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A Modified Nonlocal Continuum Electrostatic Model for Protein in Water and Its Analytical Solutions for Ionic Born Models

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Abstract. A nonlocal continuum electrostatic model, defined as integro-differential equations, can significantly improve the classic Poisson dielectric model, but is too costly to be applied to large protein simulations. To sharply reduce the model's complexity, a modified nonlocal continuum electrostatic model is presented in this paper for a protein immersed in water solvent, and then transformed equivalently as a system of partial differential equations. By using this new differential equation system, analytical solutions are derived for three different nonlocal ionic Born models, where a monoatomic ion is treated as a dielectric continuum ball with point charge either in the center or uniformly distributed on the surface of the ball. These solutions are analytically verified to satisfy the original integro-differential equations, thereby, validating the new differential equation system.

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Key words: Nonlocal continuum electrostatic models, Poisson dielectric equations, protein-water interface problem, nonlocal ionic Born models.

1 Introduction

Continuum electrostatic models play an important role in the study and simulation of protein functions and protein-ligand relations [21,27]. Based on both classical and quantum mechanical approaches, they have been well developed in terms of the Poisson and Poisson-Boltzmann equations, and have been widely applied to the calculation of electrostatic potential energy for protein simulations in both water and ionic solvent environments [1,7,10,17,22,24,28]. In these models, water is simply treated as a featureless

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continuum medium with a dielectric constant; an important structural feature — the polarization correlations among water molecules — is totally ignored.

To develop more sophisticated continuum electrostatic models that reflect this structural feature of water, an approach called "nonlocal electrostatics" has been studied in literature [2–6,18–20,26,29]. In this approach, the dielectric constant of water is replaced by a dielectric function $\epsilon(\mathbf{r},\mathbf{r}')$ of two space variables $\mathbf{r}$ and $\mathbf{r}'$ such that the linear response relation of the displacement field $\mathbf{d}(\mathbf{r})$ with the electric field $\mathbf{e}(\mathbf{r})$, which is defined as $\nabla\Phi(\mathbf{r})$, is extended as a triple integral over the water range domain D_s:

$$\mathbf{d}(\mathbf{r})=\epsilon_0\int_{D_s}\epsilon(\mathbf{r},\mathbf{r}')\nabla\Phi(\mathbf{r}')\mathrm{d}\mathbf{r}', \quad \mathbf{r}\in D_s, \tag{1.1}$$

where $\Phi(\mathbf{r})$ denotes the electrostatic potential density function. The classic Poisson dielectric model is then extended as a nonlocal continuum electrostatic model. As defined in integro-differential equations, however, the nonlocal model is too costly to be solved numerically for a large protein simulation problem. One strategy to sharply reduce the cost of solving a nonlocal model is to reformulate the nonlocal model as a set of differential equations. This strategy has been adopted by several authors, yielding some numerical algorithms and program packages for solving nonlocal models [9,13,15,23,30,32].

We observed that the complexity of a nonlocal model can be sharply reduced, provided that the gradient operator ∇ is taken out of the integration [32]. Since the domain D_s of integration may have a complicated geometry, such a switch of the gradient operator with the integral operator may produce either mathematical uncertainty or computational difficulties (e.g., using Green's formula results in a surface integral over the interface Γ between the protein and water ranges, which is difficult to compute since Γ is a molecular surface of the protein). To avoid such potential obstacles, in this paper, we simply modify the relation (1.1) by setting the domain of integration as the whole space $\mathbb{R}^3$. Such a modification is reasonable since each water molecule is also subject to the polarization correlations from all other charged atoms/ions outside the water range domain D_s. Using this modified integral of (1.1), we derive a modified nonlocal continuum electrostatic model, in which the integral terms can be expressed in terms of convolution. Using the properties of convolution, we then rigorously transform the modified nonlocal model equivalently from the integro-differential equations into a system of partial differential equations, along with proper jump conditions on the interface between the water and protein ranges. Our differential formulation is different from the one given in [13,15].

To validate our differential formulation, we use the new differential equation system to calculate the analytical solutions of two typical nonlocal ionic Born models, called the nonlocal point charge Born model and the nonlocal spherical shell Born model. In these models, a monoatomic ion is treated as a dielectric continuum ball with point charge in the center or uniformly distributed on the surface of the ball, respectively. We also find the analytical solution of a traditional nonlocal point charge Born model defined in [13,15] based on our approach. Furthermore, by direct calculation of convolution, we verify that these analytical solutions satisfy their original integro-differential equations.

This confirms the veracity of our new differential equation system and our analytical solutions. These analytical solutions will be valuable in the validation of any numerical algorithm for solving a nonlocal model.

Finally, we checked the analytical solution of the traditional nonlocal point charge Born model given in [15, (3.57) and (3.58)] and [13, (17)]. The direct calculation of convolution shows that this analytical solution does not satisfy the original integro-differential equation.

The paper is organized as follows. Section 2 presents the modified nonlocal dielectric continuum model. Section 3 reformulates this nonlocal model as a system of partial differential equations. Section 4 derives the analytical solutions of three nonlocal ionic Born models. Section 5 verifies that the analytical solutions satisfy their original intego-differential equations.

2 A modified nonlocal dielectric model for protein in water

Let D_s denote the water solvent region and D_p a cavity region that hosts a protein and is surrounded by D_s such that the whole space has the decomposition

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

where Γ denotes the interface between D_p and D_s. As usual [12,15], the protein region D_p is treated as a continuum medium with a dielectric constant, ϵ_p, while the water solvent region D_s with a dielectric function, $\epsilon(\mathbf{r},\mathbf{r}')$, such that the displacement field $\mathbf{d}$ has the following linear relationship with the electric field $\mathbf{e}$:

$$\mathbf{d}(\mathbf{r}) = \epsilon_0 \int_{\mathbb{R}^3} \epsilon(\mathbf{r},\mathbf{r}')\mathbf{e}(\mathbf{r}')\mathrm{d}\mathbf{r}', \quad \mathbf{r}\in\mathbb{R}^3. \tag{2.1}$$

Here $\mathbf{d}$ and $\mathbf{e}$ are induced from the charge density function $\rho(\mathbf{r})$ and the electrostatic potential function $\Phi(\mathbf{r})$, respectively, by

$$\mathbf{e}(\mathbf{r}) = \nabla\Phi(\mathbf{r}), \quad \mathbf{r}\in\mathbb{R}^3, \tag{2.2}$$

and

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

where $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$ is the gradient operator for $\mathbf{r} = (x,y,z)$.

While the dielectric function $\epsilon(\mathbf{r},\mathbf{r}')$ can be set in different expressions [8,13,15,30], in this paper, we define it by

$$\epsilon(\mathbf{r},\mathbf{r}') = \bar{\epsilon}(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') + \kappa(\mathbf{r})Q_\lambda(\mathbf{r}-\mathbf{r}'), \tag{2.4}$$

where δ denotes the Dirac-delta function, $\bar{\epsilon}(\mathbf{r})$ and $\kappa(\mathbf{r})$ are two piecewise constant functions defined by

$$\bar{\epsilon}(\mathbf{r}) = \begin{cases} \epsilon_p, & \mathbf{r}\in D_p, \\ \epsilon_\infty, & \mathbf{r}\in D_s, \end{cases} \quad \text{and} \quad \kappa(\mathbf{r}) = \begin{cases} 0, & \mathbf{r}\in D_p, \\ \epsilon_s - \epsilon_\infty, & \mathbf{r}\in D_s, \end{cases} \tag{2.5}$$

and $Q_\lambda(\mathbf{r})$ is set as

$$Q_\lambda(\mathbf{r})=\frac{1}{4\pi\lambda^2|\mathbf{r}|}e^{-|\mathbf{r}|/\lambda},\quad \mathbf{r}\neq 0. \tag{2.6}$$

Here ϵ_s is the dielectric constant of water solvent, λ is a positive parameter for characterizing the polarization correlations of water molecules and other charged atoms/ions, and ϵ_∞ is the permittivity factor for water in the limit of high frequency [31]. In general, $\epsilon_s>\epsilon_\infty>0$. For example, in [30], the authors selected $\epsilon_s=78.5$, $\epsilon_\infty=1.8$, $\epsilon_p=2$, and $\lambda=20$Å.

Applying (2.1), (2.2), and (2.4) to (2.3), we obtain a modified nonlocal dielectric continuum model for a protein in water:

$$\begin{cases} -\nabla\cdot(\bar{\epsilon}(\mathbf{r})\nabla\Phi(\mathbf{r})+\kappa(\mathbf{r})\int_{\mathbb{R}^3}Q_\lambda(\mathbf{r}-\mathbf{r}')\nabla\Phi(\mathbf{r}')\mathrm{d}\mathbf{r}')=\frac{1}{\epsilon_0}\rho(\mathbf{r}), & \mathbf{r}\in\mathbb{R}^3\setminus\Gamma,\\ \Phi(\mathbf{r})\to 0, & \text{as } |\mathbf{r}|\to\infty. \end{cases} \tag{2.7}$$

From the classic linear dielectric theory [12, 16] it is known that the electrostatic potential is continuous on the interface Γ,

$$\Phi(\mathbf{s}^+)=\Phi(\mathbf{s}^-),\quad \mathbf{s}\in\Gamma, \tag{2.8}$$

and the electric displacement field $\mathbf{d}$ has continuity in the normal vector direction on the interface Γ,

$$\mathbf{d}(\mathbf{s}^+)\cdot\mathbf{n}(\mathbf{s})=\mathbf{d}(\mathbf{s}^-)\cdot\mathbf{n}(\mathbf{s}),\quad \mathbf{s}\in\Gamma, \tag{2.9}$$

where $\mathbf{n}(\mathbf{s})$ denotes the unit outward normal vector of protein region D_p, and $\Phi(\mathbf{s}^\pm)$ and $\mathbf{d}(\mathbf{s}^\pm)$ denote the limits at the interface point $\mathbf{s}$ from inside and outside D_p along the direction of $\mathbf{n}(s)$. That is,

$$\Phi(\mathbf{s}^\pm)=\lim_{t\to 0+}\Phi(\mathbf{s}\pm t\mathbf{n}(\mathbf{s})),\quad \text{and}\quad \mathbf{d}(\mathbf{s}^\pm)=\lim_{t\to 0+}\mathbf{d}(\mathbf{s}\pm t\mathbf{n}(\mathbf{s})).$$

Applying (2.2) and (2.4) to (2.1) immediately yields

$$\mathbf{d}(\mathbf{r})=\begin{cases} \epsilon_0\epsilon_p\nabla\Phi(\mathbf{r}), & \mathbf{r}\in D_p\\ \epsilon_0\epsilon_\infty\nabla\Phi(\mathbf{r})+\epsilon_0(\epsilon_s-\epsilon_\infty)\int_{\mathbb{R}^3}Q_\lambda(\mathbf{r}-\mathbf{r}')\nabla\Phi(\mathbf{r}')\mathrm{d}\mathbf{r}', & \mathbf{r}\in D_s. \end{cases}$$

Thus, (2.9) implies the second interface condition as required for solving the nonlocal model (2.7):

$$\epsilon_\infty\frac{\partial\Phi(\mathbf{s}^+)}{\partial\mathbf{n}(\mathbf{s})}+(\epsilon_s-\epsilon_\infty)\int_{\mathbb{R}^3}Q_\lambda(\mathbf{s}-\mathbf{r}')\nabla\Phi(\mathbf{r}')\mathrm{d}\mathbf{r}'\cdot\mathbf{n}(\mathbf{s})=\epsilon_p\frac{\partial\Phi(\mathbf{s}^-)}{\partial\mathbf{n}(\mathbf{s})},\quad \mathbf{s}\in\Gamma, \tag{2.10}$$

where

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

For clarity, the restrictions of Φ and ρ onto the protein and water regions D_p and D_s are denoted as Φ_p, Φ_s, ρ_p, and ρ_s, respectively, such that

$$\rho(\mathbf{r})=\begin{cases}\rho_p(\mathbf{r}), & \mathbf{r}\in D_p,\\ \rho_s(\mathbf{r}), & \mathbf{r}\in D_s,\end{cases}\quad\text{and}\quad \Phi(\mathbf{r})=\begin{cases}\Phi_p(\mathbf{r}), & \mathbf{r}\in D_p,\\ \Phi_s(\mathbf{r}), & \mathbf{r}\in D_s,\end{cases}$$

In the above notation, the nonlocal dielectric model (2.7) and its two interface conditions (2.8) and (2.10) are re-written as

$$\begin{cases}-\epsilon_p\Delta\Phi_p(\mathbf{r})=\frac{1}{\epsilon_0}\rho_p(\mathbf{r}), & \mathbf{r}\in D_p,\\ -\epsilon_\infty\Delta\Phi_s(\mathbf{r})-(\epsilon_s-\epsilon_\infty)\nabla\cdot\int_{\mathbb{R}^3}Q_\lambda(\mathbf{r}-\mathbf{r}')\nabla\Phi(\mathbf{r}')\mathrm{d}\mathbf{r}'=\frac{1}{\epsilon_0}\rho_s(\mathbf{r}), & \mathbf{r}\in D_s,\\ \Phi_s(\mathbf{r})\to 0, & \text{as } |\mathbf{r}|\to\infty,\end{cases}\tag{2.11}$$

where

$$\Delta=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2},$$

and Φ_s and Φ_p satisfy the interface conditions

$$\Phi_s(\mathbf{s})=\Phi_p(\mathbf{s}),\quad \mathbf{s}\in\Gamma,\tag{2.12}$$

and

$$\epsilon_\infty\frac{\partial\Phi_s(\mathbf{s})}{\partial\mathbf{n}(\mathbf{s})}+(\epsilon_s-\epsilon_\infty)\int_{\mathbb{R}^3}Q_\lambda(\mathbf{s}-\mathbf{r}')\nabla\Phi(\mathbf{r}')\mathrm{d}\mathbf{r}'\cdot\mathbf{n}(\mathbf{s})=\epsilon_p\frac{\partial\Phi_p(\mathbf{s})}{\partial\mathbf{n}(\mathbf{s})},\quad \mathbf{s}\in\Gamma.\tag{2.13}$$

We note that the integral term of (2.7) is actually the convolution $\nabla\Phi*Q_\lambda$ of $\nabla\Phi$ with the kernel function Q_λ, i.e.,

$$(\nabla\Phi*Q_\lambda)(\mathbf{r})=\int_{\mathbb{R}^3}Q_\lambda(\mathbf{r}-\mathbf{r}')\nabla\Phi(\mathbf{r}')\mathrm{d}\mathbf{r}',$$

and the convolution has the derivative property:

$$D^\alpha(v*Q_\lambda)=(D^\alpha v)*Q_\lambda=v*D^\alpha Q_\lambda,\tag{2.14}$$

where

$$D^\alpha=\frac{\partial^{|\alpha|}}{\partial x^{\alpha_1}\partial y^{\alpha_2}\partial z^{\alpha_3}}$$

denotes the $|\alpha|$-order partial derivative for $\alpha=(\alpha_1,\alpha_2,\alpha_3)$ with α_1, α_2, and α_3 being non-negative integers and $|\alpha|=\alpha_1+\alpha_2+\alpha_3$ (See Theorem 6.30 in [25, Page 171], for example). Using (2.14), we can obtain

$$(\nabla\Phi*Q_\lambda)(\mathbf{r})=\nabla(\Phi*Q_\lambda)(\mathbf{r}),\quad\text{and}\quad \nabla\cdot(\nabla\Phi*Q_\lambda)(\mathbf{r})=(\Phi*\Delta Q_\lambda)(\mathbf{r}),\quad \mathbf{r}\in D_s.\tag{2.15}$$

By the first identity of (2.15), the interface condition (2.13) is simplified as

$$\epsilon_p \frac{\partial \Phi_p(\mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} = \epsilon_\infty \frac{\partial \Phi_s(\mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} + (\epsilon_s - \epsilon_\infty) \frac{\partial (\Phi * Q_\lambda)(\mathbf{s})}{\partial \mathbf{n}(\mathbf{s})}, \quad \mathbf{s} \in \Gamma. \tag{2.16}$$

It is also known that the kernel function $Q_\lambda(\mathbf{r})$ of (2.6) satisfies the equation

$$-\lambda^2 \Delta Q_\lambda(\mathbf{r}) + Q_\lambda(\mathbf{r}) = \delta(\mathbf{r}), \quad \mathbf{r} \in \mathbf{R}^3. \tag{2.17}$$

Doing the convolution of Φ on the both sides of the above equation yields

$$(\Phi * \Delta Q_\lambda)(\mathbf{r}) = \frac{1}{\lambda^2}[(\Phi * Q_\lambda)(\mathbf{r}) - \Phi_s(\mathbf{r})], \quad \mathbf{r} \in D_s. \tag{2.18}$$

Thus, the second identity of (2.15) can be simplified as

$$\nabla \cdot (\nabla \Phi * Q_\lambda)(\mathbf{r}) = \frac{1}{\lambda^2}[(\Phi * Q_\lambda)(\mathbf{r}) - \Phi_s(\mathbf{r})], \quad \mathbf{r} \in D_s.$$

Hence, the modified nonlocal electrostatic model (2.11) is simplified as follows:

$$\begin{cases} -\epsilon_p \Delta \Phi_p(\mathbf{r}) = \frac{1}{\epsilon_0}\rho_p(\mathbf{r}), & \mathbf{r} \in D_p, \\ -\epsilon_\infty \Delta \Phi_s(\mathbf{r}) + \frac{(\epsilon_s - \epsilon_\infty)}{\lambda^2}[\Phi_s(\mathbf{r}) - (\Phi * Q_\lambda)(\mathbf{r})] = \frac{1}{\epsilon_0}\rho_s(\mathbf{r}), & \mathbf{r} \in D_s. \\ \Phi_s(\mathbf{r}) \to 0, & \text{as } |\mathbf{r}| \to \infty, \end{cases} \tag{2.19}$$

along with the interface conditions (2.12) and (2.16).

Remark 2.1. The above model is often called the Fourier-Lorentzian nonlocal model or simply the Lorentzian model. In applications, the issue arises how to select a proper value of λ. The choice of λ depends on a particular solvent. In [2, Table 1], eight different values of λ were obtained in the range from 3 to 8 for eight different ionic solvents to fit the experimental data. Two values 15 and 30 of λ, which bracket the value $\lambda = 23$Å used in [15], were tested in [32, Figure 2.1] for 9 different types of ions in the calculation of free energy differences, showing that a nonlocal model is relatively insensitive to the choice of λ. In the case of protein in water, a typical λ-range of 10 to 20Å is suggested in [14].

3 Reformulation as differential equations

Even the new form (2.19) has greatly simplified the original nonlocal model (2.11), its finite element or finite difference approximation still leads to a fully dense linear matrix problem (see a proof in [32]). Further complexity reduction is required to yield a feasible nonlocal model for a large scale protein simulation problem.

To do so, we regard the convolution term as a unknown function,

$$u(\mathbf{r}) = \Phi * Q_\lambda(\mathbf{r}), \quad \mathbf{r} \in R^3. \tag{3.1}$$

With (2.18) and the identity $\Phi * \Delta Q_\lambda = \Delta(\Phi * Q_\lambda)$ we find that u satisfies the equation

$$-\lambda^2 \Delta u(\mathbf{r}) + u(\mathbf{r}) - \Phi(\mathbf{r}) = 0, \quad \mathbf{r} \in R^3. \tag{3.2}$$

Since $\Phi_s(\mathbf{r})$ goes to zero as $|\mathbf{r}| \to 0$, it is clear that $u(\mathbf{r})$ goes to zero too.

A combination of (3.2) with (2.19) immediately yields a system of partial differential equations for solving the unknown functions Φ_p, Φ_s, and u:

$$\begin{cases} -\epsilon_p \Delta \Phi_p(\mathbf{r}) = \frac{1}{\epsilon_0}\rho_p(\mathbf{r}), & \mathbf{r} \in D_p, \\ -\epsilon_\infty \Delta \Phi_s(\mathbf{r}) + \frac{(\epsilon_s - \epsilon_\infty)}{\lambda^2}\Phi_s(\mathbf{r}) - \frac{(\epsilon_s - \epsilon_\infty)}{\lambda^2} u(\mathbf{r}) = \frac{1}{\epsilon_0}\rho_s(\mathbf{r}), & \mathbf{r} \in D_s \\ -\lambda^2 \Delta u(\mathbf{r}) + u(\mathbf{r}) - \Phi(\mathbf{r}) = 0, & \mathbf{r} \in R^3. \end{cases} \tag{3.3}$$

We can define u_p and u_s, respectively, by

$$-\lambda^2 \Delta u_p(\mathbf{r}) + u_p(\mathbf{r}) - \Phi_p(\mathbf{r}) = 0, \quad \mathbf{r} \in D_p, \tag{3.4}$$

and

$$-\lambda^2 \Delta u_s(\mathbf{r}) + u_s(\mathbf{r}) - \Phi_s(\mathbf{r}) = 0, \quad \mathbf{r} \in D_s. \tag{3.5}$$

Since u is continuously differentiable over the whole space $\mathbb{R}^3$, which follows from (3.1), u_p and u_s can be set to satisfy the interface conditions

$$u_p(\mathbf{s}) = u_s(\mathbf{s}), \quad \frac{\partial u_p(\mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} = \frac{\partial u_s(\mathbf{s})}{\partial \mathbf{n}(\mathbf{s})}, \quad \mathbf{s} \in \Gamma. \tag{3.6}$$

In terms of u_s, the interface condition (2.13) becomes

$$\epsilon_p \frac{\partial \Phi_p(\mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} = \epsilon_\infty \frac{\partial \Phi_s(\mathbf{s})}{\partial \mathbf{n}(\mathbf{s})} + (\epsilon_s - \epsilon_\infty)\frac{\partial u(\mathbf{s})}{\partial \mathbf{n}(\mathbf{s})}, \quad \mathbf{s} \in \Gamma. \tag{3.7}$$

Hence, the differential equation system (3.3) can be re-described as the interface problem:

$$\begin{cases} -\epsilon_p \Delta \Phi_p(\mathbf{r}) = \frac{1}{\epsilon_0}\rho_p(\mathbf{r}), \\ -\lambda^2 \Delta u_p(\mathbf{r}) + u_p(\mathbf{r}) - \Phi_p(\mathbf{r}) = 0, \quad \mathbf{r} \in D_p, \end{cases} \tag{3.8}$$

and

$$\begin{cases} -\epsilon_\infty \Delta \Phi_s(\mathbf{r}) + \frac{(\epsilon_s - \epsilon_\infty)}{\lambda^2}[\Phi_s(\mathbf{r}) - u_s(\mathbf{r})] = \frac{1}{\epsilon_0}\rho_s(\mathbf{r}), \\ -\lambda^2 \Delta u_s(\mathbf{r}) + u_s(\mathbf{r}) - \Phi_s(\mathbf{r}) = 0, \qquad \mathbf{r} \in D_s, \end{cases} \tag{3.9}$$

where both $u_s(\mathbf{r})$ and $\Phi_s(\mathbf{r})$ go to zero as $|\mathbf{r}| \to \infty$, Φ_p and Φ_s satisfy the interface conditions (3.7), and u_p and u_s satisfy (3.6).

Obviously, the above system of partial differential equations is well defined with the boundary and interface conditions. It can be solved approximately by a finite difference or finite element method as a sparse linear matrix problem. Hence, it is feasible to be applied to the calculation of electrostatics for a large scale biomolecular system.

Remark 3.1. In [32], a fast solver has been developed for solving the nonlocal model of water (i.e., Eq. (3.9) with D_s being the whole space $\mathbb{R}^3$) based on a solution splitting approach. We intend to extend such a fast solver to the numerical solution of protein-water interface problem (3.8) and (3.9) in our subsequent paper.

4 Analytical solutions of three nonlocal ionic Born models

In this section, we use the differential equations (3.8) and (3.9) to calculate the analytical solutions of two nonlocal ionic Born models: One is called the point charge Born model, and the other is the spherical shell Born model. Furthermore, we also similarly find the exact solution of a traditional nonlocal point charge Born model that was considered in [13, 15]. These three models are also simply called Models A, B, and C, respectively. Here one monoatomic ion with charge q is treated as a dielectric ball with radius $a>0$ so that we have that

$$D_p=\{\mathbf{r}:|\mathbf{r}|<a\},\quad \Gamma=\{\mathbf{r}:|\mathbf{r}|=a\},\quad D_s=\{\mathbf{r}:|\mathbf{r}|>a\},\quad \text{and}\quad \rho_s(\mathbf{r})=0.$$

4.1 Point charge Born model (Model A)

In the point charge Born model, charge q is placed at the center of the ball D_p. Thus, the charge density function is $\rho(\mathbf{r})=q\delta(\mathbf{r})$, and the model is defined by the equations

$$-\epsilon_p\Delta\Phi_p(\mathbf{r})=\frac{q}{\epsilon_0}\delta(\mathbf{r}), \qquad |\mathbf{r}|<a, \tag{4.1}$$

$$\epsilon_\infty\Delta\Phi_s(\mathbf{r})+(\epsilon_s-\epsilon_\infty)\nabla\cdot v(\mathbf{r})=0, \qquad |\mathbf{r}|>a, \tag{4.2}$$

$$\Phi_p(\mathbf{s})=\Phi_s(\mathbf{s}), \qquad |\mathbf{s}|=a, \tag{4.3}$$

$$\big(\epsilon_p\nabla\Phi_p(\mathbf{s})-\epsilon_\infty\nabla\Phi_s(\mathbf{s})-(\epsilon_s-\epsilon_\infty)v(\mathbf{s})\big)\cdot\mathbf{n}=0, \qquad |\mathbf{s}|=a, \tag{4.4}$$

and $\Phi_s(\mathbf{r})\to 0$ as $|\mathbf{r}|\to\infty$. Here $v(\mathbf{r})$ is defined by

$$v(\mathbf{r})=\int_{\mathbb{R}^3}Q_\lambda(\mathbf{r}-\mathbf{r}')\nabla_{\mathbf{r}'}\Phi(\mathbf{r}')\,d\mathbf{r}'. \tag{4.5}$$

The electrostatic potential $\Phi(\mathbf{r})=\Phi(r)$ with $r=|\mathbf{r}|$ is a radial function. From Theorem A.1 in the appendix we know that $u(\mathbf{r})=u(r)$ is a radial function too. Hence, by using spherical coordinates, the partial differential equations (3.8) and (3.9) can be simplified as a system of ordinary differential equations:

$$\begin{cases} \frac{\mathrm{d}^2}{\mathrm{d}r^2}\big(r\Phi_p(r)\big)=0, \\ -\frac{\mathrm{d}^2}{\mathrm{d}r^2}\big(ru_p(r)\big)+\frac{1}{\lambda^2}[ru_p(r)-r\Phi_p(r)]=0 \quad \text{for } 0<r<a, \end{cases} \tag{4.6}$$

and

$$\begin{cases} -\frac{\mathrm{d}^2}{\mathrm{d}r^2}\big(r\Phi_s(r)\big)+\frac{(\epsilon_s-\epsilon_\infty)}{\epsilon_\infty\lambda^2}[r\Phi_s(r)-ru_s(r)]=0, \\ -\frac{\mathrm{d}^2}{\mathrm{d}r^2}\big(ru_s(r)\big)+\frac{1}{\lambda^2}[ru_s(r)-r\Phi_s(r)]=0, \qquad \text{for } a<r<\infty. \end{cases} \tag{4.7}$$

The interface conditions (3.6) and (3.7) become

$$\Phi_p(a)=\Phi_s(a), \tag{4.8}$$
$$\epsilon_p\Phi_p'(a)=\epsilon_\infty\Phi_s'(a)+(\epsilon_s-\epsilon_\infty)u_s'(a), \tag{4.9}$$
$$u_p(a)=u_s(a), \tag{4.10}$$
$$u_p'(a)=u_s'(a), \tag{4.11}$$

and the boundary conditions are given by

$$u_s(r)\to 0 \quad \text{and} \quad \Phi_s(r)\to 0, \quad \text{as } r\to\infty. \tag{4.12}$$

Because of the continuity of $u(\mathbf{r})$ for all $|\mathbf{r}|<\infty$, u_p is bounded within the ball D_p. Thus, it must satisfy

$$\lim_{r\to 0} r u_p(r)=0. \tag{4.13}$$

Let

$$\kappa=\frac{1}{\lambda}\sqrt{\frac{\epsilon_s}{\epsilon_\infty}}.$$

Because of (4.12), the solution of (4.7) is given by

$$\Phi_s(r)=\frac{1}{r}(A_1+\frac{\epsilon_\infty-\epsilon_s}{\epsilon_\infty}A_2e^{-\kappa r}), \quad a<r<\infty, \tag{4.14}$$
$$u_s(r)=\frac{1}{r}(A_1+A_2e^{-\kappa r}), \qquad a<r<\infty, \tag{4.15}$$

where A_1 and A_2 are two constants to be determined.

Solving the first equation of (4.6), we obtain that

$$\Phi_p(r)=\frac{q}{4\pi\epsilon_0\epsilon_p r}+A_3, \tag{4.16}$$

where the original Poisson equation (4.1) has been used to gain the constant $q/(4\pi\epsilon_0\epsilon_p)$.

We then solve the second equation of (4.6) to get

$$u_p(r)=\frac{1}{r}\left[A_4\sinh(r/\lambda)+A_5\cosh(r/\lambda)+\frac{q}{4\pi\epsilon_0\epsilon_p}\right]+A_3. \tag{4.17}$$

The five constants A_1, A_2, A_3, A_4, and A_5 are determined uniquely by the four interface conditions (4.8) to (4.11) and the condition (4.13). A short calculation shows that the interface condition (4.9) involves only A_1 so that A_1 is directly found from (4.9):

$$A_1=\frac{q}{4\pi\epsilon_0\epsilon_s}. \tag{4.18}$$

With (4.13), we can get the value of A_5:

$$A_5=-\frac{q}{4\pi\epsilon_0\epsilon_p}. \tag{4.19}$$

By using the interface conditions (4.8), (4.10), and (4.11), the following system of three linear equations is constructed for solving the remaining three constants A_2, A_3, and A_4:

$$\begin{pmatrix} \frac{\epsilon_\infty-\epsilon_s}{\epsilon_\infty}e^{-\kappa a} & -a & 0 \\ e^{-\kappa a} & -a & -\sinh\frac{a}{\lambda} \\ e^{-\kappa a}\lambda(1+a\kappa) & 0 & a\cosh\frac{a}{\lambda}-\lambda\sinh\frac{a}{\lambda} \end{pmatrix} \begin{pmatrix} A_2 \\ A_3 \\ A_4 \end{pmatrix} = \frac{q}{4\pi\epsilon_0\epsilon_p} \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix},$$

where

$$b_1 = \frac{\epsilon_s-\epsilon_p}{\epsilon_s}, \quad b_2 = \frac{\epsilon_s-\epsilon_p}{\epsilon_s}-\cosh\frac{a}{\lambda}, \quad \text{and} \quad b_3 = \frac{\lambda(\epsilon_s-\epsilon_p)}{\epsilon_s}+a\sinh\frac{a}{\lambda}-\lambda\cosh\frac{a}{\lambda}.$$

Solving the above linear system gives

$$A_2 = -\frac{q}{4\pi\epsilon_0\epsilon_p\epsilon_s}\frac{\epsilon_\infty e^{\kappa a}[a\epsilon_s+\lambda(\epsilon_p-\epsilon_s)\sinh\frac{a}{\lambda}]}{[a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s)]\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}, \tag{4.20}$$

$$A_3 = \frac{q}{4\pi\epsilon_0 a\epsilon_p\epsilon_s}\left(\epsilon_p-\epsilon_s-\frac{(\epsilon_\infty-\epsilon_s)[a\epsilon_s+\lambda(\epsilon_p-\epsilon_s)\sinh\frac{a}{\lambda}]}{[a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s)]\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}\right), \tag{4.21}$$

$$A_4 = \frac{q}{4\pi\epsilon_0\epsilon_p}\frac{(\epsilon_s-\epsilon_p)\lambda+a\epsilon_s\sinh\frac{a}{\lambda}+[a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s)]\cosh\frac{a}{\lambda}}{[a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s)]\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}. \tag{4.22}$$

In summary, the solution $\Phi(\mathbf{r})$ of the nonlocal point charge Born model is given by

$$\Phi_p(\mathbf{r}) = \frac{q}{4\pi\epsilon_0\epsilon_p}\left\{\frac{1}{|\mathbf{r}|}+\frac{1}{a\epsilon_s}\left(\epsilon_p-\epsilon_s-\frac{(\epsilon_\infty-\epsilon_s)[a\epsilon_s+\lambda(\epsilon_p-\epsilon_s)\sinh\frac{a}{\lambda}]}{[a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s)]\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}\right)\right\} \tag{4.23}$$

for $0<|\mathbf{r}|<a$, and

$$\Phi_s(\mathbf{r}) = \frac{q}{4\pi\epsilon_0\epsilon_s}\frac{1}{|\mathbf{r}|}\left\{1+\frac{e^{\kappa a}\frac{(\epsilon_s-\epsilon_\infty)}{\epsilon_p}[a\epsilon_s+\lambda(\epsilon_p-\epsilon_s)\sinh\frac{a}{\lambda}]}{[a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s)]\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}e^{-\kappa|\mathbf{r}|}\right\} \quad \text{for } |\mathbf{r}|>a. \tag{4.24}$$

Remark 4.1. The above expression of Φ_s can be rewritten in the form

$$\Phi_s(\mathbf{r}) = \frac{q}{4\pi\epsilon_0\epsilon_s}\frac{1}{|\mathbf{r}|}\left\{1+\frac{e^{\kappa a}\frac{(\epsilon_s-\epsilon_\infty)}{\epsilon_p}[\epsilon_s+(\epsilon_p-\epsilon_s)\frac{\sinh(a/\lambda)}{(a/\lambda)}]}{[a\sqrt{\epsilon_\infty\epsilon_s}/\lambda+(\epsilon_\infty-\epsilon_s)]\frac{\sinh(a/\lambda)}{(a/\lambda)}+\epsilon_s\cosh\frac{a}{\lambda}}e^{-\kappa|\mathbf{r}|}\right\}.$$

Since

$$\lim_{a\to0}\frac{\sinh(a/\lambda)}{(a/\lambda)}=1 \quad \text{and} \quad \lim_{a\to0}\cosh(a/\lambda)=1,$$

it is easy to get the limit

$$\lim_{a\to0}\Phi_s(\mathbf{r}) = \frac{q}{4\pi\epsilon_0\epsilon_s}\frac{1}{|\mathbf{r}|}\left[1+\frac{(\epsilon_s-\epsilon_\infty)}{\epsilon_\infty}e^{-\kappa|\mathbf{r}|}\right].$$

This gives the analytical solution of the nonlocal point charge model of water that we obtained in [32, see (5.8)] by a novel solution splitting formula.

4.2 Spherical shell Born model (Model B)

We next consider a spherical shell Born model as defined below:

$$-\epsilon_p \Delta \Phi_p(\mathbf{r}) = 0, \qquad |\mathbf{r}| < a, \tag{4.25}$$

$$\epsilon_\infty \Delta \Phi_s(\mathbf{r}) + (\epsilon_s - \epsilon_\infty)\nabla \cdot v(\mathbf{r}) = 0, \qquad |\mathbf{r}| > a, \tag{4.26}$$

$$\Phi_p(\mathbf{s}) = \Phi_s(\mathbf{s}), \qquad |\mathbf{s}| = a, \tag{4.27}$$

$$\big(\epsilon_p \nabla \Phi_p(\mathbf{s}) - \epsilon_\infty \nabla \Phi_s(\mathbf{s}) - (\epsilon_s - \epsilon_\infty) v(\mathbf{s})\big) \cdot \mathbf{n} = \frac{q}{4\pi\epsilon_0 a^2}, \quad |\mathbf{s}| = a, \tag{4.28}$$

and $\Phi_s(\mathbf{r}) \to 0$ as $|\mathbf{r}| \to \infty$. Here $v(\mathbf{r})$ is given in (4.5), and charge q has been distributed uniformly on the spherical surface $|\mathbf{r}| = a$.

Since the solution is a radial solution, the above equations can be simplified into the ordinary differential equations that are the same as the ones given in (4.6) to (4.13) except of (4.9), which is replaced by

$$\epsilon_p \Phi_p'(a) - \epsilon_\infty \Phi_s'(a) - (\epsilon_s - \epsilon_\infty) u_s'(a) = \frac{q}{4\pi\epsilon_0 a^2}. \tag{4.29}$$

Hence, its solution can be similarly obtained:

$$\begin{aligned}
&\Phi_s(r) = B_1 \frac{1}{r} + B_2 \frac{\epsilon_\infty - \epsilon_s}{\epsilon_\infty} \frac{e^{-\kappa r}}{r}, && a < r < \infty, \\
&u_s(r) = B_1 \frac{1}{r} + B_2 \frac{e^{-\kappa r}}{r}, && a < r < \infty, \\
&\Phi_p(r) = B_3, && 0 < r < a, \\
&u_p(r) = B_3 + B_4 \frac{\sinh(r/\lambda)}{r}, && 0 < r < a,
\end{aligned}$$

where (4.12) and (4.13) have been used. The constant

$$B_1 = \frac{q}{4\pi\epsilon_0 \epsilon_s} \tag{4.30}$$

is found from (4.29). The constants B_2, B_3 and B_4 are then determined by conditions (4.8), (4.10), and (4.11), from which it yields the following linear system:

$$\begin{pmatrix} \frac{\epsilon_\infty - \epsilon_s}{\epsilon_\infty} e^{-\kappa a} & -a & 0 \\ e^{-\kappa a} & -a & -\sinh\frac{a}{\lambda} \\ e^{-\kappa a}\lambda(1+a\kappa) & 0 & a\cosh\frac{a}{\lambda} - \lambda\sinh\frac{a}{\lambda} \end{pmatrix} \begin{pmatrix} B_2 \\ B_3 \\ B_4 \end{pmatrix} = -\frac{q}{4\pi\epsilon_0\epsilon_s} \begin{pmatrix} 1 \\ 1 \\ \lambda \end{pmatrix}.$$

Solving it gives

$$B_2=-\frac{q\epsilon_\infty}{4\pi\epsilon_0\epsilon_s}\frac{e^{\kappa a}\lambda\sinh\frac{a}{\lambda}}{(a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s))\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}, \tag{4.31}$$

$$B_3=\frac{q}{4\pi\epsilon_0\epsilon_s}\frac{\sqrt{\epsilon_\infty\epsilon_s}\sinh\frac{a}{\lambda}+\epsilon_s\cosh\frac{a}{\lambda}}{(a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s))\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}, \tag{4.32}$$

$$B_4=-\frac{q\lambda}{4\pi\epsilon_0}\frac{1}{(a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s))\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}. \tag{4.33}$$

Therefore, the solution of the nonlocal spherical shell Born model is found as follows:

$$\Phi_p(\mathbf{r})=\frac{q}{4\pi\epsilon_0\epsilon_s}\frac{\sqrt{\epsilon_\infty\epsilon_s}\sinh\frac{a}{\lambda}+\epsilon_s\cosh\frac{a}{\lambda}}{(a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s))\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}, \quad |\mathbf{r}|<a, \tag{4.34}$$

and

$$\Phi_s(\mathbf{r})=\frac{q}{4\pi\epsilon_0\epsilon_s}\frac{1}{|\mathbf{r}|}\left\{1+\frac{e^{\kappa a}(\epsilon_s-\epsilon_\infty)\lambda\sinh\frac{a}{\lambda}}{(a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s))\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}e^{-\kappa|\mathbf{r}|}\right\}, \quad |\mathbf{r}|>a. \tag{4.35}$$

We note that $\Phi_p(\mathbf{r})$ is now a constant function.

4.3 A traditional nonlocal point charge Born model (Model C)

We finally consider the following traditional nonlocal point charge Born model:

$$-\epsilon_p\Delta\Phi_p(\mathbf{r})=\frac{q}{\epsilon_0}\delta(\mathbf{r}), \qquad |\mathbf{r}|<a, \tag{4.36}$$

$$\epsilon_\infty\Delta\Phi_s(\mathbf{r})+(\epsilon_s-\epsilon_\infty)\nabla\cdot\hat{v}(\mathbf{r})=0, \qquad |\mathbf{r}|>a, \tag{4.37}$$

$$\Phi_p(\mathbf{s})=\Phi_s(\mathbf{s}), \qquad |\mathbf{s}|=a, \tag{4.38}$$

$$\left(\epsilon_p\nabla\Phi_p(\mathbf{s})-\epsilon_\infty\nabla\Phi_s(\mathbf{s})-(\epsilon_s-\epsilon_\infty)\hat{v}(\mathbf{s})\right)\cdot\mathbf{n}=0, \qquad |\mathbf{s}|=a, \tag{4.39}$$

where $\Phi_s(\mathbf{r})\to 0$ as $|\mathbf{r}|\to\infty$, and $\hat{v}$ is defined by

$$\hat{v}(\mathbf{r})=\int_{D_s}Q_\lambda(\mathbf{r}-\mathbf{r}')\nabla_{\mathbf{r}'}\Phi_s(\mathbf{r}')d\mathbf{r}'. \tag{4.40}$$

This model comes from [13] and [15, page 48].

For the above model, we extend $\Phi_s(\mathbf{r})$ continuously into the ball $|\mathbf{r}|<a$ by setting

$$\Phi_s(\mathbf{r})=\Phi_s(\mathbf{s}), \quad \text{for } |\mathbf{r}|<a, \quad \text{with } |\mathbf{s}|=a.$$

After this extension, $\Phi_s(\mathbf{r})$ becomes well defined in $\mathbb{R}^3$, and $\hat{v}$ can be expressed in the convolution form

$$\hat{v}(\mathbf{r})=\int_{\mathbb{R}^3}Q_\lambda(\mathbf{r}-\mathbf{r}')\nabla_{\mathbf{r}'}\Phi_s(\mathbf{r}')d\mathbf{r}'=(Q_\lambda*\nabla\Phi_s)(\mathbf{r})=\nabla(Q_\lambda*\Phi_s)(\mathbf{r}). \tag{4.41}$$

In this way, we can argue as before to obtain its analytical solution. For clarity, we set

$$w(\mathbf{r})=(Q_\lambda * \Phi_s)(\mathbf{r}).$$

Note that $w(\mathbf{r})$ may differ from $u(\mathbf{r})=(Q_\lambda*\Phi)(\mathbf{r})$ since $\Phi_s(\mathbf{r})$ may be different from $\Phi_p(\mathbf{r})$ for $|\mathbf{r}|<a$. We do calculation as before, obtaining that

$$\begin{aligned}
&\Phi_p(r)=C_3+\frac{q}{4\pi\epsilon_0\epsilon_p r}, && 0<r<a,\\
&\Phi_s(r)=C_1\frac{1}{r}+\frac{\epsilon_\infty-\epsilon_s}{\epsilon_\infty}C_2\frac{1}{r}e^{-\kappa r}, && a<r<\infty,\\
&w_p(r)=C_4\frac{1}{r}\sinh\frac{r}{\lambda}+C_1\frac{1}{a}+\frac{\epsilon_\infty-\epsilon_s}{\epsilon_\infty}C_2\frac{1}{a}e^{-\kappa a}, && 0<r<a,\\
&w_s(r)=C_1\frac{1}{r}+C_2\frac{1}{r}e^{-\kappa r}, && a<r<\infty,
\end{aligned}$$

where w_p and w_s denote the restriction of w to D_p and D_s, respectively, and we have used (4.36) and the boundary condition that w_s and Φ_s go to zero as $r\to\infty$.

With the interface condition (4.39), we find that

$$C_1=B_1.$$

We then use the interface conditions (4.38), $w_p(a)=w_s(a)$, and $w_p'(a)=w_s'(a)$ to obtain the following linear matrix system:

$$\begin{pmatrix} \frac{\epsilon_\infty-\epsilon_s}{\epsilon_\infty}e^{-\kappa a} & -a & 0\\ \frac{\epsilon_s}{\epsilon_\infty}e^{-\kappa a} & 0 & -\sinh\frac{a}{\lambda}\\ e^{-\kappa a}\lambda(1+a\kappa) & 0 & a\cosh\frac{a}{\lambda}-\lambda\sinh\frac{a}{\lambda}\end{pmatrix}\begin{pmatrix}C_2\\C_3\\C_4\end{pmatrix}=\frac{q}{4\pi\epsilon_0\epsilon_s}\begin{pmatrix}\frac{\epsilon_s}{\epsilon_p}-1\\0\\-\lambda\end{pmatrix}.$$

Its solution is found as below in terms of the values of B_1 to B_4 given in (4.30) to (4.33):

$$\begin{aligned}
&C_2=B_2,\\
&C_3=B_3-\frac{q}{4\pi\epsilon_0\epsilon_p a},\\
&C_4=B_4.
\end{aligned}$$

Therefore, the solution of the traditional nonlocal point charge Born model is given by

$$\Phi_p(\mathbf{r})=\frac{q}{4\pi\epsilon_0\epsilon_p}\left\{\frac{1}{|\mathbf{r}|}-\frac{1}{a}+\frac{\epsilon_p}{\epsilon_s}\frac{\sqrt{\epsilon_\infty\epsilon_s}\sinh\frac{a}{\lambda}+\epsilon_s\cosh\frac{a}{\lambda}}{(a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s))\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}\right\} \tag{4.42}$$

for $0<|\mathbf{r}|<a$, and

$$\Phi_s(\mathbf{r})=\frac{q}{4\pi\epsilon_0\epsilon_s}\frac{1}{|\mathbf{r}|}\left\{1+\frac{e^{\kappa a}(\epsilon_s-\epsilon_\infty)\lambda\sinh\frac{a}{\lambda}}{(a\sqrt{\epsilon_\infty\epsilon_s}+\lambda(\epsilon_\infty-\epsilon_s))\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}}e^{-\kappa|\mathbf{r}|}\right\},\quad |\mathbf{r}|>a. \tag{4.43}$$

We note that Φ_s in this problem agrees with the one in the spherical shell problem.

5 Verification of analytical solutions

In this section, we verify the analytical solutions obtained in the previous section. The key step of verification is to evaluate the convolution $Q_\lambda * \Phi$ and $Q_\lambda * \Phi_s$ since both $v(\mathbf{r})$ and $\hat{v}(\mathbf{r})$, which are defined in (4.5) and (4.40), can be reformulated as

$$v(\mathbf{r}) = \nabla(Q_\lambda * \Phi)(\mathbf{r}), \quad \text{and} \quad \hat{v}(\mathbf{r}) = \nabla(Q_\lambda * \Phi_s)(\mathbf{r}).$$

Both $Q_\lambda * \Phi$ and $Q_\lambda * \Phi_s$ will be calculated directly by using Formula (A.6), which is presented in Corollary A.1 in the appendix.

5.1 Case of the point charge Born model

We first verify our solution to the nonlocal point charge Born model defined in (4.1) to (4.5). In order to verify (4.2) and (4.4), we need to evaluate the convolution function $u(\mathbf{r}) = (Q_\lambda * \Phi)(\mathbf{r})$ analytically. Let $r = |\mathbf{r}|$. With formula (A.6), we obtain that

$$(Q_\lambda * \Phi)(\mathbf{r}) = \begin{cases} \frac{1}{r\lambda}\Big(e^{-\frac{r}{\lambda}}\int_0^r z\Phi_p(z)\sinh\frac{z}{\lambda}dz + \sinh\frac{r}{\lambda}\int_r^a z\Phi_p(z)e^{-\frac{z}{\lambda}}dz + \\ \qquad + \sinh\frac{r}{\lambda}\int_a^\infty z\Phi_s(z)e^{-\frac{z}{\lambda}}dz\Big), & |\mathbf{r}| < a, \\ \frac{1}{r\lambda}\Big(e^{-\frac{r}{\lambda}}\int_0^a z\Phi_p(z)\sinh\frac{z}{\lambda}dz + e^{-\frac{r}{\lambda}}\int_a^r z\Phi_s(z)\sinh\frac{z}{\lambda}dz + \\ \qquad + \sinh\frac{r}{\lambda}\int_r^\infty z\Phi_s(z)e^{-\frac{z}{\lambda}}dz\Big), & |\mathbf{r}| > a. \end{cases} \tag{5.1}$$

Substituting the expressions (4.23) and (4.24) of Φ_p and Φ_s to (5.1), we obtain that

$$\begin{aligned}(Q_\lambda * \Phi)(\mathbf{r}) &= \frac{q}{4\pi\epsilon_0\epsilon_p}\frac{1}{r}e^{-\frac{r}{\lambda}}\Big(\cosh\frac{a}{\lambda} - 1\Big) + A_3\frac{1}{r}e^{-\frac{r}{\lambda}}\Big(a\cosh\frac{a}{\lambda} - \lambda\sinh\frac{a}{\lambda}\Big) \\ &\quad + A_1\frac{1}{r}\Big(1 - e^{-\frac{r}{\lambda}}\cosh\frac{a}{\lambda}\Big) + A_2\frac{1}{r}e^{-\kappa r} \\ &\quad - A_2\frac{1}{r}e^{-\frac{r}{\lambda}}e^{-\kappa a}\Big(\cosh\frac{a}{\lambda} + \sqrt{\frac{\epsilon_s}{\epsilon_\infty}}\sinh\frac{a}{\lambda}\Big) \\ &= \frac{1}{r}(A_1 + A_2e^{-\kappa r}) = u_s(\mathbf{r}), \qquad \text{for } |\mathbf{r}| > a,\end{aligned}$$

where $u_s(\mathbf{r})$ and the values of A_1, A_2, and A_3, which are given in (4.15), (4.18), (4.20), and (4.21), respectively, have been used in the above direct calculation.

Similarly, we verify that

$$(Q_\lambda * \Phi)(\mathbf{r}) = u_p(\mathbf{r}), \qquad |\mathbf{r}| < a,$$

where u_p is given in (4.17).

With the above results, we verify the equations and interface conditions (4.1) to (4.5) by direct calculation.

5.2 Case of spherical shell Born model

Applying the solution expressions (4.34) and (4.35) into the formula (5.1), and then by direct calculation, we verify that our analytical solution given in (4.34) and (4.35) satisfies the equations of (4.25) to (4.28) and the boundary condition $\Phi_s(\mathbf{r})\to 0$ as $|\mathbf{r}|\to\infty$.

5.3 Case of traditional nonlocal model

Using formula (5.1) and direct calculation, we verify that the analytical solution of the traditional nonlocal point charge Born model given in (4.42) and (4.43) satisfies the original equations given in (4.36) to (4.40).

We note that "another analytical solution" of the traditional nonlocal point charge Born model was given in [15, (3.57) and (3.58)] and [13, (17)], where $\epsilon_p=1$ was assumed (i.e., the interior of the sphere is in vacuum). We recall it in our notation as below:

$$\Phi_p(\mathbf{r})=\frac{q}{4\pi\epsilon_0}\left[\frac{1}{|\mathbf{r}|}+\frac{1}{a\epsilon_s}\left(1-\epsilon_s+\frac{\epsilon_s-\epsilon_\infty}{\epsilon_\infty}\frac{\sinh(\kappa a)}{\kappa a}e^{-\kappa a}\right)\right],\quad |\mathbf{r}|<a, \tag{5.2}$$

and

$$\Phi_s(\mathbf{r})=\frac{q}{4\pi\epsilon_0\epsilon_s|\mathbf{r}|}\left(1+\frac{\epsilon_s-\epsilon_\infty}{\epsilon_\infty}\frac{\sinh(\kappa a)}{\kappa a}e^{-\kappa|\mathbf{r}|}\right),\quad |\mathbf{r}|>a, \tag{5.3}$$

from which it can be seen that they are different from ours in (4.42) and (4.43).

We show that (5.3) does not satisfy the equation (4.37) of the traditional nonlocal model. In fact, we let Φ_s be in the form

$$\Phi_s(\mathbf{r})=\frac{q}{4\pi\epsilon_0\epsilon_s|\mathbf{r}|}\left(1+\frac{\epsilon_s-\epsilon_\infty}{\epsilon_\infty}Se^{-\kappa|\mathbf{r}|}\right),\quad |\mathbf{r}|>a,$$

where S is a constant to be determined. We extend it continuously to $|\mathbf{r}|<a$ by a constant function as done in Subsection 4.3. Then, with formula (5.1), we calculate its convolution function $w(\mathbf{r})$ to get that

$$w(\mathbf{r})=(Q_\lambda * \Phi_s)(\mathbf{r})=\frac{q}{4\pi\epsilon_0\epsilon_s|\mathbf{r}|}\left(1-Se^{-\kappa|\mathbf{r}|}+(ST_2-T_1)e^{-|\mathbf{r}|/\lambda}\right),\quad |\mathbf{r}|>a,$$

where

$$T_1=\frac{\lambda}{a}\sinh\frac{a}{\lambda},\quad \text{and}\quad T_2=\frac{e^{-\kappa a}}{\epsilon_\infty a}\left\{[a\sqrt{\epsilon_s\epsilon_\infty}+\lambda(\epsilon_\infty-\epsilon_s)]\sinh\frac{a}{\lambda}+a\epsilon_s\cosh\frac{a}{\lambda}\right\}.$$

Further, with (4.41), we can reformulate equation (4.37) as

$$\epsilon_\infty\Delta\Phi_s(\mathbf{r})+(\epsilon_s-\epsilon_\infty)\Delta w(\mathbf{r})=0,\quad |\mathbf{r}|>a.$$

This yields

$$T_1=ST_2. \tag{5.4}$$

Table 1: Comparisons of the coefficients α_1, α_2, α_3, and α_4 of the solutions $\Phi(\mathbf{r})$ for the three nonlocal Born models reported in Subsections 4.1 to 4.3. These calculations were done by using $\lambda=15$, $a=1$, $q=2$, $\epsilon_p=1$, $\epsilon_\infty=1.8$, and $\epsilon_s=80$. Model C2 denotes the case of Model C with the functions given in (5.2) and (5.3) [15, (3.57) and (3.58))] and [13, (17)].

	α_1	α_2	α_3	α_4
Model A	28.79672675	−18.69545828	0.3599590845	15.19277503
Model B	0	10.71455628	Same	16.14927312
Model C	Same	−18.08217047	Same	Same as Model B
Model C2	Same	−18.07646606	Same	16.15816986

This equation does not hold when

$$S=\frac{\sinh(\kappa a)}{\kappa a}$$

and we get a contradiction. This completes the proof that the function $\Phi_s(\mathbf{r})$ of (5.3) is not the solution of the traditional nonlocal point charge Born model.

Note that the function $\Phi_s(\mathbf{r})$ we obtained in (4.43) can be expressed as

$$\Phi_s(\mathbf{r})=\frac{q}{4\pi\epsilon_0\epsilon_s|\mathbf{r}|}\left(1+\frac{\epsilon_s-\epsilon_\infty}{\epsilon_\infty}\left(-\frac{C_2}{C_1}\right)e^{-\kappa|\mathbf{r}|}\right),$$

and (5.4) does hold for

$$S=-\frac{C_2}{C_1},$$

where C_1 and C_2 are the two constants given in Section 4.3. Hence, our function $\Phi_s(\mathbf{r})$ is the exact solution of the original equation (4.36).

5.4 Comparisons of analytical solutions

From Section 4 it can be seen that the solutions of Models A, B, and C have the same form

$$\Phi(\mathbf{r})=\begin{cases}\alpha_1\frac{1}{|\mathbf{r}|}+\alpha_2, & |\mathbf{r}|<a,\\ \alpha_3\frac{1}{|\mathbf{r}|}+\alpha_4\frac{e^{-\kappa|\mathbf{r}|}}{|\mathbf{r}|}, & |\mathbf{r}|>a,\end{cases}\tag{5.5}$$

with suitable constants α_1, α_2, α_3, and α_4. Using $\lambda=15$, $a=1$Å, $q=2e_c$, $\epsilon_p=1$, $\epsilon_\infty=1.8$, and $\epsilon_s=80$, we calculated these constants and listed them in the table. Here $1\text{Å}=10^{-10}$ meter, and e_c denotes the charge of an electron, which is equal to 1.602×10^{-19} Coulomb. In calculation, we used $\epsilon_0=8.854\times10^{-12}$ Farad/meter.

The functions of (5.2) and (5.3) can also be expressed in a form of (5.5). As comparison, we calculated their values of α_1, α_2, α_3, and α_4, and listed them in the table as Model C2. It is interesting to note that although the functions of (5.2) and (5.3) does not yield the

exact solution of Model C, they have the same values of α_1 and α_3 as the exact solution, and their values of α_2 and α_4 are close to that of the exact solution:

$$(-18.07646606)-(-18.08217047)\approx 5.7044\times 10^{-3}, \quad \text{for } \alpha_2,$$

and

$$16.15816986-16.14927312\approx 8.8967\times 10^{-3}, \quad \text{for } \alpha_4.$$

This suggests that the functions of (5.2) and (5.3), which were obtained from another reformulation approach in [15, (3.57) and (3.58)] and [13, (17)] for Model C, may be used as a good approximation to the exact solution.

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Appendix

In this appendix, we present a proof to a calculation formula of convolution and an important fact that we use in our analytical solution calculation in Section 4. That is, a convolution of a radial function with another radial function remains a radial function and can be simplified to a one-dimensional integral. The following theorem can also be found in [11, page 743].

Theorem A.1. *If $f(\mathbf{r})=f(r)$ and $g(\mathbf{r})=g(r)$ are two radial functions in $\mathbb{R}^3$, then the convolution $(f*g)(\mathbf{r})=(f*g)(r)$ is a radial function, and*

$$(f*g)(r)=\frac{2\pi}{r}\int_0^\infty zf(z)[G(z+r)-G(|z-r|)]\mathrm{d}z, \quad 0<r<\infty, \tag{A.1}$$

where $r=|\mathbf{r}|$ for $\mathbf{r}\in\mathbb{R}^3$, $(f*g)(\mathbf{r})=\int_{\mathbb{R}^3} f(\mathbf{r}')g(\mathbf{r}-\mathbf{r}')\mathrm{d}\mathbf{r}'$, and G is defined by

$$G(\tau)=\int_0^\tau tg(t)\mathrm{d}t. \tag{A.2}$$

Proof. A function h is radial if and only if it satisfies

$$h(p\mathbf{r})=h(\mathbf{r}), \quad \mathbf{r}\in\mathbb{R}^3$$

for any orthogonal transformation p (a linear operator preserving the inner product $p\mathbf{r}\cdot p\mathbf{r}'=\mathbf{r}\cdot\mathbf{r}'$ for all $\mathbf{r},\mathbf{r}'\in R^3$). The calculation

$$\begin{aligned}(f*g)(p\mathbf{r})&=\int_{\mathbb{R}^3} f(p\mathbf{r}-\mathbf{r}')g(\mathbf{r}')\mathrm{d}\mathbf{r}'=\int_{\mathbb{R}^3} f(p\mathbf{r}-p\mathbf{r}')g(p\mathbf{r}')\mathrm{d}\mathbf{r}'\\&=\int_{\mathbb{R}^3} f(\mathbf{r}-\mathbf{r}')g(\mathbf{r}')\mathrm{d}\mathbf{r}'=(f*g)(\mathbf{r})\end{aligned}$$

shows that $f*g$ is indeed a radial function. Therefore, without loss of generality, we choose $\mathbf{r}=\langle 0,0,r\rangle$, which yields

$$|\mathbf{r}-\mathbf{r}'|=\sqrt{(x')^2+(y')^2+(z'-r)^2},\quad \text{for}\quad \mathbf{r}'=\langle x',y',z'\rangle.$$

Since f and g are radially symmetric, $(f*g)(\mathbf{r})$ can be written as

$$\begin{aligned}(f*g)(r)&=\int_{\mathbb{R}^3} f(|\mathbf{r}'|)g(|\mathbf{r}-\mathbf{r}'|)\mathrm{d}\mathbf{r}'\\&=\int_{\mathbb{R}^3} f(\sqrt{(x')^2+(y')^2+(z')^2})g(\sqrt{(x')^2+(y')^2+(z'-r)^2})\mathrm{d}x'\mathrm{d}y'\mathrm{d}z'.\end{aligned}$$

Changing to the spherical coordinates (z,θ,ϕ),

$$\begin{cases}x'=z\sin\phi\cos\theta,\\ y'=z\sin\phi\sin\theta,\\ z'=z\cos\phi,\end{cases}$$

where $0<z<\infty$, $0\le\theta\le 2\pi$, and $0\le\phi\le\pi$, we can get

$$\sqrt{(x')^2+(y')^2+(z')^2}=z\quad\text{and}\quad\sqrt{(x')^2+(y')^2+(z'-r)^2}=\sqrt{z^2+r^2-2zr\cos\phi},$$

and then simplify the triple integral into the iterated integral

$$\begin{aligned}(f*g)(r)&=\int_0^\infty\int_0^\pi\int_0^{2\pi} f(z)g(\sqrt{z^2+r^2-2zr\cos\phi})z^2\sin\phi\mathrm{d}\theta\mathrm{d}\phi\mathrm{d}z\\&=2\pi\int_0^\infty zf(z)\int_0^\pi g(\sqrt{z^2+r^2-2zr\cos\phi})z\sin\phi\mathrm{d}\phi\mathrm{d}z.\end{aligned}\tag{A.3}$$

Using the variable substitution $t=\sqrt{z^2+r^2-2zr\cos\phi}$, we can get

$$z\sin\phi\mathrm{d}\phi=\frac{t}{r}\mathrm{d}t.$$

The new limits of integration are

$$t=\sqrt{z^2+r^2-2zr}=|z-r|\quad\text{for}\ \phi=0\quad\text{and}\quad t=\sqrt{z^2+r^2+2zr}=z+r\quad\text{for}\ \phi=\pi.$$

Thus,

$$\int_0^\pi g(\sqrt{z^2+r^2-2zr\cos\phi})z\sin\phi\mathrm{d}\phi=\frac{1}{r}\int_{|z-r|}^{z+r} tg(t)\mathrm{d}t.$$

Hence, the integral (A.3) becomes

$$(f*g)(r)=\frac{2\pi}{r}\int_0^\infty zf(z)\int_{|z-r|}^{z+r} tg(t)\mathrm{d}t\mathrm{d}z.\tag{A.4}$$

Further, by setting

$$G(\tau)=\int_0^\tau tg(t)\mathrm{d}t, \tag{A.5}$$

the integral $\int_{|z-r|}^{z+r} tg(t)\mathrm{d}t$ can be expressed as

$$\int_{|z-r|}^{z+r} tg(t)\mathrm{d}t=G(z+r)-G(|z-r|).$$

So (A.4) is expressed in the form of (A.1). This completes the proof of Theorem A.1. □

Corollary A.1. *If f is a radial function, and*

$$Q_\lambda(\mathbf{r})=\frac{1}{4\pi\lambda^2|\mathbf{r}|}e^{-\frac{|\mathbf{r}|}{\lambda}},$$

then

$$(f*Q_\lambda)(\mathbf{r})=\frac{1}{r\lambda}\left(e^{-\frac{r}{\lambda}}\int_0^r zf(z)\sinh(\frac{z}{\lambda})\mathrm{d}z+\sinh(\frac{r}{\lambda})\int_r^\infty zf(z)e^{-\frac{z}{\lambda}}\mathrm{d}z\right), \tag{A.6}$$

where $0<r<\infty$, and $\sinh(x)=(e^x-e^{-x})/2$.

Proof. For $Q_\lambda(r)$, it is easy to find $G(\tau)$ as shown below:

$$\begin{aligned}G(\tau)&=\int_0^\tau tQ_\lambda(t)\mathrm{d}t=\int_0^\tau\frac{1}{4\pi\lambda^2}e^{-\frac{t}{\lambda}}\mathrm{d}t\\&=\frac{1}{4\pi\lambda^2}\int_0^\tau e^{-\frac{t}{\lambda}}\mathrm{d}t=-\frac{\lambda}{4\pi\lambda^2}e^{-\frac{t}{\lambda}}\Big|_0^\tau\\&=\frac{1}{4\pi\lambda}(1-e^{-\frac{\tau}{\lambda}}).\end{aligned} \tag{A.7}$$

Thus, with (A.1), we have that

$$\begin{aligned}(f*Q_\lambda)(r)&=\frac{2\pi}{r}\int_0^\infty zf(z)\frac{1}{4\pi\lambda}\left[(1-e^{-\frac{z+r}{\lambda}})-(1-e^{-|z-r|})\right]\mathrm{d}z\\&=\frac{1}{2r\lambda}\left[\int_0^r zf(z)\left(e^{-\frac{|z-r|}{\lambda}}-e^{-\frac{z+r}{\lambda}}\right)\mathrm{d}z+\int_r^\infty zf(z)\left(e^{-\frac{|z-r|}{\lambda}}-e^{-\frac{z+r}{\lambda}}\right)\mathrm{d}z\right]\\&=\frac{1}{2r\lambda}\left[\int_0^r zf(z)\left(e^{-\frac{r-z}{\lambda}}-e^{-\frac{z+r}{\lambda}}\right)\mathrm{d}z+\int_r^\infty zf(z)\left(e^{-\frac{z-r}{\lambda}}-e^{-\frac{z+r}{\lambda}}\right)\mathrm{d}z\right]\\&=\frac{1}{2r\lambda}\left[\int_0^r zf(z)\left(e^{\frac{z}{\lambda}}-e^{-\frac{z}{\lambda}}\right)e^{-\frac{r}{\lambda}}\mathrm{d}z+\int_r^\infty zf(z)\left(e^{\frac{r}{\lambda}}-e^{-\frac{r}{\lambda}}\right)e^{-\frac{z}{\lambda}}\mathrm{d}z\right]\\&=\frac{1}{r\lambda}\left(e^{-\frac{r}{\lambda}}\int_0^r zf(z)\sinh(\frac{z}{\lambda})\mathrm{d}z+\sinh(\frac{r}{\lambda})\int_r^\infty zf(z)e^{-\frac{z}{\lambda}}\mathrm{d}z\right).\end{aligned}$$

This completes the proof of Corollary A.1. □

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