Brownian HydroDynamics for Confined Electrolytes

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Outline

Electrolyte Solutions

- **Electrolyte solutions** are important for batteries, ion-selective membranes, biology, etc.
- **Thermal fluctuations** play a key role at mesoscopic systems and can affect macroscopic observables.
- We have studied bulk transport coefficients of a binary electrolyte using the **fluctuating Poisson-Nernst-Planck-Stokes** equations: **conductivity** and **collective diffusion coefficient**.
- **Fluctuating Hydrodynamics** (FHD) gives the same results as the classical **Debye-Hückel-Onsager** (DHO theory).

"Fluctuating Hydrodynamics and Debye-Hückel-Onsager Theory for Electrolytes", A. Donev and **Alejandro L. Garcia** and J.-P. Péraud and A. J. Nonaka and **John B. Bell**, Current Opinion in Electrochemistry, 13:1-10, 2019 [**ArXiv:1808.07799**].

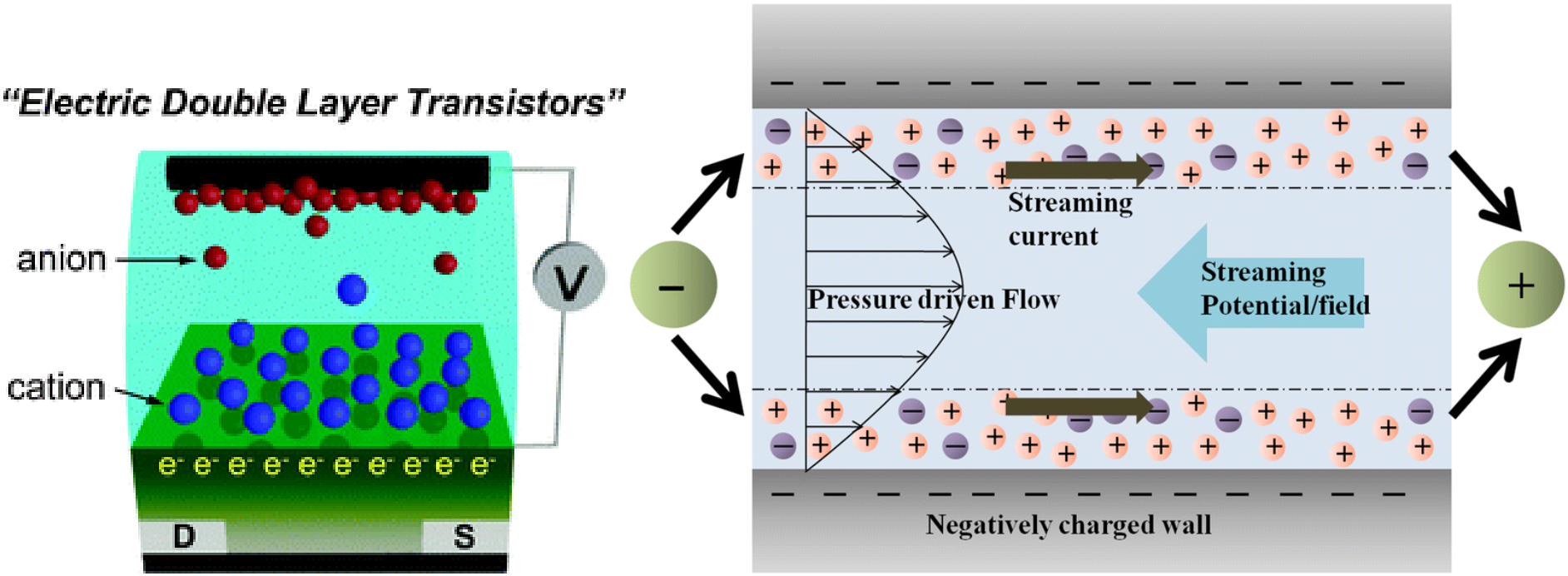
Particle-continuum modeling

- A key issue with the fluctuating continuum approach is that it only works for **dilute electrolytes** because of two key reasons:
  - There are **too few ions** per λ_D^3 volume as molarity increases (counter-intuitive!), where λ_D is Debye length.
  - It is not easy if at all possible to include **steric repulsion** and microscopic structure information in FHD.
- There are enough (too many!) water molecules though, so it does make sense to coarse-grain those into a continuum **implicit solvent**.
- This leads to **Brownian HydroDynamics** (BD-HI) with **electrostatic and hydrodynamic interactions**.

"A Discrete Ion Stochastic Continuum Overdamped Solvent Algorithm for Modeling Electrolytes" by **Daniel R. Ladiges** et al., Phys. Rev. Fluids, 6:044309, 2021 [**ArXiv:2007.03036**]

BDHI for electrolytes

Coarse-grained modeling of electrolyte solutions using **Brownian HydroDynamics**



Electrohydrodynamics, conduction in nanochannels, battery electrodes, ion channels.

Quick intro to BD-HI

- The Ito equations of **Brownian HydroDynamics** for the (correlated) positions of the N ions $\mathbf{Q}(t) = \{\mathbf{q}_1(t), \ldots, \mathbf{q}_N(t)\}$ are

$$d\mathbf{Q} = \boldsymbol{\mathcal{M}}\mathbf{F}dt + (2k_B T\,\boldsymbol{\mathcal{M}})^{\frac{1}{2}}\, d\boldsymbol{\mathcal{B}} + k_B T\,(\partial_{\mathbf{Q}} \cdot \boldsymbol{\mathcal{M}})\, dt,$$

  where $\boldsymbol{\mathcal{B}}(t)$ is a vector of Brownian motions, and $\mathbf{F}(\mathbf{Q})$ are electrostatic+steric+external forces.

- The symmetric positive semidefinite (SPD) **hydrodynamic mobility matrix** $\boldsymbol{\mathcal{M}}$ has 3×3 block $\mathbf{M}_{ij}$ that maps a force on particle j to a velocity of particle i.
- Key challenges for fast **linear-scaling**:
  - Long-ranged electrostatics ($\mathbf{F}(\mathbf{Q})$) and hydrodynamics ($\boldsymbol{\mathcal{M}}\mathbf{F}$)
  - Generating **Brownian displacements** with covariance $\sim \boldsymbol{\mathcal{M}}$ (FHD!)
  - Generating stochastic drift $\sim \partial_{\mathbf{Q}} \cdot \boldsymbol{\mathcal{M}}$ (temporal integrators)

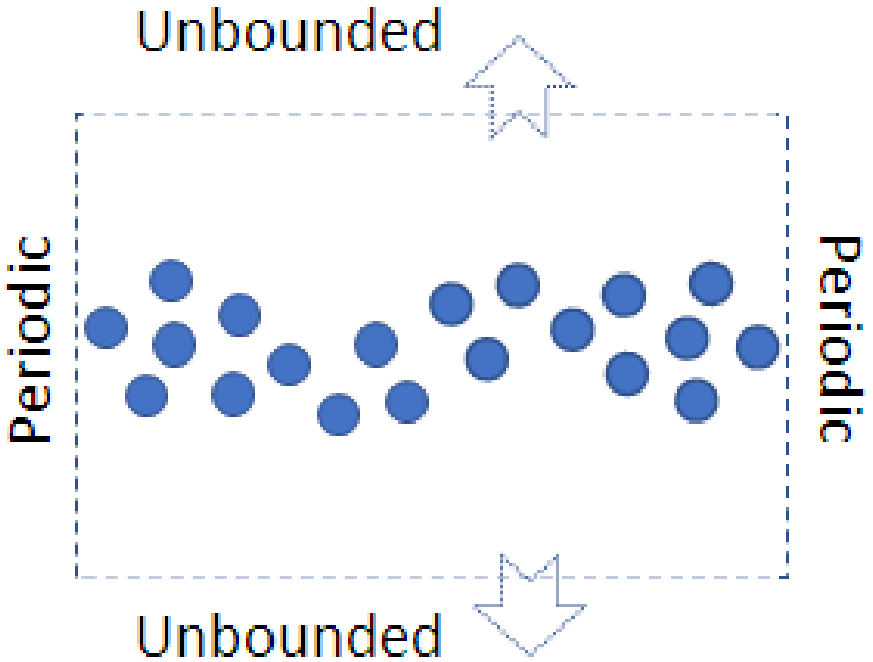
Outline

Doubly-Periodic Geometries

Poisson's equation for electrostatic potential with **Gaussian charges**:

$$\epsilon\Delta\phi(\mathbf{r}) = -f(\mathbf{r}) = \sum_{i=1}^{N} \frac{z_i}{(2\pi g_w^2)^{3/2}} \exp\left(-\frac{\|\mathbf{r}-\mathbf{q}_i\|^2}{2g_w^2}\right)$$

Start with: Electroneutral domain **doubly periodic** in $(x, y) \in [-L, L]$ and unbounded in z ($\mathbf{E} = -\nabla\phi \to 0$ as $z \to \pm\infty$)



Fourier-Chebyshev approach

For **quasi-2D** systems, f is compactly supported in $[-L, L]^2 \times [0, H]$.

$$\rightarrow \epsilon \Delta \phi = 0 \quad \text{if} \quad z < 0 \text{ or } z > H$$

Harmonic solve in xy Fourier space, $\phi(\mathbf{r}) \equiv \widehat{\phi}(k_x, k_y, z)$

$$\epsilon \left(\widehat{\phi}_{zz} - k^2 \widehat{\phi} \right) = 0$$

$$\rightarrow \widehat{\phi}(k, z) = \begin{cases} Ae^{-kz} & z > H \\ Be^{kz} & z < 0 \end{cases}$$

where in-plane wavenumber $k^2 = k_x^2 + k_y^2$.

This implies the boundary conditions

$$\widehat{\phi}_z(k, H) + k\widehat{\phi}(k, H) = 0$$

$$\underbrace{\widehat{\phi}_z(k, 0) - k\widehat{\phi}(k, 0) = 0}_{\text{Dirichlet to Neumann map!}}$$

Doubly-periodic quasi-2D Poisson equation

- Solution smooth at $z = 0/H \rightarrow$ same BCs hold for *interior* $\widehat{\phi}$!
- For $z \in [0, H]$, we get a simple 2-point Boundary Value Problem (BVP) for each $\mathbf{k}$:

$$\epsilon\left(\widehat{\phi}_{zz} - k^2\widehat{\phi}\right) = -\widehat{f}(k, z)$$

$$\widehat{\phi}_z(x, y, H) + k\phi(k, H) = 0$$

$$\widehat{\phi}_z(x, y, 0) - k\widehat{\phi}(x, y, 0) = 0$$

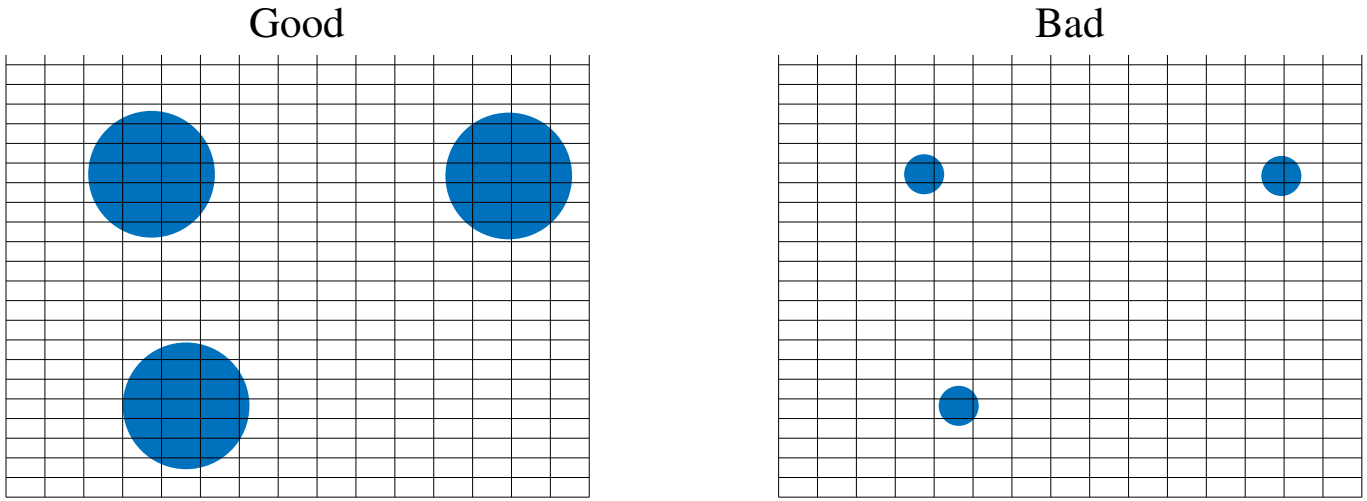
- Solve this BVP using Chebyshev spectral integral equation reformulation (**Leslie Greengard** 1991).

Particle-mesh (PPPM)

- For electrolytes, f is the charge density due to collection of **Gaussian charges**

$$f(\mathbf{r}) = \sum_{i=1}^{N} \frac{q_i}{(2\pi g_w^2)^{3/2}} \exp\left(-\frac{\|\mathbf{r}-\mathbf{z}_i\|^2}{2g_w^2}\right)$$

- Can a grid-based method work? Only if $h \sim g_w$.



Need alternative strategy for point-like (narrow) charges.

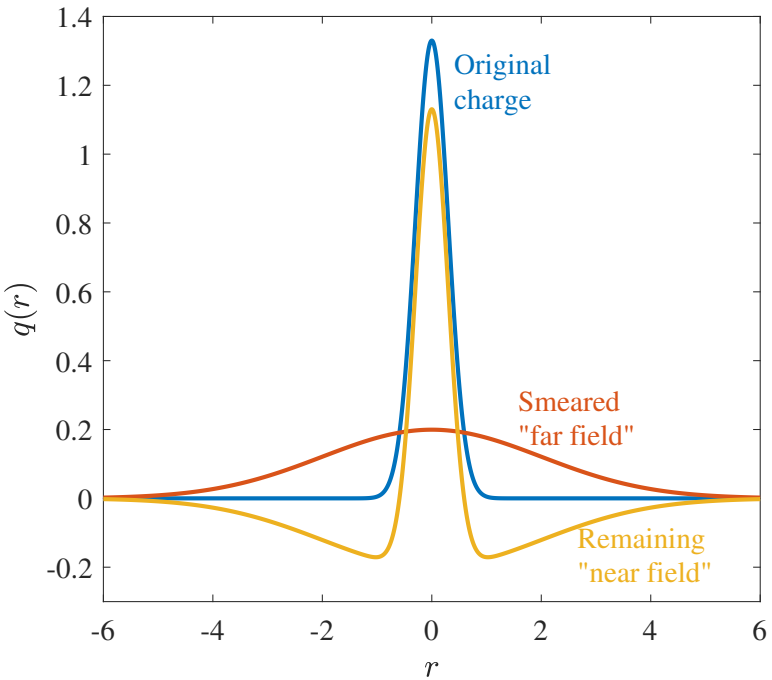
Ewald splitting

- Introduce normalized Gaussian splitting function

$$\gamma(r;\xi) \propto e^{-r^2\xi^2}$$

- **Ewald splitting** parameter ξ has units 1/length optimized for speed
- Split charge = smeared charge + neutral

$$f = \underbrace{f * \gamma}_{\text{far field}} + \underbrace{f * (1-\gamma)}_{\text{near field}}$$



Spectral Ewald method for slabs

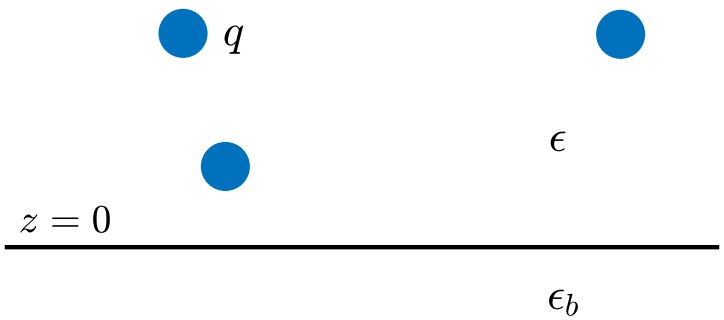
- **Near field** charge clouds have zero net charge
  - Exponentially-decaying near field interaction
  - Free space BC $\rightarrow$ analytical solution
  - Can be made nonzero at $\mathcal{O}(1)$ **neighbors** per point
- **Far field** $\epsilon\Delta\phi^{(f)} = \gamma * f$ is smooth
  - **Grid-based solver works**
  - Spread charge density to grid by convolving $f * \gamma^{1/2}$
  - Solve $\epsilon\Delta\psi = (f * \gamma^{1/2})$ on grid
  - Interpolate grid $\gamma^{1/2} * \psi$ to get $\phi^{(f)} = \epsilon^{-1}\Delta^{-1}(f * \gamma)$ at charges.

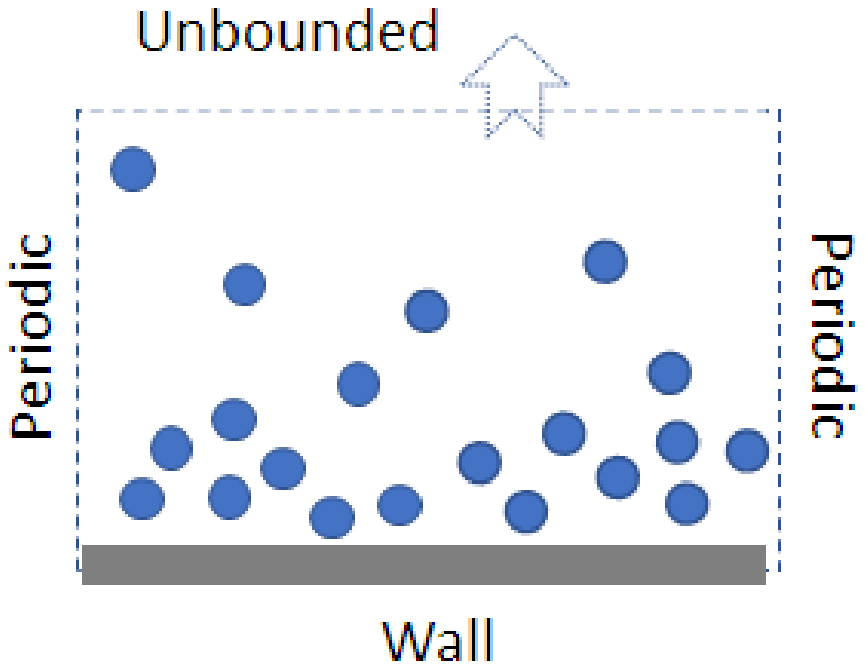
"A fast spectral method for electrostatics in doubly-periodic slit channels" by **Ondrej Maxian**, Raul P. Peláez, L. Greengard and A. Donev, J. Chem. Phys., 154, 204107, 2021 [**ArXiv:2101.07088**].

Permittivity jump - single wall

BCs for the potential ϕ at a dielectric interface: continuity of potential and displacement

$$\phi(x, y, 0^+) = \phi(x, y, 0^-)$$
$$\epsilon\phi_z(x, y, 0^+) = \epsilon_b\phi_z(x, y, 0^-)$$

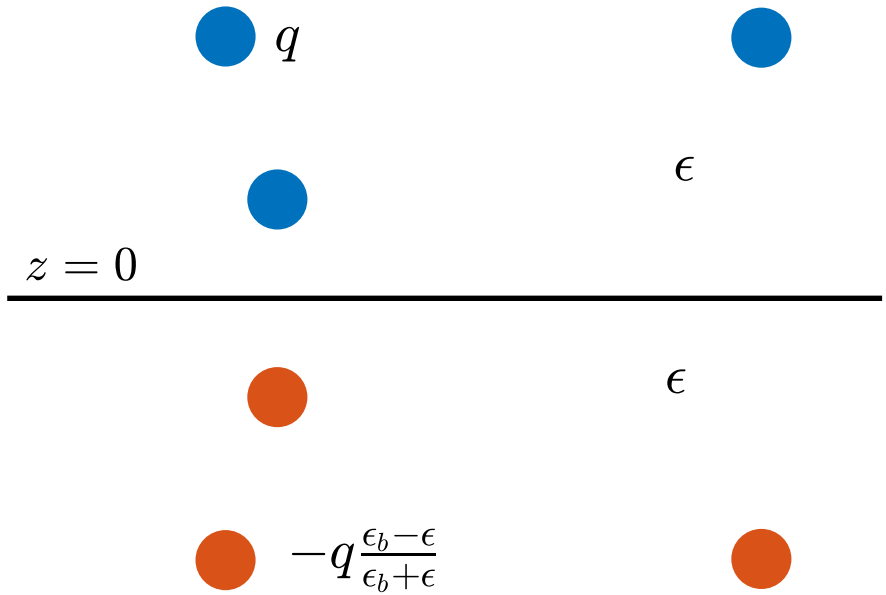




BottomWall

Image construction - single wall

Solution on $z > 0$ same as with uniform permittivity and set of *image charges*

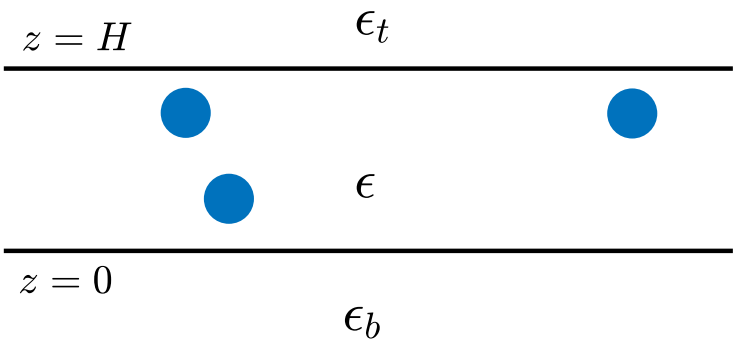


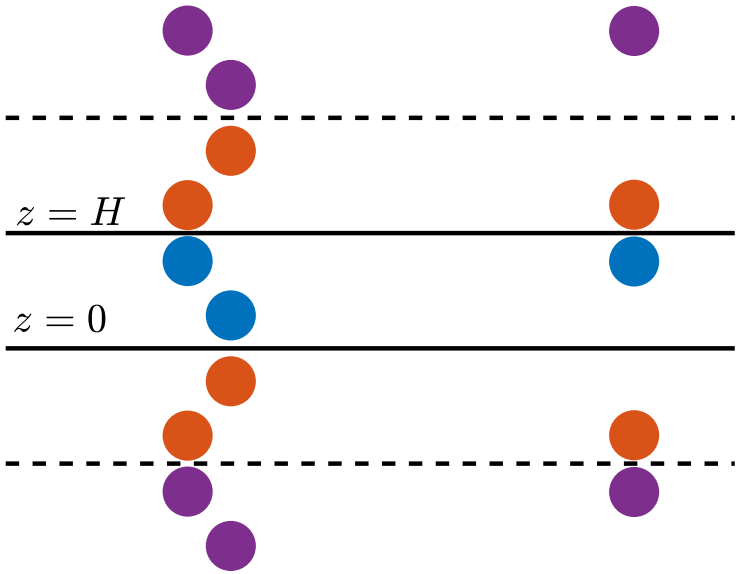
Use DP solver + Ewald splitting on the problem with images

Image construction - two walls

- Three different permittivities
- We can also add **surface charge**

$$\epsilon\phi_z(x,y,0^+) - \epsilon_b\phi_z(x,y,0^-) = -\sigma_b(x,y)$$
$$\epsilon\phi_z(x,y,H^-) - \epsilon_t\phi_z(x,y,H^+) = \sigma_t(x,y)$$

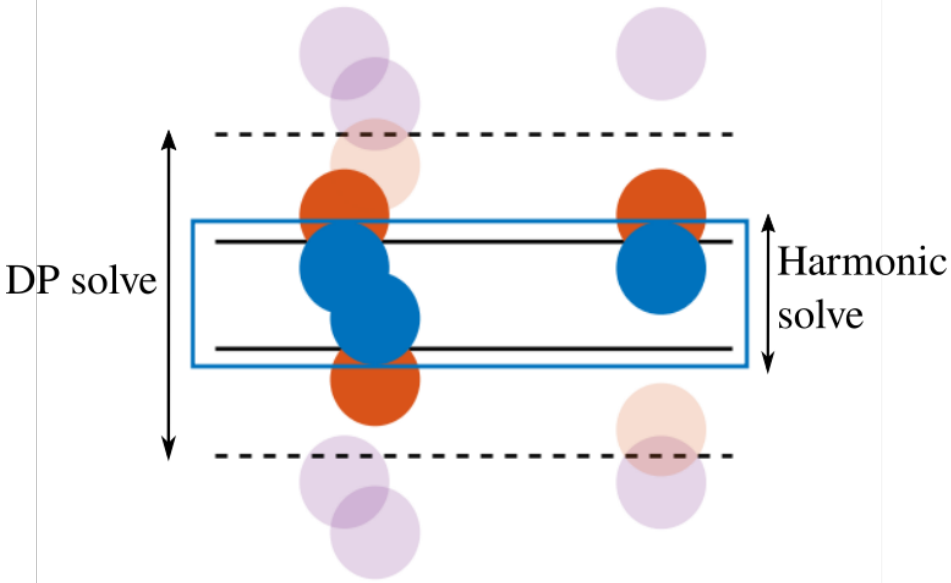




- Infinitely many images in **far-field problem** (near-field easy)

Far-field solver for slit channels

- Spread to grid = smear charges
- We only need potential in a **thicker slab**
- Find images that overlap domain
- Do initial **DP solve** with *only* these images (BCs *not* satisfied)
- Compute potential due to far-away images using a **harmonic BC correction solve**

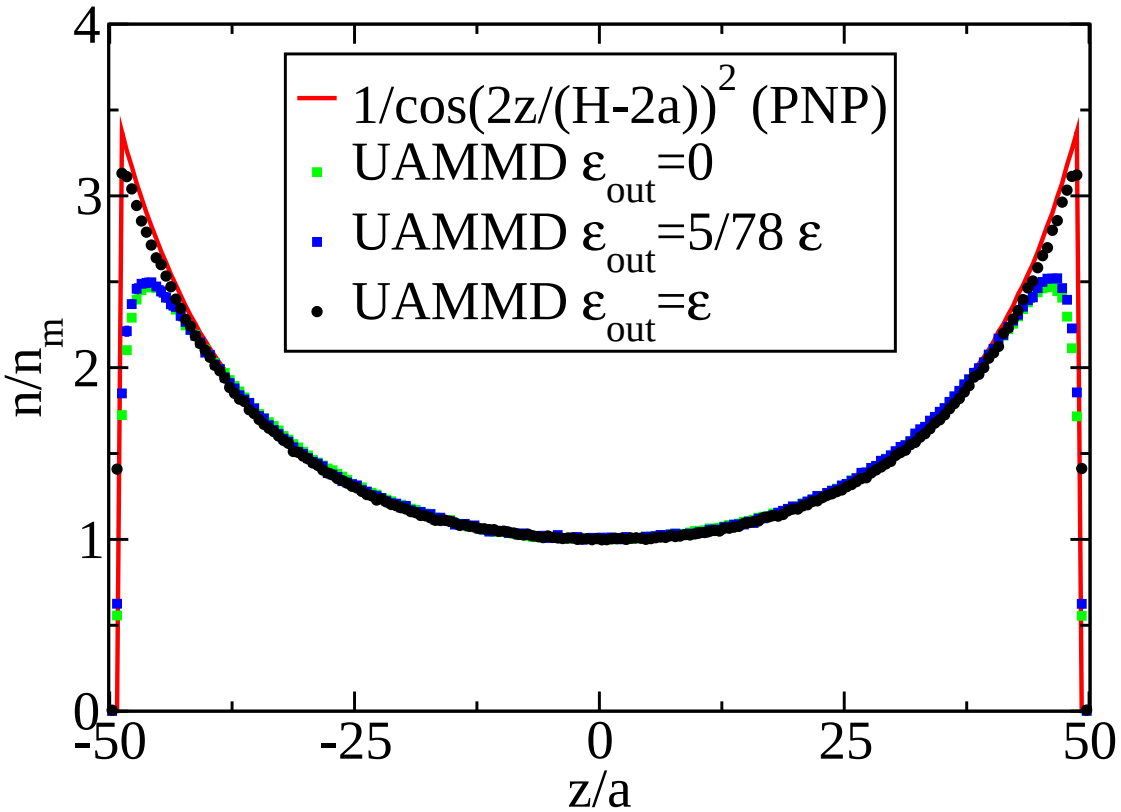


- Uses 3D FFTs + decoupled BVP solves for each wavenumber + neighbor sums (all parallelizable on GPU):
  UAMMD = Brownian dynamics GPU code by **Raul Perez Peláez**.

Dielectric effects for confined electrolytes

Equilibrium for positively-charged wall with negatively charged ions

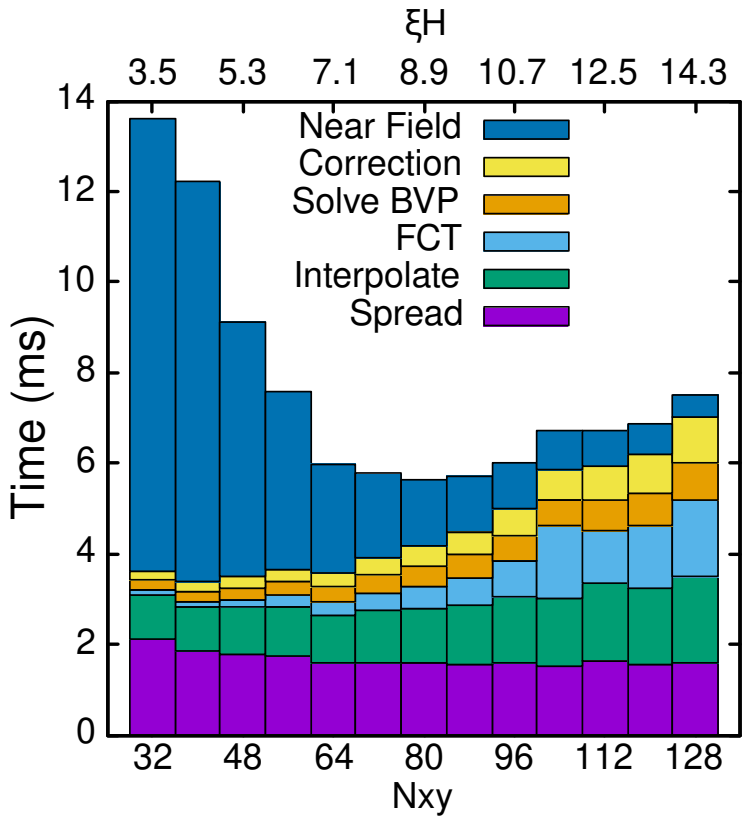
- $\epsilon_{\text{out}} = \epsilon \rightarrow$ no images, matches analytical solution of PNP equations
- $\epsilon_{\text{out}} = 5/78\epsilon \approx 0.06\epsilon \rightarrow$ Images repelled by each other (**not in PNP**!)
- $\epsilon_{\text{out}} = 0 \rightarrow$ field outside irrelevant, close to glass or vacuum (MD)



GPU acceleration

Splitting parameter ξ chosen to optimize speed

- Smaller ξ: Coarser grid, near field eats up entire cost
- Larger ξ: Finer grid, far field (spread & interpolate, FFT) cost more



- 20K charges = 6 ms per time step!

Outline

Fluctuating Hydrodynamics

- Consider N **Brownian ions/blobs** of size a with positions $\mathbf{q}_i(t)$ and velocity $\mathbf{u}_i = \dot{\mathbf{q}}_i$.
- The ions are immersed in a **fluctuating Stokes** fluid with **fluid velocity** $\mathbf{v}(\mathbf{r}, t)$, $\boldsymbol{\nabla} \cdot \mathbf{v} = 0$ and

$$\begin{aligned} \rho \partial_t \mathbf{v} + \boldsymbol{\nabla} \pi &= \eta \boldsymbol{\nabla}^2 \mathbf{v} + \sum_{i=1}^{N} \mathbf{F}_i \delta_a (\mathbf{q}_i - \mathbf{r}) + \boldsymbol{\nabla} \cdot \left(\sqrt{2\eta k_B T} \boldsymbol{\mathcal{Z}} \right) \\ \mathbf{u}_i &= \int \delta_a (\mathbf{q}_i - \mathbf{r}) \, \mathbf{v}(\mathbf{r}, t) \, d\mathbf{r} \end{aligned}$$

  along with appropriate **boundary conditions**.
- Here the **stochastic stress** is a random Gaussian tensor field $\boldsymbol{\mathcal{Z}}(\mathbf{r}, t)$ from **fluctuating hydrodynamics (FHD)**:

$$\langle \mathcal{Z}_{ij}(\mathbf{r}, t) \mathcal{Z}_{kl}(\mathbf{r}', t') \rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \, \delta(t - t') \delta(\mathbf{r} - \mathbf{r}').$$

Overdamped Limit

- In the limit of **infinite Schmidt number**, the above equations converge to the **overdamped Langevin** equations of Brownian HydroDynamics for the ion positions,

$$d\mathbf{Q} = \boldsymbol{\mathcal{M}}\mathbf{F}dt + \left(2k_B T\,\boldsymbol{\mathcal{M}}\right)^{\frac{1}{2}} d\boldsymbol{\mathcal{B}} + k_B T\left(\partial_{\mathbf{Q}}\cdot\boldsymbol{\mathcal{M}}\right)dt.$$

- Block of mobility matrix for particles i and j (including $i = j$!) is very similar to the **Rotne-Prager tensor** used in BD-HI,

$$\boldsymbol{\mathcal{M}}_{ij} = \eta^{-1}\int \delta_a(\mathbf{q}_i - \mathbf{r})\mathcal{G}(\mathbf{r},\mathbf{r}')\delta_a(\mathbf{q}_j - \mathbf{r}')\; d\mathbf{r}d\mathbf{r}',$$

  where $\mathcal{G}$ is the Green's function for the Stokes problem.

- Captures **Stokes-Einstein** and **hydrodynamic interactions**:

$$\boldsymbol{\mathcal{M}}_{ii} = \boldsymbol{\mathcal{M}}_{\text{self}} = \frac{1}{6\pi\eta a}\mathbf{I} \quad \text{defines } \textbf{ion hydrodynamic radius}$$

$$\boldsymbol{\mathcal{M}}_{ij} \approx \eta^{-1}\left(\mathbf{I} + \frac{a^2}{6}\nabla^2_{\mathbf{r}}\right)\left(\mathbf{I} + \frac{a^2}{6}\nabla^2_{\mathbf{r}'}\right)\mathcal{G}(\mathbf{r}-\mathbf{r}')\Big|^{\mathbf{r}=\mathbf{q}_j}_{\mathbf{r}'=\mathbf{q}_i}$$

Brownian HydroDynamics via FHD

- Solve a **steady-state Stokes problem** (linear scaling in N)

$$\begin{aligned} \nabla \pi^n &= \eta \nabla^2 \mathbf{v}^n + \nabla \cdot \left(\sqrt{\frac{2\eta k_B T}{\Delta t}} \mathbf{Z}^n \right) + \sum_{i=1}^{N} \mathbf{F}_i^n \delta_a \left(\mathbf{q}_i^n - \mathbf{r} \right) \\ \nabla \cdot \mathbf{v}^n &= 0. \end{aligned}$$

- **Predict** midpoint particle position:

$$\mathbf{q}^{n+\frac{1}{2}} = \mathbf{q}^n + \frac{\Delta t}{2} \int \delta_a \left(\mathbf{q}_i^n - \mathbf{r} \right) \mathbf{v}^n \left(\mathbf{r}, t \right) d\mathbf{r}$$

- **Correct** particle position,

$$\mathbf{q}^{n+1} = \mathbf{q}^n + \Delta t \int \delta_a \left(\mathbf{q}_i^{n+\frac{1}{2}} - \mathbf{r} \right) \mathbf{v}^n \left(\mathbf{r}, t \right) d\mathbf{r}.$$

"A Discrete Ion Stochastic Continuum Overdamped Solvent Algorithm for Modeling Electrolytes" by **Daniel R. Ladiges** et al., Phys. Rev. Fluids, 6:044309, 2021 [**ArXiv:2007.03036**]

Wet vs Dry Diffusion

- In the above approach, the steady Stokes equations have to be solved with a grid size smaller than a, i.e., Angstroms — not efficient.
- Two possible solutions:
  - Implement **Ewald splitting for Stokes** to decouple particle size from grid size; not trivial and still WIP.
  - Use a coarser grid of spacing $\tilde{a} > a$, but add unresolved fluid fluctuations in the form of **dry diffusion**.
- We follow the second approach in the Discrete Ion Stochastic Continuum Overdamped Solvent (DISCOS) method

$$\boldsymbol{\mathcal{M}}_{ij} = \mu_0 \mathbf{I}\delta_{ij} + \eta^{-1} \int \delta_{\tilde{a}}(\mathbf{q}_i - \mathbf{r})\boldsymbol{\mathcal{G}}(\mathbf{r}, \mathbf{r}')\delta_{\tilde{a}}(\mathbf{q}_j - \mathbf{r}')\, d\mathbf{r} d\mathbf{r}'.$$

- In DISCOS, we use second-order Stokes and Poisson solver and kernels taken from **Immersed Boundary Method**, but can also use spectral solvers (harder for Stokes).

Wet vs Dry Diffusion

- Total diffusion is now **bare** or **dry diffusion** (different for each ionic species) plus **wet diffusion**:

$$D = \frac{k_B T}{6\pi\eta a} = (k_B T)\,\mu_0 + \frac{k_B T}{6\pi\eta\delta_{\tilde{a}}} = \text{input}$$

- In confinement, no-slip conditions on the walls lead to **space-dependent mobility** (both total and bare); $\mu_0(\mathbf{q})$ can be tabulated ahead of time.
- Fundamental question: **Does the percentage split of the diffusion between wet and dry matter for macroscopic observables** like total flow or total current?
- Another way to ask this: How important are hydrodynamic interactions between ions at **short distances**?

Bulk conductivity

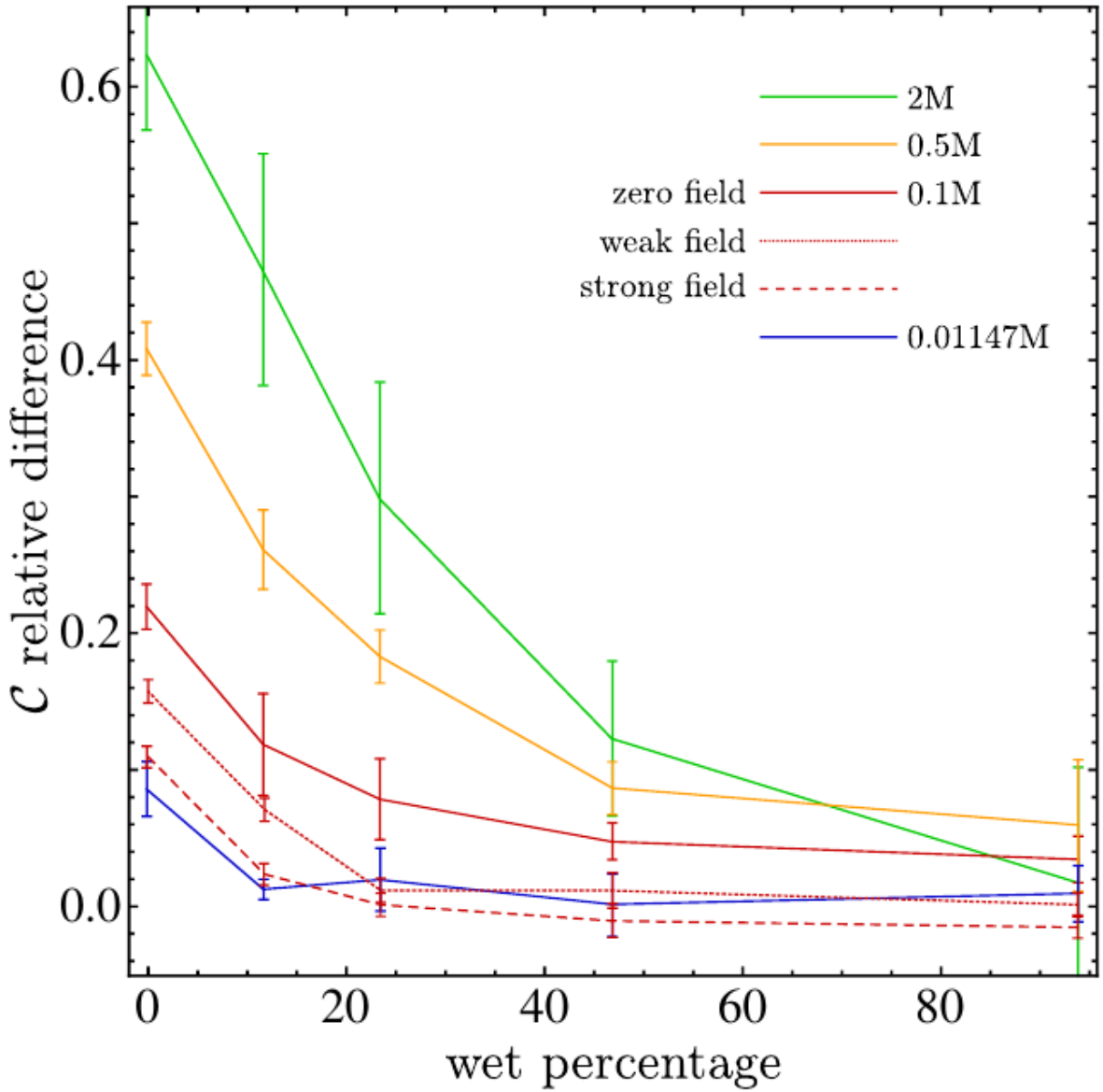
- The **bulk conductivity** of electrolyte solutions at finite concentrations has**:**
  - **relaxation corrections** due to electrostatic correlations
  - **electrophoretic corrections** due to hydrodynamic interactions (Onsager).
- Performed periodic simulations and measured conductivity at **finite fields** (non-equilbrium) at 0.1M and zero field at several concentrations,

$$\mathcal{C}_{E\to 0} = \frac{1}{6\,(k_B T)\,\mathcal{V}\tau}\int_0^{\tau} (\varsigma(t)-\varsigma(0))^2\,dt$$

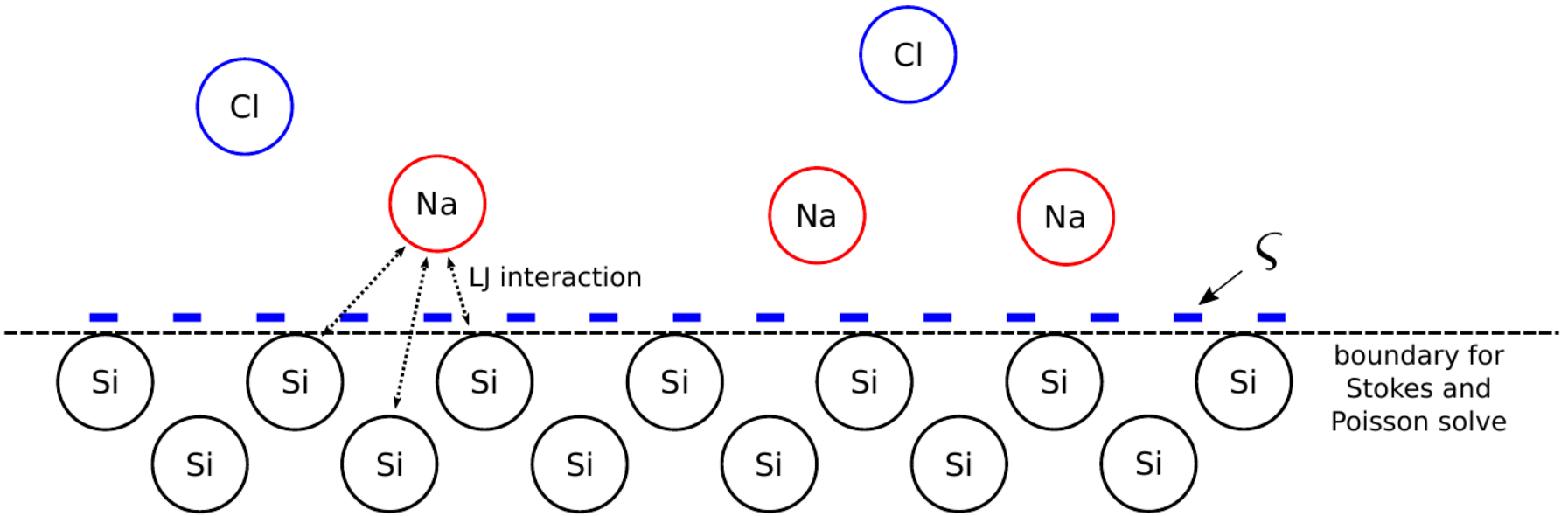
$$\varsigma(t) = \sum_{i=1}^{N} z_i \mathbf{q}_i(t) \quad \text{(center of charge)}$$

- Key conclusion: As long as **fluid grid resolves typical ion-ion distance** the bulk conductivity is approximated well.

Hydrodynamics and bulk conductivity



From MD to BD

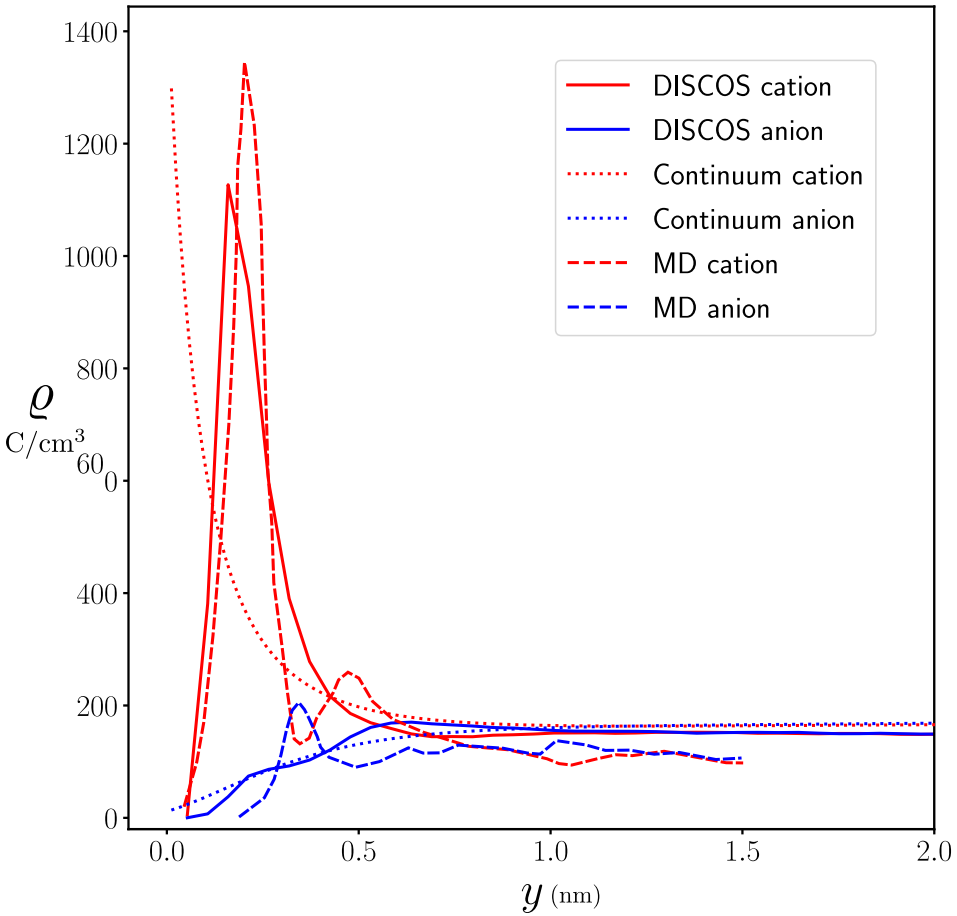


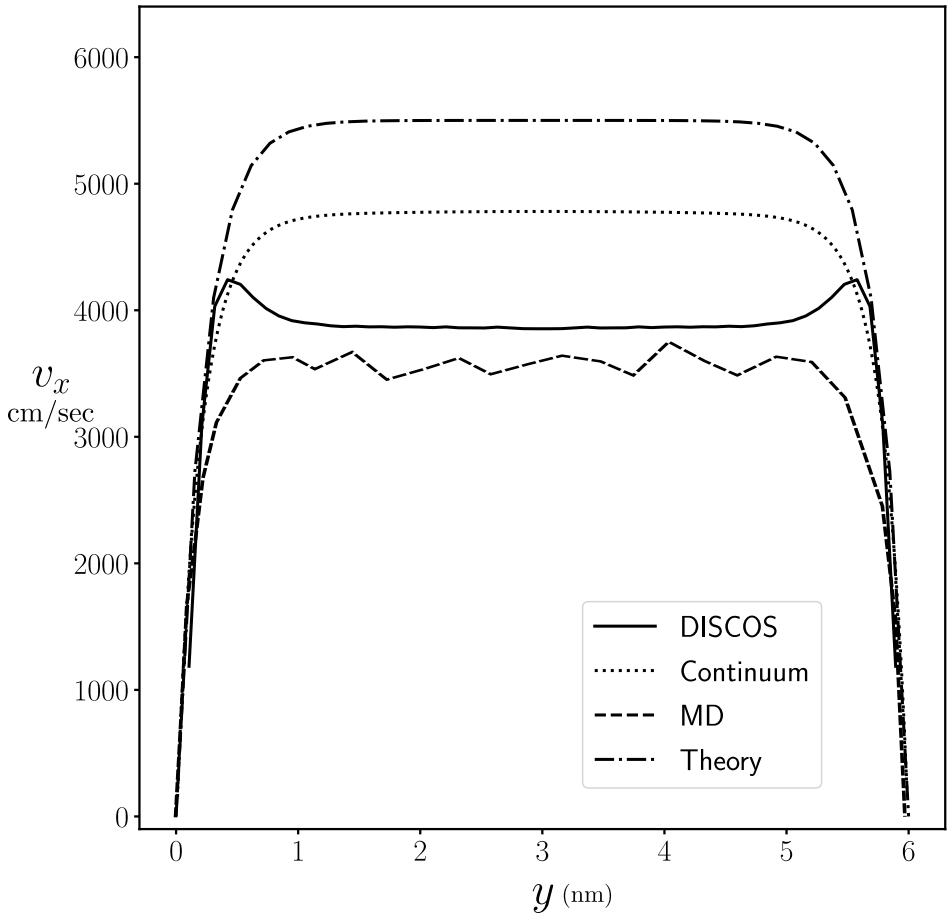
Key open question: How should one treat the **electrolyte-wall boundary in Poisson and Stokes solves?**

How to account for evanescent fields / **polarizability** / images in MD/BD, how to account for microscopic **slip** of fluid, etc.

"Modelling Electrokinetic Flows with the Discrete Ion Stochastic Continuum Overdamped Solvent Algorithm" by **Daniel R. Ladiges** et al., in preparation

Electroosmotic flow: MD vs BD





Results not very sensitive to wet-dry diffusion split, but some fluid grid is required to get flow! Work currently in progress at LBNL...

Future Directions

- Achieve a **time step size** of 1ps ($\sim 0.1a^2/D$) without sacrificing too much of physical fidelity (softer ions).
  Are there better (multistep/multistage) **temporal integrators**?
- Develop **GPU hydrodynamic solver** (done) and then add fluctuations (in progress).
  Can we do Ewald splitting for Stokes in the presence of boundaries?
- More careful comparisons to MD for nonequilibrium steady states: how to handle **BCs for implicit solvent**?
- Study **dynamical problems** (e.g., AC potentials, charging of EDLs, etc.) and compare to continuum theories.
- Bigger question: Does one need to account for the polarization / solvation / hydrogen bonds in solvent explicitly?