

# Error Analysis of the Poisson P<sup>3</sup>M Force Field Scheme for Particle-Based Simulations of Biological Systems

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The particle-particle-particle-mesh (P<sup>3</sup>M) force field scheme [1], [2] is an efficient approach to account for both the long-range and short-range electrostatic interactions in the simulation of biological systems. Resolving the particle-mesh term in real-space [2], [3] improves the original approach of Hockney *et al.* [1] by allowing for the inclusion of non-periodic boundary conditions. To date, the P<sup>3</sup>M method has not been fully utilized by the computational biophysics community due to a lack of rigorous analysis of the computational error associated with the P<sup>3</sup>M approach [4]. Performing such an analysis is the main goal of this work. The P<sup>3</sup>M approach is based on a separation of the Coulomb interaction into a long-range and short-range component by a smooth function  $f(r)$ ,

$$\frac{1}{r} = \frac{f(r)}{r} + \frac{1-f(r)}{r} \quad (1)$$

which is chosen in such a way that the first term represents the long-range interaction and the second term results in a short-range one. Within the proposed P<sup>3</sup>M formalism, the long-range force, or particle-mesh force, is calculated with an extremely efficient finite difference multi-grid Poisson solver in real space [3]. The function  $f(r)$  is then related to the "shape" of the particle used to assign its charge to the real space grid, and to interpolate the corresponding force at the particle position. The short-range force is composed of two parts that are both determined within a small domain. The first term is the particle-particle force and is computed by a direct summation of the pair-wise interaction of close neighbors, including the van der Waals interactions. The second part of the short-range calculation is a correction term, which accounts for the portion of the interaction already included in the solution of Poisson's equation. This correction term, or "reference" force, is calculated analytically and stored in a look-up table [1]. The ability of the reference force to reproduce the force calculated with the Poisson solver within the short-range domain determines the accuracy of the P<sup>3</sup>M method. Figure 1 shows a plot of the particle-particle, reference, and particle-mesh forces between two ions in a 0.5 M KCl solution as a function of ion separation. The triangular-shaped cloud (TSC) [1] assignment scheme is used and the mesh spacing is 1 nm. As can be seen, within the short-range domain (defined here as a sphere with a 2 nm radius) the reference force and particle-mesh force cancel and the short-range ion interaction is defined exclusively by the particle-particle interaction as it should be.

In order to further assess the accuracy of the P<sup>3</sup>M approach, the radial distribution function (RDF) of the ionic population [5] is calculated with Brownian dynamics for bulk electrolyte solutions, and compared with the analytic solution of the Ornstein-Zernike equation [6], using the hypernetted-chain closure relation [7]. The RDF is shown in Fig. 2 for several simulation parameters. For the parameters corresponding to Fig. 1 there is excellent agreement between the computed RDF (TSC, Grid 1.0 nm) and the analytic values. For simulations using either a smaller grid size (TSC, Grid 0.5 nm) or a lower order (in this case nearest-grid point) charge assignment/force interpolation scheme (NGP, Grid 1.0 nm) the peak RDF increased considerably. This deviation of the RDF from the analytic value is due to the fact that the reference force is not able to reproduce the values obtained by the Poisson solver, resulting in an accumulation of error in the computation of the short-range force. In this work, a complete analysis of the error associated with the real space P<sup>3</sup>M approach for biologically relevant systems is presented. Methods to improve the accuracy and efficiency of the P<sup>3</sup>M are also discussed.

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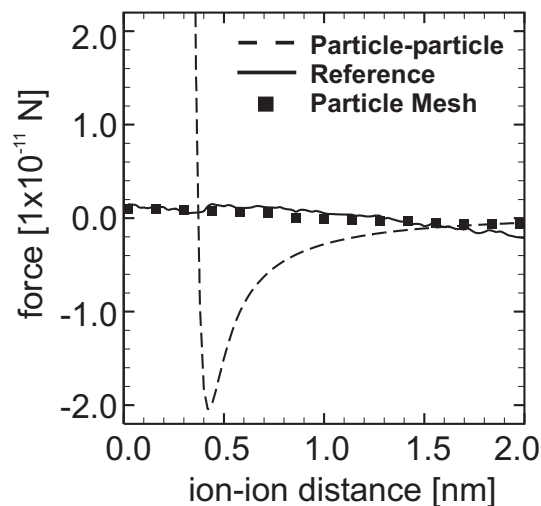


Fig. 1. Components of the force within the short-range domain computed between two ions of opposite sign charges in a 0.5 M KCl solution with no applied bias.

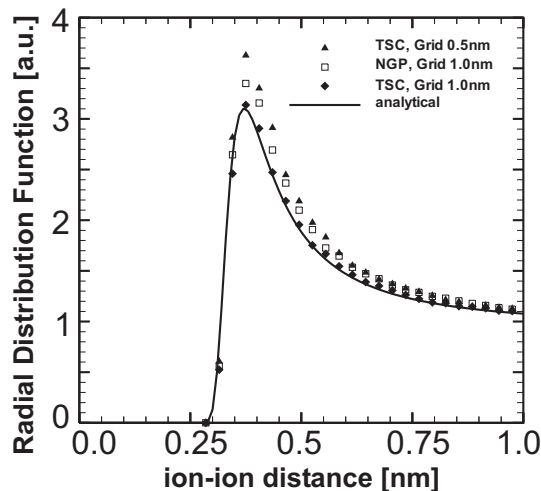


Fig. 2. Anion-cation radial distribution functions for a 0.5 M KCl solution for various charge assignment schemes and grid size configurations.

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