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# SOLVING POISSON'S EQUATION ON A DISCRETE MESH

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## ABSTRACT

In Molecular Dynamic Simulations, obtaining the energy and forces experienced by ions in a system are necessary. Solving Poisson's equation is central to obtaining both the energy and forces. This article attempts to quantify the accuracy of solving Poisson's equation using a discrete mesh (P3M methodology used). Gaussian distributed charges are considered.

Increasing the sampling frequency improves the accuracy of the result. The law of diminishing returns is applicable, creating an optimization problem.

## NOMENCLATURE

| | |
|---|---|
| $q$ | Charge |
| $\rho$ | Charge density |
| $\phi$ | Electrostatic field |
| $\psi$ | Electric field |
| $U$ | Potential energy |
| $F$ | Force |
| $\hat{f}$ | Fourier transform of $f$ |
| $F[f] = \hat{f}$ | |
| $f = F^{-1}\left[\hat{f}\right]$ | |
| $g$ | Green's function |

## INTRODUCTION

In Molecular Dynamics, particles in a box are allowed to move according to van der Waals dispersion and Coulombic forces. Van der Waal dispersion forces are typically modeled with a Lennard-Jones potential. In order to represent a bulk fluid and prevent unnatural wall effects, periodic boundary conditions are used. The bulk fluid is therefore represented as the unit cell box replicated along each axis an infinite number of times (see Fig. 1).

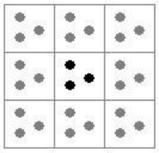

**Figure 1** Periodic Boundary Conditions

In order to overcome the difficulty in calculating energies and forces from the Coulombic interactions, an Ewald sum is used. The point charges on atoms are mathematically equal to a point charge minus a diffuse Gaussian charge (a) added to a diffuse Gaussian charge (b) (see Fig. 2).

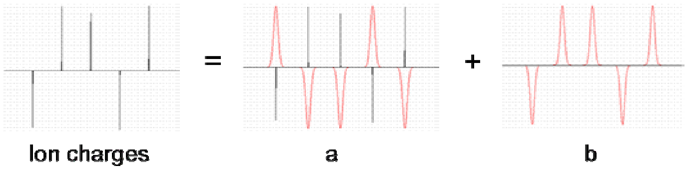

**Figure 2**

The point charge is paired with an opposite diffuse charge (a) and results in a Coulombic interaction that is easy to calculate and drops off sharply with distance. The second diffuse charge (b) can then be manipulated with an Ewald sum more easily than working with the original point charges. In the Ewald sum, Poisson's equation

$$\nabla^2 \phi = 4\pi\rho$$

is solved for the diffuse charges (b) by a Fourier transform in three dimensional space, algebraic manipulation and the inverse Fourier transform (not on a discrete mesh). From here on, the charge density will be assumed to contain the 4*Pi constant. Because the diffuse charge has a Gaussian distribution, the Fourier transform and inverse transform can be solved analytically. An analytic solution of the electrostatic field is therefore obtainable as outlined above.

The Ewald sum has been modified to be even quicker by use of a discrete mesh and a Green's function in what is known as the P3M method[1,2]. The P3M takes advantage of the fact that Poisson's equation can be solved for any charge distribution by a convolution of the charge density with the correct Green's function. In application, the P3M method assigns the diffuse charges onto a mesh by means of some assignment function. The convolution of this mesh with the appropriate Green's function is done as a simple multiplication in Fourier space to solve for the electrostatic field.

When the electrostatic field is obtained, the potential energy, electric field and forces can be obtained by the following mathematical properties:

$$U = q \cdot \phi$$

$$\psi = -\nabla \phi$$

$$F = q \cdot \psi$$

$$F = -\nabla U$$

When the P3M method is used, errors are introduced by using a mesh to approximate the continuous charge distribution and by using a solution to the Green's function on the discrete mesh. It is the purpose of this paper to quantify the error that is introduced by use of a mesh to obtain a 1-D solution to the system energy. No attempt is made to refine the Green's function used as is done by others[3,4].

## THE SYSTEM TO BE STUDIED

In order for the system to be physically meaningful, there must be a few constraints on the possible charge densities to be studied. The charge density of the cell will be specified for the x-axis for a unit length L from x=-L/2 to x=L/2. The first constraint is that there should be no net charge over a unit length. As a result, the following must be enforced for a continuous charge density

$$\int_{-L/2}^{L/2} \rho(x)dx = 0$$

or below for a discrete mesh from –L/2 < x < L/2

$$\sum_{i=1}^{N} \rho_i = 0$$

This first constraint prevents the simulated fluid from having an excess charge that would be exacerbated by the periodic boundary conditions.

The second constraint is that the charge density at x=-L/2 and x=L/2 must be equal. Requiring the charge densities be equal at the boundaries has more to do with proper charge distribution than specifying a constraint. A charge distribution could be used where the densities at the boundaries were not equal, but that would not represent the periodic system which we are trying to construct.

In addition to the constraints, there are also constraints for the solution of Poisson's equation. The solution to Poisson's equation results in the electrostatic field. To represent a periodic system, the field must be equal at the boundaries. In addition, the field strength should be adjusted so that integration over the entire field is zero (This is the reference point for energy comparison). These constraints, shown below, are similar to those for the charge density distribution.

$$\phi(-L/2) = \phi(L/2)$$

$$\int_{-L/2}^{L/2} \phi(x)dx = 0$$

By having the proper constraints for the electrostatic field, the resulting electric field obtained by differentiation will also have the correct properties. A sample charge distribution, electrostatic field and electric field which satisfy the correct constraints are given below (see Fig. 3, 4 & 5).

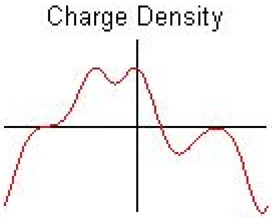

**Figure 3**

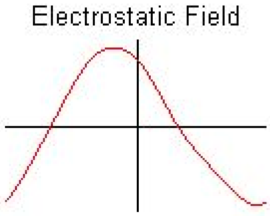

**Figure 4**

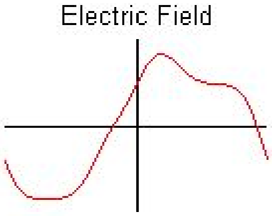

**Figure 5**

## THE GREEN'S FUNCTION

In order to solve Poisson's equation on a discrete mesh through a convolution, the proper Green's function must be obtained. It has been shown previously[4] that the continuous Green's function in reciprocal space is given by

$$\hat{g} = 1/(2\pi n/L)^2 \qquad n = 1,2,3..$$

In the definition of a Green's function, a convolution of the Green's function with the charge density will give the electrostatic field with the proper boundary conditions.

One can derive the Green's function for Poisson's equation by solving

$$-\nabla^2 g = \delta(x - x_0)$$

according to the boundary condition that

$$g(-L/2) = g(L/2) .$$

The resulting Green's function will look like Figure 6 below.

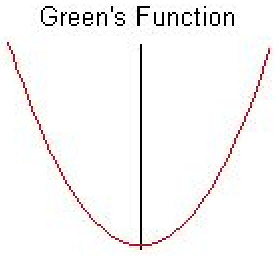

**Figure 6**

## METHODOLOGY

The charge density distribution is transformed using a Discrete Fourier Transform (DFT). In Fourier space the charge distribution is multiplied by the Green's function to get the convolution. The result is the electrostatic potential in Fourier space. It can presently be transformed into real space to give the electrostatic potential, or it can be ik differentiated to give the electric field in Fourier space. The electric field can then be transformed into real space.

The above method to give an accurate electrostatic field will be evaluated. The sum of errors at each grid point is normalized and compared according to the following equation.

$$error = \frac{1}{N}\sum_{i}\left|\phi_{grid}(x_i) - \phi_{analytic}(x_i)\right|$$

In addition, the error of the total energy of the system is calculated and compared. The error versus number of grid points for a particular charge density distribution is constructed. This correlation can then be used to discover the required grid refinement needed for a tolerable error.

Presently, the electrostatic field is used to describe the accuracy of the solution on the discrete mesh. It should be noted that any error in the electrostatic field will be amplified in the resulting electric field. The errors in any resulting forces calculated are therefore going to be much larger than the corresponding energies.

## RESULTS

Results from the error of the electrostatic field are given below. To make the graph easier to read, the x-axis is plotting using 1 / # Grid Points. As the number of grid points increase the solution approaches the analytic solution.

To make the results more general, three different charge distributions are used. Over a length of 4*Pi, the three functions were constructed according to the outlined rules above. The first function was constructed of six different Gaussian curves. The second function consisted of a cosine curve. The third function was exactly like the first, except the Gaussian's were made narrower. The results are presented below.

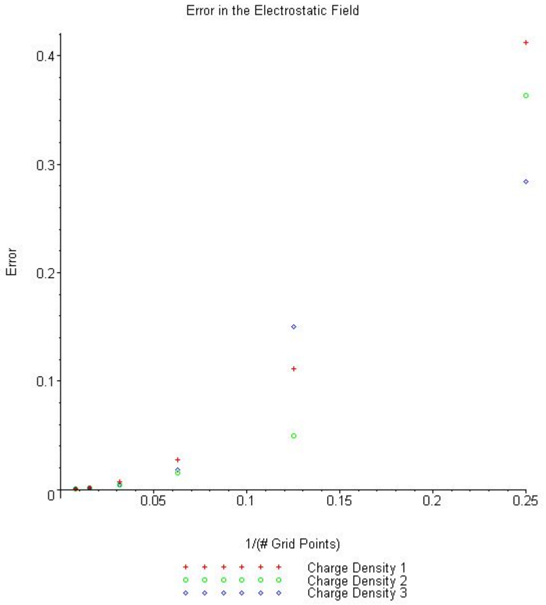

**Figure 7**

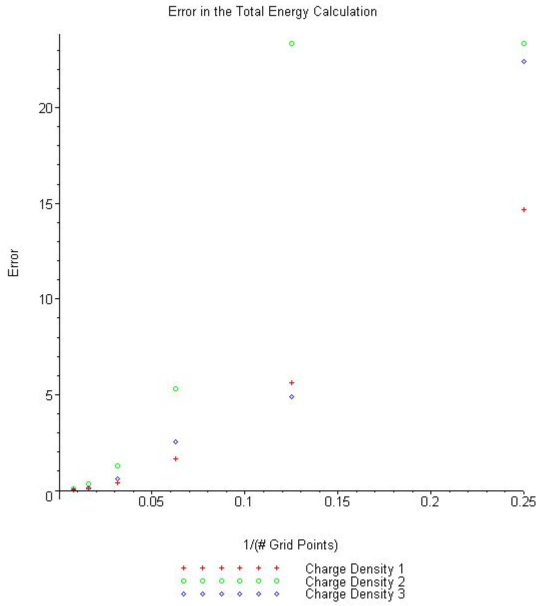

**Figure 8**

The results are straightforward. In order to achieve results that are within a 5% error, at least 16 or more points will be needed, assuming the functions are similar in curvature to the ones used. It is clear that the sampling frequency must be double the highest frequency present in the charge distribution. Such is evident by the second charge distribution in Figure 8.

## CONCLUSIONS

It is clear that any accuracy within a certain percentage can be achieved by simply refining the mesh  Like many problems, the accuracy desired is offset by increased computational time. There fore, the level of accuracy required should be found first.

## ACKNOWLEDGMENTS

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[4] Hockney, R. W., and Eastwood, J. W., 1998, Computer Simulation Using Particles, IOP, Bristol, Chap. 8.

## APPENDIX

Maple sheet available upon request.