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A New Boundary Integral Equation for Molecular Electrostatics with Charges Over Whole Space

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Abstract In this paper, a new integral equation of electrostatics is proposed as an integral form of a basic dielectric continuum model, which is traditionally represented in a form of Poisson differential equation. As an application in protein simulations, the new integral equation is reduced to a second kind Fredholm boundary integral equation on the interface between the solute and solvent regions for a piecewise constant permittivity function, together with two new integral expressions for the electrostatics within the solute and solvent regions. The new integral equation and expressions work for any charge problem over the whole space (including the one with charges on the interface). This valuable feature is verified numerically for a dielectric sphere model with a point charge inside, outside, or on the sphere in this paper.

Keywords Poisson equation · Dielectric continuum model · Fredholm integral equation · Molecular electrostatics

Mathematics Subject Classification (2000) 45B05 · 92B05 · 65N80

1 Introduction

Electrostatic interactions play an important role in molecular biology, biochemistry, electrochemistry, bioengineering, and many other fields. One commonly-used math-

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ematical model for computing the electrostatic potential density function $\phi(\mathbf{r})$ is the Poisson dielectric continuum model, which is a second-order elliptic partial differential equation defined in the whole space $\mathbb{R}^3$ with a dielectric permittivity function $\varepsilon(\mathbf{r})$ as the coefficient function and a charge density function $\rho(\mathbf{r})$ as the right hand side function [12,16]. In biomolecular applications, $\varepsilon(\mathbf{r})$ is set as a piecewise constant function, and the whole space $\mathbb{R}^3$ is split as a bounded solute region, a unbounded solvent region that surrounds the solution region, and an interface between the solute and solvent regions [12,16]. The charge density function $\rho(\mathbf{r})$ is then estimated, respectively, within the solute and solvent regions. While the charge density within the solute region can be easily estimated (via partial charges) for a protein with a given molecular structure, the charge density within the solvent region is usually estimated in terms of the concentration functions of ionic species [23,26]. Currently, the Boltzmann distribution is used to estimate the ionic concentration functions such that the Poisson dielectric equation is modified to be a nonlinear second order elliptic partial differential equation, known as the Poisson-Boltzmann equation (PBE), and it has been widely used in the calculation of molecular electrostatics for a dilute ionic solvent [15,21,26,28,35]. Several computer program packages such as DelPhi [29], UHBD [13], APBS [3], and the PBEQ module [17] of the biomolecular simulation program CHARMM [9] have been developed for solving PBE by finite-difference and finite element methods. The boundary integral equation approach has also been applied to the calculation of molecular electrostatics but is only limited to the linearized Poisson-Boltzmann equation and the Poisson dielectric equation with a charge density function nonzero only within the solute region (i.e., a protein is assumed to be inside a cavity immersed in pure water) [7,11,12,24,25,34].

However, it has been known that the PBE model may not be accurate enough for estimating molecular electrostatics, especially in the region close to the solute, where the solvent has properties dramatically different from the bulk fluid. In fact, in the PBE model, each ion is simply treated as a point charge without considering the effect of ionic volume sizes. Such an ionic size effect may be essential in some important protein modeling problems (e.g., ion channel selectivity problems). There have been many efforts to develop size-modified PBE models [23,26] and to develop new solvent models for the solvent within an ion channel by using classicla density functional theory (DFT) for hard-sphere mixture fluids [1,4,6,5]. New dielectric continuum models, which we will call Poisson-DFT models, have been proposed [30, 31] in which each ion is modeled as a hard-sphere, and the free energy terms related to a hard-sphere mixture are used to estimate the charge density within the solvent region. The Poisson-DFT model equations can be solved iteratively as a Poisson dielectric equation with a charge density function (depending on the electric potential) that may be nonzero over the whole space. The purpose of this paper is to develop a new integral formulation to solve this kind of Poisson model problem efficiently by a boundary element method [18,19].

Currently, several different boundary integral equation formulations were proposed for solving the Poisson dielectric model by a boundary element method, including the apparent-surface-charge/polarizable-continuum model (ASC/PCM) formulation [11,27]. But, they considered only an interior charge problem. That is, it has been assumed that the solvent is pure water, and there does not exist any charges

on the interface. Although an integral formulation of the Poisson dielectric model for a charge density function that may be nonzero over the whole space can be obtained by using current integral formulation techniques (such as the ones used in Juffer *et al*'s integral formulation of the linearized PBE model [20]), such a formulation was never done yet. Even so, it seems difficult to produce an integral formulation from the Poisson dielectric equation via these techniques if there exist charges on the interface due to the resulting singularity in at least one of the variables.

In this paper, a new approach is applied to the integral formulation of the molecular electrostatics induced by any charges over the whole space. In this new approach, a basic dielectric model is first introduced, and is shown to have the Poisson dielectric model as its differential form. Then, the integral formulation process begins with the basic dielectric model instead of the Poisson dielectric model such that the electrostatic potential density function can be expressed in a simple integral form in terms of a polarization charge density function and an electric charge density function. By Debye's classic dielectric theory, the unknown polarization charge density function is removed from this integral expression, resulting in a new integral equation of electrostatics.

As an important application in protein simulations, this new integral equation with a piecewise constant permittivity function is considered in this paper. We rigorously calculate the gradient of this piecewise constant permittivity function as a distribution, and simplify the new integral equation as one second kind Fredholm boundary integral equation and two integral expressions for the electrostatics within the solute and solvent regions, respectively. Since it is already in an integral form, this new integral formulation is a "natural" choice for computing molecular electrostatics by a boundary element algorithm. In contrast, in order to solve the Poisson dielectric model by a boundary element method, an integral reformulation has to be carried out. Such an integral formulation process may become difficult for some charge problems (such as the one with charges on the interface), and may require different integral equations to deal with different charge problems.

To verify our new integral formulation, numerical experiments were made in this paper for a dielectric sphere model with a point charge inside, outside, or on the sphere. For simplicity, we discretized the new integral formulation using a piecewise constant boundary finite element method, and programmed it in MATLAB. We also obtained the analytical solution of the dielectric sphere model with a point charge on the sphere ourselves since we could not find it in literature after finding the ones with a point charge inside and outside the sphere from [10, 16]. These analytical solutions were then applied to the verification of our new integral formulation. The numerical results show that the numerical solutions match well the analytical solutions for all the three point charge cases.

In our numerical experiments, the discretized boundary integral equation was simply solved by using the MATLAB direct method since our purpose here was only to verify the new integral formulation. Actually, it is a well conditioned linear system, and can be solved "optimally" (in terms of the numbers of floating point operations and computer memory locations) by a Krylov subspace iterative method enhanced by a fast multipole method. Such an optimal iterative method has been well studied in solving a boundary integral equation formulated from the linearized

Poisson-Boltzmann equation [24]. We plan to adopt it to the numerical solution of our new boundary integral equation in our future studies.

The paper is organized as follows. Section 2 introduces the basic dielectric continuum model and shows that the Poisson dielectric model is its differential form. Section 3 obtains the new integral equation of electrostatics from the basic dielectric continuum model, and then use it to derive the new integral formulation for computing biomolecular electrostatics with charges over the whole space. Section 4 reports numerical results to verify the new integral formulation.

2 Poisson dielectric model

According to the Debye classic dielectric theory [14, 16], we assume that there exist a polarization charge density function $\gamma(\mathbf{r})$ and a charge density function $\rho(\mathbf{r})$ such that a polarization field $\mathbf{p}(\mathbf{r})$, a displacement field $\mathbf{d}(\mathbf{r})$, and an electric field $\mathbf{e}(\mathbf{r})$ are defined, respectively, by the following three equations:

$$\nabla\cdot\mathbf{p}(\mathbf{r}) = \gamma(\mathbf{r}), \quad \mathbf{r}\in\mathbb{R}^3, \tag{2.1}$$

$$-\nabla\cdot\mathbf{d}(\mathbf{r}) = \rho(\mathbf{r}), \quad \mathbf{r}\in\mathbb{R}^3, \tag{2.2}$$

and

$$-\nabla\cdot(\varepsilon_0\mathbf{e}(\mathbf{r})) = \gamma(\mathbf{r})+\rho(\mathbf{r}), \quad \mathbf{r}\in\mathbb{R}^3, \tag{2.3}$$

where ε_0 is the permittivity of the vacuum, and $|\mathbf{e}|\to 0$ as $|\mathbf{r}|\to\infty$.

If there exists an electrostatic potential function $\phi(\mathbf{r})$ such that

$$\mathbf{e}(\mathbf{r}) = \nabla\phi(\mathbf{r}), \quad \mathbf{r}\in\mathbb{R}^3, \tag{2.4}$$

then (2.3) is written as the simple Poisson equation

$$\begin{cases} -\nabla^2\phi(\mathbf{r}) = \frac{1}{\varepsilon_0}(\gamma(\mathbf{r})+\rho(\mathbf{r})) & \text{for } \mathbf{r}\in\mathbb{R}^3, \\ \phi(\mathbf{r})\to 0 & \text{as } |\mathbf{r}|\to\infty, \end{cases} \tag{2.5}$$

where ∇^2 denotes the Laplacian operator.

However, the polarization charge density function $\gamma(\mathbf{r})$ is very difficult to estimate in practice. To avoid this difficulty, some assumptions have to be made on the relationships of the electric field $\mathbf{e}$ with $\mathbf{p}$ and $\mathbf{d}$. In this paper, we only consider the following classic linear relationships:

$$\text{(a)}\quad \mathbf{d}(\mathbf{r}) = \varepsilon_0\varepsilon(\mathbf{r})\mathbf{e}(\mathbf{r}); \qquad \text{(b)}\quad \mathbf{p}(\mathbf{r}) = \varepsilon_0\chi(\mathbf{r})\mathbf{e}(\mathbf{r}), \tag{2.6}$$

where $\varepsilon(\mathbf{r})$ is the relative dielectric permittivity function, and $\chi(\mathbf{r})$ is the dielectric susceptibility function satisfying that $\varepsilon(\mathbf{r}) = 1+\chi(\mathbf{r})$. A combination of the equation of (2.5) with equations (2.1) to (2.4) and the linear relationships of (2.6) defines *the basic dielectric continuum model* that we consider in this paper.

Traditionally, this basic dielectric continuum model is reformulated as a differential equation, called the Poisson dielectric model, in the form:

$$\begin{cases} -\nabla\cdot(\varepsilon(\mathbf{r})\nabla\phi(\mathbf{r})) = \rho(\mathbf{r}) & \text{for } \mathbf{r}\in\mathbb{R}^3, \\ \phi(\mathbf{r})\to 0 & \text{as } |\mathbf{r}|\to\infty, \end{cases} \tag{2.7}$$

where $\varepsilon(\mathbf{r})$ is the dielectric permittivity function defined by

$$\varepsilon(\mathbf{r}) = \varepsilon_0 \varepsilon(\mathbf{r}). \tag{2.8}$$

In fact, to get the Poisson dielectric model, we first obtain the expression of $\gamma(\mathbf{r})$ by applying the relationship (b) of (2.6) and (2.4) to (2.1). We then insert this expression to (2.5) to yield an equation without involving $\gamma(\mathbf{r})$. Finally, this equation can be easily simplified to the form of (2.7).

In protein simulations, the dielectric permittivity function $\varepsilon(\mathbf{r})$ is often set as a piecewise constant function

$$\varepsilon(\mathbf{r}) = \begin{cases} \varepsilon_p & \text{for all } \mathbf{r} \in D_p, \\ \varepsilon_s & \text{for all } \mathbf{r} \in D_s, \end{cases} \tag{2.9}$$

based on the following whole space $\mathbb{R}^3$ decomposition,

$$\mathbb{R}^3 = D_s \cup D_p \cup \partial D_p,$$

where D_p denotes the bounded solute region (hosting a protein), D_s is the solvent region surrounding D_p, ∂D_p denotes the boundary of D_p, and ε_p and ε_s are two distinct positive dielectric constants. In this case, the function ϕ in equation (2.7) may not be a strong solution, due to the discontinuity of the coefficient ε on the interface ∂D_p. Hence, the Poisson dielectric model (2.7) is modified as

$$\begin{cases} -\nabla\cdot(\varepsilon(\mathbf{r})\nabla\phi(\mathbf{r})) = \rho(\mathbf{r}) & \text{for } \mathbf{r} \in \mathbb{R}^3 \setminus \partial D_p, \\ \phi(\mathbf{r}) \to 0 & \text{as } |\mathbf{r}| \to \infty, \end{cases} \tag{2.10}$$

and subject to the following interface conditions:

$$\phi(\mathbf{s}+) = \phi(\mathbf{s}-), \quad \text{and} \quad \varepsilon_s \frac{\partial \phi(\mathbf{s}+)}{\partial \mathbf{n}(\mathbf{s})} = \varepsilon_p \frac{\partial \phi(\mathbf{s}-)}{\partial \mathbf{n}(\mathbf{s})}, \quad \forall \mathbf{s} \in \partial D_p, \tag{2.11}$$

where $\frac{\partial \phi(\mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} = \nabla\phi(\mathbf{s}) \cdot \mathbf{n}(\mathbf{s})$, $\mathbf{n}(\mathbf{s})$ denotes the unit outward normal vector of the solute domain D_p,

$$\phi(\mathbf{s}\pm) = \lim_{t\to 0+} \phi(\mathbf{s} \pm t\mathbf{n}(\mathbf{s})), \quad \text{and} \quad \frac{\partial \phi(\mathbf{s}\pm)}{\partial \mathbf{n}(\mathbf{s})} = \lim_{t\to 0+} \frac{\partial \phi(\mathbf{s} \pm t\mathbf{n}(\mathbf{s}))}{\partial \mathbf{n}(\mathbf{s})}.$$

Of course, the problem (2.10–2.11) can be cast in weak form as:

$$\begin{aligned} &\text{find } \phi \in W_q^1(\mathbb{R}^3) \text{ such that} \\ &\int_{\mathbb{R}^3} \varepsilon(\mathbf{r})\nabla\phi(\mathbf{r}) \cdot \nabla v(\mathbf{r})\, d\mathbf{r} = \int_{\mathbb{R}^3} \rho(\mathbf{r}) v(\mathbf{r})\, d\mathbf{r}, \quad \forall v \in W_p^1(\mathbb{R}^3), \end{aligned} \tag{2.12}$$

where $1/p + 1/q = 1$ and W_p^1 denotes the Sobolev space of functions whose first derivatives are p-th power integrable [8]. In this way, both of the interface conditions (2.11) as well as the decay condition at the infinity become implicit in (2.12). Taking $p > 3$ allows us to interpret the meaning of the Poisson dielectric equation when ρ includes Dirac delta-fucntions [8].

In biomolecular simulations, the charge density function ρ may be a distribution in the form

$$\rho = \sum_{j=1}^{N} q_j \delta_{\mathbf{r}_j}, \tag{2.13}$$

where q_j is the charge at the position $\mathbf{r}_j$ of the jth atom of a biomolecule, N is the total number of atoms, and $\delta_{\mathbf{r}_j}$ is the Dirac-delta measure, which is a distribution (i.e., a linear continuous functional) defined for $\mathbf{r} \in \mathbb{R}^3$ by

$$\langle \delta_{\mathbf{r}}, f \rangle = \delta_{\mathbf{r}}(f) = f(\mathbf{r}), \quad \forall f \in \mathscr{D}. \tag{2.14}$$

Here $\mathscr{D}$ denotes the test function space. It contains all arbitrarily smooth functions with a compact support on the whole space $\mathbb{R}^3$ or in an open subset Ω of $\mathbb{R}^3$ [32]. In this case, all the related equations should be re-formulated in distribution notation, or in the appropriate Sobolev space as in (2.12).

In practice, it is often sufficient to assume that $\rho(\mathbf{r})$ is a bounded function with sufficient decay at infinity, and that $\varepsilon(\mathbf{r})$ has appropriate generalized derivatives to allow the familiar integral notation during the formulation of our new integral equation. The case where ρ, γ, or other related functions are distributions can be treated similarly to what is done in the proof of Theorem 3.2. To make precise required regularity for $\rho(\mathbf{r})$, we define the norm

$$\|\rho\|_{\mathscr{R}_\sigma} = \sup_{\mathbf{r}' \in \mathbb{R}^3} \int_{\mathbb{R}^3} |\rho(\mathbf{r})| |\mathbf{r} - \mathbf{r}'|^{-\sigma} \, d\mathbf{r}, \tag{2.15}$$

and let $\mathscr{R}_\sigma$ denote the space of measurable functions for which the norm is finite.

3 New integral equation formulation

In this section, we first obtain the integral equation of electrostatics from the basic dielectric continuum model. We then apply it to the protein simulation case to get the new integral equation formulation for computing biomolecular electrostatics induced from any charges in the whole space. Furthermore, we show that both the Poisson dielectric model and the related interface conditions can be followed from the new integral equation formulation. For clarity, these results are presented in Theorems 3.1 to 3.3, respectively.

Theorem 3.1 *Let $\phi(\mathbf{r})$ be the solution of the basic dielectric continuum model. If both ρ and γ are in $\mathscr{R}_1$, and the permittivity function $\varepsilon(\mathbf{r})$ is differentiable, then ϕ satisfies the integral equation*

$$\varepsilon(\mathbf{r})\phi(\mathbf{r}) = \int_{\mathbb{R}^3} G(\mathbf{r}, \mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}' + \int_{\mathbb{R}^3} \phi(\mathbf{r}')\nabla\varepsilon(\mathbf{r}') \cdot \nabla G(\mathbf{r}, \mathbf{r}')d\mathbf{r}', \quad \mathbf{r} \in \mathbb{R}^3. \tag{3.1}$$

Proof We recall that the basic dielectric continuum model is defined by equation (2.5) together with assumptions (2.1) to (2.4) and the linear relationships of (2.6). Since $\rho \in \mathscr{R}_1$ and $\gamma \in \mathscr{R}_1$, by (2.5), the solution ϕ of the basic dielectric continuum model can be expressed in the integral form

$$\phi(\mathbf{r}) = \int_{\mathbb{R}^3} G(\mathbf{r},\mathbf{r}')\frac{\gamma(\mathbf{r}')}{\varepsilon_0}d\mathbf{r}' + \int_{\mathbb{R}^3} G(\mathbf{r},\mathbf{r}')\frac{\rho(\mathbf{r}')}{\varepsilon_0}d\mathbf{r}', \quad \mathbf{r} \in \mathbb{R}^3, \tag{3.2}$$

where $G(\mathbf{r},\mathbf{r}') = 1/(4\pi|\mathbf{r}-\mathbf{r}'|)$, which is the fundamental solution defined by

$$-\nabla^2 G(\mathbf{r},\cdot) = \delta_{\mathbf{r}}, \quad \forall \mathbf{r} \in \mathbb{R}^3. \tag{3.3}$$

To remove the function $\gamma(\mathbf{r})$ from the integral expression (3.2), we use (2.1), the item (b) of (2.6), and (2.4) to express $\gamma(\mathbf{r})$ as

$$\gamma(\mathbf{r}) = \varepsilon_0 \nabla\cdot(\chi(\mathbf{r})\nabla\phi(\mathbf{r})).$$

Thus,

$$\int_{\mathbb{R}^3} G(\mathbf{r},\mathbf{r}')\frac{\gamma(\mathbf{r}')}{\varepsilon_0}d\mathbf{r}' = \int_{\mathbb{R}^3} G(\mathbf{r},\mathbf{r}')\nabla\cdot(\chi(\mathbf{r}')\nabla\phi(\mathbf{r}'))d\mathbf{r}'. \tag{3.4}$$

We recall the first Green's formula in the form

$$\int_\Omega [g(\mathbf{r})\nabla\cdot\mathbf{F}(\mathbf{r}) + \mathbf{F}(\mathbf{r})\cdot\nabla g(\mathbf{r})]d\mathbf{r} = \int_{\partial\Omega} g(\mathbf{s})\mathbf{F}(\mathbf{s})\cdot\mathbf{n}(\mathbf{s})d\mathbf{s},$$

where Ω is a bounded domain, $\mathbf{n}(\mathbf{s})$ denotes the outward unit normal vector for $\mathbf{s} \in \partial\Omega$, $d\mathbf{r}$ denotes the volume differential, and $d\mathbf{s}$ denotes the surface differential. Using the above Green's formula twice, we get

$$\begin{aligned}
&\int_\Omega G(\mathbf{r},\mathbf{r}')\nabla\cdot(\chi(\mathbf{r}')\nabla\phi(\mathbf{r}'))d\mathbf{r}' \\
&= \int_{\partial\Omega} G(\mathbf{r},\mathbf{s})\chi(\mathbf{s})\nabla\phi(\mathbf{s})\cdot\mathbf{n}(\mathbf{s})d\mathbf{s} - \int_{\partial\Omega}\phi(\mathbf{s})\chi(\mathbf{s})\nabla G(\mathbf{r},\mathbf{s})\cdot\mathbf{n}(\mathbf{s})d\mathbf{s} \\
&+ \int_\Omega \phi(\mathbf{r}')\nabla\cdot(\chi(\mathbf{r}')\nabla G(\mathbf{r},\mathbf{r}'))d\mathbf{r}'.
\end{aligned}$$

We then set $\Omega = \{\mathbf{r}|\ |\mathbf{r}| < R\}$, a ball with radius $R > 0$. Since both $G(\mathbf{r},\mathbf{r}')$ and $\phi(\mathbf{r}')$ and their derivatives go to zero sufficiently rapidly as $|\mathbf{r}'| \to \infty$, letting $R \to \infty$ immediately gives

$$\int_{\mathbb{R}^3} G(\mathbf{r},\mathbf{r}')\nabla\cdot(\chi(\mathbf{r}')\nabla\phi(\mathbf{r}'))d\mathbf{r}' = \int_{\mathbb{R}^3}\phi(\mathbf{r}')\nabla\cdot(\chi(\mathbf{r}')\nabla G(\mathbf{r},\mathbf{r}'))d\mathbf{r}'.$$

Since $\varepsilon(\mathbf{r}) = \varepsilon_0 + \varepsilon_0\chi(\mathbf{r})$, we get that $\nabla\chi(\mathbf{r}') = \nabla\varepsilon(\mathbf{r})/\varepsilon_0$, and

$$\nabla\cdot(\chi(\mathbf{r}')\nabla G(\mathbf{r},\mathbf{r}')) = \nabla\chi(\mathbf{r}')\cdot\nabla G(\mathbf{r},\mathbf{r}') + \chi(\mathbf{r}')\nabla^2 G(\mathbf{r},\mathbf{r}'),$$

at least in the distributional sense:

$$\int_{\mathbb{R}^3}\phi(\mathbf{r}')\chi(\mathbf{r}')\nabla^2 G(\mathbf{r},\mathbf{r}')d\mathbf{r}' = -\chi(\mathbf{r})\phi(\mathbf{r}),$$

where (3.3) has been used. Therefore, (3.4) is simplified as

$$\int_{\mathbb{R}^3} G(\mathbf{r},\mathbf{r}')\frac{\gamma(\mathbf{r}')}{\varepsilon_0}d\mathbf{r}' = \int_{\mathbb{R}^3} \phi(\mathbf{r}')\nabla\chi(\mathbf{r}')\cdot\nabla G(\mathbf{r},\mathbf{r}')d\mathbf{r}' - \chi(\mathbf{r})\phi(\mathbf{r}).$$

Applying the above identity to (3.2) gives

$$\phi(\mathbf{r}) = \int_{\mathbb{R}^3} G(\mathbf{r},\mathbf{r}')\frac{\rho(\mathbf{r}')}{\varepsilon_0}d\mathbf{r}' + \int_{\mathbb{R}^3} \phi(\mathbf{r}')\nabla\chi(\mathbf{r}')\cdot\nabla G(\mathbf{r},\mathbf{r}')d\mathbf{r}' - \chi(\mathbf{r})\phi(\mathbf{r}).$$

Since $\chi(\mathbf{r})+1 = \varepsilon(\mathbf{r})/\varepsilon_0$, and $\nabla\chi(\mathbf{r}') = \nabla\varepsilon(\mathbf{r})/\varepsilon_0$, the above equation can be reformulated as (3.1). This completes the proof of Theorem 3.1.

We will refer to the integral equation of (3.1) as *the integral equation of electrostatics* since it gives an integral form of the basic dielectric continuum model.

We next consider a piecewise constant permittivity function to simplify the volume integral equation of (3.1) into a surface integral equation. In the following lemma, we obtain its gradient vector in the form of a distribution.

Lemma 3.1 *If the dielectric permittivity function $\varepsilon(\mathbf{r})$ is a piecewise constant function defined by (2.9), then its generalized gradient vector $\nabla\varepsilon$ is a distribution defined by*

$$\langle\nabla\varepsilon,\mathbf{f}\rangle = (\nabla\varepsilon)(\mathbf{f}) = (\varepsilon_s-\varepsilon_p)\int_{\partial D_p}\mathbf{f}(\mathbf{s})\cdot\mathbf{n}(\mathbf{s})d\mathbf{s} \tag{3.5}$$

for all $\mathbf{f}=(f_1,f_2,f_3)$ with f_1,f_2, and f_3 in the test function space $\mathscr{D}$.

Proof By the definition of the generalized derivative [32], the generalized gradient vector $\nabla\varepsilon$ is a distribution defined by

$$(\nabla\varepsilon)(\mathbf{f}) = -\langle\varepsilon,\nabla\cdot\mathbf{f}\rangle, \tag{3.6}$$

where $\nabla\cdot\mathbf{f} = \frac{\partial f_1}{\partial x}+\frac{\partial f_2}{\partial y}+\frac{\partial f_3}{\partial z}$ for $\mathbf{r}=(x,y,z)\in\mathbb{R}^3$, and

$$\langle\varepsilon,\nabla\cdot\mathbf{f}\rangle = \int_{\mathbb{R}^3}\varepsilon(\mathbf{r})\nabla\cdot\mathbf{f}(\mathbf{r})d\mathbf{r}.$$

By the definition of $\varepsilon(\mathbf{r})$, the above integral can be simplified as

$$\int_{\mathbb{R}^3}\varepsilon(\mathbf{r})\nabla\cdot\mathbf{f}(\mathbf{r})d\mathbf{r} = \varepsilon_s\int_{D_s}\nabla\cdot\mathbf{f}(\mathbf{r})d\mathbf{r} + \varepsilon_p\int_{D_p}\nabla\cdot\mathbf{f}(\mathbf{r})d\mathbf{r}.$$

Using the divergence theorem, we get that

$$\int_{D_s}\nabla\cdot\mathbf{f}(\mathbf{r})d\mathbf{r} = -\int_{\partial D_p}\mathbf{f}(\mathbf{s})\cdot\mathbf{n}(\mathbf{s})d\mathbf{s}, \quad \text{and} \int_{D_p}\nabla\cdot\mathbf{f}(\mathbf{r})d\mathbf{r} = \int_{\partial D_p}\mathbf{f}(\mathbf{s})\cdot\mathbf{n}(\mathbf{s})d\mathbf{s}.$$

Hence,

$$(\nabla\varepsilon)(\mathbf{f}) = -\langle\varepsilon,\nabla\cdot\mathbf{f}\rangle = (\varepsilon_s-\varepsilon_p)\int_{\partial D_p}\mathbf{f}(\mathbf{s})\cdot\mathbf{n}(\mathbf{s})d\mathbf{s}.$$

This completes the proof.

We now reduce the integral equation (3.1) into a second kind Fredholm boundary integral equation in the following theorem.

Theorem 3.2 *Let $\phi(\mathbf{r})$ be the solution of the integral equation (3.1) with $\rho \in \mathscr{R}_1$. If the dielectric permittivity function $\varepsilon(\mathbf{r})$ is a piecewise constant function defined by (2.9), then $\phi(\mathbf{s})$ for all $\mathbf{s} \in \partial D_p$ is the solution of the following Fredholm integral equation of the second kind,*

$$u(\mathbf{s}) = \frac{2g(\mathbf{s})}{\varepsilon_p + \varepsilon_s} + \frac{2(\varepsilon_s - \varepsilon_p)}{\varepsilon_p + \varepsilon_s} \int_{\partial D_p} u(\mathbf{s}') \frac{\partial G(\mathbf{s}, \mathbf{s}')}{\partial \mathbf{n}(\mathbf{s}')} d\mathbf{s}', \quad \mathbf{s} \in \partial D_p, \tag{3.7}$$

and the other values of $\phi(\mathbf{r})$ are expressed by

$$\phi(\mathbf{r}) = \begin{cases} \dfrac{1}{\varepsilon_p} g(\mathbf{r}) + \dfrac{\varepsilon_s - \varepsilon_p}{\varepsilon_p} \displaystyle\int_{\partial D_p} u(\mathbf{s}) \frac{\partial G(\mathbf{r}, \mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} d\mathbf{s} & \text{if } \mathbf{r} \in D_p, \\ \dfrac{1}{\varepsilon_s} g(\mathbf{r}) + \dfrac{\varepsilon_s - \varepsilon_p}{\varepsilon_s} \displaystyle\int_{\partial D_p} u(\mathbf{s}) \frac{\partial G(\mathbf{r}, \mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} d\mathbf{s} & \text{if } \mathbf{r} \in D_s, \end{cases} \tag{3.8}$$

where $\mathbf{n}(\mathbf{s})$ is the unit outward normal vector of the solute region D_p, $g(\mathbf{r})$ is a continuous function given by

$$g(\mathbf{r}) = \int_{\mathbb{R}^3} G(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}') d\mathbf{r}', \quad \forall \mathbf{r} \in \mathbb{R}^3, \tag{3.9}$$

$$G(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi |\mathbf{r} - \mathbf{r}'|}, \quad \text{and} \quad \frac{\partial G(\mathbf{r}, \mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} = \frac{(\mathbf{r} - \mathbf{s}) \cdot \mathbf{n}(\mathbf{s})}{4\pi |\mathbf{r} - \mathbf{s}|^3}.$$

Proof We use the notation of distributions to write the second integral term of (3.1) as

$$\int_{\mathbb{R}^3} \phi(\mathbf{r}') \nabla \varepsilon(\mathbf{r}') \cdot \nabla G(\mathbf{r}, \mathbf{r}') d\mathbf{r}' = \langle \nabla \varepsilon, \phi \nabla G(\mathbf{r}, \cdot) \rangle. \tag{3.10}$$

Thus, the integral equation (3.1) is reformulated as

$$\varepsilon(\mathbf{r}) \phi(\mathbf{r}) = g(\mathbf{r}) + \langle \nabla \varepsilon, \phi \nabla G(\mathbf{r}, \cdot) \rangle.$$

Taking appropriate limits, we see that this remains valid for ε defined by (2.9). Taking appropriate limits again using (3.5), we find for $\mathbf{r} \in \mathbb{R}^3 \setminus \partial D_p$ that

$$\langle \nabla \varepsilon, \phi \nabla G(\mathbf{r}, \cdot) \rangle = (\varepsilon_s - \varepsilon_p) \int_{\partial D_p} \phi(\mathbf{s}) \nabla G(\mathbf{r}, \mathbf{s}) \cdot \mathbf{n}(\mathbf{s}) d\mathbf{s},$$

and so the integral equation (3.1) simplifies as

$$\varepsilon(\mathbf{r}) \phi(\mathbf{r}) = g(\mathbf{r}) + (\varepsilon_s - \varepsilon_p) \int_{\partial D_p} \phi(\mathbf{s}) \frac{\partial G(\mathbf{r}, \mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} d\mathbf{s}, \quad \mathbf{r} \in \mathbb{R}^3 \setminus \partial D_p. \tag{3.11}$$

For clarity, we set

$$W(\mathbf{r}) = \int_{\partial D_p} \phi(\mathbf{s}) \frac{\partial G(\mathbf{r}, \mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} d\mathbf{s}, \quad \forall \mathbf{r} \in \mathbb{R}^3 \setminus \partial D_p, \tag{3.12}$$

which is often called the double layer potential function. From Theorem 6.17 in [22] (Page 80) it is known that $W(\mathbf{r})$ has the jump discontinuity across the interface:

$$W(\mathbf{s}\pm) = W(\mathbf{s}) \pm \frac{1}{2}\phi(\mathbf{s}), \quad \mathbf{s} \in \partial D_p, \tag{3.13}$$

where $W(\mathbf{s})$ exists as an improper integral, and $W(\mathbf{s}\pm)$ is defined by the limits

$$W(\mathbf{s}\pm) = \lim_{t\to 0+} W(\mathbf{s} \pm t\mathbf{n}(\mathbf{s})).$$

Since $g(\mathbf{r})$ is defined by a convolution, it is continuous for all $\mathbf{r} \in \mathbb{R}^3$.

We next set $\mathbf{r} = \mathbf{s} - t\mathbf{n}(\mathbf{s}) \in D_p$ for each $\mathbf{s} \in \partial D_p$ and $t > 0$. Using (3.13) and the continuity of ϕ and g, we then can get the limits

$$\lim_{t\to 0+} \varepsilon(\mathbf{s} - t\mathbf{n}(\mathbf{s}))\phi(\mathbf{s} - t\mathbf{n}(\mathbf{s})) = \varepsilon_p \phi(\mathbf{s}), \qquad \lim_{t\to 0+} g(\mathbf{s} - t\mathbf{n}(\mathbf{s})) = g(\mathbf{s}),$$

and

$$\lim_{t\to 0+} W(\mathbf{s} - t\mathbf{n}(\mathbf{s})) = W(\mathbf{s}) - \frac{1}{2}\phi(\mathbf{s}).$$

Applying these limits to (3.11) can result in the boundary integral equation (3.7).

Finally, when the solution $u(\mathbf{s})$ of (3.7) is obtained, the integral formula (3.8) follows from (3.11) immediately. This completes the proof.

Note that the solution of the boundary integral equation is the electrostatic potential density function restricted on the interface ∂D_p. Hence, the values of $\phi(\mathbf{r})$ for all $\mathbf{r} \in \mathbb{R}^3$ can be obtained from our new integral formulation.

Remark 1: *It is interesting to note that equations (3.7) and (3.8) are reduced to the equations of (2.24) to (2.26) given in [20] if the charge density function $\rho(\mathbf{r})$ is defined by (2.13). But, the authors of paper [20] did not get any equations for a charge function nonzero over the whole space. The integral formulation techniques used in [20] are also very different from ours. They rely on the Green's second identity and the interface conditions; thus, functions are required to have well behave second derivatives, and ρ cannot be nonzero on the interface. In contrast, our integral formulation uses the Green's first identity and does not need any interface condition assumptions. Hence, it demands less regularities on functions and can deal with the interface charge problem easily. Moreover, it has been done rigorously in mathematics.*

We finally show that the potential energy function $\phi(\mathbf{r})$ defined by (3.8) satisfies the Poisson dielectric equation (2.10) and the interface conditions in the following theorem.

Theorem 3.3 *If $\phi(\mathbf{r})$ is a function defined by (3.8), and $g(\mathbf{r})$ is defined by (3.9), where $\rho \in \mathscr{R}_\sigma$ for $\sigma = 1$ and 2, then $\phi(\mathbf{r})$ satisfies the Poisson dielectric equation (2.10), and the following two interface conditions:*

$$\phi(\mathbf{s}+) = \phi(\mathbf{s}-), \quad \forall \mathbf{s} \in \partial D_p, \tag{3.14}$$

and

$$\varepsilon_p \nabla\phi(\mathbf{s}-)\cdot\mathbf{n}(\mathbf{s}) = \varepsilon_s \nabla\phi(\mathbf{s}+)\cdot\mathbf{n}(\mathbf{s}), \quad \forall \mathbf{s}\in\partial D_p. \tag{3.15}$$

Proof We first show that $\phi(\mathbf{r})$ satisfies the Poisson dielectric equation (2.10). Let $W(\mathbf{r})$ be given in (3.12). Clearly, $\nabla^2 G(\mathbf{r},\mathbf{r}') = 0$ for $\mathbf{r}\neq\mathbf{r}'$. Thus,

$$\nabla^2 W(\mathbf{r}) = 0, \quad \forall \mathbf{r}\in\mathbb{R}^3\setminus\partial D_p.$$

Hence, for $\mathbf{r}\in D_p$, by (3.8) and (3.3),

$$\begin{aligned}\nabla^2\phi(\mathbf{r}) &= \frac{1}{\varepsilon_p}\nabla^2 g(\mathbf{r}) + \frac{\varepsilon_s-\varepsilon_p}{\varepsilon_p}\nabla^2 W(\mathbf{r})\\ &= \frac{1}{\varepsilon_p}\int_{\mathbb{R}^3}\nabla^2 G(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}' = \frac{1}{\varepsilon_p}\langle\nabla^2 G(\mathbf{r},\cdot),\rho\rangle\\ &= -\frac{1}{\varepsilon_p}\langle\delta_{\mathbf{r}},\rho\rangle = -\frac{1}{\varepsilon_p}\delta_{\mathbf{r}}(\rho) = -\frac{1}{\varepsilon_p}\rho(\mathbf{r}).\end{aligned}$$

Similarly, we can obtain that

$$\nabla^2\phi(\mathbf{r}) = -\frac{1}{\varepsilon_s}\rho(\mathbf{r}) \quad \text{for } \mathbf{r}\in D_s.$$

This proves that $\phi(\mathbf{r})$ satisfies the Poisson dielectric equation (2.10).

To obtain the interface conditions, we take the limits on expression (3.11) with $\mathbf{r} = \mathbf{s}\pm t\mathbf{n}(\mathbf{s})$ for $t\to 0^+$ to get

$$\varepsilon(\mathbf{s}\pm)\phi(\mathbf{s}\pm) = g(\mathbf{s}\pm) + (\varepsilon_s-\varepsilon_p)\left[W(s)\pm\frac{1}{2}\phi(\mathbf{s})\right],$$

where $\varepsilon(\mathbf{s}+)=\varepsilon_s$, $\varepsilon(\mathbf{s}-)=\varepsilon_p$, and $W(\mathbf{r})$ is the double layer potential function as given in (3.12). Thus, if $g(\mathbf{s}) = g(\mathbf{s}\pm)$, then

$$\begin{aligned}\phi(\mathbf{s}+)-\phi(\mathbf{s}-) &= \left(\frac{1}{\varepsilon_s}g(\mathbf{s}+) + \frac{\varepsilon_s-\varepsilon_p}{\varepsilon_s}\left[W(s)+\frac{1}{2}\phi(\mathbf{s})\right]\right)\\ &- \left(\frac{1}{\varepsilon_p}g(\mathbf{s}-) + \frac{\varepsilon_s-\varepsilon_p}{\varepsilon_p}\left[W(s)-\frac{1}{2}\phi(\mathbf{s})\right]\right)\\ &= \frac{(\varepsilon_p-\varepsilon_s)(\varepsilon_s+\varepsilon_p)}{2\varepsilon_s\varepsilon_p}\left[\frac{2}{\varepsilon_p+\varepsilon_s}g(\mathbf{s}) + \frac{2(\varepsilon_s-\varepsilon_p)}{\varepsilon_p+\varepsilon_s}W(\mathbf{s}) - \phi(\mathbf{s})\right] = 0\end{aligned}$$

since $\phi(\mathbf{s})$ is the solution of the boundary integral equation (3.7). This completes the proof of (3.14).

Next, applying the gradient operator to (3.11) gives

$$\nabla(\varepsilon(\mathbf{r})\phi(\mathbf{r})) = \nabla g(\mathbf{r}) + (\varepsilon_s-\varepsilon_p)\nabla W(\mathbf{r}), \quad \forall\mathbf{r}\in\mathbb{R}^3\setminus\partial D_p.$$

Based on our assumption on ρ,

$$\nabla g(\mathbf{r}) = \int_{\mathbb{R}^3}\nabla G(\mathbf{r},\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}',$$

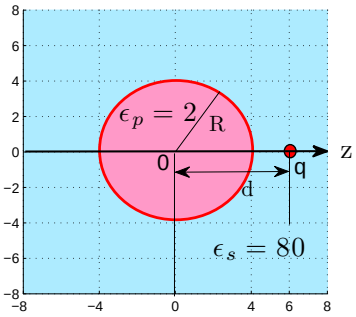

Fig. 4.1 The point charge outside the lower-dielectric sphere.

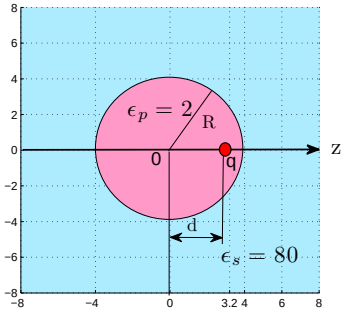

Fig. 4.2 The point charge inside the lower-dielectric sphere.

and thus ∇g is continuous across ∂D_p. Using the above identity and the continuity of the normal derivative of the double-layer potential function $W(\mathbf{r})$ (see Theorem 6.19 in [22], Page 82),

$$\nabla W(s+) \cdot \mathbf{n}(\mathbf{s}) = \nabla W(s-) \cdot \mathbf{n}(\mathbf{s}),$$

we can get (3.15). This completes the proof.

Remark 2: *Using standard approximation arguments, the results of this section can be extended to hold for singular data ρ. In particular, the integral operator in (3.7) is well defined on $L^r(\partial D_p)$ for all $1 < r < \infty$ [19]. For example, if ρ consists of a sum of delta-functions (2.13), then g defined in (3.9) is actually smooth on ∂D_p if there are no point charges on ∂D_p. For a point charge on ∂D_p, a different approach would be required since $g \notin L^r(\partial D_p)$ for any $r > 1$.*

4 Numerical verification of the new integral formulation

To verify our new integral formulation of the basic dielectric continuum model (2.5), in this section, we apply the new integral formulation to the numerical solution of a dielectric sphere model problem, where $D_p = \{\mathbf{r} | \, |\mathbf{r}| < R\}$ and $\rho = q\delta_{\mathbf{r}_0}$ with $\mathbf{r}_0 =< 0, 0, d >$ for $-\infty < d < \infty$ and q being a given point charge. The analytical solutions of this model problem with a point charge inside and outside the sphere, as illustrated in Figures 4.1 and 4.2, can be found in [10], for example. The solution with a point charge lying on the sphere is obtained by us in this section since we did not find it in the literature.

4.1 The new boundary integral formulation

Since ρ is a distribution for this model problem, the integral form of $g(\mathbf{r})$ should be rewritten as the distribution form $g(\mathbf{r}) = \rho(G(\mathbf{r}, \cdot))$, which can be found easily from

the definition of Dirac-delta measure $\delta_{\mathbf{r}}$ as shown below:

$$g(\mathbf{r}) = \rho(G(\mathbf{r},\cdot)) = q\delta_{\mathbf{r}_0}(G(\mathbf{r},\cdot)) = qG(\mathbf{r},\mathbf{r}_0) = \frac{q}{4\pi|\mathbf{r}-\mathbf{r}_0|} \quad \text{for } \mathbf{r} \neq \mathbf{r}_0.$$

Clearly, $\mathbf{n}(\mathbf{s}) = \mathbf{s}/R$, and the spheric surface $\mathbf{s} \in \partial D_p$ can be parameterized as

$$\mathbf{s} = \mathbf{s}(\varphi,\theta), \quad \forall(\varphi,\theta) \in D,$$

where $\mathbf{s}(\varphi,\theta) =< R\sin\varphi\cos\theta, R\sin\varphi\sin\theta, R\cos\varphi >$, and $D = [0,\pi]\times[0,2\pi]$. For the above parametric expression, we find

$$\left|\frac{\partial \mathbf{s}}{\partial\varphi} \times \frac{\partial \mathbf{s}}{\partial\theta}\right| = R^2\sin\varphi.$$

Thus, the surface integral of (3.7) can be transformed to a double integral on the rectangular domain D:

$$\begin{aligned}
&\int_{\partial D_p} \nabla G(\mathbf{s}',\mathbf{s})\cdot\mathbf{n}(\mathbf{s})\phi(\mathbf{s})d\mathbf{s} = \int_{\partial D_p} \frac{\mathbf{s}'-\mathbf{s}}{4\pi|\mathbf{s}'-\mathbf{s}|^3}\cdot\frac{\mathbf{s}}{R}\phi(\mathbf{s})d\mathbf{s} \\
&= \int_D \frac{\mathbf{s}'-\mathbf{s}(\varphi,\theta)}{4\pi|\mathbf{s}'-\mathbf{s}(\varphi,\theta)|^3}\cdot\frac{\mathbf{s}(\varphi,\theta)}{R}\phi(\mathbf{s}(\varphi,\theta))\left|\frac{\partial \mathbf{s}}{\partial\varphi}\times\frac{\partial \mathbf{s}}{\partial\theta}\right| d\varphi d\theta \\
&= \frac{R}{4\pi}\int_0^{2\pi}\int_0^{\pi} \frac{\mathbf{s}'-\mathbf{s}(\varphi,\theta)}{|\mathbf{s}'-\mathbf{s}(\varphi,\theta)|^3}\cdot\mathbf{s}(\varphi,\theta)\phi(\mathbf{s}(\varphi,\theta))\sin\varphi d\varphi d\theta,
\end{aligned}$$

where $s' = \mathbf{s}(\varphi',\theta')$ for a fixed point $(\varphi',\theta') \in D$. In this way, the boundary integral equation (3.7) is simplified as

$$\begin{aligned}
u(\mathbf{s}(\varphi',\theta')) &= \frac{q}{2\pi(\varepsilon_s+\varepsilon_p)}\frac{1}{|\mathbf{s}(\varphi',\theta')-\mathbf{r}_0|} \\
&+ \frac{R(\varepsilon_s-\varepsilon_p)}{2\pi(\varepsilon_s+\varepsilon_p)}\int_0^{2\pi}\int_0^{\pi}\frac{[\mathbf{s}(\varphi',\theta')-\mathbf{s}(\varphi,\theta)]\cdot\mathbf{s}(\varphi,\theta)}{|\mathbf{s}(\varphi',\theta')-\mathbf{s}(\varphi,\theta)|^3}u(\mathbf{s}(\varphi,\theta))\sin\varphi d\varphi d\theta
\end{aligned} \tag{4.1}$$

for each point $(\varphi',\theta') \in D$.

For test purposes, we consider only a piecewise constant finite element method for solving the above Fredholm equation of the second kind [18]. That is, the unknown function u is approximated as a piecewise constant function,

$$u(\mathbf{s}(\varphi,\theta)) \approx \sum_{k=1}^{N} u_k\psi_k(\varphi,\theta),$$

based on a uniform rectangular mesh partition of domain D,

$$D = \bigcup_{k=1}^{N} \triangle_k,$$

where $\triangle_k = [\varphi_i,\varphi_{i+1}]\times[\theta_j,\theta_{j+1}]$ is a rectangular element with $k = (j-1)m+i$, $\varphi_i = (i-1)h_1$, $\theta_j = (j-1)h_2$, and $N = mn$ for $i = 1,2,\ldots,m$ and $j = 1,2,\ldots,n$.

Here $h_1 = \pi/m$, $h_2 = 2\pi/n$, u_k denotes a constant approximation to $u(\mathbf{s}(\varphi,\theta))$ for $(\varphi,\theta) \in \triangle_k$, and $\psi_k(\varphi,\theta)$ is the kth basis function defined by

$$\psi_k(\varphi,\theta) = \begin{cases} 1 & \text{if } (\varphi,\theta) \in \triangle_k, \\ 0 & \text{otherwise .} \end{cases}$$

Let $K : L_2(D) \to L_2(D)$ be the integral operator defined for any $u \in L_2(D)$ by

$$Ku(\varphi',\theta') = \int_0^{2\pi}\int_0^{\pi} \frac{[\mathbf{s}(\varphi',\theta') - \mathbf{s}(\varphi,\theta)]\cdot \mathbf{s}(\varphi,\theta)}{|\mathbf{s}(\varphi',\theta') - \mathbf{s}(\varphi,\theta)|^3} u(\mathbf{s}(\varphi,\theta)) d\varphi d\theta, \ \forall (\varphi',\theta') \in D,$$

where $L_2(D)$ denotes the set of all square integrable functions on D with the inner product $\langle u, v\rangle = \int_D u(x)v(x)dx$. Then, the integral equation (4.1) can be approximated as a system of linear equations:

$$u_k\langle \psi_k, \psi_k\rangle = \frac{2}{\varepsilon_s + \varepsilon_p}\langle g, \psi_k\rangle + \frac{R(\varepsilon_s - \varepsilon_p)}{2\pi(\varepsilon_s + \varepsilon_p)} \sum_{l=1}^{N} u_l \langle K\psi_l, \psi_k\rangle \tag{4.2}$$

for $k = 1, 2, \ldots, N$.

For simplicity, all integrals on each rectangular element $\triangle_k$ are evaluated approximately by one of the following two rectangular quadratures:

$$\int_{\triangle_k} f(\varphi,\theta) d\varphi d\theta \approx h_1 h_2 f(\varphi_i, \theta_j) \ \text{ and } \int_{\triangle_k} f(\varphi,\theta) d\varphi d\theta \approx h_1 h_2 f(\varphi_{i+1}, \theta_{j+1}),$$

depending on the need of dealing with a singularity problem in double integral evaluations. Using the above quadratures and writing u_k as u_{ij} for $k = (j-1)m + i$, we can approximate the linear system (4.2) as

$$\begin{aligned} u_{kl} &= \frac{2q}{4\pi(\varepsilon_s + \varepsilon_p)} \frac{1}{|\mathbf{s}(\varphi_k,\theta_l) - \mathbf{r}_0|} \\ &+ h_1 h_2 \frac{R(\varepsilon_s - \varepsilon_p)}{2\pi(\varepsilon_s + \varepsilon_p)} \Big[\sum_{(i,j)\neq(k,l)} u_{ij} \frac{[\mathbf{s}(\varphi_k,\theta_l) - \mathbf{s}(\varphi_i,\theta_j)]\cdot \mathbf{s}(\varphi_i,\theta_j)}{|\mathbf{s}(\varphi_k,\theta_l) - \mathbf{s}(\varphi_i,\theta_j)|^3} \sin\varphi_i \\ &+ u_{kl} \frac{[\mathbf{s}(\varphi_k,\theta_l) - \mathbf{s}(\varphi_{k+1},\theta_{l+1})]\cdot \mathbf{s}(\varphi_k,\theta_l)}{|\mathbf{s}(\varphi_k,\theta_l) - \mathbf{s}(\varphi_{k+1},\theta_{l+1})|^3} \sin\varphi_k \Big], \end{aligned} \tag{4.3}$$

where $k = 1, 2, \ldots, m$ and $l = 1, 2, \ldots, n$. Note that a simple treatment has been made in the above linear system to remove the singularity point at $(i, j) = (k, l)$.

Using the natural ordering (i.e., order the mesh points (φ_i, θ_j) from left to right and then from bottom to top), we write the linear system (4.3) in the matrix form

$$[I - c(h_1, h_2)A]U = b, \tag{4.4}$$

where $c(h_1,h_2) = h_1 h_2 \frac{R(\varepsilon_s - \varepsilon_p)}{2\pi(\varepsilon_s + \varepsilon_p)}$, I denotes the identity matrix, $A = (a_{\mu,\nu})$ is a $N \times N$ matrix, and U and b are two column vectors as defined below:

$$U = (u_{11}, u_{21}, \ldots, u_{m1}, u_{12}, u_{22}, \ldots, u_{m2}, \ldots, u_{1n}, u_{2n}, \ldots, u_{mn})^t,$$

and

$$b = (b_{11}, b_{21}, \ldots, b_{m1}, b_{12}, b_{22}, \ldots, b_{m2}, \ldots, b_{1n}, b_{2n}, \ldots, b_{mn})^t.$$

Here the entries b_{kl} and $a_{\mu\nu}$ for $\mu = (l-1)m+k$ and $\nu = (j-1)m+i$ are defined by

$$b_{kl} = \frac{q}{2\pi(\varepsilon_s+\varepsilon_p)}\frac{1}{|\mathbf{s}(\varphi_k,\theta_l)-\mathbf{r}_0|} \text{ and } a_{\mu\nu} = \frac{[\mathbf{s}(\varphi_k,\theta_l)-\mathbf{s}(\varphi_i,\theta_j)]\cdot\mathbf{s}(\varphi_i,\theta_j)}{|\mathbf{s}(\varphi_k,\theta_l)-\mathbf{s}(\varphi_i,\theta_j)|^3}\sin\varphi_i.$$

Further, we set $a_{\mu\nu}=0$ if $|\mathbf{s}(\varphi_k,\theta_l)-\mathbf{s}(\varphi_i,\theta_j)|<10^{-10}$ in our actual calculations.

When U is obtained from solving the linear system (4.4), a value of the potential function $\phi(\mathbf{r})$ for $\mathbf{r}\in\mathbb{R}^3\setminus\partial D_p$ can be calculated approximately by the formula

$$\phi(\mathbf{r}) = \begin{cases} \frac{1}{\varepsilon_p}g(\mathbf{r}) + \frac{R(\varepsilon_s-\varepsilon_p)}{4\pi\varepsilon_p}h_1h_2\sum_{j=1}^{n}\sum_{i=1}^{m}\kappa(\mathbf{r},\varphi_i,\theta_j)u_{ij} & \text{if } \mathbf{r}\in D_p, \\ \frac{1}{\varepsilon_s}g(\mathbf{r}) + \frac{R(\varepsilon_s-\varepsilon_p)}{4\pi\varepsilon_s}h_1h_2\sum_{j=1}^{n}\sum_{i=1}^{m}\kappa(\mathbf{r},\varphi_i,\theta_j)u_{ij} & \text{if } \mathbf{r}\in D_s, \end{cases} \tag{4.5}$$

where

$$g(\mathbf{r}) = \frac{q}{4\pi|\mathbf{r}-\mathbf{r}_0|}, \quad \text{and } \kappa(\mathbf{r},\varphi_i,\theta_j) = \frac{[\mathbf{r}-\mathbf{s}(\varphi_i,\theta_j)]\cdot\mathbf{s}(\varphi_i,\theta_j)}{|\mathbf{r}-\mathbf{s}(\varphi_i,\theta_j)|^3}\sin\varphi_i.$$

4.2 Analytical solutions of the dielectric sphere model

When the point charge q is outside the dielectric sphere (i.e., $d>R$), the analytical solution of this model problem can be found as given in Problem 4.9 in Jackson's textbook [16] (Dr. Dezso Boda provided us with the solution manual). For completeness, we cite it as below:

$$\phi(r,\varphi) = \begin{cases} \frac{q}{4\pi\varepsilon_s}\sum_{j=0}^{\infty}\frac{1+2j}{1+j\sigma_2}P_j(\cos\varphi)\frac{r^j}{d^{j+1}} & \text{if } r<R, \\ \frac{q}{4\pi\varepsilon_s}\sum_{j=0}^{\infty}\left[1+\frac{R^{2j+1}}{r^{2j+1}}\frac{j\sigma_1}{1+j\sigma_2}\right]P_j(\cos\varphi)\frac{r^j}{d^{j+1}} & \text{if } R<r<d, \\ \frac{q}{4\pi\varepsilon_s}\sum_{j=0}^{\infty}\left[1+\frac{R^{2j+1}}{d^{2j+1}}\frac{j\sigma_1}{1+j\sigma_2}\right]P_j(\cos\varphi)\frac{d^j}{r^{j+1}} & \text{if } r>d, \end{cases} \tag{4.6}$$

where $\sigma_1=(1-\varepsilon_p/\varepsilon_s)$, $\sigma_2=(1+\varepsilon_p/\varepsilon_s)$, $0\le\varphi\le\pi$, and P_j denotes the Legendre polynomial of the jth degree.

Since $P_j(1)=1$ for all j, setting $\varphi=0$ in (4.6) gives a value of the potential energy function $\phi(\mathbf{r})$ at $\mathbf{r}=(0,0,z)\in\mathbb{R}^3$ for $z>0$. We will calculate only these values of $\phi(\mathbf{r})$ in our numerical tests.

When the point charge is inside the dielectric sphere (i.e., $d<R$), the analytical solution can be found in [10] (eq. (2) to (4), Page 848). Here we only cite it in the case of $\varphi=0$ (i.e., along the z-axis) as below:

$$\phi(r,0) = \begin{cases} \frac{q(1+\gamma)}{4\pi\varepsilon_p}\sum_{j=0}^{\infty}\left(1+\frac{\gamma}{1-\gamma+2j}\right)\frac{d^j}{r^{j+1}} & \text{if } r>R, \\ \frac{q}{4\pi\varepsilon_p}\sum_{j=0}^{\infty}\left[\frac{r^j}{d^{j+1}}+\frac{(rd)^j\gamma}{R^{2j+1}}\left(1+\frac{\gamma}{1-\gamma+2j}\right)\right] & \text{if } 0<r<d, \\ \frac{q}{4\pi\varepsilon_p}\sum_{j=0}^{\infty}\left[\frac{d^j}{r^{j+1}}+\frac{(rd)^j\gamma}{R^{2j+1}}\left(1+\frac{\gamma}{1-\gamma+2j}\right)\right] & \text{if } d<r<R, \end{cases} \tag{4.7}$$

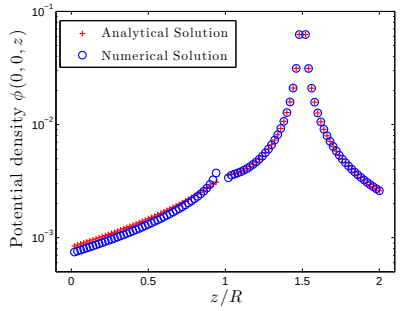

Fig. 4.3 Comparison of the numerical solutions with the analytical solution given in (4.6) for the point charge outside the dielectric sphere.

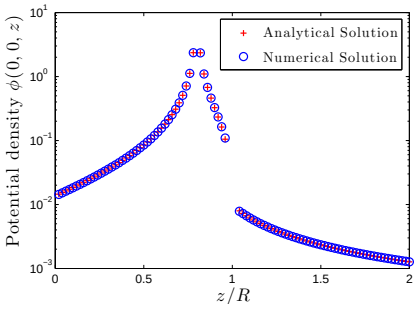

Fig. 4.4 Comparison of the numerical solutions with the analytical solution given in (4.7) for the point charge inside the dielectric sphere .

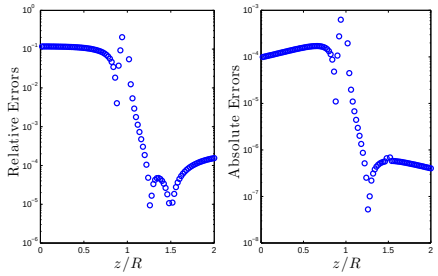

Fig. 4.5 Errors of the numerical solutions for the point charge outside the dielectric sphere compared with the analytical solution given in (4.6)

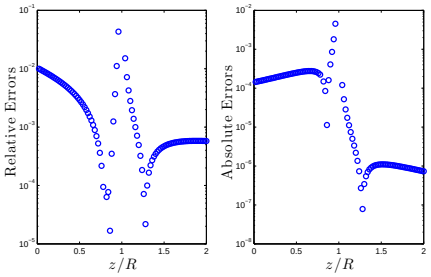

Fig. 4.6 Errors of the numerical solutions for the point charge inside the dielectric sphere compared with the analytical solution given in (4.7).

where $\gamma = (\varepsilon_p - \varepsilon_s)/(\varepsilon_p + \varepsilon_s)$. The analytical solution with point charge outside the sphere is also given in [10] (eq. (5) to (7), Page 849).

When the point charge lies on the sphere with $d = R$, we found the analytical solution in the form

$$\phi(r,\varphi) = \begin{cases} \dfrac{q}{4\pi\varepsilon_p} \displaystyle\sum_{j=0}^{\infty} \frac{1+2j}{j+(1+j)\varepsilon_s/\varepsilon_p} P_j(\cos\varphi) \frac{r^j}{R^{j+1}} & \text{if } r < R, \\ \dfrac{q}{4\pi\varepsilon_s} \displaystyle\sum_{j=0}^{\infty} \frac{1+2j}{1+j(1+\varepsilon_p/\varepsilon_s)} P_j(\cos\varphi) \frac{R^j}{r^{j+1}} & \text{if } r > R. \end{cases} \tag{4.8}$$

4.3 Numerical tests

We wrote a Matlab program and made tests with $R = 4$, $q = 5$, $\varepsilon_p = 2$, $\varepsilon_s = 80$, $n = m = 150$, and $0 < z < 8$. Here the linear system (4.4) was solved by using Matlab's direct solver of linear systems. See Figures 4.1 and 4.2 for illustratons. After

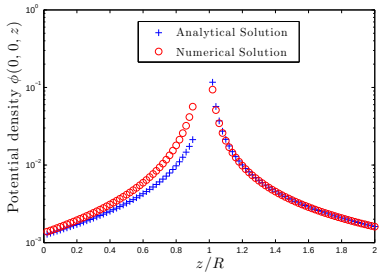

Fig. 4.7 Comparison of the numerical solutions with the analytical solution given in (4.8) for the point charge lying on the dielectric sphere.

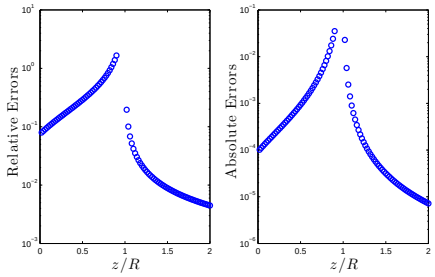

Fig. 4.8 Errors of the numerical solutions for the point charge lying on the dielectric sphere compared with the analytical solution given in (4.8).

obtaining the numerical solution of the linear system (4.4), we calculated 98 values of $\phi(\mathbf{r})$ at $\mathbf{r} = (0,0,z_k)$ for $z_k = kh$ with $h = 0.08$ and $k = 1,2,\ldots,100$ except of the two points $(0,0,R)$ and $(0,0,d)$ at which the analytical formula (4.6) is undefined. In the case of the point charge outside the dielectric sphere, we set $d = 1.5R = 6$ while in the case inside the sphere, we set $d = 0.8R = 3.2$. Using $d = R$ gives the case of the charge on the sphere. The analytical potential values were calculated by using the first 1000 terms of their series expressions (4.6) to (4.8). In the case of the point charge on the sphere, we modified the term $|\mathbf{s}(\varphi_k,\theta_l) - \mathbf{r}_0|$ as $|\mathbf{s}(\varphi_{k+1},\theta_{l+1}) - \mathbf{r}_0|$ if $\mathbf{s}(\varphi_k,\theta_l) = \mathbf{r}_0$ to avoid the singularity in the calculations of the values of $g(\mathbf{s})$ for the linear system (4.3).

The comparisons of the numerical values of $\phi(\mathbf{r}_k)$ with the corresponding analytical values are presented in Figures 4.3, 4.4, and 4.7. The absolute and relative errors of the numerical solutions are also displayed in Figures 4.5, 4.6, and 4.8 as a function of variable z/R. From these figures we can see that the numerical solutions match the analytical solutions very well. Figures 4.5, 4.6, and 4.8 display that each numerical solution value has good accuracy even though all the related integrals were calculated approximately by using the simplest rectangular quadratures.

From the above numerical tests we see that the largest errors occur at the points near the spherical surface. They can be reduced by using advanced numerical quadratures and special singular integral strategies for solving the integral equation (3.7) [**?**,18,19,33]. These numerical techniques will be considered in our future studies.

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