



Solutions to a reduced Poisson–Nernst–Planck system and determination of reaction rates

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ABSTRACT

We study a reduced Poisson–Nernst–Planck (PNP) system for a charged spherical solute immersed in a solvent with multiple ionic or molecular species that are electrostatically neutralized in the far field. Some of these species are assumed to be in equilibrium. The concentrations of such species are described by the Boltzmann distributions that are further linearized. Others are assumed to be reactive, meaning that their concentrations vanish when in contact with the charged solute. We present both semi-analytical solutions and numerical iterative solutions to the underlying reduced PNP system, and calculate the reaction rate for the reactive species. We give a rigorous analysis on the convergence of our simple iteration algorithm. Our numerical results show the strong dependence of the reaction rates of the reactive species on the magnitude of its far field concentration as well as on the ionic strength of all the chemical species. We also find non-monotonicity of electrostatic potential in certain parameter regimes. The results for the reactive system and those for the non-reactive system are compared to show the significant differences between the two cases. Our approach provides a means of solving a PNP system which in general does not have a closed-form solution even with a special geometrical symmetry. Our findings can also be used to test other numerical methods in large-scale computational modeling of electro-diffusion in biological systems.

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1. Introduction

Concentrations of ionic and molecular species are key quantities in the description of biomolecular processes at nanometer to submicron scales. For instance, the concentrations of ligands (substrates), receptors (enzymes), and ions regulate almost all biomolecular and cellular activities. Variations in such concentrations often result from molecular diffusion, reaction, and production or depletion. As the random motion arising from thermal fluctuations, molecular diffusion causes the spread of localized signals for intracellular and intercellular communications. Chemical reaction and enzymatic regulation are also associated with the diffusion, production, and depletion of molecular species. This way, molecular diffusion and enzyme reaction form a coupled system which is often associated with signal transduction, gene expression, and metabolism networking.

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Biomolecular diffusion is often driven by an electric field. In such electro-diffusion, the electrostatics can strongly affect the diffusion which in turn affects the rate of association between molecules such as the binding of a ligand to a receptor; cf. e.g., Refs. [1,2]. The electric field in a charged biomolecular system is determined not only by target macromolecules but also by the concentrations of all the charged species, including diffusive ions and small charged molecules.

Mean-field approximations of diffusive molecules or ions are often given by the system of Poisson–Nernst–Planck (PNP) equations. Such a system describes properly the coupling of electrostatics and diffusion of charged chemical species. The PNP system is a combination of Nernst–Planck equations and Poisson equation. The Nernst–Planck equations describe the time evolution of concentrations of chemical species. They are of the form

$$\frac{\partial c_i}{\partial t} - \nabla \cdot [D_i(\nabla c_i + \beta q_i c_i \nabla \psi)] = 0,$$

where $c_i = c_i(x, t)$ is the local concentration of the i th charged molecular or ionic species with charge q_i at the spatial point x at time t , D_i the diffusion constant, and β the inverse thermal energy. The Poisson equation, given by

$$\nabla \cdot \varepsilon \nabla \psi = -\rho,$$

relates the electrostatic potential ψ and the charge density ρ that consists of both fixed and mobile charges, the latter being a linear combination of all the concentrations c_i . Here ε is the product of the dielectric coefficient and the vacuum permittivity ε_0 . (More details of these equations are given in the next section.)

In case of no chemical reaction, the steady-state Nernst–Planck equations lead to the Boltzmann distributions of concentrations in terms of the electrostatic potential [3]. The Poisson equation then becomes the Poisson–Boltzmann equation [4–10]. For reactive chemical species, the non-equilibrium charge distributions deviate from the Boltzmann distribution, and the Poisson equation is needed to determine the electrostatic field. In this case, the PNP system can then be used to calculate the reaction rate. Such calculations are important, as recent studies have shown that substrate concentrations affect the reaction rates, a fact that is ignored in the usual Debye–Hückel limiting law [3,11].

The PNP system can be hardly solved analytically, even for the steady-state system with a very simple geometry. The main difficulty arises from the nonlinear coupling of the electrostatic potential and concentrations of chemical species. Numerical methods for PNP systems have been developed for simple one-dimensional settings and complex three-dimensional models, and have been combined with the Brownian dynamics simulations; cf. Refs. [12–21].

In this work, we consider a reduced PNP system for diffusion of ionic or molecular species in a solution in an electric field induced by charged molecules. The modification from the full PNP system is made by assuming that the concentration of each non-reactive molecular species is given by the Boltzmann distribution. Such distributions are linearized, mimicking the Debye–Hückel approximation. The concentration fields to be determined are those of reactive species. We focus on a spherical, uniformly charged solute particle in a solvent with multiple molecular or ionic species, and only consider the steady-state of the system. We first derive semi-analytical solutions of the underlying, reduced PNP system. We then present a simple iteration method for numerically solving the system using our semi-analytical solution formula. The convergence of our numerical method is proved. We further calculate numerically the equilibrium concentrations, electrostatic potential, and the reaction rates of reactive species. We finally compare our result with that of the case of no reactive species. Our work provides a means of solving a PNP system which in general does not have a closed-form solution even with a special geometrical symmetry. Our findings can also be used to test other numerical methods in large-scale computational modeling of electro-diffusion in biological systems.

In Section 2, we describe our reduced PNP system. In Section 3, we derive the semi-analytical solution formula and present our numerical scheme for obtaining the solution. In Section 4, we use our formula and scheme to calculate the electrostatic potential, the molecular or ionic concentrations, and the reaction rates of reactive species. In Section 5, we compare our results with the case that all the chemical species are non-reactive. Finally, in Section 6, we draw conclusions. In Appendix A, we give details of our derivation of our semi-analytical solution formulas; in Appendix B, we prove the convergence of our numerical scheme.

2. Model description

We first describe our reduced Poisson–Nernst–Planck (PNP) system for a general case in which some charged solutes are immersed in a solvent. There are multiple, diffusive ionic or molecular species in the solvent. Some of them are reactive and some are not. We then describe our reduced PNP system for a uniformly charged spherical solute in a solvent with multiple ionic or molecular species.

2.1. The general case

Let Ω denote the entire region of an underlying solvation system. Let Ω_m and Ω_s denote the solute region and solvent region, respectively. Let also Γ denote the interface that separates Ω_s and Ω_m , cf. Fig. 2.1. We shall use the interface Γ as the dielectric boundary. Let ε_m and ε_s denote the dielectric constant of the solute region Ω_m and that of the solvent region

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