Week 5: Lennard-Jones and PBCs

2MMN40: Introduction to Molecular Modeling and Simulation
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1 The Assignment

Last session we expanded our code from a single molecule to many molecules by using a topology. So far these molecules do not interact with each other as we only have interactions inside of molecules. Today we will introduce non-bonded interactions, which are responsible for the interaction between molecules. This is typically the most expensive part of a calculation, since each molecule interacts with all other molecules.

After this we will be able to simulate small interacting clusters of molecules in vacuum. In real life we are typically more interested in how molecules in a solid or liquid (bulk) interact. To simulate a theoretically infinite system, we will introduce periodic boundary conditions.

What to do:

1. Finish extending the simulator to multiple molecules, if you haven't finished that already.
2. Implement the Lennard-Jones Potential and the corresponding forces in your simulation.
3. Add the use of periodic boundary conditions.

2 Non-bonded interaction

One of the basic inter-molecular (or non-bonded) interactions is the Lennard Jones interaction:

$$U_{ij}^{\mathsf{LJ}} = 4\epsilon_{ij} \cdot \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right], \tag{1}$$

where σ and ϵ are element (i.e. atom type) dependent parameters. Implement the LJ interaction between molecules including forces (Note that the LJ-potential acts on a per atom basis). You should probably modify the topology file to account for σ and ϵ and this new type of interaction. Should the non-bonded interactions also work inside a molecule? Why or why not?

2.1 Mixing rules for the LJ parameters

If σ_i and σ_j are the constants for two different atoms i and j (say Oxygen and Carbon), then the value corresponding to their interaction will be

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j). \tag{2}$$

And for the ϵ's,

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}. \tag{3}$$

2.2 LJ-Parameters for water

Species	σ (nm)	ϵ (kJ/mol)
O	0.315061	0.66386
H	0	0

Table 1. H_2O Lennard-Jones parameters.

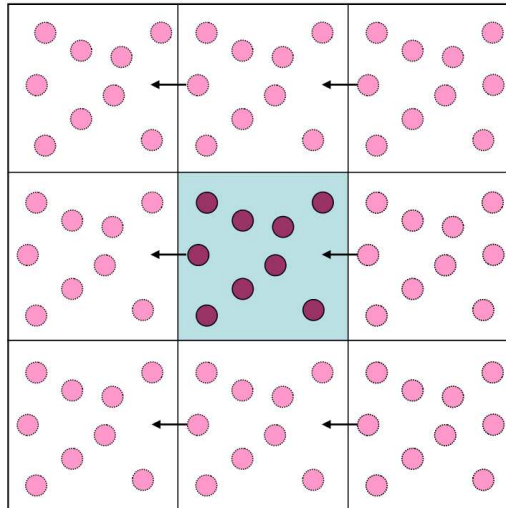# 3 Periodic Boundary Conditions (PBCs)

Figure 1. 2D version of periodic boundary conditions. The block in the middle is the simulation block and around it are periodic copies.

To simulate a large system of molecules you need to use periodic boundary conditions (PBCs). With PBCs particles which leave a box on the left side come back on the right. On each side of the box is a mirror image of the box with which the particles in the box interact. In this way it is as if the material has no surface. This is great, because otherwise we would need to model how the system interacts with the surrounding air or material. Moreover the system you simulate is theoretically infinite in all directions. This has the benefit that your simulation results correspond better to real life. Imagine a glass of water, for example, it has on the order of 10^{23} water molecules, that is an almost "infinite" amount.

To avoid double counting when using PBCS, each particle only interacts with the copy of the other particles which is closest to it. To avoid self-interaction (i.e. an interaction of a molecule with itself through a periodic boundary) you need to introduce a cutoff. There are some things you need to think about when you do this. What does it mean physically to introduce a cutoff? Is there a justification for using a cutoff from a physical/chemistry perspective? Spoiler: the answer is yes. Try to think of the reason. It would be nice if you include it in the final report.

How do you modify the distance calculation to account for the PBCs? Write down the equation and implement it, note that this will definitely depend on the box size.

There is one more important question to consider, when you write your trajectory to a file, should you project the coordinates into the box or not? What are the advantages and disadvantages? If you project the coordinates back into the box, think about whether you want to project, based on atom positions, or on the center of mass of the molecule. Note that in the first case you might have one half of a molecule on the left in you box and one half on the right.

4 Neighbourlists

As soon as you introduce a cutoff you can also introduce a neighbor list. This is a list that contains for every atom (or molecule) all its neighboring atoms (or molecules). The standard MD neighbor list is the so called Verlet list. It is, however, quite advanced.

For this project you can use a simpler neighbor list. You can simply create a list of all pairs (i, j) such that

$$\|\mathbf{r}_{ij}\| < r_{\text{cutoff}}, \tag{4}$$

where i and j are either atoms or the centers of masses of the molecules. From a mathematical point of view we can think of our system of atoms as vertices and the Lennard-Jones potential as connecting two atoms (vertices) as soon as they are within a distance r_{cutoff} and hence creating an edge. This mathematical picture is important because in computer science there are methods to represent graphs efficiently (i.e. adjancency lists, adjancency matrices etc.). You can (but we won't force you to) use one of those representations.

Note that a neighbor list must be updated during the MD simulation. Atoms that are neighbors at one point in time are not necessarily neighbors at another point in time.