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A free energy satisfying finite difference method for Poisson–Nernst–Planck equations

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ABSTRACT

In this work we design and analyze a free energy satisfying finite difference method for solving Poisson–Nernst–Planck equations in a bounded domain. The algorithm is of second order in space, with numerical solutions satisfying all three desired properties: i) mass conservation, ii) positivity preserving, and iii) free energy satisfying in the sense that these schemes satisfy a discrete free energy dissipation inequality. These ensure that the computed solution is a probability density, and the schemes are energy stable and preserve the equilibrium solutions. Both one- and two-dimensional numerical results are provided to demonstrate the good qualities of the algorithm, as well as effects of relative size of the data given.

1. Introduction

In this paper, we are interested in constructing a free energy satisfying numerical method for solving the initial boundary value problem for the Poisson–Nernst–Planck (PNP) equations,

$$\begin{cases} \partial_t c = \nabla\cdot(\nabla c + c\nabla\psi) & x\in\Omega, t>0 \\ \Delta\psi = -c & x\in\Omega, t>0, \\ c(t=0,x) = c^{\text{in}}(x), & x\in\Omega, \\ (\nabla c + c\nabla\psi)\cdot\mathbf{n} = 0, \quad \frac{\partial\psi}{\partial\mathbf{n}} = \sigma & \text{on } \partial\Omega,\ t>0, \end{cases} \tag{1.1}$$

where c is the concentration of ion species, $\Omega\subset\mathbb{R}^d$ denotes a connected closed domain with smooth boundary $\partial\Omega$, ψ is the potential governed by the Poisson equation which is necessary to determine the electrostatic field, and $\mathbf{n}$ is the unit outward normal vector. Subject to the given initial and boundary conditions, the compatibility condition

$$\int_{\partial\Omega}\sigma\,ds + \int_{\Omega} c^{\text{in}}\,dx = 0 \tag{1.2}$$

is necessarily to be imposed for solvability of the problem. By free-energy satisfying we mean that the free energy dissipation law is satisfied at the discrete level.

The PNP equations describe the diffusion of ions under the effect of an electric field that is itself caused by those same ions. The system couples the Nernst–Planck (NP) equation (which describes the drift of ions in a potential gradient by

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Ohm's law and diffusion of ions in a concentration gradient by Fick's law) and the Poisson equation (which relates charge density with electric potential). This system of equations for multiple species has been extensively used in the modeling of semiconductors (see e.g., [32]), and the membrane transport in biological ion channels (see e.g., [14]).

The PNP system can hardly be solved analytically. The main difficulty arises from the nonlinear coupling of the electrostatic potential and concentrations of chemical species. When the physical domain has a simple geometry, a semi-explicit formula was derived in [26] for the steady-state solution; the existence and stability of the steady-state solution was established a long while ago [21] in the study of the steady Van Roostbroeck model in semiconductors. It has been proved by H. Gajewski and K. Gärtner in [18] that the solution to the drift–diffusion system converges to the thermal equilibrium state as time becomes large if the boundary conditions are in thermal equilibrium. The key-point of the proof is an energy estimate with the control of the free energy dissipation. Long time behavior was also studied in [5], and further in [1,4] with refined convergence rates.

In the past decade a growing interest in PNP systems has been driven mainly by experimental and numerical advances. Computational algorithms have been constructed for both simple one-dimensional settings and complex three-dimensional models in various chemical/biological applications, and have been combined with the Brownian Dynamics simulations; cf. [3,9,11,13,17,20,22,26,29,30,33,34,36,37,39]. Many of these existing algorithms are introduced to handle specific settings in complex applications, in which one may encounter different numerical obstacles, such as discontinuous coefficients, singular charges, geometric singularities, and nonlinear couplings to accommodate various phenomena exhibited by biological ion channels [40]. For instance, [36,37] developed a finite difference scheme for liquid junction and ion selective membrane potentials, in which authors used a fully implicit discretization scheme and the Newton–Raphson solver for the resulting linear system. In [30], a 3D finite element method for the system with a singular (point-like) charge outside of the concentration region was developed. A second order PNP solver was developed in [39] in a realistic ion-channel context with the Dirichlet boundary condition. In spite of many existing computational studies, rigorous numerical analysis seems to be still lacking.

Our objective is to construct and analyze an explicit second-order PNP algorithm to incorporate main mathematical features of the PNP system so that the numerical solution remains faithful for long time simulations, i.e., the numerical solution possesses desired properties including conservation of ions, positivity of concentration and dissipation of the free energy. Therefore we consider only the standard PNP equations of form (1.1), while the reader may find intensive discussions of the modeling aspect of the PNP system in the literature.

The main properties of the solution to (1.1) are the nonnegativity principle, the mass conservation and the free energy dissipation, i.e.,

$$c^{\text{in}} \geqslant 0 \Longrightarrow c \geqslant 0 \quad \forall t > 0, \tag{1.3}$$

$$\int_{\Omega} c(t,x)\,dx = \int_{\Omega} c^{\text{in}}(x)\,dx \quad \forall t > 0, \tag{1.4}$$

$$\frac{d}{dt}\tilde{F} = -\int_{\Omega} c^{-1}|\nabla c + c\nabla\psi|^2\,dx + \frac{1}{2}\int_{\Gamma}(\sigma_t\psi - \psi_t\sigma)\,ds, \tag{1.5}$$

where the free energy $\tilde{F}$ is defined by

$$\tilde{F} = \int_{\Omega}\left[c\log c + \frac{1}{2}c\psi\right]dx.$$

If σ does not depend on time, we can use a modified functional $F = \tilde{F} + \frac{1}{2}\int_{\Gamma}\sigma\psi\,ds$ so that

$$\frac{d}{dt}F = -\int_{\Omega} c^{-1}|\nabla c + c\nabla\psi|^2\,dx \leqslant 0.$$

These properties are also naturally desired for numerical methods solving (1.1). In this paper, we develop such a method. We will demonstrate that these properties of the numerical methods could be critical in obtaining the long-time behavior of the solutions.

It is difficult for numerical schemes to preserve all three properties for PNP equations exactly at the discrete level. A recent effort toward this direction is found in [16], where the authors present an implicit second order finite difference scheme with a simple iteration so that the energy dissipation law is approximated closely.

The free energy dissipation in time is also the driving force so that the large time behavior of the solution to (1.1) is governed by the steady-state solution. In fact, the steady-state solution is necessarily of the form $c = Ze^{-\psi}$, which gives $\Delta\psi = -Ze^{-\psi}$, and Z can be further determined by integration of the Poisson equation while using the Neumann boundary data. In other words, the PNP system near steady states is close to a Poisson–Boltzmann equation (PBE)

$$\Delta\psi = \left(\int_{\partial\Omega}\sigma\,ds\right)\frac{e^{-\psi}}{\int_{\Omega}e^{-\psi}\,dx}, \quad x\in\Omega, \quad \left.\frac{\partial\psi}{\partial\mathbf{n}}\right|_{\partial\Omega} = \sigma.$$