B03 Highly accurate simulation of electrokinetic transport processes in nanopores

Abstract

Presented is a multi-component mixture, single phase solver of ionically driven flow with the Finite Volume Method implemented in OpenFOAM®. A flexible inheritance structure allows for further extensions of the Poisson-Nernst-Planck model, and quickly modifying case configurations based on dimensional and/or non-dimensional specifications at runtime. Implicit treatment of the electromigration flux provides numerical stability, while special boundary condition ensures better conservation of species flux and more accurate species concentration profiles at the boundary cells. The transport dynamics of this solver is preemptively verified with species transport between an instantaneously equilibrated reservoir and nanopore entrance.

Mathematical Modelling

State-of-the-art Poisson-Nernst-Planck equations:

$$\int_{V(t)} \frac{\partial c_i}{\partial t} d\mathbf{x} = \int_{V(t)} \underbrace{\nabla \cdot (D_i \nabla c_i)}_{\textbf{Diffusive flux}} d\mathbf{x}$$

$$+ \int_{V(t)} \underbrace{\nabla \cdot [(\underbrace{D_i \frac{e z_i}{kT}}_{\mu_i} \nabla \Psi) c_i]}_{\textbf{Electromigration flux}} \ d\mathbf{x}$$

$$\int_{V(t)} \nabla \cdot (\epsilon \nabla \Psi) \ \ d\mathbf{x} = \int_{V(t)} \underbrace{-\rho_E}_{-F\sum_1^m z_i c_i} \ d\mathbf{x}$$

Used as governing equation in:

- Transmission Line Model [1].
- Analytical solutions of nanopore charging [1,2].
- Numerical simulations used as verification for analytical solutions [3].

Currently available extensions:

- Additional advection term: $\mathbf{u} \cdot \nabla c_i$
- Decomposed electric potential [4]
  - Poisson equations for intrinsic and external contributions to the electric potential field:

$$\nabla \cdot (\epsilon \nabla \Psi) = \nabla \cdot \left(\epsilon \nabla \begin{bmatrix} \Psi_{\mathrm{Ext}} \\ \Psi_{\mathrm{Int}} \end{bmatrix} \right) = -\rho_{\mathrm{E}}$$

$$\implies \begin{cases} \nabla \cdot (\epsilon \nabla \Psi_{\mathrm{Ext}}) = 0 \\ \nabla \cdot (\epsilon \nabla \Psi_{\mathrm{Int}}) = -\rho_{\mathrm{E}} \end{cases}$$

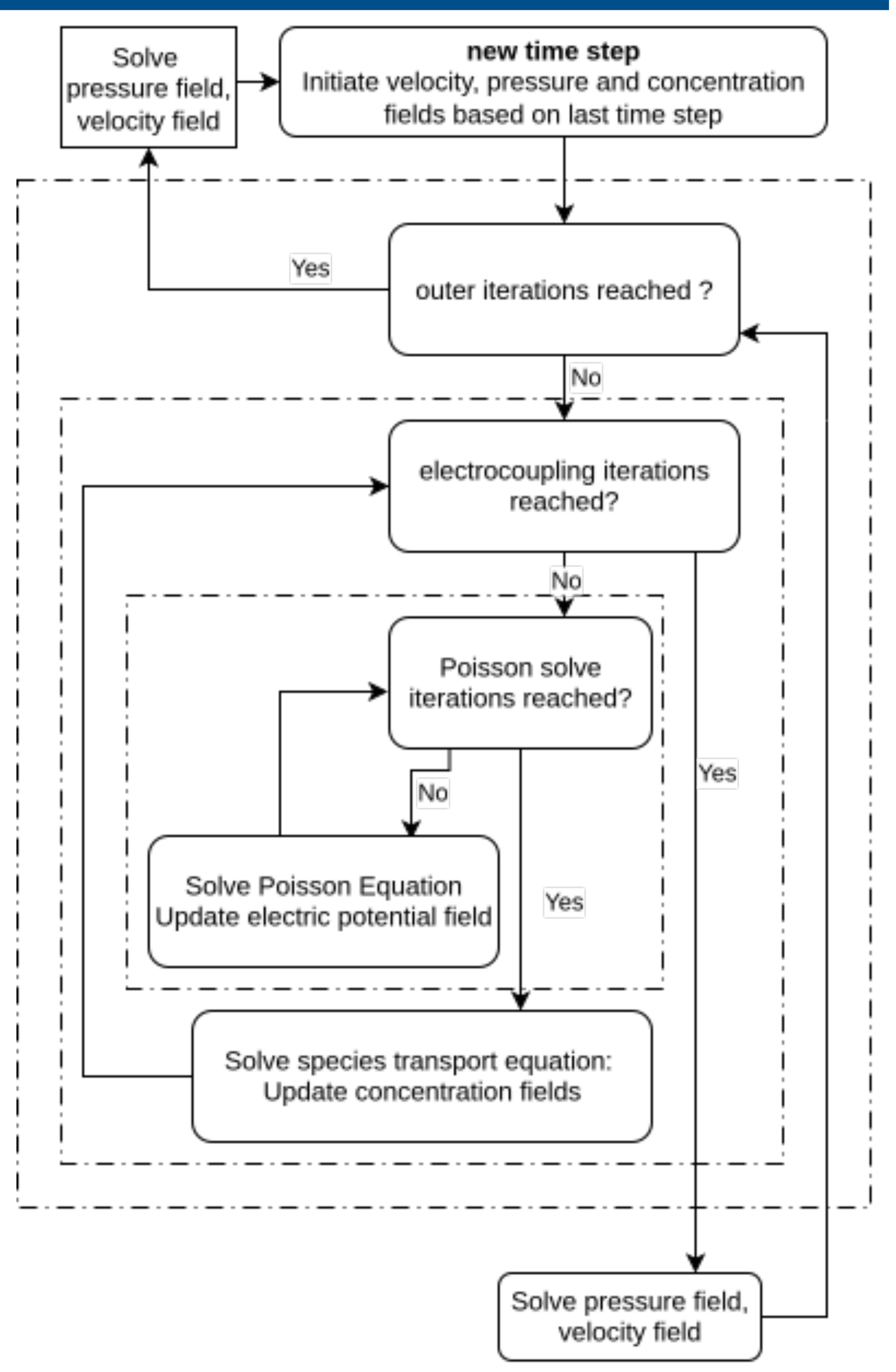
  - Electrical Force:

$$\mathbf{f}_{\mathrm{E}} = -\rho_{\mathrm{E}} \Psi_{\mathrm{Ext}}$$

Numerical Implementation

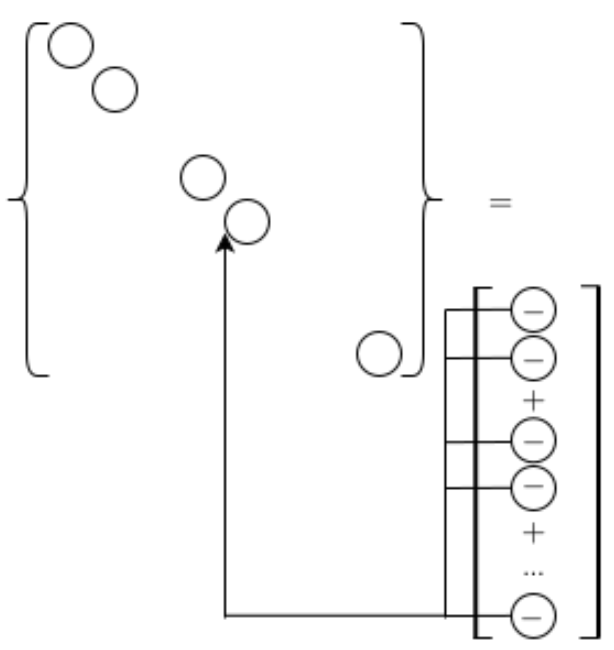
Coupling Algorithm

Segregated solver stabilization with multiple nested iterations [4].



Electromigration Flux discretization

Partially implicit discretization of a source term (supported natively within OpenFOAM®) of the electromigration flux $\nabla \cdot (D_i \frac{e z_i}{kT} \nabla \Psi) c_i$.



Boundary Conditions

Zero Ionic Flux

Neumann-type boundary condition ensuring no species flux on the domain wall boundaries:

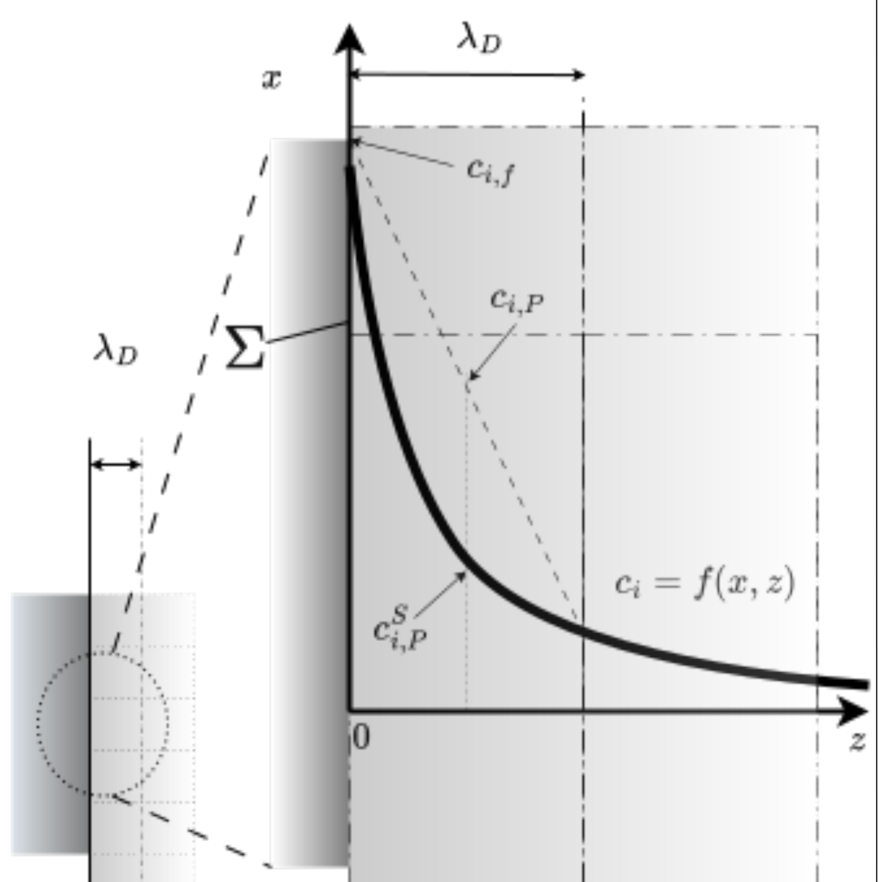
$$[\nabla \cdot c_i]_f \cdot n_{\perp} \mathbf{A}_f = - \left[\frac{\mu_i}{D_i} (\nabla \Psi) c_i \right]_f \cdot \mathbf{A}_f$$

or $\quad \nabla c_{i,P} + \frac{\mu_i}{D_i} (\nabla \Psi_f) c_{i,P} = 0$

Subgrid Zero Ionic Flux

Dirichlet-type boundary condition enforcing both no species flux on the domain walls, and exponential species distribution in the boundary cell. Proposed and first implemented in the rheoTool toolbox [1].

$$c^P_{i,P} = c^S_{i,f} \exp\left(\frac{\mu_i}{D_i}(\Psi_f - \Psi_P)\right)$$



Validation Test Cases

2D rectangular pore

Semi-infinite (close-ended) nanopore charging analysis by Aslyamov & Janssen [2].

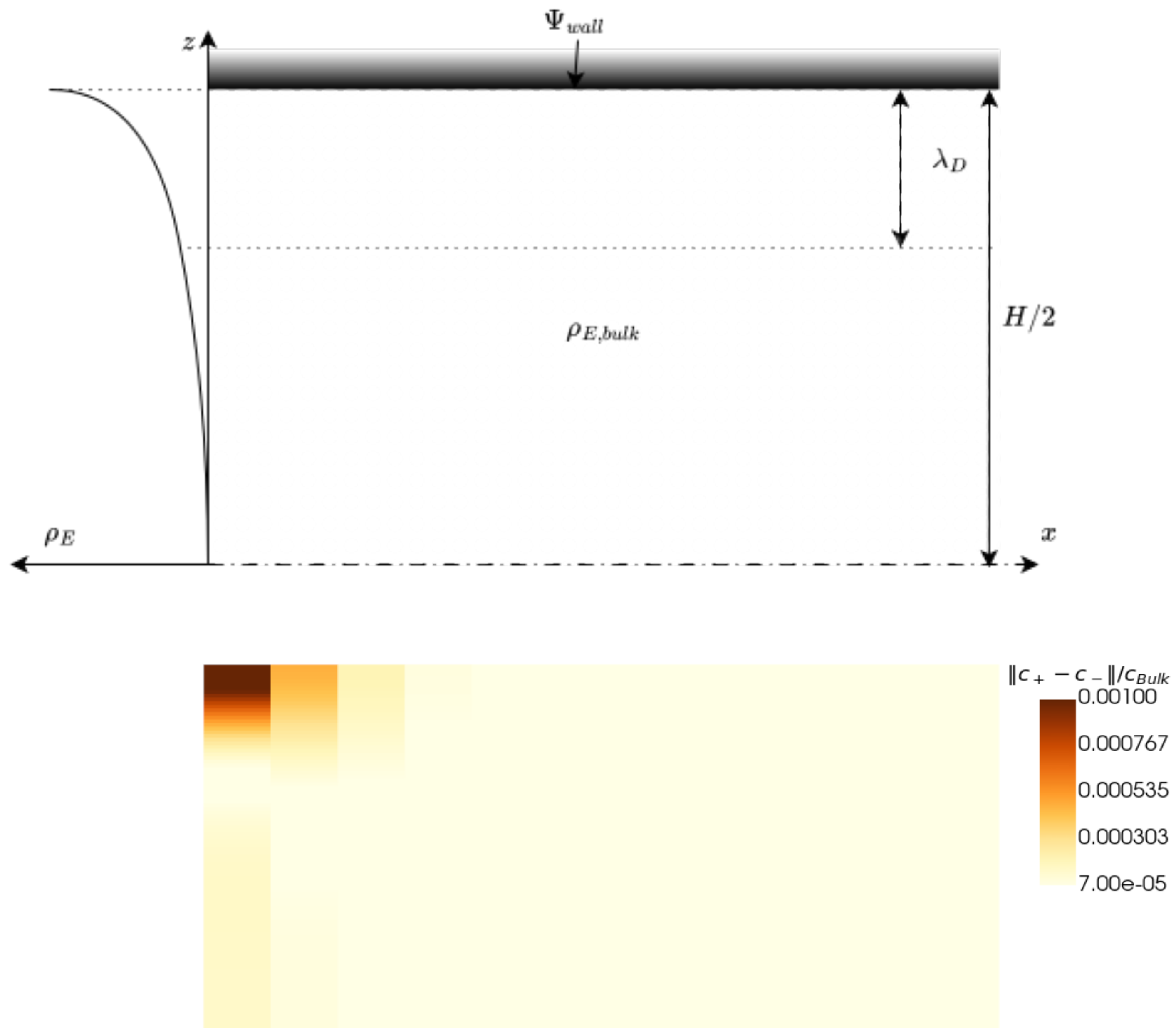


Fig.1 Sketch of case setup and simulation results for $H = 3.77 \times 10^{-6}$ m , $\lambda_D = 2.97 \times 10^{-7}$ m, $D = 1 \times 10^{-9}$ m/s^2, $c_{Bulk} = 0.001$ mol L^{-1}, $\Psi_{wall} = 0.025 \frac{k_B T}{e} = 2.59 \times 10^{-5}$ V

3D cylindrical pore

Simulation of a finite cylindrical pore by Gupta et al.[3].

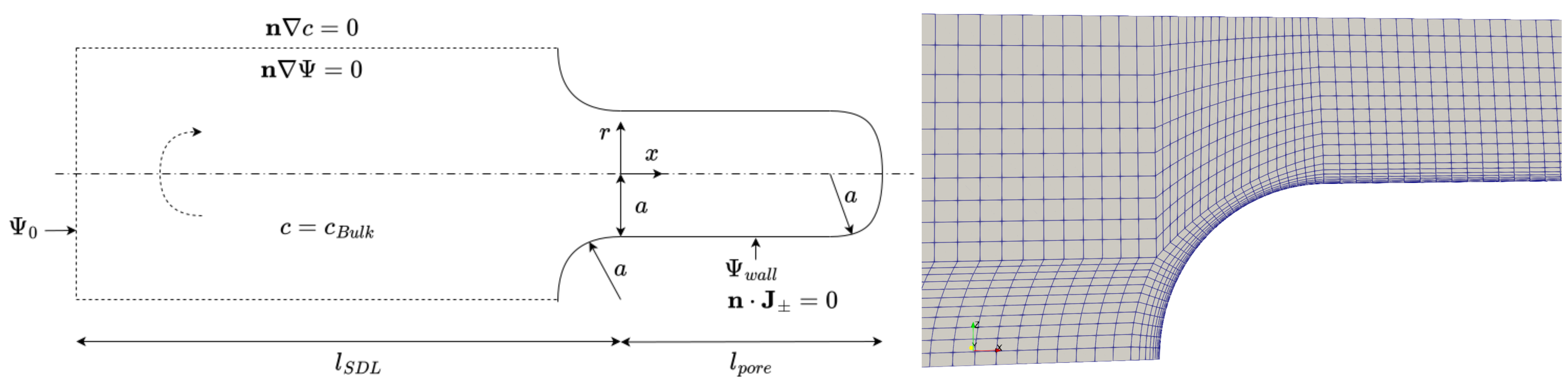


Fig.2 Sketch of case setup and mesh geometry details at pore opening (work in progress)

Outlook

- Verify late-time charging dynamics with Transmission Line Model. Doing so would require significant speedup of solver or adaptative time stepping.
- Verify early-times concentration and potential field solutions with analytical approximations provided by Henrique et al. [5].
- Compare agreement of late-time charging dynamics with different modifications to the Poisson-Nernst-Planck equations: current discussions in literature regarding species transport dynamics lack verification with late-time charging.

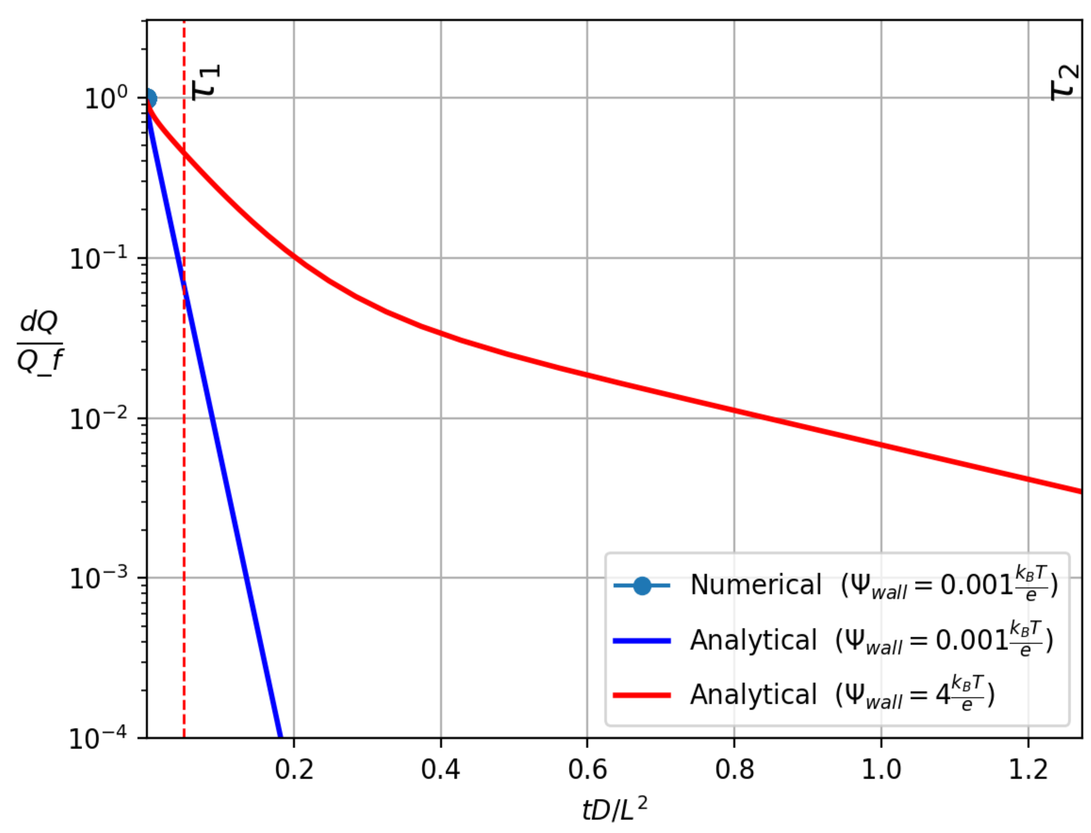


Fig.3 Analytical late-times charging rate, as compared with available early-times results.

References

[1] Mathijs Janssen. Transmission line circuit and equation for an electrolyte- filled pore of finite length. Physical Review Letters, 126(13), March 2021.

[2] Timur Aslyamov and Mathijs Janssen. Analytical solution to the poisson- nernst-planck equations for the charging of a long electrolyte-filled slit pore, 2022.

[3] Ankur Gupta, Pawel J. Zuk, and Howard A. Stone. Charging dynamics of overlapping double layers in a cylindrical nanopore. Physical Review Letters, 125(7), August 2020.

[4] Francisco Pimenta and Manuel A. Alves. Numerical simulation of electrically-driven flows using openfoam, 2018.

[5] Filipe Henrique, Pawel J. Zuk, and Ankur Gupta. Charging dynamics of electrical double layers inside a cylindrical pore: predicting the effects of arbitrary pore size. Soft Matter, 18(1):198213, 2022.