

Convergence Analysis on a Structure-Preserving Numerical Scheme for the Poisson-Nernst-Planck-Cahn-Hilliard System

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Abstract. In this paper, we provide an optimal rate convergence analysis and error estimate for a structure-preserving numerical scheme for the Poisson-Nernst-Planck-Cahn-Hilliard (PNPCH) system. The numerical scheme is based on the Energetic Variational Approach of the physical model, which is reformulated as a non-constant mobility gradient flow of a free-energy functional that consists of singular logarithmic energy potentials arising from the PNP theory and the Cahn-Hilliard surface diffusion process. The mobility function is explicitly updated, while the logarithmic and the surface diffusion terms are computed implicitly. The primary challenge in the development of theoretical analysis on optimal error estimate has been associated with the nonlinear parabolic coefficients. To overcome this subtle difficulty, an asymptotic expansion of the numerical solution is performed, so that a higher order consistency order can be obtained. The rough error estimate leads to a bound in maximum norm for concentrations, which plays an essential role in the nonlinear analysis. Finally, the refined error estimate is carried out, and the desired convergence estimate is accomplished. Numerical results are presented to demonstrate the convergence order and performance of the numerical scheme in preserving physical properties and capturing ionic steric effects in concentrated electrolytes.

AMS subject classifications: 35K35, 35K55, 65M06, 65M12

Key words: Poisson-Nernst-Planck-Cahn-Hilliard system, positivity preserving, optimal rate convergence analysis, higher order asymptotic expansion, rough error estimate, refined error estimate.

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1 Introduction

The well-known Poisson-Nernst-Planck (PNP) theory has been widely applied to describe the ion transport in many biological processes and technological applications, such as ion channels, semiconductors, and electric double layer capacitors [2, 4, 40, 60]. Although it has achieved great success in many applications, the PNP theory has many limitations due to its mean-field nature. In the mean-field approximation, ions are treated as point charges that only interact with the background electric potential arising from the charges in the system. As such, ionic steric effect and ion-ion correlation have been ignored. However, such ignored effects could be crucial to description of ion transport in some scenarios, e.g., charge dynamics in concentrated electrolytes and ions permeation through ion channels.

To overcome the limitations, various modified PNP theories with steric effects have been proposed recently. Based on a lattice gas model, ionic steric effect has been taken into account through the incorporation of entropy of solvent molecules to the electrostatic free energy [6, 31–34, 39, 44, 61]. Another approach is to consider steric effects via including the Lennard-Jones potential for hard-sphere repulsions [18, 30, 36]. To avoid computationally inefficient integro-differential equations, local approximations of nonlocal terms up to the leading order have been proposed to get reduced local models [28, 30, 36]. To get more accurate models, regularization terms of concentration gradient energies can be further included to describe the steric interactions [20–23]. The proposal of such concentration gradient terms follows the same spirit as the Ginzburg-Landau theory for the description of phase separation in mixtures.

Considering an H^{-1} gradient flow of the electrostatic free energy with the additional concentration gradient energies, one can obtain the following Poisson-Nernst-Planck-Cahn-Hilliard (PNPCH) system:

$$\begin{cases} \frac{\partial c^l}{\partial t} = D^l \nabla \cdot \left[c^l \nabla \left(z^l \phi + \ln c^l + \sum_{n=1}^M g^{ln} c^n - \sigma^l \Delta c^l \right) \right], & l=1, 2, \dots, M, \\ -\nabla \cdot (\kappa \nabla \phi) = \sum_{l=1}^M z^l c^l + \rho^f, \end{cases}$$

where ϕ is the electrostatic potential, c^l is the ion concentration for the l -th species, z^l is the valence, M is the total number of the ionic species, ρ^f is the fixed charge density, κ and D^l are coefficients arising from nondimensionalization, $G = (g^{ln})$ is the coefficient matrix for steric interactions, and σ^l is a gradient energy coefficient. Since its proposal in the work [20], the PNPCH system has been applied to study the ion transport in ion channels [22] and charge dynamics in room temperature ionic liquids [21, 23].

In this work, we consider structure-preserving numerical methods and their error estimates for the PNPCH system. For simplicity of presentation, we assume a homogeneous source term $\rho^f \equiv 0$, and $M=2$, which corresponds to only two species of ions, denoted as n and p . The analysis of this work could be easily extended to the case of