A Structure-Preserving JKO Scheme for the Size-Modified Poisson-Nernst-Planck-Cahn-Hilliard Equations

Jie Ding[1,*] and Xiang Ji[2]

[1] *School of Science, Jiangnan University, Wuxi, Jiangsu, 214122, China*
[2] *Department of Mathematics and Mathematical Center for Interdiscipline Research, Soochow University, 1 Shizi Street, Suzhou 215006, Jiangsu, China*

Abstract. In this paper, we propose a structure-preserving numerical scheme for the size-modified Poisson-Nernst-Planck-Cahn-Hilliard (SPNPCH) equations derived from the free energy including electrostatic energies, entropies, steric energies, and Cahn-Hilliard mixtures. Based on the Jordan-Kinderlehrer-Otto (JKO) framework and the Benamou-Brenier formula of quadratic Wasserstein distance, the SPNPCH equations are transformed into a constrained optimization problem. By exploiting the convexity of the objective function, we can prove the existence and uniqueness of the numerical solution to the optimization problem. Mass conservation and unconditional energy-dissipation are preserved automatically by this scheme. Furthermore, by making use of the singularity of the entropy term which keeps the concentration from approaching zero, we can ensure the positivity of concentration. To solve the optimization problem, we apply the quasi-Newton method, which can ensure the positivity of concentration in the iterative process. Numerical tests are performed to confirm the anticipated accuracy and the desired physical properties of the developed scheme. Finally, the proposed scheme can also be applied to study the influence of ionic sizes and gradient energy coefficients on ion distribution.

AMS subject classifications: 35K55, 35J05, 65M06, 65M12

Key words: Structure-preserving, size-modified Poisson-Nernst-Planck-Cahn-Hilliard equations, JKO framework, positivity.

1. Introduction

The classical Poisson-Nernst-Planck (cPNP) equation is a continuum mean-field model, which can describe the ionic transport in semiconductors, ion channels, and electrochemical devices. The cPNP equations include the Poisson's equation and the

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Nernst-Planck (NP) equations. The Poisson's equation can determine the electrical potential induced by the ionic concentration. According to the Fick and Kohlrausch laws, the NP equations describe electro-diffusion and electrophoresis. Despite its usefulness in a variety of applications, the cPNP equations show unphysical crowding of ions near charged surfaces and incorrect dynamics of ion transport, due to the ignored steric effects of ions in its mean-field derivation. To incorporate the steric effects of ions in the PNP model, one technique is to include the interaction energy, which can be the density functional theory [12, 13, 36] or the Lennard-Jones potential [9, 14, 16, 23] for the hard-sphere repulsions. Another technique is to add the entropy of solvent molecules to the electrostatic free energy [17, 19, 21, 30, 35], which is known as the Borukhov model [2]. Employing the consideration of the entropy of solvent molecules in the free energy functional, Lu *et al.* [30] get a class of size-modified Poisson-Nernst-Planck (SMPNP) equations.

In this paper, in addition to incorporating the entropy of solvent molecules in the free energy functional, we also consider the concentration gradient energies utilized in the Ginzburg-Landau theory to describe phase separation [10, 11]. A conserved H^{-1} gradient flow of the Ginzburg-Landau functional gives rise to the Cahn-Hilliard equations [3]. Therefore, the free energy arising from electrostatic energies, entropies, steric energies, and Cahn-Hilliard mixtures leads to the following size-modified Poisson-Nernst-Planck-Cahn-Hilliard (SPNPCH) equations:

$$\begin{cases} \partial_t c^l = \gamma_l \nabla \cdot c^l \nabla \left[\log v_l c^l + q^l \psi - \dfrac{v_l}{v_0} \log \left(1 - \sum_{k=1}^{M} v_k c^k \right) - \sigma^l \Delta c^l \right] \\ \qquad\qquad\qquad \text{in } \Omega, \quad l = 1, 2, \ldots, M, \\ -\kappa \Delta \psi = \sum_{l=1}^{M} q^l c^l + \rho^f \quad \text{in } \Omega, \end{cases} \quad (1.1)$$

where c^l denotes the concentration of l-th ionic species, q^l denotes the valence of l-th ionic species, v_l denotes the volume of l-th ionic species, v_0 denotes the volume of the solvent molecule, σ^l denotes gradient energy coefficient of l-th ionic species, Ω denotes the charged system, ψ denotes the electrostatic potential, ρ^f denotes the fixed charge density, and κ and γ_l denote two nondimensionalized coefficients.

In the closed system, the PNP-type equations have three physical properties: total mass conservative, the positivity of ionic concentration, and energy dissipation. Much effort is devoted to developing the PNP-type scheme to preserve the above properties by using finite difference method, finite volume method, and finite element method. A finite element scheme for the PNP-type equations was developed in [31] to ensure the positivity of ionic concentration via a variable transformation. An arbitrary-order free energy satisfying a discontinuous Galerkin method for 1-D PNP equations was constructed in [28] to meet the energy dissipation law, in which the positivity of numerical solutions is enforced by an accuracy-preserving limiter. An implicit finite difference method for PNP equations to satisfy three physical properties was designed in [8, 15].