

NUMERICAL STUDIES FOR AN INTERFACE PROBLEM INVOLVING FOURTH- AND SECOND-ORDER POISSON-FERMI ELECTROSTATIC EQUATIONS

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Abstract. A class of particular interface problems, which is derived from Bazant-Storey-Kornyshev (BSK) theory to account for the electrostatic correlation in concentrated electrolytes, is studied in this paper. It involves a modified fourth-order Poisson-Fermi equation in solvents and a second-order Poisson equation in solutes with high-contrast coefficients, where nonhomogeneous interface conditions are introduced over the interface that divides solutes from solvents. A type of interface-fitted finite element method is developed and analyzed for this interface problem, and optimal error estimates are obtained for all variables in both H^1 and L^2 norms. Numerical experiments validate all attained theoretical results through two mathematical examples, as well as the electrostatic correlation phenomenon in concentrated electrolytes through a physical example, practically, where the electrostatic stress and interactional forces in the concentrated electrolyte are computed to reveal the charge reversal phenomenon that is governed by the BSK theory.

Key words. Fourth-/second-order Poisson-Fermi interface problem, nonhomogeneous interface condition, interface-fitted finite element method, optimal convergence, electrostatic correlation, charge reversal.

1. Introduction

In biological processes and colloidal stabilities, electrostatic interactions between the charged objects in solution and their ionic atmospheres play an important role [1], such as the biological activity of proteins [2, 3, 4], the self-assembly of biomolecules [5, 6] and the ions' adsorption on lipid membranes [7, 8, 9]. The study of electrostatic interactions can have a better understanding on the molecular function in cells and improve the efficacy of biomedical drugs. The Poisson-Boltzmann (PB) continuum model that is based on the mean-field approximation has been used to simulate the distribution of ions around charged surfaces for nearly a century [10], where the ions are treated as point charges which only interact with the background electric potential arising from the charges in the system. So the ionic steric effect and electrostatic interactions between ions have been ignored. However, such ignored effects are crucial to describe the ion transport in some situations, such as the charge dynamics in concentrated electrolytes and ions permeation through ion channels. To overcome the limitations, many efforts have been made to improve the PB continuum model in order to correctly describe the spatial and related effects in electrolytes and ionic liquids [11, 12, 10, 13].

Recently, based on the Santangelo's work [14], Bazant, Storey, and Kornyshev propose a modified PB model to depict the electrostatic potential field (e.g., the solvent region Ω_1 in Fig. 1) by substituting the following fourth-order Poisson-Fermi equation for the classical second-order PB equation under the consideration

of electrostatic correlation effects [15, 16],

$$(1) \quad \epsilon_1(l_c^2 \Delta^2 \phi_1 - \Delta \phi_1) = \rho(\phi_1), \quad \mathbf{x} \in \Omega_1,$$

where ϕ_1 is the electrostatic potential defined in the solvent surrounding the solute (molecule), ϵ_1 is the dielectric constant of electrolyte, and l_c is the electrostatic length. The above new theory is therefore called BSK theory, which can be turned back to the classical PB theory by letting $l_c = 0$ in (1), leading to the following second-order Poisson-type electrostatic potential equation defined in either solvents or solutes (e.g., the solute region Ω_2 in Fig. 1):

$$(2) \quad -\epsilon_2 \Delta \phi_2 = 0, \quad \mathbf{x} \in \Omega_2,$$

where ϕ_2 and ϵ_2 are the electrostatic potential and dielectric permittivity, respectively, in the solute. Both ϵ_1 and ϵ_2 are positive. The Fermi-like charge density distribution in (1), $\rho(\phi_1)$, is defined as [15, 17, 10]:

$$\rho(\phi_1) = z_1 e C_1 + z_2 e C_2,$$

where C_1 and C_2 represent ion species concentrations in solvent, defined as [16]:

$$(3) \quad \begin{cases} C_1 = C_\infty^+ e^{-z_1 \frac{e}{K_B T} \phi_1}, \\ C_2 = C_\infty^- e^{-z_2 \frac{e}{K_B T} \phi_1}, \end{cases}$$

where e is the unit charge, K_B the Boltzmann constant and T the absolute temperature, C_∞^+ and C_∞^- indicate the far field concentrations of cations and anions in electrolytes, respectively, z_1 (resp., z_2) is the valence of cations (resp., anions) with the opposite sign (such as $z_1 = 3, z_2 = -1$), satisfying $z_1 C_\infty^+ = z_2 C_\infty^-$. Then,

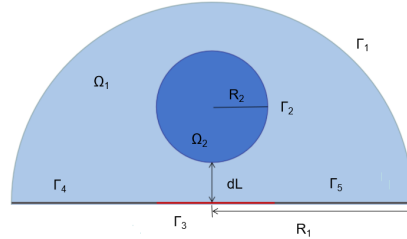


FIGURE 1. The geometry of a solvation system with an implicit solvent, where the solvent-solute interface Γ_2 separates the solvent region Ω_1 and the molecular (solute) region Ω_2 . The red segment, Γ_3 , represents a charged plate.

the following boundary conditions and interface conditions are proposed for the above interface problem involving the fourth-order Poisson-Fermi equation (1) and second-order Poisson equation (2) on either side of the interface,

$$(4) \quad \begin{cases} \phi_1 = \phi_2, & \text{on } \Gamma_2, \\ \epsilon_1 \frac{\partial \phi_1}{\partial \mathbf{n}_1} + \epsilon_2 \frac{\partial \phi_1}{\partial \mathbf{n}_2} = -\sigma, & \text{on } \Gamma_2, \\ \phi_1 = 0, & \text{on } \Gamma_1, \\ \epsilon_1 \frac{\partial \phi_1}{\partial \mathbf{n}_1} = \begin{cases} \sigma, & \text{on } \Gamma_3, \\ 0, & \text{on } \Gamma_4, \Gamma_5, \end{cases} & \\ -\Delta \phi_1 = g, & \text{on } \partial \Omega_1, \end{cases}$$