

N -Body Problem

I. Introduction

The N -body problem describes the motion of N distinct particles, acting upon one another by certain classical forces, given the initial masses, positions, and velocities of the particles. Although the 2-body problem can be solved analytically, the N -body problem for $N > 3$ has as of yet only been solved numerically.

A typical example of this is planetary motion—the planets influence one another via gravity, and are kept in a stable orbit via the opposing centripetal force. Tracking the motion of each of these bodies simply turns into a problem of re-evaluating the forces at each time step, and noting the relationship between force and momentum, $\vec{F} = \dot{\vec{p}}$, resulting in a shift of the position of the “particles” by a certain amount.

More specifically, the forces are evaluated via a potential, which is thus related to the motion of the particle, as per the relationship:

$$\nabla \vec{U} = -\vec{F} = -\dot{\vec{p}} = -m\ddot{\vec{r}}$$

An interesting N -body problem is the molecular dynamics (MD) simulation. This is a classical simulation, on the atomic or molecular scale of the motion of particles due to one another. Quantum mechanical effects are ignored on this scale due to two main approximations:

- That electrons move much quicker than nuclei and thus can be taken to move instantaneously (Born-Oppenheimer approximation)
- That nuclei, being much heavier than electrons, can be approximated as point particles that move according to Newtonian mechanics.

The potential in most MD simulations in macromolecular systems consists of bonded forces, of straight bond, angle, and dihedral terms, and of non-bonded forces including the Coulomb and Lennard-Jones potentials. Due to the balance of speed of MD simulations (as related to *ab initio* calculations) and accuracy (relative to coarse-grained calculations), MD simulations have been used for a wide variety of applications, from evaluating the surface and bulk properties of metal alloys, to minimizing proteins structures, to calculating fluid properties.

In this particular work, we simulate the bulk motion of water molecules at the atomic scale and compare calculated properties (such as density and dispersion coefficients and the radial distribution function) to experimental values.

II. Method

A. Potential

The potential used here is the CHARMM force-field potential:

$$\begin{aligned}
 U = & \sum_{\text{bonds}} k_b (b - b_0)^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + \sum_{\text{dihedrals}} k_\phi [1 + \cos(n\phi - \delta)] \\
 & + \sum_{\text{impropers}} k_\omega (\omega - \omega_0)^2 + \sum_{\text{nonbonded}} \epsilon \left[\left(\frac{R_{\min ij}}{r_{ij}} \right)^{12} - \left(\frac{R_{\min ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{\epsilon r_{ij}}
 \end{aligned}$$

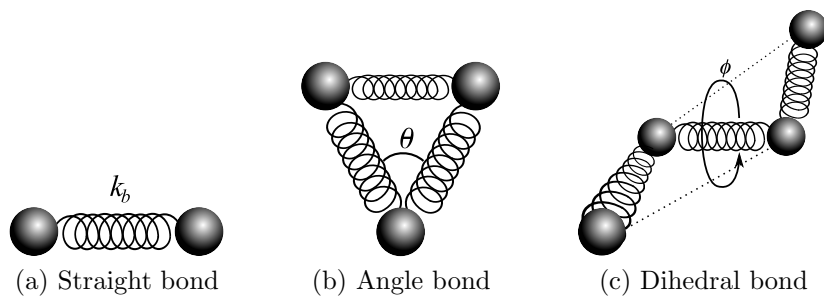
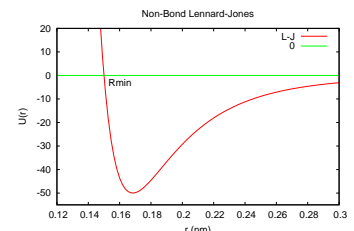


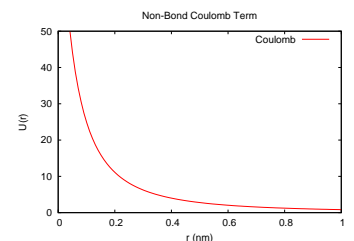
Figure 1: The bonded terms of the CHARMM force-field potential.

The first three terms describe the bonds between the atoms, using the harmonic approximation. The first term is a summation of spring-like potentials, summed over the set of particles, with spring constant k_b (see Fig. 1a), where b_0 is an equilibrium distance between the two atoms (bond length). The angle term describes an oscillation in the angle θ between three atoms, as in Fig. 1b, again, about an equilibrium angle θ_0 , with spring constant k_θ . The dihedral term is more complicated, involving four atoms. It describes the torsional motion of the atoms about the central bond. The angle is defined by the angle between the planes indicated by the dotted lines (see Fig. ??).

The last two terms describe the non-bondlike interactions. The first is the Lennard-Jones potential, which includes a repulsive and attractive term, where R_{\min} refers to the curve's zero-intersect (see Fig. 2a). This potential is formed from two distinct forces—the van der Waals force, which is attractive, and more potent at longer ranges, and the Pauli repulsion, which is repulsive, and works at short ranges. The van der Waals force is due to temporarily shifted electron clouds, which lead to small temporary dipoles within an atom or molecule with no permanent dipole moment. Pauli repulsion is a repulsion due to atoms coming too close to one another—due to the Pauli exclusion principle, the electrons cannot occupy the same quantum state, and this leads to a short-range repulsion. The final term, the Coulomb potential describes a force due to the charges of the atoms or molecules—if they are of the same sign, this force is repulsive, and if they are of different signs, the force is attractive.



(a) Lennard-Jones



(b) Coulomb

Figure 2: Non-bond terms.

In the atomic level of simulating water, the dihedral term is disregarded, as the structure of H_2O is as in Fig. 3. As indicated in the figure, $r_{\text{HH}} = 0.9572$ nm describes the straight bond between two H (shown by the dotted line), and the relatively minute spring constant $k_{\text{HH}} \approx 0$, in order to cut down on a large amount of computational time while still retaining decent accuracy. The bond between O and H (indicated by the thick line) is described by equilibrium bond length $r_{\text{OH}} = 1.5139$ nm and force constant $k_{\text{OH}} = 450 \frac{\text{kcal}}{\text{mol}\text{\AA}^2}$, while $k_{\theta} = 55.0$ gives the force constant affiliated with the angle bond, and the equilibrium angle in H_2O is 104.5° . The higher spring constant for the OH bond indicates that the bond is stiffer, or that it is less prone to deflecting from the equilibrium than the other bonds in the molecule.

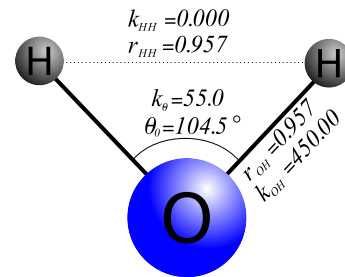


Figure 3: Water, where blue is oxygen (O), and gray is hydrogen (H).

In order to further cut down on computational power, the nonbond terms are not evaluated between every pair of atoms. Instead, atoms are only considered to interact if they are within a certain radius of one another. However, to mitigate an infinite force introduced by suddenly cutting off the potential, beyond a defined radius r_{switch} the potential is down-scaled, while beyond a defined radius $r_{\text{cut}} > r_{\text{switch}}$, the potential is cut off. Here we use $r_{\text{switch}} = 12\text{\AA}$ and $r_{\text{cut}} = 14\text{\AA}$.

Additionally, as we are simulating bulk water, we can simulate a cube of water and use Ewald summation to account for long-range forces, as those forces sum quickly in Fourier space. Thus, the summation of short-range forces can be truncated quickly in position-space, and long-range forces can be truncated quickly in Fourier-space to greatly reduce computational time with only a small loss in accuracy.

B. Simulation

We begin with a periodic lattice of water, with molecule distances set so that the resulting cube has the same density as water.

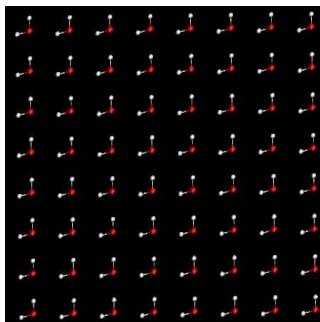


Figure 4: Initial water box before minimization.

As this periodic lattice does not look at all natural, the energy of the system is then minimized in order to mimic nature's tendency to achieve the lowest energy state. In order to achieve this quickly, Steepest descent is used as a first-order method, and Newton-Raphson is

used as a second-order technique. Steepest descent basically moves along the $-\nabla U$ direction. The algorithm is as follows:

1. Calculate the energy of the initial structure, via the potential described above
2. Calculate the energy for structures where each atom is shifted by (dx, dy, dz) .
3. Move the atoms to the positions where U decreases by the maximum possible amount
4. Iterate until a local minimum is found

The step size varies with iteration, and is determined by a linear search. Unfortunately, each step is at a right angle to the previous step, which leads to a slowly converging system, which is computationally simple per step. In order to thus augment it, Newton-Raphson method is used after several Steepest Descent iterations. Newton-Raphson simply takes an initial guess, evaluates the derivative of the function at that point, finds the zero intersect of the tangent line, and takes that zero as the next guess.

Following minimization, the actual meat of the simulation takes place. An initial temperature is assigned to the system, leading to initial velocities, via the Boltzmann distribution, which describes the distribution of speeds as:

$$P(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp \left[\frac{-mv^2}{2k_B T} \right]$$

where k_B is the Boltzmann constant, m is the mass of each molecule, and T is the temperature. Due to this intimate relationship between temperature and velocity, as well as randomization, the “true” temperature is evaluated at each timestep, following which the velocities of the molecules are adjusted to correct the temperature. The temperature is calculated via:

$$\langle \epsilon_{\text{kin}} \rangle = \left\langle \sum_{i=1}^N \frac{1}{2} m_i v_i^2 \right\rangle = \frac{3}{2} N k_B T(t)$$

and subsequently adjusted by scaling the velocities by $\left(\frac{T_{\text{ref}}}{T(t)} \right)^{1/2}$.

Let us consider what happens to atom i at each timestep. For every n timesteps, a list is generated for i containing the atoms that are within r_{cut} of i , and another list containing the atoms that are between r_{switch} and r_{cut} . At every time step, the potential between i and each of these atoms is evaluated, where the potential due to those between the switch and cut radii are scaled by a certain factor. The force is then evaluated, obtaining $\ddot{\vec{r}}$. The velocity is then found by taking $\dot{\vec{r}} dt \approx d\vec{r}$, and then the position similarly by $\vec{r} dt \approx \vec{r}$ (simply a Riemann sum). After all atoms have been thus treated, the temperature is adjusted. by scaling all the velocities as mentioned above.

To summarize:

Approximations

- Electrons move instantaneously
- Nuclei are point particles

- Bonds are described by harmonic terms
- Hydrogen atoms do not interact with one another.
- Bonds do not break
- Atoms which are a certain distance apart ($r_{\text{switch}} \leq r < r_{\text{cut}}$) interact more weakly, by a scaled amount, while atoms which are further apart ($r \geq r_{\text{cut}}$) do not interact at all
- Bulk water is periodic, so long-range terms can be summed using the Particle-mesh Ewald method.

Techniques

- Particle-mesh Ewald to evaluate long-range forces
- Steepest descent to minimize the energy of the system
- Newton-Raphson to finish minimizing the energy of the system
- Riemann sum to evaluate the change in position from the calculated acceleration

III. Results

After simulation, the water box was properly randomized, as seen in Fig. 5.

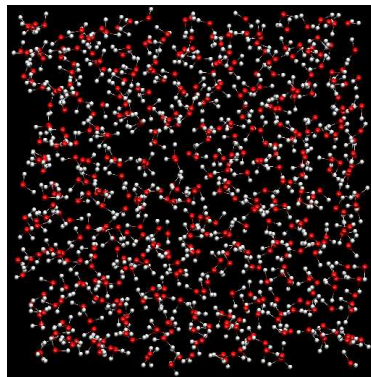


Figure 5: Water box after simulation, at 300 K.

At a final temperature of $T_f = 300.8$ K, a water box containing 512 water molecules was calculated to have the following properties:

- Volume: 15213 \AA^3
- Density: 1.006 g/cm^3
- Heat of vaporization: 10.37 kcal/mol
- Diffusion coefficient: $2.6 \times 10^{-5} \text{ cm}^2/\text{s}$

These values fit quite well with experimental values (values obtained from <http://www.lsbu.ac.uk/water/data.html>):

- Density: 1 g/cm^3
- Heat of vaporization: 10.76 kcal/mol
- Diffusion coefficient: $2.27 \times 10^{-5} \text{ cm}^2/\text{s}$

The thermodynamical quantities during the end of the simulation are given in Fig. 6, and the radial distribution function is shown in Fig. 7. The radial distribution function shows the variation of density of the substance with distance from an arbitrary particle. This was averaged over several different particles in order to obtain a less randomized curve.

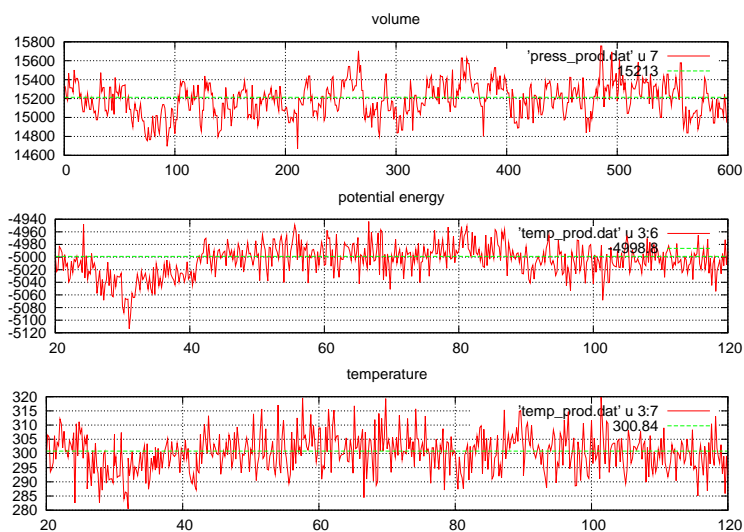


Figure 6: Thermodynamical quantities at the end of the simulation, graphing time (in $\text{ps}=10^{-12}\text{s}$) vs volume, potential energy, and temperature (from top to bottom).

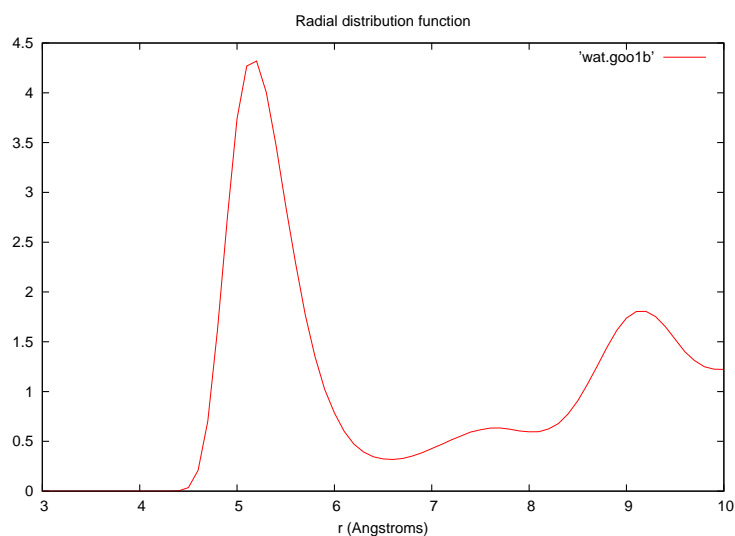


Figure 7: Radial distribution function $g(r)$