HONOURS DISSERTATION

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ABSTRACT

This is a short summary of my work...

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ACKNOWLEDGEMENTS

I would like to dedicate this work to..

ONE

INTRODUCTION

TWO

MOLECULAR DYNAMICS

2.1   Introduction

The underlying assumption behind many molecular dynamics simulations is that the particles move according to the laws of Newtonian Mechanics. The effects fo Quantum Mechanics are usually small unless very light atoms (such as hydrogen or helium) are being simulated or the particles are vibrating at very high rates [1]

The fundamental identity of Newtonian Mechnanics is Newton's Second Law of Motion (2.1.1). This equation allows the prediction of a particle's trajectory provided that an initial position and velocity is known; and the forces acting on that particle can be calculated for any position or velocity.

$$\mathbf{F} = m\mathbf{a} \tag{2.1.1}$$

If a force depends only on the position of a particle it is known as a conservative force. Almost all forces considered in molecular dynamics are of this type because atoms or molecules do not lose energy due to friction or any other dissipative process.

Conservative forces can be further subdivided into forces that depend either on absolute position such as gravity or forces can depend on position relative to another particle (intermolecular forces). Gravity is usually neglected in MD simulations as the mass of atoms and molecules is very small.

Only pairwise intermolecular forces are considered ie the total force acting on a particle is the sum of the forces caused by every other particle in the system (**??**).

While the forces caused by groups of particles should also be considered, this would severly complicate the simulation, and hence is often ignored.

In MD simulations the intermolecular forces are usually described using potentials.

2.1.1 Potentials

A potential is the function of potential energy with position, where position is usually expressed as a set of orthogonal vectors such as x, y and z in three dimensions. Conservative forces can be calculated from their potential by equation 2.1.2. The gradient of the potential, denoted by ∇ is the partial differential of the potential in each orthogonal direction.

$$\mathbf{F} = -\nabla \mathbf{U} \tag{2.1.2}$$

A very popular potential used in molecular dynamics simulations is the Lennard-Jones potential [2] (equation 2.1.3) as it is simple yet gives comparable results to experimental values.

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right] \tag{2.1.3}$$

In equation 2.1.3, ϵ is the depth of the energy well, while σ is the root of the Lennard-Jones potential which corresponds to the change from attractive to repulsive forces (see Lennard Jones Figures), this is taken to be the diameters of the particles during the collision.

THREE

BACKGROUND THEORY

3.1 Force-Driven Simulators

3.1.1 Introduction

Force-driven (or time driven) simulators are the most popular method of simulating particles due to their relative simplicity and ability to handle soft potentials. Simulators of this kind were pioneered by Rahman [3] who predicted physical properties of liquid argon with reasonable accuracy.

The distinguishing feature between force-driven and event-driven simulators is the way in which they move through time. During force-based simulations particles' positions and velocities are calculated every unit of time, Δt using the forces acting on the particles. These newly calculated values are then used to predict the next set of particle positions. This is then repeated over the desired simulation time.

3.1.2 Integrators

Once the forces acting on a particle is known, that particle's acceleration can be calculated using Newton's Second Law of Motion (equation 3.1.1).

$$\mathbf{F} = m\frac{\partial^2\mathbf{r}}{\partial t^2}$$
(3.1.1)

However, since acceleration is the second time derivative of position (velocity is the first time deriviative), calculating the particle's future position results in solving a differential equation of order 2 or higher since force, and hence acceleration likely changes with time. In order to accomplish this numerical integrators are used.

The majority of numerical integrators are based on Taylor Series (equation 3.1.2).

$$r(t + \Delta t) = r(t) + \frac{\partial r(t)}{\partial t}(\Delta t) + \frac{1}{2}\frac{\partial^2 r(t)}{\partial t^2}(\Delta t)^2 + \frac{1}{3!}\frac{\partial^3 r(t)}{\partial t^3}(\Delta t)^3 + \frac{1}{4!}\frac{\partial^4 r(t)}{\partial t^4}(\Delta t)^4 + ...$$
$$(3.1.2)$$

The simplest integrator is Euler's Method which is just the Taylor Series truncated after the acceleration term (equation 3.1.3).

$$r(t + \Delta t) = r(t) + \frac{\partial r(t)}{\partial t}(\Delta t) + \frac{1}{2}\frac{\partial^2 r(t)}{\partial t^2}(\Delta t)^2 + O(\qquad (3.1.3)$$

3.2 References

[1]   D. Frenkel and B. Smit. *Understanding Molecular Simulations*. Ed. by Second Edition. Academic Press, 2002. DOI: `10.1016/B978-012267351-1/50006-7`.

[2]   J.E. Lennard-Jones. "The Determination of Molecular Fields I & II". In: *Proc. R. Soc. Lon. Ser-A* 106A (1924), pp. 441–477. DOI: `10.1098/rspa.1924.0081`.

[3]   A Rahman. "Correlations in the Motion of Atoms in Liquid Argon". In: *Phys. Rev.* 136 (1964), A405–A411. DOI: `10.1103/PhysRev.136.A405`.