Lecture Notes: Molecular Dynamics Simulations

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1 Introduction

Molecular simulations has become an indispensable tool in developing our understanding of various systems ranging from simple monoatomic fluids to more complex fluids made up of polymers, surfactants and proteins. From the early Monte Carlo¹ and molecular dynamics² (MD) simulations of hard sphere systems and later on soft sphere fluids,^{3,4} simulation techniques have advanced significantly, and today a variety of techniques are available for evaluating thermodynamic, structural and dynamical properties. A number of standard textbooks cover this vast subject.^{5, 6, 7, 8, 9} Figure 1 illustrates the regime of length and time scales probed using classical molecular dynamics simulations which is the subject of this lecture. In this regime, the length scales range from 1-10 nm $(10^{-9}m)$ and time scales are typically in the ns $(10^{-9}s)$ regime. Classsical molecular dynamics lies between quantum simulations and systems that are mesoscopic in nature. In the mesoscale regime one is interested in probing systems on the time scale of a few μ s and length scales of 10 - 1000 nm. These systems include the structure and dynamics of phases with complex microstructure that form in oil-water-surfactant systems and dynamics of colloidal suspensions. These systems are important in detergency, wetting and biological processes at the level of the cell membrane. Several coarse grained methods are used to study system properties at the mesoscale. Coarse grained molecular dynamics, Brownian dynamics, dissipative particle dynamics and lattice Boltzmann methods are a few of the currently used methods. Ideally one would be interested in using information from smaller length and



Figure 1: Schematic representation of the various simulation methods and the corresponding length and time scales typically accessible to each method. Confined fluids, self assembled monolayers, the bilayer phase and flow past a sphere are representative of the systems discussed in this review. Quantum methods include density functional, ab inito and Carr-Parinello molecular dynamics. Atomisitic methods include molecular dynamics and Monte Carlo simulations. Mesoscale methods include coarse grained molecular dynamics, dissipative particle dynamics, Brownian dynamics and Lattice Boltzmann simulations. Continuum methods involve solution of heat, mass and momentum transport equations using a variety of numerical methods such as finite element and finite difference methods. Methods such as coarse grained molecular dynamics include the overlap region between atomistic and mesoscale simulations, while dissipative particle dynamics and Lattice Boltzmann methods include the overlap between mescoscale and continuum regimes.

time scales to carry out mesoscale simulations whereby the mesoscale model incorporates the required microscopic features of the system. This is currently an active area of research.

2 Molecular Dynamics of Soft Spheres

Consider a collection of N interacting particles. The objective of a molecular dynamics simulation is to describe the time evolution of the particle positions $\mathbf{r}_i(t)$, $i = 1 \dots N$ and momenta $\mathbf{p}_i(t)$, $i = 1 \dots N$. The primary input into the simulation is the specific form of the interparticle interaction potential which governs the dynamics of the particles. Molecular dynamics simulations are performed on broadly two classes of systems; hard sphere and soft spheres. We restrict our attention to simulations of soft spheres. Assuming that the particles can be treated classically, the particle dynamics are governed by Newton's Second Law of motion,

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i \qquad i = 1, \dots, N \tag{1}$$

where m_i is the mass of particle *i* and \mathbf{F}_i is the force acting on the *i*th particle. Eq. 1 which is in vector form represents a set of 3N coupled second order differential equations which are solved numerically to obtain the positions and momenta of the particles. In a collection of N particles the force,

$$\mathbf{F}_{i} = \sum_{j \neq i}^{N} \mathbf{f}_{ij} \tag{2}$$

is obtained by summing the forces acting on particle *i* from all other particles *j* in the system, where \mathbf{f}_{ij} is the force between two particles *i* and *j*.

Eq. 1 can also be obtained from the Lagrange equations of motion. This is a useful starting point as it provides a more general framework for deriving equations of motion for systems of particles evolving under constraints or while carrying out molecular dynamics simulations in ensembles such as the isothermal isobaric ensemble (NPT) or the canonical ensemble (NVT) where an appropriate Lagrangian is the starting point. The Lagrangian,

$$L(x_1, y_1, z_1, \dots, \dot{x}_N, \dot{y}_N, \dot{z}_N) = K(\dot{x}_1, \dot{y}_1, \dot{z}_1 \dots \dot{x}_N, \dot{y}_N, \dot{z}_N) - U(x_1, y_1, z_1, \dots, x_N, y_N, z_N)$$
(3)

where K is the kinetic energy which is only a function of the particle velocities $(\dot{x}_i, \dot{y}_i, \dot{z}_i)$ and U is the total potential energy of the collection of N particles, is only a function of the particle positions (x_i, y_i, z_i) . In Eq. 3 dots represent time derivatives and the subscript denotes the particle index. If m_i is the mass of the *i*th particle the Lagrangian,

$$L = \frac{1}{2} \sum_{i=1}^{N} m_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) - U(x_1, y_1, z_1, \dots, x_N, y_N, z_N)$$
(4)

The Lagrange equations of motion are,

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}_i}\right) - \frac{\partial L}{\partial x_i} = 0 \qquad i = 1, \dots, N$$
(5)

Substituting Eq. 4 into Eq. 5 and simplifying we obtain the following scalar forms of the equations of motion,

$$m_{i}\frac{d^{2}x_{i}}{dt^{2}} = -\frac{\partial U}{\partial x_{i}} = F_{i}^{x}$$

$$m_{i}\frac{d^{2}y_{i}}{dt^{2}} = -\frac{\partial U}{\partial y_{i}} = F_{i}^{y}$$

$$m_{i}\frac{d^{2}z_{i}}{dt^{2}} = -\frac{\partial U}{\partial z_{i}} = F_{i}^{z}$$

$$i = 1, \dots, N$$
(6)

In a molecular dynamics simulation, the above set of 3N scalar equations are solved using an appropriate numerical integration procedure. In vector notation Eqs. 6 reduces to Eq. 1.

Molecular dynamics simulations for a fixed number of particles (N) in a volume (V) with a conservative force field, yields trajectories in a Microcanonical ensemble (NVE), as the total Hamiltonian (kinetic + potential) is a constant of the equations of motion. This is true for systems that have a well defined equilibrium state in the absence of friction or other dissipative or random forces. Additionally in the absence of external forces the momentum is also a conserved quantity for particles interacting via pairwise additive forces.

2.1 Interaction Potentials and Forces

We will be mostly interested in particles that interact with pairwise additive interactions as two body potentials have been extensively used to study the phase behaviour and transport properties of a wide variety of fluids. Perhaps the most widely used two body interaction potential in molecular simulations is the two parameter 12-6 Lennard-Jones potential,

$$u(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \tag{7}$$

where ϵ_{ij} is the interaction energy between particles *i* and *j*, σ_{ij} is the atomic diameter and r_{ij} is the scalar distance between particles *i* and *j*. The first term in the Lennard-Jones potential is soft repulsive and the second term is the dispersion interaction which is attractive. The dispersion interaction arises due to fluctuating dipoles that are set up between otherwise neutral entities. The dispersion interaction is quantum mechanical in origin and the $(1/r)^6$ dependence is an exact result. The repulsive $(1/r)^{12}$ is empirical in nature. The total internal energy for a system of pairwise additive interacting particles is,

$$U = \sum_{i=1}^{N-1} \sum_{j>i} u(r_{ij}).$$
(8)

Note that the sum in Eq. 8 consists of N(N-1)/2 terms.

Now let us consider the term involving the force acting on particle i in the x direction. From Eq. 6,

$$F_{i}^{x} = -\frac{\partial U(x_{1}, y_{1}, z_{1}, \dots, x_{N}, y_{N}, z_{N})}{\partial x_{i}})$$

$$= -\frac{\partial}{\partial x_{i}} \sum_{i=1}^{N-1} \sum_{j>i}^{N} u(r_{ij})$$

$$= -\sum_{i=1}^{N-1} \sum_{j>i}^{N} \frac{\partial u(r_{ij})}{\partial x_{i}}$$

$$= \sum_{i=1}^{N-1} \sum_{j>i}^{N} f_{ij}^{x}$$
(9)

where

$$f_{ij}^x = -\frac{\partial u(r_{ij})}{\partial x_i} \tag{10}$$

is the force in the x direction on particle i due to particle j and F_i^x given in Eq. 9 is the total force acting on particle i in the x direction due to the other N - 1 particles in the system. In

vector form,

$$\mathbf{f}_{ij} = -\nabla_{i}u(r_{ij})$$

$$= -\left[\mathbf{e}_{x}\frac{\partial u(r_{ij})}{\partial x_{i}} + \mathbf{e}_{y}\frac{\partial u(r_{ij})}{\partial y_{i}} + \mathbf{e}_{z}\frac{\partial u(r_{ij})}{\partial z_{i}}\right]$$

$$= -\left[\mathbf{e}_{x}\frac{du}{dr_{ij}}\frac{\partial r_{ij}}{\partial x_{i}} + \mathbf{e}_{y}\frac{du}{dr_{ij}}\frac{\partial r_{ij}}{\partial y_{i}} + \mathbf{e}_{z}\frac{du}{dr_{ij}}\frac{\partial r_{ij}}{\partial z_{i}}\right]$$
(11)

The last line is obtained using the chain rule for differentiation. Since the scalar distance,

$$r_{ij} = \sqrt{(x_i - y_i)^2 + (y_i - y_j)^2 + (z_i - z_j)^2}$$
(12)

then,

$$\frac{\partial r_{ij}}{\partial x_i} = \frac{x_i - x_j}{r_{ij}}, \qquad \frac{\partial r_{ij}}{\partial y_i} = \frac{y_i - y_j}{r_{ij}}, \qquad \frac{\partial r_{ij}}{\partial z_i} = \frac{z_i - z_j}{r_{ij}}$$
(13)

Substituting Eqs. 13 in Eq. 11,

$$\mathbf{f}_{ij} = -\frac{du}{dr_{ij}} \frac{\mathbf{r}_{ij}}{r_{ij}},\tag{14}$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j = \mathbf{e}_x(x_i - x_j) + \mathbf{e}_y(y_i - y_j) + \mathbf{e}_z(z_i - z_j)$. The vector positions \mathbf{r}_i and \mathbf{r}_j are illustrated for a two particle system in Fig. 2.

If the functional form of the interparticle potential is known then the derivative in Eq. 14 can be evaluated. For the 12-6 Lennard-Jones interaction,

$$\frac{du}{dr_{ij}} = \frac{-24\epsilon_{ij}}{r_{ij}} \left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 \right]$$
(15)

Substituting Eq. 15 into Eq. 11 the force,

$$\mathbf{f}_{ij} = \frac{24\epsilon_{ij}}{r_{ij}^2} \left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 \right] \mathbf{r}_{ij}$$
(16)

and in scalar form, the force in the x direction is,

$$f_{ij}^{x} = \frac{24\epsilon_{ij}}{r_{ij}^{2}} \left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6} \right] (x_{i} - x_{j})$$
(17)

Similar equations follow for the y and z components of the force. The force $\mathbf{f}_{ji} = -\mathbf{f}_{ij}$ follows from Newton's Third Law. In the above derivation the forces are assumed to be centrally symmetric, i.e. the forces act only along the line of centers, \mathbf{r}_{ij} and are dependent only on the distance r_{ij} .



Figure 2: Schematic representation of vector positions for two particles i and j illustrating the direction of the force along the vector \mathbf{r}_{ij} .

3 Dimensionless Quantities

While carrying out simulations it is useful to express various quantities in suitable reduced units. Consider a set of indentical particles of mass m, interacting via a 12-6 Lennard-Jones potential with parameters ϵ and σ . Using the following reduced units (indicated by a *)

$$t^* = t\sqrt{\frac{\epsilon}{m\sigma^2}} \qquad \mathbf{r}^* = \frac{\mathbf{r}}{\sigma} \qquad \mathbf{F}^* = \frac{\mathbf{F}\sigma}{\epsilon},$$
 (18)

Newton's Second Law (Eq. 1) reduces to

$$\frac{d^2 \mathbf{r}_i^*}{dt^{*2}} = \mathbf{F}_i^* \qquad i = 1, \dots, N$$
(19)

In reduced units the accelerations are equal to the forces. In component form,

$$\frac{d^{2}x_{i}^{*}}{dt^{*2}} = F_{xi}^{*}$$

$$\frac{d^{2}y_{i}^{*}}{dt^{*2}} = F_{yi}^{*}$$

$$\frac{d^{2}z_{i}^{*}}{dt^{*2}} = F_{zi}^{*}$$
(20)

$$i = 1, \dots N \tag{21}$$

Other quantities that are evaluated in an MD simulation are the kinetic energy,

$$K = \frac{m}{2} \sum_{i=1}^{N} (v_{xi}^2 + v_{yi}^2 + v_{zi}^2)$$
(22)

In reduced units,

$$K^* = \frac{1}{2} \sum_{i=1}^{N} (v_{xi}^{*2} + v_{yi}^{*2} + v_{zi}^{*2})$$
(23)

where

$$K^* = \frac{K}{\epsilon}, \qquad v^* = v\sqrt{\frac{m}{\epsilon}}$$
 (24)

For spherical particles, the kinetic temperature is evaluated from the equipartition theorem which relates the kinetic energy to the temperature, T,

$$K = \frac{3}{2}NkT \tag{25}$$

where k is the Boltzmann constant. Defining a reduced temperature, $T^* = kT/\epsilon$

$$T^* = \frac{1}{3N} \sum_{i=1}^{N} \left(v_{xi}^{*2} + v_{yi}^{*2} + v_{zi}^{*2} \right)$$
(26)

The total linear momentum of the collection of paricles is

$$M = m \sum_{i=1}^{N} (v_{xi} + v_{yi} + v_{zi})$$
(27)

which in reduced units is,

$$M^* = \sum_{i=1}^{N} (v_{xi}^* + v_{yi}^* + v_{zi}^*)$$
(28)

4 Integrating the Equations of Motion

The equations of motion make up an initial value problem and consist of a set of coupled second order ordinary differential equations. Given the positions and velocities at t = 0 the the positions and velocities at a later time t can be obtained using a suitable algorithm. These algorithms are based on Taylor series expansions and the resulting finite difference forms. The two most popular methods are the Verlet algorithm and the Velocity Verlet algorithm. In what follows we will assume that the quantities are in reduced units and the 'stars' are henceforth omitted. Note that in reduced units, the accelerations are equal to the forces.

4.1 Verlet Algorithm

Forward and backward Taylor expansions about the position x(t) yields

$$x(t + \Delta t) = x(t) + \dot{x}(t)\Delta t + \ddot{x}(t)\frac{\Delta t^{2}}{2!} + \ddot{x}(t)\frac{\Delta t^{3}}{3!} + O(\Delta t)^{4}$$
(29)

and

$$x(t - \Delta t) = x(t) - \dot{x}(t)\Delta t + \ddot{x}(t)\frac{\Delta t^{2}}{2!} - \ddot{x}(t)\frac{\Delta t^{3}}{3!} + O(\Delta t)^{4}$$
(30)

respectively. Adding Eqs. 29 and 30,

$$x(t + \Delta t) = 2x(t) - x(t - \Delta t)\Delta t + \ddot{x}(t)\Delta t^{2} + O(\Delta t)^{4}$$
(31)

which is used to obtain the position $x(t + \Delta t)$ given the positions at t and $t - \Delta t$. Although the backward difference formula (Eq. 30) can be used to obtain $x(t - \Delta t)$ at the first time step, $x(t - \Delta t)$ can be set to x(t) for the first time step.

Once the positions have been obtained the velocities at time t,

$$v_x(t) = \frac{x(t + \Delta t) - x(t - \Delta t)}{2\Delta t},\tag{32}$$

are obtained using a central difference formula. The Verlet algorithm is popular both due to its simplicity and good energy conserving properties for moderate values of Δt . The local truncation order for the positions is of $O(\Delta t^3)$. The above equations have been derived for the positions and velocities of a given particle in the *x* direction. Similar equations hold for the other directions. Typical time steps, Δt , used in MD simulations are 1-2 fs (1 fs = 10^{-15} s).

4.2 Velocity Verlet Algorithm

In the Verlet algorithm the velocities are evaluated only from the positions and do not inolve the forces. The Velocity Verlet algorithm overcomes this drawback. In the Velocity Verlet algorithm the positions and velocities are updated using,

$$x(t + \Delta t) = x(t) + \dot{x}(t)\Delta t + \dot{x}(t)\frac{\Delta t^2}{2!}$$
(33)

and

$$v_x(t + \Delta t) = v_x(t) + \frac{1}{2}\Delta t[\ddot{x}(t) + \ddot{x}(t + \Delta t)]$$
(34)

The equation for the positions is obtained from a forward difference Taylor expansion (Eq. 29). Unlike the verlet algorithm the velocities are obtained from the forces and current positions. In order to obtain the expression for the velocities we proceed in the following manner. Taylor expansions for the velocity and accelerations are

$$v_x(t + \Delta t) = v_x(t) + \dot{v}_x(t)\Delta t + \ddot{v}_x(t)\frac{\Delta t^2}{2!} + \dots$$
(35)

$$\dot{v}_x(t+\Delta t) = \dot{v}_x(t) + \ddot{v}_x(t)\Delta t + \ddot{v}_x(t)\frac{\Delta t^2}{2!} + \dots$$
(36)

From Eq. 36

$$\ddot{v}_x(t)\frac{\Delta t^2}{2!} = [\dot{v}_x(t+\Delta t) - \dot{v}_x(t)]\frac{\Delta t}{2} + O(\Delta t^3)$$
(37)

Eq. 34 is obtained by substituting Eq. 37 into Eq. 35 and simplifying.

An alternate derivation for the Velocity Verlet algorithm using the original Verlet equations is given below. From Eq. 32

$$v_x(t + \Delta t) = \frac{x(t + 2\Delta t) - x(t)}{2\Delta t}$$
(38)

From Eq. 31

$$x(t+2\Delta t) = 2x(t+\Delta t) - x(t) + \ddot{x}(t+\Delta t)(\Delta t)^2$$
(39)

Substituting Eq. 39 in Eq. 38 we obtain,

$$v_x(t + \Delta t) = \frac{2x(t + \Delta t) - 2x(t) + \ddot{x}(t + \Delta t)(\Delta t)^2}{2\Delta t}$$

$$\tag{40}$$

Substituting $x(t + \Delta t)$ from Eq. 31 into Eq. 40 and simplifying results in Eq. 34.

4.3 Setting up the Molecular Dynamics Simulation

Initial Velocities and Velocity Scaling

Simulations are carried out in a cubic simulation box of side L. The number of particles N is determined by the density at which the simulation is to be carried out. The initial positions can be randomnly assigned avoiding overlaps or for dense systems the initial configuration can also be constructed by assigning the co-ordinates to a lattice. Initial velocities can be assigned in different ways. The velocities can be assigned using a Maxwell-Boltzmann distribution⁵ or

by simply assigning velocities from a uniform distribution of random numbers⁹, $r_x, r_y, r_z \in [-1, 1]$. Hence the velocities of the particle are,

$$v_{xi} = r_x/r,$$
 $v_{yi} = r_y/r,$ $v_{zi} = r_z/r,$ for $i = 1, ... N$

where $r = \sqrt{(r_x^2 + r_y^2 + r_z^2)}$. The velocities can be scaled to obtain a desired temperature using the following method. If T_s is the set temperature and the current temperature of the system corresponding to velocities, $v_{xi}, v_{yi}, v_{zi}, i = 1, ..., N$, using Eq. 26 is T_c then the scaled velocities,

$$v'_{xi} = v_{xi}\sqrt{\frac{T_s}{T_c}}$$
 $v'_{xi} = v_{xi}\sqrt{\frac{T_s}{T_c}}$ $v'_{xi} = v_{xi}\sqrt{\frac{T_s}{T_c}}$ for $i = 1, \dots N$

It can easily be shown that the temperature computed from v' is T_s . During the equilibration phase of the MD simulation velocity scaling using the above procedure is followed to bring the velocities to a desired set temperature. During this velocity scaling phase, the total energy is not conserved and the trajectories must not be used to compute any properties. Once sufficient time has been given for equilibration, then velocity scaling is removed and the system follows NVE dynamics. The amount of time required for equilibration depends on the system being investigated as well as the initial configuration.

Initial Momentum

While carrying out molecular dynamics in the absence of external forces, the total linear momentum of the system is a conserved quantity and the net acceleration of the center of mass is zero. Since momentum is conserved a non-zero but constant center of mass momentum can also exist. Although the presence of a non-zero center of mass is allowed, it is customary to set the center of mass velocity to zero. This is important while computing other dynamical quantities such as the mean squared displacements or time correlation functions for evaluating transport coefficients. Given the velocities v_{xi} , v_{yi} , v_{zi} , i = 1, ..., N, of a given configuration, the linear momentum is given by Eq. 28. The scaled velocities which correspond to a zero linear

momentum are obtained by subtracting the net linear momentum in a given direction.

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