Molecular dynamics

Intensive Computation

Annalisa Massini
2020-2021

Lecture 11

INTRODUCTION

http://twiki.di.uniroma1.it/pub/CI/WebHome/FosdickMolecDynamic.pdf

Introduction

- **Molecular dynamics** is concerned with simulating:
  - the motion of molecules to understand chemical reactions
  - fluid flow
  - phase transitions
  - droplet formation
  - physical phenomena that derive from molecular interactions

- These studies include both:
  - the motion of many molecules as in a fluid
  - the motion of a single large molecule consisting of hundreds or thousands of atoms, as in a protein

Introduction

- Computers are a critically important tool for these studies because there simply is no other way to trace the motion of a large number of interacting particles
- The earliest of these computations were done in the 1950s by Berni Alder and Tom Wainwright at Lawrence Livermore National Laboratory
- They studied the distribution of molecules in a liquid, using a model in which the molecules are represented as **hard spheres** which interact like billiard balls
- Using the fastest computer at that time, an IBM 704, they were able to simulate the motions of 32 and 108 molecules in computations requiring 10 to 30 hours

Introduction

- Computations using a more realistic molecular model known as **Lennard-Jones** have been performed at IBM Kingston by Lawrence Hannon, George Lie and Enrico Climenti to study the flow of fluids
- In these computations the fluid was represented by 10^4 interacting molecules
- Even though this is miniscule compared with the number of molecules in a gram of water, the behavior of the flow was like that in a real fluid

Introduction

- Another class of molecular dynamics computations is concerned with the internal motion of molecules especially proteins and nucleic acids
- The goal is to gain a better understanding of the function of these molecules in biochemical reactions
- Classical mechanics is suffcient to model the motions, but still the computational power required for following the motion of a large molecule is enormous

Introduction

- Scientific visualization is particularly important for understanding the results of a molecular dynamics simulation
- The millions of numbers representing a history of the positions and velocities of the particles is not a very revealing picture of the motion
- Visualization using pictures and animations is fundamental to recognize typical phenomena such as:
  - The formation of a vortex
  - The nature of the bending in a protein
  - The stretching of a large molecule

Introduction

- Our goal is to gain some understanding of the nature of these computations
- We use the term **particle** to refer to the interacting objects: atoms or molecules
- We will analyze three different models:
  - **Hooke's law**: the force acts as if the particles were connected to their neighbors by springs
  - **Lennard-Jones**: forces are strong repulsive at very short interparticle distances, attractive at larger distances, and extremely weak attractive at very large distances
  - **hard sphere**: particles interact as if they were billiard balls - they bounce off each other when they are a certain distance apart, otherwise they do not interact

Introduction

- After describing these models, we discuss the equations of motion for each model, and then we consider numerical methods for solving these equations

- Solving the equations of motion for the **hard sphere model** requires solving some simple problems in **geometry**
- In particular, we must determine when and where two spheres moving at constant velocity will collide (vector analysis in two and three dimensions)

Introduction

- With **Hooke's Law** and **Lennard Jones** models we must solve a system of **differential equations**
- For this we use two numerical methods:
  - **Euler's method**
  - **Verlet's method**
- Euler's method is the simplest method we could reasonably use and provides the easiest introduction to basic ideas of numerically solving the equations of motion
- Verlet's method is slightly more complex but more accurate, and is the simplest of the numerical methods used in serious molecular dynamics computations

Introduction

- Finally, we consider the **exact solution** of the equations of motion for the Hooke's Law model
- This is the only model of the three considered here that admits an exact solution
- Exact solutions are important for us because they provide a means for testing the accuracy of our numerical methods
- An understanding of this part requires some elementary knowledge of matrix eigenvalues and eigenvectors

MODELS

Models

- Models of particle systems are characterized by the nature of the interactions between the particles
- Generally it is assumed that:
  - the forces between the particles are **conservative**, that is **energy is conserved** and
  - the **total force** acting on a particle due to the other particles is the sum of the forces between pairs of particles, that is the force acting on particle i is given by an expression of the form

$$f_i = \sum_{i=1, i \neq j}^{n} f_{i,j}$$

Where f_i is the total force on particle i due to the other particles, $f_{i,j}$ is the force on particle i due to particle j, and n is the number of particles in the system

Models

- Force is a vector quantity, so the sum in equation

$$f_i = \sum_{i=1, i \neq j}^{n} f_{i,j}$$

  is a vector sum

- The order of the indices is important:
  - the first index identifies the particle acted on
  - the second index identifies the particle causing the action

- Newton's third law tells us that $f_{i,j} + f_{j,i} = 0$

Models

- There is an important relation between potential energy and force in a conservative system
- If r is the position of a particle, $f(r)$ the force acting on it, and $\phi(r)$ its potential energy (**capacity** to do work that a **body** possesses as a result of its position), then

$$f(r) = -\nabla \phi(r)$$

- Notice that:
  - f is a vector
  - ϕ is a scalar
  - ∇ is the gradient, defined as the vector whose components are the partial derivatives of the function (and represents the direction and rate of fastest increase)

Models

- For example, if

$$\phi(r) = \|r\|^2 \text{ where } r = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

- then the three components of the force are

$$f_x = -\frac{\partial \phi}{\partial x} = -2x \quad f_y = -\frac{\partial \phi}{\partial y} = -2y \quad f_z = -\frac{\partial \phi}{\partial z} = -2z$$

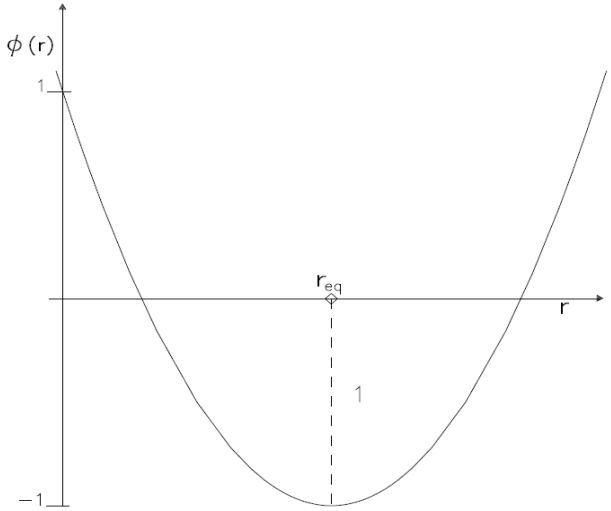
- Since potential energy is a scalar quantity, it is often more convenient to describe the model in terms of its potential energy function ϕ
- At a point of minimum potential energy, the partial derivatives of the potential energy are zero, and thus it is a point at which all of the forces are zero: **equilibrium point**

Models

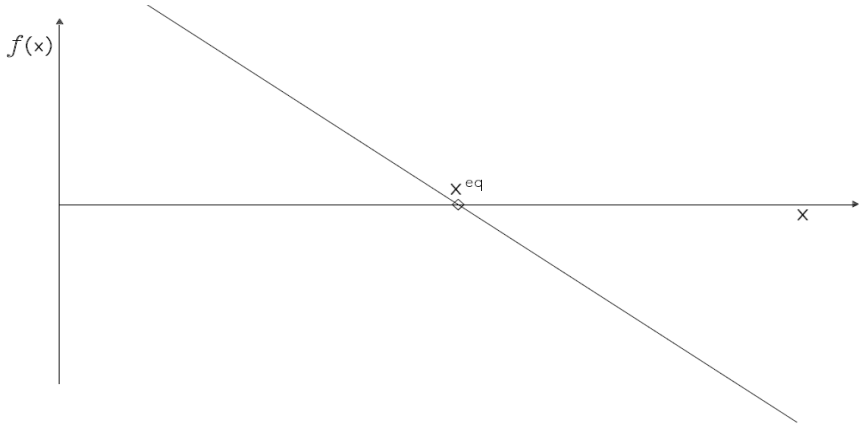
- We now consider three models, referred to as the Hooke's law model, HL for short, the Lennard-Jones model, LJ for short, and the hard sphere model, HS for short.
- The **LJ model** comes closest to representing real molecular systems, but presents the most diffcult computational challenge
- The **HL model** is an approximation to the LJ model when the particles have *low kinetic energy*, thus remaining close to their equilibrium positions
- The **HS model** is an approximation to the LJ model when the particles have *high kinetic energy*, or when attractive forces are very weak.

Hooke's Law model

- **Case 1D – 1 particle**



Potential energy in a 1D system



Force in a 1D system

- In the HL model
  - the **potential energy** of a particle is proportional to the square of its displacement from its equilibrium position
  - the **force** is proportional to the displacement of the particle from its equilibrium position and it is directed towards the equilibrium position

Hooke's Law model

- The equations for the potential energy, and force are:

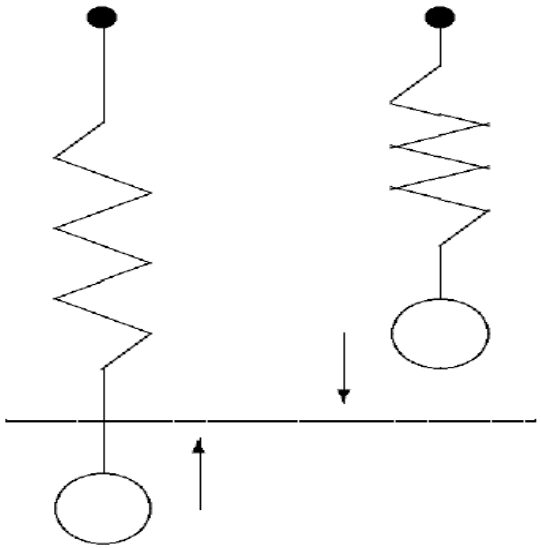
$$\phi(x) = \frac{k}{2}(x - x^{eq})^2 + \phi^{min}$$

$$f(x) = -k(x - x^{eq})$$

- where
  - k is a constant, sometimes referred to as the **force constant**
  - ϕ^{min} is a constant, the minimum potential energy
  - x^{eq} is the equilibrium position of the particle
- Notice that $f(x) = -\frac{d\phi(x)}{dx}$

Hooke's Law model

- The most familiar example of a system subject to a HL force is a small mass suspended by a spring
- It moves up and down under the influence of a HL force imposed by the spring



Hooke's Law model

- **Case 2D – 1 particles**

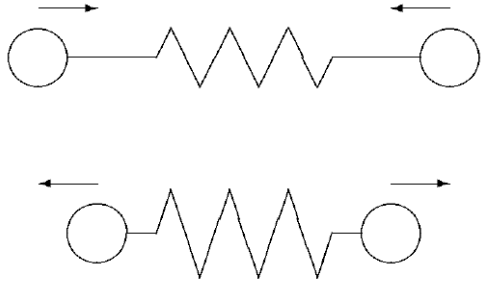
- In two dimensions this model is described by

$$\phi(x,y) = \frac{k}{2}((x - x^{eq})^2 + (y - y^{eq})^2) + \phi^{min}$$

which we may write more compactly as

$$\phi(r) = \frac{k}{2}\|r - r^{eq}\|^2 + \phi^{min}$$

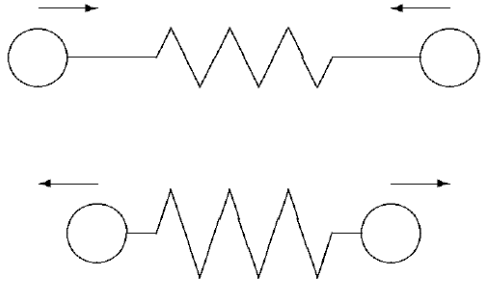
Hooke's Law model



- **Case 1D – 2 particles**

- We now consider the case of HL models for systems of more than one particle, starting with the 2-particle case
- Think of a physical system of two masses connected by a spring
- The force of the spring acts along a line joining the particles that we take to be the x axis
- When the **distance** between the particles is:
  - d the spring is neither stretched or compressed, so the system is in equilibrium
  - Less than d the spring is compressed and the force acts to drive the particles apart
  - Greater than d the spring is stretched and the force acts to bring the particles closer together

Hooke's Law model



- **Case 1D – 2 particles**

- The potential energy function

$$\phi(x_1, x_2) = \frac{k}{2}(x_1 - x_2 + d)^2 + \phi^{min}$$

- The forces can be obtained by taking the appropriate derivatives of the potential energy giving

$$f_1(x_1, x_2) = -k\,(x_1 - x_2 + d)$$
$$f_2(x_1, x_2) = k\,(x_1 - x_2 + d)$$

Hooke's Law model

- **Case 1D – 4 particles**

- The potential energy function

$$\phi(x_1, x_2, x_3, x_4) = \frac{k}{2}((x_1 - x_2 + d)^2 + (x_2 - x_3 + d)^2 + (x_3 - x_4 + d)^2) + \phi^{min}$$

- This system is in equilibrium when the particles are each a distance d from its neighbors.
- The forces are

$$f_1(x_1, x_2) = -k\,(x_1 - x_2 + d)$$
$$f_2(x_1, x_2, x_3) = -k\,(2x_2 - x_1 - x_3)$$
$$f_3(x_2, x_3, x_4) = -k\,(2x_3 - x_2 - x_4)$$
$$f_4(x_3, x_4) = -k\,(x_4 - x_3 - d)$$

- Extension of these equations to n-particle systems is easy

Hooke's Law model

- **Case 1D – 4 particles**

- The equations are simplified if we fix the equilibrium position of the first particle in the origin and we define new variables q_i as follows:

$$x_i = (i-1)d + q_i$$

- Thus, q_i denotes the displacement from the equilibrium position
- In the new variables the potential energy is:

$$\phi(q_1, q_2, q_3, q_4) = \frac{k}{2}((q_1 - q_2)^2 + (q_2 - q_3)^2 + (q_3 - q_4)^2) + \phi^{min}$$

- and the forces are

$$f_1(q_1, q_2) = -k\,(q_1 - q_2)$$
$$f_2(q_1, q_2, q_3) = -k\,(2q_2 - q_1 - q_3)$$
$$f_3(q_2, q_3, q_4) = -k\,(2q_3 - q_2 - q_4)$$
$$f_4(q_3, q_4) = -k\,(q_4 - q_3)$$

Lennard-Jones Model

- We consider a three-dimensional system

- The **potential energy function** for a pair of particles, 1 and 2, in the LJ model is given by:

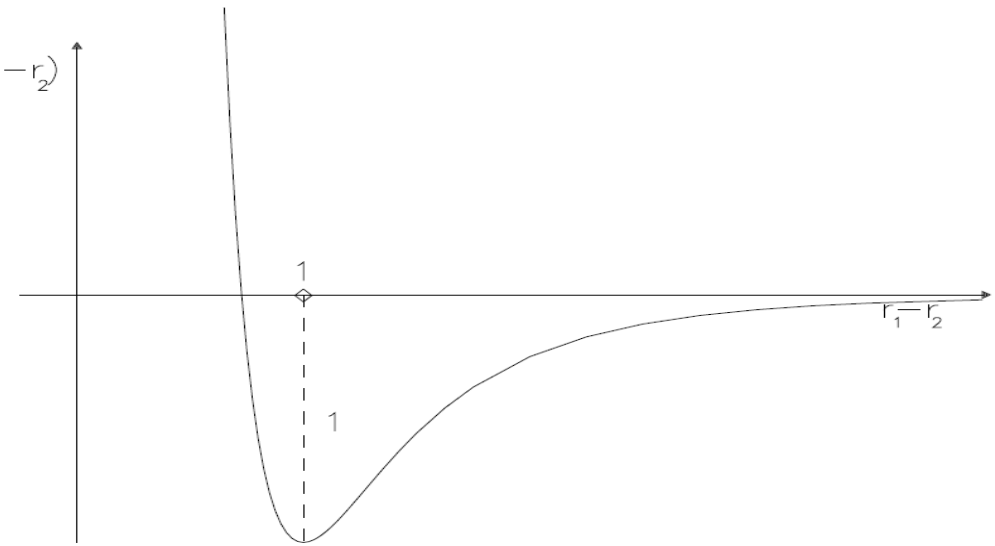
$$\phi(r_1, r_2) = \left(\frac{1}{\|r_1 - r_2\|^{12}} - \frac{1}{\|r_1 - r_2\|^{6}} \right)$$

- The units have been chosen to locate the minimum of the potential energy at $\|r_1 - r_2\| = 1$, and the value of the minimum equal to 1

Lennard-Jones Model

- In the expression of the potential energy function

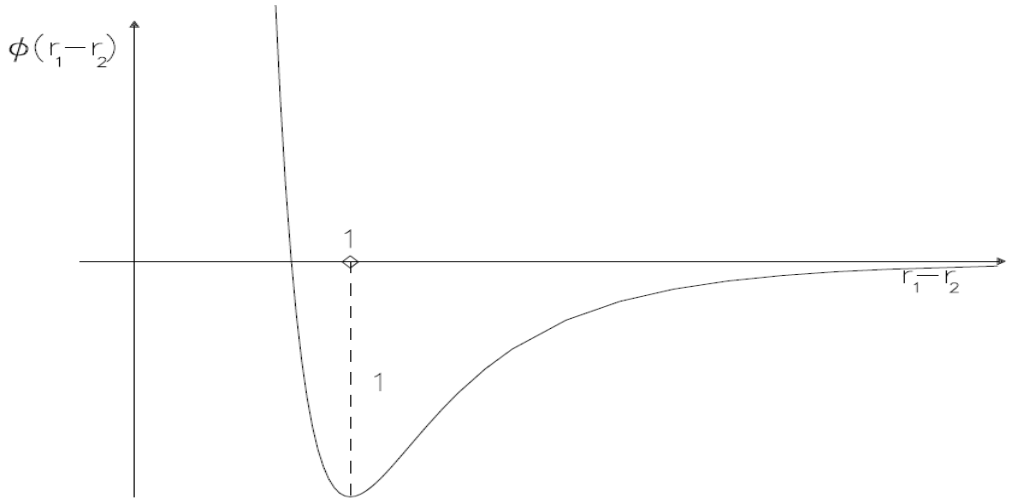
$$\phi(r_1, r_2) = \left(\frac{1}{\|r_1 - r_2\|^{12}} - \frac{1}{\|r_1 - r_2\|^{6}} \right)$$



  - the first term is the **repulsive contribution** of forces at short distance
  - the second term is the **attractive contribution** of Van der Waals forces for large distance

Lennard-Jones Model

- Considering the slope of this function we see that the force:
  - is strongly repulsive at small distances
  - is attractive at large distances
  - becomes extremely weak at very large distances
- The crossover between the repulsive region and the attractive region occurs where $\|r_1 - r_2\| = 1$, the point of minimum potential energy, where the force is zero since the derivative of ϕ is zero



Lennard-Jones Model

- The forces on particle 1 can be determined as

$$f_{1x} = 12\left(\frac{1}{\|r_1 - r_2\|^{14}} - \frac{1}{\|r_1 - r_2\|^{8}}\right)(x_1 - x_2)$$

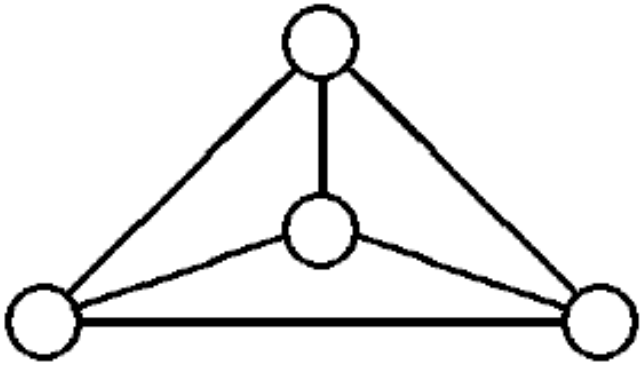
$$f_{1y} = 12\left(\frac{1}{\|r_1 - r_2\|^{14}} - \frac{1}{\|r_1 - r_2\|^{8}}\right)(y_1 - y_2)$$

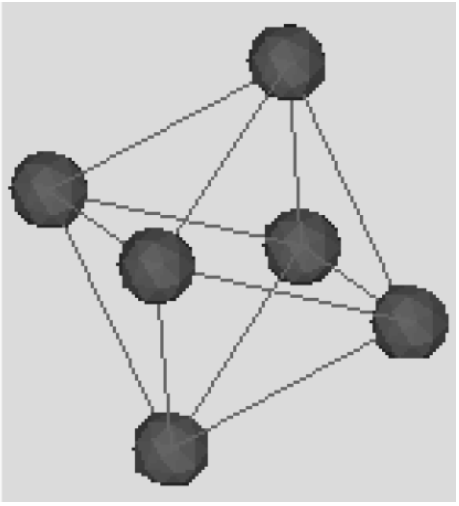
$$f_{1z} = 12\left(\frac{1}{\|r_1 - r_2\|^{14}} - \frac{1}{\|r_1 - r_2\|^{8}}\right)(z_1 - z_2)$$

- In a many-particle LJ system the force on each particle is determined by summing over the pairwise interactions, using the above formulas
- Since the force between widely separated pairs is very weak it is sometimes neglected: a cutoff distance is chosen, and the force between those particles is ignored

Lennard-Jones Model

- The equilibrium configuration is not easily determined
- If there are only four particles, then the particles are at the corners at the corners of a regular tetrahedron
- In the case of six particles, we have an octahedron





Hard sphere Model

- This model is best visualized as a collection of hard, perfectly elastic, balls - like billiard balls
- The interactions between particles are like collisions between these balls
- Two-dimensional and one-dimensional versions of this model, as well as the three-dimensional model, are studied: in two dimensions it is called the hard disk model
- The potential energy for a pair of particles is

$$\phi(r_1, r_2) = \begin{cases} 0 & \|r_1 - r_2\| > \sigma \\ \infty & \|r_1 - r_2\| \leq \sigma \end{cases}$$

Hard sphere Model

- Thus there is no force acting on the particles except at the instant when they are a distance apart
- At that point an instantaneous force is applied, causing a change in velocities
- We can think of the collision as if it were between two billiard balls of radius σ

$$\phi(r_1, r_2) = \begin{cases} 0 & \|r_1 - r_2\| > \sigma \\ \infty & \|r_1 - r_2\| \leq \sigma \end{cases}$$

Hard sphere Model

- The HS model can be viewed as an approximation to the LJ model with high-velocity particles
  - When particles in the LJ model are moving at high velocities the effect of the attractive force is quite small
  - The particles move at high speed in (approximately) straight lines until they get close enough for the repulsive force to come into play, at which time they collide as in the hard sphere model
  - The repulsive force rises so steeply in the LJ model it has almost the same effect as a collision between hard spheres of diameter slightly less than 1

EQUATIONS OF MOTION

Equations of motion

- Newton's second law gives us the equation for the motion of a particle: $ma = f$
  - where m is the particle's mass, a its acceleration, and f is the force acting on it
- From this equation and a knowledge of the initial position and the initial velocity of the particle we can, in principle, determine its position and velocity at future times
- In a system of interacting particles their motion is determined by solving one equations for each particle
- The equations are interdependent because the force on a particle is a function of the position of other particles
- Now we look at the form of these equations for the different models, then we will look at the solution of these equations

One-dimensional systems

- The equations of motion for a 1-dimensional system of two interacting particles are:

$$m_1\ddot{x}_1 = f_1$$
$$m_2\ddot{x}_2 = f_2$$

where the acceleration is represented by $\ddot{x}$ that is

$$\ddot{x}_i = \frac{d^2x_i}{dt^2}$$

- We assume that all particles have the same mass:

$$m = m_1 = m_2$$

- The equation of motion $m\ddot{x} = f$ can be written more compactly in matrix form as

$$m\begin{bmatrix}\ddot{x}_1\\ \ddot{x}_2\end{bmatrix} = \begin{bmatrix}f_1\\ f_2\end{bmatrix}$$

One-dimensional systems

- We could express the equations of motion for a system of n particles by exactly the same simple equation, with $\ddot{x}$ denoting a vector of n accelerations, and f (x) denoting a vector of n forces
- For example, the explicit matrix equation of a four-particle system is

$$m\begin{bmatrix}\ddot{x}_1\\ \ddot{x}_2\\ \ddot{x}_3\\ \ddot{x}_4\end{bmatrix}=\begin{bmatrix}f_1\\ f_2\\ f_3\\ f_4\end{bmatrix}$$

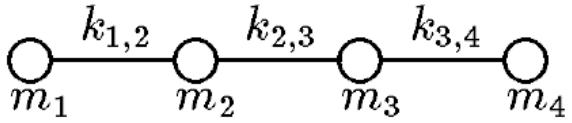
One-dimensional systems

- The equations of motion for four particles in the HL model are

$$m\ddot{q}_1 = -k\,(q_1 - q_2)$$
$$m\ddot{q}_2 = -k\,(2q_2 - q_1 - q_3)$$
$$m\ddot{q}_3 = -k\,(2q_3 - q_2 - q_4)$$
$$m\ddot{q}_4 = -k\,(q_4 - q_3)$$

- We assumed that the particles are identical so that a common force constant, and common masses are used throughout

- The equations of motion for a non-homogeneous HL model consisting of four particles with unequal masses, and unequal force are (slightly) different



One-dimensional systems

- The equations of motion for two particles with LJ forces, acting in just one dimension are

$$m\ddot{x}_1 = 12\left(\frac{1}{(x_1 - x_2)^{13}} - \frac{1}{(x_1 - x_2)^{7}}\right)$$

$$m\ddot{x}_2 = 12\left(\frac{1}{(x_2 - x_1)^{13}} - \frac{1}{(x_2 - x_1)^{7}}\right)$$

One-dimensional systems

- In a 4-particle system with LJ forces

$$m\ddot{x}_1 = 12 \sum_{j=2}^{4} \left(\frac{1}{(x_1 - x_j)^{13}} - \frac{1}{(x_1 - x_j)^{7}} \right)$$

$$m\ddot{x}_2 = 12 \sum_{j=1, j\neq 2}^{4} \left(\frac{1}{(x_2 - x_j)^{13}} - \frac{1}{(x_2 - x_j)^{7}} \right)$$

$$m\ddot{x}_3 = 12 \sum_{j=1, j\neq 3}^{4} \left(\frac{1}{(x_3 - x_j)^{13}} - \frac{1}{(x_3 - x_j)^{7}} \right)$$

$$m\ddot{x}_4 = 12 \sum_{j=1}^{3} \left(\frac{1}{(x_4 - x_j)^{13}} - \frac{1}{(x_4 - x_j)^{7}} \right)$$

One-dimensional systems

- The equations of motion for the HS model must be expressed a little differently

$$x_1 = x_1^{(0)} + \dot{x}_1^{(0)}\left(t - t^{(0)}\right)$$
$$x_2 = x_2^{(0)} + \dot{x}_2^{(0)}\left(t - t^{(0)}\right)$$

- where $x_i^{(0)}$ denotes position at time $t^{(0)}$, and the velocities, $\dot{x}_i^{(0)}$ are the velocities at time $t^{(0)}$
- If the particles are moving towards each other collide at some time, say $t^{(1)}$
- At this instant they change their velocities and the new positions are given by

$$x_1 = x_1^{(1)} + \dot{x}_1^{(1)}\left(t - t^{(1)}\right)$$
$$x_2 = x_2^{(1)} + \dot{x}_2^{(1)}\left(t - t^{(1)}\right)$$

One-dimensional systems

- Solving the equations of motion in this case amounts to:
  - determining the time of the next collision
  - moving the particles to their positions at that time
  - then determining the new velocities of the colliding particles
- This process is repeated over and over

- Thus we compute the motion from collision to collision

- If the particles are moving away from each other, then there is no collision

One-dimensional systems

- A 1-dimensional HS model where particles move away from each other is not very interesting because the particles gradually move farther and farther apart, going to $+\infty$ or $+\infty$

- But we can make it interesting if we put ***walls*** on left and right constraining the particles to remain in some interval
- When a particle hits the wall then we can assume it bounces back, i.e. reverses its velocity
- Or we can assume that the particles are conned to a circle, as if we joined left and right ends of an interval of the x axis (periodic boundary condition)

Two-dimensional systems

- We now assume

$$r = \begin{bmatrix} x \\ y \end{bmatrix}$$

- The position of the i-th particle is denoted r_i
- Then we can write the equations of motion for an n-particle system exactly as before, but with r in place of x

$$m\ddot{r} = f$$

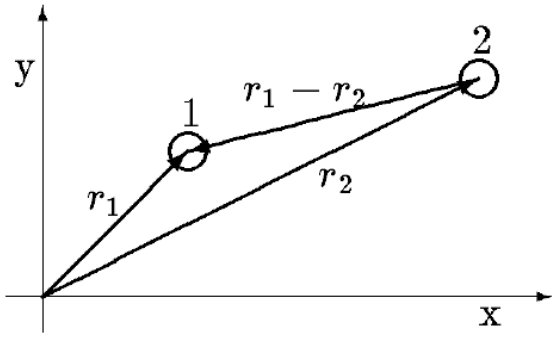
- Consider a 2-particle system with

$$r = \begin{bmatrix} r_1 \\ r_2 \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ y_1 \\ y_2 \end{bmatrix}$$

Two-dimensional systems

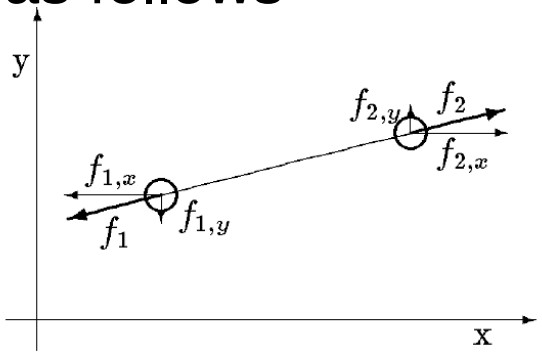
- Consider a 2-particle system with

$$r = \begin{bmatrix} r_1 \\ r_2 \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ y_1 \\ y_2 \end{bmatrix}$$



- Thus we can write the equations of motion as follows

$$m \begin{bmatrix} \ddot{x}_1 \\ \ddot{x}_2 \\ \ddot{y}_1 \\ \ddot{y}_2 \end{bmatrix} = \begin{bmatrix} f_{1x} \\ f_{1y} \\ f_{2x} \\ f_{2y} \end{bmatrix}$$



where $f_{i\,x}$ and $f_{i\,y}$ are the components of the force on particle i

- The forces are directed along the line through the centers of the two particles

Two-dimensional systems

- The equations of motion for a 2-particle HL model are

$$m\begin{bmatrix}\ddot{x}_1\\ \ddot{x}_2\\ \ddot{y}_1\\ \ddot{y}_2\end{bmatrix} = k\left(1-\frac{d}{\|r\|}\right)\begin{bmatrix}x_1-x_2\\ y_1-y_2\\ x_2-x_1\\ y_2-y_1\end{bmatrix}$$

- The equations of motion for a 2-particle LJ model are

$$m\begin{bmatrix}\ddot{x}_1\\ \ddot{x}_2\\ \ddot{y}_1\\ \ddot{y}_2\end{bmatrix} = 12\left(\frac{1}{\|r_1-r_2\|^{14}}-\frac{1}{\|r_1-r_2\|^{8}}\right)\begin{bmatrix}x_1-x_2\\ y_1-y_2\\ x_2-x_1\\ y_2-y_1\end{bmatrix}$$

Two-dimensional systems

- The equations of motion for a n-particle system have the same form, the only difference being that when $n > 2$, a pairwise sum over interactions must be made to determine f_{ix} and f_{iy}
- For example, for the LJ model

$$f_{ix} = 12 \sum_{\substack{j=1 \\ j \neq i}}^{n} \left(\frac{1}{\|r_i - r_j\|^{14}} - \frac{1}{\|r_i - r_j\|^{8}} \right) (x_i - x_j)$$

$$f_{iy} = 12 \sum_{\substack{j=1 \\ j \neq i}}^{n} \left(\frac{1}{\|r_i - r_j\|^{14}} - \frac{1}{\|r_i - r_j\|^{8}} \right) (y_i - y_j)$$

Two-dimensional systems

- The equations of motion for a 2-dimensional HS system are the obvious extension of the 1-dimensional equations

- We can write the equation for the i-th particle in vector form as

$$r_i = r_i^{(1)} + \dot{r}_i^{(1)}\left(t - t^{(1)}\right)$$

System Evolution

- The work of the computation is determining when the next collision will occur
- In 1-dimension only the particles on the left and right of a given particle are collision candidates, and only these particles remain candidates for the entire calculation - that is in one dimension neighbors remain neighbors
- In 2-dimension systems, the number of possibilities we must examine is much larger
- We might consider every pair of particles
- To do better, we can divide space into bins of a certain size, so that the collision candidates for a given particle are the other particles in the same bin or in neighboring bins

Two-dimensional systems

- Alternatively, we can use a timetable of predicted collision times
  - For every particle we determine the time and partner for its next collision, assuming no other collisions take place
  - The entry with the earliest collision time in the timetable is the next collision
  - Once we process that collision, we need to update the timetable
  - The updating process involves looking for a new collision partner for each of the two particles that just collided
  - When those collision partners have been found some other entries in the timetable may need to be updated, any that had one member of the colliding pair as a collision partner must be updated
- For 3-dimensional systems the formulas and issues are the same as for the 2-dimensional systems adding the z component