Optimal Rate Convergence Analysis of a Second Order Numerical Scheme for the Poisson–Nernst–Planck System

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Abstract. In this work, we propose and analyze a second-order accurate numerical scheme, both in time and space, for the multi-dimensional Poisson-Nernst-Planck system. Linearized stability analysis is developed, so that the second order accuracy is theoretically justified for the numerical scheme, in both temporal and spatial discretization. In particularly, the discrete $W^{1,4}$ estimate for the electric potential field, which plays a crucial role in the proof, are rigorously established. In addition, various numerical tests have confirmed the anticipated numerical accuracy, and further demonstrated the effectiveness and robustness of the numerical scheme in solving problems of practical interest.

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Key words: Poisson-Nernst-Planck system, linearized stability analysis, second order accuracy, convergence analysis.

1. Introduction

The Poisson–Nernst–Planck (PNP) system has been widely used in modeling transmembrane ion channels, semiconductor, and electrochemical devices. The Poisson's equation describes the electrostatic potential stemming from the charge density that consists of mobile ions and fixed charges. The Nernst-Planck equations model the diffusion and migration of ion species in the gradient of electrostatic potential. For symmetric 1 : 1 electrolytes, the ion transport is described by the PNP system

$$n_t = D_n \Delta n - e\beta \nabla \cdot \left(D_n n \nabla \phi \right), \qquad (1.1a)$$

$$p_t = D_p \Delta p + e\beta \nabla \cdot \left(D_p p \nabla \phi \right), \qquad (1.1b)$$

$$-\nabla \cdot \varepsilon_0 \varepsilon_r \nabla \phi = e(p-n) + \rho^f, \qquad (1.1c)$$

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where *p* and *n* are the concentrations of positive and negative charged species, D_p and D_n are their diffusion constants, *e* is the elementary charge, β is the inverse of thermal energy, ϕ is the electrostatic potential, ε_0 is the vacuum permittivity, ε_r is the relative permittivity(or dielectric coefficient), and ρ^f is the density of fixed charge.

Let *L*, *D*₀, and *c*₀ be the characteristic length, diffusion constant, and concentration, respectively. Denote another characteristic length $\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_r}{2\beta e^2 c_0}}$ for an ionic solution with bulk ionic concentration *c*₀ and homogenous dielectric coefficient ε_r . We shall introduce the following dimensionless parameters and variables:

$$\tilde{x} = x/L, \qquad \tilde{t} = tD_0/L\lambda_D, \quad \tilde{p} = p/c_0, \quad \tilde{n} = n/c_0, \qquad (1.2a)$$

$$\tilde{D}_{p} = D_{p}/D_{0}, \ \tilde{D}_{n} = D_{n}/D_{0}, \quad \tilde{\phi} = \beta e \phi, \quad \tilde{\rho}^{f} = \rho^{f}/c_{0}e.$$
 (1.2b)

Rescaling above quantities and dropping all the tildes lead to a nondimensionalized PNP system

$$\begin{cases} \partial_t p = \frac{\lambda_D}{L} D_p \nabla \cdot (\nabla p + p \nabla \phi), \\ \partial_t n = \frac{\lambda_D}{L} D_n \nabla \cdot (\nabla n - n \nabla \phi), \\ -2 \frac{\lambda_D^2}{L^2} \Delta \phi = p - n + \rho^f. \end{cases}$$
(1.3)

For ease of presentation, we choose a computational domain $\Omega = (0, 1)^3$, and consider zero Neumann boundary conditions

$$\frac{\partial \phi}{\partial n} = 0, \quad \frac{\partial p}{\partial n} = \frac{\partial n}{\partial n} = 0 \quad \text{on } \partial \Omega.$$
 (1.4)

For simplicity, we denote by $C_n = \frac{\lambda_D}{L} D_n$, $C_p = \frac{\lambda_D}{L} D_p$, and $\kappa = \frac{L^2}{2\lambda_D^2}$.

Recently, there has been growing interests in incorporating effects that are beyond the mean-field description to the PNP theory, such as the steric effect, ion-ion correlations, and inhomogeneous dielectric environment [12, 13, 16, 19, 22, 23, 27, 31]. Various versions of modified PNP theory have been developed to account for such ignored effects within the framework of the PNP theory. For instance, the steric effect of ions have been taken into account by including excess free energy of solvent entropy [13–15, 22, 33], hard-sphere interaction kernels [12, 27], or the fundamental measure theory [23]. A modified PNP model has been proposed to consider Coulombic ion-ion correlations in inhomogeneous dielectric environment [19].

Due to the nonlinear coupling of the electrostatic potential and ionic concentrations, it is not trivial to solve the PNP system analytically, even numerically. Much effort has been devoted to the development of numerical methods that possess desired properties [1–3, 5, 8–10, 17, 18, 20, 21, 24–27, 29, 32]. For instance, a hybrid numerical scheme that employs adaptive grids has been proposed to solve a two-dimensional PNP system [25]. A delicate temporal discretization scheme has been recently developed to preserve free energy dynamics [8]. Using Slotboom variables, Liu and Wang [17] have developed a free energy

satisfying finite difference scheme for a 1D PNP system. Also, they have constructed a free energy satisfying discontinuous Galerkin method, in which the positivity of numerical solutions is enforced by an accuracy-preserving limiter [18]. A finite element discretization that is able to enforce positivity of numerical solutions has been proposed for the PNP system, as well as the PNP system coupled with the incompressible Navier-Stokes equations [24].

Theoretical analysis of the numerical methods for the PNP system turns out to be very challenging, and the convergence analysis works for the nonlinear system is very limited. Motivated by the variational energy structure of the PNP system, the energy stability analysis has attracted a great deal of attentions [8, 11, 17, 18, 24], in terms of either the logarithmic free energy or a simplified electric energy. Meanwhile, a theoretical justification of the convergence analysis has not been available in these works, due to the difficulty in the nonlinear error estimate. Among the existing theoretical works on the convergence analysis, it is worthy of reviewing the following works. A semi-discrete scheme was analyzed in [30], with the spatial convergence estimate is given. A convergence proof was provided for certain class of fully discrete finite element schemes, while the convergence order has not been justified. A first order (in time) scheme was proposed and analyzed in [10], with a semi-implicit treatment for the nonlinear term, and an optimal rate convergence estimate was provided. The only theoretical analysis for a second order (in time) scheme could be found in [28], in which a fully implicit treatment for the nonlinear term is involved. The second order convergence order in time has been proved in the article, while a theoretical justification of the unique solvability of the numerical scheme is not available, due to the implicit treatment for the nonlinear term.

In this article, we propose and analyze a second order in time, centered difference numerical scheme for the PNP system (1.3). In particular, a modified version of Adams-Moulton interpolation formula is applied to the diffusion term, and the coefficient distribution at the temporal stencil points, t^{n+1} and t^{n-1} , leads to a much improved stability property than the standard Crank-Nicolson approximation, in comparison with the one used in [28]. Also, a fully explicit treatment is taken for the nonlinear convection term, with an application of second order accurate Adams-Bashforth extrapolation formula. Because of its linear nature, the unique solvability of the proposed numerical scheme is automatically assured. In addition, we provide an optimal rate convergence analysis for the numerical scheme. The key difficulty in the nonlinear error estimate has always been associated with a bound of the numerical solution in certain norms. In the PNP system, instead of obtaining the ℓ^{∞} bound of the numerical solution, which has been a standard approach, we only make use of the discrete ℓ^4 bound of the discrete gradient for the numerical solution of electric potential, namely, $\|\nabla \phi\|_4$. In turn, the discrete ℓ^4 estimate of the numerical error function for n and p has to be derived, and such an estimate could be accomplished via the Sobolev interpolation inequality at a discrete level. On the other hand, to obtain the bound for $\|\nabla \phi\|_4$, we apply the linearized stability analysis. In more details, the discrete ℓ^2 convergence estimate up to the previous time step yields a discrete H_h^2 bound of the numerical solution for ϕ , by making use of a discrete elliptic regularity inequality. Moreover, with the help of discrete Sobolev embedding, from H_h^2 to $W_h^{1,4}$, a bound for $\|\nabla\phi\|_4$ could be derived, up to the previous time step. Due to the explicit treatment of the nonlinear convection term, such a bound is sufficient to pass through the convergence estimate at the next time step, so that an induction analysis becomes available. A combination of all these techniques yields the desired convergence result, and such a convergence is unconditional, i.e., no scaling law between the time step size Δt and spatial resolution *h* is needed, since we have avoided using the inverse inequality in the analysis. This is the first such result for the PNP system.

This paper is organized as follows. In Section 2 we present the fully discrete numerical scheme. A preliminary estimate is provided in Section 3, which gives the discrete ℓ^4 and $W_h^{1,4}$ estimate of a grid function. Subsequently, the optimal rate convergence analysis is established in Section 4. Some numerical results are presented in Section 5. Finally, some concluding remarks are made in Section 6.

2. The numerical scheme

The variables *n*, *p*, ϕ are cell-centered evaluated at $(i \pm 1/2, j \pm 1/2, k \pm 1/2)$. For simplicity of presentation, we assume $N_x = N_y = N_z = N$ and $\Delta x = \Delta y = \Delta z = h$, with $h = \frac{1}{N}$. The following notations of centered differences using different stencils at different grid points are introduced to facilitate the description:

$$D_x g(x) = \frac{g(x+h/2) - g(x-h/2)}{h},$$

$$D_x^2 g(x) = \frac{g(x-h) - 2g(x) + g(x+h)}{h^2}$$

The corresponding operators in the y and z directions can be defined in a similar way; the details are skipped for breviy.

In the dynamic equation (1.1a) for *n*, the nonlinear term $\nabla \cdot (n \nabla \phi)$ can be approximated by centered difference as

$$\mathcal{N}_{h}(\nabla\phi, n) = \nabla_{h} \cdot (n\nabla_{h}\phi) = D_{x}(nD_{x}\phi) + D_{y}(nD_{y}\phi) + D_{z}(nD_{z}\phi)$$

at $\left(i \pm \frac{1}{2}, j \pm \frac{1}{2}, k \pm \frac{1}{2}\right).$ (2.1)

Similar centered difference method can be applied to dynamic equation (1.1b) for p; the corresponding approximations to the two nonlinear terms are given below:

$$\mathscr{N}_{h}(\nabla\phi,p) = \nabla_{h} \cdot \left(p\nabla_{h}\phi\right) = D_{x}\left(pD_{x}\phi\right) + D_{y}\left(pD_{y}\phi\right) + D_{z}\left(pD_{z}\phi\right), \qquad (2.2)$$

and both terms are evaluated at the mesh points ($i \pm 1/2$, $j \pm 1/2$, $k \pm 1/2$). The boundary conditions for these physical variables are implemented through finite difference approximation. The boundary extrapolation formulas for *n* and *p* can be derived in the same manner:

$$n_{i+1/2,j+1/2,-1/2} = n_{i+1/2,j+1/2,1/2}, \quad p_{i+1/2,j+1/2,-1/2} = p_{i+1/2,j+1/2,1/2}.$$
(2.3)

The other four boundary sections can be dealt with in the same way; the details are skipped for brevity.

The following second order (in time) numerical scheme is proposed:

$$\frac{n^{k+1} - n^{k}}{\Delta t} = C_{n} \Delta_{h} \left(\frac{3}{4} n^{k+1} + \frac{1}{4} n^{k-1} \right) - C_{n} \left[\frac{3}{2} \mathcal{N}_{h} (\nabla \phi^{k}, n^{k}) - \frac{1}{2} \mathcal{N}_{h} (\nabla \phi^{k-1}, n^{k-1}) \right], \quad (2.4a)$$

$$\frac{p^{k+1} - p^k}{\Delta t}$$

$$= C_p \Delta_h \left(\frac{3}{4} p^{k+1} + \frac{1}{4} p^{k-1}\right) + C_p \left[\frac{3}{2} \mathcal{N}_h (\nabla \phi^k, p^k) - \frac{1}{2} \mathcal{N}_h (\nabla \phi^{k-1}, p^{k-1})\right], \quad (2.4b)$$

$$-\Delta_h \phi^{k+1} = \kappa \left(p^{k+1} - n^{k+1} + \rho^f \right),$$
(2.4c)

$$n_{i\pm1/2,j\pm1/2,-1/2}^{k+1} = n_{i\pm1/2,j\pm1/2,1/2}^{k+1}, \quad p_{i\pm1/2,j\pm1/2,-1/2}^{k+1} = p_{i\pm1/2,j\pm1/2,1/2}^{k+1}, \quad (2.4d)$$

$$\phi_{i\pm1/2,j\pm1/2,-1/2}^{k+1} = \phi_{i\pm1/2,j\pm1/2,1/2}^{k+1}.$$
(2.4e)

Notice that the solution to the Poisson's equation with homogeneous Neumann boundary conditions is not unique, up to an additive constant. In numerical simulations, we set the electrostatic potential at one corner to be zero to single out the solution. Such a treatment does not affect the numerical simulation and analysis.

Remark 2.1. The proposed scheme is a three-step method that requires two levels of initial data. To prepare the first two levels of initial data, we use a backward Euler discretization of the Nernst–Planck equations to compute for one time step.

Remark 2.2. In the multi-step scheme, we choose specific combinations of the coefficients. A modified version of Adams-Moulton interpolation formula is applied to the diffusion term, with extra weight on the implicit time level. Such a treatment leads to a much improved stability property than the standard Crank-Nicolson approximation.

2.1. Discrete inner product and norm

For any pair of variables ϕ^a , ϕ^b which are defined at the mesh points (i + 1/2, j + 1/2, k + 1/2), (such as *n*, *p*, ϕ , etc.), the discrete *L*²-inner product is given by

$$\langle \phi^a, \phi^b \rangle = \sum_{k=0}^{N-1} \sum_{j=0}^{N-1} \sum_{i=0}^{N-1} \phi^a_{i+1/2, j+1/2, k+1/2} \phi^b_{i+1/2, j+1/2, k+1/2} h^3.$$
(2.5)

Clearly all the discrete L^2 inner products defined above are second order accurate. The corresponding discrete L^2 norms can be defined accordingly, and we denote them by $\|\cdot\|_2$.

In addition to the standard $\|\cdot\|_2$ norm, we introduce a discrete $\|\cdot\|_p$ norm for any $p \ge 1$. For example, for the phase variable ϕ , which is evaluated at the mesh points (i + 1/2, j + 1/2, k + 1/2), its discrete $\|\cdot\|_p$ norm is given by

$$\left\|\phi\right\|_{p} = \left(h^{3} \sum_{k=0}^{N-1} \sum_{j=0}^{N-1} \sum_{i=0}^{N-1} |\phi_{i+1/2,j+1/2,k+1/2}|^{p}\right)^{\frac{1}{p}}.$$
(2.6)

For its discrete gradient, the following definitions are introduced:

$$\begin{aligned} \left\| \nabla_{h} \phi \right\|_{p} &= \left(\left\| D_{x} \phi \right\|_{p}^{p} + \left\| D_{y} \phi \right\|_{p}^{p} + \left\| D_{z} \phi \right\|_{p}^{p} \right)^{\frac{1}{p}} \end{aligned}$$
(2.7a)
with
$$\begin{aligned} \left\| D_{x} \phi \right\|_{p}^{p} &= h^{3} \sum_{k=0}^{N-1} \sum_{j=0}^{N-1} \sum_{i=1}^{N-1} \left| (D_{x} \phi)_{i,j+1/2,k+1/2} \right|^{p}, \\ \left\| D_{y} \phi \right\|_{p}^{p} &= h^{3} \sum_{k=0}^{N-1} \sum_{j=1}^{N-1} \sum_{i=0}^{N-1} \left| (D_{y} \phi)_{i+1/2,j,k+1/2} \right|^{p}, \\ \left\| D_{z} \phi \right\|_{p}^{p} &= h^{3} \sum_{k=1}^{N-1} \sum_{j=0}^{N-1} \sum_{i=0}^{N-1} \left| (D_{z} \phi)_{i+1/2,j+1/2,k} \right|^{p}. \end{aligned}$$
(2.7a)

The corresponding $\|\cdot\|_p$ ($p \ge 1$) norms for the other physical variables can be defined in a similar manner.

3. Preliminary estimate

Consider a discrete grid function f, evaluated at the mesh points (i + 1/2, j + 1/2, k + 1/2). If f satisfies the discrete Neumann condition, as given by (2.3), it has a corresponding discrete Fourier Cosine transformation in quarter wave sequence:

$$f_{i+1/2,j+1/2,k+1/2} = \sum_{l,m,n=0}^{N-1} \alpha_{l,m,n} \hat{f}_{l,m,n}^{N} \cos \frac{l\pi x_{i+1/2}}{\hat{L}} \cos \frac{m\pi y_{j+1/2}}{\hat{L}} \cos \frac{n\pi z_{k+1/2}}{\hat{L}}$$

with $\alpha_{l,m,n} = \begin{cases} 1, & \text{if } l \neq 0, m \neq 0, n \neq 0, \\ \sqrt{\frac{1}{2}}, & \text{if one among } l, m, n \text{ is } 0, \\ \sqrt{\frac{1}{4}}, & \text{if two among } l, m, n \text{ are } 0, \\ \sqrt{\frac{1}{8}}, & \text{if } l = m = n = 0, \end{cases}$

where $x_{i+1/2} = (i + \frac{1}{2})h$, $y_{j+1/2} = (j + \frac{1}{2})h$, $z_{k+1/2} = (k + \frac{1}{2})h$. Then we make its extension to a continuous function:

$$f_N(x, y, z) = \sum_{l,m,n=0}^{N-1} \alpha_{l,m,n} \hat{f}_{l,m,n}^N \cos \frac{l\pi x}{\hat{L}} \cos \frac{m\pi y}{\hat{L}} \cos \frac{n\pi z}{\hat{L}},$$
(3.1)

where

$$\hat{f}_{l,m,n}^{N} = \frac{8}{\hat{L}^3} \int_0^{\hat{L}} \int_0^{\hat{L}} \int_0^{\hat{L}} \alpha_{l,m,n} f_N(x,y,z) \cos \frac{l\pi x}{\hat{L}} \cos \frac{m\pi y}{\hat{L}} \cos \frac{n\pi z}{\hat{L}} dx dy dz$$

The following result gives a bound of the discrete ℓ^4 norm of the grid function in terms of the continuous L^4 norm of its continuous version; also see the related analyses in [4,6,7], in which the periodic boundary conditions are considered.

Lemma 3.1. We have

$$\left\|f\right\|_{4} \leq \sqrt{2}^{d} \left\|f_{N}\right\|_{L^{4}}, \quad \left\|\nabla_{h}f\right\|_{4} \leq \sqrt{2}^{d} \left\|\nabla f_{N}\right\|_{L^{4}} \quad \text{with } d \text{ the dimension.}$$
(3.2)

Proof. For simplicity of presentation, we focus our analysis in the 2-D case; for the 3-D grid function, the analysis could be carried out in a similar, yet more tedious way.

We denote the following grid function

$$g_{i+1/2,j+1/2} = \left(f_{i+1/2,j+1/2}\right)^2.$$
 (3.3)

A direct calculation shows that

$$||f||_4 = (||g||_2)^{\frac{1}{2}}.$$
 (3.4)

Note that both norms are discrete in the above identity. Moreover, we assume the grid function g has a discrete Fourier expansion as

$$g_{i+1/2,j+1/2} = \sum_{l,m=0}^{N-1} \alpha_{l,m} (\hat{g}_c^N)_{l,m} \cos \frac{l\pi x_{i+1/2}}{\hat{L}} \cos \frac{m\pi y_{j+1/2}}{\hat{L}}, \qquad (3.5)$$

and denote its continuous version as

$$G(x, y) = \sum_{l,m=0}^{N-1} \alpha_{l,m} (\hat{g}_c^N)_{l,m} \cos \frac{l\pi x}{\hat{L}} \cos \frac{m\pi y}{\hat{L}}.$$
 (3.6)

With an application of the Parseval equality at both the discrete and continuous levels, we have

$$\left\|g\right\|_{2}^{2} = \left\|G\right\|_{L^{2}}^{2} = \frac{1}{4}\hat{L}^{2}\sum_{l,m=0}^{N-1} \left|\left(\hat{g}_{c}^{N}\right)_{l,m}\right|^{2}.$$
(3.7)

On the other hand, we also denote

$$H(x,y) = (f_N(x,y))^2 = \sum_{l,m=0}^{2N-2} \alpha_{l,m} (\hat{h}^N)_{l,m} \cos \frac{l\pi x}{\hat{L}} \cos \frac{m\pi y}{\hat{L}} \in \mathcal{P}_{2N-2},$$
(3.8)

where \mathscr{P}_{2N-2} is the space of trigonometric polynomials in *x* and *y* of degree up to 2N - 2. The reason for $H \in \mathscr{P}_{2N-2}$ is because $f_N \in \mathscr{P}_{N-1}$. We note that $H \neq G$, since $H \in \mathscr{P}_{2N-2}$, while $G \in \mathcal{P}_{N-1}$, although H and G have the same interpolation values on at the numerical grid points $(x_{i+1/2}, y_{j+1/2})$. In other words, g is the interpolation of H onto the numerical grid point and G is the continuous version of g in \mathcal{P}_{N-1} . As a result, collocation coefficients \hat{g}_c^N for G are not equal to \hat{h}^N for H, due to the aliasing error. In more detail, for $0 \le l, m \le N-1$, we have the following representations:

$$(\hat{g}_{c}^{N})_{l,m} = \begin{cases} (\hat{h}^{N})_{l,m} - (\hat{h}^{N})_{l+N,m} - (\hat{h}^{N})_{l,m+N} + (\hat{h}^{N})_{l+N,m+N}, & 1 \leq l \leq N-2, 1 \leq m \leq N-2, \\ (\hat{h}^{N})_{l,m} - (\hat{h}^{N})_{l+N,m} - \sqrt{2}(\hat{h}^{N})_{l,m+N} + \sqrt{2}(\hat{h}^{N})_{l+N,m+N}, & 1 \leq l \leq N-2, m = 0, \\ (\hat{h}^{N})_{l,m} - (\hat{h}^{N})_{l+N,m}, & 1 \leq l \leq N-2, m = N-1, \\ (\hat{h}^{N})_{l,m} - \sqrt{2}(\hat{h}^{N})_{l+N,m} - (\hat{h}^{N})_{l,m+N} + \sqrt{2}(\hat{h}^{N})_{l+N,m+N}, & l = 0, 1 \leq m \leq N-2, \\ (\hat{h}^{N})_{l,m} - \sqrt{2}(\hat{h}^{N})_{l+N,m} - \sqrt{2}(\hat{h}^{N})_{l,m+N} + 2(\hat{h}^{N})_{l+N,m+N}, & l = 0, m = 0, \\ (\hat{h}^{N})_{l,m} - \sqrt{2}(\hat{h}^{N})_{l+N,m}, & l = 0, m = N-1, \\ (\hat{h}^{N})_{l,m} - \sqrt{2}(\hat{h}^{N})_{l+N,m}, & l = N-1, 1 \leq m \leq N-2, \\ (\hat{h}^{N})_{l,m} - \sqrt{2}(\hat{h}^{N})_{l,m+N}, & l = N-1, m = 0, \\ (\hat{h}^{N})_{l,m}, & l = N-1, m = N-1. \end{cases}$$

With an application of Cauchy inequality, it is clear that

$$\sum_{l,m=0}^{N-1} \left| (\hat{g}_c^N)_{l,m} \right|^2 \le 4 \sum_{l,m=0}^{2N-2} \left| (\hat{h}^N)_{l,m} \right|^2.$$
(3.9)

Meanwhile, an application of Parseval's identity to the Fourier expansion (3.8) gives

$$||H||^{2} = \frac{1}{4} \hat{L}^{2} \sum_{l,m=0}^{2N-2} \left| (\hat{h}^{N})_{l,m} \right|^{2}.$$
(3.10)

Its comparison with (3.7) indicates that

$$\|g\|_{2}^{2} = \|G\|^{2} \le 4 \|H\|^{2}$$
, i.e. $\|g\|_{2} \le 2 \|H\|$ (3.11)

with the estimate (3.9) applied. Meanwhile, since $H(x, y) = (f_N(x, y))^2$, we have

$$\left\| f_N \right\|_{L^4} = \left(\|H\|_2 \right)^{\frac{1}{2}}.$$
 (3.12)

Therefore, a combination of (3.4), (3.9) and (3.12) results in

$$\|f\|_{4} = \left(\|g\|_{2}\right)^{\frac{1}{2}} \le \left(2\|H\|_{L^{2}}\right)^{\frac{1}{2}} \le \sqrt{2}\|f_{N}\|_{L^{4}}.$$
(3.13)

This finishes the proof of (3.2) for d = 2.

The 3-D case could be analyzed in the same fashion, and the details are skipped for the sake of brevity. The second inequality of (3.2) could be proved in a similar way. This finishes the proof of Lemma 3.1. $\hfill \Box$

The next proposition, which corresponds to a discrete version of Sobolev inequality, is crucial in the nonlinear stability and convergence analysis.

Proposition 3.1. The following estimate is valid:

$$\|f\|_{4} \leq \check{C}_{1} \|f\|_{2} + \check{C}_{2} \|f\|_{2}^{\frac{1}{4}} \cdot \|\nabla_{h}f\|_{2}^{\frac{3}{4}}, \qquad (3.14a)$$

$$\left\|\nabla_{h}f\right\|_{4} \leq \check{C}_{3} \left\|\Delta_{h}f\right\|_{2},\tag{3.14b}$$

where $\check{C}_1,\,\check{C}_2$ and \check{C}_3 are constants independent on h.

Proof. Parseval's identity (at both the discrete and continuous levels) implies that

$$\sum_{i,j,k=0}^{N-1} |f_{i+1/2,j+1/2,k+1/2}|^2 = \frac{1}{8} N^3 \sum_{l,m,n=0}^{N-1} |\hat{f}_{l,m,n}^N|^2,$$
(3.15a)

$$\left\|f_{N}\right\|_{L^{2}}^{2} = \frac{1}{8}\hat{L}^{3}\sum_{l,m,n=0}^{N-1}|\hat{f}_{l,m,n}^{N}|^{2}.$$
(3.15b)

This in turn results in (based on the fact that $hN = \hat{L}$)

$$\left\|f\right\|_{2}^{2} = h^{3} \sum_{i,j,k=0}^{N-1} |f_{i+1/2,j+1/2,k+1/2}|^{2} = \frac{1}{8} \hat{L}^{3} \sum_{l,m,n=0}^{N-1} |\hat{f}_{l,m,n}^{N}|^{2} = \left\|f_{N}\right\|_{L^{2}}^{2}.$$
 (3.16)

For the comparison between the discrete and continuous gradient, we start with the following Fourier expansions:

$$(D_{x}f)_{i,j+1/2,k+1/2} = \frac{f_{i+1/2,j+1/2,k+1/2} - f_{i-1/2,j+1/2,k+1/2}}{h}$$
$$= \sum_{l,m,n=0}^{N-1} \alpha_{l,m,n} \mu_{l} \hat{f}_{l,m,n}^{N} \sin \frac{l\pi x_{i}}{\hat{L}} \cos \frac{m\pi y_{j+1/2}}{\hat{L}} \cos \frac{n\pi z_{k+1/2}}{\hat{L}}, \quad (3.17a)$$

$$(\partial_x f_N)_{i,j+1/2,k+1/2} = \sum_{l,m,n=0}^{N-1} \alpha_{l,m,n} v_l \hat{f}_{l,m,n}^N \sin \frac{l\pi x_i}{\hat{L}} \cos \frac{m\pi y_{j+1/2}}{\hat{L}} \cos \frac{n\pi z_{k+1/2}}{\hat{L}}$$
(3.17b)

with

$$\mu_l = -\frac{2\sin\frac{l\pi h}{2\hat{L}}}{h}, \quad v_l = -\frac{l\pi}{\hat{L}}.$$
 (3.18)

In turn, an application of Parseval's identity yields

$$\left\| D_x f \right\|_2^2 = \frac{1}{8} \hat{L}^3 \sum_{l,m,n=0}^{N-1} |\mu_l|^2 |\hat{f}_{l,m,n}^N|^2,$$
(3.19a)

$$\left\|\partial_{x}f_{N}\right\|_{L^{2}}^{2} = \frac{1}{8}\hat{L}^{3}\sum_{l,m,n=0}^{N-1}|v_{l}|^{2}|\hat{f}_{l,m,n}^{N}|^{2}.$$
(3.19b)

The comparison of Fourier eigenvalues between $|\mu_l|$ and $|v_l|$ shows that

$$\frac{2}{\pi} |v_l| \le |\mu_l| \le |v_l| \quad \text{for} \quad 0 \le l \le N - 1.$$
(3.20)

This indicates that

$$\frac{2}{\pi} \left\| \partial_x f_N \right\|_{L^2} \le \left\| D_x f \right\|_2 \le \left\| \partial_x f_N \right\|_{L^2}.$$
(3.21)

Similar comparison estimates can be derived in the same manner to reveal

$$\frac{2}{\pi} \|\nabla f_N\|_{L^2} \le \|\nabla_h f\|_2 \le \|\nabla f_N\|_{L^2}.$$
(3.22)

It can be proved analogously that

$$\frac{4}{\pi^2} \|\Delta f_N\|_{L^2} \le \|\Delta_h f\|_2 \le \|\Delta f_N\|_{L^2}.$$
(3.23)

On the other hand, we make use of (3.2) in Lemma 3.1. For the continuous function $f_N(x, y, z)$, we have the following estimate in Sobolev embedding:

$$\|f_N\|_{L^4} \le C \|f_N\|_{H^{3/4}} \le C \|f_N\|^{\frac{1}{4}} \cdot \|f_N\|_{H^1}^{\frac{3}{4}} \le C \|f_N\|^{\frac{1}{4}} \cdot (\|f_N\| + \|\nabla f_N\|)^{\frac{3}{4}}$$

$$\le C_1 \|f_N\| + C_2 \|f_N\|^{\frac{1}{4}} \cdot \|\nabla f_N\|^{\frac{3}{4}},$$
(3.24a)

$$\left\|\nabla f_N\right\|_{L^4} \le C_3 \left\|\Delta f_N\right\|_{L^2}.\tag{3.24b}$$

Finally, a combination of the equivalence estimates (3.16), (3.22), (3.23), (3.2) in Lemma 3.1 and the Sobolev inequalities (3.24a), (3.24b) result in the desired inequalities (3.14a), (3.14b). The proof of Proposition 3.1 is finished.

4. Convergence analysis

The following is the main theorem of this paper.

Theorem 4.1. Let n_e , p_e , ϕ_e be the exact solution of the PNP (1.3) with the boundary conditions (1.4) and let $(n_{\Delta t,h}, p_{\Delta t,h}, \phi_{\Delta t,h})$ be the numerical solution of (2.4a)-(2.4e). Then the following convergence result holds as Δt and h go to zero:

$$\|n_e - n_{\Delta t,h}\|_{\ell^{\infty}(0,T;\ell^2)} + \|p_e - p_{\Delta t,h}\|_{\ell^{\infty}(0,T;\ell^2)} + \|\phi_e - \phi_{\Delta t,h}\|_{\ell^{\infty}(0,T;H_h^2)}$$

$$\leq C(\Delta t^2 + h^2),$$
 (4.1)

where the constant C depends only on the regularity of the exact solution and the fixed charge function ρ^{f} .

4.1. Consistency analysis

Our goal is to construct approximate profiles **n**, *P*, Φ and and show that they satisfy the numerical scheme (2.4a)-(2.4e) up to an $\mathcal{O}(\Delta t^2 + h^2)$ error.

We denote

$$\mathbf{n}_{i+1/2,j+1/2,k+1/2} = (n_e)(x_{i+1/2}, y_{j+1/2}, z_{k+1/2}),$$
(4.2a)

$$P_{i+1/2,j+1/2,k+1/2} = (p_e)(x_{i+1/2}, y_{j+1/2}, z_{k+1/2})$$
(4.2b)

for $0 \le i, j, k \le N - 1$ (at interior grid points). In addition, an even symmetric "ghost" point extrapolation is taken for **n** and *P*:

$$\mathbf{n}_{i+1/2,j+1/2,-1/2} = \mathbf{n}_{i+1/2,j+1/2,1/2}, \quad P_{i+1/2,j+1/2,-1/2} = P_{i+1/2,j+1/2,1/2}$$
(4.3)

following the discrete boundary condition (2.3). Similar even symmetric extrapolation formulas can be derived at four other boundary sections.

To facilitate the convergence analysis in later sections, we construct the approximate profile Φ through the following discrete Poisson's equation

$$-\Delta_h \Phi = \kappa (P - \mathbf{n} + \rho^f) \quad \text{with} \quad \Phi_{i \pm 1/2, j \pm 1/2, -1/2} = \Phi_{i \pm 1/2, j \pm 1/2, 1/2}.$$
(4.4)

Moreover, a careful analysis indicates the following consistency between Φ and ϕ_e :

$$\left\| \Phi - \phi_e \right\|_{W_h^{2,\infty}} \le Ch^2 \tag{4.5}$$

provided that ϕ_e is smooth enough. Note that $\|\cdot\|_{W_h^{2,\infty}}$ denotes the discrete $W^{2,\infty}$ norm, in which the point-wise maximum norm of the given discrete function is measured, up to its second order finite differences.

By combining all the consistency analyses above, it is straightforward to verify the following local truncation estimates:

$$\frac{\mathbf{n}^{k+1} - \mathbf{n}^{k}}{\Delta t} = C_{n} \Delta_{h} \left(\frac{3}{4} \mathbf{n}^{k+1} + \frac{1}{4} \mathbf{n}^{k-1} \right) - C_{n} \left(\frac{3}{2} \mathscr{N}_{h} (\nabla \Phi^{k}, \mathbf{n}^{k}) - \frac{1}{2} \mathscr{N}_{h} \left(\nabla \Phi^{k-1}, \mathbf{n}^{k-1} \right) \right) + \tau_{n}^{k+\frac{1}{2}}, \quad (4.6a)$$

$$\frac{P^{k+1} - P^{k}}{\Delta t} = C_{p} \Delta_{h} \left(\frac{3}{4} P^{k+1} + \frac{1}{4} P^{k-1} \right) + C_{p} \left(\frac{3}{2} \mathcal{N}_{h} (\nabla \Phi^{k}, P^{k}) - \frac{1}{2} \mathcal{N}_{h} \left(\nabla \Phi^{k-1}, P^{k-1} \right) \right) + \tau_{p}^{k+\frac{1}{2}}, \quad (4.6b)$$

$$-\Delta_h \Phi^{k+1} = \kappa \left(P^{k+1} - \mathbf{n}^{k+1} + \rho^f \right), \tag{4.6c}$$

$$\mathbf{n}_{i\pm1/2,j\pm1/2,-1/2}^{k+1} = \mathbf{n}_{i\pm1/2,j\pm1/2,1/2}^{k+1}, \quad P_{i\pm1/2,j\pm1/2,-1/2}^{k+1} = P_{i\pm1/2,j\pm1/2,1/2}^{k+1}, \quad (4.6d)$$

$$\Phi_{i\pm 1/2,j\pm 1/2,-1/2}^{k+1} = \Phi_{i\pm 1/2,j\pm 1/2,1/2}^{k+1}, \tag{4.6e}$$

where

$$\begin{split} \tau_{i,j,k}^{\mathbf{n},k+\frac{1}{2}} &= \Delta t^2 U_{i,j,k}^{\mathbf{n},k+\frac{1}{2}} + h^2 V_{i,j,k}^{\mathbf{n},k+\frac{1}{2}}, \\ \tau_{i,j,k}^{P,k+\frac{1}{2}} &= \Delta t^2 U_{i,j,k}^{P,k+\frac{1}{2}} + h^2 V_{i,j,k}^{P,k+\frac{1}{2}} \end{split}$$

with $U_{i,j,k}^{\mathbf{n},k+\frac{1}{2}}$, $U_{i,j,k}^{P,k+\frac{1}{2}}$, $V_{i,j,k}^{\mathbf{n},k+\frac{1}{2}}$, and $V_{i,j,k}^{P,k+\frac{1}{2}}$ associated with certain high order derivatives of exact solution **n** and P. Thus, we can get

$$\left\|\tau_{n}^{k+\frac{1}{2}}\right\|_{2} \leq C(\Delta t^{2}+h^{2}), \qquad \left\|\tau_{p}^{k+\frac{1}{2}}\right\|_{2} \leq C(\Delta t^{2}+h^{2}).$$
 (4.7)

We also note a discrete $W^{2,\infty}$ bound for the constructed approximate solution

$$\left\|\mathbf{n}^{k}\right\|_{W_{h}^{1,\infty}}+\left\|P^{k}\right\|_{W_{h}^{1,\infty}}+\left\|\Phi^{k}\right\|_{W_{h}^{2,\infty}}\leq C_{0}^{*}$$
(4.8)

at any time step t^k , which comes from the regularity of the constructed solution. This bound will be used in the stability and convergence analysis for the numerical error functions.

4.2. Stability and convergence analysis

The following error functions are denoted:

$$\tilde{n} = \mathbf{n} - n, \qquad \tilde{p} = P - p, \qquad \tilde{\phi} = \Phi - \phi$$
(4.9)

at the corresponding mesh points. Subtracting (2.4a)-(2.4e) from (4.6a) yields the following system for the error functions:

$$\frac{\tilde{n}^{k+1} - \tilde{n}^{k}}{\Delta t} = C_{n} \Delta_{h} \left(\frac{3}{4} \tilde{n}^{k+1} + \frac{1}{4} \tilde{n}^{k-1} \right) - C_{n} \left(\frac{3}{2} \mathcal{N}_{h} (\nabla \tilde{\phi}^{k}, \mathbf{n}^{k}) + \frac{3}{2} \mathcal{N}_{h} (\nabla \phi^{k}, \tilde{n}^{k}) - \frac{1}{2} \mathcal{N}_{h} (\nabla \tilde{\phi}^{k-1}, \mathbf{n}^{k-1}) - \frac{1}{2} \mathcal{N}_{h} (\nabla \phi^{k-1}, \tilde{n}^{k-1}) \right) + \tau_{n}^{k+\frac{1}{2}}, \quad (4.10a)$$
$$\frac{\tilde{p}^{k+1} - \tilde{p}^{k}}{\tilde{p}^{k}} = C_{n} \Delta_{h} \left(\frac{3}{2} \tilde{p}^{k+1} + \frac{1}{2} \tilde{p}^{k-1} \right) + C_{n} \left(\frac{3}{2} \mathcal{N}_{h} (\nabla \tilde{\phi}^{k}, P^{k}) + \frac{3}{2} \mathcal{N}_{h} (\nabla \phi^{k}, \tilde{p}^{k}) \right)$$

$$\frac{P}{\Delta t} = C_p \Delta_h \left(\frac{3}{4} \tilde{p}^{k+1} + \frac{1}{4} \tilde{p}^{k-1} \right) + C_p \left(\frac{3}{2} \mathscr{N}_h (\nabla \tilde{\phi}^k, P^k) + \frac{3}{2} \mathscr{N}_h (\nabla \phi^k, \tilde{p}^k) - \frac{1}{2} \mathscr{N}_h (\nabla \tilde{\phi}^{k-1}, P^{k-1}) - \frac{1}{2} \mathscr{N}_h (\nabla \phi^{k-1}, \tilde{p}^{k-1}) \right) + \tau_p^{k+\frac{1}{2}}, \quad (4.10b)$$

$$-\Delta_{h}\tilde{\phi}^{k+1} = \kappa (\tilde{p}^{k+1} - \tilde{n}^{k+1}), \qquad (4.10c)$$

$$\tilde{n}_{i\pm1/2,j\pm1/2,-1/2}^{k+1} = \tilde{n}_{i\pm1/2,j\pm1/2,1/2}^{k+1}, \quad \tilde{p}_{i\pm1/2,j\pm1/2,-1/2}^{k+1} = \tilde{p}_{i\pm1/2,j\pm1/2,1/2}^{k+1}, \quad (4.10d)$$

$$\hat{\phi}_{i\pm 1/2, j\pm 1/2, -1/2}^{k+1} = \hat{\phi}_{i\pm 1/2, j\pm 1/2, 1/2}^{k+1}.$$
(4.10e)

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First, we assume a-priori that the numerical error function (for *n* and *p*) has an ℓ^2 bound at time step t^j , j = k, k - 1:

$$\|\tilde{n}^{j}\|_{2} + \|\tilde{p}^{j}\|_{2} \le 1$$
 for $j = k, k - 1.$ (4.11)

In turn, by the discrete Poisson's equation (4.10c), we get

$$\left\|\Delta_{h}\tilde{\phi}^{j}\right\|_{2} = \left\|\kappa(\tilde{p}^{j} - \tilde{n}^{j})\right\|_{2} \le \kappa \left\|\tilde{p}^{j} - \tilde{n}^{j}\right\|_{2} \le C_{1}^{*} \quad \text{for } j = k, k - 1,$$
(4.12)

where C_1^* is constant depending on κ . Meanwhile, it is observed that $\tilde{\phi}^j$ satisfies a homogeneous Neumann boundary condition. As an application of (3.14b) in Proposition 3.1, we obtain

$$\left\| \nabla_{h} \tilde{\phi}^{j} \right\|_{4} \leq \check{C}_{3} \left\| \Delta_{h} \tilde{\phi}^{j} \right\|_{2} \leq C_{1}^{*} \check{C}_{3} := C_{2}^{*} \quad \text{for } j = k, k - 1.$$
 (4.13)

Therefore, the following discrete $W^{1,4}$ bound for the numerical solution ϕ^{j} is derived:

$$\left\|\nabla_{h}\phi^{j}\right\|_{4} \leq \left\|\nabla_{h}\Phi^{j}\right\|_{4} + \left\|\nabla_{h}\tilde{\phi}^{j}\right\|_{4} \leq CC_{0}^{*} + C_{2}^{*} := C_{3}^{*} \quad \text{for } j = k, k-1,$$
(4.14)

in which the discrete $W^{1,\infty}$ bound (4.8) for the constructed solution Φ^k was used.

Taking a discrete inner product with (4.10a) by the error function $2\tilde{n}^{k+1}$ gives

$$\begin{split} \|\tilde{n}^{k+1}\|_{2}^{2} &- \|\tilde{n}^{k}\|_{2}^{2} + \|\tilde{n}^{k+1} - \tilde{n}^{k}\|_{2}^{2} + \frac{3}{2}C_{n} \Delta t \|\nabla_{h}\tilde{n}^{k+1}\|_{2}^{2} + \frac{1}{2}C_{n} \Delta t \langle\nabla_{h}\tilde{n}^{k+1}, \nabla_{h}\tilde{n}^{k-1}\rangle_{2} \\ &= 2\Delta t \left\langle \tau_{n}^{k+\frac{1}{2}}, \tilde{n}^{k+1} \right\rangle - 3C_{n} \Delta t \left\langle \mathcal{N}_{h}(\nabla\tilde{\phi}^{k}, \mathbf{n}^{k}), \tilde{n}^{k+1} \right\rangle - 3C_{n} \Delta t \left\langle \mathcal{N}_{h}(\nabla\phi^{k}, \tilde{n}^{k}), \tilde{n}^{k+1} \right\rangle \\ &+ C_{n} \Delta t \left\langle \mathcal{N}_{h}(\nabla\tilde{\phi}^{k-1}, \mathbf{n}^{k-1}), \tilde{n}^{k+1} \right\rangle + C_{n} \Delta t \left\langle \mathcal{N}_{h}(\nabla\phi^{k-1}, \tilde{n}^{k-1}), \tilde{n}^{k+1} \right\rangle. \end{split}$$

Note that the homogeneous Neumann boundary condition for \tilde{n}^{k+1} was used in the summation by parts for the diffusion term. In addition, the Cauchy inequality could be applied to the other diffusion term associated with Adams-Moulton interpolation:

$$-\frac{1}{2} \left\langle \nabla_{h} \tilde{n}^{k+1}, \nabla_{h} \tilde{n}^{k-1} \right\rangle_{2} \leq \frac{1}{4} \left(\|\nabla_{h} \tilde{n}^{k+1}\|_{2}^{2} + \|\nabla_{h} \tilde{n}^{k-1}\|_{2}^{2} \right).$$
(4.15)

The estimate for the local truncation error term is standard:

$$2\left\langle\tau_{n}^{k+\frac{1}{2}},\tilde{n}^{k+1}\right\rangle \leq \left\|\tau_{n}^{k+\frac{1}{2}}\right\|_{2}^{2} + \left\|\tilde{n}^{k+1}\right\|_{2}^{2}.$$
(4.16)

The first nonlinear inner product on the right hand side of (4.15) is a linearized term. With an application of summation by parts, we have

$$-3C_{n}\left\langle\mathcal{N}_{h}(\nabla\tilde{\phi}^{k},\mathbf{n}^{k}),\tilde{n}^{k+1}\right\rangle \leq CC_{n}\left\|\nabla_{h}\tilde{\phi}^{k}\right\|_{2}\cdot\left\|\mathbf{n}^{k}\right\|_{\infty}\cdot\left\|\nabla_{h}\tilde{n}^{k+1}\right\|_{2}$$

$$\leq CC_{n}C_{0}^{*}\left\|\Delta_{h}\tilde{\phi}^{k}\right\|_{2}\cdot\left\|\nabla_{h}\tilde{n}^{k+1}\right\|_{2}\leq CC_{n}C_{0}^{*}\left\|\kappa(\tilde{p}^{k}-\tilde{n}^{k})\right\|_{2}\cdot\left\|\nabla_{h}\tilde{n}^{k+1}\right\|_{2}$$

$$\leq \tilde{C}_{4}\left(\left\|\tilde{p}^{k}\right\|_{2}^{2}+\left\|\tilde{n}^{k}\right\|_{2}^{2}\right)+\frac{1}{16}C_{n}\left\|\nabla_{h}\tilde{n}^{k+1}\right\|_{2}^{2},$$

$$(4.17)$$

where the discrete elliptic regularity, $\|\nabla_h \tilde{\phi}^k\|_2 \leq C \|\Delta_h \tilde{\phi}^k\|_2$, was applied in the second step, the discrete Poisson's equation (4.10c) was recalled in the third step, and $\tilde{C}_4 = C(C_n C_0^*)^2/C_n$. Similar inequality could be derived for the third nonlinear term on the right hand side of (4.15):

$$C_{n}\left\langle \mathscr{N}_{h}(\nabla\tilde{\phi}^{k-1},\mathbf{n}^{k-1}),\tilde{n}^{k+1}\right\rangle \leq \tilde{C}_{4}\left(\left\|\tilde{p}^{k-1}\right\|_{2}^{2}+\left\|\tilde{n}^{k-1}\right\|_{2}^{2}\right)+\frac{1}{16}C_{n}\left\|\nabla_{h}\tilde{n}^{k+1}\right\|_{2}^{2}.$$
(4.18)

For the second nonlinear inner product on the right hand side of (4.15), we start from the following inequality, based on summation by parts and an application of discrete Hölder inequality:

$$-3C_n\left\langle \mathscr{N}_h(\nabla\phi^k, \tilde{n}^k), \tilde{n}^{k+1} \right\rangle \le CC_n \left\| \nabla_h \phi^k \right\|_4 \cdot \left\| \tilde{n}^k \right\|_4 \cdot \left\| \nabla_h \tilde{n}^{k+1} \right\|_2.$$

$$(4.19)$$

To carry out this nonlinear estimate, we recall the discrete $W^{1,4}$ bound (4.14) for the numerical solution ϕ^k , based on the a-priori assumption (4.14). For the second term appearing on the right hand side of (4.19), we recall an application of (3.14a) in Proposition 3.1, due to a homogeneous Neumann boundary condition for \tilde{n}^k and \tilde{p}^k :

$$\left\|\tilde{n}^{k}\right\|_{4} \leq \check{C}_{1}\left\|\tilde{n}^{k}\right\|_{2} + \check{C}_{2}\left\|\tilde{n}^{k}\right\|_{2}^{\frac{1}{4}} \cdot \left\|\nabla_{h}\tilde{n}^{k}\right\|_{2}^{\frac{3}{4}},$$
(4.20a)

$$\left\|\tilde{p}^{k}\right\|_{4} \leq \check{C}_{1}\left\|\tilde{p}^{k}\right\|_{2} + \check{C}_{2}\left\|\tilde{p}^{k}\right\|_{2}^{\frac{1}{4}} \cdot \left\|\nabla_{h}\tilde{p}^{k}\right\|_{2}^{\frac{3}{4}}.$$
(4.20b)

In turn, a substitution into (4.19) shows that

$$-3C_{n}\left\langle\mathscr{N}_{h}(\nabla\phi^{k},\tilde{n}^{k}),\tilde{n}^{k+1}\right\rangle \leq CC_{n}C_{3}^{*}\left\|\nabla_{h}\tilde{n}^{k+1}\right\|_{2}\left(\check{C}_{1}\left\|\tilde{n}^{k}\right\|_{2}+\check{C}_{2}\left\|\tilde{n}^{k}\right\|_{2}^{\frac{1}{4}}\cdot\left\|\nabla_{h}\tilde{n}^{k}\right\|_{2}^{\frac{3}{4}}\right)$$
$$\leq \tilde{C}_{6}\left\|\tilde{n}^{k}\right\|_{2}^{2}+\frac{1}{8}C_{n}\left\|\nabla_{h}\tilde{n}^{k}\right\|_{2}^{2}+\frac{1}{16}C_{n}\left\|\nabla_{h}\tilde{n}^{k+1}\right\|_{2}^{2},\qquad(4.21)$$

in which the Young's inequality was applied in the last step and \tilde{C}_6 depends on C_n , C_3^* , \check{C}_1 and \check{C}_2 .

The fourth nonlinear inner product on the right hand side of (4.15) could be analyzed in the same manner; the technical details are left to interested readers:

$$C_{n} \left\langle \mathscr{N}_{h} (\nabla \phi^{k-1}, \tilde{n}^{k-1}), \tilde{n}^{k+1} \right\rangle$$

$$\leq \tilde{C}_{6} \left\| \tilde{n}^{k-1} \right\|_{2}^{2} + \frac{1}{8} C_{n} \left\| \nabla_{h} \tilde{n}^{k-1} \right\|_{2}^{2} + \frac{1}{16} C_{n} \left\| \nabla_{h} \tilde{n}^{k+1} \right\|_{2}^{2}.$$
(4.22)

Therefore, a combination of (4.15)-(4.18) and (4.21) leads to

$$\begin{aligned} \left\| \tilde{n}^{k+1} \right\|_{2}^{2} &- \left\| \tilde{n}^{k} \right\|_{2}^{2} + C_{n} \Delta t \left\| \nabla_{h} \tilde{n}^{k+1} \right\|_{2}^{2} - \frac{1}{4} C_{n} \Delta t \left\| \nabla_{h} \tilde{n}^{k-1} \right\|_{2}^{2} \\ &\leq \Delta t \left\| \tilde{n}^{k+1} \right\|_{2}^{2} + \tilde{C}_{4} \Delta t \left(\left\| \tilde{p}^{k} \right\|_{2}^{2} + \left\| \tilde{p}^{k-1} \right\|_{2}^{2} \right) + \tilde{C}_{7} \Delta t \left(\left\| \tilde{n}^{k} \right\|_{2}^{2} + \left\| \tilde{n}^{k-1} \right\|_{2}^{2} \right) \\ &+ \frac{1}{8} C_{n} \Delta t \left(\left\| \nabla_{h} \tilde{n}^{k} \right\|_{2}^{2} + \left\| \nabla_{h} \tilde{n}^{k-1} \right\|_{2}^{2} \right) + \Delta t \left\| \tau_{n}^{k+\frac{1}{2}} \right\|_{2}^{2} \end{aligned}$$

$$(4.23)$$

with $\tilde{C}_7 = \tilde{C}_4 + \tilde{C}_6 + 1$.

The discrete energy estimate for the numerical error equation (4.10b) (for p) can be performed in the same way. The following inequality could be derived in the same manner; the details are skipped for brevity:

$$\begin{split} \|\tilde{p}^{k+1}\|_{2}^{2} - \|\tilde{p}^{k}\|_{2}^{2} + C_{p} \Delta t \|\nabla_{h} \tilde{p}^{k+1}\|_{2}^{2} - \frac{1}{4} C_{p} \Delta t \|\nabla_{h} \tilde{p}^{k-1}\|_{2}^{2} \\ \leq \Delta t \|\tilde{p}^{k+1}\|_{2}^{2} + \tilde{C}_{4} \Delta t \left(\|\tilde{n}^{k}\|_{2}^{2} + \|\tilde{n}^{k-1}\|_{2}^{2}\right) + \tilde{C}_{7} \Delta t \left(\|\tilde{p}^{k}\|_{2}^{2} + \|\tilde{p}^{k-1}\|_{2}^{2}\right) \\ + \frac{1}{8} C_{p} \Delta t \left(\|\nabla_{h} \tilde{p}^{k}\|_{2}^{2} + \|\nabla_{h} \tilde{p}^{k-1}\|_{2}^{2}\right) + \Delta t \|\tau_{p}^{k+\frac{1}{2}}\|_{2}^{2}. \end{split}$$

$$(4.24)$$

Finally, a combination of (4.23) and (4.24) leads to

$$\begin{split} \|\tilde{n}^{k+1}\|_{2}^{2} - \|\tilde{n}^{k}\|_{2}^{2} + \|\tilde{p}^{k+1}\|_{2}^{2} - \|\tilde{p}^{k}\|_{2}^{2} + C_{n} \Delta t \|\nabla_{h} \tilde{n}^{k+1}\|_{2}^{2} + C_{p} \Delta t \|\nabla_{h} \tilde{p}^{k+1}\|_{2}^{2} \\ \leq \Delta t \left(\|\tilde{n}^{k+1}\|_{2}^{2} + \|\tilde{p}^{k+1}\|_{2}^{2} \right) + \tilde{C}_{8} \left(\|\tilde{n}^{k}\|_{2}^{2} + \|\tilde{p}^{k}\|_{2}^{2} + \|\tilde{n}^{k-1}\|_{2}^{2} + \|\tilde{p}^{k-1}\|_{2}^{2} \right) \\ + \frac{1}{8} C_{n} \Delta t \|\nabla_{h} \tilde{n}^{k}\|_{2}^{2} + \frac{3}{8} C_{n} \Delta t \|\nabla_{h} \tilde{n}^{k-1}\|_{2}^{2} + \frac{1}{8} C_{p} \Delta t \|\nabla_{h} \tilde{p}^{k}\|_{2}^{2} \\ + \frac{3}{8} C_{p} \Delta t \|\nabla_{h} \tilde{p}^{k-1}\|_{2}^{2} + \Delta t \left(\left\| \tau_{n}^{k+\frac{1}{2}} \right\|_{2}^{2} + \left\| \tau_{p}^{k+\frac{1}{2}} \right\|_{2}^{2} \right) \end{split}$$

$$(4.25)$$

with $\tilde{C}_8 = C(\tilde{C}_4 + \tilde{C}_7)$. Summing over time steps and an application of discrete Gronwall inequality give

$$\left\|\tilde{n}^{k+1}\right\|_{2}^{2} + \left\|\tilde{p}^{k+1}\right\|_{2}^{2} \le \tilde{C}_{9}(\triangle t^{2} + h^{2})^{2} \quad \forall \ 0 \le k \le N_{k},$$
(4.26)

which is equivalent to

$$\left\|\tilde{n}^{k+1}\right\|_{2} + \left\|\tilde{p}^{k+1}\right\|_{2} \le \tilde{C}_{10}(\Delta t^{2} + h^{2}) \quad \forall \ 0 \le k \le N_{k}.$$
(4.27)

Recovery of the a-priori bound (4.11). With the help of the $\ell^{\infty}(0, T; \ell^2)$ error estimate (4.27) for *n* and *p*, we see that the a-priori bound (4.11) is also valid for the numerical error functions \tilde{n}, \tilde{p} at time step t^{k+1} , provided that

$$\Delta t \leq \left(2\tilde{C}_{10}\right)^{-\frac{1}{2}}, \quad h \leq \left(2\tilde{C}_{10}\right)^{-\frac{1}{2}} \quad \text{with } \tilde{C}_{10} \text{ dependent on } T.$$

This completes the convergence analysis.

Combining the construction (4.2b) for **n** and *P*, and the $O(h^2)$ consistency (4.5) between Φ and ϕ_e , completes the proof of Theorem 4.1.



Figure 1: Evolution of the electrostatic potential ϕ and concentrations p and n at time T = 0, T = 0.1, and T = 1.

5. Numerical examples

5.1. Accuracy test

We now test the performance of the proposed numerical method in a two dimensional setting. The computational domain is chosen as $\Omega = (-1, 1)^2$, and we consider an asymmetric 2:1 electrolyte with $\kappa = 1$:

$$\rho^{f}(x,y) = e^{-100\left[(x+\frac{1}{2})^{2}+(y+\frac{1}{2})^{2}\right]} - e^{-100\left[(x+\frac{1}{2})^{2}+(y-\frac{1}{2})^{2}\right]} - e^{-100\left[(x-\frac{1}{2})^{2}+(y+\frac{1}{2})^{2}\right]} + e^{-100\left[(x-\frac{1}{2})^{2}+(y-\frac{1}{2})^{2}\right]}.$$

Here the fixed charge density $\rho^f(x, y)$ approximates two positive and two negative point charges located in four quadrants using Gaussian functions with small local supports. The initial data for concentrations are given by

$$p(0, x, y) = 0.1, \quad n(0, x, y) = 0.2.$$
 (5.1)

The initial distribution of electrostatic potential is obtained by solving the Poisson's equation with initial concentrations. The homogeneous Neumann boundary conditions (1.4) are applied in the numerical simulation. Fig. 1 displays the evolution of concentrations

h	ℓ^2 error in <i>p</i>	Order	ℓ^2 error in <i>n</i>	Order	ℓ^2 error in ϕ	Order
0.1	1.5913e-004	-	1.5913e-004	-	1.7003e-004	-
0.05	4.7390e-005	1.7475	4.7390e-005	1.7475	4.4962e-005	1.9190
0.025	1.1904e-005	1.9931	1.1904e-005	1.9931	1.1076e-005	2.0212
0.0125	2.4374e-006	2.2880	2.4374e-006	2.2880	2.4503e-006	2.1764

Table 1: The ℓ^2 error and convergence order for the numerical solutions of p, n, and ϕ with $\Delta t = h$.

and the potential at time T = 0, T = 0.1, and T = 1. One can observe that the initial electrostatic potential is induced by the fixed charges. As time evolves, the mobile ions are attracted to the oppositely charged fixed charges. Accordingly, the electrostatic potential at fixed charges gets screened by accumulated mobile ions of opposite signs. Our simulation results have demonstrated that the proposed numerical scheme can effectively solve problems of physical interest.

To verify the accuracy of the semi-implicit scheme (2.4a)-(2.4e), we numerically solve the problem using various spatial step sizes h and temporal step sizes Δt , with $\Delta t = h$. Table 1 lists the ℓ^2 error and convergence order for numerical solutions of p, n, and ϕ at time T = 0.5. The ℓ^2 numerical errors are obtained by a comparison between the numerical solution and a reference solution computed with a highly refined mesh. As expected, we can see that the ℓ^2 error decreases robustly as the mesh refines, and the convergence order is about two for both the concentrations and electrostatic potential.

5.2. Application

To further demonstrate the effectiveness and robustness of the numerical scheme, we apply the proposed scheme to study a singular perturbation problem when the coefficient κ in the Poisson's equation becomes large. We take the same parameters and initial conditions as the previous example, except that κ varies from 1, 50, 100, and 200. We recall that $\kappa = \frac{L^2}{2\lambda_D^2}$. Large values of κ correspond to a relatively short Debye length, comparing to the physical dimension.

Since zero-flux boundary conditions are used for the Nernst-Planck equations, the total mass of concentrations is conserved. For large κ values, the boundary layer effect comes into play and the concentration becomes high and concentrated around the fixed charges. Fig. 2 displays the electrostatic potential and concentrations at the steady state with a growing κ . As expected, the potential and concentration become more and more concentrated in the vicinity of the four fixed charges. The simulation results illustrate that the developed scheme is capable of capturing the boundary layer effects.

6. Concluding remarks

In this work, we propose and analyze a second-order accurate, both in time and space, finite difference numerical scheme for the PNP system. The nonlinear convection terms are treated in a fully explicit way, so that the unique solvability is automatically assured.



Figure 2: The electrostatic potential (Left) and the concentration (Right) at the steady state with $\kappa = 1$, $\kappa = 50$, $\kappa = 100$, and $\kappa = 200$.

In addition, a careful application of discrete Fourier analysis results in a discrete Sobolev embedding from H_h^2 into $W_h^{1,4}$, which in turns yields a desired bound for the numerical solution. With the help of such a bound, we are able to derive an optimal rate convergence analysis for the fully discrete scheme, with second order accuracy both in time and space. In addition, such a convergence is unconditional, i.e., no scaling law between the time step size Δt and spatial resolution *h* is needed, since the inverse inequality has been avoided in the analysis. The numerical results have also demonstrated the robustness, efficiency, and accuracy of the proposed numerical scheme.

We now discuss several issues and possible further refinements of our work. In this work, we propose a novel second-order accurate numerical scheme and focus on the analysis of convergence order. As a matter of fact, the mass conservation, preservation of the positivity of numerical solutions, and the free-energy decay of the charged system at a discrete level are of great importance to a numerical scheme for the PNP equations. Rigorous

proof of such desired properties is a challenging task. Some progress has been made in the literature, cf. [1, 8, 9, 11, 17, 24, 27]. In our numerical tests, we have numerically checked the positivity of the numerical solutions. It remains for future work to rigorously prove the desired properties for the proposed numerical scheme.

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