

# An Iterative Method for Finite-Element Solutions of the Nonlinear Poisson-Boltzmann Equation

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**Abstract:** A finite-element (FE) approach combined with an efficient iterative method have been used to provide a numerical solution of the nonlinear Poisson-Boltzmann equation. The iterative method solves the nonlinear equations arising from the FE discretization procedure by a node-by-node calculation. Moreover, some extensions called by Picard, Gauss-Seidel, and successive overrelaxation (SOR) methods are also presented and analyzed for the FE solution. The performances of the proposed methods are illustrated by applying them to the problem of two identical colloidal particles in a symmetric electrolyte. My numerical results are found in good agreement with the previous published results. A comprehensive survey is also given for the accuracy and efficiency of these methods.

**Key-Words:** finite-element method, Poisson-Boltzmann equation, colloidal particles interaction

## 1 Introduction

The nonlinear Poisson-Boltzmann (PB) equation describes, in some approximation, the electric potential and charge distribution in colloidal systems [1, 2]. Knowing the electrostatic potential, one can calculate other quantities such as the free energy of a colloidal system and the force of particle-particle interaction. Features of inter-particle interaction are of great importance in studying the stability of colloidal dispersions, the formation of colloidal crystals and membrane separation processes [3].

To obtain numerical solutions of the PB equation, one must solve a system of nonlinear algebraic equations resulting from a discretization by, for example, the finite-element (FE) method. The standard method for the solution is Newton's method or its variant [4]. Newton's method is a local method that converges quadratically in a sufficiently small neighborhood of the exact solution. It is very sensitive to initial guesses due to its local convergence property. We propose here an iterative method which is globally and monotonically convergent with simple upper or lower solutions of the PB equation as initial guesses [5].

The method of monotone iterations is a classical tool for the study of the existence of the solution of semilinear partial differential equations of certain types [6, 7, 8, 9]. It is also useful for the numerical solution of these types of problems approximated, for instance, by the finite difference [10, 11, 12], finite element [13], or boundary element [14, 15, 16] method.

It is a constructive method that depends essentially on only one parameter, called the monotone parameter herein, which determines the convergence behavior of the iterative process. Embedded in the widely used FE algorithm, four monotone iterative methods, namely, Jacobi, Picard, Gauss-Seidel, and SOR methods are presented and analyzed in this paper.

In the next section, we state the model problem from the colloidal system to the corresponding PB equation and FE algorithm. The model is subject to Dirichlet and Neumann types of conditions on various parts of the boundary of an irregular domain. Starting with the upper solution as an initial guess, it is shown in Section 3 that maximal sequences generated by Jacobi, Picard, Gauss-Seidel, and SOR iterations all converge monotonically from above to the unique solution of the resulting nonlinear system. In Section 4, we represent a part of our extensive numerical experiments on various confined and unconfined models to demonstrate the accuracy and efficiency of monotone properties of the proposed methods. Moreover, a short concluding remark is given in Section 5.

## 2 Description of the Problem

Owing to the symmetry, all of the problems considered have the same two-dimensional domain  $\Omega$  which is shown in Fig. 1. Segment CD is the wall of a cylindrical vessel, segment DE is the outlet, segment BC represents a midplane for the problems with two par-

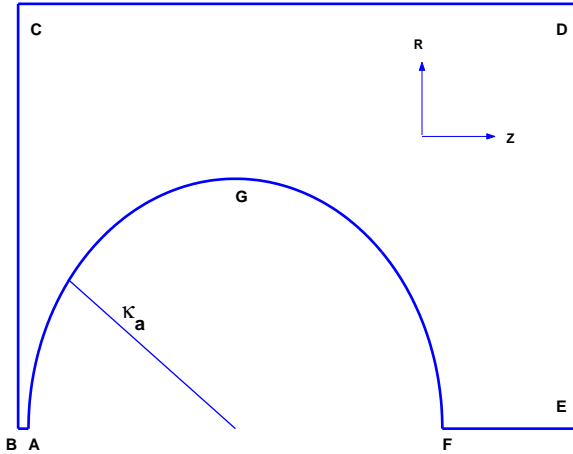


Figure 1: The domain for the problem of two interacting identical spherical particles.

ticles, segment AB is half the separation distance  $L$  and segment BE is the axis of rotational symmetry.

The dimensionless PB equation for electrostatic potential  $\Psi$  outside the spheres in cylindrical coordinates takes the form

$$\frac{\partial^2 \Psi}{\partial R^2} + \frac{1}{R} \frac{\partial \Psi}{\partial R} + \frac{\partial^2 \Psi}{\partial Z^2} = \sinh \Psi \quad (1)$$

Length, electrostatic potential, and force are respectively measured in units of Debye length  $\kappa^{-1} = (2nq_e^2/\epsilon kT)^{-1/2}$ ,  $kT/q_e$ , and  $\epsilon(kT/q_e)^2$ , where  $n$  is the concentration of any of the species in the electrolyte,  $q_e$  is the absolute value of electronic charge,  $\epsilon$  is the absolute permittivity of the electrolyte,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and the rationalized SI is used to express the factors.

To solve Eq. (1), it is necessary to define the potential  $\Psi$  and the potential gradient  $\partial\Psi/\partial N$  at the boundary  $\partial\Omega$  of the domain  $\Omega$ .  $N (= \kappa \mathbf{n})$  is the outward normal direction from the boundary  $\partial\Omega$ . In the present paper,  $\Psi = \Psi_s$  on the boundary AGF (which refers to the sphere surface), and  $\Psi = \Psi_m$  on the boundary CD (which refers to the pore wall). Axis symmetry of the geometry implies that derivatives with respect to the coordinates  $R$  on the line EF are assumed to be zero. Also, on the line DE natural boundary condition of the Neumann type is satisfied. The electric potentials within the spheres and the material surrounding the pore are constant.

The electric field is related to the potential by the equation  $\mathbf{E} = -\nabla\Psi$ . The force of interaction of the particles is obtained by means of direct integration of the total stress tensor over the appropriate surface. There are at least two possible ways of integrating: over the surface of the particle and over the midplane.

The dimensionless force obtained by integrating over the surface of the particle is calculated according to the expression

$$F_s = (\kappa_a)^2 \int_0^\pi |\nabla\Psi|^2 \cos\theta \sin\theta d\theta, \quad (2)$$

where  $\kappa_a$  is the dimensionless sphere radius. For the integration over the midplane, say  $\mathbf{M}$ , the dimensionless force is

$$F_m = \int_{\mathbf{M}} \left[ 2(\cosh \Psi - 1) + \left( \frac{\partial \Psi}{\partial R} \right)^2 - \left( \frac{\partial \Psi}{\partial Z} \right)^2 \right] R dR, \quad (3)$$

The latter case is more accurate since different pieces of the midplane contribute with the same sign.

### 3 Monotone Iterative Methods

Let  $\mathcal{T}$  be a FE partition of the domain  $\Omega$  such that  $\mathcal{T} = \{ \tau_j : j = 1, \dots, M, \bar{\Omega} = \cup_{j=1}^M \bar{\tau}_j \}$  and the system of nonlinear algebraic equations resulting from FE discretization is

$$\eta_i \psi_i - \sum_{k \in V(i)} \eta_k \psi_k = -R_i(\psi_i) + R_i^* \quad (4)$$

where the set  $V(i)$  of degrees of freedom satisfies  $\eta_k \neq 0, \forall k \in V(i), k \neq i$ , the function  $R(\cdot, \Psi)$  is nonlinear in  $\Psi$  describing the PB equation and  $R^*$  is prescribed in the boundary  $\partial\Omega$ . The diagonal dominance of the resulting matrices (i.e., M-matrices [17]) of the model problems provides not only stability of numerical solutions (i.e., no non-physical oscillations) but also convergence of iterative procedures. This is a basic hypothesis for the development of various monotone iterative schemes for (4).

**Definition 1** A vector  $\tilde{\Psi} \equiv (\tilde{\psi}_1, \dots, \tilde{\psi}_N) \in \mathbb{R}^N$  is called an upper solution of (4) if it satisfies the following inequality

$$\eta_i \tilde{\psi}_i - \sum_{k \in V(i)} \eta_k \tilde{\psi}_k \geq -R_i(\tilde{\psi}_i) + R_i^*, \quad (5)$$

and  $\hat{\Psi} \equiv (\hat{\psi}_1, \dots, \hat{\psi}_N) \in \mathbb{R}^N$  is called a lower solution if

$$\eta_i \hat{\psi}_i - \sum_{k \in V(i)} \eta_k \hat{\psi}_k \leq -R_i(\hat{\psi}_i) + R_i^*, \quad (6)$$

for  $1 \leq i \leq N$  where  $N$  is the total number of node points.

Given any ordered lower and upper solutions  $\hat{\Psi}$  and  $\tilde{\Psi}$ , we define the solution sections by

$$\begin{aligned}\langle \hat{\Psi}, \tilde{\Psi} \rangle &\equiv \{ \Psi \in \mathbb{R}^N; \hat{\Psi} \leq \Psi \leq \tilde{\Psi} \} \\ \langle \hat{\psi}_i, \tilde{\psi}_i \rangle &\equiv \{ \psi_i \in \mathbb{R}; \hat{\psi}_i \leq \psi_i \leq \tilde{\psi}_i \}.\end{aligned}$$

### 3.1 Jacobi Method

Now we introduce the maximal sequence. Let  $\bar{V}^{(0)} = \tilde{\Psi}$  be an initial iterate. We construct a sequence  $\{\bar{V}^{(m+1)}\}$  by solving the linear system

$$\begin{aligned}\eta_i \bar{v}_i^{(m+1)} &- \sum_{k \in V(i)} \eta_k \bar{v}_k^{(m)} + \bar{\gamma}_i^{(m+1)} \bar{v}_i^{(m+1)} \\ &= \bar{\gamma}_i^{(m+1)} \bar{v}_i^{(m)} - R_i(\bar{v}_i^{(m)}) + R_i^*,\end{aligned}\quad (7)$$

for  $m = 0, 1, 2, \dots$ ,  $1 \leq i \leq N$  and the monotone parameter  $\bar{\gamma}_i^{(m+1)}$  is defined by

$$\bar{\gamma}_i^{(m+1)} \equiv \frac{\partial R_i(\bar{v}_i^{(m)})}{\partial \psi_i}.\quad (8)$$

For the maximal sequence we have the following properties [18, 12].

**Lemma 2** Assume the nonlinear function  $R_i(\psi_i)$  is monotone increasing and concave up with respect to  $\psi_i$ , i.e.,  $\partial^2 R_i / \partial \psi_i^2 > 0$ . Then the maximal sequence  $\{\bar{V}^{(m)}\}$  given by (7) with  $\bar{V}^{(0)} = \tilde{\Psi}$  possesses the monotone property

$$\hat{\Psi} \leq \bar{V}^{(m+1)} \leq \bar{V}^{(m)} \leq \tilde{\Psi}, \quad m = 0, 1, 2, \dots\quad (9)$$

Moreover, for each  $m$ ,  $\bar{V}^{(m)}$  is also an upper solution.

*Proof.* Let  $e_i^{(0)} \equiv \bar{v}_i^{(0)} - \bar{v}_i^{(1)} = \tilde{\psi}_i - \bar{v}_i^{(1)}$ . By (7) we have

$$\begin{aligned}(\eta_i + \bar{\gamma}_i^{(1)})e_i^{(0)} &= (\eta_i + \bar{\gamma}_i^{(1)})\tilde{\psi}_i \\ &- \left[ \sum_{k \in V(i)} \eta_k \bar{v}_k^{(0)} + \bar{\gamma}_i^{(1)} \bar{v}_i^{(0)} - R_i(\bar{v}_i^{(0)}) + R_i^* \right] \\ &= \eta_i \tilde{\psi}_i - \sum_{k \in V(i)} \eta_k \tilde{\psi}_k + R_i(\tilde{\psi}_i) - R_i^* \geq 0.\end{aligned}$$

In view of  $e_i^{(0)} \geq 0$  for all  $1 \leq i \leq N$ . This leads to  $\bar{V}^{(1)} \leq \tilde{\Psi}$ .

Assume, by induction, that  $\bar{v}_i^{(m)} \leq \bar{v}_i^{(m-1)}$  for some  $m > 1$ . By (7)  $e_i^{(m)} \equiv \bar{v}_i^{(m)} - \bar{v}_i^{(m+1)}$  satisfies

$$\begin{aligned}(\eta_i + \bar{\gamma}_i^{(m+1)})e_i^{(m)} &= \sum_{k \in V(i)} \eta_k (\bar{v}_k^{(m-1)} - \bar{v}_k^{(m)}) \\ &- R_i(\bar{v}_i^{(m-1)}) + R_i(\bar{v}_i^{(m)}) + \bar{\gamma}_i^{(m)} \bar{v}_i^{(m-1)} \\ &- \bar{\gamma}_i^{(m)} \bar{v}_i^{(m)}.\end{aligned}$$

By  $\partial^2 R / \partial \Psi^2 \geq 0$  and the mean value theorem, we have

$$\begin{aligned}R_i(\bar{v}_i^{(m-1)}) - R_i(\bar{v}_i^{(m)}) &\leq \frac{\partial R_i(\bar{v}_i^{(m-1)})}{\partial \psi_i} \\ &\quad (\bar{v}_i^{(m-1)} - \bar{v}_i^{(m)}), \\ R_i(\bar{v}_i^{(m-1)}) - R_i(\bar{v}_i^{(m)}) &\leq \bar{\gamma}_i^{(m)} \bar{v}_i^{(m-1)} - \bar{\gamma}_i^{(m)} \bar{v}_i^{(m)}.\end{aligned}$$

This yields  $e_i^{(m)} \geq 0$  which shows that  $\bar{v}_i^{(m+1)} \leq \bar{v}_i^{(m)}$  and hence monotone property (9) thus follows by induction.

To show that  $\hat{\Psi} \leq \bar{V}^{(m+1)}$ , we assume, by induction, that  $\hat{\psi}_i \leq \bar{v}_i^{(m)}$  for some  $m > 1$ . By (6) and (7) we have

$$\begin{aligned}(\eta_i + \bar{\gamma}_i^{(m+1)})(\bar{v}_i^{(m+1)} - \hat{\psi}_i) &= -(\eta_i + \bar{\gamma}_i^{(m+1)})\hat{\psi}_i \\ &+ \left[ \sum_{k \in V(i)} \eta_k \bar{v}_k^{(m)} + \bar{\gamma}_i^{(m+1)} \bar{v}_i^{(m)} - R_i(\bar{v}_i^{(m)}) + R_i^* \right] \\ &\geq \sum_{k \in V(i)} \eta_k (\bar{v}_k^{(m)} - \hat{\psi}_k) \\ &+ \left[ \bar{\gamma}_i^{(m+1)} \bar{v}_i^{(m)} - \bar{\gamma}_i^{(m+1)} \hat{\psi}_i + R_i(\hat{\psi}_i) - R_i(\bar{v}_i^{(m)}) \right].\end{aligned}$$

By the concave up property of  $R_i(u_i)$  and the mean value theorem again, we have

$$\bar{\gamma}_i^{(m+1)} \bar{v}_i^{(m)} - \bar{\gamma}_i^{(m+1)} \hat{\psi}_i + R_i(\hat{\psi}_i) - R_i(\bar{v}_i^{(m)}) \geq 0.$$

This yields  $(\eta_i + \bar{\gamma}_i^{(m+1)})(\bar{v}_i^{(m+1)} - \hat{\psi}_i) \geq 0$  which shows

$$\bar{v}_i^{(m+1)} \geq \hat{\psi}_i.$$

To show that  $\bar{V}^{(m+1)}$  is an upper solution for each  $m$ , we observe from (7) and the monotone property of  $\{\bar{V}^{(m)}\}$  that

$$\begin{aligned}\eta_i \bar{v}_i^{(m+1)} &= \sum_{k \in V(i)} \eta_k \bar{v}_k^{(m)} - \bar{\gamma}_i^{(m+1)} \bar{v}_i^{(m+1)} \\ &+ \bar{\gamma}_i^{(m+1)} \bar{v}_i^{(m)} - R_i(\bar{v}_i^{(m)}) + R_i^*, \\ &\geq \sum_{k \in V(i)} \eta_k \bar{v}_k^{(m+1)} + \left[ -\bar{\gamma}_i^{(m+1)} \bar{v}_i^{(m+1)} \right. \\ &\quad \left. + \bar{\gamma}_i^{(m+1)} \bar{v}_i^{(m)} - R_i(\bar{v}_i^{(m)}) \right] + R_i^*.\end{aligned}$$

By the concave up property of  $R_i(u_i)$  and the mean value theorem, we have

$$\bar{\gamma}_i^{(m+1)} [\bar{v}_i^{(m)} - \bar{v}_i^{(m+1)}] \geq R_i(\bar{v}_i^{(m)}) - R_i(\bar{v}_i^{(m+1)}).$$

Therefore,

$$\eta_i \bar{v}_i^{(m+1)} \geq \sum_{k \in V(i)} \eta_k \bar{v}_k^{(m+1)} - R_i(\bar{v}_i^{(m+1)}) + R_i^*.$$

This shows that  $\bar{V}^{(m)}$  is an upper solution.

**Theorem 3** Assume conditions in Lemma 2 hold. Then the sequence  $\{\bar{V}^{(m)}\}$  generated by solving (7) with  $\bar{V}^{(0)} = \tilde{\Psi}$  converge monotonically to the solution  $\bar{V}$  of (4). Moreover

$$\hat{\Psi} \leq \bar{V} \leq \bar{V}^{(m+1)} \leq \bar{V}^{(m)} \leq \tilde{\Psi}, \quad m = 1, 2, \dots \quad (10)$$

and if  $\Psi^*$  is any solution of (4) in  $\langle \hat{\Psi}, \tilde{\Psi} \rangle$  then

$$\hat{\Psi} \leq \Psi^* \leq \bar{V}.$$

*Proof.* By Lemma 2 and the completeness property, the limit  $\lim_{m \rightarrow \infty} \bar{V}^{(m)} = \bar{V}$  exists and satisfies the relation (10). Now if  $\Psi^* \in \langle \hat{\Psi}, \tilde{\Psi} \rangle$  is a solution of (4) then  $\tilde{\Psi}$  and  $\Psi^*$  are ordered upper and lower solutions. Using  $\bar{V}^{(0)} = \tilde{\Psi}$ , Lemma 2 implies that  $\bar{V}^{(m)} \geq \Psi^*$  for every  $m$ . Letting  $m \rightarrow \infty$  gives  $\bar{V} \geq \Psi^*$ . This proves the theorem.

### 3.2 Picard and Gauss-Seidel Methods

Let  $\mathcal{A}$  be the matrix obtained by FE discretization. It can be written in the split form  $\mathcal{A} = \mathcal{D} - \mathcal{L} - \mathcal{U}$ , where  $\mathcal{D}$ ,  $\mathcal{L}$  and  $\mathcal{U}$  are the diagonal, lower-off diagonal and upper-off diagonal matrices of  $\mathcal{A}$ , respectively. The elements of  $\mathcal{D}$  are positive and those of  $\mathcal{L}$  and  $\mathcal{U}$  are nonnegative. Using  $\hat{\Psi}$  and  $\tilde{\Psi}$  as the initial iterates we can construct the three maximal sequences by the three iterative schemes defined as follows:

#### (a) Picard method

$$\begin{aligned} & (\mathcal{A} + \bar{\Gamma}_P^{(m+1)}) \bar{V}_P^{(m+1)} \\ &= \bar{\Gamma}_P^{(m+1)} \bar{V}_P^{(m)} - R(\bar{V}_P^{(m)}) + R^*, \end{aligned} \quad (11)$$

#### (b) Gauss-Seidel method

$$\begin{aligned} & (\mathcal{D} - \mathcal{L} + \bar{\Gamma}_G^{(m+1)}) \bar{V}_G^{(m+1)} = \mathcal{U} \bar{V}_G^{(m)} \\ & + \bar{\Gamma}_G^{(m+1)} \bar{V}_G^{(m)} - R(\bar{V}_G^{(m)}) + R^*, \end{aligned} \quad (12)$$

#### (c) Jacobi method

$$\begin{aligned} & (\mathcal{D} + \bar{\Gamma}_J^{(m+1)}) \bar{V}_J^{(m+1)} = (\mathcal{L} + \mathcal{U}) \bar{V}_J^{(m)} \\ & + \bar{\Gamma}_J^{(m+1)} \bar{V}_J^{(m)} - R(\bar{V}_J^{(m)}) + R^*, \end{aligned} \quad (13)$$

where

$$\bar{\Gamma}_P^{(m+1)} \equiv \text{diag}(\bar{\gamma}_{P,i}^{(m+1)}), \bar{\gamma}_{P,i}^{(m+1)} \equiv \frac{\partial R_i(\bar{v}_{P,i}^{(m)})}{\partial \psi_i}, \quad (14)$$

$$\bar{\Gamma}_G^{(m+1)} \equiv \text{diag}(\bar{\gamma}_{G,i}^{(m+1)}), \bar{\gamma}_{G,i}^{(m+1)} \equiv \frac{\partial R_i(\bar{v}_{G,i}^{(m)})}{\partial \psi_i}, \quad (15)$$

$$\bar{\Gamma}_J^{(m+1)} \equiv \text{diag}(\bar{\gamma}_{J,i}^{(m+1)}), \bar{\gamma}_{J,i}^{(m+1)} \equiv \frac{\partial R_i(\bar{v}_{J,i}^{(m)})}{\partial \psi_i}, \quad (16)$$

and the initial guesses are  $\bar{V}_P^{(0)} = \bar{V}_G^{(0)} = \bar{V}_J^{(0)} = \tilde{\Psi}$ . The following lemma gives the monotone property of these sequences.

**Lemma 4** Assume the conditions in Lemma 2 hold. Then the maximal sequence  $\{\bar{V}^{(m)}\}$  given by either one of the iterative schemes (11)-(13) with  $\bar{V}^{(0)} = \tilde{\Psi}$  possesses the monotone property (10).

**Theorem 5** Assume the conditions of Lemma 2 hold. Then each of the maximal sequences  $\bar{V}_G^{(m)}, \bar{V}_J^{(m)}, \bar{V}_P^{(m)}$  converges monotonically to the solution  $\bar{V}$  of (4) and satisfies the relation (10). Moreover,

$$\bar{V}_P^{(m)} \leq \bar{V}_G^{(m)} \leq \bar{V}_J^{(m)}, \quad (17)$$

for every  $m = 1, 2, 3, \dots$

### 3.3 SOR Method

Typically for the linear system  $\mathcal{A}x = b$  overrelaxation is based on the splitting

$$\omega \mathcal{A} = (\mathcal{D} - \omega \mathcal{L}) - [(1 - \omega) \mathcal{D} + \omega \mathcal{U}],$$

and the corresponding successive overrelaxation (SOR) method is given by the recursion

$$(\mathcal{D} - \omega \mathcal{L})x^{(m+1)} = [(1 - \omega) \mathcal{D} + \omega \mathcal{U}]x^{(m)} + \omega b,$$

where  $\omega$  is called the acceleration parameter. For the nonlinear system solved by the monotone iterative method we define

$$\begin{aligned} & (\mathcal{D} + \bar{\Gamma}_S^{(m+1)} - \omega \mathcal{L}) \bar{V}_S^{(m+1)} \\ &= [(1 - \omega)(\mathcal{D} + \bar{\Gamma}_S^{(m+1)}) + \omega \mathcal{U}] \bar{V}_S^{(m)} \\ &+ \omega [\bar{\Gamma}_S^{(m+1)} \bar{V}_S^{(m)} - R(\bar{V}_S^{(m)}) + R^*], \end{aligned} \quad (18)$$

where the monotone parameter  $\bar{\Gamma}_S^{(m+1)}$  is defined by

$$\bar{\Gamma}_S^{(m+1)} \equiv \text{diag}(\bar{\gamma}_{S,i}^{(m+1)}), \bar{\gamma}_{S,i}^{(m+1)} \equiv \frac{\partial R_i(\bar{v}_{S,i}^{(m)})}{\partial \psi_i}. \quad (19)$$

**Lemma 6** Assume the conditions in Lemma 2 hold. Moreover, if

$$0 < \omega \leq 1. \quad (20)$$

Then the maximal sequence  $\{\bar{V}_S^{(m)}\}$  given by the iterative scheme (18) with  $\bar{V}_S^{(0)} = \tilde{\Psi}$  possesses the monotone property (10). Moreover, for each  $m$ ,  $\bar{V}_S^{(m)}$  is also an upper solution.

*Proof.* Let  $E^{(0)} \equiv \bar{V}_S^{(0)} - \bar{V}_S^{(1)} = \tilde{\Psi} - \bar{V}_S^{(1)}$ . By (18) we have

$$\begin{aligned} & (\mathcal{D} + \bar{\Gamma}_S^{(1)} - \omega\mathcal{L})E^{(0)} \\ &= (\mathcal{D} + \bar{\Gamma}_S^{(1)} - \omega\mathcal{L})(\tilde{\Psi} - \bar{V}_S^{(1)}) \\ &= (\mathcal{D} + \bar{\Gamma}_S^{(1)} - \omega\mathcal{L})\tilde{\Psi} \\ &\quad - \left[ (1 - \omega)(\mathcal{D} + \bar{\Gamma}_S^{(1)}) + \omega\mathcal{U} \right] \bar{V}_S^{(0)} \\ &\quad - \omega \left[ \bar{\Gamma}_S^{(1)} \bar{V}_S^{(0)} - R(\bar{V}_S^{(0)}) + R^* \right] \\ &= \omega \left[ (\mathcal{D} - \mathcal{L} - \mathcal{U})\tilde{\Psi} + R(\tilde{\Psi}) - R^* \right]. \end{aligned}$$

Here  $\tilde{\Psi}$  is an upper solution  $\omega > 0$  and  $(\mathcal{D} + \bar{\Gamma}_S^{(1)} - \omega\mathcal{L})^{-1}$  exists and is nonnegative (cf. [17]). Therefore  $E^{(0)} \geq 0$ , i.e.,  $\bar{V}_S^{(1)} \leq \tilde{\Psi}$ .

Assume, by induction, that  $\bar{V}_S^{(m)} \leq \bar{V}_S^{(m-1)}$  for some  $m > 1$ . By (18)  $E^{(m)} \equiv \bar{V}_S^{(m)} - \bar{V}_S^{(m+1)}$  satisfies

$$\begin{aligned} & (\mathcal{D} + \bar{\Gamma}_S^{(m+1)} - \omega\mathcal{L})E^{(m)} = (\bar{\Gamma}_S^{(m+1)} - \bar{\Gamma}_S^{(m)})\bar{V}_S^{(m)} \\ &+ (\mathcal{D} + \bar{\Gamma}_S^{(m)} - \omega\mathcal{L})\bar{V}_S^{(m)} - (\mathcal{D} + \bar{\Gamma}_S^{(m+1)} - \omega\mathcal{L})\bar{V}_S^{(m+1)} \\ &= (\bar{\Gamma}_S^{(m+1)} - \bar{\Gamma}_S^{(m)})\bar{V}_S^{(m)} \\ &+ \left[ (1 - \omega)(\mathcal{D} + \bar{\Gamma}_S^{(m)}) + \omega\mathcal{U} \right] \bar{V}_S^{(m-1)} \\ &+ \omega \left[ \bar{\Gamma}_S^{(m)} \bar{V}_S^{(m-1)} - R(\bar{V}_S^{(m-1)}) + R^* \right] \\ &\quad - \left[ (1 - \omega)(\mathcal{D} + \bar{\Gamma}_S^{(m+1)}) + \omega\mathcal{U} \right] \bar{V}_S^{(m)} \\ &\quad - \omega \left[ \bar{\Gamma}_S^{(m+1)} \bar{V}_S^{(m)} - R(\bar{V}_S^{(m)}) + R^* \right] \\ &= (\bar{\Gamma}_S^{(m+1)} - \bar{\Gamma}_S^{(m)})\bar{V}_S^{(m)} \\ &+ [(1 - \omega)\mathcal{D} + \omega\mathcal{U}] (\bar{V}_S^{(m-1)} - \bar{V}_S^{(m)}) \\ &+ \bar{\Gamma}_S^{(m)} \bar{V}_S^{(m-1)} + \omega[-R(\bar{V}_S^{(m-1)})] \\ &\quad - \bar{\Gamma}_S^{(m+1)} \bar{V}_S^{(m)} - \omega[-R(\bar{V}_S^{(m)})] \\ &= [(1 - \omega)\mathcal{D} + \omega\mathcal{U}] (\bar{V}_S^{(m-1)} - \bar{V}_S^{(m)}) \\ &+ \omega \left[ \bar{\Gamma}_S^{(m)} \bar{V}_S^{(m-1)} - R(\bar{V}_S^{(m-1)}) \right. \\ &\quad \left. - \bar{\Gamma}_S^{(m)} \bar{V}_S^{(m)} + R(\bar{V}_S^{(m)}) \right]. \end{aligned}$$

Similarly, we can use (20), concave up property of  $R(\cdot)$  and the mean value theorem to have

$$(\mathcal{D} + \bar{\Gamma}_S^{(m+1)} - \omega\mathcal{L})E^{(m)} \geq 0.$$

Therefore  $E^{(m)} \geq 0$ , i.e.,  $\bar{V}_S^{(m+1)} \leq \bar{V}_S^{(m)}$ .

To show that  $\bar{V}_S^{(m+1)}$  is an upper solution, we consider (18),

$$(\mathcal{D} + \bar{\Gamma}_S^{(m+1)} - \omega\mathcal{L})\bar{V}_S^{(m+1)}$$

$$\begin{aligned} &= (\mathcal{D} + \bar{\Gamma}_S^{(m+1)})\bar{V}_S^{(m)} + \omega(-\mathcal{D} - \bar{\Gamma}_S^{(m+1)} + \mathcal{U})\bar{V}_S^{(m)} \\ &+ \omega \left[ \bar{\Gamma}_S^{(m+1)} \bar{V}_S^{(m)} - R(\bar{V}_S^{(m)}) + R^* \right]. \end{aligned}$$

After moving the terms,  $(\mathcal{D} + \bar{\Gamma}_S^{(m+1)})\bar{V}_S^{(m+1)}$ , to the right-hand side and using (20), we obtain

$$\begin{aligned} -\omega\mathcal{L}\bar{V}_S^{(m+1)} &= -\mathcal{D}\bar{V}_S^{(m+1)} + (1 - \omega)\mathcal{D}\bar{V}_S^{(m)} + \omega\mathcal{U}\bar{V}_S^{(m)} \\ &\quad + \bar{\Gamma}_S^{(m+1)} (\bar{V}_S^{(m)} - \bar{V}_S^{(m+1)}) + \omega \left[ -R(\bar{V}_S^{(m)}) + R^* \right] \\ &\geq -\mathcal{D}\bar{V}_S^{(m+1)} + (1 - \omega)\mathcal{D}\bar{V}_S^{(m)} + \omega\mathcal{U}\bar{V}_S^{(m)} \\ &\quad + \omega \left[ \bar{\Gamma}_S^{(m+1)} (\bar{V}_S^{(m)} - \bar{V}_S^{(m+1)}) - R(\bar{V}_S^{(m)}) + R^* \right]. \end{aligned}$$

By the mean value theorem and  $\bar{V}_S^{(m)} \geq \bar{V}_S^{(m+1)}$  we have

$$\begin{aligned} -\omega\mathcal{L}\bar{V}_S^{(m+1)} &\geq -\mathcal{D}\bar{V}_S^{(m+1)} + (1 - \omega)\mathcal{D}\bar{V}_S^{(m)} \\ &\quad + \omega\mathcal{U}\bar{V}_S^{(m+1)} + \omega \left[ -R(\bar{V}_S^{(m+1)}) + R^* \right] \end{aligned}$$

After adding the term,  $\omega\mathcal{D}\bar{V}_S^{(m+1)}$  and using the fact  $\omega \leq 1$ , we obtain

$$\begin{aligned} \omega(\mathcal{D} - \mathcal{L})\bar{V}_S^{(m+1)} &\geq (1 - \omega)\mathcal{D}(\bar{V}_S^{(m)} - \bar{V}_S^{(m+1)}) \\ &\quad + \omega\mathcal{U}\bar{V}_S^{(m+1)} + \omega \left[ -R(\bar{V}_S^{(m+1)}) + R^* \right] \\ &\geq \omega\mathcal{U}\bar{V}_S^{(m+1)} + \omega \left[ -R(\bar{V}_S^{(m+1)}) + R^* \right]. \end{aligned}$$

Therefore, we move the term,  $\omega\mathcal{U}\bar{V}_S^{(m+1)}$ , to the left-hand side and cancel the  $\omega$  to have

$$(\mathcal{D} - \mathcal{L} - \mathcal{U})\bar{V}_S^{(m+1)} \geq -R(\bar{V}_S^{(m+1)}) + R^*.$$

This proves that  $\bar{V}_S^{(m+1)}$  is an upper solution.

## 4 Results and Discussions

### 4.1 Interaction of Two Identical Charged Spherical Particles

This problem deals with two identical colloidal particles immersed in symmetrical 1:1 electrolyte. It was studied in several works and can serve as a test [1, 19, 20]. In the present paper, the force of interaction of two particles of the radius  $\kappa_a = 10.0$  and  $5.0$  were calculated for the separation distance  $L = 1.0$  and  $0.5$  respectively. The constant potential  $\Psi_S$  on the surfaces of both particles was equal to  $2.0$ . The Neumann boundary conditions  $\partial\Psi/\partial\mathbf{n} = \mathbf{0}$  are implied on the other boundaries of the domain.

A typical mesh and solution are shown in Fig. 2 and 3 for a case of two interacting spherical particles with  $\kappa_a = 5$ ,  $\Psi_s = 2$  and  $L = 0.25$ . Table 1 shows re-

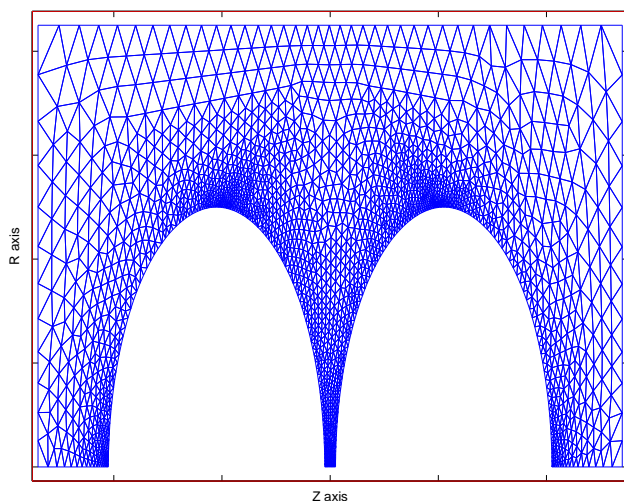


Figure 2: The mesh for the problem of two interacting identical charged spherical particles.

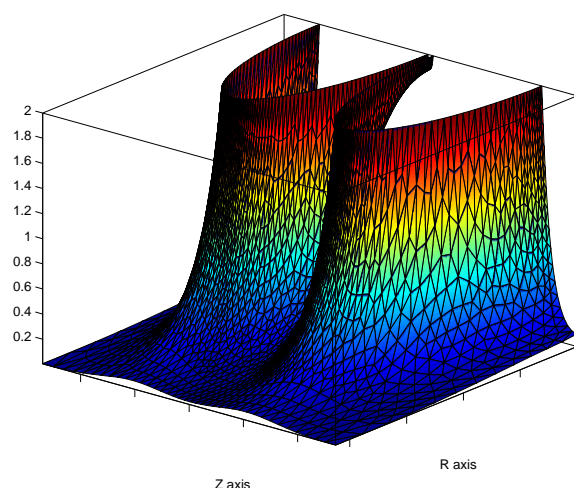


Figure 3: The numerical solution for the problem of two interacting identical charged spherical particles.

sults for the dimensionless electrostatic force between two identical spherical particles for given conditions, which compared with some previously published papers. The results are in good agreement of ours.

Table 1

The Dimensionless Force between Two Particles

$\kappa_a$	$F_m$	$F_{p1}$	$F_{p2}$	$F_{p3}$
10.0	19.852	20.101	19.892	20.048
5.0	15.509	15.509	15.476	15.545

Note that  $F_m$  is the force on the midplane,  $F_{p1}$  is the force from previous results [1],  $F_{p2}$  is the force from previous results [21], and  $F_{p3}$  is the force from previous results [19].

#### 4.2 Interaction of Two Identical Charged Spherical Particles Confined within a Charged Cylindrical Pore

This problem deals with the long-range electrostatic interaction of two charged spheres confined in a like-charged cylindrical pore. The same parameters are used, e.g., the 1:1 electrolyte, the constant potential on the cylindrical pore  $\Psi_P = 5.0$ , and the constant potential on the spheres  $\Psi_S = 3.0$ . The radius of the particles is  $\kappa_a = 1.185$  and the sphere radius to pore radius ratio is  $\lambda = 0.13$ . Fig. 4 shows the isopotential plot for two isolated spheres ( $\Psi_S = 3.0$ ) and two spheres confined in a pore ( $\Psi_S = 3.0$  and  $\Psi_P = 5.0$ ). They are found in good agreement with the published results, see, e.g., [22]. Fig. 5 shows the numerical solution for the confined case.

In order to observe the behavior of the error reduction for various iterative schemes the error  $\|e^{(m)}\|_\infty \equiv \|\bar{v}^{(m)} - \bar{v}^{(m-1)}\|_\infty$  is defined and the stopping criterion for these iterations is determined from the condition  $\|e^{(m)}\|_\infty \leq 1.0E-6$ . Fig. 6 shows the typical phenomena of monotone convergence in various schemes for the confined case ( $\Psi_S = 3.0$  and  $\Psi_P = 5.0$ ). The behaviors of the residual,  $\|A\bar{V}^{(m)} + R(\bar{V}^{(m)})\|_\infty$ , of various methods are shown in Fig. 7. Since the solution figure and the convergence behavior are similar, we skip the unconfined case ( $\Psi_S = 3.0$ ).

Table 2

The *Nit* and CPU Time Versus Various Methods

$\Psi_S = 3.0$	Picard (G)	Picard (S)	GS	Jacobi	SOR
<i>nit</i>	7	7	874	1707	252
Time (Sec)	377	27	13	20	8
$\Psi_S = 3.0$	Picard (G)	Picard (S)	GS	Jacobi	SOR
$\Psi_P = 5.0$					
<i>nit</i>	9	9	942	1767	256
Time (Sec)	385	30	14	21	8

In the table, *nit* denotes the number of iterations, Time is the CPU time (Intel Pentium D 820), Picard



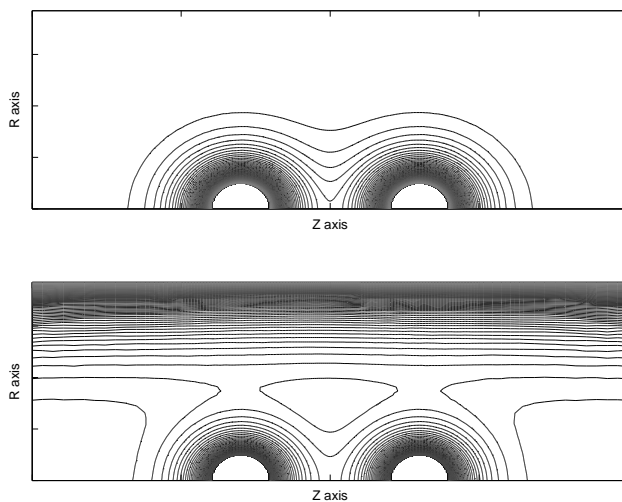


Figure 4: Calculated isopotential lines for the problem considered in subsection 4.2. A half-section of the physical geometry is shown, with the line of symmetry lying at the bottom. On the top of the graph, isolated spheres; on the bottom of the graph, spheres confined in a pore. The pore wall is at the top.

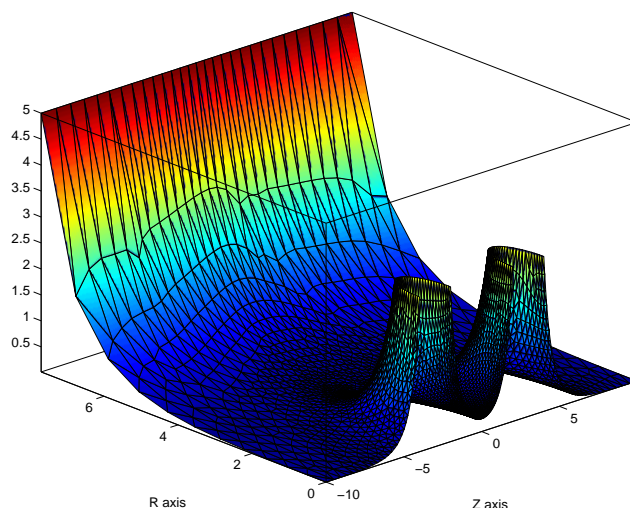


Figure 5: The numerical solution for the case of spheres confined in a pore.

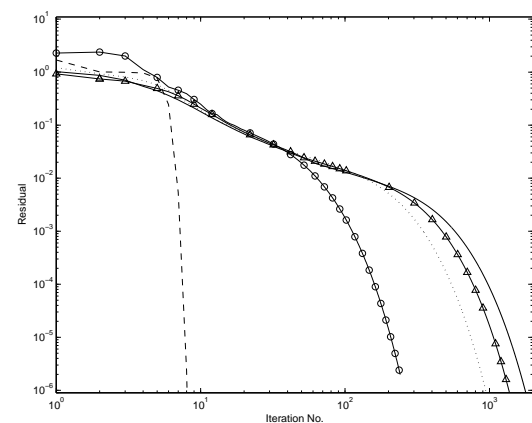


Figure 6: The residual versus the number of iterations for the case of two isolated spheres. Solid line: Jacobi method, dotted line: Gauss-Seidel method and dashed line: Picard method. Solid line with triangles: SOR method with  $\omega=0.8$ , Solid line with circles: SOR method with  $\omega=1.6$ .

(G) means Picard method with Gaussian elimination for the linear solver, Picard (S) means Picard method with Gauss-Seidel method for the linear solver, GS is the Gauss-Seidel method and SOR is successive overrelaxation method with  $\omega = 1.6$ . The convergence of the Picard method is the fastest, then the SOR method, and then the Gauss-Seidel method and the Jacobi method follows accordingly. On the one hand the iterative behavior of the Picard method is remarkable for its fast convergence. It is finished after seventh ( $\Psi_S = 3.0$ ) and ninth ( $\Psi_S = 3.0$   $\Psi_P = 5.0$ ) iterative step and more faster than Gauss-Seidel and Jacobi methods. This phenomenon verifies Theorem 5. On the other hand the memory storage and the CPU time consuming in Gaussian elimination are the drawbacks of the Picard method. Fig. 8 shows the number of iterations versus the acceleration parameter for the case of spheres confined in a pore. The best value of  $\omega$  is 1.8.

**Remark 7** In literature, reordering rows and columns is one of important ingredients used in parallel implementations of both direct and iterative solution techniques. The type of reordering used in applications depends on whether a direct or an iterative method is being considered. In 1972, George [23, 24] observed that reversing the Cuthill-McKee (RCM) ordering yields a better scheme used to enhance the effectiveness of sparse Gaussian elimination. We implement the RCM algorithm to survey the influence on the monotone iterative schemes. Figs. 9 and 10 show a more compact pattern produced by RCM scheme. However, the iteration numbers and CPU times do not be reduced for all monotone

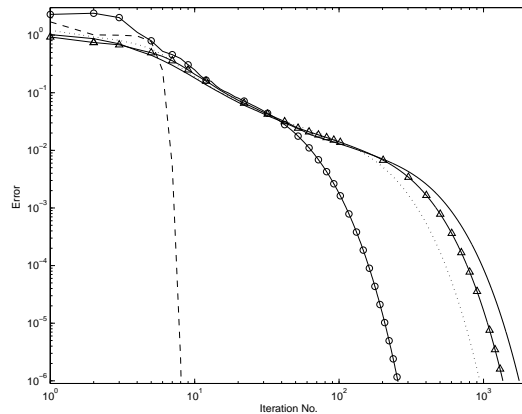


Figure 7: The error versus the number of iterations for the case of spheres confined in a pore. Solid line: Jacobi method, dotted line: Gauss-Seidel method and dashed line: Picard method. Solid line with triangles: SOR method with  $\omega=0.8$ , Solid line with circles: SOR method with  $\omega=1.6$ .

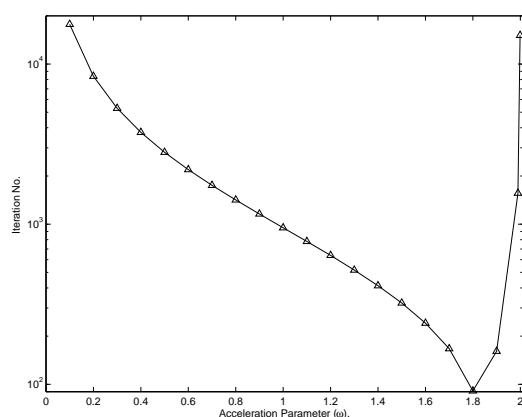


Figure 8: The number of iterations versus the acceleration parameter for the case of spheres confined in a pore.

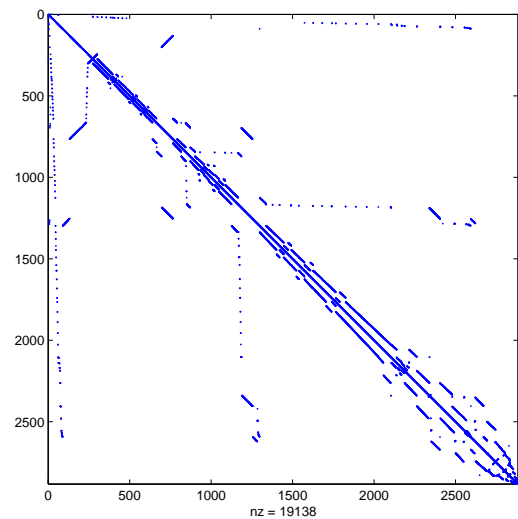


Figure 9: The matrix pattern before RCM ordering.

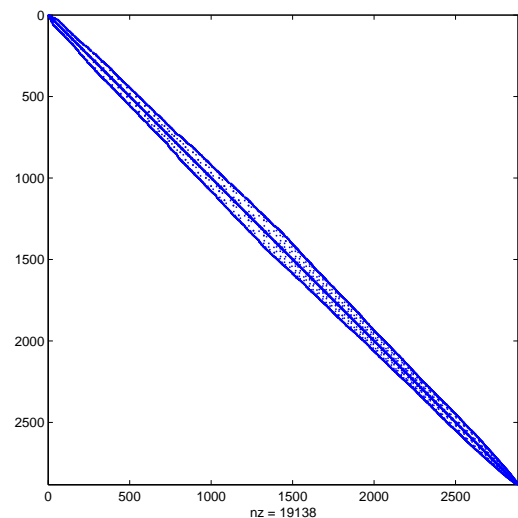


Figure 10: The matrix pattern after RCM ordering.

schemes. The incomplete LU factorization and multigrid methods should be considered to speed up the convergence in the future.

## 5 Conclusion

An iterative method for finite-element solutions named as the monotone iterative method is proposed for the study of the nonlinear Poisson-Boltzmann equation. With the help of the special nonlinear property we can construct the maximal sequences which converge decreasingly to the solution of the PB equation. These iterative methods are globally and monotonically convergent with simple upper solutions of the PB equation as initial guesses. Picard, Gauss-Seidel, Jacobi and SOR monotone iterative methods



are completely presented for the FE solutions. Several numerical examples are also given and found in good agreement with the previous published results. However, it is worthy pointing out that the theoretical analysis of convergence for the SOR method in the case  $1 < \omega < 2$  is still open, and it, we hope, will come in the near future.

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