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A FINITE DIFFERENCE SCHEME FOR SOLVING THE NONLINEAR POISSON-BOLTZMANN EQUATION MODELING CHARGED SPHERES *[1)]

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Dedicated to the 70th birthday of Professor Lin Qun

Abstract

In this work, we propose an efficient numerical method for computing the electrostatic interaction between two like-charged spherical particles which is governed by the nonlinear Poisson-Boltzmann equation. The nonlinear problem is solved by a monotone iterative method which leads to a sequence of linearized equations. A modified central finite difference scheme is developed to solve the linearized equations on an exterior irregular domain using a uniform Cartesian grid. With uniform grids, the method is simple, and as a consequence, multigrid solvers can be employed to speed up the convergence. Numerical experiments on cases with two isolated spheres and two spheres confined in a charged cylindrical pore are carried out using the proposed method. Our numerical schemes are found efficient and the numerical results are found in good agreement with the previous published results.

Mathematics Subject Classification: 65N06, 65B99.
Key words: Nonlinear Poisson-Boltzmann equation, Electrostatic interaction, Irregular domain, Monotone iterative method, Multigrid solver.

1. Introduction

The interactions between colloidal particles control the operation of many important industrial processes and also determine the properties of the final products. The nonlinear Poisson-Boltzmann equation has been used for the description of the distribution of electrostatic potential in colloidal dispersions, see, e.g., [20, 22]. Knowing the electrostatic potential, one can calculate the force of particle-particle interaction. Features of interparticle interaction are of great importance for the stability of colloidal dispersions.

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The problem of obtaining numerical solutions of the nonlinear Poisson-Boltzmann equation has a long history. In 1956, Hoskins and Levine [11] made the first such attempt for identical spheres interactions under constant surface potential. Their calculations were based on a second-order finite difference scheme and were carried out on a relatively small grid $(8 * 16)$. In [4], Bowen and Sharif considered the axi-symmetric situations of the Poisson-Boltzmann problem. While the problem is defined in the three-dimensional (3D) space, they can reduce it to a problem in two space dimensions using the geometrical symmetry. Their work used an adaptive finite element method for two interacting charged spheres enclosed in a charged cylindrical capillary. In their 1998 *Nature* paper [3], the authors found that in the absence of the charged capillary wall the two particles repelled one another over the whole range of particle separations, while in the presence of the charged wall a long range attractive force arose. However, their results were questioned by several authors, see, e.g., [14, 21]. In another *Nature* paper [9], the calculations in [3] were repeated and it was found that although the particle-particle interactions were reduced by the presence of a wall, no attraction was found.

Due to its practical importance, the problem of the long-range electrostatic attraction between like-charge spheres has recently been studied numerically by many authors, see, e.g., [1, 2, 6, 7, 8, 10]. Among these numerical schemes, few are related to the finite difference approach. This is mainly due to the difficulty given by the presence of a multi-connected domain. To overcome the difficulty, a conformal mapping approach may be used in some special cases to transform the multi-connected domain to a rectangular one. One can then solve the transformed Poisson-Boltzmann equation by using finite difference methods on the rectangular domain with a regular grid, see, e.g., [6]. In the present work, we will propose another type of finite difference scheme useful for handling general multi-connected domains. The goal is to solve the problem under consideration on the original multi-connected domain with a uniform Cartesian grid, while maintaining the simplicity of the finite difference scheme and the second-order approximation accuracy. The proposed method is flexible for complex domains on which the conformal mappings are not available. Since a uniform Cartesian grid on the domain is used, the method is simple and there is almost no extra cost in the grid generation. Moreover, our approach also allows to use the fast Poisson solvers based on multigrid methods. The method will be used to solve the Poisson-Boltzmann equation describing the long-range electrostatic attraction between like-charge spheres.

This paper is organized as follows. In Section 2, we give a description of the problem. In Section 3, a monotone iterative strategy useful for a class of semi-linear PDEs of elliptic type will be discussed. This strategy will be useful for linearizing the nonlinear Poisson-Boltzmann equation. In Section 4, a modified central finite difference scheme is introduced. Special attention is given to handle the irregular interface inside the rectangular domain. In Section 5, the proposed numerical scheme is applied to solve the nonlinear Poisson-Boltzmann equation for two identical charged spherical particles immersed in a symmetric univalent electrolyte and for two spheres confined in a like-charged cylindrical pore. We also compare our results with those available in the literature. Some concluding remarks are provided in the final section.

2. The Description of the Problem

We consider the nonlinear Poisson-Boltzmann equation

$$\Delta\Psi = \sinh\Psi, \tag{2.1}$$

where Ψ is the electrostatic potential. Usually, the above equation is defined in a 3D space, but for two isolated like-charged spherical particles immersed in a symmetric univalent electrolyte or like-charged spheres confined in a long, charged cylindrical pore, because of the symmetry of the geometry, we can rewrite the nonlinear Poisson-Boltzmann equation (2.1) as the following

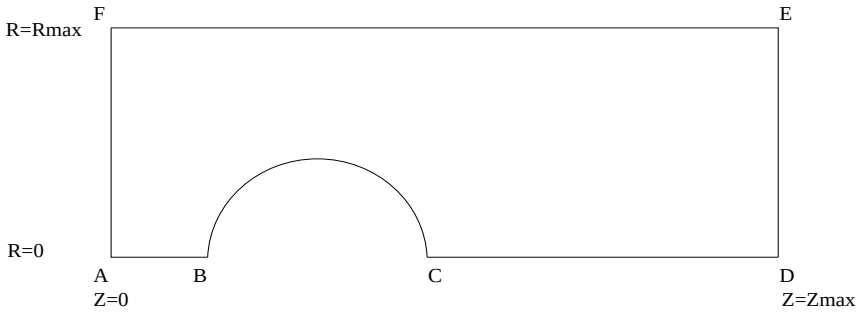

Figure 1: Quarter domain for two interacting charged spheres. Boundaries AB and CD are the Z-axis lines of symmetry while boundary AF is the R-axis line of symmetry.

2D equation in cylindrical coordinates [3, 7]:

$$\frac{\partial^2\Psi}{\partial R^2}+\frac{1}{R}\frac{\partial\Psi}{\partial R}+\frac{\partial^2\Psi}{\partial Z^2}=\sinh\Psi, \tag{2.2}$$

and solve the nonlinear equation on a quarter domain as shown in Fig. 1.

We consider the case of constant surface potential [6, 7]. In this case, the boundary conditions are given below:

- (1) For two isolated spheres:

$$\frac{\partial\Psi}{\partial R}=0 \quad \text{on AB, CD and EF,} \tag{2.3}$$
$$\frac{\partial\Psi}{\partial Z}=0 \quad \text{on AF and DE,} \tag{2.4}$$
$$\Psi=\Psi_s \quad \text{on } \widehat{BC}. \tag{2.5}$$

- (2) For two spheres confined in a charged pore:

$$\frac{\partial\Psi}{\partial R}=0 \quad \text{on AB, CD,} \tag{2.6}$$
$$\frac{\partial\Psi}{\partial Z}=0 \quad \text{on AF and DE,} \tag{2.7}$$
$$\Psi=\Psi_p \quad \text{on } EF, \tag{2.8}$$
$$\Psi=\Psi_s \quad \text{on } \widehat{BC}. \tag{2.9}$$

Knowing the electrostatic potential, the electrostatic force can be determined by [4]:

$$F=F^*\left[\epsilon_0\epsilon_r\pi\left(\frac{\kappa T}{e}\right)^2\right],$$

where ϵ_0 is the permittivity of vacuum (8.854×10^{-12} in $CV^{-1}m^{-1}$, ϵ_r is the relative dielectric constant (78.0 is used in the literature), κ is the Boltzmann constant (1.38×10^{-23}) in JK^{-1}, T is the absolute temperature (298 is used in the literature) in K, e is the elementary charge (1.602×10^{-19}) in C [3], and the dimensionless force F^* is the integration over the median plane:

$$F^*=\int_0^{R_{max}}\left[2(\cosh\Psi-1)+\left(\frac{\partial\Psi}{\partial R}\right)^2-\left(\frac{\partial\Psi}{\partial Z}\right)^2\right]\times RdR. \tag{2.10}$$

3. Monotone Iterative Method

To develop a computational algorithm for problem (2.2), we first consider a more general problem in the form

$$\begin{aligned} &-\Delta u - \frac{1}{y}\frac{\partial u}{\partial y} = f(x,y,u), \quad \text{in } I, \\ &u(x,y) = \eta, \quad \text{on } \partial I_1, \qquad \frac{\partial u}{\partial n}(x,y) = 0, \quad \text{on } \partial I_2, \end{aligned} \tag{3.1}$$

where I is the domain described in Fig. 1, ∂I_1 is the boundary $\widehat{BC}$, ∂I_2 is the boundary $\partial I \backslash \partial I_1$, $f(x,y,u)$ is a continuous function which is differentiable in u, and η is a given positive constant. It is clear that problem (2.2) is a special case of (3.1) with $\eta = \Psi_s$ and $f(x,y,u) = -\sinh(u)$. To show the existence and uniqueness of the solution to (3.1), we use the method of upper and lower solutions and its associated monotone iterations, see [16, 17, 18] for the reference. Some preliminary applications of the monotone iteration methods for the nonlinear Poisson-Boltzmann equation are also reported in [15]. We say that $\tilde{u}(x,y)$ is an upper solution of (3.1) if it satisfies the inequalities:

$$\begin{aligned} &-\Delta \tilde{u} - \frac{1}{y}\frac{\partial \tilde{u}}{\partial y} \geq f(x,y,\tilde{u}), \qquad \text{in } I, \\ &\tilde{u}(x,y) \geqslant \eta \quad \text{on } \partial I_1, \qquad \frac{\partial \tilde{u}}{\partial n}(x,y) \geqslant 0 \quad \text{on } \partial I_2. \end{aligned} \tag{3.2}$$

Similarly, $\hat{u}(x,y)$ is called a lower solution if it satisfies the above inequalities in reverse order. The pair $\tilde{u}(x,y)$ and $\hat{u}(x,y)$ is said to be ordered if $\tilde{u}(x,y) \geq \hat{u}(x,y)$. For a given pair of ordered upper and lower solutions $(\tilde{u}, \hat{u})$ we set

$$S = \{u \in C(I); \quad \hat{u} \leqslant u \leqslant \tilde{u}\}. \tag{3.3}$$

Let $\gamma(x,y)$ be any nonnegative function satisfying

$$\gamma(x,y) \geq \max\left\{-\frac{\partial f}{\partial u}(x,y,u); \quad \hat{u}(x,y) \leqslant u(x,y) \leqslant \tilde{u}(x,y)\right\}. \tag{3.4}$$

Then for any initial guess $u^{(0)}(x,y)$ we can construct a sequence $\{u^{(m)}\}$ by the linear iteration process:

$$\begin{aligned} &-\Delta u^{(m)} - \frac{1}{y}\frac{\partial u^{(m)}}{\partial y} + \gamma u^{(m)} = \gamma u^{(m-1)} + f(x,y,u^{(m-1)}) \quad \text{in } I, \\ &u^{(m)}(x,y) = \eta \quad \text{on } \partial I_1, \qquad \frac{\partial u^{(m)}}{\partial n}(x,y) = 0 \quad \text{on } \partial I_2. \end{aligned} \tag{3.5}$$

It is obvious that the sequence $\{u^{(m)}\}$ is well defined for each $m = 1, 2, \cdots$. Denote the sequence by $\{\bar{u}^{(m)}\}$ if $u^{(0)} = \tilde{u}$ is an upper solution, and by $\{\underline{u}^{(m)}\}$ if $u^{(0)} = \hat{u}$ is a lower solution, and refer to them as maximal and minimal sequences, respectively. The following result gives the monotone convergence of these sequences.

Lemma 3.1 ([16]). *Assume $f(x,y,u) \in C^1(S)$. Let $(\tilde{u}, \hat{u})$ be a pair of ordered upper and lower solutions of (3.1). Then the maximal sequence $\{\bar{u}^{(m)}\}$ converges to a maximal solution $\bar{u} = \bar{u}(x,y)$ of (3.1), and the minimal sequence $\{\underline{u}^{(m)}\}$ converges to a minimal solution $\underline{u} = \underline{u}(x,y)$ of (3.1). Moreover,*

$$\hat{u} \leqslant \underline{u}^{(m)} \leqslant \underline{u}^{(m+1)} \leqslant \underline{u} \leqslant \bar{u} \leqslant \bar{u}^{(m+1)} \leqslant \bar{u}^{(m)} \leqslant \tilde{u} \quad \text{on } I,$$

and if $\frac{\partial f}{\partial u} \leqslant 0$ in S , then $\bar{u} = \underline{u} (= u^*)$ and u^* is the unique solution of (3.1) in S.

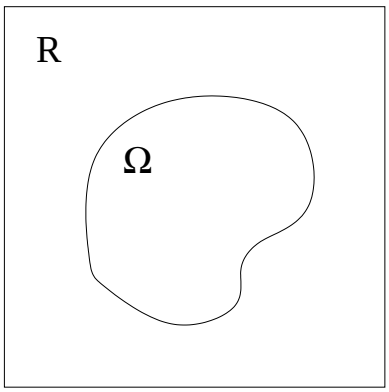

Figure 2: A sketch of a computational domain that is inside the rectangle R but outside of Ω.

We now consider (3.1) with $f(u) = -\sinh(u)$, i.e., (2.2). It follows from the facts $f(0) = -\sinh(0) = 0$ and $f(\rho) = -\sinh(\rho) < 0$ for every $\rho \geq \eta > 0$ that the pair

$$\tilde{u}(x,y) = \rho \quad \text{and} \quad \hat{u}(x,y) = 0 \tag{3.6}$$

are upper and lower solutions. Moreover,

$$\frac{\partial f}{\partial u}(u) = -\cosh(u) \leqslant 0 \quad \text{for every } u \in S. \tag{3.7}$$

As a consequence of Lemma 3.1, we have the following result.

Lemma 3.2. *Given any constant $\eta > 0$, the boundary value problem (3.1) with $f(u) = -\sinh(u)$ has a unique positive solution. Moreover, for any $\rho \geq \eta$, the sequences $\{\bar{u}^{(m)}\}$ and $\{\underline{u}^{(m)}\}$ obtained from (3.5) with $\bar{u} = \rho$ and $\underline{u} = 0$, respectively, converge to u^* and satisfy the monotonicity property:*

$$0 \leq \underline{u}^{(m)} \leq \underline{u}^{(m+1)} \leq u^* \leq \bar{u}^{(m+1)} \leq \bar{u}^{(m)} \leq \rho. \tag{3.8}$$

4. A Modified Finite Difference Scheme

First we introduce a modified finite difference scheme for the following equation in an irregular domain $R\backslash\Omega$, as shown in Fig. 2:

$$\frac{\partial^2 u}{\partial x^2} + \frac{1}{y}\frac{\partial u}{\partial y} + \frac{\partial^2 u}{\partial y^2} = f(x,y), \quad (x,y) \in R\backslash\Omega. \tag{4.1}$$

We use the zero level set of a two dimensional level set function $\varphi(x,y)$ to represent the boundary $\partial\Omega$. For example, if the inside boundary $\partial\Omega$ is the union of the boundaries of two ellipses

$$\frac{(x-x_i)^2}{a_i^2} + \frac{(y-y_i)^2}{b_i^2} = 1, \quad i = 1,2, \tag{4.2}$$

then we can choose

$$\varphi(x,y) = \min\left\{\varphi_1(x,y), \varphi_2(x,y)\right\}, \tag{4.3}$$

where $\varphi_i(x,y), i = 1,2$ are given by

$$\varphi_i(x,y) = \frac{(x-x_i)^2}{a_i^2} + \frac{(y-y_i)^2}{b_i^2} - 1. \tag{4.4}$$

With the definition of $\varphi(x, y)$, and $\varphi_{ij} = \varphi(x_i, y_j)$ in the discrete case, the boundary $\partial\Omega$ is implicitly defined by $\varphi(x, y) = 0$.

4.1. Dirichlet Boundary Conditions

If we have a Dirichlet boundary condition on ∂R, we can use a uniform Cartesian grid,

$$x_i = a + i\Delta x, \qquad i = 0, 1, \cdots, M, \qquad \Delta x = (b-a)/M, \tag{4.5}$$

$$y_j = c + j\Delta y, \qquad j = 0, 1, \cdots, N, \qquad \Delta y = (d-c)/N, \tag{4.6}$$

on the entire rectangle $[a, b] \times [c, d]$. In this case it is known that a fast Poisson solver can be applied directly. Eq. (4.1) can be written in conservative form by using the fact that the 2nd and 3rd terms in (4.1) can be combined as $(yu_y)_y/y$. Discretizing the resulting conservative form gives

$$\frac{u_{i-1,j} - 2u_{ij} + u_{i+1,j}}{(\Delta x)^2} + \frac{1}{y_j}\left(\frac{y_{j-\frac{1}{2}}u_{i,j-1} - (y_{j-\frac{1}{2}} + y_{j+\frac{1}{2}})u_{ij} + y_{j+\frac{1}{2}}u_{i,j+1}}{(\Delta y)^2}\right) = f_{ij}. \tag{4.7}$$

However, if there is an interface in the stencil, then we need to modify the finite difference scheme in order to use the given conditions on the interface. Below we consider one possible case as shown in Fig. 3; other cases can be handled in a similar way. Define $\Delta x_1 = \mathrm{OQ}$ and $\Delta y_1 = \mathrm{OP}$. We have

$$\begin{aligned}
\frac{1}{y}\frac{\partial}{\partial y}\left(y\frac{\partial u}{\partial y}\right) &\approx \frac{1}{y_j}\left[\frac{y_{j+\frac{1}{2}\Delta y_1}\frac{\partial u}{\partial y}(i, j+\frac{1}{2}\Delta y_1) - y_{j-\frac{1}{2}\Delta y_1}\frac{\partial u}{\partial y}(i, j-\frac{1}{2}\Delta y_1)}{\frac{1}{2}(\Delta y_1 + \Delta y)}\right] \\
&\approx \frac{1}{y_j}\left[\frac{y_{j+\frac{1}{2}\Delta y_1}(\frac{u_P - u_{ij}}{\Delta y_1}) - y_{j-\frac{1}{2}\Delta y_1}(\frac{u_{ij} - u_{i,j-1}}{\Delta y})}{\frac{1}{2}(\Delta y_1 + \Delta y)}\right] \\
&= \frac{1}{y_j}\Big[\frac{2}{(\Delta y_1 + \Delta y)\Delta y_1} \times y_{j+\frac{1}{2}\Delta y_1} \times (u_P - u_{ij}) - \\
&\qquad \frac{2}{(\Delta y_1 + \Delta y)\Delta y} \times y_{j-\frac{1}{2}} \times (u_{ij} - u_{i,j-1})\Big],
\end{aligned}$$

and

$$\begin{aligned}
\frac{\partial^2 u}{\partial x^2} &\approx \frac{\frac{\partial u}{\partial x}(i+\frac{1}{2}\Delta x_1, j) - \frac{\partial u}{\partial x}(i+\frac{1}{2}\Delta x_1, j)}{\frac{1}{2}(\Delta x + \Delta x_1)} \\
&\approx \frac{2}{(\Delta x_1 + \Delta x)\Delta x_1}(u_Q - u_{ij}) - \frac{2}{(\Delta x_1 + \Delta x)\Delta x}(u_{ij} - u_{i-1,j}).
\end{aligned}$$

By defining

$$\begin{aligned}
\gamma_1 &= \frac{2}{(\Delta x_1 + \Delta x)\Delta x_1}, \quad \gamma_3 = \frac{2}{(\Delta x_1 + \Delta x)\Delta x}, \\
\gamma_2 &= \left[y_{j+\frac{1}{2}\Delta y_1} \times \frac{2}{(\Delta y_1 + \Delta y)\Delta y_1}\right]\frac{1}{y_j}, \\
\gamma_4 &= \left[y_{j-\frac{1}{2}\Delta y_1} \times \frac{2}{(\Delta y_1 + \Delta y)\Delta y}\right]\frac{1}{y_j},
\end{aligned}$$

and $\gamma_0 = -(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)$, we obtain the finite difference scheme for the irregular point (i, j):

$$\gamma_3 u_{i-1,j} + \gamma_4 u_{i,j-1} - \gamma_0 u_{ij} = f(x_i, y_j) - (\gamma_1 u_Q + \gamma_2 u_P). \tag{4.8}$$

This implies that the resulting linear system is diagonally dominant.

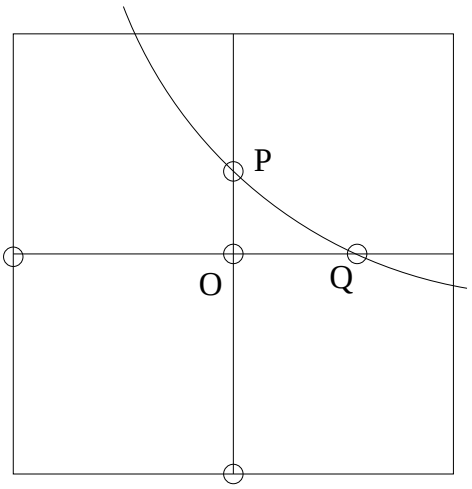

Figure 3: The stencil for the modified 5-point central difference scheme.

4.2. Neumann Boundary Conditions

For a Neumann boundary condition on ∂R, we can use the ghost point method except on the case $y = 0$ is the boundary where the given PDE has a coordinate singularity. The idea is to use the staggered grid in the y direction and uniform grid in the x direction. The corresponding grid points are given by:

$$\begin{aligned} y_j &= (j - \frac{1}{2})\Delta y, \quad \Delta y = \frac{y_{max}}{n - \frac{1}{2}}, \quad j = 1, 2, \cdots, n \\ x_i &= (i-1)\Delta x, \quad \Delta y = \Delta x, \qquad i = 1, 2, \cdots, m \end{aligned}$$

To make it simple, we suppose $\Delta x = \Delta y$. For $i = 1, \cdots, m$ and $j = 2, \cdots, n$, the conservation form (4.7) is employed to discretize (4.1). When $j = 1$, we use the non-conservative form to take care of the coordinate singularity on $y = 0$:

$$\frac{u_{i+1,1} - 2u_{i1} + u_{i-1,1}}{(\Delta x)^2} + \frac{1}{y_1}\frac{u_{i2} - u_{i0}}{2\Delta y} + \frac{u_{i0} - 2u_{i1} + u_{i2}}{(\Delta y)^2} = f_{ij}, \tag{4.9}$$

where $u_{i,0}$ is the ghost point value (i.e. the value at the points outside of the solution domain). By using the Neumann boundary condition $u_y = 0$ on $y = 0$ we have $u_{i0} = u_{i1}$. Substituting this approximation to (4.9) gives

$$\frac{u_{i+1,1} - 2u_{i1} + u_{i-1,1}}{(\Delta x)^2} + \frac{1}{y_1}\frac{u_{i2} - u_{i1}}{2\Delta y} + \frac{-u_{i1} + u_{i2}}{(\Delta y)^2} = f_{ij}. \tag{4.10}$$

This approach also preserves the diagonal dominant property of the resulting linear system. Consequently, the linear system associated with the finite difference scheme can be solved by using some multigrid solvers, such as [19].

4.3. Outline of the Numerical Algorithm

Below we give an outline of the numerical algorithm for solving Eq. (2.2):

- Set up a uniform grid (x_i, y_j) for the rectangular domain.

- Choose an upper and a lower solutions $\bar{\Psi}^{(0)}(x,y)$ and $\underline{\Psi}^{(0)}(x,y)$. If a Dirichlet boundary condition $\Psi(x,y)|_{\partial I_1} = \Psi_s(x,y) \geq 0$ is given, then we can take $\bar{\Psi}^{(0)}(x,y) = \max|\Psi_s(x,y)|$ and $\underline{\Psi}^{(0)}(x,y) = 0$. For $m = 0,1,2,\cdots$, iteratively update $\bar{\Psi}^{(m)}$ by solving

$$\frac{\partial^2 \bar{\Psi}^{m+1}}{\partial R^2} + \frac{1}{R}\frac{\partial \bar{\Psi}^{m+1}}{\partial R} + \frac{\partial^2 \bar{\Psi}^{m+1}}{\partial Z^2} - \gamma \bar{\Psi}^{m+1} = \sinh \bar{\Psi}^m - \gamma \bar{\Psi}^m, \quad (R,Z) \in I, \tag{4.11}$$

$$\bar{\Psi}^{m+1}|_{\partial I_1} = \Psi_s, \qquad \left.\frac{\partial \bar{\Psi}^{m+1}}{\partial n}\right|_{\partial I_2} = 0, \tag{4.12}$$

  where $\gamma = \max_{(x_i,y_j)\in I}\{\cosh \bar{\Psi}^m_{ij}\}$. The iterative procedure stops if $\|\bar{\Psi}^{(m+1)} - \bar{\Psi}^{(m)}\|$ is sufficiently small. The lower solution $\underline{\Psi}^{(m)}$ is obtained in a similar way.

- Use the modified finite difference method introduced in the last two subsections to discretize the linearized partial differential equations. The resulting linear system is then solved by a multigrid solver.

5. Numerical Experiments

We first validate our numerical method by checking the errors against a known exact solution. We solve the equation (4.1) on the domain $R\backslash\Omega$, where $R = [0,1]\times[0,1]$ and $\partial\Omega$ is represented by

$$\frac{(x-0.3)^2}{0.1^2} + \frac{(y-0.5)^2}{0.1^2} = 1.$$

Let $f(x,y)$ in (4.1) be given by

$$f(x,y) = -2\pi^2 \cos(\pi x)\cos(\pi y) - \frac{1}{x}\pi \sin(\pi x)\cos(\pi y). \tag{5.1}$$

It can be verified that the exact solution of the equation (4.1) is $u = \cos(\pi x)\cos(\pi y)$. The Dirichlet boundary condition along the interior boundary $\partial\Omega$ and the exterior boundary ∂R are determined from the exact solution at the boundary. Inside Ω, the solution is defined as 0. Table 1 shows the numerical errors and the corresponding convergence order. The maximum error E in Table 1 is defined by

$$E = \max_{i,j}|u(x_i,y_j) - U_{ij}|, \tag{5.2}$$

where U_{ij} is the numerical solution at (x_i,y_j). It is observed from Table 1 that the rate of convergence for the proposed numerical method for (4.1) is two.

5.1. Two Isolated Spheres

Now we solve the equation for two like-charged spheres immersed in a symmetrical 1:1 electrolyte, which has been studied extensively in the past; see, e.g., [4, 6, 7, 11]. The radius of both spheres is 5, and the two spheres are isolated with distance 0.5. The constant potential Ψ_s in (2.5) is 2.0 on the surfaces of both particles.

We first check the monotonicity of the iteration process discussed in Section 3 and included in Section 4.3. Fig. 4 represents the maximal and minimal sequence values at four typical points $(j*\Delta z, 0)$, $j = 0,1,2$ and 3, where Δz is the unit length of the partition in the Z direction. We can see clearly from Fig. 4 the monotonicity of the maximal and minimal sequences. The parameters used in the numerical computations are: $\gamma = \cosh(2.0)$, the initial upper solution $\tilde{u} = 2.0$ and the initial lower solution $\hat{u} = 0.0$.

To test the accuracy of numerical schemes for the solutions of the Poisson-Boltzmann equation, it is common to calculate the dimensionless force between the two spheres given by the

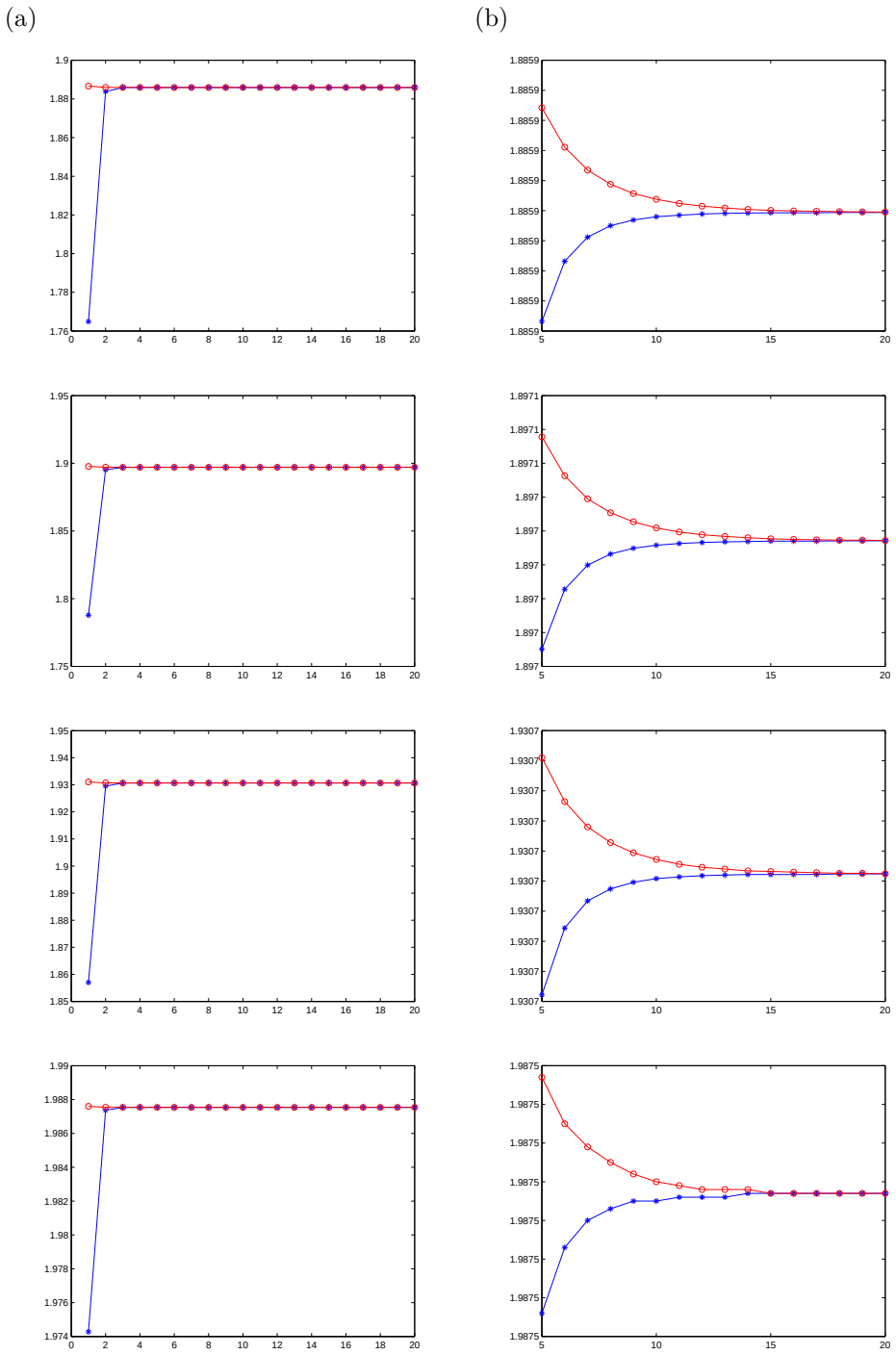

Figure 4: The computed maximal and minimal sequences at some typical points versus the iterations, 'o' is the upper solution, '*' is the lower solution. From top to bottom: numerical values at points $(j*\Delta z, 0)$ with $0 \leq j \leq 3$ against the number of iterations. The right figures are obtained by amplifying the left ones when the number iterations is between 5 and 20.

Table 1: A convergence analysis for the test problem with $f(x, y)$ given by (5.1) and the exact solution $u = \cos(\pi x)\cos(\pi y)$.

$M \times N$	E	$E_{\frac{M\times N}{2}}/E_{M\times N}$	order
33×33	5.1012×10^{-4}		
65×65	1.3622×10^{-4}	3.7448	1.9049
129×129	3.5256×10^{-5}	3.8638	1.9500

Table 2: Comparison of the dimensionless interaction force for two identical colloidal particles case.

F^*(this paper)	F^*Ref.[7]	F^*Ref.[4]	F^*Ref.[6]
15.535	15.545	15.509	15.545

formula (2.10). Table 2 gives the dimensionless interaction force obtained by using our proposed method, which is compared with some previously published results. The results obtained by using adaptive mesh refinement methods are 15.545 [7] and 15.509 [4], which are in good agreement with our result of 15.535.

5.2. Two Spheres Confined in a Charged Cylindrical Pore

This problem deals with the long-range electrostatic interaction of two charged spheres confined in a like-charged cylindrical pore. We choose the same parameters as in [3]: the 1:1 electrolyte, the constant potential on the cylindrical pore Ψ_p in (2.8) is 5.0, the constant potential on the spheres Ψ_s in (2.9) is 3.0, the radius of the particles is $a = 1.185$, and the sphere radius to pore radius ratio is $\lambda = 0.13$.

The computational results for the electrostatic force are shown in Fig. 5. It is observed that the force is always positive, i.e., there is only repulsion between the particles and no long-range attraction is found in the numerical results. We also give the isopotential plot for two isolated spheres (i.e., (2.3)-(2.5) with $\Psi_s = 3$) and two spheres confined in a pore (i.e., (2.6)-(2.9) with $\Psi_s = 3$ and $\Psi_p = 5$) in Fig. 6. They are found to be in good agreement with the published results; see, e.g., [3].

During the calculation, the stopping criteria $\epsilon = 10^{-7}$ is used for the monotone iteration to obtain the above numerical results. Moreover, mesh refinements with grids of 128×64, 256×128 and 512×256 are carried out to ensure convergence. Since the resulting linear system is diagonally dominant, the use of multigrid method speeds up the convergence of the solutions.

6. Conclusion

In this paper, we have proposed a numerical method for solving the nonlinear Poisson-Boltzmann equation on an irregular domain. The main difficulties are the nonlinearity and the fact that the solution domain is irregular. Using the special form of the nonlinear term $\sinh(\Psi)$, we apply a monotone iterative type method to linearize the nonlinear Poisson-Boltzmann equation. We then introduce a modified finite difference scheme to discretize the linearized equation on the irregular domain. Special attention is paid to make sure that the resulting linear system is diagonally dominant. Consequently, the system can be solved by some multigrid solvers. Since our method does not depend on the geometry of the domain, it is expected to be useful for solving the nonlinear Poisson-Boltzmann equation in complex geometries. One of the

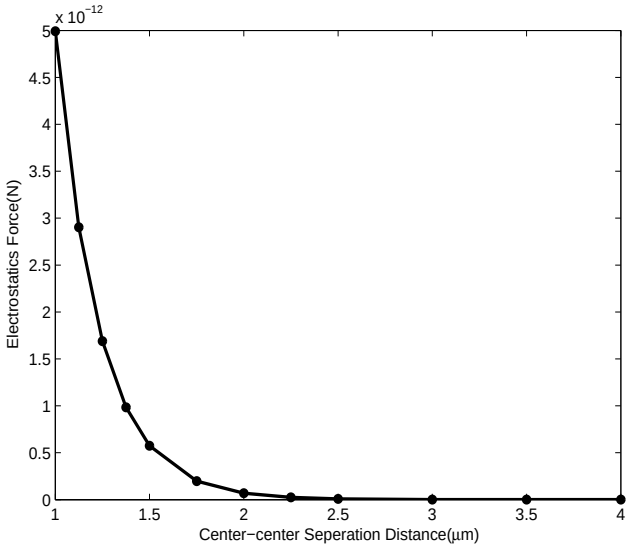

Figure 5: Two spheres confined in a charged cylindrical pore: long-range electrostatic interaction.

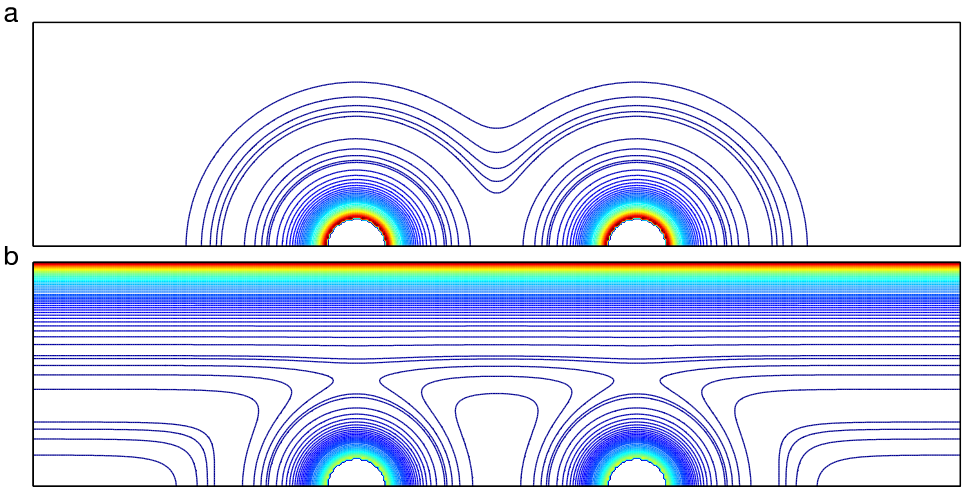

Figure 6: Two spheres confined in a charged cylindrical pore: calculated isopotential lines. A half-section of the physical geometry is shown, with the line of symmetry lying at the bottom. (a): Isolated spheres; (b): spheres confined in a pore. The pore wall is at the top.

future directions along this work is to develop some adaptive finite difference methods using the techniques proposed in this work. This may involve the use of mesh adaptivity, see, e.g., [12, 13].

The proposed numerical method for the Poisson-Boltzmann equation has been applied to the previously studied problems for electrostatic interaction of two identical particles. The numerical solutions agree well with those obtained by the adaptive finite element methods [4, 7]. Since the resulting linear system is diagonally dominant, the use of a multigrid method speeds up the convergence of the solutions.

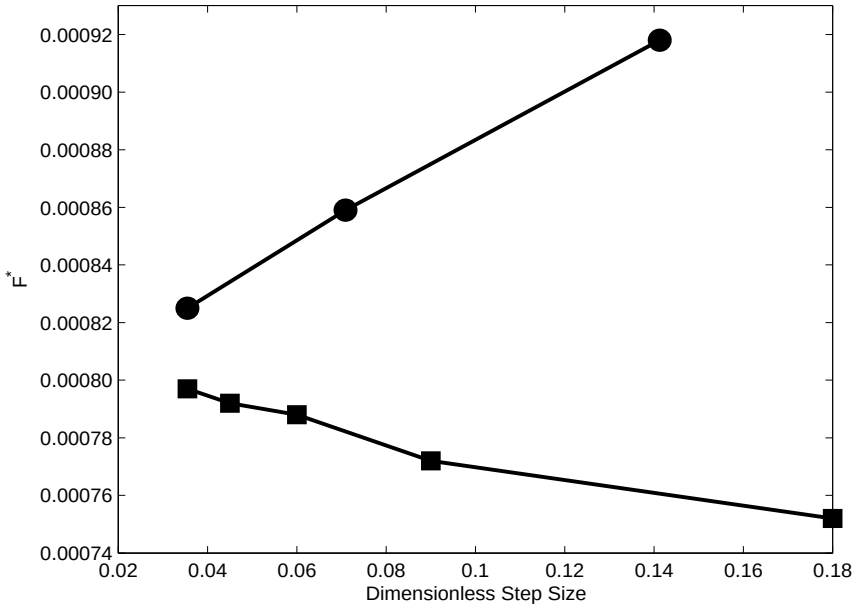

Figure 7: Comparison of the convergence of the force calculated in this paper ('•' line) and in the reference [5] (square dot line).

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