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A Multifidelity Approach to Effectively Compute the Steady-State Flow Of Ionic Solutions

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Introduction

We develop and demonstrate a new, hybrid simulation approach for charged fluids, which combines the accuracy of the nonlocal, classical density functional theory (cDFT) with the efficiency of the Poisson-Nernst-Planck (PNP) equations. The approach is motivated by the fact that the more accurate description of the physics in the cDFT model is required only near the charged surfaces, while away from these regions the PNP equations provide an acceptable representation of the ionic system. We formulate the hybrid approach in two stages. The first stage defines a coupled hybrid model in which the PNP and cDFT equations act independently on two overlapping domains, subject to suitable interface coupling conditions. At the second stage we apply the principles of the alternating Schwartz method to the hybrid model by using the interface conditions to define the appropriate boundary conditions and volume constraints exchanged between the PNP and the cDFT subdomains.

Ionic Fluid Density Models

The Poisson–Nernst–Planck equations are given as

$$\begin{aligned} \nabla\cdot\left(D_\alpha\nabla\rho_\alpha^P+\frac{D_\alpha e z_\alpha}{kT}\rho_\alpha^P\nabla\phi^P\right)=0 \quad &\text{(Nonlinear Drift–Diffusion)}\\ -\Delta\phi^P=\frac{1}{\epsilon\epsilon_0}\sum_{\alpha=1}^{N}ez_\alpha\rho_\alpha^P \quad &\text{(Gauss's Law)}, \end{aligned} \tag{1}$$

and the classical Density Functional Theory equations are given as

$$\begin{aligned} -\nabla\cdot\left[D_\alpha\rho_\alpha^D\nabla\frac{1}{kT}\left(\log\rho_\alpha^D+z_\alpha\phi+kT\frac{\delta F^{ex}}{\delta\rho_\alpha^D}\right)\right]=0\\ -\Delta\phi^D=\frac{1}{\epsilon\epsilon_0}\sum_{\alpha=1}^{N}ez_\alpha\rho_\alpha^D, \end{aligned} \tag{2}$$

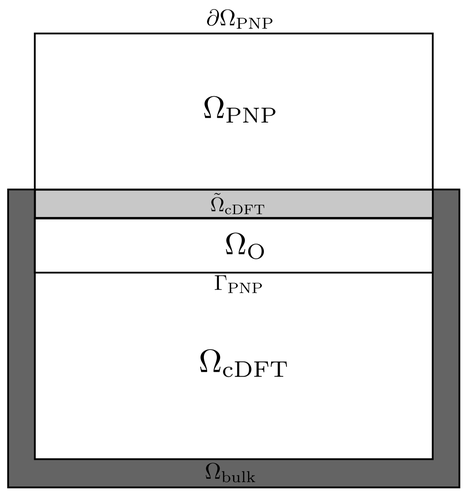
where

$$\frac{\delta F^{ex}}{\delta\rho_\alpha^D}=\underbrace{\sum_\gamma\int\frac{\partial\Phi}{\partial n_\gamma}(y)w_\alpha^{(\gamma)}(x-y)dy}_{\text{Hard Sphere}}+\underbrace{\sum_\beta\int\rho_\beta^D(y)u_{\alpha\beta}(x-y)dy}_{\text{Mean–Field Dispersion}}-\underbrace{\sum_\beta\int\left(\rho_\beta^D(y)\Delta c_{\alpha\beta}(x-y)\right)dy}_{\text{Charge Correlation}},$$

is the *excess Free Energy contributitions* to the grand free energy functional. Through phenomenological evidence, it is observed that the solution of the PNP equations is a good description of the charged particle behavior away from surfaces in the system, therefore, it is reasonable to use the cDFT equations only in the neighborhood of surfaces, and the PNP equations everywhere else in the system.

The Hybrid cDFT–PNP model

Consider the following prototypical domain configuration.



To simplify the presentation let $\mathcal{L}^{\text{cDFT}}$ and $\mathcal{L}^{\text{PNP}}$ denote the cDFT and PNP operators, respectively. We collect the densities and the chemical potentials of the N species into vectors denoted by $\boldsymbol{\rho}=(\rho_1,\rho_2,\ldots,\rho_N)$ and $\boldsymbol{\mu}=(\mu_1,\mu_2,\ldots,\mu_N)$, respectively. The coupled hybrid cDFT–PNP model comprises the subdomain governing equations

$$\begin{cases} \mathcal{L}^{\text{cDFT}}(\boldsymbol{\rho}^{\text{D}},\phi^{\text{D}},\boldsymbol{\mu}^{\text{D}})=0 \text{ in } \Omega_{\text{cDFT}}\\ \boldsymbol{\rho}^{\text{D}}=\boldsymbol{\rho}^{\text{D}}_{\text{bulk}} \quad \text{on } \Omega_{\text{bulk}}\backslash\tilde{\Omega}_{\text{cDFT}}\\ \phi^{\text{D}}=\phi^{\text{D}}_D \quad \text{on } \partial\Omega_{\text{cDFT}}\backslash\Gamma_{\text{cDFT}}\\ \boldsymbol{\mu}^{\text{D}}=\boldsymbol{\mu}^{\text{D}}_{\text{D}} \quad \text{on } \partial\Omega_{\text{cDFT}}\backslash\Gamma_{\text{cDFT}} \end{cases} \begin{cases} \mathcal{L}^{\text{PNP}}(\boldsymbol{\rho}^{\text{P}},\phi^{\text{P}})=0 \text{ in } \Omega_{\text{PNP}}\\ \boldsymbol{\rho}^{\text{P}}=\boldsymbol{\rho}^{\text{P}}_{\text{D}} \quad \text{on } \partial\Omega_{\text{PNP}}\backslash\Gamma_{\text{PNP}}\\ \phi^{\text{P}}=\phi^{\text{P}}_D \quad \text{on } \partial\Omega_{\text{PNP}}\backslash\Gamma_{\text{PNP}} \end{cases} \tag{3}$$

along with the interface conditions:

$$\begin{cases} \boldsymbol{\rho}^{\text{D}}=\boldsymbol{\rho}^{\text{P}} \quad \text{on } \tilde{\Omega}_{\text{cDFT}}\\ \phi^{\text{D}}=\phi^{\text{P}} \quad \text{on } \Gamma_{\text{cDFT}}\\ \boldsymbol{\mu}^{\text{D}}=\bar{\boldsymbol{\mu}}(\boldsymbol{\rho}^{\text{P}},\phi^{\text{P}}) \quad \text{on } \Gamma_{\text{cDFT}} \end{cases} \text{and} \quad \begin{cases} \boldsymbol{\rho}^{\text{P}}=\boldsymbol{\rho}^{\text{D}} \quad \text{on } \Gamma_{\text{PNP}}\\ \phi^{\text{P}}=\phi^{\text{D}} \quad \text{on } \Gamma_{\text{PNP}} \end{cases}, \tag{4}$$

where

$$\bar{\mu}_\alpha(\rho_\alpha^{\text{P}},\phi^{\text{P}}):=\ln\left(\rho_\alpha^{\text{P}}\right)+z_\alpha\phi^{\text{P}}+V(\mathbf{x})+\frac{\delta F_{\text{ex}}}{\delta\rho_\alpha}(\rho_\alpha^{\text{P}}) \tag{5}$$

Solution Method: Extending the Schwarz alternating method to the hybrid model

Here we use the interface conditions (4) to define the proper data exchange between the two different models in (3). This yields the following generalized Schwarz alternating procedure for the solution of the coupled hybrid problem (3)–(5):

Begin with initial guesses $\boldsymbol{\rho}_0^{\text{D}}$ and ϕ_0^{D} on Γ_{PNP}.
Set $k=k+1$ and solve:

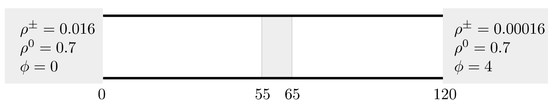
$$\text{(PNP)} \quad \begin{cases} \mathcal{L}^{\text{PNP}}(\boldsymbol{\rho}_k^{\text{P}},\phi_k^{\text{P}})=0 \quad \text{in } \Omega_{\text{PNP}}\\ \boldsymbol{\rho}_k^{\text{P}}=\boldsymbol{\rho}_{k-1}^{\text{D}} \quad \text{on } \Gamma_{\text{PNP}}\\ \phi_k^{\text{P}}=\phi_{k-1}^{\text{D}} \quad \text{on } \Gamma_{\text{PNP}} \end{cases}$$

$$\text{(cDFT)} \quad \begin{cases} \mathcal{L}^{\text{cDFT}}(\boldsymbol{\rho}_k^{\text{D}},\phi_k^{\text{D}},\boldsymbol{\mu}_k^{\text{D}})=0 \quad \text{in } \Omega_{\text{cDFT}}\\ \boldsymbol{\rho}_k^{\text{D}}=\boldsymbol{\rho}_k^{\text{P}} \quad \text{on } \tilde{\Omega}_{\text{cDFT}}\\ \phi_k^{\text{D}}=\phi_k^{\text{P}} \quad \text{on } \Gamma_{\text{cDFT}}\\ \boldsymbol{\mu}_k^{\text{D}}=\bar{\boldsymbol{\mu}}(\boldsymbol{\rho}_k^{\text{P}},\phi_k^{\text{P}}) \quad \text{on } \Gamma_{\text{cDFT}} \end{cases} \tag{6}$$

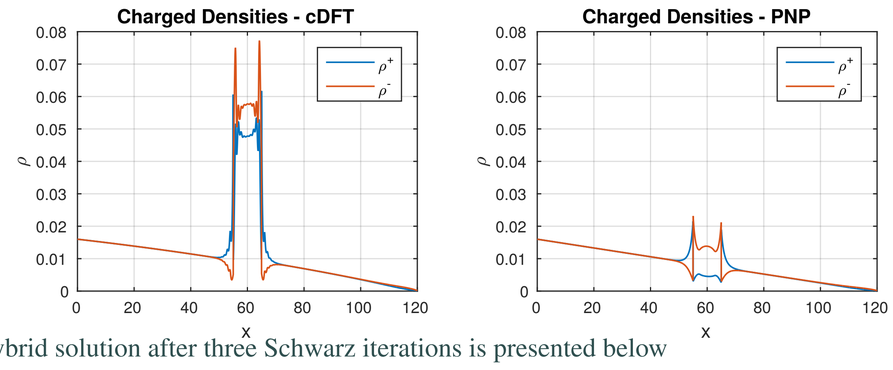
If $\text{diff}(\mathbf{u}_k^{\text{H}},\mathbf{u}_{k+1}^{\text{H}})\geq\delta$ then continue; else: stop.

Application Problem: Flow Through a Porous Membrane

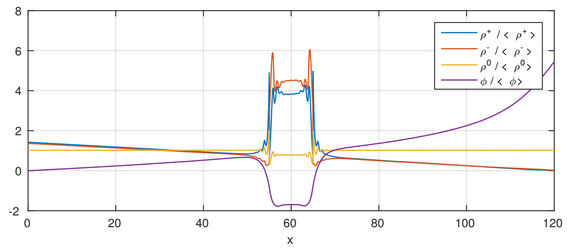
In this example we consider diffusion across a charged, semi-permeable planar membrane with thickness $10d\approx 3$ nm. The description of the problem is given in the following diagram.



As we see below, the PNP solution neglects the oscillations near the membrane predicted by the cDFT model.

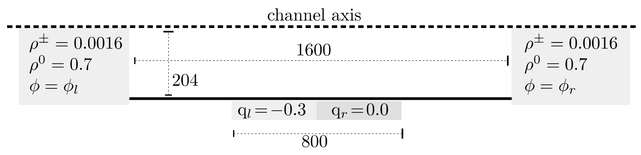


The Hybrid solution after three Schwarz iterations is presented below

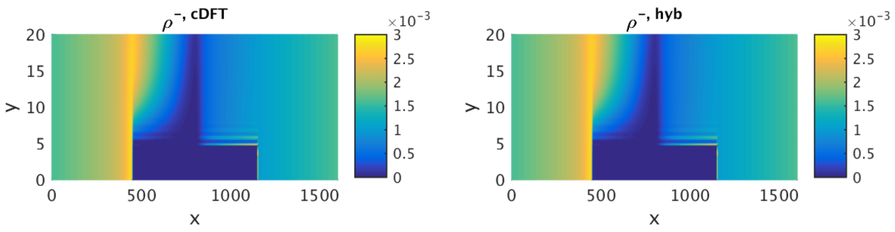


Application Problem: Flow Through a Nanochannel with Inhomogeneously Charged Walls

We consider steady-state ion transport through a nanochannel with inhomogeneously charged channel walls. Consider the nanochannel geometry of this problem below



The channel occupies the middle of the domain, with a reflective boundary at the channel's axis for computational convenience. This allows us to model only half of the device. A comparison between the PNP, cDFT, and Hybrid anion density profile near the charged wall is given below for this application problem



The computational costs are summarized in the following table comparing the normalized wall clock times of the three models.

h	PNP	cDFT	Hybrid	cDFT/Hybrid	Hybrid/PNP
1/2	0.350	1.000	0.556	1.7987	1.589
1/4	3.656	8.238	4.213	1.9557	1.152
1/5	6.811	30.260	8.604	3.5171	1.263

Summary

On this poster, we have presented a multifidelity modeling approach to computing the behavior of ionic flows in the microscale regime. We demonstrated that the hybrid solution preserves the oscillations predicted in the cDFT model. In addition, for large 2D problems, we demonstrate that we can achieve significant computational cost savings by using this approach.

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