Computational Electrokinetics: Numerical Solution of Ion-Exchanger Dynamics

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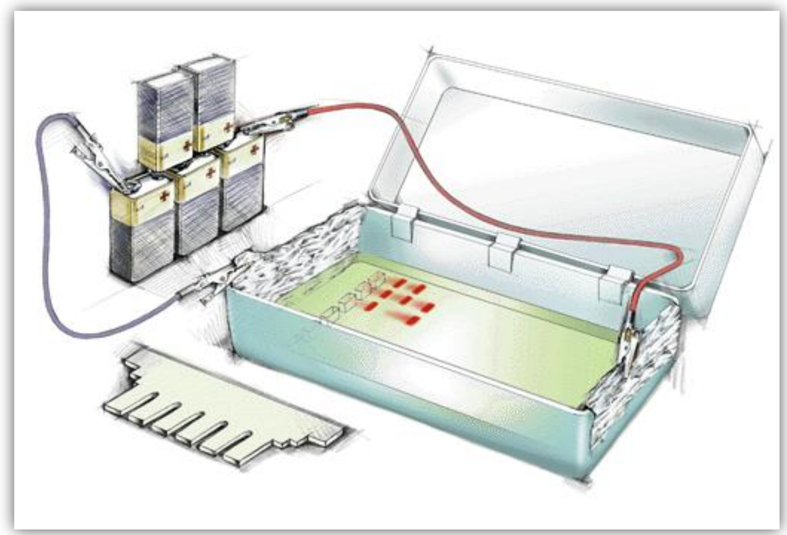
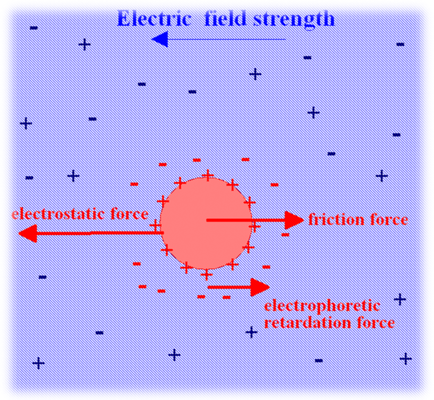
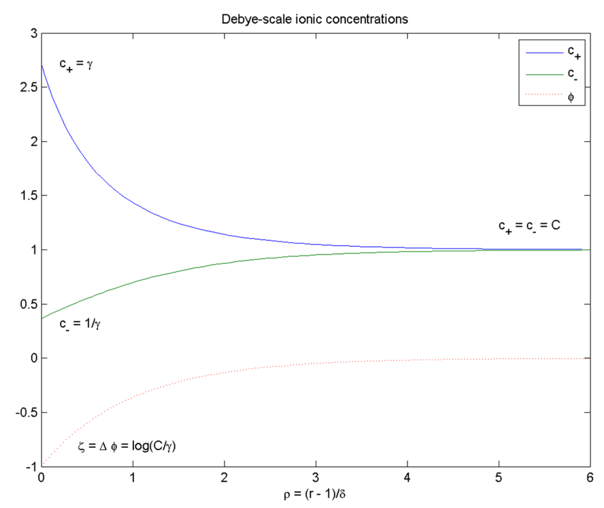
Physical phenomenon

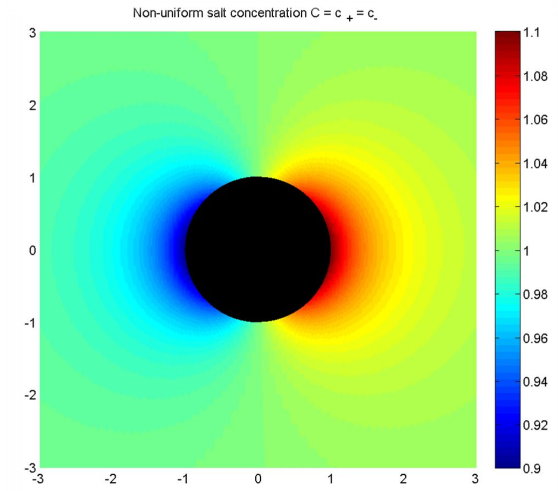
An ion-selective conducting particle is suspended in an electrolyte solution and exposed to a uniform electric field.





Due to strong electrostatic forces, most of the electrolyte remains neutral, except for a thin ("Debye") layer around the particle. This scale separation allows for a mathematical analysis using singular expansions, leading to an effective macro-scale description.



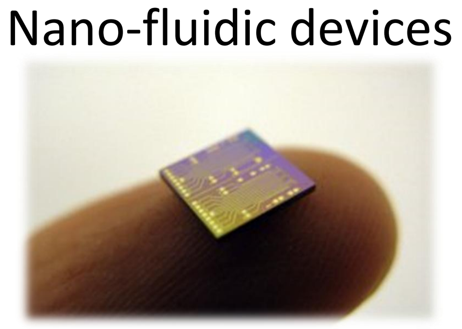


The system achieves steady-state for a specific particle velocity, where the fluid and electrostatic forces are balanced.

Applications

Electrochemical surfaces

Nano-fluidic devices



Packed bed separation devices

Ion-selective particles

Desalination processes

Macro-scale Problem[1]

Problem Variables

Φ – Electrostatic potential

C – Salt concentration

$\mathbf{V}$, P – Fluid velocity and pressure

Differential Equations

1. Charge conservation:
2. Salt conservation:
3. Stokes flow: (coupled with Coulomb force)

$$\nabla\cdot\left(C\nabla\Phi\right)=0$$

$$\Delta C-\alpha\mathbf{V}\cdot\nabla C=0$$

$$\begin{cases}\Delta\mathbf{V}-\nabla P+\Delta\Phi\nabla\Phi=0\\ \nabla\cdot\mathbf{V}=0\end{cases}$$

Boundary Conditions

At particle surface

1. Potential drop due to electrical double layer
2. Ion-selective kinetics
3. Effective slip velocity

Far-field (away from the particle)

1. Constant electric field β
2. Ambient ionic concentration
3. Fluid moves with velocity ($-\mathcal{U}$)

Force-free particle

In steady-state, the total force acting on the particle vanishes:

$$\mathbf{F}=\oiint\underline{\underline{\mathbf{S}}}\cdot\hat{\mathbf{n}}\,dA$$

$$\underline{\underline{\mathbf{S}}}=\nabla\mathbf{V}+\left(\nabla\mathbf{V}\right)^{\dagger}-P\underline{\underline{\mathbf{I}}}+\nabla\Phi\nabla\Phi-\frac{1}{2}\left\|\nabla\Phi\right\|^{2}\underline{\underline{\mathbf{I}}}$$

The steady-state problem can be formulated as:

Given β (applied field), find $\mathcal{U}$ (particle velocity) such that $\mathbf{F}=\mathbf{0}$ (steady-state).

Approximate analytic solution exists for weak-field regime ($\beta \ll 1$).

(1) Problem variables (Φ, C, $\mathbf{V}$, P) and parameters (α, β, $\mathcal{U}$) are dimensionless.

Solver Implementation

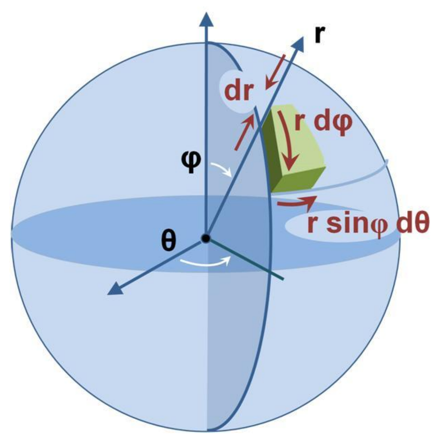
Discrete Problem

Axial symmetry for φ

➔Spherical coordinates.

➔2D Problem (r,θ)

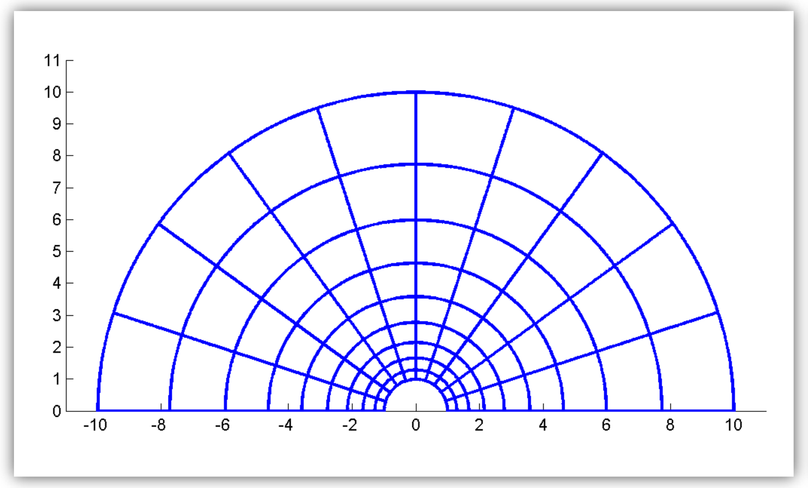
➔Non-Cartesian operators

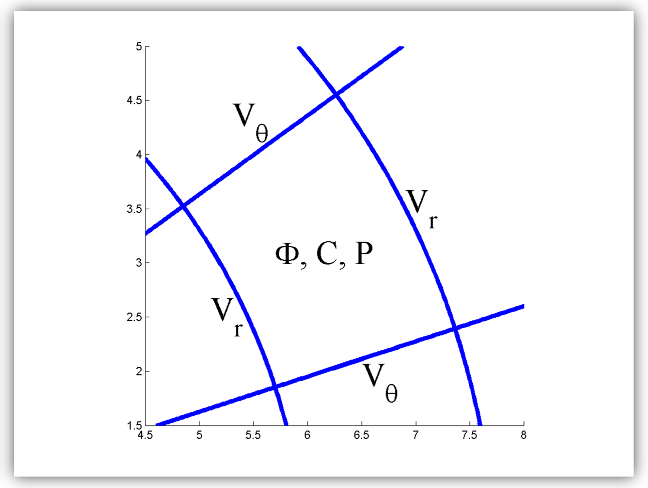


Finite Volume Method

➔ Discrete operators

➔ Sparse matrices (MATLAB)





Iterative Solver

Coupled non-linear system

➔ Newton's method: $\underline{x}=\left[\Phi\quad C\quad \mathbf{V}\quad P\right]$

$$\mathcal{L}(\underline{x}+\underline{\delta x})\approx\mathcal{L}(\underline{x})+\nabla\mathcal{L}(\underline{x})\cdot\underline{\delta x}$$

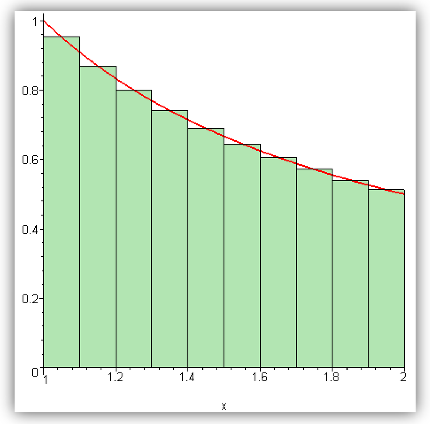
$$\mathcal{L}(\underline{x})=\underline{0}$$

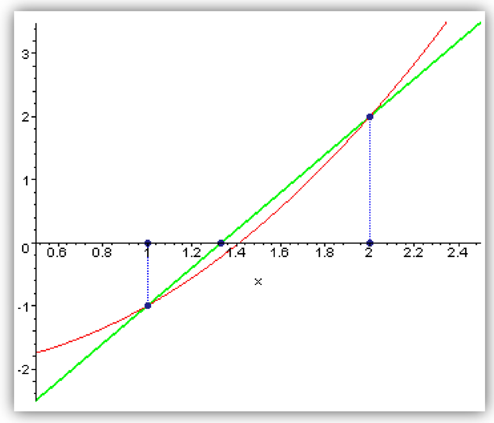
$$\Downarrow$$

$$\underline{\delta x}=-\left[\nabla\mathcal{L}(\underline{x})\right]^{-1}\cdot\mathcal{L}(\underline{x})$$

➔**F** is computed by 1D numerical integration.

➔Steady-state velocity **V** is found by Secant method **(F=0)**.





References

[1] E. Yariv, Migration of ion-exchange particles driven by a uniform electric field. Journal of Fluid Mechanics, 655:1-17, 2010.

[2] E. Yariv, An asymptotic derivation of the thin-Debye-layer limit for electrokinetic phenomena. Chemical Engineering Communications, 197 3-17, 2010