

# Implementing Particle Mesh Ewald Method for Simulating Charged Particles

Molecular simulation of materials and biopolymers is a powerful method to understand and explain physical properties and make design predictions. Usually such simulations are done with periodic box conditions (to capture the bulk nature of a real system) and involve long and short range interactions of particles. Typically, the main 2 components of these interactions are Van der Waals (1<sup>st</sup> parenthesis in Eq 1) and electrostatic term (given by coulomb's law in the 2<sup>nd</sup> parenthesis)

$$E(r) = \left( \frac{A_{rep}}{r^{12}} - \frac{B_{disp}}{r^6} \right) + \left( \frac{q_1 q_2}{r} \right) \quad (1)$$

One of the main challenges in calculating these energies in periodic systems is their slow convergence with distance. Given the pairwise nature of the potential, the obvious way forward is to implement a pairwise double loop to calculate all the pair energies. The computational cost scales with system size as  $O(N^2)$  where  $N$  is the number of particles and this can become very slow with standard systems of size  $10^3$ - $10^4$  particles<sup>1</sup>. The usual practice is truncating them at some cutoff distance and ignoring contributions beyond the cutoff distance, making the calculation scale as  $O(N)$ . From an accuracy standpoint, this can be problematic for a potential with a  $1/r^n$  term because the contribution beyond a cutoff distance  $r_c$  for a system with  $N$  particles of uniform density  $\rho$  is given by

$$U_{tail} = 2\pi N \rho \int_{r_c}^{\infty} \left[ \frac{1}{r^n} \right] r^2 dr \quad (2)$$

For potentials with  $n > 3$ , like the Van der Waals potential in (1), the truncation is reasonable as the tail decays to zero. However, the electrostatic term in (1) has  $n=1$  which means it is not convergent. Thus it is important to consider long range interactions for such a potential.

## The Ewald Sum<sup>2</sup>

A sophisticated way to overcome the problem of scaling with  $O(N^2)$  is to use the method of Ewald summation. Let's consider a system of  $N$  particles with charges  $q_i$  at positions  $r_i$  in an overall neutral cubic simulation box of length  $L$ . Since periodic boundary conditions are used, the electrostatic energy of the box is given by

$$E = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{n \in Z^3} \frac{q_i q_j}{|r_{ij} + nL|} \quad (3)$$

The sum over  $n$  takes into account the periodic images of the charges. Now the trick here is to decompose the above sum into two separate sums using a convergence function  $f(r)$  as seen in (4).

$$E = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{n \in Z^3} \frac{q_i q_j f(r)}{|r_{ij} + nL|} + E = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{n \in Z^3} \frac{q_i q_j [1 - f(r)]}{|r_{ij} + nL|} \quad (4)$$

The idea here is to distribute the two main complications of the coulomb potential – rapid variation at small values of  $r$  and slow decay at large value of  $r$  using a clever choice of  $f$ . This means

- (1) The first sum should be negligible beyond a cutoff distance. This represents what is called the real space component and can be evaluated directly. The value of  $f(r)$  should be smooth for small  $r$ .
- (2) The second sum represents the long range tail that can be calculated using a Fourier transform. At high  $r$ , the function  $f$  should decay quickly to zero so that this term is accurately represented by a small number of wave vectors  $k$ . This represents what is called the reciprocal space component of the potential.

The traditional selection for  $f(r)$  is the complementary error function  $\text{erfc}(r)$  defined by

$$f(r) = \text{erfc}(r) = \frac{2}{\sqrt{\pi}} \int_r^\infty e^{-t^2} dt \quad (5)$$

It can be derived that the final energy is given by

$$E = E^{(r)} + E^{(k)} - E^{(s)} \quad (6)$$

where the first term  $E^{(r)}$  gives the real space electrostatics sum (corresponding to the 1<sup>st</sup> sum in (4))

$$E^{(r)} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \sum_{n \in \mathbb{Z}^3} \frac{q_i q_j \operatorname{erfc}(\alpha |r_{ij} + nL|)}{|r_{ij} + nL|} \quad (7)$$

The 2<sup>nd</sup> term  $E^{(k)}$  is the contribution from reciprocal space

$$E^{(k)} = \frac{1}{2L^3} \sum_{k \neq 0} \frac{4\pi}{k^2} |\tilde{\rho}(k)|^2 \exp\left(-k^2/4\alpha\right) \quad (8)$$

To avoid overcounting in (8), a self energy term has to be subtracted from the sum. This accounts for  $E^{(s)}$ .

$$E^{(s)} = \frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^N q_i^2 \quad (9)$$

The inverse length parameter  $\alpha$  is referred to as the Ewald parameter and tunes the relative weight between the real space and the reciprocal space contribution. It is inversely proportional to the real space cutoff distance  $r_c$ . The final result of the calculation is independent of  $\alpha$  by construction. The Fourier transformed charge density  $\tilde{\rho}(k)$  is defined by

$$\tilde{\rho}(k) = \sum_{j=1}^N q_j e^{-ik \cdot r_j} \quad (10)$$

### Ewald Sum using particle mesh

An optimized version of Ewald summation generally scales with number of particles as  $O(N^{1.5})$ . For a system using cutoff for short range electrostatics, the reciprocal space sum scales as  $O(N^2)$ . It is also well known that the Poisson equation can be solved more efficiently by distributing charges on a mesh. Thus particle mesh methods have become very popular in molecular simulations. We describe below the Particle Mesh Ewald method (PME) that was proposed by Darden et. al<sup>3</sup>. and is ubiquitous in molecular dynamic simulations of proteins and polymer materials.

A key aspect of the PME method is charge assignment on the mesh that is done as follows: Define an even function  $W(r)$  such that the fraction of charge which is assigned to the mesh point  $r_p$  due to a unit charge at position  $r$  is given by  $W(r_p-r)$ . If the charge density of the system is  $\rho(r) = \sum_{i=1}^N q_i \delta(r-r_i)$ , then the mesh based charge density  $\rho_M$  defined at the mesh points  $r_p$  can be written as the following convolution

$$\rho_M(r_p) = \frac{1}{h^3} \int_{L^3} dr W(r_p - r) \rho(r) = \frac{1}{h^3} \sum_{i=1}^N q_i W(r_p - r_i) \quad (11)$$

Here  $h$  is the spacing between mesh points. Hence if there are  $N_M$  mesh points, then  $h = L/N_M$ . For PME method proposed by Darden, we use the coulomb green function as the solution to the Poisson equation that restricts the value of  $W(r)$ . For example for the 1-D case, let  $g(x)$  be the green function and  $W_p(x) = W(x_p - x)$  the charge assigned to mesh point  $p$  at position  $x_p$ . The electrostatic potential at position  $x^1$  can then be written as

$$\phi(x^1) = \sum_{p=1}^P W_p(x) g(x^1 - x_p) \quad (12)$$

where the sum is taken over all  $P$  mesh points to which the particle at position  $x$  contributed some fraction of its charge, i.e the  $P$  mesh points closest to  $x$ . Peterson<sup>4</sup> has tabulated the polynomials for  $P=3, \dots, 7$ . Note that  $W(r) = W(x)W(y)W(z)$ .

In the PME method, it is assumed that Equation (8) is applicable in the discrete case. Instead of  $\tilde{\rho}(k)$ , we use the finite Fourier transform of the mesh based charge density  $\hat{\rho}_M(k)$  given by

$$\hat{\rho}_M(k) = h^3 \sum_{r_p \in M} \rho_M(r_p) e^{-ik \cdot r_p} \quad (13)$$

The sum is over the 3-D mesh in real space and the  $k$ -vectors are from the corresponding Fourier mesh.

We propose to perform implement the PME method, and use the same to perform an MD simulation of a periodic box containing sodium and chloride ions.

## References:

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