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A regularization approach for solving Poisson's equation with singular charge sources and diffuse interfaces

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ABSTRACT

Singular charge sources in terms of Dirac delta functions present a well-known numerical challenge for solving Poisson's equation. For a sharp interface between inhomogeneous media, singular charges could be analytically treated by fundamental solutions or regularization methods. However, no analytical treatment is known in the literature in case of a diffuse interface of complex shape. This letter reports the first such regularization method that represents the Coulomb potential component analytically by Green's functions to account for singular charges. The other component, i.e., the reaction field potential, then satisfies a regularized Poisson equation with a smooth source and the original elliptic operator. The regularized equation can then be simply solved by any numerical method. By considering two benchmark problems, the proposed regularization method is numerically validated and compared with a semi-analytical quasi-harmonic method.

1. Introduction

The Poisson equation, as a mean field model, is widely used for the study of electrostatic interactions in biological and chemical systems at molecular level [1] and also for the design of semiconductor devices at the nanoscale [2]. In typical applications, two dielectric materials are concerned in the system and one of them carries fixed point charges, which are represented as Dirac delta functions in the source term of Poisson's equation. In classical settings, a sharp interface is assumed to separate two media, which yields a piecewise constant for the dielectric coefficient of Poisson's equation.

Recently, the use of diffuse interface Poisson models becomes popular [3,4]. For biological and chemical systems in molecular or nanoscales, the assumption of a sharp interface as the boundary of two dielectric materials seems to be unphysical [5]. The diffuse interface model [6], in which a smooth transition layer is assumed at material boundaries, provides an alternative to model the dielectric function. In studying electrostatic interactions of macromolecule and solvent, various free energy variational models have been

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proposed, including minimal molecular surface [7], level set [8], and phase field [9]. These models all feature a diffuse interface type dielectric boundary. In this letter, a simple Poisson's equation involving inhomogeneous media and a diffuse interface is studied. In particular, we will assume constant dielectric values inside each dielectric medium, while the dielectric function varies smoothly from one medium to another, through a narrow transition band.

The accurate treatment of singular charge sources of Poisson's equation is a well-known challenge. Mathematically, the fixed point charges are expressed in terms of the Dirac delta functions, which are unbounded at charge centers. In conventional numerical algorithms, a trilinear scheme is often used to distribute point charges to their neighboring grid points. This is known to be a very poor approximation, and motivates a recent development of a second order accurate geometric discretization of the multidimensional Dirac delta distribution [10]. We note that the numerical difficulty for representing singular functions via discrete finite values could be completely avoided if charge singularities are treated *analytically*.

For Poisson's equation with singular charges and diffuse interfaces, a family of semi-analytical methods have been proposed [4] for eleven orthogonal coordinate systems in which the three-dimensional (3D) Laplace equation is separable. The dielectric function is assumed to be variant only in one orthogonal direction, and the underlying diffuse interface can then be approximated via several pieces of quasi-harmonic diffuse interfaces. For each quasi-harmonic dielectric function, Green's functions for Poisson's equation can be calculated analytically. The singular charges are treated analytically in this approach with diffuse interfaces. Nevertheless, this semi-analytical method is limited to simple geometries. No analytical procedure is available in the literature for singular charges with complex domains and diffuse interfaces.

In a related field, a series of regularization methods have been developed for solving the Poisson–Boltzmann (PB) equation with singular charges and sharp interfaces over any domain, see the references in [11]. In regularization methods, the potential function is decomposed into a singular component plus one or two other components. Satisfying a Poisson equation with the same singular sources, the singular component can be analytically solved as Coulomb potentials or Green's functions. After removing the singular part, the other potential components are bounded, and thus can be accurately solved by finite difference or finite element methods. However, all existing regularization methods are designed for piecewise constant dielectric functions with sharp interfaces. It is unclear if regularization formulation could be established for diffuse interfaces.

This letter reports the first regularization method in the literature that is able to handle diffuse interfaces. Besides a decomposition of potential function, the success of the new method lies in a decomposition of the inhomogeneous dielectric function. The singular charge sources containing in a complex domain can then be analytically treated. The details of the proposed regularization formulation will be discussed in Section 2. This new method can be combined with any numerical discretization, and is expected to find extensive applications for various real world problems. Numerical validation for two examples will be considered in Section 3. Finally, this letter ends with a conclusion.

2. Regularization formulation

Consider a three-dimensional (3D) Poisson's equation with a Dirichlet boundary condition [4]

$$\begin{cases} -\nabla\cdot(\epsilon(\vec{r})\nabla u(\vec{r})) = \rho := 4\pi\sum_{j=1}^{N_s} q_j\delta(\vec{r}-\vec{r}_j), & \text{in } \Omega, \\ u(\vec{r}) = g(\vec{r}) & \text{on } \partial\Omega, \end{cases} \tag{1}$$

where u is the potential function and g is a boundary function. The domain Ω consists of three regions, an interior domain Ω_i, an exterior domain Ω_e, and a transition layer Ω_t in between Ω_i and Ω_e. See Fig. 1(a).

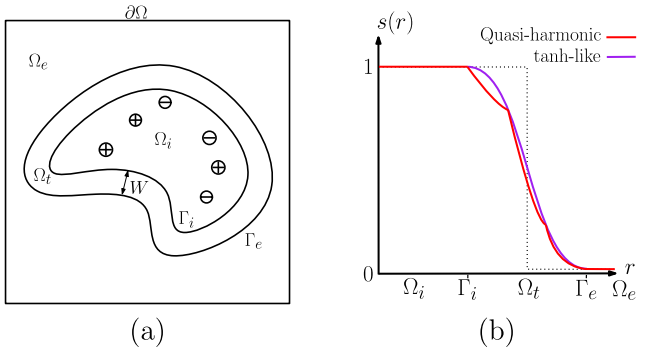


Fig. 1. (a) Domain setting of the problem; (b) Diffuse interfaces used in the spherical domain example.

The interface between Ω_i and Ω_t is denoted by Γ_i, while the one between Ω_t and Ω_e is Γ_e. There exist N_s point charges inside Ω_i with charge numbers being q_j, for $j = 1, 2, \ldots, N_s$. The dielectric function $\epsilon(\vec{r})$ takes constant values $\epsilon = \epsilon_i$ in Ω_i and $\epsilon = \epsilon_e$ in Ω_e. Here we assume $\epsilon_i < \epsilon_e$. In Ω_t, $\epsilon(\vec{r})$ varies smoothly from ϵ_i to ϵ_e, so that it is a C^2 continuous function over the entire domain Ω. Consequently, function u and its gradient ∇u are continuous everywhere in Ω, except at charge centers.

In the proposed two-component regularization, the potential u is decomposed into a Coulomb component u_C and a reaction field component u_{RF} with $u = u_C + u_{RF}$. As in the sharp interface case [11], the Coulomb potential is assumed to satisfy a homogeneous Poisson's equation with the same singular charges ρ

$$\begin{cases} -\epsilon_i \Delta u_C(\vec{r}) &= \rho(\vec{r}) \quad \text{in } \mathbb{R}^3; \\ u_C(\vec{r}) &= 0. \quad \text{as } |\vec{r}| \to \infty. \end{cases} \tag{2}$$

Thus, the singular component u_C is analytically given as the Green's function $G(\vec{r})$, i.e., $u_C(\vec{r}) = G(\vec{r}) := \sum_{j=1}^{N_s} \frac{q_j}{\epsilon_i |\vec{r} - \vec{r}_j|}$.

To deal with the diffuse interface, we propose to decompose the dielectric function into a constant base value plus a variant part, i.e., $\epsilon = \epsilon_i + \hat{\epsilon}$. Consequently, $\hat{\epsilon} = 0$ in Ω_i and $\hat{\epsilon} = \epsilon_e - \epsilon_i$ in Ω_e, with $\hat{\epsilon} \geq 0$ throughout the domain Ω. By introducing the dual decomposition into Poisson's equation (1), we have

$$-\nabla \cdot (\hat{\epsilon} \nabla u_C) - \nabla \cdot (\hat{\epsilon} \nabla u_{RF}) - \epsilon_i \Delta u_C - \epsilon_i \Delta u_{RF} = \rho, \quad \text{in } \Omega. \tag{3}$$

By subtracting (2) from (3), the Poisson equation is now free of singular sources

$$-\nabla \cdot (\hat{\epsilon} \nabla G) - \nabla \cdot (\hat{\epsilon} \nabla u_{RF}) - \epsilon_i \Delta u_{RF} = 0, \quad \text{in } \Omega, \tag{4}$$

where we have substituted u_C by the known Green's function G. Note that $G(\vec{r})$ is unbounded at charge centers inside Ω_i. However, in the proposed regularization, we have deliberately designed a nice property: $\hat{\epsilon} = 0$ in Ω_i. This enables us to simplify the new source term of Eq. (4) as,

$$\nabla \cdot (\hat{\epsilon} \nabla G) = \nabla \hat{\epsilon} \cdot \nabla G + \hat{\epsilon} \Delta G = \nabla \hat{\epsilon} \cdot \nabla G = \nabla \epsilon \cdot \nabla G. \tag{5}$$

In Eq. (5), $\hat{\epsilon} \Delta G$ is dropped out, because $\Delta G = 0$ everywhere except at charge centers within Ω_i, while $\hat{\epsilon} = 0$ in Ω_i. In the last step, we have $\nabla \epsilon = \nabla \hat{\epsilon}$ because ϵ and $\hat{\epsilon}$ differ by a constant ϵ_i. The gradient of Green's function is analytically given as $\nabla G(\vec{r}) = -\sum_{j=1}^{N_s} \frac{q_j (\vec{r} - \vec{r}_j)}{\epsilon_i |\vec{r} - \vec{r}_j|^3}$. Moreover, by the definition of ϵ, $\nabla \epsilon$ is non-vanishing only in Ω_t, while $\nabla \epsilon = 0$ for both Ω_i and Ω_e. Thus, $\nabla \epsilon \cdot \nabla G$ is finite in Ω, and one just needs to calculate it in the transition band Ω_t.

In summary, we propose a new regularized Poisson's equation for the reaction field potential

$$\begin{cases} -\nabla \cdot (\epsilon(\vec{r}) \nabla u_{RF}(\vec{r})) = \nabla \epsilon(\vec{r}) \cdot \nabla G(\vec{r}), & \text{in } \Omega, \\ u_{RF}(\vec{r}) = g(\vec{r}) - G(\vec{r}) & \text{on } \partial\Omega, \end{cases} \tag{6}$$

in which the two u_{RF} terms in Eq. (3) have been combined into one. Hence, the decomposition of dielectric function $\epsilon = \epsilon_i + \hat{\epsilon}$ is used only in the derivation. All real computations can be carried out based on $\epsilon(\vec{r})$ only. Once u_{RF} is computed from (6), the solution of the original Poisson's equation (1) is recovered by $u = u_{RF} + G$.

3. Numerical validation

In this letter, we validate the proposed regularization method by studying two benchmark examples. The diffuse interface is constructed through a level set function $s(\vec{r})$, which takes constant values $s_i = 1$ and $s_e = 0$, respectively, in Ω_i and Ω_e. In Ω_t, $s(\vec{r})$ varies smoothly from 1 to 0. The smooth dielectric function can then be calculated as $\epsilon(\vec{r}) = s(\vec{r})\epsilon_i + (1 - s(\vec{r}))\epsilon_e$, in which we take $\epsilon_i = 1$ and $\epsilon_e = 80$.

Example 1. Consider a spherical domain Ω_i with a point charge $q_1 = 1$ at its center. Assume the charge point to be the origin of our coordinate, i.e., $\vec{r}_1 = (0, 0, 0)$. A cubic computational domain $\Omega = [-10, 10]^3$ is employed. In this example, both boundaries Γ_i and Γ_e are spheres with radii being $r_i = 2$ and $r_e = 5$, respectively. In the transition layer $r_i < |\vec{r}| < r_e$, the level set function is given as $s(\vec{r}) = \frac{s_e - s_i}{2}[\tanh(k(\frac{|\vec{r}| - r_i}{r_e - r_i} - 0.5)) + 1] + s_i$, where $k = 6$ is large enough to ensure that $s(\vec{r})$ can be numerically assumed as a smooth function across Γ_i and Γ_e. An illustration of $s(r)$ for $r = |\vec{r}|$ is shown in Fig. 1(b) as a tanh-like curve.

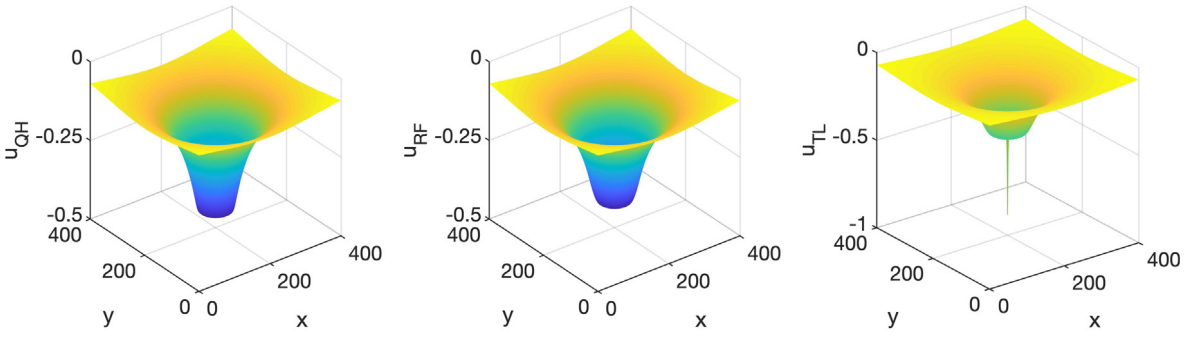
For a spherical domain, a semi-analytical method [4] is available to provide series solutions. Following [4], we first approximate the present tanh-like diffuse interface $s(r)$ by three pieces of quasi-harmonic diffuse interfaces. In particular, we will divide the transition region Ω_t into three spherical shells of the same thickness. Referring to Fig. 1(b), this amounts to cut the interval $r \in [r_i, r_e]$ into three subintervals of equal length. Then in each subinterval, one approximates $s(r)$ by a quasi-harmonic function such that its endpoint values agree with $s(r)$. This allows us to construct analytical series solution for the present example.

Besides the proposed regularization method, the trilinear method is also examined for a comparison. In both numerical methods, the central finite difference is employed to discretize the system. A uniform grid with the same mesh size in all three dimensions, i.e., $N = N_x = N_y = N_z$, is used with a spacing $h = \frac{20}{N-1}$. On boundary $\partial\Omega$, the Dirichlet boundary data is given by the Coulomb potential for exterior medium, i.e., $g(\vec{r}) = \frac{q_1}{\epsilon_e |\vec{r}|}$. For the regularization method, the reaction field potential $u_{RF}(\vec{r})$ will be reported. For both trilinear and quasi-harmonic methods, in order to directly compare with $u_{RF}(\vec{r})$, we will subtract the potential solution by Green's function, and denote the resulted solution as $u_{TL}(\vec{r})$ and $u_{QH}(\vec{r})$, respectively.

Before we present numerical results, it should be pointed out that the asymptotic limits of numerical solution and semi-analytical solution are different, because the quasi-harmonic diffuse interface is different from the tanh-like diffuse interface. Theoretically, two numerical solutions $u_{RF}(\vec{r})$ and $u_{TL}(\vec{r})$ should converge to the same place, as h goes to zero. However, the difference between $u_{RF}(\vec{r})$ and $u_{QH}(\vec{r})$ will not become smaller for a smaller h, and could be reduced only if more pieces of quasi-harmonic functions are employed for diffuse interface approximation.

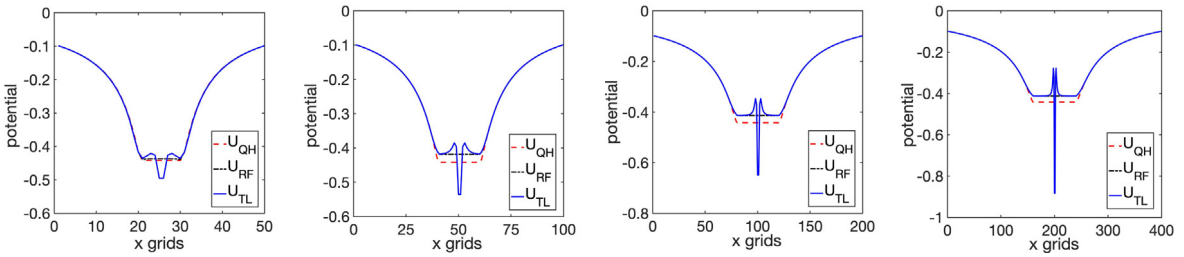
We first visually compare three solutions. By taking $N = 400$, surface plots of potential solutions u_{QH}, u_{RF} and u_{TL} on the plane $z = 0$ are shown in Fig. 2. It can be seen that the three solutions are almost identical for the majority part of the domain. For trilinear solution u_{TL}, numerical artifact is very obvious at the charge center. Excluding a small neighborhood around the origin, the difference between u_{RF} and u_{TL} is then very small. The regularization solution u_{RF} and semi-analytical solution u_{QH} have almost the same shape — a flat potential inside Ω_i with a smoothly increment outside the sphere. This indicates that the charge singularity is well taken care of in the proposed regularization method.

To see the differences in more detail, we depict three potentials along a x line with $y = 0$ and $z = 0$, see Fig. 3. For u_{RF} and u_{QH}, their difference is almost zero outside the sphere Ω_i, while inside the sphere, two



(a) u_{QH} (b) u_{RF} (c) u_{TL}

Fig. 2. Surface plot of potential solutions u_{QH}, u_{RF} and u_{TL} on the plane $z = 0$.



(a) $N = 50$ (b) $N = 100$ (c) $N = 200$ (d) $N = 400$

Fig. 3. Line plots of u_{QH}, u_{RF} and u_{TL} along a x line with $y = 0$ and $z = 0$.

Table 1
The comparison of three solutions' differences.

		$\lvert u_{QH} - u_{RF}\rvert$		$\lvert u_{QH} - u_{TL}\rvert$		$\lvert u_{RF} - u_{TL}\rvert$	
N	h	L_2	L_∞	L_2	L_∞	L_2	L_∞
50	0.408	7.66E−4	1.30E−2	9.60E−4	5.30E−2	6.12E−4	5.80E−2
100	0.202	1.82E−3	2.62E−2	1.87E−3	9.35E−2	4.53E−4	1.16E−1
200	0.101	2.19E−3	2.95E−2	2.21E−3	2.07E−1	3.23E−4	2.35E−1
400	0.050	2.29E−3	3.04E−2	2.30E−3	4.41E−1	2.29E−4	4.71E−1

flat potentials attain different heights. Moreover, the height difference here actually approaches a constant as N becomes larger, which is around 0.03. For trilinear solution u_{TL}, it obviously converges to u_{RF} in most parts, except for near the charge center. However, near the origin, the disagreement between u_{TL} and u_{RF} increases, suggesting a divergent behavior of trilinear charge distribution.

We finally quantitatively compare the difference of three solutions in L_2 and L_∞ norms for different N in Table 1. For the difference between u_{TL} and u_{RF}, the L_2 norm becomes smaller and smaller. This agrees with the above observation that both numerical solutions converge to the same place as h goes to zero. However, the L_∞ norm diverges in a rate inversely proportional to h, i.e., $O(h^{-1})$. This result fully illustrates how bad the trilinear approximation is. Fortunately, such a difficulty is analytically bypassed in our regularization method. For u_{QH} and u_{RF}, we note that the height difference between two solutions inside Ω_i is actually captured by the L_∞ norm, which is 3.04E−2 at $N = 400$. In fact, the L_∞ norm converges *quadratically* to a constant height difference. To see this, we take 3.04E−2 as the reference value for the "exact" height difference. Then the change in the L_∞ norm is 1.74E−2, 0.42E−2, and 0.09E−2, respectively, for $N = 50$, 100, and 200. This obviously is a sequence with $O(h^2)$ convergence, and demonstrates the second order accuracy of the central difference discretization underlying the regularization approach.

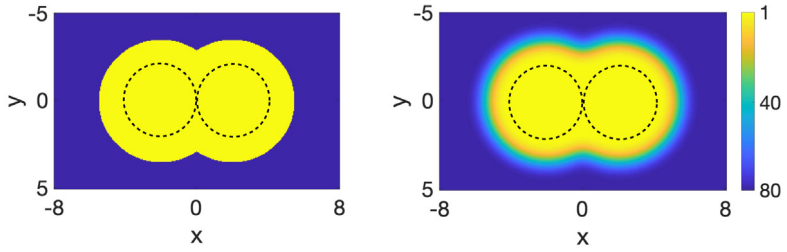


Fig. 4. Color map on the plane $z = 0$ for $\epsilon(\vec{r})$ before (left) and after (right) a Gaussian convolution in Example 2. In both figures, dashed lines represent the VdW surfaces. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Example 2. Consider two atoms with the same radius $R = 2$ and charge $q = 1$, and different centers at $(-2, 0, 0)$ and $(2, 0, 0)$. The computational domain is $\Omega = [-10, 10]^3$ with mesh size $N = 400$. To construct a diffuse interface, a solvent accessible surface (SAS) [7] is first defined based on a probe radius 1.5. Then a Heaviside function is defined as 1 and 0, respectively, for inside and outside of the SAS. At last, the Heaviside function is convoluted with a Gaussian kernel to generate a level set function $s(\vec{r})$, which is guaranteed to be 1 inside two balls while having a smooth transition outside two balls. The corresponding $\epsilon(\vec{r})$ functions before and after the convolution are illustrated in Fig. 4 on the plane $z = 0$. For this numerically generated diffuse interface, the proposed regularization method performs equally well. The electrostatic free energy of this two-atoms system is found to be -206.97 kcal/mol.

4. Conclusion

A novel regularization approach is introduced for Poisson's equation with singular charge sources and diffuse interfaces, which is the first of its kind in the literature. Through a dual decomposition of potential and dielectric functions, the proposed regularized Poisson's equation for the reaction field potential has the same elliptic operator with a smooth source function, which can be easily solved by common numerical methods. For two benchmark problems, the regularization method is validated by comparing with a semi-analytical method and conventional trilinear distribution method. The further development of the regularization method for the Poisson–Boltzmann equation and the Gaussian convolution algorithm for generating diffuse interfaces will be reported in the future.

CRediT authorship contribution statement

Siwen Wang: Software, Validation, Writing — review & editing. **Arum Lee:** Software. **Emil Alexov:** Writing — review & editing. **Shan Zhao:** Conceptualization, Methodology, Writing — original draft.

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References

[1] B. Honig, A. Nicholls, Classical electrostatics in biology and chemistry, Science 268 (1995) 1144–1149.
[2] Y. Taur, T.H. Ning, Fundamentals of Modern VLSI Devices, Cambridge University Press, 1998.
[3] L. Li, C. Li, Z. Zhang, E. Alexov, On the dielectric constant of proteins: smooth dielectric function for macromolecular modeling and its implementation in DelPhi, J. Chem. Theory Comput. 9 (2013) 2126–2136.

[4] C. Xue, S. Deng, Unified construction of Green's functions for Poisson's equation in inhomogeneous media with diffuse interfaces, J. Comput. Appl. Math. 326 (2017) 296–319.
[5] T. Hazra, S. Ahmed-Ullah, S. Wang, E. Alexov, S. Zhao, A super-Gaussian Poisson–Boltzmann model for electrostatic solvation free energy calculation: smooth dielectric distribution for protein cavities and in both water and vacuum states, J. Math. Biol. 79 (2019) 631–672.
[6] K.E. Teigen, X. Li, J. Lowengrub, F. Wang, A. Voigt, A diffuse-interface approach for modeling transport, diffusion and adsorption/desorption of material quantities on a deformable interface, Commun. Math. Sci. 4 (2009) 1009–1037.
[7] P. Bates, G.W. Wei, S. Zhao, Minimal molecular surfaces and their applications, J. Comput. Chem. 29 (2008) 380–391.
[8] L.-T. Cheng, J. Dzubiella, J.A. McCammon, B. Li, Application of the level-set method to the solvation of nonpolar molecules, J. Chem. Phys. 127 (2007) 084503.
[9] Y. Zhao, Y.Y. Kwan, J. Che, B. Li, J.A. McCammon, Phase-field approach to implicit solvation of biomolecules with Coulomb-field approximation, J. Chem. Phys. 139 (2013) 024111.
[10] R. Egan, F. Gibou, Geometric discretization of the multidimensional Dirac delta distribution - Application to the Poisson equation with singular source terms, J. Comput. Phys. 346 (2017) 71–90.
[11] W. Geng, S. Zhao, A two-component matched interface and boundary (MIB) regularization for charge singularity in implicit solvent, J. Comput. Phys. 351 (2017) 25–39.