Mathematical Description of Project: Molecular Simulation of an Na-Cl System using the Particle Mesh Ewald Method

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1 Introduction

Objective: Simulating a set of N physical particles, evolving under Newton's laws of motion.
The particles in the box interact with each other under both, Van der Waal's as well as Coulomb interactions. Van der Waal's interactions vary as r^{-6}, and are hence local interactions. They can be truncated to short range. However, Coulomb interactions vary with r^{-1}. Hence, they cannot be truncated at short range. Similarly, the short range nature of the forces prevents use of simple periodic images.

2 Mathematical Specification

2.1 Forces

Force at a position $\vec{x}$ is given by the sum of the Coulomb forces from all particles at that point:

$$\vec{F_k}(\vec{x}) = q_k \nabla_x \Phi(\vec{x} - \vec{x_k}) \tag{1}$$

$$\Phi(r) = \frac{1}{4\pi r} \tag{2}$$

$$\vec{F}(\vec{x}) = \sum_{k'} \vec{F_{k'}}(\vec{x}) \tag{3}$$

Φ = Coulomb potential

Forces on each particle can be calculated by summing over the forces due to all other particles, leading to an $\mathcal{O}(n^2)$ scaling for the calculations.

Van der Waal forces can be calculated as:

$$\vec{F}(\vec{x}) = \nabla_x \left(\frac{A_{rep}}{r^{12}} - \frac{B_{disp}}{r^6} \right) \tag{4}$$

A_{rep} = Repulsion constant
B_{disp} = Dispersion constant

2.2 Particle Mesh Ewald

The potential is split into short range and long range electrostatics. The short range electrostatics are computed using the standard N-body calculation, while the long range electrostatics are computed using the periodic image conventions.
The cost of the short range interaction is $\mathcal{O}(n^2) * \delta^3$ where delta is the fractional cutoff for the short range.
The cost of the long range electrostatics, calculated in the reciprocal space = $\mathcal{O}(N)$ (for assigning the particles) + $\mathcal{O}(N_g \log N_g)$

3 Methods

Short range forces are calculated through particle pairwise interactions. Particles are bin sorted onto a grid. This sorting is an $\mathcal{O}(N)$ operation. Short range interactions can be calculated for particles only in neighboring grid points. This interaction calculation is $\mathcal{O}(n^2) * \delta^3$. An appropriate choice of δ would lead to sub $\mathcal{O}(n^2)$ scaling.
The PME forces are calculated by depositing the charges on grid points. The mathematical formulation of these forces is outlined in writeup 1. The forces on the grid points from the charge distribution on the grid points can be calculated via the convolution of deposition function with the charges. The forces on the particles can be interpolated from the forces on the grid points. This method is similar to that implemented in HW4 for the Vortex method.
The numerical integration of the equations of motion will be calculated via the Velocity Verlet algorithm.

$$\vec{r}(t + \Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t + \frac{1}{2}\vec{a}(t)\Delta t^2 \tag{5}$$

$$\vec{v}(t + \frac{\Delta t}{2}) = \vec{v}(t) + \frac{1}{2}\vec{a}\Delta t \tag{6}$$

$$\vec{a}(t + \Delta t) = -\frac{1}{m}\nabla V(\vec{r}(t + \Delta t)) \tag{7}$$

$$\vec{v}(t + \Delta t) = \vec{v}(t + \frac{\Delta t}{2}) + \frac{1}{2}\vec{a}(t + \Delta t)\Delta t \tag{8}$$

Discretization methods: Grid decomposition
Numerical Methods: FFT, Convolution

4 Specification of Computational Solution

A computational solution to this system would involve simulating the of Na^+Cl^- ions in the periodic box. As the system would be simulated in an NVE ensemble, tracking the energies of the system over time would give a check on the accuracy. The trajectory of the particles can also be visualized in VMD to observe the dynamics of the system.