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

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Abstract: A finite-element 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. The performance of the proposed method is illustrated by applying it 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.

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 [2, 7]. 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 [11].

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 [1]. 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]. Picard, Gauss-Seidel and Jacobi monotone iterative methods are completely presented for the FE solutions.

2 Description of the Problem

Owing to the symmetry, all of the problems considered have the same two-dimensional domain Ω which

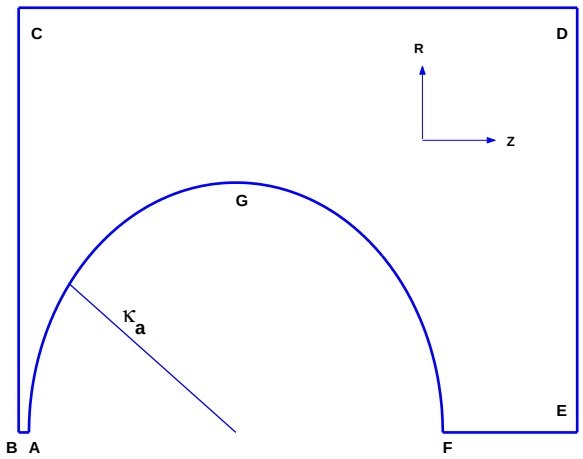

Figure 1: The domain for the problem of two interacting identical spherical particles.

is shown in Fig. 1. Segments CD is the wall of a cylindrical vessel, segment DE is the outlet, segment BC represents a midplane for the problems with two particles, segment AB is half the separation distance L and segment BE is the axis of rotational symmetry.

The dimensionless PB equation for electrostatic potential Ψ outside the spheres in cylindrical coordinates takes the form

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

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, ϵ 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.

The electric field is related to the potential by the equation $\boldsymbol{E} = -\nabla\Psi$. 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

$$F_s = (\kappa_a)^2 \int_0^{\pi} |\nabla\Psi|^2 \cos\theta \sin\theta \; d\theta, \qquad (2)$$

where κ_a is the dimensionless sphere radius. For the integration over the midplane, say **M**, the dimensionless force is

$$\begin{aligned} F_m &= \int_{\mathbf{M}} \left[2(\cosh\Psi - 1) + \left(\frac{\partial\Psi}{\partial R}\right)^2 \right. \\ &- \left. \left(\frac{\partial\Psi}{\partial Z}\right)^2 \right] R \; dR, \end{aligned} \qquad (3)$$

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

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

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 Ψ describing the PB equation and R^* is prescribed in the boundary $\partial\Omega$. The diagonal dominance of the resulting matrices (i.e., M-matrices [12]) 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 $\tilde{\Psi} \equiv (\tilde{\psi}_1, \ldots, \tilde{\psi}_N) \in \mathbb{R}^N$ is called an upper solution of (4) if it satisfies the following inequality*

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

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

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

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

3.1 Jacobi Method

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

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

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

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

Similarly, by using $\underline{V}^{(0)} = \hat{\Psi}$ as another initial iterate, we obtain a sequence $\{\underline{V}^{(m+1)}\}$ from the linear system

$$\begin{aligned} \eta_i\underline{v}_i^{(m+1)} &- \sum_{k\in V(i)} \eta_k\underline{v}_k^{(m)} + \underline{\gamma}_i^{(m+1)}\underline{v}_i^{(m+1)} \\ &= \underline{\gamma}_i^{(m+1)}\underline{v}_i^{(m)} - R_i(\underline{v}_i^{(m)}) + R_i^*, \end{aligned} \qquad (9)$$

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

$$\underline{\gamma}_i^{(m+1)} \equiv \frac{\partial R_i(\underline{v}_i^{(m)})}{\partial\psi_i}. \qquad (10)$$

For the maximal and minimal sequences we have the following properties [6, 10].

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

$$\hat{\Psi} \leq \overline{V}^{(m+1)} \leq \overline{V}^{(m)} \leq \tilde{\Psi}, \; m = 0, 1, 2, \ldots. \qquad (11)$$

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

$$\hat{\Psi} \leq \overline{V} \leq \overline{V}^{(m+1)} \leq \overline{V}^{(m)} \leq \tilde{\Psi}, \; m = 1, 2, \ldots. \qquad (12)$$

Lemma 4 *Assume the nonlinear function $R_i(\psi_i)$ is monotone increasing and concave down with respect to ψ_i, i.e., $\partial^2 R_i/\partial\psi_i^2 < 0$. Then the minimal sequence $\{\underline{V}^{(m)}\}$ given by (9) with $\underline{V}^{(0)} = \hat{\Psi}$ possesses the monotone property*

$$\hat{\Psi} \le \underline{V}^{(m+1)} \le \underline{V}^{(m)} \le \tilde{\Psi},\ m = 0, 1, 2, \ldots. \quad (13)$$

Theorem 5 *Assume conditions in Lemma 4 hold. Then the sequence $\{\underline{V}^{(m)}\}$ generated by solving (9) with $\underline{V}^{(0)} = \hat{\Psi}$ converge monotonically to the solution $\underline{V}$ of (4). Moreover*

$$\hat{\Psi} \le \underline{V} \le \underline{V}^{(m+1)} \le \underline{V}^{(m)} \le \tilde{\Psi},\ m = 1, 2, \ldots. \quad (14)$$

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 and minimal sequences by the three iterative schemes defined as follows:

(a) Picard method

$$\begin{aligned} & (\mathcal{A}+\overline{\Lambda}_P^{(m+1)})\overline{V}_P^{(m+1)} \\ = \ & \overline{\Lambda}_P^{(m+1)}\overline{V}_P^{(m)} - R(\overline{V}_P^{(m)}) + R^*, \quad (15) \\ & (\mathcal{A}+\underline{\Lambda}_P^{(m+1)})\underline{V}_P^{(m+1)} \\ = \ & \underline{\Lambda}_P^{(m+1)}\underline{V}_P^{(m)} - R(\underline{V}_P^{(m)}) + R^*, \quad (16) \end{aligned}$$

(b) Gauss-Seidel method

$$\begin{aligned} & (\mathcal{D} - \mathcal{L}+\overline{\Lambda}_G^{(m+1)})\overline{V}_G^{(m+1)} = \mathcal{U}\overline{V}_G^{(m)} \\ & +\overline{\Lambda}_G^{(m+1)}\overline{V}_G^{(m)} - R(\overline{V}_G^{(m)}) + R^*, \quad (17) \\ & (\mathcal{D} - \mathcal{L}+\underline{\Lambda}_G^{(m+1)})\underline{V}_G^{(m+1)} = \mathcal{U}\underline{V}_G^{(m)} \\ & +\underline{\Lambda}_G^{(m+1)}\underline{V}_G^{(m)} - R(\underline{V}_G^{(m)}) + R^*, \quad (18) \end{aligned}$$

(c) Jacobi method

$$\begin{aligned} & (\mathcal{D}+ \overline{\Lambda}_J^{(m+1)})\overline{V}_J^{(m+1)} = (\mathcal{L} + \mathcal{U})\ \overline{V}_J^{(m)} \\ & +\overline{\Lambda}_J^{(m+1)}\overline{V}_J^{(m)} - R(\overline{V}_J^{(m)}) + R^*, \quad (19) \\ & (\mathcal{D}+\underline{\Lambda}_J^{(m+1)})\underline{V}_J^{(m+1)} = (\mathcal{L} + \mathcal{U})\ \underline{V}_J^{(m)} \\ & +\underline{\Lambda}_J^{(m+1)}\underline{V}_J^{(m)} - R(\underline{V}_J^{(m)}) + R^*, \quad (20) \end{aligned}$$

where

$$\overline{\Lambda}_P^{(m+1)} \equiv diag(\overline{\gamma}_{P,i}^{(m+1)}), \overline{\gamma}_{P,i}^{(m+1)} \equiv \frac{\partial R_i(\overline{v}_{P,i}^{(m)})}{\partial\psi_i}, \quad (21)$$

$$\underline{\Lambda}_P^{(m+1)} \equiv diag(\underline{\gamma}_{P,i}^{(m+1)}), \underline{\gamma}_{P,i}^{(m+1)} \equiv \frac{\partial R_i(\underline{v}_{P,i}^{(m)})}{\partial\psi_i}, \quad (22)$$

$$\overline{\Lambda}_G^{(m+1)} \equiv diag(\overline{\gamma}_{G,i}^{(m+1)}), \overline{\gamma}_{G,i}^{(m+1)} \equiv \frac{\partial R_i(\overline{v}_{G,i}^{(m)})}{\partial\psi_i}, \quad (23)$$

$$\underline{\Lambda}_G^{(m+1)} \equiv diag(\underline{\gamma}_{G,i}^{(m+1)}), \underline{\gamma}_{G,i}^{(m+1)} \equiv \frac{\partial R_i(\underline{v}_{G,i}^{(m)})}{\partial\psi_i}, \quad (24)$$

$$\overline{\Lambda}_J^{(m+1)} \equiv diag(\overline{\gamma}_{J,i}^{(m+1)}), \overline{\gamma}_{J,i}^{(m+1)} \equiv \frac{\partial R_i(\overline{v}_{J,i}^{(m)})}{\partial\psi_i}, \quad (25)$$

$$\underline{\Lambda}_J^{(m+1)} \equiv diag(\underline{\gamma}_{J,i}^{(m+1)}), \underline{\gamma}_{J,i}^{(m+1)} \equiv \frac{\partial R_i(\underline{v}_{J,i}^{(m)})}{\partial\psi_i}. \quad (26)$$

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

Lemma 6 *Assume the conditions of Lemma 2 hold. Then the maximal sequence $\{\overline{V}^{(m)}\}$ given by either one of the iterative schemes (15),(17) and (19) with $\overline{V}^{(0)} = \hat{\Psi}$ possesses the monotone property (11).*

Theorem 7 *Assume the conditions of Lemma 2 hold. Then each of the maximal sequences $\overline{V}_G^{(m)}, \overline{V}_J^{(m)}, \overline{V}_P^{(m)}$ converges monotonically to the solution $\overline{V}$ of (4) and satisfies the relation (12). Moreover,*

$$\overline{V}_P^{(m)} \le \overline{V}_G^{(m)} \le \overline{V}_J^{(m)}, \quad (27)$$

for every $m = 1, 2, 3, \ldots$.

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 [2, 4, 8]. 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 Ψ_S on the surfaces of both particles was equal to 2.0. The Neumann boundary conditions $\partial\Psi/\partial\boldsymbol{n} = 0$ are implied on the other boundaries of the domain.

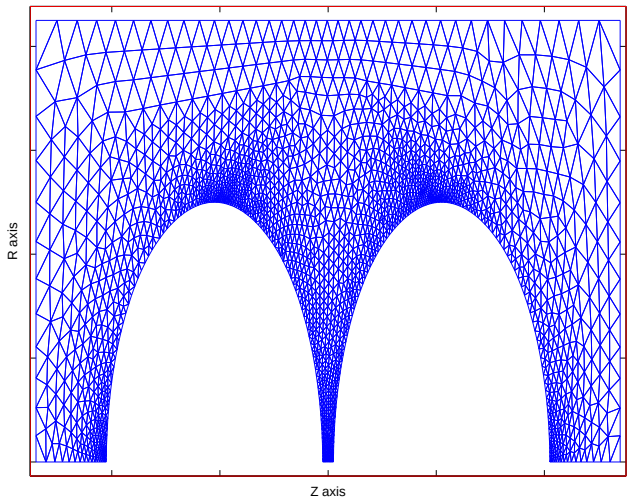

Figure 2: The mesh for the problem of two interacting identical charged spherical particles.

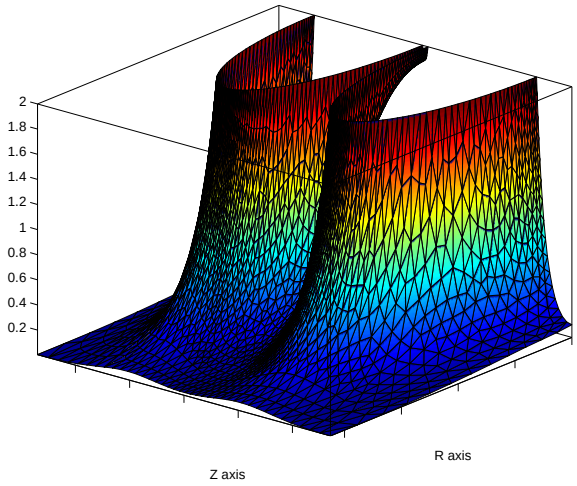

Figure 3: The numerical solution for the problem of two interacting identical charged spherical particles.

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 results 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 my results.

Table 1
The Dimensionless Force between Two Particles

κ_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 [2], F_{p2} is the force from previous results [9], and F_{p3} is the force from previous results [4].

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

This problem deal 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., [3].

In order to observe the behavior of the error reduction for various iterative schemes the error $||e^{(m)}||_\infty \equiv ||\overline{v}^{(m)} - \overline{v}^{(m-1)}||_\infty$ is defined and the stopping criterion for these iterations is determined from the condition $||e^{(m)}||_\infty \leq 1.0E{-}6$. Fig. 5 shows the typical phenomena of monotone convergence in various schemes. The convergence of Picard method is the fastest, and then Gauss-Seidel method and Jacobi method follow accordingly. This phenomenon verifies Theorem 5. On the one hand the iterative behavior of Picard method is remarkable for its fast convergence. It is finished after ninth iterative step and more faster than Gauss-Seidel and Jacobi methods. On the other hand the memory storage and the CPU time consuming in Gauss elimination are the drawbacks of Picard method.

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References:

[1] R. E. Bank and D. J. Rose, Parameter selection for Newton-like methods applicable to nonlinear partial differential equations, *SIAM J. Numer. Anal.* 17, 1980, pp. 806–822.

[2] W. R. Bowen and A. O. Sharif, Adaptive finite-element solution of the nonlinear Poisson-Boltzmann equation: a charged spherical particle at various distances from a charged cylindrical pore in a charged planar surface, *J. Coll. Interface Sci.* 187, 1997, pp. 363–374.

[3] W. R. Bowen and A. O. Sharif, Long-range electrostatic attraction between like-charge spheres in a charged pore, *Nature* 393, 1998, pp. 663–665.

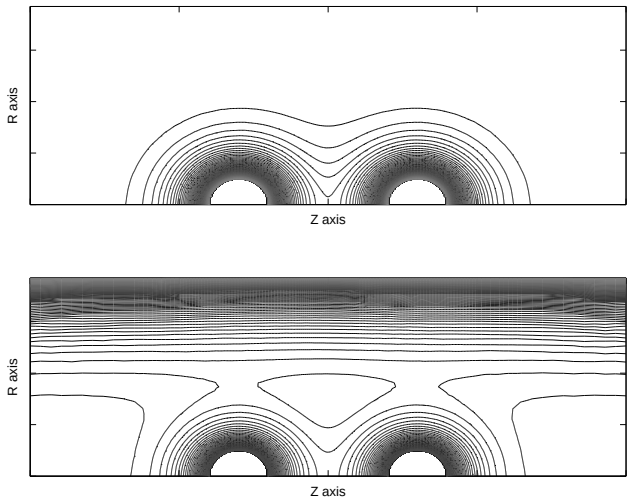

Figure 4: Calculated isopotential lines for the problem considered in subsection 4.2. A half-section of the physical geometry is shown, with the line of symmetry lying at the bottom. On the top of the graph, isolated spheres; on the bottom of the graph, spheres confined in a pore. The pore wall is at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

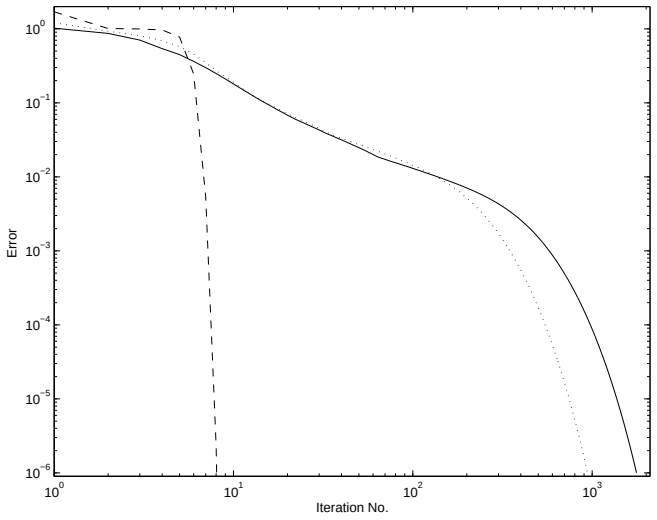

Figure 5: The error versus the number of iteration for the case of spheres confined in a pore. Solid line: Jacobi method, dotted line: Gauss-Seidel method and dashed line: Picard method.

[4] S. L. Carnie, D. Y. C. Chan, and J. Stankovich, Computation of forces between spherical colloidal particles: nonlinear Poisson-Boltzmann theory, *J. Colloid Interface Sci.* 165, 1994, pp. 116–128.

[5] R.-C. Chen and J.-L. Liu, An iterative method for adaptive finite element solutions of an energy transport model of semiconductor devices, *J. Comput. Phys.* 189, 2003, pp. 579–606.

[6] R.-C. Chen and J.-L. Liu, Monotone iterative methods for the adaptive finite element solution of semiconductor equations, *J. Comput. Applied Math.* 159, 2003, pp. 341–364.

[7] P. Dyshlovenko, Adaptive mesh enrichment for the Poisson-Boltzmann equation, *J. Comput. Phys.* 172, 2001, pp. 198–201.

[8] P.E. Dyshlovenko, Adaptive numerical method for Poisson-Boltzmann equation and its application, *Comput. Phys. Commun.* 147, 2002, pp. 335–338.

[9] J. E. Ledbetter, T. L. Croxton and D. A. McQuarrie, The interaction of two charged spheres in the Poisson-Boltzmann equation, *Can. J. Chem.* 59, 1981, pp. 1860-1864.

[10] C. V. Pao, Block monotone iterative methods for numerical solutions of nonlinear elliptic equations, *Numerische Mathematik* 72, 1995, pp. 239–262.

[11] W. B. Russell, D. A. Saville and W. R. Schowalter, *Colloidal Dispersion*, Cambridge University Press, 1989

[12] R. S. Varga, *Matrix Iterative Analysis*, Prentice-Hall, Inc. 1962