An Alternative Charge Distribution Implementation on The Ewald Summation Method

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Abstract

A re-formulated version of Ewald Summation method is presented in this paper by replacing each point charge with a triangular shape charge distribution instead of the original Gaussian shape charge distribution. With triangular shape charge distribution, we aim to be able to accelerate the computation of the reciprocal sum part of the Ewald Summation for crystal simulations with periodic boundary conditions.

1. Introduction

Fast and reliable computer simulations of particle systems is a challenging problem in the scientific computing community. The accurate treatment of interactions in a molecular system is an essential requirement for performing a reliable computer simulation. However, the long-range nature of Coulomb's law makes evaluation of the electrostatic interactions a computationally demanding task. [1]

The computational challenge of simulating particle systems lies in solving the so-called N-body problem. For a given system of N particles, an N-body solution evaluates the pairwise interactions among all the particles with O(N^2) runtime complexity. The most common method to reduce this burden is to include a cutoff radius which will limit the interaction of an atom with other atoms to a sphere of neighboring atoms in the cutoff radius range. Various methods have been developed to reduce errors introduced by the use of straight cutoff, such as shifting or scaling Coulomb's law to force the interactions of charges to become negligible at further points of the cutoff radius.

This paper aims to reformulate the efficient Ewald Summation (E.S.) technique for triangular charge shape distribution. E.S. is widely used in different forms to solve the N-body problem in Molecular Dynamics (MD) environments. MD simulations have been widely used as a tool for studying the dynamical and structural properties of bulk materials at an atomic level. The basic steps in MD simulation of a particle system are [1] : (i) define the atomic level system behavior for particle interactions and choose the appropriate model, (ii) using the model, calculate the forces effecting each particle, (iii) numerically integrate the forces using Newton's Second Law and update the coordinates. The challenging part of the above process comes from the fact that the above steps are

for only one time-step. Typically, a particle system is simulated for millions of time steps where each time step corresponds to $0.5 - 2$ femtoseconds.

The $O(N^2)$ complexity severely limits the size of the systems that can be studied even on very fast computers. Many algorithms have been developed to improve this performance. The Particle Mesh Ewald (PME), a Fourier-based Ewald Summation Method [2], is one of the many solutions derived to efficiently calculate the interactions between particles. The method, reduces the complexity of the N-body problem to $O(N\log N)$ in certain cases with controllable errors using periodic boundary conditions to evaluate long range interactions.

Molecular dynamics is typically applied to small systems dominated by surface effects interactions of atoms with the container walls. As the wall-fluid interactions will apply from each wall, most of the particles will be affected by this interaction such that a simulation of this system should provide information on the behavior of the liquid and solid surface, not information on the bulk liquid. In simulations where these surface effects are not of interest, they can be removed by using periodic boundary conditions (PBC). In PBC, the simulation cell is replicated infinitely in all three dimensions. When a particle leaves the original simulation cell, one of its images enters from the opposite side.

Molecular dynamics simulations involving explicit solvent molecules have usually been performed under one of the following boundary conditions on the Coulombic interactions [3]:

- Non-periodic boundary conditions with some treatment of the system environment interface [4].
- Periodic boundary conditions using a finite cutoff.
- Periodic boundary conditions together with a reaction field.
- Periodic boundary conditions using Ewald Summation.

All of these conditions have their most appropriate environments. The Ewald Sum certainly seems the most appropriate for crystal simulations and may be the best current choice for macromolecular solution simulations as well [5]. In the past, it has not been used for large systems due to the prohibitive cost of the usual implementation. Today with the developments in computer performance and also using parallel processing enables us to work on these large systems. Besides, with algorithmic improvements, like PME method mentioned earlier, the order of computation is further decreased down to an order of $N\log N$.

The scientific community is continuously in search of more efficient algorithms for MD simulation. One previous work was the re-formulating of the Ewald method in terms of efficient Bspline interpolation of the structure factors [6]. Use of Bsplines in place of Lagrange interpolation lead to analytic gradients as well as a significant improvement in accuracy.

The paper is organized as follows: Section 2 gives a technical introduction and aims to develop an understanding of Ewald Summation. A method to develop the original Ewald

Summation formula is also presented in this section. Section 3 synthesizes the E.S. for triangular shape charge distribution. Finally, conclusions are presented Section 4.

2. Ewald Summation

The total Coulomb energy of a system of N particles in a cubic box of size L and their infinite replicas in PBC is given as:

$$\phi = \frac{1}{2}\sum_{\mathbf{n}}{}' \sum_{i=1}^{N}\sum_{j=1}^{N}\frac{q_i q_j}{|r_{ij,\mathbf{n}}|} \qquad (2.1)$$

where q_i is the charge of particle i. The main cell is located at $\mathbf{n} = (\mathbf{0}, \mathbf{0}, \mathbf{0})$. Its image cells are located at L_n intervals in all three dimensions as **n** goes to infinity.

The unit cell vector is $\mathbf{n} = (n_1, n_2, n_3) = n_1 L\hat{x} + n_2 L\hat{y} + n_3 L\hat{z}$ where $\hat{x}, \hat{y}, \hat{z}$ are the Cartesian coordinate unit vectors. The first sum in Coulomb energy equation is primed to indicate that terms with $i = j$ are omitted when $\mathbf{n} = \mathbf{0}$.

This is a single and conditionally convergent series which means that the result depends on the order of summation [7]. Here the q_i and q_j represents the two-point charges with some constant values. From the nature of this representation we will observe that the amount of consumed time will increase geometrically with the increase in the number of particles in the system. To decrease the computation time, the charge distribution notion is used instead of point charge notion. This had enabled Ewald and Bertaut to develop an absolutely convergent series to compute Coulombic interactions.

Bertaut [8], replacing the ionic crystal by a spherically symmetric charge distribution, calculated the Coulombic interaction energy by a single absolutely convergent infinite series whose terms are a function of the lattice vectors in the reciprocal space. Bertaut's series is absolutely convergent but is not very efficient if computation time is taken as the parameter [3].

The disadvantage of Coulomb's energy equation is that basically it is a single and conditionally convergent series. These two characteristics of this formulation form an incompatibility for high speed computing environments.

Ewald Summation provided an efficient technique to evaluate the long-range interactions between particles and their periodic images. Ewald Summation re-formulates the Coulomb's equation with the sum of two rapidly converging series plus a constant term [9]. These series calculate the interactions at different ranges and the summation of these terms gives us the Coulomb energy within an error range. The Ewald Summation is formulated as:

$$\phi(r) = \phi_d(r) + \phi_r(r) + \phi_c(r) \qquad (2.2)$$

where ϕ_d is the direct (real) sum, ϕ_r is the reciprocal (imaginary) sum and ϕ_c is the constant term. The problem is to calculate the electrostatic potential experienced by one ion in the presence of all the other ions in the crystal. We consider a lattice made up of ions with positive or negative charges and shall assume that the ions are spherical. We compute the total potential ϕ at an ion as the sum of two distinct but related potentials (excluding the constant term).

Force expressions can be easily obtained from Ewald energy formulation by direct differentiation in each coordinate $\mathbf{p} = \mathrm{x}, \mathrm{y}, \mathrm{z}$. To avoid complexity, the equations in this paper will be potential energy based. And the self-term will not be shown since it, as a constant, will disappear in force calculations. The equations for these terms for the Gaussian distribution are, for the direct sum:

$$\phi_d(r) = \frac{1}{4\pi\epsilon_0} \sum_{B=1}^{N} q_B \frac{\mathrm{erfc}(\alpha|r - R_B|)}{|r - R_B|} \qquad (2.3)$$

where ϵ_0 is the permitivity of free space, α is the Ewald coefficient, N is the number of charges in the system and

$$\mathrm{erfc}(x) = 1 - \mathrm{erf}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du \qquad (2.4)$$

The reciprocal sum:

$$\phi_r(r) = \frac{1}{\epsilon_0 V} \sum_{l \neq 0} \frac{\exp(-m^2/4\alpha^2)}{m^2} \sum_{B=1}^{N} q_B \exp\big(l.m(r - R_B)\big) \qquad (2.5)$$

where V is the volume of the simulation box, m is the reciprocal space vector.

In the reciprocal sum part of the E.S., each point charge is replaced by a charge distribution of proportional magnitude and equal sign which spreads out from the lattice site in a spherically symmetrical way. Or in other words each ionic charge is distributed within a sphere of radius R so that the charge density is proportional to a normalized distribution function $\gamma(r)$, where r is the distance from the atomic center. In the direct sum part each particle is represented by the original point charge and a charge distribution of proportional magnitude and opposite sign. We see the significance of the shape of the charge distribution on the computation time clearly at Ewald Summation. By changing the width of the Gaussian type charge distribution (or the Ewald coefficient parameter) we are able the shift the amount of work done between the direct sum and the reciprocal sum parts. As the distribution gets narrower, the reciprocal sum becomes more dominant in the result. At the far end, if the distribution function is selected to be a Dirac function then the point charge and the distribution function cancels out at the direct sum and the result is generated only by the reciprocal sum. In general, this work load shifting aims to prevent a bottleneck that may come from the computation of one term; either direct or reciprocal sum parts. A lot of work has been done to find the optimum Ewald coefficient parameter [10].

It is worth pointing out that in distributed environments determining the optimum Ewald coefficient parameter should consider the structure of the distributed environment too; which adds the problem of finding an optimal value a new perspective. The size of the processing system, the structure of processing elements, the distribution algorithms, workload allocation techniques implemented are some factors that affect the optimal value.

Obtaining the Ewald Summation formula

An electrostatic potential is a long-range function, which decays only as the inverse power of the distance. An alternative to the direct application is to split the potential into three parts as mentioned before:

$$\phi(r) = \phi_d(r) + \phi_r(r) + \phi_c(r) \qquad (2.6)$$

, where $\phi(r)$ is the total potential of the system, $\phi_d(r)$ is the direct sum potential, $\phi_r(r)$ is the reciprocal sum potential and $\phi_c(r)$ is the correction term.

The total potential can be represented in terms of electric field E :

$$\phi(r) = -\int_{-\infty}^{\infty} E(\psi)d\psi = \frac{q_B}{4\pi\epsilon_0}\left(\frac{1}{r}\int_0^r (4\pi a^2\gamma(a))da + \int_r^{\infty} (4\pi a\gamma(a))da\right) \qquad (2.7)$$

where $\gamma(r)$ represents the shape of the charge distribution as a function of distance, r. The evaluation of this term for Gaussian shape charge distribution below:

$$\gamma(r) = \frac{\alpha^3}{\pi^{1.5}}\exp(-\alpha^2 r^2) \qquad (2.8)$$

yields,

$$\phi(r) = \frac{q_B}{4\pi\epsilon_0}\left(\frac{\mathrm{erfc}(\alpha r)}{r}\right) \qquad (2.9)$$

If the charge distribution is zero at some distance d,(or considered to be zero) then the electrostatic potential of the $\gamma(r)$ shaped charge will be equal to the electrostatic potential of a point charge q_B for $r > d$. Since the $\phi_d(r)$ is the difference of these potentials, it can be written as:

$$\phi_d(r) = \phi(r) - \phi_r(r) \qquad (2.10)$$

For Gaussian distribution:

$$\phi_\gamma(r) = \frac{1}{4\pi\epsilon_0}\sum_{B=1}^{N} q_B\left(\frac{1}{|r - R_B|} - \frac{\mathrm{erf}(\alpha|r - R_B|)}{|r - R_B|}\right) = \frac{1}{4\pi\epsilon_0}\sum_{B=1}^{N} q_B\frac{\mathrm{erfc}(\alpha|r - R_B|)}{|r - R_B|} \qquad (2.11)$$

In the case of a finite distribution (e.g. triangular shape charge distribution) the upper limit of the second integral in equation (2.7) should be the point where the distribution hits zero (e.g. $1/\alpha$).

The derivation of the reciprocal sum part for a particular charge distribution involves computing the Fourier transformation of the charge distribution.

The Fourier transform of a charge distribution, $\gamma(r)$ is:

$$\hat{\gamma}(k) = \int_0^{\infty}\left(4\pi r^2\gamma(r)\frac{\sin(2\pi kr)}{2\pi kr}\right)dr = \int_0^{\infty}\left(\frac{2r}{k}\gamma(r)\sin(2\pi kr)\right)dr \qquad (2.12)$$

which for Gaussian distribution yields:

$$\hat{\gamma}(k) = \exp(-k^2\pi^2/\alpha^2) \tag{2.13}$$

With the reciprocal sum potential

$$\phi_r(r) = \frac{1}{\epsilon_0 V}\sum_{l\neq 0}\frac{\hat{\gamma}(m/2\pi)}{m^2}\sum_{B=1}^{N} q_B \exp\left(l.\, m(r - R_B)\right) \tag{2.14}$$

For Gaussian distribution we get:

$$\phi_r(r) = \frac{1}{\epsilon_0 V}\sum_{l\neq 0}\frac{\exp(-m^2/4\alpha^2)}{m^2}\sum_{B=1}^{N} q_B \exp\left(l.\, m(r - R_B)\right) \tag{2.15}$$

3. Triangular Distribution

In this section we will re-derive E.S. formulation, which was detailed above, for triangular shape charge distribution.

The triangular shape charge distribution is represented by:

$$SI2 = \begin{cases} \frac{3\alpha^4}{\pi}\left(\frac{1}{\alpha} - |\mathbf{r}|\right) & \text{for } |\mathbf{r}| \leq 1/\alpha \\ 0 & \text{for } |\mathbf{r}| > 1/\alpha \end{cases}$$

This equation represents a spherically symmetric triangular shape charge distribution whose magnitude is zero when the distance from the atomic center is more than $1/\alpha$. The Ewald coefficient parameter is the only parameter that effects the width of the distribution. The magnitude for $|\mathbf{r}| \leq 1/\alpha$ is given as $\frac{3\alpha^4}{\pi}\left(\frac{1}{\alpha} - |\mathbf{r}|\right)$. The reason why the triangular distribution is represented in this form comes from the definition of the direct sum component. At any point where $|\mathbf{r}| > 1/\alpha$, the net direct sum potential due to the point charge and the charge distribution is zero. Therefore, when computing the force or potential at a point, we can neglect, without error, all charges at a distance greater than $r = 1/\alpha$.

To verify the result; potential component is computed by:

$$\phi_d(r) = \frac{1}{4\pi\epsilon_0}\sum_{B=1}^{N} q_B\left(\frac{1}{|r - R_B|} - \frac{1}{|r - R_B|}\int_0^{1/\alpha}(4\pi a^2\gamma(a))da\right) = 0 \tag{3.1}$$

For the Gaussian the integral becomes:

$$\int_0^{1/\alpha}\left(4\pi a^2\frac{3\alpha^4}{\pi}\left(\frac{1}{\alpha} - |\mathbf{r}|\right)\right)da = 1 \tag{3.2}$$

Since the triangular distribution is defined in two different regions ($|\mathbf{r}| \leq 1/\alpha$ and $|r| > 1/\alpha$), we need to derive the potential for these two regions separately. For $|\mathbf{r}| \leq 1/\alpha$

$$\phi_\gamma(r) = \frac{q_B}{4\pi\epsilon_0}\left(\frac{1}{r}\int_0^r \left(4\pi a^2 3\frac{\alpha^4}{\pi}\left(\frac{1}{\alpha}-a\right)\right)da + \int_r^{1/\alpha}\left(4\pi a 3\frac{\alpha^4}{\pi}\left(\frac{1}{\alpha}-a\right)\right)da\right) \qquad (3.3)$$
$$= \frac{q_B}{4\pi\epsilon_0}\left(\alpha(2+r^2\alpha^2(-2+r\alpha))\right)$$

To get the force for the direct sum in this region we simply take the partial derivation of the direct sum potential:

$$\frac{q_B}{4\pi\epsilon_0}\left(\partial_r\left(\frac{1}{r}-\left(\alpha(2+r^2\alpha^2(-2+r\alpha))\right)\right)\right) = \frac{q_B}{4\pi\epsilon_0}\left(\frac{-1+r^3\alpha^3(4-3r\alpha)}{r^2}\right) \qquad (3.4)$$

For $|r| > 1/\alpha$:

$$\phi_d(r) = \frac{q_B}{4\pi\epsilon_0}\left(\frac{1}{r}\int_0^{1/\alpha}\left(4\pi a^2 3\frac{\alpha^4}{\pi}\left(\frac{1}{\alpha}-a\right)\right)da\right) = \frac{q_B}{4\pi\epsilon_0}\left(\frac{1}{r}\right) \qquad (3.5)$$

And the direct sum force in this region is:

$$\frac{q_B}{4\pi\epsilon_0}\left(\partial_r\left(\frac{1}{r}-\frac{1}{r}\right)\right) = 0 \qquad (3.6)$$

And the reciprocal sum potential can be found by:

$$\begin{aligned}\phi_r(r) \quad &= \frac{q_B}{4\pi\epsilon_0}\int_0^{1/\alpha}\left(4\pi r^2\frac{3\alpha^4}{\pi}\left(\frac{1}{\alpha}-r\right)\frac{\mathrm{Sin}[2\pi kr]}{2\pi kr}\right)dr \\ &= \frac{q_B}{4\pi\epsilon_0}\left(\frac{3\alpha^3\mathrm{Sin}\left[\frac{k\pi}{\alpha}\right]\left(-k\pi\mathrm{Cos}\left[\frac{k\pi}{\alpha}\right]+\alpha\mathrm{Sin}\left[\frac{k\pi}{\alpha}\right]\right)}{k^4\pi^4}\right)\end{aligned} \qquad (3.7)$$

4. Conclusion

The preference between the Gaussian and the triangular should depend on the acceptable error and computation time.

The minimum error is possibly achieved by the Gaussian distribution. In the existence of a parallel reciprocal sum, if the total consumed time can be decreased to the time consumed by the direct sum then we can expect the triangular to perform better than the Gaussian at small and large cutoffs (in time) and to perform better in the means of both error and time at small cutoffs.

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