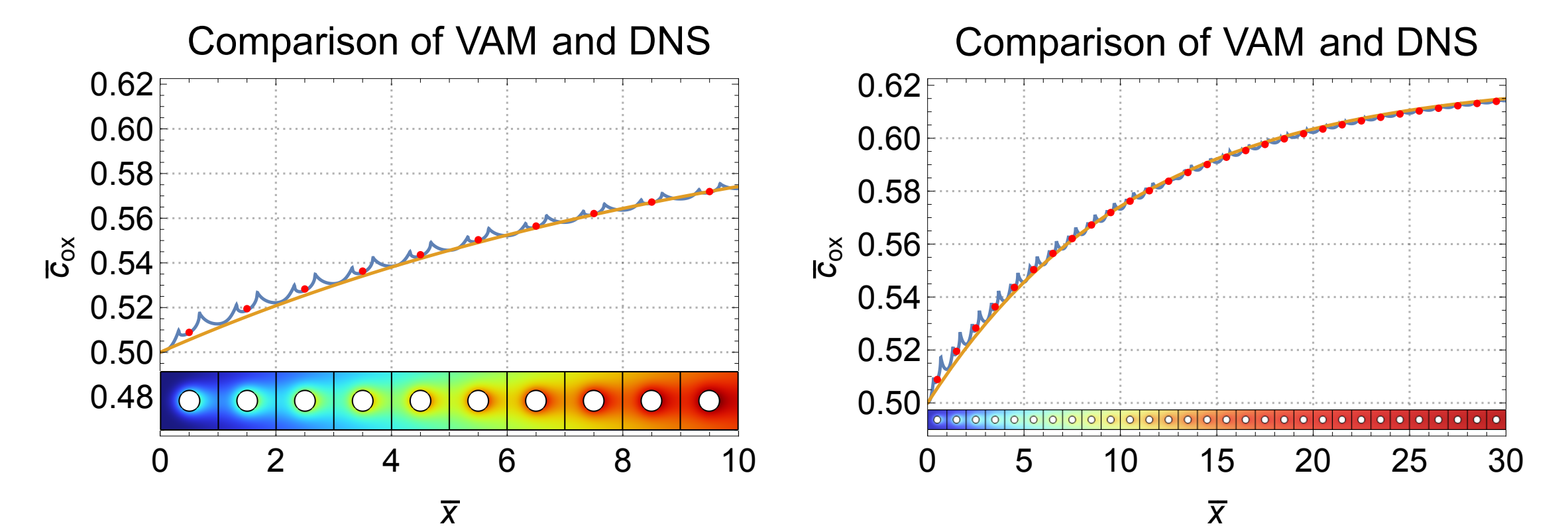
with the intrinsic volume and surface averages, and the equilibrium concentration

$$\langle \cdot \rangle^\beta = \frac{1}{V_\beta} \int_{V_\beta} \cdot dV, \quad \langle \cdot \rangle_{\beta\gamma}^\beta = \frac{1}{V_\beta} \int_{A_{\beta\gamma}} \cdot d\bar{A}, \quad \langle \bar{c}_{\text{ox}}^{\text{eq}} \rangle^\beta = \frac{1}{1 + \exp(-\bar{\eta})}.$$

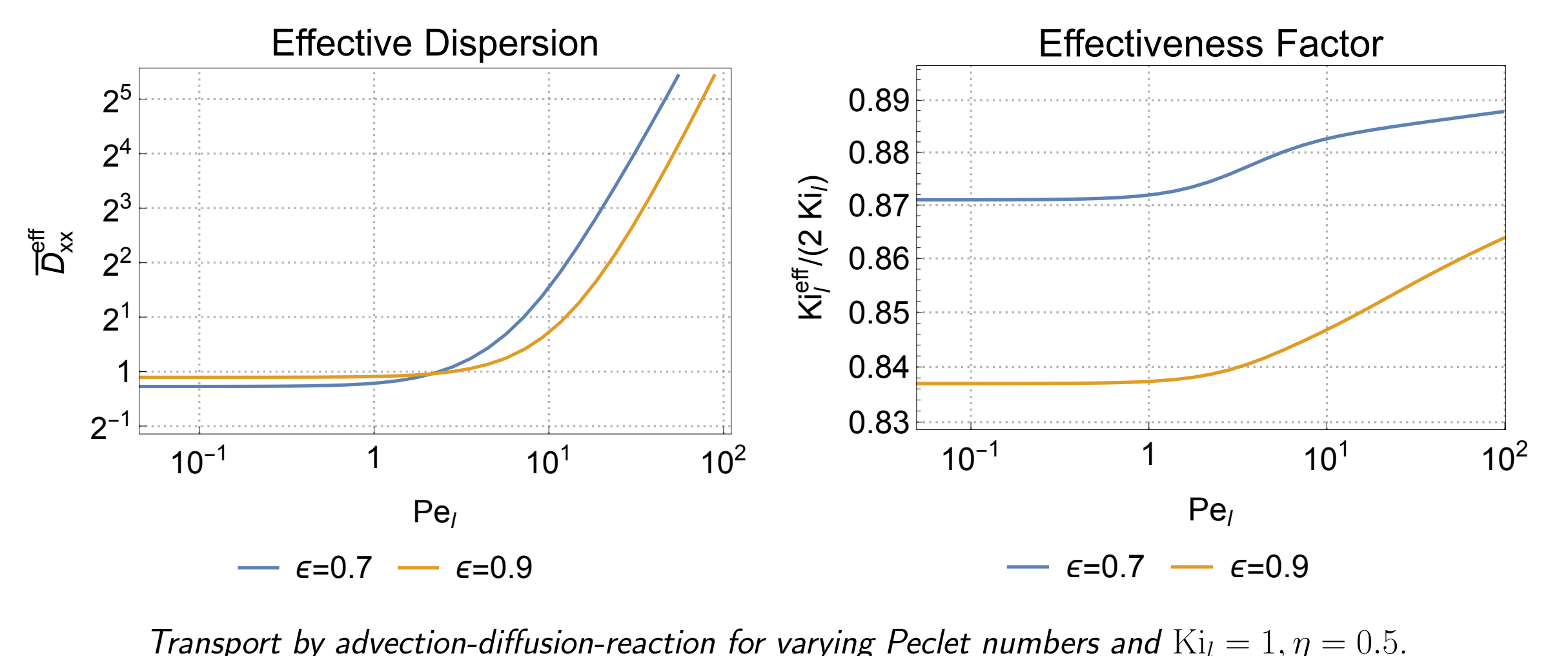
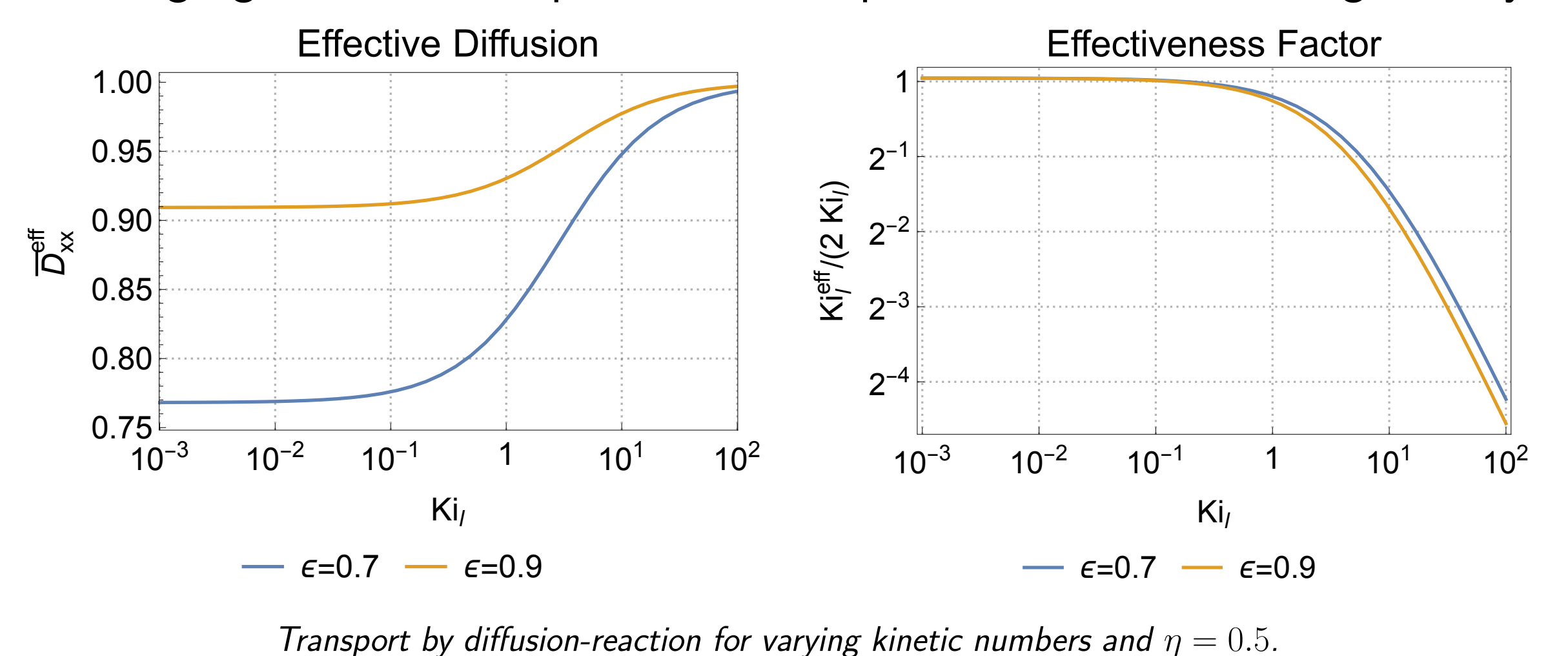
The periodic field variables  $\mathbf{f}$  and  $s$  are determined by closure problems [1] for the local concentration deviation,  $\tilde{c}_{\text{ox}} = \bar{c}_{\text{ox}} - \langle \bar{c}_{\text{ox}} \rangle^\beta = s \langle \bar{c}_{\text{ox}} \rangle^\beta + \mathbf{f} \cdot \nabla \langle \bar{c}_{\text{ox}} \rangle^\beta$ .

## Results

We verify the up-scaled macroscopic description with a direct numerical solution for a 1D advection-diffusion-reaction transport problem using the SCd pore-scale geometry:



The following figures show computed effective parameters for the SCd geometry:



## Conclusions and Applications

- The developed framework based on the method of volume averaging allows studying the dependency and sensitivity of the effective parameters in terms of different pore-scale geometries and dimensionless transport parameters.
- We are developing reduced surrogate models for the effective parameters, which can be used in place of common simplified analytical or empirical relations to efficiently simulate the effect of different pore-scale geometries within porous electrodes in macroscopic redox flow battery cell models.

## References

- [1] F. J. Valdés-Parada, C. G. Aguilar-Madera, and J. Álvarez-Ramírez, "On diffusion, dispersion and reaction in porous media," Chemical Engineering Science, vol. 66, no. 10, pp. 2177–2190, May 2011.
- [2] S. Whitaker, The Method of Volume Averaging, vol. 13. Dordrecht: Springer Netherlands, 1999.