A Computational Viewpoint on Classical Density Functional Theory

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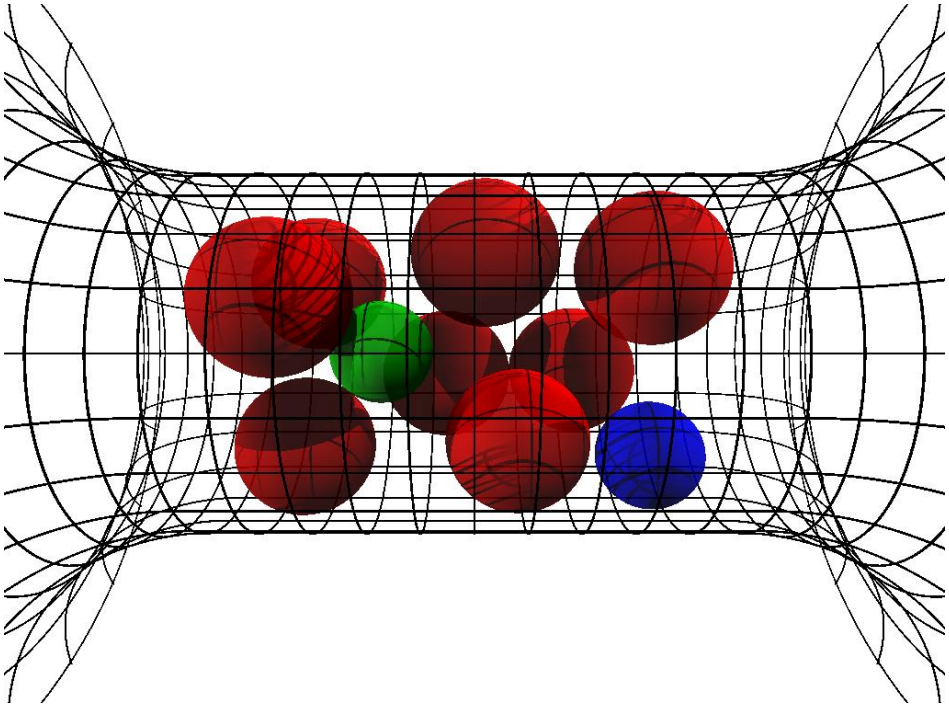
Geometric Modeling in Biomolecular Systems
SIAM Life Sciences 14, Charlotte, NC August 6, 2014

Outline

What is CDFT?

A fast, accurate theoretical tool to understand the fundamental physics of inhomogeneous fluids



What is CDFT?

For concentration $\rho_i(\vec{x})$ of species i, solve

$$\min_{\rho_i(\vec{x})} \Omega[\{\rho_i(\vec{x})\}]$$

where Ω is the free energy.

What is CDFT?

For concentration $\rho_i(\vec{x})$ of species i, solve

$$\frac{\delta\Omega}{\delta\rho_i(\vec{x})} = 0$$

which are the Euler-Lagrange equations.

What is CDFT?

DFT

- Computes ensemble-averaged quantities directly
- Can have physical resolution in time (μs) and space (Å)
- Requires an accurate Ω
- Requires sophisticated solver technology
- Can predict experimental results!

For example,

D. Gillespie, L. Xu, Y. Wang, and G. Meissner,
J. Phys. Chem. B 109, 15598, 2005

Outline

Equilibrium

$$\rho_i(\vec{x}) = \exp\left(\frac{\mu_i^{\text{bath}} - \mu_i^{\text{ext}}(\vec{x}) - \mu_i^{\text{ex}}(\vec{x})}{kT}\right)$$

where

$$\begin{aligned}\mu_i^{\text{ex}}(\vec{x}) &= \mu_i^{\text{HS}}(\vec{x}) + \mu_i^{\text{ES}}(\vec{x}) \\ &= \mu_i^{\text{HS}}(\vec{x}) + \mu_i^{\text{SC}}(\vec{x}) + z_i e\phi(\vec{x})\end{aligned}$$

and

$$-\epsilon\Delta\phi(\vec{x}) = e\sum_i \rho_i(\vec{x})$$

Details

The theory and implementation are detailed in

Knepley, Karpeev, Davidovits, Eisenberg, Gillespie,
An Efficient Algorithm for Classical Density Functional Theory in Three Dimensions: Ionic Solutions,
JCP, 2012.

Outline

Hard Spheres (Rosenfeld)

$$\mu_i^{\mathrm{HS}}(\vec{x}) = kT \sum_\alpha \int \frac{\partial \Phi^{\mathrm{HS}}}{\partial n_\alpha}(n_\alpha(\vec{x}'))\omega_i^\alpha(\vec{x} - \vec{x}')\, d^3x'$$

where

$$\Phi^{\mathrm{HS}}(n_\alpha(\vec{x}')) = -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \vec{n}_{V1} \cdot \vec{n}_{V2}}{1 - n_3} + \frac{n_2^3}{24\pi(1 - n_3)^2}\left(1 - \frac{\vec{n}_{V2} \cdot \vec{n}_{V2}}{n_2^2}\right)^3$$

Hard Sphere Basis

$$n_\alpha(\vec{x}) = \sum_i \int \rho_i(\vec{x}')\omega_i^\alpha(\vec{x} - \vec{x}')\, d^3x'$$

where

$$\omega_i^0(\vec{r}) = \frac{\omega_i^2(\vec{r})}{4\pi R_i^2} \qquad \omega_i^1(\vec{r}) = \frac{\omega_i^2(\vec{r})}{4\pi R_i}$$

$$\omega_i^2(\vec{r}) = \delta(|\vec{r}| - R_i) \qquad \omega_i^3(\vec{r}) = \theta(|\vec{r}| - R_i)$$

$$\vec{\omega}_i^{V1}(\vec{r}) = \frac{\vec{\omega}_i^{V2}(\vec{r})}{4\pi R_i} \qquad \vec{\omega}_i^{V2}(\vec{r}) = \frac{\vec{r}}{|\vec{r}|}\delta(|\vec{r}| - R_i)$$

Hard Sphere Basis

All n_α integrals may be cast as convolutions:

$$\begin{aligned} n_\alpha(\vec{x}) &= \sum_i \int \rho_i(\vec{x}')\omega_i^\alpha(\vec{x}' - \vec{x})d^3x' \\ &= \sum_i \mathcal{F}^{-1}\left(\mathcal{F}\left(\rho_i\right) \cdot \mathcal{F}\left(\omega_i^\alpha\right)\right) \\ &= \sum_i \mathcal{F}^{-1}\left(\hat{\rho}_i \cdot \hat{\omega_i^\alpha}\right) \end{aligned}$$

and similarly

$$\mu_i^{\mathrm{HS}}(\vec{x}) = kT \sum_\alpha \mathcal{F}^{-1}\left(\frac{\partial \hat{\Phi}^{\mathrm{HS}}}{\partial n_\alpha} \cdot \hat{\omega_i^\alpha}\right)$$

Hard Sphere Basis

Spectral Quadrature

There is a fly in the ointment:

- standard quadrature for ω^α is very inaccurate ($\mathcal{O}(1)$ errors),
- and destroys conservation properties, e.g. total mass

We can use spectral quadrature for accurate evaluation,

- combining FFT of density, $\hat{\rho}_i$,
- with analytic FT of weight functions.

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Spectral Quadrature

$$\hat{\omega}_i^0(\vec{k}) = \frac{\hat{\omega}_i^2(\vec{k})}{4\pi R_i^2} \qquad \hat{\omega}_i^1(\vec{k}) = \frac{\hat{\omega}_i^2(\vec{k})}{4\pi R_i}$$

$$\hat{\omega}_i^2(\vec{k}) = \frac{4\pi R_i \sin\left(R_i|\vec{k}|\right)}{|\vec{k}|} \qquad \hat{\omega}_i^3(\vec{k}) = \frac{4\pi}{|\vec{k}|^3}\left(\sin\left(R_i|\vec{k}|\right) - R_i|\vec{k}|\cos\left(R_i|\vec{k}|\right)\right)$$

$$\hat{\omega}_i^{V1}(\vec{k}) = \frac{\hat{\omega}_i^{V2}(\vec{k})}{4\pi R_i} \qquad \hat{\omega}_i^{V2}(\vec{k}) = \frac{-4\pi\imath}{|\vec{k}|^2}\left(\sin\left(R_i|\vec{k}|\right) - R_i|\vec{k}|\cos\left(R_i|\vec{k}|\right)\right)$$

Hard Sphere Basis

Numerical Stability

Recall that

$$\Phi^{\mathrm{HS}}(n_\alpha(\vec{x}')) = \ldots + \frac{n_2^3}{24\pi(1-n_3)^2}\left(1 - \frac{\vec{n}_{V2}\cdot\vec{n}_{V2}}{n_2^2}\right)^3$$

and note that we have analytically

$$\frac{\left|n^{V2}(x)\right|^2}{\left|n^2(x)\right|^2} \leq 1.$$

However, discretization errors in ρ_i near sharp geometric features can produce large values for this term, which prevent convergence of the nonlinear solver. Thus we explicitly enforce this bound.

Outline

Bulk Fluid (BF) Electrostatics

$$\mu_i^{\mathrm{SC}} = \mu_i^{\mathrm{ES},bath} - \sum_j \int_{|\vec{x}-\vec{x}'|\leq R_{ij}} \left(c_{ij}^{(2)}(\vec{x},\vec{x}') + \psi_{ij}(\vec{x},\vec{x}') \right) \Delta\rho_j(\vec{x}')\, d^3x'$$

Using $\lambda_k = R_k + \frac{1}{2\Gamma}$, where Γ is the MSA screening parameter, we have

$$c_{ij}^{(2)}\left(\vec{x},\vec{x}'\right) + \psi_{ij}\left(\vec{x},\vec{x}'\right) = \frac{z_i z_j e^2}{8\pi\epsilon} \left(\frac{|\vec{x}-\vec{x}'|}{2\lambda_i\lambda_j} - \frac{\lambda_i+\lambda_j}{\lambda_i\lambda_j} + \frac{1}{|\vec{x}-\vec{x}'|} \left(\frac{(\lambda_i-\lambda_j)^2}{2\lambda_i\lambda_j} + 2 \right) \right)$$

Bulk Fluid (BF) Electrostatics

$$\mu_i^{\mathrm{SC}} = \mu_i^{\mathrm{ES},bath} - \sum_j \int_{|\vec{x}-\vec{x}'|\leq R_{ij}} \left(c_{ij}^{(2)}(\vec{x},\vec{x}') + \psi_{ij}(\vec{x},\vec{x}') \right) \Delta\rho_j(\vec{x}')\, d^3x'$$

It's a convolution too!

Bulk Fluid (BF) Electrostatics

$$\mu_i^{\mathrm{SC}} = \mu_i^{\mathrm{ES},bath} - \sum_j \int_{|\vec{x}-\vec{x}'|\leq R_{ij}} \left(c_{ij}^{(2)}(\vec{x},\vec{x}') + \psi_{ij}(\vec{x},\vec{x}') \right) \Delta\rho_j(\vec{x}')\, d^3x'$$

$$\mathcal{F}\left(\Delta\rho_j\right) = \mathcal{F}\left(\rho_j - \rho_{\mathrm{bath}}\right) = \mathcal{F}\left(\rho_j\right) - \mathcal{F}\left(\rho_{\mathrm{bath}}\right)$$

- $\mathcal{F}\left(\rho_j\right)$ was already calculated
- $\mathcal{F}\left(\rho_{\mathrm{bath}}\right)$ is constant
- $\mathcal{F}\left(c_{ij}^{(2)}\left(\vec{x},\vec{x}'\right) + \psi_{ij}\left(\vec{x},\vec{x}'\right)\right)$ is constant

so we only calculate the inverse transform on each iteration.

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FFT is also inaccurate!

Bulk Fluid (BF) Electrostatics

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$$\hat{c}_{ij}^{(2)} + \hat{\psi}_{ij} = \frac{z_i z_j e^2}{\epsilon|\vec{k}|} \left(\frac{1}{2\lambda_i\lambda_j} I_1 - \frac{\lambda_i+\lambda_j}{\lambda_i\lambda_j} I_0 + \left(\frac{(\lambda_i-\lambda_j)^2}{2\lambda_i\lambda_j} + 2 \right) I_{-1} \right)$$

where

$$I_{-1} = \frac{1}{|\vec{k}|}\left(1 - \cos\left(|\vec{k}|R\right)\right)$$

$$I_0 = -\frac{R}{|\vec{k}|}\cos\left(|\vec{k}|R\right) + \frac{1}{|\vec{k}|^2}\sin\left(|\vec{k}|R\right)$$

$$I_1 = -\frac{R^2}{|\vec{k}|}\cos\left(|\vec{k}|R\right) + 2\frac{R}{|\vec{k}|^2}\sin\left(|\vec{k}|R\right) - \frac{2}{|\vec{k}|^3}\left(1 - \cos\left(|\vec{k}|R\right)\right)$$

Outline

Reference Fluid Density (RFD) Electrostatics

Expand around $\rho_i^{\text{ref}}\left(\vec{x}\right)$, an inhomogeneous reference density profile:

$$\mu_i^{SC}\left[\left\{\rho_k\left(\vec{y}\right)\right\}\right] \approx \mu_i^{SC}\left[\left\{\rho_k^{\text{ref}}\left(\vec{y}\right)\right\}\right] - kT\sum_i \int c_i^{(1)}\left[\left\{\rho_k^{\text{ref}}\left(\vec{y}\right)\right\};\vec{x}\right]\Delta\rho_i\left(\vec{x}\right)d^3x - \frac{kT}{2}\sum_{i,j}\iint c_{ij}^{(2)}\left[\left\{\rho_k^{\text{ref}}\left(\vec{y}\right)\right\};\vec{x},\vec{x}'\right]\Delta\rho_i\left(\vec{x}\right)\Delta\rho_j\left(\vec{x}'\right)d^3x\,d^3x'$$

with

$$\Delta\rho_i\left(\vec{x}\right) = \rho_i\left(\vec{x}\right) - \rho_i^{\text{ref}}\left(\vec{x}\right)$$

Reference Fluid Density (RFD) Electrostatics

$$\rho_i^{\text{ref}}\left[\left\{\rho_k\left(\vec{x}'\right)\right\};\vec{x}\right] = \frac{3}{4\pi R_{SC}^3\left(\vec{x}\right)}\int_{\left|\vec{x}'-\vec{x}\right|\leq R_{SC}\left(\vec{x}\right)} \alpha_i\left(\vec{x}'\right)\rho_i\left(\vec{x}'\right)d^3x'$$

Choose α_i so that the reference density is

- charge neutral, and
- has the same ionic strength as ρ_i

This can model gradient flow

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Reference Fluid Density (RFD) Electrostatics

We can rewrite this expression as an averaging operation:

$$\rho^{ref}(\vec{x}) = \int \rho(\vec{x}') \frac{\theta\left(|\vec{x}' - \vec{x}| - R_{SC}(\vec{x})\right)}{\frac{4\pi}{3} R_{SC}^3(\vec{x})} dx'$$

where

$$R_{SC}(\vec{x}) = \frac{\sum_i \tilde{\rho}_i(\vec{x}) R_i}{\sum_i \tilde{\rho}_i(\vec{x})} + \frac{1}{2\Gamma(\vec{x})}$$

We close the system using

$$\Gamma_{\mathrm{SC}}[\rho](\vec{x}) = \Gamma_{\mathrm{MSA}}\left[\rho^{\mathrm{ref}}(\rho)\right](\vec{x}).$$

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Consistency checks

- Check n_α of constant density against analytics
- Check that n_3 is the combined volume fraction
- Check that wall solution has only 1D variation

Sum Rule Verification

Hard Spheres

$$\beta P_{\text{bath}}^{HS} = \sum_i \rho_i(R_i)$$

where

$$P_{\text{bath}}^{HS} = \frac{6kT}{\pi}\left(\frac{\xi_0}{\Delta} + \frac{3\xi_1\xi_2}{\Delta^2} + \frac{3\xi_2^3}{\Delta^3}\right)$$

using auxiliary variables

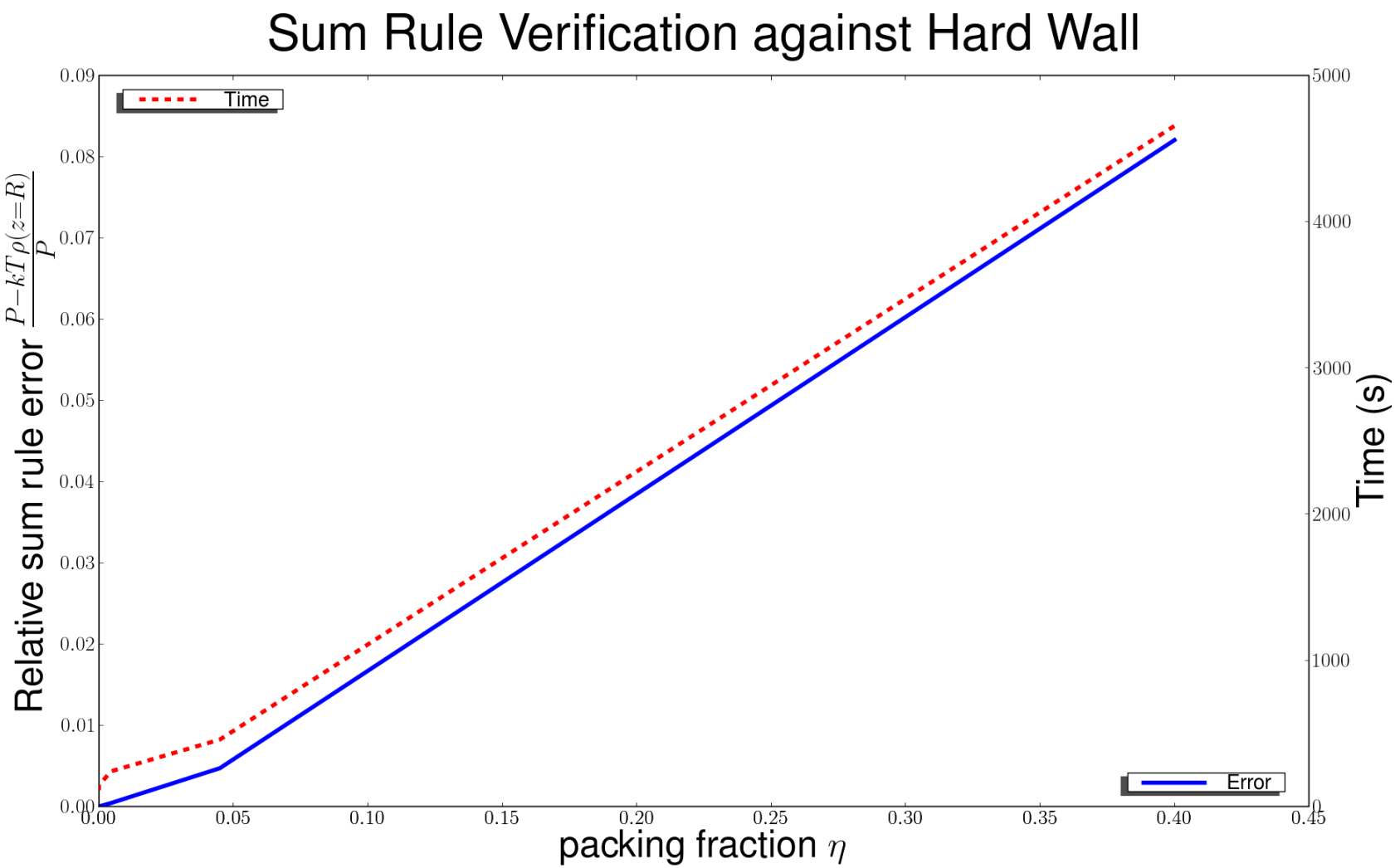
$$\xi_n = \frac{\pi}{6}\sum_j \rho_j^{bath}\sigma_j^n \qquad n \in \{0, \ldots, 3\}$$

$$\Delta = 1 - \xi_3$$

Sum Rule Verification

Hard Spheres

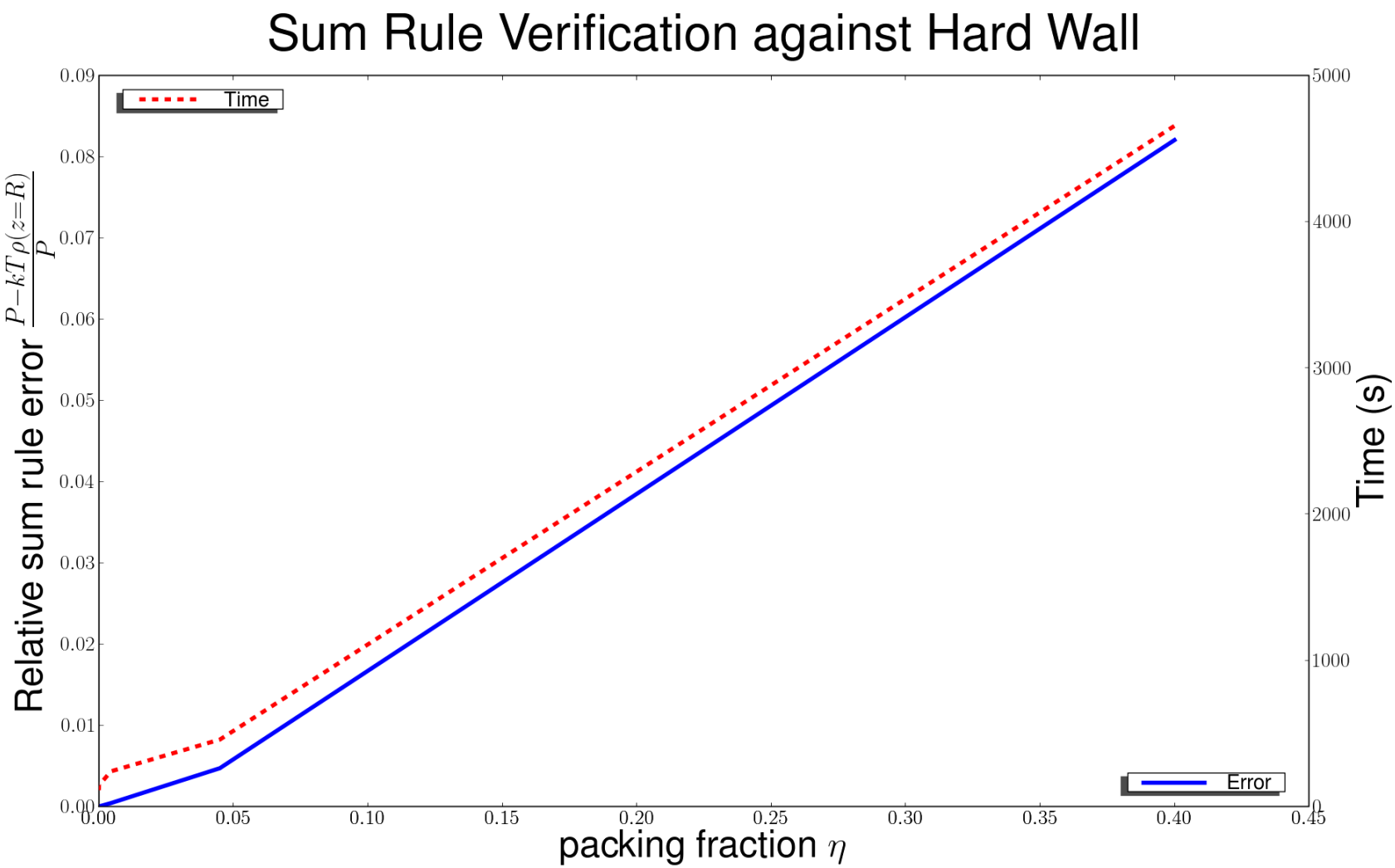
Relative accuracy and Simulation time for $R = 0.1\text{nm}$



Sum Rule Verification

Hard Spheres

Volume fraction ranges from 10^{-5} to 0.4 (very difficult for MC/MD)



Ionic Fluid Verification

Charged Hard Spheres

R_{cation}	0.1nm
R_{anion}	0.2125nm
Concentration	1M
Domain	$2 \times 2 \times 6\,\text{nm}^3$ and periodic
Uncharged hard wall	$z = 0$
Grid	$21 \times 21 \times 161$

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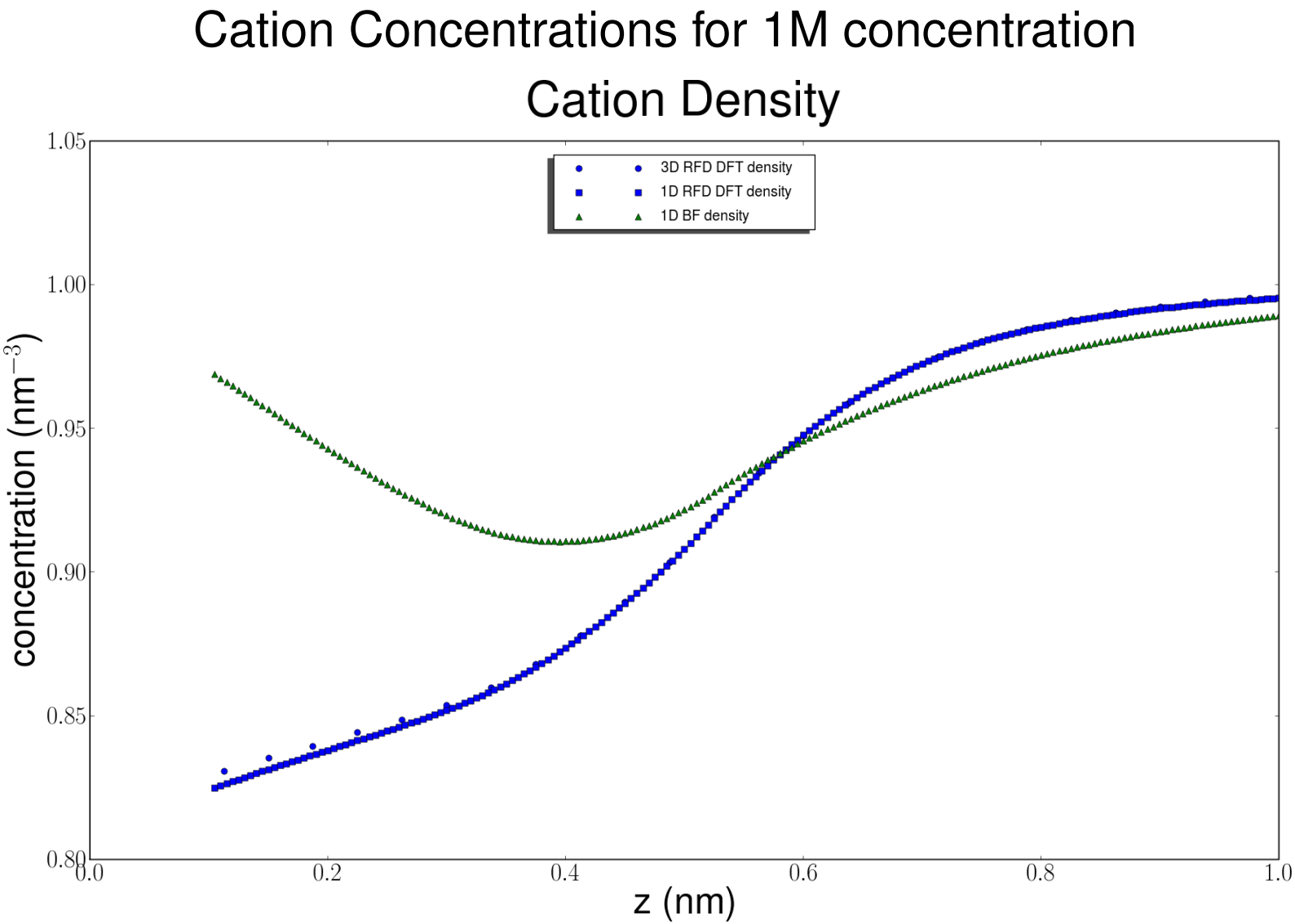

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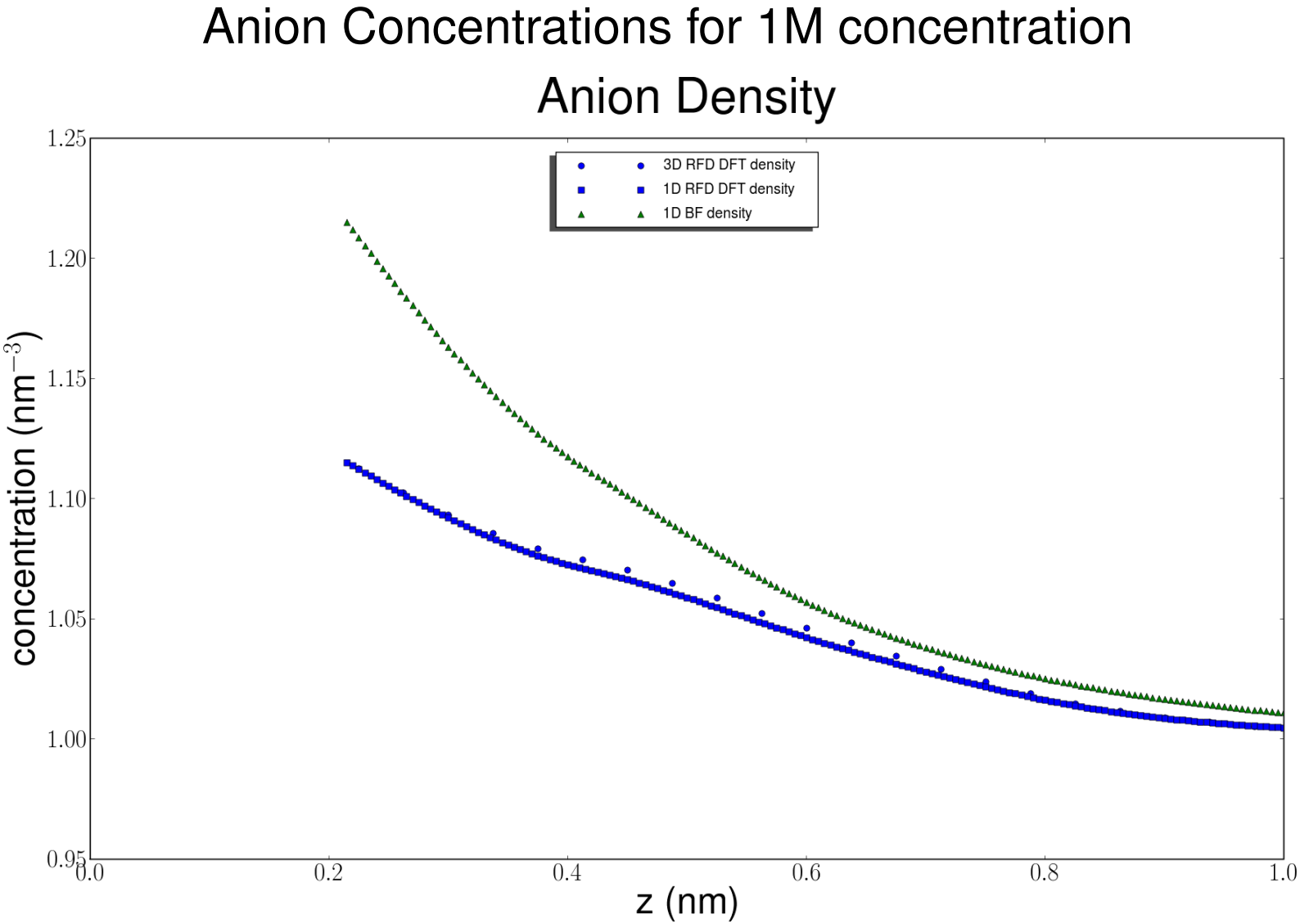
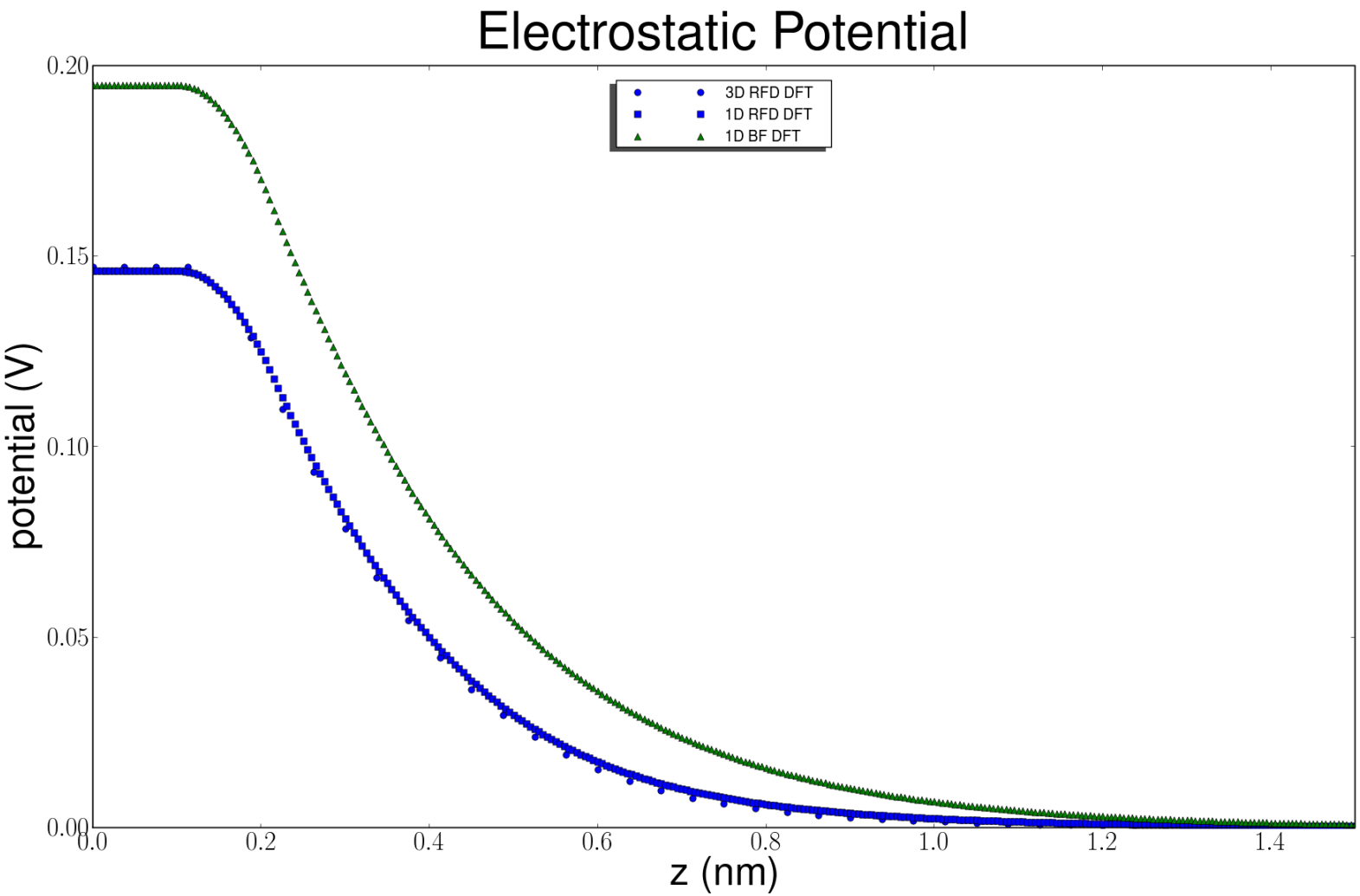


Ionic Fluid Verification

Charged Hard Spheres

Mean Electrostatic Potential for 1M concentration



Ionic Fluid Verification

Charged Hard Spheres

These results were first reported in 1D in
Density functional theory of the electrical double layer: the RFD functional,
J. Phys.: Condens. Matter 17, 6609, 2005.

Main Points

Real Space vs. Fourier Space

- $\mathcal{O}(N^2)$ vs. $\mathcal{O}(N \lg N)$
- Accurate quadrature only available in Fourier space

Electrostatics

- Bulk Fluid (BF) model can be qualitatively wrong
- Reference Fluid Density (RFD) model demands complex algorithm

Solver convergence

- Picard was more robust
- Newton rarely entered the quadratic regime
- Still no multilevel alternative (interpolation?)

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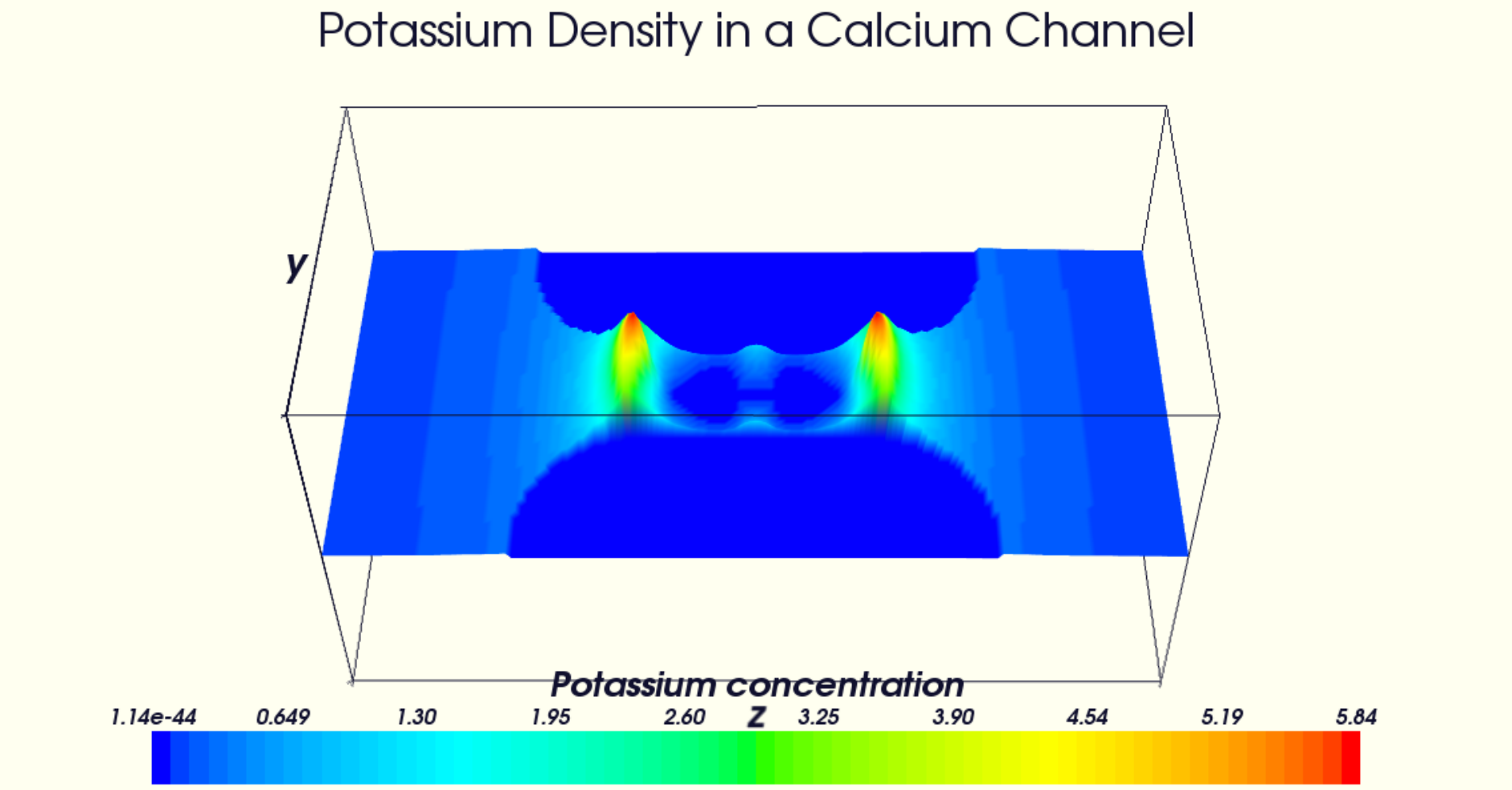

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