DEVELOPMENT AND APPLICATIONS OF REAL-SPACE ELECTROSTATIC INTERACTION METHODS FOR CHARGE-MULTIPOLES IN CONDENSED PHASE ENVIRONMENTS

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by

Madan Lamichhane,

_____

Kathie E. Newman, Director

_____

J. Daniel Gezelter, Director

Graduate Program in Physics

Notre Dame, Indiana

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DEVELOPMENT AND APPLICATIONS OF REAL-SPACE

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Abstract

by

Madan Lamichhane

$$a^2 + b^2 = c^2$$

$$E = mc^2$$

$$\frac{e}{m} = c^2$$

$$a^2 + b^2 = \frac{e}{m}$$

DEDICATION

To my father Late Hari Bahadur Lamichhane and mother Dropati Lamichhane

for their hard work, consistent support, love, and inspiration.

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CHAPTER 1

INTRODUCTION

In computer simulation of condensed phase molecular systems, molecules are commonly represented by atomic sites that interact by a parametrized forcefield. This forcefield aims to reproduce observable phenomena, by incorporating the proper physics into the simulation. There are mainly two types of interaction; intramolecular and intermolecular, which determines the static and dynamic properties of the molecular systems. Intramolecular interaction is the interaction within a single molecules which includes, bonding, bending, torsion etc whereas intermolecular interaction is the interaction between two or more molecules which includes van der Waals and electrostatic interactions due to full or partial charges located on or near the atomic sites. The computation of these electrostatic interactions is the most expensive portion of a molecular simulations. Due to this, there have been significant efforts to develop practical, efficient, and accurate methods for evaluating electrostatic interactions.

The Ewald method is one of the most well known and accurate method but it is computationally expensive scaling as $O(N^2)$, where N is the total number of particles. The appropriate selection of damping paramenter and suitable algorithm can decrease computational cost to $O(N^{3/2})$[18]. Modification of the Ewald method, including a particle mesh and fast Fourier transform (FFT) have decreased its cost down to $O(N \log N)$ [3, 5, 15, 23]. But these modified Ewald methods (par-

ticle mesh Ewald (PME), particle-particle particle-mesh Ewald (P3ME)) are still computationally expensive. In addition to this, the Ewald method requires an inherent periodicity which can be problematic in a number of protein/solvent and ionic solution environments [6, 9, 10, 13, 20, 21, 25]. To address these problems a lot of interest is currently growing in developing efficient real space electrostatic methods which scales linearly with the system size i.e. $O(N)$. This method was originally proposed by wolf *et al.* [26] and extended initially by Zahn *et al.*[4] then by C.J. Fennell and J. D. Gezelter [6]. All these methods were limited to charge-charge interactions between atomic cites. Our research developed real-space electrostatic interaction methods for higher order charge-multipoles (dipoles and quadrupoles) and studied their applications and performance in various condensed phase environments. This research also studied various static, dynamic, and dielectric properties for molecular systems using newly developed real space methods.

This dissertation consists of five chapters. First chapter is an introductory chapter initially outlines the background and motivation of the research. It also briefly discusses the basic principles of widely used molecular simulation methods: Molecular Dynamics (MD) and Monte Carlo (MC) simulations, where the newly developed electrostatic methods are very useful. Similarly this chapter also describes traditional Ewald as well as various improved Ewald based methods: P3ME, PME, and Multiple-based Ewald. Additionally it presents the problems caused due to the spherical truncation in real-space methods and discusses various technique implemented to resolve this problem in the past.

Chapter 2 presents the mathematical formulation of our newly developed real-space electrostatic methods: Gradient-shifted Force (GSF), Shifted-potential

(SP), and Taylor-shifted force (TSF). It also compares energy constant evaluated using newly developed methods with analytical results for different types dipolar and quadrupolar crystals.

The accuracy newly developed methods have been tested against Ewald in Chapter 3. Furthermore various static and dynamic properties evaluated from real space methods are also compared with traditional Ewald method. The test of total energy conservation is very important in MD simulations which is also studied in this chapter.

Chapter 4 describes three different ways of evaluating the dielectric properties for dipolar and quadrupolar liquids using Flcutuation, Perturbation, and Potential of Mean Force (PMF) methods. This chapter also explores the correction factor required to obtain correct dielectric using GSF, SP, and TSF methods. In addition, the dielectric properties; susceptiblity and dielectric constant, obtained using all three different methods are compared with each other as well as with previous simulation result in case of Stockmayer fluid.

Finally Chapter 5 summarizes, draw conclusion and discusses future directions, applications, and limitations of my research.

1.1 Molecular Dynamics (MD) Simulation

Molecular dynamics is computer simulation method for studying static and dynamic properties for molecular systems. In this method, each atom or molecule interacts with other molecules in the system and evolve dynamically following classical equation of motion. The numerical step-by-step process for MD is outlined in Figure 1.1.

In MD simulation, first of all molecules are initialized by assigning their ini-
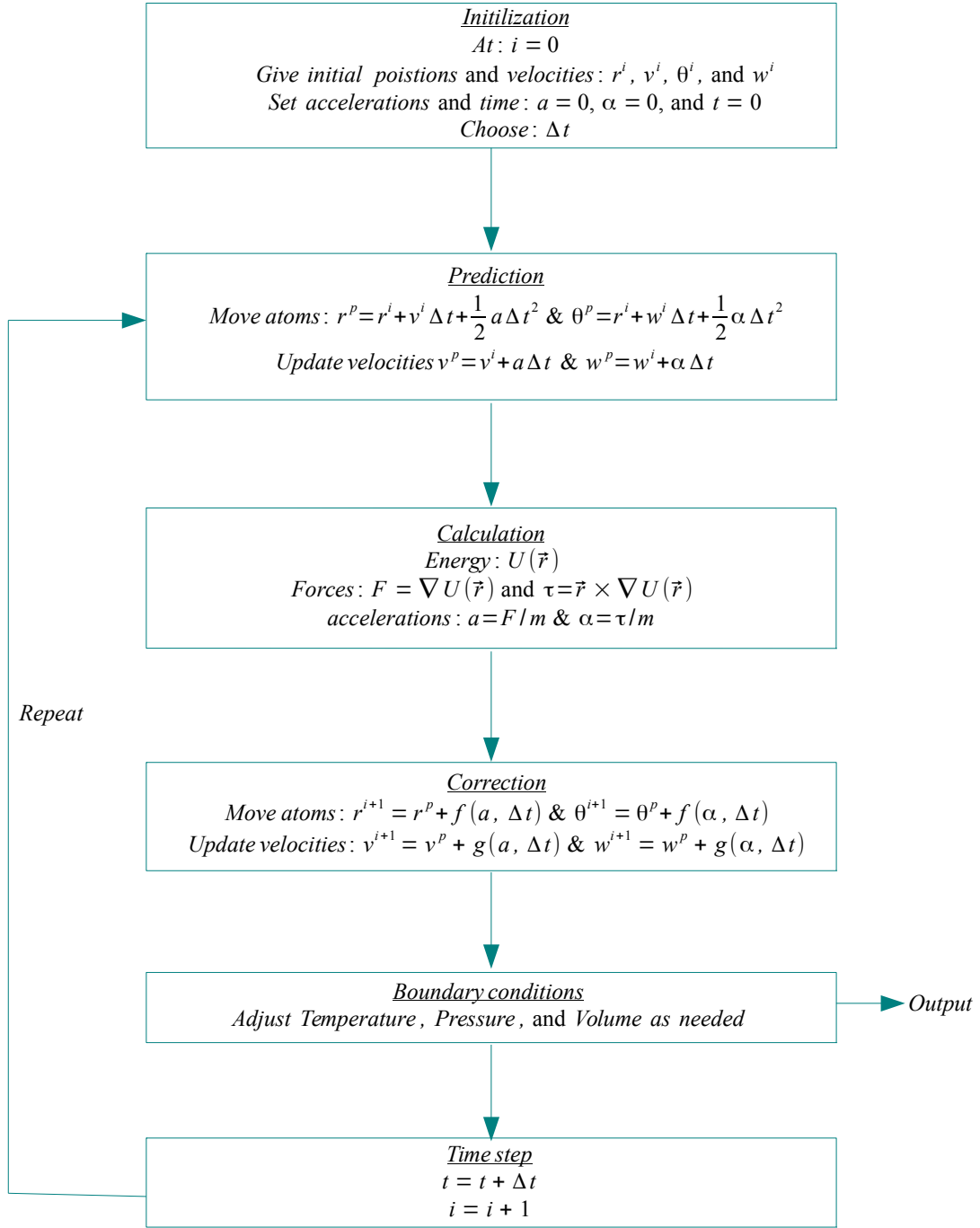
Figure 1.1. Schematic figure showing step-by-step process in Molecular dynamics simulation algorithm.

tial positions and velocities at given boundary conditions. Molecules are usually initialized in such a way so that system does not take very long time to reach equilibrium. Before moving a molecule in the system, we need to evaluate its potential energy which is mainly due to intramolecular interactions within the molecule itself as well as intermolecular interactions with all other molecules in the system. We can write the potential energy for a molecule in a system as shown in below:

$$U(\mathbf{r}) = \overbrace{U_{bond} + U_{bend} + U_{torsion}}^{Intramolecular\ interactions} + \overbrace{U_{electrostatic} + U_{van\ der\ Waals}}^{Intermolecular\ interactions} + ... \qquad (1.1)$$

In equation 1.1 the energy due to bonding, bending, and torsion represents intramolecular interactions whereas electrostatic and van der Waals represents intermolecular interactions. The force and torque acting on the molecule is obtained using following equations.

$$\mathbf{F}(\mathbf{r}) = \nabla_r U(\mathbf{r}) \qquad (1.2\text{a})$$

$$\mathbf{T}(\mathbf{r}) = \mathbf{r} \times \nabla_r U(\mathbf{r}). \qquad (1.2\text{b})$$

The force and torque provides the required dynamics to the molecule at a given time step. The same process is repeated for every molecules in the system. Once the molecules move forward by time step following prescribed equation of motion, their positions and velocities are adjusted according to applied boundary conditions (i.e temperature, pressure, volume etc) in the system. After adjusting positions and velocities, again we can evaluate the potential energy for each

molecule and repeat same process till the simulation completes its predetermined simulation time.

In MD simulations, the intermolecular interactions are most expensive parts of simulation. Among them van der Waals interaction is short range interaction usually described by Lennard-Jones (LJ) potential can be written as,

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right], \tag{1.3}$$

where σ is diameter of a molecule and ϵ determines well depth of the attractive potential. Above equation 1.3 clearly shows it decays much faster with the distance therefore considered as short-range interaction. The repulsive part of the LJ potential $\frac{1}{r^{12}}$ prevents two or more molecules to occupy same position. The electrostatic interactions are considered as long-range interaction. If we consider charge-charge interactions between molecules then they interact with Coulomb's law

$$U_{electrostatic}(r) = \frac{1}{4\pi\epsilon_o} \frac{q_1 q_2}{r}. \tag{1.4}$$

Equation 1.4 shows that electrostatic interaction decay much slower with the distance i.e. $\frac{1}{r}$. If we consider lowest order moment in the molecule as a dipole then the electrostatic interaction falls off by $\frac{1}{r^3}$. Even for considering lowest order moment in molecule as quadrupole, the electrostatic interaction decays as $\frac{1}{r^5}$ which is slower than LJ interaction. Since the electrostatic interaction decays slowly we need to consider large number of molecules around a molecule to capture right physical behaviour due to interactions. But it causes computational inefficiency when considered interactions with large number of molecules around it. The most important challenge in the molecular dynamics communities have been to capture

right electrostatic behaviour of a molecule considering small number molecules around it. There have been many efforts in the past to develop efficient and accurate algorithms to evaluate electrostatic interaction in molecular simulation, which will be discussed in detail in the following section 1.3 . Still those electrostatic methods have got some limitations. In addition to that those methods can also be generalized to higher order charge-multipoles. We will also discuss about how our newly developed electrostatic methods will resolve these issues.

Real liquid systems consists of very large number of molecules. But for computational efficiency only small number of particles (few thousands) are usually considered in molecular simulations. On the other hand, if we want to study and predict bulk properties of the material considering small number of molecules, the large fraction of molecules will be near the edge of the sample contributing huge surface effect. To eliminate surface effect, Periodic Boundary Conditions (PBC) have long been employed in various simulations [16].

1.1.1 Peridic Boundary Condition (PBC)

In PBC, the simulation box is replicated throughout the space to form an infinite lattice. In the course of simulation, if a molecule moves in the central box then its images in every replicated boxes also move in the similar fashion. Similarly if a molecule leaves the central box then the one of its images will enter the box through opposite face as shown in Figure 1.2 to conserve total number of particle in a central box. Therefore the system acts like there is no wall at the boundary of the central box which eliminates the surface effect in the computation. In this method if we want to evaluate potential energy of a molecule, we can consider its interactions with nearest molecules or images using minimum image convention

[1]. Even if you use minimum energy convention, for each molecule we need to calculate large number of pairwise distances at each simulation time step. Consider a system of N molecules, if we want to evaluate potential energy for a ith molecule we need to find its distances r_{ij} with every j^{th} molecules or images in the system. To evaluate total energy of the system, $\frac{1}{2}N(N-1)$ number of distinct distances should be calculated at each time step, which makes computation very expensive. If the interaction between molecules is short-ranged then we can consider small distance around the molecule and assume that molecule only interacts with the molecules within that region. Providing small cutoff region around the molecule and evaluating interactions only within that region, we can make MD simulation very efficient.

1.1.2 Spherical truncation and Neighbour list

Often in liquid simulations the small spherical cutoff region (r_{cut}) is considered around a molecule to take account of its interaction with molecules, beyond which there is no interaction between the molecules. Consider a system of molecules with box size L employed in PBC then r_{cut} should be less than $L/2$ in simulation. If $r_{cut} > L/2$ then molecule may interact with other molecules as well as their images at the same time which is problematic in molecular dynamic simulation. The spherical truncation implemented in PBC is shown in figure 1.2.

But evaluating every pair distances between molecules at every time step to determine whether or not a particular molecule is within cutoff region is computationally expensive. Therefore the cutoff sphere of r_{cut} is surrounded by the another larger sphere of radius r_{list} as shown in figure 1.3. At the beginning of the simulation a list of the molecules i.e. neighbour list is constructed around
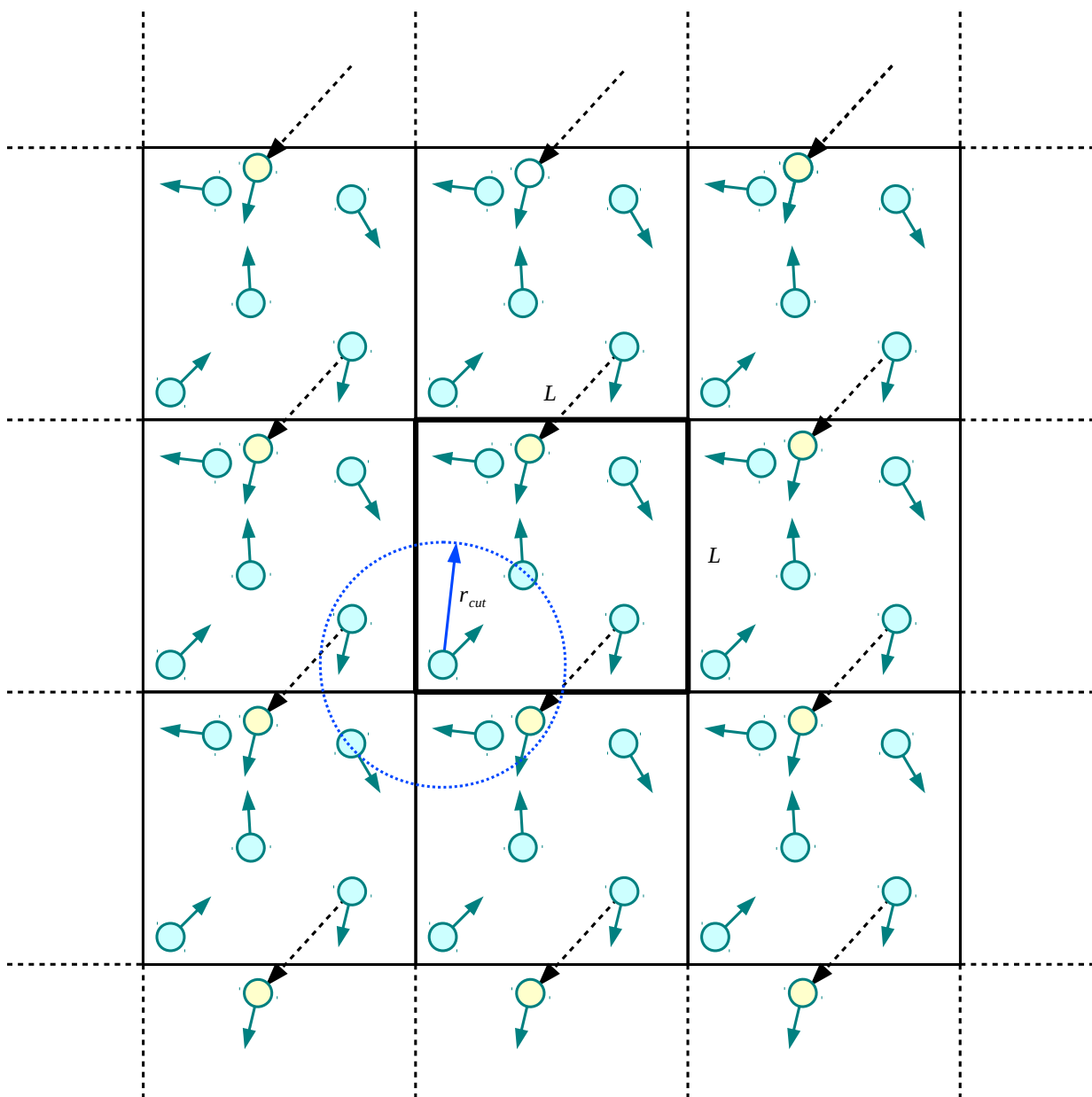
Figure 1.2. Periodic Boundary Condition for two dimensional (2D) molecular system. The central box is outlined using thicker line and replicated through out the plane to form 2D lattice. Usually in simulations, the potential energy of a molecule is evaluated considering interactions with the molecules and images within a cutoff region as shown in blue circle
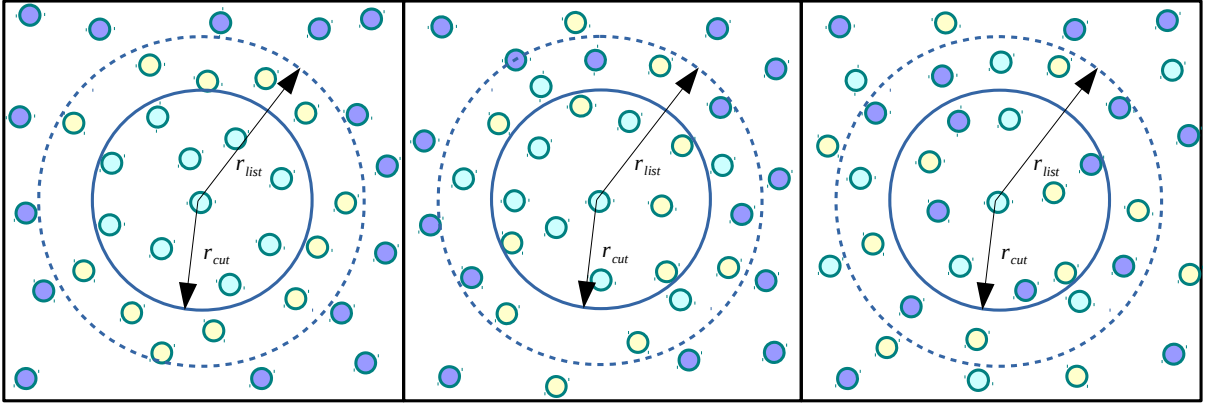
Figure 1.3. Region of neighbour list around the cutoff sphere. The molecules in cutoff region, neighbour list, and outer region are indicated by green, yellow, and violet circles. The neighbour list should be reconstructed before molecules in the outer region starts to penetrate cutoff region.

each molecule for which the pair separation $r_{ij} < r_{list}$. For few time step, only the molecules in the neighbour list are selected to check whether or not they are within the cutoff sphere. After few time step, neighbour list is again reconstructed by evaluating pair distances between the molecules. This reconstruction time for the neighbour list is mainly determined by the dynamics of the molecules in the simulation.

1.2   Monte Carlo (MC) Simulation

To study any physical and statistical properties of the system, we need to generate large number of different configurations with the consideration of constraints imposed in the system. Monte Carlo method uses probabilistic interpretation of the system to generate various configurations of the system. Each configuration depends only upon its processor but does not depend on the all the other config-

urations that were visited previously. For a canonical system, the probability of obtaining a given configuration is given by Boltzmann factor, $e^{-\frac{\Delta E}{k_B T}}$. Metropolis et. al developed the selection criteria for acceptance of the subsequent configuration of the system [17]. According to their method, the new configuration of the system is accepted either $\Delta E < 0$ or $e^{-\frac{\Delta E}{k_B T}} > r$, where r is the random number between 0 and 1. The evaluation of the potential energy difference between subsequent configurations i.e ΔE is very important in the MC simulation. For computational efficiency, this method also utilize pairwise electrostatic interactions including cutoff region r_{cut} as well as periodic boundary condition. Therefore developing efficient and accurate electrostatic interaction method has always been subject of interest in the MC communities.

1.3 Electrostatic Methods

Consider a system of N particles in a cubic box of length L replicated infinitely in the 3D-space then the electrostatic potential energy of the particle with charge q_i and located at r_i is given by

$$U_i = \sum_{n}' \sum_{j=1}^{N} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|}, \tag{1.5}$$

where q_j represents all other charges located at position $\mathbf{r}_j$ or in periodic replicas. Similarly $\mathbf{n}$ is the cell-coordinate vector can be expressed as $\mathbf{n}L = n_1 L \, \hat{x} + n_2 L \, \hat{y} + n_3 L \, \hat{z}$, where $n_1, n_2,$ and n_3 number of cell along x, y, and z directions and can vary from 0 to *infinity*. The prime in the first sum indicates that $i = j$ should be ignored for central box i.e. $n = 0$. The factor $\frac{1}{4\pi\epsilon_o}$ has been dropped in the equation 1.5 for simplicity. The total potential energy of the system can be

evaluated as,

$$U = \sum_{\substack{i=1 \\ i \neq j}}^{N} U_i = \frac{1}{2} \sum_{n}' \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|}, \tag{1.6}$$

where factor of $\frac{1}{2}$ in the second part of the equation is due to removing $i \neq j$ in the summation. Since the electrostatic interaction (Coulomb interactions) is the long-range interactions hence very time consuming in the molecular simulation. On the other hand the potential energy evaluated using equation **??** converges conditionally to the correct value depending on the order of summation taken into account during calculation[2]. Therefore there have been many efforts to reduce computational time and remove its conditional convergent behaviour during simulation will be discussed in the following subsections.

1.3.1 Ewald Method

This method was originally proposed by Ewald in 1921 to evaluate electrostatic interactions in PBC. In this method, the electrostatic interaction can divided into two rapidly converging real and reciprocal space sums as well as a constant self-term [24].

$$U_{real} = \frac{1}{2} \sum_{i,j}^{N} \sum_{n}' q_i q_j \frac{\text{erfc}(\alpha r_{ij,n})}{r_{ij,n}}, \tag{1.7a}$$

$$U_{reciporcal} = \frac{1}{2\pi V} \sum_{i,j}^{N} \sum_{\mathbf{m} \neq 0} \frac{\exp(-(\pi \mathbf{m}/\alpha)^2 + 2\pi i \mathbf{m}.\mathbf{r}_{ij})}{\mathbf{m}^2}, \tag{1.7b}$$

$$U_{self} = -\frac{\alpha}{\sqrt{\pi}} \sum_{i=1}^{N} q_i{}^2, \tag{1.7c}$$

where V is the volume of the simulation box, $\mathbf{m}$ is a reciprocal-space vector, and α is damping parameter which determines the rate of convergence in the real

and reciprocal space. The self-term in the equation 1.7c is to remove artificial interactions of a charge with its images located in the periodic replicas of the box. Since $\text{erf}(x) + \text{erfc}(x) = 1$ we can write 1.6 as,

$$U = \frac{1}{2} \sum_{n}^{\prime} \sum_{i=1}^{N} \sum_{j=1}^{N} q_i q_j \frac{\text{erfc}(\alpha r_{ij,n}) + \text{erf}(\alpha r_{ij,n})}{r_{ij,n}}. \qquad (1.8)$$

The equation 1.7a is obtained by taking complementary error function term and the equation 1.7b can be obtained taking Fourier transform of the error function term in equation 1.8.

Physically each point charge in the system can be assumed to be surrounded by a Gaussian distribution of equal magnitude and opposite signed charge (see figure 1.4) with density,

$$\rho_i(r) = q_i \left(\frac{\alpha}{\sqrt{\pi}} \right)^3 \exp(-\alpha^2 r^2), \qquad (1.9)$$

where α is a damping parameter determines the distribution of the charge, r is the position from the center of distribution. The imposed charge distribution around a charge screens the interactions between the charges making interaction a short-ranged and converges rapidly with distance. These Gaussian distributions are counteracted by other Gaussian distributions of the charges of same magnitude but opposite in sign as shown in figure 1.4[24]. The sum of potential energy due to second type of charge distributions converge in the reciprocal space.

For minimum image convention scheme, i.e. each particle can interact with its nearest charge or image, the total number of interactions is $\frac{1}{2}N(N-1)$ in Ewald method. *Recerz* and *Jacobs* suggested that by choosing proper simulation parameters and minimum image convention schemes we can make reciprocal potential
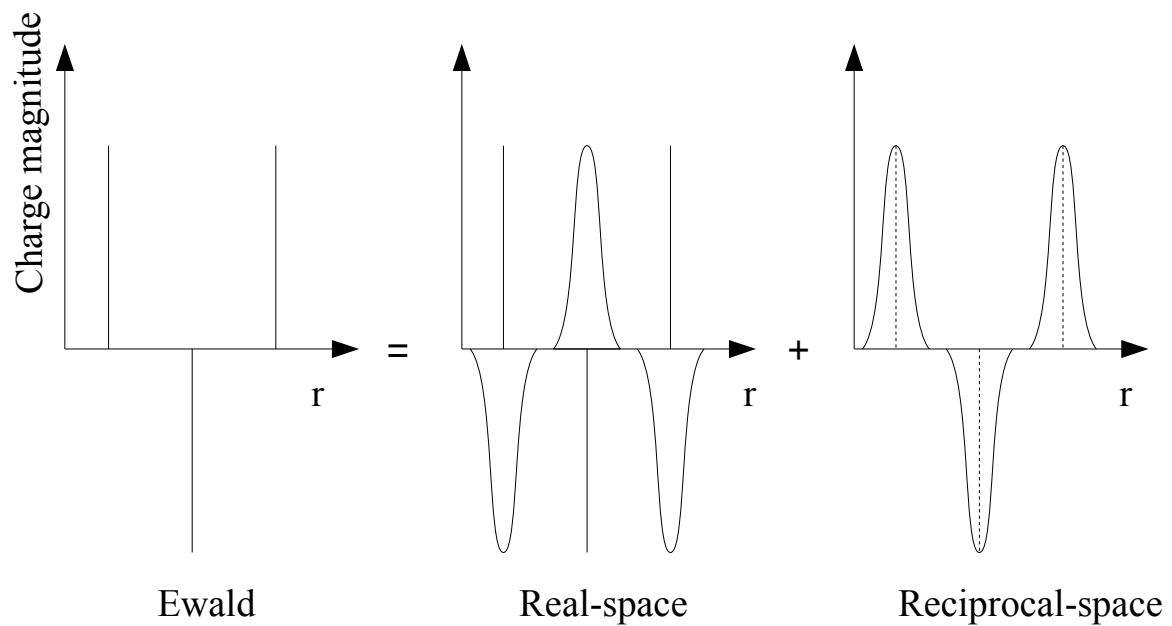
Figure 1.4. In Ewald method point charge is surrounded by the Gaussian distribution of the equal and opposite-signed charge evaluated in real-space. These Gaussian distributions are compensated by the corresponding opposite-singed distribution of the charges calculated in the reciprocal-space

very small as compared to real-space potential so that it can be ignored [22]. How-ever this method is only applicable for larger system and strongly dependent on configurations of the system. Perram et al. subdivided box into $m crossm crossm$ sub-boxes and selected damping parameter $\alpha = m\sqrt{-\log(\delta)}$, where δ is the relative error constant for neglecting maximum term in the real-space sum, and using this technique they were able to reduce computational time to $O(N^{3/2})$.

1.3.2 Fourier-based Ewald Methods

The Ewald method has been modified using Fast Fourier transform (FFT) to reduce complexity to $O(Nlog(N))$. In these method charges are interpolated to 3D grid and reciprocal sum is evaluated using FFT. The particle-particle particle-mesh Ewald (PPPME) and particle-mesh Ewald (PME) methods are two widely used Fourier-based Ewald methods.

1.3.2.1 Particle-Particle Particle-Mesh Ewald (PPPME)

The PPPME method was originally developed Hockmney and Eastwood [8] then extended by Luty et al.[14] and Rajagopal et al. [19]. In this method elec-trostatic interaction is divided into short ranged real-space sum and long ranged reciprocal-space sum. The charges in the system are approximated as uniformly decreasing spherical charge density. The short-ranged potential within the cutoff radius $r < r_{cut}$ is calculated using electrostatic interactions between charge distri-butions. To calculate long-ranged potential, first of all charges are assigned to the 3D grid as shown in figure **??** then transformed to the Fourier space for evaluating electrostatic potential. Since charges are assigned to the grid, it is very efficient to evaluate electrostatic interaction in the reciprocal space. Once potential energy is

evaluated, inverse Fourier transformed is applied to calculate energy in real-space and this energy is numerically differentiated to get force acting on the grid. Finally we can interpolate electrostatic force (or energy) from the grid to particle locations to obtain actual force acting on the particle.

Although PPPME has complexity $O(N\log N)$, for computational accuracy, we should either refine mesh or use better interpolation technique, both of which are computational expensive. In addition to this, using numerical differentiation to calculate force may introduced error in calculation. Therefore higher order differentiation schemes are often used in force calculation. In order to get optimal performance, all of the parameters; charge-distribution, interpolation technique, and differentiation schemes should be properly selected for a particular system which makes this method system-specific [**?**].

1.3.2.2   Particle-Mesh Ewald (PME)

This method is the modification of the PPPME method, in which the potential energy is divided into real-space and reciprocal-space sums and evaluated using the Ewald's Gaussian distribution of charge. The real-space sum within the cutoff sphere is evaluated using actual electrostatic interactions between charges whereas the reciprocal sum is calculated in Fourier-space using the idea of 3D grid as explained in PPPME method. Similarly unlike PPPME, this method evaluates force analytically differentiating electrostatic energy at a given grid point, which reduces memory requirement significantly. This method has also $O(N\log N)$ complexity and uses interpolation to map back electrostatic force from grid to particles. Therefore we should discover optimal interpolation technique to obtain excellent speed and accuracy for a simulation of given system and makes it system depen-

dent.

There are many Ewald-based methods that have been developed for calculating electrostatic interaction in molecular simulations but they are not being widely used because of efficiency and difficulty in implementation. In addition, one particular method can not be used for all kind of molecular environments. We have already discussed widely used Ewald and Ewald-based methods.

1.3.3 Real Space Methods

Before discussing about the real space methods, it is better to discuss about the fundamental property of the electrostatic interactions in the real condensed phase environments. The electrostatic interaction between two charged particles decays as $1/r$. But molecular system usually composed of an equal number of positive and negative charges. Thus the range of interaction between a particular charge and rest of the other charges in the system are different than the interaction between two bare charges. Consider a one dimensional (1D) crystal lattice composed of positive and negative charges. The potential energy of a particular ion can be considered as a sum of interactions with positive and negative ion pairs as shown in Figure 1.5(a). Mathematically the potential energy for 1D crystal with alternating charges is given by a Madelung sum,

$$
\begin{aligned}
U^{Mad} &= -2q_iq_j \left(\frac{1}{a} - \frac{1}{2a} \right) - 2q_iq_j \left(\frac{1}{3a} - \frac{1}{4a} \right) - 2q_iq_j \left(\frac{1}{5a} - \frac{1}{6a} \right) + ... \\
&= - \left(\frac{2q_iq_j}{(1.414)^2a} \right) - \left(\frac{2q_iq_j}{(3.464)^2a} \right) - \left(\frac{2q_iq_j}{(5.477)^2a} \right) + ...
\end{aligned}
\tag{1.10}
$$

In equation(1.10) we see that the interaction energy of a single ion with the pairs converges faster than $(1/r)$. Similarly, in a two dimensional (2D) lattice, the

(a)

(b)
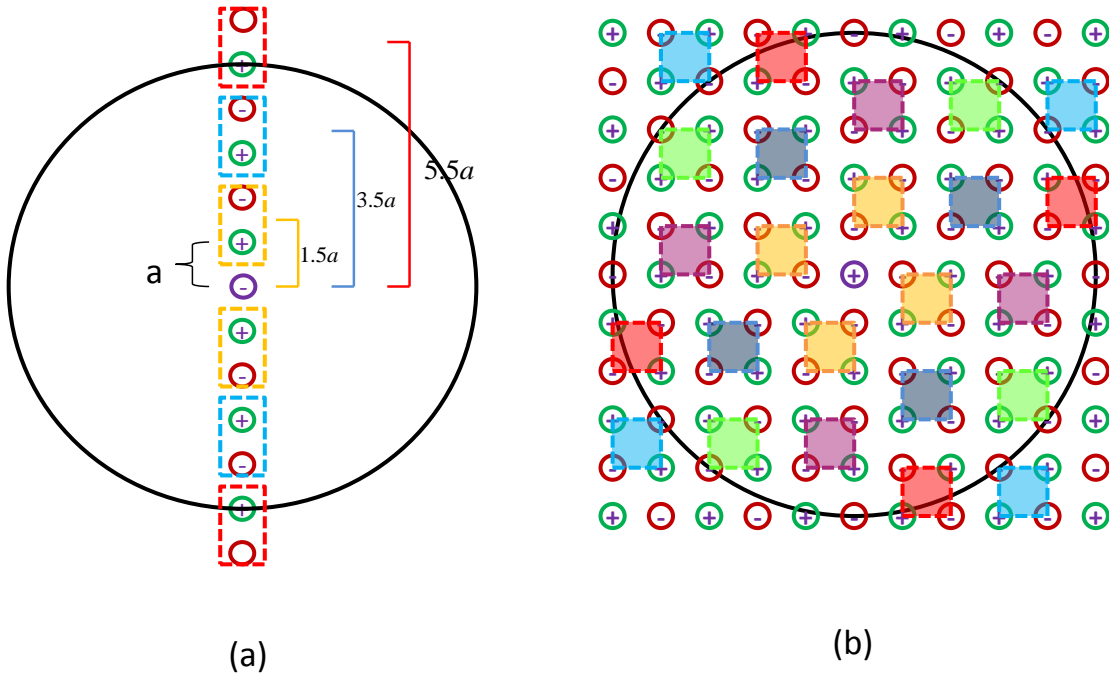
Figure 1.5. Schematic diagram showing grouping of ions in (a) 1D (b) 2D crystals. The interaction of the central ion with the group of ions decays faster than $1/r$. The direct spherical truncation breaks the ordering of the ions at the cut off sphere providing a net charge within the cutoff sphere. The breaking of the charge ordering increases with the crystal dimension resulting in a large net charge in the higher dimensional crystal.

potential energy of an ion can be described as a sum of positive and negative four body groups as seen in Figure 1.5(b). The interaction energy between an ion and group of four ions decays much faster than the charge-charge interaction. For a three-dimensional (3D) crystal, the potential energy of an ion can be considered as due to its interaction with the group of eight ions forming a cube. From this generalization, we can conclude that the electrostatic interaction energy for an ion in the crystalline system is a short-ranged as compared to charge-charge interaction. Therefore, even the relatively small size of the system should be able to represent bulk long-ranged interactions of the system.

In order to reduce the computational expense of a molecular dynamics simulation, interactions between particles are only considered if the particles exist within a cutoff distance r_c, of one another. We first consider how the energy of a system behaves if we truncate the interactions at the cutoff radius. Figure 1.6 shows (black line) that the electrostatic potential energy does not converge to the Madelung energy upon increasing the cutoff radius for the direct truncation. On the other hand the energy is found to be closer to the Madelung constant when the net charge within the cutoff radius is zero (Figure 1.7). This oscillation in the potential energy is due to the breaking in charge ordering on the surface of the cutoff sphere which results in a net charge within the cutoff sphere. The size of the net charge is proportional to the dimension of the crystal. Although the interaction energy is short ranged, the direct truncation results in severe oscillation in the 3D crystal as shown in Figure 1.6. Dipolar (or quadrupolar) crystals are also formed by ordering of the dipolar (or quadrupolar) molecules. Therefore similar oscillatory behaviour in the potential energy is seen due to the breaking of the ordering of dipoles (or quadrupoles) on the surface of the truncated sphere. Even
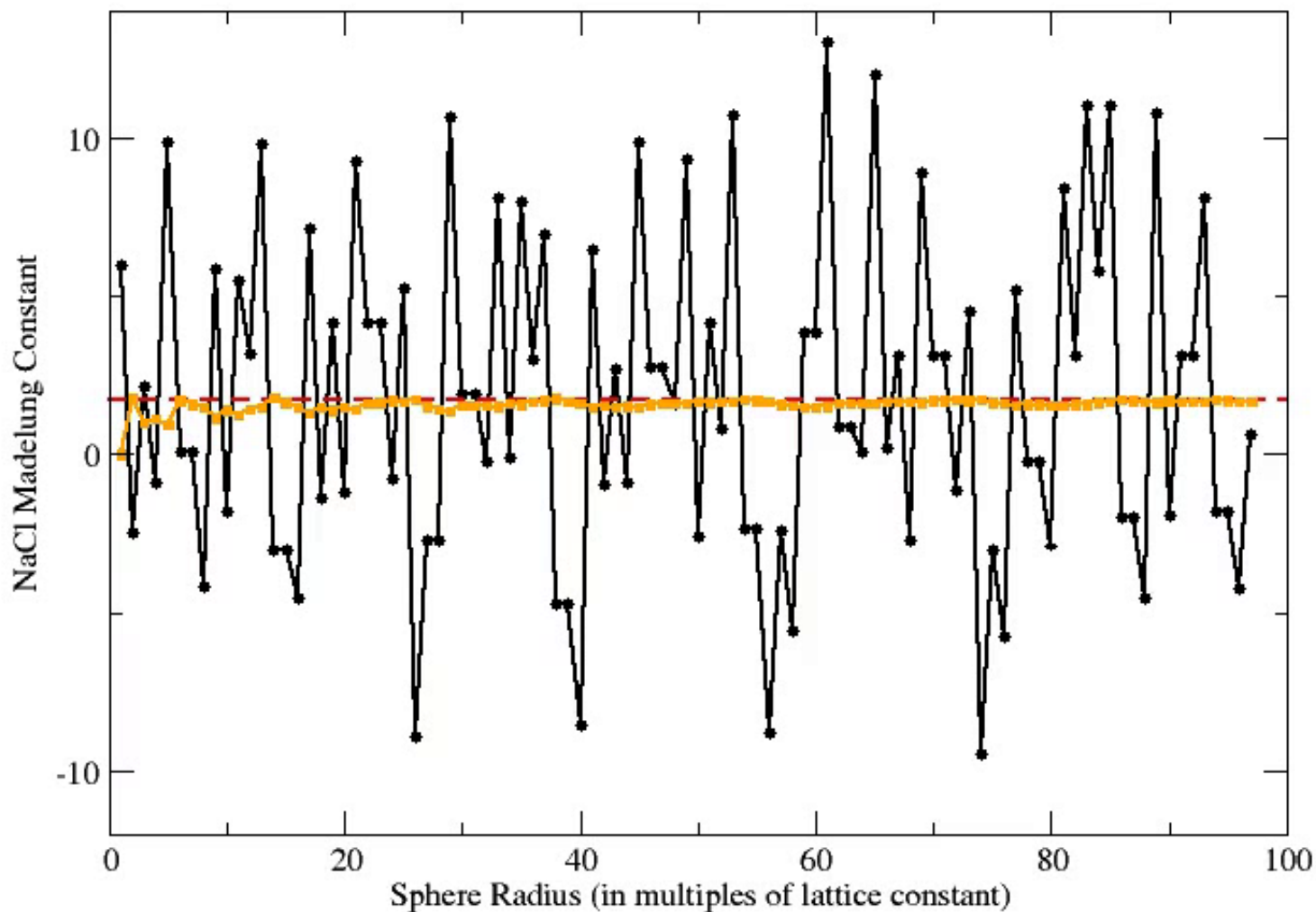
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Figure 1.6. Convergence of the lattice energy constants for a NaCl crystal as a function of cutoff radius for the direct (hard) cutoff method (black line). The orange line in the left figure is for charge neutralized cutoff sphere (when image charged placed on the surface of the cutoff sphere). The red dotted line represents Madelung energy for NaCl crystal
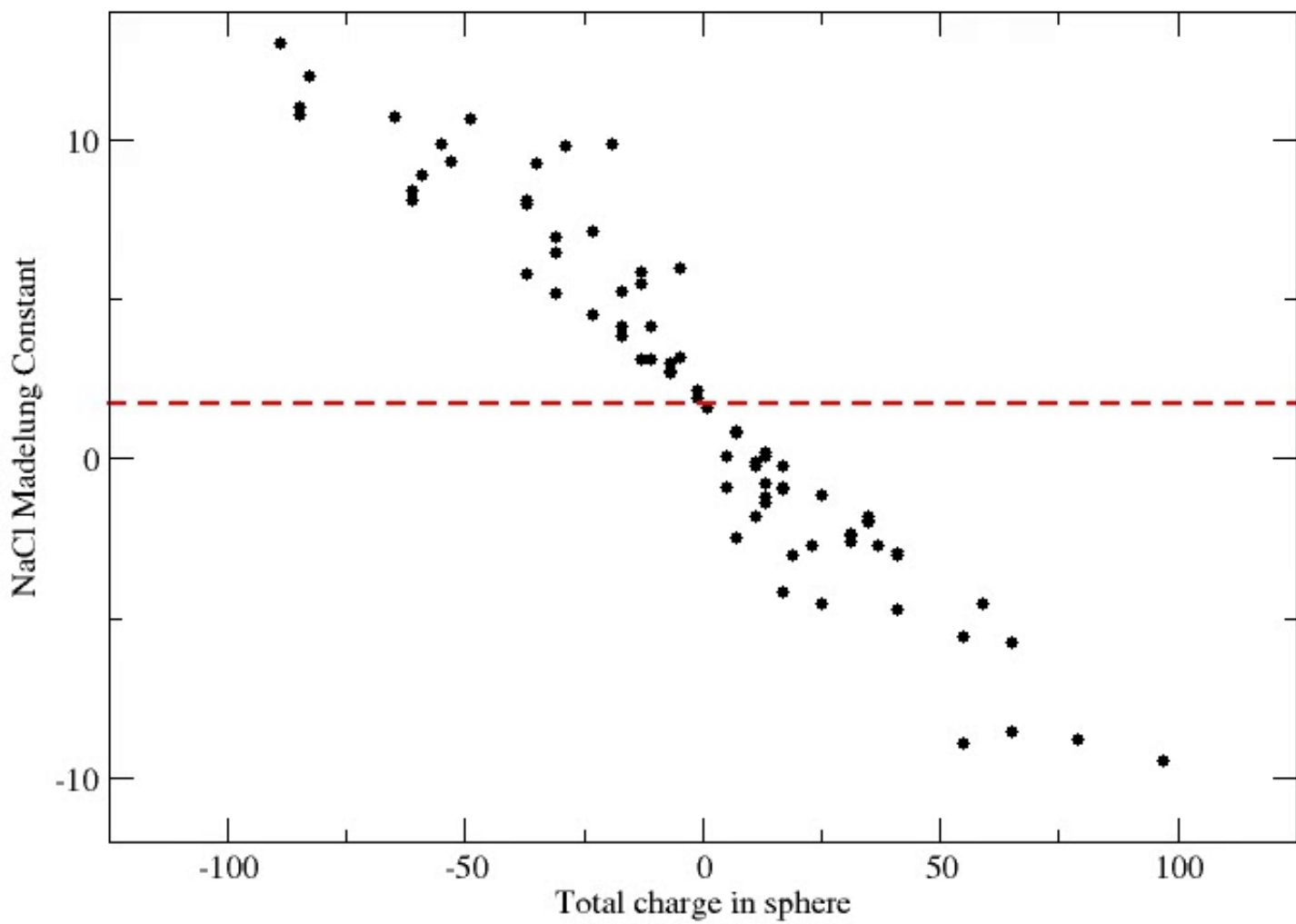
Figure 1.7. Convergence of the lattice energy constants for a NaCl crystal as a function of net charge within a cutoff sphere. The red dotted line represents Madelung energy for NaCl crystal

in liquids there is local ordering of the molecules due to electrostatic interaction and similar oscillatory behaviour in the electrostatic potential has been seen in the direct truncation.

Wolf *et al.* proposed the idea of placing an image charge on the surface of cutoff sphere for every charge found within the sphere. The image charges would have opposite charge of those found within the sphere, thus guarantee charge neutralization within the cutoff sphere [26]. This charge neutralization converges the potential energy to the correct Madelung energy as shown in Figure 1.6 (orange line). In molecular dynamics (MD) simulations, the energy, force and torque should approach zero as the distance between molecules approaches the cutoff radius in order to conserve total energy. However Wolf's forces and torques derived from the potential do not go to zero at the cutoff radius, which makes it inappropriate to use in MD simulations. More recently, Zahn *et al.* and Fennell and Gezelter proposed the damped shifted force (DSF) potential, which incorporates Wolf's approach of image charges while ensuring the forces and torques approach zero at the cutoff radius [4, 6]. Fukuda has also recently been successful with the neutralization of higher order moments in a system of point charges [7].

In our research, we have generalized Wolf's shifted potential (SP) to the higher order electrostatic multipoles. Similarly, we have also developed the gradient shifted force (GSF) and Taylor shifted force (TSF) potentials which are the extension of the damped shifted force (DSF) for higher order charge-multipoles. In the following chapter 2, I will discuss about the development of the SP, GSF, and TSF methods and evaluate the energy constants for various dipolar and quadrupolar crystals using newly developed methods and compare result with analytical

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method [11]. Similarly in the chapter 3, I will derive different physical proper-
ties such as; co-ordination number, orientational relaxation time, diffusivity, and
mean potential energy for the mixed liquid phase systems using our methods and
compare results with Ewald method. Additionally, I will also compare the con-
servation of energy in the molecular dynamics simulations for SP, GSF, and TSF
methods with the Ewald method [12].Chapter 4 discusses about how to use our
methods to calculate correct dielectric properties for the condensed dipolar and
quadrupolar systems. Finally I will conclude summary of my research in chapter
5.

BIBLIOGRAPHY

1. M. P. Allen. Introduction to molecular dynamics simulation, 2004.

2. M. P. Allen and D. J. Tildesley. *Computer Simulation of Liquids*. Clarendon Press, New York, NY, USA, 1989. ISBN 0-19-855645-4.

3. T. Darden, D. York, and L. Pedersen. Particle mesh ewald: An nlog(n) method for ewald sums in large systems. *The Journal of Chemical Physics*, 98(12), 1993.

4. Z. Dirk, S. Bernd, and M. K. Stefan. Enhancement of the wolf damped coulomb potential: static, dynamic, and dielectric properties of liquid water from molecular simulation. *The Journal of Physical Chemistry B*, 106(41): 10725–10732, 2002. doi: 10.1021/jp025949h. URL `http://dx.doi.org/10.1021/jp025949h`.

5. U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen. A smooth particle mesh ewald method. *The Journal of Chemical Physics*, 103(19), 1995.

6. C. J. Fennell and J. D. Gezelter. Is the ewald summation still necessary? pairwise alternatives to the accepted standard for long-range electrostatics. *The Journal of Chemical Physics*, 124(23):234104, 2006. doi: http://dx.doi.org/10.

1063/1.2206581. URL `http://scitation.aip.org/content/aip/journal/jcp/124/23/10.1063/1.2206581`.

7. I. Fukuda. Zero-multipole summation method for efficiently estimating electrostatic interactions in molecular system. 139(17):174107, 2013. doi: http://dx.doi.org/10.1063/1.4827055. URL `http://scitation.aip.org/content/aip/journal/jcp/139/17/10.1063/1.4827055`.

8. R. W. Hockney and J. W. Eastwood. *Computer simulation using particles.* CRC Press, 1988.

9. P. H. Hünenberger and J. A. McCammon. Ewald artifacts in computer simulations of ionic solvation and ion – ion interaction: A continuum electrostatics study. *J. Chem. Phys.*, 110(4):1856–1872, 1999.

10. P. H. Hünenberger and J. A. McCammon. Effect of artificial periodicity in simulations of biomolecules under ewald boundary conditions: a continuum electrostatics study. *Biophys. Chem.*, 78:69–88, 1999.

11. M. Lamichhane, J. D. Gezelter, and K. E. Newman. Real space electrostatics for multipoles. i. development of methods. *The Journal of Chemical Physics*, 141(13):134109, 2014. doi: http://dx.doi.org/10.1063/1.4896627. URL `http://scitation.aip.org/content/aip/journal/jcp/141/13/10.1063/1.4896627`.

12. M. Lamichhane, K. E. Newman, and J. D. Gezelter. Real space electrostatics for multipoles. ii. comparisons with the ewald sum. *The Journal of Chemical Physics*, 141(13):134110, 2014. doi: http://dx.doi.org/10.1063/1.4896628.

URL `http://scitation.aip.org/content/aip/journal/jcp/141/13/10.1063/1.4896628`.

13. B. A. Luty and W. F. van Gunsteren. Calculating electrostatic interactions using the particle-particle particle-mesh method with nonperiodic long-range interactions. *J. Phys. Chem.*, 100(7):2581–2587, 1996.

14. B. A. Luty, M. E. Davis, I. G. Tironi, and W. F. V. Gunsteren. A comparison of particle-particle, particle-mesh and ewald methods for calculating electrostatic interactions in periodic molecular systems. *Molecular Simulation*, 14(1):11–20, 1994. doi: 10.1080/08927029408022004. URL `http://dx.doi.org/10.1080/08927029408022004`.

15. B. A. Luty, I. G. Tironi, and W. F. van Gunsteren. Latticesum methods for calculating electrostatic interactions in molecular simulations. *The Journal of Chemical Physics*, 103(8), 1995.

16. M.Born and T. V. Karman. *Physik*, Z(13):297, 1912.

17. N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller. Equation of state calculations by fast computing machines. *The Journal of Chemical Physics*, 21(6), 1953.

18. J. W. Perram, H. G. Petersen, and S. W. D. Leeuw. An algorithm for the simulation of condensed matter which grows as the 3/2 power of the number of particles. *Molecular Physics*, 65(4):875–893, 1988. doi: 10.1080/00268978800101471. URL `http://dx.doi.org/10.1080/00268978800101471`.

19. G. Rajagopal and R. Needs. An optimized ewald method for long-ranged potentials. *Journal of Computational Physics*, 115(2):399 – 405, 1994. ISSN 0021-9991. doi: http://dx.doi.org/10.1006/jcph.1994.1205. URL `http://www.sciencedirect.com/science/article/pii/S0021999184712058`.

20. J. E. Roberts and J. Schnitker. How the unit cell surface charge distriubution affects the energetics of ion-solvent interactions in simulations. *J. Chem. Phys.*, 101(6):5024–5031, 1994.

21. J. E. Roberts and J. Schnitker. Boundary conditions in sumulations of aqueous ionic solutions: A systematic study. *J. Phys. Chem.*, 99:1322–1331, 1995.

22. Z. A. Rycerz and P. W. M. Jacobs. Ewald summation in the molecular dynamics simulation of large ionic systems. *Molecular Simulation*, 8(3-5):197–213, 1992. doi: 10.1080/08927029208022476. URL `http://dx.doi.org/10.1080/08927029208022476`.

23. J. Shimada, H. Kaneko, and T. Takada. Efficient calculations of coulombic interactions in biomolecular simulations with periodic boundary conditions. *Journal of Computational Chemistry*, 14(7):867–878, 1993. ISSN 1096-987X. doi: 10.1002/jcc.540140712. URL `http://dx.doi.org/10.1002/jcc.540140712`.

24. A. Y. Toukmaji and J. A. B. Jr. Ewald summation techniques in perspective: a survey. *Computer Physics Communications*, 95(23):73 – 92, 1996. ISSN 0010-4655. doi: http://dx.doi.org/10.1016/0010-4655(96)00016-1. URL `http://www.sciencedirect.com/science/article/pii/0010465596000161`.

25. W. Weber, P. H. Hünenberger, and J. A. McCammon. Molecular dynamics

simulations of a polyalanine octapeptide under ewald boundary conditions: Influence of artificial periodicity on peptide conformation. *J. Phys. Chem. B*, 104(15):3668–3675, 2000. doi: 10.1021/jp9937757. URL `http://dx.doi.org/10.1021/jp9937757`.

26. D. Wolf, P. Keblinski, S. R. Phillpot, and J. Eggebrecht. Exact method for the simulation of coulombic systems by spherically truncated, pairwise r1 summation. *The Journal of Chemical Physics*, 110(17), 1999.