

# Scientific Computing II

## Molecular Dynamics

### Exercise 13: Pair Potentials and Forces

There are different potentials describing the interaction between two entities. Examples are the harmonic potential for two bodies which are connected by a spring or the gravitational potential for any pair of objects in our universe. For this exercise, you will need:

- Hard sphere potential:  $U_{HS}(r) = \begin{cases} \infty & \forall r \leq d \\ 0 & \forall r > d \end{cases}$
- Soft sphere potential:  $U_{SS}(r) = \epsilon \left(\frac{\sigma}{r}\right)^n$
- Van der Waals potential:  $U_W(r) = -4\epsilon \left(\frac{\sigma}{r}\right)^6$
- Lennard-Jones potential:  $U_{LJ}(r) = \alpha\epsilon \left(\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m\right)$

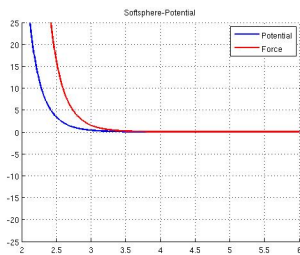
- (a) From the formula for the pair potential, the force which acts upon the two bodies can be derived. Calculate the force for the given potentials.
- (b) Draw an approximate graph of all potentials and forces.
- (c) Examine the calculated force functions and try to find qualitative differences between them. Consider especially the following properties:
  - attraction or repulsion
  - influence of the distance
  - usability on a computer

**Solution:**

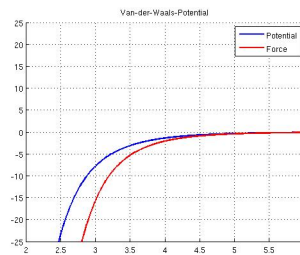
(a) Forces:

Name	potential	force	attractive(-) / repulsive(+)
Hard Sphere	$\infty \quad \forall r \leq d$ $0 \quad \forall r > d$	$0 \quad r \neq d$ $\infty \quad r = d$	+
Soft Sphere	$\epsilon \cdot \left(\frac{\sigma}{r}\right)^n$	$\frac{n \cdot \epsilon}{r} \cdot \left(\frac{\sigma}{r}\right)^n$	+
Van der Waals	$-4\epsilon \cdot \left(\frac{\sigma}{r}\right)^6$	$\frac{-24\epsilon}{r} \cdot \left(\frac{\sigma}{r}\right)^6$	-
Lennard-Jones-12-6	$4\epsilon \cdot \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right)$	$\frac{24}{r}\epsilon \cdot \left(2\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right)$	+ -

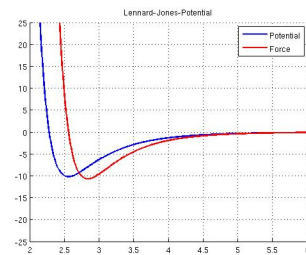
(b) Graphs:



Soft-Sphere potential.



Van-der-Waals potential.



Lennard-Jones-12-6 potential.

- (c)
- Hard-Sphere: not time-integratable, therefore a different kind of algorithm is required.
  - The potentials model attraction, repulsion, or both.
  - One thing in common: force and potential decrease very quickly with increasing distance, therefor called short-range potentials (as opposed to long-range potentials like gravitation or Coulomb charges)

**Exercise 14: Multi-Centered Molecules**

For single-centered molecules, the force on molecule  $i$  equals the sum of all forces between molecule  $i$  and all other molecules:  $\vec{F}_i = \sum_{j \neq i} \vec{F}_{ij}$ .

Using the force, the acceleration of molecule  $i$  is given by the following formula:

$$\ddot{\vec{x}}_i = \frac{\vec{F}_i}{m_i} = \frac{\sum_{j \neq i} \vec{F}_{ij}}{m_i}$$

For multi-centered molecules, there are some more values to be considered to be able to represent rotations:

- values considered for single-centered molecules: force  $\vec{F}$ , mass  $m$ , acceleration  $\ddot{\vec{x}}$ .
- values only to be considered for multi-centered molecules: torque  $T$ , moment of inertia  $I$ , angular acceleration  $\dot{\omega}$ .

Find the formula for the angular acceleration that is analogue to the formula for the acceleration  $\ddot{\vec{x}}$ .

**Solution:**

Consider two non-spherical molecules:  $i$  with 2 interaction sites and another molecule  $j$  with 3 interaction sites. Apart from translation, we also have to consider rotational motion now.

- Compute force between molecule  $i$  and molecule  $j$ :

$$F_{ij} = F_{i1,j1} + F_{i1,j2} + F_{i1,j3} + F_{i2,j1} + F_{i2,j2} + F_{i2,j3},$$

i.e. the sum over all site-site pairs.

- Compute the total force on molecule  $i$ :  $F_i = \sum_{i \neq j} F_{ij}$
- The force on each site results in a torque  $\tau$ :

$$\tau = \sum_{s \in \text{sites } i} d_s \times F_s,$$

where  $d_s$  denotes the distance of site  $s$  from the center of mass, and  $F_s$  the force on center  $s$ .

- The relationship between angular acceleration  $\frac{\partial \omega}{\partial t}$  and torque  $\tau$  is  $\tau = I \times \frac{\partial \omega}{\partial t}$ .
- Thus, angular acceleration  $\frac{\partial \omega}{\partial t} = I^{-1} \times \tau$ .

**Exercise 15: Internal degrees of freedom**

Consider the following model of a molecular fluid:



- Molecules consist of two atoms, which interact via a harmonic potential:

$$U_{harmonic}(r_{ij}) = \frac{1}{2}k(r_{ij} - r_0)^2,$$

where  $k$  models the bond strength and  $r_0$  the equilibrium bond length between the two atoms.

- Atoms of different molecules interact by the Lennard-Jones potential.
- The time integration is carried out for each atom, based on the forces on that atom.

Set up the formulas to

- calculate the total potential in the computational domain for  $N$  molecules ( $2N$  atoms).
- calculate the force on an atom due to the potential model,

- (c) describe the system of differential equations that describes the movement of the atoms! Formulate the Velocity-Störmer-Verlet integration scheme in order to solve that system.
- (d) To efficiently calculate the force, we use the truncated Lennard-Jones potential with a cut-off radius  $r_c$ .

Give the runtime complexity with respect to the number of particles, and explain shortly why this complexity is obtained.

- (e) Outlook: Derive the Shake-algorithm to enforce fixed bond-lengths for the diatomic fluid under consideration.  
How does it compare to rigid-body motion in exercise 14?

**Solution:**

- (a) Let  $neigh(i)$  denote the neighbouring atom of atom  $i$ .

Potential calculation: first possibility

$$U = \sum_i^{2N} \sum_{j \neq i, j \neq neigh(i)}^{2N} \frac{1}{2} U_{LJ}(r_{ij}) + \sum_{i,j=neigh(i)}^{2N} \frac{1}{2} U_{harmonic}(r_{ij}).$$

or

$$U = \sum_i^{2N} \sum_{j \neq i}^{2N} \frac{1}{2} U_{LJ}(r_{ij}) + \frac{1}{2} \sum_{i,j=neigh(i)}^{2N} (U_{harmonic}(r_{ij}) - U_{LJ}(r_{ij})).$$

- (b) Force calculation: Force  $F_i$  on molecule  $i$

$$F_i = \sum_{j \neq i, j \neq neigh(i)}^{2N} F_{LJ}(r_{ij}) + \sum_{j=neigh(i)}^{2N} F_{harmonic}(r_{ij}).$$

with  $F_{LJ}(r_{ij}) = -\nabla U_{LJ}(r_{ij}) = \frac{24\epsilon}{r_{ij}} \left( 2 \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right)$

and  $F_{harmonic}(r_{ij}) = -\nabla U_{harmonic}(r_{ij}) = -k(r_{ij} - r_0)$

- (c) ODEs for movement:

$$\ddot{x}_j = \frac{F_j}{m_j}$$

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

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

- (d) O(N): in order to find neighbouring particles for one molecule, only the neighbouring cells have to be searched, i.e. the distance for a constant number of particles has to be calculated. This has to be done for N molecules.

- (e) The Shake-algorithm allows to enforce constraints (e.g. fixed bond-length between two atoms) for molecules which are not completely rigid, e.g. a polymer chain.

We formulate a constraint  $\sigma$  to fix the distance between two atoms  $i$  and  $j$  to equal  $b_{ij}$ :

$$|r_i - r_j|^2 = b_{ij}^2$$

$$\sigma = r_{ij}^2 - b_{ij}^2 = 0$$

The equation of motion can be formulated as

$$m_i \ddot{r}_i = f_i + g_i \quad (1)$$

$f_i$  denotes the force on molecule  $i$  resulting from inter- and intramolecular interactions, while the force-like term  $g_i$  expresses the effect of the constraint on molecule  $i$ :

$$g_i = -\lambda \nabla \sigma = -2\lambda r_{ij}$$

Integrating Eq. (1) with the Störmer-Verlet gives

$$r_i(t + \Delta t) = 2r_i(t) - r_i(t - \Delta t) + \frac{\Delta t^2}{m_i}(f_i + g_i) \quad (2)$$

$$= r'_i(t + \Delta t) + \frac{\Delta t^2}{m_i}g_i \quad (3)$$

$$= r'_i(t + \Delta t) - 2\frac{\Delta t^2}{m_i}\lambda r_{ij}, \quad (4)$$

where  $r'_i(t + \Delta t)$  is the current approximation to the atom's final position and  $r_{ij}$  is the current distance between atoms  $i$  and  $j$ . Approximating  $\lambda$ , we obtain new approximate positions  $r''_i, r''_j$ :

$$r''_i = r'_i - 2\frac{\Delta t^2}{m_i}\lambda r_{ij} \quad (5)$$

$$r''_j = r'_j + 2\frac{\Delta t^2}{m_j}\lambda r_{ij} \quad (6)$$

So we can determine  $\lambda$  from the constraint:  $r''_{ij} = b_{ij}$ :

$$r''_{ij} = (r'_i - 2\frac{\Delta t^2}{m_i}\lambda r_{ij} - r'_j + 2\frac{\Delta t^2}{m_j}\lambda r_{ij})^2 \quad (7)$$

$$= (r_{ij} - 2\Delta t^2(\frac{1}{m_i} + \frac{1}{m_j})\lambda r_{ij})^2 = b_{ij}^2 \quad (8)$$

Solving for  $\lambda$  and updating  $r_i, r_j$  ensures the constraints again.

Note: for more complex molecules with several constraints, Eq. (8) is linearized and  $\lambda$  is determined only up to order of  $\Delta t^2$ , and the positions of all atoms are determined iteratively:

$$\lambda = \frac{r_{ij}'^2 - b_{ij}^2}{4\Delta t^2 \left(\frac{1}{m_i} + \frac{1}{m_j}\right) r_{ij}' r_{ij}'},$$

then the positions  $r_i, r_j$  are updated accordingly. This is done for all constraints and repeated, until for all constraints holds  $|r_{ij}' - b_{ij}^2| < \epsilon b_{ij}^2$ .

Alternatively, a system of linear equations can be set up and solved for the correction factors  $\lambda_k$ . As the resulting matrix is usually sparse, the methods previously discussed in the lecture are well-suited.

Note that only the positions fulfill the constraints, the atoms may have relative velocities. This short-coming can be treated with the Rattle algorithm.

#### **Comparison to rigid-body motion:**

- Time integration becomes more expensive.
- With Shake, molecules may be kept partially or completely rigid.

Source:

D.C. Rapaport: The Art of Molecular Dynamics Simulation,  
Cambridge University Press, 2010.