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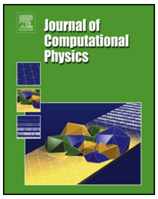

An implicit boundary integral method for computing electric potential of macromolecules in solvent

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ABSTRACT

A numerical method using implicit surface representations is proposed to solve the linearized Poisson–Boltzmann equation that arises in mathematical models for the electrostatics of molecules in solvent. The proposed method uses an implicit boundary integral formulation to derive a linear system defined on Cartesian nodes in a narrowband surrounding the closed surface that separates the molecule and the solvent. The needed implicit surface is constructed from the given atomic description of the molecules, by a sequence of standard level set algorithms. A fast multipole method is applied to accelerate the solution of the linear system. A few numerical studies involving some standard test cases are presented and compared to other existing results.

1. Introduction

The mathematical modeling and numerical simulation of electrostatics of charged macromolecule-solvent systems have been extensively studied in recent years, due to their importance in many branches of electrochemistry; see, for instance, [8,23,26,27,39,53,57,60,65,71,76,89] and references therein for recent overviews of the developments in the subject.

There are roughly two classes of mathematical models for such macromolecule-solvent systems, depending on how the effect of the solvent is modeled: explicit solvent models in which solvent molecules are treated explicitly, and implicit solvent models in which the solvent is represented as a continuous medium. While explicit solvent models are believed to be more accurate, they are computationally intractable when modeling large systems. Implicit models are therefore often an alternative for large simulations, see [6,19,22,50,90] and references therein for recent advances. The Poisson–Boltzmann model is one of the popular implicit solvent models in which the solvent is treated as a continuous high-dielectric medium [16,21,28,41,51,56,69,70,80]. This model, and many variants of it, has important applications, for instance in studying biomolecule dynamics of large proteins [4,5,10,12,33,90]. Many efficient and accurate computational schemes for the numerical solution of the model have been developed [3,7,9,18,24,30,31,36,51,54,81,88].

To introduce the Poisson–Boltzmann model, let us assume that the macromolecule has N_c atoms centered at $\{\mathbf{z}_j\}_{j=1}^{N_c}$, with radii $\{r_j\}_{j=1}^{N_c}$ and charge number $\{q_j\}_{j=1}^{N_c}$ respectively. Let Γ be the closed surface that separates the region occupied by the macromolecule and the rest of the space. The typical choice of Γ is the so-called *solvent excluded surface*, which is defined

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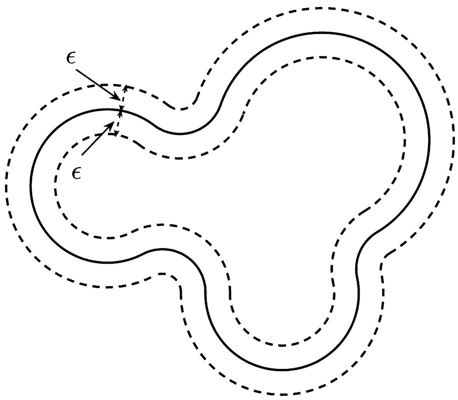

Fig. 1. A view of the "*solvent excluded surface*" in 2D is shown by the middle solid curve, and the narrowband Γ_ϵ is shown here by the space bounded between the dashed curves.

as the boundary of the region outside the macromolecule which is accessible by a probe sphere with some small radius, say ρ_0; see Fig. 1 for an illustration. We use Ω to denote the region surrounded by Γ that includes the macromolecule.

We use a single function ψ to denote the electric potential inside and outside of Ω. In the Poisson–Boltzmann model, ψ solves the Poisson's equation for point charges inside Ω, that is,

$$-\nabla \cdot (\varepsilon_I \nabla \psi(\mathbf{x})) = \sum_{k=1}^{N_c} q_k \delta(\mathbf{x} - \mathbf{z}_k), \quad \text{in } \Omega$$

where ε_I denotes the dielectric constant in Ω. Outside $\overline{\Omega}$, that is in the solvent that excludes the interface Γ, ψ solves the Poisson's equation for a continuous distribution of charges that models the effect of the solvent, that is,

$$-\nabla \cdot (\epsilon_E \nabla \psi) = \rho_B(T, \mathbf{x}, \psi(\mathbf{x})), \quad \text{in } \mathbb{R}^3 \setminus \overline{\Omega}$$

where ε_E denotes the dielectric constant of the solvent, which often has much higher value than that of the macromolecule, $\varepsilon_E \gg \varepsilon_I$. The source term ρ_B is a nonlinear function coming from the Boltzmann distribution with T denoting the temperature of the system. More precisely, for solvent containing m ionic species,

$$\rho_B(T, \mathbf{x}, \psi(\mathbf{x})) := e_c \sum_{i=1}^{m} c_i \bar{q}_i e^{-e_c \bar{q}_i \psi(\mathbf{x})/k_B T}, \quad \mathbf{x} \in \mathbb{R}^3 \setminus \overline{\Omega}$$

where $c_i, \bar{q}_i$ are the concentration and charge of the ith ionic species, e_c is the electron charge, k_B is the Boltzmann constant, and T is the absolute temperature.

The nonlinear term $\rho_B(T, \mathbf{x}, \psi)$ in the Poisson–Boltzmann system poses significant challenges in the computational solution of the system. In many practical applications, it is replaced by the linear function $-\bar{\kappa}_T^2 \psi(\mathbf{x})$ where the parameter $\bar{\kappa}_T = \sqrt{\frac{2e^2 \mathbb{I}}{k_B T}}$ is called the Debye–Hückel screening parameter with k_B, e, and $\mathbb{I}$ being the Boltzmann constant, the unit charge, and the ionic strength respectively. This leads to the linearized Poisson–Boltzmann equation (PBE) for the electrostatic potential ψ. It takes the following form

$$\begin{aligned}
-\nabla \cdot (\varepsilon_I \nabla \psi(\mathbf{x})) &= \sum_{k=1}^{N_c} q_k \delta(\mathbf{x} - \mathbf{z}_k), && \text{in } \Omega, \\
-\nabla \cdot (\varepsilon_E \nabla \psi(\mathbf{x})) &= -\bar{\kappa}_T^2 \psi(\mathbf{x}), && \text{in } \overline{\Omega}^c, \\
\psi(\mathbf{x})_{|\Gamma_+} &= \psi(\mathbf{x})_{|\Gamma_-}, && \text{on } \Gamma, \\
\varepsilon_E \frac{\partial \psi}{\partial n}_{|\Gamma_+} &= \varepsilon_I \frac{\partial \psi}{\partial n}_{|\Gamma_-}, && \text{on } \Gamma, \\
|\mathbf{x}| \psi(\mathbf{x}) \to 0, \quad |\mathbf{x}|^2 |\nabla \psi(\mathbf{x})| &\to 0, && \text{as } |\mathbf{x}| \to \infty.
\end{aligned} \tag{1}$$

Here the operator $\partial/\partial n \equiv \mathbf{n}(\mathbf{x}) \cdot \nabla$ denotes the usual partial derivative at $\mathbf{x} \in \Gamma$ in the outward normal direction $\mathbf{n}(\mathbf{x})$ (pointing from Γ outward). The usual continuity conditions, continuity of the potential and the flux across Γ, are assumed, and the radiation condition, which requires ψ decay to zero far away from the macromolecule, is needed to ensure the uniqueness of solutions to the linearized Poisson–Boltzmann equation. See e.g. [3,7,10,16,30,31,50,53,70,80,81].